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# ISOTOPE EFFECTS—I

## HYDROGEN ISOTOPE EFFECTS IN ACETYLACETONE AND ITS ENOL

M. J. T. Robinson,* K. M. Rosen and J. D. B. Workman
The Dyson Perrins Laboratory, South Parks Road, Oxford OX1 3QY, England

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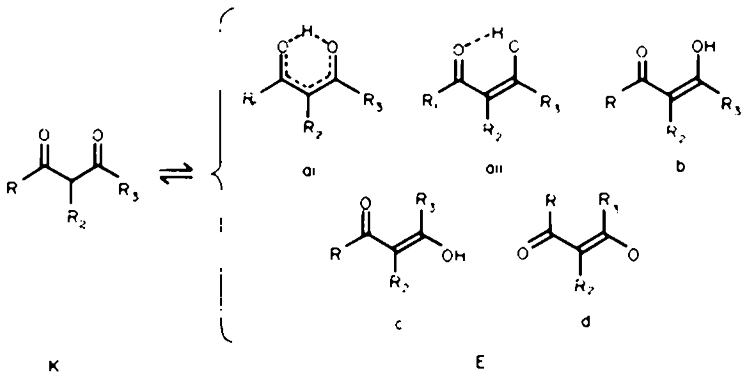
**Abstract**—Aspects of the effects of deuteriation on the properties of acetylacetone (pentan-2,4-dione) and its enol have been reinvestigated and new isotope effects have been sought in order to understand better the nature of the hydrogen bridge in the enol (1E). There is *no* substantial hydrogen isotope effect on the enthalpy of enolisation of 1 (contrary to Ref. 5) but there are unusually large isotope effects on $\nu_{max}$ (contrary to Ref. 5) and on the band shape of the long wavelength ($\sim 37,000\ cm^{-1}$) UV absorption and on the $^{13}C$ NMR chemical shift of the C(3) atoms in 1E. It is concluded that these and other properties of the enol 1E can be qualitatively explained if the hydrogen bridge in 1E is not quite symmetrical but has two symmetrically placed potential energy minima close together for the hydrogen atom leading to a lengthening of the O···O distance on deuteriation.

Acetylacetone (pentane-2,4-dione) (1K) and its enol 1E (Fig. 1) have been a classic example of tautomerism since Meyer first measured the enol content.[1] The principle form of the enol appears to cyclic with a symmetric (or nearly symmetric) hydrogen bridge[2,3] and might be expected to show unusual spectroscopic and equilibrium isotope effects. The effect of isotopic substitution at O<u>H</u> in 1E in hydrogen NMR spectra is well established experimentally[4] but the explanation is in doubt (see below). The hydrogen isotope effects on the equilibrium $1K \rightleftharpoons 1E$ ($\delta\Delta H^\circ - 10.5\ kJ\ mol^{-1}$)[5] and on the low frequency $\pi \rightarrow \pi^*$ band near $37,000\ cm^{-1}$ (no change in $\epsilon_{max}$, a small but unspecified increase in $\nu_{max}$)[5] reported before this work began, however, were respectively inexplicably large and very small. We were originally interested in using UV spectra to determine the hydrogen isotope effect on the equilibrium $1K \rightleftharpoons 1E$, previously studied by $^1H$ NMR, but preliminary experiments showed quite different results from those reported and we accordingly investigated several aspects of hydrogen isotope effects on 1. These isotope effects and other properties of the enol are related qualitatively to a model of the enol H-bond at the end of this paper.

Although the cyclic form (a in Fig. 1) is undoubtedly the predominant form of the enol in the gas phase and in most solvents the possible importance of the trans enols 1Ec and 1Ed (Fig. 1) and of the *cis* enol 1Eb without an intramolecular H-bond (Fig. 1) must be considered. The original "evidence" for **10**Ec or **10**Ed[6] was based on a misconception. A much more recent claim for "*trans*" enols[7] (based on IR and UV spectra) in 4-7 was withdrawn[8] following criticism[9] only to reappear[10] (NMR spectra) from another source. We note that there is a rather good correlation between the amounts of O-alkylation of 1[11] and the proportion of "*trans*" enol detected by a $^1H$ NMR signal near δ - 5.4 ppm[10] and we have separated commercial "5" into 5 (essentially 5K; no "enol" absorption near δ = 5.4 ppm developed even after several months) and the enol ether, 4-isopropoxypent-3-en-2-one, by GLC. Weak concentration dependent IR



| | $R_1$ | $R_2$ | $R_3$ |
|---|---|---|---|
| 1 | Me | H | Me |
| 2 | Me | Me | Me |
| 3 | H | H | H |
| 4 | Me | Et | Me |
| 5 | Me | i-Pr | Me |
| 6: | Me | s-Bu | Me |

| | $R_1$ | $R_2$ | $R_3$ |
|---|---|---|---|
| 7. | Me | s-Bu | Me |
| 8: | t-Bu | H | t-Bu |
| 9: | $CF_3$ | H | $CF_3$ |
| 10: | Me | H | Ph |
| 11: | Ph | H | Ph |

