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

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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 $r(C–C)$ = 1.42(1) Å and $r(C=C)$ = 1.35(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 $\mu\beta$ is estimated to be 1200×10^{-48} esu which is calculated from the Pockel coefficient (r_{33}) determined by electrooptic measurements of poled 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.[1] The nitro group also 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.[2] We have been interested in the chemistry of nitro compounds for some years and found several new reactions and reagents involving the nitro group.[3] Since nitro compounds having other heteroatoms have special properties and reactivity, their potential both as nitromethylene heterocyclic insecticides[4] and building blocks for the controlled synthesis of sensitive molecules have been studied.[5] In 1983, we reported a new synthesis of β-phenylthio nitroalkenes, β-sulfinyl nitroalkenes and β-sulfonyl nitroalkenes starting from nitroalkenes,[6] compounds which have proved to be useful electron-deficient alkenes for Michael addition and the Diels–Alder reaction.[7] Nitro enamines have also been extensively used as useful reagents for organic synthesis.[8] 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.[9] In this paper we report a simple method for the preparation from 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-phenylthionitro-
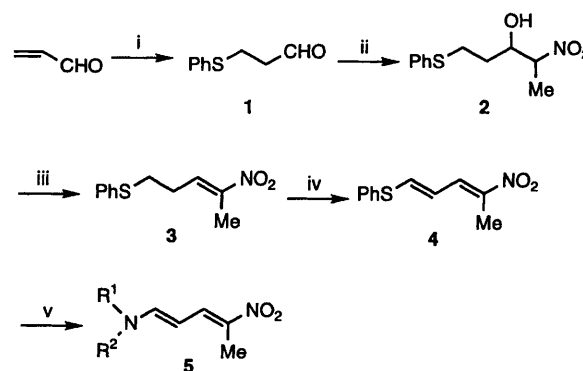
Scheme 1 *Reagents and conditions:* i, PhSH, 0 °C, RT, 3 h; ii, EtNO₂, DBU, RT, 24 h; iii, Al₂O₃, 50 °C, 24 h; iv, SO₂Cl₂, 0 °C, 30 min, then Et₃N, 0 °C, 30 min; v, R¹R²NH, RT, 8 h

alkenes by chlorination of β-phenylthionitroalkanes with sulfuryl chloride followed by dehydrochlorination of the product on treatment with triethylamine.[6] This method is very attractive, since the starting materials, β-phenylthionitroalkanes, are readily prepared by the Michael addition of thiophenol with nitroalkenes; a variety of alkyl or aryl groups can also be introduced into β-phenylthionitroalkenes by the choice of suitable nitroalkenes.[10] We have attempted the preparation of δ-phenylthionitrodienes by this method in which chlorination and dehydrochlorination of the δ-phenyl-thionitroalkenes is a simple extension of the original method (Scheme 1). The Michael addition of thiophenol to acrolein gave 3-phenylthiopropanal **1** in quantitative yield. The nitro-aldol condensation of **1** with nitroethane followed by dehydration with basic alumina in dichloromethane at 40 °C[11] gave 2-nitro-5-phenylthiopent-2-ene **3** 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 nitroenamines from β-phenylthionitro-alkenes.[12] Thus, 4-nitro-1-(pyrrolidin-1-yl)penta-1,3-diene **5a** and 1-diethylamino-4-nitropenta-1,3-diene **5b** were prepared

