

oxygen atom O(2). The location of the C γ [C(4)] atom is in position II [*trans* to N(1)]. Orientation of the side group as a whole in relation to the backbone is shown in Fig. 4(b). This orientation is similar to that observed in DL- α -amino-n-butyric acid (Ichikawa & Iitaka, 1968) and L-ornithine hydrochloride (Chiba *et al.*, 1967).

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Crystal and Molecular Structure of [1]Benzothieno[2,3-*b*][1]benzothiophene (C₁₄H₈S₂)*

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[1]Benzothieno[2,3-*b*][1]benzothiophene, C₁₄H₈S₂, crystallizes in the monoclinic space group *P*2₁ with two molecules in a unit cell of dimensions: $a = 9.935 \pm 0.003$, $b = 4.027 \pm 0.001$, $c = 13.622 \pm 0.004$ Å and $\beta = 97.90 \pm 0.03^\circ$. The structure was determined from three-dimensional integrated precession data. The final *R* index, based on 960 observed reflexions, is 0.059. Distribution of the bond lengths in the thiophene nucleus of the molecule indicates an extensive π delocalization which is probably due to the participation of the nonbonded electrons on the sulphur atoms in the conjugation. Results of a simple HMO calculation support this indication. The crystal consists of rigid, planar molecules stacked along the *b* axis. Results of a Shomaker-Trueblood type rigid-body motion analysis are consistent with the molecular arrangement.

Introduction

The chemistry of [1]benzothieno[2,3-*b*][1]benzothiophene (TNTN), as well as preliminary results of its structure, have been described recently (Dayagi, Goldberg & Shmueli, 1970). Following the results and im-

plication of the chemical study, it was considered of interest to carry out a comparative structural investigation of TNTN and some of its oxidized derivatives. The main interest in such a study is to assess the influence of the two extreme oxidation states of sulphur on the detailed structures of the otherwise analogous heterocyclic molecules (Fig. 1). This assessment may be of value in estimating the effect of the electronic configuration of sulphur on the structure and chemistry of related compounds and in comparing experimental

* Presented at the Meeting of the Israel Crystallography Society, Technion, Haifa, 7 April 1970 (Goldberg & Shmueli, 1970).

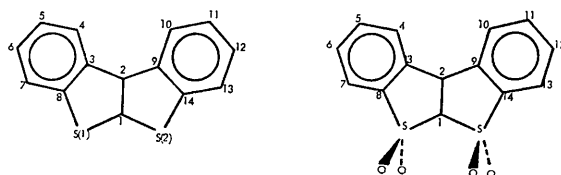


Fig. 1. TNTN and its disulphone derivative.

results with theoretical predictions concerning conjugation in unsaturated heterocyclic sulphides and sulphones (Longuet-Higgins, 1949; Koch & Moffitt, 1951; Bossa, 1969).

The purpose of the present study is to determine and discuss the detailed geometry and packing mode of the TNTN molecule in the crystalline state. The structure of the disulphone derivative of TNTN (Fig. 1), as well as the conclusions from the above-mentioned comparative study, are presented in the paper that follows this one (Goldberg & Shmueli, 1971).

Experimental

The crystal data on TNTN, obtained during the early stage of this work (Dayagi *et al.*, 1970) and used in the present study, are shown in Table 1.

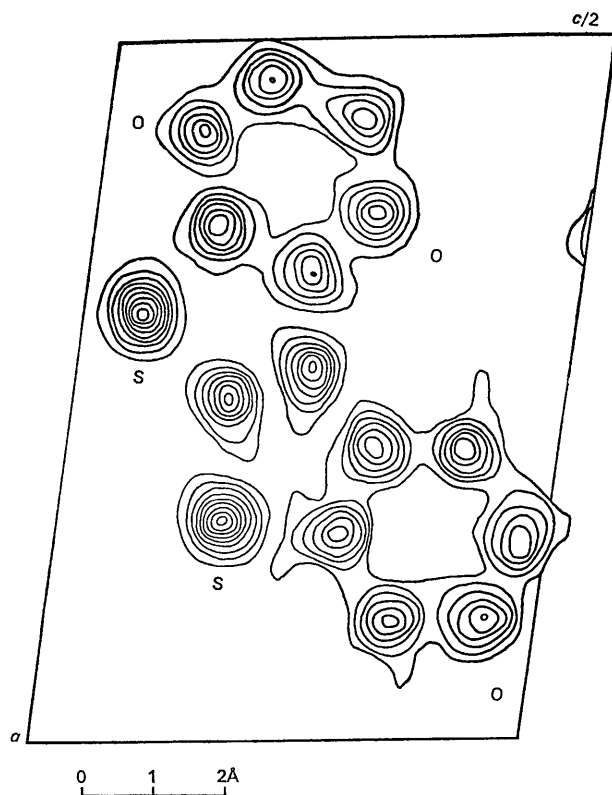


Fig. 2. Electron density projection down the b axis. Contours at intervals of $1 \text{ e.}\text{\AA}^{-2}$ for the carbon atoms and at intervals of $3 \text{ e.}\text{\AA}^{-2}$ for sulphur. The first contour represents $1 \text{ e.}\text{\AA}^{-2}$.

