Acta Cryst. (1985). C**41**, 227–229

Structures of a Series of Sulphonate Disubstituted Diacetylenes. I. 2,4-Hexadiynylene Bis(2-mesitylenesulphonate), $C_{24}H_{26}O_6S_2$

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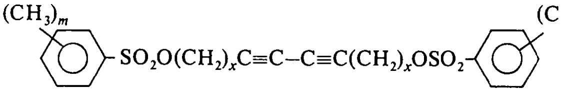
(*Received* 21 *March* 1984; *accepted* 26 *September* 1984)

Abstract. $M_r = 474{\cdot}59$, monoclinic, $P2_1/a$, $a = 5{\cdot}774\,(2)$, $b = 25{\cdot}864\,(3)$, $c = 7{\cdot}982\,(1)$ Å, $\beta = 95{\cdot}05\,(2)°$, $U = 1187{\cdot}4$ Å^3, $Z = 2$, $D_m = 1{\cdot}31\,(1)$, $D_x = 1{\cdot}326$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}70926$ Å, $\mu = 0{\cdot}215$ mm^{-1}, $F(000) = 500$, $T = 300$ K, $R = 0{\cdot}0433$ for 1418 counter reflections. The diacetylene molecules pack so that the potentially reacting carbon atoms, for *trans*-1,4-addition polymerization of adjacent molecules, are separated by a distance of 5·473 (2) Å. This accounts for the lack of solid-state polymerization for this compound, although its molecular conformation is similar to those of other, reactive, sulphonates of the same series.

Introduction. This paper is one of a series in which we present crystal structure data for diacetylenes with substituents containing sulphonate groups. Here and in following papers we present crystal structure data for various members of the general system (I).



(I)

where $2 \le m \le 5$, $1 \le x \le 4$.

The purpose of these investigations is to study the effects of the number and the positions of methyl groups on the benzene ring, in conjunction with increasing flexibility and carbon-chain length of the end group, on the reactivity of the diacetylene.

Experimental. Title compound (MSHD) prepared by reaction of mesitylenesulphonyl chloride with 2,4-hexadiyne-1,6-diol as previously reported for other sulphonate derivatives of diacetylenes (Ando, Bloor, Hubble & Williams, 1980). Recrystallization from methanol gave white crystalline solid (C = 60·59, H = 5·41, S = 13·35%; $C_{24}H_{26}O_6S_2$ requires C = 60·74, H = 5·52, S = 13·51%). Several diacetylenes with sulphonate-containing substituents crystallize in reactive and unreactive modifications (Ando *et al.*, 1980; Enkelmann, 1980). MSHD was obtained in only one modification, which did not polymerize either on heating to just below the melting point or on exposure to UV radiation or X-rays. Single crystals suitable for X-ray study grown by slow evaporation of methanol solutions; D_m by flotation in 1-propanol/bromoform; crystal $0{\cdot}5 \times 0{\cdot}35 \times 0{\cdot}12$ mm. Lattice parameters determined by least squares from setting angles of 25 reflections automatically centred on Enraf–Nonius CAD-4 diffractometer. Graphite-monochromated Mo $K\alpha$ radiation, $\omega/2\theta$ scans, $1{\cdot}5 < \theta < 27°$; scan rate 1·2–6·6° min^{-1}; ω scan width $(0{\cdot}8 + 0{\cdot}35\tan\theta)°$; aperture setting 4 mm; three standard reflections, monitored every hour, showed no decay. 2576 reflections measured, 2417 unique, $R_{\rm int} = 0{\cdot}018$, 1418 $[I_o > 1{\cdot}5\sigma(I_o)]$ used in refinement; index range h −6/5, k 0/32, l 0/10. Structure solved by direct methods using *SHELX* (Sheldrick, 1976). All non-H atoms located in best E map and subsequent difference map revealed positions of H atoms. Least-squares anisotropic refinement of positions of non-H atoms, isotropic refinement of all H atoms gave final $R = 0{\cdot}0433$; best agreement obtained with unit weights. $\Delta/\sigma(\max.) = 0{\cdot}08$, residual electron density within $\pm 0{\cdot}25$ e Å^{-3}. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). Final atomic parameters are listed in Table 1.* Computations were performed on the Queen Mary College ICL 2980 computer.

