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| Title | CHEMISTRY OF NON-KEKULÉ TYPE ODD-ALTERNANT AND EVEN-ALTERNANT HYDRCARBONS |
| Author(s) | Hara, Osamu |
| Citation | 大阪大学, 1977, 博士論文 |
| Version Type | VoR |
| URL | https://hdl.handle.net/11094/24457 |
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# CHEMISTRY OF NON-KEKULÉ TYPE
# ODD-ALTERNANT AND EVEN-ALTERNANT HYDRCARBONS

Osamu Hara

# Contents

Chapter 1. Introduction

Chapter 2. Benzo[cd]pyrenyl System

Chapter 3. Methylenebenzo[cd]pyrene

Chapter 4. Syntheses and Chemical Reactivities of 5- and 6-Diphenylmethylenebenzo[cd]pyrene

Chapter 5. Dibenzo[de;jk]pentacenyl System

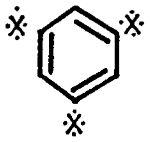
Chapter 6. Triangulenyl System

# Chapter 1. Introduction

## 1.1. Classification of Conjugated systems

In general, conjugated systems are divided into two categories, e.g., alternant and non-alternant.1) A conjugated system is termed alternant if the atoms in this system can be divided into two groups, starred and unstarred, in such a way that no two atoms of like parity are directly linked. It is easily seen that conjugated systems are alternant if, and only if, they contain no odd-membered rings. In butadiene (1), benzene (2), allyl (3), and benzyl (4), for example, this starring procedure can be carried out successfully, each starred atom being attached only to unstarred one and vice versa. These systems are therefore alternant.


(1)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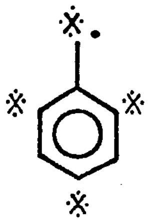
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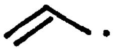
It should be noted that the classification includes conjugated systems with both even and odd numbers of atoms which are called even alternant and odd alternant, respectively.

An even alternant hydrocarbon (even AH) such as butadiene and benzene is a normal neutral conjugated hydrocarbon containing an even number of electrons which will pair up in the π-orbitals of lowest energy available to them. Therefore, such a system, with all the electrons paired, is called a closed shell system. An odd alternant hydrocarbon (odd AH) such as allyl and benzyl must exist as an ion or a radical, the latter of which being neutral but containing an odd number of electrons so that one remains unpaired. Allyl system provides a simplest example of the odd alternant conjugated system, the cation (3a) and anion (3b) having closed shell with two and four electrons, respectively, while the radical (3c) has three electrons. While azulene (5) and fulvene (6) are non-alternant in which the starring procedure failing because they have odd-membered rings.

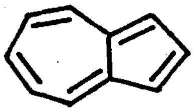
(3a)

(3c)



(3b)

(6)



(5)

In a simple Hückel MO approach, the π-MO's of an even AH are written as

$$\Phi_\mu = \sum_i a_{\mu i}\psi_i$$

Coulson and Rushbrooke[2)] showed that the π-MO's of such an even AH exhibit striking regularities so called pairing theorem. e.g., the π-MO's of an even AH appear in pairs $\Phi_\mu^+$ and $\Phi_\mu^-$ with energies $\alpha+E_\mu$ and $\alpha-E_\mu$, α being the Coulomb integral for carbon atom.

Thus, the MO's of an even AH appear in pairs, spaced equally from the central level of α in energy as shown in Fig. 1a. The pairing theorem also applied to odd AH's. In this

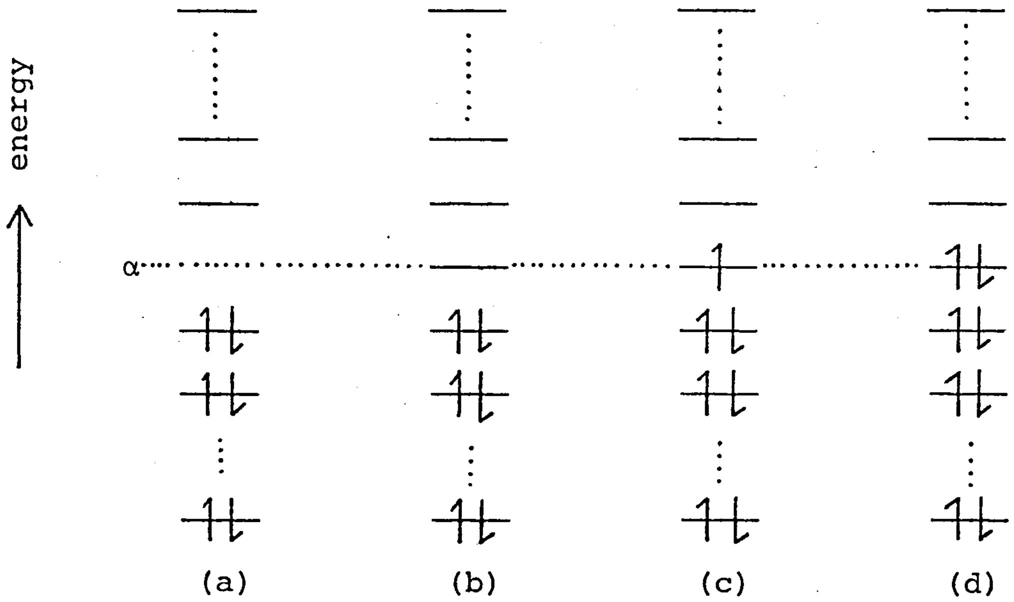
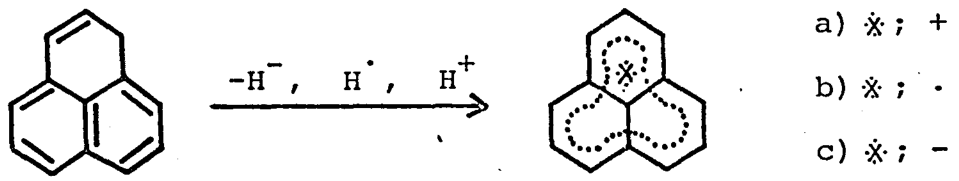


Fig. 1. Orbital Energy Diagram for (a) even AH, (b) odd AH Cation, (c) odd AH Radical, and (d) odd AH Anion.

case, since the number of AO's is odd, the number of MO's must also be odd. Therefore, there must be one unpaired MO of energy $\alpha$ left over. Such odd MO is described as a nonbonding MO (NBMO) and is denoted as $\Phi_0$. The electronic configurations for odd AH cation, radical, and anion are shown in Fig. 1b, 1c, and 1d, respectively.

## 1.2. Phenalenyl System

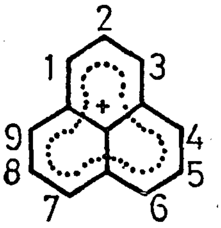
One of the most intriguing examples of odd AH is the phenalenyl system. Like allyl (3) and benzyl (4), the phenalenyl system (5) comprises the cation (5a), radical (5b), and anion (5c). These are produced from phenalene (6) both in theory and in practice by the loss of hydride ion, hydrogen atom, and proton, respectively.



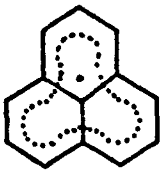
(6) (5)

Simple Hückel MO calculations predict that the phenalenyl system has a nonbonding and six bonding molecular orbitals with the energies indicated in Fig. 2. The phenalenyl cation (5a) possesses twelve π-electrons which exactly fill pairwise the six bonding molecular orbitals. The extra one and two electrons of the radical (5b) and the anion (5c) occupy the nonbonding molecular orbital. Therefore, all three entities should have the same magnitude of π-electron energy and also a same π-electron delocalization energy of 5.82 β. Due to its symmetry (a three-fold rotational axis and three two-fold axes), the electron density distribution in the phenalenyl cation (5a) and in the anion (5c) are found at positions 1,3,4,6,7 and 9 to be +0.167 and -0.167, respectively. The most striking feature is that the central carbon atom has no charge since the nonbonding MO coefficient at this atom vanishes, even though this is a starred atom. From these considerations, the phenalenyl system is best represented as a symmetrical peripheral form such as formula shown above. These assumptions have been revealed by the successful syntheses of the cation (5a)[3] and radical (5b)[4] in 1956 and the anion (5c)[5] in 1950.

Some aspects of phenalene chemistry have been compiled by Reid,[6] Hunig,[7] Prinzbach,[8] and Murata.[9]



(5a)



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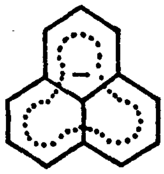


(5c)

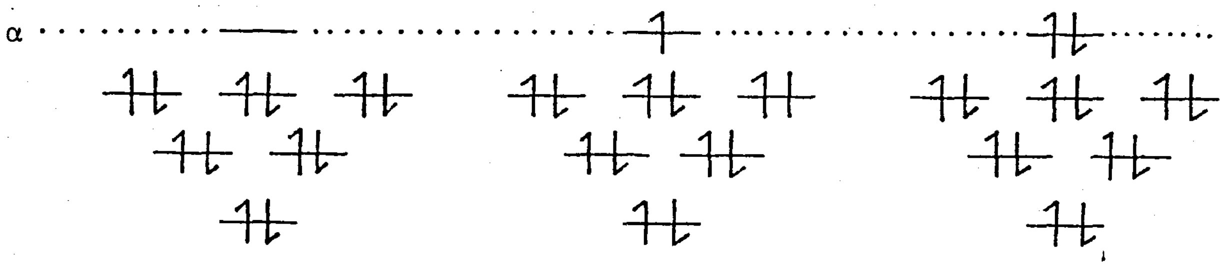
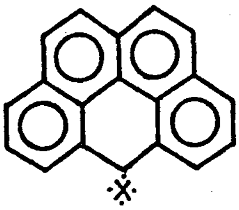


Fig. 2. Hückel Molecular Orbitals of the Phenalenyl Systems.

The benzo[cd]pyrenyl system (7), a representative of higher benzolog of the phenalenyl system, is also an odd AH and will be discussed in Chapter 2.



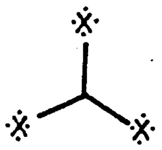
(7)

## 1.3. Compounds Containing Triplet Ground State

One of the well-known results of simple Hückel molecular orbital theory is that a non-Kekulé even alternant hydrocarbon with n starred atoms and m unstarred atoms should posses n-m NBMO's composed entirely of atomic orbitals of starred atoms.

In the ground state the electrons tend to occupy the orbitals of lower energy, so as a rule each bonding MO,s will contain two electrons with opposite signs, leaving n-m NBMO's.
By Hund's rule the most stable configuration is that with the highest multiplicity. Therefore, in the case of n-m=2, a neutral hydrocarbon of this class should exist in a triplet ground state.

Some simple examples are trimethylenemethane (8), m-xylylene (9), and 1,8-naphthoquinodimethane (10). Tetramethyleneethane (11) is, which contains two NBMO's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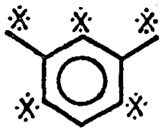
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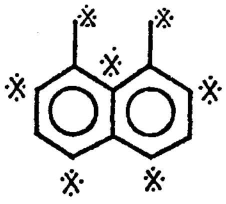
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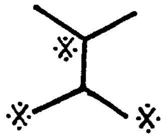

(11)

although n-m=0, is an exeptional example. Hückel molecular orbitals for trimethylenemethane is illustrated in Fig. 3 as an example.

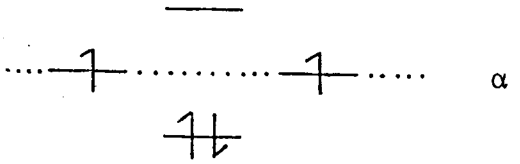
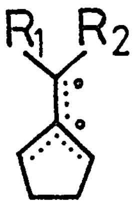


Fig. 3. Hückel Molecular Orbitals of (8).

Recently, Dowd and co-workers10) have demonstrated that the triplet state of parent trimethylenemethane (8) is the ground state. Similarly, it was verified that various substituted trimethylenemethane (12)11), the derivative of tetramethylene-ethane (13)12), and the tetraphenyl derivative of m-xylylene (14) exist as a triplet ground state in conformity with the theoretical predictions.

On the other hand, Pagni14) reported the preparation and characterization of the bridged 1,8-naphthoquinodimethane (15). In this case, the esr spectrum of (15) shows that the triplet state lies 200 cal/mol above the singlet ground state.



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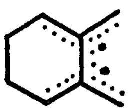

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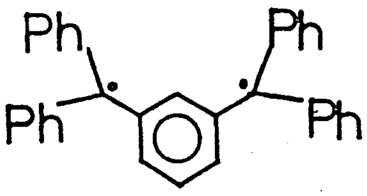

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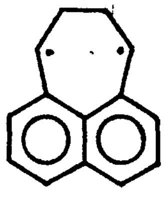
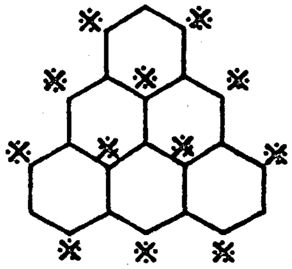


(15)

However, there exists only a few experimental investigation of higher benzologs of non-Kekulé even alternant hydrocarbons having two NBMO's, such as triangulene (16), dibenzo[de;hi]-tetracene (17), and dibenzo[de;jk]pentacene (18). These systems are regarded as good model compounds for comparison of the physical and chemical properties with the theoretical predictions, in paticular whether the neutral species exist in triplet or singlet ground state, because of their rigid structures. Therefore, we are interested in these systems in connection with the phenalenyl system.

We have attempted to synthesize and characterize the ionic and neutral species of triangulenyl and dibenzo[de;jk]pentacenyl systems. The details of the results will be described in Chapter 5 and 6.



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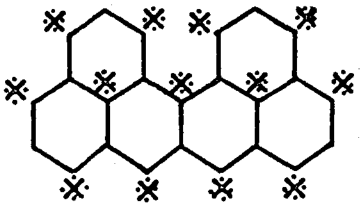

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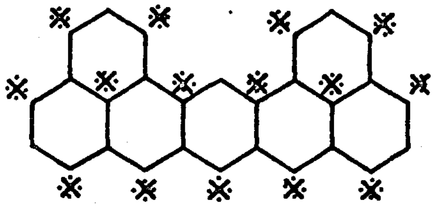

(18)

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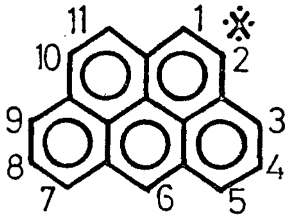
# Chapter 2. Benzo[cd]pyrenyl System

## 2.1. Introduction

In our continuing studies on the chemistry of phenalenyl system¹⁾ we have extended our attention to the higher benzolog of phenalenyl, benzo[cd]pyrenyl system (1). The benzo[cd]-pyrenyl systems, cation (1a), radical (1b) and anion (1c), are odd-alternant hydrocarbons as in the case of phenalenyl system (see Sec. 1.2). Simple HMO calculations predict that the benzo[cd]pyrenyl system (1) possesses nine bonding MO's and one nonbonding MO with the energies indicated in Fig. 1.
The benzo[cd]pyrenyl cation (1a) possesses eighteen π-electrons which exactly fill pairwise the nine bonding MO's. The extra one and two π-electrons of the radical (1b) and the anion (1c) occupy the nonbonding MO. Therefore all three entities should



(1)

(2)

a) ※ = +
b) ※ = •
c) ※ = −

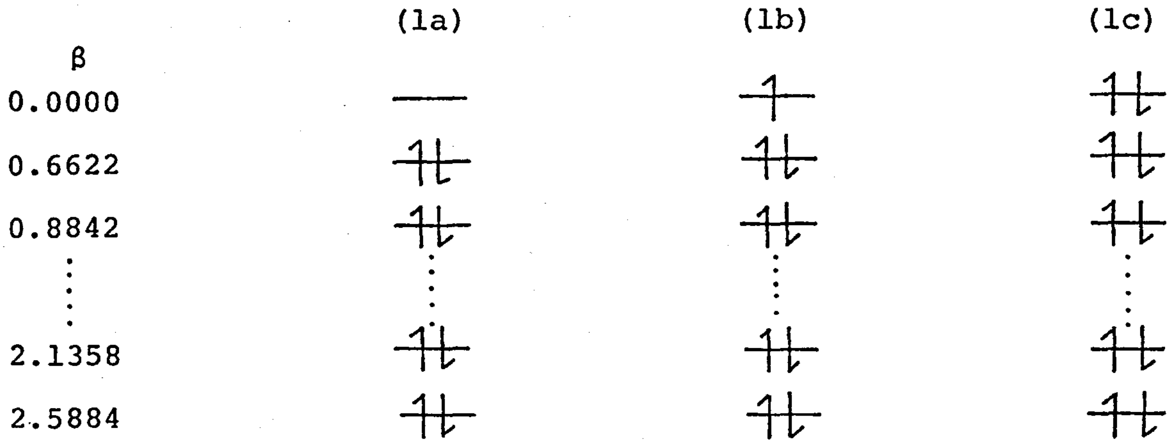


Fig. 1. Hückel Molecular Orbitals of Benzo[cd]pyrenyl System (1).

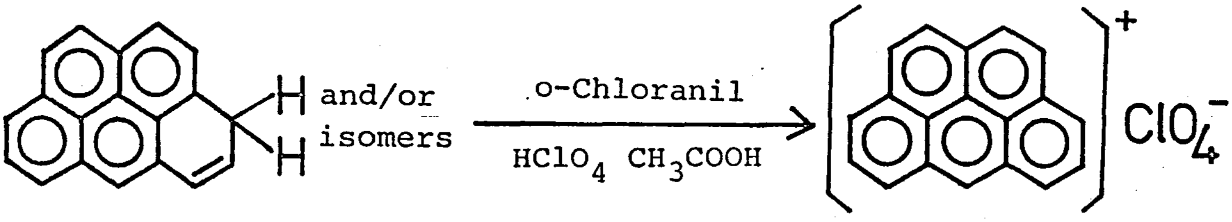
have the same magnitude of π-electron energy and also same π-electron delocalization energy of 8.6966 in β-unit.

Since the absolute value of the charge density at atom i in an odd-alternant hydrocarbon ion is $a_{oi}^2$, where $a_{oi}$ being the nonbonding molecular orbital coefficient of atom i$^{2)}$, charge densities of the benzo[cd]pyrenyl cation (1a) and anion (1c) have readily been calculated and are given in Table 1.

Reid and Bonthron$^{2)}$ have already reported the synthesis of the benzo[cd]pyrenyl cation (1a) as crystalline perchlorate by treatment of the precursor hydrocarbon (3) and/or its isomers with o-chloranil and perchloric acid. According to molecular orbital theory the reaction of conjugated carbonium ion with nucleophiles should occur at the carbon atom of highest charge

Table 1. Coefficients of the NBMO and Hückel Charge Densities of the Benzo[cd]pyrenyl System (1).

| Position (i) | | 2,10,11a | 3,5,7,9 | 6 | 5b,11c |
|---|---|---|---|---|---|
| $\lvert a_{0i} \rvert$ | | 0.2462 | 0.3693 | 0.4924 | 0.1231 |
| Charge Density | (1a) | +0.0606 | +0.1364 | +0.2425 | +0.0152 |
| | (1b) | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| | (1c) | -0.0606 | -0.1364 | -0.2425 | -0.0152 |



(3)

(1a)

density. Because the cation (1a) possesses several sites with different charge densities as shown in Table 1, the cation (1a) is of interest to test this prediction. The results revealed that the reaction of (1a) with nucleophiles occurs at the position of highest charge density as predicted by Hückel molecular orbital theory.

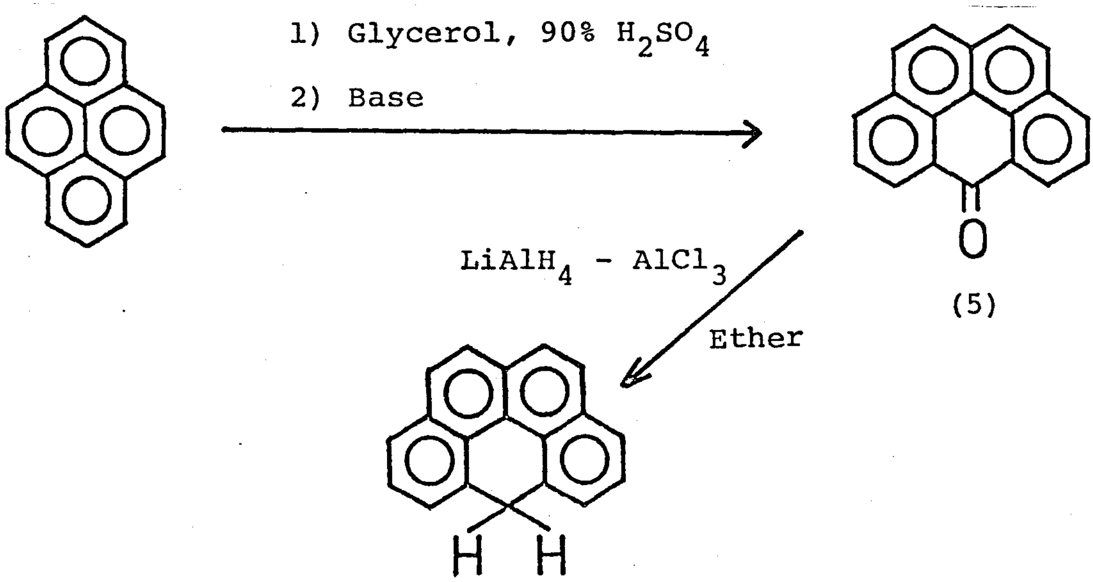
Recently, the radical (1b) is also prepared from 3H-benzo-[cd]pyrene (3) and/or isomers by air oxidation like the phenalenyl radical (2b)[3] and characterized by esr spectroscopy by Reddoch and Paskovich.[4] Like the phenalenyl radical (2b), the radical (1b) is quite stable at room temperature if protected from further reaction with oxygen.

Although the generation of the anion (1c) from 6H-benzo[cd]-pyrene (4) with sodium ethoxide was described in the literature by Jutz[5] none of the spectroscopic properties of (1c) have been reported.

In this context, we described herein the syntheses and the characterization of the cation (1a) and the anion (1c) together with the relationship between their proton chemical shifts and the Hückel $\pi$-charge densities at the respective carbon atoms

## 2.2. Synthesis of the Benzo[cd]pyrenyl Cation

6H-Benzo[cd]pyren-6-one (5), available in two steps from the pyrene by the known procedure2), was converted to the desired 6H-benzo[cd]pyrene (4) by lithium aluminum hydride-aluminum chloride complex reduction. Compound (4) is crystallized from cyclohexane as pale yellow plates of mp 121-128°C [Lit. 134°6), 123-124°7), and 124-130°C2)]. The identy of (4) follows from its nmr spectrum (Fig. 2) which shows 2H singlet at $\delta$ 4.89 along with the aromatic protons multiplet at $\delta$ 7.4-7.8 (10H). Inspection of the spectrum, no other isomeric hydrocarbons could be detected.



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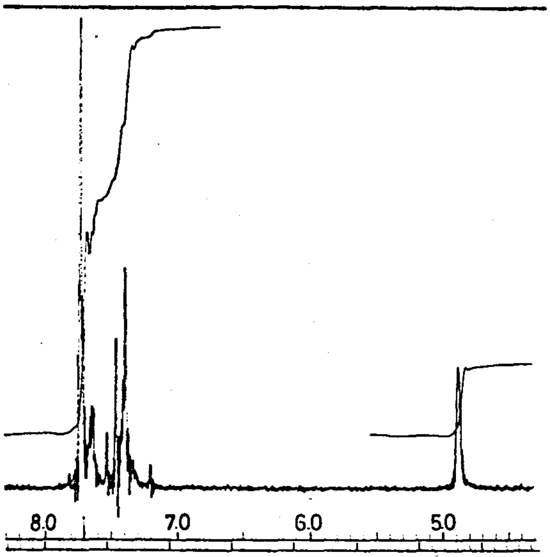

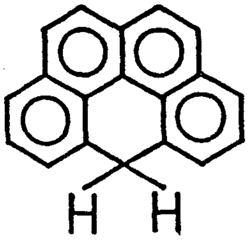

(4)

Fig. 2. The Nmr Spectrum of (4) in $CDCl_3$.

The cation (1a) was prepared from (4) with o-chloranil and 70% perchloric acid in acetonitrile according to the procedure of Reid.[2)] While the product shows the identical electronic spectrum with that of (1a) reported by Reid, its nmr (Fig. 5) was quite different from that of the Reid's cation.*
However, since the nmr spectrum of our product, $\delta$ 8.30 (2H, t, J=7.8 Hz, H-4,8), $\delta$ 8.39 (2H, d, J=9.0 Hz, H-1,11), $\delta$ 8.65 (2H, d, J=9.0 Hz, H-2,10), $\delta$ 9.11 (2H, d, J=7.8 Hz, H-3,9), $\delta$ 9.13 (2H, d, J=7.8 Hz, H-5,7), and $\delta$ 10.01 (1H, s, H-6), is fully consistent with the proposed cationic structure and the elemental

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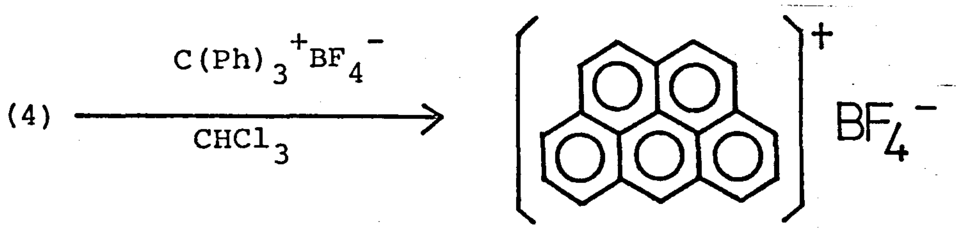
* Reid and Bonthrone have been reported the nmr spectral data of benzo[cd]pyrenyl perchlorate as two groups of signals centered at $\delta$ 8.62 and 9.25.

analysis of the product is also in good agreement with the expected values, the product is believed to be a true benzo[cd]-pyrenyl cation.

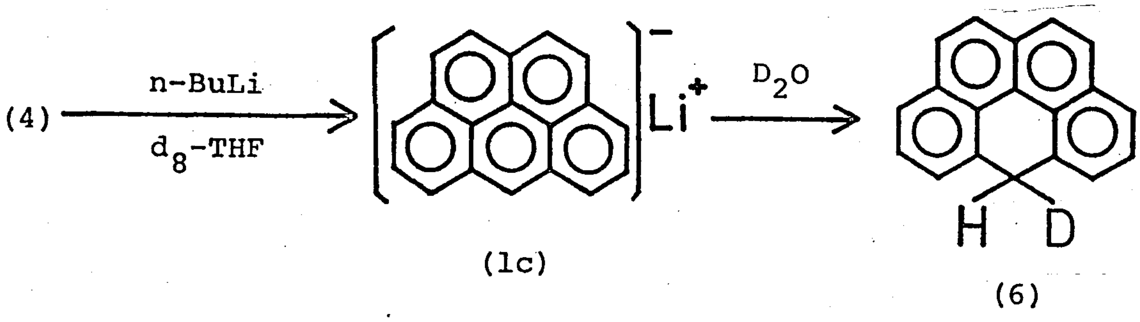
The tetrafluoroborate of the cation (1a) was also easily obtained from (4) by hydride abstraction with triphenylmethyl fluoroborate in chloroform in high yield.



(1a)

## 2.3. Synthesis of Benzo[cd]pyrenyl Anion

Formation of the benzo[cd]pyrenyl anion (1c) was achieved by direct proton abstraction from the precursor hydrocarbon (4) with butyllithium. Thus, treatment of (4) in $d_8$-tetrahydrofuran (freshly distilled over $LiAlH_4$) with butyllithium in hexane containing small amount of ether at -78°C in vacuo gave a dark brown solution of the benzo[cd]pyrenyl anion (1c) in quantitative yield.



Existence of the anion (1c) was revealed by the fact that the solution could be quenched by deuterium oxide to produce exclusively 6-monodeuterio-6H-benzo[cd]pyrene (6). The structure of (6) was confirmed on the basis of its mass and nmr spectra. The mass spectrum of (6) shows the parent peak at m/e 241. The deuterium incorporation at C-6 position, where the maximum negative charge density is found in the anion (1c), was established by its nmr spectrum (Fig. 3) which exhibits a single benzylic proton broad singlet at δ 4.98 (1H) and aromatic protons multiplet at δ 7.4-7.8 (10H). Fig. 4 shows the visible spectrum of (1c) in tetrahydrofuran.

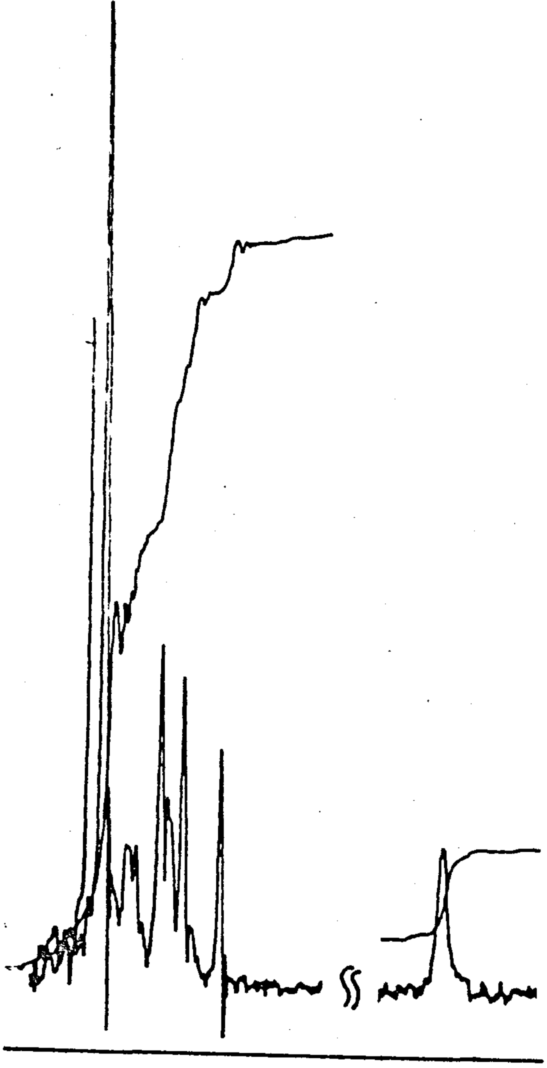
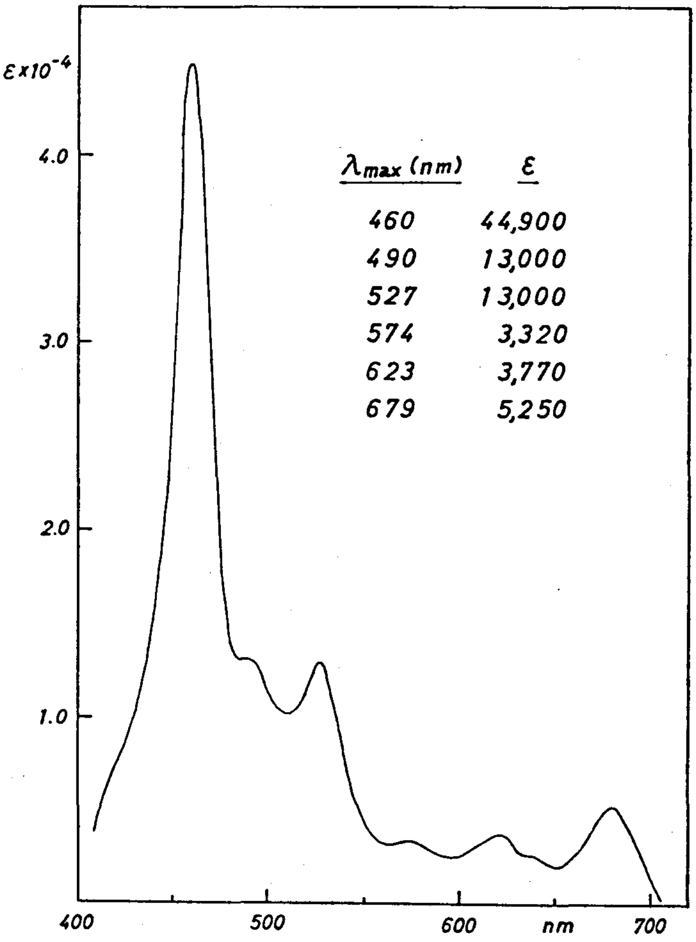


Fig. 3. The NMR Spectrum of (6) in $CDCl_3$.



| $\lambda_{max}$ (nm) | ε |
|---|---|
| 460 | 44,900 |
| 490 | 13,000 |
| 527 | 13,000 |
| 574 | 3,320 |
| 623 | 3,770 |
| 679 | 5,250 |

Fig. 4. The Visible Spectrum of (1c) in THF.
The ε values were estimated assuming quantitative conversion of (4) into (1c).

## 2.4. Nmr Spectra of Benzo[cd]pyrenyl Cation and Anion

Since the early 1960's the relationship between the $^1$H-nmr and $^{13}$C-nmr chemical shift and the local π-charge density of the corresponding carbon atom of aromatic molecules have been extensively investigated. In many cases so far investigated, it has become apparent that there is a simple linear correlation between the chemical shift and the π-charge density.8) Furthermore this argument have successfully been applied to a series of several dianions, such as sym-dibenzocyclooctatetraenyl dianion by Katz9a) and some perturbed [12]annulenyl dianions by Trost.9b)

We wish to present here the nmr spectra of the ionic species of benzo[cd]pyrenyl system, (1a) and (1c) in connection with the charge distribution in these ions derived from the non-Kekulé hydrocarbon.

The nmr spectrum (100 MHz) of (1c) recorded at 0°C is given in Fig. 5 compared with that of the cation (1a). Table 2 summarized chemical shifts and coupling constants taken from these spectra. The first-order analysis of the signals is in full accord with the delocalized structures (1a) and (1c) with $C_{2v}$-symmetry. H-1 and H-2 of (1a) and (1c) were assigned according to the calculated π-electron density at their

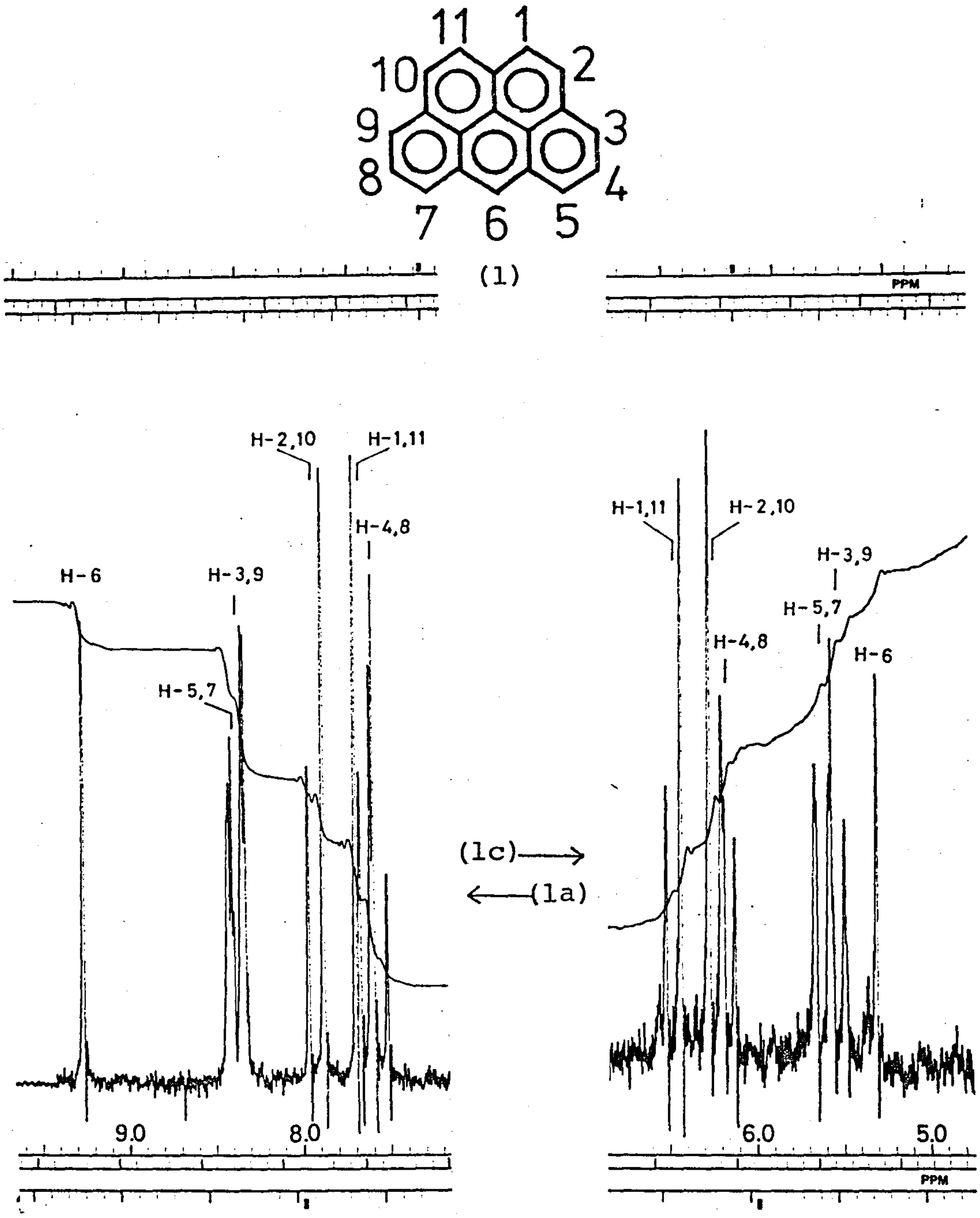


Fig. 5. The NMR Spectrum of (1a) (left) in $CF_3COOH$ and (1c) (right) in $d_8$-THF.

Table 2. The NMR Data of (1a) and (1c).

| | Cation (1a)[a] | | | | | Anion (1c) | | |
|---|---|---|---|---|---|---|---|---|
| Position | Obs. Chem. Shift[b] | Correct. Chem. Shift | Coupl. Const. | Ring Current Correct.[d] | Charge Density | Obs. Chem. Shift[c] | Correct. chem. Shift | Coupl. Const. |
| 1,11 | δ8.39 | δ7.34 | $J_{1,2}$ | 1.05 | 0.0000 | δ6.47 | δ5.42 | $J_{1,2}$ |
| 2,10 | 8.65 | 7.64 | =9.0Hz | 1.01 | ±0.0606 | 6.24 | 5.23 | =8.2Hz |
| 3, 9 | 9.11 | 8.17 | $J_{3,4}$ | 0.94 | ±0.1364 | 5.53 | 4.59 | $J_{3,4}$ |
| 4, 8 | 8.30 | 7.79 | $=J_{4,5}$ | 0.51 | ±0.0000 | 6.20 | 5.69 | $=J_{4,5}$ |
| 5, 7 | 9.13 | 8.11 | =7.8Hz | 1.02 | ±0.1364 | 5.63 | 4.61 | =7.5Hz |
| 6 | 10.01 | 8.50 | | 1.51 | ±0.2424 | 5.31 | 3.80 | |

a) perchlorate.

b) δ-values from TMS in $CF_3COOH$.

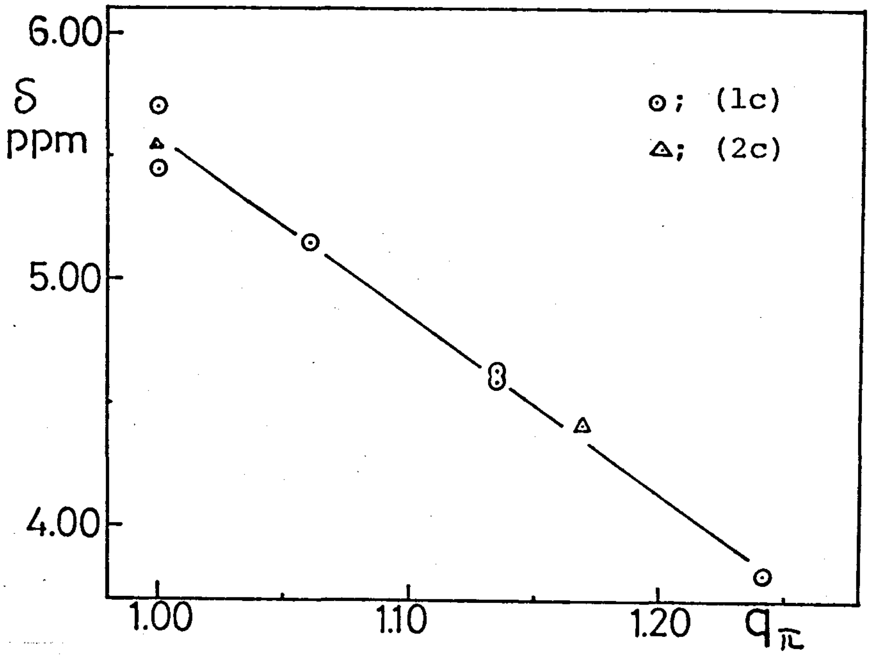
c) δ-values were determined in $d_8$-THF, relative to the lowfield THF signal assumed to lie at δ 3.63 from TMS.

d) The sum of ring current corrections for adjacent benzene rings by the simple point dipole approximation calculated by using the formula, $(12.0)a^2\Sigma R_i^{-3}$.[9a]

respective carbon atoms. The substantial up and down-field shift of H-6 in (1a) and (1c) is attributable to the largest positive (+0.2424 for (1a)) and negative charge density (-0.2424 for (1c)) respectively at C-6.

Fig. 6 is a plot of the nmr chemical shift (after correction for the ring current effects of the adjacent rings,[9)] see Table 2) of the protons of the cation (1a) and anion (1c) versus the Hückel charge density of the corresponding carbon atom. This plot provides good straight lines respectively and the points for lithium phenalenide (2c)[10)] also fall almost exactly on the line of (1c). The excellent correlation between the nmr chemical shift and the Hückel charge density provides evidence that the positive and negative charge exists on the alternate carbon atoms of the respective molecule of (1a) and (1c) as predicted by HMO method. This accord stresses the merits of the simple theory of non-Kekulé hydrocarbons even in terms of a Hückel molecular orbital treatment.

These results described above lead to the conclusion that the benzo[cd]pyrenyl system is a typical odd-alternant system as well as phenalenyl system.



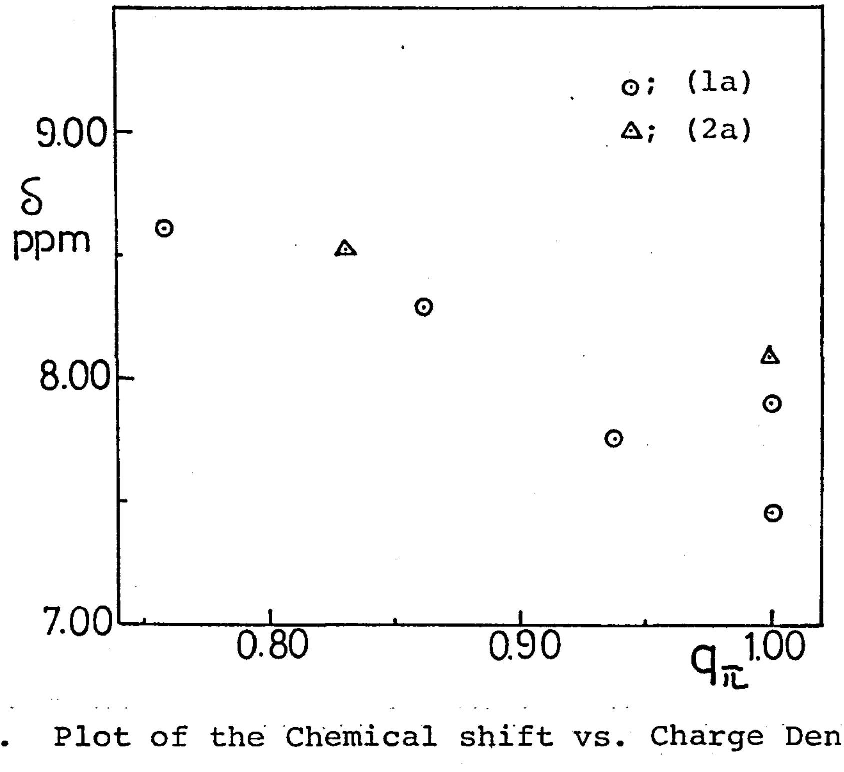
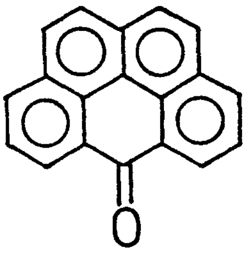


Fig. 6. Plot of the Chemical shift vs. Charge Density of (1c) [upper] and (1a) [lower].

