

THE STRUCTURE OF THE PROTONATED AZO-LINK IN  
2,2'-AZO-ISOBUTANE\*

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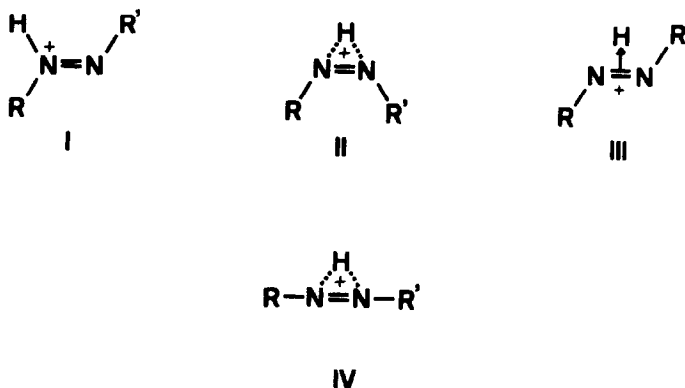
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Since the recognition by H a n t z s c h <sup>1)</sup> that the azo-group is susceptible to protonation, the acid-base equilibrium of azo-compounds has been extensively investigated. It is therefore surprising that the structure of the azonium-cation, i.e. the conjugated acid of the base  $R-N=N-R'$  should still be open to debate. Apart from H a n t z s c h's original proposal, in which the incoming proton is  $\sigma$ -bonded to one or other of the nitrogen atoms (I), various other geometries have been put forward on the basis of physico-chemical data of protonated azo-compounds.

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\*Part XIII of the Series: "Elektronenstruktur und physikalisch-chemische Eigenschaften von Azoverbindungen".

Part XII: Helv. Chim. Acta 46, 1109 (1963).

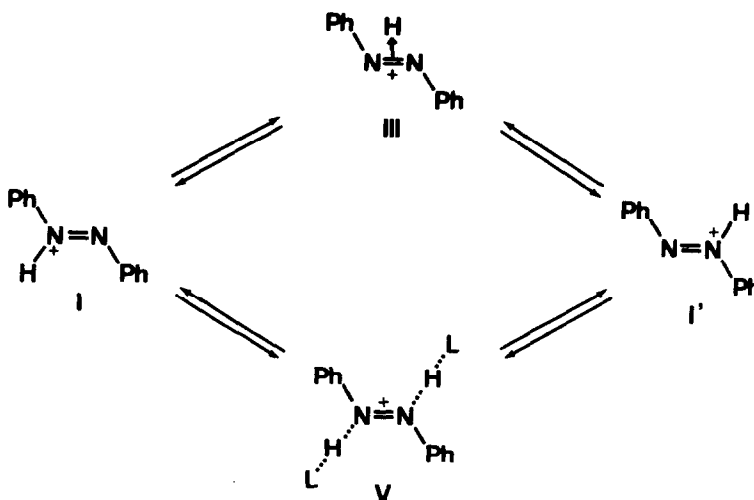


From determinations of the acid dissociation constants of substituted azobenzenes J a f f é and G a r d n e r <sup>2)</sup> had concluded that the proton,  $H^+$  at least in the diphenyl-azonium cation ( $R, R' = \text{phenyl}$ ) - is bonded in the nodal plane of the  $\pi$ -system to both lone pairs of the azo link. The conjugate acid of azobenzene should therefore assume the cis-configuration (II), independent of the configuration of the free base. This was disproved by showing that cis- and trans-azobenzene yield different conjugate acids <sup>3)</sup>.

C i l e n t o <sup>4)</sup> has suggested that in certain donor-substituted azobenzenes the proton of the conjugate acid might form a  $\pi$ -complex (III) with the azo-link, without involving the nitrogen lone pairs. Again, this conclusion, based on an analysis of the pH dependence of the electronic spectra of p,p'-bisdimethylamino-azobenzene, has been shown to be open to question <sup>5)</sup>. Lately, the

unspecified formulation IV has been used mainly by J a f f é and his co-workers <sup>6)</sup> to express their belief that the azo-link acts as a single basic center and that symmetric azo-compounds  $R-N=N-R$  yield symmetric azonium cations. However, it is difficult to understand what the geometry for the symmetric conformation of minimum energy implied by IV could be.

