The Crystal and Molecular Structure of 12-Ethoxy-2,3-benzo-6,5-naphtho[b]-[7,12]-thiaphosphorin-7,7,12-trioxide*

By N. N. Dhaneshwar, A. G. Kulkarni,† S. S. Tavale and L. M. Pant

National Chemical Laboratory, Poona, India

Crystals of 12-ethoxy-2,3-benzo-6,5-naphtho[b] [7,12]-thiaphosphorin-7,7,12-trioxide, $C_{18}H_{15}O_4SP$, are monoclinic, space group $P2_1/n$ with $a = 14\cdot71 \pm 0\cdot01$, $b = 8\cdot07 \pm 0\cdot02$, $c = 14\cdot30 \pm 0\cdot01$ Å; $\beta = 94\cdot0 \pm 0\cdot2°$; $\varrho_o = 1\cdot406$ g cm^{-3}, ϱ_c (for $Z = 4$) $= 1\cdot405$ g cm^{-3}. The structure was solved by direct methods using visually estimated data, and refined by the least-squares method to an R value of 0·115 for 1906 observed reflexions. The e.s.d.'s in bond lengths not involving hydrogen atoms are 0·006–0·020 Å and in bond angles, 0·4–1·1°. The dihedral angle between the plane of the naphthalene ring and that of the benzene ring on either side of the sulphur and phosphorus atoms is 133·8°; P lies in the naphthalene plane and S is 0·153 Å out of it, whereas S lies in the benzene plane and P is 0·159 Å out of it. The S=O and S–C bonds around S have a slightly distorted tetrahedral configuration suggesting greater s character of S=O bonds than of S–C bonds; the distortion in tetrahedral configuration around P is more severe. The ethyl group undergoes large anisotropic thermal vibrations owing to loose van der Waals contacts with atoms of neighbouring molecules.

Introduction

In recent years, the structure analyses of phenothiazine (Bell, Blount, Briscoe & Freeman, 1968) and a number of its derivatives such as chlorpromazine (McDowell, 1969) have been reported. These compounds are known to be biologically active and many of them have found commercial use as drugs. In their search for similar new biologically active systems, Tilak and coworkers have synthesized the phosphorus analogues of these compounds (Acharekar, Gogte & Tilak, 1972). In this paper, the structure analysis of one of these compounds, 12-ethoxy-2,3-benzo-6,5-naphtho[b] [7,12]-thiaphosphorin-7,7,12-trioxide, is reported; its structural formula is given below.
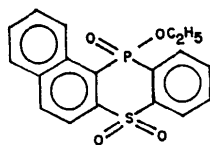
Experimental

The crystals, grown from aqueous alcohol, are monoclinic, space group $P2_1/n$ with $a = 14\cdot71 \pm 0\cdot01$, $b = 8\cdot07 \pm 0\cdot02$, $c = 14\cdot30 \pm 0\cdot01$ Å; $\beta = 94\cdot0 \pm 0\cdot2°$; $\varrho_o = 1\cdot406$ g cm^{-3}, ϱ_c (for $Z = 4$) $= 1\cdot405$ g cm^{-3}. Axial lengths were measured with the help of high-angle reflexions in

---

zero-layer Weissenberg photographs with the films mounted in the Straumanis arrangement; β was determined by the method of triangulation (Jeffery, 1971). Data were collected with unfiltered Cu radiation from zero to seventh-layer Weissenberg photographs about the b axis and from zero to third-layer photographs about the [101] axis; the crystals used for the two sets of photographs had cross-sections 0·4 × 0·7 and 0·4 × 0·8 mm² respectively. The data were processed in the usual way (Takwale & Pant, 1971); absorption was neglected.

