



Title	The Molecular Structures of Bridge Compounds : Diborane and Trimethylaluminum
Author(s)	Ogawa, Teiichiro
Citation	大阪大学, 1966, 博士論文
Version Type	VoR
URL	https://hdl.handle.net/11094/1148
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The Molecular Structures of Bridge Compounds;
Diborane and Trimethylaluminum

Teiichiro Ogawa

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1. List of Papers

- (I) Least Square Calculation of Potential Constants and Their Standard Errors of Diborane.

Teiichiro Ogawa and Tatsuo Miyazawa,
Spectrochimica Acta, 20, 557-564 (1964).

- (II) The Far Infrared Spectra of Trimethylaluminum.

Teiichiro Ogawa, Kozo Hirota and Kunio Fukushima,
Bull. Chem. Soc. Japan, 37, 1243-1244 (1964).

- (III) Vibrational Assignments and Intramolecular Force Field of Trimethylaluminum.

Teiichiro Ogawa, Kozo Hirota and Tatsuo Miyazawa,
Bull. Chem. Soc. Japan, 38, 1105-1110 (1965).

- (IV) Electronic Structure of Diborane and Hyperconjugation Effect.

Teiichiro Ogawa and Kozo Hirota,
J. Mol. Spectroscopy, submitted in 1965.

2. Introduction

The bridge compounds as diborane and trimethylaluminum have been studied by many authors since their structure and reactivities are peculiar. The structure of diborane was once considered to be of an ethane type, but the study by the electron diffraction has established that two hydrogen atoms of diborane lie between two boron atoms. This conclusion was also confirmed by the studies of vibrational spectra. Meanwhile the electronic structure of this bridge was interpreted in various ways as the protonated double bond, the half-bond, the three center bond etc. The case of trimethylaluminum is similar to the case of diborane. The molecular structure of trimethylaluminum was decided to be a bridged one by the X-ray diffraction study but the detailed electronic structure has not been fully examined.

The purpose of the present study is to elucidate the structure of these molecules more clearly and to interpret them with electronic theory. The measurements of the vacuum ultraviolet spectra of diborane and the far infrared spectra of trimethylaluminum were carried out. The normal vibrations and the electronic energies were calculated and the infrared and ultraviolet spectra were assigned on the bases of the theoretical calculations.

3. General Discussion

3.1. General Descriptions on the Structure of the Bridge Compounds

The research on boron hydride has a long and interesting history. Although the corresponding halides of boron have monomer structure BX_3 , the simple substance BH_3 has not been prepared; instead, diborane (B_2H_6) are found to be the simplest boron hydride. The fundamental difficulty in the structural problem is that there seems to be not enough valence electrons in the molecules to fill the molecular orbitals.

Stock developed the vacuum technique to manipulate the reactive substances and concluded there were little doubt that B_2H_6 had similar structure to C_2H_6 by the use of X-ray, near infrared spectra and reactivities (1). Sidgwick suggested (2) that there were one-electron bonds in B_2H_6 , and Pauling explained (3) the stability of this molecule by the resonance theory that several configurations with different pairs of hydrogen atoms attached by one-electron bonds were included in the final structure. Mulliken predicted (4) that B_2H_6 should probably be paramagnetic, but experimental measurements showed diamagnetism at room temperature. Mulliken then discussed (5) the electronic structure for a ethane-like model by the use of MO method. Electron diffraction of gaseous diborane was studied by Bauer (6) who interpreted his observations on the basis of

the ethane model and pointed out a faint inner peak which could not be explained by the bridge model.

The bridge model was first proposed by Dilthey in 1921 (7). Longuet-Higgins and Bell advocated (8) the bridge structure with no direct link between the two boron atoms. The suggested structure was resonance hybrid among two covalent structures and two ionic structures (both had two single bonds and two no bonds). They suggested that Bauer's curve of the electron diffraction was predicted equally by the bridge model. The main argument in their paper was the assignments of the vibrational spectra. The ethane-like structure failed to explain the number of strong bands. Pitzer gave (9) the electronic interpretation to the bridge model in terms of a protonated double bond. Mulliken went (10) into more detail and gave the MO description for the bridge model. He showed the electronic structure must be essentially the same as that in ethylene. Rundle (11) interpreted the bridge bonds as half bonds and Longuet-Higgins (12) as three-center bonds.

