Structure of the Unreactive Modification of 2,4-Hexadiynylene Bis(*p*-bromobenzenesulphonate)

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Abstract. $C_{18}H_{12}Br_2O_6S_2$, $M_r = 548 \cdot 2$, triclinic, $P\bar{1}$, $a = 9 \cdot 066$ (1), $b = 5 \cdot 028$ (2), $c = 11 \cdot 175$ (2) Å, $\alpha = 80 \cdot 91$ (2), $\beta = 94 \cdot 30$ (1), $\gamma = 88 \cdot 21$ (2)° at 300 K, $U = 501 \cdot 1$ Å^3, D_m (300 K) = $1 \cdot 79$ (1), $D_c = 1 \cdot 817$ Mg m^{-3}, $Z = 1$, $F(000) = 270$, μ(Cu $K\alpha$) = $6 \cdot 999$ mm^{-1}, λ(Cu $K\alpha$) = $1 \cdot 54178$ Å. The final $R = 0 \cdot 039$ for 1376 counter reflections. The details of the crystal structure account for the absence of solid-state reactivity in this crystal modification.

Introduction. Many diacetylenes (general formula $R-C\vdots C \cdot C\vdots C-R'$) undergo solid-state polymerization reactions (Wegner, 1969, 1972), polymerization being initiated by thermal, mechanical or photochemical techniques. The ability of a particular diacetylene to undergo a solid-state transformation into a polymeric material is governed by the molecular packing of the molecules, which in turn is decided by the properties of the side groups R and R' (Baughman, 1974; Wegner, 1977). This work is part of a study of the structural properties of a series of diacetylene monomers with similar end groups in an attempt to correlate the effect of small changes in these groups with solid-state reactivity. The structures of 2,4-hexadiynylene bis-(*p*-toluenesulphonate) (TS) (Enkelmann, Leyrer & Wegner, 1979), 2,4-hexadiynylene bis(*p*-methoxybenzenesulphonate) (MBS) (Fisher, Ando, Bloor & Hursthouse, 1979; Williams, Ando, Bloor & Hursthouse, 1980), 2,4-hexadiynylene bis(β-naphthalenesulphonate) (NS) (Williams, Ando, Bloor & Hursthouse, 1979) and 2,4-hexadiynylene bis(*p*-chlorobenzenesulphonate) (CBS) (Mayerle & Clarke, 1978) have already been published.

The title compound (BBS) was prepared by the reaction of *p*-bromobenzenesulphonyl chloride with 2,4-hexadiyne-1,6-diol using the method reported by Wegner (1971) for the analogous ditosylate (TS) derivative. Recrystallization from acetone gave a light-brown crystalline solid (C = $39 \cdot 39$, H = $2 \cdot 52$, S = $11 \cdot 15$, Br = $29 \cdot 29\%$; $C_{18}H_{12}Br_2O_6S_2$ requires C = $39 \cdot 41$, H = $2 \cdot 19$, S = $11 \cdot 68$, Br = $29 \cdot 19\%$). Single crystals suitable for X-ray study were obtained by slow evaporation of an acetone solution. A crystal of approximate dimensions $0 \cdot 6 \times 0 \cdot 1 \times 0 \cdot 1$ mm was selected for data collection. It was observed that, as in some previously studied systems, *i.e.* CBS (Enkelmann, 1978) and MBS (Fisher *et al.*, 1979; Williams *et al.*, 1980), two crystal modifications were obtained; first, moderately sized plate-like crystals of an unreactive modification and, secondly, dendritic microcrystals of a reactive modification (see also Enkelmann, 1980). Lattice parameters were obtained by least squares from the setting angles for 25 reflections automatically centred on a Nonius CAD-4 diffractometer. Intensities were collected with Ni-filtered Cu $K\alpha$ radiation in the $\omega/2\theta$ scan mode. The scan rate was variable between $1 \cdot 2$ and $6 \cdot 6$° min^{-1}. The ω scan width was $(0 \cdot 85 + 0 \cdot 15 \tan \theta)$° and the aperture setting was 4 mm. Two intensity-control reflections, monitored after every hour of exposure, showed no decay. The data were reduced to 1890 unique reflections, of which 1376 had $I_o > 1 \cdot 5\sigma(I_o)$ and were used in the refinement.

