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X-Ray Structural Study of a 1:2:1 Inclusion Complex of Non-centrosymmetric 1,6,9,14-Tetrahydroxy-1,6,9,14-tetra-*t*-butylcyclohexadeca-2,4,7,10,12,15-hexayne, Ethanol, and Water

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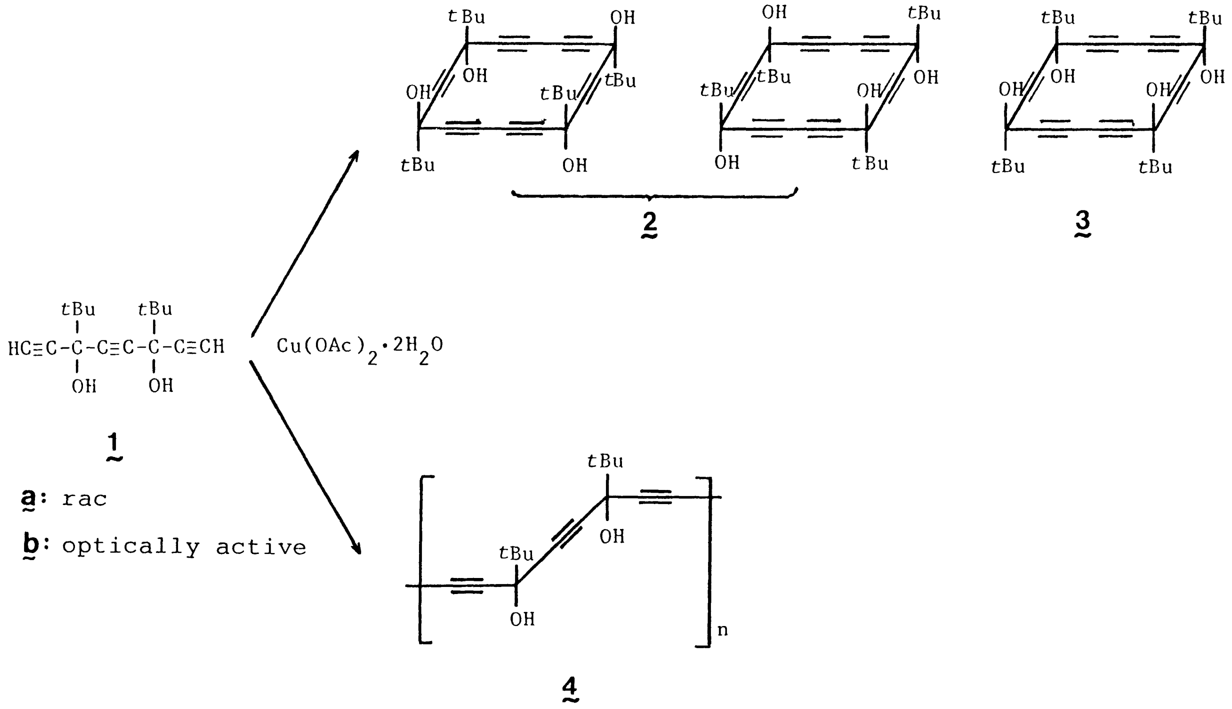
The structure of the title cyclic hexayne has been elucidated by X-ray analysis of its 1:2:1 inclusion complex with EtOH and H_2O. The important role of H_2O in consolidating the disordered, hydrogen-bonded host lattice is also clarified.

Previously we reported that oxidative coupling of racemic (**1a**) and optically active (**1b**) 3,6-di-*t*-butylocta-1,4,7-triyne-3,6-diol gives cyclic dimeric (**2** or **3**) and optically-active polymeric (**4**) products, respectively.$^{1)}$ However, the cyclic dimer was not firmly established as either the racemic (**2**) or the *meso* (**3**) compound.



Recrystallization of (**2**) (white powder, mp 300 °C)[1] from absolute ethanol did not give crystals of good quality. However, use of aqueous ethanol as a solvent yielded colorless prisms (mp not sharp) of the title complex (**5**), whose stoichiometry and structure were then elucidated by X-ray crystallography. The present study has shown the cyclic hexayne to be the non-centrosymmetric isomer (**2**) and (**5**) to be an inclusion compound.

