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Structure of 3,5-Octadiynylene Bis(*p*-toluenesulphonate)

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Abstract. $C_{22}H_{22}O_6S_2$, $M_r = 446{\cdot}53$, triclinic, $P\bar{1}$, $a = 7{\cdot}034\,(3)$, $b = 9{\cdot}590\,(1)$, $c = 9{\cdot}692\,(2)$ Å, $\alpha = 116{\cdot}61\,(2)$, $\beta = 111{\cdot}70\,(2)$, $\gamma = 85{\cdot}48\,(2)^\circ$ at 294 K, D_m (294 K) = 1·355 (10), D_c (294 K) = 1·373 Mg m^{-3}, $Z = 1$; $F(000) = 234$, μ(Cu $K\alpha$) = 2·417 mm^{-1}, λ(Cu $K\alpha$) = 1·54178 Å; final $R = 0{\cdot}055$ for 2000 counter reflections collected at 294 K. The details of the crystal structure explain why the compound does not undergo solid-state polymerization under the influence of heat or UV irradiation.

Introduction. Many disubstituted diacetylenes (general formula R–C⋮C.C⋮C–R') undergo solid-state polymerization (Wegner, 1969, 1972), polymerization being achieved by thermal, mechanical or photochemical techniques. The ability of a specific diacetylene to undergo a solid-state transformation into a polymeric material is governed by the packing of the molecules in the crystal lattice and by the properties of the side groups R and R' (Baughman, 1974; Wegner, 1977). The extensively studied 2,4-hexadiynylene bis(*p*-toluenesulphonate) (TSHD), with $R = R' = -CH_2-O-SO_2-C_6H_4-CH_3$, is the best known example of such a transformation (Enkelmann, Leyrer & Wegner, 1979). Comparative studies on several other diacetylenes with similar side groups have been reported (Williams, Ando, Bloor & Hursthouse, 1979). The present work was conducted as part of a study of the structural properties of the series of bis(*p*-toluenesulphonate) diacetylenes in which extra CH_2 groups are inserted between the side group R, as above, and the central diacetylenic unit.

The title compound (TSOD) was prepared by the reaction of *p*-toluenesulphonyl chloride with 3,5-octadiyne-1,8-diol by the method reported (Wegner, 1971) for the analogous hexadiynylene (TSHD) derivative. The crude product was separated from the reaction mixture by precipitation with ice-water and, after several recrystallizations from acetone, gave a pale-yellow crystalline solid, m.p. 398 K (C = 58·71, H = 5·23, S = 13·43%; $C_{22}H_{22}O_6S_2$ requires C = 59·18, H = 4·96, S = 14·36%). Single crystals suitable for X-ray study were obtained by evaporation of an acetone solution. A crystal 0·7 × 0·2 × 0·1 mm was selected for data collection.

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 on the same instrument with Ni-filtered Cu $K\alpha$ radiation and an $\omega/2\theta$ scan mode. The scan rate was variable between 1·2 and 6·6° min^{-1}. The ω scan width was $(0{\cdot}8 + 0{\cdot}15 \tan\theta)^\circ$, and the aperture setting was 4 mm. Two control reflections, monitored after every hour of exposure, showed no decay of the crystal. In each 96-step scan, the outer 16 steps on each side constituted left (B_l) and right (B_r) backgrounds, and the central 64 steps the peak count (C). The integrated intensity (I_o) of a reflection and its e.s.d. $\sigma(I_o)$ were calculated from $I_o = |C - 2(B_l + B_r)|$ and $\sigma(I_o) = |C + 4(B_l + B_r)|^{1/2}$. The data were reduced to 2224 unique reflections, of which 2000 had $I_o > 2\sigma(I_o)$ and were used in the refinement.

The structure was solved by direct methods with *SHELX* (Sheldrick, 1976). All non-hydrogen atoms were located in the best E map, and subsequent difference maps revealed the positions of the H atoms. Least-squares anisotropic refinement of the non-hydrogen atoms and free, isotropic refinement of all H atoms gave a final R of 0·055. The weighting scheme $w = 1/[\sigma^2(F_o) + 0{\cdot}001F_o^2]$ gave flat agreement analyses. The final atomic positional parameters are in Table 1.* The crystallographic computations were performed on the Queen Mary College ICL 1904S and ICL 2980, and on the University of London CDC 7600 computers.