Determination and refinement of the structure

Normalized values of about 250 structure factors were used in the Sayre-equation program written by Long (1965); the set of signs corresponding to the highest consistency index (0·89) was used to obtain a three-dimensional Fourier map. This map revealed two half-molecules fairly clearly. However, the refinement of the structure on the basis of two half-molecules stopped at an R value of about 0·37 and there were some serious discrepancies between F_o and F_c. It was soon apparent that the signs of F's used to obtain the Fourier map were with respect to a false centre of symmetry and therefore gave an approximate structure along with its inverted image in the map. On shifting the origin to the correct centre of symmetry, the structure refined normally. A comparison of the signs of F_c on the completion of the structure analysis with the various sets of signs obtained from the Sayre-equation program showed that the set corresponding to the next highest consistency index (0·84) was the correct one. The refinement was carried out by the block-diagonal least-squares method; in the later stages, hydrogen atoms were included and anisotropic temperature factors

Table 1. *Final atomic and thermal parameters and their estimated standard deviations* (*in parentheses*)

Anisotropic thermal parameters are of the form $T = \exp[-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + 2b_{12}hk + 2b_{23}kl + 2b_{13}hl)]$.

(*a*) Non-hydrogen atoms ($\times 10^4$)

	x	y	z	b_{11}	b_{22}	b_{33}	b_{12}	b_{23}	b_{13}
C(1)	3283 (5)	673 (10)	−503 (5)	43 (4)	91 (13)	35 (4)	−9 (6)	4 (5)	2 (3)
C(2)	3872 (6)	1424 (12)	−1103 (6)	50 (5)	176 (18)	40 (4)	−21 (8)	25 (7)	3 (3)
C(3)	4618 (6)	2292 (12)	−707 (6)	43 (5)	143 (17)	60 (5)	−18 (7)	12 (7)	19 (4)
C(4)	4795 (6)	2383 (11)	254 (7)	29 (4)	116 (15)	73 (6)	−3 (6)	−12 (7)	4 (3)
C(5)	4224 (5)	1555 (11)	866 (6)	32 (4)	124 (15)	47 (4)	6 (6)	−20 (6)	−3 (3)
C(6)	3441 (5)	713 (10)	468 (5)	41 (4)	118 (14)	34 (4)	4 (6)	2 (6)	−2 (3)
C(7)	4449 (7)	1648 (13)	1842 (7)	46 (5)	226 (22)	49 (5)	1 (8)	−42 (8)	−7 (4)
C(8)	5211 (7)	2529 (16)	2191 (8)	49 (5)	275 (26)	74 (7)	10 (10)	−79 (11)	−3 (5)
C(9)	5745 (7)	3343 (14)	1591 (8)	42 (5)	222 (24)	92 (8)	−13 (9)	−71 (11)	−6 (5)
C(10)	5554 (6)	3285 (13)	628 (9)	34 (4)	164 (20)	106 (9)	−11 (8)	−27 (10)	5 (5)
C(11)	2311 (6)	−2160 (10)	497 (6)	47 (4)	82 (13)	45 (4)	7 (6)	6 (6)	10 (3)
C(12)	2189 (6)	−2124 (10)	−483 (6)	35 (4)	99 (14)	55 (5)	6 (6)	7 (6)	−4 (3)
C(13)	2007 (7)	−3564 (11)	−994 (6)	65 (5)	113 (15)	44 (4)	2 (7)	−30 (6)	−13 (4)
C(14)	1914 (8)	−5021 (13)	−531 (8)	71 (7)	127 (18)	86 (7)	−19 (9)	−8 (9)	−1 (5)
C(15)	2025 (8)	−5092 (12)	410 (9)	72 (7)	91 (17)	107 (9)	0 (8)	31 (9)	21 (6)
C(16)	2228 (7)	−3675 (11)	943 (6)	64 (6)	117 (15)	46 (5)	9 (8)	13 (6)	17 (4)
C(17)	1003 (8)	404 (17)	1530 (11)	65 (7)	241 (29)	133 (11)	−8 (12)	6 (14)	49 (7)
C(18)	380 (8)	1790 (17)	1532 (13)	43 (6)	239 (30)	183 (15)	−18 (11)	−52 (16)	26 (7)
O(1)	3035 (5)	−909 (9)	2108 (4)	83 (5)	222 (14)	29 (3)	−9 (7)	15 (5)	−4 (3)
O(2)	1859 (4)	872 (7)	1161 (4)	48 (3)	82 (9)	62 (4)	4 (4)	−8 (4)	25 (3)
O(3)	2518 (5)	−609 (9)	−2029 (4)	70 (4)	213 (14)	26 (3)	−6 (6)	1 (5)	−8 (2)
O(4)	1536 (4)	800 (8)	−946 (4)	52 (3)	126 (11)	59 (4)	13 (5)	16 (5)	−11 (3)
S	2305 (1)	−236 (3)	−1088 (1)	47 (1)	106 (3)	31 (1)	−10 (2)	11 (1)	−8 (1)
P	2670 (1)	−384 (3)	1180 (1)	47 (1)	102 (4)	30 (1)	−1 (2)	0 (1)	8 (1)

