

## Structure of 2,4-Hexadiynylene Bis( $\beta$ -naphthalenesulphonate)

BY RICHARD L. WILLIAMS, DAVID J. ANDO AND DAVID BLOOR

*Department of Physics, Queen Mary College, Mile End Road, London E1 4NS, England*

AND MICHAEL B. HURSTHOUSE

*Department of Chemistry, Queen Mary College, Mile End Road, London E1 4NS, England*

(Received 13 March 1979; accepted 23 April 1979)

### Abstract

$C_{26}H_{18}O_6S_2$ , monoclinic,  $P2_1/n$ ,  $a = 13.4457$  (9),  $b = 5.4213$  (3),  $c = 15.9033$  (9) Å,  $\beta = 100.964$  (5)° at 300 K;  $D_m$  (300 K) = 1.40,  $D_c$  (300 K) = 1.432 Mg m<sup>-3</sup>,  $Z = 2$ ;  $F(000) = 508$ ,  $\mu(Cu K\alpha) = 2.349$  mm<sup>-1</sup>,  $\lambda(Cu K\alpha) = 1.54178$  Å. The final  $R = 0.054$  for 1878 counter reflections collected at 300 K. The details of the crystal structure explain why the compound does not undergo solid-state polymerization under the influence of heat or UV irradiation.

### Introduction

Many diacetylenes (having the general formula  $R-C\equiv C:C\equiv C-R'$ ) undergo solid-state polymerization reactions (Wegner, 1969, 1972), polymerization being initiated by thermal, mechanical or photochemical techniques. Whether or not a specific diacetylene can undergo a solid-state transformation into a polymeric material is governed by the molecular packing of the molecules and by the properties of the side groups  $R$  and  $R'$  (Baughman, 1974; Wegner, 1977). This work was conducted as part of a study of the spectroscopic and structural properties of a series of diacetylene monomers with similar end groups in an attempt to correlate the effect of small changes in these groups with solid-state reactivity.

### Experimental

The title compound (NS) was prepared by the reaction of  $\beta$ -naphthalenesulphonyl chloride with 2,4-hexadiyne-1,6-diol with the method reported by Wegner (1971) for the analogous ditosylate (TS) derivative. Extraction with ether and recrystallization from acetone gave a light-brown crystalline solid, m.p. 405 K ( $C = 63.47$ ,  $H = 3.85$ ,  $S = 12.28\%$ ;  $C_{26}H_{18}O_6S_2$  requires  $C = 63.36$ ,  $H = 3.66$ ,  $S = 13.05\%$ ). Small plate-like crystals, suitable for X-ray study, were grown from a

saturated solution in acetone by evaporation at room temperature. A crystal  $0.5 \times 0.4 \times 0.1$  mm was selected for data collection.

Oscillation and Weissenberg photographs of other crystals were used to obtain the space group and approximate lattice parameters. Accurate lattice parameters were obtained by least squares from the setting angles for 25 reflections automatically centred on a Nonius CAD-4 diffractometer. Intensities were collected on the same instrument with Ni-filtered  $Cu K\alpha$  radiation and an  $\omega/2\theta$  scan mode. The scan rate was variable between 1.2 and 6.6° min<sup>-1</sup>. The  $\omega$  scan width was  $(0.75 + 0.25 \tan \theta)^\circ$ , and the aperture setting was 4 mm. Two intensity-control reflections, monitored after every hour of exposure, showed no decay of the crystal. In each 96-step scan, the outer 16 steps on each side constituted left ( $B_l$ ) and right ( $B_r$ ) backgrounds, and the central 64 steps the peak count ( $C$ ). The integrated intensity ( $I_o$ ) of a reflection and its e.s.d.  $\sigma(I_o)$  were calculated from  $I_o = |C - 2(B_l + B_r)|$  and  $\sigma(I_o) = |C + 4(B_l + B_r)|^{1/2}$ . The data were reduced to 2164 unique reflections, of which 1883 had  $I_o > 1.5\sigma(I_o)$  and were used in the refinement.

