Structure of Azuleno[1,2-*b*]thiophene

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Abstract. $C_{12}H_8S$, m.p. 375–376 K, orthorhombic, *Pnma*, $a = 7.954$ (2), $b = 19.194$ (5), $c = 6.021$ (2) Å, $D_m = 1.33$, $D_x = 1.332$ Mg m^{-3}, $Z = 4$. Final $R = 0.105$ for 504 reflexions. The molecules form a sheet parallel to (010). The sheets are stacked along **b**. The structure is disordered as in azulene. The molecule is planar within 0.06 (2) Å. The bond-length alternation in the seven-membered ring is significant, the shortest C–C length being 1.27 (2) Å between positions 5 and 6 [C(7)–C(8)], and the longest 1.58 (2) Å between 4a and 9a [C(11)–C(12)].

Introduction. For benz[*a*]azulene (1) the bond-length alternation in the seven-membered ring has been indicated to be characteristic of polyenes by the analysis of the NMR spectra (Bertelli & Crews, 1970). The title compound (2) is a novel azulenoid heterocyclic compound considered to form a 14π-electronic system, as does (1) (Fujimori, Fujita, Yamane, Yasunami & Takase, 1980). The NMR vicinal coupling constants indicate that the degree of the bond-length alternation of (2) is smaller than that of (1), but larger than that of azuleno[1,2-*b*]furans, depending on the aromaticity of the fused ring attached to the azulene ring (Fujimori, Fukazawa, Yamane, Yasunami & Takase, 1981). In this connexion, it is desirable to determine the molecular structures of these compounds by X-ray crystallography.

Crystals of (2) were obtained from a hexane solution as thin green plates with {010} developed faces, and bounded by {201} and {001}. Systematic absences were 0*kl* for *k* + *l* odd and *hk*0 for *h* odd, indicating the space group to be *Pn*2₁*a* or *Pnma*. During the analysis *Pn*2₁*a* was ruled out.

Since the crystals sublimed gradually, a specimen of dimensions 0.23 × 0.05 × 0.50 mm was coated with an adhesive agent (Cemedaine) and mounted on a Rigaku four-circle diffractometer. The intensities were measured up to $2\theta = 120°$ with the ω–2θ scan method [scan speed 4° min^{-1} in 2θ; scan range (°) in 2θ:

$1.2 + 0.15 \tan \theta$] using Ni-filtered Cu radiation ($\lambda = 1.5418$ Å) at 40 kV and 200 mA. Background was measured for 5 s on either side of the peak. Three reference reflexions showed no intensity deterioration. The intensities were corrected for Lorentz and polarization factors, but not for absorption [μ(Cu $K\alpha$) = 2.59 mm^{-1}]. In total 587 independent reflexions were collected, of which 504 with $|F_o| > \sigma(F)$ were used in the refinement.

The structure was solved by the Patterson method. At first the space group was assumed to be *Pn*2₁*a* based on the molecular symmetry and $Z = 4$. A Fourier synthesis, which was phased with the non-

Table 1. *Final atomic parameters of the non-hydrogen atoms* (×10⁴, *except* B_{eq}) *and of the hydrogen atoms* (×10³, *except* B_{iso}), *with e.s.d.'s in parentheses*

$B_{eq} = (\frac{4}{3}) \sum_i \beta_{ii}/a_i^{*2}$. The occupancy factor is 0.5 for all atoms.

