The structure of benzoyldimedone from X-ray diffraction analysis

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The structure of benzoyldimedone was established by X-ray diffraction analysis. The only tautomer was found. In this tautomer, the enol proton is covalently bound to the oxygen atom that is remote from the phenyl group. The role of steric and electronic factors in stabilization of the enol structure is analyzed. The geometric characteristics of the ring formed through an intramolecular hydrogen bond are discussed.

Key words: X-ray diffraction analysis, tautomerism, intramolecular hydrogen bond, β-diketones, β-triketones, conjugation, 2-benzoyl-5,5-dimethylcyclohexane-1,3-dione.

β-Diketones and β-triketones attract attention of researchers[1,2] because of their use in synthetic practice, including the synthesis of biologically active compounds, and the presence of the keto-enol and enol-enol tautomerism. Besides, the enol tautomers of these compounds were found to have a strong intramolecular hydrogen bond. The tautomeric properties and the presence of the H bond are responsible for the high lability of the structures and high reactivities of these compounds both when substituents are introduced and when the temperature and the solvent are varied. The regularities of the influence of these factors on the enol tautomers and their structures remain in many respects unclear.

NMR spectral studies demonstrated[3] that in the case of acetyldimedone, unlike acetylacetone,[2] the replacement of the methyl group by the phenyl fragment leads to a shift of the enol-enol tautomeric equilibrium toward the tautomer containing the enol proton at the O atom that is remote from the phenyl group. Previously,[4] based on the data of low-temperature neutron diffraction study,[5] it has been concluded that there is only one potential well for the H bond in the benzoylacetone molecule. This conclusion is inconsistent with abundant data on the structures of β-diketones[2] and is, apparently, somewhat untimely. The structures of β-diketones have been studied in detail by X-ray and neutron diffraction analysis.[6—13] The structures of β-triketones have been studied only in two works.[14,15] In this work, the structure of the benzoyldimedone molecule was studied by X-ray diffraction analysis.

Experimental

Single crystals of 2-benzoyl-5,5-dimethylcyclohexane-1,3-dione were prepared by slow evaporation from a 1 : 1 ether—hexane mixture with cooling to ~10 °C. A crystal of dimensions 0.8×0.6×0.36 mm was chosen for X-ray diffraction study. The three-dimensional X-ray diffraction data set was collected on an automated four-circle Nicolet R3m diffractometer (Mo-Kα radiation, graphite monochromator, θ/2θ scan technique, $2\theta_{max} = 60°$). A total of 2193 reflections were measured, of which 1975 reflections were independent ($R_{int} = 0.0150$). The crystals are monoclinic; space group $P2_1/n$. The unit cell parameters are as follows: $a = 7.225(3)$ Å; $b = 15.187(4)$ Å; $c = 12.005(3)$ Å; $\beta = 102.72(3)°$; $V = 1284.9(7)$ Å^3; $Z = 4$; $d_{calc} = 1.263$ g cm^{-3}; $\mu = 0.87$ cm^{-1}. The structure was solved by the direct method. The positions of the H atoms were located from the difference Fourier synthesis. The structure was refined by the full-matrix least-squares method with anisoptropic thermal parameters for nonhydrogen atoms and isotropic thermal parameters for H atoms. The final values of the R factors were as follows: $R_1 = 0.0367$, $wR_2 = 0.1029$ ($I > 2\sigma(I)$); $R_1 = 0.0370$, $wR_2 = 0.1032$ (based on all data). All calculations were carried out using the SHELX-97 program package.[16—18] The atomic coordinates, bond lengths, and bond angles of the β-triketone were deposited with the Cambridge Structural Database.

