structure seems to be stabilized by electrostatically favourable molecular packing in addition to the conventional van der Waals forces.

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The Crystal and Molecular Structure of 2,4-Hexadiynylene Bis(*p*-chlorobenzenesulfonate)

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2,4-Hexadiynylene bis(*p*-chlorobenzenesulfonate) crystallizes in the triclinic space group $P\bar{1}$ with one molecule in a unit cell of dimensions $a = 8{\cdot}941$ (1), $b = 11{\cdot}170$ (1), $c = 5{\cdot}030$ (2) Å, $\alpha = 100{\cdot}81$ (1), $\beta = 91{\cdot}19$ (3), and $\gamma = 94{\cdot}19$ (1)°. The structure was solved by direct methods and refined by full-matrix least squares to a final R for 1723 observed reflections of 0·045. The centrosymmetric molecules pack in columns along the c axis. The details of the packing, dominated by non-bonded Cl–Cl and Cl–C(phenyl) interactions, clearly explain why the molecule does not undergo solid-state polymerization upon thermal or X-ray irradiation.

Introduction

Considerable effort has been expended during the past decade on the solid-state polymerization of organic molecules. The mechanism for such polymerization by one class of compounds, the diacetylenes, was first proposed by Wegner (1969) and later elaborated upon by Baughman (1974). Since the reactivity of the

diacetylene monomers depends primarily on their spatial arrangement in the crystal lattice, it is perhaps surprising that the title compound remains inert under conditions causing complete polymerization of the closely related 2,4-hexadiynylene bis(*p*-toluenesulfonate) (hereafter referred to as the ditosylate). To understand the unreactivity of the title compound, we have determined its structure and report the results here.

Experimental

The compound was prepared by the reaction of *p*-chlorobenzenesulfonyl chloride with 2,4-hexadiyne-1,6-diol by the method reported by Wegner (1971) for the analogous ditosylate derivative. Recrystallization from CH_2Cl_2/hexane yielded colorless needles, many of which appeared to be twinned or cracked along the long axis. From a needle that showed no obvious defects when examined with a polarizing microscope, a fragment of approximate dimensions 0·075 × 0·23 × 0·27 mm perpendicular to the faces (100), (010), and (001), respectively, was cleaved. The crystal was mounted on the end of a glass fiber with nail enamel and transferred to an Enraf–Nonius CAD-4 automatic diffractometer where, following machine location and centering of 14 reflections, a preliminary unit cell and orientation matrix were computed. Subsequent to this, 20 high-angle reflections were computer centered and the initial cell constants refined to give a triclinic unit cell, based on graphite-monochromatized Cu $K\alpha_1$ radiation (λ = 1·54051 Å), with the cell parameters listed in Table 1.

Several open-counter ω scans gave peak widths at half-height of 0·15–0·25°. Data of the form $(\pm h,\pm k,l)$ were collected using θ–2θ scans and graphite-monochromatized Cu $K\alpha$ radiation to θ = 76°. The scan range was calculated according to the formula $\Delta\theta = (0{\cdot}9 + 0{\cdot}2\tan\theta)°$ and was extended by 25% on each end of the scan range for background measurement. The scan rate, based on a fast prescan, was computed such that 10^4 counts were to be obtained, if possible, in the maximum time of 90 s allowed for each reflection. An aperture with a height of 4 mm and a variable width of $(4{\cdot}0 + 0{\cdot}9\tan\theta)$ mm was placed in front of the scintillation counter at a distance of 173 mm from the crystal. Three standard reflections monitored after every 50 reflections declined in intensity by ~17% over the course of data collection. The final intensities were scaled accordingly. This decline in intensity was accompanied by the appearance of a gradually deepening amber tint to the crystal. We believe this to be decomposition and not the onset of polymerization observed with various other diacetylene molecules. 2166 reflections were collected, 1833 of which were unique. The 333 reflections that were collected twice were averaged, giving an R of 0·039. Of the 1833 unique reflections, 1723 were judged to be observed by the criterion $F^2 \geq 3\sigma(F^2)$. The data were corrected for Lp and absorption effects. The transmission coefficients ranged between 0·399 and 0·706 based on a linear transmission coefficient μ = 48·83 cm^{-1}.

