

## The $C_{2v}$ Structure of Enolic Acetylacetone

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**Abstract:** It has often been postulated that the lowest energy enolic form of Acetylacetone (AcAc) assumes  $C_s$  symmetry, i.e., has a double-minimum potential possibly exhibiting a low barrier to internal proton transfer and not a single minimum,  $C_{2v}$ . Recent theoretical calculations and experimental work support the  $C_s$  hypothesis but the literature on this fascinating molecule is divided. Toward this objective, the high-resolution rotational spectra of enolic acetylacetone and 3 isotopologues have been obtained, revealing  $C_{2v}$  symmetry. The two methyl groups exhibit a very low barrier to internal rotation, thus making AcAc internally highly dynamic.

### Introduction

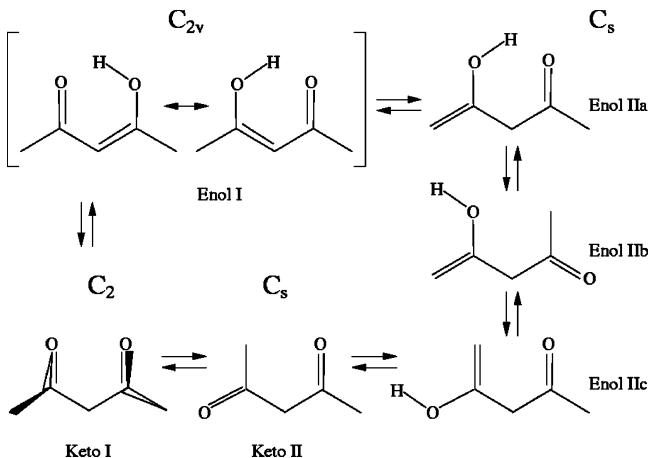
Acetylacetone (AcAc) allows for several tautomeric forms at different conformations in dynamic equilibrium (see Scheme 1) and multiple pathways of internal motions between equivalent positions; together with malonaldehyde (MA) it can be considered a prototype molecule for studying keto–enol tautomerization.

Two different shapes (shown in Chart 1) of the lowest energy enolic conformation of AcAc have been proposed: In most cases a  $C_s$ , and in some cases a  $C_{2v}$  enolic form was invoked for acetylacetone. We present here the pure rotational spectrum of acetylacetone, measured in supersonic expansions, which provides strong evidence for the symmetric nature of the internally highly dynamic molecule.

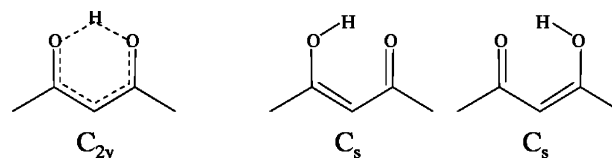
Some time ago, microwave (MW) spectra showed unambiguously that in MA,<sup>1</sup> 2-methyl-MA,<sup>2</sup> and 2-nitro-MA<sup>3</sup> the enol tautomeric species contains a hydrogen bonded ring comprising two equivalent structures with  $C_s$  symmetry (analogous to the two proposed  $C_s$  structures in Chart 1) connected through a transition state with  $C_{2v}$  symmetry (similar to the  $C_{2v}$  structure in Chart 1). A proton tunneling barrier of 3.3 kcal/mol was determined for MA.<sup>4</sup>

AcAc has been the subject of many experimental<sup>5–15</sup> and theoretical investigations,<sup>16–22</sup> even more than MA, but the

**Scheme 1.** Enolic and Keto Forms of Acetylacetone



**Chart 1.** Plausible Lowest Energy Enolic Forms of Acetylacetone



keto–enol tautomerization ratio as well as the structures of the two forms remain elusive, with conflicting results, linked to

