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Structures of a Series of Sulfonate Disubstituted Diacetylenes. V. 3,5-Octadiynylene Bis(2-mesitylenesulfonate)

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Abstract. $C_{26}H_{30}O_6S_2$, $M_r = 502·6$, monoclinic, $P2_1/n$, $a = 19·951$ (2), $b = 6·139$ (3), $c = 10·528$ (2) Å, $\beta = 92·26$ (2)°, $V = 1288·5$ Å^3, $Z = 2$, $D_m = 1·28$ (1), $D_x = 1·29$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 0·20$ mm^{-1}, $F(000) = 532$, $T = 300$ K. Final $R = 0·052$ for 1139 counter reflections. The triple-bond length is 1·188 (6) Å, the central single bond 1·383 (10) Å and the interbond angle 178·5 (5)°. The absence of a topochemical polymerization for this diacetylene monomer is a direct consequence of the molecular packing.

Introduction. The solid-state reactivity of crystals of disubstituted diacetylenes is controlled by the packing of the monomer molecules in the crystal. This paper reports a further structure in this series of compounds. Details concerning the background to these studies can be found in part I of the series (Werninck, Blair, Milburn, Ando, Bloor, Motevalli & Hursthouse, 1985).

Experimental. Title compound (MSOD) prepared by the general method used previously (Werninck *et al.*, 1985). Recrystallization from methanol gave a white crystalline solid (C = 61·97, H = 6·01, S = 12·56%; $C_{26}H_{30}O_6S_2$ requires C = 62·13, H = 6·02, S = 12·56%). Only one modification of MSOD was obtained which did not polymerize either on heating to just below the melting point or on exposure to UV radiation, γ-rays, or X-rays. Single crystals suitable for X-ray study grown by slow evaporation from acetone solutions; crystal *ca* 0·325 × 0·275 × 0·125 mm selected for data collection. D_m, lattice parameters and intensity data measured as described previously (Werninck *et al.*, 1985). Three intensity-control reflections, monitored after every hour of data collection, showed no decay. 2717 reflections measured, θ 1·5–25°, 2266 unique, $R_{\rm int} = 0·018$, 1139 [$F_o > 4·0\sigma(F_o)$] used in refinement, index range h ±23, k +7, l +12. No absorption corrections applied. Structure solved by direct methods using *SHELX76* (Sheldrick, 1976). All non-H atoms located in best E map and subsequent difference map revealed positions of H atoms. Least-squares anisotropic refinement (based on F) of positions of non-H atoms and methylene and phenyl H atoms freely refined isotropically (methyl H atoms refined as part of rigid groups) gave R and wR of 0·0516 and 0·0652, respectively, $w = 1/[\sigma^2(F) + 0·0005F^2]$; Δ/σ(max.) = 0·30; $\Delta\rho$ within ±0·25 e Å^{-3}. Final atomic parameters are listed in Table 1.* Computations made at Queen Mary College using the Chemical Crystallography VAX11/750 computer; f, f' and f'' values from *International Tables for X-ray Crystallography* (1974). *CHEMGRAF* (Davies, 1983) drawings of the structure are shown in Figs. 1 and 2, which show the atom numbering; bond lengths are given in Table 2.

Discussion. The inclusion of an additional CH_2 group in the end groups of MSOD means that the molecular conformation is not comparable with those of most of the other disubstituted diacetylenes for which we have reported structures (Werninck *et al.*, 1985, and references therein). The only related compound studied is the 3,5-octadiynylene bis(*p*-toluenesulfonate) (TSOD) (Williams, Ando, Bloor, Hursthouse & Motevalli, 1980), and even in this the molecular conformation differs. In TSOD, the terminal conjugated ring lies approximately parallel to the diacetylene moiety while in MSOD it is approximately

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, all bond angles, bond lengths involving H atoms, intermolecular contact distances and an additional figure have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42780 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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orthogonal. In addition, in TSOD the molecules do not form stacks while in MSOD they do.

The diacetylene units are separated by 6·139 (3) Å along the stack direction (*b* axis) with the diacetylene moieties close to a parallel stack. For such a large separation of monomers the angle of tilt with respect to the stack axis would have to lie between 36 and 40° if Schmidt's (1967) criterion of less than 4 Å separation of the potentially reactive C(2) atoms is to be satisfied. This is clearly not the case, in accord with the absence of solid-state polymerization in MSOD. The large separation along **b** is due to the fact that the planes of the mesitylene groups lie close to the *b* axis forcing the monomer units apart.