Table 1. *Crystal data*

$\text{C}_{14}\text{H}_8\text{S}_2$, M.W. = 240.35
Crystal system: monoclinic
Space group: $P2_1$ or $P\frac{2_1}{m}$ (systematic absences $0k0, k=2n+1$)
$a = 9.935 \pm 0.003 \text{ \AA}$
$b = 4.027 \pm 0.001$
$c = 13.622 \pm 0.004$
$\beta = 97.90 \pm 0.03^\circ$
$d_{\text{meas}} = 1.46 \text{ g.cm}^{-3}$ (measured by flotation in a benzene-chloroform mixture).
$d_{\text{calc}} = 1.478 \text{ g.cm}^{-3}$ for $Z=2$.

The somewhat meagre space-group information (only three $0k0$ reflexions were absent due to the short b axis) in conjunction with the results of the intensity moment test (Foster & Hargreaves, 1963) and with packing considerations, indicated that $P2_1$ is the space group of TNTN. Results of the moment test (Table 2), strongly suggesting that the (010) projection is centrosymmetric, were confirmed by subsequent structure determination (Dayagi, *et al.*, 1970). An examination of interatomic distances in the projection pointed to $P2_1$ as being the only possible space group. These details were only briefly indicated in the account of the early work on TNTN.

Table 2. *Results of intensity moment test on $h0l$ reflexions*

	Average experimental moments*	Theoretical moments	
		$p1$	$p2$
$\langle z^2 \rangle$	2.54–2.70	1.89	2.66
$\langle z^3 \rangle$	9.60–10.80	5.06	10.65

* Moments were computed from overlapping equal groups of 20 to 50 reflexions in a $\sin^2 \theta$ range. Lower and upper limits of the average experimental moment range correspond to averaging over 20 to 50 reflexion groups, respectively. 340 $h0l$ reflexions (including unobserved) were used.

Three-dimensional integrated precession intensity data were collected using $\text{Mo K}\alpha$ radiation. Eight layers ($h0l-h2l$ and $0kl-4kl$) were recorded from a crystal whose approximate linear dimensions were $0.15 \times 0.6 \times 0.8 \text{ mm}$. A total of 2230 intensities was measured mainly with a Joyce-Loebl Mark IIICS recording microdensitometer, although intensities of some weaker reflexions were estimated visually. Intensities of the 'unobserved' reflexions were estimated as $\frac{1}{2}I_{\text{min}}$, where I_{min} is the smallest observed intensity value.

Data from the series of timed exposures taken for each layer were scaled by the computed film-to-film ratios. Each reflexion was assigned a weighting parameter determined by its estimated accuracy and by the number of measurements in which the reflexions was involved. Lorentz and polarization corrections were applied and all data were brought to a common

scale by a least-squares procedure (Rabinovich, unpublished) similar to that described by Rollett & Sparks (1960). A total of 452 reflexions, common to different layers, was used to this end. Absorption corrections were not applied, as the linear absorption coefficient for Mo *K*α radiation is only about 4.4 cm⁻¹. After data processing was completed, 1248 independent *F*_o's, including 285 *F*_o's corresponding to the 'unobserved' reflexions, were available for study.

All computations were carried out on a CDC 3400 computer at the Tel-Aviv University Computation Centre. Programs used in this work are listed at the end of the paper.

Determination and refinement of structure

The solution of the *b*-axis projection of TNTN by the heavy-atom method is described elsewhere (Dayagi *et al.*, 1970). Results of that study provided the *x* and *z* coordinates of all the non-hydrogen atoms. The electron density projection on the *a*-*c* plane of the unit cell is reproduced in Fig. 2.

The trial structure was deduced by examining the projection, assuming that the molecule was planar and that the bond lengths and angles were those found in thiophene (Cox, Gillot & Jeffrey, 1949) and in a benzene ring (*International Tables for X-ray Crystallography*, 1962*b*). Based on these considerations, the molecular plane was found to be inclined about 27.5° with respect to the plane of the projection. This led to a

separation of 3.57 Å between the planes of adjacent molecules related by translation along [010]; the 3.57 Å value agreed well with the value obtained at the end of the refinement. The *y* coordinates of all the non-hydrogen atoms were now referred to the centre of one of the sulphur atoms which was kept fixed at *y*=0 to specify the origin of the polar space group. Two cycles of isotropic least-squares refinement, based on the trial structure obtained as described above, resulted in the agreement index, *R*_{hkl}=0.14. A total of 960 observed reflexions was included in the calculation. Additional four cycles of block-diagonal (2–3 atoms per block) refinement, in which individual isotropic temperature factors were assigned to the atoms, lowered the agreement index to *R*_{hkl}=0.096. Constant weights were used in these two calculations.