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the interpretation of the experimental data or to the nature of the theoretical calculations. All investigations agree that Enol I and Keto I are the two lowest energy tautomers, while the ketonic conformer Keto II and other enolic isomers involving a pentenic carbon frame (Enol IIa, IIb, IIc shown in Scheme 1) are expected at higher energies.<sup>16</sup> The ketonic form allows for skeletal torsion out of the planar structure which then originates two conformational species (as shown in Figures S1 and S2 of the Supporting Information), having two equivalent (Keto I exhibiting  $C_2$  symmetry with two internal  $\text{CH}\cdots\text{O}$  hydrogen bonds forming two six-membered rings) or nonequivalent (Keto II exhibiting  $C_s$  symmetry with one internal  $\text{CH}\cdots\text{O}$  hydrogen bond forming one six-membered ring) methyl rotors.

An early electron diffraction (ED) investigation concluded that the lowest energy enolic form has  $C_{2v}$  symmetry (see Chart 1) and that it is 65% abundant at 100 °C,<sup>5</sup> while the most recent ED investigation, performed with an ultrafast electron diffraction apparatus, suggests the lowest energy enolic form to have  $C_s$  symmetry and to be 78% abundant at 155 °C.<sup>15</sup> Both values are quite different from that reported in the gas phase by other methods (~90% at 100 °C by gas IR spectral measurements (see ref 9 in ref 5) and ~95% at 50 °C by gas  $^1\text{H}$  NMR measurements<sup>11</sup>). It should be noted that the NMR spectrum was measured at a fairly high pressure, 200 Torr, where one cannot exclude dimerization, especially of the enolic form. The ED and rotational spectroscopy studies were carried out at much lower pressures.

There is a wealth of evidence in the literature using very different techniques that all support  $C_s$  symmetry for the molecular shape in solid state, liquid, and gas phase: (i) X-ray crystallography;<sup>9</sup> (ii) neutron crystallography;<sup>8</sup> (iii) liquid-phase NMR;<sup>14</sup> (iv) gas-phase vibrational spectroscopy;<sup>13</sup> (v) gas-phase ED.<sup>7,15</sup> However, (i), (ii), and (iii) are of limited significance for the comparison with the gas phase: it is not uncommon that only one configuration is found in the crystal but conformational equilibria in the gas phase. The IR study (iv) is very qualitative. Finally, while the examination of diffraction data (v) including the O—O nonbonding distance which is much larger than that of  $C_{2v}$  geometry appears to be careful, we note that this analysis is based on several assumptions for the keto-tautomer, and thus the results for the enol-tautomer carry with them the appropriateness of those assumptions.

As already shown for MA, rotationally resolved spectroscopy is a powerful method for unraveling these kind of problems. However, both lowest energy tautomers, Enol I and Keto I, are complicated systems from a dynamical point of view since they have two methyl groups that can undergo low-barrier internal rotation. The enolic form potentially has an additional large amplitude motion of the proton between two oxygens (see Chart 1). However, since the motion of the proton could be either an internal proton transfer or a near-harmonic vibration, it is difficult to say a priori if the two methyl groups of Enol I are equivalent or not.

We present here the assignment of the pure rotational spectrum of the lowest energy enolic species Enol I of AcAc and all of its singly substituted  $^{13}\text{C}$ -isotopologues. Their analysis, individually and in combination, provides a wealth of evidence supporting  $C_{2v}$  symmetry for its shape. The structural parameters of the carbon frame are derived quantitatively with high precision.

## Methods

Two different experimental setups have been used: a high-resolution supersonic-jet Fourier transform microwave (MW) spectrometer and a millimeter-wave (MMW) free-jet absorption spectrometer, which provide complementary results. Acetylacetone, supplied by Aldrich, is a liquid at room temperature and has been used in mixtures of about 1% with a rare gas without further purification.

