

## Structure of 2,4-Hexadiyn-1-ol at 110 K

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**Abstract.**  $C_6H_6O$ , monoclinic,  $P2_1/a$ ,  $a = 4.893$  (3),  $b = 28.471$  (17),  $c = 4.131$  (2) Å,  $\beta = 101.67$  (6)° at 300 K; and  $a = 4.875$  (2),  $b = 28.117$  (18),  $c = 4.028$  (1) Å,  $\beta = 102.25$  (4)° at 110 K;  $D_m$  (300 K) = 1.1,  $D_c$  (300 K) = 1.109 g cm<sup>-3</sup>,  $Z = 4$ ;  $F(000) = 200$ ,  $\mu(\text{Mo } K\alpha) = 0.45$  cm<sup>-1</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å. The structure was solved by direct methods with diffractometer data and refined to  $R = 0.13$  for 494 observed reflexions collected at 110 K. The crystal structure accounts for the observed solid-state reactivity of 2,4-hexadiyn-1-ol.

**Introduction.** Many diacetylenes (general formula  $R-C:C:C-R'$ ) undergo solid-state polymerization reactions (Wegner, 1969, 1972). Polymerization may be 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 diacetylene molecules which have a relatively small number of atoms in these side groups. The crystal structures of 2,4-hexadiyne (Himes, 1953) and 2,4-hexadiyne-1,6-diol (Hädicke, Penzien & Schnell, 1971) have already been published.

The structure presented here provides information which assists in the interpretation of spectroscopic data (Fisher, Batchelder & Bloor, 1978), and illustrates the importance of the nature of the side groups  $R$  and  $R'$  in the solid-state polymerization of diacetylenes.

Samples of 2,4-hexadiyn-1-ol were prepared by the coupling of propargyl chloride and propargyl alcohol in an alkaline solution containing  $Cu^+$  ions as a catalyst (Wegner, 1975). Crystals (m.p. 42°C) used for the structure determination were grown from a solution in 40–60° petroleum ether. These were compared with a second batch grown by a sublimation technique. Both batches gave equivalent Weissenberg photographs.

Freshly prepared crystals are colourless, but rapidly turn pink on exposure to daylight at room temperature.

This colouration is due to the formation of a small amount of polymer within the crystals. A crystal  $0.2 \times 0.3 \times 0.2$  mm was selected for data collection. Although it was estimated that this specimen contained only a few per cent of polymer, its quality was probably lower than that usually required for the collection of single-crystal intensity data. During the period of data collection, the crystal was cooled in a stream of cold nitrogen gas. The temperature of the crystal was maintained at 110 K ( $\pm 3$  K). Cooling the crystal during data collection prevented in-beam polymerization.

Oscillation and Weissenberg photographs were used to obtain the space group and approximate lattice parameters. Weissenberg photographs of crystals at 300 and 110 K showed no evidence of any phase transition between these temperatures.

Accurate lattice parameters were calculated using a least-squares analysis of setting angles for fifteen reflexions automatically centred on a Nonius CAD-4 diffractometer. Intensity data were collected on the same instrument using graphite-monochromated  $Mo K\alpha$  radiation and an  $\omega/2\theta$  scan mode. The scan rate was variable and was determined by a fast prescan. All the reflexions which yielded a net count of more than 5 during the prescan were rescanned slowly to give a total count of 2000 subject to a maximum scanning time of 60 s. The  $\omega$  scan width was determined as  $\text{scan} = (0.6 + 0.2 \tan \theta)^\circ$ , and the aperture setting as  $\text{apt.} = (3.0 + 0.5 \tan \theta)$  mm. Two intensity-control reflexions monitored after every 50 reflexions showed no decay of the crystal during data collection. 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 reflexion and its estimated standard deviation  $\sigma(I_o)$  were calculated from the equations:  $I_o = |C - 2(B_l + B_r)|$  and  $\sigma(I_o) = |C + 4(B_l + B_r)|^{1/2}$ . The data reduced to 996 unique reflexions of which 494 had  $I_o > 1.5\sigma(I_o)$  and were used in the refinement.