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* Lists of structure factors, thermal parameters and dihedral angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35267 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Atomic coordinates* ($\times 10^4$, *for* H $\times 10^3$)

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

	x	*y*	*z*
C(1)	−78 (3)	−4267 (2)	5587 (3)
C(2)	−221 (4)	−3009 (2)	6587 (3)
C(3)	−354 (4)	−1458 (2)	7838 (3)
C(4)	304 (3)	−147 (2)	7590 (3)
C(5)	2567 (3)	4075 (2)	9328 (2)
C(6)	2514 (3)	5431 (2)	10664 (3)
C(7)	3419 (3)	5610 (2)	12288 (3)
C(8)	4431 (4)	4378 (3)	12519 (3)
C(9)	4507 (4)	3013 (2)	11207 (2)
C(10)	3562 (3)	2861 (2)	9603 (2)
C(11)	3330 (6)	7085 (3)	13753 (4)
O(1)	2517 (2)	−168 (1)	7985 (2)
O(2)	2603 (3)	1236 (2)	6430 (2)
O(3)	5745 (2)	726 (2)	8290 (2)
S	3683 (1)	1129 (0)	7932 (0)
H(1)	−171 (7)	−130 (5)	777 (5)
H(2)	71 (6)	−123 (4)	907 (5)
H(3)	5 (4)	80 (3)	836 (3)
H(4)	−35 (4)	−26 (3)	647 (4)
H(5)	200 (4)	405 (3)	832 (4)
H(6)	179 (4)	635 (3)	1050 (3)
H(8)	527 (5)	451 (4)	1371 (4)
H(9)	545 (5)	225 (4)	1149 (4)
H(10)	351 (5)	790 (5)	1369 (4)
H(11)	446 (9)	723 (7)	1488 (8)
H(12)	208 (8)	679 (7)	1384 (6)

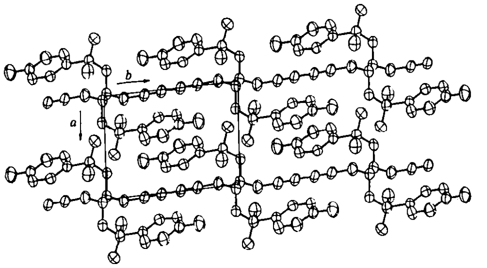

Fig. 2. Molecular plot viewed along **c**. 50% probability ellipsoids are shown (*ORTEP*, Johnson, 1965).

Table 2. *Interatomic distances* (Å) *and angles* (°)

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

C(1)–C′(1)	1·385 (4)	S–C(10)	1·749 (2)
C(1)–C(2)	1·188 (3)	C(10)–C(5)	1·388 (2)
C(2)–C(3)	1·462 (3)	C(5)–C(6)	1·374 (3)
C(3)–C(4)	1·516 (3)	C(6)–C(7)	1·396 (3)
C(4)–O(1)	1·459 (2)	C(7)–C(8)	1·393 (3)
O(1)–S	1·572 (1)	C(8)–C(9)	1·372 (3)
S–O(2)	1·419 (1)	C(9)–C(10)	1·390 (2)
S–O(3)	1·426 (2)	C(7)–C(11)	1·507 (3)
C(3)–H(1)	0·94 (4)	C(8)–H(8)	1·04 (3)
C(3)–H(2)	1·08 (4)	C(9)–H(9)	1·01 (4)
C(4)–H(3)	0·95 (3)	C(11)–H(10)	0·84 (4)
C(4)–H(4)	0·96 (3)	C(11)–H(11)	1·04 (6)
C(5)–H(5)	0·90 (3)	C(11)–H(12)	0·99 (6)
C(6)–H(6)	1·03 (2)		
C′(1)–C(1)–C(2)	179·6 (2)	S–C(10)–C(5)	120·4 (1)
C(1)–C(2)–C(3)	178·9 (2)	S–C(10)–C(9)	119·0 (1)
C(2)–C(3)–C(4)	112·3 (2)	C(5)–C(10)–C(9)	120·6 (2)
C(3)–C(4)–O(1)	106·1 (2)	C(10)–C(5)–C(6)	119·2 (2)
C(4)–O(1)–S	118·2 (1)	C(5)–C(6)–C(7)	121·6 (2)
O(1)–S–O(2)	109·7 (1)	C(6)–C(7)–C(8)	117·6 (2)
O(1)–S–O(3)	103·7 (1)	C(6)–C(7)–C(11)	121·7 (2)
O(2)–S–O(3)	119·7 (1)	C(8)–C(7)–C(11)	120·7 (2)
O(1)–S–C(10)	103·8 (1)	C(7)–C(8)–C(9)	122·0 (2)
O(2)–S–C(10)	108·9 (1)	C(8)–C(9)–C(10)	119·0 (2)
O(3)–S–C(10)	109·9 (1)		

Discussion. Molecular plots, obtained with *ORTEP* (Johnson, 1965), are shown in Figs. 1 and 2, and the bond lengths and angles are given in Table 2. A comparison of bond lengths and angles and dihedral angles between TSOD and the related monomer TSHD (Enkelmann *et al.*, 1979) shows that there are no significant differences due to inclusion of an extra CH_2 group other than the obvious change in conformation, and a small rotation of the aromatic ring about the S–C(10) bond to bring it into the plane of C(10)–S–O(2).