Scheme 2 showing compounds 5a and 5b structures at top.
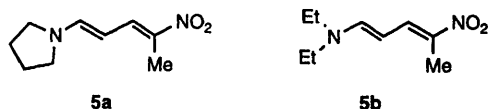
by the reaction of **4** with pyrrolidine and diethylamine, respectively. The configurations of the double bonds were determined to be E by ^{1}H NMR spectroscopy or X-ray crystallography as discussed later. Other nucleophiles such as the carbanions derived from active methylene compounds or various organometallics may react with **4** to give various nitro dienes. If other α,β-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 nitropolyenes. Some modifications are required for the general synthesis of nitropolyenes. The modified method is presented in Scheme 2, where the nitro-aldol reaction of (*E*)-3-phenylthiopropenal **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,^{13} 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%).^{14} The present sequence of reactions may be useful for a general synthesis of β-phenylthio-α,β-unsaturated aldehydes starting from α,β-unsaturated nitriles. The nitro-aldol condensation of **8** with nitroethane followed by dehydration with basic alumina gave **4** (60%). The aldehyde **8** was converted into (2*E*,4*E*)-5-phenylthiopenta-2,4-dienal **9** on treatment with *N*-2,2-bis(trimethylsilyl)ethylidene-*tert*-butylamine.^{15} The aldehyde **8** may be converted into polyene-aldehydes terminating with a phenylthio group by repeating this procedure. The dienes or polyenes 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 polyenes whose conjugated length can be controlled. Furthermore, the Wittig reaction of **9** or related polyenals followed by coupling with Grignard reagents in the presence of transition metals will provide a new method for the preparation of polyenes of controlled configuration.^{16} 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 δ 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 δ 2.15 as a singlet. These results suggest that **5a** consists of one stereoisomer, the large coupling constant (J 12.2 Hz) suggesting a 1*E*,3*E* 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*E*,3*E* 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 polyenes. Molecule **5a** is essentially planar in *E,E* configuration with r(C–C) =
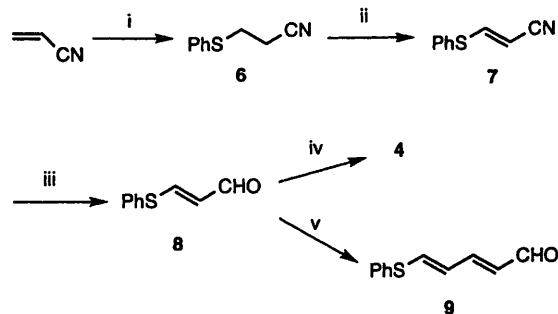
Scheme 2 *Reagents and conditions*: i, PhSH, RT, 3 h, ii, SO$_2$Cl$_2$, 0 °C, 30 min, then Et$_3$N, 0 °C, 30 min; iii, DIBAL, toluene, RT, 24 h; iv, EtNO$_2$, DBU, RT, 24 h, then Al$_2$O$_3$, 50 °C; v, (Me$_3$Si)$_2$CH-CH=NCMe$_3$, ZnBr$_2$, 5 h, then ZnCl$_2$, H$_2$O, RT, 1 h
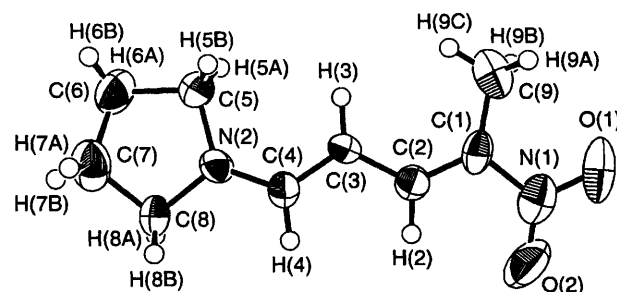

Fig. 1 X-Ray molecular structure of compound **5a**, with crystallographic numbering scheme

