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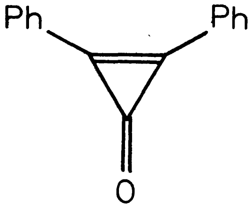
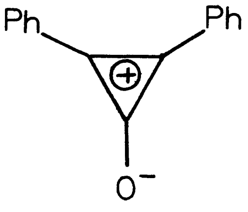
X-RAY DETERMINATION OF THE STRUCTURE OF ANHYDROUS DIPHENYLCYCLOPROPENONE. VARIATIONS OF THE MOLECULAR GEOMETRY DUE TO HYDROGEN BONDING

Harumichi TSUKADA, Hirotaka SHIMANOUCHI, and Yoshio SASADA
Faculty of Science, Tokyo Institute of Technology,
Ookayama, Meguro-ku, Tokyo 152

The crystal structure of anhydrous diphenylcyclopropenone was determined and the structural features are compared with those in its monohydrate. The systematic variation of the molecular geometry found is attributable to the contribution from a dipolar ionic form, enhanced by the formation of the hydrogen bond.

As a part of the serial work on the non-benzenoid aromatic compounds, we previously reported the crystal structure of diphenylcyclopropenone monohydrate, in which there are two kinds of hydrogen-bonding scheme.[1] The structure was refined further on the basis of the intensity data measured on a four-circle diffractometer. The result shows some systematic changes of the detailed molecular geometry ascribable to the difference in hydrogen-bonding scheme. The present analysis of the anhydrous crystal has been undertaken in order to reveal the effect of hydrogen bonding on the molecular geometry of this highly-strained non-benzenoid aromatic system. When we have completed the determination of the present anhydrous crystal structure, an independent structure determination of the monohydrate has been published by Ammon,[2] but his conclusion is somewhat different from ours. This prompts us to report the detailed molecular structure in the anhydrous crystal in connection with our result on the hydrate crystal, which might give new information about the chemistry of this system.


(I)


(Ia)

The anhydrous single crystals of diphenylcyclopropenone (I) were obtained by use of carefully-purified benzene as a solvent for crystallization. Crystal data: $\underline{M}$ = 206.2. Orthorhombic, $\underline{a}$ = 25.27(1), $\underline{b}$ = 7.475(6), $\underline{c}$ = 17.91(1) Å, $\underline{U}$=3383 Å^3, $\underline{D}_m$ = 1.21, $\underline{D}_c$ = 1.21 g·cm^{-3}, $\underline{Z}$ = 12, $\underline{F}$(000) = 1296, space group Pbcn, μ(Cu-$\underline{K\alpha}$) = 5.99 cm^{-1}. Three-dimensional intensity data were collected on equi-inclination Weissenberg photographs using Cu-$\underline{K\alpha}$ radiation (λ = 1.5418 Å) and measured by a TV densitometer.[3] The structure was solved by the direct methods. Three reflections, 19 0 6, 21 1 3 and 12 2 5 were chosen for origin specification. Phase determination was performed by the manual symbolic addition procedure followed by the refinement using the program of the tangent formula.4) An *E* map synthesized with 266 reflections clearly revealed the structure. Structural parameters of the anisotropic heavy atoms and the isotropic hydrogens have been refined by the block-diagonal matrix least-squares method to the final *R* of 0.095.

It was shown that eight molecules(A) occupy general positions and the remaining four molecules(B) lie in special positions across the crystallographic C_2 axis, which coincides with the C=O bond. The molecules(B) are disordered; an alternative orientation of the three-membered ring is shown by the dotted lines in Fig. 1. This reasonably explains the diffuse lines along the reciprocal lattice row parallel to the c* direction in the Weissenberg photographs. No abnormally short intermolecular contacts are found, except those between the disordered three-membered rings.

