

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

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Abstract

$C_{20}H_{18}O_8S_2$, triclinic, $P\bar{1}$, $a = 9.875(2)$, $b = 10.226(2)$, $c = 5.798(2)$ Å, $\alpha = 96.59(2)$, $\beta = 76.92(2)$, $\gamma = 116.03(2)^\circ$ at 300 K; $D_m = 1.445$, $D_c = 1.460$ Mg m⁻³, $Z = 1$; $F(000) = 234$, $\mu(\text{Mo } K\alpha) = 0.254$ mm⁻¹, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å. Final $R = 0.045$ for 1673 counter reflections collected at 300 K. The crystal structure accounts for the absence of solid-state reactivity in this crystal modification.

(abbreviated to CBS) crystallizes at room temperature in an unreactive crystal modification, the structure of which has been determined by Mayerle & Clarke (1978). Recently, a metastable reactive modification has been found by Enkelmann (1978). The bis(*p*-methoxybenzenesulphonate), $X = \text{OCH}_3$, (abbreviated to MBS) has similar, stable unreactive and metastable reactive phases (Bloor, Ando, Fisher & Hubble, 1979). We report here the crystal structure of the unreactive modification and compare it with the two known related structures mentioned above.

Introduction

The solid-state polymerization of diacetylenes, $R-C\equiv C:C:C-R'$, has been known for many years (Sondheimer, Amiel & Wolovsky, 1957). The topochemical nature of the reaction and its potential for the formation of macroscopic polymer crystals was first realized by Wegner (1969). However, not all diacetylenes are reactive, and many of those that are become disordered during the transformation from monomer to polymer. Crucial factors in the solid-state reactivity are the molecular packing and interactions (Baughman, 1974; Wegner, 1977), which are largely determined by the monomer end groups. This work was carried out as part of a study of monomers with similar end groups in an attempt to quantify the effects of small changes in these groups on solid-state reactivity. The monomers studied were those with $R = R' = -\text{CH}_2-\text{O}-\text{SO}_2-\text{C}_6\text{H}_4-X$, where X is CH_3 , F, Cl, Br, H and OCH_3 .

The bis(*p*-tosylate), $X = \text{CH}_3$, (abbreviated to TS) is highly reactive and has been extensively studied. The crystal structures of the polymer at 300 K (Kobelt & Paulus, 1974) and 120 K (Enkelmann, 1977; Bloor, Fisher, Batchelder, Kennedy, Cottle, Lewis & Hursthouse, 1979) and of the monomer at 120 K (Enkelmann, Leyrer & Wegner, 1979) have been reported. The bis(*p*-chlorobenzenesulphonate), $X = \text{Cl}$,

Experimental

Samples of MBS were prepared by reaction of *p*-methoxybenzenesulphonyl chloride with 2,4-hexadiyne-1,6-diol, analogous to the preparation of TS (Wegner, 1971). MBS samples were purified by recrystallization from a range of solvents. Two crystal modifications were obtained: firstly, large plate-like crystals of an unreactive modification and, secondly, small dendritic crystals of a reactive modification. Crystallization behaviour is unusual in that both forms can be obtained from the same solutions for a number of different solvents. The proportion of each form appears to be controlled by crystallization kinetics rather than purity.

Plate-like crystals of the inactive modification (m.p. 393 K) were grown from an acetone solution by slow evaporation. Several crystals which had dimensions in their longest axis of up to several mm and which were typically less than 1 mm thick in their other dimensions were selected for examination by X-ray photography. Oscillation and Weissenberg photographs of these relatively large crystals indicated that they were triclinic but that all the crystals were split. Cleaving a crystal in directions parallel and perpendicular to the long axis produced a single crystal $0.7 \times 0.8 \times 0.5$ mm which was suitable for the collection of X-ray diffraction data.