The structure was solved with *MULTAN* (Germain, Main & Woolfson, 1971) using 200 reflections with $E > 1{\cdot}4$. The values of $\langle|E^2-1|\rangle$ and $\langle|E|\rangle$ indicated the structure to be centrosymmetric. An E map computed with the phases obtained from the set with the highest combined figure of merit revealed all the non-hydrogen atoms. The structure was then refined by full-matrix least-squares methods. All positional parameters and isotropic temperature factors were varied and the structure refined to an R of 0·17. The refinement was continued with the assignment of anisotropic temperature parameters to the non-hydrogen atoms. The aromatic H atoms were placed in fixed, calculated positions while the methylene H atoms were placed in the fixed positions at which they were found on a difference Fourier map. The structure refined to convergence at R = 0·045, based on 127 variables and 1723 observations and using as weights $w = 4F_o^2/\sigma^2(F_o^2)$. The maximum shift in any parameter at the end of the last least-squares cycle was <0·001 that of its standard deviation. The neutral scattering factors of Cl, S, O, and C were taken from *International Tables for X-ray Crystallography* (1974, pp. 72–98) as were the corrections for the anomalous scattering of all the

Table 1. *Crystal data*

2,4-Hexadiynylene bis(*p*-chlorobenzenesulfonate)
Molecular formula: $C_{18}H_{12}S_2O_6Cl_2$, M_r = 459·30
Triclinic, space group $P\bar{1}$

a = 8·941 (1) Å	Z = 1
b = 11·170 (1)	D_c = 1·550 g cm^{-3}
c = 5·030 (2)	D_x = 1·56
α = 100·81 (1)°	
β = 91·19 (3)	
γ = 94·19 (1)	

Table 2. *Final atomic positional parameters* (×10^4)

Standard deviations are in parentheses.

	x	y	z
Cl	376 (1)	3549 (1)	7818 (2)
S	5569 (1)	2405 (1)	−49 (1)
O(1)	6994 (2)	2590 (1)	1925 (4)
O(2)	5397 (2)	1163 (1)	−1403 (3)
O(3)	5793 (3)	3343 (2)	−1579 (4)
C(1)	9448 (3)	330 (2)	660 (6)
C(2)	8482 (3)	884 (2)	1773 (6)
C(3)	7344 (3)	1580 (3)	3241 (6)
C(4)	4086 (2)	2714 (2)	2115 (5)
C(5)	3337 (3)	1777 (2)	3102 (5)
C(6)	2197 (3)	2034 (2)	4888 (6)
C(7)	1826 (3)	3234 (3)	5619 (6)
C(8)	2569 (3)	4173 (2)	4630 (7)
C(9)	3707 (3)	3914 (2)	2860 (6)

non-hydrogen atoms (*International Tables*, 1974, pp. 149–150). The scattering factors of H were those of Stewart, Davidson & Simpson (1965). The final atomic positional parameters are listed in Table 2.* All computations were done with an IBM 360/195 computer using programs described previously (Mayerle, 1977).

Results and discussion

The atom-labeling scheme and the anisotropic thermal ellipsoids of the title compound are shown in Fig. 1. Bond distances and angles are listed in Table 3.

