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Crystal and Molecular Structure of [1]Benzothieno[2,3-*b*][1]Benzothiophene Disulphone (C₁₄H₈O₄S₂)*

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[1]Benzothieno[2,3-*b*][1]benzothiophene disulphone, C₁₄H₈O₄S₂, crystallizes in the monoclinic space group *P*₂₁/*c* with four molecules in a unit cell of dimensions: $a = 11.084 \pm 0.006$, $b = 8.599 \pm 0.002$, $c = 15.325 \pm 0.008$ Å and $\beta = 116.82 \pm 0.05^\circ$. The structure was determined to study the extent of conjugation of a sulphone group with an unsaturated ring system. The determination was effected by an automatic application of the symbolic-addition procedure. The final *R* index, based on about 1500 observed reflexions, is 0.071. The central C–C double-bond distance of 1.361 ± 0.006 Å and the (average) C–S bond distance of 1.753 ± 0.004 Å indicate an appreciable conjugation of the sulphone groups with the central part of the molecule. The molecule is bent about the central C–C bond with its nearly planar halves forming an angle of about 5° . Results of a Schomaker–Trueblood type thermal-motion analysis suggest that the rigid-body model is not quite appropriate for describing the overall molecular motion.

Introduction

The investigation of the structure of [1]benzothieno[2,3-*b*][1]benzothiophene disulphone (TNTNO) was undertaken as a part of a comparative study involving heterocyclic molecules with a similar skeleton, but differing in the electronic configuration of the sulphur atoms. Molecular dimensions of the closely related [1]benzothieno[2,3-*b*][1]benzothiophene (TNTN) (Goldberg & Shmueli, 1971) indicate an extensive charge delocalization throughout the condensed ring system, and reflect the ability of divalent sulphur as a heteroatom to participate in the resonance. Upon the oxidation of TNTN to TNTNO (Dayagi, Goldberg & Shmueli, 1970) the non-bonded electrons on the sulphur atoms of TNTN become absorbed in the S=O bond orbitals of the sulphone groups of TNTNO, whose limited but significant extent of conjugation with unsaturated ring systems was first predicted by Koch & Moffitt (1951).

The aim of the present study is to determine the detailed molecular structure and packing arrangement

of TNTNO in the crystalline state, and to compare the molecular dimensions of TNTN and TNTNO in view of the different configurations of sulphur atoms and the different extents of charge delocalization expected in these closely related compounds.

Experimental

Slow cooling of a saturated solution of TNTNO in ethyl methyl ketone yielded yellow, well-developed crystals. The diffraction symmetry and systematically absent reflexions, as shown by Weissenberg and precession photographs taken with Cu *K*α radiation, assigned the crystal to the monoclinic space group *P*₂₁/*c*. A least-squares fit of unit-cell dimensions to about 30 high-angle reflexions observed on Weissenberg photographs [$\lambda(\text{Cu } K\alpha_1) = 1.5405$, $\lambda(\text{Cu } K\alpha_2) = 1.5443$ Å] gave the following results: $a = 11.084 \pm 0.006$, $b = 8.599 \pm 0.002$, $c = 15.325 \pm 0.008$ Å and $\beta = 116.82 \pm 0.05^\circ$. These Weissenberg photographs were calibrated with powder lines obtained from a thin copper wire. Observed density, measured by flotation in a dioxane – CCl₄ mixture, is 1.55 g.cm⁻³. Calculated density, for four molecules of TNTNO (C₁₄H₈O₄S₂) in the unit cell, is 1.551 g.cm⁻³.

Integrated precession intensity data were collected with Mo *K*α radiation. Two similarly shaped crystals,

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with approximate dimensions of 0.1 × 0.4 × 0.6 mm and 0.1 × 0.3 × 0.5 mm, respectively, were used for the intensity-data collection. A total of 3340 reflexions was recorded on 12 layers (*Ok*l-*4kl*, *h0l*-*h3l*, and *hk0*-*hk2*) including 1060 reflexions that were too weak to be measured. Intensities of 2380 reflexions were measured with a Joyce-Loebl recording microdensitometer and these of the 'unobserved' reflexions were estimated as $\frac{1}{2} I_{\min}$, where I_{\min} was the weakest observed intensity.

The data from the series of timed exposures taken for each layer were scaled up by the computed film-to-film ratios, and each reflexion was assigned a weighting

parameter given by $w_o(I) = \frac{I^2}{\sigma^2(I)}$, where I is the rela-

tive intensity and $\sigma(I)$ is the corresponding error estimate. Lorentz and polarization factors were applied and all data were brought to a common arbitrary scale by a least-squares procedure (Rabinovich, unpublished) similar to that described by Rollett & Sparks (1960). A total of 480 reflexions, common to different layers, was involved in the correlation of data. After data processing was completed, 2450 independent F_o values, including 930 F_o 's that corresponded to the 'unobserved' reflexions, were available for study.

Absorption corrections were not applied since the linear absorption coefficient of TNTNO for Mo $K\alpha$ radiation is only about 4.1 cm⁻¹.

Determination of structure

The orientation of the molecular plane was indicated, by a sharpened Patterson projection down the *b* axis, to be roughly parallel to (10 $\bar{2}$). This indication was further supported by $F_{20\bar{4}}$ which is the largest structure amplitude. However, neither the sharpened Patterson projection down the *a* axis nor the sharpened Harker section $P(x \frac{1}{2} z)$ offered a convenient means of locating the sulphur atoms; the former, because of the large number of solutions it presented, and the latter, because of a heavy non-Harker background which could be explained in terms of the vector set of a TNTNO molecule oriented with its plane roughly parallel to the *b* axis, as indicated above. Therefore, it was decided to try to solve the structure first by a direct method of sign determination. Nevertheless, the information so far obtained was very useful, as shown below.

Approximate scale and temperature factors were obtained from a Wilson plot (Wilson 1942; Rogers 1965).