A careful reinvestigation of the acid-base equilibria and of the NMR and electronic spectra of sterically hindered azobenzenes <sup>7)</sup> has shown that H a n t z s c h's proposal of unsymmetric protonation and of an non-symmetric structure of the azonium cation yields the soundest explanation of the observed data. In symmetric azobenzene systems ( $R, R' = \text{phenyl}$ ) and in solvents of high proton activity the tautomerism  $I \rightleftharpoons I'$  may proceed either intramolecularly with III as a transition state or intermolecularly by proton exchange with the solvent (V).



Qualitative arguments based on simple MO-considerations concerning the relative energies of the free base, the azonium cation I or I', and the hypothetical transition state III and V suggest that the lifetime of I or I' in systems with R = alkyl instead of R = aryl should be long enough to allow resolution of the NMR proton signals of the non-equivalent R-groups.

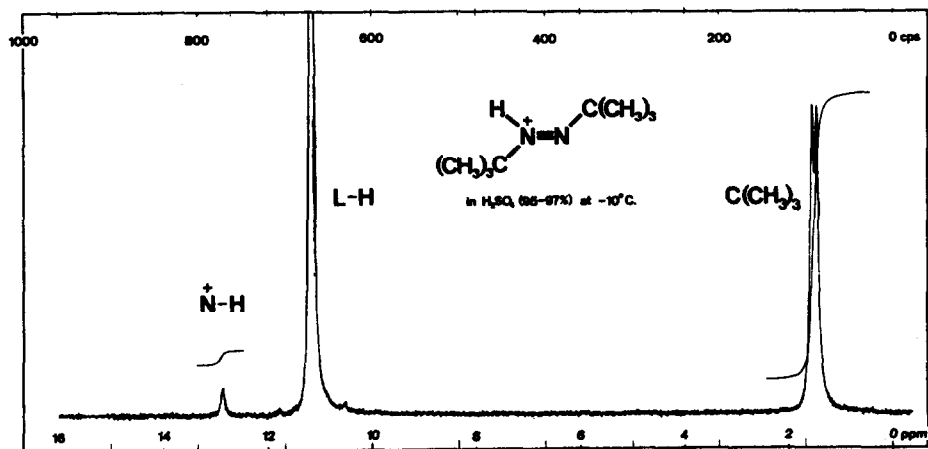


Fig. 1. The NMR spectrum of 2,2'-azoisobutane (Varian A-60 NMR spectrometer; external standard TMS in chloroform).

As shown in Fig. 1, this is indeed the case. 2,2'-Azoisobutane (VI) dissolved in 95 to 97% sulfuric acid at  $-10^{\circ}\text{C}$  yields an azonium cation to which structure I ( $\text{R} = \text{C}(\text{CH}_3)_3$ ) is assigned on the basis of its NMR spectrum. Indeed, the NMR spectrum shows two methyl proton signals at 88 and 93 cps (relative ratio 1:1) and a signal at 772 cps assigned to the azonium proton (ratio methyl proton signals to azonium proton signal 18:1). The NMR spectrum of VI in 96 to 98% deuterio sulfuric acid (99.0% deuterium) recorded under standard conditions at  $35^{\circ}\text{C}$  yields only the split signal of the methyl-protons. This proves that the observed splitting of this signal is not due to coupling with a symmetrically bonded azonium proton, e.g. II, III or IV. As expected, the separation of

the methyl signals decreases with increasing temperature and depends furthermore on the H<sub>2</sub>O (resp. D<sub>2</sub>O) content of the acid medium. The solutions in sulfuric acid are stable enough so that VI can be recovered unchanged after periods exceeding 2 days.

The choice of VI as a test compound was motivated by its inability to undergo an acid-catalysed prototropic rearrangement, which leads to isomeric hydrazones in the case of alkyl azo-derivatives with a proton in the position alpha to the azo-link<sup>8)</sup>.

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#### Literature

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