

compound is characteristic of that in fredericamycin A (Fig. 1a, Misra *et al.*, 1982). The bond lengths C(1)—O(1) and C(4)—O(2) [1.216(9) and 1.202(9) Å respectively] indicate that the carbonyl groups are properly positioned for further synthesis. The distribution of bond lengths and angles around the 'spiro' atom C(5) shows some interesting features. The internal angle in both the five-membered rings at C(5) [average angle 102.4(6)°] compares well with the theoretical value of 103.4° obtained in a VF calculation on (S)-(—)-spiro[4.4]nonane-1,6-dione (Altona, de Graaff, Leeuwstein & Romers, 1971). However, the bond lengths around the spiro C atom show larger variations [from 1.52(1) to 1.59(1) Å] than those predicted by the theoretical calculations [1.519 to 1.529 Å]. It is clear that the large variations in the title compound arise from steric interactions between the atoms in the neighbourhood of the spiro junction and also from the forced aromatic nature of the two parts of the molecule. The angle between these two planes is 89.9(6)° which provides the necessary spatial requirements for further synthetic feasibility towards fredericamycin A.

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## Structures of a Series of Sulfonate Disubstituted Diacetylenes. III. 4,6-Decadiynylene Bis(pentamethylbenzenesulfonate)

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**Abstract.** C<sub>32</sub>H<sub>42</sub>O<sub>6</sub>S<sub>2</sub>, *M<sub>r</sub>* = 586.80, monoclinic, *C2/c*, *a* = 21.632(3), *b* = 18.669(2), *c* = 15.063(2) Å, β = 97.65(1)°, *U* = 6029.0 Å<sup>3</sup>, *Z* = 8, *D<sub>m</sub>*(300 K) = 1.29(1), *D<sub>x</sub>* = 1.29 Mg m<sup>-3</sup>, λ(Cu Kα) = 1.5418 Å, μ = 1.836 mm<sup>-1</sup>, *F*(000) = 2512, *T* = 300 K, final *R* = 0.0463 for 2766 counter reflections. The molecule adopts a Z-shaped conformation with the aromatic rings on either side of the diacetylene group. The lack of solid-state polymerization for this compound is a consequence of this molecular conformation, which sterically inhibits any topochemical reaction of the diacetylene moieties in adjacent molecules.

**Introduction.** This paper forms part of a series in which we correlate crystal structure and solid-state reactivity of diacetylenes with substituent groups containing sulfonate groups. Details of the background to these studies are given in the first paper in the series (Werninck, Blair, Milburn, Ando, Bloor, Motevalli & Hursthouse, 1985).

**Experimental.** Title compound (PMDD) prepared by the general method reported previously (Ando, Bloor, Hubble & Williams, 1980). Recrystallization from methanol gave a white crystalline solid (*C* = 65.13,

H = 7.24, S = 10.00%; C<sub>32</sub>H<sub>42</sub>O<sub>6</sub>S<sub>2</sub> requires C = 65.50, H = 7.21, S = 10.93%). PMDD obtained in only one modification, which did not polymerize either on heating to just below the melting point or on exposure to UV radiation,  $\gamma$ -rays or X-rays. Single crystals suitable for X-ray study grown by slow evaporation of acetone solutions at room temperature;  $D_m$  by flotation in 1-propanol/bromoform. Crystal of approximate dimensions 0.20 × 0.20 × 0.60 mm used for data collection. Lattice parameters determined by least-squares fitting of setting angles of 25 reflections automatically centred on a CAD-4 diffractometer. Intensities collected with Ni-filtered Cu  $K\alpha$  radiation,  $\omega/2\theta$  scan mode, with  $3 \leq \theta \leq 70^\circ$ , scan rate 1.2 to 6.6° min<sup>-1</sup>,  $\omega$ -scan width (0.8 + 0.35 tan $\theta$ )°, aperture setting 4 mm. Three intensity control reflections, monitored after every hour of data collection, showed some decay, corrected for during the data processing. 4747 reflections measured, 4464 unique,  $R_{\text{int}} = 0.028$ , 2766 [ $I_o > 3.0\sigma(I_o)$ ] used in refinement, index range:  $h \pm 24$ ,  $k 0/20$ ,  $l 0/16$ . Structure solved by direct methods using *SHELX76* (Sheldrick, 1976). All non-H and most H