1.42 (1) Å and r(C=C) = 1.35(1) and 1.371 (9) Å. The geometry of molecule **5a** is in good agreement with the calculated geometry of 1-(*N,N*-dimethylamino)-4-nitrobuta-1,3-diene (C–C = 1.42 Å and both C=C = 1.37 Å).^{17} Recent calculations on 1-amino-4-nitrobutadiene show that C–C is 1.433 Å, the C=C close to NO$_2$ is 1.337 and the other C=C is 1.347.^{17} The dipole moment and static hyperpolarizability of polyenes with donor-acceptor substituents are calculated from these data.^{17} The atoms C(6), C(7) and O(2) deviated slightly with 0.20(1), 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 $Pna2_1$ (#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.^{18} 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 π-donors and π-acceptors have been proposed as effective candidates for NLO materials.^{19} Recent theoretical studies have shown that donor-acceptor polyenes are greatly
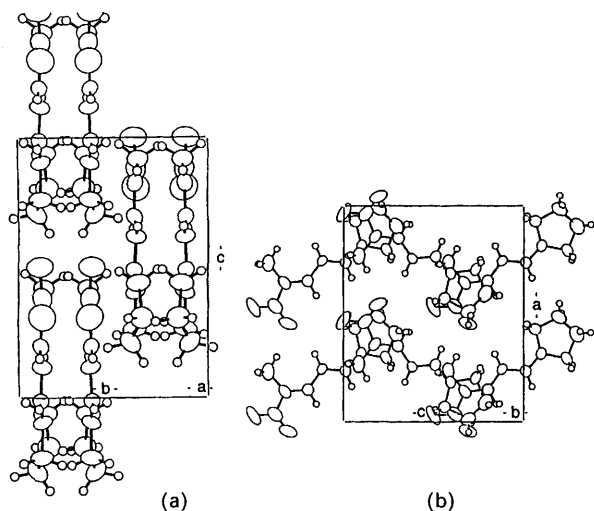
Fig. 2 Single crystal X-ray structure of compound **5a**: (a) view along the *a* axis, (b) along the *b* axis

Table 1 Selected bond lengths (Å) for compound **5a**

O(1)–N(1)	1.259(9)	C(1)–C(9)	1.47(1)
O(2)–N(1)	1.24(1)	C(2)–C(3)	1.42(1)
N(1)–C(1)	1.42(1)	C(3)–C(4)	1.371(9)
N(2)–C(4)	1.323(8)	C(5)–C(6)	1.54(1)
N(2)–C(5)	1.461(9)	C(6)–C(7)	1.46(1)
N(2)–C(8)	1.47(1)	C(7)–C(8)	1.51(1)
C(1)–C(2)	1.35(1)		

Table 2 Selected bond angles (°) for compound **5a**

O(1)–N(1)–O(2)	123.6(9)	C(2)–C(1)–C(9)	125.8(8)
O(1)–N(1)–C(1)	116(1)	C(1)–C(2)–C(3)	128.5(8)
O(2)–N(1)–C(1)	120.0(9)	C(2)–C(3)–C(4)	119.8(8)
C(4)–N(2)–C(5)	123.9(7)	N(2)–C(4)–C(3)	126.9(8)
C(4)–N(2)–C(8)	122.6(6)	N(2)–C(5)–C(6)	103.4(7)
C(5)–N(2)–C(8)	113.4(7)	C(5)–C(6)–C(7)	106.3(7)
N(1)–C(1)–C(2)	117.2(8)	C(6)–C(7)–C(8)	108.4(9)
N(1)–C(1)–C(9)	116.8(9)	N(2)–C(8)–C(7)	102.7(8)

superior to the corresponding polyaromatics, particularly for electrooptic modulation.[17,18] 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 calculation.[18] We have, therefore, measured some optical properties of **5a** and compared them with those of 5-dimethylamino-5'-nitro-2,2'-bithiophene **10**[20] and 4-dimethylamino-4'-nitrobiphenyl **11**[20] which have 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 absorption maxima of compounds **4**, **5a**, **5b**, **10** and **11** in various solvents are summarized in Table 3. The data for compounds **10** and **11** are taken from ref. 20. A large solvatochromic effect was observed in compounds **5** and **10**: for example, the differences for the absorption maxima in hexane and DMF of **5** and **10** are 60 and 80 nm, respectively. In contrast, that of **11** is < 25 nm. The linear bathochromicity of the absorption of the longest wavelength of these compounds was observed by an increase in the solvent polarity. Correlations of absorption shifts for **5** with solvent polarity are similar to those of merocyanine dyes the solvatochromism of which has been well studied.[21] The ground-to-excited state dipole moment change, $\Delta\mu$, was estimated from the solvatochromism data.[21] The data listed in Table 3 suggest that $\Delta\mu$ of values **5** and **10** are larger than that of **11**. The X-ray structure analyses show that **5** and **10** are almost completely
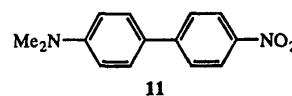
Table 3 Absorption properties of compounds 4 and 5