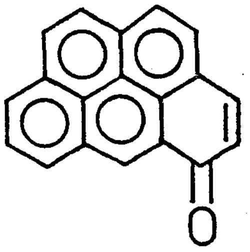
## 2.5. Synthesis of 3H-Benzo[cd]pyren-3-one

In this section we describe the synthesis and characterization of 3H-benzo[cd]pyren-3-one (8).

A series of ketones having a benzo[cd]pyrene skeleton such as (5), (7), (8), and (9) are of great interest both theoretically and experimentally. Among them, 6H-benzo[cd]pyren-6-one (5) and 5H-benzo[cd]pyren-5-one (7) are already synthesized.$^{2)}$ Although Reid have proposed the structures (8) or (9) to one of the minor hydration products of benzo[cd]pyrenyl perchlorate, none of its spectroscopic data and its precise structure have been reported to data.



(5)



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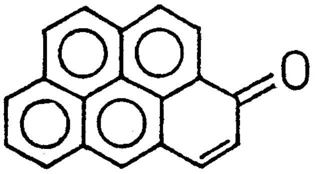
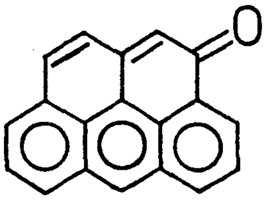


(8)

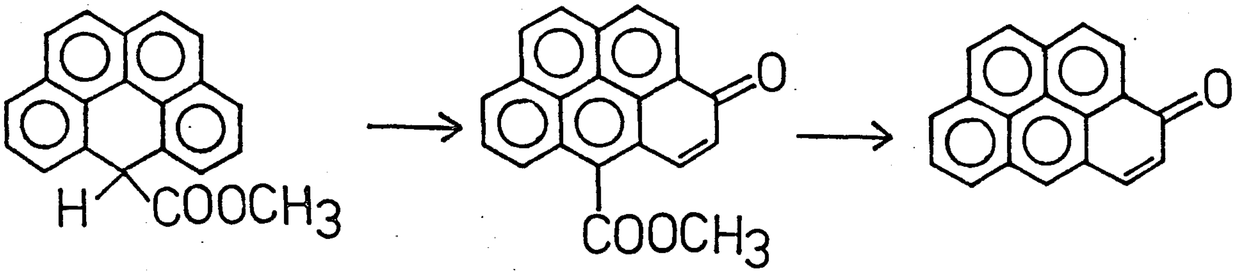


(9)

On the other hand, Zahradnik$^{11)}$ have closely studied theoretically and experimentally on the $pK_{BH^+}$ of (5), (7), phenalenone (10), and various derivatives of (10). Similarly, Culbertson and Pettit$^{12)}$ have determined the basic strength of some aromatic aldehydes and ketones, and have shown that the basicity could well be interpreted in terms of perturbed MO theory.

In this context, it is of much interest to synthesize 3H-benzo[cd]pyren-3-one (8). We have found that the ester (11), whose preparation is described in succeeding chapter, is readily oxidized with atmospheric oxygen to give the keto-ester (12) via hydrogen migration.

Thus, stirring a ether solution of the ester (11) containing a small amount of triethylamine at room temperature under exposing to air for several weeks gave the keto ester (12) as reddish orange needles with mp 239-240°C in 64% yield along with a trace amount of the recovered ester (11). The structure of (12) was confirmed by elemental analysis and spectroscopic properties. The mass spectrum of (12) shows intense peaks at m/e 312 ($M^+$, 100%), 281 ($M^+$-$OCH_3$, 34%), 253 ($m^+$-$CO_2CH_3$, 21%), and 225 ($M^+$-$CO_2CH_3$-CO, 18%). Its nmr spectrum shows a singlet at $\delta$ 4.22 ($OCH_3$) and two pairs of doublets at $\delta$ 6.88 (H-4, $J_{4,5}$=10.0 Hz), 7.87 (H-5), 8.15 (H-1, $J_{1,2}$=8.5 Hz), and 8.66 (H-2) along with a multiplet at $\delta$ 7.78-8.27 (H-7, 8, 9, 10, 11) [see Fig. 7].



(11) (12) (8)

These assignments could be confirmed by the double resonance experiments, the irradiation at $\delta$ 8.66 converted the doublet at $\delta$ 8.15 into a singlet and the other irradiation at $\delta$ 6.88 the doublet at $\delta$ 7.87 into a singlet. The significant downfield shift of H-2 is caused by the anisotropy effect of the carbonyl group at C-3. Its ir spectrum shows two streching bands characteristic to the ring and ester carbonyls at 1630 and 1725 $cm^{-1}$, respectively, which are consistent with the structure of (12).

Hydrolysis of the keto-ester (12) with aqueous alcoholic sodium hydroxide followed by decarboxylation in boiling quinoline with copper powder gave 3H-benzo[cd]pyren-3-one (8) as dark brown prisms, mp 194-196°C in 15-20% yield.

The structure of (8) was confirmed from its spectroscopic data. Its mass spectrum shows intense peaks at m/e 254 ($M^+$, 100%) and 226 ($M^+$-CO, 61%) and its nmr spectrum shows three doublets at $\delta$ 6.76 (H-4, $J_{4,5}$=8.5 Hz), 7.68 (H-5), and 8.69 (H-2, $J_{1,2}$=8.5 Hz) along with multiplet at $\delta$ 7.8-8.2 (other protons). These spectroscopic evidences are fully consistent with the structure of (8) [see. Fig. 8]. The carbonyl streching frequency of (8) are shown in Table 3 compared with those of the model compounds, (5), (7), and (10). It is noted that the band of (8) is fairly low frequency and is comparable to that of (7) [see. Table 3]. This presumably suggested that the basicity of

(8) would be almost identical with that of (7). The basicity of (8) is now currently examined.

Table 3. The Carbonyl Stretching Band of (5), (7), (8), and (10).

| (5) | (7) | (8) | (10) |
|---|---|---|---|
| 1651[(2)]<br>($CHCl_3$) | 1628[2)]<br>($CHCl_3$) | 1629<br>($CHCl_3$) | 1637<br>(nujor) |

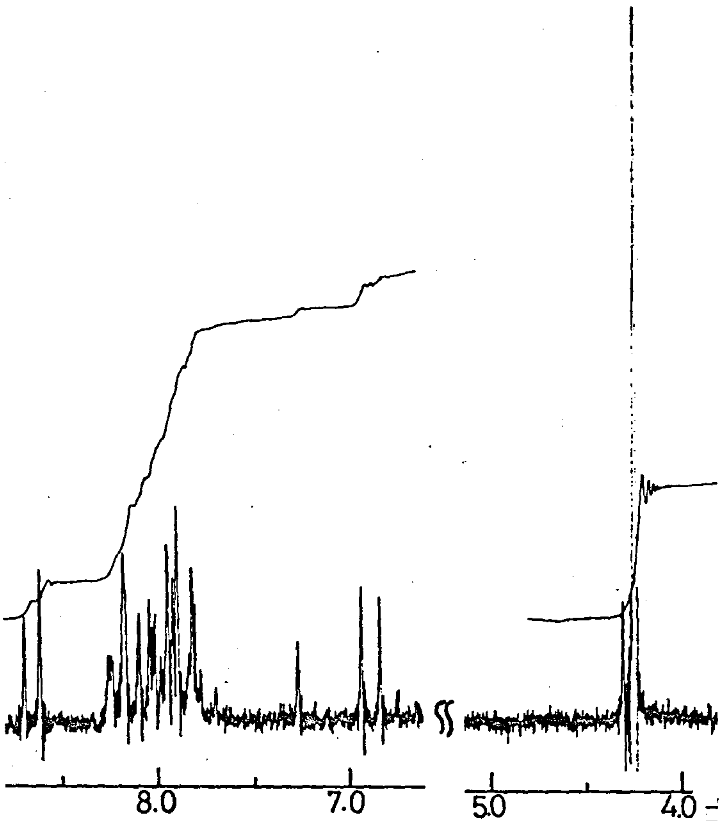


Fig. 7. The NMR Spectrum of (12).

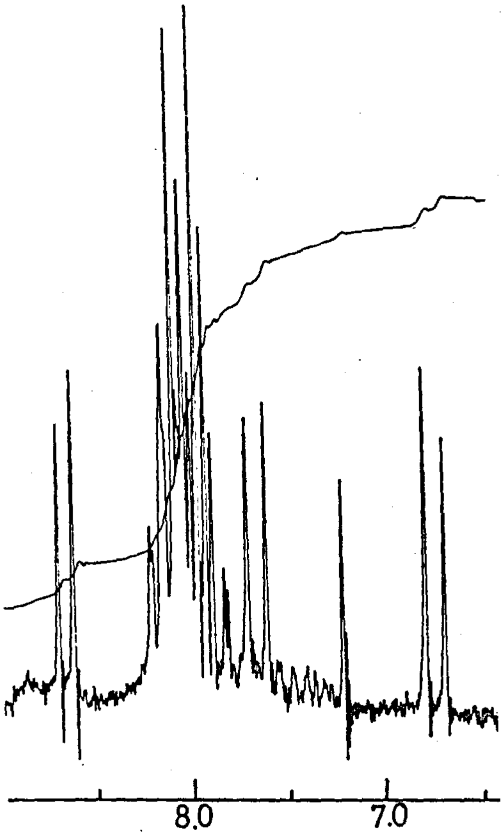


Fig. 8. The NMR Spectrum of (8).

## 2.6. Experimental

EXP. 1. NMR spectral measurement of lithium benzo[cd]pyrenide (1c):

To a degassed solution of 6H-benzo[cd]pyrene (4) 5 mg (0.02 mmol) in 0.4 ml 0f freshly distilled (over $LiAlH_4$) THF-$d_8$ was added 0.03 mmol of butyllithium in hexane (containing small amount of ether) at -60°C. The dark brown mixture was filtered with a sintered glass fused to the apparatus and the transparent solution was tipped into an nmr sample tube also connected to the apparatus. The tube was cut off and drawn free. All the manipulations were carried out in vacuo. The nmr spectrum of the solution was determined with a 100 MHz nmr spectrometer at temperature range of -40-0°C. After the measurement of the nmr spectrum the solutin was quenched with $D_2O$ in THF to give 6-deuterio- 6H -benzo[cd]pyrene (6) as a sole product.

(1c):

NMR($\delta$ in THF-$d_8$). 5.31(s, 1H, H-6), 5.53(d, H-3,9, $J_{3,4}=J_{8,9}=$ 7.5 Hz), 5.63(d, 2H, H-5,7, $J_{4,5}=J_{7,8}=$7.5 Hz), 6.20(dd, 2H, H-4,8), 6.24, 6.47(ABq, 4H, H-1, 2,10,11, $J_{1,2}=J_{10,11}=$8.2 Hz).

(6):

MS. m/e 241($M^+$, 58%), 240($M^+$-1, 100%), 239($M^+$-2, 16%).

Exp. 2. Electronic spectral measurement of lithium benzo[cd]-pyrenide (1c):

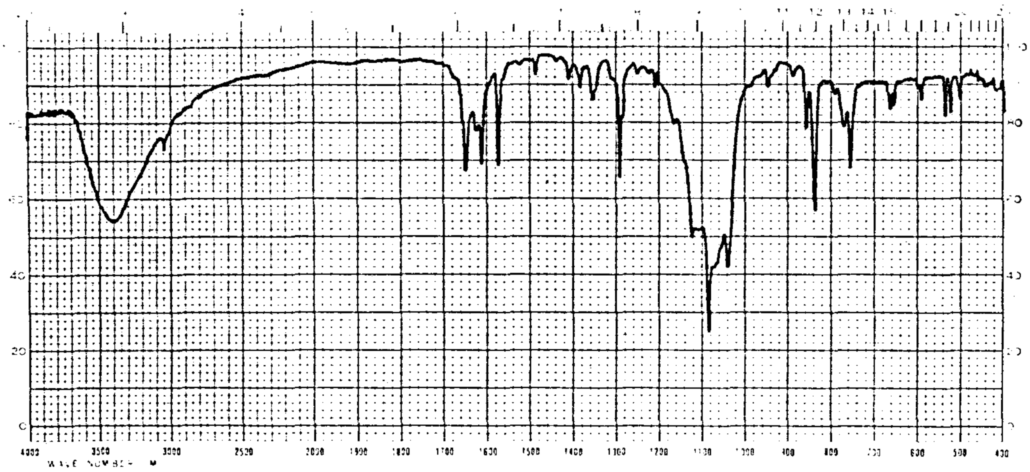
To a degassed solution of 6H-benzo[cd]pyrene (4) 0.586 mg in 10 ml of freshly distilled (over $LiAlH_4$) THF was added excess butyllithium in hexane under nitrogen atmosphere at -70°C. The slightly brown solution was tipped into a quartz cell fused to the reaction vessel and the visible spectrum of (1c) was measured quickly at room temperature (at about 5°C). The ε-values of (1c) were estimated assuming quantitative conversion of (4) into (1c).

ES(THF). $\lambda_{max}$(log ε). 679(3.72), 623(3.58), 574(3.50), 527(4.12), 490(4.12), 460(4.65).

Exp. 3. Benzo[cd]pyrenyl tetrafluoroborate (1a):

To a stirred solution of 6H-benzo[cd]pyrene 480 mg (2 mmol) in 15 ml of dry chloroform was added 726 mg (2.2 mmol) of triphenylmethyl tetrafluoroborate all at once at room temperature. Black solids precipitated immediately. The mixture was gently refluxed for 1 hr and cooled to room temperature. The black solid mass was collected by means of filtration and washed several times with dry chloroform in a dry box to give 554 mg (1.7 mmol) of (1a) in a 85% yield.

IR(KBr).



Exp. 4. Air oxidation of 6-carbomethoxy-6H-benzo[cd]pyrene (12):

A solution of 6-carbomethoxy-6H-benzo[cd]pyrene (11) 150 mg (0.5 mmol) in 80 ml of ether containing trace of triethylamine was stirred at room temperature for several weeks. The mixture was evaporated and the residue was chromatographed on alumina eluting with benzene to give trace of recovered ester and 130 mg (83 %) of 6-carbomethoxy-3H-benzo[cd]pyrene-3-one (12). Recrystallization from benzene gave 100 mg (64 %)of pure (12) as reddish orange needles, mp 239-240°C.

Anal. Calcd for $C_{21}H_{12}O_3$ : C, 80.76; H, 3.87%.

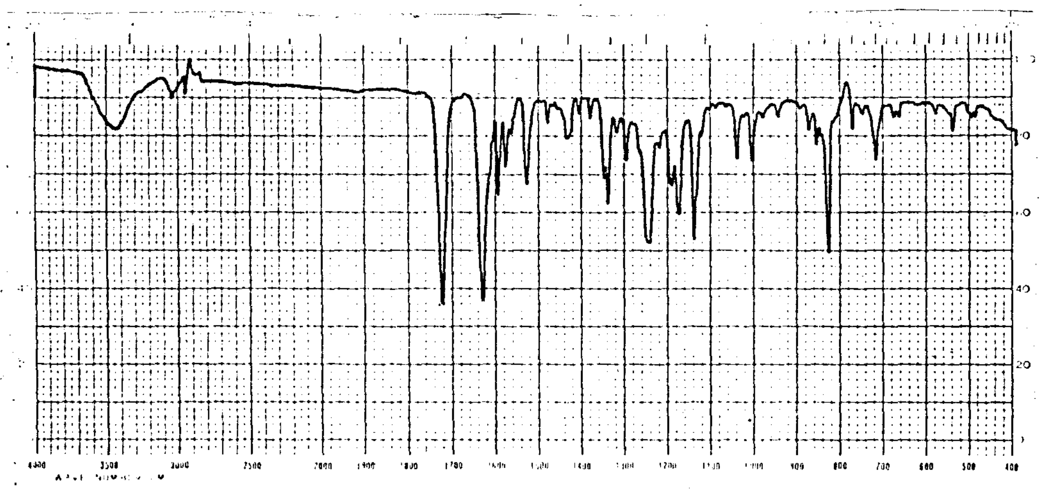
Found : C, 80.58, H, 3.78%.

MS. m/e 312($M^+$,100%), 281($M^+$-$OCH_3$, 34%), 253($M^+$-$CO_2CH_3$, 21%), 225($M^+$-$COOCH_3$, CO, 18%).

NMR(δ in $CDCl_3$). 4.22(s, -$OCH_3$), 6.88(d, H-4, $J_{4,5}$=10.0 Hz), 7.87(d, H-5), 8.15(d, H-1, $J_{1,2}$=8.5 Hz), 8.66 (d, H-2), 7.78-8.27(m, H-7,8,9,10,11).

ES($CH_3CN$). $\lambda_{max}$(log ε); 413(4.28), 398(4.23), 304(4.23), 292 (4.12), 254(4.20), 248(4.21), 226(4.66), 204(4.79).

IR(KBr). $\nu_{C=O}$; 1630, 1725 $cm^{-1}$.



Exp. 5. 3H-Benzo[cd]pyrene-3-one:

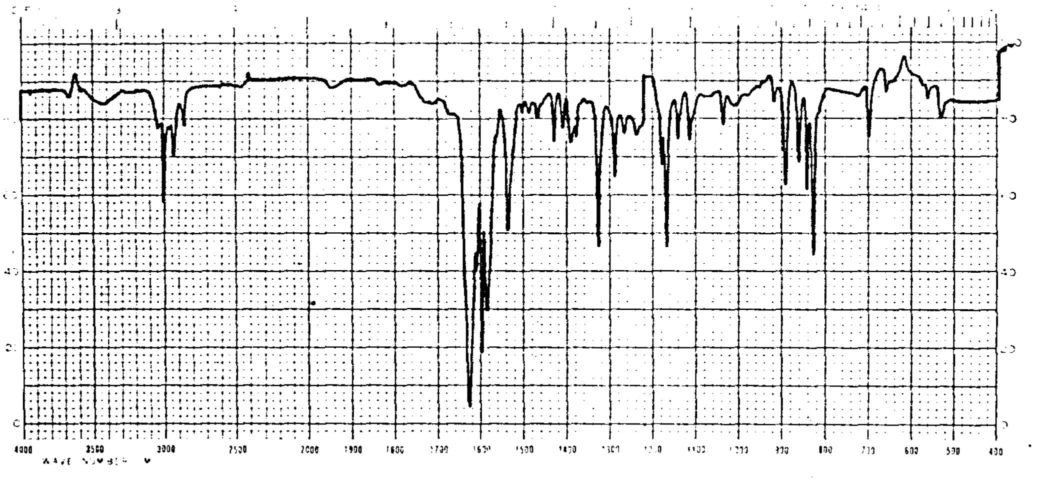
A suspension of the foregoing keto-ester (12) 100 mg (0.32 mmol) in 60 ml of ethanol and 20 ml of 10% sodium hydroxide aqueous solution was stirred for 2 days at room temperature. To the reddish brown solution was added 30 ml of water and 10 ml of benzene. The aqueous layer was acidified with hydrochloric acid and extracted with ether. The extract was dried over magnesium sulfate and evapolated in reduced pressure to give crude carboxylic acid as reddish brown solids. The acid 20 mg of copper powder in 8 ml of anhydrous quinoline was refluxed. After gas evolution was ceased the mixture was additionally refluxed for 15 min. To the mixture was added 20 ml of chloroform and the organic layer was washed 2N hydrochloric acid several times, saturated aqueous solution of sodium hydrogen carbonate, and water. After dried over magnesium sulfate the solution was evaporated in reduced pressure and the residue was chromatographed on alumina eluting with benzene and benzene-chloroform (1:1) to give 20 mg (26%) of the crude ketone (8). Recrystallization from benzene-hexane afforded reddish brown prisms, with mp 194-196°C.

MS. m/e 254($M^+$, 100%), 226($M^+$-CO, 61%).

NMR($\delta$ in $CDCl_3$). 6.76(d, H-4, $J_{4,5}$=8.5 Hz), 7.68(d, H-5), 8.69 (d, H-2, $J_{1,2}$=8.5 Hz), 7.8-8.2(m, others).

ES($CH_3OH$). $\lambda_{max}$(log $\varepsilon$); 407(4.29), 301(4.17), 293 sh(4.05), 249 (4.17), 224(4.65).

IR($CHCl_3$). $\nu_{C=O}$; 1629 $cm^{-1}$.



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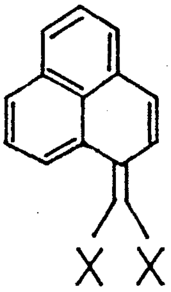
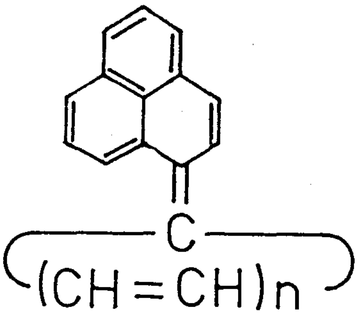
# Chapter 3. Methylenebenzo[cd]pyrene

## 3.1. Introduction

In our current interest in the chemistry of phenalene, we have recently reported the syntheses and the chemical and physical properties of various phenafulvenes (1)$^{1)}$ and phenafulvalenes (2),$^{2)}$ which are cross conjugated π-electron system containing a phenalene ring.



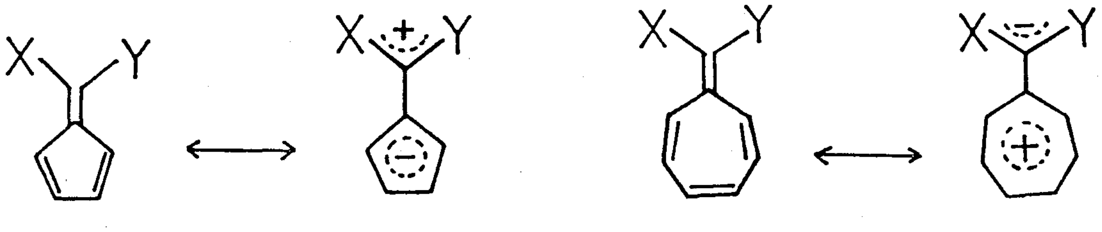
(1)



(2)

The fulvenes, nonalternant hydrocarbons characterized by the presence of a cross conjugated electron system within a five-membered ring have been known for more than seventy years, since Thile$^{3)}$ discovered the formation of yellow to red condensation products of cyclopentadiene with aldehydes and ketones. The bright color of the fulvenes has attracted many chemists in the course of time. Over the last two decades, systematic investigation has been carried out, stimulated by the application of the method of molecular orbital theory to these compounds. On the other hand, heptafulvene is the seven-membered analog of fulvene, isomeric with cyclooctatetraene and styrene. Its properties have been anticipated theoretically by B. Pullman and A. Pullman4) but its attempted synthesis has failed. In the time since 1961 publication by Doering and Wiley5) of their first synthesis of heptafulvene, the comparison of chemical and physical properties between fulvene (3) and heptafulvene (4) still remains a subject of active investigation.

According to Hückel (4n+2)π-rule, it was predicted that the cyclopentadiene moiety in fulvene tends to form a stable anion and the cycloheptatriene moiety in heptafulvene to form a stable cation, both possessing a group of six π-electrons. Therefore, the exocyclic double bond of (3) and (4) is polar in nature and the terminal carbon being positive in the former, negative in the latter case. The extent of the polarity was estimated from the dipole-



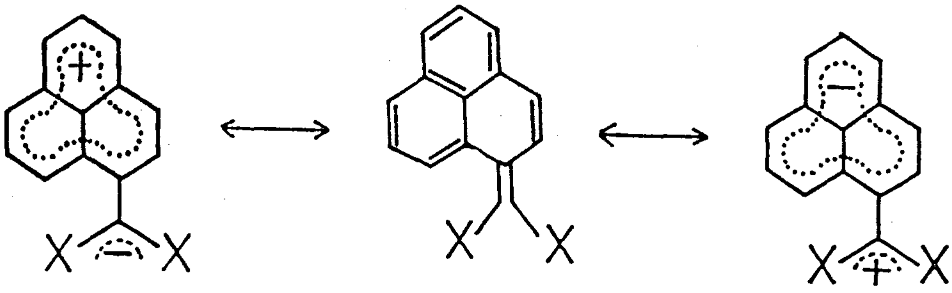
(3) (3') (4) (4')

Fig. 1 Fulvene and Heptafulvene.

moment of suitably substituted fulvenes (or their benzologs) or from the spectral shift as a function of substituents. However, the experimentally estimated polarity is not so large as predicted by simple Hückel molecular orbital calculations, which are based upon the assumption that the exchange integrals of all C=C bonds and Coulomb integrals of all atoms are set to be equal, respectively. Meanwhile, these above experimental results were supported by recent improved molecular orbital calculations[6)] which consider fairly large bond alternation commonly exists in non-alternant hydrocarbons such as the fulvenes, unlike alternant bydrocarbons such as benzene and naphthalene.

However, it was experimentally pointed out that the fulvene and the heptafulvene derivatives which carry appropriate polar substituents at the methylene group were fairly polarized in such a way in Fig. 1. The syntheses and the peculiar physical and chemical properties of the fulvenes have been reviewed in detail by Bergmann[7)] and Yates.[8)]

In view of these precedents, the fulvenes containing a phenalene moiety, so-called phenafulvene (1), are of interest because of the electronic characteristics of the phenalene system described in Chapter 1, and are distinct from the normal fulvenes. Namely, it might be expected that the phenafulvene (1) will be polarized in such a way that the positive or the negative end of the dipole is localized in the phenalene ring by the substituent is electron attractive or electron donative respectively, as depicted in Fig. 2. And this prediction above has been revealed by the syntheses of some phenafulvene derivatives.[1,9]



(1a)
X; electron attractive substituent

(1)

(1b)
X; electron donative substituent

Fig. 2. Phenafulvenes.

More recently, from the same standpoint as phenafulvenes, various phenafulvalenes which are cross conjugated systems composed of a phenalene and a odd membered ring hydrocarbon such as cyclopentadiene or heterocycles, pyrane and thiopyrane, were synthesized and characterized as reviewed by Murata.[2] Meanwhile, the benzo[cd]pyrenyl system possesses several sites with different absolute values of the nonbonding molecular orbital coefficients as given in Table 1 in Chapter 2. Accordingly the methylenebenzo[cd]pyrenes are particularly interesting by the reason described below in addition to the connection with phenafulvenes.
Since perturbed molecular orbital theory[10] indicates that when

the even alternant hydrocarbon R' is generated from union with K such as methyl through atom i in an odd alternant hydrocarbon R, such as benzo[cd]pyrene as depicted in Fig. 3, the difference in

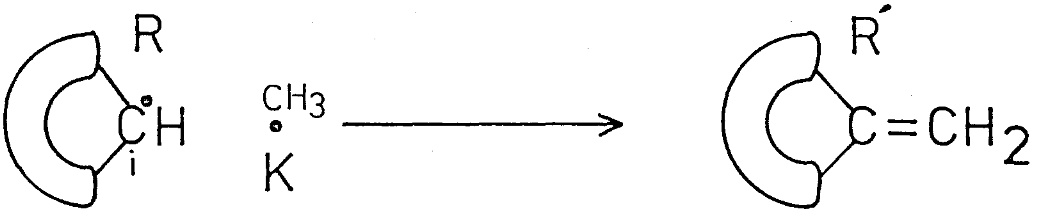
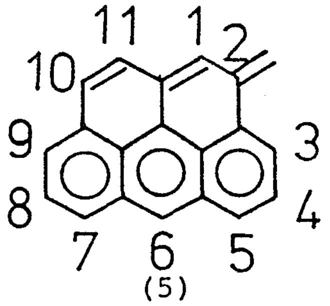


Fig. 3. Union of Methyl with odd AH R to Regenerate the even AH R′.

π-energy $\delta E_{RR'}$ between R and R', being the π-energy of union of odd-alternant hydrocarbon with methyl, will be given by $\delta E_{RR'} = 2\beta a_{0i}$. Where $a_{0i}$ is nonbonding molecular orbital coefficient of atom i in R through which union takes place. Further, when union K is a heteroatom the extent of charge separation of newly generated double bond should decrease with increasing $|a_{0i}|$. Here are possible four isomers of the methylenebenzo[cd]pyrenes which can be shown by Kekulé structures as illustrated below.

In order to gain the experimental evidences of above theoretical considerations we examined the syntheses and characterizations of some derivatives of (6), (7), and (8) along with



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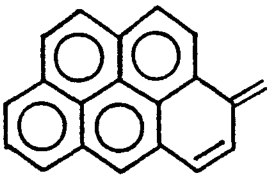
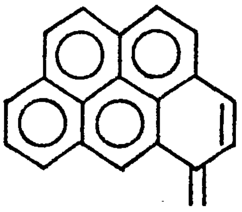
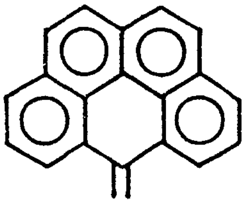


(6)



(7)



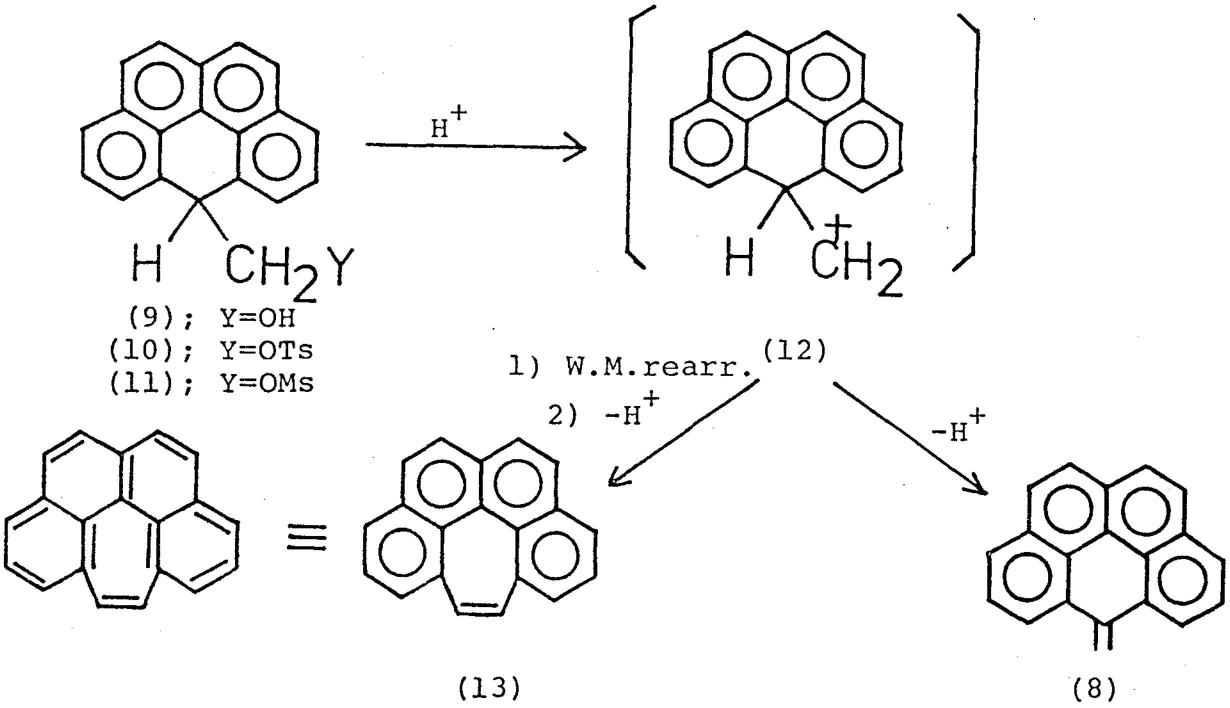
(8)

preparation and attempted isolation of the parent 6-methylenebenzo[cd]pyrene (8).

## 3.2. 6-Methylenebenzo[cd]pyrene

### 3.2.1. Preparation and Dimerization of the Parent 6-Methylenebenzo[cd]pyrene

As shown in Scheme 1, it was expected that solvolysis of the alcohol (9) or the corresponding tosylate (10) or mesylate (11) in acidic media could afford the parent 6-methylenebenzo[cd]-pyrene (8) through loss of a proton from the intermediate carbonium ion (12) and/or the ring expansion product (13) consisting of a heptafulvene moiety in its π-system via Wagner-Meerwein type rearrangement.



Scheme 1.

The alcohol (9) and the mesylate (11) were obtained according to Scheme 2. Treatment of the hydrocarbon (14) in tetrahydrofuran with butyllithium at -60°C followed by introduction of carbon dioxide gas gave the crude 6H-benzo[cd]pyrene-6-carboxylic acid as a sole isolated product. Expectedly, site of the carboxylation is in accord with the carbon atom carring highest charge density predicted by Hückel MO theory (see. Section 2.1). The carboxylic acid was converted to its methylester (15) with diazomethane in ether under nitrogen atmosphere because (15) is readily oxydized in solution by atmospheric oxygen as described in Section 2.5. Lithium aluminum hydride reduction of (15) in ether at -20°C produced the alcohol (9) whose mesylate (11) was available by the known procedures11) in 25% overall yield based on the hydrocarbon (14). However, the tosylate (10) could not form by the usual method with tosylchloride in pyridine though none of the significant reason to be considered.

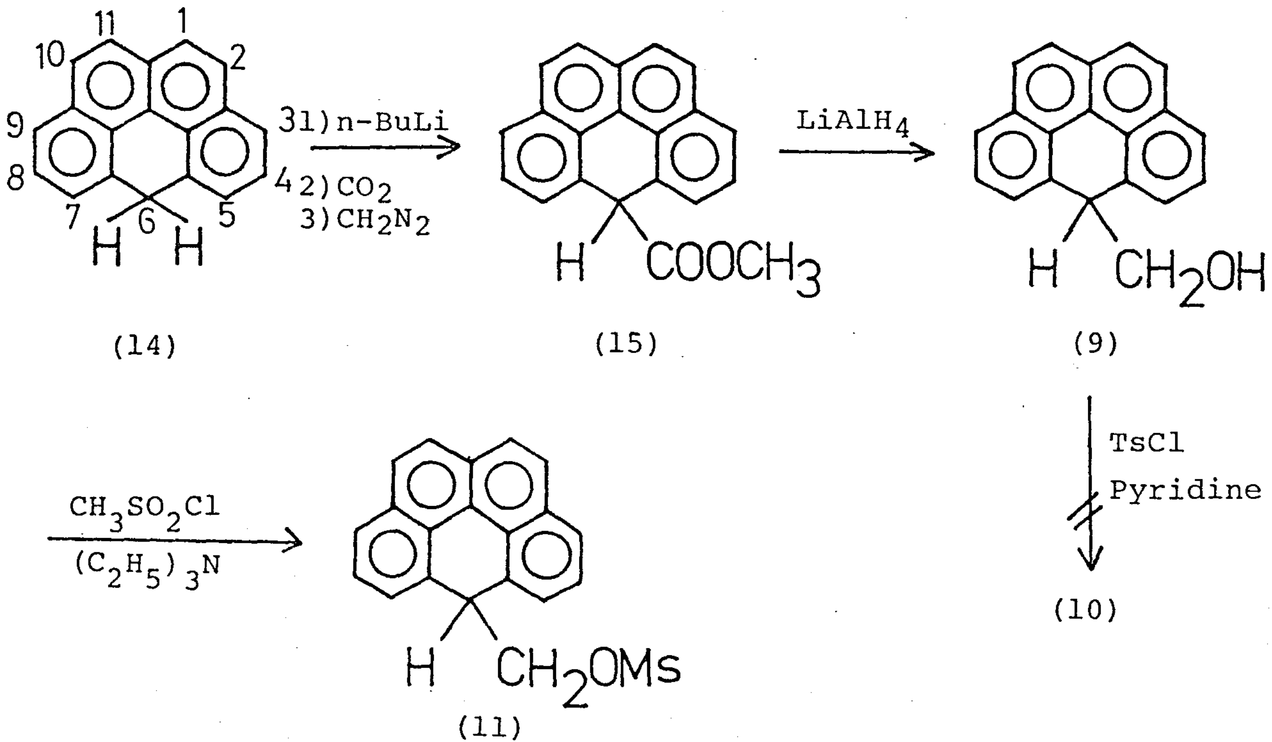
The structures of (15), (9), and (11) were based on their elemental analyses and spectroscopic properties. Their nmr spectral data were summarized in Table 1 and were in complete accord with these structures respectively.

The mesylate (11) was solvolized in gently refluxing dry acetic acid for 1 hr under nitrogen atmosphere. Chromatographic

Table 1. The NMR Spectral Data of (15), (9), and (11) in $CDCl_3$

( $\delta$-value from TMS ).

| | (15) | (9) | (11) |
|---|---|---|---|
| $-CH_3$ or $-OH$ | 3.51, s | 1.6, s | 2.39, s |
| $-CH_2-$ | | 3.60, d<br>J=6.5Hz | 4.28, d<br>J=6.5Hz |
| H-6 | 5.81, bs | 4.67, t<br>J=6.5Hz | 5.04, bt<br>J=6.5Hz |
| aromatic-H | 7.41-7.81 | 7.49-7.91 | 7.57-7.97 |



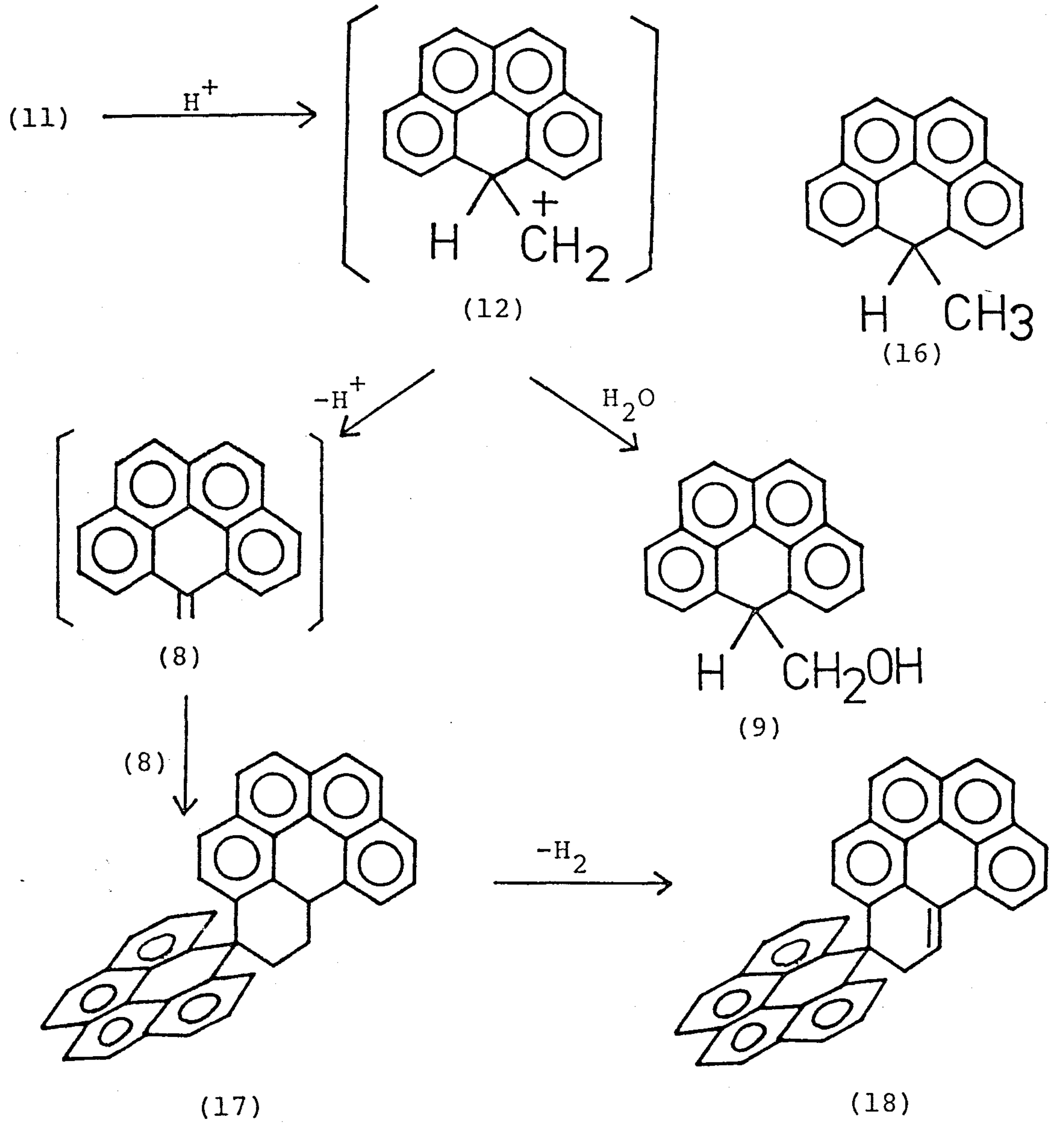
Scheme 2.

separation of the products gave (17) in 50% yield along with a trace amount of (18). Analogously formolysis of the mesylate (11) at 50°C gave (17) in 15% yield and a trace amount of (18) in addition to the alcohol (9) in 26% yield and a small amount of a reductive product (16) as shown in Scheme 3. In the latter case the formation of the alcohol in a considerable amount and the decrease in the formation of (17) are not striking feature since formic acid, as is generally known, gradually decomposes even at room temperature into water and carbon monoxide. Thus, the intermediate carbonium ion (12) has partly converted to the alcohol (9) by hydroxidation with water. The formation of the reductive product (16), however, remaines unsolved.

On the other hand it is remarkable that formolysis of the mesylate (11) at the relatively high temperature of 80°C for 10 min gave exclusively the dehydrated spiro dimer (18) besides the alcohol (9) and the hydrocarbon (16) in the similar yields with those of the formolysis at 50°C.

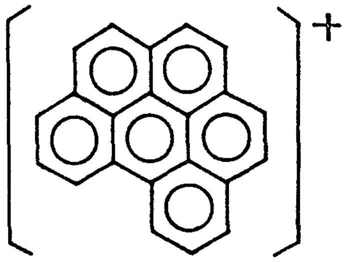
The structures of the alcohol (9) and the reductive product (16) were identified from their nmr spectra which were identical to those of their authentic samples. The authentic (16) was synthesized by lithiation of (14) with butyllithium followed by methylation with methyl iodide as described in the following section.

The product (17) is air sensitive pale yellow crystals with mp 158-162°C (decmp.). Both the elemental analysis, which afforded satisfactry values for a mlecular formular $C_{40}H_{24}$, and the mass spectrum of (17), ($M^+$, 25%), 276 (the benzoperylene ion



Scheme 3.

(19), 100%), clearly indicated it to be a dimer of (8). The structure of (17) was convincingly established on the basis of its nmr spectrum which shows a benzyl methin signal at δ 5.01 (t, J=7.5 Hz)) and four methylene protons signal at δ 2.38-2.68 (m) along with nineteen aromatic protons signal at δ 7.00-7.94 (m). The assignments of signals at δ 5.01 and 2.38-2.68 were confirmed by double resonance experiment, thus irradiation at about δ 2.6 changed the broad triplet at δ 5.01 into a broad singlet and contrary irradiation at δ 5.01 changed the multiplet at δ 2.38-2.68 to AA'BB'-like multiplet (see Fig. 4). Further supportive evidence of the structure (17) was gained by the fact that the absorption spectrum of (17) is closely similar to that of the hydrocarbon (16) in absorption maxima and intensities as shown in Fig. 6.



