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## 10-Hydroxy-3-methoxy-2,4a-ethano-5,8-methanoperhydronaphthalene: An Example of Steric Preference in Photochemical Addition\*

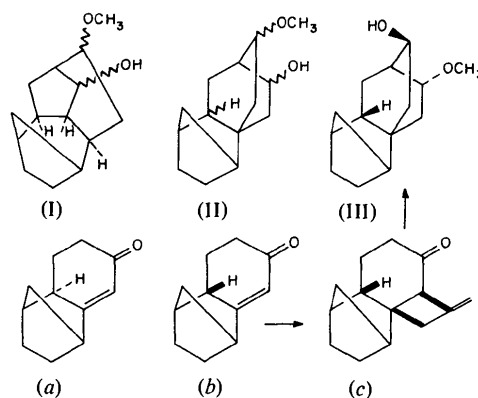
BY A. D. HARDY† AND F. R. AHMED‡

*Division of Biological Sciences, National Research Council of Canada, Ottawa, Canada K1A 0R6*

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**Abstract.**  $C_{14}H_{22}O_2$ , monoclinic,  $C2/c$ ,  $a = 11.821$  (2),  $b = 6.435$  (2),  $c = 31.567$  (2) Å,  $\beta = 92.24$  (2)°,  $V = 2399.4$  Å<sup>3</sup>,  $Z = 8$ ,  $D_x = 1.231$ ,  $D_m = 1.239$  g cm<sup>-3</sup> (floatation in KI solution at 22°C). The structure has been determined by X-ray analysis, and its synthesis has been found to conform to the photoaddition rule. The direct method was used and block-diagonal least-squares refinement led to  $R = 0.042$ ,  $R_w = 0.039$  for the 1759 observed reflexions. The molecules are inter-linked by hydrogen bonds to form separate continuous chains.

**Introduction.**  $C_{14}H_{22}O_2$  was synthesized by K. Wiesner and his collaborators by a method that they wished to utilize in the synthesis of delphinium alkaloids. The method was based on the re-arrangement postulated for the biogenesis of this type of skeleton (Valenta & Wiesner, 1956), and the product was predicted to be (I). Further chemical studies, however, ascertained that the compound had failed to re-arrange as predicted and (II) was then proposed. The actual structure found by this analysis was (III).



Determination of the stereochemistry of the compound was needed in order to clarify the steric preference of the photochemical addition by which the system was constructed. From this work, Wiesner (1973) concluded that the starting material was (b) rather than (a), (b) being converted with complete stereospecificity into the allene photoadduct (c). The conversion of (c) to (III) had been accomplished by standard methods which left no doubt that the methoxy group in (III) was derived from the ketone function in (c).

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† Postdoctorate Fellow.

‡ To whom correspondence should be addressed.

Also, according to Wiesner (1973), this structure upholds the photoaddition rule (Wiesner, Poon, Jirkovský & Fishman, 1969), although it is completely unlike the examples on which the rule was originally based. The rule states that the stereochemistry of addition of olefins to  $\alpha,\beta$ -unsaturated ketones is dictated *exclusively* by the preferential stability of the excited state.

The X-ray data were measured on a Picker diffractometer with Ni-filtered Cu radiation and a crystal  $0.870 \times 0.537 \times 0.065$  mm, mounted with  $b^*$  along the  $\phi$  axis. The unit-cell parameters were based on angular settings of high-order axial reflexions, and the intensities were measured by the  $\theta$ - $2\theta$  scan method. The intensities were corrected for background, crystal decomposition, and for Lorentz-polarization and absorption effects [ $\mu(\text{Cu } K\alpha) = 6.37 \text{ cm}^{-1}$ ]. The absorption corrections to the intensities were calculated by Gaussian integration (Ahmed, 1970) and were in the range 1.04–1.40. Of 2033 reflexions within  $\sin \theta/\lambda = 0.588$ , 1759 were accepted as observed.