	λ_{max}/nm (log ε)				
Compds.	Hexane	CH$_2$Cl$_2$	DMF	MeCN	MeOH
4	350 (4.30)	374 (4.42)	377 (4.38)	372 (4.38)	366 (4.28)
5a	392 (4.69)	451 (4.69)	456 (4.70)	452 (4.72)	460 (4.46)
5b	386 (4.69)	447 (4.68)	454 (4.70)	453 (4.38)	464 (4.72)
10[a]	466	535	549	534	524
11[a]	375		400[b]		

[a] Data from ref. 20. [b] In formamide.
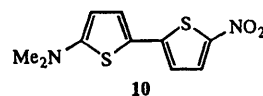
planar whilst **11** is non-planar;[20] therefore, butadiene and bithiophene skeletons provide more efficient electron-delocalization pathways than biphenyl. Thus, the donor- and acceptor-substituted conjugated diene **5a** is expected to exhibit NLO activity comparable to **10** and **11**. First, the macroscopic NLO properties of **4**, **5a** and **11** were qualitatively compared for powdered samples by measuring the SHG intensity at 532 nm with a Nd-YAG laser (1064 nm).[22] Compound **5a** was SHG active, the efficiency being 2.5 times that of urea, whilst compound **4** showed little SHG activity. The literature reports that the SHG activities of **11** and related compounds are *ca.* 3 times that of urea.[23] Thus, the SHG activity of **5a** is as high as that of biphenyls with donors and acceptors. In general, polyenes with donor and acceptors are not useful for SHG due to reabsorption of the converted light; however, highly conjugated systems may find other applications such as an optical modulator (Pockels effect).[18] The molecular hyperpolarizability (β) was estimated by electrooptical measurements using a semiconducting laser (1300 nm) on poled solid solutions of **5a** in polymers. This method has been used for rapid and reliable characterization of new chromophores.[24] The electro-optic activity of poled polymer [poly(methyl methacrylate) with **5a** by 5 wt%] was measured by the literature method.[22] The molecular nonlinearity of **5a** was estimated to be $\mu\beta = 1200 \times 10^{-48}$ 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.[18] 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 **10** or **11**. Since small molecules are favoured for applications as optical modulators using poled polymers, polyenes 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 ethenyl units and the effect per unit volume is a maximum for 20 units[17]) are now in progress.

Experimental

Melting points were determined with a Yanaco micro-melting point apparatus and are uncorrected. IR spectra were determined on a Hitachi 260-10 spectrometer. ^{1}H NMR 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 on 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

elementary analyser. These analyses were all performed at the Advanced Instrumentation Center for Chemical Analysis, Ehime University.

3-Phenylthiopropanal 1[14]

To a cooled solution of acrolein (5.6 g, 0.1 mol) in THF (100 cm^3) was added thiophenol (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 1 (15 g, 91%), which was pure enough for the use in the next step; colourless oil; ν_{max}(neat)/cm^{-1} 3056, 2932, 1724, 1582, 1482, 1026, 740 and 692; δ_H(CDCl$_3$) 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); δ_C(CDCl$_3$, 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-Nitro-1-phenylthiopentan-3-ol 2

To a solution of 1 (1.66 g, 10 mmol) and nitroethane (0.83 g, 11 mmol) in acetonitrile (10 cm^3) was added DBU (0.14 cm^3, 1 mmol). The resulting solution was stirred at room temperature for 24 h after which it was poured into water containing dilute HCl. The mixture was extracted with diethyl ether and the extract dried (MgSO$_4$), and evaporated to give crude 2. Purification by column chromatography (silica gel, hexane–ethyl acetate) gave 2 (2.1 g, 87%) as a colourless oil; ν_{max}(neat)/cm^{-1} 3450, 3060, 2940, 1550, 1482, 1442, 1394, 1358, 742 and 692; δ_H(CDCl$_3$) 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 (CI, isobutane): m/z 242 (M$^+$ + 1, 16), 195 (62), 167 (82), 150 (22), 123 (100) and 110 (60) (Found: C, 54.43; H, 5.25; N, 5.68. C$_{11}$H$_{15}$NO$_3$S requires C, 54.79; H, 5.43; N, 5.81%).

