

Fig. 2. (a) ORTEP (Johnson, 1965) drawing projected along the C(22)···C(34) and C(32)···C(28) direction. (b) View of the shaded central ring in (a).

C(34)] is deformed to a boat form as shown in Fig. 2(b). The flip angles of C(23) and C(29) against the least-squares plane involving C(22), C(32), C(28) and C(34) are 14.5 (6) and 15.2 (6)°, respectively, and they are larger than that in the case of [2.2]paracyclophane (12.6°), where two benzene rings are connected by two ethano bridges at *para* positions (Hope, Bernstein & Trueblood, 1972). This deformation also affects the reactivity of TBPA towards electrophiles, *e.g.* singlet O₂. Judging from the HOMO coefficients calculated by the Hückel MO method, positions C(23) and C(29) are the most reactive sites for electrophiles. The boat-shaped

deformation of the central benzene ring may introduce a facial selectivity towards electrophiles. Thus the reaction of singlet O₂ with TBPA at these positions should occur from the inner side to give the *endo*-peroxide stereoselectively.

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Studies on Nonlinear Optical Materials: Structure of Diphenylmethyl (Z)-1-(1-Methylthio-2-nitrovinyl)tetrahydropyrrole-2-carboxylate

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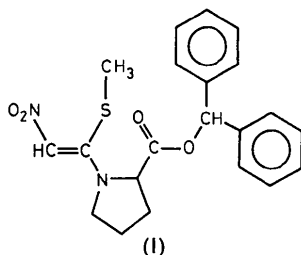
Abstract. C₂₁H₂₂N₂O₄S, *M_r* = 398.5, orthorhombic, *P*2₁2₁2₁, *a* = 9.799 (1), *b* = 11.853 (1), *c* = 17.316 (2) Å, *V* = 2011.4 Å³, *Z* = 4, *D_m* = 1.320, *D_x* = 1.314 Mg m⁻³, Cu *Kα*, λ = 1.5418 Å, μ = 1.63 mm⁻¹, *F*(000) = 840.0, *T* = 293 K, *R* = 0.055 for 1735 significant reflections. In the 1-methylthio-2-nitrovinyl moiety the C=C bond, 1.368 (7) Å, is significantly longer than in ethylene, 1.336 (2) Å. The second harmonic generation (SHG) efficiency of this

compound is only 0.25 of the urea standard. The correlation between the molecular packing and SHG is discussed.

Introduction. Nonlinear optical organic materials are gaining widespread recognition and are under intensive investigation owing to their potential applications in the field of optical signal processing (Chemla & Zyss, 1987). Organic crystals exhibiting second harmonic generation (SHG) are currently being developed (Nicoud, 1988). On the molecular level, this is made possible by the molecules bearing donor

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and acceptor groups at each end of a conjugated system resulting in an effective intramolecular charge transfer through a highly polarizable π -electron system. 'Push-pull' ethylenes with donor and acceptor groups on the vicinal C atoms of ethylene have been studied for SHG (Kanagapushpam, Venkatesan & Cameron, 1988). In particular, the crystal structure must be noncentrosymmetric together with a suitable packing arrangement (Oudar, 1977). A typical strategy adopted to achieve a noncentrosymmetric system is to add a chiral group. The title compound (I) was synthesized bearing in mind the above aspects in order to achieve appreciable SHG efficiency. The title compound is a 'push-pull' ethylene with nitro and thiomethyl groups as acceptor and donor groups respectively. The proline moiety was introduced to cause chirality in the system.