Magnitudes of the normalized structure factors were then evaluated as

$$|E(\mathbf{h})| = \left[\frac{|F_o(\mathbf{h})|^2}{K^2 p(\mathbf{h}) \sigma_2(\mathbf{h})} \right]^{1/2} \exp \left(B \frac{\sin^2 \theta}{\lambda^2} \right) \quad (1)$$

(Rogers, 1965), where K and B are scale and temperature factors, respectively, $F_o(\mathbf{h})$ is the observed structure amplitude (on a relative scale) of reflexion \mathbf{h} (*hkl*), $p(\mathbf{h})$ is the average-intensity multiple (Rogers, 1950) and

$$\sigma_2(\mathbf{h}) = \sum_{n=1}^N f_n(\mathbf{h})$$

where $f(\mathbf{h})$ is the scattering factor of an atom at rest. The program employed assigns the average multiple to each reflexion, given the point group and the lattice type of the crystal. Atomic scattering factors in (1) were computed from the analytical approximate expression of Forsyth & Wells (1959). Average values of some functions of E and the distribution of the E values among the data are compared with corresponding theoretical results in Table 1.

The sign of $E_{20\bar{4}}$ was indicated by the \sum_2 relationship (Hauptman & Karle, 1954) to be negative with a probability of 97%. The negative sign of $20\bar{4}$ was also suggested by the need to keep the molecules away from centres of symmetry and to prevent them from lying on screw axes. This latter restriction was based on the previously indicated molecular orientation and on some pertinent packing considerations.

A \sum_2 listing (Karle & Karle, 1966) was constructed from 196 reflexions with $E \geq 1.70$, and the signs of three large E 's, which entered into many combinations, were arbitrarily chosen as positive, thus fixing the space-group origin (Hauptman & Karle, 1953). The starting set of signs comprised $E_{225} = +3.58$, $E_{51\bar{8}} = +3.34$, $E_{230} = +3.06$, $E_{20\bar{4}} = -3.00$ and the corresponding symmetry-related reflexions. Out of the 196 reflexions, 189 were allotted signs in two 7-minute runs of an automatic routine whose algorithm is based on the iterative application of the symbolic-addition procedure (Karle & Karle, 1966). The lowest acceptable probability for a positive sign of a triple product (Woolfson, 1961) was 95% during the first stage of sign determination. An increased \sum_2 listing, prepared from 333 reflexions with $E \geq 1.50$, and a repeated application of the automatic routine yielded 119 more signs. The acceptable probability for the positive sign of a triple product was lowered to 93% during the second stage. Thus, 308 signs of independent, normalized structure factors were indicated. Altogether, seven signs were inconsistent with the Sayre equation, and after their re-examination with

Table 1. Some functions of $|E|$ and the percentage distribution of their magnitudes

	Experimental	Theoretical	
		Centrosymmetric	Noncentrosymmetric
$\langle E \rangle$	0.817	0.798	0.886
$\langle E^2 - 1 \rangle$	0.924	0.968	0.736
$\langle E^2 \rangle$	1.003	1.000	1.000
$ E > 3$	0.24	0.3	
$ E > 2$	3.6	5.0	
$ E > 1$	35.5	32.0	

the aid of the Σ_2 listing four were corrected and retained.

The E map, computed with the remaining 305 E 's as coefficients, led to the determination of the structure. The map contained two peaks with (relative) heights of about 1000, separated by 3.2 Å, which were taken to correspond to the sulphur atoms. These two peaks plus 18 more, with heights ranging from 250 to 400, were clustered about a plane whose orientation was close to that of (10 $\bar{2}$). Background noise was appreciable, but its height did not exceed 100. The distribution of the 20 peaks showed that they correspond to all the non-hydrogen atoms of TNTNO. In fact, four cycles of overall isotropic least-squares refinement, with constant weight, of the atomic parameters indicated by the E map, resulted in a structure with acceptable intramolecular distances. The discrepancy factor, based on 1520 observed reflexions, was $R_{hkl}=0.135$ after the fourth cycle. All the 305 signs on which the E map was based were found to be correct. Overall scale and temperature factors resulting from the first refinement were $K=0.19$ and $U_o=0.033$ Å², respectively; the corresponding quantities obtained from the Wilson plot were: $K=0.17$ and $U_o=0.023$ Å². The discrepancy factor converged to $R_{hkl}=0.112$ after an additional cycle of refinement in which individual isotropic temperature factors were assigned to all the nonhydrogen atoms.

In subsequent calculations, the molecule was subdivided into three parts corresponding to blocks on the diagonal of the normal-equations matrix. One part comprised the thiophthene nucleus with the oxygen atoms while the other two each contained four benzene-carbon atoms and, eventually, the hydrogen atoms attached to them.

The weights employed were $w_1 = \left[aK^2 + \frac{bF_o^2}{4w_o} \right]^{-1}$, or $w_2 = \frac{w_1}{4F_o^2}$, according to whether M_1 or M_2 was to be minimized, where $M_1 = \sum w_i [F_o^i - (K|F_c|)^i]^2$ and $w_o = \frac{I^2}{\sigma^2(I)} = \frac{F_o^4}{\sigma^2(F_o^2)}$ is the weighting parameter assigned to each reflexion during data processing. Thus, for $a=0$ and $b=1$, $w_1 = \frac{1}{\sigma^2(F_o)}$ and $w_2 = \frac{1}{\sigma^2(F_o^2)}$, while for $a=1$ and $b=0$, w_1 is a constant weight which, however, depends on the layer (or on the overall) scale factor K . Constants a and b were chosen in the above manner in most calculations. Weighted discrepancy factors are given by $r_i = \frac{M_i}{\sum w_i F_o^{2i}}$ with $i=1$ or 2 according to whether M_1 or M_2 is minimized.

Three cycles of anisotropic refinement, based on positional and thermal parameters of the non-hydrogen atoms, reduced the R value to 0.088. Six large structure amplitudes ($F_{21\bar{4}}$, $F_{30\bar{4}}$, $F_{20\bar{4}}$, $F_{20\bar{2}}$, $F_{11\bar{2}}$, and $F_{20\bar{2}}$), which were probably affected by extinction, were excluded from the refinement at this stage.

Coordinates of the hydrogen atoms were calculated,

assuming that the hydrogen atoms are coplanar with the benzene rings, that the C-H bonds parallel the long diagonals of the rings, and that the C-H bond distance is 0.95 Å.