(19)

On the other hand, while the pronounced sensitivity of other product (18) resulted from the relatively high temperature formolysis makes the results of both elemental analysis and mass spectral measurement unsatisfactory, the structure of (18) was confirmed by its nmr and electronic spectra and chemical evidence. The nmr spectrum of (18) (Fig. 5) shows a doublet at δ 3.18 (2H, J=5.0 Hz) and triplet at δ 6.47 (1H, J=5.0 Hz) along

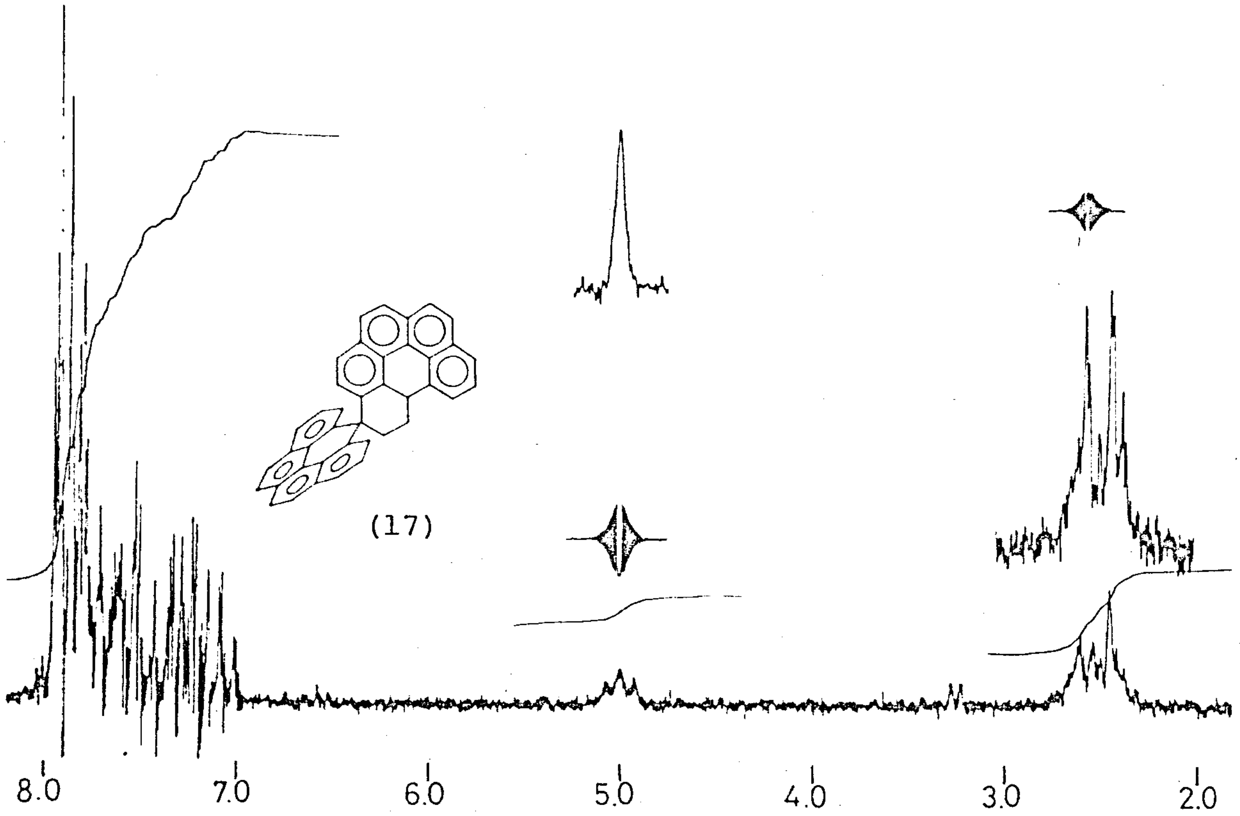


Fig. 4. The NMR Spectrum of (17) in $CDCl_3$.

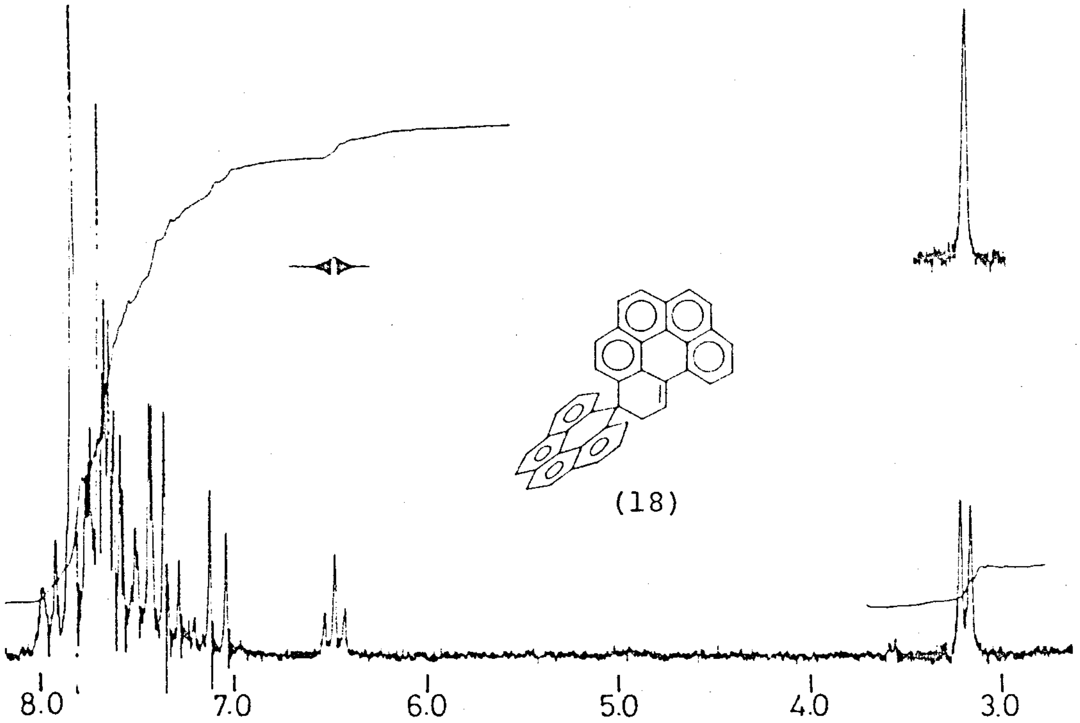


Fig. 5. The NMR Spectrum of (18) in $CDCl_3$.

with multiplet of the nineteen aromatic protons at about δ 7.03-7.93. Irradiation at δ 6.47 converted the doublet at δ 3.18 into a clear singlet as shown in Fig. 5.

In the electronic spectrum of (18), as depicted in Fig. 6, there is characteristic extension of the long wavelength absorption maxima into the visible region.  This clearly suggested the

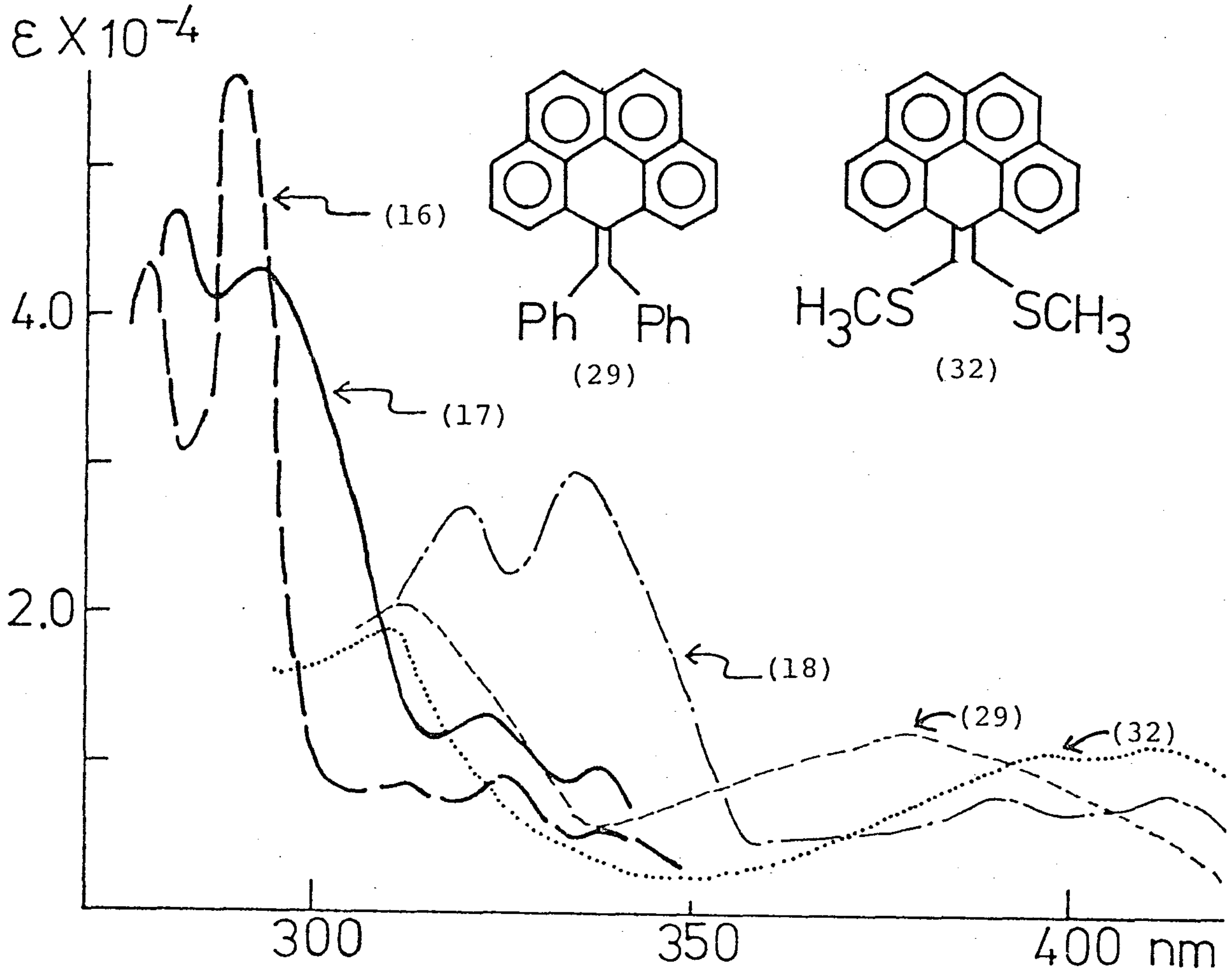


Fig. 6.  The Electronic Spectra of (17), (18), (16), (29), and (32).

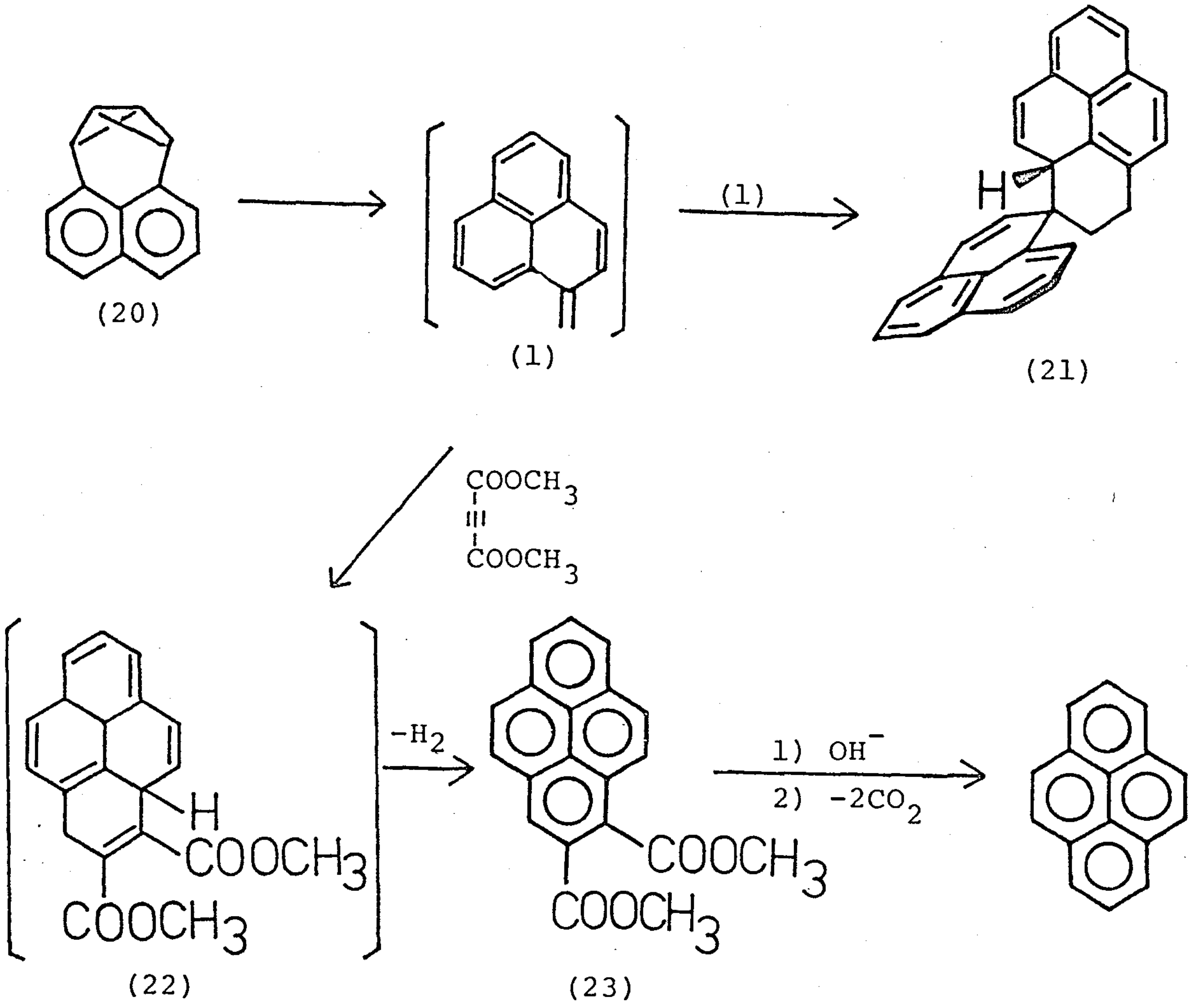
existence of a 6-methylenebenzo[cd]pyrene chromophore in its molecule. This conclusion was also supported by the comparison of the spectrum of (18) with those of some derivatives of 6-methylenebenzo[cd]pyrene, (32) and (29), whose preparations will be described in following sections. In an attempt to further confirm the structure (18), the dihydro-compound (17) was oxidized in benzene with iodine. The product was produced in 45% yield and identified as (18) by its nmr and electronic spectra.

### 3.2.2. Mechanistic Aspects of solvolysis of the mesylate (11)

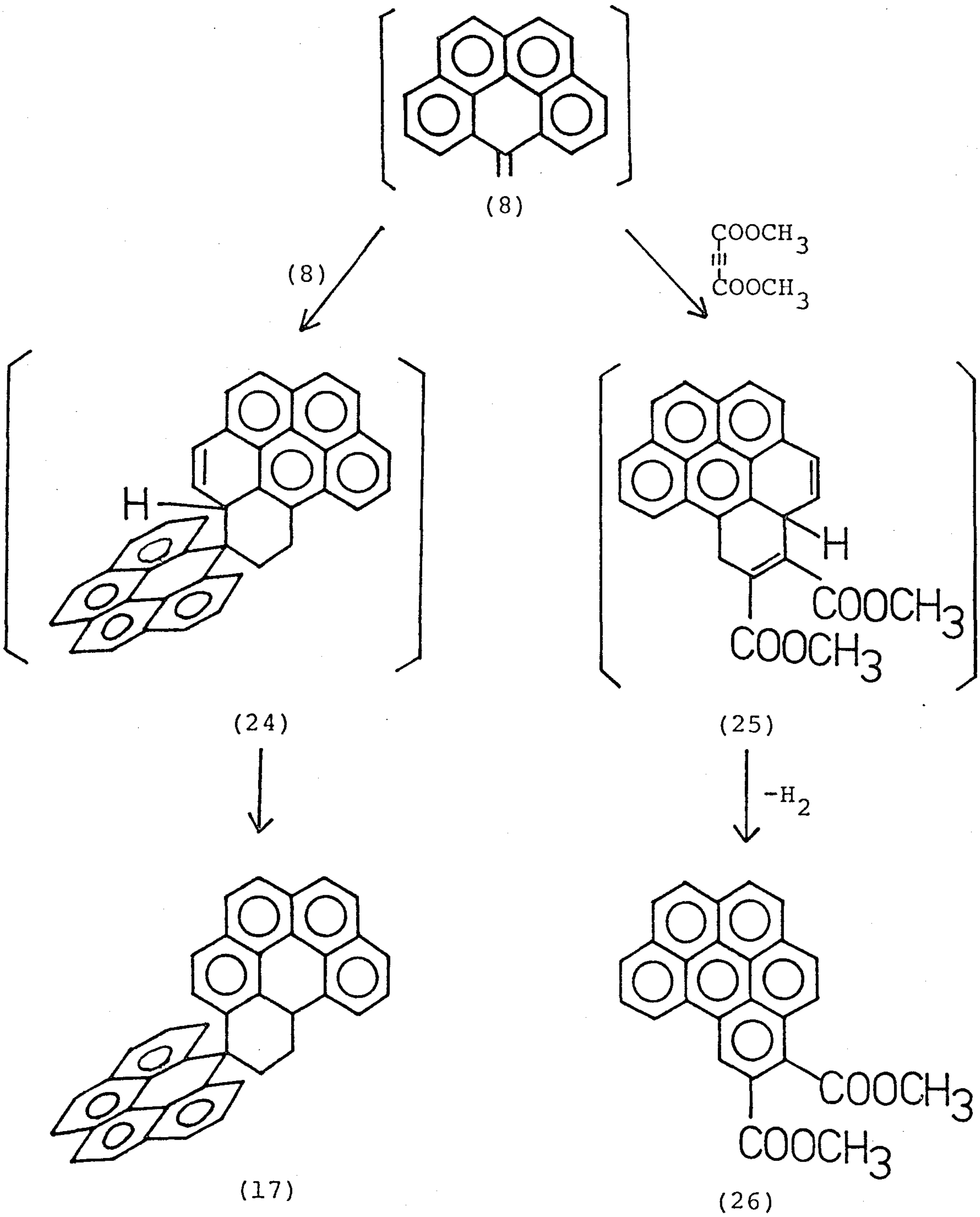
From the mechanistic viewpoint we will consider the results described in preceding section on the basis of the product analysis and trapping experiment.

First, we consider the formation of the spiro dimers, (17) and (18). In the case of phenafulvene we have already reported12) the formation of its dimer by transition metal promoted isomerization of naphtho[1,8]tricydo[4.1.0.0$^{2,7}$]heptene (20). Namely, when (20) was treated with transition metal complex, such as Pd or Rh, a rapid reaction occured to give a phenafulvene dimer (21) together with other products. Furthermore, the transient formation of phenafulvene was revealed by trapping experiment with dimethyl acetylenedicarboxylate. The above isomerization was carried out in the presence of dimethyl acetylenedicarboxylate to give the dimethylester of pyrenedicarboxylic acid (23) presumably via (22), which could be hydrolized and decarboxylated to afford pyrene as depicted in Scheme 4.

Therefore, the formation of the dimer (17) in the solvolysis of (11) is considered to proceed closely analogous pathway



Scheme 4.

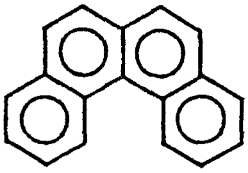

(8)
(8)
COOCH3
COOCH3
H
(24)
H
COOCH3
COOCH3
(25)
-H2
(17)
COOCH3
COOCH3
(26)

Scheme 5.

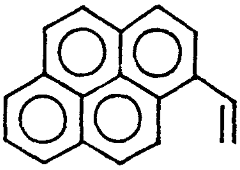
with that of the formation of the phenafulvene dimer (21). Thus, the results obtained in the solvolysis of the mesylate (11) can be explained as a mechanism shown in Scheme 5.

The intermediate carbonium ion (12) generated from the mesylate (11) converted into 6-methylenebenzo[cd]pyrene (8) through loss of a proton, which readily dimerized into the transient dimer (24) because (8) is not stable enough to be isolated as well as phenafulvene. In this case, however, the striking feature is that unlike the case of the phenafulvene dimerization (24) has undergone hydrogen migration to rsult in the dimer (17). The ease of the hydrogen migration may be attributed to the difference in π-electron energy between benzo[a]phenanthrene and 1-vinylpyrene moieties in these molecules, (17) and (24). Thus, variable-β SCF molecular orbital calculations revealed benzo[a]phenanthrene (27) is more stable than 1-vinylpyrene (28) by 11 Kcal/mol.

The substantial difference in stability of (27) and (28) is at least mainly responsible for the following finding e. g., there are significant differences in stability and reactivity

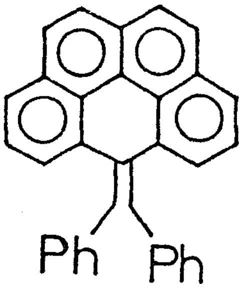


(27)

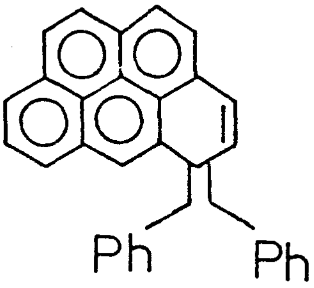


(28)

between 6-diphenylmethylenebenzo[cd]pyrene (29) and 5-diphenylmethylenebenzo[cd]pyrene (30) [vide infra].



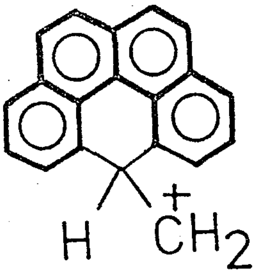
(29)



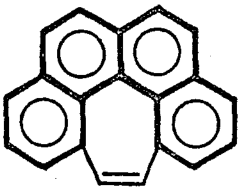
(30)

In this case too, trapping experiment with dimethyl acetylenedicarboxylate has been performed to prove the existence of 6-methylenebenzo[cd]pyrene as a intermediate. The mesylate (11) was treated in formic acid at 40-50°C for 4 hr in the presence of dimethyl acetylenedicarboxylate followed by the usual work-up and purification with column chromatography on alumina to give a mixture of the alcohol (9) and 5,6-dicarbomethoxybenzo[ghi]perylene (26) along with (16) and (17). Although (26) could not be isolated, the structures of (9) and (26) were identified by the nmr spectral characteristics and the relative ratio of (9) and (26) (23% and 3.4%) was determined by the integration of the spectrum. The pure (26) is characterized as described in Section 3.2.3.

Next, we must consider the experimental fact that the expected ring expansion product (13) can not be isolated in the solvolysis of the mesylate (11). The reason is assumed to be the increased molecular strain caused by the ring expansion reaction because of the rigidity of the benzo[a]phenanthrene moiety in the carbonium ion (12). In order to test this working hypothesis the solvolysis of the alcohol (9) in polyphosphoric acid was carried out, which is considered to be more drastic conditions than those described above. However, when the alcohol (9) was heated at 80°C for a few minutes or 40-50°C for 1 hr under nitrogen atmosphere, the dehydrated spiro dimer (18) was resulted as a sole product through column chromatography on alumina. Although the reason for the unsuccesful synthesis of (13) is not clear at this stage, most important factor is presumed to be the rigidity of the benzo[a]phenanthrene skeleton.



(12)



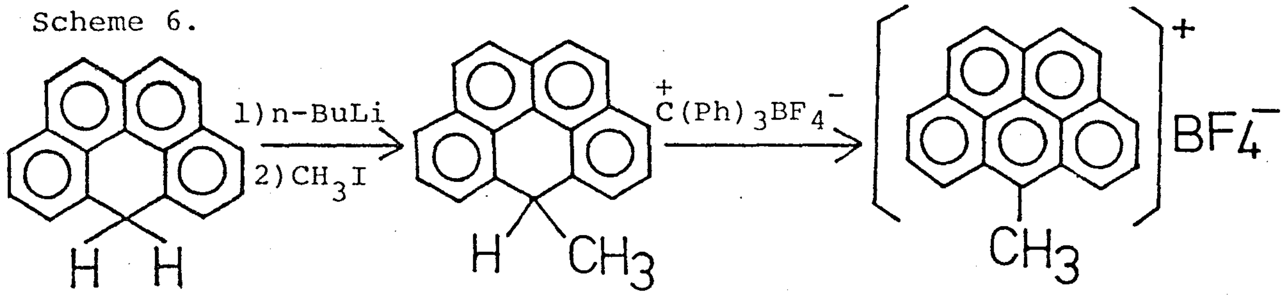
(13)

### 3.2.3. Attempted Isolation of the Parent 6-Methylenebenzo[cd]-pyrene

In preceding sections we have indicated the formation of 6-methylenebenzo[cd]pyrene (8) as a transient intermediate species but its isolation failed. However, since the synthesis of (8) is of much interest to know both its electronic state and thermal stability in comparison with that of the parent phenafulvene (1), we examined the synthesis of (8) through the alternate pathway.

To this end, 6-methylbenzo[cd]pyrenium tetrafluoroborate (31) was chosen as an attractive key intermediate, which might convert to (8) by loss of a proton. 6-methyl-6H-benzo[cd]-pyrene (16) was readily accessible from (14) through lithiation with butyllithium followed by methylation with excess methyl-iodide in 92% yield. Treatment of (16) with slight excess of triphenylmethyl tetrafluoroborate in chloroform gave a 83% yield of the desired carbonium ion (31) (see Scheme 6). The compound

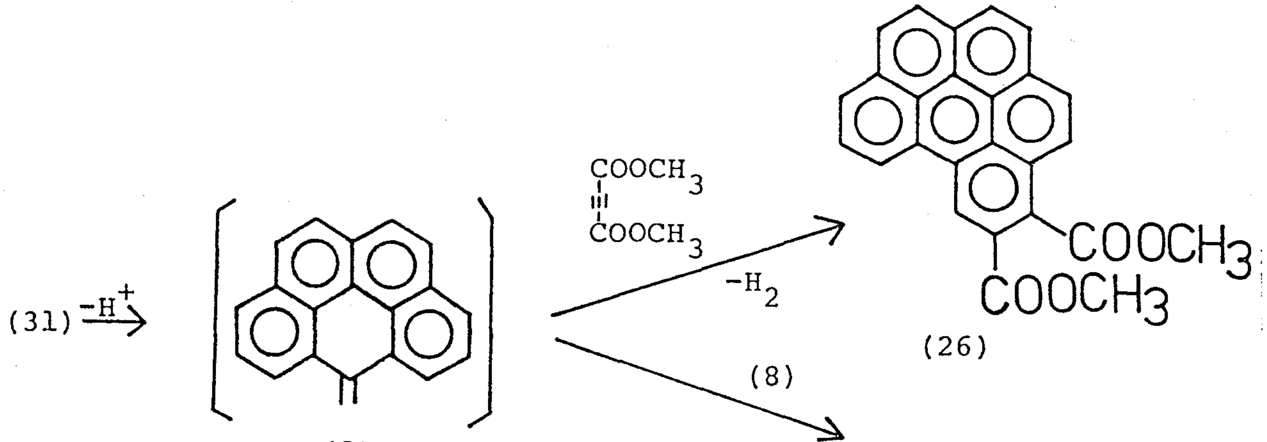
Scheme 6.



(14) (16) (31)

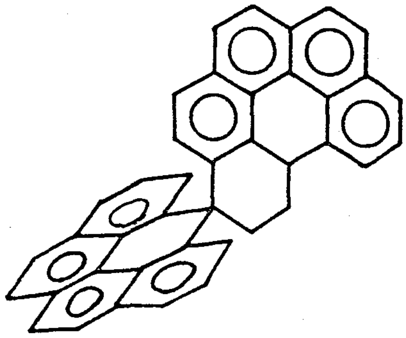
(16) is air sensitive yellow crystals, mp 122-124°C. The structure of (16) is clearly supported by its spectroscopy. Its mass spectrum shows intense peaks at m/e 254 ($M^+$, 17%) and 239 ($M^+-CH_3$, 100%), and its nmr spectrum shows signals at $\delta$ 1.56 (d, $-CH_3$, J=7.3 Hz), and $\delta$ 4.77 (q, H-6, J=7.3 Hz) along with multiplet at $\delta$ 7.5-7.9 (aromatic protons),which are in good agreement with the structure (16). The compound (31) has high melting point ( >350°C) and decomposed on exposing to moisture with fading to yellow. The ir spectrum of (31) displays a strong band at about 1080 $cm^{-1}$ suggesting the existence of tetrafluoroborate anion. Its nmr spectrum shows an AB-quartet at $\delta$ 8.33 (d, J=8.6 Hz, H-1,11) and $\delta$ 8.57 (d, J=8.6 Hz, H-2,10), a doublet of doublets at $\delta$ 8.41 (J=7.0 Hz and 6.5 Hz, H-4,8), a doublet at $\delta$ 9.12 (J=6.5 Hz, H-3,9), a doublet at $\delta$ 9.51 (J=7.0 Hz, H-5,7), and a singlet at $\delta$ 3.87 ($-CH_3$), which are in full accord with the structure of (31).

The proton abstruction reaction from the carbonium ion (31) was carried out. When a solution of triethylamine or 1,5-diazabicyclo[5.4.0]undecene-5 (DBU) in chloroform was added to the suspension of the carbonium ion (31) in chloroform at 0°C under nitrogen atmosphere the spiro dimer (17) was obtained as an isolated product through usual work-up and column chromatography on alumina. The reaction was conducted in the presence of dimethyl acetylenedicarboxylate and, after usual work-up the products were chromatographed twice on alumina and recrystallized from hexane-benzene to give the analytically pure dicarbomethoxybenzo[ghi]perylene (26) in 5% yield as reddish brown crystals



(8)

Scheme 7.



(17)

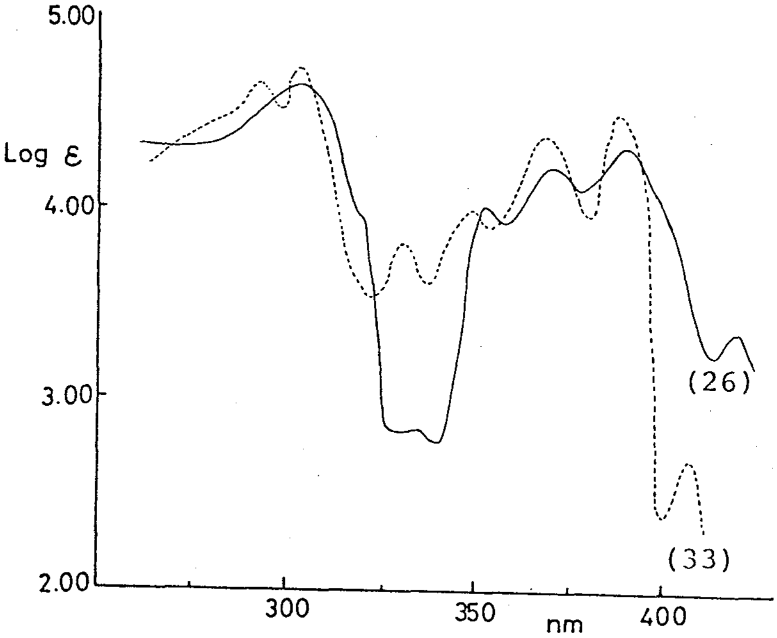


Fig. 7 The Electronic Spectra of (26) and (33).

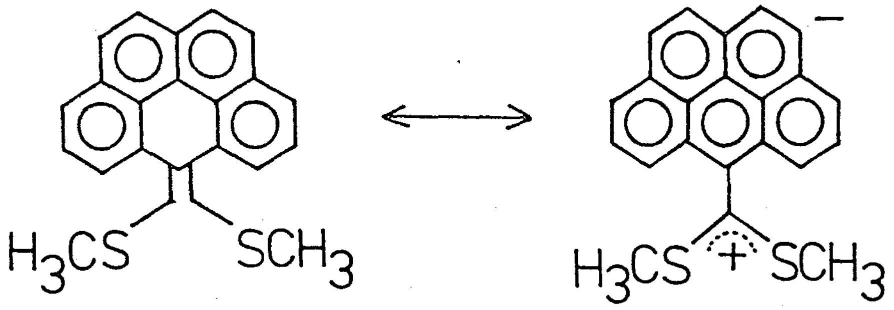
with mp 239-240°C. The structure of (26) was confirmed through combination of its elemental analysis and mass, electronic, and nmr spectroscopy. Its mass spectrum shows intense peaks at m/e 392 ($M^+$, 100%), 361 ($M^+$-$OCH_3$, 28%), and 274 ($M^+$-2$COOCH_3$, 28%), and nmr spectrum shows a pair of singlets of methoxy groups at $\delta$ 4.10 and 4.17, a doublet of doublets at $\delta$ 8.92 (H-8, $J_{8,9}$= 7.7 Hz, $J_{8,10}$=1.5 Hz), and a singlet at $\delta$ 9.41 (H-7) along with other aromatic protons multiplet at $\delta$ 7.87-8.28, which are in full accord with the structure of (26). Further proof of this structure was gained from its electronic spectrum. As can be seen in Fig. 7, the absorption spectrum of (26) is closely similar to that of its parent hydrocarbon (33)$^{13)}$ both in absorption maxima and in intensities.

On the other hand, while the proton abstraction reaction from (31) with triethylamine was performed even at about -10-15°C, which is a limit temperature range of the reaction to proceed, monitered by thin layer chromatography on alumina, none of the hydrocarbon product except for the dimer (17) could be detected.

In conclusion, as well as phenafulvene (1), the desired parent 6-methylenebenzo[cd]pyrene (8) can not be isolated due to its pronounced thermal instability as far as it is generated under the conditions described above.

## 3.3. Synthesis and Characterization of 6-Bis(methylthio)methylenebenzo[cd]pyrene

We attempted to synthesize 6-bis(methylthio)methylenebenzo[cd]pyrene (32) as a first example of substituted methylenebenzo[cd]pyrene containing polar group on the exocyclic methylene carbon atom. The compound (32) is of much interest since it was expected that there is a significant contribution of charge separated resonance form, such as (32'), to the ground state of (32).

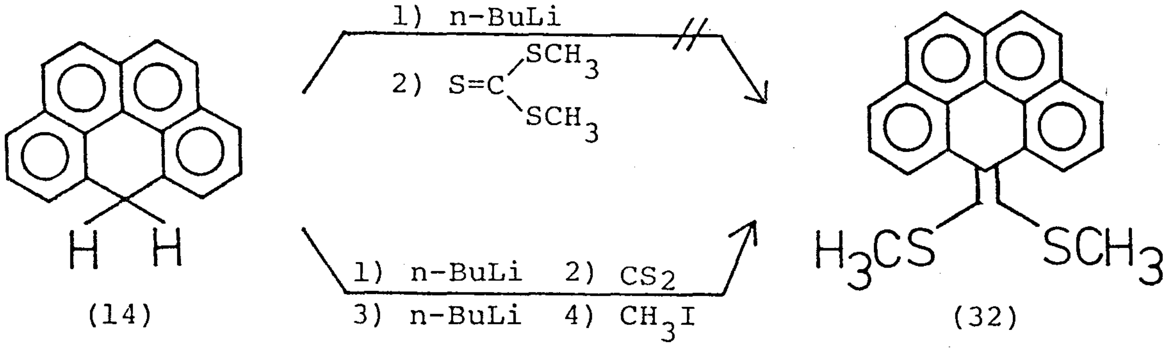


(32) (32')

Although in order to synthesize (32) we firstly examined the reaction of 6H-benzo[cd]pyrene (14) and butyllithium followed by condensation with dimethyl trithiocarbonate as illustrated in Scheme 8, we have failed in obtaining the desired compound (32), because the condensation reaction could not proceed at -10°C. Even at this temperature the intermediate benzo[cd]pyrenyl anion gradually decomposed. However, the successful synthesis of (32) was achieved by stepwise reactions shown in Scheme 8. Thus, 6H-benzo[cd]pyrene (14) was allowed to lithiation with an equimolar amount of butyllithium in tetrahydrofuran under nitrogen atmosphere followed by condensation of the anion with an equimolar amount of carbon disulfide. The resultant mixture was once more treated with an equimolar amount of butyllithium followed by quenching of the resulted anion with a large excess of methyl iodide to give the crude product (32). Recrystallization of the crude product from hexane-benzene afforded the analytically pure (32) in 28% yield as yellow prisms, mp 143-143.5°C.

The structure of (32) is convincingly assigned from its elemental analysis and spectroscopic data.

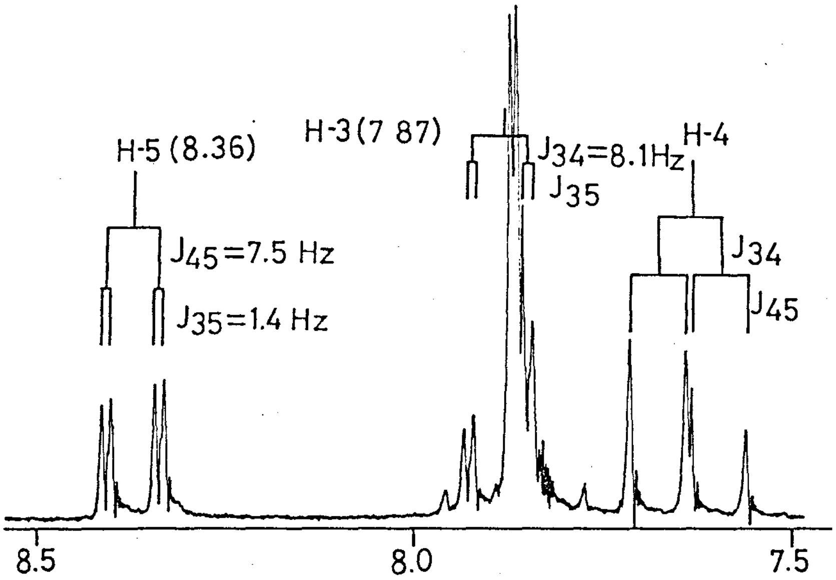
Scheme 8.

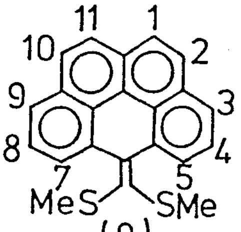


Its mass spectrum shows intense peaks at m/e 344 ($M^+$, 48%), 328 ($M^+-CH_4$, 44%), 314 ($M^+-2CH_3$, 10% ), and 282 ($M^+-CH_3$, $SCH_3$ 100%) and its nmr spectrum shows a singlet at $\delta$ 2.19 (2-$CH_3$), a doublet of doublets at $\delta$ 7.63 (H-4,8, $J_{3,4}=J_{8,9}=8.1$ Hz, $J_{4,5}=J_{7,8}=7.5$ Hz), a AB-quartet at $\delta$ 7.82 and 7.90 (H-1,2,10,11, $J_{1,2}=J_{10,11}=9.0$ Hz), a doublet of doublets at $\delta$ 7.87 (H-3,9, $J_{3,5}=J_{7,9}=1.4$ Hz), and a doublet of doublets at $\delta$ 8.36 (H-5,7). The above assignments were confirmed by double resonance experiment, the irradiation at $\delta$ 7.63 changed the doublet of doublets at $\delta$ 8.36 assigned to H-5 and 7 into doublet with coupling constant J=1.4 Hz. The first-order analysis of the spectrum and a symmetrical pattern of the signals coupled with an equivalence of two methylthio groups are in full accord with the assigned structure of (32). The electronic spectrum of (32) is shown in Fig. 6.

The exclusive formation of (32) is in good agreement with the predictions from Hückel molecular orbital theory as in the case of the preparation of 6-methyl-6H-benzo[cd]pyrene described in preceding section. Thus, electrophilic reaction in lithium benzo[cd]pyrenide should be preferentially allowed to occur at C-6 position.

The characteristic feature in this molecule (32) is that the methyl protons signal in its nmr spectrum has appeared in





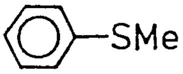
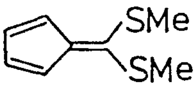
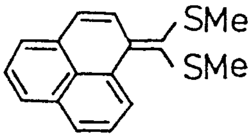
(9)

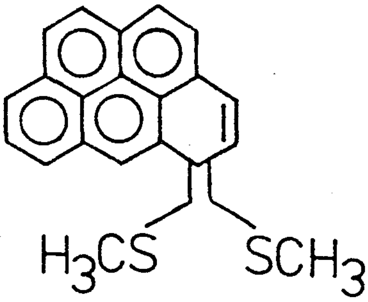
Fig. 8. The NMR Spectrum of (32) in $CDCl_3$.

rather upfield region compared with those of model compounds listed in Table 2.[1)] Despite the presence of powerful electron donating methylthio groups, it was concluded the minor contribution of the charge separated resonance form such as (32') to the ground state of (32).

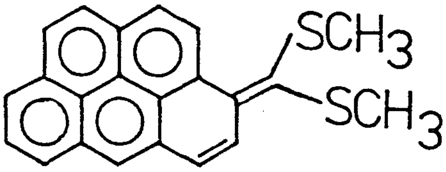
This fact is believed to be caused by the steric and electronic effects. That is to say, the π-electron conjugation between the methylthio groups and the benzo[cd]pyrenyl moiety through the exocyclic double bond was strongly inhibited by the nonplanarity of the molecule which is derived from the close proximity of two peri-hydrogens, H-5 and H-7, and two methylthio groups. Furthermore, the largest nonbonding molecular orbital coefficient at the site bearing the exocyclic double bond, C-6, in the benzo[cd]pyrenyl system is partly responsible for the minor charge separation in (32). Detailed interpretation must await the syntheses of hitherto unknown isomeric compounds such as (35), (36), and (37).

Table 2.

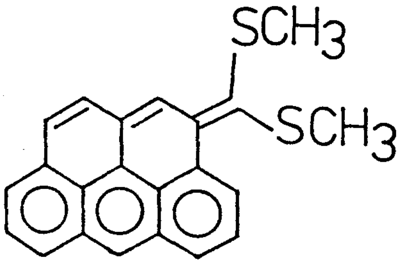
| Compounds | δ (ppm) |
|---|---|
|  | 2.25 |
|  | 2.42 |
|  | 2.48 |
|  | 2.40<br>2.47 |



(35)



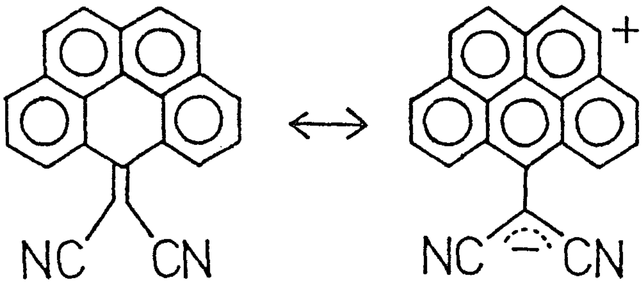
(36)



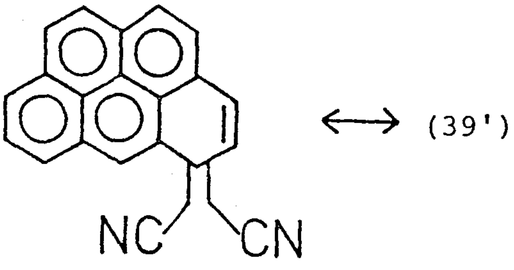
(37)

## 3.4. Syntheses and Characterization of 3- and 5-Dicyanomethylenebenzo[cd]pyrene

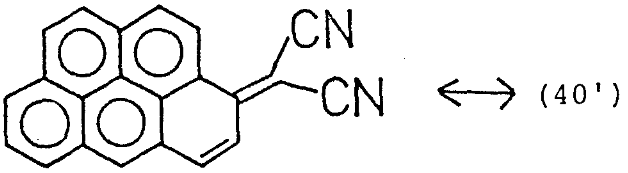
As a part of our study of the chemistry of methylenebenzo[cd]pyrene, we tried to synthesize its derivatives which contain nitrile groups at the exocyclic methylene group such as (38), (39), and (40). In these molecules it is expected that there is a large contribution of charge separated resonance form, such as (38') and so on, to the ground state because of incorporation of two strongly electron attractive nitrile groups.



(38) (38')

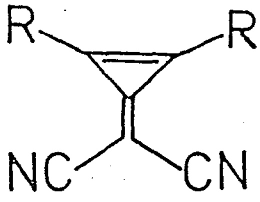


(39)

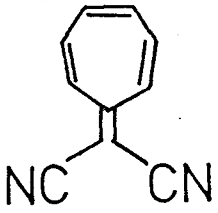


(40)

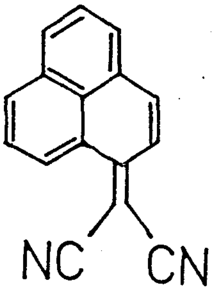
Recently a number of various fulvene type compounds have been prepared. The stabilities of the fulvenes are markedly affected by the introduction of electron withdrawing groups at the exocyclic position, which results in stabilization of the dipolar form. Evidently, the dicyanomethylenecyclopropenes (41)[14] and 8,8-dicyanoheptafulvene (42)[15] are known to be stable compounds. In the case of the phenafulvene (43),[16] dicyano substitution at exocyclic position is to stabilize the molecule because of the well-known electron stability of the phenalenium cation. Similar situation would also be expected in the isomeric derivatives of (38), (39), and (40) which might be supposed as good model compounds to examine the theoretical consideration as described in Section 3.1.



