Table 1. *Atomic coordinates* (×10^4 *for* C, ×10^3 *for* H) *and equivalent isotropic thermal parameters* (×10^3)

$$U_{eq} = \tfrac{1}{3}\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq} or U_{iso} (Å^2)
C(1)	7499 (7)	3842 (3)	1696 (9)	73 (2)
C(2)	8194 (7)	4312 (3)	143 (12)	84 (3)
C(3)	9058 (7)	4084 (3)	−1765 (11)	82 (3)
C(4)	9255 (6)	3368 (3)	−2234 (11)	69 (2)
C(5)	8547 (5)	2894 (2)	−699 (9)	54 (2)
C(6)	7681 (5)	3121 (3)	1243 (9)	56 (2)
C(7)	7064 (8)	2500	2609 (14)	64 (3)
H(1)	691 (7)	397 (3)	335 (11)	116 (24)†
H(2)	811 (7)	483 (3)	59 (12)	124 (27)†
H(3)	949 (7)	444 (3)	−303 (13)	95 (24)†
H(4)	969 (6)	316 (3)	−391 (10)	99 (21)†
H(71)	748 (10)	250	452 (15)	104 (31)†
H(72)	580 (10)	250	282 (19)	101 (32)†

† U_{iso}.

Discussion. The atomic coordinates are listed in Table 1,* interatomic distances and bond angles are presented in Fig. 1 (e.s.d.'s: C—C 0·006–0·009 Å, C—H 0·06–0·09 Å; C—C—C 0·4–0·5°, C—C—H 3–4°). The molecule is planar [maximum deviation from the mean plane is for C(5), 0·013 (6) Å] and possesses C_{2v} symmetry. The intermolecular contacts correspond to normal van der Waals interactions. The projection of the structure onto (001) is shown in Fig. 2. The most important difference between our results and those of Burns & Iball (1954) and Brown & Bortner (1954) involves the value of the angle C(6)—C(7)—C(6′), 102·7° against 105·6 and 106° respectively.

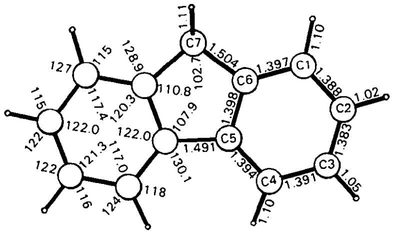

Fig. 1. Interatomic distances (Å) and bond angles (°).

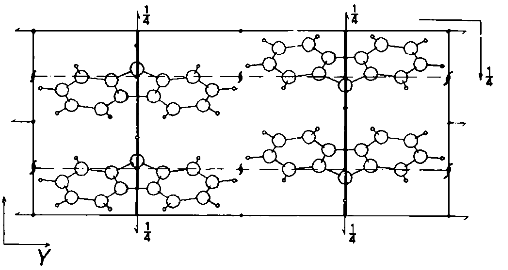

Fig. 2. Projection onto the (001) plane.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39291 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Acta Cryst. (1984). C**40**, 1211–1214

A Polarized, Twisted, Ethylene: Structure of 3,3-Bis(methylthio)-2-nitro-2-propene-1-nitrile, $C_5H_6N_2O_2S_2$

By Nirupa U. Kamath and K. Venkatesan

Department of Organic Chemistry, Indian Institute of Science, Bangalore 560 012, *India*

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Abstract. $M_r = 190$, monoclinic, $P2_1/n$, $a = 4{\cdot}123$ (1), $b = 13{\cdot}096$ (3), $c = 15{\cdot}126$ (3) Å, $\beta = 93{\cdot}8$ (2)°, $V = 814{\cdot}9$ Å^3, $Z = 4$, $D_m = 1{\cdot}540$ (3), $D_x = 1{\cdot}548$ (3) g cm^{-3}, $\lambda(\text{Cu } K\alpha) = 1{\cdot}5418$ Å, $\mu = 53{\cdot}64$ cm^{-1}, $F(000) = 392{\cdot}0$, $T = 293$ K. Final $R = 0{\cdot}054$ for 1119 significant reflections. The C=C bond length is 1·376 (4) Å which indicates only a moderate polarization, with a DNMR rotational barrier of 80·2 kJ mol^{-1}. The molecule is twisted about the C=C double bond by 12·8°. A reasonable correlation between rotational barrier (DNMR studies) and C=C bond lengths (X-ray measurements) has been obtained.

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Introduction. The purpose of the present investigation on the polarized ethylenes (Kamath & Venkatesan, 1984; Adhikesavalu & Venkatesan, 1981, 1982, 1983*a,b*) is twofold: first, to study the molecular geometry of push–pull ethylenes with different donor and acceptor substituents; secondly, to look for any possible correlation that may be present between the C=C bond lengths and the rotational barrier about the ethylene bond for this class of molecules. The results are presented in this paper.