**(a) Supersonic-Jet FTMW (FT-MW) Spectroscopy.** The details of the Coaxially Oriented Beam-Resonator Arrangement (COBRA) FT-MW spectrometer,<sup>23,24</sup> which covers the range 2–26.5 GHz, have been described previously.<sup>25</sup> The molecular beam was generated as a pulsed supersonic expansion of an AcAc/Ne mixture at a total backing pressure of 2 bar. Using a 1-mm diameter nozzle orifice, molecular pulses of about 0.25 ms duration were found optimal. The molecular response after MW impulse excitation was recorded in the time domain; its signal frequencies were determined by Fourier transformation. The pulsed supersonic jet, exhibiting rotational temperatures of 2 K, was introduced coaxially to the axis of the Fabry–Pérot resonator, and consequently each observed transition appears as a Doppler doublet. The line center is determined as the arithmetic mean of the peak frequencies of the two Doppler components. The accuracy of spectral line positions is estimated to be better than 2 kHz. All frequency measurements were referenced to a global position system (GPS) controlled frequency standard ( $10^{-11}$ ).

**(b) Free Jet Absorption Millimeter Wave (FJA-MMW) Spectroscopy.** The Stark modulated FJA-MMW spectrometer covering the frequency range 60–80 GHz has already been described elsewhere.<sup>26,27</sup> A mixture of AcAc seeded in argon, at pressures between 50 and 300 mbar, was expanded through a nozzle with a diameter of 0.35 mm, to  $2 \times 10^{-3}$  mbar. Estimated rotational temperatures in the range from 10 to 30 K were reached. The accuracy of the spectral line positions is about 0.10 MHz. All frequency measurements were referenced to a rubidium frequency standard.

## Results and Analysis

We recorded some MMW spectra of AcAc 10 years ago, but at that time we failed to assign them, partially for the reasons mentioned above and partially for our bias toward a  $C_s$  shape. It was only after we proceeded to the centimeter range of the MW region that we could assign 32 rotational transitions with a pulsed supersonic-jet FT-MW spectrometer and, after that, transitions in the MMW range. All of them appeared to belong to a single state (as shown in Table S1 of the Supporting Information) and were fitted with a semirigid rotor Hamiltonian,<sup>28</sup>

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**Table 1.** Spectroscopic Constants for the  $A_1$  State of the Lowest Energy Enolic Tautomer of AcAc and Its Singly Substituted  $^{13}\text{C}$ -Isotopologues (Watson's S-Reduction,  $I^r$  Representation)

	normal <sup>a</sup>	$^{13}\text{C}_{\text{CH}_3}$	$^{13}\text{C}_{\text{CO}}$	$^{13}\text{C}_{\text{CH}}$
$A/\text{MHz}$	6032.2431(4) <sup>b</sup>	5985.9431(7)	6030.3379(7)	5985.978(2)
$B/\text{MHz}$	1723.2640(3)	1686.4769(3)	1714.6758(3)	1723.3104(5)
$C/\text{MHz}$	1350.6909(2)	1325.7598(2)	1345.3859(2)	1348.4150(3)
$P_{\text{cc}}/\text{u}\text{\AA}^2$	1.442	1.447	1.452	1.446
$N^c$	79	9	9	9
$\sigma/\sigma_{\text{exp}}^d$	0.47	0.35	0.3	0.71

<sup>a</sup> The following centrifugal distortion constants have been determined for the normal species:  $D_1 = 0.017(3)$  kHz,  $D_{JK} = 9.97(1)$  kHz,  $D_K = 12.80(4)$  kHz,  $d_1 = -0.028(1)$  kHz,  $d_2 = -0.0540(6)$  kHz,  $H_{JK} = 0.26(9)$  Hz,  $H_K = 6.9(3)$  Hz,  $H_{KJ} = -15.7(3)$  Hz. These values have been fixed in the parametric fits of the less abundant isotopologues. <sup>b</sup> Errors in parentheses are expressed in units of the last digit. <sup>c</sup> Number of transitions in the fit. <sup>d</sup> Reduced deviation of the fit, relative to measurement errors of 2 and 100 kHz for the MW-FT and mmw lines, respectively.

thereby determining the spectroscopic parameters shown in Table 1.

