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Molecular Crystal Structure of Acetylacetone at 210 and 110 K: Is the Crystal Disorder Static or Dynamic?

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The molecular and crystal structure of acetylacetone (AA) was studied at 210 and 110 K in order to reveal the nature of the hydrogen bond and possible crystal disorder. The single crystal was grown by an in situ crystallization from the melt using an IR laser beam producing a molten zone in a Lindeman capillary. At both temperatures the crystals are orthorhombic (space group *Pnma*, $Z = 4$) with molecules having a crystallographic mirror plane perpendicular to the mean molecular plane. The intramolecular hydrogen bond is characterized by the O···O distances 2.541(2) and 2.547(1) Å at 210 and 110 K, with the central hydrogen atom equally distributed over the two positions near the oxygens. So, the hydrogen bond in AA has two distinct potential minima that are in agreement with previous NMR data and recent quantum-chemical calculations. The bond lengths C−O and C−C in the *cis*-enol fragment have averaged values (1.291(1) and 1.402(1) Å at 110 K) corresponding to the superposition of two enol isomers due to the crystallographic symmetry. The nature of the crystal disorder (static or dynamic) is discussed using analysis of the atomic anisotropic displacement parameters. Charge density analysis in AA has been performed using the high-order X-ray diffraction data at 110 K and a multipole model.

Introduction

β-Diketones belong to the well-known class of tautomeric compounds that are widely used in organic and inorganic chemistry. Over the years, the keto−enol tautomeric equilibrium, the structure of both keto and enol forms, and the nature of the strong intramolecular O−H···O hydrogen bond in the enol form of *β*-diketones were subject of intensive studies using a large variety of different methods, including IR, Raman, microwave, and NMR spectroscopies, X-ray and neutron diffraction measurements, quantum-chemical calculations, and some other techniques.[1,2] In recent years, interest in these systems has been renewed due to the development of new NMR spectroscopy methods for the study of solid samples,[3] new opportunities of the high-resolution, low-temperature X-ray and neutron diffraction analysis,[4] and essential progress in ab initio quantum-chemical calculations of the relatively large molecular systems.

An increased interest in compounds with the short (strong) hydrogen bonds including *cis*-enol forms of *β*-diketones is related to the study of transfer of a proton from one oxygen atom to another along the hydrogen bond—one of the most important and general reactions in chemistry. Proton transfer plays a crucial role in many processes such as acid−base neutralization reactions, electrophilic addition, and many others.[5] It has also a great importance in catalysis and several biochemi-

cal processes, ranging from enzymatic reactions to tautomeric interconversion in DNA bases.[6] It was established by numerous studies that in most cases the proton transfer usually takes place via relatively short hydrogen bonds at the distances $d(O···O) \leq 2.55-2.60$ Å, and nowadays namely these bonds became a subject of very intensive theoretical and experimental investigations,[7−10] so in a number of very recent publications they even have received the special name "low barrier hydrogen bonds" (LBHB).[11]

A detailed review of the relevant spectroscopic and structural data on proton transfer and hydrogen bonding in *cis*-enol forms of *β*-diketones was given by Emsley.[1] It was shown that these enols are stabilized by intramolecular OHO hydrogen bonds which often were considered as being centered and somehow incorporated into delocalized "aromatic" *π*-electron systems. Further studies have demonstrated that despite their large strength, hydrogen bonds in *cis*-enols are neither centered nor involved directly in the ring's aromatic stabilization although they are certainly coupled to it. (Nowadays, however, this concept has again received additional attention; see below.) For most structural studies of *cis*-enols the O···O distances were found to be in the rather narrow interval 2.55−2.45 Å with the position of central hydrogen atom near one of the two oxygens. This result indicated that enol tautomers have double-minimum potential, but the barrier between minima might be relatively small. In accord with Emsley's classification based not only on the available X-ray or neutron diffraction data but on the IR and NMR measurements as well, the given interval 2.55−2.45

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Å corresponds to the changeover from the weak or normal hydrogen bonds (double minimum, high barrier) to the very strong ones (wide single minimum potential or very small barrier that is below the ground state of the central H, D atoms; namely, these bonds have received the abbreviation LBHB.[11]) This structural feature of *cis*-enols makes the definition of the hydrogen bond type in these compounds rather uncertain.

More recently, an analysis of the molecular geometry in the six-member cyclic enol fragment (HOCR=CR−CR=O) for a large series of β-diketones using the structure-correlation method[12] and the Cambridge Database was made by Gilli et al.[13−15] It was shown that for cyclic *cis*-enols there is a correlation between the strength of the hydrogen bond estimated by both $d(O\cdots O)$ and $d(O-H)$ distances and the measure of electronic delocalization in the system of conjugated double bonds. This correlation was interpreted in terms of the "resonance-assisted hydrogen bond" concept (RAHB), which is essentially a synergistic reinforcement of hydrogen bonding and π-delocalization. The proposed model was found to be in good agreement with NMR and IR data and most recent ab initio calculations. The most important results of this investigation that are in line with Emsley's conclusions[1] are as follows: a very short and narrow interval of the $O\cdots O$ distances in *cis*-enols (2.43−2.55 Å); a strong electronic delocalization in the heteroconjugated fragment that was evidenced in the C−O and C−C bond lengths "intermediate" between typical values for the single and double bonds; a lowering of the $\nu(OH)$ frequencies (2566−2675 cm^{-1}) and downfield shift of the enolic proton resonance (15.3−17.0 ppm). It was noted also that the enolic proton has never been found exactly in the middle of the $O\cdots O$ distance even for the strongest hydrogen bonds, thus suggesting a double-well shape of the H-bond potential. Only in the very recent low-temperature (at 8 and 20 K using X-ray and neutron diffraction, respectively) study of benzoylacetone,[16] having one of the shortest intramolecular $O\cdots O$ distance 2.492(3) Å among all known *cis*-enols, was the hydrogen bond found to be almost centered. (H−O distances are equal to 1.33(1) and 1.25(1) Å with the very large vibration amplitude of the central H atom along the hydrogen bond equal to 0.34 Å.)