Fig. 1. Keto-enol tautomerism in β-dicarbonyl compounds, with possible structures for the enol forms

bands in the region 3400–3636 cm$^{-1}$ were interpreted as evidence for free and intermolecularly H-bonded OH in enols of 10[12] but the assignments have not been confirmed. *If* a *trans* enol is present in **1** and similar compounds in significant amounts it must be in mobile equilibrium (NMR timescale) with the predominant *cis* form. It is known, however, that the very large chemical shift of the enolic OH̱ is remarkably insensitive to solvents[13] (except for strong bases or solvents that can exchange hydrogen rapidly); Chan *et al.*[4] attributed a small temperature dependent effect in **1E** in butyl ether to ~ 1% of an *inter*molecularly H-bonded form, more likely to be **1Eb** than **1Ec** or **1Ed**. From such evidence it seems that if *trans* or acyclic *cis* enols are present in mobile equilibrium with the cyclic *cis* enol **1Ea** their concentration must be low under most conditions so that **1** can be treated as a simple system **1K** ⇌ **1E** and "enol" will imply Ea (Fig. 1) in the rest of this paper.

*Hydrogen isotope effect on the enthalpy of enolisation of* **1**

Although less sensitive than UV, NMR is probably the best method for measuring the temperature dependence of the equilibrium **1K** ⇌ **1E**. Using $^1$H NMR Thompson and Allred[5] found $\Delta H^\circ$(**1K**-$d_0$) = − 10.0 kJ mol$^{-1}$, in good agreement with other measurements,[14] but the isotope effect was surprisingly large because $\Delta H^\circ$ (**1K**-3,3-$d_2$) = + 0.5 kJ mol$^{-1}$, although the isotope effect on $\Delta G^\circ$ was small. They were unable to explain this unprecedented isotope effect, as were Dahlberg and Long,[15] who found only a small isotope effect on $\Delta G^\circ$(**2K**). It seemed likely that **1**-$d_2$ had not come to equilibrium (the enol content was reported as 19% at 310K and 18.6% at 254K).[5] We found that neither **1**-$d_0$ nor **1**-$d_2$ reached equilibrium in 8 hr at − 20°. Very small amounts of triethylamine greatly accelerated the reactions and ~ 0.01% of the base led to complete equilibration in ≯2 hr at 254K, without any change in the position or breadth of the OH̱ signal in **1**-$d_0$, nor any significant amount of $^1$H–$^2$H exchange in the Me groups in **1**-$d_2$. The equilibrium constants at 3 temperatures (Table 1) were determined from the integrals for the Me peaks and gave $\Delta H^\circ$(**1K**-$d_0$) = − 9.54 ± 0.21 kJ mol$^{-1}$ and $\Delta H^\circ$(**1K**-3,3-$d_2$) = − 8.08 ± 0.21 kJ mol$^{-1}$. The isotope effect, 1.5 ± 0.3 kJ mol$^{-1}$, is clearly much more reasonable in magnitude than the earlier estimate. It cannot at present be related to changes in vibration frequencies because the thorough vibrational analysis of **1E**-$d_1$ and **1E**-$d_2$[16] cannot yet be matched for **1K**.[17]

Since our work was completed[18] Kol'tsov and Ershov[19] (whose work only came to our notice very recently through the index to *Chem. Abs.* **82** (1975)) have reported similar results and conclusions.

*Hydrogen isotope effects on the* $\pi \rightarrow \pi^*$ *absorption band of* **1E**

Relatively few measurements of hydrogen isotope effects on allowed electronic transitions have been made and the reported values are not very large for hydrogens on the ring in benzene (the transition energy for the 0–0 band, 453 kJ mol$^{-1}$, is *raised* by 0.4 kJ mol$^{-1}$ for each $^1$H replaced by $^2$H)[20] or in the side chains of aromatic compounds.[21] This is not surprising because the CH($\sigma$-) bonds are not directly involved in the ($\pi$-) electron systems responsible for the transitions and would not be expected to change in vibration frequency very much between the ground and electronically excited states.