2-Nitro-5-phenylthiopent-2-ene 3

A mixture of 2 (2.4 g, 10 mmol) and chromatographic alumina (activity I according to Brockmann; 5 g) in CH$_2$Cl$_2$ (10 cm^3) was stirred at 50 °C for 24 h after which the reaction mixture was filtered and the alumina washed with CH$_2$Cl$_2$. The filtrate was evaporated to give crude 3 which after column chromatography (silica gel, hexane–ethyl acetate) gave pure 3 (1.7 g, 75%) as a pale yellow oil; ν_{max}(neat)/cm^{-1} 3100, 2970, 1700, 1582, 1552, 1522, 1482, 1442, 1390, 1334, 1088, 1026, 742, 720 and 692; δ_H(CDCl$_3$) 2.07 (3 H, d, J 0.9), 2.50 (2 H, m), 3.04 (2 H, t, J 7.2), 7.11 (1 H, t, J 7.8) and 7.33 (5 H, m); δ_C(CDCl$_3$) 12.5, 27.7, 32.2, 126.6, 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. C$_{11}$H$_{13}$NO$_2$S 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 CH$_2$Cl$_2$ (10 cm^3) at 0 °C was added SO$_2$Cl$_2$ (0.80 cm^3, 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 CH$_2$Cl$_2$ (10 cm^3). The resulting solution was cooled at 0 °C and triethylamine (1.39 cm^3, 10 mmol) was added at 0 °C. The reaction mixture was stirred at 0 °C for 30 min, and then poured into water containing dilute HCl. The mixture was extracted with CH$_2$Cl$_2$ and the extract dried (MgSO$_4$) and evaporated to give crude 4. Purification by column chromatography (silica gel, hexane–ethyl acetate) gave pure 4 (1.5 g, 70%) as yellow crystals; mp 88–90 °C; ν_{max}(KBr)/cm^{-1} 3050, 2920, 1630, 1554, 1442, 1304, 1166, 958, 878 and 750; δ_H(CDCl$_3$) 2.16 (3 H, s), 6.22 (1 H, dd, J 14.7, 11.9), 7.13 (1 H, d, J 14), 7.42 (5 H, m) and 7.62 (1 H, d, J 11.9); δ_C(CDCl$_3$) 12.7, 120.3, 128.8, 129.6, 131.6, 131.9, 132.3, 143.6 and 143.8; m/z 221 (M$^+$, 32), 175 (16), 160 (13), 125 (14), 109 (41), 97 (22) and 82 (100) (Found: C, 59.64; H, 4.92; N, 6.43. C$_{11}$H$_{11}$NO$_2$S requires C, 59.78; H, 4.98; N, 6.33%).

(1E,3E)-4-Nitro-1-(pyrrolidin-1-yl)penta-1,3-diene 5a

A solution of 4 (1.1 g, 5 mmol) and pyrrolidine (10 mmol) in MeOH (5 cm^3) was stirred at room temperature for 8 h, and then poured into water. The mixture was extracted with CH$_2$Cl$_2$, and the extract dried (MgSO$_4$) and evaporated. The residue was subjected to column chromatography (silica gel, hexane–ethyl acetate) to give 5a (0.78 g, 80%) as orange crystals; mp 122–123 °C; ν_{max}(KBr)/cm^{-1} 2920, 2870, 1620, 1596, 1386, 1304, 1256, 1184, 972 and 872; δ_H(CDCl$_3$) 2.01 (4 H, m), 2.15 (3 H, s), 3.41 (4 H, m), 4.99 (1 H, t, J 12.2), 7.15 (1 H, d, J 12.2) and 7.92 (1 H, d, J 12.2); δ_C(CDCl$_3$) 12.5, 25.1, 47.0, 52.2, 94.7, 132.7, 140.8 and 150.3; m/z 183 (M$^+$ + 1, 9), 182 (M$^+$, 92), 165 (61), 134 (28), 112 (100), 70 (47) and 55 (65) (Found: C, 59.13; H, 7.55; N, 15.34. C$_9$H$_{14}$N$_2$O$_2$ requires C, 59.32; H, 7.74; N, 15.37%).