Note that the main bonding features of the thiophene nucleus of TNTN were already apparent at this stage of the refinement. The weighting functions used were

$$w_1 = \left[(aK)^2 + \frac{(bF_o)^2}{4w_o} \right]^{-1} \text{ or } w_2 = \frac{w_1}{4F_o^2}$$

according to whether *M*₁ or *M*₂ was to be minimized, where

$$M_i = \sum w_i [F_o^i - (K|F_c|)^i]^2, \quad i=1,2.$$

Constants *a* and *b* were taken as *a*=0 and *b*=1 or *a*=1 and *b*=0 (for constant weight). The weighting parameter (*w*_o), which was assigned to the measured intensities, is



Fig. 3. Best plane section through the three-dimensional difference density. Contours at intervals of 0.05 e.Å⁻³. Zero contour is represented by a dashed line. Heavy lines denote the projection of the molecule on the best plane after the completion of refinement.

given by $w_0 = \frac{F_o^4}{\sigma^2(F_o^2)}$ so that for $a=0$ and $b=1$, $w_1 = \frac{1}{\sigma^2(F_o)}$ and $w_2 = \frac{1}{\sigma^2(F_o^2)}$. Agreement factors are given by

$$R = \frac{\sum |F_o - K|F_c||}{\sum F_o} \quad \text{and} \quad r_i = \frac{\sum w_i [F_o^i - (K|F_c|)^i]^2}{\sum w_i F_o^{2i}}$$

with $i=1$ or 2 according to whether weighting scheme w_1 or w_2 was used.

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

Three cycles of anisotropic refinement, based on the parameters of all the non-hydrogen atoms, brought R down to 0.077. The eight separate layer scale factors* were then refined with all the other parameters kept fixed. This was followed by one cycle of anisotropic refinement (with the layer scale factors kept fixed) resulting in a further decrease of the agreement index to $R_{hkl}=0.069$.

Available atomic coordinates were then referred to the axial system of the molecular tensor of inertia, revealing an almost exact planarity of the molecule. A section, through the best molecular plane, of the three-dimensional difference density (Fig. 3) showed eight maxima whose positions correspond well with the expected locations of the hydrogen atoms. The height of these peaks ranges from $0.25 \text{ e.}\text{\AA}^{-3}$ to $0.55 \text{ e.}\text{\AA}^{-3}$, while the average value of the density in the lowest portions of the map is $-0.25 \text{ e.}\text{\AA}^{-3}$. Additional detail includes peaks that probably correspond to the residual density in the bonds.

The refinement was resumed including the coordinates of the hydrogen atoms. The eight layer scale factors and the equal isotropic temperature factors ($u_o = 0.05 \text{ \AA}^2$), which were assigned to the hydrogen atoms, were kept fixed during subsequent calculations. Two cycles of anisotropic refinement, which also included the unobserved reflexions, reduced the agreement factor to $R_{hkl}=0.060$ (for observed reflexions only). A large structure amplitude, $F_{11\bar{2}}$, which was probably affected by extinction, was excluded from the calculations at this stage. The weighting scheme used in the final stages of the refinement was w_2 , with constants a and b equal to unity.

Constant weights assigned to the unobserved reflexions were obtained from the condition: $\langle w\Delta^2 \rangle = 1$ (Cruickshank, Pilling, Bujosa, Lovell & Truter, 1961),

where $\Delta = K^{-1}F_o - |F_c|$. The refinement of the structure was concluded with one cycle of anisotropic refinement, based on all atomic parameters except the isotropic temperature factors of the hydrogen atoms and the y coordinate of S(1) which were kept fixed throughout the refinement. Final agreement indices are: $R_{hkl}=0.059$ for observed reflexions, $R_{hkl}=0.082$ for all reflexions and $r_2=0.015$.

Atomic scattering factors used were given by Dawson (1960) for sulphur, by Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955) for carbon 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. Atomic positional and thermal parameters with their standard deviations, estimated during the last cycle of the refinement, are shown in Tables 3 and 4 respectively.

Table 3. Atomic coordinates as fractions of cell edges

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

	x	y	z
S(1)	0.3910 (2)	0.0000	0.0602 (1)
S(2)	0.6896 (2)	-0.0375 (7)	0.1705 (1)
C(1)	0.5199 (6)	0.0675 (17)	0.1567 (4)
C(2)	0.4788 (6)	0.2244 (19)	0.2385 (4)
C(3)	0.3364 (6)	0.2988 (17)	0.2225 (4)
C(4)	0.2542 (6)	0.4545 (24)	0.2837 (4)
C(5)	0.1170 (7)	0.4924 (28)	0.2524 (6)
C(6)	0.0595 (8)	0.3811 (23)	0.1615 (6)
C(7)	0.1356 (7)	0.2294 (23)	0.0972 (5)
C(8)	0.2749 (6)	0.1851 (18)	0.1291 (4)
C(9)	0.5892 (6)	0.2674 (18)	0.3165 (4)
C(10)	0.5944 (7)	0.4151 (19)	0.4108 (4)
C(11)	0.7145 (8)	0.4267 (21)	0.4732 (5)
C(12)	0.8316 (8)	0.2981 (21)	0.4462 (5)
C(13)	0.8353 (7)	0.1490 (20)	0.3538 (5)
C(14)	0.7109 (6)	0.1337 (18)	0.2904 (4)
H(4)	0.290 (8)	0.575 (27)	0.347 (6)
H(5)	0.068 (8)	0.611 (26)	0.297 (6)
H(6)	-0.034 (9)	0.356 (27)	0.131 (6)
H(7)	0.097 (8)	0.132 (26)	0.037 (6)
H(10)	0.503 (8)	0.510 (35)	0.430 (5)
H(11)	0.709 (8)	0.491 (37)	0.540 (6)
H(12)	0.934 (7)	0.339 (25)	0.489 (6)
H(13)	0.906 (8)	0.017 (33)	0.340 (6)

Thermal-motion analysis and packing arrangement

Anisotropic vibration components, U_{ij} , shown in Table 4 were subjected to an analysis carried out by the method of Schomaker & Trueblood (1968) with the aid of a program written by Shmueli (1970).

