

Structure of 3,5-Octadiyne-1,8-diol at 120 K

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Abstract. $\text{OHH}_2\text{C}-\text{H}_2\text{C}-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-\text{CH}_2-\text{CH}_2\text{OH}$, monoclinic, $P2_1/c$, with $a = 4.847(2)$, $b = 19.58(1)$, $c = 8.130(2)$ Å, $\beta = 95.41(4)^\circ$ at 120 K. $D_m(298\text{ K}) = 1.36$, $D_c(120\text{ K}) = 1.402\text{ g cm}^{-3}$, $Z = 4$. $F(000) = 296$, $\mu(\text{Cu K}\alpha) = 6.15\text{ cm}^{-1}$, $\lambda(\text{Cu K}\alpha) = 1.54178$ Å. The structure was refined to $R = 0.042$ for 1016 counter reflections. The crystal structure accounts for the observed solid-state reactivity of 3,5-octadiyne-1,8-diol.

Introduction. Many diacetylenes (general formula $R-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-R'$) undergo solid-state polymerization reactions of the type illustrated in Fig. 1 (Wegner, 1969, 1972, 1977). Polymerization may be initiated by thermal, photochemical or mechanical techniques. The ability of a specific diacetylene monomer to polymerize in the solid state is governed by the molecular packing of the diacetylene molecules and by the nature 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 having a relatively small number of atoms in these side groups. The structures of 2,4-hexadiyne (Himes, 1953), 2,4-hexadiyne-1,6-diol

(Hädicke, Penzien & Schnell, 1971) and 2,4-hexadiyn-1-ol (Fisher, Batchelder & Hursthouse, 1978) have been published.

3,5-Octadiyne-1,8-diol was prepared by the oxidative coupling of 3-butyn-1-ol (99%, Aldrich Chemical Company Ltd) in water, in the presence of ammonium chloride, cuprous chloride and concentrated hydrochloric acid (Bowden, Heilbron, Jones & Sargent, 1947). The product was extracted with ether and recrystallized twice from toluene to give a pale-pink, crystalline solid, m.p. 43.5°C . (C = 69.67; H = 7.31%. $\text{C}_8\text{H}_{10}\text{O}_2$ requires C = 69.50; H = 7.30%.) Plate-like crystals, suitable for X-ray study, were grown from a saturated solution in toluene at room temperature.

Freshly prepared crystals are colourless, but rapidly turn pink on exposure to daylight at room temperatures. This colouration is due to the formation of trace amounts of polymer. A crystal $0.5 \times 0.8 \times 0.1$ mm was selected for data collection, during which the crystal was cooled in a stream of cold nitrogen gas to $120(\pm 3)$ K, which seemed to be effective in preventing 'in-beam' polymerization.

Photographs of other crystals were used to obtain the space group and approximate values for the lattice parameters. Accurate values for the latter were calculated by least-squares analysis of 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 and was determined by a fast prescan of $6.6^\circ\text{ min}^{-1}$. The ω -scan width was determined as $\text{scan} = (0.8 + 0.2 \tan \theta)^\circ$ and the aperture setting was 4 mm. Regions equal to 25% of the ω -scan width were scanned on either side of each peak. Counts measured in these regions constituted left (B_l) and right (B_r) backgrounds of the peak count, C . The net intensity for each peak was taken as $I_o = |C - 2(B_l + B_r)|$ and the standard deviation as $\sigma(I_o) = |C + 4(B_l + B_r)|^{1/2}$. Those peaks which gave $\sigma(I)/I > 0.3$ when measured during the prescan were not rescanned. All other peaks were rescanned subject to a maximum scanning time of 60 s. Two intensity

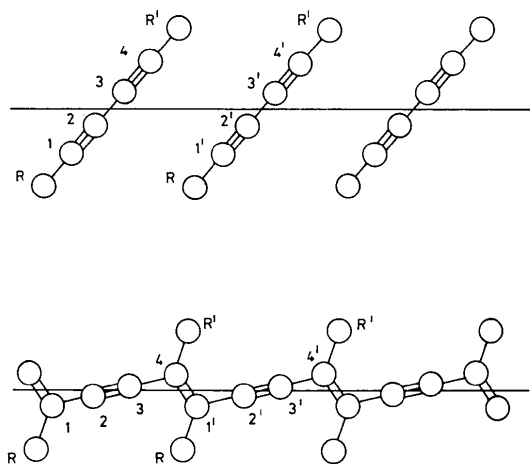


Fig. 1. 1,4-Addition polymerization of diacetylenes.

control reflections which were monitored after every 3600 s of X-ray exposure did not show any decay of the crystal. Data collected in the range $3 < \theta < 60^\circ$ reduced to 1198 unique, observed reflections of which 1016 obeyed the condition $I_o > 1.5\sigma(I_o)$ and were used in the structure refinement.