(41)



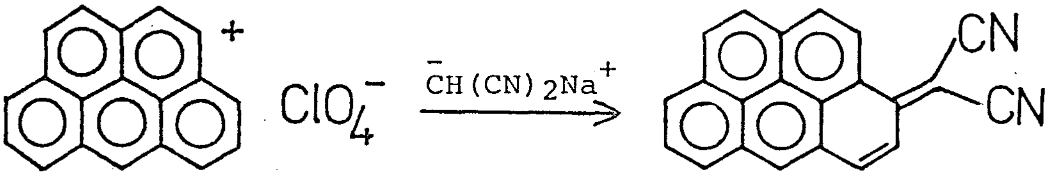
(42)



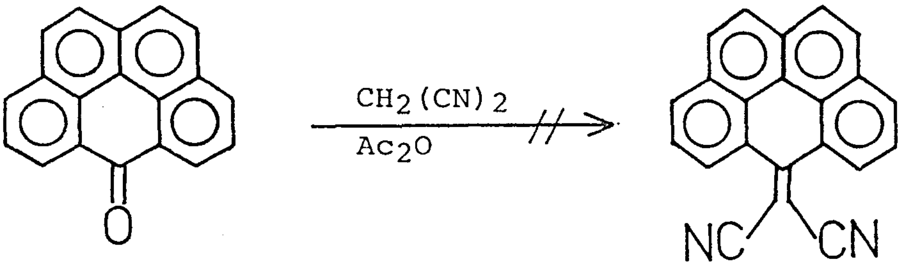
(43)

Attempted synthesis of (38) by the condensation reaction of the benzo[cd]pyrenyl perchlorate with the sodium salt of malononitrile failed to give (38). Instead the only product isolated was found to be the isomeric (40) as deep purple needles, mp > 350°C, in 7.3% yield. The structure of (40) is unequivocally proved through its nmr spectrum (vide infra).

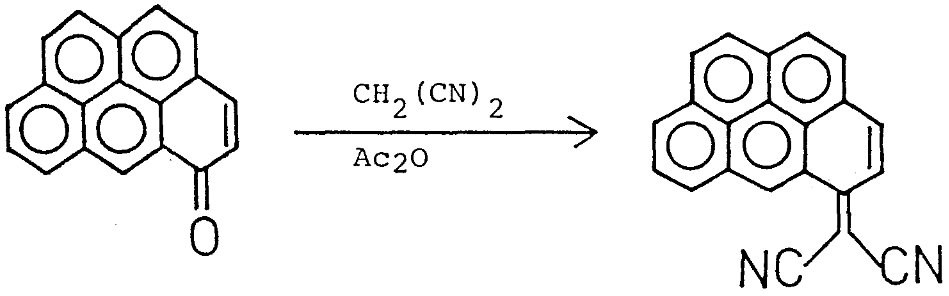
Although an alternate route to (38) consists of dehydrative condensation of the ketone (44) and malononitrile in acetic anhydride, no reaction occured and the ketone (44) was recovered quantitatively.



(40)



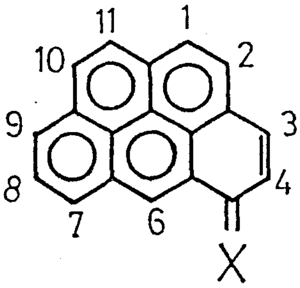
(44) (38)



(45) (39)

On the other hand, similar direct condensation of the ketone (45)[17)] and malononitrile in refluxing acetic anhydride gave 5-dicyanomethylenebenzo[cd]pyrene (39) as deep purple crystals, mp 297-298°C in 8.3% yield.

The structures of (39) and (40) were established through their elemental analyses and spectroscopic properties. Mass spectra of the both products exhibit molecular ion peak at m/e 302 as base peak and both ir spectra exhibit strong band at 2200 $cm^{-1}$ which suggests the existence of conjugated nitrile group. The observed nmr spectral data of (39) and (40) were summarized in Table 3 and 4. Because of their low solubility in usual organic solvents the acceptable spectrum of (39) shown in Fig. 9 was recorded by using pulse Fourier-Transform technique, and the spectrum of (40) shown in Fig. 11 was recorded in arsen trichloride by CW method. As can be seen in Table 3 and 4, H-4 and H-6 of (39), and H-2 and H-4 of (40) are more deshielded than the respective protons of the corresponding ketones (45) and (46). Similar observation was found in the case of phenalenone (47) and dicyanomethylenephenalene (43).[9a)] Accordingly, the structure of (39) and (40) were convincingly borne out by the fact that the nmr spectrum of either (39) or (40) has closely similar pattern to that of (45) or (46), respectively.



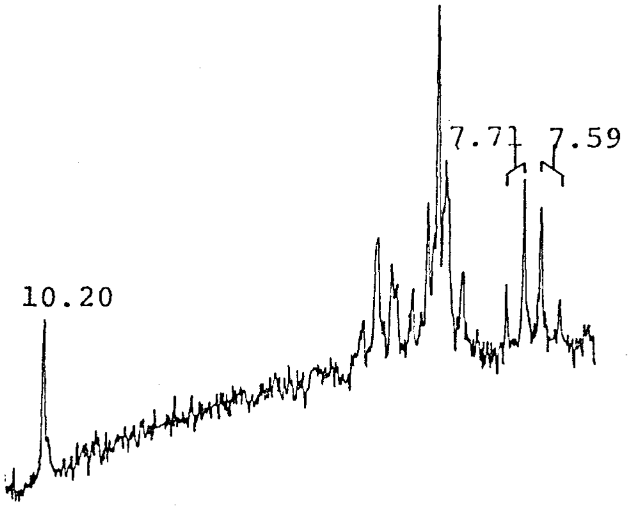


Fig. 9. The NMR Spectrum of (39) in $CDCl_3$.

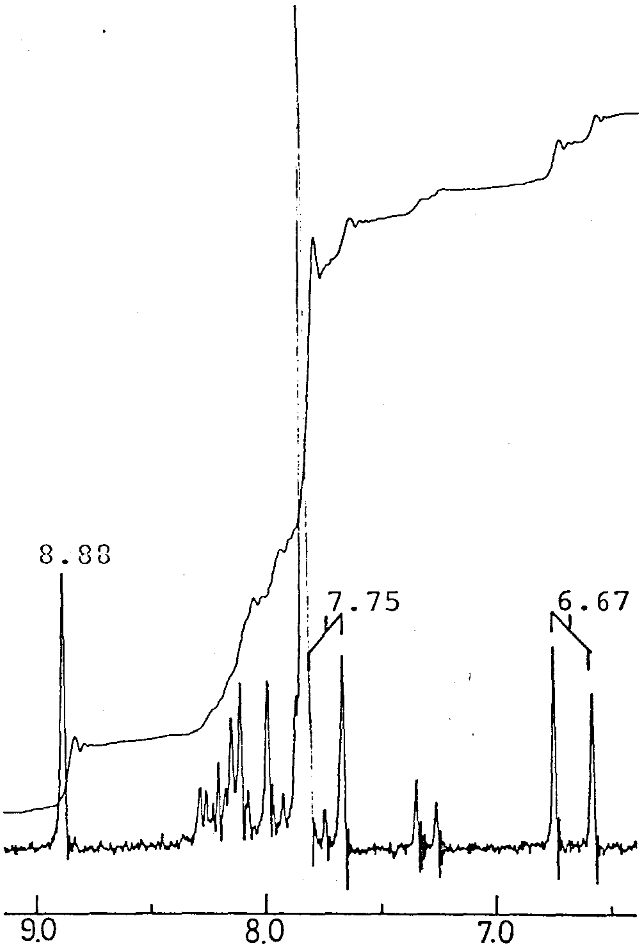
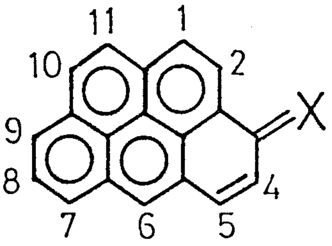
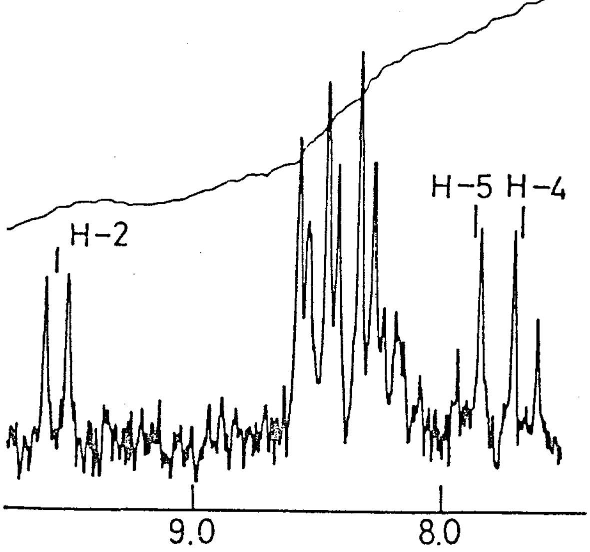


Fig. 10. The NMR Spectrum of (45) in $CDCl_3$.

Table 3. The NMR Spectral Data of (39) and (45).

| Proton | (39) | | (45) | |
|---|---|---|---|---|
| | Multipl. and Chem.Shift (δ) | Coupl. Const. | Multipl. and Chem. Shift (δ) | Coupl. Const. |
| 3 | d, 7.71 | $J_{3,4}$ | d, 7.75 | $J_{3,4}$ |
| 4 | d, 7.59 | =9.0Hz | d, 6.67 | =9.9Hz |
| 6 | s, 10.20 | | s, 8.88 | |
| others | m, 8.0-8.4 | | m, 7.7-8.3 | |





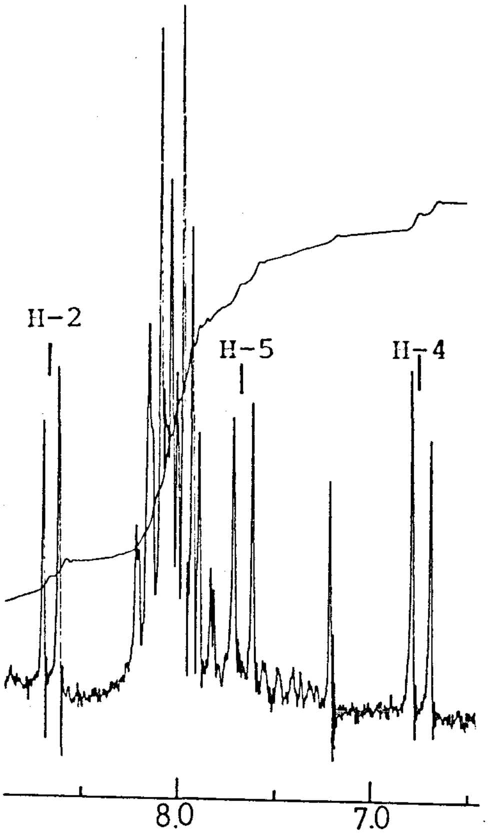


Fig. 11. The NMR Spectrum of (40) in $AsCl_3$.

Fig. 12. The NMR Spectrum of (46) in $CDCl_3$.

Table 4. The NMR Spectral Data of (40) and (46).

| Proton | (40) Multipl. and Chem. Shift (δ) | (40) Coupl. Const. | (46) Multipl. and Chem. Shift (δ) | (46) Coupl. Const. |
|---|---|---|---|---|
| 2 | d, 9.55 | $J_{1,2}$ =9.0Hz | d, 8.69 | $J_{1,2}$ =8.5Hz |
| 4 | d, 7.68 | $J_{4,5}$ =9.0Hz | d, 6.76 | $J_{4,5}$ =8.5Hz |
| 5 | d, 7.86 | | d, 7.68 | |
| others | m, 8.2-8.6 | | m, 7.8-8.2 | |

Let us consider the above mentioned experimental results. Inspite of the prediction that the reaction of the benzo[cd]-pyrenyl cation with nucleophiles should preferentially occur at C-6 position of highest charge density,[17)] the actual product of the cation and sodium salt of malononitrile was (40). When a steric factor is taken into account, attack of C-3 and/or C-5 is some advantage than that of C-6. In the case of the reaction, however, even in a low yield the preferential formation of (40) is puzzling, since the Hückel charge densities at these carbon atoms are calculated to be equal. The failure of the reaction between the ketone (44) and malononitrile seems attributable to the relatively large steric effect and/or low reactivity of (44) compared with (45). The latter reason can be expected from the difference between (44) and (45) in carbonyl stretching frequency and basicity.[18)] (see Sec. 2.5).

The electronic spectra of (39) and (40) were depicted in Fig. 13 along with the corresponding ketones (45) and (46). As can be seen in Fig. 13, the longest wavelength absorption maximum of (39) is shifted bathochromically than that of (40) as in the case of the respective ketones (45) and (46).

The results shown here indicate that the significance of the contribution of the dipolar form such as (39') and (40'), respectively is assumed to be in the same extent with those of the corresponding ketones (45) and (46). Since the synthesis of (38) is not achieved to date the exact comparison of these dicyanomethylenebenzo[cd]pyrenes remains a subject of further study.

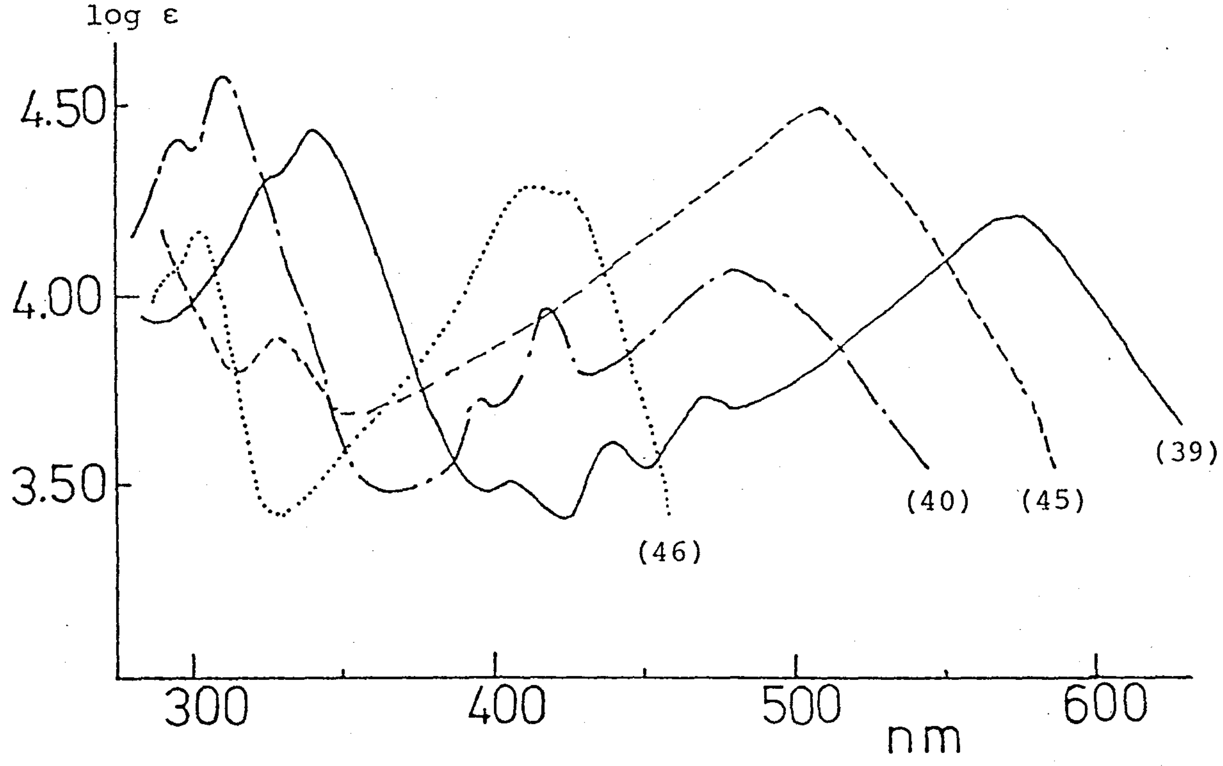


Fig. 13. The Electronic Spectra of (39), (40), (45), and (46).

## 3.5. Experimental

Exp. 1. 6-Carbomethoxy-6H-benzo[cd]pyrene (15):

To a stirred solution of 6H-benzo[cd]pyrene (14) (4.2 g, 17.5 mmol) in 30 ml of dry THF was added 17.5 mmol of butyllithium in hexane at -60°C under nitrogen atmosphere. After stirring the dark brown solution at the same temperature for 30 min carbon dioxide (dried through concd. sulfuric acid and over phosphorous pentoxide) was bubbled into the solution, which was warmed to 0°C over 3 hr under carbon dioxide bubbling. After acidified with dil. hydrochloric acid, the reaction mixture was extracted with ether. The ether layer was washed with water and extracted with saturated aqueous solution of sodium hydrogen carbonate. After washing with ether the aqueous layer was acidified with concd. hydrochloric acid in an ice bath to give colorless precipitates. The solids were extracted with ether and the ether layer was washed with water and dried over anhydrous sodium sulfate. The crude carboxylic acid was treated with diazomethane under nitrogen atmosphere to give crude methyl ester (15). The product was chromatographed on alumina eluting with hexane-benzene (1:1) and recrystallized from hexane-benzene to give analytically pure (15) as pale yellow needles in a 63% yield, mp 149-150°C.

Anal. Calcd for $C_{21}H_{14}O_2$ : C, 84.54; H, 4.73%.
Found : C, 84.32; H, 4.72%.

MS. m/e 298($M^+$, 12%), 239($M^+$-$COOCH_3$, 100%).

IR(KBr). $\nu_{C=O}$; 1725 $cm^{-1}$.

NMR($\delta$ in $CDCl_3$). 3.51(s, 3H, $-CH_3$), 5.81(bs, 1H, H-6), 7.41-7.81 (m, 10H, aromatic protons).

ES(hexane). $\lambda_{max}$(log $\varepsilon$); 373(2.23), 367(2.41), 362(2.45), 354 (2.76), 338(3.68), 325(3.92), 311(3.89), 290(4.65), 279(4.56), 235(4.52), 219(4.67).

Exp. 2. 6-Hydroxy-6H-benzo[cd]pyrene (9):

A solution of (15) (1.19 g, 4 mmol) in 120 ml of dry ether was added dropwise to a suspension of lithium aluminum hydride (152 mg, 4 mmol) in 20 ml of dry ether at -20°C over 2 hr under nitrogen atmosphere. After stirring for 3 hr at the same temperature the reaction mixture was quenched with ether saturated with water. The product was extracted with benzene and the organic layer was washed successively with dil. hydrochloric acid, saturated aqueous solution of sodium hydrogen carbonate and water. After the organic layer was dried over anhydrous sodium sulfate and evaporated under reduced pressure, the dark red residue was recrystallized from hexane-benzene (2:3) under nitrogen atmosphere to give 870 mg (80%) of (9) as brownish prisms, mp 119.5-122°C.

Anal. Calcd for $C_{20}H_{14}O$: C, 88.86; H, 5.22%.

Found : C, 89.15; H, 5.39%.

MS. m/e 270($M^+$, 3.2%), 239($M^+$-$CH_2OH$, 100%).

NMR ($\delta$ in $CDCl_3$). 1.6(bs, 1H, -OH), 3.60(d, 2H, J=6.5 Hz, -$CH_2$-O), 4.67(t, 1H, J=6.5 Hz, H-6), 7.49-7.91(m, 10H, aromatic protons).

ES($CH_3CN$). $\lambda_{max}$(log $\varepsilon$); 373(2.56), 366(2.50), 354(2.84), 336(3.65), 323(3.87), 310(3.85), 287(4.68), 277(4.57), 268 sh(4.31), 234(4.41), 220(4.61).

Exp. 3. 6-Mesyloxymethyl-6H-benzo[cd]pyrene (11):

To a stirred solution of (9) 270 mg (1 mmol) in 6 ml of dry methylene chloride containing 1.6 mmol of triethylamine was added dropwise 1.3 mmol of methanesulfonyl chloride in 7 ml of dry methylene chloride at -10°C over 30 min under nitrogen atomosphere. After stirring for 2 hr at the same temperature the solution was poured into ice water. The organic layer and the combined methylene chloride extracts were washed successively with cold dil. hydrochloric acid, saturated aqueous solution of sodium hydrogen carbonate and water, and dried over anhydrous magnesium sulfate. The solvent was evaporated under reduced pressure to give 277 mg (80%) of nearly pure mesylate (11) as brown yellow crystals. The crude mesylate was dissolved in 5 ml of methylene chloride and 5 ml of hexane under nitrogen atmosphere and the solution was concentrated to a volume of 4 ml. The solution was cooled gradually to -40°C to give a 172 mg (50%) of the analytically pure mesylate (11) as pale yellow needles, mp 120-122°C (dec.).

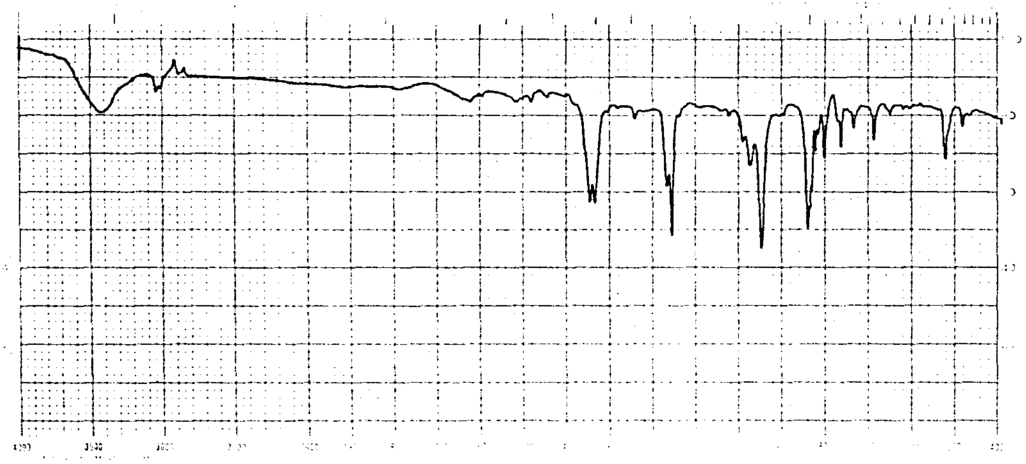
Anal. Calcd for $C_{21}H_{16}O_3S$: C, 72.39; H, 4.63; S, 9.20%.
Found : C, 72.13; H, 4.61; S, 9.05%.

MS. m/e 348($M^+$, 3%), 252($M^+$-OMs, 33%) 239($M^+$-$CH_2$OMs, 100%).

NMR(δ in $CDCl_3$). 2.39(s, 3H, $-SO_2-CH_3$), 4.28(d, 2H, J=6.5 Hz, $-CH_2-SO_2-$), 5.04(bt, J=6.5 Hz, 1H, H-6), 7.57-7.97(m, 10H, aromatic protons).

ES($CH_3CN$). $\lambda_{max}$(log ε); 365(2.80), 353(2.88), 335(3.72), 322(3.92), 310(3.90), 286(4.76), 276(4.64), 266(4.34), 234(4.51), 226(4.48), 219(4.69).

IR(KBr).



Exp. 4. Acetolysis of mesylate (11):

A solution of the mesylate (11) 140 mg (0.4 mmol) in 15 ml of dry acetic acid and 96 mg (0.8 mmol) of anhydrous sodium dihydrogen phosphate as a buffer was refluxed for 1 hr under nitrogen atmosphere. The reaction mixture was poured into water and extracted with benzene. The extracts were washed successively twice with saturated aqueous solution of sodium hydrogen carbonate and water, dried and the solvent was evaporated under reduced pressure. The residue was chromatographed twice on the deactivated alumina containing 3% of water eluting with hexane-benzene (9:1) to give 50 mg (50%) of the nearly pure spiro dimer (17) as pale yellow crystals, mp 158-162°C (decomp.).

Anal. Calcd for $C_{40}H_{20}$: C, 95.21; H, 4.79%.

Found : C, 94.98; H, 4.73%.

MS. m/e 504($M^+$, 25%), 276(benzo[ghi]perylene ion, 100%).

NMR(δ in $CDCl_3$). 2.68-2.38(m, 4H, H-6,6'7,7'), 5.01(bt, 1H, J=7.5 Hz, H-7a), 7.00-7.94(m, 19H, aromatic protons).

ES(hexane). $\lambda_{max}$(log ε); 338(4.00), 323(4.13), 293(4.63), 282 (4.67), 262 sh(4.43), 258 sh(4.22), 256(4.24), 249(4.19), 233(4.63), 219(4.74).

Exp. 5. Formolysis of mesylate (11):

A solution of the mesylate (11) 140 mg (0.4 mmol) in 14 ml of 99% formic acid and 96 mg (0.8 mmol) of anhydrous sodium dihydrogen phosphate as a buffer was heated to 40-50°C for 4 hr under nitrogen atmosphere. The solution was worked up by procedures same to those described in Exp. (4). The crude products were chromatographed on the deactivated alumina containing 3% of water eluting gradiently with hexane, hexane-benzene (9:1), and benzene. The solvents of the each fractions were stripped to give 4 mg of the reductive product (16) from the hexane eluate, 15 mg (15%) of the spiro-dimer (17) from the hexane-benzene eluate, and 26 mg, (26%) of the alcohol (9) from the benzene eluate. The structures of (16) and (9) were confirmed from the nmr spectra which are identical with those of the respective authentic compounds.

Exp. 6. Formolysis of mesylate (11) at high temperature:

A solution of the mesylate (11) 140 mg (0.4 mmol) in 14 ml of 99% formic acid and 96 mg (0.8 mmol) of anhydrous sodium dihydrogen phosphate as a buffer was heated from room temperature to 80°C over 15 min and maintained at this temperature for 10 min under nitrogen atmosphere. The reaction mixture was worked up by procedures same to those described in Exp. (4). The crude products were chromatographed on the deactivated alumina containing 3% of water eluting gradiently with hexane, hexane-benzene (9:1), and benzene to give 8 mg (7%) of (16), 15 mg (15%) of the dehydrospiro-dimer (18) as yellow crystals, and 23 mg (23%) of the alcohol (9).

(18):

MP. gradually decomposed at about 80°C.

NMR($\delta$ in $CDCl_3$). 3.18(d, 2H, J=5.0 Hz, H-6,6'), 6.47(t, 1H, J=5.0 Hz, H-7), 7.03-7.93(m, 19H, aromatic protons).

ES(hexane). $\lambda_{max}$(log $\varepsilon$); 413(3.92), 390(3.91), 334(4.47), 320(4.44), 279(4.66), 265 sh(4.61), 232(4.82), 216(4.96).

Exp. 7. Trapping of methylenbenzo[cd]pyrene. Formation of 5,6-dicarbomethoxybenzo[ghi]perylene (26):

A solution of the mesylate (11) 140 mg (0.4 mmol) in 14 ml of 99% formic acid containing 96 mg (0.8 mmol) of dimethyl acetylenedicarboxylate was heated at 40-50°C for 4 hr in the presence of 96 mg (0.8 mmol) of anhydrous sodium dihydrogen phosphate as a buffer under nitrogen atomophere. The reaction mixture was worked up by procedures same to those described in Exp. (4). The products were chromatographed on the deactivated alumina containing 2.5% of water eluting gradiently with hexane, hexane-benzene (9:1), and benzene to give 5 mg (4%) of (16), 10 mg (10%) of (17), and 30 mg of the mixture of (26) and the alcohol (9). The structures of (26) and (9) were identified by the nmr spectral characteristics and the relative ratio of (26) and (9) was determined by the integration of the spectrum.

Exp. 8. Dehydrogenation of spiro-dimer (17):

A solution of 55 mg (0.11 mmol) of the spiro-dimer (17) and 38 mg (0.3 mmol) of iodine in 6 ml of benzene was stirred at room temperature for 30 min under nitrogen atmospher. The solvent of the reaction mixture was stripped under reduced pressure. The products were chromatographed on the deactivated alumina containing 2.5% of water eluting with benzene and again on the same deactivated alumina eluting with hexane-benzene (9:1) to give 20 mg (45%) of the nearly pure dehydrospiro-dimer (18) as yellow crystals, which was identical in every respects with the authentic sample.

Exp. 9. Formation of dehydrospiro-dimer (18):

100 mg (0.33 mmol) of alcohol (9) was added to 15 ml of polyphosphoric acid and heated at 50-60°C for 1 hr under nitrogen atmosphere. The greenish black mixture was poured into ice

water and extracted with benzene. The extracts were washed successively with saturated aqueous solution of sodium hydrogen carbonate and water. The benzene solution was dried over anhydrous magnesium sulfate and the solvent was stripped. The residue was chromatographed on the deactivated alumina containing 2.5% of water eluting with hexane-benzene (9:1) to give 25 mg (31%) of the dehydrospiro-dimer (18) as yellow crystals.

Exp. 10. 6-Methyl-6H-benzo[cd]pyrene (16):

To a stirred solution of 6H-benzo[cd]pyrene (14) 1.56 g (6.5 mmol) in 70 ml of dry THF was added 6.5 mmol of butyllithium in hexane at -60°C under nitrogen atmosphere. After stirring the dark brown solution at the same temperature for 30 min a large excess of methyl iodide was added at once. The mixture was stirred for 1 hr at -50°C and warmed to room temperature gradually. The reaction mixture was poured into water and the products were extracted with benzene. After the organic layer was washed successively with 2N-hydrochloric acid, saturated aqueous solution of sodium hydrogen carbonate and water, was dried over anhydrous magnesium sulfate. After removal of the solvent the brown residue was chromatographed on alumina eluting with hexane-benzene (1:1). Evaporation of the solvent gave the crude compound (16), which was recrystallized from cyclohexane under nitrogen atmosphere to give pure (16) (1.51 g, 92%) as yellow crystals, mp 122-124°C.

Anal. Calcd for $C_{20}H_{14}$ : C, 94.45; H, 5.55%.

Found : C, 94.24; H, 5.55%.

MS. m/e 254($M^+$, 17%), 239($M^+$-$CH_3$, 100%).

NMR($\delta$ in $CDCl_3$). 1.56(d, 3H, J=7.3 Hz, -$CH_3$), 4.77(q, 1H, J=7.3 Hz, H-6), 7.5-7.9(m, 10H, aromatic protons).

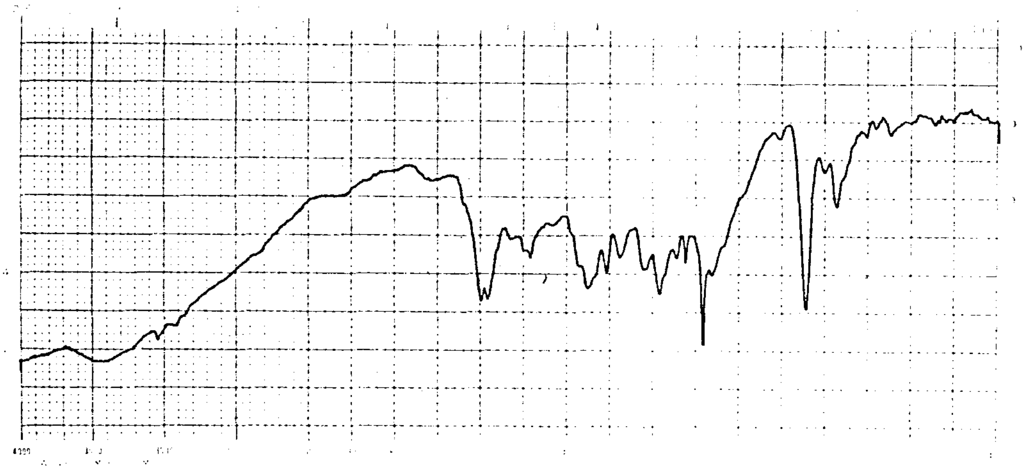
ES(hexane). $\lambda_{max}$(log $\varepsilon$); 338(3.77), 325(3.97), 312(3.95), 289(4.75), 278(4.64), 268.5(4.39).

Exp. 11. 6-Methylbenzo[cd]pyrenium tetrafluoroborate (31):

To a stirred solution of (16) 1.5 g (6.0 mmol) in 40 ml of dry chloroform was added powder of triphenylmethyl tetrafuloroborate 2.05 g (6.5 mmol) at room temperature. Black solids precipitated at once and the mixture was warmed at 50°C for 2 hr. After cooling to room temperature, the black solid mass was collected by filtration and washed with dry chloroform several times in a dry box. The product was dried in vacuo to give 1.7 g (5.0 mmol) of (31) in 83% yield, mp >350°C.

NMR($\delta$ in $CF_3COOH$). 3.87(s, 3H, -$CH_3$), 8.33(d, 2H, $J_{1,2}=J_{10,11}=$ 8.6 Hz, H-1,11), 8.57(d, 2H, H-2,10), 8.41 (dd, 2H, $J_{3,4}=J_{8,9}=$6.5 Hz, $J_{4,5}=J_{7,8}=$7.0 Hz), 9.12(d, 2H, H-3,9), 9.51(d, 2H, H-5,7).

IR(KBr).



Exp. 12. Dimerization of 6-methylenebenzo[cd]pyrene (8):

To a suspension of the cation (31) 340 mg (1 mmol) in 20 ml of dry chloroform was added dropwise 150 mg (3.0 mmol) of trietylamine in 5 ml of dry chloroform at 0°C over 15 min under nitrogen atmosphere. After stirring for additional 1 hr the reaction mixture was poured into 2N-hydrochloric acid and the organic layer was washed successively with saturated aqueous solution of sodium hydrogen carbonate and water. After removal of the solvent the brown residue was chromatographed on the deactivated alumina containing 2.5% of water eluting with hexane-benzene (9:1) to give 105 mg (42%) of analytically pure spiro-dimer

(17) as pale yellow crystals, mp 158-162°C (dec), which was identical in every respects with the product of Exp. (4) and (5).

Exp. 13. Trapping of 6-methylenebenzo[cd]pyrene (8):

To a suspension of 6-methylbenzo[cd]pyrenium tetrafluoroborate (31) 170 mg (0.5 mmol) in 15 ml of dry chloroform containing dimethyl acetylenedicarboxylate 120 mg (1.0 mmol) was added dropwise 75 mg (1.50 mmol) of triethylamine in 10 ml of dry chloroform at room temperature over 30 min under nitrogen atmosphere. After additional stirring for 3 hr the reaction mixture was poured into water. The organic layer was washed successively with water, 2N-hydrochloric acid, saturated aqueous solution of sodium hydrogen carbonate and water, and dried over anhydrous magnesium sulfate. After removal of the solvent the residue was chromatographed twice on alumina eluting with benzene. Evaporation of the solvent gave 39 mg (20%) of crude product. The analytical sample of (26) was obtained by recrystallization from hexane-benzene as reddish brown crystals in 5% yield, mp 239-240°C.

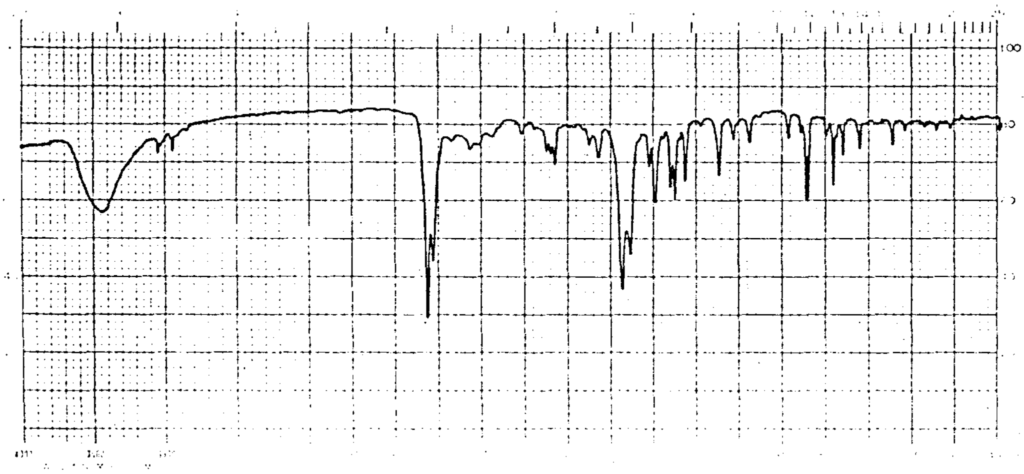
Anal. Calcd for $C_{26}H_{16}O_4$ : C, 79.58; H, 4.11%.
Found : C, 80.10; H, 4.19%.

MS. m/e 392($M^+$, 100%), 361($M^+$-$OCH_3$, 28%), 274($M^+$-2$COOCH_3$, 28%).

NMR(δ in $CDCl_3$). 4.17(s, 3H, $-CH_3$), 4.10(s, 3H, $-CH_3$), 7.87-8.28 (m, 8H, H-1,2,3,4,9,10,11,12), 8.92(dd, 1H, $J_{8,9}$=7.5 Hz, $J_{8,10}$=1.5 Hz, H-8), 9.41(s, 1H, H-8).

ES($CHCl_3$). $\lambda_{max}$(log ε); 419(3.37), 389(4.34), 369(4.23), 351(4.01), 335 sh(2.85), 303(4.65), 292 sh(4.50), 272(4.33).

IR(KBr).



Exp. 14. 6-Bis(methylthio)methylenebenzo[cd]pyrene (32):

To a stirred solution of 6H-benzo[cd]pyrene (14) (60 mg, 0.25 mmol) in 10 ml of dry THF was added butyllithium (0.25 mmol) in hexane at -60°C under nitrogen atmosphere. After stirring for 15 min at same temperature, the mixture was warmed to -20°C. Carbon disulfide (19 mg, 0.25 mmol) in dry THF 2 ml was added all at once. After stirring at -20°C for 30 min, the mixture was cooled to -40°C. To the stirred solution was added butyllithium (0.25 mmol) in hexane and the solution was warmed gradually to -10°C in a period of 1 hr. A large excess of methyl iodide was added to the solution and the mixture was stirred for 30 min. The mixture was quenched with saturated aqueous ammonium chloride solution, and extracted with benzene. The organic layer was washed successively with saturated aqueous sodium hydrogen carbonate solution and water, and dried over anhydrous sodium sulfate. After removal of the solvent the red residue was chromatographed on alumina eluting with hexane-benzene (1:1). Evaporation of the yellow eluate gave 30 mg of crude (32). The crude product was recrystallized from hexane-benzene to give 24 mg of yellow prisms, mp 143-143.5°C, in 28% yield.

Anal. Calcd for $C_{22}H_{16}S_2$ : C, 76.76; H, 4.69; S, 18.61%.

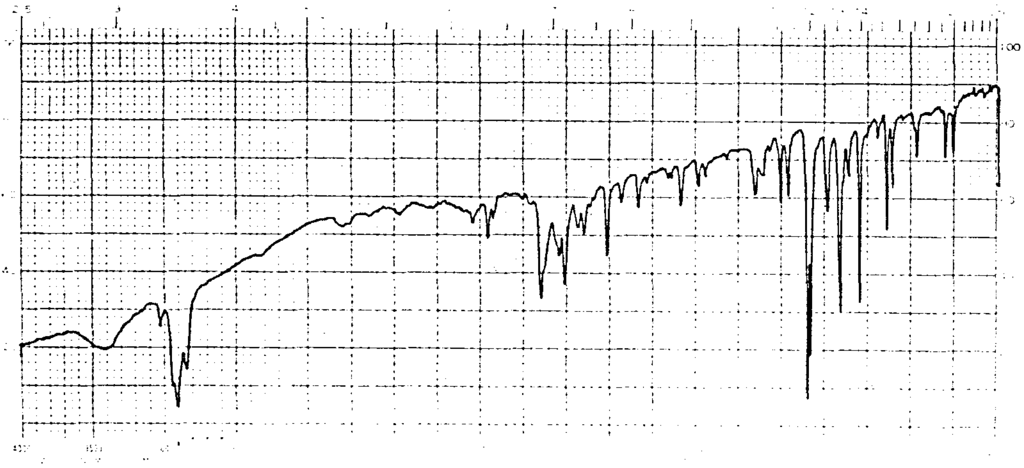
Found : C, 76.23; H, 4.77; S, 18.23%.

MS. m/e 344($M^+$, 48%), 328($M^+$-$CH_4$, 44%), 314($M^+$-2$CH_3$, 10%), 282($M^+$-$CH_3$, $SCH_3$, 100%).

NMR(δ in $CDCl_3$). 2.19(s, 6H, 2-$SCH_3$), 7.63(dd, 2H, H-4,8, $J_{3,4}$=$J_{8,9}$=8.1 Hz, $J_{4,5}$=$J_{7,8}$=7.5 Hz), 7.82, 7.90(ABq, 4H, H-1,2,10,11, $J_{1,2}$=$J_{10,11}$=9.0 Hz), 7.87(dd, 2H, H-3,9, $J_{3,5}$=$J_{7,9}$=1.4 Hz), 8.36(dd, 2H, H-5,7).

ES(in hexane). $\lambda_{max}$(log $\varepsilon$); 410(4.06), 396(4.05), 310(4.28),
285(4.29), 220(4.79).

IR(KBr).



Exp. 15. 5-Dicyanomethylenebenzo[cd]pyrene (39):

To a refluxed partial suspension of 5H-benzo[cd]pyren-5-one (45) (197 mg, 0.76 mmol) in 8 ml of dry acetic anhydride was added 200 mg (3.1 mmol) of malononitrile under nitrogen atmosphere, and the mixture was refluxed for 2 hr. After addition of additional 100 mg (1.15 mmol) of malononitrile, the solution was further refluxed for 2 hr. After the dark purple solution was cooled to room temperature, precipitated black solid mass was collected and washed with ether. The product was repeatedly chromatographed three times on silica gel eluting with benzene-chloroform (1:1). Recrystallization from toluene gave 19 mg (8.3%) of (39) as deep purple crystals, mp 297-298°C.

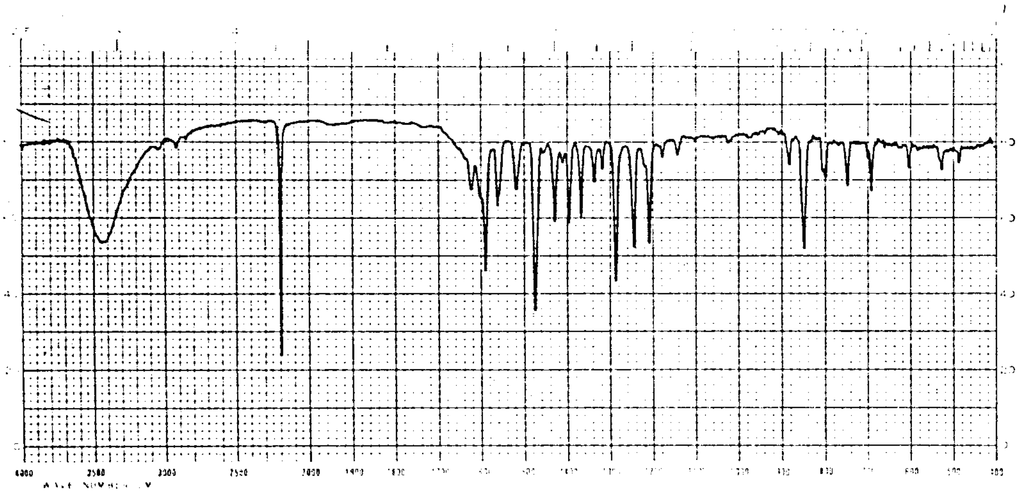
Anal. Calcd for $C_{22}H_{10}N_2$ : C, 87.40; H, 3.33; N, 9.27%.
Found : C, 87.56; H, 3.42; N, 9.30%.

MS. m/e 302($M^+$, 100%).

NMR(δ in $CDCl_3$). 7.59(d, H-4, $J_{3,4}$=9.0 Hz), 7.71(d, H-3), 8.02-8.45(m, H-1,2,7,8,9,10,11), 10.20(s, H-6).