The RAHB concept has recently received an additional confirmation in the theoretical study of the enol form of acetylacetone (AA) using completely optimized calculations at the Hartree−Fock and second-order Møller−Plesset (MP2) levels with the basis sets up to D95++** and the semiempirical calculations AM1, PM3, and SAM.[17] It was established that intramolecular hydrogen bond stabilizes the *cis*-enol form by 12.5 kcal/mol, which is about 6−8 kcal/mol more than expected for a simple O−H···O interaction. Moreover, the enhanced stabilization was found to be larger than that for other resonance-stabilized H bonds, and this was attributed to the aromatic character of the 6π-electron system in AA.

Despite the large interest in structural studies of *cis*-enols, the crystal structures of the simplest representatives of this series such as malondialdehyde (MDA) and acetylacetone (AA) were not known until now, although their molecular structures were studied by microwave spectroscopy,[18,19] electron diffraction,[20−22] and some other techniques including as well modern quantum-chemical calculations.[17,23] MDA was shown to exist as planar *cis*-enol with $O\cdots O$ distance 2.553 Å and an asymmetric hydrogen bond corresponding to the double-well potential minimum[18,19] that was confirmed by an ab initio calculation.[23] The microwave spectrum of trideuterated MDA showed[19] a nontunneling molecule with C_s symmetry and $O\cdots O$ distance

of 2.574 Å; the C_s structure follows also from the X-ray photoelectron spectroscopy data.[24]

The molecular structure of AA has been somewhat controversial. On the basis of two separate electron diffraction studies, Karle et al.[21] determined the enol form of AA to be symmetrical with the very short $O\cdots O$ distance of 2.381 Å and the H bond in the plane of the ring. On the contrary, Shibata[22] reported an unsymmetric enol structure with a longer $O\cdots O$ distance of 2.512 Å and the H position significantly out of the molecular plane. The difference between these two reports may be related to Shibata's assumption that his AA sample was 100% enol (at 21 °C), while Karle's gas-phase electron diffraction study was performed at 100−110 °C and it was assumed that enol containment was only 66 ± 5%. Photoelectron spectroscopy of AA does not give a clear answer about the symmetry of the hydrogen bond in a free state because of an overlap of one of the peaks with the signal of keto form.[25] The only known X-ray structure with the AA molecule in a crystal was reported for its cocrystal with an organic drug complex where AA was included as a solvent.[26] The H bond was found to be asymmetric ($O\cdots O$ distance 2.535 Å, O−H 1.03 Å, and H···O 1.46 Å, the hydrogen atom being 0.36 Å above the molecular plane), and in the enol fragment a significant difference was found between the formal single and double C−C and C−O bonds (1.412, 1.338 Å and 1.331, 1.238 Å, respectively). It was noted that in this particular case the asymmetry of the hydrogen bond in AA may be induced by the asymmetry of crystal environment, but the nonplanarity of the six-member H-bonded cycle seems to be rather strange.

Taking into account the absence of accurate diffraction data for AA in the solid state and some controversial conclusions about its molecular structure, in the present work we have performed low-temperature single-crystal X-ray diffraction analysis of acetylacetone at 210 K and high-resolution study of the same crystal at 110 K. We expected that a multitemperature experiment will allow to reveal the nature of the intramolecular hydrogen bond in this compound in the solid state. The data at 110 K were used for an electron density distribution analysis in AA using the multipole model.

Experimental Section and Structure Refinement

At room temperature acetylacetone is a liquid with the melting point of ca. 250 K. The single crystal was grown from the melt by an in situ crystallization technique[27] using a miniature zone-melting method with an IR-laser beam producing a molten zone in a thin Lindeman glass capillary of diameter 0.3 mm.

X-ray diffraction data were collected with a "Siemens P4" diffractometer (graphite monochromator, Mo Kα radiation) first at the temperature 210 K and then at 110 K. The second data set was collected up to $2\theta \leq 90°$ for the half-sphere of reflections in order to obtain high-resolution data. The crystallographic data, experimental conditions, and results of the conventional refinements are presented in Table 1. All intensities were corrected for the cylindrical crystal shape and absorption. The structure was solved and refined with the direct methods and full-matrix least-squares procedure in the anisotropic−isotropic (for hydrogen atoms) approximation using the SHELX PLUS (version 4.05) program package. The extinction correction was found to be negligible.