Observational equations for the components of the translation, libration and screw-motion tensors, denoted by **T**, **L** and **S** respectively, incorporated the constraint that the trace of **S** should vanish. The initial origin was chosen at the centre of mass and the calculation was referred to the axial system of the molecular tensor of inertia. Unit weights were assigned to

* Refinement commenced with all data on one common scale. At this stage, the data were separated into eight groups corresponding to the eight layers from which they were collected.

all observations. The calculation, some of whose results are shown in Table 5, was concluded with the correction of atomic positions for the effects of librational motion by the method of Schomaker & Trueblood (1968).

The root-mean-square discrepancy, corrected for the number of degrees of freedom, between observed and calculated U_{ij} 's is 0.0046 Å² as compared with 0.0032 Å² which is the average estimated standard deviation of observed U_{ij} 's. Although the r.m.s. discrepancy is somewhat large, the comparison of individual observed and calculated U_{ij} 's shows that the thermal parameters fit the rigid-body model reasonably well. The results of the analysis are further supported by the thermal parameters being consistent with the modes of molecular motion conceivable within the limitations imposed by the packing.

The molecules of TNTN are stacked along the *b* axis in such a way that the overlap between adjacent molecules in the stack (Fig. 4) is minimized, as is usually observed in similar cases (Gaultier, Hauw & Breton-Lacombe, 1969). Projection of the structure on the *a-c* plane (Fig. 5) shows that the stacks are also stabilized by S...S short contacts.* According to the results of the rigid-body motion analysis, the direction associated with the smallest amplitude of libration is only about 3° away from the central bond, which is expected considering the interference of the packing with this type of motion. On the other hand, the amplitude of vibrational translation is largest in a direction 8.5° away from the long molecular axis; the motion in that direction is hindered mainly by the relatively loose H...H contacts.

* Similar short contacts between two pairs of sulphur atoms related by a twofold screw axis have been observed in 1,2-benzodithiol-3-one oxime (Andreotti, Cavalca, Manfredotti & Musatti, 1969) and several other close approaches between sulphur atoms have been found and quoted by Walker, Folting & Merritt (1969).

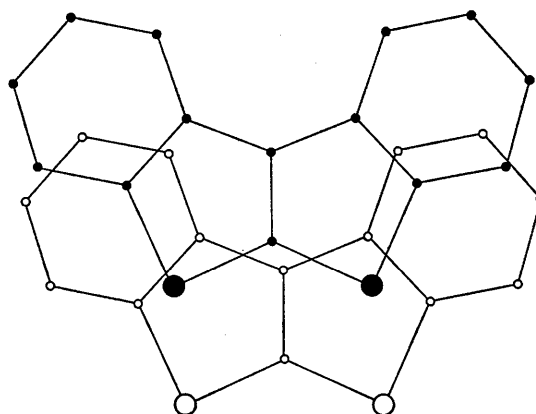


Fig. 4. Projection of two adjacent stacked molecules of TNTN on the best plane of one of them.

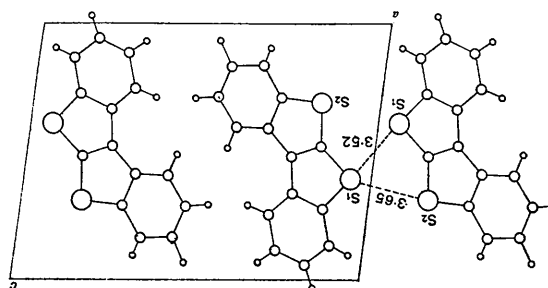


Fig. 5. Projection of the structure down the *b* axis.

Intermolecular close approaches, observed in the structure, are listed in Table 6.

Molecular structure

Bond lengths and angles along with their standard deviations are shown in Tables 7 and 8, respectively. Fig. 6 illustrates the molecular geometry of TNTN.

Table 4. Anisotropic vibration components U_{ij} (Å²)

E.s.d.'s in parentheses are given in units of the last decimal place. Anisotropic temperature factor is defined as: $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{23}klb^*c^* + 2U_{13}lhc^*a^* + 2U_{12}hka^*b^*)]$, where *h*, *k*, *l* and *a**, *b**, *c** are reflexion indices and unit-cell edges, respectively.