	x	y	z	B_{eq} or B_{iso} (Å²)
C(1)	4036 (20)	919 (8)	6420 (28)	6.9 (8)
C(2)	3264 (22)	654 (9)	4606 (33)	8.2 (10)
S(3)	2541 (7)	1212 (3)	2686 (9)	8.5 (3)
C(4)	2538 (18)	3042 (8)	2656 (25)	6.4 (7)
C(5)	2588 (17)	3795 (7)	2778 (19)	5.2 (6)
C(6)	3093 (21)	4282 (9)	4312 (31)	7.5 (9)
C(7)	3923 (20)	4094 (7)	6233 (23)	5.9 (7)
C(8)	4378 (17)	3547 (8)	7267 (26)	6.3 (7)
C(9)	4512 (16)	2217 (7)	7527 (25)	5.9 (7)
C(10)	3258 (16)	1883 (7)	4274 (23)	5.1 (7)
C(11)	3198 (13)	2662 (6)	4205 (20)	4.2 (6)
C(12)	4073 (16)	2815 (7)	6500 (24)	6.2 (7)
C(13)	4013 (19)	1648 (7)	6341 (24)	5.8 (7)
H(1)	445 (18)	59 (7)	736 (28)	6 (4)
H(2)	316 (20)	20 (8)	474 (28)	8 (5)
H(4)	204 (13)	271 (5)	154 (17)	3 (3)
H(5)	191 (19)	395 (7)	157 (25)	6 (4)
H(6)	296 (19)	473 (7)	444 (27)	7 (5)
H(7)	439 (18)	438 (7)	736 (27)	6 (4)
H(8)	517 (17)	345 (6)	880 (23)	4 (3)
H(9)	505 (20)	221 (7)	890 (26)	8 (5)

hydrogen atoms of the fused five-membered rings, revealed the molecular image as though the structure were disordered with respect to an additional mirror plane parallel to (010) and bisecting the long molecular axis. The disordered structure was refined by a block-diagonal least-squares method, with *Pnma* assumed. The H atoms were found on a difference Fourier map and included in the refinements. At the final stage of the refinement, the atomic shifts for the non-H atoms were less than 20% of the corresponding standard deviations (σ), and those of the H atoms were less than σ. The final R was 0·105 for 504 reflexions. The quantity minimized was $\sum w(|F_o| - |F_c|)^2$, with $w = 1·0$ for $|F_o| \leq 25·0$ and $(25·0/|F_o|)^2$ for $|F_o| > 25·0$. Refinements by a full-matrix least-squares method did not give meaningful results.

The atomic scattering factors used were taken from *International Tables for X-ray Crystallography* (1974).
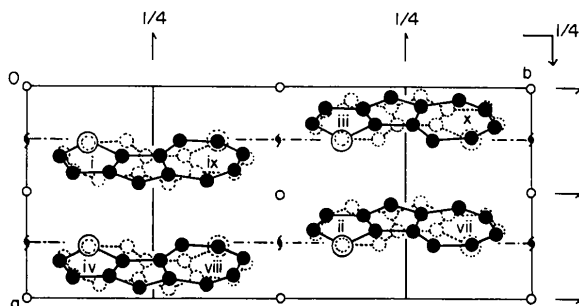
The computations were carried out at the Crystallographic Research Center, Institute for Protein Research, Osaka University, and at the Okayama University Computer Center. The programs used were *SIGM*, *HBLS*-V and *DAPH* (Ashida, 1973), and *MOLCON* (Fujii, 1979).

Table 2. *Least-squares planes and displacements* (Å) *of the atoms from the planes* ($X = ax$, $Y = by$, $Z = cz$)

(I) The thiophene ring (ring A)

$$0·884X - 0·029Y - 0·466Z - 0·973 = 0$$

C(1)*	0·015 (21)	C(13)*	−0·020 (19)
C(2)*	−0·005 (24)	C(9)	−0·033 (25)
S(3)*	−0·006 (11)	C(11)*	−0·051 (26)
C(10)*	0·016 (18)		

(II) The five-membered ring through C(10), C(11), C(12), C(9) and C(13) (ring B)

$$0·891X + 0·005Y - 0·453Z - 1·148 = 0$$

C(10)*	0·013 (18)	C(1)	−0·031 (27)
C(11)*	−0·003 (16)	S(3)	−0·069 (23)
C(12)*	−0·008 (18)	C(4)	−0·045 (24)
C(9)*	0·017 (19)	C(8)	0·059 (26)
C(13)*	−0·019 (19)		

(III) The seven-membered ring (ring C)

$$0·885X + 0·022Y - 0·466Z - 1·179 = 0$$

C(11)*	0·006 (15)	C(8)*	0·015 (19)
C(4)*	−0·008 (18)	C(12)*	−0·016 (17)
C(5)*	0·025 (17)	C(9)	−0·021 (22)
C(6)*	−0·029 (22)	C(10)	−0·005 (21)
C(7)*	0·008 (19)		

Dihedral angles (°) between the planes

(I) and (II) 2·1 (8)   (II) and (III) 1·3 (6)   (I) and (III) 2·9 (6)

* Atoms used for calculation of the planes.