ES($CH_3CN$). $\lambda_{max}$(log ε); 573(4.21), 470(3.75), 439(3.62), 405(3.52), 332(4.45), 274(4.12), 263 sh(4.13), 228 sh(4.63), 215(4.80).

IR(KBr). $\nu_{C\equiv N}$; 2200 $cm^{-1}$.



Exp. 16. 3-Dicyanomethylenebenzo[cd]pyrene (40):

To a suspension of benzo[cd]pyrenium perchlorate 170 mg (0.5 mmol) in dry THF 10 ml was added dropwise 1.0 mmol of sodium salt of malononitrile in 5 ml of dry THF (prepared from molononitrile and an equimolar amount of sodium hydride) at 0°C over 15 min. The mixture was stirred at 0°C for 1.5 hr. After water was added to the resulting dark red solution, the mixture was extracted with chloroform. The organic layer was washed successively with dil. hydrochloric acid, saturated aqueous solution of sodium hydrogen carbonate, and water, and dried over anhydrous sodium sulfate. After removal of the solvent, the residual black solids were chromatographed on alumina eluting with benzene. Recrystallization of the crude (40) obtained from toluene gave 11 mg (7.3%) of analytically pure (40) as deep purple needles, mp 350°C.

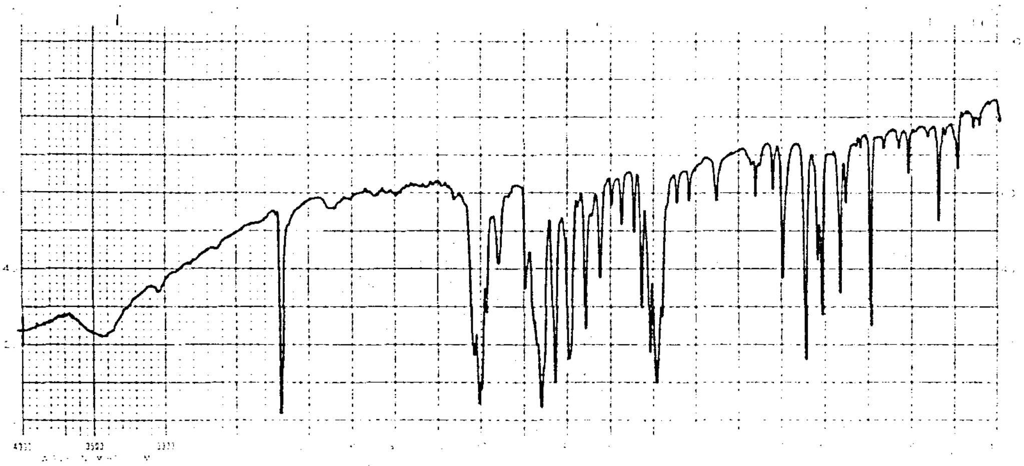
Anal. Calcd for $C_{22}H_{10}N_2$: C, 87.40; H, 3.33; N, 9.27%.
Found : C, 87.04; H, 3.39, N, 9.37%.

MS. m/e 302($M^+$, 100%).

NMR(δ in $AsCl_3$). 7.68(d, H-4, $J_{4,5}$=9.0 Hz), 7.86(d, H-5), 8.2-8.6(m, 7H, H-1,6,7,8,9,10,11), 9.55(d, H-2, $J_{1,2}$=9.0 Hz).

ES(in $CH_3CN$). $\lambda_{max}$(log ε); 505(4.48), 328 sh(3.90), 206(4.98).

IR(KBr). $\nu_{C\equiv N}$; 2200 $cm^{-1}$



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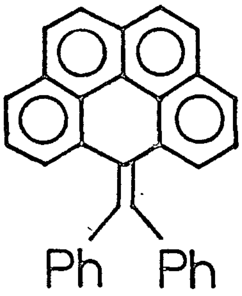
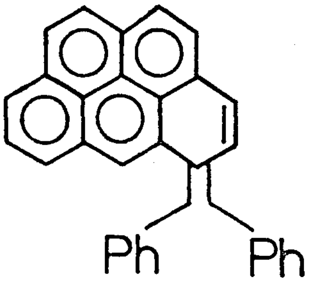
# Chapter 4. Syntheses and Chemical Reactivities of 5- and 6-Diphenylmethylenebenzo[cd]pyrene

## 4.1. Syntheses of 5- and 6-Diphenylmethylenebenzo[cd]pyrene

In our current interest in the cross-conjugated methylenebenzo[cd]pyrene, we are next encouraged to examine syntheses of 6- and 5-diphenylmethylenebenzo[cd]pyrene, (1) and (2).

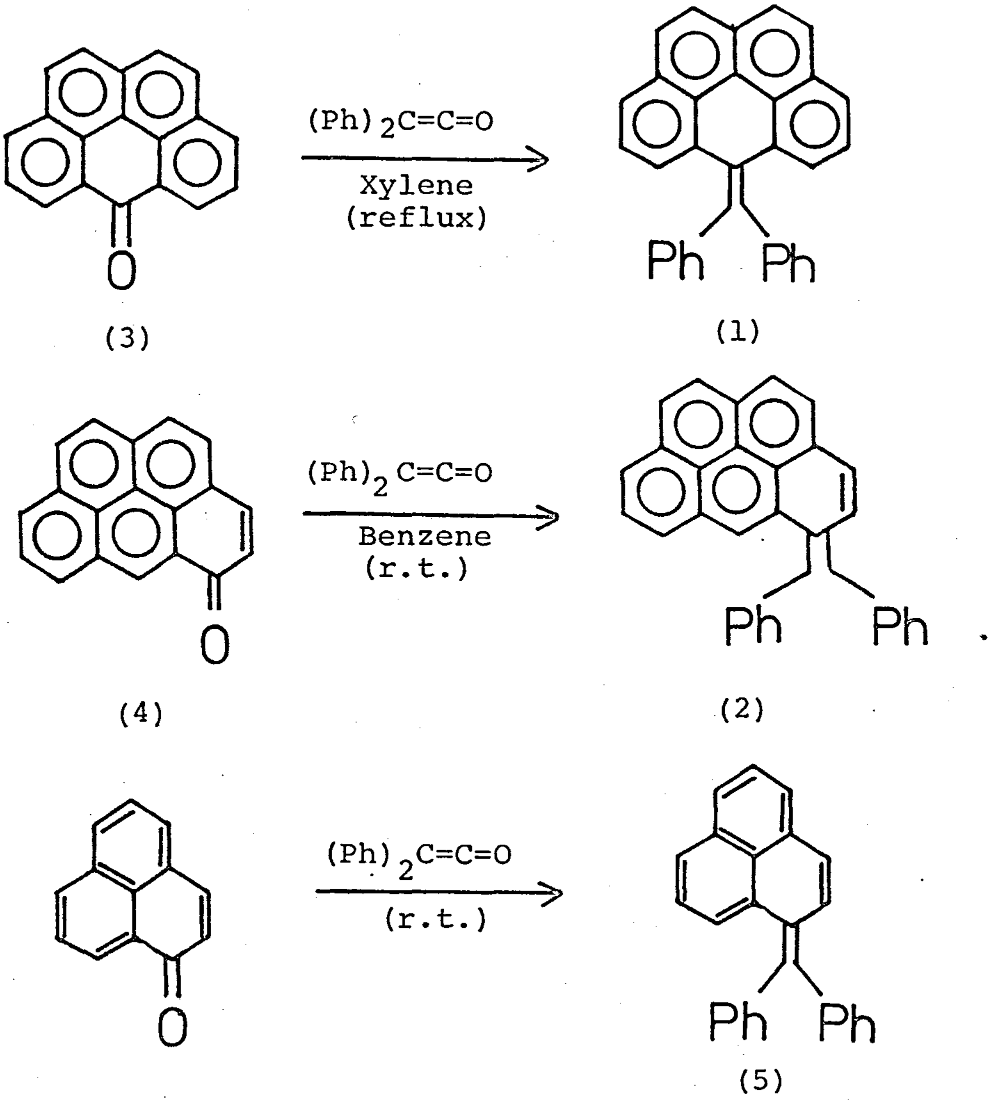


(1)



(2)

Although phenyl group could not be expected to have characteristic properties as a strong electron attractive or donative substituent, there should be expected some differences in their physical and chemical properties between (1) and (2). Our successful approach to (1) and (2) has been achieved by utilization of the ketones, (3) and (4), and diphenylketene through decarboxylation from intermediate β-lactone. This method has successfully been



applied to the synthesis of diphenylphenafulvene (5) by Gommper.1)

Treatment of the ketone (3) and slight excess of diphenylketene in refluxing xylene under nitrogene atmosphere for a few hours gave after chromatographic separation, a 15% yield of the desired 6-diphenylmethylenebenzo[cd]pyrene (1), yellow prisms, mp 249-250°C, along with the recovered starting ketone (3) in 75% yield.

The structure of (1) can be deduced from its elemental analysis and spectroscopic properties. Its mass spectrum exhibits parent peak at m/e 404 as base peak. Its nmr spectrum is depicted in Fig. 1, whose first order analysis is in complete accord with the structure of (1) with $C_{2v}$-symmetry. Thus, it shows a doublet of doublets at $\delta$ 7.13 (H-4,8, $J_{3,4}=J_{4,5}=J_{7,8}=J_{8,9}=8.0$ Hz), a broad singlet of the ten phenyl protons at $\delta$ 7.19, a doublet of doublets at $\delta$ 7.43 (H-3,9, $J_{3,5}=J_{7,9}=1.5$ Hz), a doublet of doublets at $\delta$ 7.72 (H-5,7), and a singlet at $\delta$ 7.88 (H-1,2,10,11). The above assignments were identified through the following double resonance experiment, the irradiation at $\delta$ 7.13 converted the doublet of doublets at $\delta$ 7.72 into broad singlet.

On the other hand, treatment of the ketone (4) with diphenylketene in benzen at room temperature under nitrogen atmosphere immediately led to a dark red solution from which an air sensitive red product (2) was obtained along with two by-products, (6) and (7). On exposing to air the red product (2) readily decomposed with fading to yellow and yielded two products (6) and (7) which are identical with by-products of the above reaction whose structures will be discussed in Section 4.2. Therefore, isolation and purification of the main red product have to be carried out through careful chromatography on silica gel under nitrogen atmosphere monitered by electronic spectroscopy. The resulted main product is air-sensitive dark red needles (in 50% yield) whose structure was assigned to (2) based on its elemental analysis and spectroscopic properties. Its mass spectrum exhibits intense peaks at m/e 404 ($M^+$, 100%), 327 ($M^+-C_6H_5$, 36%), and 326 ($M^+-C_6H_6$, 59%), and its nmr spectrum (Fig. 2) exhibits two doublets at $\delta$ 6.83 and 7.03 (H-4 and 3, $J_{3,4}$=9.9 Hz) and multiplet at $\delta$ 7.1-8.1 (other protons). Although complets assignments of all protons are impossible, there is a pare of doublets characteristic to H-3 and H-4 of (2) in olefinic region.

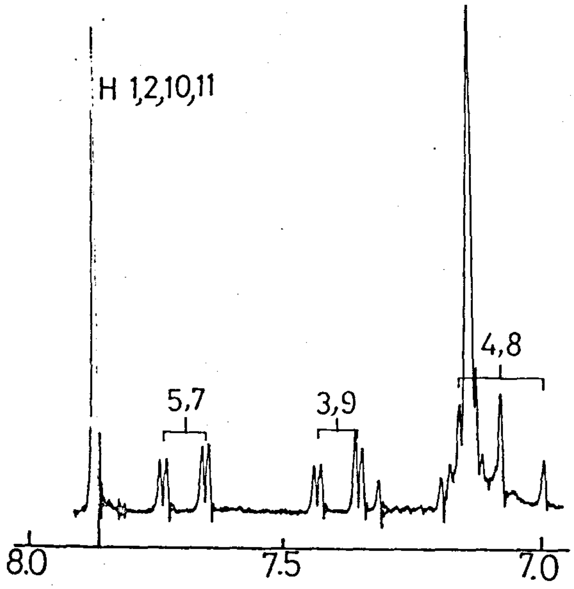


Fig. 1. The NMR Spectrum of (1) in $CDCl_3$.

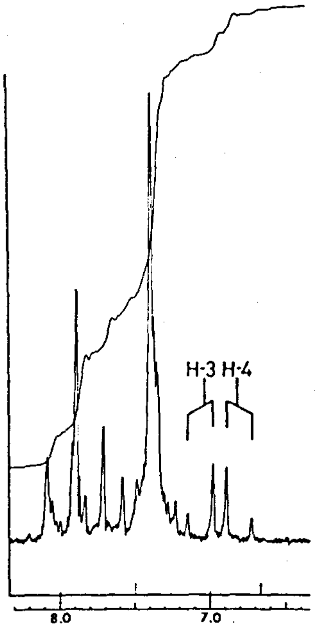


Fig. 2. The NMR spectrum of (2) in $CDCl_3$.

Electronic spectra of (1) and (2) were illustrated in Fig. 3. Since due to its pronounced air sensitivity the compound (2) was contaminated with trace amounts of (6) and (7), the exact intensity of the spectrum could not be observed.

As shown in Fig. 3 a remarkable bathochromic shift of the longest wavelength absorption maximum of (2) by 110 nm was found compared with that of (1). The shift is qualitatively consistent with theoretical prediction based on perturbed MO theory.2)

The rate of the condensation reaction of diphenylketen with the ketone (3) was extremely slower than that of the reaction with (4), e.g., the ketone (4) reacted immediately with diphenylketene even at room temperature, whereas the ketone (3) could not

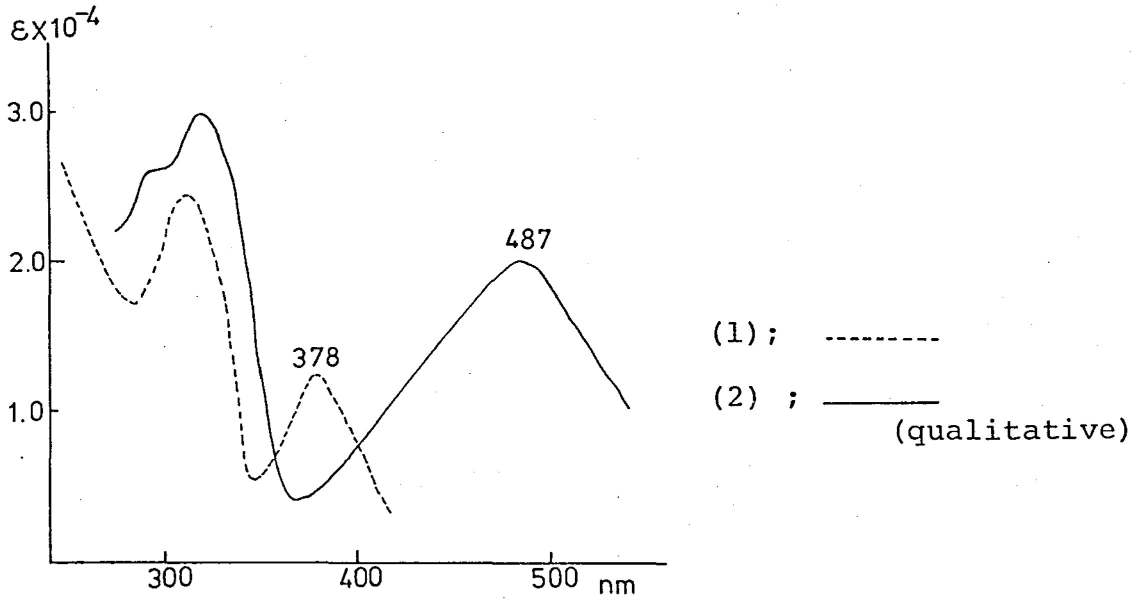
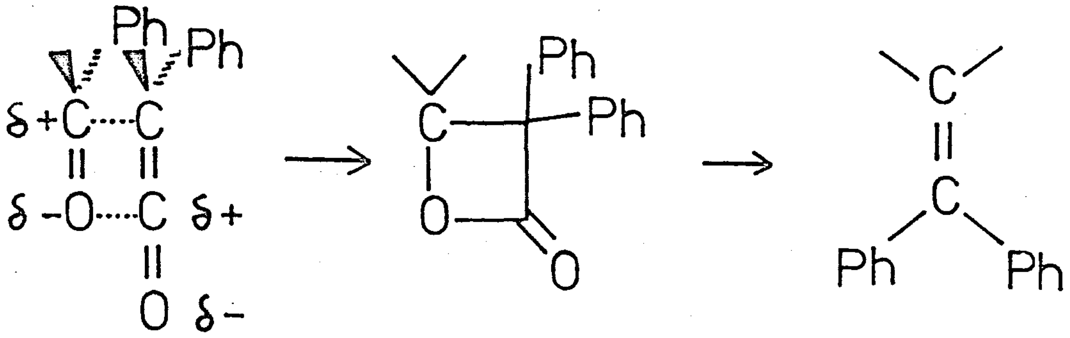


Fig. 3. The Electronic Spectra of (1) and (2).

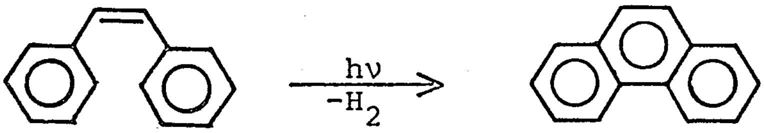
react at room temperature. Furthermore, the yield of (1) was much lower than that of (2). In view of the fact that the reaction of diphenylketene with the carbonyl compound is known to proceed via polar cycloaddition pathway, the above mentioned difference in reactivity between (3) and (4) is reasonably interpreted in terms of the lower polarity of the carbonyl group of (3) compared with that of (4), which is reflected to its higher frequency of carbonyl stretching band and its lower basicity[3)] (see Section 2.5). This finding is consistent with the result observed in Section 3.4 that the ketone (3) failed to give the condensation product with malononitrile while the ketone (4) gave the expected product.



Scheme 1.

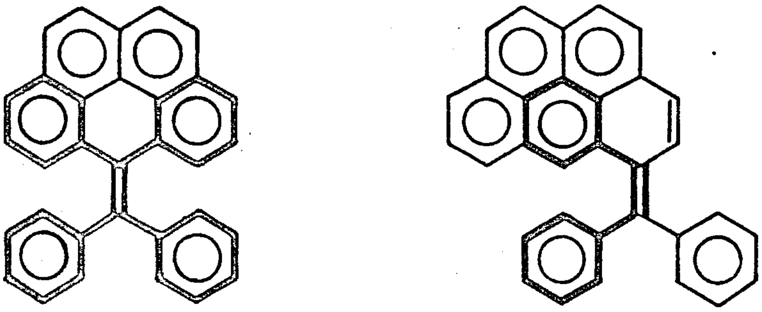
## 4.2. Chemical Reactivities of 5- and 6-Diphenylmethylenebenzo[cd]pyrene

Since the discovery of the photochemical conversion of stilbene (8) into phenanthrene (9) similar type of reactions of many stilbene analogs have been actively investigated and the mechanism has been argued in detail. At present photodehydrocyclizations have proved to be very useful synthetic route to a number of polycyclic aromatic compounds.[4)]



(8) (9)

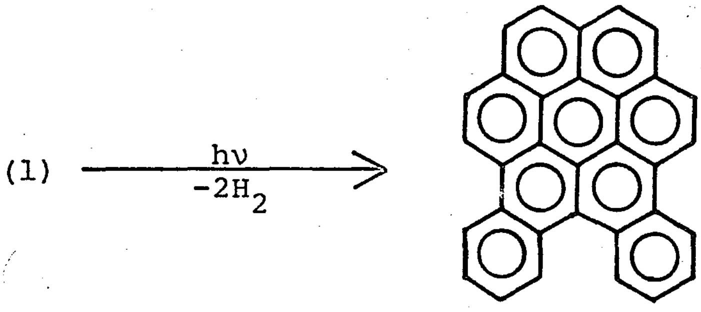
In view of these facts, we decided to investigate on the photo-conversion of (1) and (2) which contain stilbene moiety in their molecules as illustrated in Fig. 4. When a benzene solution of (1) and three mole equivalents of iodine was irradi-



(1) (2)

Fig. 4.

ated through pyrex filter with high pressure Hg lamp under nitrogen atmosphere at about 0°C, after chromatographic separation the double cyclization product (10) was afforded as yellow needles in 30% yield. The structure of (10) was identified through elemental analysis and, mass and electronic spectroscopy. Its nmr spectral measurement has, however, failed even by using pulse Fourier-Transform technique because of its extremely low solubility in usual organic solvents. Both elemental analysis and mass spectrum of (10), m/e 400 ($M^+$, 100%), clearly indicated it to be a product in which two moles of hydrogens were eliminated.



(10)

Electronic spectrum of (10) was depicted in Fig. 5 along with those of coronene (11) and its higher benzologs such as benzo[a]coronene (12), dibenzo[aj]coronene (13), and tribenzo[adg]coronene (14).[5)] Inspection of these absorption spectra now provides a rational explanation for the structure of (10). Thus, [1] as might be expected, there is a steady displacement of β and p-bands toward longer wavelength with increasing the

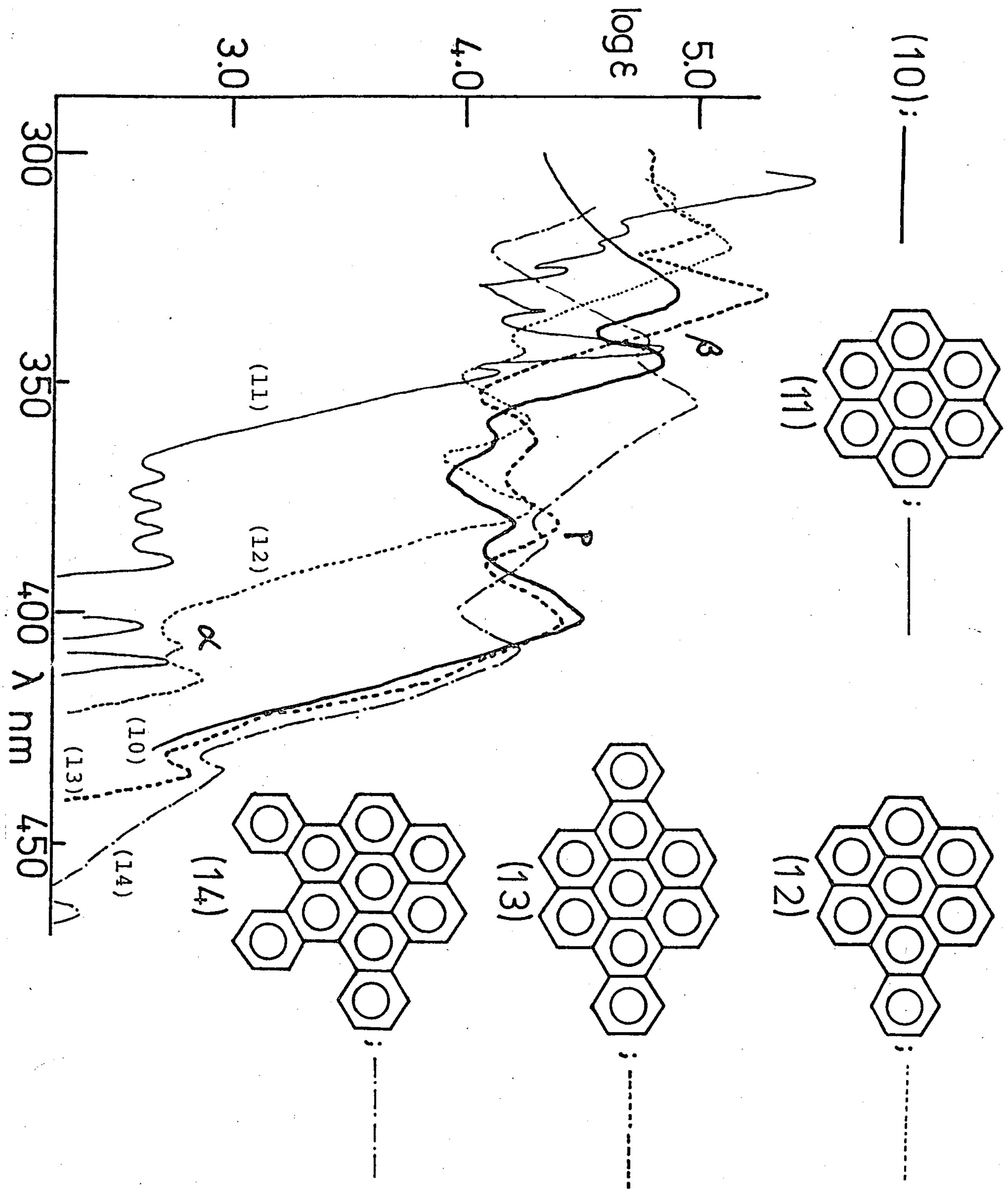


Fig. 5. The Electronic Spectra of (10), (11), (12), (13), and (14) in Benzene.

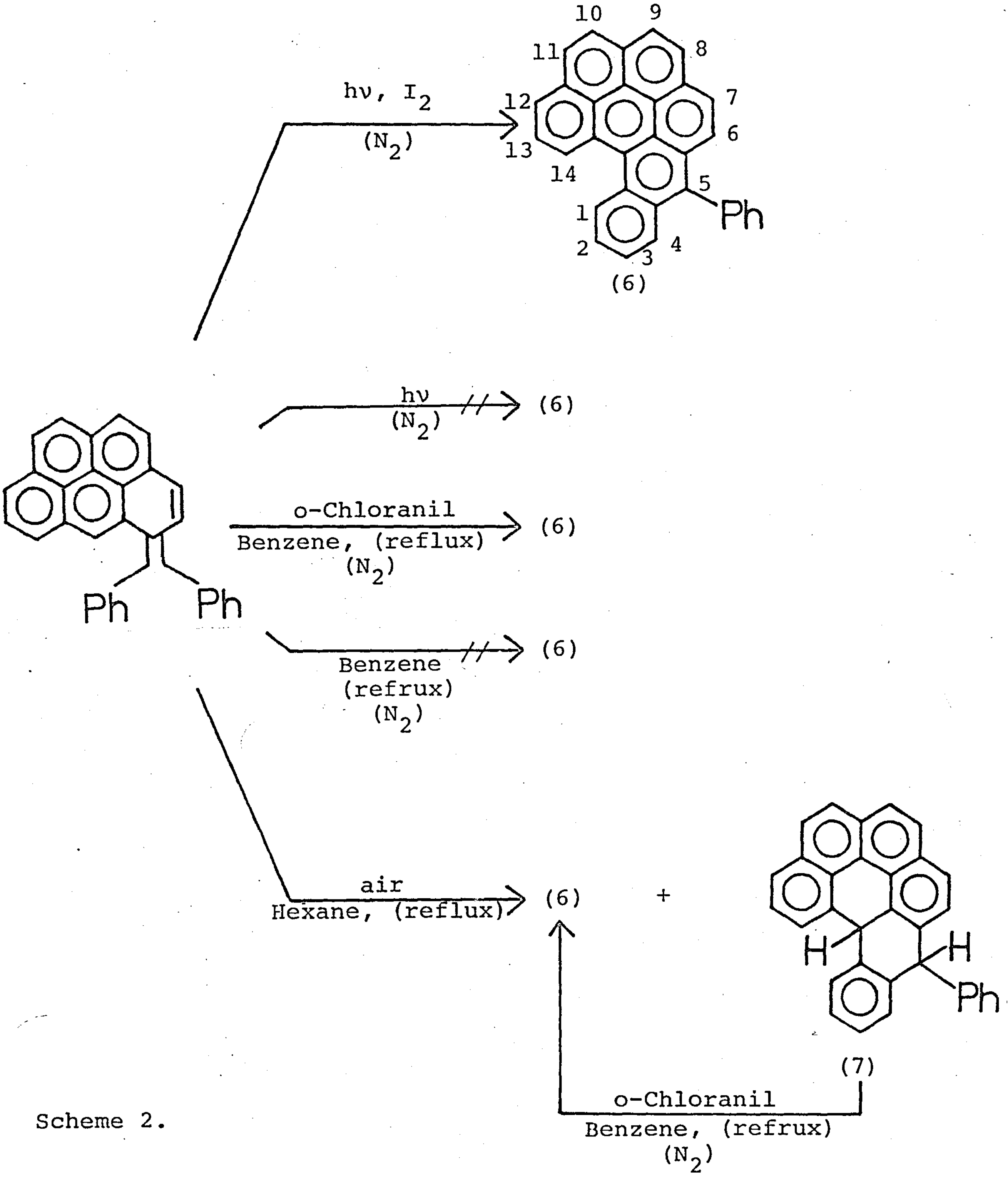
number of benzene rings condensed to coronene moiety in the spectra of (11), (12), (13), and (14), and the absorption maxima at 344 and 361 nm of (10) are consistent with those for the coronene condensed with two benzene rings. [2] The longest wavelength absorption band with low intensity at around 430 nm observed in (10) is closely similar to those of (13) and (14) indicating the presence of a coronene chromophore fused with two or three benzene rings.

From the above considerations, the product (10) is believed to have the structure of (10). Similar photodehydrocyclization of (2) gave (6) in 67% yield.

Since the photoreaction of (2) without iodine resulted in recovery of the starting material, it is apparent that iodine is essential for the dehydrocyclization step in this reaction.

On the other hand, in the presence of a slight excess of o-chloranil under nitrogen afforded (6), yellow needles mp 237-238°C, in 27% yield. Since the above cyclization had failed either at room temperature or without o-chloranil, this reaction evidently requires heat and oxidizing agent.

The structure of (6) was established by elemental analysis and mass and nmr spectroscopic properties. Its mass spectrum shows molecular ion peak at m/e 402 as a base peak and its nmr spectrum shows signals at $\delta$ 9.31 (dd, H-14, $J_{13,14}$=8.0 Hz, $J_{12,14}$=


10
9
11
8
12
7
13
6
14
5
Ph
1
2
3
4
(6)
hν, I2
(N2)
hν
(N2)
(6)
o-Chloranil
Benzene, (reflux)
(N2)
(6)
Ph
Ph
Benzene
(refrux)
(N2)
(6)
air
Hexane, (reflux)
(6)
+
H
H
Ph
(7)
o-Chloranil
Benzene, (refrux)
(N2)

Scheme 2.

1.0 Hz) and δ 9.46 (dd, H-1, $J_{1,2}$=8.0 Hz, $J_{1,3}$=1.0 Hz) along with multiplet at δ 7.50-8.43. Assignments of H-1 and H-14 have been achieved by the following double resonance experiments as illustrated in Fig. 6, the irradiation at around δ 7.7 converted the doublet of doublets at δ 9.46 into broad singlet and another irradiation at around δ 8.1 converted the doublet of doublets at δ 9.31 into broad singlet. This experiment also suggests that H-2 and H-13 resonate at around δ 7.7 and 8.1, respectively. Taking into account the induced diamagnetic anisotropy effects of the adjacent benzene rings, it seems to be reasonable to assume that H-13 appears at lower field than H-2. In addition, one of the by-products in the preparation of (2) from the ketone (4) and diphenylketene as described in preceding section was identified as (6) based on its electronic spectrum, which is depicted in Fig. 8.

In order to gain further insight into mechanistic aspects of the conversion of (2) into (6) and (7) with atmospheric oxygen, in addition to structural elucidation of the other product (7), we tried to examine the following experiments.

Heating a hexane solution of (2) exposing to air for several hours gave a mixture of (6) and (7). Although complete separation of (6) and (7) has failed, fractional recrystallization twice from benzene afforded the analytically pure (7) as

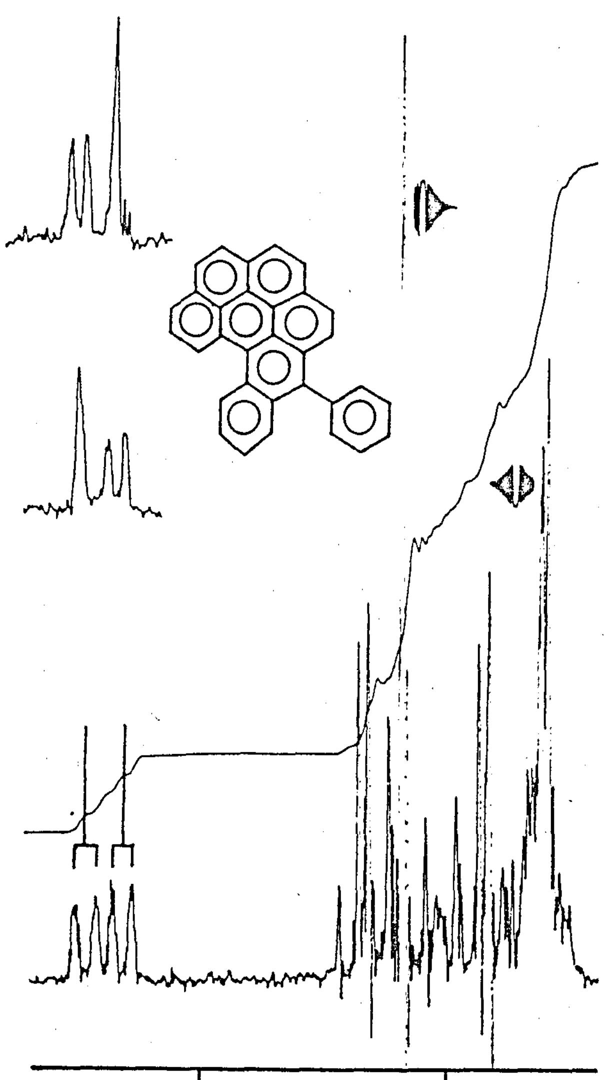


Fig. 6. The NMR Spectrum of (6) in $CDCl_3$.

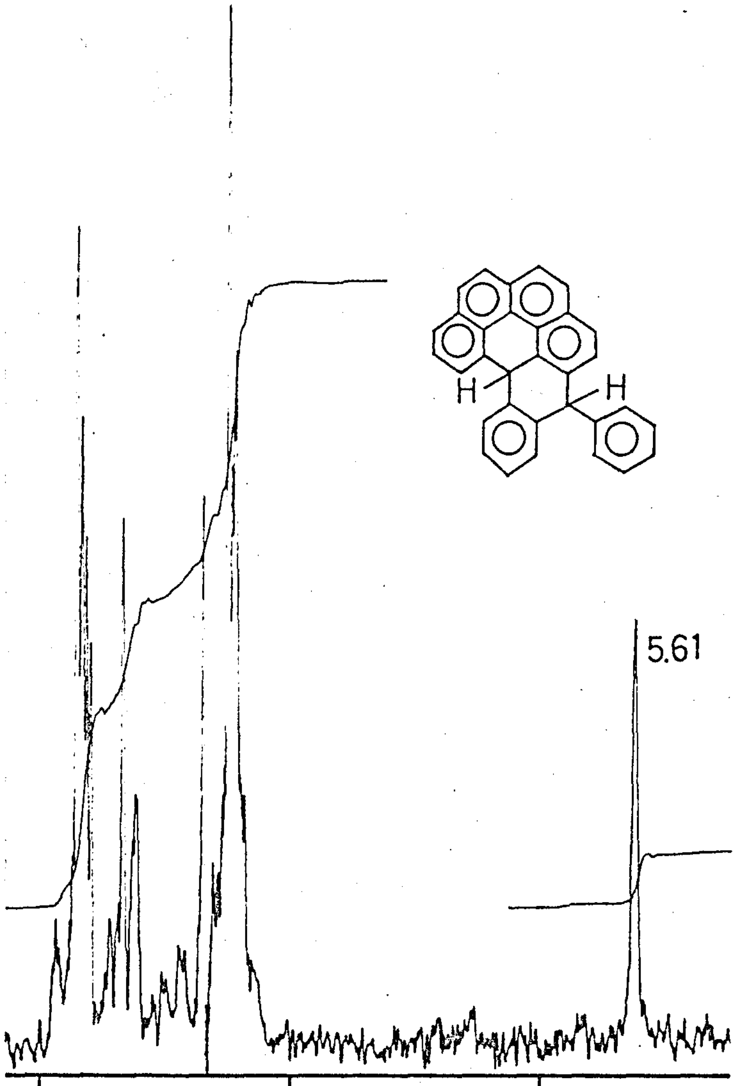


Fig. 7. The NMR Spectrum of (7) in $CDCl_3$.

colorless needles, mp 247-249°C, in 16% yield. The pure (6) could not be separated from the mixture, however, heating it with o-chloranil in benzene resulted in the formation of almost pure (6) in 26% yield based on (2). On the other hand, treatment of the pure (7) with o-chloranil under the similar conditions gave (6) in about 65% yield. Elemental analysis and mass spectrum of (7), which shows intense peaks at m/e 404 ($M^+$, 15%), 402 ($M^+$-$H_2$, 54%), and 326 ($M^+$-$C_6H_6$, 100%), indicated it to be an isomer of (2). This is supported experimentally by its readily conversion to (6) with a loss of hydrogen. Final confirmation of this structure assignment was obtained from its nmr spectrum and electronic spectrum. As can be seen in Fig. 8, its electronic spectrum is closely similar to that of the model compound (19)

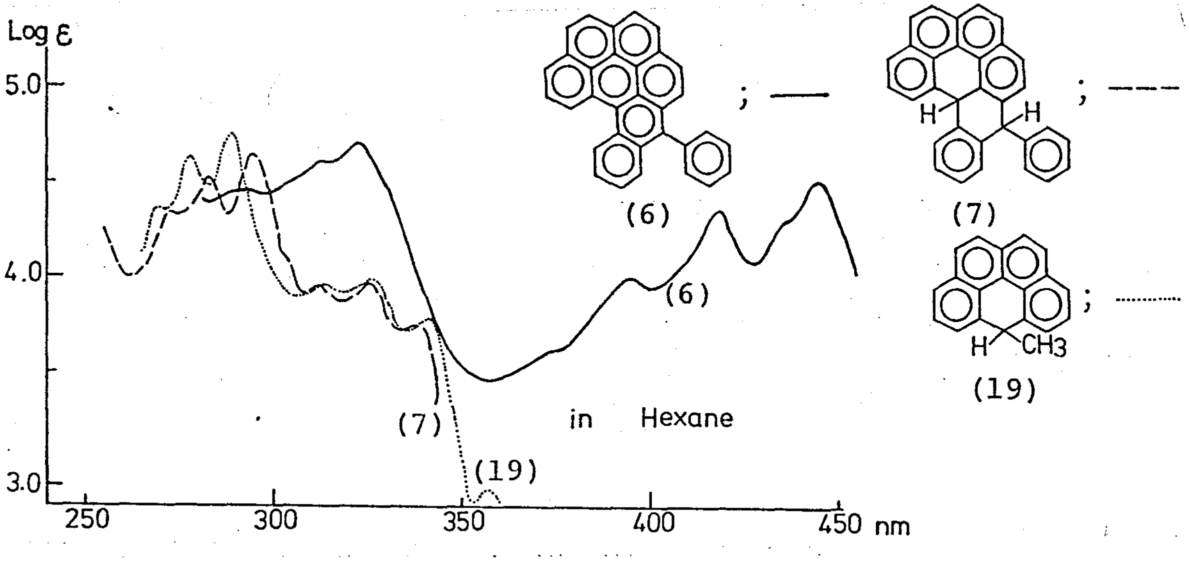
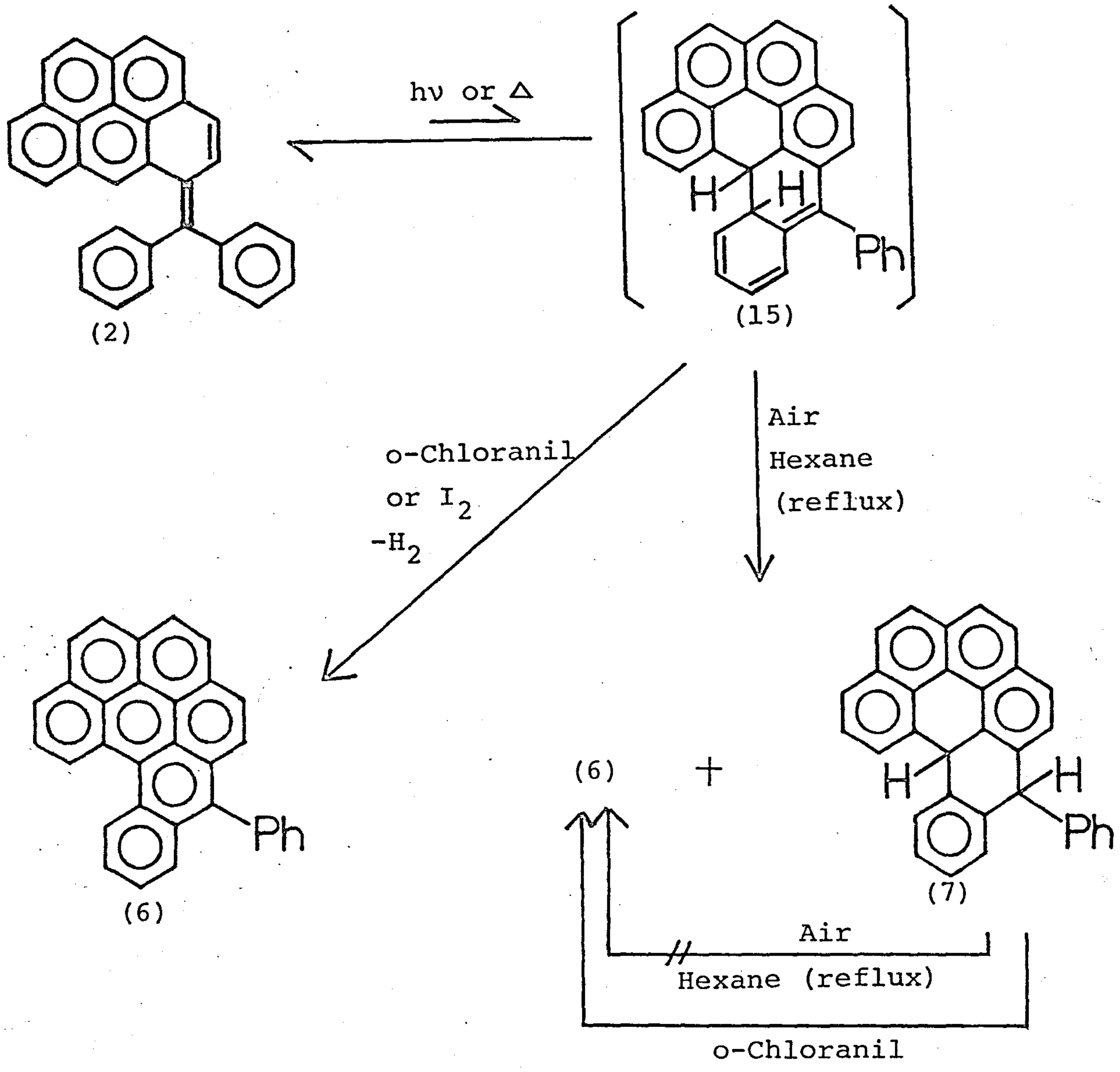


Fig. 8. The Electronic Spectra of (6), (7), and (19).

in absorption maxima and intensities. This strongly suggests the existence of a benzo[a]phenanthrene chromophore. Its nmr spectrum shows a broad singlet at $\delta$ 5.61 and multiplet at $\delta$ 7.18-7.98 in a relative ratio 1:9 (see Fig. 7). Two methines hydrogens H-5, and H-14b, are magnetically nonequivalent, however, it is not striking that their chemical shifts are almost identical each other, since both hydrogens are located in triply benzylic positions. Therefore its nmr spectrum was convincingly consistent with the structure of (7). However, There should be expected four stereoisomers for (7), which will be discussed below along with mechanistic considerations.