The structure was solved by direct methods using *SHELX* (Sheldrick, 1976). All non-H atoms were located in the best E map and a subsequent difference map revealed the positions of the H atoms. Least-squares anisotropic refinement of the positions of the non-H atoms and free, isotropic refinement of all H-atom positions gave a final R of $0 \cdot 039$. The best agreement was obtained with a unit weighting scheme. The data were corrected for absorption by the method of North, Phillips & Mathews (1968). Final atomic parameters are listed in Tables 1 and 2. Computations were performed on the Queen Mary College ICL 2980 computer.*

Table 1. *Fractional coordinates* ($\times 10^4$) *and equivalent isotropic temperature factors* ($\text{Å}^2 \times 10^3$) *for the non-H atoms*

The latter are obtained from the equation $U_{eq} = (U_{11} \times U_{22} \times U_{33})^{1/3}$. E.s.d.'s are given in parentheses.

	x	y	z	U_{eq}
C(1)	9441 (5)	9351 (11)	310 (5)	58 (3)
C(2)	8501 (5)	8250 (11)	835 (5)	59 (3)
C(3)	7366 (7)	6818 (13)	1511 (6)	68 (4)
C(4)	4174 (5)	7999 (9)	2699 (4)	44 (2)
C(5)	3838 (6)	7274 (11)	3895 (4)	54 (3)
C(6)	2710 (6)	5553 (11)	4151 (5)	60 (3)
C(7)	1941 (5)	4588 (11)	3210 (5)	56 (3)
C(8)	2268 (6)	5289 (11)	2022 (5)	58 (3)
C(9)	3396 (5)	7045 (10)	1762 (4)	50 (3)
O(1)	7038 (4)	8135 (8)	2534 (3)	62 (2)
O(2)	5899 (5)	11658 (8)	3345 (3)	76 (3)
O(3)	5431 (4)	11449 (7)	1156 (3)	58 (2)
S	5635 (1)	10126 (3)	2389 (1)	51 (1)
Br	379 (1)	2257 (2)	3558 (1)	88 (1)

Table 2. *Fractional coordinates* ($\times 10^3$) *and isotropic temperature factors* ($\text{Å}^2 \times 10^3$) *for the H atoms*

	x	y	z	U
H(1)	760 (7)	498 (13)	183 (6)	97 (22)
H(2)	641 (6)	700 (11)	98 (5)	82 (18)
H(3)	437 (5)	821 (10)	454 (5)	71 (16)
H(4)	243 (6)	516 (10)	494 (5)	78 (17)
H(5)	169 (6)	450 (11)	136 (5)	85 (18)
H(6)	369 (5)	768 (9)	92 (4)	57 (13)

Discussion. Molecular plots, obtained with *ORTEP* (Johnson, 1965), are shown in Figs. 1 and 2, and bond lengths and angles are given in Tables 3 and 4. A comparison between BBS and the analogous CBS (in its inactive modification) (Mayerle & Clarke, 1978) shows that the lattice parameters, molecular conformation and bond lengths and angles are all very similar, an expected result since the only difference between the two compounds is in the halogen atom at the extremes of the molecule. Mayerle & Clarke (1978), in their discussion of the structure of CBS, point out the importance of the interaction between the Cl atoms and phenyl rings of adjacent molecules along the short axis, and the same reasoning must also apply to BBS. Compilation of data from available X-ray structure determinations (Bloor, 1982) shows that solid-state reaction is possible if the separation of the reacting atoms, C(2) and C(2′) in the adjacent BBS molecules, is less than 4·0 Å (Schmidt, 1967). The minimum separation of these atoms is set by molecular contact of the diacetylene moieties. For a given separation of the diacetylene units it is then possible to calculate upper and lower limits for the angle between the axes of the diacetylene moieties and their stacking direction. These
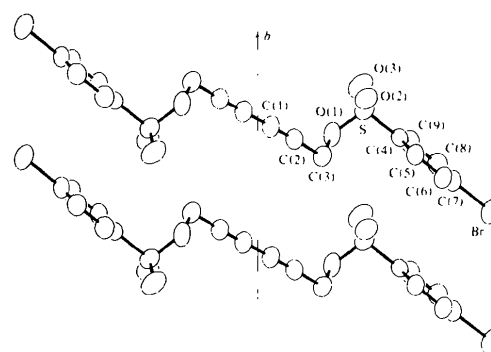

Fig. 1. View of the structure perpendicular to the *ab* plane. 50% probability ellipsoids are shown.
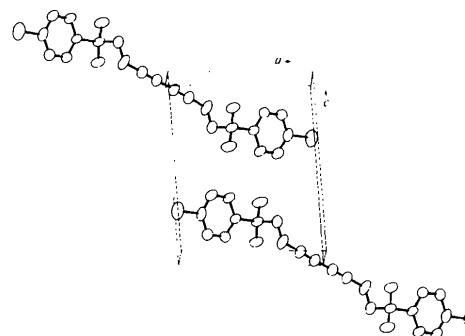

Fig. 2. View of the structure perpendicular to the *ac* plane. 50% probability ellipsoids are shown.