The structure was solved by direct methods using the *SHELX* program (Sheldrick, 1976). All non-hydrogen

Table 1. Atomic coordinates ( $\times 10^4$  for O and C;  $\times 10^3$  for H)

Estimated standard deviations are given in parentheses. The overall isotropic temperature factors for the H atoms refined to  $0.016(12) \text{ \AA}^2$ .

|         | x          | y         | z         |
|---------|------------|-----------|-----------|
| C(1)    | -2739 (38) | 1859 (4)  | 670 (38)  |
| C(2)    | -551 (31)  | 1535 (14) | 2347 (36) |
| C(3)    | 1304 (30)  | 1274 (4)  | 3682 (34) |
| C(4)    | 3388 (31)  | 971 (4)   | 5244 (36) |
| C(5)    | 5234 (32)  | 710 (4)   | 6632 (35) |
| C(6)    | 7494 (37)  | 395 (4)   | 8289 (36) |
| O(1)    | -2837 (25) | 2289 (3)  | 2535 (25) |
| H(C1)   | -476 (25)  | 168 (4)   | 103 (27)  |
| H'(C1)  | -239 (24)  | 200 (3)   | -207 (30) |
| H(C6)   | 726 (24)   | 39 (4)    | 1102 (28) |
| H'(C6)  | 972 (26)   | 54 (4)    | 809 (28)  |
| H''(C6) | 778 (25)   | 38 (4)    | 558 (29)  |
| H(O1)   | -42 (28)   | 245 (4)   | 267 (27)  |

Table 2. Interatomic distances ( $\text{\AA}$ ) and bond angles ( $^\circ$ )

Estimated standard deviations are given in parentheses.

|             |          |                |             |
|-------------|----------|----------------|-------------|
| C(1)—O(1)   | 1.43 (1) | C(1)—C(2)—C(3) | 178.1 (1.6) |
| C(1)—C(2)   | 1.46 (2) | C(2)—C(3)—C(4) | 178.7 (1.6) |
| C(2)—C(3)   | 1.20 (2) | C(3)—C(4)—C(5) | 179.3 (1.6) |
| C(3)—C(4)   | 1.37 (2) | C(4)—C(5)—C(6) | 179.4 (1.6) |
| C(4)—C(5)   | 1.20 (2) | C(2)—C(1)—O(1) | 112.8 (1.2) |
| C(5)—C(6)   | 1.47 (2) |                |             |
| O(1)—H(O1)  | 1.2 (1)  |                |             |
| O(1)—H(O1)' | 1.5 (1)  |                |             |
| O(1)⋯O(1)'  | 2.71 (2) |                |             |

atoms were located in the 'best'  $E$  map, and all H atoms were revealed in an electron density synthesis phased on the C and O atoms. Least-squares refinement of all atomic positions gave a final  $R$  of 0.13.

The atomic fractional coordinates are given in Table 1,\* and interatomic distances and angles are presented in Table 2. Fig. 1 shows a projection of the unit-cell contents viewed perpendicular to the  $ab$  plane (ORTEP, Johnson, 1965).

The crystallographic computations were done on the Queen Mary College ICL 1904S and the University of London CDC 7600 computers.

**Discussion.** In a recent review (Wegner, 1977) it was suggested that the following packing conditions are necessary for diacetylenes to undergo solid-state polymerization of the type illustrated in Fig. 2:  $3.4 < S_1 < 4.0 \text{ \AA}$ , where  $S_1 = d_1 \sin \gamma_1$ ;  $\gamma_1 \approx 45^\circ$ ;  $d_2 = 4.9 \pm 0.1 \text{ \AA}$ ; and  $\gamma_2 = 13.5^\circ$ .

For 2,4-hexadiyn-1-ol,  $d_1 = 4.87 \text{ \AA}$ ,  $\gamma_1 = 49.6^\circ$ ,  $S_1 = 3.71 \text{ \AA}$ , and polymer chains form parallel to  $a$ . These

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33487 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

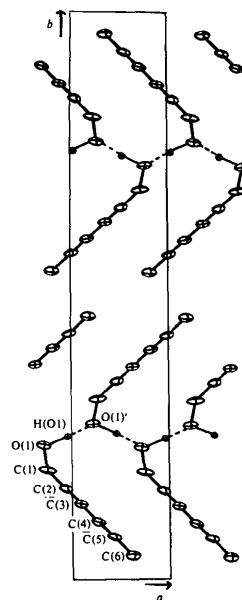


Fig. 1. Molecular plot viewed normal to  $ab$  (50% probability ellipsoids).