The results of the structure solution and refinement have demonstrated that at both temperatures the AA molecules in the crystal occupy a special position (4c in the space group *Pnma*) with the crystallographic mirror plane passing through the C(3)−H(3) bond and perpendicular to the mean molecular
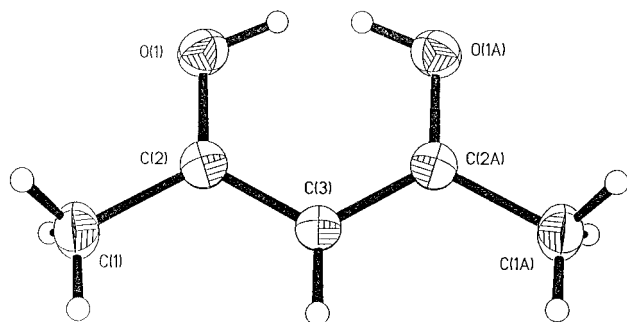
Figure 1. General view of the AA molecule in crystal at 110 K with the atom presentation as the thermal probability ellipsoids ($p = 50\%$) and atomic numbering scheme.

TABLE 1: Crystal Data and Experimental Conditions for Structure Refinement

	210 K	110 K
empirical formula	$C_5H_8O_2$	$C_5H_8O_2$
molecular weight, M	100.12	100.12
crystal system	orthorhombic	orthorohombic
space group	*Pnma*	*Pnma*
a, Å	8.463(3)	8.396(3)
b, Å	16.031(5)	15.984(5)
c, Å	4.146(1)	4.066(1)
V, Å³	562.4(8)	545.6(5)
Z	4	4
d_{calc} (g/cm³)	1.182	1.219
μ (mm⁻¹)	0.087	0.087
$F(000)$	216	216
2θ range (deg)	50	90
scan type	Wyckoff	Wyckoff
scan range in ω (deg)	1.80	1.80
no. of reflections collected	1923	5890
no. of unique reflections	515	2269
R_{merg}	0.108	0.048
no. of obs reflections ($F \geq 4.0\sigma$)	373	1089
no of parameters	53	53
reflns/params ratio	7.04	20.55
R	0.0645	0.0481
R_w	0.0791	0.0527
goodness of fit	1.026	1.478
weight scheme	$1/\sigma^2(F) + 0.003F^2$	$1/\sigma^2 + 0.0008F^2$
largest difference peak/hole, e/Å³	0.19/−0.21	0.43/−0.17

plane. Thus, the symmetry of the AA molecule in crystal is close but not exactly the *mm*2. This is quite usual situation for many organic molecules (for example, see ref 4) when in crystals they lose very often such symmetry elements as the *m*-plane and/or 2-fold axis.

The central hydrogen atom H(1) was found to be disordered over two equivalent positions near the oxygens at normal O−H distances of ca. 0.90 Å. Several different models and refinements were tested in order to reveal the nature of this disorder, and they will be discussed below in detail. A general view of AA in the crystal at 110 K with the non-hydrogen atom presentation as the thermal probability ellipsoids ($p = 50\%$) and atomic numbering scheme is presented in Figure 1; atomic coordinates and anisotropic (isotropic for hydrogen atoms) displacement parameters corresponding to the data at 210 and 110 K are given in Table 2.

To visualize the charge density distribution in AA, in the present work we have performed a multipole refinement of the X-ray data using a model of the rigid nonspherical pseudoatom by Hansen and Coppens[28] and the XD package program.[29] To

take into account the molecular and crystal symmetry, a local symmetry constraint ("3" for C(1), "*m*" for C(2), O(1), and "*mm*2" for C(3), H(3) atoms) and chemical constraints (H atoms of methyl group) were imposed on multipole coefficients. This reduced the number of refined multipole parameters with the multipole expansion up to the hexadecapole level ($l = 4$) for C, O atoms and dipole level ($l = 1$) for hydrogens. The multipole refinement converged to $R = 0.0372$, $R_w = 0.0482$, and GOF = 1.08, which was a significant improvement in comparison with the conventional one. Lowering of the local symmetry did not change results significantly.

Results and Discussion

Our data definitely show that acetylacetone in the crystal exists in the *cis*-enol form with the central hydrogen atom H(1) equally distributed over the two positions near the oxygens. So, the hydrogen bond in AA has two separated potential minima. The crystal symmetry of AA requires to assume that its X-ray structure is a superposition of two nondistinguishable *cis*-enol isomers, but the nature of crystal disorder (static or dynamic) is a question of further discussion.

Several different refinements were tested to reveal the hydrogen atom position and the nature of the hydrogen bond and disorder. First, we tried to refine the structure with the central position of the H(1) atom in the mirror plane, but the results of this refinement for both temperatures were not significant and resulted in the very large isotropic squared displacement amplitude for this atom (0.14 Å² at 100 K). This is not surprising however for systems with strong hydrogen bonds, but further anisotropic refinement of this atom (which was expected to provide an elongated thermal ellipsoid along the hydrogen bond) failed.

A refinement of the crystal structure in the acentric space group *Pna*2$_1$ (all atoms in general positions, standard space group setting was used with the corresponding unit cell axes interchange) resulted in a reasonable asymmetric molecular geometry, but subsequent difference Fourier synthesis revealed again two positions for hydrogens at normal distances of ca. 0.90 Å from both O atoms, and their refined occupancies were found to be equal. In addition, this refinement resulted in very strong correlations between the refined parameters, and the standard deviations in the molecular geometry were 3−4 times larger than for refinement in the space group *Pnma*.

