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Structure of the 1:1 complex of Trithia(5)heterohelicene* and 7,7,8,8-Tetracyano-*p*-quinodimethane

By M. Konno, Y. Saito, K. Yamada† and H. Kawazura†

The Institute for Solid State Physics, The University of Tokyo, Roppongi-7, Minato-ku, Tokyo 106, *Japan*

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Abstract. $C_{16}H_8S_3.C_{12}H_4N_4$, $M_r = 500{\cdot}6$, $C2/c$, $a = 21{\cdot}478\ (4)$, $b = 8{\cdot}548\ (3)$, $c = 13{\cdot}841\ (3)$ Å, $\beta = 114{\cdot}86\ (2)°$, $U = 2305{\cdot}7\ (7)$ Å^3, $D_m = 1{\cdot}448$, $D_x = 1{\cdot}442$ Mg m^{-3}, $Z = 4$, μ(Mo $K\alpha$) = 0·341 mm^{-1}. The structure was refined to an R value of 0·048 for 1543 observed reflections collected by X-ray diffractometry. Heterohelicene and TCNQ molecules are stacked alternately in infinite columns along **c**. The heterohelicene molecule is overcrowded. The bending between adjacent rings relieves the repulsion between H(8) and H(8′). Thus the molecule has a helical structure, the terminal five-membered rings being inclined at an angle of 29·6° to each other.

Introduction. Attention has been paid to the hexahelicene molecule as an inherently dissymmetric chromophore (Newman & Lednicer, 1956; Moscowitz, 1961). The CD and ORD spectra of heterohelicene molecules were quite different from those of the hexahelicene molecule (Groen & Wynberg, 1971). The present investigation was undertaken to throw some light on this phenomenon and to study the charge-transfer interaction between TCNQ and heterohelicene molecules. Crystals are greenish-black needles. Preliminary oscillation and Weissenberg photographs depicted a monoclinic lattice with systematic absences hkl with $h + k$ odd and $h0l$ with h, l odd, consistent with space groups $C2/c$ and Cc. A successful structure analysis was accomplished in $C2/c$. Intensity data were collected on an automated four-circle diffractometer using graphite-monochromated Mo $K\alpha$ radiation. The intensities of reflections with $2\theta \leq 55°$ were measured by means of the 2θ–ω scan technique. 1543 independent reflections with $|F| \geq 3\sigma$ were collected. Lorentz and polarization corrections were applied but no correction for absorption was made.

Sharpened Patterson maps gave the positions of three S atoms. Fourier maps phased by these atoms revealed the non-hydrogen atoms. After several refinements by block-diagonal least-squares methods, all the H atoms could be located. The final refinement was carried out by the full-matrix least-squares program *RADIEL* (Yang, Becker & Coppens, unpublished) with anisotropic temperature factors for non-hydrogen atoms and isotropic for H. The final R value was 0·048. The scattering factors of Stewart, Davidson & Simpson (1965) were used for H atoms and all other scattering factors were taken from *International Tables for X-ray Crystallography* (1974). The final atomic parameter shifts were all less than one tenth of the corresponding standard deviations. Final atomic parameters are listed in Table 1.‡

Discussion. Thermal ellipsoids of the non-hydrogen atoms of a heterohelicene molecule are shown in Fig. 1. The heterohelicene molecule possesses a crystallographic C_2 axis passing through the central S atom and the center of the C(14)–C(14′) bond. A planar configuration through the entire molecule is expected, owing to the conjugation of double and single bonds; however, the steric repulsion between the two terminal

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* IUPAC name: thieno[3,2-*e*:4,5-*e*′]bis(benzo[*b*]thiophene).

† Present address: Faculty of Pharmaceutical Sciences, Josai University, Sakado, Saitama 350-02, Japan.

