A Nuclear Magnetic Resonance Study of the Intramolecular Hydrogen Bond in Acetylacetone

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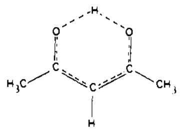
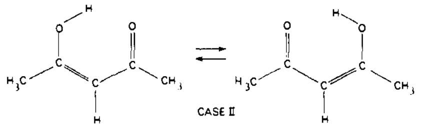
Abstract: Selected ^{13}C and ^{2}H spin-lattice relaxation times have been determined for the enol form of pentane-2,4-dione and its perdeuterated analogue; from a consideration of these relaxation times, deuterium quadrupole coupling constants are derived from which it is concluded that the intramolecular hydrogen bond in the enolic form is of the double minimum type. This conclusion is supported by chemical shift and liquid crystal studies.

Pentane-2,4-dione (acetylacetone), **1**, exists as an equilibrium mixture of the tautomeric diketo and enol forms.[2] The uncatalyzed rate of interconversion between these forms is relatively slow and their simultaneous nuclear magnetic resonance (NMR) spectroscopic observation is thus possible. Under normal conditions of measurement, the enolic form dominates the equilibrium.[3]

The relative stability of the enol derives, at least partially, from the formation of an intramolecular hydrogen bond. Although the strength of this bond has not been measured directly, a value of approximately 10–15 kcal/mol may be estimated.[4] At present there is considerable interest in the nature of the potential function describing this bond; that is, is the hydrogen bond strong enough for the proton to effectively reside in a single well potential function (case I), or is it in a double well potential function with the proton being rapidly transferred between the minima (case II). The ground state molecular geometries associated with cases I and II are C_{2v} and C_s, respectively.[5]



CASE I



CASE II

A number of studies have attempted to define the nature of the hydrogen bond potential function in **1**; there is, however, sufficient serious disagreement between these reports that the nature of the potential must be regarded as still undetermined. For example, on the basis of electron diffraction studies,[6] it has been concluded that the C_{2v} structure is the lowest energy form of the enol; on the other hand, infrared spectroscopic studies have indicated that equilibrating C_s structures best describe the enolic form.[7] Additional evidence has been advanced in favor of case I[8] and case II[9] interpretations.

For a hydrogen bond of the type found in acetylacetone, O(1)–H–O(2), the electric field gradient, *eq*, experienced by the bridging proton is a sensitive function of its position relative to the terminal oxygen atoms;[10,11] for a given O(1)–O(2) distance, the more symmetric the positioning of the proton, the smaller the field gradient. A determination of the electric field gradient at the bridging hydrogen nucleus thus provides a measure of the symmetry of the hydrogen bond. This gradient may be conveniently probed through its interaction with the nuclear electric quadrupole moment of deuterium.

This report primarily concerns the determination of the quadrupole coupling constant (QCC), e^2q_zQ/h, for the bridging deuterium of acetylacetone-d_8 and a discussion of these results in terms of a hydrogen bond potential function.

Results and Calculations

Expressions for the nuclear magnetic relaxation times of quadrupolar nuclei attached to molecules undergoing anisotropic rotational diffusion have been derived by Huntress.[12] In this formulation, the relaxation times are dependent on (i) the quadrupolar coupling constant (e^2q_zQ/h), (ii) the asymmetry parameter

$$\eta = (q_x - q_y)/q_z \tag{1}$$

(q_i being the electric field gradient along the ith axis of the coordinate system, S_1, that diagonalizes the quadrupole coupling tensor), (iii) the angles relating S_1 to the principal coordinate system of the molecule (the coordinate system in which the moment of inertia tensor is diagonal), and (iv) the diffusion constants, D_i ($i = x, y, z$), about the molecular axes.

No assumptions regarding the interdependence of the diffusion constants were made by Huntress. McClung's formulation of extended diffusion[13] of a symmetric top molecule, however, predicts that in the diffusion limit

$$D_i = kT\tau_J/I_i \tag{2}$$

where kT is the Boltzmann factor, I_i is the moment of inertia about the ith axis, and τ_J is the *single* angular momentum correlation time for the molecule.