It has been reported[5] that there is no hydrogen isotope effect on $\nu_{max}$ (36,800 cm$^{-1}$ ≡ 440.3 kJ mol$^{-1}$) for **1E** in cyclohexane but that there is a small change in intensity consistent with $K_H > K_D$, although no numerical data were given. When we treated solutions of **1** (~ 10$^{-4}$ M) in aprotic organic solvents with $H_2O$ and with $D_2O$ in parallel experiments at 288K we observed a *large* isotope effect of $\nu_{max}$ (Table 2), the effect being most clearly seen in the difference spectrum (Fig. 2). After several hours both solutions had reached equilibrium and numerical integration showed that the *band areas* were equal to within 1%, although the ratio of extinction coefficients ($\epsilon^D_{max}/\epsilon^H_{max}$) is significantly greater than unity, i.e. there is an isotope effect on the band shape (the band is *narrower* for **1E**-O-d than for **1E**-$d_0$) as well as on $\nu_{max}$. Qualitatively similar results have been found for other cyclic enols, aromatic primary amines and some H-bonded complexes.[22] In experiments with completely enolic analogues of **1** it has been found[22] that there are no significant isotope effects on band areas as such so that the equality of band areas for **1**-$d_0$ and **1**-$d_2$ implies that there is no hydrogen isotope effect on the equilibrium in **1** in several solvents, a result consistent with the $^1$H NMR result for the neat liquid.

The contrast between the present and earlier results[5] for **1** can be explained by the different experimental techniques. Thompson and Allred prepared **1**-$d_2$ and then made up very dilute solutions (~ 10$^{-4}$ M) in cyclohexane

Table 1. Hydrogen isotope effect on the equilibrium **1K** ⇌ **1E**, based on integration of $^1$H NMR signals for the C-methyl groups

| Species | T/K | n$^a$ | K$^b$ |
|---|---|---|---|
| **1**-$d_0$ | 313 | 18 | 3.54 0.05 |
| **1**-$d_2$ | | 11 | 3.77 0.07 |
| **1**-$d_0$ | 273 | 36 | 6.15 0.07 |
| **1**-$d_2$ | | 27 | 5.78 0.10 |
| **1**-$d_0$ | 253 | 42 | 8.42 0.12 |
| **1**-$d_2$ | | 38 | 7.93 0.13 |

**1**-$d_0$: $\Delta H^\circ$ = −9.5±0.4 kJ mol$^{-1}$; $\Delta S^\circ$ = −19.9±1.5 J mol$^{-1}$ K$^{-1}$

**1**-$d_2$: −8.1±0.8 ; −14.9±2.9

$^a$Number of integrals measured after variations had become random.

$^b$Errors quoted are twice the standard error.

Table 2. Hydrogen isotope effects on the long wavelength absorption of 1E

| Solvent | $\bar{\nu}$/cm$^{-1}$ [a] ($\nu_{max}$/cm$^{-1}$)[b] | $\Delta\bar{\nu}$[a] ($\Delta\nu_{max}$)[b] | E[c] /kJ mol$^{-1}$ |
|---|---|---|---|
| Water | 36,470 | 240 | 2.9 |
| | (36,380) | (220) | 2.6 |
| DME-water[d] | 36,360 | 250 | 3.0 |
| (40:60) | (36,420) | (350) | 4.2 |
| DME-water[d] | 36,700 | 270 | 3.2 |
| (99:1) | (36,705) | (350) | 4.2 |
| MeCN-water[e] (99:1) | (36,790) | (260) | 3.1 |
| Cyclohexane[ef] | (36,800) | (305) | 3.6 |
| Vapour[e-g] | (37,760) | (320) | 3.8 |

[a] $\bar{\nu}$ = centroid of band: limits of numerical integration set at absorbances equal to 10% or less of the maximum absorbance.

[b] $\nu_{max}$ estimated by extrapolation of mid-points of horizontal chords: reproducibility of $\nu_{max}$ ~ ±25 cm$^{-1}$ for each solvent but very small residual vibrational fine structure makes $\Delta\nu_{max}$ vary more than $\Delta\bar{\nu}$ from solvent to solvent.

[c] Change of transition energy.

[d] DME = 1,2-dimethoxyethane.

[e] It has not yet been possible to get sufficiently reproducible intensities for numerical integration to be worthwhile.

[f] Cells were "seasoned" with $H_2O$ or $D_2O$.

[g] Saturated vapour at 25°C in 2 mm cells.

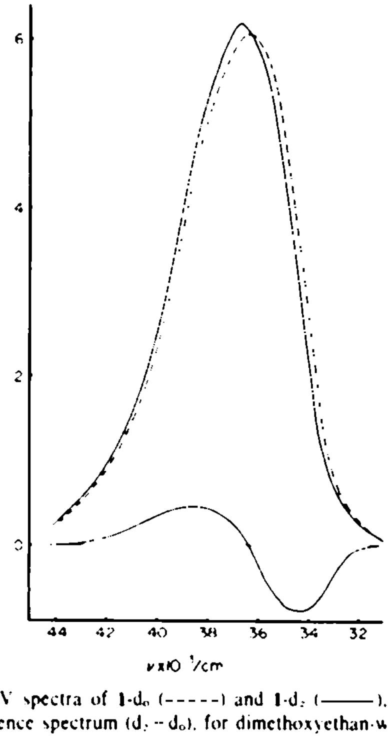


Fig. 2. UV spectra of 1-$d_0$ (-----) and 1-$d_2$ (———), and the difference spectrum ($d_2 - d_0$), for dimethoxyethan-water.

