Acta Cryst. (1986). C**42**, 1049–1050

Structures of a Series of Sulfonate Disubstituted Diacetylenes. IV. 2,4-Hexadiynylene Bis(pentamethylbenzenesulfonate)

By Majid Motevalli, Philip A. Norman and Michael B. Hursthouse

*Department of Chemistry, Queen Mary College, Mile End Road, London E*1 4*NS, England*

Alan R. Werninck, Harry W. Milburn and Elizabeth Blair

*Department of Chemistry, Napier College of Commerce and Technology, Colinton Road, Edinburgh EH*10 5*DT, Scotland*

and David Bloor and David J. Ando

*Department of Physics, Queen Mary College, Mile End Road, London E*1 4*NS, England*

(*Received* 21 *January* 1985; *accepted* 21 *January* 1986)

Abstract. $C_{28}H_{34}O_6S_2$, $M_r = 530{\cdot}7$, triclinic, $P\bar{1}$, $a = 6{\cdot}446\,(3)$, $b = 9{\cdot}296\,(2)$, $c = 11{\cdot}776\,(2)$ Å, $\alpha = 73{\cdot}75\,(2)$, $\beta = 75{\cdot}22\,(3)$, $\gamma = 85{\cdot}61\,(3)°$, $V = 655{\cdot}0$ Å^3, $Z = 1$, $D_m = 1{\cdot}29\,(1)$, $D_x = 1{\cdot}35$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 0{\cdot}199$ mm^{-1}, $F(000) = 282$, $T = 300$ K. Final $R = 0{\cdot}0434$ for 1952 counter reflections. The triple-bond length is 1·189 (5) Å, the central bond 1·375 (7) Å and the interbond angle 179·0 (3)°. The monomer adopts a conformation which prevents the close approach of the potentially reacting C atoms, necessary for *trans*-1,4-addition polymerization of adjacent molecules, and this accounts for the lack of solid-state polymerization of this diacetylene.

Introduction. This paper continues the series in which we correlate crystal structure and solid-state reactivity of diacetylenes with substituent groups containing sulfonate units. Details of the background to these studies can be found in the first paper of the series (Werninck, Blair, Milburn, Ando, Bloor, Motevalli & Hursthouse, 1985).

Experimental. Title compound (PMHD) prepared by the general method reported previously (Ando, Bloor, Hubble & Williams, 1980). Recrystallization from methanol gave a white crystalline solid (C = 63·05, H = 6·45, S = 11·58%; $C_{28}H_{34}O_6S_2$ requires C = 63·37, H = 6·46, S = 12·08%). Only one modification of PMHD 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* 0·375 × 0·375 × 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. 2669 reflections measured, θ 1·5–26°, 2561 unique, $R_{\text{int}} = 0{\cdot}007$, 1952 $[F_o > 3{\cdot}0\sigma(F_o)]$ used in refinement, index range $h \pm 7$, $k -10/11$, $l\,0/14$. No absorption corrections applied. Structure solved by direct methods using *SHELX*76 (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 free, isotropic refinement of all H atoms gave final $R = 0{\cdot}0434$; max. Δ/σ in final cycle 0·76; unit weights used; residual electron density within $\pm 0{\cdot}28$ e Å^{-3}. Final atomic parameters are listed in Table 1.* Computations 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 Fig. 1, which shows the atom numbering, and Fig. 2; bond lengths are given in Table 2.

Discussion. The molecular conformation of PMHD is similar to that of the inactive modification of 2,4-hexadiynylene bis(methoxybenzenesulfonate) (MBSHD) (Fisher, Ando, Bloor & Hursthouse, 1979). In this case, the end group is rotated about the C(3)—O(3) bond by approximately 90° from that found in reactive monomers with similar side groups (Ando *et al.*, 1980). The torsion angles for PMHD,

---

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, all bond angles, bond lengths involving H atoms and intermolecular contact distances have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42779 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

0108-2701/86/081049-02$01.50

MBSHD and the reactive forms of the bis(benzenesulfonate) (BSHD) and bis(*p*-toluenesulfonate) (TSHD) analogues are given in Table 3. While BSHD and TSHD have nearly identical conformations despite different lattice packing, in the case of PMHD the orientation of the plane of the phenyl ring is rotated by about 40°, relative to that in MBSHD. This is due to steric constraints imposed by the bulky methyl groups for PMHD.