Table 1 (*cont.*)

(*b*) Hydrogen atoms ($\times 10^3$)

	x	y	z
H(2)	367 (7)	140 (14)	−180 (7)
H(3)	508 (7)	276 (14)	−111 (7)
H(7)	405 (7)	100 (15)	225 (8)
H(8)	538 (9)	267 (17)	287 (8)
H(9)	637 (8)	408 (16)	173 (8)
H(10)	593 (8)	404 (15)	9 (9)
H(13)	189 (8)	−357 (13)	−168 (7)
H(14)	171 (9)	−589 (14)	−89 (8)
H(15)	203 (8)	−599 (14)	76 (9)
H(16)	221 (8)	−379 (14)	160 (7)
H(17)	113 (9)	−2 (18)	193 (10)
H'(17)	70 (9)	−58 (17)	111 (10)
H(18)	70 (9)	284 (18)	173 (11)
H'(18)	−30 (9)	141 (17)	178 (11)
H''(18)	31 (9)	201 (18)	96 (11)

were introduced, and the refinement continued with Cruickshank's weighting scheme. Final R is 0·115 for 1906 observed reflexions.* The final atomic and thermal parameters along with their e.s.d.'s (obtained from the diagonal terms of the least-squares inverse matrices) are given in Table 1.

The intramolecular bond lengths and angles are shown in Fig. 1, and the equations of the planes referred to the a',b,c orthogonal axes are given in

---

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30740 (19 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. *Equations of planes*

(1) Naphthalene ring

$$-0·5553X' + 0·8279Y + 0·0792Z' = -2·3305 \text{ Å}$$

(2) Benzene ring

$$0·9781X' - 0·1676Y - 0·1234Z' = 3·5509 \text{ Å}$$

Dihedral angle between the naphthalene ring plane and the benzene plane is 133·8°.

Deviations of atoms from planes (Å)

	(1)	(2)
C(1)	0·022	
C(2)	−0·029	
C(3)	−0·018	
C(4)	0·005	
C(5)	−0·009	
C(6)	0·028	
C(7)	−0·021	
C(8)	−0·020	
C(9)	0·016	
C(10)	0·026	
C(11)		0·000
C(12)		−0·009
C(13)		0·012
C(14)		−0·007
C(15)		−0·002
C(16)		0·006
S	0·153	0·010
P	0·010	0·159
H(2)	0·045	
H(3)	−0·129	
H(7)	−0·084	
H(8)	0·011	
H(9)	0·013	
H(10)	0·160	
H(13)		−0·032
H(14)		−0·124
H(15)		0·057
H(16)		−0·120

Table 2 along with the angle between them and the deviations of the atoms from these planes.

Description of the structure and discussion

The central ring of the molecule is in a boat conformation; the molecule is folded about the line through the sulphur and phosphorus atoms. The dihedral angle between the least-squares planes of the naphthalene ring and the benzene ring on either side of the S and P atoms is 133·8°; P lies in the naphthalene plane and S is 0·153 Å away from it, whereas S lies in the benzene plane and P is 0·159 Å away from it (Table 2).

The bond lengths and angles around the sulphur atom agree well with those in other similar structures cited by Chu & Chung (1973) in Table 4 of their paper. The C–S–C bond angle is 103·3° while the O–S–O angle is 118·7°; the other four angles around the sulphur atom are near the tetrahedral value within about 2°; a similar situation is found in the structure of 9-isobutylthioxanthene-10,10-dioxide (Chu & Chung, 1973); these bond angles probably imply more s character in the two S–O bonds than in the two S–C bonds (P. M. Nair; personal discussion).

The C–P–C angle is 104·9° whereas the O–P–O angle is 115·9°. The contraction of the C–P–C angle and the expansion of the O–P–O angle from the tetrahedral value is similar to the contraction of the C–S–C angle and expansion of the O–S–O angle, though these changes are smaller in magnitude. However, some other angles around the phosphorus also deviate appreciably from the tetrahedral value.

