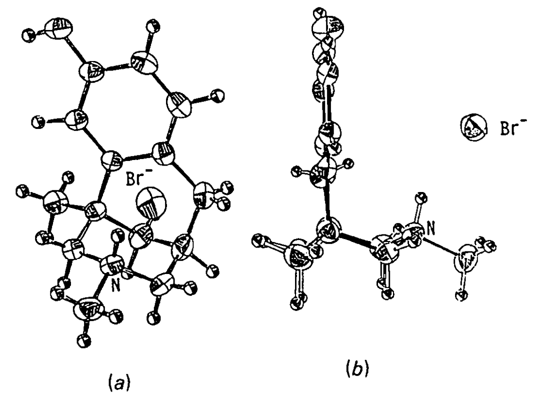

Fig. 2. Perspective views of the molecule (*a*) normal to the molecular plane and (*b*) from the side.

the center of the benzene ring, 4·11 Å, is rather short compared to the corresponding value in (2), 4·69 Å. It is noteworthy that, in spite of these considerable structural differences, the present compound still retains analgesic activity. A Br atom connects two adjacent molecules by two hydrogen bonds, O···Br 3·23 Å [H(O)···Br 2·39 Å] and N···Br 3·35 Å [H(N)···Br 2·53 Å], resulting in an infinite chain in the crystal packing.

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Structure of 2,4-Hexadiynylene Bis(benzenesulphonate), $C_{18}H_{14}O_6S_2$

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Abstract. $M_r = 390·43$, monoclinic, $P2_1/c$, $a = 13·079\ (3)$, $b = 5·280\ (1)$, $c = 13·977\ (6)$ Å, $\beta = 111·19\ (3)°$, $U = 899·95$ Å^3, $Z = 2$, $D_m = 1·42\ (1)$, $D_x = 1·441$ Mg m^{-3}, Cu $K\alpha$, $\lambda = 1·54184$ Å, $\mu = 2·832$ mm^{-1}, $F(000) = 404$, $T = 300$ K, $R = 0·0438$ for 1271 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 3·746 (6) Å. This accounts for the occurrence of solid-state polymerization for this compound. The bond lengths and angles agree with those of similar compounds.

Introduction. The fact that many disubstituted diacetylenes (general formula R-C⋮C·C⋮C-R') can be polymerized in the solid state to give extended-chain polymers was first recognized by Wegner (1969, 1971, 1972). Since this discovery there have been extensive investigations of the solid-state chemistry of diacetylenes (see Bloor, 1982, 1983*a*, and references therein) and of the properties of the resulting polymers (see Bloor, 1981, 1983*b*, and references therein). The solid-state reactivity of the diacetylene monomers is determined by the packing of the molecules in the crystal, which is in turn dependent on the properties of the monomer end groups R and R' (Baughman, 1974; Wegner, 1977; Bloor, 1982). Crystal structure data have been used to test the criteria proposed for solid-state reactivity (Baughman, 1974; Schmidt, 1967). Available data show that Schmidt's criterion

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that the reacting C atoms, C(1) and C(4) on neighbouring diacetylene molecules, must be separated by less than 4 Å is adequate (Bloor, 1982, 1983*a*,*b*).

So far little progress has been made in using this knowledge as a tool to predict the reactivity of diacetylene monomers. Crystal structure data for a series of diacetylenes with chemically similar side groups are required to enable further insights to be gained into the relationship of molecular and crystal structure. Some data are already available for the series of symmetric diacetylenes containing a sulphonate group in the substituents: 2,4-hexadiynylene bis(*p*-toluenesulphonate) (TSHD) (Enkelmann, Leyrer & Wegner, 1979), 2,4-hexadiynylene bis(methoxybenzenesulphonate) (MBSHD) (Fisher, Ando, Bloor & Hursthouse, 1979), 2,4-hexadiynylene bis(naphthalenesulphonate) (NSHD) (Williams, Ando, Bloor & Hursthouse, 1979), 2,4-hexadiynylene bis(*p*-chlorobenzenesulphonate) (CBSHD) (Mayerle & Clarke, 1978), 2,4-hexadiynylene bis(*p*-bromobenzenesulphonate) (BBSHD) (Williams, Ando, Bloor, Motevalli & Hursthouse, 1982), 3,5-octadiynylene bis(*p*-toluenesulphonate) (TSOD) (Williams, Ando, Bloor, Hursthouse & Motevalli, 1980) and 5,7-dodecadiynylene bis(*p*-toluenesulphonate) (TSDDD or TS-12) (Siegel, Sixl, Enkelmann & Wenz, 1982). We have therefore embarked upon the syntheses of further members of this series in order to study their crystal structures and solid-state reactivity.