In the case of Al_2X_6 , the earlier results of electron diffraction measurements (13) showed that aluminum halides had the bridge structure and the results of the Raman spectra gave the same conclusion (14). In the case of trimethylaluminum, however, the results of electron diffraction showed it had an ethane-like structure (15), though the results of the Raman spectrum (14) showed it had a bridge structure.

As is mentioned above, two different structures had been advocated by various authors; nevertheless convincing arguments for the bridge structure began to be proposed from the end of 1940's. Price (16) investigated the infrared spectrum of diborane under greater resolving power and indicated a striking similarity with the spectrum of ethylene. He concluded the rotational structure ruled out the ethane-type structure but agreed very well with the bridge model. Hedberg and Schomaker re-examined the electron diffraction of diborane and concluded it had the bridge structure (17). Lewis and Rundle (18) concluded trimethylaluminum dimer had a bridge structure with a skeletal symmetry of D_{2h} by X-ray diffraction of single crystal. Since then, the geometrical structures of diborane, aluminum trihalide dimers and trimethylaluminum dimer have been decided to be of the bridge structure and the objects of research have turned its direction into the interpretation and the properties of the bridge structure. The present study is one of such attempts on the problem.

3.2. Thermochemical Study on Diborane

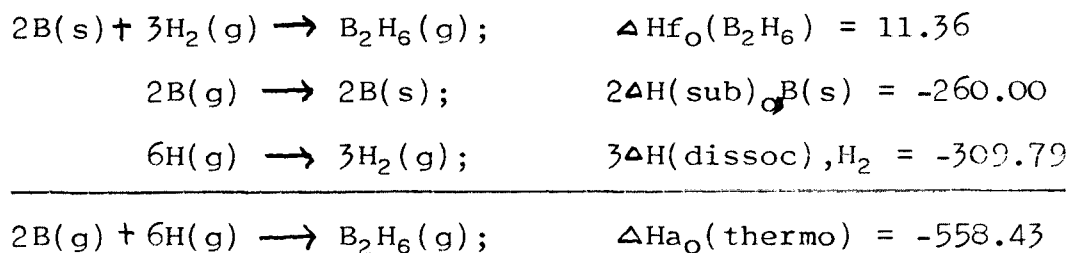
The specific heat of diborane was measured over the temperature range 100 - 300°K (19). A barrier of the rotation of BH_3 groups in a ethane-like structure were calculated to be about 10,000 cal/mol, which was considerably higher than the typical value (3,000 cal/mol for ethane).

But, in the bridge model, the calculated specific heat satisfactorily agreed with the observed value (8).

The resonance energy for diborane was calculated (20) to be 23.9 Kcal/mol, since the enthalpy of formation of BH_3 was calculated to be -15.7 Kcal/mol from the equation of the electronegativities and the observed enthalpy of formation of B_2H_6 was -7.5 Kcal/mol $[23.9 = -7.5 - 2 \times (-15.7)]$. The heat of dissociation for $\text{B}_2\text{H}_6(\text{g}) = 2\text{BH}_3(\text{g})$ was estimated as 28.5 Kcal/mol (21) by the thermochemical measurement of the reaction of methylamine with diborane. The value was also determined (22) as 32~38 Kcal/mol by the analysis of kinetics of the decomposition of BH_3CO .

However, BH_3 itself had never been observed experimentally and the above results contained more or less questionable postulates. On the other hand mass-spectrometric investigation may give a direct value for the dissociation energy. The result of the low-pressure dissociation of B_2H_6 gave a value of dissociation energy $D_0(\text{BH}_3-\text{BH}_3) = 55 \pm 8$ Kcal/mol (23).