Results and Discussion

Analysis of the structural data demonstrated that benzoyldimedone in the crystal exists only as the *cis*-enol tautomer with an intramolecular hydrogen bond. The keto group is in the α position with respect to the phenyl ring (Fig. 1). The principal geometric parameters are given in Table 1. The phenyl ring in the molecule is planar (the average deviation of the atoms from the mean plane is 0.008 Å). The conformation of the cyclohexene ring is determined by the presence of the conjugated double bonds C(3)=C(2)—C(1)=O(1). As a consequence, five carbon atoms, *viz.*, C(1), C(2), C(3), C(4), and C(6), are in a single plane (the average deviation of the atoms from the mean plane is 0.046 Å), but the C(5) atom deviates from this plane. The angle between this plane and the plane through the C(4),

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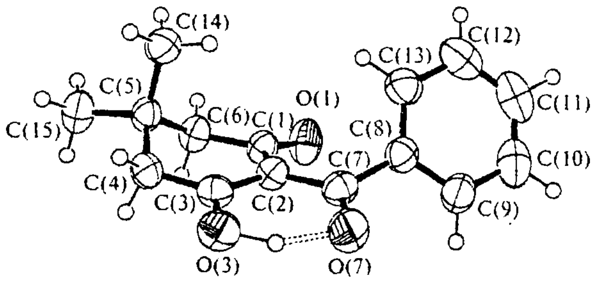

Fig. 1. Molecular structure of benzoyldimedone based on X-ray diffraction data.

Table 1. Bond lengths in the benzoyldimedone molecule

Bond	d/Å	Bond	d/Å
C(1)—O(1)	1.219(2)	C(3)—C(4)	1.485(2)
C(1)—C(2)	1.469(2)	C(4)—C(5)	1.526(2)
C(1)—C(6)	1.509(2)	C(5)—C(6)	1.529(2)
C(2)—C(3)	1.389(2)	C(7)—O(7)	1.260(2)
C(2)—C(7)	1.447(2)	C(7)—C(8)	1.486(2)
C(3)—O(3)	1.311(2)		

C(5), and C(6) atoms is 46.7°. The central ring in the molecule (see Fig. 1) is formed through the strong O(3)—H(3O)...O(7) intramolecular hydrogen bond (O(3)...O(7) = 2.468(2) Å, O(3)—H(3O) = 1.10(3) Å, O(7)...H(3O) = 1.44(3) Å, and O(3)-H(3O)...O(7) = 153(2)°). This ring is also planar; the average deviation of the C(3), O(3), C(2), C(7), and O(7) atoms from the mean plane is 0.045 Å; the dihedral angles between the mean plane of this ring and the mean planes of the phenyl and the cyclohexene rings are 46.50(6)° and 10.6(1)°, respectively.

The O(3)...O(7) distance (2.468(2) Å) is very short; however, it falls in the range of distances typical of acyclic β-diketones.[6–12,19] The C(7)—O(7) (the "bound" carbonyl group) distance (1.260(2) Å) is somewhat longer than the corresponding distances found in most of the known β-diketones. The C(3)—O(3) bond length (1.311(2) Å) is typical of benzoylmethanes,[19] but it is shorter than those in acetylacetone (1.331 Å)[6] and malonic dialdehyde (1.320 Å).[11] The C(2)—C(3) bond length (1.389(2) Å) is among the largest values known for β-diketones whose structures have been studied.[6–13,19] The C(2)—C(7) distance (1.447(2) Å) is substantially longer than those in diarylmethanes, benzoylacetone, and acetylacetone and is close to the value found in malonic dialdehyde.[6–12,19] This distance virtually coincides with the average distance for the model structures (1.454 Å),[20] in which the bridging H atom is replaced by the alkyl group, and is more typical of the structures without an intramolecular hydrogen bond.