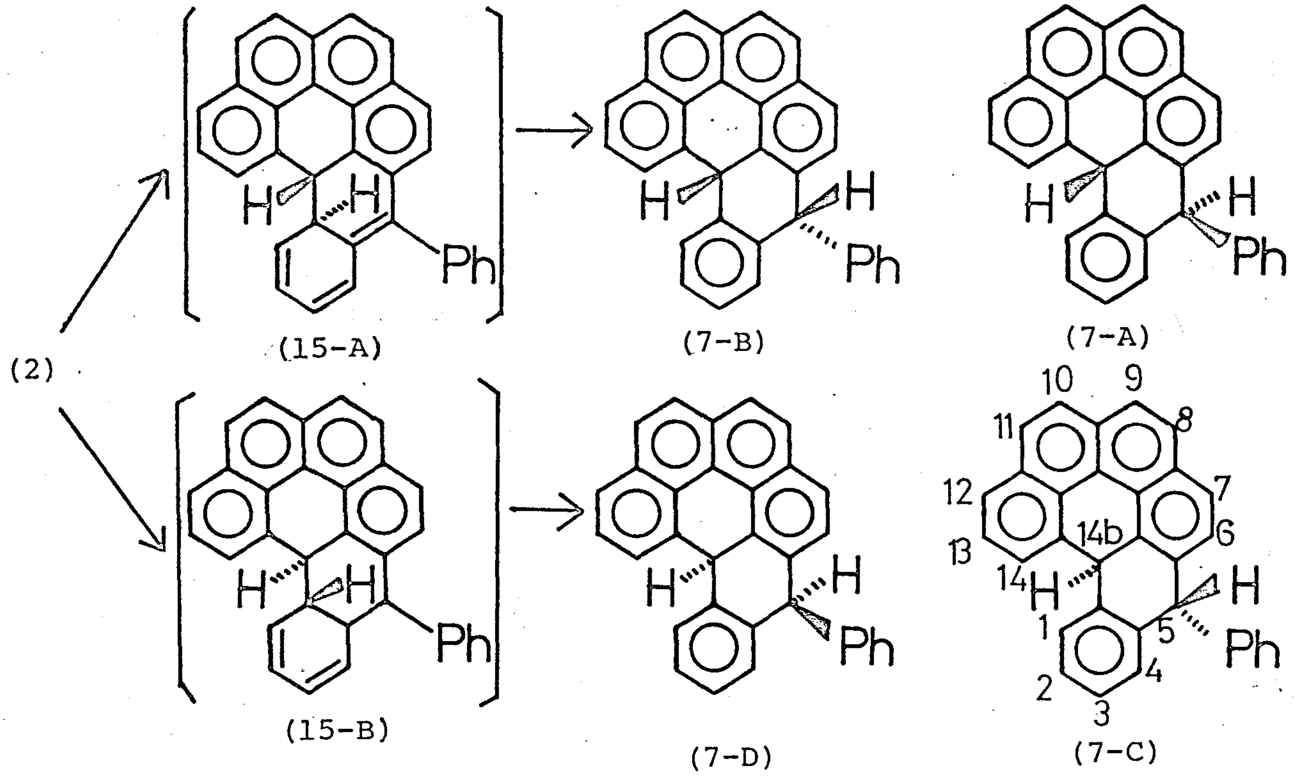
The above mentioned results of thermal- or photo-promoted conversion of (2) into (6) and/or (7) can be interpreted in terms of the mechanism shown in Scheme 3 which was identical with that already proposed[4)] for stilbene.

Equilibrium between (2) and the cyclized intermediate (15) was at first attained thermally and/or photochemically. Subsequently the transient intermediate (15) would transformed into (6) by the action of dehydrogenation agent such as chloranil or iodine, or into a mixture of (6) and (7) by the thermal reaction exposing to air. The driving force of the formation of (7) is the regeneration of the aromatic benzen ring. In this case the compound (7) was considered not to be an intermediate for the formation of (6) since (7) is remained intact under the same reaction conditions.



Scheme 3.

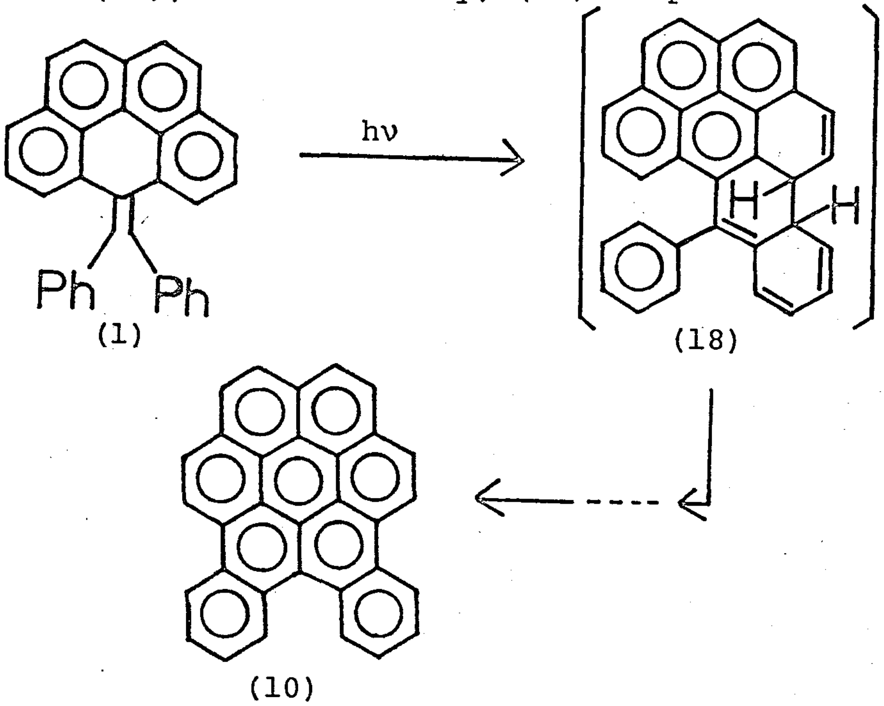
There are four possible stereoisomers for (7) whose structures are given below. Inspection of dreiding models reveals that, if the molecule existed in a configuration illustrated as (7-B) or (7-D), the hydrogens attached to C-4 and C-6 would have substantial nonbonding interaction due to the close proximity to the phenyl group at C-5 whereas that of the configuration of (7-A) or (7-C) may not. Then, although the latter configurations, (7-A) and (7-C), would newly give rise nonbonding interaction between hydrogen at C-14b and the phenyl group, it, on



Scheme 4.

the whole, can be said that there is some steric advantage of (7-A) and (7-C) compared with (7-B) and (7-D). Therefore the structure of (7) seems more likely to be (7-A) and (7-C) than (7-B) and (7-D) in terms of the steric considerations. Unfortunately, conclusive evidence for the stereochemistry of (7) can not be obtained so far.

Finally, we will discuss the difference in the reactivity between (1) and (2) toward cyclization. Greater reactivity of (2) compared to (1) can be reasonably understood through the difference in π-energy between benzo[a]phenanthrene (16) and 1-vinylpyrene (17), that is to say, (16) is predicted to be more



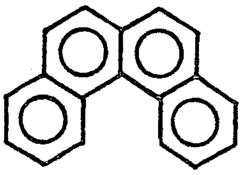
(1)

(18)

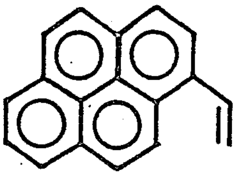
(10)

Scheme 5.

stable than (17) by 11 Kcal/mol (see Section 3.2.2). Thus, as can be seen from Scheme 5, cyclization of (1) must be involved an unfavorable transition from the more stable benzo[a]phenanthrene skeleton (16) to the less stable 1-vinylpyrene skeleton (17), whereas in the case of cyclization of (2), the relative stability is reversed. Such an argument can also be applied to hydrogen migration of the methylenebenzo[cd]pyrene dimer as described in Section 3.2.2.



(16)



(17)

## 4.3. Experimental

Exp. 1. 6-Diphenylmethylenebenzo[cd]pyrene (1):

To a refluxed solution of 6H-benzo[cd]pyren-6-one (3) (127 mg, 0.5 mmol) in 10 ml of dry xylene was added dropwise (1.2 ml, 0.65 mmol) of diphenylketene in 4 ml of dry xylene under nitrogen atmosphere over 5 min. The solution was refluxed for 2.5-3.0 hr. After removal of the solvent the red residue was chromatographed on the deactivated alumina containing 3% of water eluting gradiently with hexane, hexane-benzene (10:1), and benzene. Evaporation of the solvent gave 30 mg (15%) of (1) from hexane-benzene eluate and 95 mg (75%) of recovered ketone (3) from benzene eluate. Recrystallization from hexane-benzene gave (1) as yellow prisms, mp 249-250°C.

Anal. Calcd for $C_{32}H_{20}$: C, 95.02; H, 4.98%.
Found : C, 94.87; H, 5.02%.

MS. m/e 404 ($M^+$, 100%), 326 ($M^+-C_6H_6$, 17%).

NMR(δ in $CDCl_3$). 7.13(dd, H-4,7, $J_{3,4}=J_{4,5}=J_{7,8}=J_{8,9}=8.0$ Hz), 7.19(bs, phenyl protons), 7.43(dd, H-3,9, $J_{3,5}=J_{7,9}=1.5$ Hz), 7.72(dd, H-5,7), 7.88(s, H-1,2,10,11).

ES(hexane). $\lambda_{max}$(log ε); 378(4.10), 311(4.39), 258(4.38), 216 (4.85).

Exp. 2. 5-Diphenylmethylenebenzo[cd]pyrene (2):

To a stirred suspension of 5H-benzo[cd]pyren-5-one 127 mg (0.5 mmol) in 8 ml of thiophene-free benzene was added 1.3 ml (0.7 mmol) of diphenylketene under nitrogen atmosphere.
The red transparent solution was stirred for 30 min at room temperature. After evaporation of the solvent below 5°C the red residue was chromatographed on silica gel eluting with hexane under nitrogen atmosphere. There were collected seven fractions containing the desired (2), the first fraction gave trace of (2) and trace of 5-phenyldibenzo[a,ghi]perylene (6) and the last three fractions gave 20 mg of a mixture of (2) and 5,14b-dihydro-5-phenyldibenzo[a,ghi]perylene (7). The solvent of remaining fractions was evaporated below 0°C to give 100 mg (50%) of the analytically pure (2) as red needles, mp 125-130°C.
All manipulations were carried out under nitrogen atmosphere in order to avoid conversion of (2) into (6) and (7).

Anal. Calcd for $C_{32}H_{20}$: C, 95.02; H, 4.98%.

Found : C, 95.20; H, 4.92%.

MS. m/e 404($M^+$, 100%), 327($M^+-C_6H_5$, 36%), 326($M^+-C_6H_6$, 59%).

NMR($\delta$ in $CDCl_3$). 6.83(d, H-4, $J_{3,4}$=9.9 Hz), 7.03(d, H-3), 7.1-8.1(m, other protons).

ES(hexane). $\lambda_{max}$(log $\varepsilon$); 487, 319, 295, 217.

Exp. 3. Photocyclization of 6-diphenylmethylenebenzo[cd]-pyrene (1):

A solution of (1) 20 mg (0.05 mmol) and iodine 38 mg (0.15 mmol) in 75 ml of benzene was irradiated through pyrex filter with a 450 w high-pressure mercury lamp for 2 hr at about 0°C under nitrogen atmosphere. After removal of the solvent the residue was chromatographed twice on alumina with benzene. The crude product was recrystallized from xylene to give 6 mg (30%) of (10) as yellow needles, mp > 360°C.

Anal. Calcd for $C_{32}H_{16}$ : C, 95.97; H, 4.05%.
Found : C, 95.58; H, 4.03%.

MS. m/e 400($M^+$, 100%).

ES(benzene). $\lambda_{max}$(log $\varepsilon$); 402(4.39), 381(4.26), 361(4.16), 344(4.86), 333 sh(4.91), 331(4.91), 296(4.55).

Exp. 4. Thermal cyclization of (2) in the presence of air:

A solution of (2) 100 mg (0.25 mmol) in hexane was refluxed exposing to air for 6-8 hr. After removal of the solvent the residue was chromatographed on alumina eluting with hexane-benzene (1:1). Evaporation of the solvent gave a mixture of (6) and (7). The mixture was recrystallized twice from benzene to give 16 mg (16%) of the analytically pure (7) as colorless needles, mp 247-249°C.

(7)

Anal. Calcd for $C_{32}H_{20}$ : C, 95.02; H, 4.98%.

Found : C, 94.83; H, 5.05%.

MS. 404($M^+$, 15%), 402($M^+-H_2$, 54%), 326($M^+-C_6H_6$, 100%).

NMR(δ in $CDCl_3$). 5.61(s, 2H, H-5, 14b), 7.18-7.98(m, 18H, aromatic protons).

ES(benzene). $\lambda_{max}$(log ε); 357(2.99), 343(3.74), 328(3.99), 314(3.98).

ES(hexane). $\lambda_{max}$(log ε)*; 341(3.79), 326(3.99), 313(3.97), 303 sh(4.11), 294.5(4.65), 283(4.52), 272(4.35), 265(4.30), 242(4.44), 237 sh(4.51), 233 sh(4.55), 214(4.76).

* The measurement of the absorption maximum of the longest wavelength at about 355 in hexane is impossible due to the low solubility of (7) in hexane.

Exp. 5. 5-Phenyldibenzo[a, ghi]perylene (6):

A solution of (2) 118 mg (0.29 mmol) in hexane was refluxed exposing to air for 6-8 hr and the solvent was evaporated. A solution of the residue and the o-chloranil 100 mg (0.4 mmol) in 5 ml of benzene was refluxed for 3 hr. After removal of the solvent the residue was chromatographed on alumina eluting with benzene. Evaporation of the solvent gave 40 mg of (6). The crude (6) was recrystallized from hexane-benzene to give 19 mg (26% based on (2)) of (6) as yellow needles, mp 237-238°C.

Anal. Calcd for $C_{32}H_{18}$ : C, 95.49; H, 4.51%.
Found : C, 95.39; H, 4.53%.

MS. m/e 402($M^+$, 100%).

NMR($\delta$ in $CDCl_3$). 9.31(dd, 1H, H-1, $J_{1,2}$=8.0 Hz, $J_{1,3}$=1.0 Hz), 9.46(dd, 1H, H-14, $J_{13,14}$=8.0 Hz, $J_{12,14}$=1.0 Hz), 7.50-8.43(m, 16H, other protons).

ES(hexane). $\lambda_{max}$(log $\varepsilon$); 444(4.51), 436 sh(4.30), 418(4.36), 394(4.00), 374 sh(3.61), 322(4.71), 312(4.61), 293(4.46), 274(4.45), 262 sh(4.33), 259 sh(4.25), 250(4.42), 244 sh(4.45), 231(4.79), 216(4.89).

Exp. 6. Photocyclization of (2):

A solution of (2) 24 mg (0.06 mmol) and iodine 23 mg (0.09 mmol) in 60 ml of benzene was irradiated through pyrex filter with a 45 w high-pressure mercury lamp for 20 min at about 0°C under nitrogen atmosphere. After removal of the solvent the residue was chromatographed on alumina eluting with benzene and again on silica gel eluting with hexane to give 16 mg (67%) of nearly pure (6).

Exp. 7. Oxidation of (2) with o-chloranil:

A solution of (2) 24 mg (0.06 mmol) and o-chloranil 20 mg (0.08 mmol) in 2 ml of benzene was stirred at room temperature under nitrogen atmosphere. Progress of the reaction was monitored by electronic spectra. The reactant (2) remained unchanged even after 20 hr. The solution was refluxed overnight under nitrogen atmosphere. After removal of the solvent the residue was chromatographed on alumina eluting with benzene. Rechromatography on silica gel with hexane afforded almost pure (6) 6.5 mg (27%).

Exp. 8. Dehydrogenation of (7) with o-chloranil:

A solution of 3 mg (0.0075 mmol) of (2) and o-chloranil 4 mg (0.016 mmol) in 1 ml of benzene was refluxed for 4 hr under nitrogen atmosphere. After removal of the solvent the residue was chromatographed on alumina with hexane-benzene (1:1) to give 2 mg (67%) of nearly pure (6).

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4) a) A. Schönberg, "Preparative Organic Photochemistry", Springer-Verlag New York., 13 (1968).

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# Chapter 5. Dibenzo[de;jk]pentacenyl System

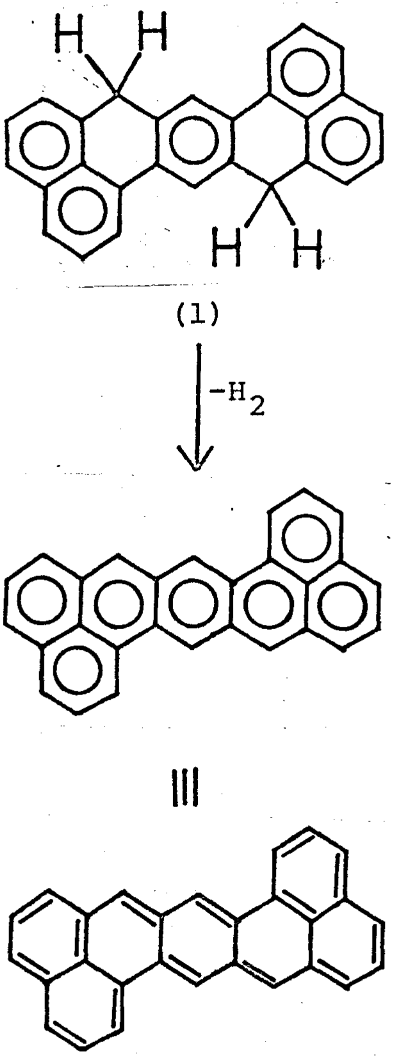
## 5.1. Introduction

Our interest in non-Kekulé hydrocarbons led us to explore the chemistry of dibenzopentacenyl system.

Let us consider the chemistry of isomeric compounds dihydroheptazethrene (1) and 7,9-dihydrodibenzo[de;jk]pentacene (3). It might be supposed that upon dehydrogenation of the compounds (1) and (3) would give the fully conjugated products (2) and (4), respectively. The former of these products, (2), actually exists as heptazethrene, and can be produced in this manner by Clar[1,2] and his co-workers. However, dehydrogenation of (3) leads only to a polymeric product. This is probably due to the fact that Kekulé structures cannot be written for (4).

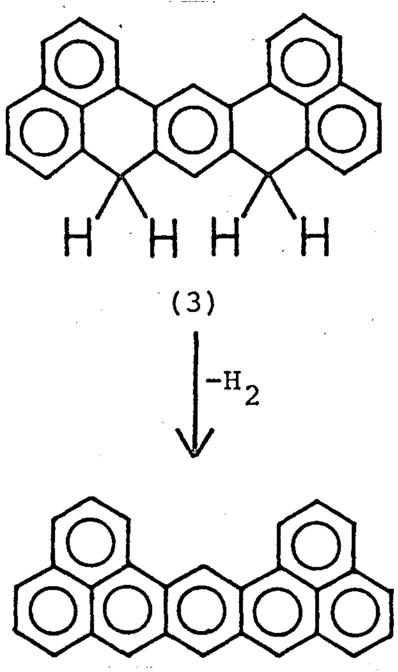
The dibenzo[de;jk]pentacenyl system (4) is a non-Kekulé even alternant hydrocarbon consisting of twentyeight carbon atoms which are divided into fifteen starred and thirteen unstarred carbon atoms as shown in following formula. Therefore, simple Hückel MO theory predicts that the dibenzo[de;jk]pentacenyl system should posses thirteen bonding and two nonbonding molecular orbitals with the energies depicted in Fig. 1.

As a result there are two ionic species, the dication (4a)



(1)

(2)



(3)

(4)

and the dianion (4c), with closed shell electronic configurations. On the other hand, the neutral species of (4), namely (4b), should exist as a diradical with triplet ground state because of the existence of a doubly degenerate pair of nonbonding molecular orbitals and the restriction of Hund's rule.

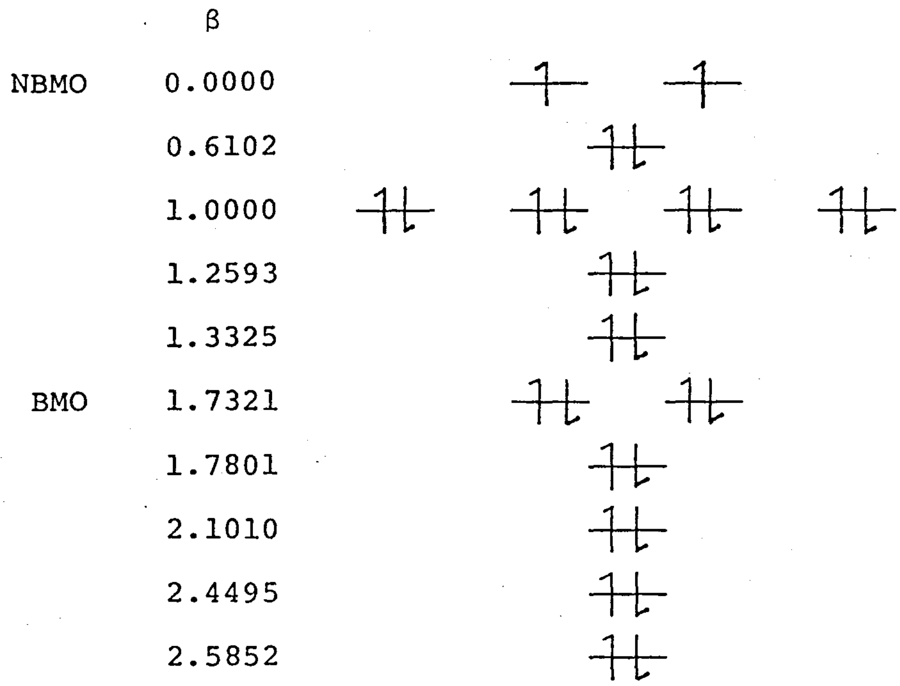
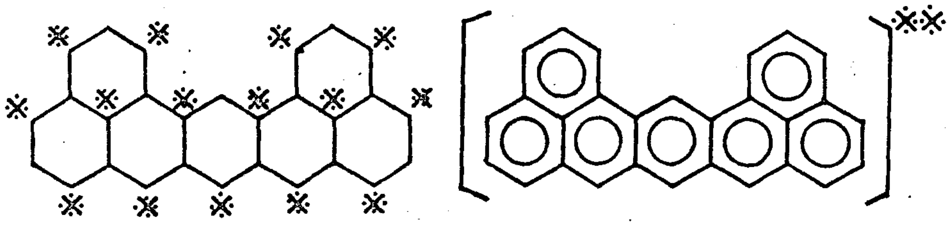


Fig. 1. Hückel Molecular Orbitals of Dibenzo[de;jk]pentacenyl System (4). The electronic state given above exhibits that for biradical (4b).



a) ; ※= +

b) ; ※= ·

c) ; ※= −

(4)

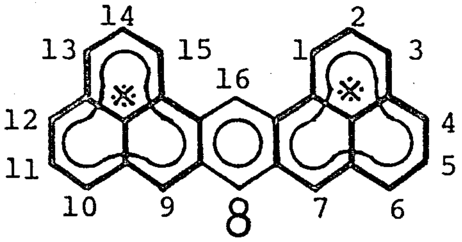
Since the absolute value of the π-charge density at atom i in a non-Kekulé even alternant hydrocarbon ion is calculated as

$$q_i = a_{0i}^2 + a_{0i}^{'2}$$

where $q_i$ is the charge density at atom i and $a_{0i}$ and $a_{0i}'$ are the respective coefficients of atom i in the nonbonding molecular orbitals$^{3)}$, charge densities of the dibenzo[de;jk]pentacenyl dication (4a) and dianion (4c) have readily been calculated and are given in Table 1. It should be noted that the fairly large charge density is found at C-8 both in the dication (4a) and the dianion (4c). Taking into account this situation the dibenzo[de;jk]pentacenyl system seems not to be a simple benzolog containing two phenalene systems (5) but to be an entirely novel non-Kekulé hydrocarbon.

Table 1. Hückel Charge Density of (4a) and (4c).

| Position | 1,15,3,13 | 4,12,6,10 | 7,9 | 8 | others |
|---|---|---|---|---|---|
| $\lvert q \rvert$ | 0.1037 | 0.1650 | 0.2670 | 0.1839 | 0.0000 |

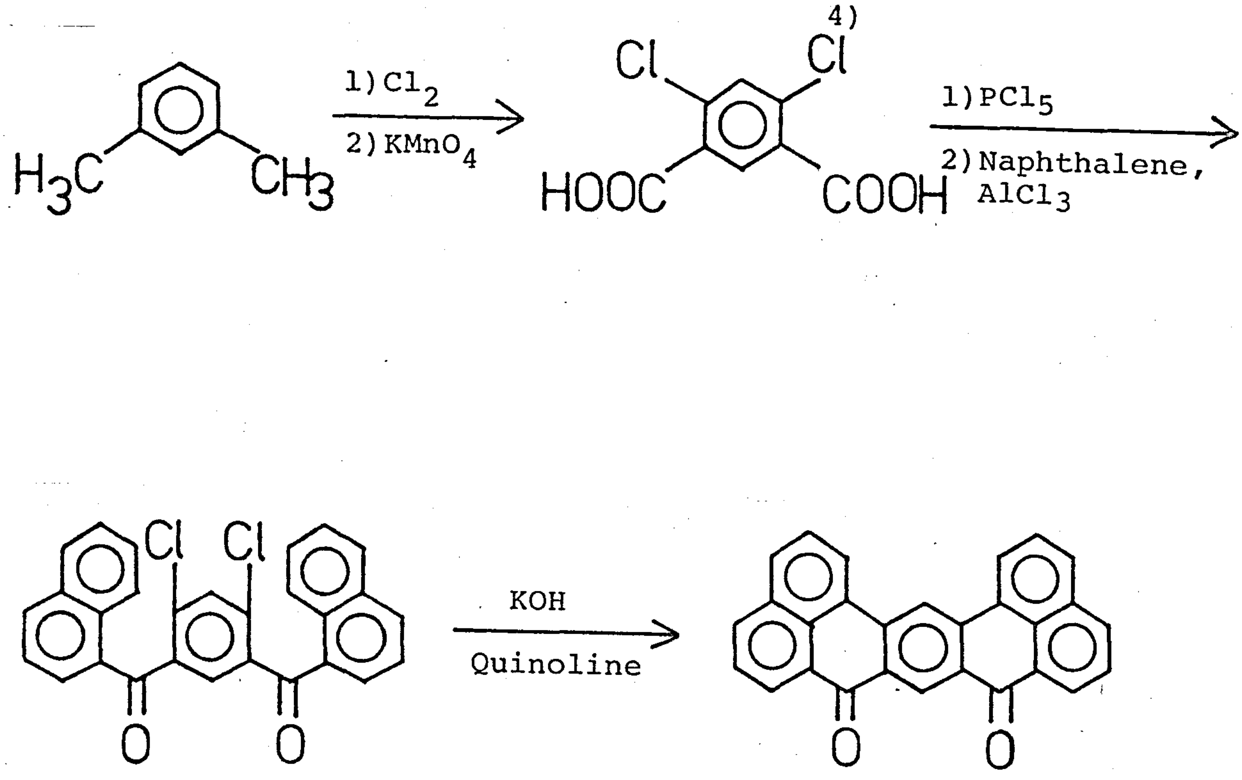


(5)

## 5.2. Synthesis of 7,9-Dihydrodibenzo[de;jk]pentacene

The attractive key intermediate for formation of dibenzo[de;jk]pentacenyl cation and anion seems to be 7,9-dihydrodibenzo[de;jk]pentacene-7,9-quinone (6) which was described in the literature by Clar$^{1,2)}$. The Clar's synthesis of (6) was illustrated in the following scheme. However no experimental

Scheme 1.

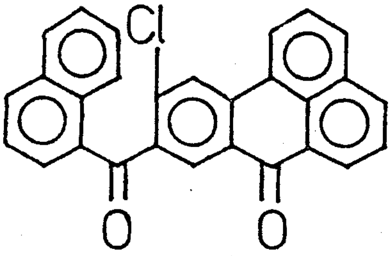


(7) (6)

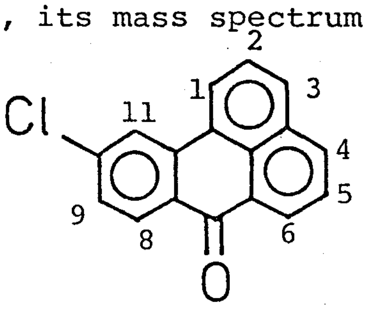
details concerning the double cyclization steps of (7) are avairable. Refluxing (7) and potassium hydroxide pellets in quinoline for 2.5-3.0 hr gave after chromatographic separation, a 5% yield of the desired quinone (6) along with two minor products, (8) and (9) in very low yields. The structures of (8) and (9) were deduced from their elemental analyses and spectroscopic data.

The ir spectrum of (8) displays a very broad band at about 1660 $cm^{-1}$ suggesting the existence of two kinds of structurally similar carbonyl groups. The nmr spectrum of (8) (see Fig. 2) in arsen trichloride exhibits signals at $\delta$ 7.41-8.85 as multiplet only in the region of aromatic protons. Additionally the structure of (8) was supported chemically by the fact that the quinone (6) could be obtained from (8) by the same way as applied to (7) in about 20% yield. Consequently it is apparent that (8) is a single cyclization product of (7).

The assigned structure of the other by-product (9) was also deduced from its elemental analysis, its mass spectrum ($M^+$, 264)



(8)



(9)

and its nmr spectum shown in Fig. 3. The obserbed chemical shifts and coupling constants in the 100 MHz nmr spectrum of (9), summarized in Table 2, are fully consistent with the assigned structure of (9). The complete assignments of signals as shown in Table 2 were performed by using the following double resonance experiments.

Irradiation at δ 8.60 (H-6) converted the doublet of doublets at δ 7.67 (H-5) into doublet with J=8.2 Hz. Another irradiation at δ 8.29 (H-8) changed the doublet of doublets at δ 7.37 (H-9) into doublet with J=1.9 Hz.

Table 2. The NMR Spectral Data of (9).

| Proton | Chem. Shift (δ ppm) | Multiplicity | Coupl. Constant (Hz) |
|---|---|---|---|
| 1 | 8.15 | dd | $J_{1,2}$=7.5<br>$J_{2,3}$=8.0<br>$J_{1,3}$=1.3<br>$J_{4,5}$=8.2<br>$J_{5,6}$=7.5<br>$J_{4,6}$=1.5<br>$J_{8,9}$=8.5<br>$J_{9,11}$=1.9 |
| 2 | 7.52 | dd | |
| 3 | 7.89 | dd | |
| 4 | 8.08 | dd | |
| 5 | 7.67 | dd | |
| 6 | 8.60 | dd | |
| 8 | 8.29 | d | |
| 9 | 7.37 | dd | |
| 11 | 8.06 | d | |

To confirm the desired quinone (6), the following spectral measurements were made since no spectroscopic properties of (6) were given in the literature. The ir spectrum of (6) exhibits two carbonyl absorption bands at 1647 and 1702 $cm^{-1}$ characteristic to quinone moiety. The symmetrical nature of (6) was paticularly easy to identify by its 100 MHz nmr spectrum (Fig. 4) which was measured in arsen trichloride because of its extremely low solu-

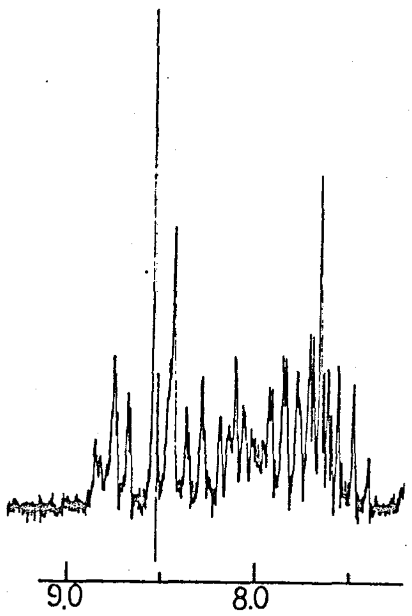


Fig. 2. The NMR Spectrum of (8) in $AsCl_3$.

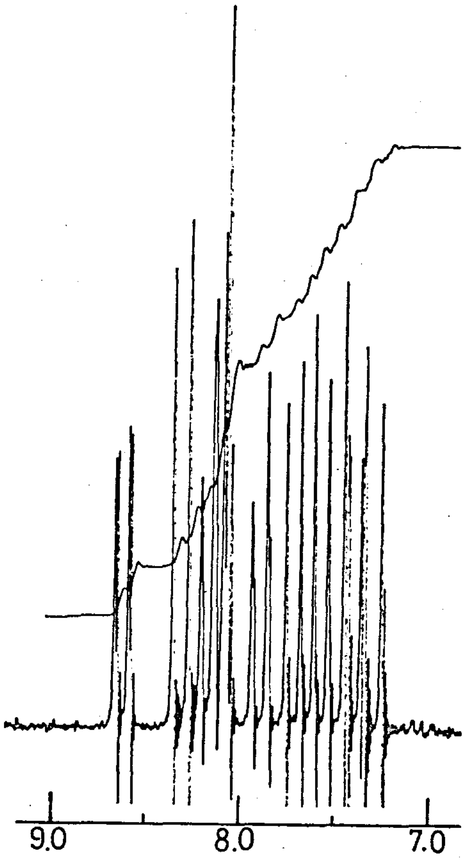
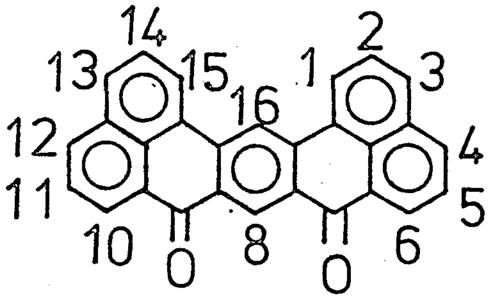


Fig. 3. The NMR Spectrum of (9) in $CDCl_3$.

bility in usual organic solvents. Result obtained is summarized in Table 3.

The symmetrical pattern of the nmr spectrum of the quinone (6) is in good agreement with the given structure with $C_{2v}$-symmetry. In addition, the assignments of the nmr spectrum of (6) given in Table 3 are reasonable in comparison with the chemical shifts and coupling constants of the corresponding protons of (9)(see Table 2) and 6H-benzo[cd]pyren-6-one (10) shown in Table 4.



(6)

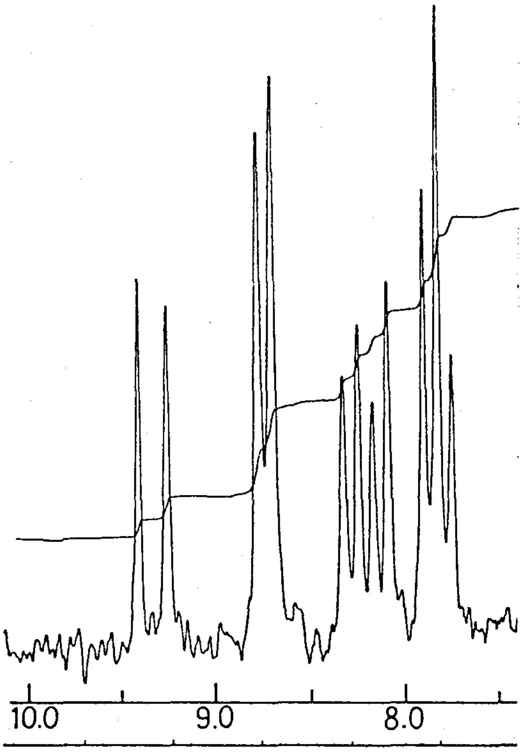


Fig. 4. The NMR Spectrum of (6) in $AsCl_3$.

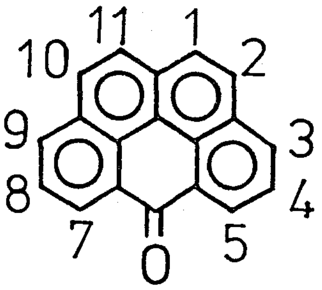
Table 3. The NMR Spectral Data of (6).

| Proton | Chem. Shift ($\delta$ ppm) | Multiplicity | Coupl. Const. (Hz) |
|---|---|---|---|
| 1, 15 | 8.74 | d | $J_{1,2}=J_{14,15}$ =7.5<br>$J_{2,3}=J_{13,14}$ =8.0 |
| 2, 14 | 7.82 | dd | |
| 3, 13 | 8.12 | d | |
| 4, 12 | 8.27 | d | $J_{4,5}=J_{11,12}$ =8.0<br>$J_{5,6}=J_{10,11}$ =7.5 |
| 5, 11 | 7.82 | dd | |
| 6, 10 | 8.74 | d | |
| 8 | 9.41 | s | |
| 16 | 9.25 | s | |

Table 4. The NMR Spectral Data of (10) in $CDCl_3$.

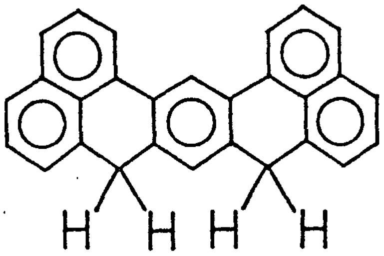
| | |
|---|---|
| H-1,11<br>H-2,10 } $\delta$ 7.84, 7.72 (ABq), | $J_{1,2}=J_{10,11}=8.9$ Hz |
| H-3, 9 $\delta$ 8.11, (dd), | $J_{3,4}=J_{8,9}=1.5$ Hz |
| H-4, 8 $\delta$ 7.72, (dd), | $J_{3,5}=J_{7,9}=1.5$ Hz |
| H-5, 7 $\delta$ 8.69, (dd), | $J_{4,5}=J_{7,8}=7.5$ Hz |

(10)



7,9-Dihydrodibenzo[de;jk]pentacene-7,9-quinone, available by the known scheme described above, was converted to the desired 7,9-dihydrodibenzo[de;jk]pentacene (11), which is regarded as a possible precursor of our target compounds, (4a), (4b), and (4c), by lithium aluminum hydride-aluminum chloride complex reduction in 40-50% yield.

$$(6)\quad \xrightarrow[\text{Ether}]{\text{LiAlH}_4\text{-AlCl}_3}$$



(11)

While the hydrocarbon (11) decomposes on activated alumina in a column chromatography, isolation and purification of (11) were conveniently achieved through chromatography on deactivated alumina (with 2.5% water) and recrystallization from toluene under nitrogen atmosphere. Compound (11) is highly air-sensitive in solution but is stable enough to be stored for a quite long period in a pure crystalline state.

The structure of (11) was confirmed on the basis of its elemental analysis and its spectroscopic properties. The elemental analysis and the mass spectrum of (11) were in full accord with a molecular formula of $C_{28}H_{18}$. Further structural assignment of (11) follows from its nmr spectrum (Fig. 5) which shows a single benzylic protons singlet at δ 4.53 (4H, H-7,7',9, 9') along with a singlet at δ 7.17 (1H, H-8), a doublet at δ 8.13 (2H, H-1,15, J=7.0 Hz), a singlet at δ 8.67 (1H, H-16), and other aromatic protons multiplet at δ 7.36-7.76 (10H).

On the other hand, it has been shown by Clar[2)] that the reduction product of the quinone (6) with zinc dust and acetic acid in pyridine is 7,9-dihydrodibenzo[de;jk]pentacene. However, the reported melting point (345°C) and the electronic spectrum of his compound (3) are quite different from those of our product (11). As can be seen from Fig. 6, the absorption

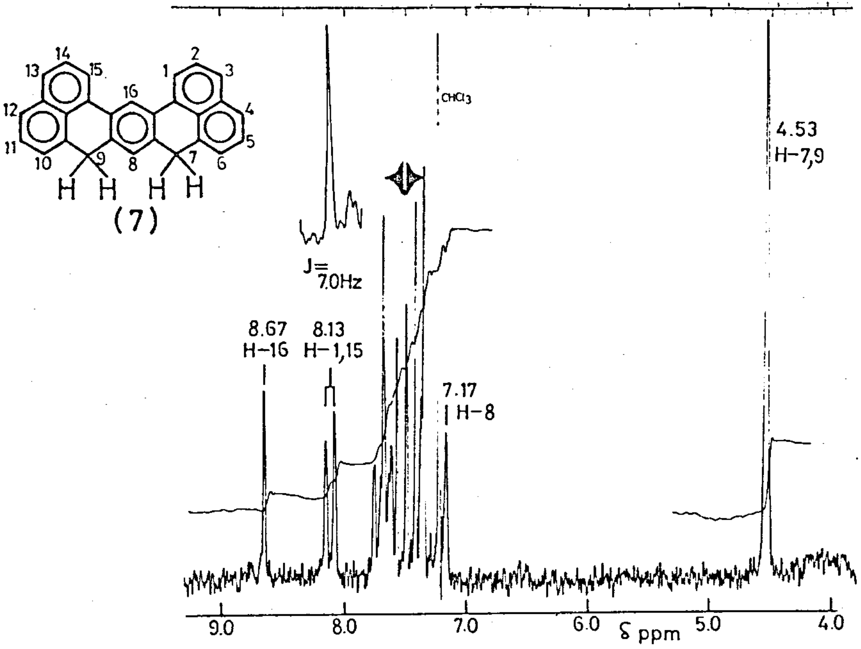


Fig. 5. The NMR Spectrum of (11) in $CDCl_3$.

spectrum of our compound (11), unlike Clar's hydrocarbon (3), is closely similar to that of the model compound, 7H-benzanthrene (12), both in absorption maxima and in intensities. In conclusion, Clar's hydrocarbon (3) should be assigned as one of the possible isomers involving the methylene group(s) at different position(s).

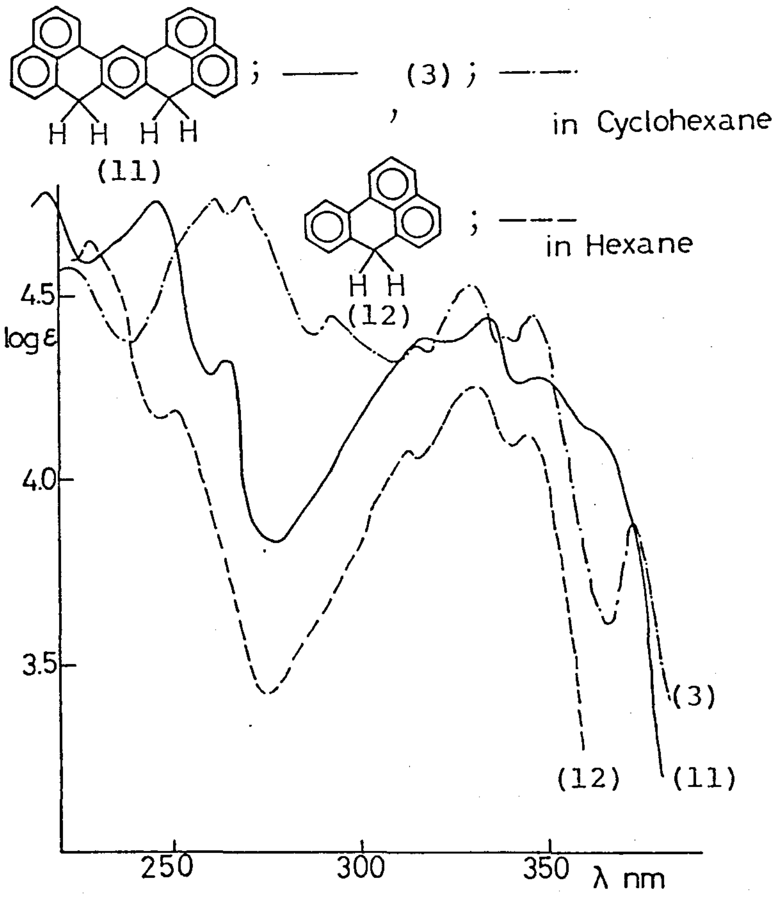


Fig. 6. The Electronic Spectra of (3), (11), and (12).

## 5.3. Synthesis of Dibenzo[de;jk]pentacenyl Dication

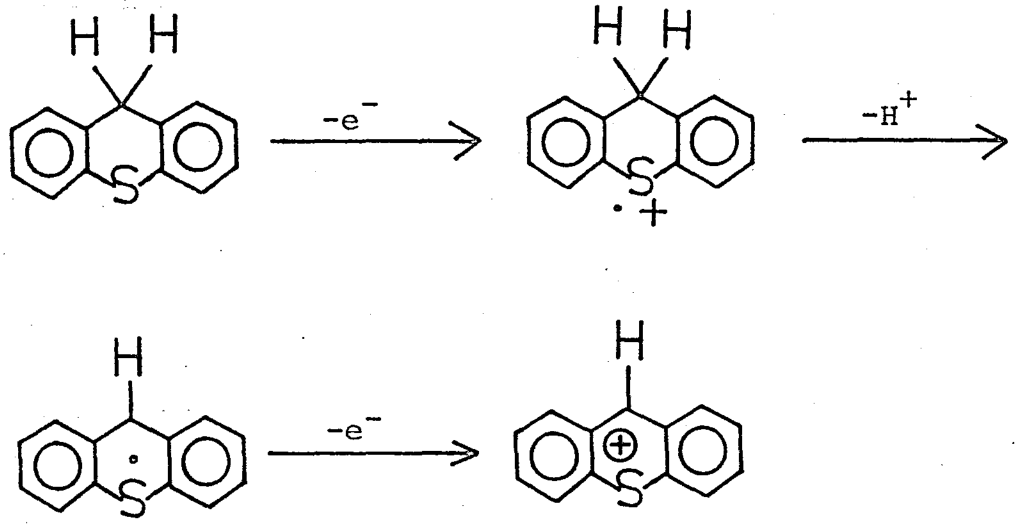
In the past decade, Olah and his co-workers[6)] have actively investigated a large number of carbonium ions which are obtained in strong acidic media such as pentafluoroantimonate in fluorosulfonic acid. On the other hand, Hogeveen[7)] and Lukas[8)] have studied kinetically the mechanisms of the generation of various carbonium ions from the corresponding alkanes by the oxidation with pentafluoroantimonate in hydrogenfluoride or fluorosulfonic acid.