The packing of the molecules in the crystal is shown in Fig. 2. The ethyl group undergoes large anisotropic thermal vibrations owing to loose coupling with atoms of the neighbouring molecules; consequently, the observed dimensions of the ethyl group have larger errors; in particular, the positions of the hydrogen atoms attached to C(17) and C(18) are rather uncertain. The disposition of the ethyl group with respect to the rest of the molecule seems to be governed by the non-bonded interactions between atoms C(17) and O(1), and C(17) and C(11); these distances are 3·22 and 3·25 Å respectively.

C(1)–S–O(4) 108·5(4)°
C(12)–S–O(3) 108·3(4)°
C(6)–P–O(2) 100·2(4)°
C(11)–P–O(1) 109·7(4)°

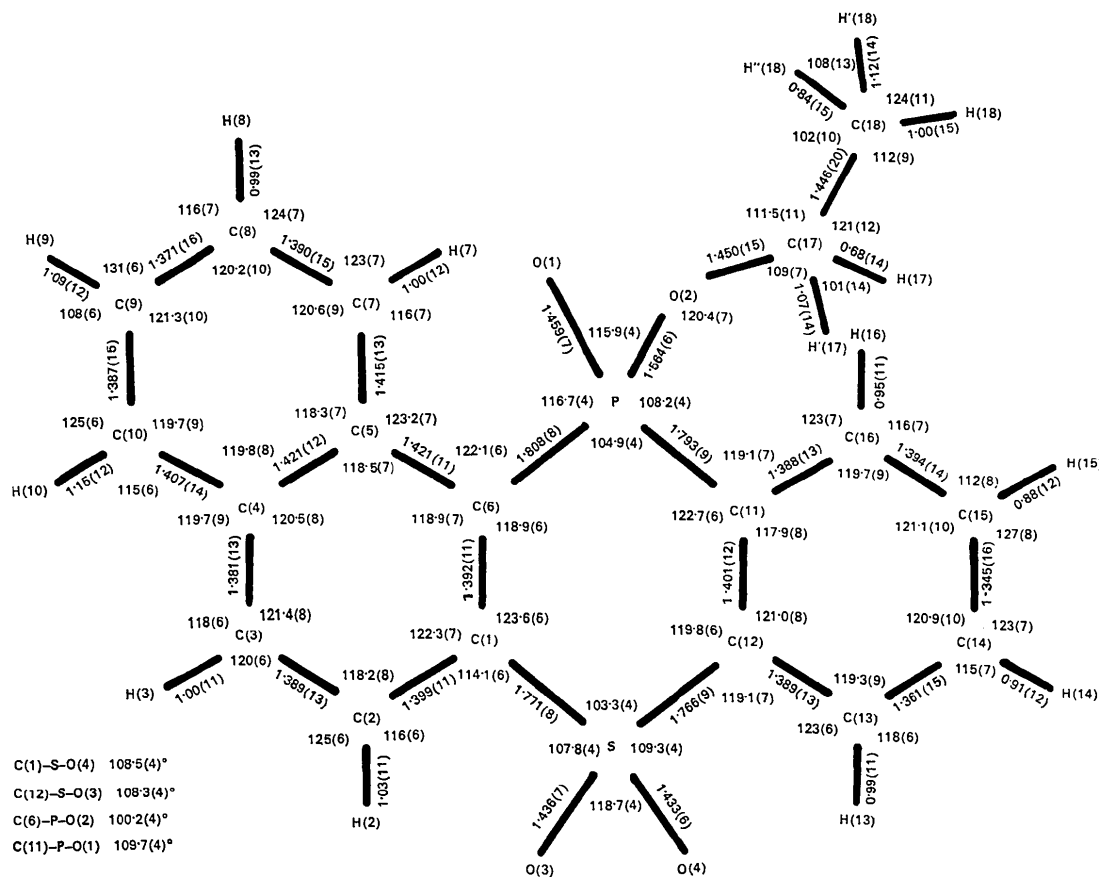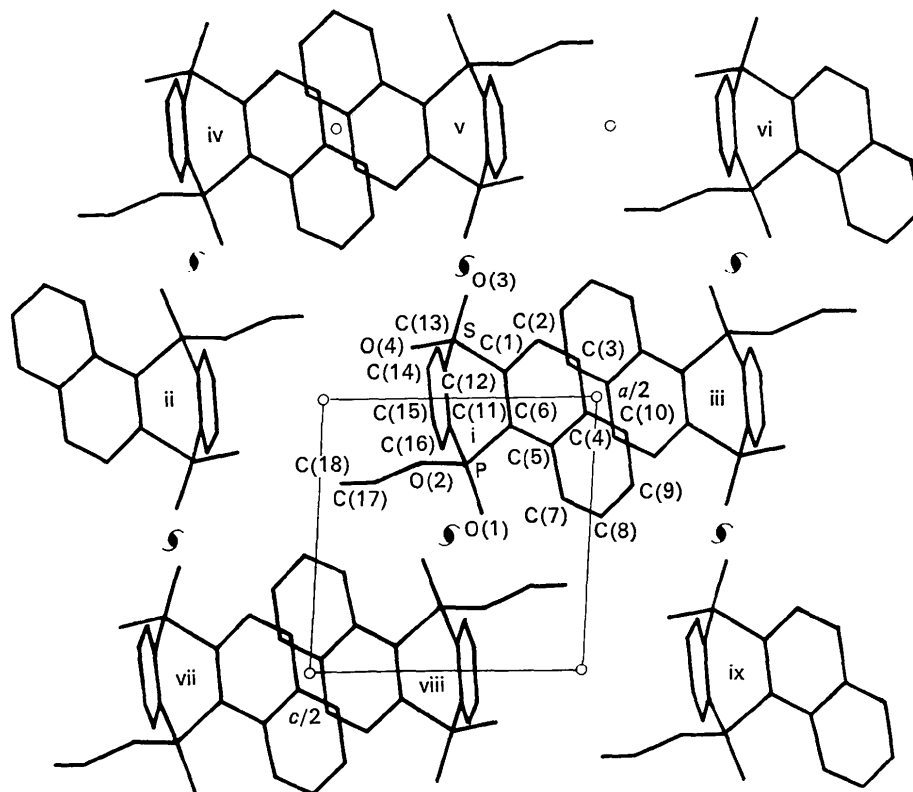Fig. 1. Bond lengths (Å) and angles (°) along with e.s.d.'s (in parentheses).