The structure was solved by direct methods with *SHELX* (Sheldrick, 1976). All non-hydrogen atoms were located in the best *E* map and all the methylene H atoms were positioned initially with the *AFIX* facility in *SHELX*. The next derived Fourier map revealed the positions of the hydroxyl H atoms. Subsequent anisotropic refinement of the non-hydrogen atoms and free, isotropic refinement for all H atoms gave a final value for *R* of 0.042. A weight of $1/[\sigma^2(F) + 0.0003 \times F_o^2]$ gave flat agreement analyses.

The atomic coordinates for the non-hydrogen atoms, and parameters for the H atoms are given in Tables 1 and 2. Interatomic distances and angles are presented in Table 3. Plots obtained with *ORTEP* (Johnson, 1965) are given in Figs. 2 and 3.*

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33798 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic coordinates ($\times 10^4$) for the O and C atoms

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

	<i>x</i>	<i>y</i>	<i>z</i>
C(1)	-1431 (4)	3608 (1)	5827 (2)
C(2)	-2911 (4)	4255 (1)	6287 (2)
C(3)	-940 (3)	4757 (1)	7030 (2)
C(4)	800 (3)	5135 (1)	7656 (2)
C(5)	2805 (3)	5569 (1)	8368 (2)
C(6)	4575 (3)	5944 (1)	8992 (2)
C(7)	6764 (4)	6392 (1)	9726 (2)
C(8)	7837 (4)	6885 (1)	8486 (2)
O(1)	-3296 (3)	3119 (1)	5055 (1)
O(2)	5743 (2)	7344 (1)	7797 (1)

Table 2. Atomic coordinates ($\times 10^4$) and isotropic temperature factors ($\text{\AA}^2 \times 10^3$) for the H atoms

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

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i>
H(C1)	-594 (43)	3397 (10)	6725 (25)	512 (56)
H'(C1)	-92 (44)	3731 (9)	4966 (25)	469 (52)
H(C2)	-4167 (41)	4169 (8)	7080 (23)	407 (50)
H'(C2)	-3907 (38)	4460 (9)	5218 (25)	437 (52)
H(C7)	6140 (33)	6659 (8)	10603 (20)	249 (40)
H'(C7)	8256 (38)	6113 (9)	10173 (20)	319 (44)
H(C8)	8613 (39)	6651 (9)	7571 (24)	410 (48)
H'(C8)	9285 (36)	7174 (9)	9011 (21)	302 (42)
H(O1)	-4112 (50)	2860 (13)	5809 (34)	661 (72)
H(O2)	4830 (47)	7135 (11)	7010 (28)	537 (66)

Table 3. Interatomic distances (\AA) and angles ($^\circ$)

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

O(1)—C(1)	1.420 (2)	O(1)—C(1)—C(2)	112.0 (0.1)
C(1)—C(2)	1.520 (2)	C(1)—C(2)—C(3)	111.0 (0.1)
C(2)—C(3)	1.460 (2)	C(2)—C(3)—C(4)	175.7 (0.1)
C(3)—C(4)	1.198 (2)	C(3)—C(4)—C(5)	179.7 (0.1)
C(4)—C(5)	1.377 (2)	C(4)—C(5)—C(6)	179.4 (0.2)
C(5)—C(6)	1.204 (2)	C(5)—C(6)—C(7)	178.8 (0.2)
C(6)—C(7)	1.459 (2)	C(6)—C(7)—C(8)	112.9 (0.1)
C(7)—C(8)	1.522 (2)	C(7)—C(8)—O(2)	112.6 (0.1)
C(8)—O(2)	1.429 (2)		

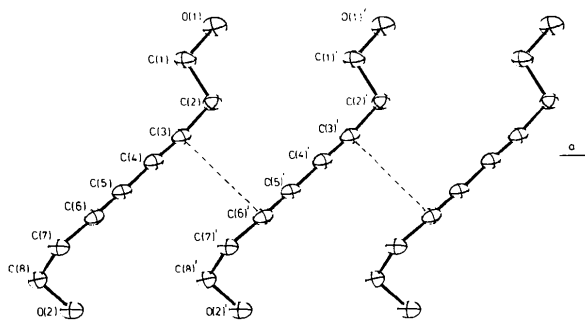


Fig. 2. Monomer molecules viewed normal to *ab*. 50% probability ellipsoids (*ORTEP*, Johnson, 1965).

