Spectroscopic Study of Keto–Enol Tautomerization in Phenol Derivatives

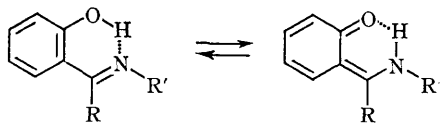
By GERALD O. DUDEK and EMILY PITCHER DUDEK

(*Departments of Chemistry: Harvard University, Cambridge, Mass.* 02138, *and Wellesley College, Wellesley, Mass.* 02181)

PROTON magnetic resonance investigations of ^{15}N-substituted Schiff bases derived from β-diketones and substituted naphthols have been useful in evaluating imine–amine equilibria.[1] It is therefore of interest to determine the equilibrium in benzene derivatives, particularly since

[1] G. O. Dudek and E. P. Dudek, *J. Amer. Chem. Soc.*, 1964, **86**, 4283.

the second form (Ib) is a quinoid structure without the "defect aromaticity" present in the naphthalene and anthracene compounds.[2,3]



(a) (b)

(I) R=R'=Me
(II) R=Me, R'=Ph
(III) R=H, R'=Ph

At room temperature, the p.m.r. spectrum of *o*-([^{15}N]-methylacetimidoyl)phenol (I; R = R' = Me) possesses a broad singlet (about 17 c./sec. wide) for the low-field proton signal (δ = 16·5 p.p.m.)[4] in both chloroform and methylene chloride solutions. As the sample temperature is lowered, the low-field signal splits into a doublet from spin-coupling to the ^{15}N-nucleus. This indicates an appreciable contribution from the second tautomer (Ib). At 0°, J_{obs} is 21·0 c./sec. and at −50°, the observed coupling is 32·4 c./sec. in chloroform solution. If $J(^{15}N–H)$ is assumed equal to 88 c./sec.,[1] then the proton is on nitrogen about 1/3 of the time. Using the computational procedure of Part VII,[1] $-\Delta H$ for the equilibrium is $1{\cdot}5_0$ kcal./mole in chloroform and $1{\cdot}4_8$ in methylene chloride solution. Extrapolating the lower-temperature data back to room temperature, the calculated ^{15}N–H spin coupling is about 17 c./sec. The discrepancy between the observed and calculated values can be attributed to some intermolecular proton exchange at room temperature. This point is being investigated.

When methanol is the solvent for (I), the acidic proton resonance is broadened by intermolecular exchange with the solvent at room temperature and accordingly cannot be observed. However, at −46°, exchange with the solvent is negligible and J_{obs} is 68·2 c./sec. (δ = 16·67 p.p.m.). Therefore in hydroxylic solvents, the quinoid form predominates.

With *o*-([^{15}N]-phenylacetimidoyl)phenol, the spectra indicate that the proton residence time on nitrogen is greatly reduced so that tautomer (IIa) (R' = Ph, R = Me) predominates. In chloroform solution, even at −40°, the acidic proton signal is only a broadened singlet (about 2·4 c./sec. wide), and the resonance is at appreciably higher fields as compared to the methyl derivatives (δ = 15·0 p.p.m.).

The salicylaldehyde adduct, *o*-([^{15}N]-phenylformimidoyl)phenol is also completely in the enol–imine form (IIIa, R' = Ph, R = H) with no p.m.r. evidence for the existence of any keto–amine tautomer.[5] However at 0° in ethanol solution, J_{obs} is 13·1 c./sec., indicating the presence of about 15% of the non-aromatic form. Regrettably the solubility of many of these compounds in alcohol is low. The effect of hydroxylic solvents on the equilbrium therefore cannot be completely determined by p.m.r. spectroscopy. However, the data on hand indicate that hydrogen-bonding solvents markedly stabilize the quinoid form.

The u.v. data of Kazitsyna, *et al.*[6] is supported by the evidence presented here. The band observed at 396 mμ for (I) is due to the quinoid form, and we can now estimate ϵ_0 for this compound as 5900.

These results are best interpreted in light of the detailed *X*-ray-crystallographic analysis of salicylic acid.[7,8] The structural data "suggests that the quinoid structure is the major valence-bond structure contributing to the overall resonance state of the molecule." The hydrogen bond of salicylic acid in solution is weak compared to the other *ortho*-substituted phenols such as salicylaldehyde, *o*-hydroxyacetophenone, *etc.*[9]

Since the *X*-ray results indicate that salicylic acid is largely quinoid, and the p.m.r. results presented here indicate that phenols such as (I) and (II) are largely quinoid, it therefore may be a better approximation to regard *all* phenols with *strong* hydrogen bonds as quinoids than to regard them as benzene derivatives. Obviously the amount of non-aromatic form will depend upon both compound and solvent, with the *o*-hydroxyacetophenone Schiff-bases in alcohol solution being

[2] S. M. Bloom and R. F. Hutton, *Tetrahedron Letters*, 1963, 1993.
[3] I. M. Hunsberger, *J. Amer. Chem. Soc.*, 1959, **72**, 5626.
[4] In p.p.m. down-field from internal tetramethylsilane. See Ref. 1 for details.
[5] L. J. Charatte, *Spectrochim. Acta*, 1963, **19**, 1275.
[6] L. A. Kazitsyna, *et al.*, *Doklady Akad. Nauk. S.S.S.R.*, 1959, **125**, 807; *J. Gen. Chem. U.S.S.R.*, 1961, **31**, 286.
[7] W. Cochran, *Acta Cryst.*, 1953, **6**, 260.
[8] M. Sundaralingam and L. H. Jensen, *Acta Cryst.*, 1965, **18**, 1053.
[9] The strength of the hydrogen bond is used as a measure of the extent of tautomeric interaction, G. Dudek, *J. Org. Chem.*, 1965, **30**, 548.

the most quinoid of the compounds being considered here.

Other ^{15}N-Schiff bases derived from phenols are under investigation and will be reported in detail later.

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