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# ESTIMATION OF AZO - HYDRAZO TAUTOMERIC EQUILIBRIUM IN ORTHO-HYDROXY-AZOCOMPOUNDS BY N.M.R.

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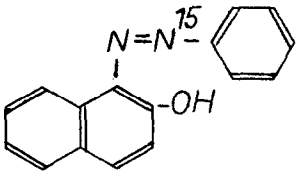
N.M.R. spectroscopy has recently been used [1] for a solution of the old problem of azo - hydrazo tautomerism in ortho and para hydroxyazocompounds. Nevertheless similarly with UV [2] and IR [3] studies only qualitative and unreliable results have been received on this problem, viz. that azophenols are true azocompounds, azonaphthols are mixtures of the tautomeric forms or pure hydrazones, and azoanthrols and azopyrazolones are pure hydrazones, and tautomeric equilibrium is solvent and temperature dependent in some cases.

For estimation of the azo-hydrazo equilibrium constant we propose to use N.M.R. spectroscopy of the azocompounds containing $N^{15}$ isotopes in their molecule. The spin of the $N^{15}$ nucleus is 1/2, therefore no magnetic quadrupole moment is present. Furthermore, the $N^{15}$ - H spin coupling constant is known, so that if presumption of the fast intramolecular exchange of the protone between azophenol and quinone forms is fulfilled, direct calculation of the tautomeric equilibrium constant $K = \frac{[azo]}{[hydrazo]}$ is possible from the equation[4,6]

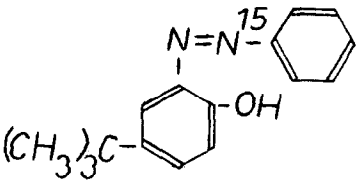
$$K = \frac{J_{N^{15}-H} - J_{obsd.}}{J_{obsd.}}$$

where $J_{N^{15}-H}$ is true spin coupling constant [x] and $J_{obsd.}$ is observed spin coupling in the studied system.

In this preliminary communication we give results of such N.M.R. study of 1-phenylazo-2-naphthol (I) and 2-hydroxy-5-tert.butylazobenzene (II) in a few solvents.




I




II

The both compounds were prepared by coupling of benzenediazonium chloride (95 % isotopic purity) with β-naphthol and para tert.butylphenol. The results are given in the table 1. From a plot of ln K vs. 1/T, $-\Delta H$ value of 1-phenylazo-2-naphthol in $CH_2Cl_2$ has been obtained over the range of 148°C, $-\Delta H$ = -0.69 Kcal/mole.

Calculations of the equilibrium constant and % of hydrazones have been carried out under presumption that proton in hydrazones is bonded to $N^{15}$ atom only and that there is no a long - range spin - spin coupling between $N^{15}$ nucleus and the proton of the hydroxyl group. Justification of such calculation is supported by results of N.M.R. study of $N^{15}$ Schiff bases [6], where such long-range spin - spin coupling has not been observed and $J_{N^{15}-H}$ constant has been 88 cps too. Safe conclusions will be given after N.M.R. study of the compounds where the both atoms of the azogroup are isotopes $N^{15}$. Such compounds are now being prepared.

Other $N^{15}$ - azocompounds derived from phenols, naphthols, anthrols, and pyrazolones are under investigation together with the study of effect of temperature, solvent and substituents on the value of the azo-hydrazo tautomeric equilibrium.

x $J_{N^{15}-H}$ has generaly various values [5,6], $J_{N^{15}-H}$ may vary somewhat with NH bond length and hybridization of the nitrogen, 88 cps yielded the most linear

plot of ln K vs. 1/T (100, 90, 88 and 86 cps were tried). Effect of solvents on $J_{N15-H}$ can be expected to cause max. error 5 % in K and hydrazone resp.[7].

Table 1.

| compd. | solvent | temp. °C | $J_{N15-H}$ obsd. cps | K = [azo]/[hydrazo] | % hydrazo |
|---|---|---|---|---|---|
| 1-phenylazo-2-naphthol | $CH_2Cl_2$ | + 29 | 58.5 | 0.505 | 66.3 |
| | | + 22 | 60.0 | 0.467 | 68.0 |
| | | + 12 | 61.3 | 0.435 | 69.7 |
| | | + 1 | 63.7 | 0.382 | 72.1 |
| | | - 32 | 68.9 | 0.278 | 78.2 |
| | | - 52 | 72.4 | 0.216 | 82.1 |
| | | - 72 | 76.6 | 0.149 | 86.8 |
| | | - 92 | 79.9 | 0,101 | 91.0 |
| | | -107 | 81.8 | 0.076 | 93.0 |
| | | -119 | 83.6 | 0.053 | 95.0 |
| | $CDCl_3$ | + 20 | 65.0 | 0.354 | 73.8 |
| | $CCl_4$ | + 20 | 51.0 | 0.725 | 57.0 |
| | $(CH_3)_2SO$ | + 20 | 60.0 | 0.467 | 68.0 |
| 2-hydroxy-5-tert.butyl-azobenzene | $CH_2Cl_2$ | + 20 | -80 2 | | 2.2 |
| | $(CH_3)_2SO$ | + 20 | 0 | | 0 |
| | $C_2H_5OH$ 95 % | - 10 | 2 | | 2.2 |

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