The compound was kindly provided by Professor Jan Sandström, University of Lund, Sweden.

Experimental. Single crystals of title compound obtained from toluene by slow evaporation, approximate dimensions $0{\cdot}1 \times 0{\cdot}2 \times 0{\cdot}7$ mm, D_m measured by flotation in KI solution. Preliminary Weissenberg photographs indicated that the crystals are monoclinic. Lattice parameters refined using a least-squares fit to the settings for 17 accurately centred reflections. Nonius CAD-4 diffractometer, graphite monochromator, Cu $K\alpha$ radiation, $\omega/2\theta$ scan mode, $\theta \leq 60°$, scan speed $1°\ \text{min}^{-1}$. During data collection two standard reflections ($12\bar{2}$ and 222) showed only statistical variation within $\pm 2\%$. 1527 reflections collected, range of *hkl*: *h* ±4, *k* 0–14, *l* 0–16, only 1119 significant, $F_o \geq 3\sigma(|F_o|)$. Data not corrected for absorption. Structure solved by direct methods (*MULTAN*80; Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). Full-matrix refinement (*SHELX*76; Sheldrick, 1976) of a scale factor, positional and anisotropic thermal parameters (isotropic thermal parameters for H atoms, located from a difference map) converged to $R = 0{\cdot}054$, $R_w = 0{\cdot}066$, $S = 4{\cdot}19$; $\sum w(|F_o| - |F_c|)^2$ minimized where $w = 17{\cdot}822/\sigma^2(F)$. Δ/σ for non-H atoms $\sim 0{\cdot}003$. Final difference map featureless. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). Illustrations drawn with *ORTEP*II (Johnson, 1976).

Discussion. A perspective view with atom numbering is shown in Fig. 1. Bond lengths and angles for non-H atoms are shown in Fig. 2. Positional coordinates and thermal parameters of non-H atoms are shown in Table 1.* Some important torsion angles are provided in Table 2.

Table 1. *Final fractional coordinates* ($\times 10^4$) *and equivalent isotropic temperature factors* ($\times 10^2$) *of non-*H *atoms*

E.s.d.'s are given in parentheses.

The temperature factor is of the form: $U_{\rm eq} = \frac{1}{3}\sum_i\sum_j a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j$.

	x	*y*	*z*	$U_{\rm eq}$(Å^2)
S(1)	2584·8 (20)	262·0 (5)	7683·1 (5)	5·37 (3)
S(2)	5444·4 (19)	1965·4 (6)	6726·8 (5)	5·33 (3)
C(3)	4108 (6)	1499 (2)	7703 (2)	3·81 (8)
C(2)	4037 (6)	2085 (2)	8457 (2)	3·95 (8)
C(1)	2276 (7)	1808 (2)	9193 (2)	4·57 (10)
N(1)	781 (8)	1592 (3)	9772 (2)	6·73 (11)
N(2)	5461 (7)	3079 (2)	8538 (2)	5·31 (9)
O(1)	5023 (7)	3578 (2)	9202 (2)	7·53 (10)
O(2)	7051 (7)	3389 (2)	7937 (2)	7·41 (9)
C(4)	4102 (10)	−315 (3)	8702 (3)	5·85 (12)
C(5)	4932 (11)	918 (4)	5963 (2)	6·81 (14)

Table 2. *Some important torsion angles* (°) *with e.s.d.'s in parentheses*

C(4)–S(1)–C(3)–S(2)	139·3 (2)	S(1)–C(3)–C(2)–N(2)	175·3 (2)
C(4)–S(1)–C(3)–C(2)	−44·6 (3)	S(2)–C(3)–C(2)–N(2)	−8·8 (4)
C(5)–S(2)–C(3)–S(1)	−2·4 (2)	C(3)–C(2)–N(2)–O(1)	173·5 (3)
C(5)–S(2)–C(3)–C(2)	−178·5 (3)	C(1)–C(2)–N(2)–O(1)	−0·6 (4)
S(1)–C(3)–C(2)–C(1)	−11·2 (4)	C(3)–C(2)–N(2)–O(2)	−6·3 (4)
S(2)–C(3)–C(2)–C(1)	164·7 (2)	C(1)–C(2)–N(2)–O(2)	179·7 (3)

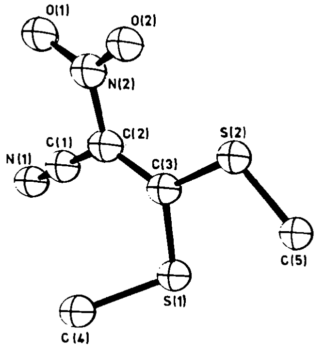

Fig. 1. A perspective view of the molecule viewed down **a** with the numbering scheme.