‡ Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35159 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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five-membered rings (III) and (III′) severely distorts the molecule to form a helical structure. Equations of the least-squares planes for each ring and deviations of the atoms from them are given in Fig. 1 and Table 2. Nonbonded short contacts in the inner core occur between H(8)···H(8′), C(8)···H(8′) and C(8)···C(8′) with distances of 2·06 (4), 2·62 (2) and 3·246 (6) Å respectively. These are considerably shorter than the sum of the van der Waals radii of about 1·8 and 1·2 Å for C and H atoms. Moreover, H(7) and H(8) show extraordinary displacements of 0·08 (3) and 0·07 (3) Å from plane (III) owing to the steric hindrance. However, individual five- and six-membered rings have fairly good planarity in order to retain the aromatic character within each ring. Considerable bending between adjacent rings seems to release molecular strain. The terminal five-membered rings are inclined at an angle of 29·6° to each other. The six-membered ring is characterized as having a boat conformation with bending of C(14) and C(11) in the same direction from the plane through the other four atoms. The torsion angles around the inner core reflect the pitch of the helix and are 17·9 (3) and 9·0 (3)° around the central C(14)–C(14′) and C(14)–C(9) bonds respectively. A similar helical shape is observed in benzo[*d*]naphtho[1,2-*d*′]benzo[1,2-*b*:4,3-*b*′]dithiophene (Stulen & Visser, 1969), where the torsion angles range from 6·5 to 21·5°.

Bond distances and angles of the heterohelicene and TCNQ moelcules are shown in Fig. 2. The S–C bond distance of the central five-membered ring is in good agreement with the value of 1·740 Å observed in dibenzothiophene (Schaffrin & Trotter, 1970). However, S–C bond distances of the terminal five-membered ring are significantly shorter and may be

Table 1. *Fractional atomic coordinates* (×10⁴, *for* H ×10³) *and equivalent isotropic temperature factors with e.s.d.'s in parentheses*

	x	y	z	U_{eq} (Å^2 × 10^3)
S(1)	0000	−3394 (2)	2500	83 (1)
S(2)	2063 (1)	1995 (2)	3357 (1)	76 (1)
N(1)	2303 (2)	704 (4)	714 (3)	84 (2)
N(2)	1073 (2)	4900 (4)	493 (3)	89 (2)
C(1)	577 (2)	971 (4)	195 (2)	45 (2)
C(2)	626 (2)	−714 (4)	171 (2)	47 (2)
C(3)	−84 (2)	1627 (4)	15 (2)	49 (2)
C(4)	1137 (2)	1899 (4)	389 (2)	51 (2)
C(5)	1791 (2)	1249 (4)	569 (3)	62 (2)
C(6)	1101 (2)	3579 (4)	442 (3)	63 (2)
C(7)	1425 (2)	3148 (4)	3416 (3)	66 (2)
C(8)	830 (2)	2388 (4)	3145 (3)	55 (2)
C(9)	854 (2)	783 (4)	2874 (2)	49 (2)
C(10)	1517 (2)	393 (4)	2976 (3)	61 (2)
C(11)	1712 (2)	−1138 (5)	2864 (3)	76 (2)
C(12)	1264 (2)	−2318 (4)	2705 (3)	80 (2)
C(13)	608 (2)	−1976 (4)	2611 (3)	64 (2)
C(14)	362 (2)	−439 (3)	2602 (2)	50 (2)
H(2)	106 (1)	−122 (3)	33 (2)	51 (9)
H(3)	−14 (1)	270 (3)	−4 (2)	54 (9)
H(7)	152 (1)	415 (3)	367 (2)	42 (8)
H(8)	45 (1)	284 (3)	318 (2)	46 (8)
H(11)	215 (2)	−127 (4)	291 (2)	67 (10)
H(12)	141 (2)	−341 (5)	266 (3)	105 (14)

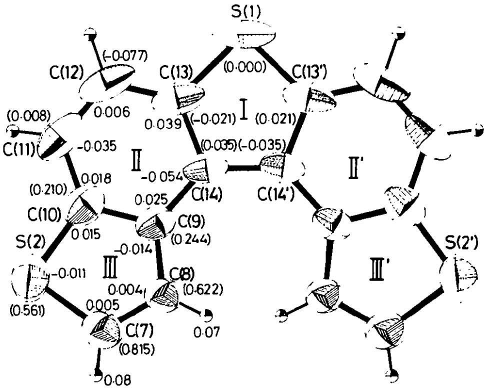

Fig. 1. An *ORTEP* plot (Johnson, 1965) of the thermal ellipsoids at 50% probability for a heterohelicene molecule. Numbers in parentheses are atomic displacements from plane (I); other numbers are displacements from planes (II) and (III). Mean e.s.d.'s of atomic shifts from planes (I), (II) and (III) are 0·013, 0·015 and 0·005 Å respectively. The atoms marked with a prime are related to those without a prime by a twofold axis.

