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Structures of a Series of Sulphonate Disubstituted Diacetylenes. II. 4,6-Decadiynylene Bis(3-durenesulphonate),* $C_{30}H_{38}O_6S_2$

By Richard J. Day, David J. Ando, David Bloor and Philip A. Norman

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

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

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

and Majid Motevalli and Michael B. Hursthouse

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

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Abstract. $M_r = 558\cdot75$, monoclinic, $P2_1/n$, $a = 6\cdot311\,(1)$, $b = 17\cdot862\,(2)$, $c = 12\cdot921\,(2)$ Å, $\beta = 96\cdot94\,(1)^\circ$, $V = 1445\cdot87$ Å^3, $Z = 2$, $D_m = 1\cdot28\,(1)$, $D_x = 1\cdot28$ Mg m^{-3}, $\lambda(\mathrm{Cu}\,K\alpha) = 1\cdot54178$ Å, $\mu = 1\cdot892$ mm^{-1}, $F(000) = 596$, $T = 300$ K, final $R = 0\cdot0406$ for 2184 counter reflections. The aromatic rings lie on either side of the diacetylene unit forming an S-shape. The molecular conformation adopted by the monomer sterically inhibits a topochemical reaction of the diacetylene units in nearest-neighbour molecules, and accounts for the lack of solid-state polymerization for this compound.

Introduction. This paper is a further part of a series in which we are seeking to establish a correlation between the solid-state reactivity and the crystal structure of diacetylenes with common substituent groups containing sulphonate moieties. The background details to these studies are described in the first paper of the series (Werninck, Blair, Milburn, Ando, Bloor, Motevalli & Hursthouse, 1985) and further members of this class of diacetylenes are described in papers III (Day, Bloor, Ando, Norman, Hursthouse, Motevalli, Milburn, Blair & Werninck, 1985), IV (Motevalli, Norman, Hursthouse, Werninck, Milburn, Blair, Bloor & Ando, 1985) and V (Bloor, Ando, Motevalli, Norman, Hursthouse, Milburn, Werninck & Blair, 1985).

Experimental. Title compound (DSDD) prepared by the general method reported previously (Ando, Bloor, Hubble & Williams, 1980). Recrystallization from methanol gave a light-cream crystalline solid (C = 64·14, H = 6·93, S = 11·45%; $C_{30}H_{38}O_6S_2$ requires C = 64·69, H = 6·85, S = 11·48%). Only one modification of DSDD 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 of approximate dimensions 0·30 × 0·30 × 0·125 mm selected 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, scan rate 1·2–6·6° min^{-1}, ω-scan width $(0\cdot8 + 0\cdot15\tan\theta)^\circ$, aperture setting 4 mm. Two intensity control reflections, monitored after every hour of data collection, showed no decay. 3198 reflections measured, θ 3–70°, 2758 unique, $R_{\mathrm{int}} = 0\cdot018$, 2184 $[F_o > 3\cdot0\sigma(F_o)]$ used in refinement, index range $h \pm 7$, k 0/21, l 0/15. 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 free, isotropic refinement of all H atoms gave final $R = 0\cdot0406$, $wR = 0\cdot0485$, $w = 1/[\sigma^2(F_o) + 0\cdot0001F_o^2]$. $\Delta/\sigma(\max.) = 0\cdot36$; $\Delta\rho$ within $\pm 0\cdot3$ e Å^{-3}. Data corrected for absorption by method of North, Phillips & Mathews (1968); transmission 0·81–1·00. Final atomic parameters are listed in Table 1.† Computations made at Queen Mary College using the Chemical Crystallography VAX11/750 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.

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* Durene is 1,2,4,5-tetramethylbenzene.

† 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 Publiction No. SUP 42279 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Fractional atomic coordinates* ($\times 10^4$) *and equivalent isotropic temperature factors* (Å$^2 \times 10^4$ *for* C *and* O; Å$^2 \times 10^5$ *for* S)

$U_{eq} = (U_{11}U_{22}U_{33})^{1/3}$. E.s.d.'s are given in parentheses.