Consequently, when eq 2 holds,

$$D_i/D_j = I_j/I_i \tag{3}$$

and the measurement of the quadrupole relaxation time of a single nucleus for which the quadrupole coupling constant, asymmetry parameter, and orientation are known, enables one to completely define the motion of the molecule. The measurement of two relaxation times will, in principle, enable one to extract additional information.

The deuterium spin-lattice relaxation times for the H(2) and H(1) deuterium atoms in acetylacetone-d_8 and the ^{13}C spin-lattice relaxation time for C(1) of acetylacetone are given in Table I (the numbering scheme is provided in Figure 1; C(1) is the carbon atom directly bonded to H(1)).

From the $^{13}C(1)$ and $^{2}H(1)$ relaxation times, a C(1)–H(1) bond length of 1.08 Å, setting $\eta = 0$, and assuming that the motions of acetylacetone and acetylacetone-d_8 are identical, we calculate[14] a quadrupole coupling constant of 197 kHz for the C(1) deuteron. Since the motion of the perdeuterio compound is most likely somewhat slower than the perprotio compound due to an increase in molecular weight, this value of the quadrupolar coupling constant is probably somewhat larger than the actual value. Additionally, our use of an equilibrium C–H bond distance in place of an average C–H bond distance leads to a somewhat larger than actual value of the quadrupolar coupling constant.

From the relaxation data, taking the $^{2}H(2)$ quadrupole coupling constant to be 197 kHz, and assuming eq 2, the reduced angular momentum correlation time for acetylacetone at 308 K is $\tau_J(kT/I_i)^{0.5} = 0.04$. Thus, the assumption of ro-

Table I. ^2H and ^{13}C Relaxation Times for Acetylacetone and Acetylacetone-d_8

Compd	Nucleus	Temp, °C	T_1, s
Acetylacetone-d_8	$^2H(1)$	35	0.612 ± 0.007^a $(-0.999)^b$
Acetylacetone-d_8	$^2H(2)$	35	0.706 ± 0.009 (-0.999)
Acetylacetone-d_8	$^2H(1)$	0	0.346 ± 0.005 (-0.999)
Acetylacetone-d_8	$^2H(2)$	0	0.446 ± 0.011 (-0.996)
Acetylacetone-d_8	$^2H(1)$	63	0.914 ± 0.023 (-0.997)
Acetylacetone-d_8	$^2H(2)$	63	1.046 ± 0.011 (-0.999)
Acetylacetone	$^{13}C(1)$	35	16.4 ± 0.4 (-0.996)

[a] The reported errors are standard deviations; the actual errors are most probably somewhat greater. [b] The values in parentheses give the correlation coefficients for the respective plots of ln $(M_\infty - M_t)$ vs. t (see Experimental Section).

Table II. Calculated Quadrupole Coupling Constants and Associated Parameters $^2H(2)$ at Various Points along the Topomerization Pathway[a,b]

q	γ, deg	ζ, deg	θ, deg	η	QCC, kHz
0.75	107.1	23.5	49.4	0.59	66
0.50	109.6	13.5	56.9	0.25	127
0.25	112.1	7.6	60.3	0.17	209
0.0	114.6	4.5	60.9	0.12	311
−0.25	117.1	3.2	59.7	0.10	434

[a] Values in the table refer to malondialdehyde and are taken from ref 15. [b] The various symbols retain the meaning given them in the text.

tational diffusion appears to be consistent with the relaxation data (see ref 13).

Karlström et al.[15] have reported a series of ab initio calculations on malondialdehyde. For H(2), these authors have determined the quadrupole coupling constant, the asymmetry parameter (η), and deviation (ζ) of the largest component of the quadrupole coupling tensor from the O–H(2) bond internuclear axis as a function of the reaction coordinate, q, describing the C_s–C_{2v} topomerization. These data are summarized in Table II. The reaction coordinate may be described as follows: q specifies a structural parameter according to the formula $p = qp_{C_{2v}} + (1 - q)p_{C_s}$, where p is a bond length or bond angle, p_{C_s} is a corresponding value for the minimum energy C_s form and $p_{C_{2v}}$ for the minimum energy C_{2v} form (see ref 15).