Oscillation and Weissenberg photographs of the cleaved crystal confirmed that the crystal system was triclinic and gave approximate values for the lattice parameters. Accurate values were calculated from the setting angles of 25 reflections measured on a Nonius CAD-4 diffractometer at 300 K. The crystal data are given in Table 1. Intensities were recorded on the same instrument with graphite-monochromated Mo $K\alpha$ radiation and an $\omega/2\theta$ scan mode (Fisher, Batchelder & Hursthouse, 1978). The crystal, which possessed a slight amber tint, showed no evidence of darkening on exposure to X-rays. Data collected in the range $1.5 < \theta < 25.0^\circ$ amounted to 1789 unique reflections of which 1673 obeyed the condition $I > 1.5\sigma(I)$ and were used in the structure refinement.

Table 1. *Crystal data for the unreactive modification of MBS [2,4-hexadiynylene bis(*p*-methoxybenzenesulphonate)]*

Molecular formula: C ₂₀ H ₁₈ O ₈ S ₂ , $M_r = 450.46$	
Triclinic, space group $P1$	
$a = 9.875$ (2) Å	$Z = 1$
$b = 10.226$ (2)	$D_c = 1.460$ Mg m ⁻³
$c = 5.798$ (2)	$D_m = 1.445$
$\alpha = 96.59$ (2)°	$V = 512.3$ Å ³
$\beta = 76.92$ (2)	
$\gamma = 116.03$ (2)	

Table 2. *Atomic coordinates for the unreactive modification of MBS: ($\times 10^4$ for O, C and S; $\times 10^3$ for H)*

E.s.d.'s are given in parentheses. The overall isotropic temperature factor for the H atoms refined to 0.07 \AA^2 .

	x	y	z
C(1)	4941 (2)	566 (2)	-4286 (4)
C(2)	4835 (2)	1551 (2)	-3069 (4)
C(3)	4633 (3)	2766 (3)	-1702 (4)
C(4)	8011 (2)	3288 (2)	-547 (3)
C(5)	8813 (2)	3575 (2)	-2856 (3)
C(6)	9814 (2)	2941 (2)	-3823 (3)
C(7)	9989 (2)	2026 (2)	-2461 (3)
C(8)	9133 (2)	1697 (2)	-163 (4)
C(9)	8164 (2)	2332 (2)	809 (3)
C(10)	11948 (3)	1778 (3)	-5512 (4)
O(1)	5138 (1)	2985 (1)	551 (2)
O(2)	6774 (2)	4348 (2)	3196 (3)
O(3)	7208 (2)	5360 (2)	-708 (3)
O(4)	10978 (2)	1396 (2)	-3211 (3)
S	6820 (1)	4150 (1)	706 (1)
H(C3)	524 (3)	363 (3)	-227 (5)
H'(C3)	349 (3)	264 (3)	-132 (4)
H(C10)	1265 (3)	129 (3)	-586 (5)
H'(C10)	1271 (4)	270 (4)	-555 (6)
H''(C10)	1142 (4)	157 (3)	-679 (6)
H(C5)	864 (3)	418 (3)	-374 (4)
H(C6)	1045 (3)	322 (2)	-534 (4)
H(C8)	924 (3)	109 (3)	92 (5)
H(C9)	767 (3)	221 (3)	242 (5)

Structure determination

The structure was solved by direct methods with *SHELX* (Sheldrick, 1976). All non-hydrogen atoms were located in the best E map and all the H atoms in a difference synthesis phased on the C, O and S atoms. Least-squares refinement of all atomic positions gave a final R of 0.045. The weighting scheme $w = 1/[\sigma^2(F_o) + 0.002F_o^2]$ gave flat agreement analyses. The atomic coordinates are listed in Table 2, bond distances and angles in Table 3.* Projections of the structure down a and c are given in Figs. 1 and 2.

The calculations were made on the Queen Mary College ICL 1904S and the University of London CDC 7600 computers.