Another possible opportunity for the crystal disorder in AA may be related to a crystal twinning which could arise either from nucleation or a phase transition between the melting point and 210 K. If the correct space group is acentric, the missing *m*-plane in the space group *Pnma* might be the twin operation, and this would result in small changes in intensities. However, our attempts to refine the "twinned" crystal structure with the SHELX-93 program package (using the TWIN option) did not improve the results in comparison with those in the acentric space group without twinning. So, all refinements indicate that most probably the true space group for AA crystal is *Pnma* with the disordered central hydrogen atom.

The proof for the noncentral position of H(1) atom followed from the "deformation" (difference) electron density map (Figure 2) where the electron density of this atom was not subtracted from the total density. Two distinct maxima corresponding to two "halves" of the H(1) atom were found in this map at expected distances from the oxygens. This map may be compared with a conventional "X−X" deformation electron density map presented in Figure 3. To construct this map, a quasi-high-order refinement has been performed using the

TABLE 2: Atomic Coordinates ($\times 10^4$ and $\times 10^3$ for Hydrogen Atoms), Their Equivalent Isotropic Displacement Parameters U_{iso} ($\times 10^3$ and $\times 10^2$ Å^2 for Hydrogens), and Anisotropic Displacement Parameters U_{ij} ($\times 10^4$ Å^2) for Non-Hydrogen Atoms

atom	X	Y	Z	U_{iso}
O(1)	4752(2)	6707(1)	−1723(4)	62(1)
	4706(1)	6703(1)	−1763(2)	30(1)
C(1)	6617(4)	593(1)	1290(8)	65(1)
	6599(1)	5920(1)	1313(3)	32(1)
C(2)	5947(3)	6739(1)	177(5)	50(1)
	5920(1)	6736(1)	181(2)	25(1)
C(3)	6582(4)	7500	1188(7)	50(1)
	6577(1)	7500	1202(3)	24(1)
H(1)	449(5)	724(3)	−232(15)	7(2)
	436(3)	721(2)	−233(9)	5(1)
H(1a)	748(4)	602(2)	273(9)	9(1)
	731(2)	598(1)	285(5)	6(1)
H(1b)	723(7)	568(4)	−45(19)	17(2)
	695(3)	564(1)	−55(7)	9(1)
H(1c)	586(5)	566(3)	241(13)	13(1)
	578(2)	564(1)	248(5)	6(1)
H(3)	742(4)	750	256(8)	4(1)
	739(3)	750	272(6)	4(1)

atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O(1)	625(14)	623(13)	618(14)	−57(7)	−59(9)	−63(7)
	283(3)	319(3)	305(3)	−34(2)	−32(2)	−25(2)
C(1)	750(19)	493(14)	721(17)	−7(9)	11(15)	12(10)
	370(4)	240(3)	357(5)	5(3)	−10(4)	11(3)
C(2)	517(15)	556(14)	425(15)	2(7)	85(9)	−10(8)
	244(3)	266(3)	227(3)	5(3)	40(2)	0(2)
C(3)	502(19)	502(17)	486(17)	0	−22(15)	0
	239(4)	241(3)	245(5)	0	−16(4)	0

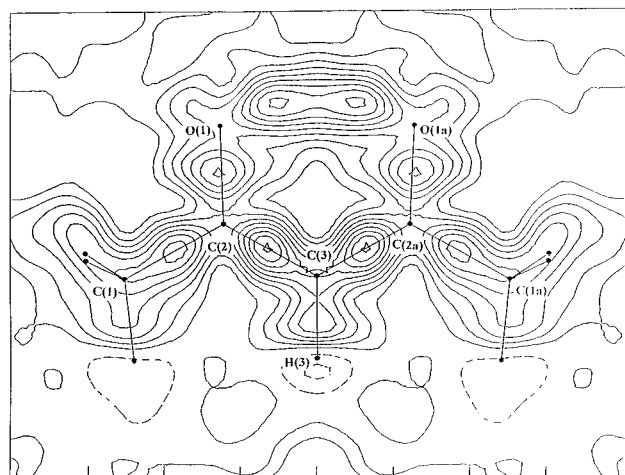*a* First line, data at 210 K; second line, data at 110 K.

Figure 2. "Difference" electron density map in the molecular plane of AA. Electron density of the central H(1) atom is not subtracted from the total density. Positive contours are given through 0.05 e/Å^3 and negative through 0.1 e/Å^3.
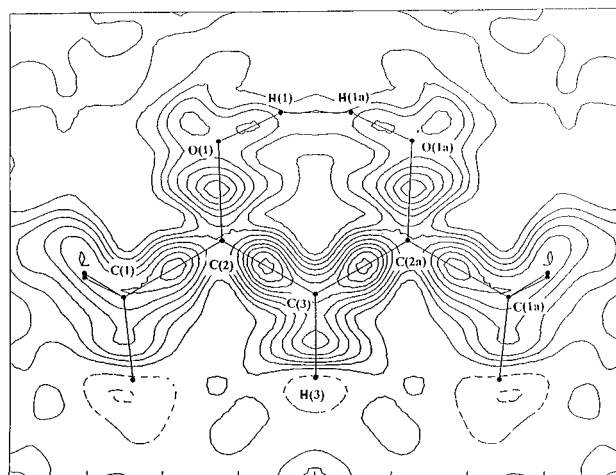

Figure 3. Convential "X−X" deformation electron density in the molecular plane of AA. Interval between isolines the same as in Figure 2.