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* Lists of structure factors, anisotropic thermal parameters, non-bonded distances and bond lengths and angles involving H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39779 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

0108-2701/85/020227-03$01.50

Table 1. *Fractional coordinates* ($\times 10^5$ *for* S; $\times 10^4$ *for* C, O; $\times 10^3$ *for* H) *and equivalent isotropic temperature factors* [Å$^2 \times 10^4$; $U_{\rm iso}$ (Å$^2 \times 10^3$) *for* H *atoms*]

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

	x	y	z	$U_{\rm eq}/U_{\rm iso}$*
C(1)	391 (7)	97 (2)	4273 (5)	580
C(2)	1060 (6)	265 (2)	3028 (5)	564
C(3)	1952 (7)	474 (2)	1529 (5)	551
C(4)	3344 (6)	1368 (1)	−810 (4)	449
C(5)	3263 (6)	1201 (1)	−2490 (4)	497
C(6)	1578 (7)	1426 (2)	−3610 (5)	555
C(7)	9 (7)	1788 (2)	−3139 (5)	555
C(8)	192 (7)	1951 (2)	−1493 (5)	574
C(9)	1831 (6)	1752 (2)	−299 (4)	506
C(10)	4820 (10)	804 (3)	−3202 (6)	731
C(11)	−1808 (11)	2011 (3)	−4402 (8)	808
C(12)	1835 (11)	1971 (3)	1452 (7)	725
O(1)	6383 (4)	636 (1)	101 (3)	692
O(2)	6669 (5)	1457 (1)	1635 (4)	818
O(3)	3611 (4)	879 (1)	2083 (3)	553
S(1)	52852 (20)	10773 (5)	7501 (10)	547
H(31)	281 (7)	18 (2)	84 (5)	74 (13)
H(32)	94 (7)	59 (2)	68 (5)	73 (13)
H(6)	144 (6)	130 (1)	−472 (5)	59 (11)
H(8)	−76 (7)	225 (2)	−116 (5)	72 (12)
H(101)	599 (7)	84 (2)	−290 (5)	60 (16)
H(102)	459 (8)	77 (2)	−442 (6)	99 (16)
H(103)	441 (9)	38 (2)	−266 (6)	116 (18)
H(111)	−308 (11)	203 (3)	−404 (8)	140 (30)
H(112)	−209 (9)	183 (2)	−532 (7)	112 (22)
H(113)	−156 (10)	240 (3)	−499 (8)	151 (24)
H(121)	308 (11)	208 (3)	189 (8)	133 (27)
H(122)	139 (8)	177 (2)	204 (6)	71 (17)
H(123)	123 (11)	239 (3)	118 (8)	168 (27)

* $U_{\rm eq} = (U_{11}U_{22}U_{33})^{1/3}$.

Discussion. *CHEMGRAF* (Davies, 1983) drawings of the structure are shown in Figs. 1 and 2, and bond lengths and angles are given in Table 2.

A comparison with the analogous 2,4-hexadiynylene bis(benzenesulphonate) (BSHD) (Ando, Bloor, Hursthouse & Motevalli, 1985) and 2,4-hexadiynylene bis(*p*-toluenesulphonate) (TSHD) (Enkelmann, Leyrer & Wegner, 1979) shows that the molecular conformations are similar for all three compounds (TSHD, BSHD and MSHD). This conformation allows a reactive packing of the monomer units. Despite this, MSHD is unreactive in the solid state since it does not satisfy Schmidt's criterion for reactivity, *i.e.* the C(2)–C(2′) distance, in adjacent molecules, is more than 4 Å (Schmidt, 1967; Ando *et al.*, 1980; Bloor, 1982, 1983). For the measured separation of the MSHD monomers, *i.e.* 5·473 (2) Å, Schmidt's criterion can be satisfied if the angle between the diacetylene moieties and the *a* axis lies between 36 and 43°. These values are set by close packing of the diacetylene units and a C(2)–C(2′) distance of 4 Å. The value observed for MSHD, 66·3 (4)°, falls outside this range so that the C(2)–C(2′) distance is too large for reaction to occur.