for UV measurements; at such low concentrations only a few μg of $H_2O$ from the atmosphere, solvent or cell walls would have been needed to convert most of 1E–0,3-$d_2$ into 1E-3-d in the spectroscopic cell. When we treated 1 ($\sim 10^{-}$ M in cyclohexane) with a few μl of $D_2O$ in a UV cell there was a fairly rapid change in $\nu_{max}$ from 36,800 to 37,105 cm$^{-1}$, with no further change during several hours, although the intensity stabilised only slowly. In another series of experiments with 1M solutions of β-diketones it was confirmed by $^1$H and $^{13}$C NMR that only the OH proton exchanges rapidly.[1] We conclude that the hydrogen isotope effect on the UV spectrum of **1E** depends almost entirely on the O<u>H</u> and that Thompson and Allred failed to observe an isotope effect in 1E-0,3-$d_2$ because the O<u>D</u> rapidly exchanged with traces of water before the spectrum could be measured.

### *Hydrogen isotope effects on $^1$H and $^{13}$C NMR spectra of* 1E

The NMR resonance of the enolic proton in **1E** is at exceptionally low field (15.8 ppm)† and is insensitive to solvent effects over a wide range of non-polar and moderately polar solvents. More surprisingly the temperature dependence (−0.003 ppm/K at 298K), which cannot be attributed to an equilibrium between inter- and intra-molecularly H-bonded systems,[4] and isotope effect ($\delta^D - \delta^H = -0.58$ ppm at 298K)[4] are very large. Chan *et al.*[4] interpreted the last two observations by a two state system (ΔE = 4.85 kJ mol$^{-1}$ for the protium system) in which the effect of deuteriation is to decrease the energy separation by ~2.4 kJ mol$^{-1}$. The two states were assumed to be the symmetrical (O<u>H</u> at δ = 16.1 ppm) and unsymmetrical (O<u>H</u> at δ = 12.1 ppm) *bond-stretch* isomers of the cyclic *cis* enol (Fig. 1; i and ii), with no isotope effects on the temperature invariant chemical shifts of O<u>H</u> in the two states.

Unfortunately the narrow temperature range used (5–82°C)[4] (278–355K) does not allow a critical test of the two state model because the latter predicts that dδ/dT is almost constant over a rather wide range of temperature near 300K. We found great difficulty in keeping 1 and 2 in solution in a solvent that did not lead to excessive broadening or change in position of the enolic proton signal and could not get below 200K (using chloroform). The results for 1E (200–310K) were almost randomly scattered about a straight line but for 2E there was a

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†At very low concentration in $CCl_4$;[24] there is a small concentration dependence (see also Experimental).

significant curvature, opposite to that expected for 1E using Chan's two state model, for δ(OH) against T (Fig. 3). Neither of these diketones is suitable for NMR over a very wide temperature range and until such a compound can be studied we conservatively conclude that hydrogen chemical shifts do not provide strong evidence for bond stretch isomers i and ii for 1Ea (Fig. 1) that are without precedent.

The $^{13}C$ NMR chemical shifts of the C1(3) nuclei (Fig. 1) in the enols of β-diketones are at very low field (191.3 ppm for 1E) compared with the averages expected for the hypothetical unsymmetrical *cis* enols (i.e. i and iii) with ordinary single and double bonds using additivity relationships and are very sensitive to substituent effects. These chemical shifts have been interpreted as inconsistent with a markedly unsymmetrical hydrogen bridge in the *cis*-enol by Shapet'ko *et al.*,[25] who observed a simple additivity for the substituent effects, covering ~ 30 ppm, of $R_1$ and $R_3$ (Fig. 1) on the chemical shifts of the C1(3) C atoms. We have observed large isotope effects ($\delta^D - \delta^H$ − 0.59 to −0.75 ppm; Table 3) on these chemical shifts when the enolic OH is deuteriated; no other $^{13}C$ chemical shifts through two bonds are commonly −0.1 ppm/D[26] and the large effects for the enols of β-diketones imply that the enol structure is unusually sensitive to molecular vibrations if an equilibrium between two or more forms of the *cis*-enol is ruled out.