Dunitz and Seiler weight scheme[30] with the coefficient B = 6.0. Both maps in Figures 2 and 3 contain distinct positive maxima at all chemical bonds, and in addition, the map in Figure 3 contains also the maxima at the position of oxygen lone pairs. An interesting feature of this map is the absence of significant positive DED in the middle of O···O distance (less than 0.05 e/Å^3), which might be an additional argument against the centered hydrogen bond in the crystal of acetylacetone.

The molecular geometry parameters of AA at 210 and 110 K are summarized in Table 3. There is no significant difference between the two data sets; therefore, in further discussion we will use only more accurate data at 110 K. Multipole refinement did not change the molecular geometry significantly. The bond lengths C(2)−O(1) and C(2)−C(3) in the enol fragment are equal to 1.291(1) and 1.402(1) Å, which are in excellent

agreement with the average values 1.289 and 1.399 Å for the "unperturbed" C−O, C=O (1.353(4) and 1.225(3) Å) and C−C, C=C (1.454(4) and 1.344(3) Å) distances in enols in accord with Gilly's analysis.[13]

The O···O distance in the AA crystal is equal to 2.547(1) Å, which is larger than earlier reported values in the gas phase[21,22] and the cocrystal of AA[26] (see above). In a very recent and most accurate ab initio calculation of AA by Dannenberg and Rios,[17] the O···O distance was found to be 2.549 Å for an asymmetric enol with C_s symmetry, which is in very good agreement with our data. It is interesting to note that, for the symmetric C_{2v} structure with the H atom equally bonded to each of the oxygens, the calculated O···O distance was 2.363 Å. This structure may be a ground or a transition state, and the energy

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TABLE 3: Molecular Geometry of Acetylacetone (Data Are Given for 210 and 110 K)[a]

	210 K	110 K
O(1)−C(2)	1.283(2)	1.291(1)
C(1)−C(2)	1.486(3)	1.497(1)
C(2)−C(3)	1.397(2)	1.402(1)
O(1)···O(1a)	2.541(2)	2.547(1)
O(1)−H(1)	0.91(5)	0.89(3)
H(1)···H(1a)	0.86(11)	0.94(5)
H(1)···O(1a)	1.74(5)	1.78(3)
C(1)−C(2)−C(3)	121.3(2)	121.2(1)
C(1)−C(2)−O(1)	117.2(2)	117.0(1)
O(1)−C(2)−C(3)	121.5(2)	121.8(1)
C(2)−C(3)−C(2a)	121.6(3)	121.0(1)
C(2)−O(1)−H(1)	110(3)	113(2)
O(1)−H(1)−O(1a)	147(5)	155(2)

[a] Bond lengths are in Å and bond angles in deg.

difference between C_s and C_{2v} structures was found to be only ≈1 kcal/mol.

In comparison with available structural data for *cis*-enols (see refs 1 and 13−16), the hydrogen bond in AA is one of the longest for this class of compounds, and therefore Emsley[1] has characterized it as the "case 2"—double minimum H bond with a rather small barrier for the hydrogen and larger barrier for the deuteron atom (or "medium" H bonds with the interval of O···O distances 2.70−2.55 Å). On further decreasing the O···O distances to 2.55−2.45 Å (case 3—"strong" hydrogen bonds in accord with this classification) it might happen that the hydrogen's movement is free of the barrier while that of the deuteron is still constrained to one well. This is probably the case of many other *cis*-enols. In both these cases, however, an upfield shift of the $\Delta\delta(^1H, {}^2H)$ values should be observed in NMR spectra on deuteration of the hydrogen bond because the deuteron remains in the shielded position while the hydrogen is free to move into the deshielded region of space between two oxygens. Experimental NMR data[31−33] for AA, benzoyl-acetone, and dibenzoylmethane show substantial upfield shifts of the $\Delta\delta(^1H, {}^2H)$ values and corresponding $\Delta\delta(^1H, {}^3H)$ values as well. At even shorter O···O distances (2.45−2.35 Å) corresponding to the "case 4" of hydrogen bonds,[1] both hydrogen and deuteron atoms are above the barrier, and their time-averaged positions coincide again. Nevertheless, on deuteration a downfield shift, i.e., negative $\Delta\delta(^1H, {}^2H)$ values, should be observed. For *cis*-enols, however, this effect has not been detected,[34] but similar hydrogen bonds probably exist in other systems such as $H_5O_2^+$, H(maleate), and dioxime−metal complexes.

