279. Crystallographic and Spectroscopic Evidence for an Intramolecular (OH···π)-Interaction

by **W. Bernd Schweizer, Jack D. Dunitz, Rolland A. Pfund, Gerardo M. Ramos Tombo**
and **Camille Ganter**

Organic Chemistry Laboratory, Swiss Federal Institute of Technology, ETH-Zentrum, CH-8092 Zürich

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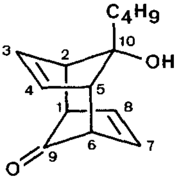
Summary

Crystallographic and spectroscopic evidence for an intramolecular (OH···π)-interaction in *anti*^{9,10}-10*endo*-hydroxy, 10*exo*-butyltricyclo[4.2.1.1^{2,5}]deca-3,7-dien-9-one (**1**) is presented.

The existence of intramolecular H-bonding of hydroxyl groups to the π-electron cloud of a C,C-double bond has been extensively propounded, mainly from IR. spectroscopic evidence1), but has never, to the best of our knowledge, been confirmed by X-ray analysis.

We now report an example of an intramolecular (O–H···π)-interaction, where the position of the H-atom has been unequivocally determined from an electron-density difference map.

In the course of our studies on nucleophilic additions to C,C-double bonds2) we have determined the structure of the olefinic alcohol **1**3), which crystallizes with a triclinic unit cell: $a=6.235(2)$, $b=7.960(2)$, $c=12.078(4)$ Å; $\alpha=79.61(3)$, $\beta=76.83(3)$, $\gamma=85.59(3)°$; $Z=2$. The arrangement of the heavy atoms was found without difficulty by direct methods [7], assuming the centrosymmetric space group $P\bar{1}$, and refined by full-matrix least-squares analysis [7] [8]. At an intermediate stage, all H-atoms were located from a (F_o-F_c)-difference synthesis and included



1

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1) See the reviews [1] [2] and the more recent papers [3] [4] [5].

2) For Part IV, see [6].

3) *anti*^{9,10}-10*endo*-Hydroxy, 10*exo*-butyltricyclo[4.2.1.1^{2,5}]deca-3,7-dien-9-one.

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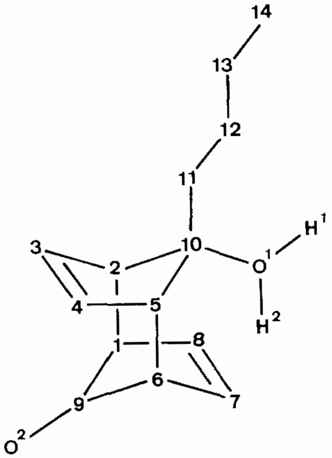
in the refinement with isotropic temperature factors, the other atoms being treated as anisotropic. The final R was 0.036, $R_w = 0.044$ (modified weights $w = \sigma^{-2}(F) \cdot \exp(r \cdot \sin^2(\theta/\lambda^2))$ [9], with $r = 7$ Å^2)[4]).

The interesting feature of the packing *(Fig.)* is the intermolecular approach of a pair of alcoholic O-atoms (O · · · O: 3.092 Å) across the assumed center of symmetry. For an ordered structure in the assumed space group $P\bar{1}$ there would have to be either two H-atoms or none between these O-atoms, whereas H-bonding would demand one. The difference map shows a pair of symmetrically disposed peaks, each at distance of 0.70(4) Å from its closest O-atom but only approximately half the strength of the peaks associated with the other H-atoms. Two additional



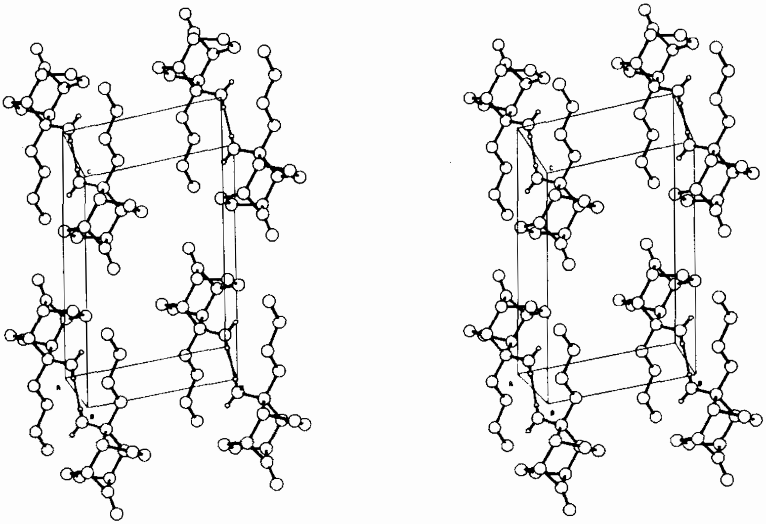


Figure. *Stereographic view of the unit cell of* **1**

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[4] Atomic coordinates of **1** have been submitted to the *Cambridge Crystallographic Data Centre.*

half-strength peaks occur at approximately the same distance from the O-atoms but directed towards the center of the C,C-double bond (H···C(3) and H···C(4): 2.11 and 2.16 Å, respectively). When the two possible positions of the H-atoms are included in the structure model, each with 50% population parameter, their isotropic vibration parameters U converge to values of 0.04 to 0.05 Å^2, approximately the same as for the other H-atoms in the molecule. We cannot distinguish experimentally between the disordered structure in space group $P\bar{1}$ and the ordered one in space group $P1$, but we think the former is more likely.

The persistence of this intramolecular (OH···π)-interaction in solution is indicated by the following IR. and ^{1}H-NMR. evidence: a concentration-independent (O–H)-stretch vibration[5] at 3600 cm^{-1} in CCl_4 solution and a concentration-independent resonance for the hydroxylic H-atom[5] at $\delta = 4.07$ ppm (t, $^4J = 1.5$ Hz) in $CDCl_3$ solution. The IR. spectrum of a nujol suspension shows two absorption bands of comparable intensity at 3576 and 3517 cm^{-1}, for which the crystal structure provides an obvious interpretation.

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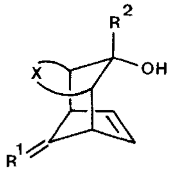
[5] In analogy to **1** other compounds of the general type **a** (see [6] and earlier paper in this series) show the same spectroscopical behaviour.



a

R^1: O or H,H
R^2: H or alkyl
X: CH=CH, CH_2–CH_2 or CH_2–CH_2–CH_2