The O–D Out-of-plane Deformation of Enolized β-Dicarbonyl Compounds

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Summary The O–D out-of-plane deformation of enolized β-dicarbonyls is a useful indication of the strength of intramolecular hydrogen-bond systems.

THE strength of intramolecular hydrogen bonding in β-dicarbonyl compounds has been discussed in terms of the frequency shift of the carbonyl stretching vibration and the chemical shift of the enolic proton.[1-3] There are some difficulties in determining the strength of the hydrogen bond from the vibrational spectrum.[3] The hydroxyl stretching vibration exhibits a broad, weak band in the region of 2500—3000 cm^{-1}, and it is extremely difficult to define its centre. The C=O stretching is strongly perturbed by the C=C stretching vibration. The in-plane deformation of the hydroxy-group does not show a clear absorption, because of the superposition of the C–O stretching and the CH_3 bending deformation. Further, the hydroxyl out-of-plane deformation, π(OH), appears usually as a shoulder band or a hidden band at around the same frequency as the strong methyl rocking absorption or the in-plane C–H deformation and the skeletal deformation of the aryl groups. Thus, the ν(OH) and π(OH) frequencies are not available for the purpose of present study (*cf. o*-substituted phenols.[5])

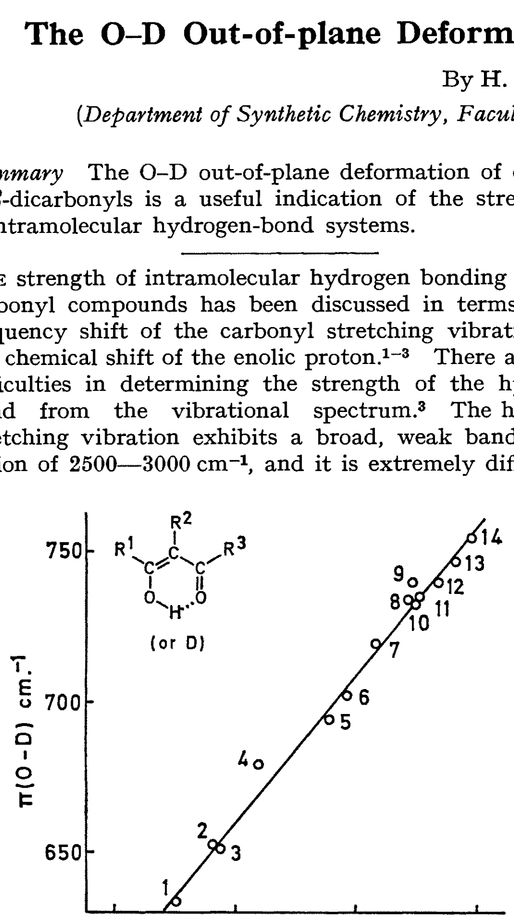

FIGURE. *Plot of* π(O–D) *frequencies against chemical shifts of the enolic protons.* 1. *Hexafluoroacetylacetone.* 2. *Methyl α-phenylthioacetoacetate.* 3. *Ethyl α-phenylthioacetoacetate.* 4. *Trifluoroacetylacetone.* 5. 3-*Chloropentane*-2,4-*dione.* 6. *Acetylacetone*-(*pentane*-2,4-*dione*). 7. *Benzoylacetone.* 8. 3-*Cyanopentane*-2,4-*dione.* 9. 3-*Nitropentane*-2,4-*dione.* 10. *Dibenzoylmethane.* 11. 3-*Methylthiopentane*-2,4-*dione.* 12. 3-*Acetylpentane*-2,4-*dione.* 13. *Tetra-acetylethane.* 14. 3-*Methoxycarbonylpentane*-2,4-*dione.*

The O–D out-of-plane deformation may be used to evaluate the strength of an intramolecular hydrogen bond in β-dicarbonyl compounds. Deuteriation of the enolic proton was easily performed by shaking with D_2O or CH_3OD. The π(OD) absorption was observed as a new band in the range 580—750 cm^{-1}. The Figure shows a plot of the frequency of π(OD) in CS_2 against τ_{OH} in CCl_4. This linear relationship indicates that formation of the stronger intramolecular hydrogen bond results in a higher frequency-shift of π(OD) and a lower magnetic-field shift of τ_{OH}.

Miyazawa and Pitzer[4] have reported the relationship between the torsional force-constant and the double-bond character of the C–O bond for formic acid. The O–D out-of-plane deformation can be expressed as a torsional vibrational mode around the C–O bond of the enolic ring.[5] Therefore, this frequency mode should be related to the double-bond character of the C–O bond) being dependent upon the extent of delocalization of the π-electrons of the enolic ring. Thus, the linear relationship between the frequency of π(OD) and τ_{OH} suggests that the intramolecular hydrogen bond is closely associated with π-conjugation of the enolic ring. The *X*-ray crystallographic study of tetra-acetylethane[6] shows that a symmetrical hydrogen bond and two effectively equal C–O bonds are formed. The deuteriated compound exhibits a high π(O–D) frequency at 747 cm^{-1} as expected, its π(OH) probably being hidden by the strong absorption at around 1000 cm^{-1}. The relationship demonstrated provides an alternative and more reliable indication of the strength of intramolecular hydrogen bonds in β-dicarbonyl compounds, such as β-triketones, β-diketones, and β-keto-esters.

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