Table 2. *Least-squares planes of the heterohelicene and quinodimethane moieties and deviations of the atoms from the planes*

The equation for a plane is in the form $AX + BY + CZ + D = 0$, where X, Y, Z and D are in Å relative to orthogonal axes a, b and c^*. Asterisks indicate atoms included in the calculations of the planes.

Plane (I): central five-membered ring

$$0\cdot1283X + 0\cdot0003Y - 0\cdot9917Z + 3\cdot3009 = 0\cdot0$$

Plane (II): six-membered ring

$$0\cdot1358X + 0\cdot1165Y - 0\cdot9839Z + 3\cdot4131 = 0\cdot0$$

Plane (III): terminal five-membered ring

$$0\cdot1403X + 0\cdot2553Y - 0\cdot9566Z + 3\cdot2604 = 0\cdot0$$

Plane (IV): quinodimethane moiety

$$-0\cdot1879X - 0\cdot0382Y + 0\cdot9815Z = 0\cdot0$$

Deviations (Å) of atoms from plane (IV)

C(1)*	−0·003 (3)	S(1)	3·465 (2)	S(2′)	2·973 (2)
C(2)*	0·001 (3)	S(2)	3·607 (2)	C(7′)	2·599 (4)
C(3)*	0·001 (3)	C(7)	3·905 (4)	C(8′)	2·746 (4)
C(4)*	0·001 (3)	C(8)	3·808 (4)	C(9′)	3·186 (3)
C(5)	−0·000 (4)	C(9)	3·473 (3)	C(10′)	3·315 (4)
C(6)	0·032 (4)	C(10)	3·369 (4)	C(11′)	3·595 (4)
N(1)	0·005 (4)	C(11)	3·189 (4)	C(12′)	3·665 (4)
N(2)	0·069 (4)	C(12)	3·196 (4)	C(13′)	3·515 (4)
C(13)	3·323 (4)	C(14)	3·360 (3)	C(14′)	3·378 (3)

Dihedral angles between planes (°)

(I)–(II)	6·7	(II)–(III′)	21·5	(IV)–(III)	12·8
(I)–(III)	14·8	(III)–(III′)	29·6	(IV)–(II′)	9·3
(II)–(III)	8·1	(IV)–(I)	4·1	(IV)–(III′)	17·2
(II)–(II′)	13·4	(IV)–(II)	5·4		

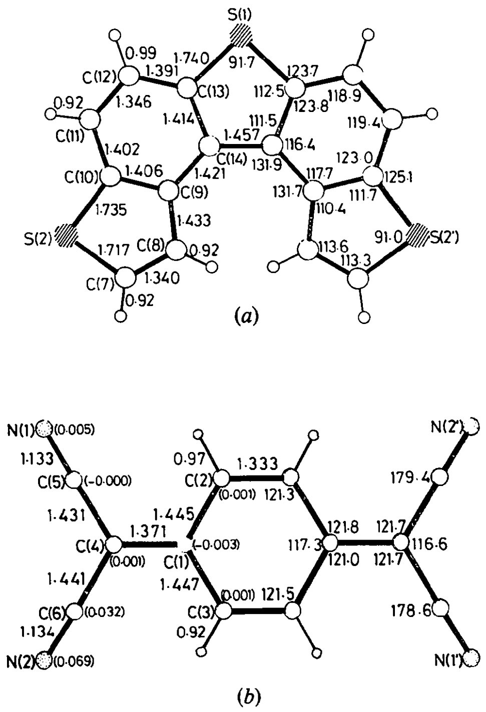

Fig. 2. Bond distances (Å) and angles (°). (*a*) Heterohelicene molecule. (*b*) TCNQ molecule. Numbers in parentheses are the atomic displacements from plane (IV) through the quinodimethane moiety. The e.s.d.'s are 0·004 Å for S–C bonds, 0·004–0·007 Å for C–C and C–N bonds, 0·03–0·04 Å for C–H bonds, 0·02° for bond angles involving S atoms, and 0·03–0·04° for all other angles.

