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THE NON-AROMATIC CHARACTER OF PHENYL OSAZONES AND OTHER bis-PHENYLHYDRAZONES

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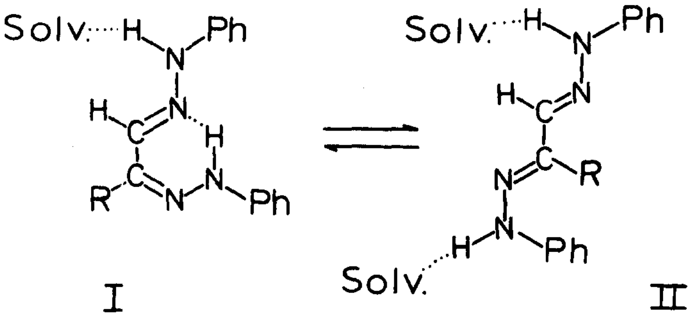
In the recent literature reports have appeared which suggest that the phenyl osazones which have chelate structures are non-classical aromatic systems (1,2) in which π-electron delocalization is achieved through the hydrogen bond (2). Evidence cited for this contention includes (1) the two dimensional X-ray crystal structure of xylose p-bromophenyl osazone which shows that five atoms of the chelate ring (hydrogen is not located) and the two p-bromophenyl groups are planar (3) and (2) polarographic studies which are said to indicate an energy difference of about 10 kcal/mole between chelate phenyl osazones and methyl phenyl osazones which cannot form chelates (1,4,5). We do not find these observations compelling, and we wish to point out that evidence is available which clearly shows that the chelate isomers of the phenyl osazones are not aromatic systems.

An equilibrium between chelate and non-chelate isomers of the phenyl osazones and other bis-phenylhydrazones is established on standing in dimethyl sulfoxide solution (6). The non-chelate form has been assigned structure II (6). The composition of the equilibrium is a function of the size of R. When R = H or CH_3, the non-chelate form is the only species which is observed. As the size of R is increased, repulsion between R and the syn NHC_6H_5 group becomes important and I is favored (6). When R = CH_2OH,



the ratio of I:II is about 1:1; for R = $(CHOH)_nCH_2OH$ (n= 1,2, or 3) the ratio is about 4:1 and for R = C_6H_5 I is essentially the only isomer observed (6). In dimethyl sulfoxide solution the non-chelate structure is stabilized significantly by the extra hydrogen bond to solvent. In less strongly hydrogen bonding solvents one would anticipate that the equilibrium would shift in favor of the chelate structure. This is in fact observed for R = H,CH_3 (6). Each of these compounds immediately after dissolving in deuteriochloroform shows a very small amount of the chelate isomer, but on standing the concentration of the chelate isomer increases substantially. The equilibrium thus has been approached from both sides showing that in the crystalline state some bis-phenylhydrazones exist as the non-chelate form while sugar phenyl osazones and certain other bis-phenylhydrazones exist as the chelate in the crystalline state.

The existence of equilibria between compounds of types I and II and the dependence of the equilibrium on the nature of R and on solvent shows clearly that the energy difference between I and II is very small. This is inconsistent with any substantial difference in π-electron delocalization energies for I and II.

Additional evidence for the absence of aromatic character comes from the absence of ring current in the chelates. Ring current has been suggested as a sound physical test for aromaticity in a system said to be a non-classical aromatic system (2). The absence of ring current in the chelate isomers of bis-phenylhydrazones is most aptly demonstrated by the n.m.r. spectrum of pyruvaldehyde bis-phenylhydrazone (6). In deuteriochloroform the methyl proton resonances of the chelate and non-chelate isomers of pyruvaldehyde bis-phenylhydrazone appear at δ 1.97 and 2.07 respectively (6). Both methyl groups are in a normal position for CH_3-C=N, and the chelate methyl resonance is actually at higher field than that of the non-chelate isomer.

The evidence summarized above shows that there is no significant stabilization of the chelate isomer relative to the non-chelate isomer of the phenyl osazones and other bis-phenylhydrazones in good hydrogen bonding media. The major portion of the stabilization of the chelate form (which is still small) in poor hydrogen bonding solvents thus is primarily due to the chelate hydrogen bond and not to a substantial difference in π-electron delocalization energies in the two isomers. It is clear that the chelates do not show a ring current. There is thus no basis in fact for the contention that phenyl osazones are best described as non-classical aromatic systems.

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