The heat of formation and the energies of diborane were discussed by Glockler (24). From the heat of formation ΔH_{fO} (25), the heat of formation from atoms ΔH_{aO} was obtained from the set of thermochemical equations: (Kcal/mol)



On the other hand, the heat of formation ΔH_{aO} could be determined from the sum of bond energies which were correlated with the internuclear distances:

$$E(BB) \approx 228.10 - 103.63 \, r(BB),$$

$$E(BH) \approx 177.92 - 90.20 \, r(BH).$$

The coefficients of the above equations were estimated from the bond energies of solid boron and B_2 radical, BH and BH_2 radicals, respectively. The heat of formation from bond energies $\Delta H_{aO}(\text{dist})$ was estimated: (Kcal/mol)

1 (BB)	1.77Å	44.67
4 (BH)	1.19Å	70.58
4 (BH')	1.33Å	57.95
<hr/>		
$\Delta H_{aO}(\text{dist})$	=	558.79

Two values of ΔH_{aO} agreed well with each other. It is noteworthy that the heat of formation of diborane was interpreted on the basis of B-B bond.

3.3. Ultraviolet Spectra and Recent Theory on Electronic Structure

Blum and Herzberg (26) measured the ultraviolet spectra of diborane and found a band at 1820Å of weak intensity. They discussed the band on the basis of Mulliken's theory on an ethane-like structure of diborane.

Price (16) examined the ultraviolet absorption spectra of diborane at low pressure down to 1000Å using a 1 meter

normal incidence grating vacuum spectrograph. He found the first strong absorption band at 1350\AA and the second absorption band of similar strength at 1200\AA . Though he reported a good experimental result, he gave no discussion on the assignments or on the electronic structure.

The first of the quantitative theory on the electronic structure is the work by Hamilton (27). He concentrated his attention on bridge bonds. He considered the terminal B-H bonds were sufficiently localized to allow a simplified treatment of the problem as a four-center, four-electron problem. He calculated the energies and the charge distributions by the use of Roothaan's SCF method on the basis of Slater orbitals. His numerical results were not satisfactory, but his results correspond to the present study in the order of the orbital energies.

The LCAO-SCF calculation for the twelve-electron system was carried out by Yamazaki (26). Exact values for all one- and two-center integrals of Slater orbitals were used in his study. The dissociation energy was calculated as 0.29 au. in poor agreement with the experimental value of 0.82 au. The net electronic charge on bridge hydrogen atom was calculated as -0.24e. The order of the energies of orbitals again corresponds to the present study. Hoffmann and Lipscomb (29) calculated the electronic energies and charge distribution for the whole series of boron hydrides in an extended Huckel approximation.

The most elaborate calculation on the electronic structure of diborane was carried out by Burnelle and Kaufman (30) with the nonempirical LCAO-SCF method, taking all electrons of the molecule into account and calculating exactly all the integrals on the basis of Gaussian atomic orbitals. His set of Gaussians contained 54 functions, $9s + 3p$ on each boron and $3s$ on each hydrogen and was called to be the largest calculation reported at that time.

In all treatments hitherto reported, electrons were treated as σ electrons, and the dissociation energy, the ionization potential and the charge distribution were calculated. But the transition energies were not satisfactory for assigning the observed bands.

In the fourth paper (IV) of the present study, the vacuum ultraviolet spectrum of diborane was re-examined and the electronic structure was calculated by the method of LCAO-SCF. The hyperconjugation effect of the bridge hydrogen atoms was taken into consideration and the system was treated as a three-center, two-electron problem. The integrals were mostly calculated non-empirically, although some of them were evaluated by making some approximations. The transition energies were evaluated to be 6.7 (forbidden) and 10.5 eV. (allowed), and they correspond well to the experimental values of 6.9 (weak) and 9.2 eV. (strong), respectively. The characteristics of the present calculation as compared with others lie in its π electron approxi-

mation with the use of the hyperconjugation theory and its assignments of the observed spectrum.