	x	y	z	U_{eq}
C(1)	4760 (4)	4626 (1)	−40 (2)	56 (1)
C(2)	4348 (4)	3974 (1)	−119 (2)	58 (1)
C(3)	3830 (5)	3176 (1)	−203 (2)	63 (1)
C(4)	5281 (4)	2691 (1)	540 (2)	60 (1)
C(5)	5427 (4)	2932 (1)	1663 (2)	56 (1)
C(6)	3488 (3)	4181 (1)	2993 (1)	45 (1)
C(7)	2015 (3)	4614 (1)	2342 (1)	45 (1)
C(8)	2346 (4)	5384 (1)	2310 (2)	53 (1)
C(9)	4120 (4)	5684 (1)	2883 (2)	63 (1)
C(10)	5613 (4)	5264 (1)	3490 (2)	61 (1)
C(11)	5324 (3)	4492 (1)	3564 (2)	51 (1)
C(12)	117 (4)	4302 (2)	1661 (2)	63 (1)
C(13)	823 (7)	5896 (2)	1659 (3)	83 (1)
C(14)	7538 (6)	5658 (3)	4064 (3)	95 (1)
C(15)	7010 (6)	4050 (3)	4245 (3)	85 (1)
O(1)	3263 (2)	2904 (1)	1956 (1)	56 (1)
O(2)	725 (3)	3094 (1)	3134 (2)	88 (1)
O(3)	4405 (3)	2842 (1)	3809 (1)	85 (1)
S(1)	2932 (1)	3206 (1)	3065 (1)	595 (2)

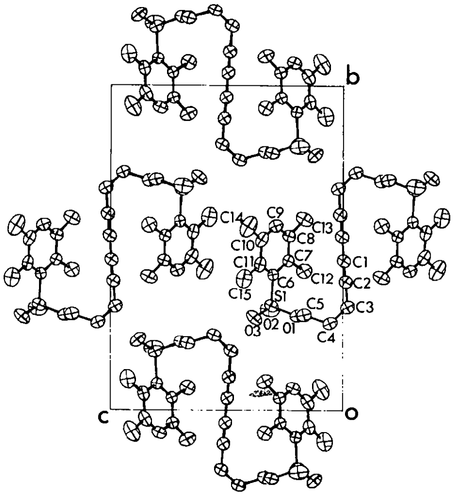

Fig. 1. View of the structure perpendicular to the *bc* plane. 50% probability ellipsoids are shown.

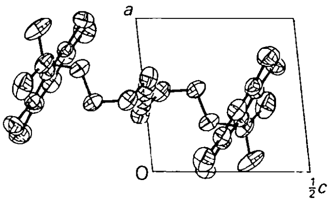

Fig. 2. View of the molecule perpendicular to the *ac* plane. 50% probability ellipsoids are shown.

Table 2. *Interatomic distances* (Å) *and angles* (°)

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

C(2)—C(1)	1·195 (4)	C(1)—C(1^i)	1·372 (5)
C(3)—C(2)	1·464 (4)	C(4)—C(3)	1·516 (5)
C(5)—C(4)	1·506 (5)	O(1)—C(5)	1·462 (4)
C(7)—C(6)	1·408 (4)	C(11)—C(6)	1·411 (4)
S(1)—C(6)	1·781 (4)	C(8)—C(7)	1·392 (4)
C(12)—C(7)	1·505 (5)	C(9)—C(8)	1·374 (4)
C(13)—C(8)	1·507 (6)	C(10)—C(9)	1·373 (4)
C(11)—C(10)	1·396 (4)	C(14)—C(10)	1·517 (6)
C(15)—C(11)	1·518 (5)	S(1)—O(1)	1·569 (3)
S(1)—O(2)	1·420 (3)	S(1)—O(3)	1·413 (3)

C(3)—C(2)—C(1)	179·2 (2)	C(1^i)—C(1)—C(2)	179·4 (2)
C(5)—C(4)—C(3)	114·1 (3)	C(4)—C(3)—C(2)	113·4 (3)
C(11)—C(6)—C(7)	122·5 (3)	O(1)—C(5)—C(4)	106·8 (3)
S(1)—C(6)—C(11)	120·8 (2)	S(1)—C(6)—C(7)	116·7 (2)
C(12)—C(7)—C(6)	124·5 (3)	C(8)—C(7)—C(6)	118·1 (3)
C(9)—C(8)—C(7)	118·9 (3)	C(12)—C(7)—C(8)	117·4 (3)
C(13)—C(8)—C(9)	119·2 (3)	C(13) C(8) C(7)	121·8 (3)
C(11)—C(10)—C(9)	119·4 (3)	C(10)—C(9)—C(8)	123·6 (3)
C(14)—C(10)—C(11)	121·8 (4)	C(14)—C(10)—C(9)	118·7 (4)
C(15)—C(11)—C(6)	124·9 (4)	C(10)—C(11)—C(6)	117·3 (3)
S(1)—O(1)—C(5)	117·2 (2)	C(15)—C(11)—C(10)	117·7 (3)
O(2)—S(1)—C(6)	110·0 (2)	O(1)—S(1)—C(6)	103·9 (2)
O(3)—S(1)—C(6)	111·6 (2)	O(2)—S(1)—O(1)	104·4 (2)
O(3)—S(1)—O(2)	117·5 (2)	O(3)—S(1)—O(1)	108·2 (2)

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

Discussion. Direct comparison of the conformation of DSDD with other sulphonate-containing diacetylenes is not possible because it is the only compound with a —$(CH_2)_3$— sequence between the diacetylene and sulphonate moieties that has been reported so far. There are, however, similarities with the structures of the —(CH_2)-linked compounds 2,4-hexadiynylene bis(*p*-methoxybenzenesulphonate) (MBSHD) (Fisher, Ando, Bloor & Hursthouse, 1979) and 2,4-hexadiynylene bis(pentamethylbenzenesulphonate) (PMHD) (Motevalli *et al.*, 1985). In all three compounds, the aromatic rings lie on either side of the diacetylene unit forming an S- (or a Z-) shape, as shown in Fig. 1. For DSDD the additional CH_2 links allow the terminal groups to be folded back through a larger angle than for MBSHD and PMHD.