Experimental. A plate-like single crystal of the title compound of approximate dimensions $0.20 \times 0.7 \times 0.30$ mm was used. D_m by flotation. Preliminary oscillation and Weissenberg photographs indicated that the crystals were orthorhombic, space group $P2_12_12_1$; lattice parameters refined by a least-squares fit to settings for 25 accurately centred unique reflections in the range $8 < \theta < 28^\circ$. Nonius CAD-4 diffractometer, graphite-monochromated $\text{Cu } K\alpha$ radiation, 2404 independent reflections to a 2θ value of 140° , scan speed 1° min^{-1} , $\omega/2\theta$ scan mode. Three standard reflections ($\bar{1}3\bar{2}$, 104, $\bar{1}\bar{3}0$) showed only statistical fluctuations within $\pm 2\%$; hkl range h : 0 to 11, k : 0 to 14, l : 0 to 21. Data corrected for Lorentz and polarization factors, but not for absorption. 1735 significant reflections with $|F_o| \geq 3\sigma(F_o)$. Structure solved by direct methods (*MULTAN80*; Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). Full-matrix least-squares refinement (*SHELX76*; Sheldrick, 1976) of scale-factor, positional and anisotropic thermal parameters for non-H atoms and positional and isotropic thermal parameters for H atoms (all located from the difference map) converged to $R = 0.055$, $wR = 0.066$, $S = 0.73$ for 342 parameters. The function minimized was $\sum w(|F_o| - |F_c|)^2$ where $w = 0.1992/[\sigma^2(F) + 0.0103|F_o|]$. In the final cycles of refinement, Δ/σ for non-H atoms was 0.083; Δ/σ for H atoms was 0.100; $\Delta\rho_{\text{max}} = 0.24$, $\Delta\rho_{\text{min}} = -0.29 \text{ e } \text{\AA}^{-3}$. Atomic scat-

tering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV).*

Discussion. A perspective view and numbering scheme of the molecule is illustrated in Fig. 1. The atomic positional coordinates and thermal parameters for non-H atoms are listed in Table 1. Intramolecular distances and bond angles are presented in Table 2.

The substituents at the vicinal C atoms of the ethylene bond $\text{C}(1)=\text{C}(2)$ have lengthened the $\text{C}=\text{C}$ bond to $1.368(7) \text{ \AA}$ which is significantly longer than found in ethylene [$1.336(2) \text{ \AA}$; Bartell, Roth, Hollowell, Kuchitsu & Young, 1965]. The $\text{C}=\text{C}$ bond length indicates only a moderate ground-state polarization. It is interesting to note that the —SMe group at the donor end appears to have taken little part in electron donation as seen from the $\text{C}(1)-\text{S}(1)$ bond length, $1.753(5) \text{ \AA}$, which is comparable to a $\text{C}-\text{S}$ single bond, 1.751 \AA (Allen, Kennard, Watson, Brammer, Orpen & Taylor, 1987). Instead, the proline moiety, which was included to cause chirality, has actually taken part in electron conjugation through the N-atom lone pair. Such a conjugation can be clearly inferred from the $\text{N}(1)-\text{C}(1)$ distance of $1.334(6) \text{ \AA}$ which is very short compared with the 1.416 \AA reported for a $[\text{C}(sp^2)]\text{N}-\text{C}(sp^2)$ bond (Allen, Kennard, Watson, Brammer, Orpen & Taylor, 1987). On the acceptor side, the $\text{N}(2)-\text{C}(2)$ bond length of 1.383 \AA is also very much shorter than the standard value for a $\text{C}(sp^2)-\text{N}$ bond of $1.452(2) \text{ \AA}$ (Ammon, Mazzochi, Regan & Colicelli, 1979). The bond lengths $\text{N}(2)-\text{O}(3)$ and $\text{N}(2)-\text{O}(4)$ are $1.234(7)$ and $1.287(7) \text{ \AA}$ respectively. From the observed bond length changes, it may be concluded that there is significant electron delocalization about the conjugated system. The proline system has taken part as a donor group in preference to the thiomethyl

* Lists of structure factors, anisotropic thermal parameters, bond lengths and angles involving H atoms, and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54734 (13 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: LI0088]

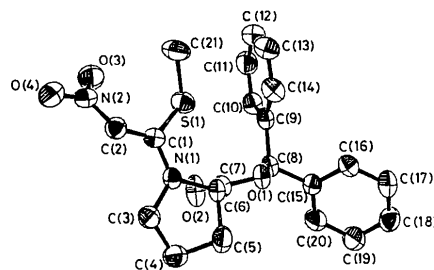


Fig. 1. Perspective view of the title molecule with the atom numbering.