compared with that of 1·718 Å observed in the thiophene molecule (Harshbarger & Bauer, 1970). The C–C bond distances of the inner core are longer than those reported in dibenzothiophene, which has a small deviation, as a whole, from the mean molecular plane. The C(9)–C(14) bond distance in the inner core is the longest within the six-membered ring. In contrast, the outermost C–C bond, C(11)–C(12), parallel to the former, is the shortest among those. These features appear to be due to the steric hindrance between terminal rings, and similar trends were observed in the crystals of hexahelicene derivatives (Lightner, Hefelfinger, Powers, Frank & Trueblood, 1972; Frank, Hefelfinger & Lightner, 1973). The bond angles C(14')C(14)C(9) and C(14)C(9)C(8) in the inner core are 131·9 and 131·7° and are larger than the corresponding angles of 123·7 and 125·1° in the periphery. Bond distances of the TCNQ moiety seem to be close to the values expected for a non-ionic TCNQ molecule. Figs. 3 and 4 show projections of the structure along **b** and **c**. TCNQ and heterohelicene molecules are stacked alternately, plane-to-plane along **c**. As shown in Table 2, the inclination between the heterohelicene molecule and the quinodimethane moiety is large due to the helical shape of the former. However, there is direct overlap between the four fused rings of the heterohelicene molecule and the TCNQ molecule. The mean interplanar distance between them is 3·388 Å, not involving C(7) and C(8) which have unusually large deviations from the plane of the TCNQ molecule. The measurements of the absorption spectra indicated that a π–π charge-transfer interaction between these molecules is predominant (Yamada,

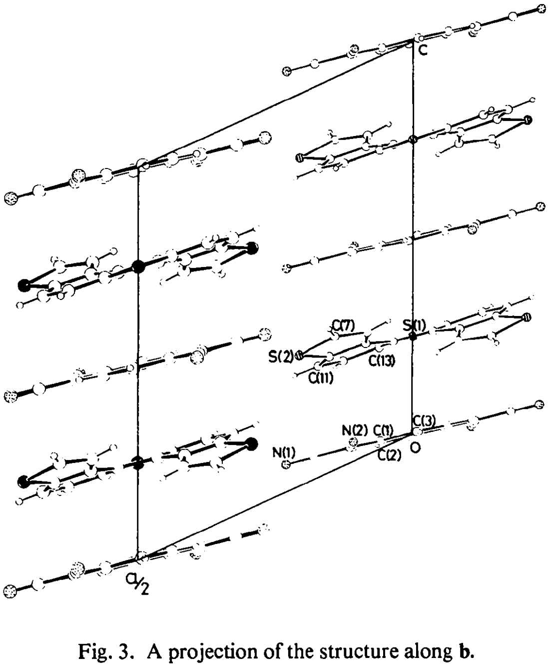

Fig. 3. A projection of the structure along **b**.