Experimental. Title compound (BSHD) prepared by reaction of *p*-benzenesulphonyl chloride with 2,4-hexadiyne-1,6-diol as previously reported for other sulphonate derivatives of diacetylenes (Ando, Bloor, Hubble & Williams, 1980). Recrystallization from acetone gave colourless crystalline solid (C = 55·48, H = 3·81, S = 15·99%; $C_{18}H_{14}O_6S_2$ requires C = 55·37, H = 3·61, S = 16·42%). Slow growth from acetone solution provided crystals suitable for X-ray study; D_m by flotation in 1-propanol/bromoform. Crystal 0·30 × 0·20 × 0·12 mm. Although some of the diacetylenes with sulphonate-containing end groups exhibit two crystal modifications the title compound was obtained in only one modification, which polymerized extremely slowly at room temperature. Lattice parameters determined by least squares from setting angles of 25 reflections automatically centred on Enraf–Nonius CAD-4 diffractometer. Ni-filtered Cu $K\alpha$ radiation, $\omega/2\theta$ scans; $3 < \theta < 70°$; scan rate 1·3–6·7° min^{-1}; ω scan width $(0·9 + 0·3 \tan\theta)°$; aperture setting 4 mm; three standard reflections, monitored every hour, showed no decay. 1978 reflections measured, 1711 unique, $R_{\rm int} = 0·0162$, 1271 $[I_o > 3\sigma(I_o)]$ used in refinement; index range h −15/14, k 0/6, l 0/16. 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 $R = 0·0438$ and $wR = 0·0434$; $w = 1/[\sigma^2(F_o) + 0·00001\ F_o^2]$; data corrected for absorption by method of North, Phillips & Mathews (1968), transmission factors 1·0–0·74. $\Delta/\sigma(\max.) = 0·004$, residual electron density within ±0·3 e Å^{-3}. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). Final atomic parameters are listed in Table 1.*

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

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

	x	y	z	$U_{\rm eq}/U_{\rm iso}$*
C(1)	148 (2)	−4082 (6)	4726 (3)	713
C(2)	418 (2)	−2530 (6)	4256 (3)	727
C(3)	756 (3)	−646 (8)	3674 (3)	780
C(4)	3005 (2)	44 (6)	3225 (2)	612
C(5)	3835 (3)	−1545 (7)	3774 (3)	740
C(6)	4249 (3)	−3235 (8)	3273 (4)	886
C(7)	3847 (4)	−3339 (8)	2222 (4)	950
C(8)	3026 (4)	−1730 (9)	1677 (3)	937
C(9)	2597 (3)	−9 (7)	2158 (3)	759
O(1)	1675 (2)	3773 (4)	3133 (2)	825
O(2)	1798 (2)	381 (4)	4357 (1)	721
O(3)	3292 (2)	3171 (4)	4727 (2)	959
S(1)	2443 (1)	2169 (2)	3861 (1)	707
H(31)	29 (2)	79 (6)	356 (2)	84 (11)
H(32)	90 (2)	−128 (6)	309 (2)	91 (12)
H(5)	405 (2)	−154 (6)	454 (2)	90 (11)
H(6)	479 (3)	−424 (6)	364 (3)	101 (13)
H(7)	418 (4)	−444 (9)	189 (3)	166 (20)
H(8)	278 (3)	−178 (7)	104 (2)	92 (13)
H(9)	206 (2)	118 (5)	183 (2)	68 (9)

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

Discussion. Molecular plots, obtained with *CHEMGRAF* (Davies, 1983), are shown in Figs. 1 and 2, and bond lengths and angles are given in Table 2. A comparison with the analogous TSHD (Enkelmann *et al.*, 1979) shows that the molecular conformations and bond lengths and angles are all very similar. The unit cell of BSHD, however, is slightly smaller than that of TSHD in the **a** and **c** directions owing to the smaller size of the end groups. Consideration of the series of monomers shows that three molecular conformations occur, typified by TSHD and the unreactive forms of CBSHD and MBSHD. Only the former allows the monomers to pack close enough to satisfy Schmidt's (1967) criterion for reactivity (Ando, Bloor, Hubble & Williams, 1980; Bloor, 1982). For the observed separation of BSHD monomers along **b**, *i.e.*