Fig. 1. Projection of the crystal structure along **c**. The arrangement of the molecules shown by solid lines corresponds to that in the $Pn2_1a$ cell. The disordered molecules about m are shown by broken lines. The symmetry code for the molecules is shown in the respective thiophene ring: (i) x,y,z; (ii) $1 - x, \frac{1}{2} + y, 1 - z$; (iii) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} + z$; (iv) $\frac{1}{2} + x, y, \frac{1}{2} - z$; (v) $\frac{1}{2} + x, y, \frac{3}{2} - z$; (vi) $\frac{1}{2} - x, \frac{1}{2} + y, -\frac{1}{2} + z$; (vii) $1 - x, 1 - y, 1 - z$; (viii) $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} - z$; (ix) $x, \frac{1}{2} - y, z$; (x) $\frac{1}{2} - x, 1 - y, \frac{1}{2} + z$; (xi) $\frac{1}{2} - x, 1 - y, -\frac{1}{2} + z$; (xii) $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} - z$.
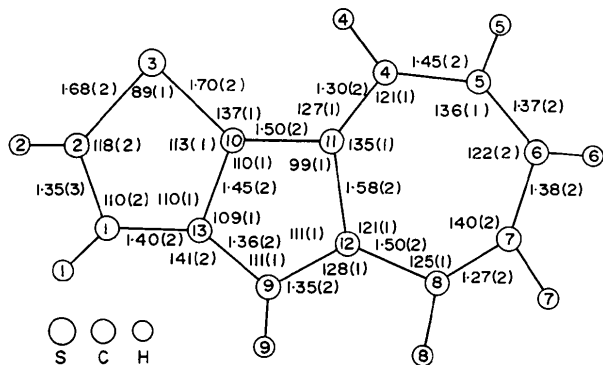
Table 3. *Torsion angles* (°) *in the rings, with e.s.d.'s in parentheses*

(I) Ring A

C(13)—C(1)—C(2)—S(3)	2·2 (2·2)
C(1)—C(2)—S(3)—C(10)	−0·2 (1·6)
C(2)—S(3)—C(10)—C(13)	−1·8 (1·3)
S(3)—C(10)—C(13)—C(1)	3·4 (1·7)
C(10)—C(13)—C(1)—C(2)	−3·4 (2·0)

(II) Ring B

C(13)—C(10)—C(11)—C(12)	1·5 (1·4)
C(10)—C(11)—C(12)—C(9)	0·6 (1·4)
C(11)—C(12)—C(9)—C(13)	−2·6 (1·7)
C(12)—C(9)—C(13)—C(10)	3·5 (1·8)
C(9)—C(13)—C(10)—C(11)	−3·1 (1·7)

(III) Ring C

C(11)—C(4)—C(5)—C(6)	−6·1 (2·8)
C(4)—C(5)—C(6)—C(7)	7·5 (3·1)
C(5)—C(6)—C(7)—C(8)	−5·0 (3·5)
C(6)—C(7)—C(8)—C(12)	0·4 (3·5)
C(7)—C(8)—C(12)—C(11)	2·8 (2·4)
C(8)—C(12)—C(11)—C(4)	−3·5 (2·4)
C(12)—C(11)—C(4)—C(5)	3·6 (2·5)

Fig. 2. Bond lengths (Å) and angles (°) involving the non-H atoms, and numbering of the atoms. The e.s.d.'s are shown in parentheses.