	U_{11}	U_{22}	U_{33}	U_{12}	U_{23}	U_{13}
S(1)	0.0441 (9)	0.0346 (9)	0.0246 (6)	-0.0040 (12)	-0.0061 (8)	0.0044 (6)
S(2)	0.0344 (8)	0.0336 (9)	0.0369 (7)	0.0086 (12)	-0.0007 (9)	0.0119 (6)
C(1)	0.0342 (30)	0.0292 (34)	0.0224 (24)	-0.0098 (35)	0.0015 (24)	0.0073 (23)
C(2)	0.0362 (32)	0.0270 (32)	0.0244 (25)	0.0000 (37)	0.0006 (37)	0.0097 (23)
C(3)	0.0296 (31)	0.0260 (34)	0.0320 (29)	0.0009 (33)	0.0071 (26)	0.0100 (25)
C(4)	0.0392 (33)	0.0394 (40)	0.0388 (28)	-0.0073 (52)	0.0102 (37)	0.0144 (26)
C(5)	0.0437 (38)	0.0416 (44)	0.0741 (46)	0.0118 (60)	0.0106 (53)	0.0240 (35)
C(6)	0.0439 (40)	0.0514 (57)	0.0579 (43)	-0.0031 (49)	0.0109 (41)	0.0072 (35)
C(7)	0.0406 (39)	0.0512 (52)	0.0515 (39)	-0.0141 (50)	0.0152 (40)	-0.0028 (33)
C(8)	0.0315 (31)	0.0289 (35)	0.0345 (29)	0.0000 (36)	0.0062 (27)	0.0090 (25)
C(9)	0.0328 (31)	0.0284 (34)	0.0276 (27)	-0.0039 (36)	0.0041 (27)	0.0048 (24)
C(10)	0.0450 (34)	0.0328 (43)	0.0293 (27)	-0.0005 (42)	-0.0001 (28)	0.0028 (26)
C(11)	0.0628 (46)	0.0331 (43)	0.0370 (30)	-0.0110 (50)	-0.0085 (33)	0.0010 (32)
C(12)	0.0447 (42)	0.0438 (50)	0.0501 (38)	-0.0186 (46)	0.0064 (39)	-0.0074 (33)
C(13)	0.0372 (37)	0.0364 (41)	0.0520 (40)	0.0014 (40)	0.0127 (35)	-0.0015 (31)
C(14)	0.0326 (32)	0.0284 (34)	0.0285 (27)	-0.0038 (34)	0.0011 (27)	0.0032 (25)

As mentioned above, the TNTN molecule is almost exactly planar in so far as the non-hydrogen atoms are concerned. The equation of the best plane, passing through these atoms, is given by

$$2.498x + 3.576y - 5.668z = 0.628 \text{ \AA}$$

where x , y and z are the fractional coordinates of a point, in the plane, referred to the crystal axes and the right-hand side is the distance of the plane from the unit-cell origin. Deviations of all atoms from this plane are listed in Table 9. Some hydrogen atoms deviate

Table 5. Results of rigid-body motion analysis

(a) Description of the motion:

Components of the tensors and the unit vectors along their principal axes are referred to the inertial system defined below. Calculation is referred to the origin which symmetrizes \mathbf{S} and reduces the trace of \mathbf{T} (Schomaker & Trueblood, 1968). Coordinates of this origin, in the inertial system with its origin at the centre of mass, are: $q_i = 0.16$, $q_m = 0.07$, and $q_n = -0.13 \text{ \AA}$.

Tensor of inertia:	Eigenvalues			Eigenvectors*		
	533		l	8.737	-0.175	4.751
	1359		m	4.017	-1.844	-11.440
	1892		n	2.498	3.576	-5.668
Tensor elements $\times 10^5$ (e.s.d. $\times 10^5$)						
Tensor	11	22	33	12	23	13
L (rad ²)	247 (62)	95 (20)	264 (17)	-4 (18)	8 (19)	-14 (33)
T (Å ²)	3451 (119)	2488 (159)	2055 (220)	97 (114)	-151 (163)	-120 (132)
S (rad·Å)	55 (58)	-71 (42)	17 (72)	-18 (43)	-3 (17)	59 (26)
R.m.s. amplitudes						
	3.0°		-0.4969	0.0537	0.8662	
L	2.8		-0.8764	-0.0007	-0.4976	
	1.8		-0.0261	-0.9986	0.0469	
	0.186 Å		-0.9890	-0.1124	0.0960	
T	0.159		-0.1349	0.9517	-0.2757	
	0.141		-0.0604	-0.2856	-0.9564	
Principal axes						

(b) Vibration tensors $V_{ij}\dagger$ ($\times 10^4 \text{ \AA}^2$) referred to the inertial system:

		V_{11}	V_{12}	V_{13}	V_{22}	V_{23}	V_{33}
S(1)	(obs)	411	91	-14	260	0	363
	(calc)	428	91	-3	330	-39	354
S(2)	(obs)	386	-87	40	274	10	371
	(calc)	429	-58	5	301	-19	353
C(1)	(obs)	351	58	-60	277	-64	221
	(calc)	374	13	-5	251	-24	263
C(2)	(obs)	377	4	10	230	-26	254
	(calc)	346	7	-13	251	-17	205
C(3)	(obs)	333	-57	12	316	-37	211
	(calc)	362	-25	-14	309	-29	229
C(4)	(obs)	450	-35	-48	434	-112	265
	(calc)	466	-103	-12	351	-31	313
C(5)	(obs)	574	-264	31	565	17	410
	(calc)	498	-203	-10	539	-54	406
C(6)	(obs)	463	-48	-15	644	-53	425
	(calc)	395	-148	-14	722	-70	396
C(7)	(obs)	373	62	-56	735	-92	350
	(calc)	344	0	-15	639	-61	344
C(8)	(obs)	346	-46	4	347	-32	244
	(calc)	345	21	-13	410	-43	270
C(9)	(obs)	325	24	-9	326	-34	235
	(calc)	362	34	-14	285	-3	220
C(10)	(obs)	410	67	33	336	6	332
	(calc)	468	101	-16	320	11	299
C(11)	(obs)	558	175	-43	408	79	379
	(calc)	498	198	-17	483	23	378
C(12)	(obs)	382	137	-92	696	-6	347
	(calc)	396	153	-15	649	18	368
C(13)	(obs)	344	-26	50	615	14	318
	(calc)	344	14	-8	574	3	328
C(14)	(obs)	316	34	-15	319	-8	263
	(calc)	345	-3	-8	368	-4	260