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

	x	y	z	U_{eq}*
C(1)	4568 (5)	678 (3)	10071 (3)	412
C(2)	3801 (5)	1850 (3)	10181 (3)	430
C(3)	2848 (6)	3289 (4)	10298 (3)	506
C(4)	3500 (4)	3260 (3)	7377 (2)	332
C(5)	5551 (4)	3348 (3)	6576 (2)	374
C(6)	6375 (4)	2065 (3)	6226 (3)	412
C(7)	5188 (5)	746 (3)	6651 (3)	397
C(8)	3068 (4)	735 (3)	7343 (2)	365
C(9)	2181 (4)	2008 (3)	7697 (2)	339
C(10)	6834 (6)	4789 (4)	6023 (4)	573
C(11)	8627 (6)	2091 (6)	5394 (4)	653
C(12)	6167 (8)	−682 (5)	6364 (5)	668
C(13)	1749 (8)	−683 (4)	7752 (4)	592
C(14)	−154 (5)	1987 (4)	8394 (3)	472
O(1)	900 (4)	5550 (3)	7622 (2)	703
O(2)	4383 (4)	5538 (3)	8106 (2)	678
O(3)	1522 (3)	3885 (2)	9442 (2)	462
S(1)	2602 (1)	4729 (1)	8080 (1)	456

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

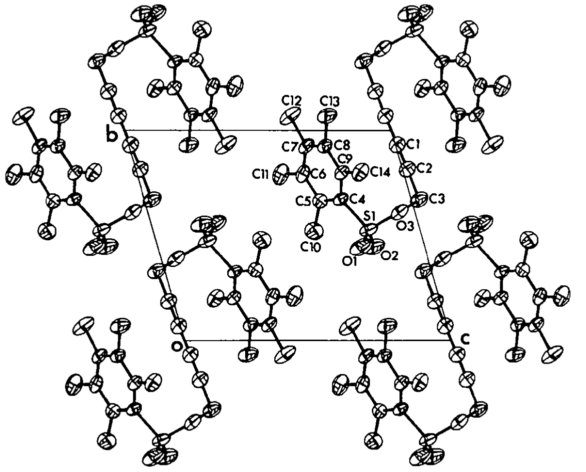

Fig. 1. View of the structure perpendicular to the *bc* plane. 50% probability ellipsoids are shown.

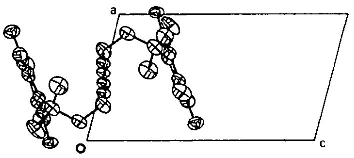

Fig. 2. View of one molecule perpendicular to the *ac* plane. 50% probability ellipsoids are shown.

Table 2. *Interatomic distances* (Å)

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

C(2)—C(1)	1·189 (5)	C(1)—C(1^i)	1·375 (7)
C(3)—C(2)	1·456 (5)	O(3)—C(3)	1·451 (5)
C(5)—C(4)	1·408 (5)	C(9)—C(4)	1·401 (5)
S(1)—C(4)	1·776 (5)	C(6)—C(5)	1·393 (5)
C(10)—C(5)	1·519 (6)	C(7)—C(6)	1·394 (5)
C(11)—C(6)	1·528 (6)	C(8)—C(7)	1·400 (5)
C(12)—C(7)	1·512 (6)	C(9)—C(8)	1·397 (5)
C(13)—C(8)	1·516 (6)	C(14)—C(9)	1·518 (6)
S(1)—O(1)	1·422 (3)	S(1)—O(2)	1·430 (3)
S(1)—O(3)	1·576 (4)		

Symmetry code: (i) 1·0 − x, −y, 2·0 − z.

Table 3. *Selected dihedral angles* (°) *for PMHD, MBSHD, BSHD and TSHD, showing principal differences*

Atomic labelling as in Fig. 1. Previous labellings have been changed for consistency with PMHD. E.s.d.'s are typically 0·2°.

	PMHD	MBSHD	BSHD	TSHD
C(2)—C(3)—O(3)—S(1)	81·2	95·6	170·6	170·4
C(3)—O(3)—S(1)—O(2)	35·5	36·7	40·3	37·9
C(3)—O(3)—S(1)—O(1)	162·1	165·2	170·3	169·3
C(3)—O(3)—S(1)—C(4)	−81·5	−79·7	−76·0	−76·7
C(5)—C(4)—S(1)—O(3)	136·8	100·3	109·8	103·4
C(9)—C(4)—S(1)—O(3)	−39·5	−80·8	−70·1	−76·0
C(5)—C(4)—S(1)—O(2)	−22·4	−16·4	−5·7	−11·6
C(9)—C(4)—S(1)—O(2)	153·9	162·5	174·3	169·0
C(5)—C(4)—S(1)—O(1)	−111·3	−149·3	−141·1	−146·2
C(9)—C(4)—S(1)—O(1)	72·4	29·6	39·0	34·4

Angles were calculated from the following data: MBSHD (Fisher *et al.*, 1979); BSHD (Ando, Bloor, Hursthouse & Motevalli, 1985); TSHD (Aime, Lefebvre, Bertault, Schott & Williams, 1982).

In the conformation adopted by PMHD the side groups prevent close approach of the potentially reactive C(2) atoms in adjacent molecules, as can be seen from Fig. 1. Solid-state reactivity is prevented in this case by steric hindrance.

This work was supported by grants from the SERC.

References

Aime, J. P., Lefebvre, J., Bertault, M., Schott, M. & Williams, J. O. (1982). *J. Phys.* (*Paris*), **43**, 307–322.

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.

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

Fisher, D. A., Ando, D. J., Bloor, D. & Hursthouse, M. B. (1979). *Acta Cryst.* B**35**, 2075–2079.

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

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.