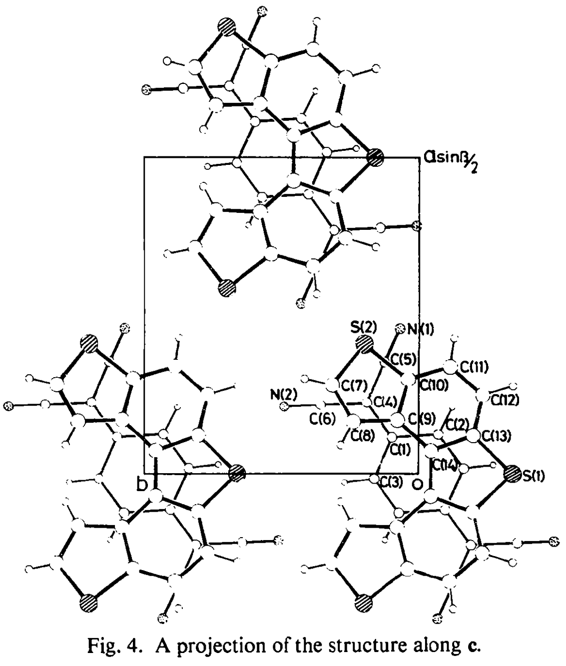

Fig. 4. A projection of the structure along **c**.

Yamada & Kawazura, 1978). Among adjacent columns, short contacts are found between S(2) and C(7) of the original unit and N(1'), shifted by (**a** + **b**)/2, at distances of 3·477 (4) and 3·305 (4) Å respectively.

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Structure of 5,5,5',5'-Tetramethyl-2,2'-bi-1,3,2λ^5-dioxaphosphorinane 2,2'-Disulphide

BY JANINA KAROLAK-WOJCIECHOWSKA, MICHAŁ WIECZOREK AND ZDZISŁAW GAŁDECKI

Institute of General Chemistry, Technical University of Łódź, Żwirki 36, 90-924 *Łódź, Poland*

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Abstract. $C_{10}H_{20}O_4P_2S_2$, monoclinic, $C2/m$, a = 11·861 (12), b = 8·765 (8), c = 7·685 (5) Å, β = 81·05 (10)°, Z = 2, $F(000)$ = 348. The dioxaphosphorinane rings adopt a chair conformation. The P=S bond of 1·903 (1) Å is equatorial. The P–P bond is 2·182 (2) Å. The molecule has a centre of symmetry at the middle of this bond and a mirror plane which is perpendicular to **b**.

Introduction. The present determination continues investigations on the crystal and molecular structure of derivatives with a 1,3,2-dioxaphosphorinane ring (Cameron, Gałdecki & Karolak-Wojciechowska, 1976; Cameron & Karolak-Wojciechowska, 1977). The title compound was prepared by Stec & Zwierzak (1967); it crystallizes in two different crystal forms (Gałdecki & Karolak-Wojciechowska, 1971). In this paper we report the crystal and molecular structure of one of these crystalline forms. The crystal system and approximate cell dimensions were determined from Weissenberg photographs. 663 unique reflections were measured on a Picker FACS-1 four-circle diffractometer. 617 reflections with $I > 2\sigma(I)$ were employed in the analysis. The data were corrected for Lorentz–polarization effects, but not for absorption.

Systematic absences hkl with $h + k = 2n$ indicate space groups $C2/m$, Cm or $C2$. A centrosymmetric structure was suggested by normalized structure factor statistics. The molecules occupy special positions and must be on a mirror plane and twofold axis. The structure was solved with *MULTAN* 74 (Main, Woolfson, Lessinger, Germain & Declercq, 1974) which was applied to 196 reflections with $|E| > 1·20$. The P and S atoms were located from the E map based on the phases obtained. All atoms other than H were located from the difference synthesis with phases based on these two atoms.

The atomic positions were refined by a full-matrix least-squares method, with anisotropic temperature factors for non-hydrogen atoms, until R dropped to 0·10. A difference synthesis then revealed all the H atoms. Refinement was continued with H atoms included with isotropic temperature factors. For the 617 observed reflections the final R = 0·074 and $R_w = (\sum w^{1/2}\Delta/\sum w^{1/2}|F_o|)$ = 0·089. The weighting function $w = 1/[\sigma^2(F) + 0·0366F^2]$ was applied. The final parameters are listed in Tables 1 and 2.*

Discussion. Bond lengths and angles are shown in Table 3. Fig. 1 displays the atom labelling. The packing of the molecules is shown in Fig. 2.

The 1,3,2-dioxaphosphorinane rings adopt the chair conformation with torsion angles O(12)–P–O(11)–C(11) – 24·8 (2), P–O(11)–C(11)–C(12) –

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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 35062 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.