Besides the rotational constants  $A$ ,  $B$ , and  $C$ , the planar moment of inertia

$$P_{\text{cc}} = (I_a + I_b - I_c) = (-\Delta_c)/2 \quad (1)$$

is also reported. The magnitude of the planar moment  $P_{\text{cc}}$ , 1.442  $\text{u}\text{\AA}^2$ , is even smaller than the value, ca. 3.2  $\text{u}\text{\AA}^2$ , expected from a rigid, heavy atom planar structure with two pairs of methyl protons contributing to it.

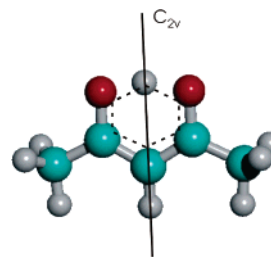
## Discussion

At first, we can note in Table 1 that the values of the rotational constants  $B$  of the normal species and its  $^{13}\text{C}_{\text{CH}}$  isotopologue practically coincide. Since the  $B$  constant is invariant (within small zero-point vibrational contributions) upon the isotopic substitution of the methine group, the methinic carbon atom lies on the  $b$ -axis of the inertia principal axes system of both isotopologues, which is only consistent with structures containing a  $C_2$  axis of symmetry.

The possibility to satisfactorily fit the observed spectrum with a conventional Hamiltonian is a second fact supporting  $C_{2v}$  symmetry. Otherwise, as in the case of MA, severe interactions (causing line shifts up to 10 GHz)<sup>1</sup> would be expected between the rotational spectra of the two inversion tunneling states.

Furthermore, with the free-jet absorption MMW spectrometer we obtain relatively high "rotational temperatures" (on the order of 30 K whereas only 2 K are reached in the supersonic-jet FT-MW spectrometer) after the supersonic expansion, such that we should have observed the rotational spectrum of the second tunneling state, if present. Since the first state is not perturbed, the same should be true for the second state, and its assignment should have been straightforward. We observed no spectral evidence for a second tunneling state. Theoretically, it might be possible that its absence can be explained by strong interactions of the proton in plane motion with the internal rotation of the methyl groups. Nevertheless we find this unlikely, since the scales of the proton tunneling and internal rotation interactions should differ significantly.

A fourth bit of evidence supporting  $C_{2v}$  structure comes from the 36/28 statistical weight, in favor of the states with an odd

**Figure 1.** The  $C_{2v}$  enolic form of AcAc contains three pairs of equivalent hydrogens and follows Fermi–Dirac statistics for three pairs of equivalent methyl hydrogens.

value of  $(K_{+1} + K_{-1})$ . As shown in Figure 1, the  $C_{2v}$  enolic form of AcAc contains three pairs of equivalent methyl hydrogens which follow the Fermi–Dirac statistics, i.e., the overall wave function

$$\psi_{\text{tot}} = \psi_e \cdot \psi_v \cdot \psi_R \cdot \psi_s \quad (2)$$

must be antisymmetric. Both the electronic wave function  $\psi_e$  and the vibrational wave function  $\psi_v$  are symmetric in the ground state, while the spin function  $\psi_s$  (36  $A_g$ ; 28  $A_u$ ) does have a ratio 9/7 between symmetric and antisymmetric components; for this reason, the rotational transitions with an antisymmetric initial state  $\psi_R$  will have a favorable intensity ratio of 9/7, with respect to the symmetric ones. With the  $C_2$  symmetry axis lying along the  $b$ -axis, the even functions are characterized by an even value of  $(K_{+1} + K_{-1})$ , and vice versa. The observed intensity variations are consistent with the 9/7 intensity ratio.

Also, transitions doubly overlapped due to the near prolate degeneracy of levels with the same  $K_{-1}$  have very weak Stark effects, which would not be true even if a small value of  $\mu_a$  exists, as in the case of a  $C_s$  symmetric, e.g., proton double-minimum potential, enolic form.