Table 1. Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic temperature factors ($\text{\AA}^2 \times 10^4$) for non-H atoms with *e.s.d.*'s in parentheses

$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	U_{eq}
C(1)	5223 (5)	2749 (4)	7012 (2)	389 (12)
C(2)	3969 (5)	3142 (4)	6794 (3)	482 (14)
C(3)	4977 (6)	3675 (5)	8285 (3)	521 (16)
C(4)	5809 (6)	3561 (6)	8985 (4)	611 (20)
C(5)	7286 (6)	3564 (5)	8688 (4)	571 (19)
C(6)	7208 (4)	2945 (4)	7919 (3)	413 (13)
C(7)	7543 (5)	1706 (4)	8022 (3)	412 (13)
C(8)	9342 (5)	350 (4)	7843 (3)	396 (12)
C(9)	9239 (5)	-53 (4)	7014 (3)	429 (13)
C(10)	8980 (6)	-1183 (4)	6870 (3)	494 (15)
C(11)	8832 (7)	-1587 (6)	6125 (4)	664 (20)
C(12)	8953 (7)	-855 (6)	5511 (4)	666 (21)
C(13)	9220 (8)	267 (6)	5643 (4)	663 (20)
C(14)	9379 (6)	659 (5)	6397 (3)	552 (17)
C(15)	10745 (5)	328 (4)	8187 (3)	404 (12)
C(16)	11869 (5)	746 (4)	7779 (3)	474 (15)
C(17)	13164 (5)	715 (5)	8121 (4)	554 (17)
C(18)	13337 (6)	298 (6)	8849 (4)	599 (18)
C(19)	12234 (7)	-104 (7)	9265 (4)	694 (22)
C(20)	10949 (6)	-104 (5)	8918 (3)	582 (18)
C(21)	5971 (9)	2154 (8)	5499 (3)	736 (26)
S(1)	6245 (1)	1797 (1)	6497 (1)	529 (4)
O(1)	8864 (3)	1527 (2)	7875 (2)	418 (9)
O(2)	6758 (4)	980 (3)	8217 (3)	630 (14)
O(3)	3257 (5)	1650 (4)	6059 (3)	682 (14)
O(4)	1914 (5)	3068 (5)	6208 (3)	796 (17)
N(1)	5761 (4)	3085 (3)	7682 (2)	380 (10)
N(2)	3038 (5)	2601 (4)	6321 (2)	548 (14)

Table 2. Bond distances (\AA) and angles ($^\circ$) involving non-H atoms with *e.s.d.*'s in parentheses

