

AN X-RAY ANALYSIS OF DIPHENYLCYCLOPROPENONE MONOHYDRATE

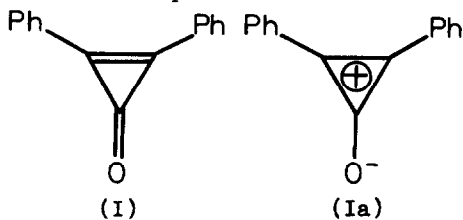
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(Received in Japan 4 May 1973; received in UK for publication 25 May 1973)

Since its synthesis in 1959,¹⁾ diphenylcyclopropenone (I) has commanded considerable interest in connexion with its strained, highly polar, and pseudoaromatic nature. In order to examine the structural-chemical basis of these properties, an X-ray analysis of diphenylcyclopropenone monohydrate was undertaken as a part of our crystallographic studies on the non-benzenoid aromatic compounds.



The monohydrate crystals, colourless needles with m.p. 87°C, were obtained by recrystallization of (I) from water-saturated benzene solution. The crystals are orthorhombic, space group Pbca; $a = 25.06 \text{ \AA}$,

$b = 9.28 \text{ \AA}$, $c = 20.66 \text{ \AA}$, $U = 4803 \text{ \AA}^3$; $D_m = 1.239 \text{ g/cm}^3$; $D_c = 1.241 \text{ g/cm}^3$; $Z = 16$ (two crystallographically independent formula units per asymmetric unit). The intensity data were recorded on Weissenberg photographs using CuK α radiation and measured visually. A total of 4135 independent structure factors were obtained. The structure was solved by the direct method and refined by the least-squares method. At the present stage, the R factor was 0.136.

The molecules are nearly planar as a whole, although the phenyl groups are slightly twisted in a same sense with respect to the three-membered ring. The bond lengths (in \AA) and angles (in degrees) in the independent molecules are shown in the Figure. Differences in lengths between the formal single and double bonds in the three-membered ring are smaller than those in diphenylcyclopropenone.²⁾ The C-O bonds are longer than those in aliphatic ketones.

These suggest a considerable large contribution from a canonical form (Ia) in the hydrate crystals.

All the water molecules participate in the hydrogen bond with the carbonyl oxygen atoms. The two independent molecules exhibit different hydrogen bonding; the molecules 1 and 2 are bonded to one and two water molecules respectively. In the crystal, such hydrophilic regions are separated by the hydrophobic ones involving a characteristic stacking of the aromatic rings. Since the aromatic ketones generally do not seem to form stable hydrate crystals, the present crystal structure suggests the highly polar nature of the molecule itself from the crystallographic point of view.

It has been reported that the hydrate formation has pronounced effect on the infrared absorption spectra of (I).³⁾ An X-ray analysis of anhydrous diphenylcyclopropanone is now in progress.

The authors wish to express their thanks to Professor Y. Kitahara for continuing interest and to Dr. M. Funamizu for supplying the sample.

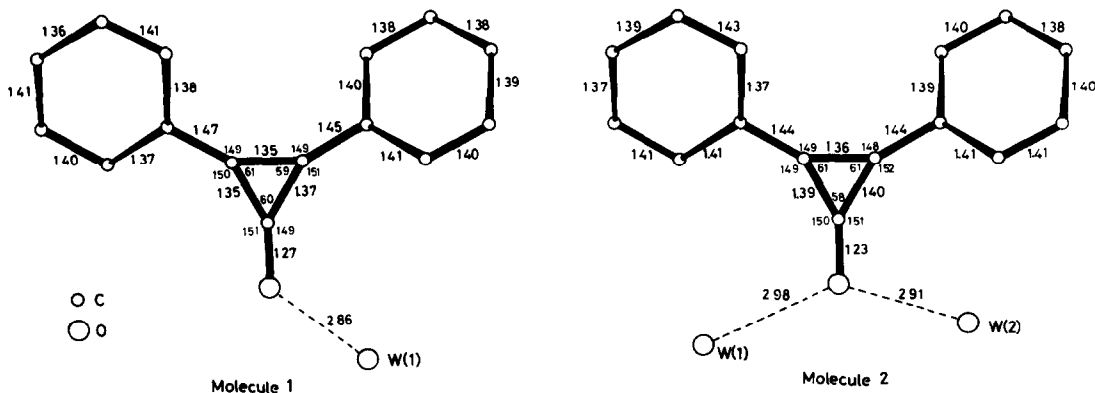


Figure. The e.s.d.'s are 0.016 - 0.021 Å and 0.9 - 1.6°.

- 1) R. Breslow, R. Haynie and J. Mirra, *J. Amer. Chem. Soc.*, **81**, 247 (1959).
M. E. Vol'pin, Y. D. Koreshkov and D. N. Kursanov, *Izv. Akad. Nauk SSSR, Otd. Khim Nauk*, (1959), 560; *Chem. Abstr.*, **53**, 21799 (1959).
- 2) L. L. Reed and J. P. Schaefer, *Chem. Commun.* (1972), 528.
- 3) F. Toda and K. Akagi, *Tetrahedron Letters*, (1968), 3735.