Recently, Pagni[9)] has studied on the process in which hydrocarbons containing extensive π-systems, such as cycloheptatriene, phenalene and others, are oxidized to the corresponding carbonium ions with fluorosulfonic acid, concd. sulfuric acid, and other oxidizing agents. As a result, he[9,10)] proposed the mechanism through radical cation as displayed in Scheme 2, not a direct hydride abstraction.

Our approach to the dibenzo[de;jk]pentacenyl dication (4a) has been through utilization of the above mentioned reaction.

When the hydrocarbon (11) is dissolved in 97% dideuteriosulfuric acid a dark green solution results, the species in which has been shown by nmr spectrum (see Fig. 7) to be the dication (4a), which indicates that (11) may undergo oxidative hydrides

Scheme 2.



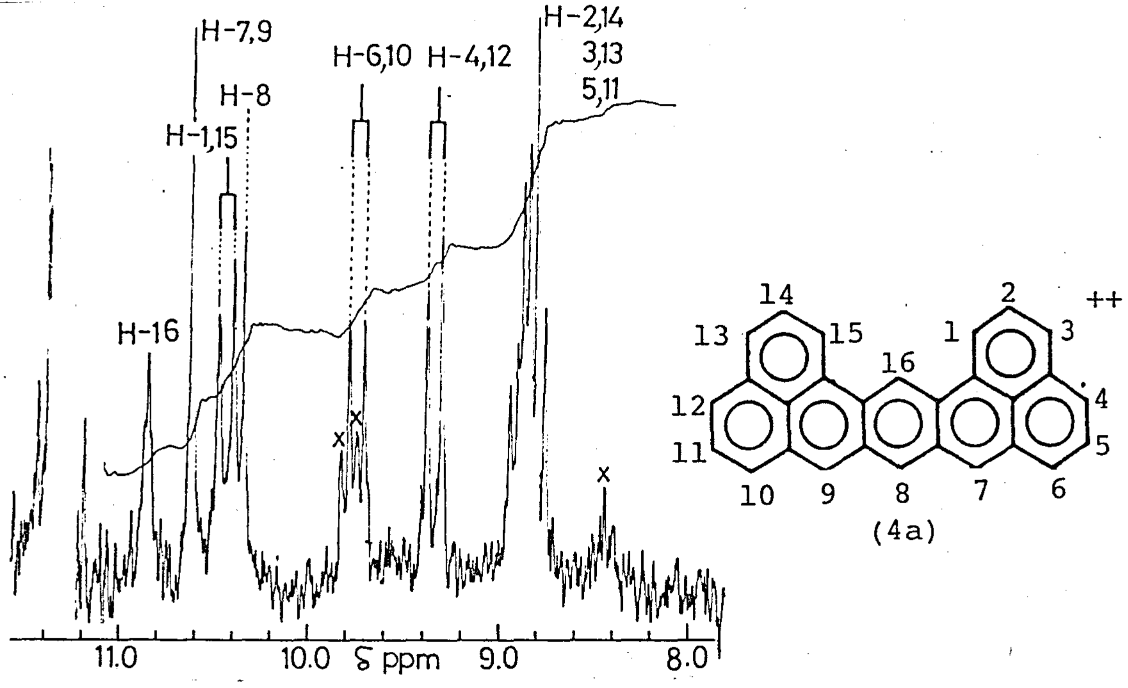


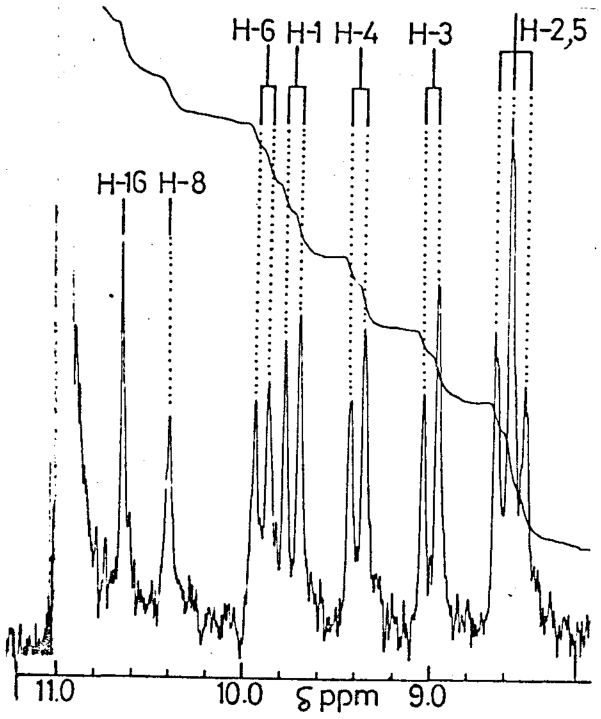
Fig. 7. The NMR Spectrum of (4a) in $D_2So_4$.

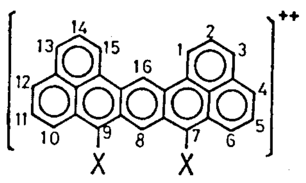
abstraction similar to that for reported by Pagni. As shown in Fig. 7, all signals appear as symmetrical pattern in fairly low magnetic region.

The nmr assignments in (4a) (see Table 5) were based upon the consideration of both the deshielding effects due to the positive charge densities on the respective carbon atoms predicted by Hückel molecular orbital calculation (see Table 1) and the diamagnetic ring current effect of the neighboring benzene rings (see Table 7). Thus, the first-order anlysis of the spectrum is in full accord with the delocalized structure of (4a) with $C_{2v}$-symmetry. Significant feature of the spectrum is that the signals attributable to H-7,8,9 and 16 resonate at considerable low magnetic field (within $\delta$ 10.3 to $\delta$ 10.8). The assignments of the signals at $\delta$ 10.34 and 10.86 to H-8 and H-16, respectively, were determined according to the fact that the ring current effects affected to H-7 (9) and H-8 were suspected as in the same order in magnitude while the protons attached to C-7 and C-9 should be more deshielded than H-8 because the charge density on C-7 (9) is larger than that on C-8 (see Table 1).
The remaining protons are reasonably assigned when we take into account the effects of $\pi$-charge density and anisotropy of ring currents associated with the neighboring benzene rings.

It should be noted the three signals indicated by check marks (X) in Fig. 7 are believed to be those of by-products which formed on oxidation process by dideuteriosulfuric acid since the heights of these signals have varied as compared with those assigned to (4a) for each experiment. Furthermore, the formation of the dication (4a) is reproducible within three experiments.

On the other hand, presumably due to the formation of the dihydroxy dication (13) the quinone (6) could be dissolved reversibly in 97% sulfuric acid. Treatment of (6) with 97% dideuteriosulfuric acid led to the formation of a dark red





(4a) X=H
(13) X=OH
(13-D) X=OD

Fig. 8. The NMR Spectrum of (6) in $D_2So_4$.

solution whose nmr spectrum depicted in Fig. 8. From the inspection of the spectrum, e.g., its symmetrical pattern and the comparison of the chemical shifts with those of (4a), it is evident that the quinone (6) exists as the dication (13-D) in 97% dideuteriosulfuric acid.

Assignments of the nmr spectrum of (13-D) given in Table 5 are straightforward, on the whole, based on the comparison with those of the dication (4a) and of the phenalenium (14) and hydroxyphenalenium cation (15) reported in the literature11) (see Table 6).

Table 5. The NMR Spectral Data of (4a) and (13-D).

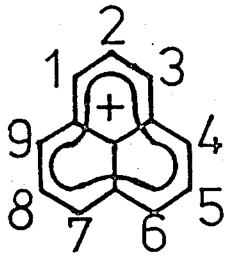
| Proton | (4a) Chem. Shift* (δ ppm) | (4a) Coupl. Const. (Hz) | (13-D) Chem. Shift* (δ ppm) | (13-D) Coupl. Const. (Hz) |
|---|---|---|---|---|
| 1,15 | 10.44 | $J_{1,2}$ $=J_{14,15}$ $=8.0$ | 9.74 | $J_{1,2}$ $=J_{14,15}$ $=J_{2,3}$ $=J_{13,14}$ $=7.5$ |
| 2,14 | 8.94-8.74 | | 8.58 | |
| 3,13 | | | 8.98 | |
| 5,11 | | $J_{4,5}$ $=J_{11,12}$ $=J_{5,6}$ $=J_{10,11}$ $=8.0$ | 8.58 | |
| 4,12 | 9.34 | | 9.36 | $J_{4,5}$ $=J_{11,12}$ $=J_{5,6}$ $=7.5$ |
| 6,10 | 9.75 | | 9.92 | |
| 7, 9 | 10.61 | | — | |
| 8 | 10.34 | | 10.67 | |
| 6 | 10.86 | | 10.40 | |

* δ-values from external TMS.

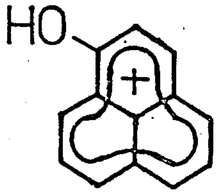
Table 6. The Chemical Shifts (δ) of (14) in $AsCl_3$ and (15) in $CF_3COOH$.11)

| Proton | (14)* | (15) |
|---|---|---|
| 1 | 9.30 | / |
| 2 | 8.48 | 7.76 |
| 3 | 9.30 | 8.88 |
| 4 | 8.48 | 8.78 |
| 5 | 9.30 | 8.20 |
| 6 | 8.48 | 8.86 |
| 7 | 9.30 | 9.01 |
| 8 | 8.48 | 8.30 |
| 9 | 9.30 | 9.46 |

* Phenalenium Hexachloroantimonate



(14)



(15)

Fig. 9 exhibits the electronic spectra of the dication (4a) and the dihydroxy dication (13), the ε-values of (4a) were estimated assuming quantitative conversion of (11) to (4a).

Our efforts were then directed towards isolation of the dication (4a) as a bistetrafluoroborate. To this end we applied the usual hydride abstraction reaction with triphenylmethyl tetrafluoroborate.

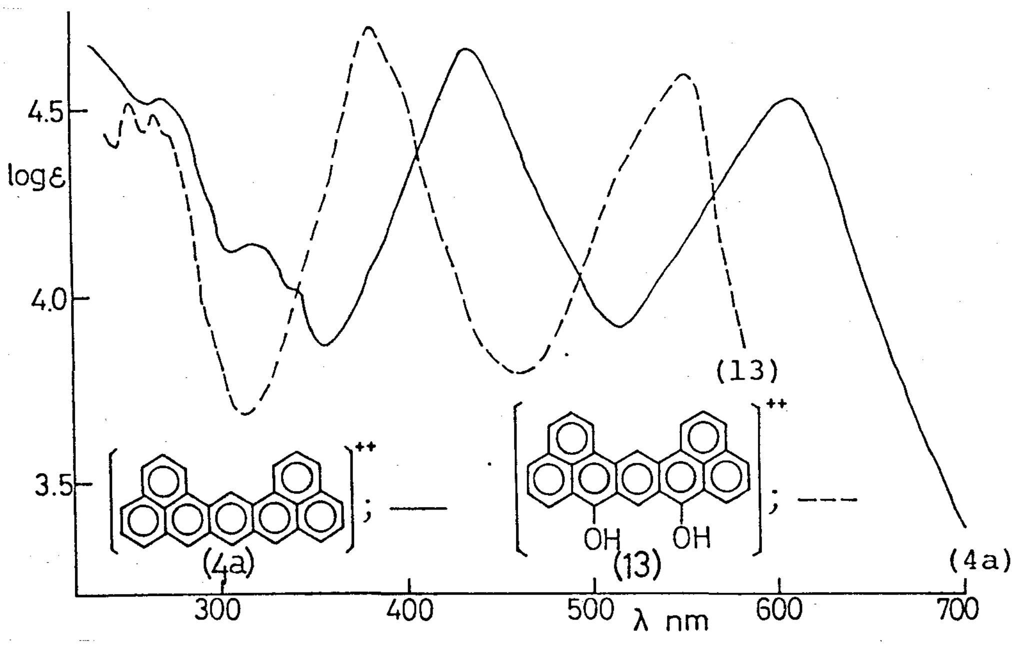
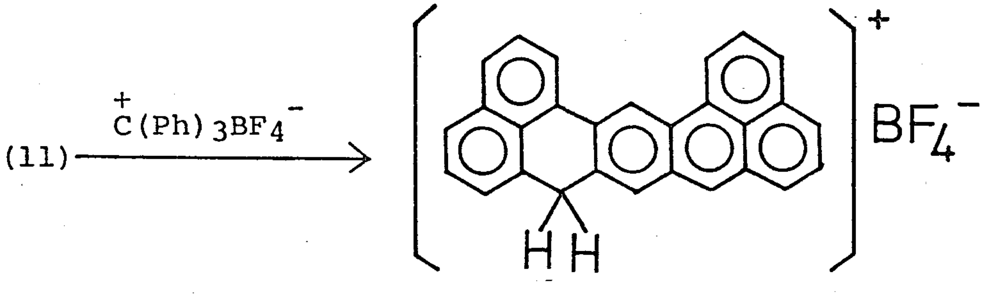


Fig. 9. The Electronic Spectra of (4a) and (13).

Thus, treatment of (11) with two molar equivalents of triphenylmethyl tetrafluoroborate in a mixture of chloroform and acetonitrile resulted in the precipitation of black solids which are soluble in arsen trichloride or slightly in trifluoroacetic acid as a dark green solution. The product had high melting poind ( > 300°C) and extremely low solubility in usual



(16)

organic solvents and decomposed on exposing to moisture with fading to yellow.

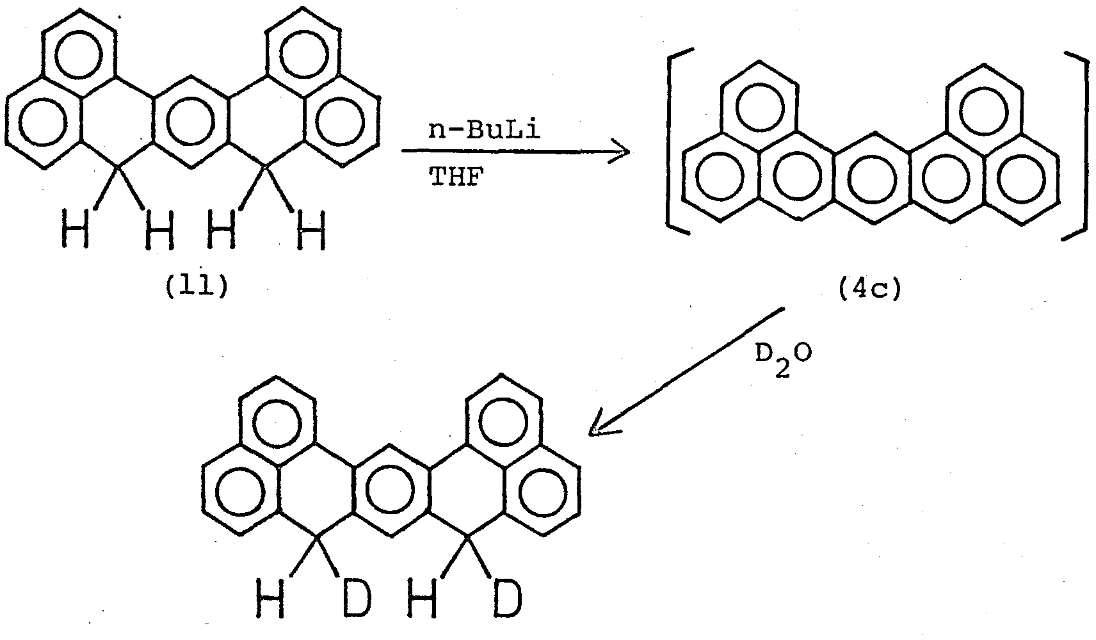
The ir spectrum of the product displays a strong broad band at 1020-1140 $cm^{-1}$ suggesting the existence of tetrafluoroborate anion. Its nmr spectrum in arsen trichloride shows along with signals of aromatic protons at $\delta$ 9.68-7.60, a two hydrogens singlet at $\delta$ 4.90 indicating preservation of an intact methylene group. These spectroscopic evidences strongly suggested that the product might be the monocation formulated as (16). This presumption was further revealed by the transformation of the product into the dication (4a). Thus, a solution of (16) in 97% dideuteriosulfuric acid shows the exactly identical nmr spectrum with that of (4a) obtained from the hydrocarbon (11). Unfortunately the expected dication bistetrafluoroborate could not be obtained so far through the direct hydride abstraction reaction.

In summary, we have demonstrated that the dication (4a) can be generated from the precursor hydrocarbon (11). The dication can be regarded as a fully delocalized divalent cation with $C_{2v}$-symmetry as predicted by Hückel molecular orbital theory. Although there exists no excellent linear relationship between the chemical shifts and the charge densities as dipicted in Fig. 12, it is clear that the positive charges reside on the alternate starred atoms.

## 5.4. Synthesis of Dibenzo[de;jk]pentacenyl Dianion

In view of the precidents that the phenalenyl[11] and benzo[cd]pyrenyl anions, which can be prepared from the corresponding hydrocarbons by direct proton abstraction, we were encouraged to examine the possibility of this transformation in the preparation of the dibenzo[de;jk]pentacenyl dianion.

When 7,9-dihydrodibenzo[de;jk]pentacene (11) is treated with butyllithium in tetrahydrofuran at -60°C a dark greenish brown solution results, the major component of which has been shown by chemical and spectroscopic evidences to be the desired dibenzo[de;jk]pentacenyl dianion (4c). That is to say, treatment of (11) in freshly distilled tetrahydrofuran with butyllithium



(11) (4c) (17)

under nitrogen atmosphere at -60°C followed by quenching with deuterium oxide to give the hydrocarbon (17). Incorporation of two deuteriums in (17) is borne out by its mass spectrum which showed parent ion peak at m/e 356. The sites of the deuterium incorporation are unequivocally proved to be C-7 and C-9 positions because the compound (17) exhibits a broad 2H singlet at $\delta$ 4.50 along with the aromatic protons signals identical with those of (11) in nmr spectrum as shown in Fig. 10 (see also Fig. 5). Exclusive deuteriation at C-7 and C-9 is well accord with the maximum charge density found on these carbon atoms (vide infra).

Because of the extremely low solubility of the dianion (4c) in tetrahydrofuran, which is presumably attributed to the doubly

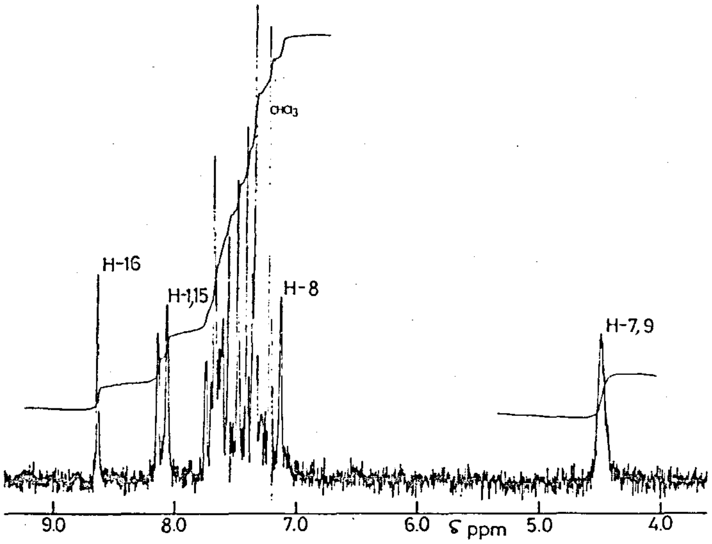


Fig. 10. The NMR Spectrum of (17) in $d_8$-THF.

charged molecule composed of twenty eight carbon atoms, and the instability of (4c) at temperature above -40°C nmr determination of this species appears to be difficult. Successful measurement of the nmr spectrum of (4c), however, could be achieved by the usual method with slight modification as follows.

The solvents of butyllithium such as hexane and ether, which would lower the solubility of (4c), were removed to some extent in vacuo and then to this butyllithium a degassed solution of (11) in $d_8$-tetrahydrofuran was added at -40 to -45°C. The resulting solution contains the dianion (4c). The reason why we choose the temperature range as above is that the proton abstraction from (11) without decomposition of the resulting dianion could be performed only under the limited temperature range because of the high viscosity of the evaporated butyllithium solution.

Since no satisfactory CW spectrum could be obtained owing to a very low concentration of (4c), the acceptable spectrum shown in Fig. 11 was recorded at -40°C by using CAT technique. On account of the very intense signals of both the solvents and the residual protons of $d_8$-tetrahydrofuran in the high field region, pulse Fourier-Transform technique could not be employed for our case.

As is the case of the phenalenyl and benzo[cd]pyrenyl anions, it seems reasonable that the similar linear relationship between chemical shifts and Hückel charge densities also exists in the present dianion (4c). With the aid of this assumption, all nmr parameters of (4c) are readily obtained by means of first-order analysis and are summarized in Table 7. This is fully consistent with the expected delocalized structure with $C_{2v}$-symmetry.

In paticular the up-field shifts of signals H-7,9,6,10,4,12 and 8 are ascribable to the relatively large negative charge

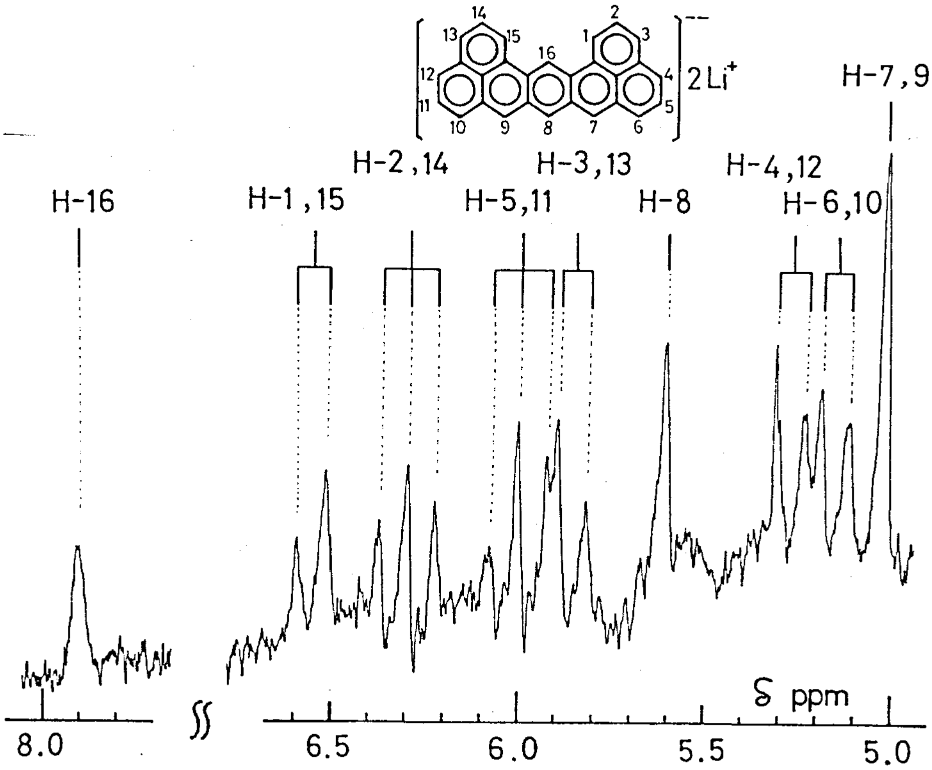


Fig. 11. The NMR Spectrum of (4c) in $d_8$-THF.

Table 7. The NMR Spectral Date of (4c).

| Position | Obs. Chem. Shift[a)] | Ring Current Correct.[b)] | Correct. Chem. Shift | Hückel Charge Density |
|---|---|---|---|---|
| 1,15 | 6.62 | 1.67 | 4.95 | -0.1037 |
| 2,14 | 6.36 | 0.71 | 5.65 | 0.0000 |
| 3,13 | 5.93 | 0.97 | 4.96 | -0.1037 |
| 4,12 | 5.33 | 0.93 | 4.40 | -0.1650 |
| 5,11 | 6.07 | 0.58 | 5.49 | 0.0000 |
| 6,10 | 5.22 | 1.02 | 4.20 | -0.1650 |
| 7, 9 | 5.08 | 1.60 | 3.48 | -0.2670 |
| 8 | 5.67 | 1.67 | 4.00 | -0.1839 |
| 16 | 7.89 | 2.46 | 5.43 | 0.0000 |

a) δ-Values were determined in $d_8$-THF, relative to the low-field THF signal assumed to lie at δ 3.63 from TMS.

b) The sum of ring current corrections for adjacent benzene rings by the simple point approximation calculated by using the formula, $(12.0)a^2\Sigma_i R_i^{-3}$.12) densities on the respective carbon atoms. On the other hand, low-field signals of H-16, 1, and 15 can be accounted for by the deshielding effect due to the induced diamagnetic ring current of the adjacent benzene rings.

As shown in Fig. 12, plot of the nmr chemical shifts (after correcting for respective ring current effects, see Table 7) of the protons of the dianion (4c) versus the Hückel charge densities of the corresponding carbon atoms has been made, and the data fitted a good straight line. The points for lithium phenalenide and benzo[cd]pyrenide also fall almost on the same line of (4c).

Consequently, from the excellent linear correlation between the nmr chemical shift and the Hückel charge density it is evident that the excess negative charge resides on the alternate carbon atoms of the dianion (4c) as predicted by Hückel molecular orbital calculations. The good agreement of the experimental and theoretical results leads to the conclusion that the dibenzo[de;jk]pentacenyl system (4) is a typical instance of non-Kekulé even alternant systems and strongly suggests that the diradical (4b) should exist in triplet ground state.
Further experiments aimed to detect the diradical are progress.

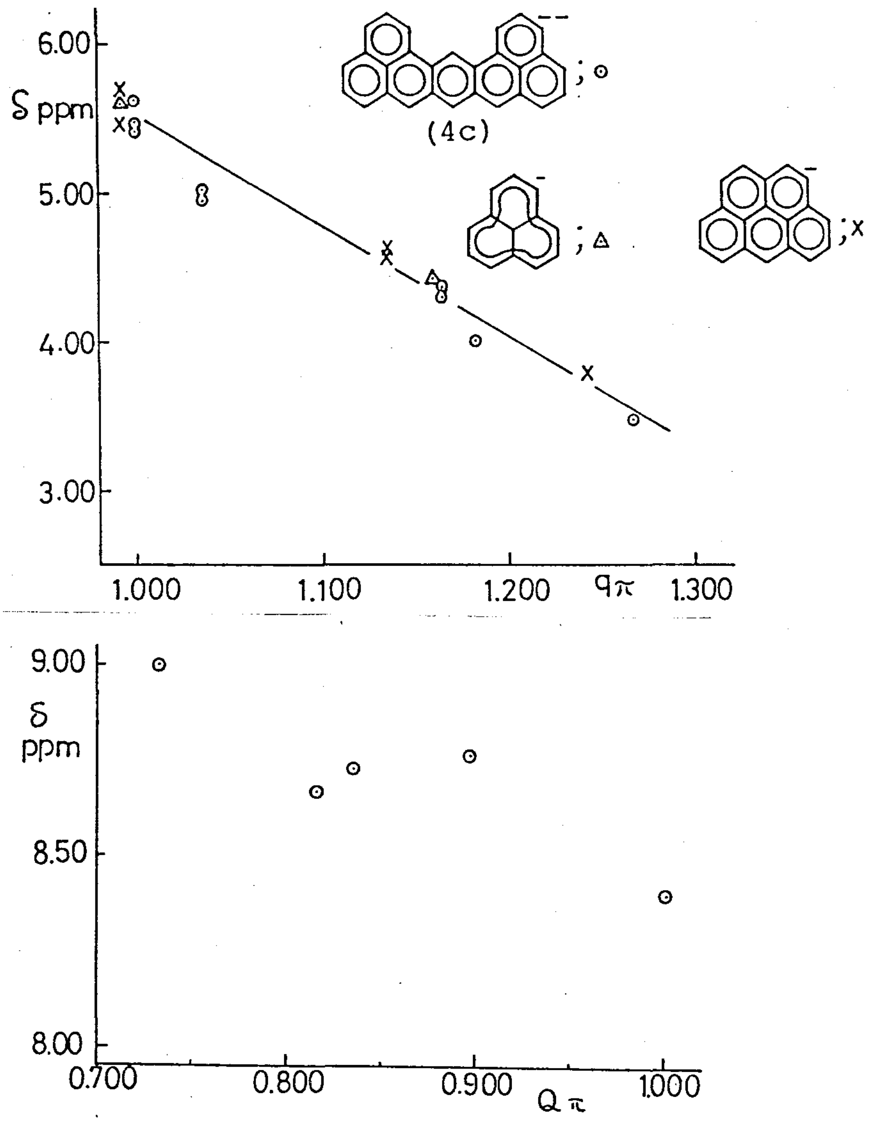


Fig. 12. Plot of Chemical Shift vs. Charge Density of (4c) [upper] and (4a) [lower].

## 5.5. Experimental

Exp. 1. 7,9-Dihydrodibenzo[de;jk]pentacene-7,9-quinone (6):

10 g (22 mmol) of 1,3-dichloro-4,6-(α-naphthoyl)-benzene was dissolved in 60 ml of boiling quinoline and potassium hydroxide pellets (2.5 g) were added gradually over 30 min. The mixture was gently refluxed for 2.5-3.0 hr and then poured into dilute hydrochloric acid (50 ml). The dark brown solids were collected by means of filtration and boiled with dilute hydrochloric acid and then with dilute aquous solution of sodium hydroxide. On cooling, the collected dark brown solids by filtration were ground in a mortar and chromatographed on alumina eluting gradiently with benzene, benzene-chloroform (1:1), and chloroform. The solvent of the each fraction was stripped to give two derivatives of 7H-benzanthrone (8) and (9) from benzene and benzene-chloroform eluates respectively, and the desired quinone (6) from chloroform eluate. Recrystallization of the crude (8) and (9) from toluene gave pure (8) as yellow needles with mp 291-293°C in 2-3% yield and pure (9) as brownish yellow needles with mp 187.5-189°C in 2-3% yield respectively. The pure quinone (6) was purified by the reported[1,2] procedures.

(8):

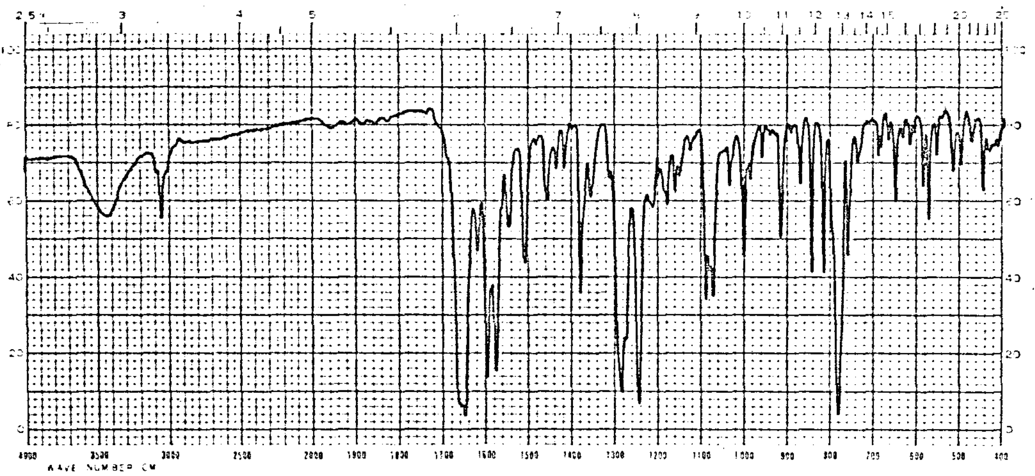
Anal. Calcd for $C_{28}H_{15}O_2Cl$: C, 80.29; H, 3.69; Cl, 8.46%

Found : C, 80.39; H, 3.61; Cl, 8.27%

NMR (δ in $AsCl_3$). 7.41— 8.85 (m).

ES ($CH_3CN$). $\lambda_{max}$ (log ε); 385(4.20), 309(4.28), 237(4.68), 212(4.91).

IR (KBr). $\nu_{C=O}$ ; 1658 $cm^{-1}$.



(9):

Anal. Calcd for $C_{17}H_9ClO$: C, 77.14; H, 3.43; Cl, 13.39%.

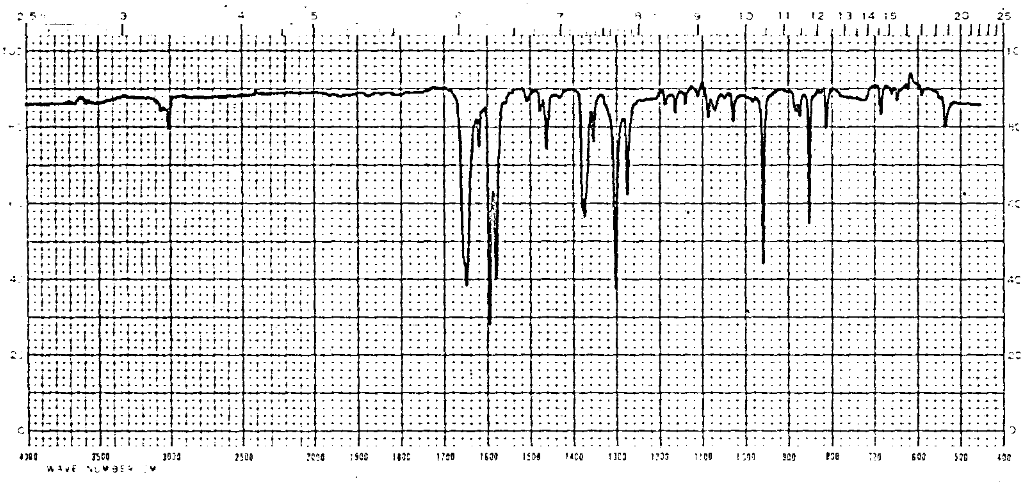
Found : C, 76.99; H, 3.59; Cl, 12.91%.

MS. m/e 264 ($M^+$, 100%), 236 ($M^+$-CO, 25%), 201 ($M^+$-CO, Cl, 27%).

NMR ($\delta$ in $CDCl_3$). 7.37(dd, 1H, H-9, $J_{8,9}$=8.5 Hz, $J_{9,11}$=1.9 Hz), 7.52(dd, 1H, H-2, $J_{1,2}$=7.5 Hz, $J_{2,3}$=8.0 Hz), 7.67(dd, 1H, H-5, $J_{4,5}$=8.2 Hz, $J_{5,6}$=7.5 Hz), 7.89(dd, 1H, H-3, $J_{1,3}$=1.3 Hz), 8.06(d, 1H, H-11), 8.08(dd, 1H, H-4, $J_{4,6}$=1.5 Hz), 8.15(dd, 1H, H-1), 8.29(d, 1H, H-8), 8.60 (dd, 1H, H-6).

ES ($CH_3CN$). $\lambda_{max}$ (log $\varepsilon$); 382(4.08), 304(4.09), 284(4.02), 273(3.94), 253(4.40), 242(4.51), 232(4.50), 211(4.72).

IR($CHCl_3$). $\nu_{c=o}$; 1649 $cm^{-1}$.



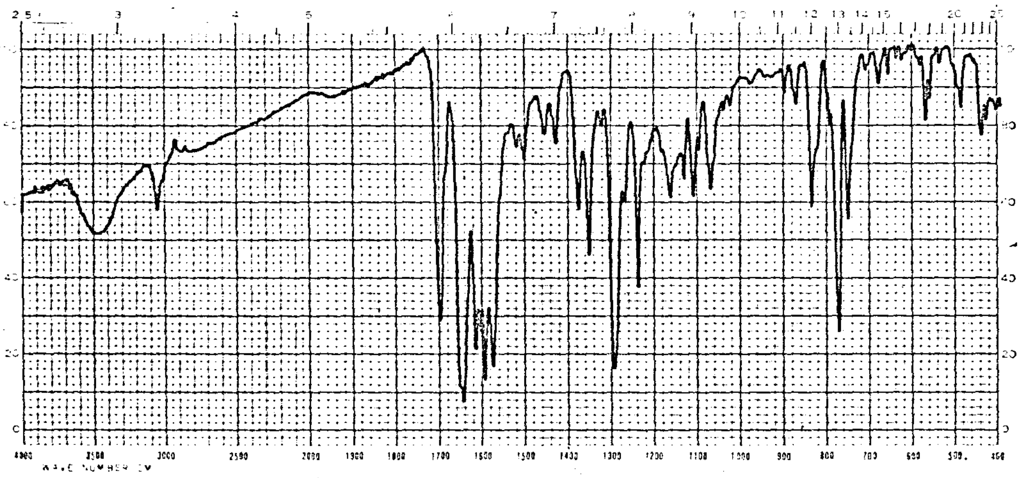
(6):

MS. m/e 382 ($M^+$, 100%), 354 ($M^+$-CO, 20%), 326 ($M^+$-2CO, 35%).

NMR ($\delta$ in $AsCl_3$). 7.82(dd, 4H, H-2,5,11,14, $J_{1,2}=J_{14,15}=7.5$ Hz, $J_{2,3}=J_{13,14}=8.0$ Hz, $J_{4,5}=J_{11,12}=8.0$ Hz, $J_{5,6}=J_{10,11}=7.5$ Hz), 8.12(d, 2H, H-3, 13), 8.27(d, 2H, H-4, 12), 8.74(d, 4H, H-1,15,6, 10), 9.25(s, 1H, H-16), 9.41(s, 1H, H-8).

ES($CH_3CN$). $\lambda_{max}$ (log $\varepsilon$); 428(4.36), 405(4.27), 330(4.31), 301.5(4.35), 290(4.27), 277(4.24), 228(4.67).

IR(KBr). $\nu_{C=O}$; 1647, 1702 $cm^{-1}$.



Exp. 2. 7,9-Dihydrodibenzo[de;jk]pentacene (11):

To a stirred suspension of lithium aluminium hydride 540 mg (14 mmol) in 120 ml of anhydrous ether was added 3.74 g (28 mmol) of anhydrous aluminum chloride all at once under nitrogen atmosphere in an ice bath. The mixture was stirred at room temperature for 2 — 3 hr, the solids were allowed to settle and the clear supernatant solution was transfered into another flask. To the solution was added 76.4 mg (0.2 mmol) of finely powdered diketone (6) over 30 min at room temperature under nitrogen atmosphere. The reaction mixture was stirred overnight and quenched with ether saturated with water, and dil. hydrochloric acid and 50 ml of benzene was added. The organic layer was washed successively with satulated aqueous solution of sodium hydrogen carbonate and water, and dried over anhydrous magnesium sulfate. After removal of the solvent the yellow residue was chromatographed on the deactivated alumina containing 2.5% of water eluting with hexane-benzene (2:1) to give 35 mg (50%) of crude (11). The crude product was recrystallized from toluene under nitrogen atmosphere to give slightly pale yellow needles, mp 213-214°C (decomp.).

Anal. Calcd for $C_{28}H_{18}$ : C, 94.98; H, 5.12%.

Found : C, 94.67; H, 5.07%.

MS. m/e 354 ($M^+$, 100%), 353 (M-1, 97%), 352 (M-2, 42%).

NMR ($\delta$ in $CDCl_3$). 4.53(s, 4H, H-7,7',9,9'), 7.17(s, 1H, H-8), 7.36-7.76(m, 10H, H-2,3,4,5,6,10,11 12,13,14), 8.13(d, 2H, H-1,15, $J_{12}=J_{14,15}=7.0$ Hz), 8.67 (s, 1H, H-16).

ES(cyclohexane). $\lambda_{max}$ (log $\varepsilon$); 362(4.14), 347(sh, 4.29), 332 (4.44), 316(4.37), 264(4.32), 246(4.76), 217(4.78), 210(4.77).

Exp. 3. Dibenzo[de;jk]pentacenyl dication (4a) in concd sulfuric acid.

To 0.5 ml of 97% $D_2SO_4$ was added 13 mg (0.04 mmol) of 7,9-dihydrodibenzo[de;jk]pentacene (11) under stirring at room temperature. The mixture was stirred for 30 min at the same temperature to give a dark green solution of the dicatin (4a). The nmr spectrum was determined with a 100 MHz nmr spectrometer.

NMR ($\delta$ in $D_2SO_4$). 8.74-8.94(m, 6H, H-2,3,5,11,13,14), 9.34(d, 2H, H-4,12, $J_{4,5}=J_{11,12}=8.0$ Hz), 9.75(d, 2H, H-6,10, $J_{5,6}=J_{10,11}=8.0$ Hz), 10.34(s, 1H, H-8), 10.44(d, 2H, H-1,15, $J_{1,2}=J_{14,15}=8.0$ Hz), 10.61(s, 2H, H-7,9), 10.86(s, 1H, H-16).

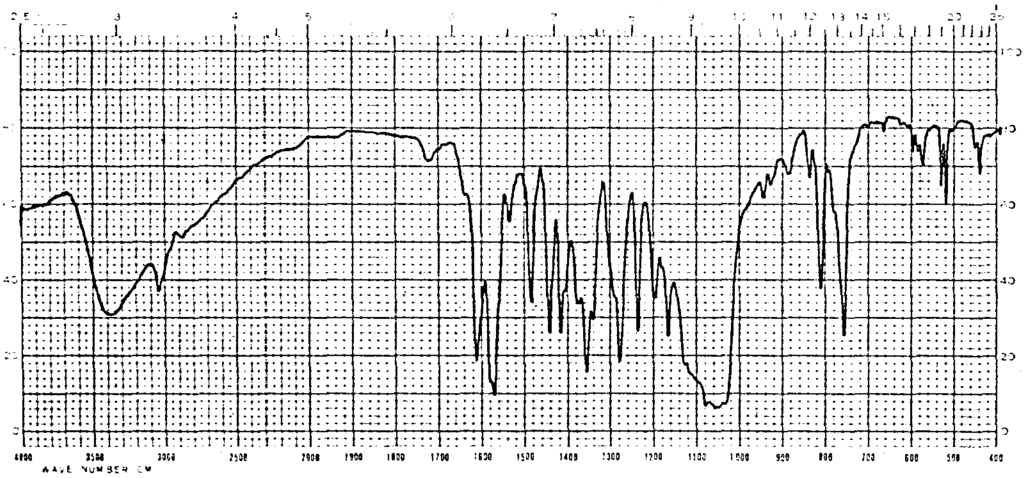
ES(97% $H_2SO_4$). $\lambda_{max}$ (log $\varepsilon$*) 606(4.51), 434(4.66), 342(sh, 4.02), 320(4.14), 270(4.53), 262(4.52).

* The $\varepsilon$-values were estimated assuming quantitative conversion of (11) into (4a).

Exp. 4. 7H-Dibenzo[de;jk]pentacenyl tetrafluoroborate (16):

To a stirred solution of 7,9-dihydrodibenzo[de;jk]pentacene (11) 35.4 mg (0.1 mmol) in 4 ml of anhydrous chloroform was added dropwise 70 mg (0.21 mmol) of triphenylmethyl tetrafluoroborate in 3 ml of anhydrous acetonitrile over 2 min at 0°C and then dark green solids precipitated. The mixture was stirred at room temperature and filtered, and the separated dark green precipitates were washed twice with anhydrous chloroform under dry nitrogen atmosphere to give 22 mg (50%) of (16), mp > 300°C. NMR (δ in $AsCl_3$). 4.90(s), 7.60-9.68(m).

IR (KBr).