It is known that an intramolecular hydrogen bond may be weakened by further intermolecular interactions between atoms of the hydrogen bridge with other neighboring atoms in the crystal. In the structure of AA, however, we did not find significantly shortened intermolecular contacts that may influence the O···O distance. Therefore, it is reasonable to assume that hydrogen-bond characteristics in this crystal should be probably close to those for this molecule in a free state. Nevertheless, one interesting feature of the crystal packing of AA should be noted, namely, intermolecular contacts between the H(3) atom, and O(1′) and H(1′) atoms [as well as O(1′a) and H(1′a) atoms because of crystal symmetry] of the neighboring molecule in the crystal (symmetry transformation between the nonprimed and primed atoms is $^1/_2 + x, y, ^1/_2 - z$). There are endless chains of similar contacts in the crystal structure along the *a*-axis. Although these distances should not be considered as significantly shortened ones [H(3)···O(1′) contact is equal to 2.84 Å, the H(3)···H(1′) 2.54 Å, and C(3)···O(1′)
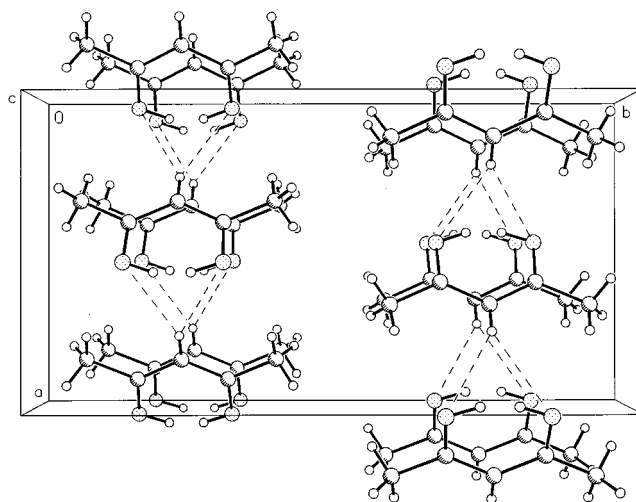

Figure 4. Crystal packing diagram of AA down the *c*-axis. Molecular chains and layers are shown; C−H···O interactions are indicated by dotted lines.

3.432 Å], they might be responsible for a possible intermolecular cooperative tautomeric process in the crystal of AA. The crystal packing diagram down the shortest *c*-axis is presented in Figure 4. Parallel chains of planar molecules form layers along the *c*-axis separated by the H···H contacts between the Me groups along the *b*-axis. This packing array may explain qualitatively an unusual anisotropic thermal expansion of the AA crystal. The ratio of expansivity of *a*:*b*:*c* = 2.7:1.0:6.6, so the least expandable crystal *b*-axis is related to direction of these H···H contacts; on the contrary, the most shrinkable on cooling (and shortest) crystal *c*-axis is almost perpendicular (76.6°) to the mean molecular plane.

The more disputable question in the present study is the nature of structure disorder in AA crystal—is it dynamic (fast exchange of central hydrogen between two oxygens) or static (high barrier prevents hydrogen jumps, and crystal structure represents random packing of the two fixed tautomers into equivalent positions in the crystal). The "averaged" and ordered structure may be also a true resonance hybrid with approximately centered enol hydrogen, but this is not the case for AA because of the rather large O···O distance in this compound. Probably the last situation is realized in the structure of benzoylacetone.[16]

Generally, in the case of asymmetric *cis*-enol molecules and/or occupying a general positions in a crystal, the kind of disorder may be resolved via multitemperature X-ray (or neutron) diffraction analyses. Chemical (asymmetric *cis*-enol molecule) or crystallographical (molecule occupies a general position in a crystal structure) nonequivalence of oxygen atoms will produce some asymmetry of the double-minima potential, and therefore lowering the temperature (in the case of dynamic disorder) will result in ordering the structure and changing of the molecular geometry, because the enol hydrogen will prefer the lower potential minimum. On the other hand, in the case of static disorder we should not expect significant changes in geometry and/or hydrogen occupancies. Both these cases may be distinguished by the Hirshfeld's "rigid bond" test.[35]

The case of disorder in acetylacetone, however, is a special one because the hydrogen bond in this crystal has a so-called "crystal-imposed" symmetry. Therefore, multitemperature diffraction data alone cannot distinguish between the static or dynamic disorder without breaking the crystal symmetry (as a result of possible phase transition on further cooling or applying a high pressure). To get conclusions about nature of disorder in AA, it is necessary to use additional information.
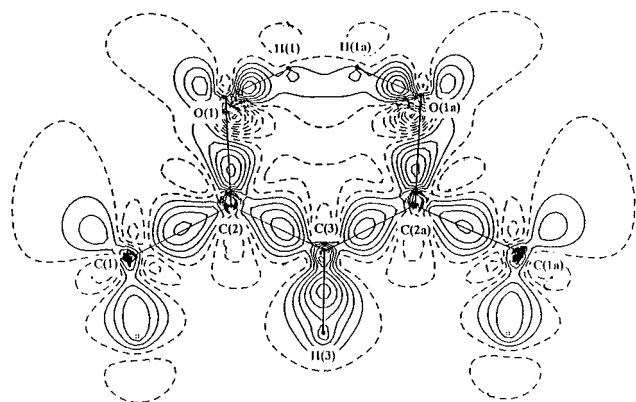
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Figure 5. Static multipole deformation electron density in the molecular plane of AA. Interval between isolines 0.1 e/Å³.