C(1)—C(2)	1.368 (7)	C(9)—C(10)	1.386 (7)
C(1)—S(1)	1.753 (5)	C(9)—C(14)	1.369 (7)
C(1)—N(1)	1.334 (5)	C(10)—C(11)	1.383 (9)
C(2)—N(2)	1.383 (7)	C(11)—C(12)	1.378 (10)
C(3)—C(4)	1.467 (9)	C(12)—C(13)	1.374 (10)
C(3)—N(1)	1.473 (7)	C(13)—C(14)	1.394 (9)
C(4)—C(5)	1.536 (8)	C(15)—C(16)	1.399 (7)
C(5)—C(6)	1.522 (8)	C(15)—C(20)	1.382 (7)
C(6)—C(7)	1.515 (7)	C(16)—C(17)	1.401 (7)
C(6)—N(1)	1.486 (6)	C(17)—C(18)	1.364 (10)
C(7)—O(1)	1.336 (6)	C(18)—C(19)	1.384 (9)
C(7)—O(2)	1.204 (6)	C(19)—C(20)	1.395 (9)
C(8)—C(9)	1.516 (7)	C(21)—S(1)	1.800 (6)
C(8)—C(15)	1.498 (7)	O(3)—N(2)	1.235 (7)
C(8)—O(1)	1.473 (5)	O(4)—N(2)	1.248 (7)
C(2)—C(1)—S(1)	126.3 (4)	C(10)—C(11)—C(12)	119.5 (6)
C(2)—C(1)—N(1)	119.5 (4)	C(11)—C(12)—C(13)	119.8 (7)
S(1)—C(1)—N(1)	114.1 (3)	C(12)—C(13)—C(14)	120.0 (6)
C(1)—C(2)—N(2)	126.7 (5)	C(9)—C(14)—C(13)	120.9 (5)
C(4)—C(3)—N(1)	104.6 (5)	C(8)—C(15)—C(16)	121.1 (4)
C(3)—C(4)—C(5)	104.3 (5)	C(8)—C(15)—C(20)	120.3 (5)
C(4)—C(5)—C(6)	104.1 (5)	C(16)—C(15)—C(20)	118.6 (5)
C(5)—C(6)—C(7)	110.7 (4)	C(15)—C(16)—C(17)	119.4 (5)
C(5)—C(6)—N(1)	103.6 (4)	C(16)—C(17)—C(18)	120.8 (6)
C(7)—C(6)—N(1)	110.4 (4)	C(17)—C(18)—C(19)	120.6 (6)
C(6)—C(7)—O(1)	110.0 (4)	C(18)—C(19)—C(20)	118.7 (6)
C(6)—C(7)—O(2)	126.0 (5)	C(15)—C(20)—C(19)	121.8 (5)
O(1)—C(7)—O(2)	124.0 (5)	C(1)—S(1)—C(21)	104.6 (3)
C(9)—C(8)—C(15)	115.5 (4)	C(7)—O(1)—C(8)	117.7 (4)
C(9)—C(8)—O(1)	108.3 (4)	C(1)—N(1)—C(3)	123.5 (4)
C(15)—C(8)—O(1)	107.0 (4)	C(1)—N(1)—C(6)	125.7 (4)
C(8)—C(9)—C(10)	119.2 (4)	C(3)—N(1)—C(6)	110.8 (4)
C(8)—C(9)—C(14)	122.6 (5)	C(2)—N(2)—O(3)	121.8 (5)
C(10)—C(9)—C(14)	118.3 (5)	C(2)—N(2)—O(4)	118.0 (5)
C(9)—C(10)—C(11)	121.4 (5)	O(3)—N(2)—O(4)	120.0 (5)

group. This can be attributed to the more nucleophilic nature of the N atom in the proline in comparison to the —SMe group.

The remaining bond lengths and bond angles have expected values within the limits of experimental

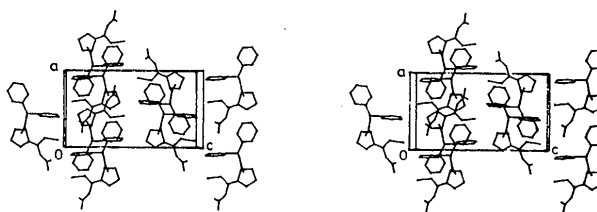


Fig. 2. Stereoview of the packing of molecules in the unit cell viewed down the *b* axis.

error. The stereo packing of the molecule is displayed in Fig. 2. There are no hydrogen-bonding interactions involved in the crystal structure.

Although the compound has crystallized in a non-centrosymmetric space group and also possesses a highly delocalized conjugated system bearing a chiral moiety, the SHG efficiency is observed to be one fourth of that of urea (Eaton & Wang, 1990). The SHG efficiency on a powder sample was measured using an Nd-YAG laser ($\lambda = 1064$ nm) by Eaton & Wang. Since SHG depends on the dipole moment change between the excited state and the ground state of the molecule (Zyss & Berthier, 1982), low SHG efficiency could be attributed to a small difference in dipole moments ($\Delta\mu$). Further, the polar axis makes angles of 26.1, 70.1 and 74.0° with the three crystallographic twofold axes along *a*, *b* and *c* axes of the crystal. These values differ significantly from the theoretically calculated angle of 54.7° for nonlinear interactions in crystals belonging to the point group 222 (Zyss & Oudar, 1982), which could be the reason for the low observed SHG. Further, the observed value of about 75° between the charge-transfer axis and the crystallographic *b* and *c* axes, not very different from 90°, would not favour large SHG activity because in this packing mode the molecular hyperpolarizabilities tend to cancel.