The sixth proof of  $C_{2v}$  symmetry comes from the detection of the three  $^{13}\text{C}$  isotopologues in natural abundance. The spectroscopic constants of the  $^{13}\text{C}$  isotopologues are also reported in Table 1. In the presence of  $C_s$  symmetry, the single isotopic  $^{13}\text{C}$  substitution of both the methyl and carbonyl carbons would generate two different isotopomers. However, we found only one spectrum for each substitution position, with an intensity of 2% relative to the normal species and twice the intensity of the  $^{13}\text{C}$  isotopomer substituted at the methine carbon. This reflects that the two methyl and the two carbonyl carbons constitute two pairs of equivalent nuclei, requiring  $C_2$  or higher symmetry. Furthermore, the planar moments  $P_{\text{cc}}$  of the normal species and all of its singly substituted  $^{13}\text{C}$  isotopologues are practically invariant and thus guarantee a heavy-atom-planar structure. Having a  $C_2$  symmetry axis while requiring planarity for the carbon frame is only compatible with a molecular  $C_{2v}$  symmetry.

The lowest energy enolic tautomer is expected to have a pseudo inertial defect  $\Delta_c$  of  $-6.40$   $\text{u}\text{\AA}^2$ , due to the methyl hydrogens out of the heavy atom planar frame. However, from eq 1 and the rotational constants of Table 1, we obtained the value  $\Delta_c = -2.88$   $\text{u}\text{\AA}^2$ . Such a small inertial value with respect to the value anticipated for a hypothetically rigid molecule has been observed for the  $A_1$  state of

**Table 2.** Substitution Co-Ordinates  $r_s$  of Carbon Atoms of the Lowest Energy Enolic Tautomer of AcAc

$r_s$			structural parameters <sup>a</sup>	
<sup>13</sup> C <sub>CH<sub>3</sub></sub>	<sup>13</sup> C <sub>CO</sub>	<sup>13</sup> C <sub>CH</sub>	$r(\text{C}_{\text{CH}_3}-\text{C}_{\text{CO}})/\text{\AA}$	1.472(3)
$ a /\text{\AA}$	2.5337(6)	1.216(1)	$r(\text{C}_{\text{CH}}-\text{C}_{\text{CO}})/\text{\AA}$	1.376 <sup>c</sup>
$ b /\text{\AA}$	0.820(2)	0.164(9)	$\alpha(\text{C}_{\text{CH}_3}-\text{C}_{\text{CO}}-\text{C}_{\text{CH}})/\text{deg}$	124.3 <sup>c</sup>
			$\alpha(\text{C}_{\text{CO}}-\text{C}_{\text{CH}}-\text{C}_{\text{CO}})/\text{deg}$	125.7 <sup>c</sup>

<sup>a</sup> The nonbonding distances  $r(\text{C}_{\text{CH}_3}-\text{C}_{\text{CH}_3})$ ,  $r(\text{C}_{\text{CH}_3}-\text{C}_{\text{CH}})$ , and  $r(\text{C}_{\text{CO}}-\text{C}_{\text{CO}})$  are 5.067(2) Å, 2.524<sup>c</sup> Å, and 2.432(2) Å, respectively.