atoms revealed by difference map; remaining H atoms (on methyl groups) inserted in idealized positions. Least-squares anisotropic refinement of non-H atoms and free isotropic refinement of all H atoms gave final  $R = 0.0463$  and  $wR = 0.0498$ ,  $w = 1/[\sigma^2(F_o) + 0.0005 \times F_o^2]$ , giving acceptable agreement analysis.  $\Delta/\sigma$  (max.) = 0.64;  $\Delta\rho$  within  $\pm 0.25 \text{ e \AA}^{-3}$ . Data corrected for absorption by method of North, Phillips & Mathews (1968); transmission 0.9690–0.9986. Final atomic parameters are listed in Table 1.\* Computations made at Queen Mary College using the Chemical Crystallography VAX 11/750 computer. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). *CHEMGRAF* (Davies, 1983) drawings of the structure are shown in Fig. 1, which shows the atom numbering, and Fig. 2; bond lengths and angles are given in Table 2.

\* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and bond lengths and angles involving H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. 42595 (24 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional atomic coordinates for the C and O ( $\times 10^4$ ) and S atoms ( $\times 10^3$ ) and equivalent isotropic temperature factors ( $\text{\AA}^2 \times 10^3$  for C and O;  $\text{\AA}^2 \times 10^4$  for S), with e.s.d.'s in parentheses

	x	y	z	$U_{\text{eq}}^*$
C(1)	1296 (2)	2031 (2)	-1399 (2)	60 (1)
C(2)	1182 (2)	1404 (2)	-1417 (2)	62 (2)
C(3)	1059 (2)	635 (2)	-1477 (3)	65 (2)
C(4)	1634 (2)	195 (2)	-1602 (3)	62 (2)
C(5)	1942 (2)	422 (2)	-2389 (3)	56 (1)
C(6)	1644 (2)	1617 (2)	-3878 (2)	42 (1)
C(7)	2193 (2)	2025 (2)	-3823 (2)	47 (1)
C(8)	2139 (2)	2767 (2)	-3780 (2)	52 (1)
C(9)	1563 (2)	3090 (2)	-3788 (2)	54 (1)
C(10)	1028 (2)	2676 (2)	-3773 (2)	55 (1)
C(11)	1065 (2)	1931 (2)	-3818 (2)	47 (1)
C(12)	2845 (2)	1710 (3)	-3773 (4)	71 (2)
C(13)	2728 (3)	3230 (4)	-3735 (6)	93 (3)
C(14)	1513 (4)	3902 (2)	-3800 (4)	90 (2)
C(15)	412 (3)	3026 (4)	-3715 (5)	102 (3)
C(16)	472 (2)	1502 (3)	-3774 (4)	69 (2)
S(1)	16554 (4)	6787 (4)	-40885 (6)	528 (3)
O(1)	1489 (1)	336 (1)	-3193 (2)	54 (1)
O(2)	2252 (1)	435 (1)	-4234 (2)	78 (1)
O(3)	1141 (1)	498 (1)	-4745 (2)	75 (1)
C(17)	1444 (2)	2746 (2)	-1352 (2)	63 (2)
C(18)	1579 (2)	3371 (2)	-1307 (2)	64 (2)
C(19)	1742 (2)	4128 (2)	-1206 (3)	67 (2)
C(20)	1184 (2)	4608 (2)	-1126 (3)	62 (2)
C(21)	827 (2)	4389 (2)	-384 (3)	56 (1)
C(22)	791 (1)	3310 (2)	1252 (2)	42 (1)
C(23)	175 (2)	3075 (2)	1260 (2)	49 (1)
C(24)	63 (2)	2333 (2)	1245 (2)	49 (1)
C(25)	548 (2)	1849 (2)	1210 (2)	50 (1)
C(26)	1147 (2)	2091 (2)	1167 (2)	48 (1)
C(27)	1284 (1)	2826 (2)	1192 (2)	46 (1)
C(28)	-383 (3)	3567 (3)	1273 (5)	74 (2)
C(29)	-595 (2)	2062 (2)	1286 (3)	69 (2)
C(30)	418 (3)	1048 (2)	1207 (4)	75 (2)
C(31)	1668 (3)	1556 (3)	1090 (5)	72 (2)
C(32)	1947 (2)	3063 (2)	1154 (4)	60 (1)
S(2)	9820 (4)	42399 (4)	13453 (6)	493 (3)
O(4)	1256 (1)	4411 (1)	455 (1)	50 (1)
O(5)	1491 (1)	4340 (1)	2036 (2)	67 (1)
O(6)	446 (1)	4674 (1)	1374 (2)	62 (1)

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

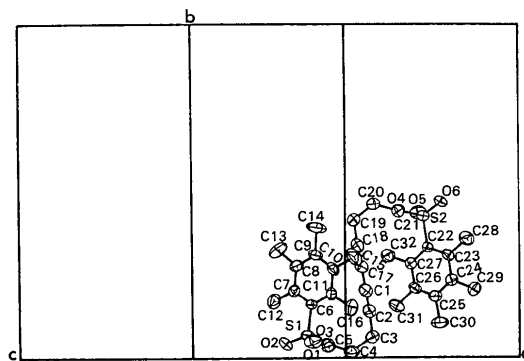


Fig. 1. View of a molecule projected along [101], with the cell outline included. 50% probability ellipsoids are shown.