Coordinates of the hydrogen atoms were included in further calculations, but their equal isotropic temperature factors (estimated as $U_o=0.05$ Å²) were kept fixed. Two more cycles of anisotropic refinement, which included only observed reflexions, resulted in $R_{hkl}=0.075$.

'Unobserved' reflexions, for which $|F_c| > K^{-1}F_o$, were now introduced into the refinement (Dunning & Vand, 1969). In view of the uncertainty in the intensity threshold value, reflexions for which $K^{-1}F_o > |F_c| > K^{-1}F_o - 1.8$ were also included; the arbitrarily chosen value of 1.8 constitutes 25% of the strongest $K^{-1}F_o$ for an unobserved reflexion. About 500 unobserved reflexions were excluded by this criterion. Two cycles of anisotropic refinement, which included 1950 reflexions based on all atomic parameters except the temperature factors of the hydrogen atoms, resulted in $R_{hkl}=0.074$ for observed reflexions only and in $R_{hkl}=0.084$ for all reflexions. Before the final cycle of anisotropic refinement, nine moderately weak reflexions, for which $|K^{-1}F_o - |F_c|| > 5$, were excluded from the calculation. Final discrepancy indices are: $R_{hkl}=0.071$ (observed only), $R_{hkl}=0.078$ (including unobserved), and $r_2^*=0.015$.

Note that main bonding features of TNTNO, which are discussed later, were already apparent at the very start of the refinement.

Atomic scattering factors used were given by Dawson (1960) for sulphur, by Berghuis, Haanappel, Poters, Loopstra, MacGillavry & Veenendaal (1955) for carbon, by Hoerni & Ibers (1954) for oxygen, and by the results of an exact quantum-mechanical calculation, quoted in *International Tables for X-ray Crystallography* (1962a) for hydrogen.

A list of observed and final calculated structure amplitudes can be obtained from the authors upon request. Final atomic positional and thermal parameters with their estimated standard deviations are shown in Tables 2 and 3, respectively.

Description of Structure

Packing

The molecular arrangement is shown in Figs. 1 and 2, and short intermolecular contacts are given in Table 4.

The generally close packing of the molecules is reflected in the arrangement of the molecules about the centres of symmetry at (000) and (0 $\frac{1}{2}$ $\frac{1}{2}$) and in the extensive network of C...O contacts spread throughout the structure. Molecules packed across the centres are

* The function minimized during the final cycle was M_2 and the w_2 weighting scheme was used accordingly with constants a and b equal to unity.

staggered with respect to each other, and have their planar parts separated by about 3.4 Å. All short C...C contacts (Table 4) arise from this arrangement, which is probably due in part to van der Waals interactions and in part to electrostatic interactions between the highly polar sulphone groups ($\mu = 4.4$ Debye for diethyl sulphone; Phillips, Hunter & Sutton, 1945).

Table 2. Atomic coordinates as fractions of the cell edges

E.s.d.'s are given in parentheses in the units of the last decimal place.

	<i>x</i>	<i>y</i>	
S(1)	-0.3438 (1)	0.3096 (2)	0.2001 (1)
O(1-1)	-0.4362 (3)	0.2764 (5)	0.2398 (3)
O(1-2)	-0.3583 (4)	0.2265 (4)	0.1151 (2)
S(2)	-0.0739 (1)	0.1606 (1)	0.3727 (1)
O(2-1)	-0.1365 (3)	0.1079 (4)	0.4319 (2)
O(2-2)	-0.0311 (4)	0.0469 (4)	0.3240 (2)
C(1)	-0.1757 (4)	0.3035 (5)	0.2907 (3)
C(2)	-0.1156 (4)	0.4458 (5)	0.3101 (3)
C(3)	-0.2061 (4)	0.5696 (5)	0.2476 (3)
C(4)	-0.1788 (5)	0.7261 (6)	0.2457 (3)
C(5)	-0.2812 (6)	0.8208 (6)	0.1795 (4)
C(6)	-0.4047 (6)	0.7621 (7)	0.1170 (4)
C(7)	-0.4353 (5)	0.6051 (7)	0.1175 (4)
C(8)	-0.3316 (5)	0.5129 (5)	0.1841 (3)
C(9)	0.0208 (4)	0.4446 (5)	0.3933 (3)
C(10)	0.1103 (5)	0.5674 (6)	0.4331 (3)
C(11)	0.2332 (5)	0.5374 (6)	0.5152 (3)
C(12)	0.2670 (5)	0.3900 (6)	0.5545 (3)
C(13)	0.1778 (5)	0.2646 (6)	0.5142 (3)
C(14)	0.0573 (4)	0.2986 (5)	0.4352 (3)
H(4)	-0.095 (5)	0.769 (7)	0.284 (4)
H(5)	-0.261 (6)	0.928 (7)	0.181 (4)
H(6)	-0.484 (5)	0.830 (6)	0.070 (4)
H(7)	-0.520 (6)	0.564 (7)	0.079 (4)
H(10)	0.087 (5)	0.667 (6)	0.407 (4)
H(11)	0.302 (5)	0.633 (6)	0.541 (4)
H(12)	0.370 (5)	0.359 (6)	0.613 (4)
H(13)	0.199 (6)	0.162 (6)	0.546 (4)

Table 4. Intermolecular short contacts*

First designated atom belongs to the reference molecule and has the coordinates *x*, *y*, *z* given in Table 2.

C(1)—C(11) ¹	3.584 Å	C(3)—C(12) ¹	3.410 Å
C(2)—C(11) ¹	3.472	C(9)—C(10) ¹	3.564
C(2)—C(12) ¹	3.503	C(10)—C(14) ¹	3.499
O(1-1)—C(6) ²	3.384	O(2-2)—C(3) ⁵	3.280
O(1-2)—C(6) ³	3.334	O(2-2)—C(4) ⁵	3.343
O(2-2)—C(4) ⁴	3.155	O(2-1)—C(13) ⁶	3.390
O(2-2)—C(5) ⁴	3.290	O(2-1)—H(13) ⁶	2.49
O(1-2)—C(11) ⁵	3.326	O(2-2)—H(4) ⁴	2.49
O(2-2)—C(2) ⁵	3.261	O(1-1)—H(12) ⁷	2.44

Key to coordinates of second atom:

1.	- <i>x</i> , 1- <i>y</i> , 1- <i>z</i>	5.	- <i>x</i> , <i>y</i> - $\frac{1}{2}$, $\frac{1}{2}$ - <i>z</i>
2.	-1- <i>x</i> , <i>y</i> - $\frac{1}{2}$, $\frac{1}{2}$ - <i>z</i>	6.	- <i>x</i> , - <i>y</i> , 1- <i>z</i>
3.	-1- <i>x</i> , 1- <i>y</i> , - <i>z</i>	7.	<i>x</i> -1, $\frac{1}{2}$ - <i>y</i> , <i>z</i> - $\frac{1}{2}$
4.	<i>x</i> , <i>y</i> -1, <i>z</i>		

* The C...C, O...C and O...H contacts listed are shorter than 3.6, 3.4 and 2.6 Å respectively.