### Structure determination

The structure was solved by direct methods with *SHELX* (Sheldrick, 1976). All non-hydrogen atoms were located in the best  $E$  map and a subsequent difference map revealed the positions of the H atoms. Least-squares anisotropic refinement of the positions of

Table 1. *Crystal data for NS [2,4-hexadiynylene bis( $\beta$ -naphthalenesulphonate)] at 300 K*

Molecular formula: $C_{26}H_{18}O_6S_2$ , $M_r = 490.54$	
Monoclinic, space group $P2_1/n$	
$a = 13.4457$ (9) Å	$Z = 2$
$b = 5.4213$ (3)	$D_m = 1.40$ Mg m <sup>-3</sup>
$c = 15.9033$ (9)	$D_c = 1.432$
$\beta = 100.964$ (5)°	

the non-hydrogen atoms and free, isotropic refinement of all H-atom positions gave a final  $R$  of 0.054. The crystal data are listed in Table 1, and the final atomic positional parameters in Tables 2 and 3. The crystallographic computations were performed on the Queen Mary College ICL 1904S and ICL 2980 computers.\*

### Discussion

Molecular plots, obtained with *ORTEP* (Johnson, 1965), are shown in Figs. 1 and 2, and the bond lengths and angles are given in Tables 4 and 5. A comparison of bond lengths and angles between NS and analogous compounds, TS (Enkelmann, Leyrer & Wegner, 1979), the bis(*p*-chlorobenzenesulphonate) ester (CBS)

\* Lists of structure factors, thermal parameters and dihedral angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34421 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Coordinates ( $\times 10^4$ ) for the C, O and S atoms

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

	$x$	$y$	$z$
C(1)	448 (2)	9388 (5)	-3 (2)
C(2)	1227 (2)	8340 (5)	-4 (2)
C(3)	2170 (2)	7048 (5)	3 (2)
C(4)	3969 (2)	5733 (4)	1564 (1)
C(5)	4726 (2)	7025 (4)	1304 (1)
C(6)	5268 (2)	8825 (4)	1851 (1)
C(7)	5009 (2)	9230 (4)	2667 (1)
C(8)	4227 (2)	7823 (5)	2910 (1)
C(9)	3704 (2)	6107 (5)	2375 (2)
C(10)	6033 (2)	10283 (5)	1604 (2)
C(11)	6517 (2)	12065 (6)	2133 (2)
C(12)	6269 (2)	12438 (6)	2941 (2)
C(13)	5539 (2)	1079 (5)	3205 (2)
O(1)	2199 (1)	4984 (3)	583 (1)
O(2)	2992 (1)	1542 (3)	1333 (1)
O(3)	3697 (1)	3256 (4)	134 (1)
S	3253 (0)	3614 (1)	871 (0)

Table 3. Atomic coordinates ( $\times 10^3$ ) for the H atoms

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

	$x$	$y$	$z$
H(1)	266 (2)	803 (6)	16 (2)
H(2)	225 (2)	646 (6)	-59 (2)
H(5)	490 (2)	670 (5)	78 (2)
H(8)	409 (2)	801 (5)	347 (2)
H(9)	314 (3)	511 (6)	252 (2)
H(10)	619 (2)	1016 (6)	106 (2)
H(11)	701 (3)	1301 (7)	192 (3)
H(12)	665 (3)	1345 (7)	337 (2)
H(13)	545 (3)	1128 (6)	379 (2)

(Mayerle & Clarke, 1978), and the bis(*p*-methoxybenzenesulphonate) ester (MBS) (Fisher, Ando, Bloor & Hursthouse, 1979), shows that there are no significant differences other than the conformational differences due to rotation of the side groups about C(3)—O(1) (Fisher *et al.*, 1979). Some bond lengthening and shortening occurs around the naphthyl group possibly due to interaction with the sulphonyl groups.