The final atomic parameters are given in Table 1.* The crystal structure viewed along **c** is shown in Fig. 1. Bond lengths and angles involving the non-H atoms are shown in Fig. 2. The least-squares planes and deviations of the atoms from the planes are given in Table 2, and the endocyclic torsion angles in Table 3.

Discussion. The molecules form a sheet parallel to (010). The sheets are stacked along **b** by van der Waals interactions. The possible cells which generate the apparent space group $Pnma$ by adding the symmetry operation m for disordering are its subgroups $Pn2_1a$ and $P2_12_12_1$. The difference in the symmetry operations of an **a** glide plane for $Pn2_1a$ and a 2_1 axis along **a** for $P2_12_12_1$ has no effect on the molecular arrangements, since the molecular planes are substantially parallel to **b**. In the sheets the molecules are packed in the same alternate hexagonal array viewed along **b** for both cells. The dihedral angle between the molecular planes of the nearest neighbours is 55·8 (3)°. All the interatomic contacts in the sheets are normal van der Waals interactions, but those between sheets are rather loose for both cells, consistent with the morphology of the crystals: $C(7)\cdots C(2^{ii})$ 3·77 (3), $H(6)\cdots S(3^{iii})$ 3·5 (2) Å for $Pn2_1a$; $C(7)\cdots C(6^{vii})$ 3·93 (3), $C(7)\cdots C(6^x)$ 3·97 (3) Å for $P2_12_12_1$.

Similar disordering has been found in azulene (Robertson, Shearer, Sim & Watson, 1962), in which the possible cells are $P2_1$ and Pa, and the disordered cell $P2_1/a$ is generated by adding $\bar{1}$ to them.

Owing to parameter interactions among the disordered atoms, the standard deviations of the atomic coordinates are largely underestimated, especially for C(1), C(2), C(5), C(6) and C(7). Thus, a detailed discussion of the molecular geometry may be meaningless. However, the observed bond alternation in the

seven-membered ring is in accordance with that suggested for (1) by the NMR data (Bertelli & Crews, 1970). C(4)—C(5) is longer than C(7)—C(8) as expected from the NMR data (Fujimori et al., 1980, 1981). The molecule is planar within 0·06 (2) Å. However, the seven-membered ring is twisted around the C(5)—C(6) bond and takes a twist-chair conformation, whose characteristic feature can be described in terms of the endocyclic torsion angles (Hendrickson, 1961; Kashino, Sasahara, Kataoka & Haisa, 1981).

References

ASHIDA, T. (1973). *The Universal Crystallographic Computing System – Osaka.* The Computation Center, Osaka Univ., Japan.

BERTELLI, D. J. & CREWS, P. (1970). *Tetrahedron,* **26**, 4717–4728.

FUJII, S. (1979). *The Universal Crystallographic Computing System – Osaka.* The Computation Center, Osaka Univ., Japan.

FUJIMORI, K., FUJITA, T., YAMANE, K., YASUNAMI, M. & TAKASE, K. (1980). *The 13th Symposium on Nonbenzenoid Aromatic Compounds,* Nagoya, Japan. Abstr. pp. 267–270.

FUJIMORI, K., FUKAZAWA, H., YAMANE, K., YASUNAMI, M. & TAKASE, K. (1981). *The 14th Symposium on Nonbenzenoid Aromatic Compounds,* Okayama, Japan. Abstr. pp. 94–97.

HENDRICKSON, J. B. (1961). *J. Am. Chem. Soc.* **83**, 4537–4547.

International Tables for X-ray Crystallography (1974). Vol. IV, pp. 72–75. Birmingham: Kynoch Press.

KASHINO, S., SASAHARA, N., KATAOKA, S. & HAISA, M. (1981). *Bull. Chem. Soc. Jpn,* **54**, 962–966.

ROBERTSON, J. M., SHEARER, H. M. M., SIM, G. A. & WATSON, D. G. (1962). *Acta Cryst.* **15**, 1–8.

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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 36888 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.