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Table 1. *Fractional coordinates* ($\times 10^4$) *with e.s.d.'s in parentheses and equivalent isotropic temperature factors* ($\text{Å}^2 \times 10^4$) *for the non-*H *atoms*

	x	*y*	*z*	U_{eq}*
C(1)	48 (2)	148 (8)	5649 (4)	623
C(2)	116 (2)	386 (8)	6766 (4)	648
C(3)	205 (3)	761 (9)	8143 (5)	739
C(4)	694 (3)	2456 (11)	8393 (5)	997
C(5)	2015 (2)	3458 (7)	10241 (4)	499
C(6)	2526 (3)	4246 (7)	9474 (4)	587
C(7)	3125 (3)	3133 (9)	9529 (4)	662
C(8)	3245 (3)	1328 (8)	10250 (4)	634
C(9)	2738 (3)	615 (8)	11004 (4)	615
C(10)	2120 (2)	1622 (7)	11022 (4)	528
C(11)	2467 (3)	6214 (9)	8581 (5)	909
C(12)	3911 (3)	120 (10)	10243 (5)	877
C(13)	1602 (3)	619 (8)	11866 (5)	707
O(1)	724 (2)	2884 (6)	9753 (3)	670
O(2)	1032 (2)	5085 (6)	11523 (3)	843
O(3)	1180 (2)	6490 (6)	9387 (4)	919
S(1)	1218 (1)	4727 (2)	10249 (1)	651

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

Table 2. *Interatomic distances* (Å)

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

C(2)–C(1)	1·188 (6)	C(1)–C(1^{i})	1·383 (10)
C(3)–C(2)	1·471 (7)	C(4)–C(3)	1·443 (8)
O(1)–C(4)	1·455 (6)	C(6)–C(5)	1·410 (7)
C(10)–C(5)	1·406 (7)	S(1)–C(5)	1·771 (7)
C(7)–C(6)	1·376 (8)	C(11)–C(6)	1·533 (9)
C(8)–C(7)	1·359 (8)	C(9)–C(8)	1·381 (8)
C(12)–C(8)	1·521 (9)	C(10)–C(9)	1·381 (7)
C(13)–C(10)	1·519 (8)		
S(1)–O(1)	1·577 (5)	S(1)–O(2)	1·423 (4)
S(1)–O(3)	1·413 (5)		

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

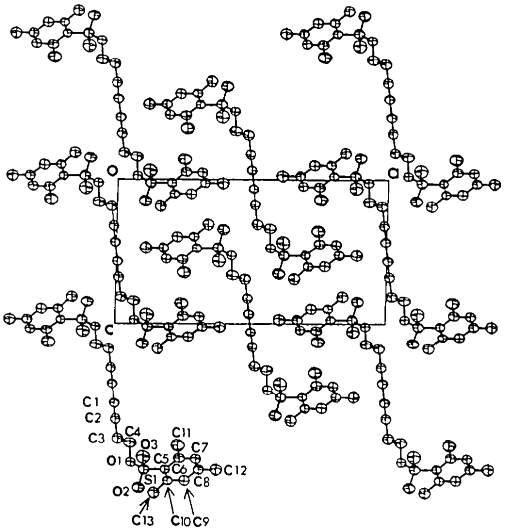

Fig. 1. View of the structure perpendicular to the *ac* plane. 50% probability ellipsoids are shown.

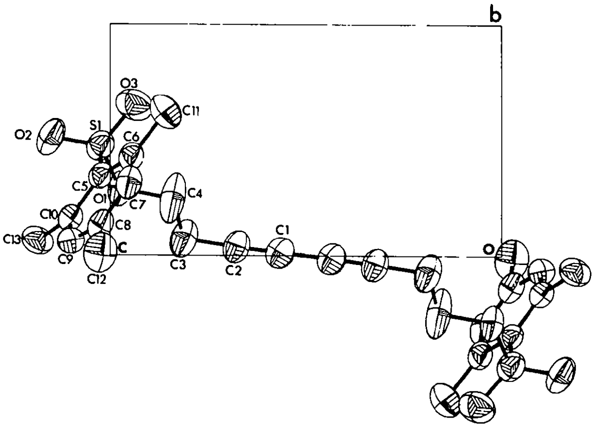

Fig. 2. View of the molecule perpendicular to the *bc* plane. 50% probability ellipsoids are shown.

References

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

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

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

Sheldrick, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

Werninck, A. R., Blair, E., Milburn, H. W., Ando, D. J., Bloor, D., Motevalli, M. & Hursthouse, M. B. (1985). *Acta Cryst.* C**41**, 227–229.

Williams, R. L., Ando, D. J., Bloor, D., Hursthouse, M. B. & Motevalli, M. (1980). *Acta Cryst.* B**36**, 2155–2157.