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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 39778 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

5·280 (1) Å, the limits for the angle between the axis of the diacetylene moiety and **b**, set by close packing at the van der Waals radius and a C(2)–C(2′) distance of 4 Å, are 40 and 49°. The observed angle, 45·2 (4)°, falls within this range, in accord with the solid-state reactivity of BSHD.

More surprising is the much slower polymerization rate of BSHD relative to TSHD since the molecular packing is very similar. Application of the theory of lattice-strain-controlled polymerization, which has been applied successfully to TSHD (Baughman, 1978; Baughman & Chance, 1980), would suggest slightly slower polymerization for BSHD than for TSHD. The very large difference observed is, however, difficult to explain on this model even if the defect density of the BSHD crystals were higher than that of the TSHD crystals.

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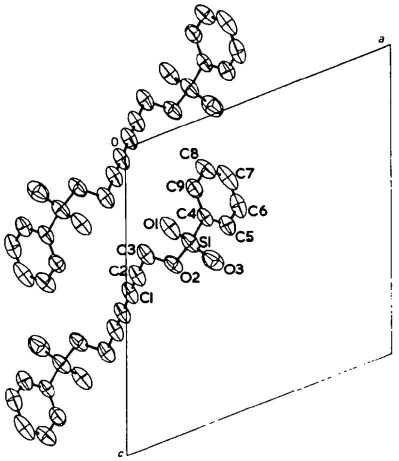

Fig. 1. View of the structure perpendicular to the *ac* plane. 50% probability ellipsoids are shown.

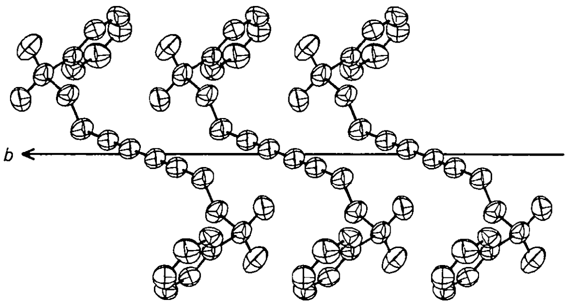

Fig. 2. View of the structure perpendicular to the *ab* plane. 50% probability ellipsoids are shown.

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

C(2)–C(1)	1·181 (5)	C(1)–C(1$^{\text{i}}$)	1·375 (7)
C(3)–C(2)	1·452 (5)	O(2)–C(3)	1·457 (5)
C(5)–C(4)	1·367 (5)	C(9)–C(4)	1·391 (5)
S(1)–C(4)	1·751 (5)	C(6)–C(5)	1·362 (6)
C(7)–C(6)	1·371 (7)	C(8)–C(7)	1·365 (6)
C(9)–C(8)	1·366 (6)	S(1)–O(1)	1·422 (3)
S(1)–O(2)	1·583 (4)	S(1)–O(3)	1·416 (3)
C(3)–C(2)–C(1)	179·3 (4)	O(2)–C(3)–C(2)	106·9 (4)
C(9)–C(4)–C(5)	120·6 (4)	S(1)–C(4)–C(5)	120·1 (4)
S(1)–C(4)–C(9)	119·3 (4)	C(6)–C(5)–C(4)	119·7 (5)
C(7)–C(6)–C(5)	120·5 (5)	C(8)–C(7)–C(6)	119·5 (5)
C(9)–C(8)–C(7)	121·3 (5)	C(8)–C(9)–C(4)	118·4 (5)
S(1)–O(2)–C(3)	117·1 (3)	O(1)–S(1)–C(4)	109·6 (2)
O(2)–S(1)–C(4)	103·2 (2)	O(2)–S(1)–O(1)	108·6 (2)
O(3)–S(1)–C(4)	109·3 (2)	O(3)–S(1)–O(1)	121·5 (2)
O(3)–S(1)–O(2)	103·1 (2)		

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

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