Discussion

The absence of solid-state reactivity in this crystal modification is a clear consequence of the crystal packing. Although the monomer units are packed along c with a tilt angle (γ_1) close to the optimum value of 45° (Fig. 3) the separation (d_1) of 5.8 \AA is larger than

* Lists of structure factors, thermal parameters and dihedral angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34434 (26 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Bond distances (Å) and angles (°) for the unreactive modification of MBS*

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

C(1)–C(1)	1.376 (4)	C(1)–C(2)–C(3)	175.5 (2)
C(1)–C(2)	1.192 (3)	C(2)–C(3)–O(1)	111.7 (2)
C(2)–C(3)	1.459 (3)	C(3)–O(1)–S	118.7 (1)
C(3)–O(1)	1.461 (2)	O(1)–S–O(2)	103.2 (1)
O(1)–S	1.579 (1)	O(1)–S–O(3)	109.1 (1)
S–O(2)	1.428 (2)	O(2)–S–O(3)	119.9 (1)
S–O(3)	1.423 (1)	O(1)–S–C(4)	105.2 (1)
S–C(4)	1.750 (2)	O(2)–S–C(4)	109.9 (1)
C(4)–C(5)	1.383 (3)	O(3)–S–C(4)	108.6 (1)
C(5)–C(6)	1.393 (3)	S–C(4)–C(5)	119.8 (1)
C(6)–C(7)	1.379 (3)	C(4)–C(5)–C(6)	119.9 (2)
C(7)–C(8)	1.395 (8)	C(5)–C(6)–C(7)	119.4 (2)
C(8)–C(9)	1.368 (3)	C(6)–C(7)–C(8)	120.4 (2)
C(4)–C(9)	1.398 (2)	C(7)–C(8)–C(9)	120.5 (2)
C(7)–O(4)	1.361 (2)	C(8)–C(9)–C(4)	119.3 (2)
O(4)–C(10)	1.436 (3)	C(9)–C(4)–C(5)	120.5 (2)
C(3)–H(C3)	0.87 (3)	C(9)–C(4)–S	119.7 (1)
C(3)–H'(C3)	1.05 (3)	C(6)–C(7)–O(4)	123.9 (2)
C(5)–H(C5)	0.94 (2)	C(8)–C(7)–O(4)	115.7 (2)
C(6)–H(C6)	0.95 (2)	C(7)–O(4)–C(10)	117.4 (2)
C(8)–H(C8)	0.98 (3)	C(1')–C(1)–C(2)	179.3 (2)
C(9)–H(C9)	0.95 (3)		
C(10)–H(C10)	1.00 (3)		
C(10)–H'(C10)	0.91 (3)		
C(10)–H''(C10)	0.95 (3)		

that necessary for a reaction to be likely (Wegner, 1977; Baughman, 1974). In addition, the configurations of the side groups are not conducive to reactivity. Reaction between the C(2) atoms of the monomer (shown as 1' and 4 in Fig. 3) would require a large distortion of the C(3)—O(1)—S linkages. Indeed O(1) is clearly positioned to prevent the close approach of the C(2) atoms on adjacent monomers. In TS the phenyl rings are nearly orthogonal to the polymerization direction, the *b* axis (Fig. 4). In MBS they are almost parallel to *c* and provide a further hindrance to polymerization. Any possibility of reaction in the *ac* plane, which shows a more favourable orientation of the side groups (Fig. 2), is precluded by the *S*-shape of the molecule, and the fact that the side groups are interposed between the diacetylenic units of the monomer molecules.

The structures for the reactive TS and the unreactive CBS are shown in Figs. 4 and 5 respectively. Comparison with Fig. 2 shows that the configurations

of the three monomers differ in only one respect: the side groups are rotated about C(3)—O(1) with respect to the central linear diacetylenic group. Precise comparisons are best made by considering torsion angles of the C(2)—C(3) and O(1)—S bonds about C(3)—O(1). These are -170 , 97.8 and -95.5° for TS, CBS, and MBS, respectively. Other small differences occur, for instance, in the tilt angle of the phenyl rings, but these are a few degrees at most and are clearly secondary to the rotations about C(3)—O(1) (see Table 4 for a comparison of MBS and CBS). In a related compound

Table 4. Principal differences in dihedral angles for MBS and CBS ($^\circ$)