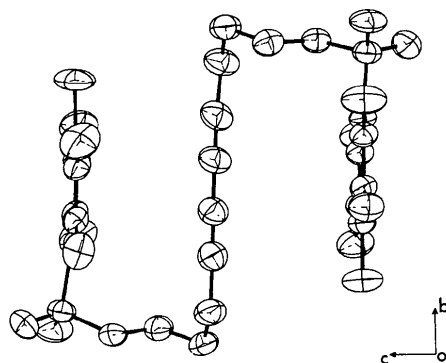


Fig. 2. View of a molecule perpendicular to the bc plane. 50% probability ellipsoids are shown.

**Discussion.** Only one other diacetylene compound with a  $-(CH_2)_3-$  sequence between the sulfonate moieties has been reported, this being 4,6-decadiynylene bis-(durennesulfonate) (DSDD) (Day, Ando, Bloor, Norman, Blair, Werninck, Milburn, Motevalli & Hursthouse, 1985), so a direct comparison with a range of very similar diacetylenes is not possible. There are similarities with some of the methyl substituted bis-(benzenesulfonate esters) of 2,4-hexadiyne-1,6-diol, in particular 2,4-hexadiynylene bis(*p*-methoxybenzenesulfonate) (MBSHD) and 2,4-hexadiynylene bis-(pentamethylbenzenesulfonate) (PMHD) (Fisher, Ando, Bloor & Hursthouse, 1979; Motevalli, Norman, Hursthouse, Werninck, Milburn, Blair, Bloor & Ando, 1986). In these compounds the aromatic rings lie to either side of the diacetylene moiety forming a *Z* shape.