We will assume that the results of Karlström et al.[15] for malondialdehyde are applicable to acetylacetone-d_8 and make use of their values for the quadrupole coupling constant, η, and ζ. Using the $^2H(1)$ quadrupole coupling constant of 197 kHz in conjunction with Huntress' equations (4.16 and 4.18)[12] and the assumption that eq 3 holds, we can calculate the ratio of the $^2H(1)$ to $^2H(2)$ spin-lattice relaxation times as a function of q.

For these calculations we take the z axis of the principal coordinate system of the molecule to be along the C(1)–H(1) bond and the y axis to be perpendicular to the plane of symmety common to the C_{2v} and C_s forms (see Figure 1). With this definition, the coordinate system which diagonalizes the quadrupole coupling tensor and the principal coordinate system of the molecule are connected by a rotation about the y axis. Therefore the irreducible tensor components, $F^{(m)}$, occurring in Huntress' equation (4.16)[12] are

$$F^{(2)} = F^{(-2)} = 0.5e^2q_zQ\{(\sqrt{6}/4)\sin^2\theta + (\eta/\sqrt{6})((1 + \cos^2\theta)/2)\} \quad (4A)$$

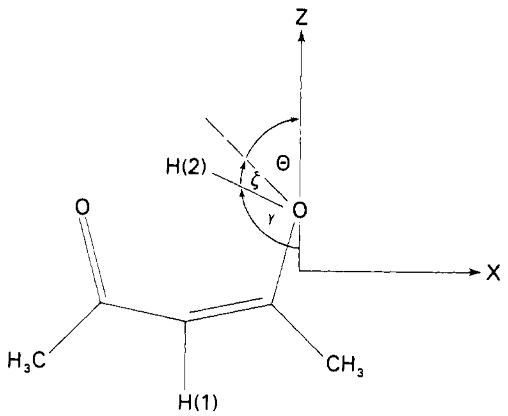


Figure 1. Coordinate, angle, and numbering schemes used in the discussion of acetylacetone and acetylacetone-d_8. The y axis of the Cartesian coordinate system is directed out of the plane of the paper. In the numbering scheme, C(1) is the carbon atom directly bound to H(1).

$$F^{(1)} = -F^{(-1)} = 0.5e^2q_zQ\{(-\sqrt{6}/2)\cos\theta\sin\theta + (\eta/\sqrt{6})\cos\theta\sin\theta\} \quad (4B)$$

$$F^{(0)} = 0.5e^2q_zQ\{((3\cos^2\theta - 1)/2) + (\eta/2)\sin^2\theta\} \quad (4C)$$

where θ is the angle of rotation about the y axis and the remaining symbols retain their previous meaning.

Assuming that the internal angles of **1** and malondialdehyde are the same, we take $\theta = 180 - (\gamma + \zeta)$, where γ is the angle between the molecular z axis and the O–$^2H(2)$ internuclear axis for a given value of the reaction coordinate, q, and ζ is the angle of deviation of the largest component of the field gradient tensor from the $^2H(2)$–O bond direction at the same given value of q (see Figure 1). Values for θ, γ, and ζ as a function of q are found in Table II.

For $^2H(1)$ relaxation, with $\eta = 0$ and $\theta = 0$, the only nonvanishing component of eq 4 is $F^{(0)} = 0.5e^2q_zQ$. For the relaxation of $^2H(2)$ we can distinguish two cases: (a) when $^2H(2)$ is exchanging between the two oxygen atoms with a rate that is fast compared to the decay of the correlation function ("fast exchange"), and (b) when $^2H(2)$ is exchanging slowly with respect to the decay of the correlation function ("slow exchange").

For slow exchange, all five components of $F^{(m)}$ must be included and the relaxation time reduces to Huntress' equation (6.1)[12] (with the appropriate changes in the definition of the principal coordinate system). However, for fast exchange, the components given in eq 4 must be replaced by their average value over the two-site exchange,[16] that is