Table 1. *Refined fractional coordinates* ( $\times 10^4$ )

	<i>x</i>	<i>y</i>	<i>z</i>
C(1)	663 (1)	1212 (3)	637 (1)
C(2)	1561 (1)	-109 (3)	882 (1)
C(3)	1148 (1)	-272 (3)	1332 (1)
C(4)	523 (1)	1779 (3)	1444 (1)
C(5)	1044 (1)	3661 (3)	1225 (1)
C(6)	868 (1)	3503 (3)	746 (1)
C(7)	-547 (1)	805 (3)	776 (1)
C(8)	-667 (1)	1532 (3)	1243 (1)
C(9)	678 (2)	1804 (3)	1934 (1)
C(10)	1863 (2)	2663 (4)	2057 (1)
C(11)	2656 (2)	1007 (3)	1870 (1)
C(12)	1849 (1)	-761 (3)	1741 (1)
C(13)	883 (2)	-482 (3)	2051 (1)
C(14)	1661 (2)	4946 (3)	128 (1)
O(1)	1859 (1)	4318 (2)	555 (0)
O(2)	-811 (1)	-1343 (2)	712 (0)
H(1)	678 (14)	917 (27)	328 (5)
H(2,1)	1629 (14)	-1549 (28)	756 (5)
H(2,2)	2331 (14)	617 (27)	867 (5)
H(3)	538 (13)	-1477 (26)	1318 (5)
H(5,1)	1897 (14)	3666 (28)	1291 (5)
H(5,2)	679 (15)	4974 (30)	1329 (5)
H(6)	200 (13)	4428 (24)	637 (5)
H(7)	-1099 (14)	1623 (28)	578 (5)
H(8,1)	-1101 (17)	500 (33)	1407 (6)
H(8,2)	-1129 (14)	2852 (28)	1241 (5)
H(9)	35 (16)	2563 (33)	2075 (6)
H(10,1)	1911 (16)	2678 (31)	2372 (6)
H(10,2)	2003 (16)	4225 (32)	1949 (6)
H(11,1)	3237 (15)	492 (30)	2092 (6)
H(11,2)	3060 (15)	1656 (30)	1614 (5)
H(12)	2192 (15)	-2190 (30)	1736 (6)
H(13,1)	171 (16)	-1357 (32)	1981 (6)
H(13,2)	1149 (15)	-611 (30)	2356 (6)
H(14,1)	1334 (17)	3884 (33)	-48 (6)
H(14,2)	2399 (17)	5346 (32)	15 (6)
H(14,3)	1081 (19)	6103 (37)	130 (7)
HO(2)	-1607 (21)	-1332 (40)	696 (7)

The C and O atoms were located from an *E* map evaluated with 255 reflexions ( $|E| \geq 1.5$ ) whose phases had been determined by symbolic addition, and the H atoms were derived from a subsequent difference map. The atomic parameters were refined by block-diagonal least squares, minimizing  $\sum w(|F_o| - |F_c|)^2$ , with  $w = 1/\{1 + [(|F_o| - 35)/30]^4\}$ , where  $2.6 \leq |F_o| \leq 230.1$ , for only the observed reflexions. In the final cycle  $R = 0.042$ ,  $R_w = 0.039$  and  $[\sum w(\Delta F)^2/(m - n)]^{1/2} = 0.84$  for the observed reflexions, and the mean and maximum shift/e.s.d. = 0.26 and 1.64. The residual electron density in the final difference map was within  $\pm 0.20 \text{ e } \text{Å}^{-3}$ . The atomic coordinates are listed in Table 1.\* The scattering factors were those of Hanson, Herman, Lea & Skillman (1964) for C and O, and of Stewart, Davidson & Simpson (1965) for H. All calculations were performed with the NRC system (Ahmed, Hall, Pippy & Huber, 1973).

**Discussion.** The two orthogonal projections presented in Fig. 1 show that the molecular structure corresponds to (III), not (II). The bond lengths and angles are shown in Fig. 2. The 16  $\text{C}(sp^3)\text{-C}(sp^3)$  bond lengths are 1.524–1.560 (3) (mean 1.539 Å), and the three  $\text{C}(sp^3)\text{-O}(sp^2)$  are 1.417–1.438 (2) (mean 1.428 Å). Although the mean values of these two types of bonds are very close to the average values of 1.537 (5) and 1.426 (5) Å respectively (Sutton, 1965), some of the bonds deviate significantly from these average values. This pattern, however, has been observed previously in many organic compounds with highly substituted C atoms. Because of overcrowding, three short intramolecular  $\text{H} \cdots \text{H}$  van der Waals contacts (below 2.20 Å) are observed, as shown in Fig. 1.

\* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32376 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

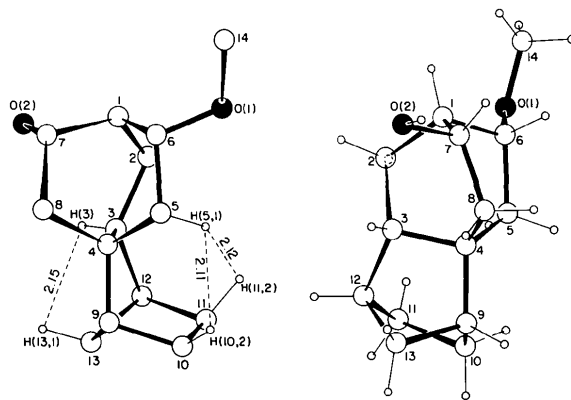


Fig. 1. Two orthogonal views of the molecular structure. The  $\text{H} \cdots \text{H}$  intramolecular van der Waals contacts below 2.20 Å are shown as dotted lines.

Table 2. Torsion angles within the rings

The numerical values correspond to the bonds in the order listed in the first column.

Ring		Torsion angles (°)					
A	C(2)–C(3)–C(4)–C(5)–C(6)–C(1)–	–33.4	–32.8	65.4	–21.9	–46.6	79.1
B	C(1)–C(2)–C(3)–C(4)–C(8)–C(7)–	–35.9	–33.4	81.2	–48.6	–16.9	65.8
C	C(1)–C(7)–C(8)–C(4)–C(5)–C(6)–	–51.9	–16.9	69.1	–47.8	–21.9	74.2
	Idealized twist-boat	–33.1	–33.1	70.6	–33.1	–33.1	70.6
D	C(3)–C(4)–C(9)–C(10)–C(11)–C(12)–	–16.0		81.5	–63.8	–10.2	75.6
	Idealized boat	0		60	–60	0	60
E	C(12)–C(13)–C(9)–C(4)–C(3)–	–60.9		52.4	–22.9	–16.0	48.7
F	C(9)–C(13)–C(12)–C(11)–C(10)–	–59.8		53.9	–27.3	–10.2	44.3

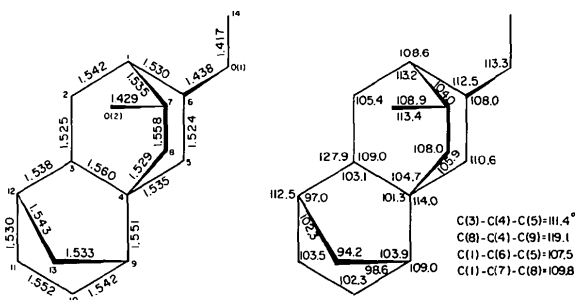


Fig. 2. Bond lengths (Å) and angles (°). The estimated standard deviations are  $\leq 0.003$  Å for the bond lengths, and  $\leq 0.2^\circ$  for the angles. C–H = 0.95–1.08 (mean 0.97) and O–H = 0.94 Å.

The average endocyclic valency angle is  $108.2^\circ$  for the six- and  $100.0^\circ$  for the five-membered rings. The latter is in agreement with the value of  $99.8^\circ$  calculated by Sim (1965) for bicycloheptane. The smallest endocyclic angle ( $94.2^\circ$ ) occurs as expected at the bridging C(13) of the bicycloheptane (norbornane) skeleton. The exocyclic C(2)–C(3)–C(12) angle of  $127.9^\circ$  is the largest C–C–C angle in the structure.

The torsion angles within the rings are listed in Table 2. The six-membered rings A, B and C, as defined in Table 2, are in the distorted twist-boat conformation, and ring D is a distorted boat. The five-membered rings are: E in the twist conformation ( $q_2 = 0.62$ ,  $\varphi_2 = 57^\circ$ , Cromer & Pople, 1975), and F in a distorted-envelope conformation ( $q_2 = 0.61$ ,  $\varphi_2 = 26^\circ$ ). C(13) is 0.88 Å from the mean plane of the four remaining atoms of each of the rings E and F.

The molecules are interlinked by a hydrogen bond O(2)–H...O(1') to form separate continuous chains parallel to  $\mathbf{a} \pm \mathbf{b}$ . The corresponding geometry is O(2)–H = 0.94, H...O(1') = 1.90, O(2)...O(1') = 2.812 Å, and O(2)–H...O(1') =  $163.6^\circ$ .

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