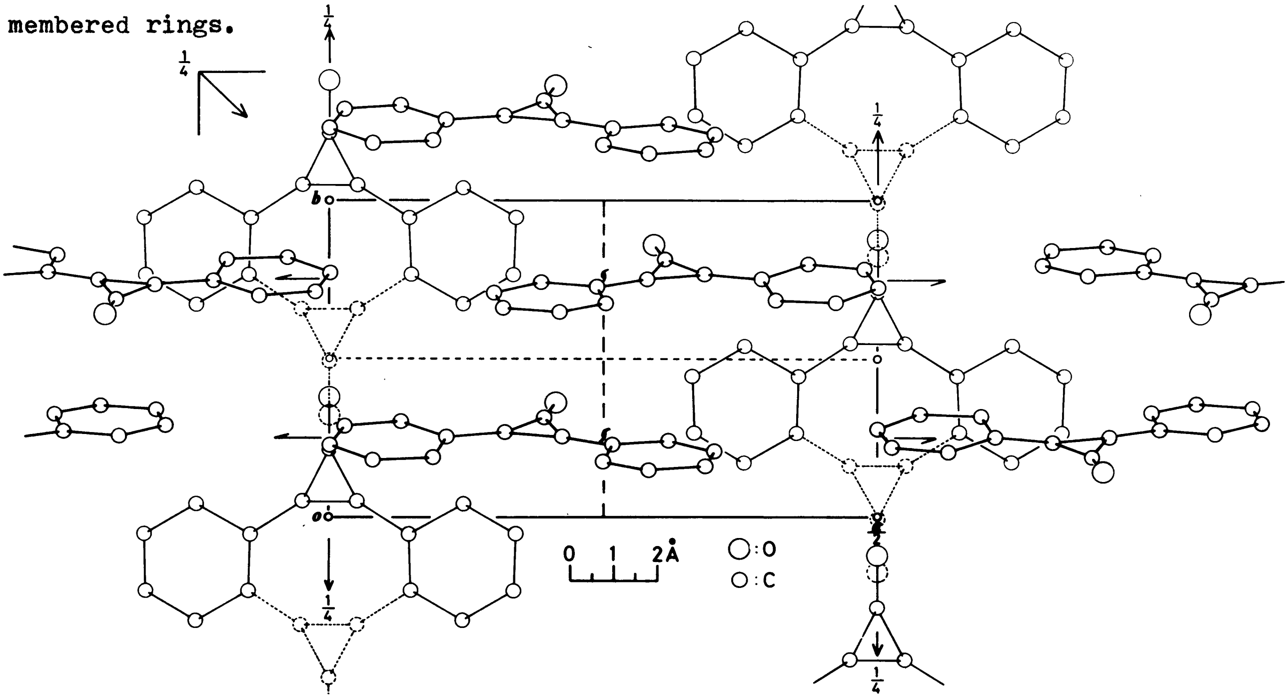


Fig. 1. Crystal structure viewed along the c axis. The molecules related by the screw diad along the c axis are omitted for clarity.

Although some parameters of the molecule(B) cannot be properly refined due to heavy overlapping with the disordered atoms, the reliable molecular geometry could be deduced from the molecule(A) as shown in Fig. 2. The molecule is almost planar as that in its monohydrate crystal.1) The torsion angles about the inter-ring bonds between the three-membered ring and the phenyl group are 2.1° and 2.3°.

The molecular geometries of (I) in anhydrous and hydrated states5) are compared in Fig. 3. It is clearly shown that the distances of C-O and C-C bonds in the three-membered ring systematically vary with the number of the hydrogen bonds involving the oxygen atom. That is, the C=O and C=C double-bond lengths progressively become longer and the C-C single bond becomes shorter according as the increasing number of hydrogen bond, zero for anhydrous state, one for molecule 1, and two for molecule 2 in the monohydrate. This is best understood if one assumes that the contribution from (Ia) is enhanced by the hydrogen bonding.

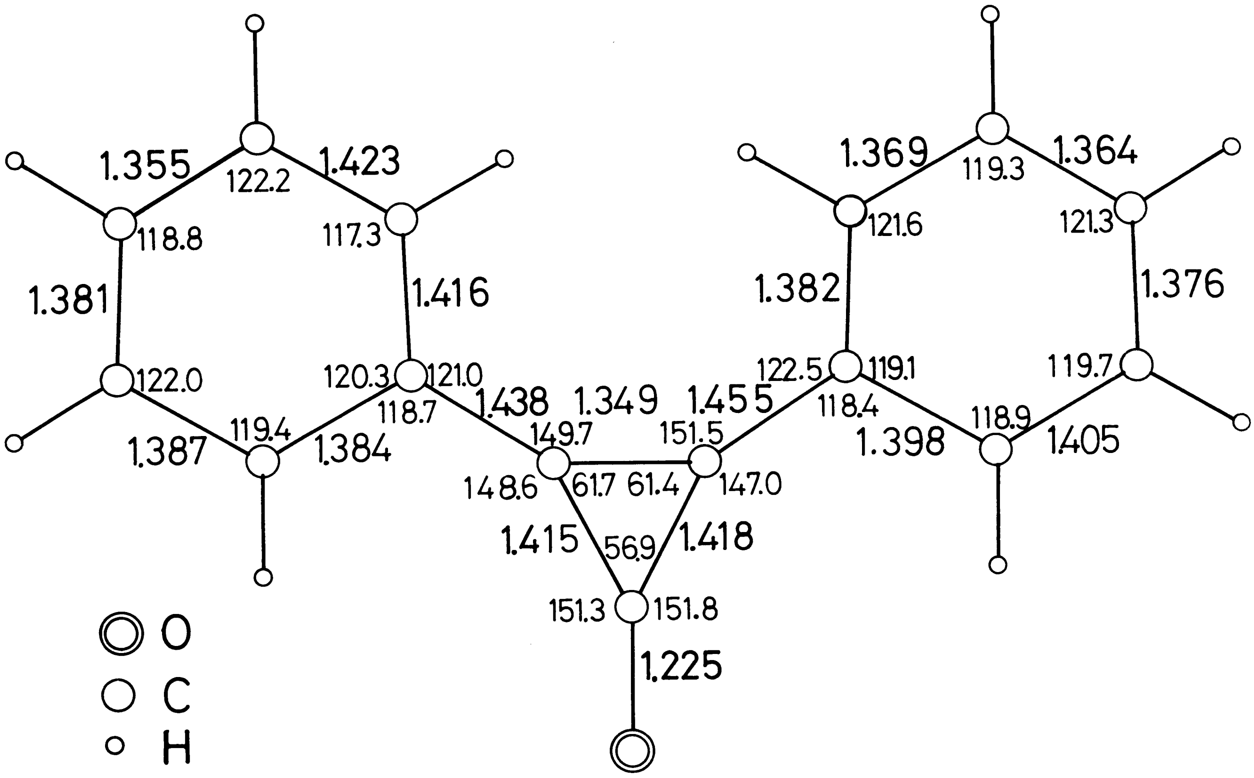
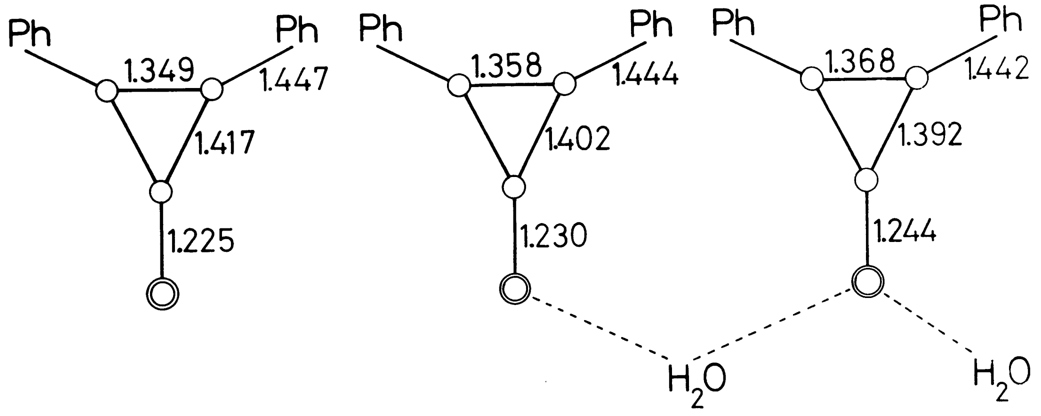