$$F^{(m)} = 0.5\{F^{(m)}(\theta) + F^{(m)}(-\theta)\} \quad (5)$$

The effect of the exchange is such that $F^{(1)} = -F^{(-1)}$ goes to zero, while $F^{(0)}$ and $F^{(\pm 2)}$ remain unchanged. Figure 2 shows the calculated ratio of $^2H(2)$ to $^2H(1)$ spin-lattice relaxation times in acetylacetone-d_8 as a function of the reaction coordinate, q, for both the fast and slow exchange limits. We have assumed that D_i/D_j is constant as a function of q and equal to I_j/I_i calculated for the C_{2v} form; see Figure 3. The experimental value of $T_1(O^2H(2))/T_1(C^2H(1))$ for **1** is 1.15 at 30 °C. Values of the T_1 ratio at 0 and 63 °C were approximately the same, being 1.14 and 1.29, respectively. These values intersect the theoretical curves for the slow and fast exchange limits at approximately $q = 0.4$ and 0.3, respectively.

Chemical Shift and Line Width Studies. The chemical shift of the bridging proton in acetylacetone has previously been observed to be temperature dependent.[9a,17] These measurements have been repeated quantitatively using anhydrous material and additional measurements have been carried out in the gas phase; the results are summarized in Table III.

Table III. ^1H and ^2H Chemical Shift and Line Width Data for the O–H and O–^2H Resonances of Acetylacetone and Acetylacetone-d_8

Compd	Concn, mol fract	Shift,[a] ppm	Temp, °C	$W_{1/2}$,[b] Hz	Temp range, °C	$\Delta\delta/\Delta T \times 10^2$,[c] ppm/°C
Acetylacetone	1.0	13.573	39.6	0.8	−20–126	−0.295 ± 0.005 (−0.998)[d]
Acetylacetone	0.36[e]	13.603	39.6	0.7	−18–90	−0.278 ± 0.005 (−0.999)
Acetylacetone	0.34[f]	13.619	39.6	0.7	−3–106	−0.284 ± 0.005 (−0.999)
Acetylacetone	0.18[f]	13.618	39.6	0.7	−3–116	−0.295 ± 0.005 (−0.999)
Acetylacetone	1.0[g]	13.729[h]	39.6		92–165	−0.386 ± 0.011 (−0.997)
Acetylacetone-d_8	1.0	13.003	39.6		0–122	−0.243 ± 0.006 (−0.997)

[a] Measured on the δ scale, relative to the enolic CH_3 group for acetylacetone and the CD_3 group for acetylacetone-d_8. [b] Determined at 60 MHz and the temperature given in the preceding column. [c] The change in shift with temperature calculated by fitting the data for the chemical shift vs. T to a straight line by the method of least squares. [d] The correlation coefficient for the respective plots of shift vs. T. [e] In cyclohexane-d_{12}. [f] In di-n-butyl ether. [g] Gas-phase spectra, obtained in the Fourier transform mode. [h] Determined by extrapolation using the least-squares fit value for $\Delta\delta/\Delta T$.

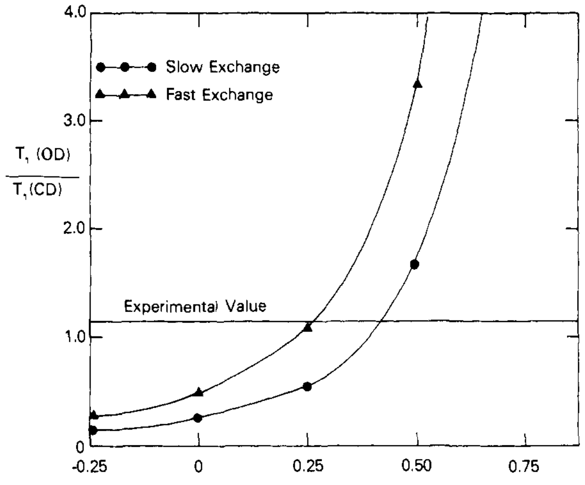


Figure 2. Calculated values for $T_1(OD)/T_1(CD)$ as a function of the reaction coordinate, q, in the slow and fast exchange limits. The experimental T_1 ratio (30 °C) is 1.15 and is indicated as a horizontal line.

For neat acetylacetone or acetylacetone solutions in cyclohexane (0.36 M) or n-butyl ether (0.15 and 0.35 M), the chemical shift is a linear function of the temperature over the investigated range, the variation in shift being approximately -0.3×10^{-2} ppm/°C (the negative sign indicates that the shift is to higher field with increasing temperature). For acetylacetone in the gas phase the shift variation is somewhat greater than in solution, being approximately -0.4×10^{-2} ppm/°C.