Wegner (1977) suggested that the following packing conditions are necessary for diacetylenes to polymerize in the solid state by the 1,4-addition of adjacent monomer molecules:  $3.40 < S_1 < 4.00$  Å, where  $S_1 = d_1 \sin \gamma_1$ , and  $\gamma_1 \approx 45^\circ$  (Fig. 3). In NS, the diacetylene units are separated by 5.42 Å along  $b$  ( $d_1$  in Fig. 3), and are orientated at an angle of  $62^\circ$  ( $\gamma_1$  in Fig. 3), with  $S_1 = 4.80$  Å. These parameters clearly lie well outside the optimum values proposed by Wegner. The large spacing along  $b$  (the axis along which polymer chains

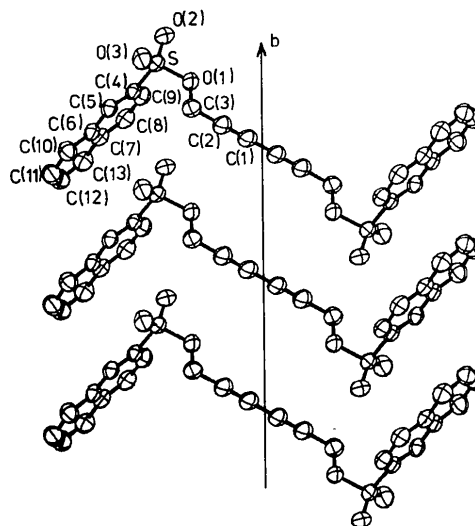


Fig. 1. Molecular plot viewed along  $c$ . 50% probability ellipsoids are shown (*ORTEP*, Johnson, 1965).

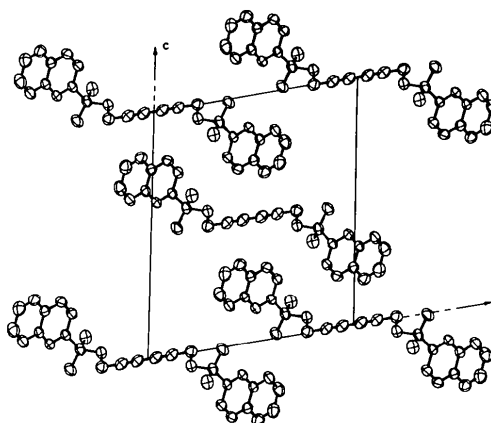


Fig. 2. Molecular plot viewed normal to  $ac$ . 50% probability ellipsoids are shown (*ORTEP*, Johnson, 1965).

propagate in the reactive TS) is caused by the physical size of the side groups and the contact between the sulphonyl group on one molecule and the CH<sub>2</sub> group on the adjacent molecule of the stack. This contact results from the strong naphthyl–naphthyl interaction which attempts to increase the face-to-face packing of these groups. These interactions also increase  $\gamma$  to a value somewhat larger than the limit required for polymerization to take place.

The dihedral angles reveal that the conformation of NS is remarkably similar to that of TS. However, because of the packing requirements of the substituent groups, the NS molecule has been rotated about the

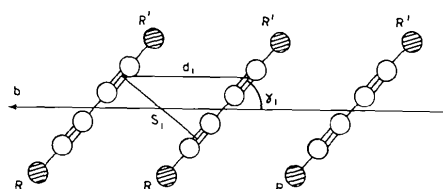


Fig. 3. Monomer packing requirements for the solid-state polymerization of diacetylenes (Wegner, 1977).

central diacetylene axis by some 30° with respect to the TS molecule. Thus it would seem that, although on a molecular level NS is very similar to TS, the intermolecular interactions which determine the crystal structure and prevent thermal- and UV-induced polymerization are similar to those in CBS.

A more detailed comparison of the molecular conformations of these four monomers, NS, TS, CBS and MBS, will be presented elsewhere (Williams, Ando & Bloor, 1979).

This work was supported by grants from the SRC and The Royal Society. One of us (RLW) thanks the SRC for a studentship.