The single molecule in the unit cell is required to be centrosymmetric. There is nothing unusual about its internal geometry. The C(1)–C(2) triple-bond distance of 1·187 (3) Å is essentially identical to the values of 1·185 (20) Å reported for diacetylenedicarboxylic acid dihydrate (Dunitz & Robertson, 1947), 1·18 (3) Å found in diphenyldiacetylene (Wiebenga, 1940), and only slightly shorter than the value of 1·21 (1) Å reported for 2,4-hexadiyne-1,6-diol (Hädicke, Penzien & Schnell, 1974). The value of 1·382 (5) Å for the length of the formally single bond [C(1)–C(1′)] between the two triple bonds compares with the value of 1·39 (3) Å reported by Wiebenga (1940) and that of 1·36 (1) Å reported by Hädicke *et al.* (1974). Dunitz & Robertson (1947) reported a length for this bond of 1·33 (2) Å in diacetylenedicarboxylic acid dihydrate, a value that seems slightly low. There is nothing unusual about the C(2)–C(3) distance of 1·455 (3) Å. The C(3)–O(1) length of 1·460 (3) Å is within a standard deviation of the value of 1·45 (10) Å reported for 2,4-hexadiyne-1,6-diol (Hädicke *et al.*, 1974). The S–O bond lengths of 1·577 (2), 1·422 (2), and 1·417 (2) Å compare well with the values of 1·583 (2), 1·422 (2), and 1·414 (2) Å in poly[1,2-bis(*p*-tolylsulfonyloxymethylene)-1-buten-3-ynylene] (Kobelt & Paulus, 1973), the polymer derived from the *p*-tosylate analog of the title compound. The C(4)–S length of 1·746 (2) Å is slightly shorter than the value of 1·752 (3) Å reported for the *p*-tosylate polymer, but not significantly so. The values of the bond angles about sulfur are essentially identical to those reported for that polymer.

The facile polymerization of the ditosylate under X-ray irradiation precludes determination of that monomer directly. This study was undertaken with the expectation that systematic modification of the ditosylate would provide clues to its high reactivity as well as more fundamental information on the solid-state packing of diacetylenes. Substitution of chlorine for the methyl groups of the ditosylate seems a logical choice since the van der Waals radii of chlorine and methyl are quite similar. This suggests that changes in packing (and reactivity) caused by the introduction of chlorine would be due to electronic interaction of the chlorine with adjacent molecules rather than to simple bulk steric effects. In addition, the well known influence of halogen substitution on solid-state olefin dimerization (Schmidt, 1971) made the use of chlorine interesting.

It was therefore intriguing to note that the bis(*p*-chlorobenzenesulfonate) showed no tendency to react under thermal and photochemical conditions which cause complete polymerization of the ditosylate (Wegner, 1971). The origin of this lack of reactivity is evident from examination of the packing arrangement of the compound, shown in Fig. 2. The molecules pack approximately face-to-face in columns along the *c* axis, the centers of the molecules being 5·030 Å apart. The slight deviation from exact face-to-face packing most likely results from the necessity to accommodate the non-planarity of the $-SO_3CH_2-$ grouping. The most important non-bonded interactions are of two types. The first is between an aromatic moiety and the Cl atom attached to the translationally equivalent phenyl group along the stack, the distance from the Cl atom to the aromatic plane being 3·76 Å. This interaction,

* Lists of structure factors, anisotropic thermal parameters and H atom positions have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32843 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

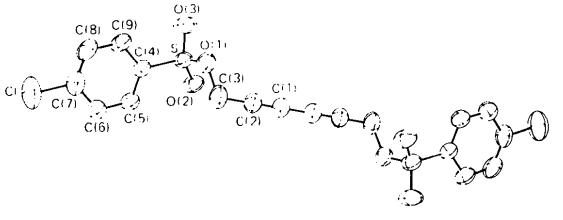

Fig. 1. The 2,4-hexadiynylene bis(*p*-chlorobenzenesulfonate) molecule. The 50% probability ellipsoids are depicted.

Table 3. *Bond distances* (Å) *and angles* (°)

S–O(1)	1·577 (2)	O(1)–S–O(2)	108·8 (1)
S–O(2)	1·422 (2)	O(1)–S–O(3)	104·0 (1)
S–O(3)	1·417 (2)	O(2)–S–O(3)	119·6 (1)
S–C(4)	1·746 (2)	C(4)–S–O(1)	103·8 (1)
C(1)–C(1′)	1·382 (5)	C(4)–S–O(2)	109·6 (1)
C(1)–C(2)	1·187 (3)	C(4)–S–O(3)	109·8 (1)
C(2)–C(3)	1·455 (3)	C(1′)–C(1)–C(2)	179 (1)
C(3)–O(1)	1·460 (3)	C(1)–C(2)–C(3)	177·5 (5)
C(4)–C(5)	1·378 (3)	C(2)–C(3)–O(1)	110·4 (2)
C(4)–C(9)	1·390 (3)	C(3)–O(1)–S	118·1 (2)
C(5)–C(6)	1·383 (4)	S–C(4)–C(5)	119·7 (2)
C(6)–C(7)	1·389 (4)	S–C(4)–C(9)	119·0 (2)
C(7)–Cl	1·734 (3)	C(5)–C(4)–C(9)	121·2 (2)
C(7)–C(8)	1·378 (4)	C(4)–C(5)–C(6)	119·4 (2)
C(8)–C(9)	1·377 (4)	C(5)–C(6)–C(7)	118·9 (2)
		C(6)–C(7)–C(8)	121·8 (2)
		C(6)–C(7)–Cl	118·8 (2)
		C(8)–C(7)–Cl	119·4 (2)
		C(7)–C(8)–C(9)	119·1 (2)
		C(8)–C(9)–C(4)	119·5 (2)