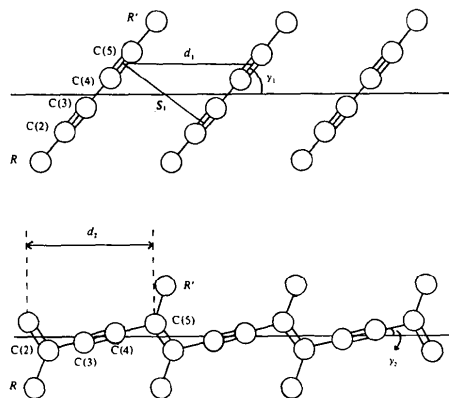


Fig. 2. Packing requirements for the solid-state polymerization of diacetylenes (Wegner, 1977).

parameters clearly satisfy the Wegner criteria, so this compound would be expected to polymerize. However, it is found that once polymerization has proceeded to the point where about 30% of the 2,4-hexadiyn-1-ol has polymerized, then cracks which are parallel to the crystallographic  $a$  axis begin to form, and this inhibits further solid-state polymerization. This effect occurs for samples polymerized by photoirradiation or by pressure polymerization. A plausible explanation for this cracking is that in the crystal structure the  $\text{CH}_2\text{OH}$  groups are more rigidly fixed in position by the system of hydrogen bonds (illustrated by broken lines in Fig. 1) than are the methyl groups which neighbour each other on adjacent chains. The movement of the acetylenic C atoms during polymerization will therefore affect the positions of the methyl C atoms, which will tend to be

pulled apart. Thus, as each new polymer chain is formed, considerable strains will be imposed in the crystal.

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### Acide Acétoxy-3 $\beta$ e Oléanène-12(13) Oïque-28 $\beta$ a

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**Abstract.** C<sub>32</sub>H<sub>50</sub>O<sub>4</sub>,  $M_r = 498$ , orthorhombic,  $P2_12_12_1$ ,  $a = 14.50$  (3),  $b = 7.33$  (1),  $c = 27.14$  (2) Å,  $V = 2884$  Å<sup>3</sup>,  $Z = 4$ ,  $D_m = 1.11$  (5),  $D_c = 1.15$  g cm<sup>-3</sup>,  $F(000) = 1088$ , 1846 observed reflexions,  $\lambda(\text{Cu } K\alpha) = 1.54178$  Å,  $T = 294$  K. Ring *E* has a chair conformation.

**Introduction.** Cette aglycone extraite de l'écorce de *Piptadeniastrum africanum* de la famille des Mimosaceae de Côte d'Ivoire a été identifiée comme étant l'acide oléanolique [acétoxy-3 $\beta$ e oléanène-12(13) oïque-28 $\beta$ a].

Ces extraits d'écorce sont utilisés en pharmacopée indigène. Il nous a paru intéressant, dans le cadre des recherches poursuivies par les différentes sections du groupe des substances naturelles de l'Université Nationale de Côte d'Ivoire, de déterminer la structure cristalline de cet extrait (Comeau, Druet & Braun, 1974).

Les cristaux se présentent sous la forme de parallélépipèdes. Le cristal utilisé pour les mesures d'intensité diffractée avait les dimensions suivantes: 0,25 × 0,12 × 0,05 mm.

Une étude sur chambre de Weissenberg et de

précession nous a permis de déterminer le groupe spatial ainsi qu'une première valeur des paramètres. 1846 réflexions non nulles ont été mesurées sur le diffractomètre automatique Enraf-Nonius CAD-3 à la température ambiante en utilisant le rayonnement Cu

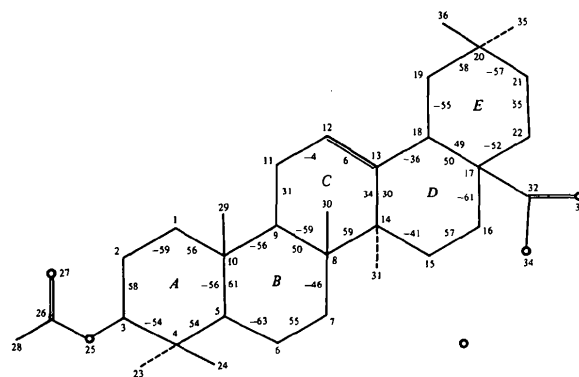


Fig. 1. Numérotation des atomes et angles de torsion (°).