The geometry of some C-H...O contacts [e.g. C(13)...H(13)...O(2-1)] suggests a weak hydrogen bond. Since, however, no spectroscopic study has been done, the nature of these contacts cannot be indicated.

Best plane

The best molecular plane, based on the carbon and sulphur atoms with unit weights, was found by a method similar to that of Schomaker, Waser, Marsh & Bergman (1959). Deviations of the atoms from the best plane indicate that the molecule is slightly bent about the central C-C bond (Fig. 3), and all (heavy) atoms of the ring system can be located close to two planes intersecting at the central bond at an angle of about 5°. Deviations of the atoms from the three planes are given in Table 5. Bending is probably due to the stag-

Table 3. Anisotropic vibration components U_{ij} (Å²)

E.s.d.'s are given in parentheses in units of the last decimal place.

The anisotropic temperature factor is defined as:

$$\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2klb^*c^*U_{23} + 2lhc^*a^*U_{31})]$$

where *h*, *k*, *l* and *a*^{*}, *b*^{*}, *c*^{*} are the reflexion indices and reciprocal unit-cell edges, respectively.

	U_{11}	U_{22}	U_{33}	U_{12}	U_{23}	U_{31}
S(1)	0.0339 (7)	0.0389 (7)	0.0387 (6)	-0.0070 (6)	-0.0085 (6)	0.0072 (6)
S(2)	0.0415 (7)	0.0247 (6)	0.0385 (6)	-0.0044 (6)	0.0014 (5)	0.0168 (6)
O(1-1)	0.0474 (21)	0.0670 (27)	0.0821 (26)	-0.0206 (22)	-0.0072 (23)	0.0314 (22)
O(1-2)	0.0702 (25)	0.0506 (22)	0.0427 (19)	0.0017 (22)	-0.0171 (18)	0.0089 (19)
O(2-1)	0.0593 (23)	0.0381 (19)	0.0565 (21)	-0.0044 (19)	0.0099 (17)	0.0306 (20)
O(2-2)	0.0644 (24)	0.0304 (17)	0.0613 (22)	-0.0019 (19)	-0.0095 (17)	0.0323 (21)
C(1)	0.0293 (24)	0.0320 (23)	0.0344 (22)	-0.0004 (22)	0.0034 (21)	0.0101 (22)
C(2)	0.0284 (23)	0.0330 (23)	0.0294 (21)	-0.0039 (23)	0.0066 (20)	0.0134 (20)
C(3)	0.0343 (25)	0.0374 (25)	0.0249 (21)	0.0035 (24)	-0.0032 (21)	0.0134 (20)
C(4)	0.0468 (29)	0.0343 (27)	0.0383 (25)	0.0019 (27)	0.0022 (23)	0.0162 (24)
C(5)	0.0521 (34)	0.0423 (28)	0.0505 (29)	0.0131 (31)	0.0120 (28)	0.0262 (29)
C(6)	0.0505 (33)	0.0497 (32)	0.0475 (30)	0.0176 (32)	0.0089 (27)	0.0203 (29)
C(7)	0.0314 (26)	0.0639 (37)	0.0393 (28)	0.0090 (30)	-0.0070 (28)	0.0071 (24)
C(8)	0.0420 (26)	0.0308 (23)	0.0366 (23)	-0.0010 (24)	-0.0031 (21)	0.0231 (22)
C(9)	0.0236 (21)	0.0342 (23)	0.0229 (19)	-0.0018 (22)	-0.0019 (19)	0.0031 (18)
C(10)	0.0326 (25)	0.0362 (26)	0.0380 (25)	-0.0058 (25)	0.0015 (22)	0.0156 (23)
C(11)	0.0321 (26)	0.0513 (31)	0.0323 (24)	-0.0047 (27)	-0.0080 (24)	0.0097 (23)
C(12)	0.0357 (27)	0.0527 (32)	0.0340 (26)	0.0085 (28)	-0.0008 (24)	0.0132 (24)
C(13)	0.0402 (27)	0.0399 (26)	0.0315 (22)	-0.0030 (27)	0.0044 (22)	0.0114 (22)
C(14)	0.0338 (24)	0.0302 (22)	0.0285 (20)	-0.0071 (22)	-0.0019 (19)	0.0144 (20)