### *Isotope effects and the nature of the hydrogen bond in* 1E

The common formula for the *cis*-enol 1E with an unsymmetrical hydrogen bond has little or no experimental basis. The electron diffraction results for 1E[2,3] and 9E[27] exclude any marked inequality in the $O^1$–H and $O^3$–H distances (Fig. 4). This (near) symmetry is in agreement with Shigorin's[28] suggestion of an aromatic structure and with substituent effects on $^{13}C$ chemical shifts,[25] although $^{13}C$ isotope effects on skeletal vibration frequencies have been interpreted as evidence for a small inequality in C–C bond lengths.[19] There is a surprising discrepancy between the two electron diffraction studies of acetylacetone so far as the O···O distance is concerned (238 ± 2 pm,[2] 252 pm[3]). The later workers suggest[3] that the earlier estimate is low and that the error was seriously underestimated but their own measurements are in doubt. Their estimate of the enol content in the gas phase at 290K (97%)[3] is much higher than the directly measured value (91 ± 1%; 298K).[10] Since failure to maintain complete tautomeric equilibrium during vaporisation of the sample (no precautions to prevent this were mentioned)[3] would give a *lower* proportion of enol (80% in the liquid at 298K) and because the O···O distance is greater in 1K than in 1E (the O···O peaks overlap in the radial distribution function) there must be doubt about the value 252 pm[3] for r(O···O) in 1E. A similar criticism does not appear to apply to the earlier work because failure to maintain equilibrium is much less likely at higher temperatures but unfortunately there is disagreement about the gas phase equilibrium at 380 K.† We suggest that the O···O distance in 1E is more likely to be near 238 pm than 252 pm.

Molecular orbital calculations of varying sophistication have reached contradictory conclusions about the symmetry of the hydrogen bonds in 1E and related enols

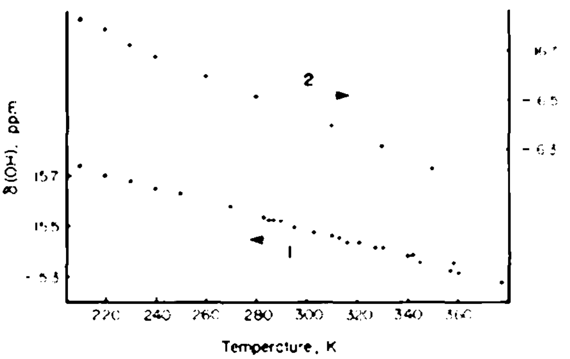

Fig. 3. Temperature dependence of the $^1H$ NMR chemical shift (form internal $Me_4Si$) of the enol proton in 1E (•, this paper; ●, data from Ref. 4, with allowance for the change in internal reference) and in 2E (■).

Table 3. Hydrogen isotope effects on the $^{13}C$ NMR chemical shifts[a] (δ, ppm from $Me_4Si$) of the enols of β-diketones resulting from deuteration of the enol OH (2M in $CDCl_3$) at 300K

| Compound | δ(C1(3)) | δ(C2) | δ, Other C atoms |
|---|---|---|---|
| 1E | 191.28 | 100.44 | 24.76 (Me) |
| 1E-d[b,c] | −0.66 | 0 | 0 |
| 1K | 202.07 | 58.53 | 30.75 (Me) |
| 1K-d[b] | 0 | 0 | 0 |
| 2E[d] | 190.61 | - | - |
| 2E-d[b] | −0.76 | - | - |
| 8E | 201.36 | 90.62 | 39.43 ($\underline{C}Me_3$), 27.40 ($C\underline{Me}_3$) |
| 8E-d[b] | −0.70 | 0 | 0 0 |
| 11E | 185.64 | 92.98 | 4 other lines, no |
| 11E-d[b] | −0.59 | +0.06 | isotope shifts. |
| ( -[e] | 197.76 | 161.74 | 5 lines not assigned) |
| ( -d[b] | −0.06 | −0.22 | no isotope shifts ) |

[a] Digital resolution 0.05 ppm. [b] Isotope shifts quoted. [c] Corrected for incomplete deuteriation. [d] Remaining resonances not assigned except for C=O, 205.39 ppm (isotope shift −0.05 ppm), in 2K. [e] Salicylaldehyde; –CH=O and C-OH only assigned.

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† The value ~90% enol derived[3] from Funck and Mecke[29] must be seriously in error because the latters' work leads to a huge variation of ΔH° with temperature[29] and serious discrepancies with other data (for $\Delta G^\circ_{298}$[30] and ΔH°[31]).