Fig. 2. Structure projected on (010). Symmetry code: i x,y,z; ii $\bar{x},\bar{y},\bar{z}$; iii $1-x,\bar{y},\bar{z}$; iv $x-\frac{1}{2},\frac{1}{2}-y,z-\frac{1}{2}$; v $\frac{1}{2}-x,\frac{1}{2}+y,-\frac{1}{2}-z$; vi $\frac{1}{2}+x,\frac{1}{2}-y,z-\frac{1}{2}$; vii $x-\frac{1}{2},\frac{1}{2}-y,\frac{1}{2}+z$; viii $\frac{1}{2}-x,\frac{1}{2}+y,\frac{1}{2}-z$; ix $\frac{1}{2}+x,\frac{1}{2}-y,\frac{1}{2}+z$. The marks on the scale represent 0, 0·5, and 1 Å.

with the compound and for their kind interest in this work. Our sincere thanks are also due to Dr P. M. Nair for valuable discussions of the theoretical chemical aspects of the structure.

References

ACHAREKAR, A. R., GOGTE, V. N. & TILAK, B. D. (1972). *Indian J. Chem.* **10**, 129–132.

BELL, J. D., BLOUNT, J. F., BRISCOE, O. V. & FREEMAN, H. C. (1968). *J. Chem. Soc.* (*D*), pp. 1656–1657.

CHU, S. S. C. & CHUNG, B. (1973). *Acta Cryst.* **B29**, 2253–2259.

JEFFERY, J. W. (1971). *Methods in X-ray Crystallography*, p. 173. London, New York: Academic Press.

LONG, R. E. (1965). UCLA Dissertation, Parts II and III.

McDOWELL, J. J. H. (1969). *Acta Cryst.* **B25**, 2175–2181.

TAKWALE, M. G. & PANT, L. M. (1971). *Acta Cryst.* **B27**, 1152–1158.