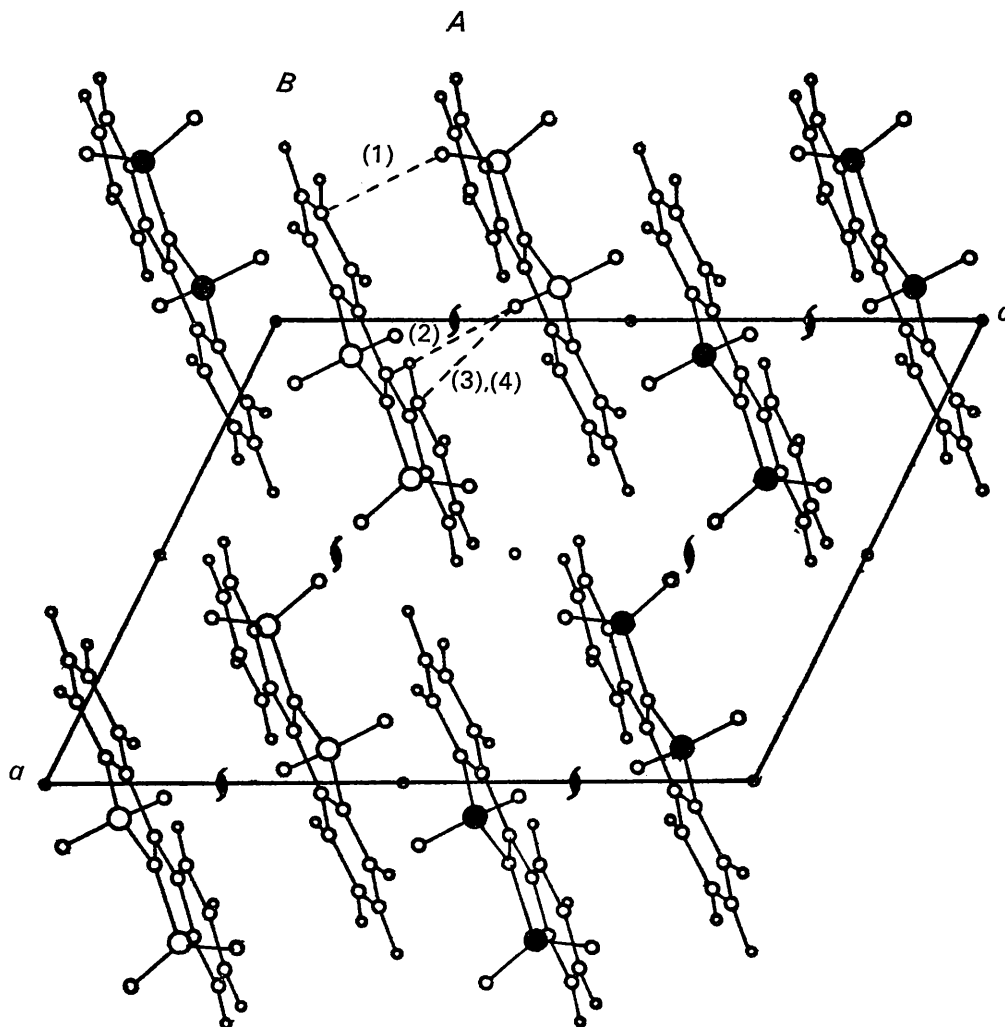


Fig. 1. Projection of the structure down the b axis. Contacts indicated by dashed lines are: (1) $O(1-2) \cdots C(11) = 3.326$, (2) $O(2-2) \cdots C(2) = 3.261$, (3) $O(2-2) \cdots C(3) = 3.280$ and (4) $O(2-2) \cdots C(4) = 3.343$ Å.

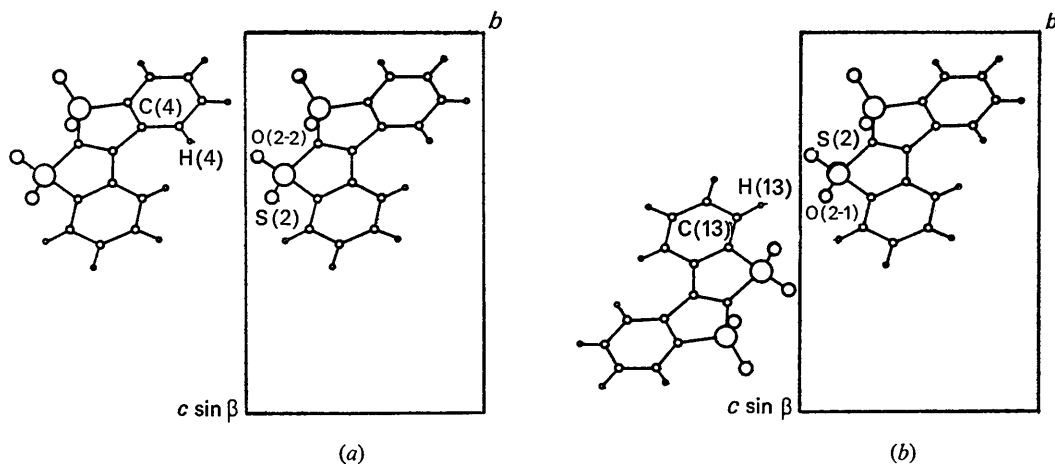


Fig. 2. Projections of parts of the structure down the a axis: (a) two molecules related by a translation along $[010]$, (b) two molecules related by a centre of symmetry at $(00\frac{1}{2})$.

gering of centrosymmetrically related molecules, whereby one half of the molecule is outside the region of overlap and is exposed to several crowded C---O contacts; the 'free' half of the molecule is bent towards the adjacent centre, as expected, from the directions of the C---O contacts which involve oxygen atoms O(2-2) and O(1-2) of molecule *A* and the carbon atoms of molecule *B* across the screw axis (Fig. 1).

Table 5. Equations of the best planes and deviations (Å) from the planes

Plane 1	$-8.234x + 1.509y + 13.981z = 6.059$ Å
2	$-7.828x + 1.512y + 14.271z = 6.001$
3	$-8.469x + 1.765y + 13.658z = 5.993$

x, *y*, *z* are fractional coordinates and the right-hand side is the distance of the plane from the unit-cell origin.

	1	2	3
S(1)	-0.036*	-0.013	0.197
S(2)	-0.003	-0.139	0.006
C(1)	0.088	0.017	0.002
C(2)	0.097	-0.005	0.009
C(3)	0.041	-0.006	0.138
C(4)	0.056	-0.002	0.158
C(5)	-0.005	-0.003	0.288
C(6)	-0.062	0.008	0.379
C(7)	-0.083	0.000	0.367
C(8)	-0.020	0.003	0.235
C(9)	0.061	-0.120	-0.014
C(10)	0.055	-0.175	-0.010
C(11)	-0.033	-0.336	0.014
C(12)	-0.083	-0.411	0.006
C(13)	-0.067	-0.346	-0.008
C(14)	-0.006	-0.214	-0.006
O(1-1)	-1.303	-1.254	1.464
O(1-2)	1.156	1.210	-0.986
O(2-1)	-1.266	-1.394	1.251
O(2-2)	1.203	1.064	-1.223

* Italicized values refer to the atoms used to define the planes.