Because disorder in AA is related to the crystal-imposed symmetry, it is clear that at both temperatures Hirshfeld's "rigid-bond" analysis will result in rather large values of Δ_{AB}, representing differences between the mean-square displacement amplitudes of C, O atoms along the C–O and C–C vectors in the enol fragment. Assuming in accord with Gilli[13] (see above) that the difference between the C–O and C=O bond lengths in the "nonperturbed" enol fragment is equal to $1.353 - 1.225 = 0.128$ Å, the estimated value for the corresponding $\Delta_{C,O}$ difference might be as large as 0.0041 Å² (respectively, estimated $\Delta_{C,C}$ value is 0.0030 Å²; see refs 12 and 36 for details). So, the contribution of a fast tautomerism or static disorder must result in significant "nonrigidity" of the bonds in enols (note for comparison that the "rigid" bond in the absence of disorder is usually characterized by a value of $\Delta \leq 0.0010$ Å²). Calculation of Δ values using conventional refinement of data at 210 and 110 K as well as high-order and multipole refinements of the low-temperature data at 110 K confirmed our expectations. Thus, at 210 K the values of Δ for bonds O(1)–C(2), C(2)–C(3), and C(1)–C(2) were found to be rather large (0.0016, 0.0056, and 0.0014 Å²), which is quite clearly an indication of their nonrigidity. We should note, however, that for this data set an estimated standard deviation $\sigma(\Delta)$ is also large (0.0027 Å²). At 110 K different refinements resulted in the Δ values in the intervals 0.0017–0.0026 Å² for C(1)–O(2), 0.0027–0.0035 Å² for C(2)–C(3), and 0.0005–0.0008 Å² for C(1)–C(2) bonds with the $\sigma(\Delta) = 0.0011$ Å². This result also proves the nonrigidity of bonds in the enol fragment of AA and crystal disorder. It is interesting that the Δ value for the C(1)–C(2) bond is the smallest in comparison with other bonds in the enol fragment (this bond is rigid), and namely this single bond does not participate in the tautomeric process.

A map of the static multipole deformation electron density in the molecular plane of AA is presented in Figure 5. The main features of this map are very similar to those in Figures 2 and 3, but peak heights in the static map are larger. Topological analysis of the experimental multipole electron density distribution in AA using Bader's "atoms in molecules" approach[37] revealed bond (3,−1) critical points in all chemical bonds with the expected values of bond ellipticities 0.14 and 0.48 for the partially multiple C(2)–O(1) and C(2)–C(3) bonds. An interpretation of these data is rather difficult, however, taking into account the structure disorder.

Concluding Remarks

The results of the present X-ray diffraction analysis of the molecular and the crystal structure of acetylacetone (AA) clearly

demonstrated that the intramolecular hydrogen bond in this simplest *cis*-enol molecule is characterized by the two distinct potential minima with the central hydrogen atom equally distributed over two positions near the oxygens. The O···O distance in AA equal to 2.547(1) Å is one of the longest in a series of known *cis*-enols and is in accord with Emsley's classification for such a bond that corresponds to the changeover from the normal hydrogen bonds (double minimum, high barrier) to the very strong ones ("low barrier hydrogen bonds"). The molecular and crystal-imposed symmetry of AA requires to assume a crystal disorder, so its X-ray structure must be a superposition of the two *cis*-enol isomers. For a symmetric molecule having an asymmetric intramolecular hydrogen bond, similar crystal disorder is probably quite expected because of the negligible effect on the lattice enthalpy (two isomers are strictly similar) and of the small gain of the lattice entropy (R ln 2) or of free energy (RT ln $2 = 0.41$ kcal/mol at 289 K).

In the special case of the molecular and crystal symmetry of AA a multitemperature analysis of the anisotropic displacement parameters ("rigid-bond" test) cannot distinguish between the static or dynamic disorder. We may suggest, however, that disorder in the AA crystal probably may have dynamic nature (fast tautomerism). The next two arguments are in line with this suggestion. In particular, detailed theoretical calculation of AA by Dannenberg and Rios[17] resulted in the very small barrier of the H atom transfer of only 2.5 kcal/mol, which should be below the ground vibrational state of the central H atom. In addition, very recent calculations of the potential function and reaction rate for a proton transfer in AA using both classical and quantum-mechanics computer simulations[38,39] confirmed the low values of the barrier and a rather high rate constant, especially at low temperatures. Further diffraction studies of this compound at lower temperatures (<100 K) and/or high pressures might be interesting because of possible phase transition in the AA crystal and breaking molecular crystallographic symmetry that will allow to obtain more definite information about the crystal disorder and the nature of hydrogen bond in this important compound.

References and Notes

(1) Emsley, J. *Struct. Bonding* **1984**, *57*, 147−191.

(2) *The Chemistry of Enols*; Rappoport, Z., Ed.; John and Wiley Sons: New York, 1990.

(3) Vila, A. J.; Lagier, C. M.; Olivieri, A. C. *J. Chem. Soc., Perkin Trans. 2* **1990**, 1615.

(4) *Accurate Molecular Structures. Their Determination and Importance;* Domenicano, A., Hargittai, I., Eds.; IUCr Monographs on Crystallography; Oxford University Press: New York, 1992.

(5) Robinson, G. V.; Thislethwaite, P. J.; Lee, J. *J. Phys. Chem.* **1986**, *90*, 4224.

(6) Jeffrey, G. A.; Saenger, W. *Hydrogen Bonding in Biological Structures*; Springer: Berlin, 1991.

(7) Tuckerman, M. E.; Marx, D.; Klein, M. L.; Parrinello, M. *Science* **1997**, *275*, 817−820.