3.4. Infrared Spectra and Intermolecular Potential Function of Diborane

The vibrational spectra are useful tools for studying molecular structures. The Raman spectrum of liquid diborane was studied by Anderson and Burg (31) and the infrared spectrum of the gas by Stitt (18). Then Lord and Nielsen (32) measured both the Raman and the infrared spectra of $B_2^{11}H_6$, $B_2^{10}H_6$ and $B_2^{10}D_6$ and gave the consistent assignments. Taylor et al. (33), Lehmann et al. (34) and Kaufman et al. (35) added the experimental data of $B_2^{11}D_6$ etc. Recently, after the present study (I) was published, Smith and Mills (36) reported a high-resolution infrared spectra of diborane and analysed the rotational structure and the Coriolis perturbations. They slightly modified the assignments by Lord and Nielsen.

The normal vibrations of diborane were treated by Bell and Longuet-Higgins (8), by Sverdlov and Zaitseva (36) and by Venkateswarlu and Radhakrishnan (37). The latter two authors calculated with general force fields with twenty-nine and fifty-six parameters, respectively. The numbers of parameters in their studies were too many to discuss the assignments and the molecular structure of diborane.

The purpose of the study by Bell and Longuet-Higgins was to clarify the priority of the bridge model to the

ethane model. They indicated the observed spectrum was much more complex than that of ethane and gave the assignments for the bridge model. Normal vibrations were calculated by the use of a valence force field with six quadratic force constants and two interaction terms (between B-B and H'-H'; ' bridge). The tendency of the values of force constants in his study is close to that of the present study and some of the conclusions were intimated in his study. However, the experimental data cited by him were poor and the method of calculation was not developed at that time.

In the present study (I), the improved way of calculation and the electronic computer were available. A statistical method has been formulated for the evaluation of standard errors of the potential constants which are calculated from vibrational frequencies. The standard errors are caused not only by the experimental uncertainties in the observed frequencies but also by deviations of the calculated frequencies from the observed ones.

The normal vibrations of diborane were calculated with reference to Lord and Nielsen's assignments in the present study. The potential function has seven valence force constants and four interaction constants, and ten of them were adjusted by the least square method so as to yield the best fit for the thirty-six observed frequencies of $B_2^{11}H_6$ and $B_2^{10}D_6$. The standard errors of these potential constants were also calculated. The bridge bond stretching

constant was calculated to be 1.77 ± 0.04 md/Å which was about half as great as the terminal bond stretching constant. A bond was considered between two boron atoms. The force constant of this boron-boron bond was 2.72 ± 0.21 md/Å. In conclusion, owing to the improvements both in the experimental data and in the method for the calculation, the characteristics of the molecular structure are clarified more exactly in the present study.

3.5. The N. M. R. Spectra and the Reactivity of Diborane

The nuclear magnetic resonance spectra of diborane in the liquid nitrogen temperature were reported by Ogg (39) and were discussed by Shoolery (40). The major feature was the lack of symmetry of the proton resonance spectra which showed the existence of more than one bonding sites for the protons in the molecule. The proton resonance spectra showed well-resolved splitting by B^{11} nucleus which made the clear assignments possible for each spectrum. The resonance of the bridge protons was found at higher magnetic field, which indicated a more hydride-ion like character of the bridge proton. To verify these conclusions, the B^{11} spin orientations were stirred for observing both of the proton resonance spectrum separately or the splitting, by proton, of the B'' resonance spectrum was observed. Both results were explained correctly by the bridge model. The theoretical discussion of the chemical shift of the bridge proton relative to the terminal proton was given in several

approximations based on Pople's and Ramsey's theories of magnetic shielding (41). The analysis gave the result that the bridge protons showed resonance at higher fields than do the BH_2 terminal protons in accordance with the experimental results. Recent experimental results in the higher resolution confirmed the above interpretation (42).

The important reactions of diborane are the substitution of the terminal hydrogen with the halides and the alkyls, the cleavage into BH_3 with the nucleophilic reagents, the cleavage into BH_4^- with the electrophilic reagents and the polymerization into higher boron hydrides. In any case, however, the acidic character of the bridge hydrogen was not observed.(43).

