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A new synthesis of 1-phenylthio- and 1-alkylamino-4-nitrobuta-1,3-diienes

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A new synthesis of push-pull dienes such as 4-nitro-1-phenylthiopenta-1,3-diene 4 and 1-dialkylamino-4-nitropenta-1,3-diene 5, is described. The X-ray crystal analysis shows that 4-nitro-1-(pyrrolidin-1-yl)penta-1,3-diene 5a is essentially planar in an E,E-configuration with r(C=C) = 1.424(1) Å and r(C=C) = 1.351(1) and 1.371(9) Å. Compounds 5 showed a large solvatochromic effect similar to that of merocyanine dyes.

Molecule 5a exhibits second harmonic generation (SHG) activity whose efficiency is 2.5 times that of urea (determined by a powder method at 1064 nm). For 5a, the molecular nonlinearity μθ is estimated to be 1200 × 10⁻⁶ esu which is calculated from the Pockel coefficient (r₁₁) determined by electrooptic measurements of dipole polymers of 5a in poly(methyl methacrylate) at 1300 nm. This value is relatively large for such small conjugated molecules, where donors and acceptors are bridged by only 4π electron systems.

Introduction

As a result of the powerful electron-withdrawing properties of the nitro group together with its potential for transformation into a variety of other functionalities, compounds containing this group have found widespread application as synthetic intermediates. The nitro group plays an important role as a typical electron acceptor for charge-transfer interactions, and many nitro compounds substituted with electron donors have been investigated for optoelectronic materials. We have been interested in the chemistry of nitro compounds for some years and found several new reactions and reagents involving the nitro group. Since nitro compounds having other heterocatoms have special properties and reactivity, their potential both as nitromethylene heterocyclic insecticides and building blocks for the controlled synthesis of sensitive molecules have been studied.

In 1983, we reported a new synthesis of β-phenylthio nitroalkenes, β-sulfinyl nitroalkenes and β-sulfonyl nitroalkenes starting from nitroalkenes, which compounds have proved to be useful electron-deficient alkenes for Michael addition and the Diels–Alder reaction. Nitro enamines have also been extensively used as useful reagents for organic synthesis. In such compounds, the nitro group cooperates with the sulfur or amino groups to modify both the properties and reactivity. Nitro dienes substituted with sulfur or amino functional groups at the other terminal position are also expected to be useful reagents for the construction of highly functionalized molecules. However, such dienes have been little studied because of difficulty in preparing them. In this paper we report a simple method for the preparation of acrolein or acrylonitrile of 4-nitro-1-phenylthiopenta-1,3-diene 4 and the conversion of this into 1-dialkylamino-4-nitropenta-1,3-diene 5 on treatment with dialkylamines. As these dienes are conjugated with electron donors and acceptors, they have the potential to show interesting optoelectronic properties. Here we also report the preliminary results of nonlinear optical (NLO) activity and the X-ray crystal structure of a new push-pull diene 5.

Results and discussions

Synthesis of push-pull dienes

Earlier, we reported the preparation of β-phenylthionitroalkenes by chlorination of β-phenylthionitroalkanes with sulfuryl chloride followed by dehydrochlorination of the product on treatment with triethylamine. This method is very attractive, since the starting materials, β-phenylthionitroalkanes, are readily prepared by the Michael addition of thiophenol to nitroalkenes; a variety of alkyl or aryl groups can also be introduced into β-phenylthionitroalkenes by the choice of suitable nitroalkenes. We have attempted the preparation of 3-phenylthionitroalkenes by this method in which chlorination and dehydrochlorination of the 3-phenylthionitroalkenes is a simple extension of the original method (Scheme 1). The Michael addition of thiophenol to acrolein gave 3-phenylthiopropanal in quantitative yield. The nitroaldol condensation of 1 with nitroethane followed by dehydration with basic alumina in dichloromethane at 40 °C gave 2-nitro-5-phenylpent-2-ene in 60–70% yield. The subsequent chlorination of 3 with sulfuryl chloride and elimination of HCl on treatment with triethylamine at 0 °C gave 4-nitro-1-phenylthiopenta-1,3-diene 4 in good overall yields. The phenylthio group of 4 was readily replaced by alkylamino groups on treatment with alkylamines in methanol at room temperature to give 5 in 70–80% yield, which was analogous to the preparation of nitrogenamines from β-phenylthionitroalkenes.