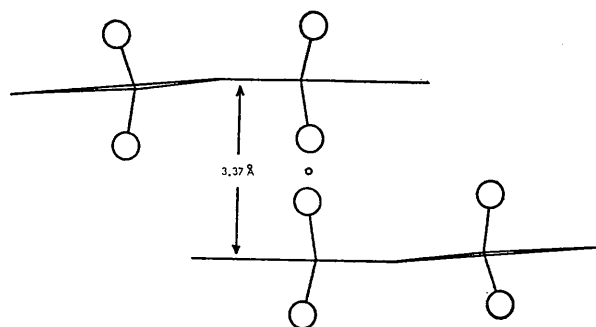


Fig. 3. Projection of a centrosymmetrically related pair down the *m* axis (see Table 6), illustrating the bending of the molecules.

Thermal motion

All atomic parameters were transformed to the axial system of the molecular tensor of inertia which based on all non-hydrogen atoms of TNTNO. The orientation of this axial system is defined in Table 6. Anisotropic thermal parameters of nonhydrogen atoms were analysed in terms of rigid-body motion parameters by the method of Schomaker & Trueblood (1968) and with the aid of a program written by Shmueli (1970). Some results of the analysis are presented in Table 7.

The root-mean-square discrepancy of ΔU_{ij} is 0.0056 Å², which is rather high if compared with the average estimated standard deviation of the observed U_{ij} 's [$\sigma(U_{ij}) = 0.0022$ Å²]. The r.m.s. discrepancy is reduced to 0.0046 Å² when the oxygen atoms are excluded from the analysis, indicating that the oxygen atoms are, to some extent, vibrating independently of the rest of the atoms. Apart from the uncorrected systematic errors

Table 6. Orientation of the inertial system

Orthogonal unit base vectors *l*, *m*, and *n*, taken along the principal axes of the tensor of inertia, are referred below to the reciprocal base vectors *a**, *b** and *c**.

	<i>a</i> *	<i>b</i> *	<i>c</i> *	Description
<i>l</i>	-6.091	3.406	-6.248	In the mean molecular plane, normal to C(1)-C(2)
<i>m</i>	-4.333	-7.739	0.077	Along C(2)-C(1)
<i>n</i>	-8.184	1.563	13.997	Normal to the mean molecular plane

Table 7. Rigid-body motion parameters

Components of the tensors and the unit vectors along their principal axes are referred to the axial system of inertia defined in Table 6. The calculation is referred to the origin which symmetrizes *S* and reduces the trace of *T* (Schomaker & Trueblood, 1968). Coordinates of this origin, in the inertial system with its origin at the centre of mass, are: $q_1 = -0.57$, $q_2 = -1.02$ and $q_3 = -0.02$ Å.

Tensor	Tensor elements × 10 ⁵ (e.s.d. × 10 ⁵)						
	11	22	33	12	23	13	
<i>L</i> (rad ²)	353 (36)	102 (23)	201 (17)	-33 (16)	-31 (17)	46 (24)	
<i>T</i> (Å ²)	3287 (136)	2696 (159)	2603 (231)	-8 (124)	-113 (159)	241 (142)	
<i>S</i> (rad - Å)	88 (54)	-74 (42)	-14 (68)	62 (37)	-8 (19)	-23 (26)	
	R.m.s. amplitudes			Principal axes			
		3.5°	0.9479	-0.1495	0.2814		
<i>L</i>		2.5	0.3079	0.2026	-0.9296		
		1.7	0.0819	0.9678	0.2381		
		0.183 Å	-0.9489	0.0639	-0.3092		
<i>T</i>		0.166	0.1897	-0.8981	0.3967		
		0.157	-0.2524	0.4351	0.8643		

in the data, another factor which may bear on the r.m.s. discrepancy is the probable presence of internal vibration modes, as indicated by the disparity of the observed vibration components; principal values of the vibration tensors (Table 8) are consistently higher for that part of the molecule, which is not involved in the close packing about the centre of symmetry.

Nevertheless, the description of the motion is physically reasonable, as the direction of largest libration is about 18° away from the long axis which corresponds to the smallest moment of inertia. Furthermore, the axis of smallest libration nearly coincides with the central bond, and libration about this direction is probably inhibited by the numerous short contacts directed nearly perpendicularly to the mean molecular plane.

Table 8. *Principal values of observed and calculated vibration tensors ($\times 10^4 \text{ \AA}^2$)*

	Observed			Calculated		
	U_1	U_2	U_3	U_1	U_2	U_3
S(1)	539	438	242	576	502	283
S(2)	447	384	230	494	427	274
C(3)	417	321	228	346	330	296
C(9)	368	345	179	339	289	253
C(4)	504	392	332	438	383	307
C(10)	430	370	271	386	374	281
C(5)	637	457	321	605	486	316
C(11)	542	403	266	493	471	304
C(6)	678	499	322	715	475	326
C(12)	579	354	318	536	435	316
C(7)	742	425	278	670	441	327
C(13)	504	370	296	482	394	283
C(8)	439	322	272	477	374	312
C(14)	396	280	245	381	337	260
O(1-1)	850	771	319	727	665	283
O(2-1)	614	588	288	644	614	259
O(1-2)	967	568	290	851	578	278
O(2-2)	668	576	273	653	506	289
C(1)	418	307	279	409	362	270
C(2)	411	290	202	340	277	261

Molecular structure

Bond lengths and angles along with their standard deviations are presented in Tables 9 and 10. The schematic drawing of the molecule is shown in Fig. 4. Bond lengths corrected for librational motion (Schomaker & Trueblood, 1968) are included in Table 9. However, in view of the presumably large uncertainty inherent in these small corrections discussion of the structure is based on the uncorrected values.

The t test (Cruickshank, 1965), applied to all chemically equivalent bonds and angles not involving hydrogen positions, shows that the internal consistency of the crystallographically independent quantities is good. The value of t does not exceed 1.6 for any of the pairs of equivalent bonds and angles, except the C(7)–C(8) and C(13)–C(14) bond pair for which $t = 2.75$. Thus, the difference between these two bonds might be considered significant.