3.6. The Structure of Trialkylaluminum

Although $\text{B}(\text{CH}_3)_3$ is in a monomer state at room temperature, it has been proved trialkylaluminum are in a dimer state. However, trialkylaluminum has been found to dissociate at higher temperatures. The dissociation constants and the dissociation energies were measured by Laubengayer and Gilliam (44) by the determination of the molecular weight of the vapor at various temperatures. The degree of dissociation of trimethylaluminum was found to be 0.075 at 100°C and 0.340 at 156°C , and the molar heat of dissociation was found to be 20.2 ± 1.0 Kcal. No measurements were made above 156°C because $\text{t}^\wedge\text{rimethylaluminum}$ decomposed at

higher temperatures. Triethylaluminum was found to dissociate more than trimethylaluminum; 0.88 at 151°C. The heat of combustion of $\text{Al}_2(\text{CH}_3)_6$ was estimated (45) to be 10.55 Kcal/g. The heat of formation of trimethylaluminum monomer in the liquid state was estimated as -36.1 Kcal/mol by the heat of reaction with acetic acid (46).

As is mentioned before, the X-ray investigation of single crystal settled the structural problem of trimethylaluminum. Lewis and Rundle (18) analysed a low-temperature diagram by the Weissenberg method and determined the atomic positions. They tried to calculate the dimerization energy by a simplified LCAO method and concluded Al-Al interactions were not negligible in this molecule.

Among several modern physical methods, nuclear magnetic resonance and infrared spectrum are especially important for studying the configurations of various alkylaluminums and their derivatives. Remarkable characteristics among these compounds are:

- a) In order to have the dimer structure, at least one $-\text{CH}_2\text{R}-$ group is necessary between aluminum atoms. In other words, only the $-\text{CH}_2\text{R}-$ groups may occupy both of the two bridge positions in a molecule.
- a) The alkyl group exchanges among various positions at room temperature, but is held at each position at the dry-ice temperature. The nuclear magnetic resonance spectrum of diborane was measured but no exchange of hydrogen atoms was reported.

The ultraviolet spectrum of the trimethylaluminum has not been reported, but no absorption band was found up to 2000Å in the present study (47).

3.7. Vibrational Spectra and Intermolecular Potential of Trimethylaluminum

The vibrational spectra of alkylaluminum was reported by various authors (14, 48-50). Hoffmann (51) measured both the Raman and infrared spectra of various aluminum compounds and gave the comprehensive assignments to those compounds. Although methyl, ethyl, n-propyl and n-butyl aluminum is dimer, i-butyl aluminum is monomer and he explained this finding by a steric effect, The observed infrared region in his study, however, was confined above 400 cm^{-1} and no calculation on normal vibrations was given in his paper.

The present author et al. (52) reported the far infrared spectra of trimethylaluminum in the region from 400 to 120 cm^{-1} and a preliminary result on the calculations of the normal vibrations. Gray (53) measured the infrared spectrum down to 300 cm^{-1} and also reported the infrared spectrum of deuterated trimethylaluminum. He modified the assignments of Hoffmann by the analysis of the spectral shift on deuteration.

Onishi and Shimanouchi (54) observed the infrared spectrum of trimethylaluminum in the 700~280 cm^{-1} region. They calculated the normal vibrations of trimethylaluminum on referring to trichloroaluminum. Their calculations are

for the skeletal vibrations on the basis of the Urey-Bradley force field modified with a resonance term. Their potential function has fourteen force constants and ten of them were adjusted by a least-square method. The assignments used in their calculation were those by Hoffmann.

The far infrared spectra of trimethylaluminum in the region from 700 to 65 cm^{-1} were reported in the second paper (II) of the present study. Trimethylaluminum was purified by vacuum distillation and then transferred into a liquid cell made of two polyethylene films 0.5 mm thick. The spectra in the region above 400 cm^{-1} were similar to those described in the literature. Two absorption bands were found at 367 and 175 cm^{-1} in the observed far infrared region.