Thus, 4-nitro-1-(pyrrolidin-1-yl)penta-1,3-diene 5a and 1-dialkylamino-4-nitropenta-1,3-diene 5b were prepared.

by the reaction of 4 with pyrrolidine and diethylamine, respectively. The configurations of the double bonds were determined to be \( E \) by \(^1\)H NMR spectroscopy or X-ray crystallography as discussed later. Other nucleophiles such as the carbanions derived from active methylene compounds or various organometallics may react with 4 to give various nitro dienes. If other \( \alpha,\beta \)-unsaturated aldehydes and nitroalkanes are used as starting materials, 4 having a variety of substituents may be prepared. However, the present method is not suitable for the preparation of nitro trienes or longer nitropolynenes. Some modifications are required for the general synthesis of nitropolynenes. The modified method is presented in Scheme 2, where the nitro-aldol reaction of \((E)-3\)-phenyliothiapropenal 8 with nitroalkanes is a key step for the preparation of 4. The requisite compound 8 was readily prepared by Michael addition of thiophenol to acrylonitrile, followed by chlorination and dehydrochlorination, and the reduction of the nitrile to the aldehyde. The direct conversion of 1 into 8 by chlorination with sulfuryl chloride and dehydrochlorination results in the formation of 8 in low yield (<10%). The present sequence of reactions may be useful for a general synthesis of \( \beta \)-phenylthio-\( \alpha,\beta \)-unsaturated aldehydes starting from \( \alpha,\beta \)-unsaturated nitriles. The nitro-aldol condensation of 8 with nitroethane followed by dehydroxylation with basic alumina gave 4 (60%). The aldehyde 8 was converted into \((2E,4E)-5\)-phenyliophenota-2,4-dienal 9 on treatment with \( \text{N}-\text{N}-\text{bis(trimethylsilyl)} \)-hexadenedi-\( \text{tert} - \text{butylamine.} \) The aldehyde 8 may be converted into polyene-aldehydes terminating with a phenylthio group by repeating this procedure. The dienes or polynones thus prepared can be considered as versatile intermediates owing to the presence of the two reactive terminal functions. The nitro-aldol condensation of such phenylthio-polyenals followed by the substitution of the phenylthio group with the amino group may give push-pull polynones whose conjugated length can be controlled. Furthermore, the Wittig reaction of 9 or related polynenals followed by coupling with Grignard reagents in the presence of transition metals will provide a new method for the preparation of polynones of controlled configuration. Further studies with these reagents are in progress.