A selected crystal of **5** with dimensions of 0.40x0.40x0.40 mm^3 was sealed inside a 0.5 mm Lindemann glass capillary, and intensity data were collected on a Nicolet R3m/V diffractometer at 22 °C using Mo-$\underline{K}_\alpha$ radiation ($\bar{\lambda}$ = 0.71073 Å) according to established procedures.[2]

Crystal data: **5**, $C_{32}H_{40}O_4 \cdot 2C_2H_5OH \cdot H_2O$, FW = 598.81, tetragonal, space group $\underline{P}\bar{4}\underline{n}2$ (No. 118), $\underline{a}$ = 10.464(3), $\underline{c}$ = 17.153(6) Å, V = 1878(1) $Å^3$, $\underline{Z}$ = 2, $\underline{F}$(000) = 652, $\underline{D}_m$ (flotation in KI/H_2O) = 1.067, $\underline{D}_c$ = 1.059 g cm^{-3}, μ = 0.41 cm^{-1}, $2\theta_{max}$ = 50°, 1681 unique reflections. The structure was solved by direct phase determination based on random starts and negative quartets.[3,4] The cyclic hexayne molecule (Fig. 1) is located at Wyckoff position 2($\underline{c}$) of site symmetry 222, and the water molecule O2 occupies position 2($\underline{a}$) of site symmetry $\bar{4}$. Half site-occupancy and disorder of the ethanol molecule, which occupies a general position, became evident in the course of refinement. In the model adopted, the ethanol molecule is represented by atoms O3[½], C9[½], C10[¼] and C11[¼] with site occupancy factors enclosed in square brackets. Atoms C9, C10, and C11 were varied isotropically, and all other non-hydrogen atoms anisotropically. The methyl H atoms in the cyclic hexayne were generated geometrically (C-H fixed at 0.96 Å), and the hydroxyl H(O1) atom was located from a difference map. These H atoms were included in structure-factor calculations in least-squares cycles with assigned isotropic temperature factors. Refinement of 1403 observed data $[|\underline{F}_o| > 3\sigma(|\underline{F}_o|)]$ on 114 parameters using the weighting scheme $\underline{w} = [\sigma^2(|\underline{F}_o|) + 0.0025|\underline{F}_o|^2]^{-1}$ converged to $\underline{R}_F$ = 0.089. All computations were performed on a DEC MicroVAX-II computer with the SHELXTL PLUS package.[3-6]

The measured dimensions of the cyclic dimer of $\underline{D}_2$ molecular symmetry is given in the legend of Fig. 1. The $\underline{C}_2$ axis passing through the mid-points of the C4-C4^b and C4^a-C4^c bonds runs parallel to the crystallographic $\underline{c}$ axis. Another $\underline{C}_2$ axis passes through the centers of the C2-C2^a and C2^b-C2^c bonds, whereas the third is normal to the mean plane of the molecule. The central sixteen-membered ring is distinctly non-planar, and its edges are distorted from linearity in a barrel-like manner, as shown by the values of the relevant bond angles and torsion angles in Fig. 1. In accordance with expectation, the unconjugated C≡C bond is found to be significantly shorter than the conjugated one, and the *t*-butyl group is in a staggered arrangement with respect to the ring atoms.