The normal vibrations of trimethylaluminum were calculated and vibrational assignments of this molecule were carried out in the third paper (III) of the present study. The methyl group of trimethylaluminum was treated as a single dynamic unit. The observed spectra were assigned on the basis of the result of the calculation. The refined treatment of the normal vibrations has 9 parameters which were adjusted by a least-square method and the standard errors of potential constants were calculated. The bands at 367 and 175 cm^{-1} found in the far infrared region were assigned to ν_{17} , and ν_{18} and ν_{14} , respectively. The present assignments are different from Onishi and Shimano-

uchi (54) for the ν_3 , ν_4 , ν_{12} and ν_{15} bands. The potential function of this molecule was found to be similar to that of diborane and similar conclusions on the bond structure were obtained.

The characteristic of the present calculations common to diborane and trimethylaluminum is the postulate of the B-B and Al-Al bonds.

3.8. The Structure of Trichloroaluminum and Related Compounds

The aluminum halides were determined to have a dimer structure (13, 14) and their dissociation was studied by Fischer and Rahlfs (55) by the determination of the vapor pressure and the vapor density. The degree of dissociation at the sublimation temperature (180°C) and the molar heat of dissociation of Al_2Cl_6 were found to be 0.0002 and 29.0 Kcal, respectively. The trichloroaluminum dimer dissociates into the monomers completely at 900°C (56). In the solid state, the Raman spectrum (57), the X-ray data (58) and the electrical conductivity (59) showed that only trichloro compound among aluminum halides had the ionic lattice, though tribromoaluminum kept its dimer structure.

In any way, trichloroaluminum forms dimer molecules in the liquid state and in the vapor state at not a high temperature. The similarity in its bridge structure with trimethylaluminum may suggest many common characteristics for both molecules. However, the angle of bridge is considerably different between them. In the case of trimethyl-

aluminum $\angle\text{C-Al-C}$ (bridge) = 110° (18) and in the case of trichloroaluminum $\angle\text{Cl-Al-Cl}$ (bridge) = 80° (13). As a result, the Al-Al distance for the former is 2.57 \AA which is approximately equal to the sum of Pauling's tetrahedral covalent radii (18, 20), while that for the latter is 3.38 \AA which is too long to form a bond between them. The longer distance of Al-Al may not allow the postulate of Al-Al bond as in the case of diborane and trimethylaluminum. In conclusion, though apparently the structure is similar, the normal vibrations of Al_2Cl_6 could not be treated as those of B_2H_6 and $\text{Al}_2(\text{CH}_3)_6$.

The assignments of the Raman spectra of aluminum halides dimer were given by Bell and Longuet-Higgins (8), together with a preliminary result of the calculations of the normal vibrations. Then, Klemperer (56) measured the infrared spectrum of the vapor of trichloro aluminum dimer and gave a rough picture of its force field by the use of a valence force field with eight parameters. Onishi and Shimanouchi (54) calculated the normal vibrations with a modified Urey-Bradley field. They assumed the Urey-Bradley repulsive potential term for the pair of aluminum atoms of the bridge and introduced a resonance interaction term in the potential function of the bridge.

The ultraviolet spectrum of trichloroaluminum was not found in the literature, but there is no conspicuous bands in the region up to 1550 \AA (60).

3.9. N. M. R. Study of Aluminum Compounds

The nuclear magnetic resonance is a powerful tool to determine the structure of boron and aluminum compounds. Considering the bridge structure of trimethylaluminum, it was surprising that the proton magnetic resonance spectrum of the liquid at room temperature consisted of a single peak rather than a pair of signals corresponding to two positions of hydrogen atoms. After the measurements in lower temperatures were carried out, the above finding was found to indicate that all the protons were magnetically equivalent at room temperature. Muller and Pritchard (61) measured the proton magnetic resonance of trimethylaluminum in cyclopentane at -75°C , and found a pair of signals with relative intensities 1:2 corresponding to protons in bridging and in terminal methyl groups, respectively. They detected no further splitting of resonance lines which showed that the protons in each methyl group were equivalent at -75°C . The chemical shifts for the protons of the bridging and the terminal methyl groups were determined to be 9.53 p.p.m. and 10.67 p.p.m., respectively. As the temperature is raised, the peaks first broaden and then coalesced into a sharp single peak at 10.79 p.p.m. This behavior was considered to be characteristic of an exchange process and the activation energy was determined to be between 6 and 14 Kcal/mol. Since the heat of dissociation was 20.2 Kcal/mol (44), this finding showed trimethylaluminum dimer did not

split into monomer during the exchange reaction. Allred and McCoy (62) obtained the similar conclusion.