**Structure analyses**

The configurations of the double bonds for compounds 4, 5, 8 and 9 can be determined by \(^1\)H NMR (CDCl\(_3\)) spectroscopy. The three protons attached at the double bonds of 5a resonate at \( \delta 4.99 \) (t, \( J \) 12.2), 7.15 (d, \( J \) 12.2) and 7.92 (d, \( J \) 12.2) and the methyl protons resonate at \( \delta 2.15 \) as a singlet. These results suggest that 5a consists of one stereoisomer, the large coupling constant \( (J_{12.2} \text{ Hz}) \) suggesting a 1,3,5E configuration. In the same way, the coupling constants of the protons attached at the double bonds of 4, 5b, 8 and 9 are all in the range of 12-15 Hz, which suggests the \( E \) configuration for these double bonds. Although compound 7 consisted of an \( E,Z \) mixture (\( E:Z = 3:2 \)), reduction of 7 into 8 with DIBAL resulted in the selective formation of the pure \( E \)-isomer. This selectivity is mainly a result of the isomerization of the Z-form into the more stable \( E \)-form during the reduction. The 1,3,5E configuration of 5a was further confirmed by X-ray crystal analyses. The X-ray crystal structure of compound 5a is shown in Fig. 1, and the bond lengths and bond angles are given in Tables 1 and 2, respectively. The X-ray crystal data provide important information for the geometry of push-pull dienes which are essential for the theoretical prediction of the dipole moment and hyperpolarizability of new push-pull polynones. Molecule 5a is essentially planar in \( E \) configuration with \( r(C-C) = 1.42 \) (Å) and \( r(C-C) = 1.35 \) (Å) and 1.371 (Å). The geometry of molecule 5a is in good agreement with the calculated geometry of 1-(1,1-dimethylamino)-4-nitrobuta-1,3-diene (\( C-C = 1.42 \) Å and both \( C-C = 1.37 \) Å). Recent calculations on 1-amino-4-nitrobutadieene that C-C is 1.43 Å, the C-C close to NO\(_2\) is 1.337 and the other C-C is 1.347. The dipole moment and static hyperpolarizability of polynones with donor-acceptor substitutions are calculated from these data. The atoms C(6), C(7) and O(2) deviated slightly with 0.20(1) and 0.18(1) and 0.16(1) Å, respectively, from the least-squares plane defined by C(1), C(2), C(3) and C(4) atoms. Fig. 2(a) and (b) show a view of the unit cell along the \( a \) and \( b \) axes, respectively. The molecule 5a is located parallel to the \( ac \) plane and stacks along the \( b \) axis in the crystal. There are no particularly important contacts, but it should be noted that these may lie outside van der Waals limits. The dipole moment of 5a exists on the \( ac \) plane. From the space group \( Pnma2_1 \) (\#33 point group mm2), the \( c \) axis component of the dipole moment remains in the solid state, but the component along the \( a \) and \( b \) axes counteract each other due to the two-fold screw axis symmetry parallel to the \( c \) axis. The \( c \) axis component of the dipole moment in the crystal plays an important part of the second harmonic generation (SHG) activity. Thus, 5a packs in a noncentrosymmetric space group and it is expected to be SHG active in a solid state.

**Optical properties of 5**

Donor-acceptor substituted conjugated compounds offer great promise as materials for non-linear optical (NLO) devices. Numerous classes of compounds have been explored for this purpose and the effects of donor-acceptor and conjugated systems on non-linearities have been extensively studied. Among them, amino and nitro substituted aromatic rings have been most extensively studied. As the aromatic resonance energy of thiophene is less than that of benzene, electron polarization involving charge separated resonance structures is expected to be easier in the thiophene series and to increase the molecular hyperpolarizability. Thus, many thiophenes substituted with \( \pi \)-donors and \( \pi \)-acceptors have been proposed as effective candidates for NLO materials. Recent theoretical studies have shown that donor-acceptor polynones are greatly
superior to the corresponding polyaromatics, particularly for electrooptic modulation. Although polyene systems suffer from the disadvantage that they are less stable and more difficult to prepare than aromatic systems, it is important to verify the predictions concerning NLO activity which are obtained by theoretical calculations. We have, therefore, recently been characterized. As donors and acceptors are constant, only the conjugated systems being changed, the effects of conjugated systems on NLO can be investigated. The linear bathochromicity of compounds 4 and 5 was estimated by electrooptical measurements using a semiconducting laser (1300 nm) on polished solid solutions of 5a in polymers. This method has been used for rapid and reliable characterization of new chromophores. The electrooptic activity of polystyrene (poly(methyl methacrylate)) with 5a by 5 wt% was measured by the literature method. The molecular nonlinearities of 5a was estimated to be $\mu B = 1200 \times 10^{-48}$ esu from a $r_{33}$ value. This value is higher than that of 4-dimethylamino-4'-nitrobiphenyl and is as high as that of 4-dimethylamino-4'-nitrostilbene. The estimation of molecular hyperpolarizability is very rough but the results seem reasonable judging from the solvatochromism data of 5a. Although the present results are simply qualitative, it should be noted that a molecule as small as 5a exhibits a NLO activity comparable to large molecules such as 4 or 11. Since small molecules are preferred for applications as optical modulators using poled polymers, polynones are good candidates for new NLO materials. Extension of the double bonds in 5a by the present method and verification of the interesting theoretical predictions about the structure–function relationships of NLO activity (the calculated hyperpolarizabilities of push–pull polyenes increase rapidly with an increasing number of ethynyl units and the effect per unit volume is a maximum for 20 units) are now in progress.