* Referred to the reciprocal base vectors \mathbf{a}^* , \mathbf{b}^* and \mathbf{c}^* .

† Observed V_{ij} 's are formed from the U_{ij} 's by a method similar to that given by Cruickshank *et al.* (1961).

Table 6. *Intermolecular contact distances shorter than 3.7 Å (excluding hydrogen atoms)*

First-designated atom of each pair belongs to the reference molecule and has the coordinates *x*, *y*, *z* listed in Table 3.

		Symmetry operation applied to the second atom
C(5)—C(13)	3.566 Å	(1)
S(1)—C(3)	3.673	(2)
S(1)—C(8)	3.644	(2)
S(2)—C(9)	3.651	(2)
C(1)—C(2)	3.614	(2)
C(3)—C(4)	3.621	(2)
C(9)—C(10)	3.662	(2)
C(4)—C(8)	3.641	(3)
C(6)—C(7)	3.632	(3)
C(11)—C(13)	3.617	(3)
C(5)—C(7)	3.663	(3)
C(10)—C(14)	3.595	(3)
C(12)—C(13)	3.652	(3)
S(1)—S(1)	3.522	(4)
S(1)—C(1)	3.641	(4)
S(1)—S(2)	3.646	(5)

Key to symmetry operations:

(1)	$x-1, y, z$
(2)	$x, y-1, z$
(3)	$x, y+1, z$
(4)	$1-x, y-\frac{1}{2}, -z$
(5)	$1-x, \frac{1}{2}+y, -z$

from the best plane by possibly significant amounts, but their positions are not considered accurate enough to warrant an interpretation of these deviations.

Table 9. *Deviations of atoms from the best plane*

S(1)	-0.008 Å	C(7)	0.020 Å	H(4)	-0.18 Å
S(2)	0.005	C(8)	0.011	H(5)	-0.04
C(1)	-0.025	C(9)	-0.007	H(6)	0.18
C(2)	-0.019	C(10)	-0.013	H(7)	0.12
C(3)	-0.020	C(11)	-0.001	H(10)	-0.01
C(4)	-0.024	C(12)	0.014	H(11)	0.16
C(5)	0.006	C(13)	0.014	H(12)	-0.15
C(6)	0.031	C(14)	0.020	H(13)	0.23

The TNTN molecule appears to have an *mm2* symmetry (excluding hydrogen atoms) within experimental error. In fact, the difference between any two chemically equivalent bonds does not exceed 1.5 standard deviations of this difference. A similar result is obtained for the comparison of corresponding angles.

The distribution of the bond lengths, within the central part of the molecule, reflects the ability of divalent sulphur as a heteroatom to participate in conjugation. Thus, the C(1)—C(2) bond distance of 1.394 Å is much longer than that of a formal double bond (1.337 Å; *International Tables*, 1962*b*). The C(2)—C(3)

Table 7. *Bond lengths*

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

	Uncorrected	Corrected*		Uncorrected	Corrected*
C(1)—C(2)	1.391 (8) Å	1.394 Å	C(4)—C(5)	1.379 (9) Å	1.382 Å
S(1)—C(1)	1.725 (5)	1.729	C(5)—C(6)	1.367 (11)	1.370
S(2)—C(1)	1.723 (6)	1.727	C(6)—C(7)	1.376 (12)	1.378
S(1)—C(8)	1.751 (7)	1.754	C(7)—C(8)	1.404 (9)	1.406
S(2)—C(14)	1.758 (6)	1.762	C(9)—C(10)	1.410 (8)	1.413
C(2)—C(3)	1.433 (9)	1.435	C(10)—C(11)	1.368 (9)	1.370
C(2)—C(9)	1.429 (8)	1.432	C(11)—C(12)	1.369 (11)	1.371
C(3)—C(8)	1.410 (8)	1.413	C(12)—C(13)	1.399 (10)	1.402
C(9)—C(14)	1.413 (9)	1.415	C(13)—C(14)	1.409 (9)	1.412
C(3)—C(4)	1.394 (9)	1.397	C(10)—H(10)	1.05 (9)	
C(4)—H(4)	1.01 (8)		C(11)—H(11)	0.95 (8)	
C(5)—H(5)	0.95 (9)		C(12)—H(12)	1.11 (7)	
C(6)—H(6)	0.97 (8)		C(13)—H(13)	0.92 (10)	
C(7)—H(7)	0.94 (8)				