	MBS	CBS
C(2)—C(3)—O(1)—S	-95.5	97.8
C(3)—O(1)—S—O(2)	-165.3	-162.7
C(3)—O(1)—S—O(3)	-36.9	-34.2
C(3)—O(1)—S—C(4)	79.5	82.5
O(1)—S—C(4)—C(5)	-100.2	-91.1
O(1)—S—C(4)—C(9)	80.8	87.4
O(2)—S—C(4)—C(5)	-149.4	-156.5
O(2)—S—C(4)—C(9)	29.7	25.0
O(3)—S—C(4)—C(5)	-16.5	-23.3
O(3)—S—C(4)—C(9)	162.5	158.2

All other dihedral angles differ by less than $\pm 3^\circ$. Angles for CBS were calculated from the data of Mayerle & Clarke (1978). E.s.d.'s are typically 0.2° for MBS and CBS.

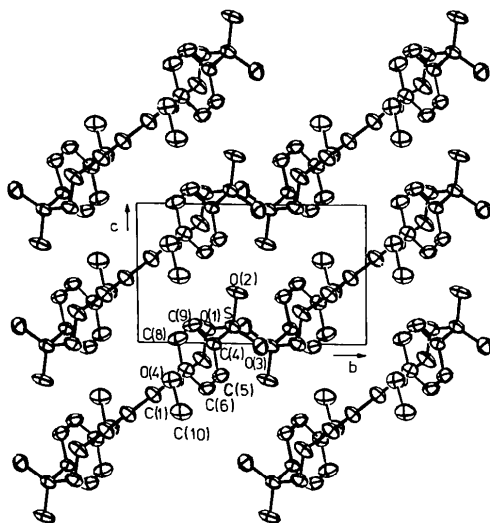


Fig. 1. Molecular plot of MBS viewed down *a*. 50% probability ellipsoids (ORTEP; Johnson, 1965).

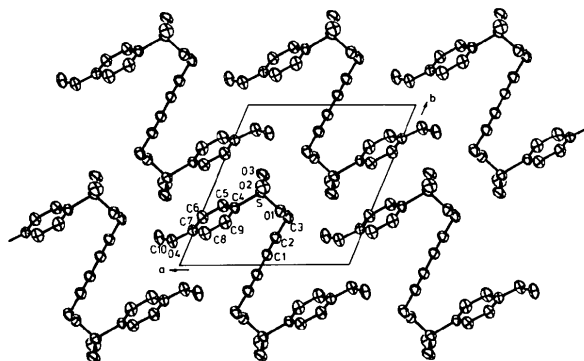


Fig. 2. Molecular plot of MBS viewed down *c*. 50% probability ellipsoids (ORTEP; Johnson, 1965).

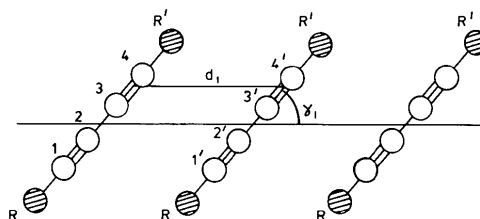


Fig. 3. Monomer packing requirements for the solid-state polymerization of diacetylenes, $4.8 < d_1 < 5.6$ Å and $\gamma_1 \approx 45^\circ$ (Wegner, 1977).

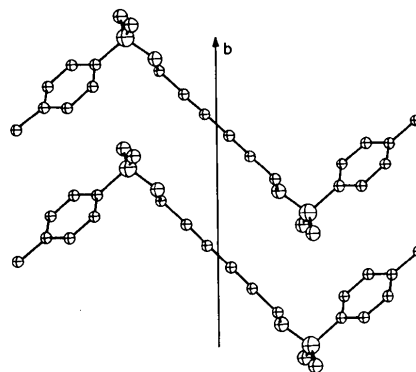
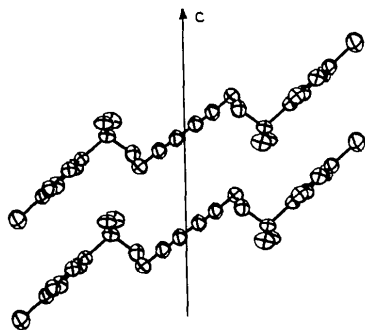


Fig. 4. TS monomer molecules viewed normal to *b*, orthogonal to the central diacetylene unit (Enkelmann, Leyrer & Wegner, 1979).