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

C(2)–C(1)	1.196 (6)	C(17)–C(1)	1.373 (6)
C(3)–C(2)	1.462 (6)	C(4)–C(3)	1.522 (8)
C(5)–C(4)	1.497 (7)	O(1)–C(5)	1.461 (5)
C(7)–C(6)	1.404 (5)	C(11)–C(6)	1.397 (6)
S(1)–C(6)	1.780 (5)	C(8)–C(7)	1.393 (5)
C(12)–C(7)	1.521 (8)	C(9)–C(8)	1.382 (6)
C(13)–C(8)	1.533 (10)	C(10)–C(9)	1.395 (6)
C(14)–C(9)	1.519 (8)	C(11)–C(10)	1.395 (6)
C(15)–C(10)	1.497 (9)	C(16)–C(11)	1.520 (8)
O(1)–S(1)	1.578 (4)	O(2)–S(1)	1.412 (4)
O(3)–S(1)	1.427 (4)	C(18)–C(17)	1.201 (6)
C(19)–C(18)	1.461 (6)	C(20)–C(19)	1.520 (8)
C(21)–C(20)	1.499 (7)	O(4)–C(21)	1.466 (5)
C(23)–C(22)	1.405 (5)	C(27)–C(22)	1.409 (5)
S(2)–C(22)	1.787 (5)	C(24)–C(23)	1.405 (5)
C(28)–C(23)	1.519 (8)	C(25)–C(24)	1.391 (6)
C(29)–C(24)	1.521 (8)	C(26)–C(25)	1.383 (6)
C(30)–C(25)	1.522 (7)	C(27)–C(26)	1.403 (5)
C(31)–C(26)	1.522 (8)	C(32)–C(27)	1.509 (7)
O(4)–S(2)	1.570 (4)	O(5)–S(2)	1.422 (3)
O(6)–S(2)	1.420 (3)		
C(17)–C(1)–C(2)	178.0 (4)	C(3)–C(2)–C(1)	177.2 (4)
C(4)–C(3)–C(2)	113.1 (5)	C(5)–C(4)–C(3)	113.7 (4)
O(1)–C(5)–C(4)	107.8 (4)	C(11)–C(6)–C(7)	121.8 (4)
S(1)–C(6)–C(7)	120.8 (3)	S(1)–C(6)–C(11)	117.3 (3)
C(8)–C(7)–C(6)	117.9 (4)	C(12)–C(7)–C(6)	124.4 (4)
C(12)–C(7)–C(8)	117.6 (4)	C(9)–C(8)–C(7)	120.9 (4)
C(13)–C(8)–C(7)	119.2 (5)	C(13)–C(8)–C(9)	119.8 (5)
C(10)–C(9)–C(8)	120.5 (4)	C(14)–C(9)–C(8)	119.9 (5)
C(14)–C(9)–C(10)	119.6 (5)	C(11)–C(10)–C(9)	119.9 (4)
C(15)–C(10)–C(9)	120.4 (5)	C(15)–C(10)–C(11)	119.7 (5)
C(10)–C(11)–C(6)	118.6 (4)	C(16)–C(11)–C(6)	123.4 (4)
C(16)–C(11)–C(10)	118.0 (4)	O(1)–S(1)–C(6)	103.6 (2)
O(2)–S(1)–C(6)	112.3 (3)	O(2)–S(1)–O(1)	108.7 (2)
O(3)–S(1)–C(6)	109.2 (2)	O(3)–S(1)–O(1)	104.5 (2)
O(3)–S(1)–O(2)	117.4 (3)	S(1)–O(1)–C(5)	117.4 (3)
C(18)–C(17)–C(1)	179.4 (4)	C(19)–C(18)–C(17)	177.3 (4)
C(20)–C(19)–C(18)	113.3 (5)	C(21)–C(20)–C(19)	113.0 (4)
O(4)–C(21)–C(20)	107.8 (4)	C(27)–C(22)–C(23)	121.9 (4)
S(2)–C(22)–C(23)	120.8 (3)	S(2)–C(22)–C(27)	117.3 (3)
C(24)–C(23)–C(22)	117.9 (4)	C(28)–C(23)–C(22)	124.6 (4)
C(28)–C(23)–C(24)	117.5 (4)	C(25)–C(24)–C(23)	120.8 (4)
C(29)–C(24)–C(23)	119.1 (4)	C(29)–C(24)–C(25)	120.0 (4)
C(26)–C(25)–C(24)	120.3 (4)	C(30)–C(25)–C(24)	119.9 (4)
C(30)–C(25)–C(26)	119.8 (4)	C(27)–C(26)–C(25)	121.0 (4)
C(31)–C(26)–C(25)	119.8 (4)	C(31)–C(26)–C(27)	119.3 (4)
C(26)–C(27)–C(22)	118.0 (4)	C(32)–C(27)–C(22)	123.1 (4)
C(32)–C(27)–C(26)	118.9 (4)	O(4)–S(2)–C(22)	103.9 (2)
O(5)–S(2)–C(22)	109.5 (2)	O(5)–S(2)–O(4)	104.7 (2)
O(6)–S(2)–C(22)	112.1 (2)	O(6)–S(2)–O(4)	108.2 (2)
O(6)–S(2)–O(5)	117.3 (2)	S(2)–O(4)–C(21)	117.5 (3)

This conformation is also adopted by PMDD (see Figs. 1 and 2). For both the decadiynylene derivatives, DSDD and PMDD, the longer  $CH_2$  sequences provide larger angles through which the substituted benzenesulfonate groups can be folded back on themselves (Fig. 2).

Potential reaction of the diacetylene moieties is prohibited for PMDD by steric factors. Along the *c* axis, the aromatic groups of the same molecule are interposed between the diacetylene units. The only possible reaction is along the *ac* diagonal. In this case, however, the reaction is prevented by a number of factors. Firstly, the monomers are arranged in pairs with the diacetylene moieties parallel in each pair, but non-parallel from one pair to another. Very few examples of reactions of non-parallel diacetylenes are known (but see Patel, Duesler, Curtin & Paul, 1980). Thus, at best, a localized reaction could occur producing a dimer, but further propagation to form a polymer chain would be unlikely. Secondly, the monomer units are so far apart that no carbon atoms have separation distances less than the 4 Å necessary for a solid-state topochemical reaction to occur (Schmidt, 1967). In fact, the distance between C(2) and C(2') at  $-x, y, \frac{1}{2}-z$ , which must react if a *trans*-1,4-addition reaction is to occur, is 5.691 (3) Å. Finally, the lattice packing provides steric hindrance that would present a large energy barrier for reaction, *i.e.* considerable rearrangement of the side groups would be necessary to allow a reaction to take place.

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