

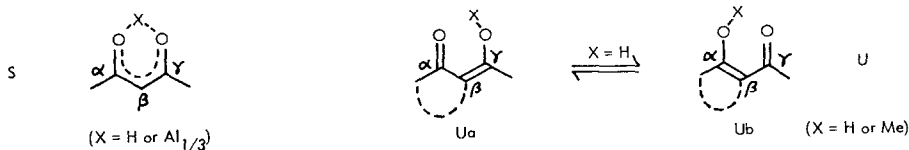
CARBON-13 N.M.R. EVIDENCE FOR AN UNSYMMETRICAL HYDROGEN BOND IN THE CIS-ENOLS OF β -DIKETONES

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Abstract. Comparison of ^{13}C chemical shifts for enols of β -diketones with those for aluminium complexes and enol ethers shows that the enols are unsymmetrical.







THERE has been a conflict of evidence as to whether the cis-enol of a β -diketone such as acetyl-acetone, $\text{CH}_3\text{C}(\text{O})\text{CH}=\text{C}(\text{O})\text{CH}_3$, has a symmetrical structure (S), following Shigorin's suggestion (1) that it is a quasi-aromatic species, or is an equilibrium between two unsymmetrical 'classical' structures ($\text{U}_a \rightleftharpoons \text{U}_b$). The remarkable deshielding of the C_α and C_γ carbon atoms in U_E (compared with that calculated for an unperturbed hydroxy unsaturated ketone) is consistent with considerable delocalisation but does not in itself establish a symmetrical structure.



Shapetko concluded (2) from a study of substituent effects on carbon-13 chemical shifts in acyclic β -diketones that the cis-enols are essentially symmetrical as in S (although he has since used other n.m.r. data as evidence for the unsymmetrical structure $\text{U}_a \rightleftharpoons \text{U}_b$ (3)). This was in agreement with, eg, electron diffraction studies (4) but not with, eg, isotope effects on skeletal vibration frequencies (5); most of the evidence has been reviewed recently (6).

In contrast to the uncertainty about the cis-enols of β -diketones, malondialdehyde (7) and β -ketoaldehydes (8) are accepted as having unsymmetrical cis-enols, in which the equilibrium $\text{U}_a \rightleftharpoons \text{U}_b$ is very sensitive to substituent effects, particularly if C_α and C_β are made part of a ring (8). It appeared likely that the large, approximately additive, substituent effects on carbon-13 chemical shifts, δ , in cis-enols observed by Shapetko (2) could be explained mainly as substituent effects on the equilibrium $\text{U}_a \rightleftharpoons \text{U}_b$ because it is expected that C_α will be deshielded relative to C_γ in U_a and vice versa in U_b (9). We have compared a series of β -dicarbonyl compounds (10) with their aluminium complexes (exemplifying compounds with the symmetrical structure S) (11) and, where possible (12), enol methyl ethers (as models for U_a or U_b). Only the C_α and C_γ -carbon atoms show large and consistent changes in δ with structure which are quoted in Table 1 (10). From these values we have calculated changes ($\Delta\delta$) in δ , resulting from converting an enol into an aluminium complex ($\text{E} \rightarrow \text{A}$) or into an enol ether ($\text{E} \rightarrow \text{M}$), and the overall change ($\Sigma\Delta\delta$) (Table 2). The assignments of resonances for the β -ketoaldehydes were simple (CW off resonance decoupling). Proton coupled spectra were used to distinguish the $\text{CO}-\text{CH}_3$ from the ring CO resonances in the enols $\underline{3E}$ and $\underline{6F}$. This failed for the aluminium complexes, however, because the presence of diastereomeric complexes in solution split each

TABLE 1. Chemical shifts δ^a (p.p.m. downfield from SiMe_4) for $\text{C}\alpha$ and $\text{C}\gamma$ in the cis-enols of β -dicarbonyl compounds (E), their aluminium complexes (A), and enol methyl ethers (M) (in chloroform as solvent at 300K).

Compound	$\text{C}\alpha$			$\text{C}\gamma$		
	E	A ^b	M	E	A ^b	M
1. 	191.28	191.44	197.16	191.28	191.44	168.09
2. 	210.32	205.84	207.90 ^c 176.71 ^d	159.38	179.36	154.48 ^c 186.00 ^d
3. 	205.03	197.32	-	175.80	187.39	-
4. 	209.83	206.29	208.32 ^c 179.09 ^d	151.85	169.63	149.96 ^c 183.62 ^d
5. 	184.90	193.38	200.17 ^c 171.51 ^d	187.56	181.08	157.41 ^c 189.45 ^d
6. 	182.05	188.87	-	198.94	191.87	-

^aDigital resolution 0.054 p.p.m.

^bAverage of four transitions: uncertainty ~ 0.1 p.p.m.

^cCorresponds to enol Ua.

^dCorresponds to enol Ub

carbonyl resonance into four components (one for the symmetrical diastereomer, three for the unsymmetrical) (13) leading to unresolved multiplets in proton coupled spectra. The close parallel between corresponding changes in related formyl- and acetyl-ketones, however, leaves no reasonable doubt about the assignments for the aluminium complexes 3A and 6A.

The changes in chemical shifts $\Delta\delta$ in going from the enols to the aluminium complexes (E \rightarrow A) are notable for the following reasons:

- The values of $\Delta\delta$ for 2-6 (E \rightarrow A) are large and opposite in sign for $\text{C}\alpha$ and $\text{C}\gamma$ in each instance: this excludes a basically symmetrical enol S and requires both a significant difference between Ua and Ub and an equilibrium constant $K \neq 1$ (acetylacetone, 1, is uninformative because $K \equiv 1$ and S and Ua \rightleftharpoons Ub become indistinguishable on this basis).
- The values of $\Delta\delta$ for corresponding carbon atoms are opposite in sign for five- (2-4) and six- (5,6) membered ring compounds, and are consistent with Garbisch's generally accepted conclusion that Ua is favoured for 2E and Ub for 5E (8).