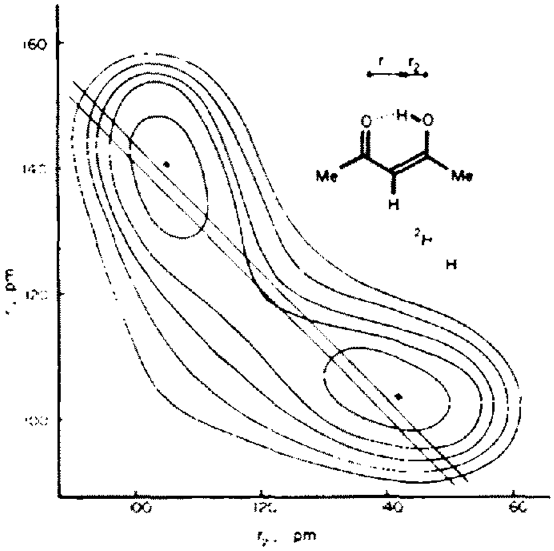

Fig. 4. A qualitative energy surface with two potential energy minima (•) for the O···H···O stretching vibrations in 1E (energy contours are arbitrary) based on *ab initio* calculations[12] for the sections with constant r(O···O) (= $r_1 + r_2$) but with the relative energies for such sections altered to give minima at r(O···O) 242 pm. This general type of energy surface with a saddle point at a *lower* value of r(O···O) than the two minima for strong but unsymmetrical hydrogen bonds leads to a contraction[26] in r(O···O) for $^1$H and to a lesser extent for $^2$H.

such as 3E. The most recent have resolved some of the earlier discrepancies[12] but *ab initio* calculations for the enol of malonaldehyde 3E (1E should be very similar)[12] do not agree.[12,13] The calculations both require that the hydrogen is 20 pm from the line of centres of the O atoms for r(O···O) ≈ 220–260 pm whereas the electron diffraction measurements favour an almost linear hydrogen bond but the difference is not important for our argument.

The *ab initio* calculations show that the most important influence on the magnitudes of the excess charges on the O (negative) and H (positive) atoms in the enol bridge in 3E is the O···O distance, the magnitudes decreasing as r(O···O) increases.[12] This correlates with several properties of the enols 1E–11E:

(a) the *deshielding* effects of large alkyl substituents $R_2$ on the enol OH because steric repulsions between $R_2$ and $R_1$ and $R_3$ force the O atoms closer together (compare δ(OH̲) 1E, 15.8 ppm;[24] 2E, 16.4;[23] 5E, 17.3 ppm;[8] (see also Experimental);

(b) the larger r(O···O) (225 pm)[22]† and the relative shielding of the OH̲ in 9E (δ(OH̲) – 13.0)[14] compared with 1E;

(c) the negative value of dδ(OH̲)/dT for 1E,[4] because the anharmonicity of the low frequency vibration that stretches O···O will make the average value of r(O···O) increase with temperature and so decrease the excess positive charge on the OH̲.

None of these qualitatively explicable consequences of the very strong H-bonds in the *cis*-enols, however, serve to distinguish between a symmetric system and one with two PE minima close together and separated by a low barrier.

If there was a single PE minimum for the enolic H atom in 1E the anharmonicity of the stretching of the O···H···O distance would make the average distance greater for $^1$H than for $^2$H because the amplitude of vibration is larger for $^1$H than for $^2$H (cf. the deuterium isotope effect, 2.4 pm, on the length of the symmetric H-bond in (HFH)$^-$).[25] Such a decrease of r(O···O) in 1E on deuteriation would be expected from the *ab initio* results for 3E to give a greater positive charge on $^2$H than on $^1$H, contrary to the observed isotope effect on the hydrogen chemical shift. A similar contradiction would appear between the substituent effects of groups $R_1$ and $R_3$[24] and of deuteriation of the OH on the $^{13}$C chemical shifts of the C1(3) atoms if deuteriation were to increase r(O···O).

The alternative hypothesis, that there are two PE minima close together for the bridge hydrogen in 1E leads one to expect a *lengthening* of r(O···O) on deuteriation. Such a lengthening of strong unsymmetrical *inter*molecular H-bonds by deuteriation is well known[26] and has been explained by a strongly negative interaction force constant for the symmetric and antisymmetric vibrations of a system A···H···A.[26] The PE surface shown in Fig. 4, essentially based on the *ab initio* calculations for 3E[12] but with the PE minima at larger values of r(O···O), in agreement with the electron diffraction measurements, leads to a simple qualitative picture of the effect of deuteriation on the bond length and related properties of 1E. The individual PE minima, separated by a low barrier, are markedly unsymmetrical and the resulting anharmonicity of the motion of the H atom makes the latters most probable positions nearer to the midpoint of O···O than are the two PE minima. The total energy for such a vibrational motion is lowered by *shortening* r(O···O) from the value for the PE minima,[26] the shortening being greater for $^1$H than for $^2$H. The shortening of r(O···O) will increase the positive charge on the hydrogen, the effect being greater for $^1$H than for $^2$H, in agreement with the observed difference in chemical shifts. If one accepts that the dominant influence on δ(OH̲) in the *cis*-enols is the charge on the hydrogen, which is related to r(O···O),[12] then the difference between 1E (δ – 15.8 ppm,[24] r(O···O) – 238 pm[21]) and 9E (δ = 13.0 ppm,[14] r(O···O) = 255 ppm[22]) are consistent with deuteriation of 1E increasing r(O···O) by 2–3 pm (δ(OH) decreases by 0.6 ppm[4]). This increase in bond length is rather less than the largest changes observed in *inter*molecular H-bonds,[26] as would be expected for the more constrained cyclic system.