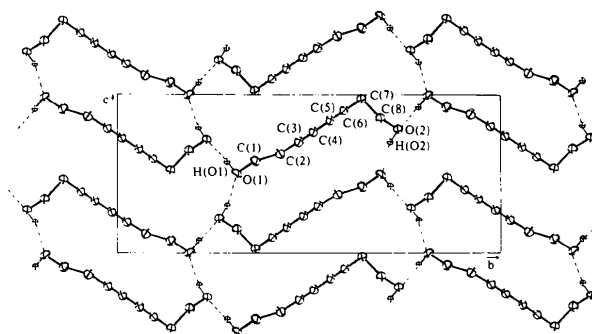


Fig. 3. Molecular plot viewed normal to *bc*. 50% probability ellipsoids (*ORTEP*, Johnson, 1965).

Discussion. The molecular packing is suitable for solid-state polymerization to occur by the 1,4-addition of adjacent monomer molecules (Fig. 1) (Wegner, 1977). The route by which polymerization occurs is illustrated in Figs. 1 and 2. C(3) and C(6') are 3.65 \AA apart, which is sufficiently small for intermolecular bonding to occur if enough energy (in the form of UV or X-ray radiation) is imparted to the monomer molecules.

Successive cross-linking would form polymer molecules with chain axes parallel to *a*. There is sufficient freedom for the diacetylene segments of 3,5-octadiyne-1,8-diol to be rearranged during polymerization without the series of hydrogen bonds (illustrated by the broken lines in Fig. 3) being disrupted. This contrasts significantly with the behaviour of 2,4-hexadiyn-1-ol (Fisher, Batchelder & Hursthouse, 1978) where rather severe hydrogen-bonding restrictions at one end of each monomer molecule affect the polymerization process. Crystallographic studies of polymeric 3,5-octadiyne-1,8-diol are in progress.

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Conformational Analysis of Progestational Agents: 11 β -Fluoro-19-nor-17 α -pregn-4-en-20-yn-17 β -ol

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Abstract. C₂₀H₂₇FO, *M_r* = 302.4, monoclinic, *P*2₁, *a* = 10.2844 (7), *b* = 11.2118 (6), *c* = 7.2248 (4) Å, β = 94.604 (5)° (λ = 1.5418 Å, *T* = room temperature), *V* = 830.4 Å³, *Z* = 2, ρ_x = 1.210 g cm⁻³. The 11 β -fluoro substituent places about the same steric strain on the molecule as H. The result in overall conformation is essentially the same as the unsubstituted compound without the bowing caused by other 11 β substituents.

Introduction. A correlation between the steric size of the 11 β substituent and the progestational activity of lynestrenol derivatives has been proposed (van der Broek *et al.*, 1977) and the variation in activity appears related to changes in the overall conformation of the molecule caused by the introduction of the 11 β substituent rather than to the direct interaction of the 11 β substituent with the receptor site. Because the progestational activity of the title compound is only slightly

enhanced by 11 β -fluoro substitution, it is of interest to compare its conformation with that of lynestrenol.

Crystal data were measured on a crystal of dimensions 0.20 × 0.50 × 0.80 mm on an Enraf–Nonius CAD-4 automatic diffractometer using Ni-filtered Cu *K* α radiation. The condition *k* = 2*n* limiting the 0*kl* reflections determined the space group to be *P*2₁. The lattice parameters were refined by a least-squares fit to measured 2 θ values of 75 reflections in the range 49 < 2 θ < 70°. Integrated relative intensities for 1784 independent reflections with 2 θ < 150° were measured using ω -2 θ scans; 1746 of these intensities were determined to be observed above background (*I* > 2 σ _{*i*}).

The intensities were reduced to structure factor amplitudes, and phase angles sufficient to locate the missing F atom were derived using the coordinates of the isomorphous structure of lynestrenol (Rohrer, Lauffenburger, Duax & Zeelen, 1976). The H atoms