^{17}O N.M.R. Studies of Enol and Phenol Compounds with Intramolecular Hydrogen Bonds

Vyacheslav V. Lapachev,* Il'ya Ya. Mainagashev, Svetlana A. Stekhova, Martin A. Fedotov, Viktor P. Krivopalov, and Vladimir P. Mamaev

Institute of Organic Chemistry, Siberian Division of the Academy of Sciences, Novosibirsk 630090, U.S.S.R.

The natural abundance 40.67 MHz ^{17}O n.m.r. spectra of enol and phenol (naphthol) compounds with intramolecular hydrogen bonds are reported and the chemical shifts of the chelated hydroxy groups are assigned.

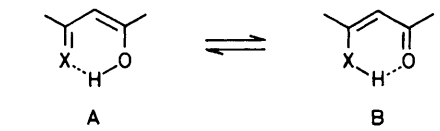
The fast 1,5-sigmatropic A $\rightleftarrows$ B tautomerism shown by six-membered enol chelates with intramolecular hydrogen bonds is one of the most common types of tautomeric interconversion.[1,2] These equilibria should be amenable to study by ^{17}O n.m.r. spectroscopy, which provides a reasonably wide range of chemical shifts.[3] However, the available ^{17}O n.m.r. data for enol compounds are controversial and do not allow the range of shifts of enol oxygen to be established. In the 1960's, the spectra of a number of highly enolised β-dicarbonyl compounds were reported,[4] but only the averaged position of the oxygen signals was obtained, since the fast A $\rightleftarrows$ B equilibrium made it impossible to obtain hydroxylic oxygen shifts. This information may be obtained from the spectra of β-ketoesters, which show no enolisation of ester groups and, consequently, no fast exchange. Lambert and Wharry have recently reported the ^{17}O n.m.r. spectra of ethyl acetoacetate (**1**) analogues.[5] They did not, however, take into account the presence of two tautomers in the mixture (K $\rightleftarrows$ E), which makes their assignment of signals doubtful.

We report here the ^{17}O n.m.r. signals for the chelated hydroxy groups of the enol and phenol (naphthol) compounds (**1**)—(**12**).

In the ^{17}O n.m.r. spectra of ethyl acetoacetate (**1**) (Figure 1), the signals of the keto and enol forms may be easily differentiated by their intensities; as shown by ^{1}H n.m.r. spectroscopy, the content of the keto and enol tautomers is 92 and 8%, respectively. Further assignments have been made in accordance with ref. 6 and are in good agreement (see Figure 1) with the data for ethyl benzoylacetate (**2**) (17% of enol) and the trifluoroacetoacetate (**3**) (>90% of enol).

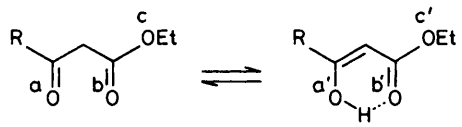
As seen in the case of the enols (**1**)—(**3**), the signal position of hydroxylic oxygen is sensitive to the neighbouring group R. By contrast, in the (2-hydroxyphenyl)-di- and tri-azines the δ_{OH} value is almost independent of the nature of the chelate's basic moiety. For these chelates the δ_{OH} value remains practically constant (90—97 p.p.m.), in spite of considerable variations in the basicity of the azine fragment. Very similar δ_{OH} values (85—90 p.p.m.) are also shown by phenol chelates with a carbonyl group as the basic fragment.[7] Therefore, in spite of considerable variations in the structure of the six-membered chelate [(2-hydroxyphenyl)-di- and tri-azines; *o*-hydroxyacetophenones[7]], the δ_{OH} range of phenolic oxygen is comparatively narrow (85—97 p.p.m.). In related chelates of the enol type the δ_{OH} range is wider (95—125 p.p.m.), however.

Reuben and Samuel[8] have assigned the signal at 315 p.p.m.



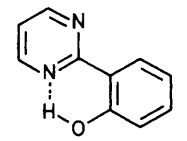
A B

X = O, NR, S

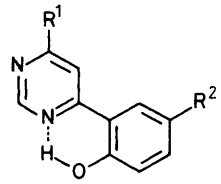


K E

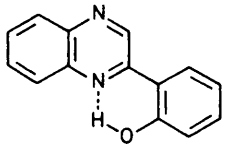
(1) R = Me
(2) R = Ph
(3) R = CF_3



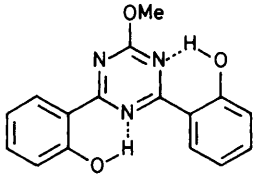
(4)



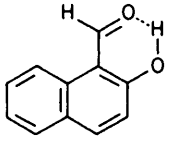
(5)–(9)



(10)



(11)



(12)

^{17}O N.m.r. chemical shifts in p.p.m.

Compound	δ_{OH}
(4)	96
(5) R^1=H, R^2=H	94
(6) R^1=H, R^2=Br	95
(7) R^1=H, R^2=OMe	90
(8) R^1=Cl, R^2=H	95
(9) R^1=NEt_2, R^2=H	97
(10)	95
(11)	97
(12)	95

to the hydroxy group of 1-phenylazo-2-naphthol (see also ref. 9). However such a strong shift of the signal could not be induced by hydrogen bonding or annelation, as illustrated by our ^{17}O n.m.r. studies of the naphthol (**12**); the shift of the hydroxy group is almost unaffected by annelation. The signal at 315 p.p.m.[8] seems therefore to be that of the hydroxylic and keto oxygens of the hydroxy and oxo tautomers of 1-phenylazo-2-naphthol averaged by fast exchange. Comparison of our data (95—125 p.p.m. range) with the enol chemical shifts (−40 to +40 p.p.m.) adopted by Gorodetsky[4] suggests that his results (see also ref. 10) on the enol–enol tautomerism of β-diketones need to be revised. The disagreement between our signal assignment for ethyl acetoacetate and that by Lambert and Wharry[5] might be due to the lower sensitivity of their instrument.

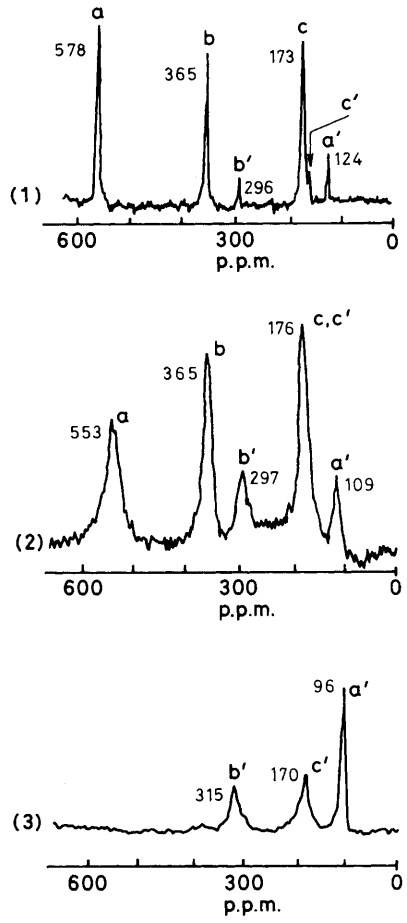


Figure 1. ^{17}O N.m.r. spectra of ketoesters (**1**)—(**3**) in $CHCl_3$ at *ca.* 300 K (Bruker CXP-300 spectrometer 10^4—10^6 scans, chemical shifts in p.p.m. downfield from external H_2O).

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