The bridging deuteron in acetylacetone-d_8 displays a temperature dependence similar to the ^1H species; the magnitude of the change, however, is somewhat diminished (-0.24×10^{-2} ppm/°C). As noted previously,[9a] a large isotope effect on the chemical shift of the bridging hydrogen atom is evidenced. At 40 °C, the chemical shift difference between the enolic CD_3 groups and the bridging deuterium atom is ca. 12.99 ppm; the corresponding shift difference for the perprotio compound was ca. 13.53 ppm. Relative to the enolic methyl group signal, no isotope effect for the remaining resonances of the keto and enolic forms is noted.

The line widths ($W_{1/2}$) of the bridging proton in acetylacetone as well as other β-diketones have occasionally been reported as being broad, and ranging in value from several to 20 Hz,[8a,9c,18] depending on conditions. The cause of this broadening has not, in general, been clarified.[19] For solutions of acetylacetone in di-n-butyl ether, however, it has been claimed that the broad signal of the bridging proton is due to slow chemical exchange between the closed (internally hydrogen bound) and open (solvent hydrogen bound) enolic structures. In this instance $W_{1/2}$ for the enolic signal varied from ca. 2 to 8 Hz as a function of temperature (at 100 MHz); it was further found that this broadening was concentration and frequency dependent.[9c] We have repeated these experiments with **1** in n-butyl ether, under anhydrous conditions, and have found that although a slight broadening (ca. 0.3 Hz) of the signal takes place as a function of temperature (from −20 to 140 °C), the line width remained less than 1 Hz (at 60 MHz). It therefore appears that there is no experimental basis for postulating an open form.

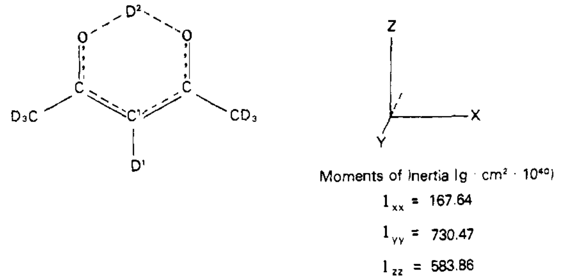


Figure 3. Coordinate system (as in Figure 1) and moments of inertia for the C_{2v} form of acetylacetone-d_8.

The temperature- and frequency-dependent broadening that was observed for n-butyl ether solutions of **1**[9c] and reported for other β-diketones[8a,18] is most probably due to traces of water. The maximum broadening of the enolic signal due to water will be given by the expression

$$W_{1/2} = 2p_{H_2O}\Delta\nu$$

where p_{H_2O} is the relative mole fraction of water and $\Delta\nu$ is the chemical shift difference (in hertz) between the enolic signal and the water signal in the absence of exchange (the factor of 2 derives from the two water protons which can exchange with the single bridging proton). Since the chemical shift difference between the water and enolic proton signals is on the order of 10 ppm, it is apparent that even traces of water in solution will significantly broaden the bridging proton resonance. It is also clear that water will affect the observed chemical shift. This would be extremely severe in dilution studies if the solvent were not anhydrous.

We have analyzed our solutions for water content gas chromatographically. These studies indicated that traces of water still remained; by extrapolation, and assuming no water contamination during transfer from the NMR tube to the injection port of the gas chromatograph, the line width of the bridging proton should be approximately 0.5 Hz.

Discussion

From Figure 2 it is seen that the $^2H(2)/^2H(1)T_1$ ratio (at 30 °C) intersects the theoretical curves at $q \approx 0.30$ in the fast exchange limit and 0.40 in the slow exchange limit; the associated values of the quadrupole coupling constant are approximately 210 and 150 kHz, respectively. It is not possible to determine which limit best describes the behavior of acetylacetone and this ambiguity must unfortunately remain.[20] The important point, however, is that regardless of which limit prevails (or if intermediate behavior prevails), the point of intersection describes a hydrogen bond of the double minimum type, case II.