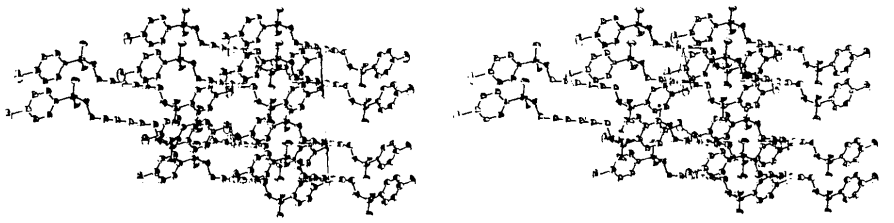

Fig. 2. The packing arrangement of the molecules. The origin of the cell is at the lower left rear corner. The *a* axis runs horizontally from left to right, *b* vertically from bottom to top, and *c* completes the right-handed coordinate system.

probably the single most important attractive interaction along the stack, is the major difference between this compound and the polymerizable *p*-tosylate analog and, as will be discussed below, is responsible for the molecule's inability to undergo solid-state polymerization. The other main attractive non-bonded interaction is between Cl atoms in adjacent stacks. The two atoms, linked by the line labeled *X* in Fig. 2 and centrosymmetrically related by the equation $x,y,z \rightarrow -x, 1-y, 2-z$, are separated by a distance of 3·673 (2) Å. In addition, each Cl atom has a neighboring Cl atom in the next stack at a distance of 4·762 (2) Å. The net result is a saw-tooth arrangement of Cl atoms running through the crystal. This can be clearly seen in Fig. 2. Other short non-bonded intrastack interactions of probable significance are those of 3·250 (3) Å between C(9)—O(3) and 3·324 (3) and 3·349 (3) Å between C(3)—O(2) and C(3)—O(3) respectively. Space-filling models show that the latter two are, in fact, oxygen–methylene hydrogen interactions. As will be discussed below, these too play a role in determining the difference in reactivity between the *p*-tosyl and *p*-chlorophenyl compounds.

The unreactivity of this compound is best analyzed in terms of Baughman's least-motion derived empirical criteria for diacetylene solid-state reactivity (Baughman, 1974). Although the monomer center-to-monomer center distance of 5·030 Å is within the range consistent with high reactivity, the angle between the molecular axis [the C(2)—C(2′) vector] and the stacking axis, γ_1 in Baughman's notation, is 67·0 (1)°. As a direct consequence, the distance between C(2) and its centrosymmetrically related counterpart in the next molecule along the stack, the two carbons which must become bonded in the polymerization process, is 4·962 (5) Å. This and, in particular, the angle γ_1 are outside the limits predicted by Baughman to be consistent with even low reactivity.