The large hydrogen isotope effect for the long wavelength allowed UV transition in 1E, and other enols,[7] could be due either to a large difference in zero point energies between the ground and excited electronic states or to a Frank-Condon effect if the two states differ in geometry significantly for the hydrogen. The first possibility would require an enormous change in vibration frequencies for the hydrogen (the difference in zero point energies for the O–$^1$H and O–$^2$H stretching vibrations in 1E and 1E-$d_1$ is only about 350 cm$^{-1}$) and, e.g. is out of scale with the observed isotope effect on the O–O band of the $^1B_{2u} \leftarrow {}^1A_{1g}$ transition of benzene ( + 30 cm$^{-1}$/$^2$H).[29] It seems more probable that electronic excitation in 1E changes the equilibrium position of the hydrogen in the O···H···O bridge. The observed effect is qualitatively understandable if the ground state has a double minimum and the excited state a single minimum (Fig. 5) so that the lesser probability of finding $^2$H than $^1$H near the centre of the O···H···O bond decreases the probability of tran-

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†9E is essentially completely enolic so that this electron diffraction result cannot be in error from a failure to estimate the enol content accurately, in contrast to 1E.

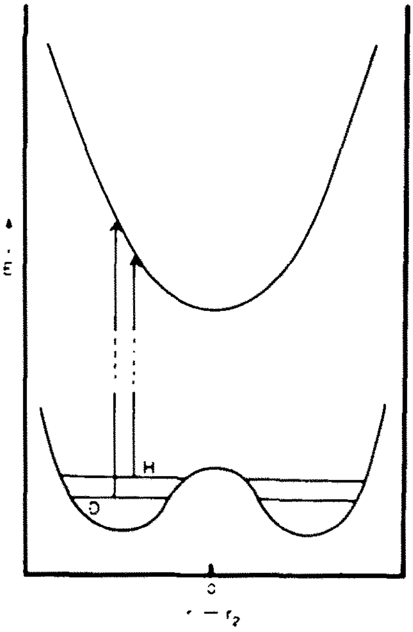

Fig. 5. The difference in the most probable excitation energies for 1E-d₀ (H) and 1E-d₂ (D) resulting from vertical transitions to a single minimum excited state from a double minimum ground state in which the maximum probability for hydrogen is nearer the central saddle point for $^1$H than for $^2$H (Fig. 4). (For clarity the transitions are shown as if taking place between a single section of each potential energy surface, although the difference between $^1$H and $^2$H is in part attributable to a difference between $^1$H and $^2$H is in part attributable to a difference in the mean value of *r*(O···O) Fig. 4.)

sitions to low vibrational states of the excited state and so increases the average transition energy.[†] The isotopic effect on the width of the band is also accounted for because the greater amplitude of vibration of $^1$H than $^2$H also takes the former further out from the centre of the O···O distance. This explanation for the hydrogen isotope effects on the UV absorption of 1E must be regarded as very tentative until more is known about the excited electronic states of such enols.

## EXPERIMENTAL

NMR *spectra.* $^1$H chemical shifts of enolic OH protons were measured with a Perkin Elmer R32 spectrometer (90 MHz, TMS lock and reference), using averages of several spectra scanned in both directions and calibrated with a frequency counter; temperatures (± 1K) were checked with a methanol sample.[1] The base catalysed tautomeric equilibria in 1-d₀ and 1-d₂ were measured on a Perkin Elmer R10 spectrometer (60 MHz, temperatures claimed to be controlled to ± 0.1K, checked as before) using integrals for C Me peaks and the results (Table 1) were based on 10–40 scans after equilibrium had been reached (random fluctuations only in the integrals); normal precautions for integration were observed and a high spinning rate was maintained to prevent spinning side bands coinciding with nearby peaks. Several preliminary runs were made in order to select the concentration of NEt₃ ( 0.01%) that would give equilibration in ≯2 h without a detectable effect on the position or width of the OH resonance (in 1-d₀). FT $^{13}$C spectra were measured with a Brüker WH90 spectrometer (22.63 MHz, $^2$H lock) and Nicolet B-NC 12 computer. FIDs were accumulated in 4K memory addresses and 4K empty addresses were added before Fourier transformation. Isotopic shifts induced by deuteriation of the enol OH were determined from solutions in CDCl₃ which were shaken with known amounts of either H₂O, or D₂O, or mixtures of both (typically 5 moles water/mole diketone): exchange equilibrium was reached in < 1 min. Rapid intermolecular exchange between O–$^1$H and O–$^2$H in 1E gave rise to weighted average $^{13}$C chemical shifts and the isotope shift in Table 3 is corrected for residual $^1$H. Exchange was slower in other instances and the separate C(3) resonances could be observed when mixtures of H₂O and D₂O were used in the exchange.