Table 5. *Intramolecular and intermolecular distances (Å) for the unreactive modification of MBS*

C(2)–C(4)	(<i>x, y, z</i>)	3.42	O(2)–C(3)	(1 – <i>x, 1 – y, –z</i>)	4.02	O(4)–C(10)	(2 – <i>x, –y, –1 – z</i>)	3.41
C(2)–C(10)	(1 + <i>x, y, z</i>)	3.56	O(3)–C(3)	(1 – <i>x, 1 – y, –z</i>)	3.20	O(4)–O(4)	(2 – <i>x, –y, –1 – z</i>)	3.43
C(3)–O(4)	(1 + <i>x, y, z</i>)	3.53	O(2)–H(C3)	(1 – <i>x, 1 – y, –z</i>)	3.58	O(2)–C(6)	(2 – <i>x, 1 – y, –z</i>)	3.36
C(3)–C(10)	(1 + <i>x, y, z</i>)	3.57	O(2)–H'(C3)	(1 – <i>x, 1 – y, –z</i>)	3.52	O(3)–C(7)	(2 – <i>x, 1 – y, –z</i>)	3.59
O(2)–C(5)	(<i>x, y, 1 + z</i>)	3.72	O(3)–H(C3)	(1 – <i>x, 1 – y, –z</i>)	3.12	O(2)–C(10)	(2 – <i>x, 1 – y, –z</i>)	3.78
O(2)–H(C5)	(<i>x, y, 1 + z</i>)	2.90	O(3)–H'(C3)	(1 – <i>x, 1 – y, –z</i>)	2.53	O(3)–C(10)	(2 – <i>x, 1 – y, –z</i>)	4.37

Fig. 5. Molecular plot of CBS viewed down *b*. 50% probability ellipsoids (Mayerle & Clarke, 1978).

(Williams, Ando, Bloor & Hursthouse, 1979), 2,4-hexadiynylene bis(β -naphthalenesulphonate), the C(2)–C(3)–O(1)–S torsion angle has been found to be -166.6° .

It follows from these results that the potential barrier for the rotation of the side group about C(3)–O(1) is rather shallow, within the range of torsion angles $+90^\circ$ to -90° . Smaller angles are unlikely because of steric hindrance due to the interaction of the diacetylenic C atoms with either the sulphonyl O atoms or the phenyl ring. In consequence the actual disposition of the diacetylenic group will depend strongly on the side-group interactions and packing. In TS and CBS the monomers pack in stacks (Figs. 4 and 5), and the interactions between the side groups have been discussed by Mayerle & Clarke (1978). In CBS the most important interaction for adjacent monomers was identified as the Cl–phenyl-ring interaction. This leads to contact between the sulphonyl O and the methylene H atoms, which increases the stack spacing relative to TS where the phenyl–phenyl interaction is important. However, they failed to note the configurational changes, which result from the different interactions and account primarily for the differences in reactivity.

In MBS the side groups stack in staggered pairs along the *cb* diagonal with alternate side groups belonging to the adjacent arrays of monomers which are aligned in the same direction. This maximizes the interaction of the methoxy O(4) with the same atom in the symmetry-related monomer at (2 – *x, –y, –1 – z*) (Table 5) and the pairwise interaction of the phenyl groups. Contact is produced between the sulphonyl

O(3) and the methylene H atoms on the symmetry-related monomer at (1 – *x, 1 – y, –z*). The C...H spacings are 3.12 and 2.53 Å. The optimum packing of the side groups achieved in this manner necessitates a large change in monomer configuration relative to TS and CBS, which is again the major cause of the absence of a solid-state reaction.