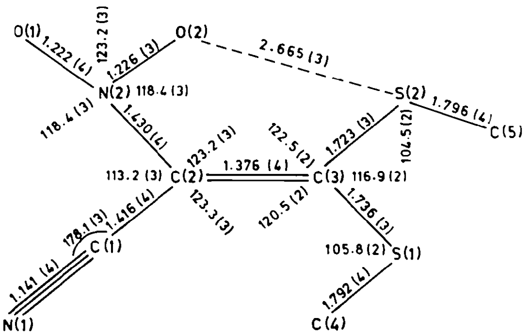

Fig. 2. Bond lengths (Å) and angles (°) of non-H atoms (e.s.d.'s are given in parentheses).

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* Lists of structure factors, anisotropic thermal parameters, H-atom positions and their isotropic temperature factors, and bond lengths and angles involving H have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39304 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The C=C double bond [1·376 (4) Å] is longer than the value for this bond in ethylene [1·336 (2) Å; Bartell, Roth, Hollowell, Kuchitsu & Young, 1965]. It is also observed that the bonds C(2)–N(2) [1·430 (4) Å] and C(2)–C(1) [1·416 (4) Å] are slightly shorter than the standard values for C(sp^2)–N [1·452 (2) Å; Ammon, Mazzocchi, Regan & Colicelli, 1979] and C(sp^2)–C(sp) bonds [1·437 (2) Å; Little, Pautler & Coppens, 1971]. In addition, we see that the S(2)–C(3) [1·723 (3) Å] and S(1)–C(3) [1·736 (3) Å] bond lengths are also slightly shorter than the value of 1·764 (1) Å found in tetrakis(methylthio)ethylene measured at 238 K (Collins & Davis, 1978).

These bond-length changes indicate that there is a small but significant push–pull effect in this molecule. The shortening of the S(2)–C(3) bond to a greater extent than the S(1)–C(3) bond may be attributed to the attractive intramolecular interaction between the S and O atoms with an S(2)···O(2) distance of 2·665 (3) Å. This distance is considerably shorter than the sum of the van der Waals radii of 3·32 Å [r(O) = 1·52; r(S) = 1·80 Å; Bondi, 1964]. The C(5)–S(2)···O(2) angle does not deviate far from linearity [171·4 (3)°]. In fact, a shorter S···O distance would give rise to an approximately linear O···S–C angle which would ensure maximum utilization of empty p and d orbitals of S in bonding (which is a favourable situation for an interaction).

Very short non-bonded interactions between S and O have been discussed in the literature (*e.g.* Kálmán & Párkányi, 1980; Barnes, Paton & Nicholls, 1982; Garratt, Przybylska & Cygler, 1983; Varughese, Przybylska, Sestanj, Bellini & Humber, 1983).

Cohen-Addad, Savariault & Lehmann (1981) have examined the X–N map of the structure of 2-(2-chlorobenzoylimino)-1,3-thiazolidine in which a short S···O contact [2·684 (2) Å] exists and these authors have found no deformation charge density between S and O.

From the study of the directional preferences of non-bonded atomic contacts with divalent S (Rosenfield, Parthasarathy & Dunitz, 1977), it may be concluded that in the present structure O(2) acts as a nucleophile, as it approaches the S atom along the LUMO of S, the O atom being out of the plane defined by C(3), S(2) and C(5) by 27°.

The twist angle, defined as the angle between the planes through the atoms S(1), C(3), S(2) and C(1), C(2), N(2) is 12·8 (3)°. The pyramidality at C(3) and C(2) is appreciable. The values of the out-of-plane bending at atoms C(3) (χ_{C3}) and C(2) (χ_{C2}), calculated using the method described by Winkler & Dunitz (1971), are 4·1 (3) and 6·5 (3)° respectively.

The C=C torsional barrier in 1,2-dideuterioethylene is 261·2 kJ mol^{-1} (Douglas, Rabinovitch & Looney, 1955). Push–pull substituents on ethylene considerably lower the free energy of activation ($\Delta G^{\neq}$) to rotation around the double bond to below 105 kJ mol^{-1}. In the case of methyl 2-[bis(dimethylamino)methylene]-3-oxobutyrate trihydrate (Kamath & Venkatesan, 1984) [l(C=C) = 1·461 (4) Å], the $\Delta G^{\neq}$ value is less than 33·6 kJ mol^{-1} (Sandström, 1983).