*UV spectra.* Spectra were measured on a Cary 14 spectrometer with the following precautions. The relative pathlengths of a matching pair of cells (*A*, *B*; 1, 2, 5 or 10 mm) were determined by comparing the absorbances for water and KNO₃ solutions for ordinary "direct" spectra, i.e. solution against solvent, and for difference spectra. Each measurement of an isotope effect involved preparing a solution of 1 in the chosen aprotic organic solvent and then treating aliquots with equal molar amounts of H₂O or D₂O (mixtures prepared by weight) and measuring spectra until both samples (*H* and *D*) had reached equilibrium: the change in $\nu_{max}$ was complete in the first spectrum but the absorbance stabilised only slowly. Eight spectra were then measured as follows:

| | Sample beam | Reference beam |
|---|---|---|
| 1 | Solvent in cell *A* | Solvent in cell *B* |
| 2 | Solvent in cell *B* | Solvent in cell *A* |
| 3 | *H* in cell *B* | Solvent in cell *A* |
| 4 | *D* in cell *B* | Solvent in cell *A* |
| 5 | *D* in cell *B* | *H* in cell *A* |
| 6 | *H* in cell *B* | *H* in cell *A* |
| 7 | *H* in cell *A* | *H* in cell *B* |
| 8 | *D* in cell *A* | *H* in cell *B* |

Spectra 1 and 2 were repeated with cleaning of the cells until they diverged by no more than 0.01 absorbance above some minimum wavelength for each solvent, e.g. 220 nm for dimethoxyethane (DME). Subtraction of 2 from 3 and from 4 gave the ordinary ("observed direct") spectrum of *H* and *D*. Subtraction of the mean of 6 and 7 from the mean of 5 and 8 gave the observed difference spectrum **Δ**. From the absorbance values of these spectra were calculated extinction coefficients $\epsilon_i$ at equal intervals $\delta\nu_i$) and thence "calculated" spectra **H** and **D**:

$$\mathbf{H} = \frac{1}{2}(H + D - \Delta) \qquad \mathbf{D} = \frac{1}{2}(H + D + \Delta).$$

The integrated intensities were then obtained by numerically integrating the spectra **H** and **D** between limits at which $\epsilon$ was a small fraction of $\epsilon_{max}$, e.g. as little as $0.01\epsilon_{max}$ for 1E in DME—water (note that the limits of $\nu$ for integration are *not* the same for **H** and **D**), provided other bands do not overlap. Analogously the centroids, $\bar{\nu}$, were estimated from

$$\bar{\nu} = \int \epsilon_i \nu_i \mathrm{d}\nu \bigg/ \int \epsilon_i \mathrm{d}\nu$$

using the same limits for $\nu$ as for the integrated intensities. The differences between the centroids $\bar{\nu}^H$ and $\bar{\nu}^D$ are both more precisely measurable (using the entire band) and more obviously a measurement of the isotope shifts (there is an isotope effect on the band shape) than the differences in $\nu_{max}$ (determined by visual inspection, with the difference spectrum used merely to confirm qualitatively the existence of an isotope effect,[21] in previous work on isotope effects on broad absorption bands), provided that the band is isolated, as is the case with 1E, so that numerical integration can include essentially the whole band. The use of the observed difference spectrum, which has a lower absolute noise level than either direct spectra separately, to constrain the difference between the "calculated" spectra is superior to previous methods for estimating isotope or other small effects on broad absorption bands, particularly for very small changes in $\nu_{max}$.[22]

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[†] Qualitatively similar but smaller hydrogen isotope effects have been observed for aromatic amines,[22] in which the pyramidal nitrogen atom becomes planar, or nearly so, in the excited state

*Compounds and solvents.* All the compounds used were redistilled or recrystallised commercial samples. The $^1$H NMR signal of the OH in 1E (1M in CDCl$_3$) remained broad after repeated distillation of 1 but was reduced to 1–2 Hz, with $\delta = 15.5$ ppm (see Ref. 24 for the small concentration dependence of this chemical shift), by drying over a molecular sieve (Linde Type 4A) followed distillation from fresh molecular sieve in dry N$_2$ at 15 mm pressure and finally dissolving 1 in CDCl$_3$ and distilling the solution from molecular sieve in a vacuum line. When such a solution was treated with a trace of water the OH resonance broadened and moved to higher field, showing that the very broad resonances that have sometimes been reported, e.g. $w_{1/2} = 18$ Hz, $\delta = 15.0$ ppm,[25] were caused by intermolecular exchange with water, not with other molecules of the enol 1E. Solvents were spectroscopic grades except for DME, which was stored over sodium for several weeks before distillation from LiAlH$_4$ under N$_2$.

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