These results show the crucial role of side-group interactions in determining solid-state reactivity. However, these interactions are seen to have their major effect through the changes in monomer molecule configuration necessary to optimize crystal packing. The dramatic effect of these changes is well illustrated by the occurrence of the reactive phase of MBS (Bloor, Ando, Fisher & Hubble, 1979), which is more reactive than TS, but which can be crystallized simultaneously with the unreactive phase. Thus the crystal-lattice energies must be similar but we can conclude that the monomer molecule configurations and packing are different.

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Konformation von 2,3,4-Tri-*O*-benzoyl- β -D-xylopyranosylfluorid und 2,3,4-Tri-*O*-acetyl- β -D-xylopyranosylfluorid im Kristall

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Abstract

In the course of conformational studies on xylopyranosyl halides the crystal structures of 2,3,4-tri-*O*-benzoyl- β -D-xylopyranosyl fluoride ($C_{26}H_{21}FO_7$) (III) and 2,3,4-tri-*O*-acetyl- β -D-xylopyranosyl fluoride ($C_{11}H_{13}FO_7$) (VI) were determined by X-ray diffraction. (III) is triclinic, space group *P1*, with lattice constants $a = 11.152(5)$, $b = 10.028(5)$, $c = 10.897(4)$ Å, $\alpha = 90.20(1)$, $\beta = 111.87(1)$, $\gamma = 89.30(1)^\circ$, $Z = 2$. (VI) is orthorhombic, space group *P2₁2₁2₁*, with lattice constants $a = 16.190(7)$, $b = 11.210(6)$, $c = 7.353(4)$ Å, $Z = 4$. Solution of the phase problem and refinement were carried out for (VI) without difficulty. For (III), however, the structure could be solved in *P1*, although it could be proven from chemical reasons and from the result of the refinement that *P1* must be the correct space group. The two independent molecules of this structure are related almost centrosymmetrically, with the deviation from this symmetry caused mainly by the F atoms. (III) has the all-axial 1C_4 conformation and (VI) the equatorial 4C_1 conformation in the crystal although for both molecules the 1C_4 conformation dominates in solution.

Einleitung

Die 2,3,4-Tri-*O*-acyl- β -D-xylopyranosylhalogenide weisen in Lösung (Chloroform) eine Konformer-

verteilung auf, bei der die ungewöhnliche tetraaxiale 1C_4 -Konformation bevorzugt vorhanden ist. So liegen, wie die Tabelle 1 zeigt, die Tri-*O*-benzoyl-pyranosylhalogenide (I), (II) und (III) praktisch vollständig, die Tri-*O*-acetyl-pyranosylhalogenide zu etwa 80% in der 1C_4 -Konformation vor. Zum Vergleich ist in Tabelle 1 das Tetrabenzoat (IV) mit aufgeführt, bei dem die Konformationsanteile ausgeglichen sind. Als Ursache für die starke Bevorzugung der tetraaxialen 1C_4 -Konformation können folgende zwei Effekte angeführt

Tabelle 1. Konformation von substituierten Xylopyranosen in Lösung und im Kristall

Verbindung	1C_4 -Anteil in Lösung	Konformation im Kristall	Literatur
(I)	90%	1C_4	(1) (2)
(II)	98	2S_0	(3) (4)
(III)	98	1C_4	vorliegende Arbeit (5)
(IV)	50	1C_4	(4) (6)
(V)	79	4C_1	(7) (8) (9)
(VI)	84	4C_1	vorliegende Arbeit (5)

Literatur: (1) Luger, Durette & Paulsen (1974); (2) Bock, Pedersen & Rasmussen (1973); (3) Luger, Kothe & Paulsen (1976); (4) Durette & Horton (1971); (5) Hall & Manville (1969); (6) Luger, Kothe & Paulsen (1977); (7) Kothe, Luger & Paulsen (1974); (8) Holland, Horton & Jewell (1967); (9) Paulsen, Garrido-Espinosa, Trautwein & Heyns (1968).