(1E,3E)-1-Diethylamino-4-nitropenta-1,3-diene 5b

This compound was prepared as an orange oil in 75% yield by the reaction of 4 with diethylamine in the same way as described in the preparation of 5a; δ_H(CDCl$_3$) 1.24 (6 H, t, J 7.2), 2.15 (3 H, s), 3.32 (4 H, q, J 7.2), 5.09 (1 H, t, J 12.4), 6.93 (1 H, d, J 12.4) and 7.93 (1 H, d, J 12.4); δ_C(CDCl$_3$) 12.4, 12.6, 42.5, 50.1, 93.2, 132.3, 141.2 and 152.7; m/z 185 (M$^+$ + 1, 120), 184 (M$^+$, 100), 167 (37), 114 (54) and 86 (45) (Found: C, 58.36; H, 8.57; N, 15.13. C$_9$H$_{16}$N$_2$O$_2$ requires C, 58.67; H, 8.76; N, 15.20%).

3-(Phenylthio)propenenitrile 7[13]

To a cooled solution of 3-(phenylthio)propanonitrile 6 (1.63 g, 10 mmol) in CH$_2$Cl$_2$ (10 cm^3) at 0 °C was added SO$_2$Cl$_2$ (0.80 cm^3, 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 CH$_2$Cl$_2$ and the solution cooled to 0 °C when triethylamine (1.39 cm^{-3}, 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 7 (1.37 g, 85%) as an E,Z mixture ($E:Z$ = 3:2) and a pale yellow oil; ν_{max}(neat)/cm^{-1} 3052, 2212, 1568, 1480, 1444, 932, 856, 832, 788, 746, 704 and 692; δ_H(CDCl$_3$) 4.98 (1 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); δ_C(CDCl$_3$, 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, 152.1 (E form) and 152.4 (Z form); m/z 163 (M$^+$ + 2, 2.5), 162 (M$^+$ + 1, 16), 161 (M$^+$, 100), 160 (M$^+$ – 1, 51), 134 (42), 117 (17) and 91 (15). These spectral data were identical with those of the literature.[13]

(E)-3-(Phenylthio)propenal 8 from 7

To a cooled solution of 7 (1.61 g, 10 mmol) in toluene (20 cm^3) was added DIBAL (10 mmol) at 0 °C. The resulting mixture was stirred at room temperature for 24 h and then poured into cold water containing dilute sulfuric acid. The mixture was extracted with diethyl ether and the extract dried (MgSO$_4$) and evaporated. Column chromatography (silica gel, hexane–ethyl acetate) of the residue gave 8 (1.35 g, 85%) as a pale yellow oil; ν_{max}(neat)/cm^{-1} 3056, 2816, 2724, 1676, 1564, 1478, 1442, 1124, 946, 856 and 834; δ_H(CDCl$_3$) 5.97 (1 H, dd, J 7.6, 15.0), 7.45 (5 H, m), 7.67 (1 H, d, J 15.0) and 9.43 (1 H, d, J 7.6); δ_C(CDCl$_3$, 67 MHz) 121.4, 127.12, 129.8, 130.9, 133.4, 156.8 and 189.8; m/z 166 (M$^+$ + 2, 5), 165 (M$^+$ + 1, 9), 164 (M$^+$, 72), 163 (M$^+$ – 1, 34), 135 (22), 110 (100) and 86 (54). These spectral data were identical with those in the literature.[14]

Preparation of 4 from 8

To a solution of 8 (1.64 g, 10 mmol) and nitroethane (0.83 g, 11 mmol) in acetonitrile (10 cm^3) was added DBU (0.14 cm^3, 1 mmol). The resulting solution was stirred at room temperature

for 24 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**.