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Structure of 1-Acetylthymine

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Abstract. $C_7H_8N_2O_3$, $M_r = 168.50$, monoclinic, $P2_1/n$, $a = 5.074$ (3), $b = 8.611$ (3), $c = 17.476$ (4) Å, $\beta = 94.57$ (4)°, $V = 761.2$ (5) Å³, $Z = 4$, $D_x = 1.467$ g cm⁻³, $\lambda(\text{Cu } K\alpha) = 1.54178$ Å, $\mu = 9.5$ cm⁻¹, $F(000) = 352$, $T = 294$ K, $R = 0.038$ for 833 observed reflections. With respect to other thymine derivatives substituted at N(1), N(1)—C(2) and N(1)—C(6) bond distances in the title compound are the longest reported to date, while the C(5)—C(6) bond distance is the shortest observed so far. An intramolecular hydrogen bond between H(6) and O(1) is revealed from the structure analysis. Intermolecular hydrogen bonds are inferred from the structure with H(6)(x, y, z) of one molecule interacting with O(1)($1-x, 1-y, 1-z$) of the other. This system appears to be the first reported example in which an H atom bonded to C participates in a bifurcated hydrogen bond. An additional intermolecular hydrogen bond is observed between O(4)(x, y, z) and H(3)($-x-1, -y, 1-z$). The title compound packs as a series of parallel planar π -stacked ribbons of molecules, with adjacent ribbons separated by approximately 3.2 Å.

Introduction. Within our program of study on modified nucleosides, we have synthesized the title compound as a precursor to the synthesis of a strategically altered nucleoside. The present structural study was undertaken to examine the effects of the electron-withdrawing acetyl substituent at N(1) on the structure of the pyrimidine ring, and as a basis for comparison with our future compounds incorporating this molecule as a fragment.

Experimental. The title compound was synthesized using the method of Spector & Keller (1958). Data

were collected using a colorless crystal of dimensions $0.30 \times 0.45 \times 0.40$ mm on a Rigaku AFC6S diffractometer equipped with an evacuated beam collimator and detector tunnel. Graphite-monochromated Cu $K\alpha$ radiation was employed with the intensities measured 400 mm from the crystal. Measured data to $2\theta = 110^\circ$ included reflections h 0–5, k 0–9, l –18–18. Scans were of the ω 2θ type, where the ω -scan speed was $32^\circ \text{ min}^{-1}$. The scan width in ω was $(1.68 + 0.30 \tan\theta)^\circ$ and weak reflections were rescanned up to eight times and the counts accumulated. Of the 1185 reflections measured, 1047 were considered unique; for averaged data, $R_{\text{int}} = 0.022$. 839 reflections were classified as observed having $F^2 \geq 3\sigma(F^2)$. Three standard reflections monitored throughout data collection showed less than 1% change in their intensities over the period of the experiment indicating no decay correction was required. Lorentz-polarization corrections were applied and an empirical absorption correction was included in the data-processing step (transmission factors, 0.95–1.00, based on ψ scans of three reflections). Six reflections (120, 12 $\bar{1}$, 200, 020, 101 and 002) had intensities that far exceeded the linear range of the detector and were flagged so as not to be used in structure solution and refinement.

The structure was solved by direct methods and refined using programs in the *TEXSAN* (Molecular Structure Corporation, 1985) software package. The structure was refined on F , initially with non-H atoms only. H-atom positions were subsequently determined from difference Fourier maps and included for the remaining cycles of refinement. Using all of the observed data, convergence was reached at $R = 0.038$ and $wR = 0.055$. For all data, $R = 0.044$ and $wR = 0.056$. The function minimized throughout refinement was $\sum w\Delta^2$ ($\Delta = |F_o| - |F_c|$),

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