Average C–C bond lengths within the benzene rings of TNTNO are 1.383 and 1.387 Å for rings *A* and *B*,

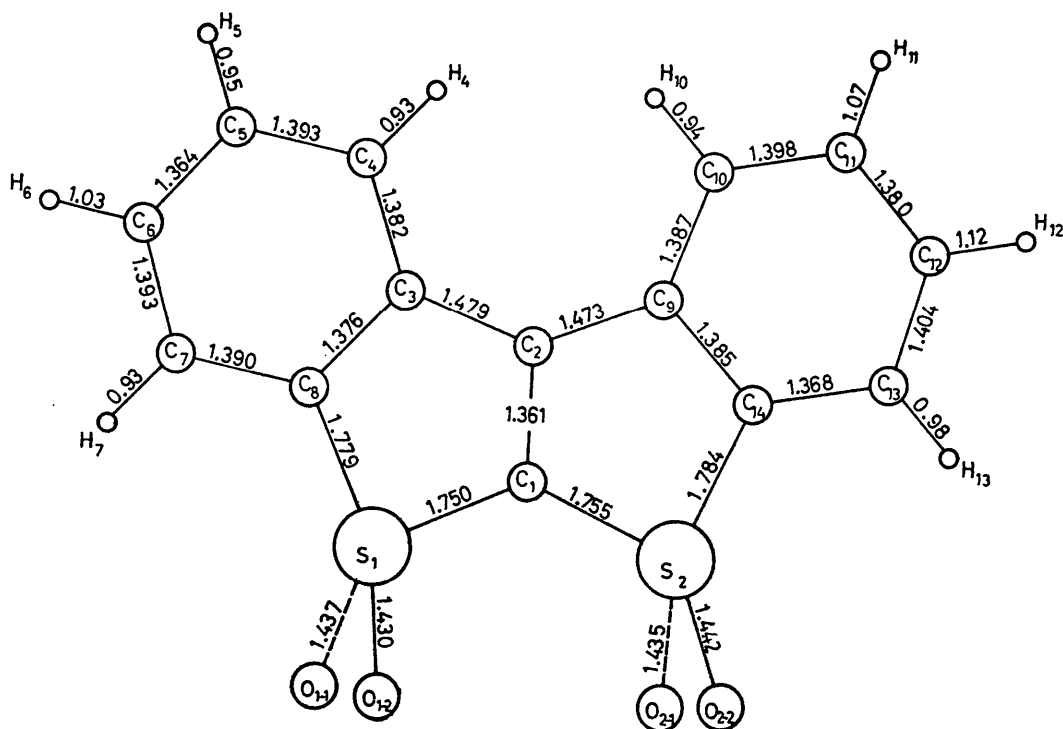


Fig. 4. Schematic drawing of the TNTNO molecule. Bond distances shown are not corrected for libration.

respectively (Fig. 4); they agree well with values usually found in aromatic structures.

Distribution of the bond lengths in the thiophene nucleus of TNTNO clearly shows, as might be expected, the effect of 'trapping' the non-bonded electrons on the sulphur atoms of TNTN (Goldberg & Shmueli, 1971) by the S=O bond orbitals. For ease of comparison, the thiophene nuclei of both molecules are schematically illustrated in Fig. 5. Thus, in TNTNO the C(2)–C(3) and C(2)–C(9) bond lengths average 1.467 Å, which agrees well with the value of a single bond between two C(sp²) atoms in similar structures, e.g. in fluorene (Burns & Iball, 1955) and in dibenzothiophene sulphone (Kronfeld & Sass, 1968). The longer C–S bond distances (1.784 and 1.779 Å) agree well with the value of 1.774 Å found in orthonic acid by Hall & Maslen (1967) and with corresponding values found for an S–C(sp²) single bond in other related compounds, quoted by these authors.

On the other hand, the shorter C–S bonds (1.750 and 1.755 Å) and the central C(1)–C(2) bond (1.361 Å) are

indicative of a partial double-bond character (*International Tables for X-ray Crystallography*, 1962*b*). Fig. 5 shows that the shorter C–S bonds and the C(1)–C(2) bond in TNTNO are closer to a single and a double bond, respectively, than the corresponding bonds in TNTN. Deviations of these bond distances in TNTNO from the formal single- and double-bond values are consistent with the prediction, first offered by Koch & Moffitt (1951), concerning the conjugation of a sulphone group with an unsaturated ring system. The perpendicularity of the planes of the sulphone group and of the ring system, a condition met by TNTNO, is, according to Koch & Moffitt, the preferred geometrical arrangement for relatively strong conjugation to take place. Therefore, we believe that the above-mentioned deviations of the three central bonds are mainly due to this effect. Thus, the charge delocalization within the TNTNO molecule may be described as being partially confined to three distinct regions: the benzene rings *A* and *B* and the central part comprising the sulphone groups and the S(1)–C(1), S(2)–C(1), and C(1)–C(2) bonds.

Table 9. Bond lengths

E.s.d.'s are given in parentheses in units of the last decimal place.

	Uncorrected	Corrected*		Uncorrected	Corrected*
C(1)–C(2)	1.361 (6) Å	1.364 Å	S(2)–C(1)	1.755 (4) Å	1.759 Å
S(1)–C(1)	1.750 (4)	1.752	S(2)–C(14)	1.784 (4)	1.787
S(1)–C(8)	1.779 (5)	1.783	C(2)–C(9)	1.473 (5)	1.475
C(2)–C(3)	1.479 (6)	1.483	C(9)–C(10)	1.387 (6)	1.390
C(3)–C(4)	1.382 (7)	1.386	C(10)–C(11)	1.398 (5)	1.401
C(4)–C(5)	1.393 (7)	1.396	C(11)–C(12)	1.380 (7)	1.384
C(5)–C(6)	1.364 (7)	1.366	C(12)–C(13)	1.404 (7)	1.406
C(6)–C(7)	1.393 (8)	1.396	C(13)–C(14)	1.368 (5)	1.371
C(7)–C(8)	1.390 (6)	1.393	C(9)–C(14)	1.385 (6)	1.389
C(3)–C(8)	1.376 (6)	1.378	S(2)–O(2-1)	1.442 (5)	1.445
S(1)–O(1-1)	1.437 (5)	1.440	S(2)–O(2-2)	1.435 (4)	1.439
S(1)–O(1-2)	1.430 (4)	1.433	C(10)–H(10)	0.94 (5)	
C(4)–H(4)	0.93 (5)		C(11)–H(11)	1.07 (5)	
C(5)–H(5)	0.95 (6)		C(12)–H(12)	1.12 (5)	
C(6)–H(6)	1.03 (5)		C(13)–H(13)	0.98 (5)	
C(7)–H(7)	0.93 (6)				

* Corrected for the effects of librational motion by the method of Schomaker & Trueblood (1968).