The reaction of the diacetylene moieties is prevented for DSDD by steric factors. In the *bc* plane the aromatic units are interposed between the diacetylene units. Along the *a* axis the monomer molecules form stacks but the necessary displacement of the C(2) atoms would bring them into close contact with the CH_3 units of the durene ring in the adjacent molecule (see Fig. 1). In addition, a considerable, energetically unfavourable, distortion of the molecule would be necessary for the formation of a polymer chain along the *a* axis. Finally the separation of potentially reactive C atoms, *i.e.* C(2) and C(2)′, is 6·260 (2) Å, much larger than the 4 Å maximum separation given by the Schmidt criterion for solid-state reactivity (Schmidt, 1967).

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Structures of Three Pyrazaboles:* 1,3,5,7-Tetramethylpyrazabole, $C_{10}H_{18}B_2N_4$; 4,4-Bis(1-pyrazolyl)pyrazabole, $C_{12}H_{14}B_2N_8$; and 4,4,8,8-Tetrakis(1-pyrazolyl)pyrazabole, $C_{18}H_{18}B_2N_{12}$

By C. P. Brock and K. Niedenzu

Department of Chemistry, University of Kentucky, Lexington, KY 40506–0055, *USA*

and E. Hanecker and H. Nöth†

Institute for Inorganic Chemistry, University of Munich, D-8000 *Munich* 2, *Federal Republic of Germany*

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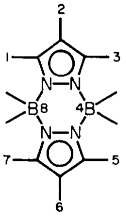
Abstract. 1,3,5,7-Tetramethylpyrazabole (hereafter, ME4PZB): M_r = 215·9, monoclinic, $P2_1/c$, a = 7·552 (1), b = 12·047 (4), c = 13·814 (6) Å, β = 91·27 (2)°, V = 1256·5 (7) Å^3, Z = 4, D_x = 1·141 g cm^{-3}, Mo $K\alpha$, graphite monochromator, λ = 0·71069 Å, μ = 0·65 cm^{-1}, F(000) = 464, T = 295 K, final R = 0·055 for 199 variables and 1424 reflections. 4,4-Bis(1-pyrazolyl)pyrazabole (hereafter BISPZB): M_r = 291·9, triclinic, $P\bar{1}$, a = 8·721 (2), b = 9·351 (2), c = 9·407 (2) Å, α = 93·75 (2), β = 100·75 (2), γ = 92·73 (2)°, V = 750·7 (2) Å^3, Z = 2, D_x = 1·291 g cm^{-3}, Mo $K\alpha$, graphite monochromator, λ = 0·71069 Å, μ = 0·79 cm^{-1}, F(000) = 304, T = 295 K, R = 0·035 for 255 variables and 1957 reflections. 4,4,8,8-Tetrakis(1-pyrazolyl)pyrazabole (hereafter TETPZB): M_r = 424·0, monoclinic, $P2_1/n$, a = 8·849 (2), b = 21·765 (2), c = 11·672 (1) Å, β = 109·51 (1)°, V = 2118·9 (5) Å^3, Z = 4, D_x = 1·329 g cm^{-3}, Mo $K\alpha$, graphite monochromator, λ = 0·71069 Å, μ = 0·82 cm^{-1}, F(000) = 880, T = 296 K, final R = 0·036 for 362 variables and 1880 reflections. In all three structures the pyrazabole adopts a pronounced boat conformation. A comparison with the nine other known pyrazabole structures, however, shows that the central B_2N_4 ring is quite flexible, and that its observed conformation is sensitive to substituent and packing effects.

Introduction. The pyrazaboles, which have the general structure and numbering scheme shown below,



are a class of heterocycles containing four-coordinate boron and exhibiting remarkable chemical and thermal stability. Recent efforts by one of us to exploit this stability (Clarke, Niedenzu, Niedenzu & Trofimenko, 1985) have focused on synthesizing polymeric pyrazaboles containing B atoms as spiro centers. In

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* Alternative name for pyrazabole: 3a,4a,7a,8a-tetraaza-4,8-dibora-*s*-indacene.

† Contribution No. 151 in the series 'Chemistry of Boron'.

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