Therefore, a very contradictory situation is observed for the conjugated system of the benzoyldimedone pseudocycle. On the one hand, the C(3)—O(3) and C(2)—C(3) distances are short and typical of the conjugation that is close to the maximum observed value. On the other hand, the C(2)—C(7) distance is noticeably longer than that expected based on the observed short O(3)...O(7) distance (2.468(2) Å).[19]

Theoretically, this peculiarity can be explained by at least three reasons. The first two reasons reside in the electronic effects of the "free" C(1)=O(1) carbonyl group and the phenyl ring. These effects should distort the conjugation according to a scheme common to β-diketones. The "free" group and the "bound" carbonyl group compete for the electrons of the π system of the C(2)=C(3) double bond. Meanwhile, the phenyl ring provides electrons of its π system. The third reason consists in spatial interactions between the phenyl ring and the "free" carbonyl group. All effects act in the same direction. However, the mesomeric effect of the phenyl ring is, apparently, of least importance because the dihedral angle between the planes of the phenyl ring and the ring with the participation of the hydrogen bond reaches almost 50°. Besides, this interaction should lead to the shortening of the C(7)—C(8) distance, but the spatial interactions between the "free" carbonyl group and the phenyl ring hinder this shortening.

The spatial interactions between the phenyl ring and the "free" carbonyl group not only lead to the elongation of the C(2)—C(7) bond but also are responsible for the shift of the tautomeric equilibrium in solution (compared to acetyldimedone) to the enol with the endocyclic double bond.[3,21]

Thus, for comparison, the length of the C(2)—C(7) bond in the alternative tautomer should be close to that of the double bond and be approximately equal to the C(2)—C(3) bond length in the enol (*i.e.*, this distance should be equal to ~1.39 Å instead of 1.45 Å). However, this short bond would induce large hindrances to the location of the phenyl group (according to Taft, its steric constant is −0.90, which is smaller only than that for the *tert*-butyl group[22]). Therefore, the enol in the crystalline state possesses a large space for location of bulky substituents due to the longer C(2)—C(7) bond. In solutions, this effect is observed when the methyl group is replaced by the phenyl ring, thus enhancing stabilization of the enol containing the "bound" carbonyl group at the α position with respect to the phenol ring.

A comparison of the structures of benzoyldimedone and the triketone containing the five-membered ring, *viz.*, acetylindanedione, which has been studied in detail by X-ray diffraction analysis,[15] demonstrated that these compounds differ mainly in the direction of enolization. It was found that acetylindanedione in the crystalline state exists as the enol tautomer containing an intramolecular hydrogen bond and an exocyclic double bond. The O...O distance is 0.18 Å shorter, which is reflected in the degree of equalization of the bonds of the ring with the participation of the intramolecular hydrogen bond. In particular, the O—H distance in benzoyldimedone is longer than that in acetylindanedione and, correspondingly, the O...H distance is shorter. The interatomic distances for the "free" carbonyl group and for the single bond that links this group with the remaining conjugated system coincide to within the experimental error (C(1)=O(1) are 1.219(2) and 1.220(2) Å and C(1)—C(2) are 1.469(2) and 1.473(2) Å in benzoyldimedone and acetylindanedione, respectively).

Shigorin suggested[2] that the hydrogen bond is strengthened in molecules in which this bond is "involved" in the system of the conjugated bonds O=C—C=C—O. Later on, this phenomenon was studied by IR spectroscopy, in particular, in the work devoted to β-diketones.[23]

These concepts were evolved[13,19] based on the data of X-ray diffraction studies and analysis of the published data, and the phenomenon under consideration was called a resonance-assisted hydrogen bond (RAHB).

We calculated the Q parameters for benzoyldimedone and acetylindanedione. According to the results of the previous studies,[13,19] this parameter characterizes the symmetry of π delocalization in the O=C—C=C—O fragment in systems with RAHB. Our calculations demonstrated that the data for acetylindanedione exactly fit the linear dependence of the Q parameter on the O...O distance, which has been found previously for dibenzoylmethanes.[19] However, the Q value for benzoyldimedone is noticeably larger than that expected based on this dependence. Apparently, this is a consequence of the above-mentioned anomalously long C(2)—C(7) distance.

Thus, the formation of short O...O distances in combination with a significant distortion of conjugation in the O=C—C=C—O system, which is typical of β-diketones, is possible for β-triketones. These instance is difficult to explain only by the presence of the additional "free" carbonyl group.

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