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

Table 8. *Bond angles and their standard deviations (excluding hydrogen atoms)*

S(1)—C(1)—S(2)	131.1 (0.4)°	C(3)—C(8)—S(1)	112.7 (0.4)°
S(1)—C(1)—C(2)	114.4 (0.4)	C(8)—S(1)—C(1)	89.9 (0.3)
C(1)—C(2)—C(3)	111.4 (0.5)	C(1)—S(2)—C(14)	89.8 (0.3)
C(1)—C(2)—C(9)	111.7 (0.5)	C(2)—C(1)—S(2)	114.5 (0.4)
C(2)—C(3)—C(4)	130.6 (0.5)	S(2)—C(14)—C(9)	112.7 (0.4)
C(2)—C(3)—C(8)	111.4 (0.5)	S(2)—C(14)—C(13)	124.8 (0.5)
C(3)—C(2)—C(9)	136.8 (0.6)	C(14)—C(9)—C(2)	111.3 (0.5)
C(3)—C(4)—C(5)	120.0 (0.6)	C(14)—C(9)—C(10)	117.7 (0.5)
C(4)—C(5)—C(6)	121.1 (0.8)	C(2)—C(9)—C(10)	131.0 (0.6)
C(5)—C(6)—C(7)	121.6 (0.7)	C(9)—C(10)—C(11)	120.0 (0.6)
C(6)—C(7)—C(8)	117.7 (0.6)	C(10)—C(11)—C(12)	121.4 (0.6)
C(7)—C(8)—C(3)	121.6 (0.6)	C(11)—C(12)—C(13)	122.2 (0.6)
C(7)—C(8)—S(1)	125.6 (0.5)	C(12)—C(13)—C(14)	116.2 (0.6)
C(8)—C(3)—C(4)	118.0 (0.5)	C(13)—C(14)—C(9)	122.5 (0.6)

and C(2)–C(9) bonds average out to 1.434 Å. This distance is much shorter than the lengths of the bonds that link both benzene rings in carbazole (1.467 Å; Lahiri, 1969) and in fluorene (1.482 Å; Burns & Iball, 1955). The sulphur–carbon bond distances in TNTN also indicate that these bonds have a partial double-bond character when compared with the single bond, C(*sp*²)–S(II) of 1.78 Å reported by several authors (*e.g.*, Hordvik & Sletten, 1966; Christie & Selinger, 1968). Their average values, 1.728 and 1.758 Å, compare well to 1.72 and 1.74 Å observed in thiophthene (Cox *et al.*, 1949). A similar distribution of bond lengths within the thiophene nucleus was also observed in the recently published structure of dibenzothiophene (Schaffrin & Trotter, 1970).

Lengths of the C–C bonds within the benzene rings are normal in the sense that such distances are usually observed in aromatic compounds. Note, however, that bond lengths within the rings increase gradually towards the central part of the molecule, thus leading to possibly significant differences (*e.g.* C(5)–C(6) and C(3)–C(8)).

The disparity of the S–C bonds found in TNTN and in thiophthene (Cox *et al.*, 1949) is also present, although to a lesser extent, in *trans*-β-2-thienylacrylic acid (Block, Filippakis & Schmidt, 1967) and in 2-formylthiophene thiosemicarbazone (Mathew & Palenik, 1969). The results of these two substituted thiophenes indicate, as pointed out in the relevant papers, a π delocalization due to the sulphur atom as well as to the substituent. In all these cases, the longer S–C bond is the one connecting sulphur to the carbon atom that seems to be more actively engaged in the π delocalization (*e.g.*, benzene carbon C(8) in TNTN and the substituted carbon in *trans*-β-2-thienylacrylic acid).

Bond distances in TNTN mentioned in the above discussion are corrected for librational motion. Corrections, however, do not exceed 0.004 Å (Table 7) and, hence, the uncorrected bond lengths would lead to the same interpretation of the bonding features.

Discussion of the molecular structure of TNTN is concluded with the results of a simple molecular orbital calculation (HMO–LCAO; Streitwieser, 1961). Following the results of a comprehensive study of related compounds (Zahradník, Párkányi, Horák & Koutecký, 1963; Zahradník & Párkányi, 1965), it was assumed that sulphur contributes only its 3*p* electrons to the π system. Values of Coulomb integrals (α) and exchange integrals (β) used in the calculations were:

$$\begin{aligned}\alpha_s &= \alpha_c + \beta_{C-C} \\ \alpha_{C(S)} &= \alpha_c + 0.1\beta_{C-C} \\ \beta_{C-S} &= 0.7\beta_{C-C}\end{aligned}$$

(Zahradník & Párkányi, 1965; Bossa, 1969). Here, the subscript C(S) denotes a carbon atom bonded to sulphur and α_c and β_{C–C} are the Coulomb and exchange integrals of a carbon atom and of a C–C bond respectively, within a benzene ring.

The molecular orbital calculation, employing the above parameters, was also performed for thiophene (Bak, Christensen, Rastrup-Andersen & Tannenbaum, 1956), thiophthene (Cox *et al.*, 1949) and thianthrene (Lynton & Cox, 1956; Rowe & Post, 1958), and a bond-order bond-length correlation curve was constructed from which the calculated C–S bond lengths were read off.