Using the $\Delta\delta$ and $\Sigma\Delta\delta$ values semiquantitatively we may define the unsymmetrical enol structures Ua and Ub more closely. In the five-membered ring compounds 2-4 the relatively large angle between the C-O bond vectors enforced by the ring makes the hydrogen bond relatively long (~ 275 nm (14) compared with 252 nm in 1E(4)) and weak (15). The five-membered ring,

TABLE 2. Changes ($\Delta\delta$) and sums of changes ($\Sigma\Delta\delta$) of the chemical shifts of atoms C α and C γ in the reactions E \rightarrow A and E \rightarrow M for compounds 1-6 in Table 1.

Reaction	$\Delta\delta$		$\Sigma\Delta\delta$		$\Delta\delta$		$\Sigma\Delta\delta$
	C α	C γ			C α	C γ	
1. E \rightarrow A	+0.16	+0.16	+0.32	E \rightarrow M	+5.88 ^a	-23.19 ^a	-17.31
2.	-4.48	+19.98	+15.50		-2.42 ^b	-4.90 ^b	-7.32 ^b
3.	-7.71	+11.59	+3.88		-33.61 ^c	+26.62 ^c	-6.99 ^c
4.	-3.54	+17.78	+14.24		-	-	-
5.	+8.48	-6.48	+2.00		-1.51 ^b	-1.89 ^b	-3.40 ^b
6.	+6.82	-7.07	-0.25		-30.74 ^c	+31.77 ^c	+1.03 ^c
					+15.27	-30.15	-14.88
					-	-	-

^aData from the cis-enol ether; data for the trans-isomer is similar

^bEnol and enol ether both correspond to Ua

^cEnol is Ua(X=H) but enol ether is Ub(X=Me)

moreover, strongly favours Ua over Ub, the extreme example being 4E (8), so that the enol ethers 2M and, particularly, 4M are rather good models for the enols 2E and 4E. The consequences are:

- The sum ($\Sigma\Delta\delta$) of the $\Delta\delta$ values for the change E \rightarrow M in 2 and in 4 are relatively small because either the $\Delta\delta$ s are small (the ether being a good model for the enol) or the $\Delta\delta$ s are large (~ 30 p.p.m.) and similar in magnitude but opposite in sign (the change from UaE to UbM in effect 'exchanging' the enol and carbonyl carbon atoms).
- The $\Delta\delta$ values for the formation of the aluminium complexes (E \rightarrow A) are opposite in sign but very unequal in magnitude for C α and C γ in 2E and 4E and $\Sigma\Delta\delta$ is strongly positive, as is to be expected if there is a large deshielding due to delocalisation in the complexes but little in the enols (16).

The $\Delta\delta$ and $\Sigma\Delta\delta$ values for the corresponding conversions of open chain and (relatively unstrained) six-membered ring compounds 5E and 6E (10) complement those for the five-membered ring compounds. These values show little or no net gain in deshielding for the change E \rightarrow A ($\Sigma\Delta\delta$ is small) but a large net shielding for E \rightarrow M (with loss of delocalisation) for 1 and 5. Thus the enol ethers are relatively poor models for the enols in these instances. This strongly suggests that there is considerable delocalisation in the enols of 1, 5, and 6, and most other β -diketones that form cis-enols (10), although the $\Delta\delta$ values for E \rightarrow A for 5 and 6 (and other nearly strainfree systems) show that these enols are not fully symmetrical, as in S. All but one of the spectra were measured on a Bruker WH90 pulsed FT spectrometer operating at 22.63 MHz, using chloroform solutions that were 2M in the β -diketone or (mixture) of enol methyl ethers and usually about 0.5-1M in the aluminium complexes (the chemical shifts were shown to be insensitive to changes in concentration in several instances).

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9. See, eg, J.B. Stothers, Carbon-13 NMR Spectroscopy, Academic Press, New York and London, 1972, p. 337.
10. For economy in space data is given only for compounds 1-6; data for other β -diketones we have studied does not add to or alter our present conclusions.
11. The choice of diamagnetic metal is unimportant for the carbon-13 chemical shifts of complexes of β -diketones; see, eg, J.C. Hammel and J.A.S. Smith, J. Chem. Soc. (A), 1970, 1855.
12. Diazomethane reacted with 1, 5, and some other relatively strain-free β -formylcycloketones to give single enol methyl ethers UaM; the ketones 3 and 6, however, failed to react with diazomethane or with many other methylating reagents. The five-membered ring β -formylketones 2 and 4 gave both enol ethers UaM and UbM with diazomethane.
13. These resonances often appeared as single bands in ordinary wide sweep spectra used to determine chemical shifts but all were resolved into four lines, spanning up to 0.4 p.p.m. in narrow sweep (eg, 500 Hz) spectra.
14. Calculated from accepted bond lengths and bond angles assuming a planar molecule.
15. The weakness of the hydrogen bonds in 2-4 is shown in several ways, eg, the shielding of the OH protons compared with those in 1, 5, 6, and many other β -diketones; the rapid intermolecular exchange of the OH; and in 4E by the presence of intermolecular hydrogen bonding (8).
16. 2-Acetylcyclopentanone 3 is intermediate in behaviour between the strained β -formylketones 2 and 4 and the unstrained β -dicarbonyl compounds such as 1, 5, and 6, and requires further study.

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