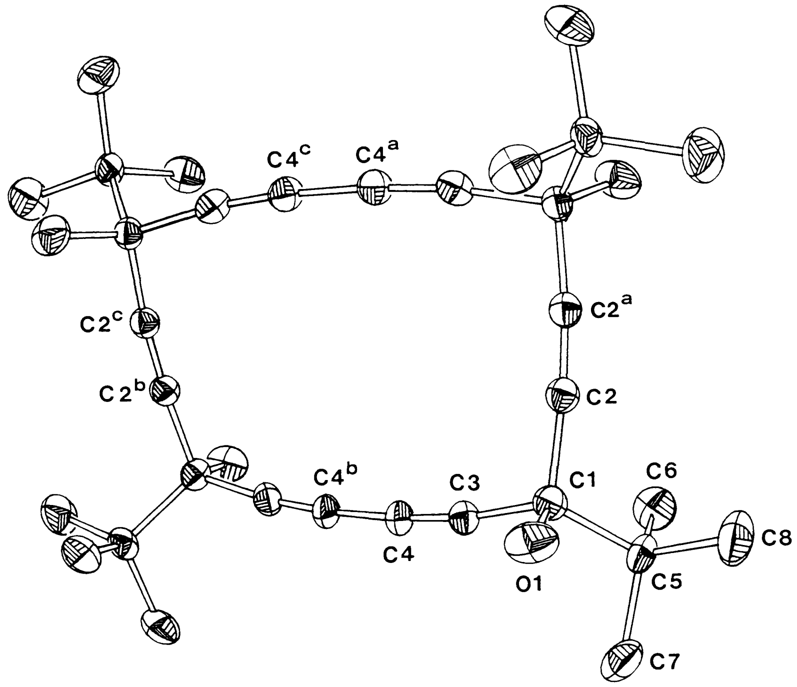


Fig. 1. The structure of the cyclic hexayne molecule with atom labelling. Thermal ellipsoids are drawn at the 30% probability level. Selected molecular dimensions (bond lengths in Å, angles in degrees, estimated standard deviations in parentheses): C1-C2 1.472(6), C2-C2^{a} 1.168(6), C1-C3 1.494(6), C3-C4 1.184(6), C4-C4^{b} 1.381(6), C1-C5 1.571(6), C1-O1 1.429(5); C1-C2-C2^{a} 173.8(3), C1-C3-C4 172.3(3), C3-C4-C4^{b} 175.3(3), C2-C1-C3 105.9(3), C2-C1-C5 111.6(3), C3-C1-C5 111.1(3), C2-C1-O1 108.6(4), C3-C1-O1 109.8(3), C5-C1-O1 109.7(5); torsion angles C1-C2-C2^{a}-C1^{a} 21.1(4), C1-C3-C4-C4^{b} -24.3(4) C3-C4-C4^{b}-C3^{b} 20.8(4), O1-C1-C5-C6 -178.0(5). Symmetry code: $^{a}\frac{1}{2}-\underline{y}$, $\frac{1}{2}-\underline{x}$, $\frac{1}{2}-\underline{z}$; $^{b}-\underline{x}$, $1-\underline{y}$, $\underline{z}$; $^{c}-\frac{1}{2}+\underline{y}$, $\frac{1}{2}+\underline{x}$, $\frac{1}{2}-z$.

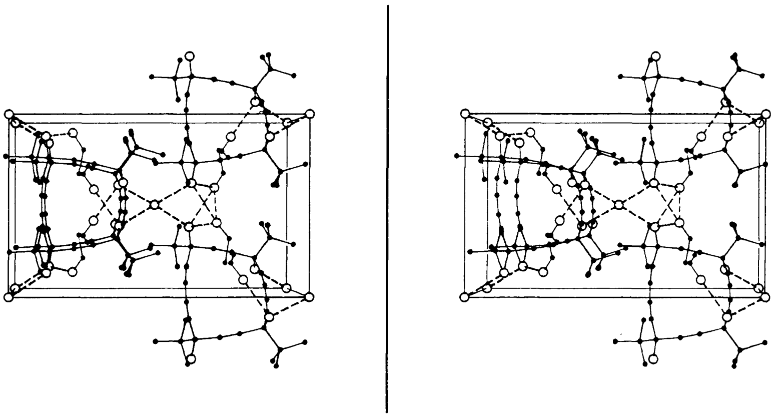


Fig. 2. Stereodrawing of the crystal structure of 5. The origin of the unit cell lies at the upper left corner, with a pointing toward the reader, b vertically downward, and c from left to right. Broken lines represent O...O hydrogen bonds. Note that the ethanol molecule is two-fold disordered, and one of the possible methyl carbon positions (atom C11) has been omitted for clarity.

A stereo view of the crystal packing is illustrated in Fig. 2. The water molecule forms hydrogen bonds [$O1\cdots O2 = 2.806(5)$ Å] with the hydroxyl groups of four neighboring hexayne molecules. The ethanol molecule is disordered over two sites, and its methyl group furthermore exhibits two-fold positional disorder. The O atoms of the hexayne and disordered ethanol molecules are also linked by hydrogen bonds [$O1\cdots O3^{a} = 2.662(8)$, $O1\cdots O3(\frac{1}{2}+y, \frac{1}{2}+x, \frac{1}{2}-z) = 2.843(8)$ Å]. Compound **5** can thus be considered as an inclusion complex comprising a host lattice built of hexayne and water molecules which accommodates the ethanol guest species. It is conceivable that two 'half' ethanol molecules related by a crystallographic C_2 axis may be replaced by another guest species of similar bulk and hydrogen-bonding capability, such as 1,2-ethanediol, to form an isomorphous inclusion complex. When the guest molecule fails to satisfy these requirements, the disordered hydrogen-bond system of the present host lattice will most likely be disrupted, and the complex is expected to crystallize in a space group of lower symmetry.

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