The proton resonance of aluminum methyl chlorides was observed in order to determine whether methyl groups or chlorine atoms occupied the bridge position (63, 64). Hoffmann (65) measured the proton magnetic resonance of various aluminum compounds to study the exchange between the bridge and the terminal positions. He concluded the order of strength to occupy the bridge position were:

Cl, CH₃, i-butyl.

The rate of exchange is slow in ether solution (66).

3.10. The Reactivity of Aluminum Compound

The aluminum compounds mentioned above are reactive and not stable in the air. Their reactivity are useful in the organic synthesis and in the polymerization. Investigations on this subjects are carried out by many researchers, including the present author (Appendix (2, 3)), and his colleagues (67). The infrared spectrum and the nuclear magnetic resonance spectrum are useful tools for such purpose.

Trimethylaluminum forms complexes as an electron acceptor with electron donating reagents. The structure of the complex formed by trimethylaluminum and diphenylamine was studied by Kawai, Ogawa and Hirota (Appendix (2, 3)) under high vacuum. The ultraviolet spectrum of diphenylamine in

the complex showed a blue shift and vibrational structures characteristic of weakly-perturbed benzene rings, which indicated phenyl rings in the complex were not appreciably conjugated. The proton magnetic resonance spectrum of the complex showed a pair of peaks at 2.90 p.p.m. and 10.58 p.p.m. with relative intensities 5:3 corresponding to protons in the phenyl groups and in terminal methyl groups. The spectra of the mixture of the complex and trimethylaluminum at various ratios and their dependence on the temperature were measured. The structure of the complex was concluded to be a dimer of the formula $[(C_6H_5)_2NAl(CH_3)_2]_2$.

The role of aluminum compounds in the polymerization of olefins are complicated and many investigations are now going on.

4. Summary

The vacuum ultraviolet spectrum of diborane and the far infrared spectra of trimethylaluminum were measured and two new bands of trimethylaluminum were observed in the far infrared regions. The observed bands both in the ultraviolet and in the infrared regions were assigned with the help of theoretical treatments.

Through the analysis of normal vibrations and electronic energies, the author obtained the following conclusions;

- (1) The infrared and ultraviolet spectra are assigned on the basis of the postulate of B-B and Al-Al bonds.
- (2) The bridge B-H and Al-C bonds are weaker than the normal bonds and they have little directional properties. These findings correspond well to π character of bridge bonds.
- (3) The hyperconjugation effect takes important role in the bridge.

5. Acknowledgments

The author thanks Professor Kozo Hirota and Professor Tatsuo Miyazawa for their valuable discussions and their encouragement during the whole work, without which the present study has not been accomplished. The author is grateful to his colleagues and to Professor Saburo Nagakura of Tokyo University for their discussions, and Dr. Koji Kaya of Tokyo University for his collaboration in the measurement of vacuum ultraviolet spectra.

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6. Appendix

The author published several papers in addition to those listed above.

- (1) Electron Spin Resonance and Electronic Absorption Spectra of the Radical Anions of Pyridine and Acridine.

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- (2) Spectroscopic Studies of the Complex Produced by Trimethylaluminum and Diphenylamine.

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- (3) Ultraviolet and Nuclear Magnetic Resonance Spectra of the Complex Produced by the Reaction of Trimethylaluminum with Diphenylamine.

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- (4) Infrared Spectra of Adsorbed Formic Acid.

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- (5) Infrared Study of the Adsorption of Formic Acid on Evaporated Nickel Film and Interaction of the Chemisorbed Species with Formic Acid.

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