Overall agreement between observed and calculated bond lengths (Table 10), as well as the consistency in the bond-order and observed bond-length relationship,

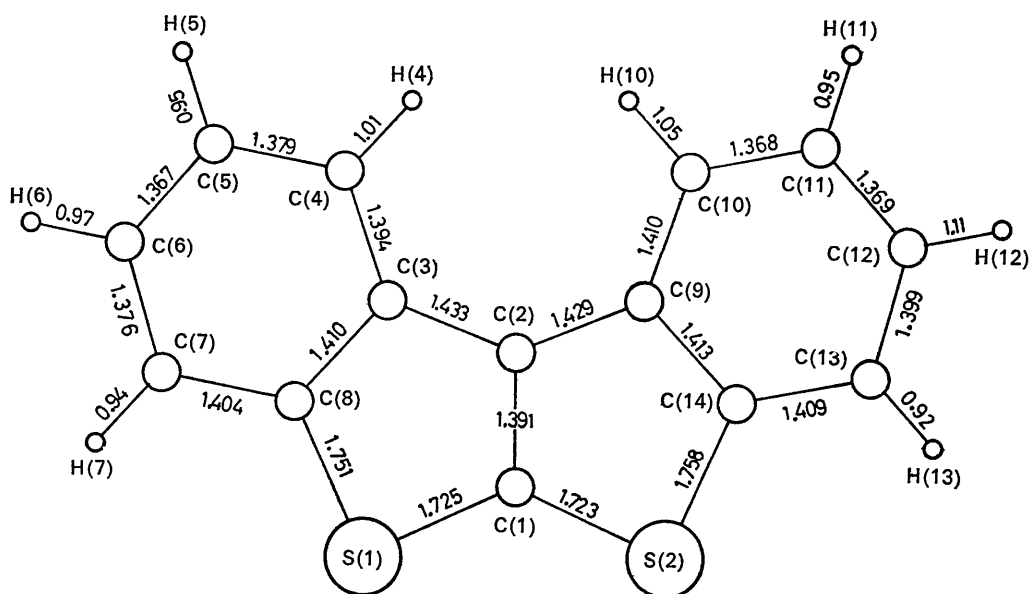


Fig. 6. Schematic drawing of TNTN molecule. Bond distances shown are not corrected for libration.

are satisfactory; indeed, they are much more satisfactory than expected in view of the approximations involved.

Table 10. *Results of the HMO calculation*

Observed bond lengths are given as average values of the corresponding equivalent bond pairs.

	Distance (corrected for libration)	Distance predicted from bond order	Bond order
S(1)-C(1)	1.728 Å	1.73 Å	0.405
S(1)-C(8)	1.758	1.74	0.358
C(1)-C(2)	1.394	1.393	0.689
C(2)-C(3)	1.434	1.438	0.438
C(3)-C(4)	1.405	1.410	0.595
C(4)-C(5)	1.376	1.392	0.695
C(5)-C(6)	1.371	1.402	0.637
C(6)-C(7)	1.390	1.394	0.686
C(7)-C(8)	1.409	1.405	0.625
C(8)-C(3)	1.414	1.414	0.574

A similar calculation that employed parameters based on the participation of the *d* orbitals of sulphur in the π system (Zahradník *et al.*, 1963) gave slightly different results. Although there is no general consensus regarding the more appropriate model to use in calculating the electronic structure of sulphur, recent studies (Bielefeld & Fitts, 1966; Bossa, 1969) indicate that the inclusion of *d* orbitals is of little importance if the bond orders are given rough calculations.

Computing

Most computer programs used in this work were obtained from the Department of Chemistry at the Weizmann Institute of Science, through the courtesy of Dr D. Rabinovich, and were adapted by the authors to the CDC 3400 computer at the Tel-Aviv University. Other programs were developed during this work. Their names, functions of the programs, and the names of their authors are listed below.

CELDIM, least-squares fit of cell dimensions, B. Kaufmann.

PRECPROC, intensity data processing, D. Rabinovich.

DATAP5, Lorentz, polarization and absorption corrections, Coppens, Leiserowitz & Rabinovich, 1965.

CROSWGHT, correlation of layer scale factors, D. Rabinovich & B. Kaufmann.

FOURSEC2 and *FOURCOMP*, Fourier syntheses, P. Coppens and U. Shmueli, respectively.

BDLS, least-squares refinement, successively modified by W. C. Hamilton, P. Coppens, F. L. Hirshfeld and D. Rabinovich from *ORFLS* (Busing & Levy, 1962).

ORTHO, calculations in the inertial system, F. L. Hirshfeld & D. Rabinovich.

DISTAN and *INDIS*, crystal and molecular geometry, P. Coppens modified by F. L. Hirshfeld and L. Leiserowitz respectively.

TMA, thermal-motion analysis, Shmueli, 1970.

SYMTEST, intensity statistics, U. Shmueli.

HUCKEL, molecular orbital calculations, I. Goldberg & U. Shmueli.

MOLPLT, drawings, B. Kaufmann.

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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,

* Presented at the meeting of the Israel Crystallography Society, Technion, Haifa, 7 April 1970 (Goldberg & Shmueli, 1970).