<sup>b</sup> imaginary coordinate  $|a|/i$  Å = 0.09(2) set to zero. <sup>c</sup> Errors are not quoted because these values have been obtained assuming zero for the imaginary  $|a|$ -coordinate of <sup>13</sup>C<sub>CH</sub>.

molecules with two quite freely rotating methyl groups, as given in the following equations:<sup>29</sup>

$$\begin{aligned}
 A_{\text{AA}} &= A_r + 2 F W_{\text{AA}}^{(2)} \rho_a^2 \\
 B_{\text{AA}} &= B_r + 2 F W_{\text{AA}}^{(2)} \rho_b^2 \\
 C_{\text{AA}} &= C_r
 \end{aligned}
 \quad (3)$$

There  $A_r$ ,  $B_r$ , and  $C_r$  are the “rigid” rotational constants, i.e., the molecule in the hypothetical limit of a very high barrier. The coefficients  $W_{\text{AA}}^{(2)}$  are Herschbach’s barrier-dependent perturbation sums relative to the  $A_1$  levels of the vibrational ground state,<sup>30</sup>  $F$  is the reduced constant of the motion, and  $\rho_g = \lambda_g I_a / I_g$ .

The experimental value of the inertial defect of the  $A_1$  species is reproduced when  $W_{\text{AA}}^{(2)} = 0.52$ , which corresponds to a value of the reduced barrier  $s = 4 V_3/9F = 5$  and to  $V_3 = 0.163$  kcal/mol. This is a very low barrier, with only one bound vibrational state (comprising its AA, AE, or EA, and EE manifold of torsional wave functions according to local mode theory which can be symmetry classified as  $A_1$ , G, and  $E_1$  or  $E_3$ , respectively, using the molecular symmetry (MS) group  $G_{36}$ ). The splitting between the AA and the EE, AE, and EA component lines are predicted to be very large, up to several tens of GHz. It is very difficult to locate the spectral position of these component lines because, differently from the AA component lines, they do not follow a pseudo semirigid Hamiltonian, since they also depend on odd power terms of the angular momenta. Thus, in the case of such a low but not yet free barrier, it becomes increasingly difficult to treat the spectroscopic observations because generic models able to fit the data to the experimental accuracy are not readily available.

Although the rotational constants are perturbed by the internal rotation contributions of eq 3, we can obtain quantitative structural information with the prerequisite for these effects to be the same for the normal species and all of its <sup>13</sup>C substituted

isotopologues, by Kraitchman’s equations.<sup>31</sup> While this assumption is generally accepted, the invariance of the planar moments  $P_{\text{cc}}$  upon substitution provides additional justification. Nevertheless, small changes in the zero-point vibrational amplitude for different isotopes of a nucleus become noticeable if its coordinate is vanishing. In AcAc the  $B$  constant rises upon <sup>13</sup>C-substitution of the methine group, yielding an unphysical imaginary coordinate. The substitution coordinates  $r_s$  obtained for the three inequivalent carbon nuclei are compiled in Table 2.

## Conclusions

Our assignment and analysis of the rotational spectrum of the  $A_1$  state extensively unravels the problem of the conformation of the lowest energy enolic tautomer of AcAc. In contrast to the conclusions reached in a very recent paper,<sup>15</sup> our data are in complete agreement with a potential of the enolic proton exhibiting a single symmetric minimum. Thus, there might be a large amplitude vibrational motion, but there is no evident proton tunneling. The observed  $C_{2v}$  species was predicted to be the global energy minimum only by one set of the available ab initio calculations, MP2/D95++\*\*, including zero-point vibrational corrections, reported by Dannenberg and Rios.<sup>16</sup>

The present report constitutes a leap forward in the analysis of the tautomeric equilibrium of AcAc by rotational spectroscopy, providing strong evidence in support of  $C_{2v}$  symmetry for the shape of the lowest energy enolic tautomer. Future steps directed toward the internal dynamics of both tautomers will be the following: (i) the assignment of the rotational spectrum of the keto form(s); (ii) the investigation of the deuterated species, for which the dramatic effects on the spectrum caused by the low barrier to internal rotation of the methyl groups will be significantly reduced, due to the considerable mass change upon H–D isotopic substitution.

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**Supporting Information Available:** Tables (2) of frequencies of rotational transition of the  $A_1$  state of Enol I-acetylacetone and its singly substituted <sup>13</sup>C-isotopologues; Figures (2) of Keto I- and Keto II-acetylacetone. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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