Exp. 5. 7,9-Dideuterio-7,9-dihydrodibenzo[de;jk]pentacene (17):

To a solution of 7,9-dihydrodibenzo[de;jk]pentacene (11) 13 mg (0.04 mmol) in 4 ml of freshly distilled (over $LiAlH_4$) THF was added 0.09 mmol of butyllithium in hexane at -60°C under nitrogen atmosphere. After the solution was stirred for 15 min at the same temperature, was quenched with THF containing $D_2O$ at -40°C, and was warmed gradually to room temperature under stirring. Dil. hydrochloric acid and 20 ml of benzene were added to the yellow solution. The organic layer was washed successively with saturated aqueous solution of sodium hydrogen carbonate and water and dried over anhydrous magnesium sulfate. After removal of the solvent the yellow residue was chromatographed on the deactivated alumina containing 2.5% of water eluting with hexane-benzene (1:1) to give 10 mg (72%) of pure 7,9-dideuterio-7,9-dihydrodibenzo[de;jk]pentacene (17).

MS. m/e 356 (52%, $M^+$), 355 (94%, $M^+$-1), 354 (100%, $M^+$-2), 353 (68%, $M^+$-3).

NMR ($\delta$ in $CDCl_3$). 4.50(bs, 2H, H-7,9), 7.16(s, 1H, H-8),
7.35-7.76(m, 10H, H-2,3,4,5,6,10,11,12,13,14),
8.13(d, 2H, H-1,15, $J_{1,2}=J_{14,15}=7.0$ Hz),
8,64(s, 1H, H-16).

Exp. 6. Dilithium dibenzo[de;jk]pentacenide (1c):

The solvents (hexane and ether) of butyllithium (0.05 mmol) were removed to some extent in vacuo and then to this butyllithium a degassed solution of 7,9-dihydrodibenzo[de;jk]pentacene (11) 2 mg (0.0074 mmol) in 0.4 ml of freshly distilled (over $LiAlH_4$) $d_8$-THF was added at -40°C in vacuo. The mixture was shaken at this temperature. The resultant dark greenish brown mixture was filtered with a sintered glass fused to the apparatus and the clear solution was tipped into an nmr sample tube also connected to the apparatus. The tube was cut off and drawn free. All the manipulations were carried out in vacuo. The nmr spectrum of (4c) was determined by using CAT technique with a 100 MHz nmr spectrometer at -40°C.

NMR ($\delta$ in $d_8$-THF). 5.08 (s, 2H, H-7,9), 5.22 (d, 2H, H-6,10, $J_{5,6}=J_{10,11}=7.5$ Hz), 5.33 (d, 2H, H-4, 12, $J_{4,5}=J_{11,12}=7.5$ Hz), 5.67 (s, 1H, H-8), 5.93 (d, 2H, H-3,13), 6.07 (dd, 2H, H-5,11), 6.36 (dd, 2H, H-2,14), 6.62 (d, 2H, H-1,15, $J_{1,2}=J_{14,15}=7.5$ Hz), 7.89 (s, 1H, H-16).

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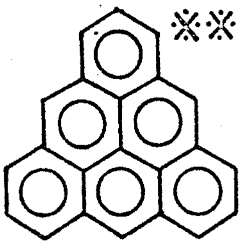
# Chapter 6. Triangulenyl System

## 6.1. Introduction

As a part of our program initiated to promote our attention in the chemistry of the phenalenyl system,$^{1)}$ we now taken up the triangulenyl system (1) as our next target compound being also a non-Kekulé type even alternant hydrocarbon system as is the dibenzo[de;jk]pentacenyl system (2). As described in preceding chapter the excellent conformity of the experimental results with the theoretical predictions has observed and this encouraged us to investigate the triangulenyl system.

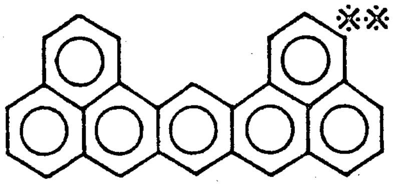


(1)

a) ※= +

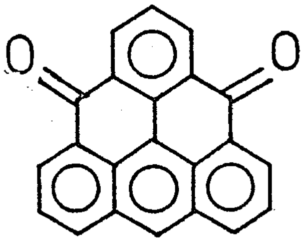
b) ※= ·

c) ※= -

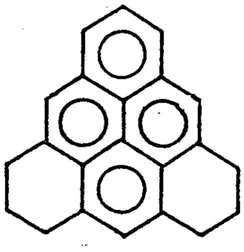


(2)

In 1953, Clar$^{2)}$ has reported the syntheses of triangulene-4,8-quinone (3) and related compounds and suggested that so-called Clar's hydrocarbon, triangulene (16), would be impossible to prepare because no Kekulé structure could be written for (1). Thus, dehydrogenation of hexahydro- and dodecahydrotriangulene, (4) and (5), led only to polymeric products.



(3)



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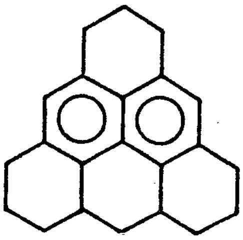
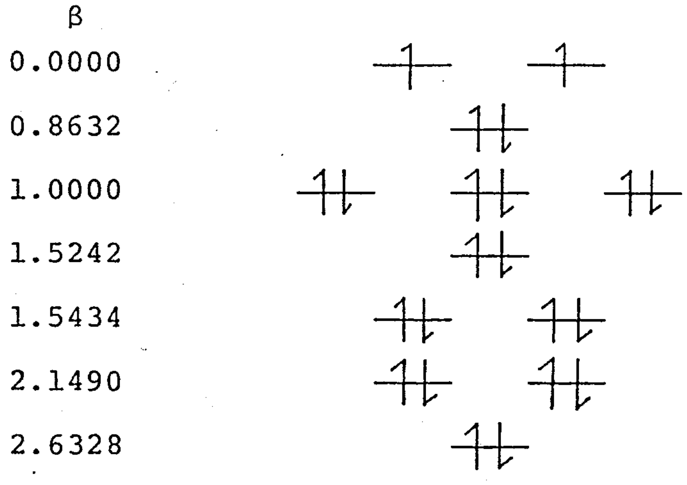
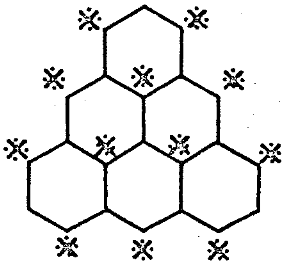


(5)

In terms of the valence bond theory,[3)] (1) has 22 carbon atoms in the molecule and has no resonance structure with more than 10 double bonds which means that (1) should have 22-20=2 nonbonding molecular orbitals. This prediction was also proved theoretically by Longuet-Higgins[2)] using molecular orbital theory. Thus, as in the case of (2) Hückel molecular orbital calculations predict its molecular orbitals and the π-charge





(1)

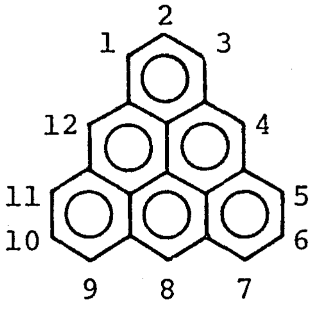
Fig. 1. Hückel Molecular Orbitals of (1).

density, q, on the respective carbon atoms in (1a) and (1b) as given in Table 1. Therefore, (1) might exist as diradical and divalent ions in the neutral and ionic forms, respectively.

Inspite of intense interest in triangulenyl system, no report of an attempt to observe such species is available to date. In this chapter we address the preparation and characterization of the hitherto elusive triangulenyl dianion (1c) and a derivative of the dication (1a).

Table 1. Hückel Charge Density of (1a) and (1c).

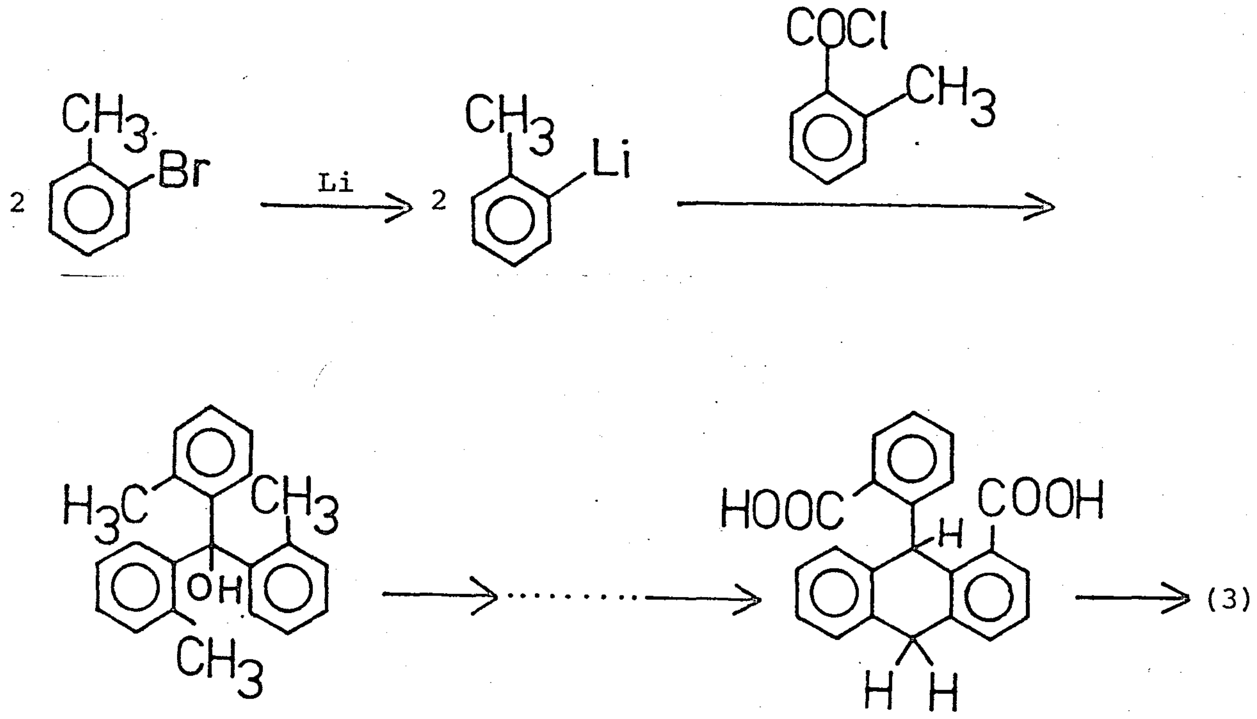
| Position | $\lvert q \rvert$ |
|---|---|
| 1,3,5,7,9,11 | 0.1818 |
| 2,6,10 | 0.0000 |
| 4,8,12 | 0.2424 |



(1)

## 6.2. Synthesis of Dihydrotriangulene

As an attractive key intermediate for formation of the cation, anion, and radical have choosed the reported triangulene-4,8-quinone. The quinone (3) was prepared by using the Clar's method$^{2)}$ starting from o-bromotoluene and toluoyl chloride through eight steps as illustrated briefly below. To confirm the structure of (3), the following spectral measurements were made since no spectroscopic properties of (3) were given in the literature. Mass spectrum of (3) exhibits molecu-



lar ion peak at m/e 306 (100%) and two peaks assigned to the fragment ions corresponding to loss of one and two carbonyls respectively at m/e 278 (13%) and 250 (9%). In its ir spectrum, a relatively low frequency carbonyl stretching band at 1645 $cm^{-1}$ is in accord with the structure of (3). Furthermore, the structure with $C_{2v}$-symmetry was convincingly identified by its nmr spectrum (Fig. 2) which was measured in arsen trichloride because of its extremely low solubility in usual organic solvents. Observed chemical shifts and coupling constants and first-order assignments were summarized in Table 2. In order to gain dihydrotriangulene, reduction of the quinone (3) was examined. Treatment of the quinone (3) with lithium aluminum hydride-aluminum chloride complex in ether at room temperature affords dihydrotriangulene as yellow needles with mp 178-181°C after column chromatography on deactivated alumina with water. Because of its pronounced air-sensitivity its elemental analysis could not afford the satisfactory values for dihydrotriangulene. However, the structural assignment to (6) is easily borne out by mass and nmr spectroscopy. The mass spectrum of (6) shows molecular ion peak at m/e 278 (100%) and nmr spectrum (Fig. 3) shows signals at $\delta$ 4.14 (m, H-3,3'), $\delta$ 4.89 (s, H-8,8'), $\delta$ 6.14 (dt, H-2, $J_{1,2}$=10.0 Hz, $J_{2,3}$=4.0 Hz), and $\delta$ 6.71 (dt, H-1, $J_{1,3}$= 2.0 Hz) along with multiplet at $\delta$ 7.24-7.64 of aromatic protons.

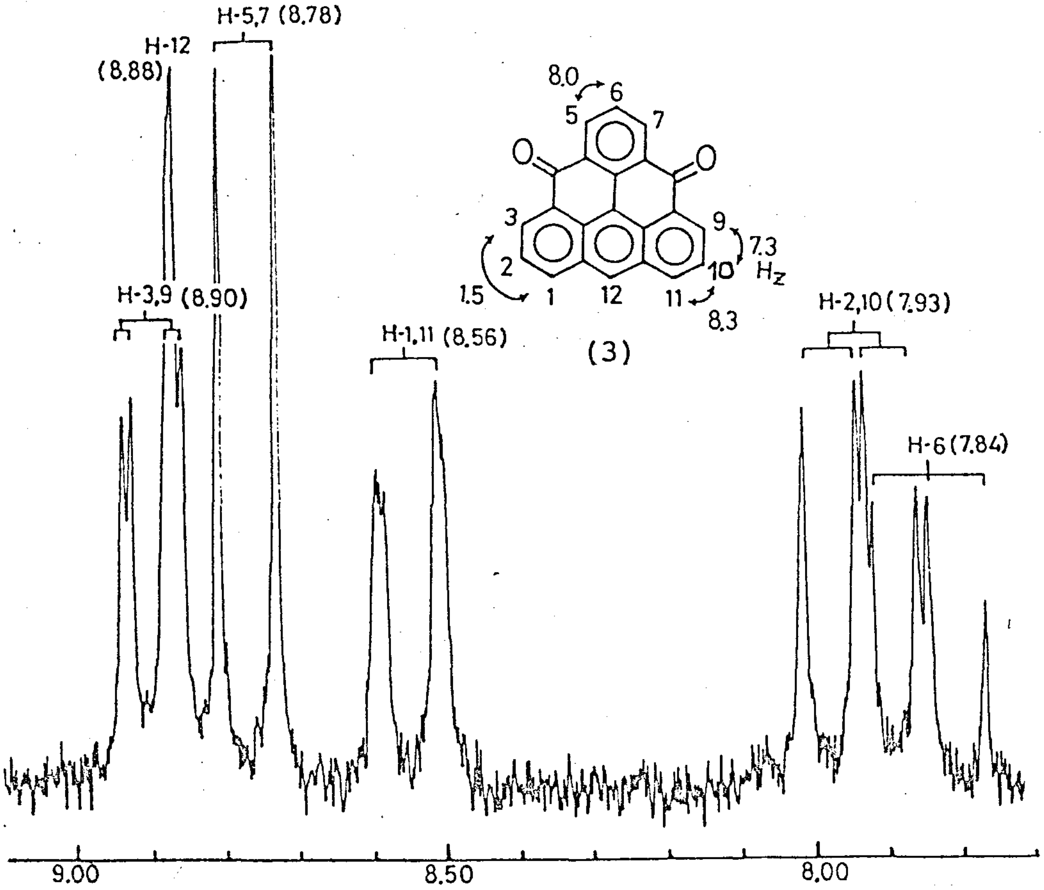
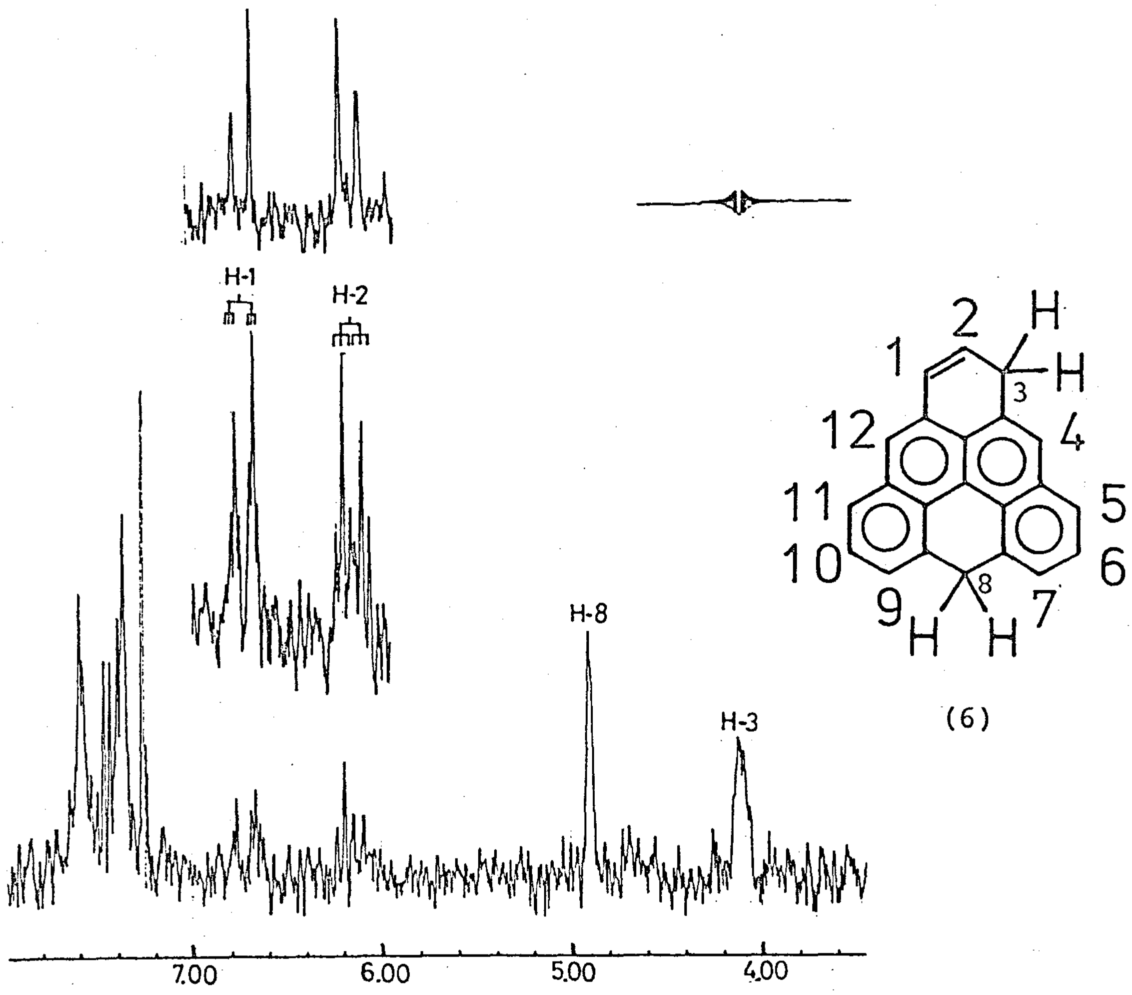


Fig. 2. The NMR Spectrum of (3) in $AsCl_3$.

Table 2. The NMR Spectral Data of (3).

| Proton | Chem. Shift(δ) | Multipl. | Coupl. Const.(Hz) |
|---|---|---|---|
| H-1,11 | 8.56 | dd | $J_{1,2}=J_{10,11}=8.3$ |
| 2,10 | 7.93 | dd | $J_{2,3}=J_{9,10}=7.3$ |
| 3, 9 | 8.90 | dd | $J_{1,3}=J_{9,11}=1.5$ |
| 5, 7 | 8.78 | d | $J_{5,6}=J_{6,7}=8.0$ |
| 6 | 7.84 | t | |
| 12 | 8.88 | s | |

These assignments were confirmed by the following spin decoupling experiment. The irradiation at δ 4.14 assigned to H-3 and 3' converted the two doublet of triplets at δ 6.14 and 6.71 assigned to H-1 and 2 into a clear pair of doublets with coupling constant 10.0 Hz.

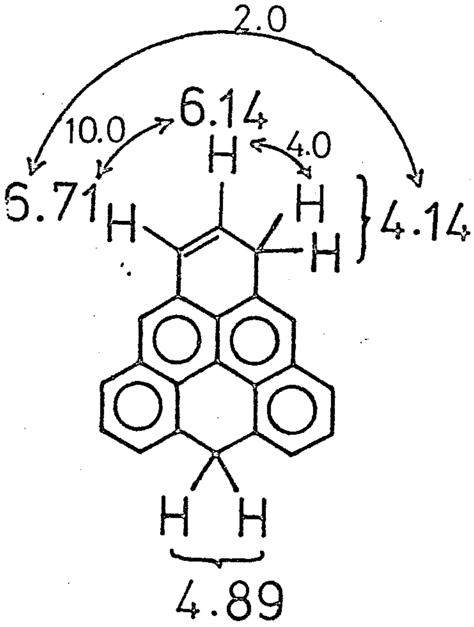


(6)

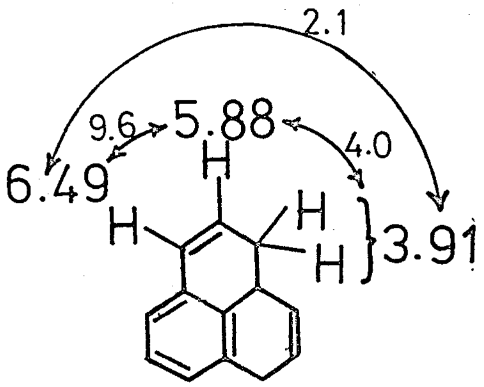
Fig. 3. The NMR Spectrum of (6) in $CDCl_3$.

Furthermore, the chemical shifts and the coupling constants of H-1,2,3, and 8 are in fair agreement with those of the corresponding protons of phenalene (7)$^{5)}$ and 6H-benzo[cd]pyrene (8), repectively (see Fig. 4).

The assigned structure (6) is unambiguously supprted by the presence of an $ABX_2$ spin system at δ 6.71, 6.14 and 4.14, and a 2H singlet at δ 4.89 in its nmr spectrum.



(6)



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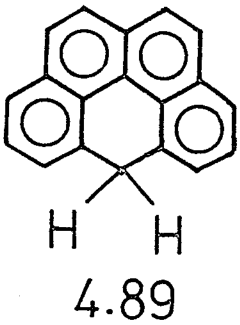


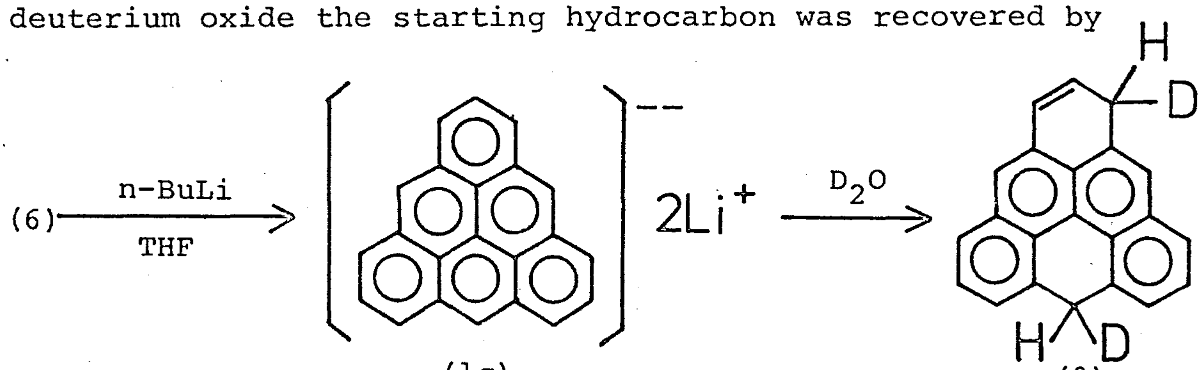
(8)

Fig. 4. The Chemical Shifts (δ) and Coupling Constants (Hz) of (6), (7), and (8).

## 6.3. Synthesis of Triangulenyl Dianion

In view of the result that there has been a good linear correlation between chemical shift and Hückel charge density in the phenalenyl and benzo[cd]pyrenyl anions and the dibenzo-[de;jk]pentacenyl dianion, a similar relation may be expected in the triangulenyl dianion (1c). To this end we examined the direct proton abstraction reaction of dihydrotriangulene (6) described in the preceding section.

Treatment of a solution of 3,8-dihydrotriangulene (6) in tetrahydrofuran with butyllithium at -78°C under nitrogen atmosphere produced a clear dark red solution. In this reaction the formation of the desired triangulenyl dianion (1c) was revealed by the following chemical and spectroscopic evidences. When the above reaction mixture was quenched with deuterium oxide the starting hydrocarbon was recovered by



(1c)

(9)

careful work-up. Incorporation of two deuterium atoms in the product was identified by its mass spectrum which shows parent ion peak at m/e 280 (79%) along with base peak at m/e 279. Although the sites of the deuterium incorporation are assumed to be at C-3 and 8 through the proton FT-nmr spectrum of (9), conclusive evidence could not be obtained so far due to shortage of the sample (9).

A solution of (1c) for direct nmr spectral measurement was prepared by treatment of a degassed solution of (6) in freshly distilled (over lithium aluminum hydride) $d_8$-tetrahydrofuran with butyllithium in hexane containing small amount of ether at -78°C in vacuo. The nmr spectrum which is recorded at -50°C displays very simple pattern as shown in Fig. 5. The first-

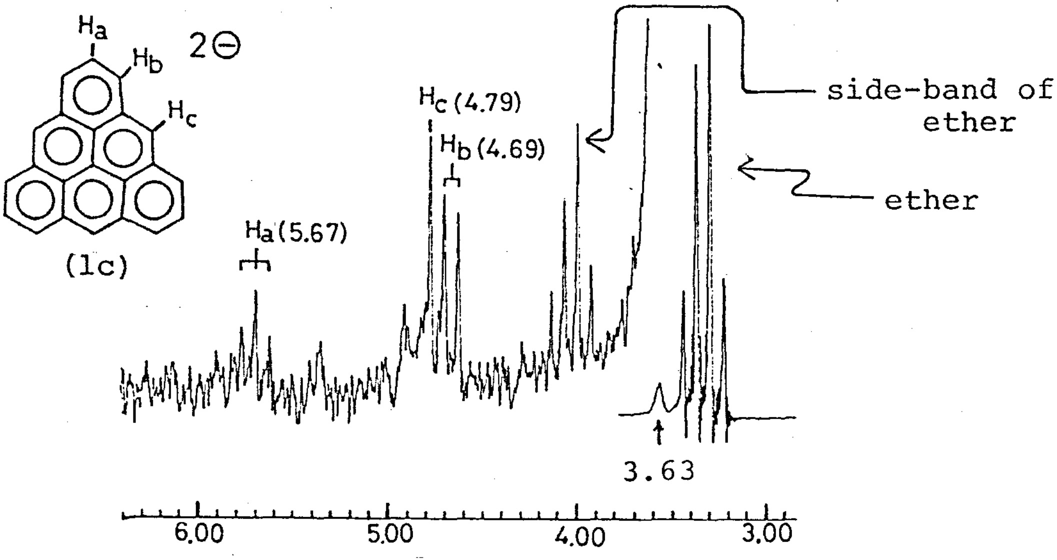


Fig. 5. The NMR Spectrum of (1c) in $d_8$-THF.

order analysis of the spectrum was easily achieved and was in complete accord with the expected delocalized structure with $D_{3h}$-symmetry (see Table 3). This analysis makes it possible to examine the relationship between the chemical shifts (after correction of the ring-current effect of the neighboring benzene rings by point dipole approximation) and Hückel charge densities of the corresponding carbon atoms. The relationship is summarized in Table 3 and displayed in Fig. 6.

As can be seen in Fig. 6, the plots for the present dianion (1c) do not fall on the same line which holds for (10), (11), and (2c), however, almost parallel linear relationship observed is partly due to their different charge distribution, i.e., negative

Table 3. The NMR Spectral Data of (1c).

| position | Obs. Chem. Shift[a)] | Ring Current Correct.[b)] | Hückel Charge Density | Coupl. Const. (Hz) |
|---|---|---|---|---|
| 1,3,5,7,9,11 | 4.72 | 1.45 | -0.1818 | $J_{1,2}=J_{2,3}=J_{5,6}$ |
| 2,6,10 | 5.70 | 0.85 | 0.0000 | $=J_{6,7}=J_{9,10}$ |
| 4,8,12 | 4.82 | 1.96 | -0.2424 | $=J_{10,11}=7.5$ |

a) δ-values were determined in $d_8$-THF, relativeto the low-field signal assumed to lie at δ 3.63 from TMS.

b) The sum of ring current corrections for adjacent benzene rings by the simple point dipole approximation calculated by using the formular, $(12.0)a^2\sum_i R_i^{-3}$. 6) charges in (10), (11), and (2c) exist entirely and/or predominantly in their peripheral carbon atoms whereas substantial negative charges are found on inner carbon atoms in the case of (1c).

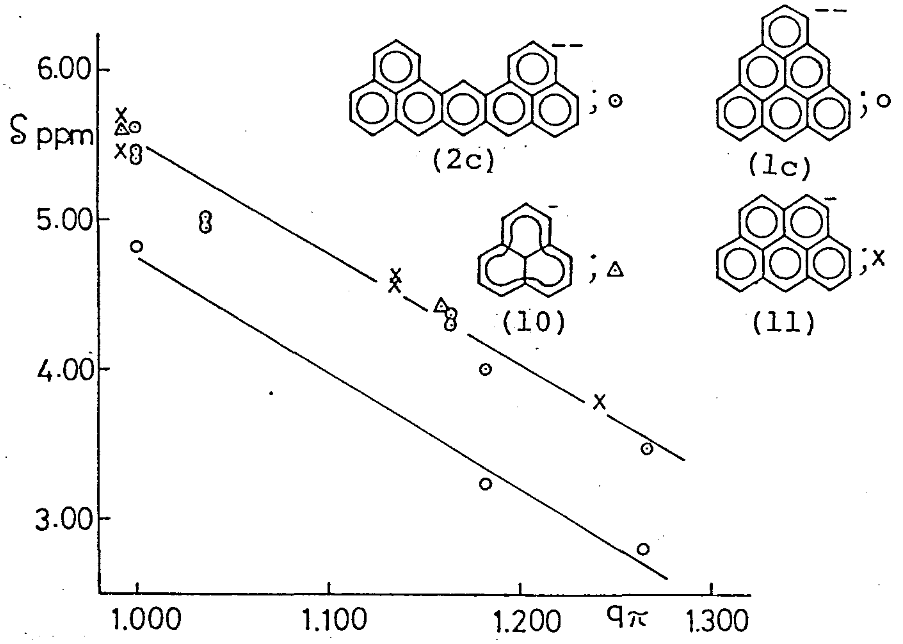
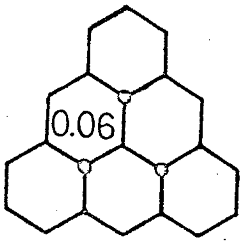
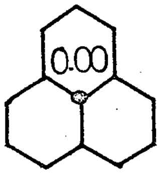


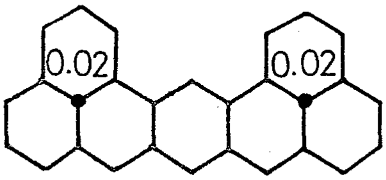
Fig. 6. Plot of Chemical Shift vs. Charge Density of (1c), (2c), (10), and (11).



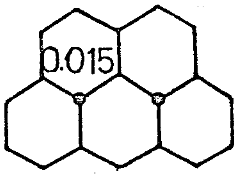
(1c)



(10)



(2c)

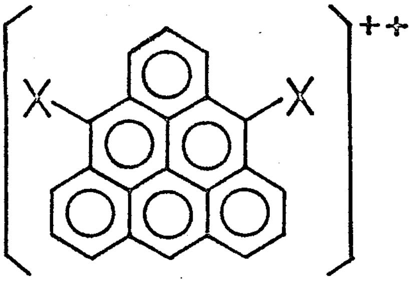


(11)

## 6.4. Dihydroxy Triangulenyl Dication

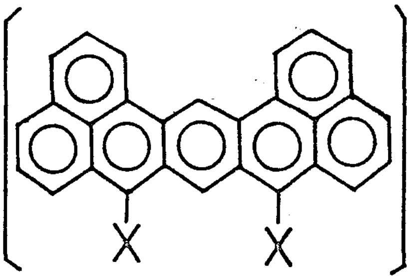
In this section we describe the formation of the dihydroxy triangulenyl dication and attempted synthesis of the parent triangulenyl dication which is the other novel triangulenyl system containing a closed shell electronic configuration as mentioned previously (Section 6.1).

As in the case of the dihydroxy dibenzo[de;jk]pentacenyl dication (13), the formation of the dihydroxy triangulenyl dication (12) was observed by using the following procedures. Thus, treatment of the quinone (3) with 97% dideuteriosulfuric acid led to the formation of a dark red solution whose nmr spectrum is shown in Fig. 7. This spectrum featured a simple symmetrical pattern and a markedly downfield chemical shift for



(12) ; X=OH

(12-D); X=OD



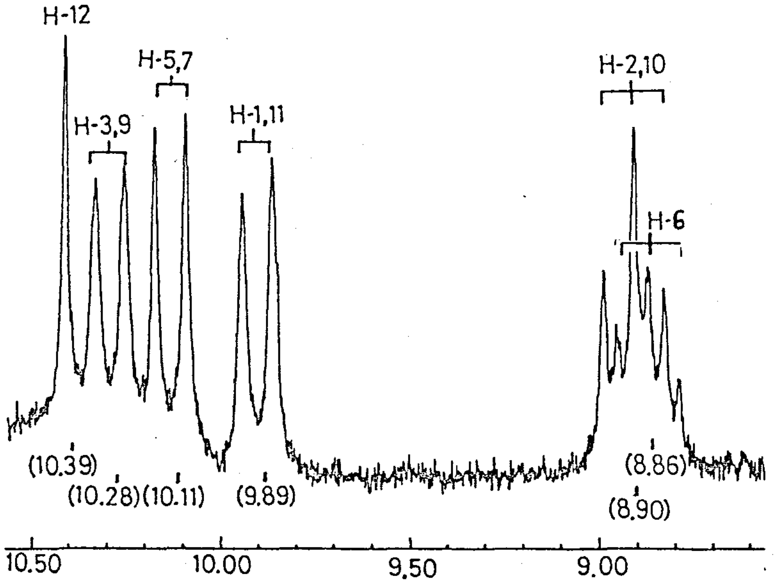
(13) ; X=OH

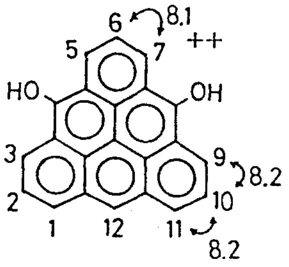
(13-D); X=OD

(see Sec. 5.3)

the all aromatic protons ($\delta$ 8.86-10.39), similar to that of (13-D) ($\delta$ 8.7-10.86), which was taken to indicate a cationic structure for (13).

Assignments of the nmr spectrum of (12-D) given in Fig. 7. were borne out based on the following considerations. The relatively downfield shifts of signals assigned to H-1, 3, 5, 7, 9, 11, and 12 compared with the other protons can be interpreted in terms of the Hückel charge densities on the corresponding carbon atoms (see Table 1). When both anisotropic effect of the hydroxyl group and meta-coupling in an aromatic ring are taken into consideration, two broad doublets at $\delta$ 10.28 and 9.89 can be assigned to H-3, 9 and H-1, 11, respectively. The remaining sharp





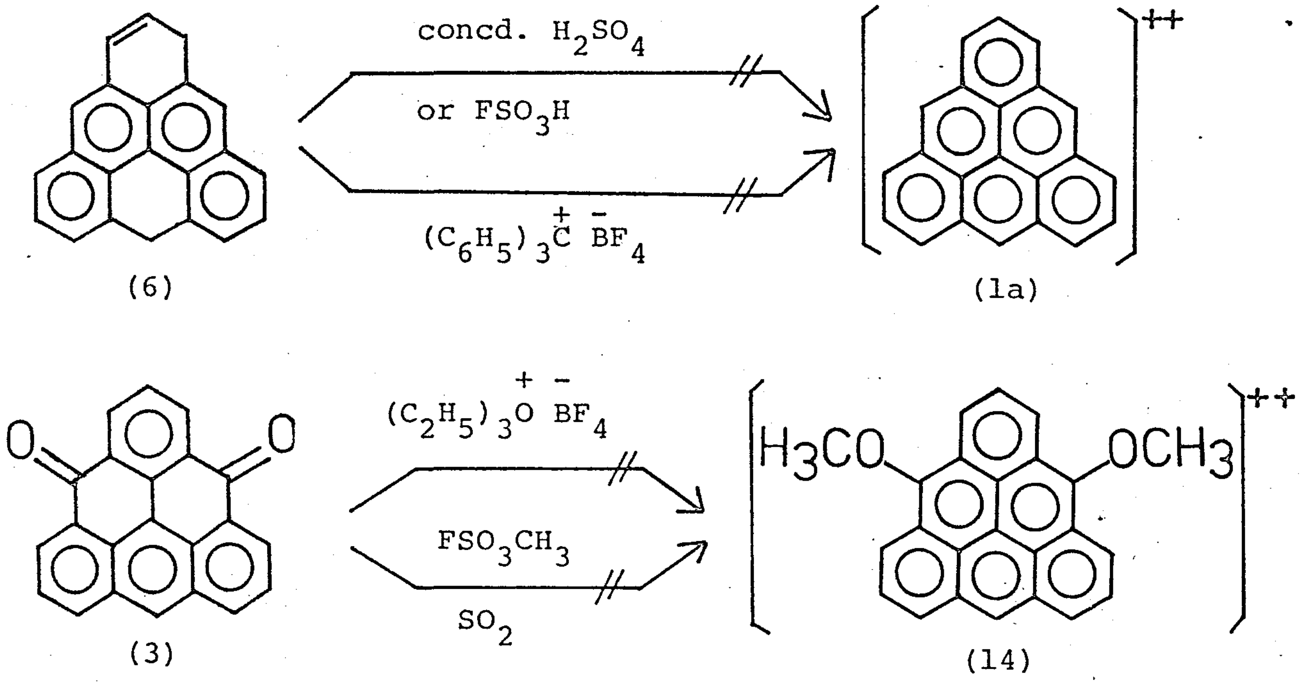
(10)

Fig. 7. The NMR Spectrum of (3) in $D_2SO_4$.

doublet at $\delta$ 10.11 was therefore assigned to H-5, 7. Two triplets integrating for one and two protons at $\delta$ 8.86 and 8.90 were easily assigned to H-6 and H-2, 10, respectively. Finally, a singlet at $\delta$ 10.39 was unequivocally attributed to H-12. These assighnments of the spectrum are compatible with the delocalized 4,8-dihydroxytriangulenyl dication with $C_{2v}$-symmetry.

In order to gain the parent triangulenyl dication (1a) and its dimethoxy derivative (14) we tried the following reactions as illustrated in Scheme 1. Unfortunately, all attempted syntheses have failed.

Scheme 1.



In summary, in this chapter we have demonstrated the syntheses of the triangulenyl dianion (1c) and the derivative of the triangulenyl dication (12) which are fully delocalized divalent ionic species with $D_{3h}$– and $C_{2v}$-symmmetry, respectively as predicted by Hückel molecular orbital theory.

Although it is difficult to prepare a fairly large amount of the precursor hydrocarbon (6), we are currently investigating the formation of the dication (1a) and the radical (1b) the latter of which is theoretically predicted to be exist in triplet ground state.

## 6.5. Experimental

### Exp. 1. 3,8-Dihydrotriangulene (6):

The complex of lithium aluminum hydride 540 mg (14 mmol) and aluminum chloride 3.74 g (28 mmol) was prepared by the same procedures as described in Exp. 2 of Chapter 5. To the ether solution of the complex was added 80 mg (0.26 mmol) of the finely powdered quinone (3) over 2 hr at room temperature under nitrogen atmosphere. The orange reaction mixture was stirred for 2 days and quenched with ether saturated with water, and dilute hydrochloric acid and 60 ml of hexane was added. The organic layer was separated and washed successively with saturated aqueous solution of sodium hydrogen carbonate and water, and dried over anhydrous magnesium sulfate. After removal of the solvent the dark purple residue was chromatographed on the deactivated alumina with 10% of water eluting with hexane to give 17 mg (23%) of almost pure (6) as yellow needles, mp 178-181°C (decomp.).

MS. m/e 278($M^+$,100%), 277($M^+$-1, 91%), 276($M^+$-2, 59%).

NMR($\delta$ in $d_8$-THF). 4.14(m, H-3,3', $J_{1,3}=J_{1,3'}=2.0$ Hz, $J_{2,3}=J_{2,3'}=$ 4.0 Hz), 4.89(bs, H-8,8'), 6.14(dt, H-2, $J_{1,2}=$ 10.0 Hz), 6.71(dt, H-1), 7.24-7.64(m, aromatic protons).

Exp. 2. 3,8-Dideuterio-3,8-dihydrotriangulene (9):

To a degassed solution of 3,8-dihydrotriangulene (6) 11 mg (0.036 mmol) in 2 ml of freshly distilled (over $LiAlH_4$) tetrahydrofuran was added 0.144 mmol of butyllithium in hexane at -70°C under nitrogen atmosphere. After stirring for 15 min at the same temperature, the solution was quenched with $D_2O$ and was warmed gradually to room temperature under stirring.
Dil. hydrochloric acid and petr. ether was added to the reddish solution. The organic layer was separated and washed with saturated aqueous solution of hydrogen carbonate and water and dried over anhydrous magnesium sulfate. After removal of the solvent the red residue was chromatographed on the deactivated alumina containing 10% of water eluting with petr. ether to give yellow crystals of (9).

MS. (30ev); m/e 281($M^+$+1, 15%), 280($M^+$, 100%), 279(($M^+$-1, 16%).
(80ev); m/e 281($M^+$+1, 16%), 280($M^+$, 79%), 279($M^+$-1, 100%).

Exp. 3. Dilithium triangulenide (1c):

To a degassed solution of 3,8-dihydrotriangulene (6) 5 mg (0.018 mmol) in 0.4 ml of freshly distilled (over $LiAlH_4$) $d_8$-tetrahydrofuran was added 0.072 mmol of butyllithium in hexane (containing small amount of ether) at -78°C. The dark red mixture was filtered with a sintered disk fused to the apparatus and the clear solution was tipped into an nmr sample tube also fused to the apparatus. The tube was cut off and drawn free. All the manipulations were carried out in vacuo. The nmr spectrum of (1c) was determined with a 100 MHz nmr spectrometer at -50°C.

NMR($\delta$ in $d_8$-THF). 4.72(d, H-1,3,5,7,9,11, $J_{1,2}=J_{2,3}=J_{5,6}=J_{6,7}=J_{9,10}=J_{10,11}=7.5$ Hz), 4.82(s, H-4,8,12), 5.70 (t, H-2,6,10).

All the melting points are uncorrected. The NMR spectra were recorded on a Varian A-60 (60 MHz) or XL-100 (100 MHz) spectrometer. The infrared spectra were recorded on a Hitachi EPI-$G_2$ spectrometer. The electronic spectra were determined on a Hitachi 124 double beam spectrophotometer. The mass spectra were obtained on a Hitachi RM-50 spectrometer operating at 20 or 70 eV.

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# Acknowledgements

This reserch has been performed under the direction of Professor Ichiro Murata. I express my deep gratitude and sincere appreciation to Professor Ichiro Murata.

I am sincerely gratitude to Drs. T. Nakazawa, K. Yamamoto, K. Nakasuji, and Y. Sugihara for their valuable discussions and useful suggestions during this work. I am particularly indebted to Dr. K. Yamamoto for his kind advice and reading a part of the manuscript.

I appreciate the help received from Mr. M. Okumiya, Mmes. K. Hayashi, and T. Hirobe with elemental analyses, from Dr. K. Ri, and Messrs. M. Doi and S. Adachi with NMR measurements, and from Mr. H. Adachi with the mass spectral analyses.

Sincere thanks are also due to the many members of the Murata group, especially to Mr. K. Tanaka for his participation in some of the present work, and to Miss Osumi for her nice typing.

Finally I would like to record my hearty appreciation to my parent for their constant encouragement throughout this work and my fiancée Y. Matsumoto for her generous assistance in completion of this manuscript.