**Experimental**

Melting points were determined with a Yanaco micro-melting point apparatus and are uncorrected. IR spectra were recorded on a JEOl JNM-GSX270 instrument for solutions in CDCl$_3$ with tetramethylsilane as an internal standard. Coupling constants $J$ are given in Hz. Mass spectra were determined with a Hitachi M-80B instrument at 20 eV. UV–VIS spectra were recorded on a Shimadzu 2200 spectrometer. Microanalyses were performed on a Perkin-Elmer 240C

**Table 1**

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<th>Compds.</th>
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<td>374 (4.42)</td>
<td>377 (4.38)</td>
<td>372 (4.38)</td>
<td>366 (4.28)</td>
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<tr>
<td>5a</td>
<td>392 (4.69)</td>
<td>451 (4.69)</td>
<td>456 (4.70)</td>
<td>452 (4.72)</td>
<td>460 (4.46)</td>
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<tr>
<td>5b</td>
<td>386 (4.69)</td>
<td>447 (4.68)</td>
<td>454 (4.70)</td>
<td>453 (4.38)</td>
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* Data from ref. 20. In formamide.
3-Phenylthiopropanal 1

To a cooled solution of acrolein (5.6 g, 0.1 mol) in THF (100 cm³), was added hydriodic acid (11 g, 0.1 mol) dropwise at 0–5 °C. The resulting solution was stirred at room temperature for 3 h after which it was evaporated to give crude 1 (15 g, 91%), which was pure enough for the use in the next step; colourless oil, vₙ₉₂ (neat)/cm⁻¹ 3056, 2932, 1724, 1582, 1482, 1026, 740 and 692; δₛ(CDCCl₃) 2.73 (2 H, t, J 7.0), 3.15 (2 H, t, J 7.0), 7.28 (5 H, m) and 9.71 (1 H, s); δₛ(CDCCl₃), 67 MHz 26.2, 43.1, 126.5, 123.8, 129.0, 129.8 and 200.2; m/z 166 (M⁺, 18) and 109 (100).

3-Phenyl-1-(4-nitrophenyl)pentan-3-ol 2

A mixture of 2-(2.4 g, 10 mmol) and chromatographic alumina (activity 1 according to Brockmann; 5 g) in CH₂Cl₂ (10 cm³) was stirred at 50 °C for 24 h after which the reaction mixture was filtered and the alumina washed with CH₂Cl₂. The filtrate was evaporated under reduced pressure and the residue was subjected to column chromatography (silica gel, hexane-ethyl acetate) to give pure 2 (2.1 g, 87%) as a colourless oil; vₙ₉₂ (neat)/cm⁻¹ 3450, 3060, 2940, 1550, 1482, 1442, 1394, 1358, 742 and 692; δₛ(CDCCl₃) 1.47 and 1.50 (3 H, d, J 8.2 each diastereomer), 1.74 (2 H, m), 2.87 (1 H, s), 3.03 and 3.13 (2 H, m, each diastereomer), 4.47 (2 H, m) and 7.35 (5 H, m); MS (Cl isotopologue): m/z 204 (M⁺ + 1, 16), 195 (62), 167 (82), 150 (22), 123 (100) and 110 (60) (Found: C, 54.43; H, 5.25; N, 5.68; C₁₁H₁₄NO₂S requires C, 54.79; H, 5.43; N, 5.81%).