Table 3. *Interatomic distances* (Å)

E.s.d.'s are given in parentheses.

C(1)–C(1^i)	1·392 (10)	C(4)–C(5)	1·388 (7)
C(1)–C(2)	1·175 (7)	C(5)–C(6)	1·377 (8)
C(2)–C(3)	1·463 (8)	C(6)–C(7)	1·379 (8)
C(3)–O(1)	1·454 (8)	C(7)–C(8)	1·375 (8)
O(1)–S	1·576 (6)	C(8)–C(9)	1·389 (7)
S–O(2)	1·423 (4)	C(9)–C(4)	1·376 (7)
S–O(3)	1·429 (4)	C(7)–Br	1·890 (7)
S–C(4)	1·749 (6)		

Symmetry code: (i) $2 - x, 2 - y, -z$.

Table 4. *Interatomic angles* (°)

E.s.d.'s are given in parentheses.

C(1^i)–C(1)–C(2)	177·7 (6)	S–C(4)–C(5)	119·0 (5)
C(1)–C(2)–C(3)	178·2 (6)	S–C(4)–C(9)	119·7 (4)
C(2)–C(3)–O(1)	110·1 (6)	C(4)–C(5)–C(6)	119·4 (6)
C(3)–O(1)–S	118·4 (5)	C(5)–C(6)–C(7)	119·1 (5)
O(1)–S–O(2)	103·6 (3)	C(6)–C(7)–Br	119·1 (5)
O(1)–S–O(3)	108·7 (3)	C(6)–C(7)–C(8)	121·9 (6)
O(1)–S–C(4)	103·8 (3)	Br–C(7)–C(8)	119·0 (5)
O(2)–S–O(3)	120·1 (3)	C(7)–C(8)–C(9)	119·0 (6)
O(2)–S–C(4)	109·9 (3)	C(8)–C(9)–C(4)	119·2 (5)
O(3)–S–C(4)	109·3 (3)	C(9)–C(4)–C(5)	121·3 (5)

quantities, termed d_1 and γ_1 in previous papers (Williams *et al.*, 1979; Fisher *et al.*, 1979), correspond to b and the angle between the diacetylene axis and the b axis in BBS. The b axis in BBS is 5·028 Å and the estimated range of angles between the diacetylene units and the b axis for reactivity is 40 to 49°. The actual value of the angle is 65·6° which is clearly outside this range, in contrast to the reactive ditosylate (TS) derivative.

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Structure of 4-Ethoxyindeno[1,2-d]azepine

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Abstract. $C_{15}H_{13}NO$, m.p. 388–390 K, monoclinic, $P2_1/a$, $a = 23·752$ (4), $b = 5·834$ (1), $c = 8·485$ (2) Å, $\beta = 92·22$ (2)°, $V = 1174·8$ (4) Å^3, $D_m = 1·268$, $D_x = 1·262$ Mg m^{-3}, $Z = 4$. Final $R = 0·044$ for 1650 non-zero reflexions. The indenoazepine ring is planar within 0·102 (2) Å, the azepine ring taking a twist-boat conformation. The bond alternation in the azaazulene ring is more remarkable than in the azulene ring. The observed bond lengths are in agreement with those calculated by the LCAO–SCF–MO method.

Introduction. 4-Ethoxyindeno[1,2-d]azepine (1) is a novel non-benzenoid aromatic compound, whose NMR and electronic spectra suggest the presence of a fully conjugated 14π ring system (Kimura, Satake & Morosawa, 1979). The present study has been undertaken in order to determine the precise molecular structure of (1), which has an electron-withdrawing $\diagup$C=N– bond in the seven-membered ring.

Crystals were grown from an acetone solution by slow evaporation as purplish-blue plates with developed faces {100}. The intensity data were collected with a specimen of 0·15 × 0·25 × 0·13 mm 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 θ) using Ni-filtered Cu $K\alpha$ radiation ($\lambda = 1·5418$ Å) at 40 kV and 200 mA. Background was measured for 4 s on either side of the peak. In total 1754 reflexions were collected, of which 1650 non-zero reflexions were used in the refinement. The intensities were corrected for Lorentz and polarization factors, but not for absorption [μ(Cu $K\alpha$) = 0·59 mm^{-1}].

The structure was solved by *MULTAN* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978), and refined by a block-diagonal least-squares method

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