In order to define the equilibrium position of the deuteron along the C_s–C_{2v} topomerization pathway, we have utilized the results of ab initio calculations on malondialdehyde. These calculations were, however, necessary on a more fundamental basis; in their absence it would not have been possible to determine the bridging deuteron's quadrupole coupling constant due to the nonnegligible and variable asymmetry and bond deviation parameters, η and ζ, respectively. At this point it is probably worthwhile to examine two approximate methods for determining the bridging deuteron's quadrupole coupling constant.

The roughest approximation would be to assume that the correlation times for both deuterons were equal and that η and ζ were negligible. With these assumptions,

$$\mathrm{QCC}(\mathrm{O}^2\mathrm{H}(2)) = \mathrm{QCC}(\mathrm{C}^2\mathrm{H}(1))\{T_1(\mathrm{C}^2\mathrm{H}(2))/T_1(\mathrm{O}^2\mathrm{H}(2))\}^{0.5} \quad (6)$$

Use of eq 6 in conjunction with the values found for the relaxation times and the quadrupole coupling constant for ^{2}H(1) leads to a value of approximately 184 kHz for the QCC of ^{2}H(2).

A more sophisticated approximation would consider the effects of anisotropic motion while still ignoring the asymmetry and bond deviation parameters. Since tumbling about the molecular z axis will be slower than about the x axis due to the larger moment of inertia about the former, the correlation time associated with the ^{2}H(2) atom will be longer than that associated with ^{2}H(1). Considerations of anisotropic motion (Huntress' equation (4.29))[12] will thus lead to a quadrupole coupling constant less than the previously estimated 184 kHz. The exact value will, however, be a function of the O–^{2}H(2)–O angle (the remaining geometric parameters may be regarded as sufficiently well defined). For reasonable values of the O–^{2}H(2)–O bond angle, 180 ± 40°, the dependence of the quadrupole coupling constant will not be overly severe; the complete curves are given in Figure 4 for both the conditions when the ^{2}H transfer rate is slow and fast relative to the reciprocal of the overall correlation time. At this level of approximation the H(2) QCC is determined to be greater than 120 kHz.

We should like to emphasize that, while the above approximations afford a value for the QCC of the bridging deuteron, they do *not* define the form of the potential function; to do so one must turn to an empirical correlation. Such a correlation has been established from solid-state studies,[11] where it has been found that hydrogen bonds of the single minimum type have quadrupole coupling constants of approximately 55 kHz, while hydrogen bonds of the double minimum type have quadrupole coupling constants in the range of ca. 100–200 kHz. Within these two approximations for the determination of the QCC of ^{2}H(2), and utilizing the empirical correlation of Blinc and Hadzi,[10] one can conclude that acetylacetone possesses a double minimum hydrogen bond.

For completeness, we sought to measure the QCC for the bridging deuteron in acetylacetone by a more direct method. Our first attempt employed solid-state techniques (broadband NMR)[11] using ostensibly microcrystalline acetylacetone-d_2 (the methyl groups were not deuterated); due to sensitivity related problems this attempt was not successful. A study of acetylacetone dissolved in a liquid crystal was, in contrast, more rewarding. A range of possible values for the QCC was derived from these measurements, bracketing approximately 125–200 kHz.[21] It was not possible to further refine the data. These values, however, are in the range expected for a double minimum hydrogen bond.

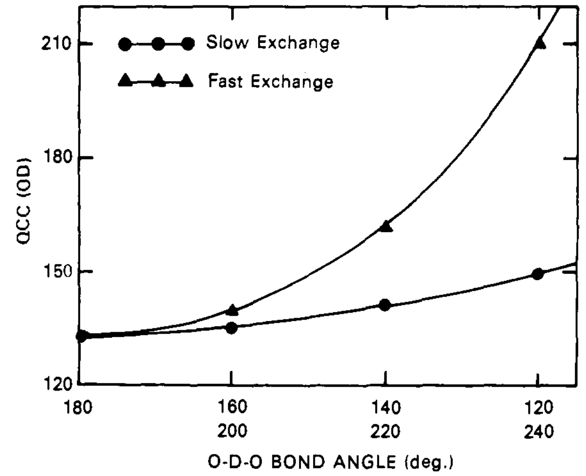


Figure 4. Calculated values for the quadrupole coupling constant of ^{2}H(2) as a function of the O–^{2}H–O bond angle assuming that $\zeta = \eta = 0$; see Discussion.