(8) Pan, Y.; McAllister, M. A. *J. Am. Chem. Soc.* **1997**, *119*, 7561−7566.

(9) Garcia-Viloca, M.; Gonzalez-Lafont, A.; Lluch, J. M. *J. Am. Chem. Soc.* **1997**, *119*, 1081−1086.

(10) Platts, J. A.; Laidig, K. E. *J. Phys. Chem.* **1996**, *100*, 13455−13461.

(11) Cleland, W. W. *Biochemistry* **1992**, *31*, 317.

(12) Stebler, M.; Buergi, H.-B. *J. Am. Chem. Soc.* **1987**, *109*, 1395.

(13) Gilli, G.; Bellucci, F.; Ferretti, V.; Bertolasi, V. *J. Am. Chem. Soc.* **1989**, *111*, 1023−1028.

(14) Bertolasi, V.; Gilli, P.; Ferretti, V.; Gilli, G. *J. Am. Chem. Soc.* **1991**, *113*, 4917−4925.

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(15) Gilli, P.; Bertolasi, V.; Ferretti, V.; Gilli, G. *J. Am. Chem. Soc.* **1994**, *116*, 909−915.

(16) (a) Madsen, G. K. H.; Iversen, B. B.; Larsen, F. K.; Kapon, M.; Reisner, G. M.; Herbstein, F. H. *J. Am. Chem. Soc.*, in press. (b) Herbstein, F. H.; Iverson, B. B.; Kapon, M.; Larsen, F. K.; Madsen, G. K. H.; Reisner, G. M. Manuscript in preparation.

(17) Dannenberg, J. J.; Rios, R. *J. Phys. Chem.* **1994**, *98*, 6714−6718.

(18) Rowe, W. F., Jr.; Duerst, R. W.; Wilson, E. B. *J. Am. Chem. Soc.* **1976**, *98*, 4021.

(19) Baughaun, S. L.; Duerst, R. W.; Rowe, W. F.; Smith, I.; Wilson, E. B. *J. Am. Chem. Soc.* **1981**, *103*, 6296.

(20) Andreassen, A. L.; Bauer, S. H. *J. Mol. Struct.* **1972**, *12*, 381.

(21) Lowry, A. H.; D'Antonio, C. G. P.; Karle, J. *J. Am. Chem. Soc.* **1971**, *93*, 6399.

(22) Iijima, K.; Ohnogi, A.; Shibata, S. *J. Mol. Struct.* **1987**, *156*, 111−118.

(23) Barone, V.; Adamo, C. *J. Chem. Phys.* **1996**, *105*, 11007−11019.

(24) Brown, R. S. *J. Am. Chem. Soc.* **1977**, *99*, 5497.

(25) Brown, R. S.; Tse, A.; Nakashima, T.; Haddon, R. C. *J. Am. Chem. Soc.* **1979**, *101*, 3157.

(26) Camerman, A.; Mastopaolo, D.; Camerman, N. *J. Am. Chem. Soc.* **1983**, *105*, 1584−1586.

(27) Boese, R.; Nussbaumer, M. In *Correlations, Transformations, and Interactions in Organic Crystal Chemistry*, *IUCr Crystallographic Symposia*; Jones, D. W., Katrusiak, A., Eds.; Oxford University Press: Oxford, U.K., 1994; Vol. 7, p 20.

(28) Hansen, N. K.; Coppens, P. *Acta Crystallogr., Ser. A* **1978**, *34*, 909−921.

(29) Koritzanszky, T.; Howard, S.; Mallinson, P. R.; Su, Z.; Richter, T.; Hansen, N. K. *XD−A Computer Program Package for Multipole Refinement and Analysis of Electron Densities from Diffraction Data*, Version 1997.

(30) Dunitz, J. D.; Seiler, P. *Acta Crystallogr., Ser. B* **1973**, *29*, 589.

(31) Chan, S.; Lin, L.; Clutter, D.; Dea, P. *Proc. Natl. Acad. Sci. U.S.A.* **1970**, *65*, 816.

(32) Shapet'ko, N. N.; Bogachev, Yu. S.; Radushnova, I. L.; Shigorin, D. N. *Dokl. Acad. Nauk USSR* **1976**, *231*, 409.

(33) Altman, L. A.; Laungani, D.; Gunnarsson, G.; Wennerström, H.; Forsen, H. *J. Am. Chem. Soc.* **1978**, *100*, 8264.

(34) Emsley, J.; Ma, L. Y. Y.; Bates, P. A.; Motevalli, M.; Hursthouse, M. *J. Chem. Soc., Perkin Trans. 2* **1989**, 527−533.

(35) Hirshfeld, F. L. *Acta Crystallogr., Ser. A* **1976**, *32*, 239.

(36) Vila, A. J.; Lagier, C. M.; Olivieri, A. C. *J. Mol. Struct.* **1992**, *274*, 215−222.

(37) Bader, R. F. W. *Atoms in Molecules: A Quantum Theory*; Oxford University Press: Oxford, U.K., 1990; 438 pp.

(38) Hinsen, K.; Roux, B. *J. Chem. Phys.* **1997**, *106* (9)*,* 3567−3576.

(39) Hinsen, K.; Roux, B. *J. Comput. Chem.* **1997**, *18*, 368−380.