This argument can be understood more clearly by reference to Fig. 3. Wegner's (1969) proposed mechanism for diacetylene polymerization involves rotation of the molecular axis toward the stacking axis followed by 1,4-addition between the terminal acetylenic carbons. In the polymerized material the angle between molecular and stacking axes is only 13° (Kobelt & Paulus, 1973). Thus, in the absence of translation along

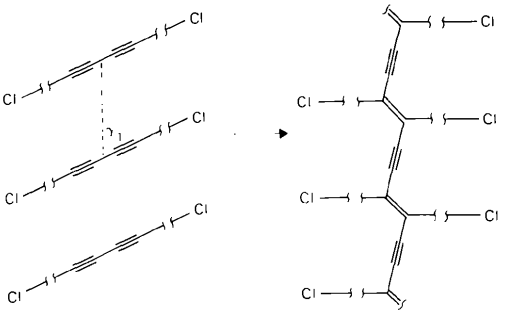

Fig. 3. Wegner model for the solid-state polymerization of diacetylenes.

the molecular axis, each molecule would have to rotate through an angle of ~54° to bring the potentially reacting atoms into proximity. For comparison, in 2,4-hexadiyne-1,6-diol, the most reactive diacetylene for which a monomer structure has been obtained (Hädicke *et al.*, 1974), the required rotation is only 28° ($\gamma_1 = 41°$).

Reduction of γ_1 from 67·0° in the present material to 41° in the diol is tantamount to translation along the molecular axis. However, as can be seen in Fig. 2, such a translation would disrupt the Cl–phenyl intrastack and, to a lesser degree, the Cl–Cl interstack interactions discussed above. We emphasize that this translation is a static one in that the molecules do not actually undergo a translation but instead crystallize in a slipped arrangement.

Although the present compound and the *p*-tosylate polymer crystallize in different space groups, the individual stacks are very much alike and can be compared directly. Close examination of the $CH_2OS(O)_2C_6H_4X$ groups in the two compounds reveals their conformations to be almost identical and the packing along the stacks to be nearly so. Since the groups attached to the diacetylenic nucleus undergo little or no movement during polymerization (Wegner, 1969), it can be assumed that a very similar relationship holds for the two monomers. The difference in the reactivity of the two molecules can thus be explained in the following manner. In the *p*-chloro compound the presence of the strong attractive interaction between the

Cl atom and the next aromatic group along the stack causes the molecules to pack as discussed above and, in the process, brings about the oxygen–methylene hydrogen contact noted previously. The weakening of the interaction between the *p* substituent and the adjacent phenyl ring in the ditosylate monomer [crude atom–atom potential calculations using the parameters of Bates & Busing (1974) show the contribution of this type of interaction to the lattice energy to be significantly less in the ditosylate] allows the molecules to stack in a form which is translationally slipped relative to the *p*-chloro compound, thereby reducing the oxygen–methylene hydrogen interactions and generally allowing the diacetylenic groups to pack slightly closer. Most importantly, the translation reduces γ_1 to ~45° and brings the two potentially reactive carbon atoms into proximity, thereby allowing facile polymerization. Thus the introduction of the chlorine atom is found to cause a profound change in solid-state reactivity *via* a rather subtle alteration of the intrastack packing.

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The Crystal Structure and Absolute Configuration of (−)-2-*exo*-Aminobicyclo[3.2.1]octane-2-carboxylic Acid Monohydrate*

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$C_9H_{15}NO_2.H_2O$ is monoclinic, space group $P2_1$, with a = 12·590 (13), b = 6·477 (8), c = 5·810 (7) Å, β = 100·68 (31)°, Z = 2. The structure was refined to an R of 0·051 for 851 counter reflections. The absolute configuration was determined by the Bijvoet method and corresponds to the (1*R*,2*R*,5*S*) configuration. The asymmetric substitution of the amino and carboxyl groups at C(2) significantly affects the mirror symmetry of the bicyclo[3.2.1]octane system.

Introduction

In the course of studies on the effect of cyclic and bicyclic amino acid analogues on the free amino acid pool of rat brain (Zand, Sellinger, Water & Harris, 1974) and on cerebellar protein synthesis (Zand & Water, 1977) it was found that 2-aminobicyclo[3.2.1]-octane-2-carboxylic acid (hereafter 2-ABO) inhibited a cell-free neuronal homogenate protein synthesizing system. In order to compare the dimensions and stereochemistry of the analogue with the amino acids that were in competition with each other during protein synthesis, it was important to determine the structure of the analogue and its absolute configuration. In protein synthesis, the amino acid must be recognized by the amino acylsynthetase and the amino acid synthetase complex must in turn be recognized by the appropriate tRNA. For this analogue, recognition and activation

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