Table 10. Bond angles and their e.s.d.'s (not including hydrogen atoms)

	Angle	e.s.d.		Angle	e.s.d.
O(1-1)–S(1)–C(8)	111.5°	0.3°	C(8)–S(1)–C(1)	91.1°	0.2°
O(1-1)–S(1)–O(1-2)	118.6	0.2	S(2)–C(1)–C(2)	112.4	0.3
O(1-1)–S(1)–C(1)	111.4	0.2	C(1)–S(2)–C(14)	91.3	0.2
O(1-2)–S(1)–C(8)	110.5	0.2	O(2-1)–S(2)–C(1)	109.5	0.2
O(1-2)–S(1)–C(1)	110.4	0.2	O(2-1)–S(2)–C(14)	112.2	0.2
S(1)–C(1)–C(2)	112.8	0.3	O(2-1)–S(2)–O(2-2)	118.7	0.2
S(1)–C(1)–S(2)	134.3	0.3	O(2-2)–S(2)–C(1)	111.2	0.2
C(1)–C(2)–C(3)	112.6	0.3	O(2-2)–S(2)–C(14)	110.6	0.2
C(1)–C(2)–C(9)	113.1	0.4	S(2)–C(14)–C(9)	111.0	0.3
C(2)–C(3)–C(8)	112.1	0.4	S(2)–C(14)–C(13)	124.5	0.3
C(2)–C(3)–C(4)	128.5	0.4	C(14)–C(9)–C(2)	112.3	0.4
C(3)–C(8)–S(1)	111.5	0.3	C(14)–C(9)–C(10)	119.1	0.3
C(3)–C(4)–C(5)	118.1	0.4	C(9)–C(10)–C(11)	117.8	0.4
C(4)–C(5)–C(6)	121.6	0.5	C(10)–C(11)–C(12)	121.6	0.4
C(5)–C(6)–C(7)	121.6	0.5	C(11)–C(12)–C(13)	121.0	0.4
C(6)–C(7)–C(8)	115.8	0.4	C(12)–C(13)–C(14)	115.9	0.4
C(7)–C(8)–C(3)	123.6	0.4	C(13)–C(14)–C(9)	124.6	0.4
C(7)–C(8)–S(1)	125.0	0.4	C(3)–C(2)–C(9)	134.1	0.4
C(8)–C(3)–C(4)	119.4	0.4	C(2)–C(9)–C(10)	128.7	0.4

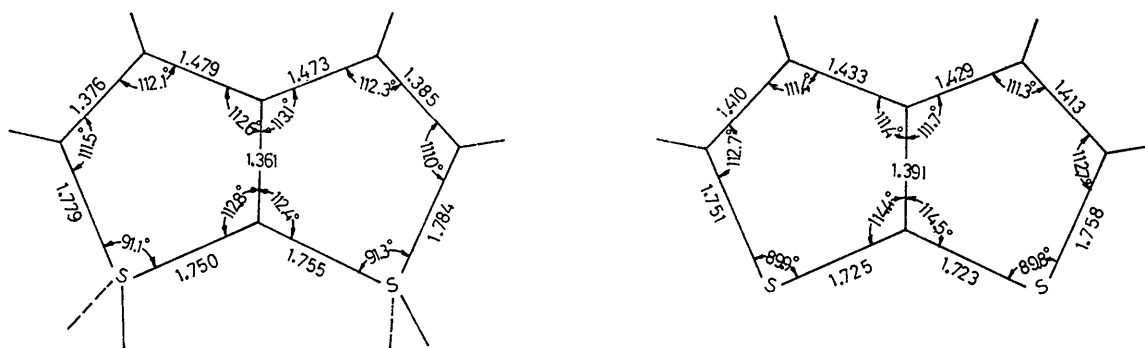


Fig. 5. Thiophthene nuclei of (a) TNTNO and (b) TNTN.

Average values of the S–O bond distances and O–S–O angles are 1.436 Å and 118.7°, respectively, the differences between the four independent S–O bonds being insignificant. Thus, the dimensions of the sulphone groups in TNTNO are closely similar to those reported for several sulphone structures (*cis*-2-butene episulphone, Desiderato & Sass, 1967; 4,4'-dichlorodiphenyl sulphone, Sime & Abrahams, 1960; β -isoprene sulphone, Jeffrey, 1951), except for dibenzothiophene sulphone in which an S–O bond distance of 1.49 Å was found (Kronfeld & Sass, 1968).

In view of these described and discussed results, it is of interest to extend the comparative study to the related disulphoxide and monosulphone derivatives of TNTN. Crystal data and chemical information on the monosulphone derivative have been published elsewhere (Dayagi *et al.*, 1970), and work on this compound is now in progress at this laboratory.

Computing

All computations were carried out on a CDC 3400 computer at the Tel-Aviv University Computation Centre with FORTRAN programs, most of which are listed elsewhere (Goldberg & Shmueli, 1971). Additional programs employed, and written in this laboratory, are *WILPLOT*, construction of the Wilson plot (Wilson, 1942; Rogers, 1965), U. Shmueli.

DIRECTO, application of the \sum_1 relationship (Hauptman & Karle, 1954), I. Goldberg and U. Shmueli.

DIRECT 1, construction of the \sum_2 listing (Karle & Karle, 1966), U. Shmueli and I. Goldberg.

DIRECT 2, automatic application of the symbolic-addition procedure (Karle & Karle, 1966), U. Shmueli.

We are grateful to our colleagues of the Weizmann Institute of Science, in particular Dr D. Rabinovich, for granting us free access to their library of computer programs. It is a pleasure to thank Mr I. Weissbren and Mr A. Tagger of the Tel-Aviv University Computation Centre for help and advice in programming, Dr S. Dayagi for useful chemical information on the compound, and Mr H. Horovitz for technical assistance.

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