2-Nitro-5-phenylthiophen-2-ene 3

A mixture of 2 (2.4 g, 10 mmol) and chromatographic alumina (activity 1 according to Brockmann; 5 g) in CH₂Cl₂ (10 cm³) was stirred at 50 °C for 24 h after which the reaction mixture was filtered and the alumina washed with CH₂Cl₂. The filtrate was evaporated to give crude 3 which after column chromatography (silica gel, hexane-ethyl acetate) gave pure 3 (1.7 g, 79%) as a pale yellow oil; vₙ₉₂ (neat)/cm⁻¹ 3052, 2922, 1724, 1550, 1482, 1444, 1390, 1334, 1088, 1026, 742, 720 and 692; δₛ(CDCCl₃) 2.07 (3 H, d, J 7.0), 2.50 (2 H, m), 3.04 (2 H, t, J 7.7), 7.11 (1 H, t, J 7.8) and 7.33 (5 H, m); δₛ(CDCCl₃) 12.5, 27.7, 32.2, 126.5, 129.0, 129.9, 133.4, 134.8 and 148.5; m/z 223 (M⁺, 20), 177 (100), 123 (99), 110 (46) and 109 (35) (Found: C, 59.21; H, 5.58; N, 6.12; C₁₁H₁₄NO₂S requires C, 59.16; H, 5.87; N, 6.27%).

(1E,3E)-4-Nitro-1-phenylthiopenta-1,3-diene 4

To a cooled solution of 3 (2.23 g, 10 mmol) in CH₂Cl₂ (10 cm³) at 0 °C was added SO₂Cl₂ (0.80 cm³, 10 mmol) slowly, and the resulting solution was stirred at 0 °C for 30 min. After this it was evaporated under reduced pressure and the residue was dissolved again in CH₂Cl₂ (10 cm³). The resulting solution was cooled at 0 °C and triethylamine (1.39 cm³, 10 mmol) was added at the same time. The resulting mixture was stirred for 30 min after which it was evaporated under reduced pressure. The residue was dissolved again in CH₂Cl₂ and the solution cooled to 0 °C when triethylamine (1.39 cm³, 10 mmol) was added at the same temperature. The resulting mixture was stirred for 30 min at 0 °C and worked up in the same way as described in the preparation of compound 4. Column chromatography (silica gel, hexane-ethyl acetate) gave pure 4 (1.37 g, 85%) as an E,Z mixture (E : Z = 3 : 2) and a pale yellow oil; vₙ₉₂ (neat)/cm⁻¹ 3052, 2922, 1724, 1550, 1484, 1444, 932, 788, 746, 704 and 692; δₛ(CDCCl₃) 4.89 (8 H, d, J 15.6, E form), 5.37 (1 H, d, J 10.4, Z form), 7.29 (1 H, d, J 10.4, Z form), 7.44 (5 H, m), 7.46 (1 H, d, J 15.6, E form); δₛ(CDCCl₃), 67 MHz 92.9 (E form), 93.5 (Z form), 115.5 (Z form), 117.1 (E form), 130.0, 131.3, 131.9, 133.5, 134.5 (E form) and 152.4 (Z form); m/z 185 (M⁺ + 1, 120), 184 (M⁺, 100), 167 (34, 17), 114 (54) and 86 (45) (Found: C, 58.36; H, 8.57; N, 15.13. C₁₁H₁₄NO₂ requires C, 58.67; H, 8.76; N, 15.20%).