Wegner (1977) suggested that the following packing conditions are necessary for diacetylenes to polymerize in the solid state by the 1,4-addition of adjacent monomer molecules: $3{\cdot}40 < S_1 < 4{\cdot}00$ Å, where $S_1 = d_1 \sin \gamma_1$, and $\gamma_1 \simeq 45°$ (Fig. 3). It is clear that TSOD does not pack in a manner favourable for solid-state polymerization. The extra CH_2 group makes the side group too bulky to allow the molecules to stack in a simple fashion, as in TSHD, and instead induces a more staggered arrangement in which the close approach of monomer units, necessary for polymerization to occur, is impossible.

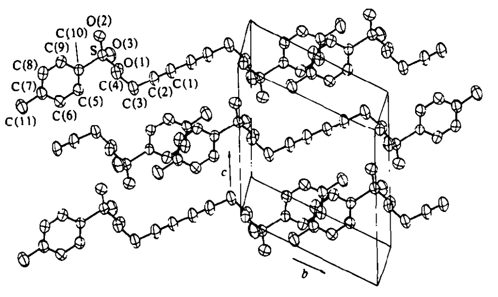

Fig. 1. Molecular plot viewed normal to *bc*. 50% probability ellipsoids are shown (*ORTEP*, Johnson, 1965).

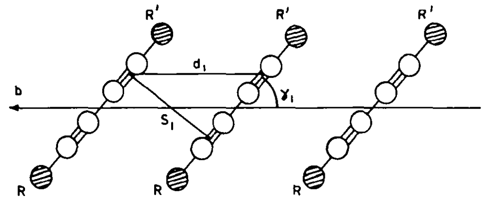

Fig. 3. Monomer packing requirements for the solid-state polymerization of diacetylenes (Wegner, 1977).

Work is in progress to investigate the structural properties of the related compounds 4,6-decadiynylene bis(*p*-toluenesulphonate) (TSDD) and 5,7-dodecadiynylene bis(*p*-toluenesulphonate) (TSDDD).

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Tétrakis(propylthio)-2,2′,6,6′ Azoxy-3,3′ Pyridine

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Abstract. $C_{22}H_{32}N_4OS_4$, triclinic, $P\bar{1}$, $a = 10{\cdot}874\ (3)$, $b = 15{\cdot}835\ (4)$, $c = 8{\cdot}683\ (3)$ Å, $\alpha = 101{\cdot}91\ (1)$, $\beta = 106{\cdot}41\ (1)$, $\gamma = 107{\cdot}46\ (1)°$, $V = 1296{\cdot}8$ Å^3, $Z = 2$, $D_x = 1{\cdot}271$ Mg m^{-3}, $\mu(\text{Cu}\,K\alpha) = 33{\cdot}9$ mm^{-1}. The structure was solved by direct methods and refined to a final R value of 0·047 for 4177 observed reflections. The planarity of the pyridine—NO—N—pyridine group allows charge delocalization along the central part of the molecule.

Introduction. Lors de la condensation de la chloro-2 nitro-3 pyridine, en milieu basique avec du mercaptan propylique, en vue de la préparation du thioéther, un produit secondaire de la réaction a été isolé en quantité non négligeable au Laboratoire de Chimie Pharmaceutique du Professeur C. L. Lapière.

La formule élémentaire et la structure moléculaire de ce nouveau composé ont été déterminées par radiocristallographie.

Parmi les 4581 réflexions mesurées sur un diffractomètre à quatre cercles Hilger & Watts, avec la radiation Cu $K\alpha$, 4177 ont été considérées comme observées $[I > 2\sigma(I)]$.

L'application du programme *MULTAN* 77 (Main, Lessinger, Woolfson, Germain & Declercq, 1977) a révélé les quatre atomes de soufre ainsi que les atomes d'azote et d'oxygène. Les positions des autres atomes non hydrogène ont été trouvées grâce à des synthèses de Fourier-différence successives. La structure a ensuite été affinée par moindres carrés, en gardant fixes les positions des atomes d'hydrogène. Les intensités ont été pondérées suivant le schéma de Cruickshank (1961), $w = (a + |F_o| + b|F_o|^2)$ avec $a = 2F_o(\text{min.})$ et $b = 2/F_o(\text{max.})$.

La valeur finale du facteur R conventionnel est de 4,73%. La Fig. 1 montre la numérotation des atomes et la Fig. 2, due au programme *PLUTO* (Motherwell, 1976), montre la conformation de la molécule. Les coordonnées des atomes non hydrogène figurent dans le Tableau 1,* tandis que les Tableaux 2 et 3 donnent respectivement les longueurs des liaisons interatomiques et des angles de valence.

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* Les listes des facteurs de structure, des facteurs de température anisotropes et les positions calculées des atomes d'hydrogène ont été déposées au dépôt d'archives de la British Library Lending Division (Supplementary Publication No. SUP 35198: 31 pp.). On peut en obtenir des copies en s'adressant à: The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, Angleterre.

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