An alternative criterion for reactivity of disubstituted diacetylenes has been proposed by Baughman (1974), who calculated the root-mean-square displacement of the molecules during reaction, which required that this

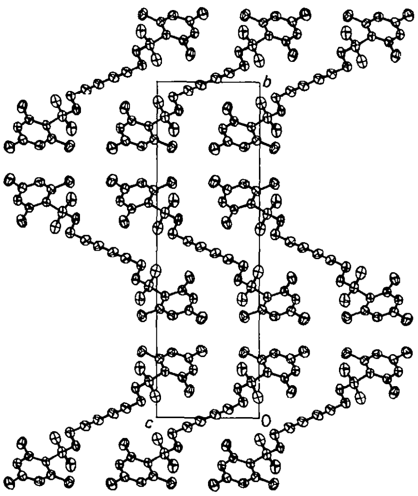

Fig. 1. View of the structure perpendicular to the *bc* plane. 50% probability ellipsoids are shown.

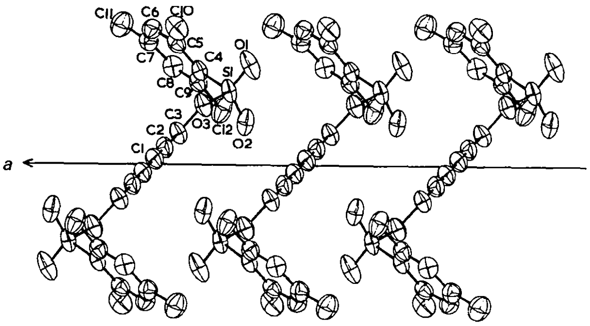

Fig. 2. View of the structure perpendicular to the *ab* plane. 50% probability ellipsoids are shown.

Table 2. *Interatomic distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

C(2)–C(1)	1·180 (6)	C(1)–C(1$^{\rm i}$)	1·377 (8)
C(3)–C(2)	1·448 (6)	O(3)–C(3)	1·461 (5)
C(5)–C(4)	1·406 (5)	C(9)–C(4)	1·407 (6)
S(1)–C(4)	1·769 (5)	C(6)–C(5)	1·389 (6)
C(10)–C(5)	1·508 (8)	C(7)–C(6)	1·379 (6)
C(8)–C(7)	1·374 (6)	C(11)–C(7)	1·504 (8)
C(9)–C(8)	1·381 (6)	C(12)–C(9)	1·508 (8)
S(1)–O(1)	1·425 (4)	S(1)–O(2)	1·414 (4)
S(1)–O(3)	1·585 (4)		

C(3)–C(2)–C(1)	178·2 (4)	O(3)–C(3)–C(2)	106·7 (4)
C(9)–C(4)–C(5)	121·6 (4)	S(1)–C(4)–C(5)	120·4 (4)
S(1)–C(4)–C(9)	117·9 (4)	C(6)–C(5)–C(4)	116·6 (4)
C(10)–C(5)–C(4)	126·8 (5)	C(10)–C(5)–C(6)	116·7 (4)
C(7)–C(6)–C(5)	123·3 (5)	C(8)–C(7)–C(6)	118·1 (5)
C(11)–C(7)–C(6)	121·0 (5)	C(11)–C(7)–C(8)	120·9 (5)
C(9)–C(8)–C(7)	122·5 (5)	C(8)–C(9)–C(4)	117·8 (4)
C(12)–C(9)–C(4)	125·7 (5)	C(12)–C(9)–C(8)	116·5 (5)
S(1)–O(3)–C(3)	116·9 (3)	O(1)–S(1)–C(4)	111·1 (3)
O(2)–S(1)–C(4)	110·6 (3)	O(2)–S(1)–O(1)	119·2 (3)
O(3)–S(1)–C(4)	103·0 (2)	O(3)–S(1)–O(1)	107·5 (3)
O(3)–S(1)–O(2)	104·0 (3)		

Symmetry code: (i) $-x$, $-y$, $1{\cdot}0-z$.

be a minimum, hence defining a least-motion reaction path. The r.m.s. displacement for MSHD is also large so that it does not provide a critical test of the criteria. The crystal structure data for other diacetylenes suggests, however, that the simple criterion of Schmidt is adequate for the assessment of solid-state reactivity of diacetylenes.