Fig. 2. Bond distances (Å) and angles (°) of the molecule(A). The e.s.d.'s are 0.006 - 0.014 Å and 0.4 - 0.9°.



(a) (b) (c)

Fig. 3. Comparison of bond lengths (Å). (a) Present study. (b) Molecule 1 in the monohydrate. (c) Molecule 2 in the monohydrate. Values for chemically equivalent bonds are averaged.

The C=O bond length in the present crystal is considerably longer than that in cyclopropanone (1.191 Å).(6) and the difference between the longer and shorter C-C bonds in the three-membered ring is smaller than those in quinones(7-8) and tropones.(9-14) From these structural chemical points of view, (I) itself is regarded to have considerable contribution from the dipolar ionic form (Ia). Moreover, it is suggested that the contribution is sensitively enhanced by the weak intermolecular interaction such as hydrogen bond. Thus, the studies of the two different crystal structures may provide an insight into the variety of the chemical properties of this conjugated system which behaves as an aromatic compound in a protic solvent(15) and shows some olefinic character in an aprotic environment.(16)

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References

1) H. Tsukada, H. Shimanouchi, and Y. Sasada, Tetrahedron Lett., 1973, 2455.
2) H. L. Ammon, J. Amer. Chem. Soc., 95, 7093 (1973).
3) T. Izumi, Japan. J. Appl. Phys., 1971, 1724.
4) J. Karle, and I. L. Karle, Acta Crystallogr., 21, 849 (1966).
5) The values for the monohydrate are based on the further refined structure.
6) J. M. Pochan, J. E. Baldwin, and W. H. Flygare, J. Amer. Chem. Soc., 91, 1896 (1969).
7) J. Trotter, Acta Crystallogr., 13, 86 (1960).
8) A. L. Macdonald, and J. Trotter, J. Chem. Soc. Perkin II, 1973, 476.
9) H. Shimanouchi, T. Ashida, Y. Sasada, M. Kakudo, I. Murata, and Y. Kitahara, Bull. Chem. Soc. Japan, 40, 779 (1967).
10) T. Hata, H. Shimanouchi, and Y. Sasada, Tetrahedron Lett., 1969, 753.
11) D. W. J. Cruickshank, G. Filippini, and O. S. Mills, Chem. Commun., 1972, 101.
12) K. Ibata, T. Hata, H. Shimanouchi, and Y. Sasada, Chem. Commun., 1972, 339.
13) M. J. Barrow, O. S. Mills, and G. Filippini, Chem. Commun., 1973, 66.
14) K. Ibata, H. Shimanouchi, and Y. Sasada, Chem. Lett., 1973, 269.
15) I. Agranat, and M. R. Pick, Tetrahedron Lett., 1972, 3111.
16) J. Ciabattoni, and G. A. Berchtold, J. Org. Chem., 31, 1336 (1969).

* Reed has also analysed the same hydrate crystal independently. (Private communication)

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