(2E,4E)-3-Phenylthiopenta-2,4-dienal 9

To a mixture of **8** (1.64 g, 10 mmol) and $ZnBr_2$ (0.23 g, 1 mmol) in THF (20 cm³) was added a solution of N-2,2-bis(trimethylsilyl)ethylidene-tert-butylamine[15] (2.67 g, 10 mmol), and the resulting mixture was stirred for 5 h at room temperature. A solution of $ZnCl_2$ (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; ν_{max}(neat)/cm⁻¹ 3028, 2812, 1676, 1608, 1582, 1554, 1442, 1380, 1268, 1188, 1154, 1122, 980, 848 and 744; δ_H(CDCl₃) 5.93 (1 H, dd, J 15.0, 8.0), 6.30 (1 H, dd, J 11.3, 15.0), 7.06 (1 H, d, J 15.0), 7.3–7.5 (5 H, m) and 9.50 (1 H, d, J 8.0); δ_C(CDCl₃, 67 MHz) 125.0, 128.7, 128.8, 129.6, 130.3, 132.1, 142.0, 150.2 and 193.4; m/z 190 (M⁺, 14), 128 (8), 110 (5) and 81 (100) (Found: C, 69.28; H, 5.12; S, 16.32. $C_{11}H_{10}SO$ requires C, 69.44; H, 5.24; S, 16.68%).

Crystallographic analysis of 5a

Crystal data. $C_9H_{14}N_2O_2$, $M = 128.22$, orthorhombic, space group $Pna2_1$, $a = 12.34(1)$, $b = 7.587(6)$, $c = 10.403(7)$ Å, $V = 974(2)$ Å³, $Z = 4$, $D_c = 1.242$ g cm⁻³, crystal dimension $0.80 \times 0.40 \times 0.05$ mm, μ(Mo-Kα) = 0.83 cm⁻¹, $F(000)$ = 392. The X-ray diffraction data were collected by using a Rigaku AFC-5R automated four-circle diffractometer with Mo-Kα radiation monochromatized by graphite [λ(Mo-Kα) = 0.710 69 Å, 2θ–ω scans, $2\theta_{max}$ = 54.9°]. The structure was solved by direct methods using the MITHRIL program[25] and refined by the full-matrix least-squares method on F^2 with weight $w = 1/\sigma^2(F^2)$. An empirical absorption correction (Ψ-scan method) was used.[26] Anisotropic thermal parameters were used for the refinement of non-H atoms. The positions of the H atoms were calculated from positions of non-H atoms. Final refinement converged at $R = 0.047$ and $R_w = 0.082$ for 422 observed [$I > 2\sigma(I)$] reflections from 1321 data. Calculations were done on a VAX station 3200 computer with the TEXSAN program[27] which used the atomic scattering factors taken from 'International Tables for X-Ray Crystallography'[28] and took anomalous dispersion into account. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Notice to Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 207/15.

NLO measurements

NLO measurements were carried out by Dr S. Aramaki at the Mitsubishi Chemistry Corporation, Research Center, Midoriku, Yokohama, Japan. Measurements of the powder SHG efficiencies (relative to urea) were performed with the fundamental (1064 nm) of a Q-switched Nd:YAG laser by a modification of the Kurtz powder technique.[22] The electrooptic activity of the poled polymer was measured by the same setup as described in the literature.[24] The Pockels coefficients (r_{33}) were determined from poled poly(methyl methacrylate) films doped with 5 wt% **5a**. Polymer films were formed by spin-coating on ITO glass. Then on the top of the films, gold electrodes were deposited. The sample was poled at 110 °C in a 0.5 MV cm⁻¹ electric field for 10 min. The electric field induced birefringence was measured by overlapping a 20V$_{rms}$ AC

voltage and r_{33} was determined to be 1.2 pm/V at 1300 nm. The $\mu\beta$ value was calculated to be 1200×10^{-48} esu.[24]

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