The larger monomer separation for MSHD relative to TSHD and BSHD [5·774 (2) compared with 5·159 (1) and 5·280 (1) Å] is due to the presence of the larger number of bulky methyl groups.

This work was supported by grants from the SERC.

References

Ando, D. J., Bloor, D., Hubble, C. L. & Williams, R. L. (1980). *Makromol. Chem.* **181**, 453–467.

Ando, D. J., Bloor, D., Hursthouse, M. B. & Motevalli, M. (1985). *Acta Cryst.* C**41**, 224–226.

Baughman, R. H. (1974). *J. Polym. Sci. Polym. Phys. Ed.* **12**, 1511–1535.

Bloor, D. (1982). *Developments in Crystalline Polymers* I, edited by D. C. Bassett, pp. 151–193. London: Applied Science Publishers.

Bloor, D. (1983). *Mol. Cryst. Liq. Cryst.* **93**, 183–199.

Davies, K. (1983). *SNOOPI.* Molecular plotting program in *CHEMGRAF* suite. Univ. of Oxford, England.

Enkelmann, V. (1980). *J. Mater. Sci.* **15**, 951–958.

Enkelmann, V., Leyrer, R. J. & Wegner, G. (1979). *Makromol. Chem.* **180**, 1787–1795.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

Schmidt, G. M. J. (1967). *Reactivity of Photoexcited Organic Molecules*, p. 227. New York: John Wiley.

Sheldrick, G. M. (1976). *SHELX.* Program for crystal structure determination. Univ. of Cambridge, England.

Acta Cryst. (1985). C**41**, 229–232

The Structure of the 2/1 'Channel' Inclusion Compound between Deoxycholic Acid and Pinacolone, $2C_{24}H_{40}O_4.C_6H_{12}O$

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(*Received* 6 *March* 1984; *accepted* 26 *September* 1984)

Abstract. $M_r = 885{\cdot}32$, orthorhombic, $P2_12_12_1$, $a = 27{\cdot}132\ (7)$, $b = 13{\cdot}543\ (2)$, $c = 14{\cdot}228\ (2)$ Å, $V = 5228\ (2)$ Å^3, $Z = 4$, $D_x = 1{\cdot}12$ Mg m^{-3}, Cu $K\alpha$, $\lambda = 1{\cdot}5418$ Å, $\mu = 0{\cdot}6$ mm^{-1}, $F(000) = 1952$, room temperature, $R = 0{\cdot}078$ and $R_w = 0{\cdot}079$ for 3067 independent reflections with $I > 1{\cdot}5\,\sigma(I)$. The crystal packing is very similar to those found in the deoxycholic acid inclusion compounds with norbornadiene and quadricyclane (tetracyclo[2.2.1.0^{2,6}.0^{3,5}]heptane), and is characterized by an assembly of antiparallel pleated bilayers of the steroid molecules, which pack together leaving empty spaces occupied by the guest molecules. The cross section of the channels is almost square. The centers of gravity of pinacolone, which assumes in the channels two different orientations related by a pseudo twofold axis, have coordinates approximately equal to those of norbornadiene and quadricyclane.

Introduction. The reversible valence isomerization of norbornadiene (NBD) to quadricyclane (QDC) is an attractive process for the chemical storage of solar energy (Hautala, Little & Sweet, 1977). Because of the lack of overlap between the electronic absorption spectrum of NBD and the solar radiance spectrum, the direct conversion NBD→QDC by sunlight is precluded. However, this conversion is still achievable by means of photosensitizers. Since the quantum efficiency of the reaction and the purity of QDC could be improved inside the channels of an inclusion compound, those of the deoxycholic acid (DCA) were chosen for this purpose.

The inclusion compounds between DCA and NBD (DCANBD; D'Andrea, Fedeli, Giglio, Mazza & Pavel, 1981) and QDC (DCAQDC; Coiro, Giglio, Mazza & Pavel, 1984) were studied in order to establish whether the DCA host lattices are nearly equal. Since the DCA host lattice does not change, it is possible to foresee that it can easily tolerate the lattice-controlled photoinduced reaction NBD→QDC, without destroying the crystal structure of the inclusion compound. Furthermore, the structural information gained from the crystal packing of DCANBD and DCAQDC is useful for the choice of

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