X-ray crystallographic measurements of the C=C bond length for a large number of push–pull ethylenes are now available (Adhikesavalu, Kamath & Venkatesan, 1983) and the rotational-barrier values ($\Delta G^{\neq}$) have been reported for some of them (Sandström, 1983). It is interesting to note (Fig. 3) that, although the barriers have been measured with different solvents such as o-dichlorobenzene and dichlorofluoromethane, there is a reasonable correlation between $\Delta G^{\neq}$ and C=C length, the rotational barrier decreasing as the bond length increases. The observed correlation indicates that the electronic factor arising from the overlap of the π-electrons of the C=C bond is a dominant one.

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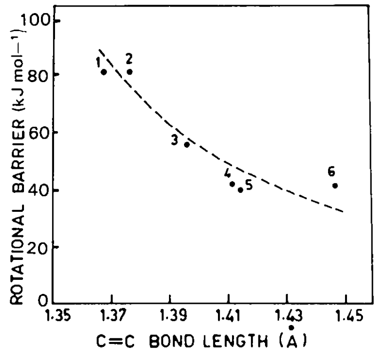

Fig. 3. Correlation plot of rotational barrier *vs* C=C double-bond length. References: $\Delta G^{\neq}$ values of compounds (1)–(6) [79·8 (bromine-free analogue), 80·2, 55·4, 41·2, 39·9, 39·9 kJ mol^{-1} (for the bromine-free 1,3-dibenzyl analogue)] in Sandström (1983) and references therein. X-ray data: (1) 2-p-bromobenzoyl-3,3-bis(methylthio)-2-propene-1-nitrile, 1·369 (7) (Abrahamsson, Rehnberg, Liljefors & Sandström, 1974); (2) 3,3-bis(methylthio)-2-nitro-2-propene-1-nitrile, 1·376 (4) (present work); (3) [dimethylamino(methylthio)methylene]malononitrile, 1·397 (8) (Adhikesavalu & Venkatesan, 1983*a*); (4) 3-[bis(dimethylamino)methylene]-3-phenyl-2-propanone, 1·409 (4) (Kamath & Venkatesan, 1984); (5) 3-(1,3-dimethyl-2-imidazolidinylidene)-2-phenyl-2-propene-1-nitrile, 1·415 (8) (Kamath & Venkatesan, 1983, unpublished results); (6) 2-p-bromobenzoyl-1,3-dimethyl-4-imidazolidinylideneacetonitrile, 1·448 (4) Å (Abrahamsson *et al.*, 1974).

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Acta Cryst. (1984). C**40**, 1214–1217

Structure of 3,5,3′-Triiodothyronamine* Bis(salicylato)borate (1:1) Salt, T_3AM.BSA, $C_{14}H_{13}I_3NO_2^+.C_{14}H_8BO_6^-$

By Vivian Cody

Medical Foundation of Buffalo, Inc., 73 *High St, Buffalo, New York* 14203, *USA*

(*Received* 24 *November* 1983; *accepted* 24 *February* 1984)

Abstract. $M_r = 891{\cdot}0$, monoclinic, $P2_1/c$, $a = 14{\cdot}886$ (4), $b = 14{\cdot}514$ (4), $c = 15{\cdot}870$ (4) Å, $\beta = 108{\cdot}92$ (2)°, $V = 3243{\cdot}4$ (3) Å^3, $Z = 4$, $D_x = 1{\cdot}82$ g cm^{-3}, λ(Mo $K\alpha_1$) = 0·71069 Å, $\mu = 29{\cdot}7$ cm^{-1}, $F(000) = 1696$, $T = 298$ K. Final $R = 0{\cdot}064$ for 8316 unique significant reflections. This is the first structural report of both molecules. T_3AM is *cisoid*, the 3′-iodine proximal, the protonated side chain extended, and the diphenyl ether conformation twist-skewed, an observation previously found only for the parent thyroid hormone containing an amino-acid side chain. BSA has tetrahedral B coordination with the planes of each salicylate moiety bisecting one another.

Introduction. It has been shown that the activity of the thyroid hormones (tetra-, triiodothyronines: T_4, T_3) and their metabolites depends primarily on specific structural requirements for optimal binding to their serum and nuclear-binding proteins. Thyroid-hormone conformational preferences have been delineated from analogue structural studies (Cody, 1980, 1981) in order to define the contribution of each hormone substituent to its overall activity. Decarboxylation of the thyronine amino acid to a thyronamine is one analogue type that has had little study.

Recent studies have shown that 3,5,3′-triiodothyronamine (T_3AM), the decarboxylation product of the active hormone T_3, has no thyromimetic activity at the nuclear receptor level, but does show adrenergic and dopaminergic effects (Meyer & Hesch, 1982, 1983). These data show that T_3AM specifically inhibits β-adrenergic receptor binding in turkey erythrocytes and α-adrenergic receptor binding in human platelets. These effects are not observed for the thyroid hormones themselves.

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* Systematic name: 4-(4-hydroxy-3-iodophenoxy)-3,5-diiodophenethylamine.

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