We now wish to comment on the sign and magnitude of the isotope effect on the bridging hydrogen atom's chemical shift and the temperature dependence of the chemical shift of this resonance. Specifically, we wish to comment on the relationship between these variables and the potential function for hydrogen bonding in **1**.

The isotope effect may be defined on the δ scale as

$$\Delta\delta(^1\mathrm{H}, {}^2\mathrm{H}) = \delta^1\mathrm{H} - \delta^2\mathrm{H}$$

The quantities that determine the magnitude of $\Delta\delta(^1\mathrm{H}, {}^2\mathrm{H})$ are the vibrational wave functions, Ψ_v, for the ground and low-lying excited states and the variation of δ with nuclear configuration. In a previous communication,[22] we have explored the relationship between hydrogen bond potential function and deuterium isotope effects and have concluded that the observed effect in acetylacetone ($\Delta\delta = 0.5$) furnishes evidence for a double minimum hydrogen bond potential function, case II. We refer to this communication[22] for further details.

The chemical shifts of intermolecular hydrogen bonds have long been known to be temperature dependent.[23] Initially it was assumed that the shifts to higher fields that occurred on heating resulted from a disruption of the hydrogen-bond network; that is, that there was a reduction in the average degree of association. An alternative explanation, based on the temperature-dependent degree of excitation of the hydrogen bond stretching mode, was later suggested by Muller and Reiter.[24] When an appropriate average over the vibrational levels was used to evaluate H-bond chemical shifts, a temperature dependence similar to that found experimentally for a number of hydrogen-bonded systems was obtained, even though the calculations assumed no dissociation of the hydrogen-bonded species.[24] Values of $\Delta\delta/\Delta T$ calculated by these authors ranged from approximately 0.2 to 0.8 × 10^{-2} ppm/°C.

We interpret the temperature-dependent chemical shift of the bridging hydrogen atom of acetylacetone in terms of the above model of Muller and Reiter.[24] Thus, the upfield shift which occurs on raising the sample temperature is brought about by a population redistribution (Boltzmann) between ground and low-lying excited states of the vibrational modes, which alter (lengthen) and O–O distance. According to this model, deuteration should result in a different value of $\Delta\delta/\Delta T$ for the deuterated compound due to changes in vibrational energy levels. This is indeed the case, but a detailed interpretation is difficult. The difference in $\Delta\delta/\Delta T$ between the liquid and gas phases shows that the vibrational energy levels and probably the hydrogen-bond potential are slightly dependent on the solvent. However, the similarity in shift between the gas and liquid shows that the chemical shift of the hydrogen-bond proton is largely intramolecular in origin.

On the basis of the relaxation data as well as the liquid crystal and chemical shift studies reported in this communication, it seems certain that the hydrogen bond in acetylacetone is double minimum in form.

Experimental Section

1,1,1,3,3,5,5,5-Octadeuteriopentane-2,4-dione (acetylacetone-d_8). Acetylacetone (10 ml) was refluxed overnight with 100 mL of 99.7% D_2O in the presence of 1 g of K_2CO_3. Acetylacetone was then extracted with dichloromethane (three 50-mL portions), dried over anhydrous $CaSO_4$, and distilled (bp 132-136 °C).[25] The deuterium incorporation was ca. 90% as determined by comparison of integrated ^1H NMR signals in the deuterated and nondeuterated compounds.

3,3-Dideuteriopentane-2,4-dione (acetylacetone-d_2). Acetylacetone (10 mL) was stirred overnight with 25 mL of D_2O followed by workup as described above. A second exchange cycle was carried out. The resulting acetylacetone had a deuterium incorporation >95%.

NMR Sample Preparation. All samples were dried over anhydrous $CaSO_4$, freshly prepared by dehydrating under vacuum at 280 °C for 3 h. Samples were dried repeatedly until $W_{1/2}$ for the O-H proton became <1 Hz (60 MHz, 42 °C). The final dryings were carried out on a vacuum line and samples were then vacuum transferred to thin-wall NMR tubes and sealed. In this manner neat samples of acetylacetone, acetylacetone-d_8, as well as samples of acetylacetone in cyclohexane and di-*n*-butyl ether were prepared.