Table 4. *Interatomic distances* (Å)

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

C(1)–C(1)'	1.377 (5)	C(6)–C(7)	1.423 (3)
C(1)–C(2)	1.192 (4)	C(7)–C(8)	1.412 (4)
C(2)–C(3)	1.446 (4)	C(8)–C(9)	1.363 (4)
C(3)–O(1)	1.446 (3)	C(4)–C(9)	1.417 (3)
O(1)–S	1.589 (2)	C(6)–C(10)	1.412 (4)
S–O(2)	1.423 (2)	C(10)–C(11)	1.362 (4)
S–O(3)	1.425 (2)	C(11)–C(12)	1.402 (5)
S–C(4)	1.748 (2)	C(12)–C(13)	1.356 (4)
C(4)–C(5)	1.363 (3)	C(13)–C(7)	1.419 (3)
C(5)–C(6)	1.413 (3)		
C(3)–H(1)	0.85 (3)	C(12)–H(12)	0.95 (4)
C(3)–H(2)	1.01 (4)	C(13)–H(13)	0.96 (4)
C(5)–H(5)	0.92 (3)	C(8)–H(8)	0.96 (3)
C(10)–H(10)	0.92 (3)	C(9)–H(9)	0.99 (3)
C(11)–H(11)	0.95 (4)		

Table 5. *Interatomic angles* (°)

C(1')–C(1)–C(2)	179.5 (3)	C(6)–C(7)–C(8)	119.4 (2)
C(1)–C(2)–C(3)	179.3 (3)	C(7)–C(8)–C(9)	121.3 (2)
C(2)–C(3)–O(1)	107.3 (2)	C(8)–C(9)–C(4)	118.5 (2)
C(3)–O(1)–S	117.4 (1)	C(9)–C(4)–C(5)	122.3 (2)
O(1)–S–O(2)	102.9 (1)	C(9)–C(4)–S	117.6 (2)
O(1)–S–O(3)	108.5 (1)	C(5)–C(6)–C(10)	122.2 (2)
O(2)–S–O(3)	120.0 (1)	C(6)–C(10)–C(11)	120.9 (3)
O(1)–S–C(4)	103.2 (1)	C(10)–C(11)–C(12)	120.0 (3)
O(2)–S–C(4)	110.7 (1)	C(11)–C(12)–C(13)	121.2 (3)
O(3)–S–C(4)	110.0 (1)	C(12)–C(13)–C(7)	120.5 (3)
S–C(4)–C(5)	120.0 (2)	C(13)–C(7)–C(6)	118.5 (2)
C(4)–C(5)–C(6)	119.7 (2)	C(13)–C(7)–C(8)	122.1 (2)
C(5)–C(6)–C(7)	118.7 (2)	C(7)–C(6)–C(10)	119.0 (2)

## References

- BAUGHMAN, R. H. (1974). *J. Polym. Sci. Polym. Phys. Ed.* **12**, 1511–1535.
- ENKELMANN, V., LEYER, R. J. & WEGNER, G. (1979). *J. Am. Chem. Soc.* In the press.
- FISHER, D. A., ANDO, D. J., BLOOR, D. & HURSTHOUSE, M. B. (1979). *Acta Cryst.* **B35**, 2075–2079.
- JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794, revised. Oak Ridge National Laboratory, Tennessee.
- MAYERLE, J. J. & CLARKE, T. C. (1978). *Acta Cryst.* **B34**, 143–147.
- SHELDRICK, G. M. (1976). *SHELX*. Program for crystal structure determination. Univ. of Cambridge, England.
- WEGNER, G. (1969). *Z. Naturforsch. Teil B*, **24**, 824–832.
- WEGNER, G. (1971). *Makromol. Chem.* **145**, 85–94.
- WEGNER, G. (1972). *Makromol. Chem.* **154**, 35–48.
- WEGNER, G. (1977). *Chemistry and Physics of One-dimensional Metals*, edited by H. J. KELLER, pp. 297–314. New York: Plenum.
- WILLIAMS, R. L., ANDO, D. J. & BLOOR, D. (1979). In preparation.