3-(Phenylthio)propenonitrile 5

To a cooled solution of 3-(phenylthio)propenonitrile (6.13 g, 10 mmol) in CH₂Cl₂ (10 cm³) at 0 °C was added SO₂Cl₂ (0.80 cm³, 10 mmol) slowly, the reaction mixture being kept at 0 °C. The resulting solution was stirred at 0 °C for 30 min after which it was evaporated under reduced pressure. The residue was dissolved again in CH₂Cl₂ and the solution cooled to 0 °C when triethylamine (1.39 cm³, 10 mmol) was added at the same time. The resulting mixture was stirred for 30 min at 0 °C and worked up in the same way as described in the preparation of compound 4. Column chromatography (silica gel, hexane-ethyl acetate) gave pure 5 (1.1 g, 5 mmol) as an E,Z mixture (E : Z = 3 : 2) and a pale yellow oil; vₙ₉₂ (neat)/cm⁻¹ 3052, 2922, 1724, 1550, 1484, 1444, 932, 788, 746, 704 and 692; δₛ(CDCCl₃) 4.89 (8 H, d, J 15.6, E form), 5.37 (1 H, d, J 10.4, Z form), 7.29 (1 H, d, J 10.4, Z form), 7.44 (5 H, m), 7.46 (1 H, d, J 15.6, E form); δₛ(CDCCl₃), 67 MHz 92.9 (E form), 93.5 (Z form), 115.5 (Z form), 117.1 (E form), 130.0, 131.3, 131.9, 133.5, 134.5 (E form) and 152.4 (Z form); m/z 185 (M⁺ + 1, 120), 184 (M⁺, 100), 167 (34, 17), 114 (54) and 86 (45) (Found: C, 58.36; H, 8.57; N, 15.13. C₁₁H₁₄NO₂ requires C, 58.67; H, 8.76; N, 15.20%).
for 2 h and then poured into water containing dilute HCl. The same work-up as described in the preparation of 2 gave the crude nitro alcohol, which was treated with chromatographic alumina in the same way as described in the preparation of 3 to give 4 (1.32 g, 60%). Spectral data of this product were identical with those of 4 prepared from 3.

\[ \text{(2E,4E)-3-Phenylthiopenta-2,4-dienal} 9 \]

To a mixture of 8 (1.64 g, 10 mmol) and ZnBr₂ (0.23 g, 1 mmol) in THF (20 cm³) was added a solution of N-2,2-bis(trimethylsilyl)ethylideneter-butylamine\(^{15}\) (2.67 g, 10 mmol), and the resulting mixture was stirred for 5 h at room temperature. A solution of ZnCl₂ (2 g) in water (20 cm³) and diethyl ether (25 cm³) were then added to the reaction mixture after which it was stirred for 1 h at room temperature. Filtration of the reaction mixture through Celite and extraction with diethyl ether followed by the customary work-up gave crude 9. This was purified by column chromatography (silica gel, hexane-ethyl acetate) to give pure 9 (1.33 g, 70%) as a pale yellow oil; \( \nu_{\text{max}}(\text{neat})/\text{cm}^{-1} = 3028, 2812, 1676, 1608, 1582, 1554, 1442, 1380, 1268, 1188, 1154, 1122, 980, 848, 744; \)

\[ \delta_{\text{CDCl₃}} (5.93 (1 H, dd, 0.71069 \text{Hz}) \text{pm} 125.0, 128.7, 128.8, 129.6, 130.3, \]


2 The NLO properties of these dyes are examined for the first time in this work.


10 Another method for the preparation of 1-nitro-4-arythio-1,3-dienes by the reaction of 1,4-dinitro dienes with anethiols has been reported (see, Z. F. Pavlova, Y. A. Kesem, E. S. Lipina, G. A. Berkova and V. V. Perkalin, Zh. Org. Khim., 1985, 21, 2300).

11 An alternative method for the preparation of β-alkylthionitroalkanes which is based on the diisocyanates of N-nitro ketones (see, M. Node, T. Kawabata, M. Fujimoto and K. Fuji, Synthesis, 1984, 33, 234; M. E. Jung and D. E. Grove, J. Chem. Soc., Chem. Commun., 1987, 753). The method starting from nitroalkanes is more convenient and general than that using N-nitro ketones, since various nitroalkanes are readily prepared by the reaction of aldehydes and nitroalkanes or nitrilation of double bonds.\(^{1}\)