^{1}H NMR Spectral Measurements. Varian XL-100/15 and A-60A NMR spectrometers were employed for continuous wave measurements; an external lock (H_2O) was utilized for the XL-100 measurements. Chemical shifts were determined using either the side-band modulation technique (for the A-60 measurements) or frequency counter (for the XL-100 measurements). The temperature measurements at 60 MHz were based on the chemical shift separation of the protons of an ethylene glycol or methanol sample utilizing the temperature-shift correlation of Van Geet.[26] At 100 MHz, the temperature measurements were derived from a copper-constantan thermocouple (ice/water reference) built into the probe. Gas-phase measurements were performed on the XL-100 spectrometer operating in the Fourier transform mode. A 2.5-cm long sealed glass ampule fitted into a 10-mm NMR tube served as the sample holder. A separate experiment showed that the temperature gradient in the ampule was <1.3 °C/cm at the highest temperature employed.

^{2}H and ^{13}C NMR Measurements. ^2H NMR spectra were recorded on a Varian XL-100/15 spectrometer operating in the Fourier transform mode; an external lock (H_2O) was used. The temperature was measured with a thermocouple as mentioned above. A JEOL FX-60 Fourier transform spectrometer was employed for the ^{13}C measurements; in order to obtain an internal deuterium lock, a 5-mm NMR tube containing the sample was fitted inside a 10-mm NMR tube containing D_2O.

Spin-Lattice Relaxation Measurements. The $(D\text{-}180\text{-}\tau\text{-}90)_n$ pulse sequence was used for all spin-lattice relaxation time measurements; the delay time, D, between the 180° pulses was in all instances $>5T_1$. For each T_1 determination, 10-15 different τ values (extending to $2\text{-}3T_1$) were utilized. The relaxation time was evaluated by fitting $[\ln(M_0 - M_\tau), \tau]$ data sets to a straight line by the method of least squares. All samples were degassed on the vacuum line (four times at ca. 10^{-4} Torr) and sealed. Measurements were performed on nonspinning samples and sample heights were adjusted so as to lie completely within the transmitter coil.

References and Notes

(1) Present address: Reproduction Research Branch, National Institute of Child Health and Human Development, National Institutes of Health, Bethesda, Maryland 20014.

(2) For a review of tautomerism in β-diketones, see S. Forsén and M. Nilsson in "The Chemistry of the Carbonyl Group", Vol. 2, J. Zabiky, Ed., Interscience, New York, N.Y., 1970, p 157ff.

(3) See, for example, G. Allen and R. Dwek, *J. Chem. Soc. B*, 161 (1966).

(4) R. S. Drago and T. D. Epley (*J. Am. Chem. Soc.*, **91**, 2883 (1969)) have noted a correlation between $\Delta H°$ and the frequency shift, $\Delta\nu_{OH}$, in the infrared stretching frequency of the O-H bond upon formation of an intermolecular hydrogen bond, $\Delta H° \approx (0.15\Delta\nu_{OH} + 3)$ kcal/mol; using ν_{OH} in **1** of ca. 2700 cm^{-1} and ν_{OH} in dilute phenol (to approximate nonhydrogen bonded **1**), we arrive at $-\Delta H° = 16.5$ kcal/mol. Granacher (*Helv. Chem. Acta*, **34**, 272 (1961)) has related NMR chemical shift changes ($\Delta\delta$) upon hydrogen bonding to $\Delta H°$, $\Delta\delta = -0.4 + \Delta H°$; using $\delta_{free}(OH) = 4.3$ (the value for dilute phenol), we calculate $-\Delta H°$ to be approximately 12 kcal/mol. Additionally, M. J. S. Dewar and co-workers (*J. Chem. Soc. A*, 25 (1971)) have calculated the difference in energy between the cis and trans (cis and trans refer to the position of the OH bond relative to the C(O)-C(H) bond) forms of the enol and claim that the difference in energy content reflects primarily the H-bond strength; this value is 11.5 kcal/mol. While a highly accurate measure of the H-bond energy is lacking, there is little doubt that the bond is strong.

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