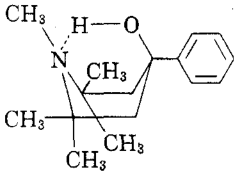
amounts of the boat form of I in the pure state and in solution. This is unique with the monocyclic piperidine derivatives and undoubtedly results from the combination of three factors: (1) extreme steric strain of three opposing axial groups in the chair form, (2) lack of interference between the two "flagpole" substituents in the boat form, but rather (3) stabilization of the boat form by hydrogen bond formation between the two "flagpole" substituents.[6]



I

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(6) Added in proof: Barton [*J. Chem. Soc.*, 2907 (1957)] recently reported similar conclusions concerning the conformation of the A ring of 2-β-bromolanostan-3-one.

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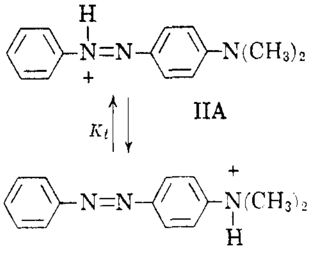
Tautomeric Equilibria. III. The Structure of the Conjugate Acid of *p*-Dimethylaminoazobenzene

Sir:

The structure of the conjugate acid of *p*-dimethylaminoazobenzene has been the subject of considerable discussion and controversy in recent years.[1] We are currently engaged in an extensive program having for one of its aims the unequivocal determination of this structure by a variety of methods. One of the lines of attack has given such a clear-cut decision that we believe preliminary publication in this form is indicated.

We have now determined the pK_a of the conjugate acid of *p*-phenylazo-*N*,*N*,*N*-trimethylanilinium methyl sulfate and of the second conjugate acid of *p*-dimethylaminoazobenzene by a spectrophotometric technique. In the process the spectra of *p*-phenylazo-*N*,*N*,*N*-trimethylanilinium ion (I) and of the first conjugate acid of *p*-dimethylaminoazobenzene (II) were needed. The spectra, in 5% sulfuric acid as solvent, are given in Fig. 1. The spectra are readily explained by the assumption, proposed by earlier workers[1b] that II is an equilibrium mixture of II A and II B.



IIA

IIB

The band at 316 mμ, due to II B, occurs at a lower intensity than the same band in I. The 516 mμ band, then, must be ascribed to II A. The equilibrium appears to shift slightly with solvent composition; with increasing sulfuric acid concentration in the range from 5–30%, the height of the 516 mμ peak increases, and simultaneously the height of the 316 mμ peak decreases. Making the perfectly reasonable assumption that the spectra of I and II B agree exactly, not only in wave length but also in intensity, we calculate an equilibrium constant $K_t = [\mathrm{IIA}]/[\mathrm{IIB}] = 1.2$ in 5% sulfuric acid, and $K_t = 2.2$ in 20% sulfuric acid.

The pK_a measurements confirm the above conclusions. Since no H_+-Scale is available the calculations were based on Hammett's H_0-Scale.[2] Although this procedure may partially invalidate the absolute values found, it is unlikely to have a profound effect on the difference between the pK_a's of the two compounds, which is the only quantity of importance for the present argument. The pK_a values found in this way were: IH^+, -3.65 ± 0.03; IIH^+, -3.04 ± 0.06.

Since

$$\begin{aligned} pK_a\,(\mathrm{IH}^+) &= -\log\,[\mathrm{I}][\mathrm{H}^+]/[\mathrm{IH}^+] \\ pK_a\,(\mathrm{IIH}^+) &= -\log\,[\mathrm{IIA} + \mathrm{IIB}][\mathrm{H}^+]/[\mathrm{IIH}^+] \\ &= -\log\,[\mathrm{IIB}](1 + K_t)[\mathrm{H}^+]/[\mathrm{IIH}^+] \end{aligned}$$

and assuming that the basicities of I and IIB are identical, *i.e.* that the effect of the groups $-\overset{+}{\mathrm{N}}(\mathrm{CH_3})_3$ and $-\overset{+}{\mathrm{N}}\mathrm{H}(\mathrm{CH_3})_2$ on the basicity of azobenzene is the same, it follows that

$$pK_a\,(\mathrm{IIH}^+) = pK_a\,(\mathrm{IH}^+) - \log\,(1 + K_t)$$

hence $K_t = 3.0$. Since this value applies to a solution approximately 50% in sulfuric acid, the agreement with the spectroscopic values is excellent.

Thus it appears unequivocally established that the first conjugate acid of *p*-dimethylaminoazobenzene is an equilibrium mixture of IIA and IIB and the value of the equilibrium constant, although solvent dependent, in moderately concentrated sulfuric acid solution is about 1–3. The implications of this finding relating to substituted dimethylaminoazobenzenes will be examined in a later paper.

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(1) (a) M. T. Rogers, T. W. Campbell, and R. W. Maatman, *J. Am. Chem. Soc.*, **73**, 5122 (1951); H. H. Jaffé, *J. Chem. Phys.*, 21, 415 (1953); I. M. Klotz, H. A. Fiess, J. Y. Chen Ho, and M. Mellody, *J. Am. Chem. Soc.*, **76**, 5136 (1954); (b) W. S. McGuire, I. F. Izzo, and S. Zuffanti, *J. Org. Chem.*, 21, 632 (1956); G. Cilento, E. C. Miller, and J. A. Miller, *J. Am. Chem. Soc.*, **78**, 1718 (1956); E. Sawicki, *J. Org. Chem.*, **22**, 365 (1957).

(2) L. P. Hammett, *Physical Organic Chemistry*, McGraw-Hill, New York, 1940, p. 267.

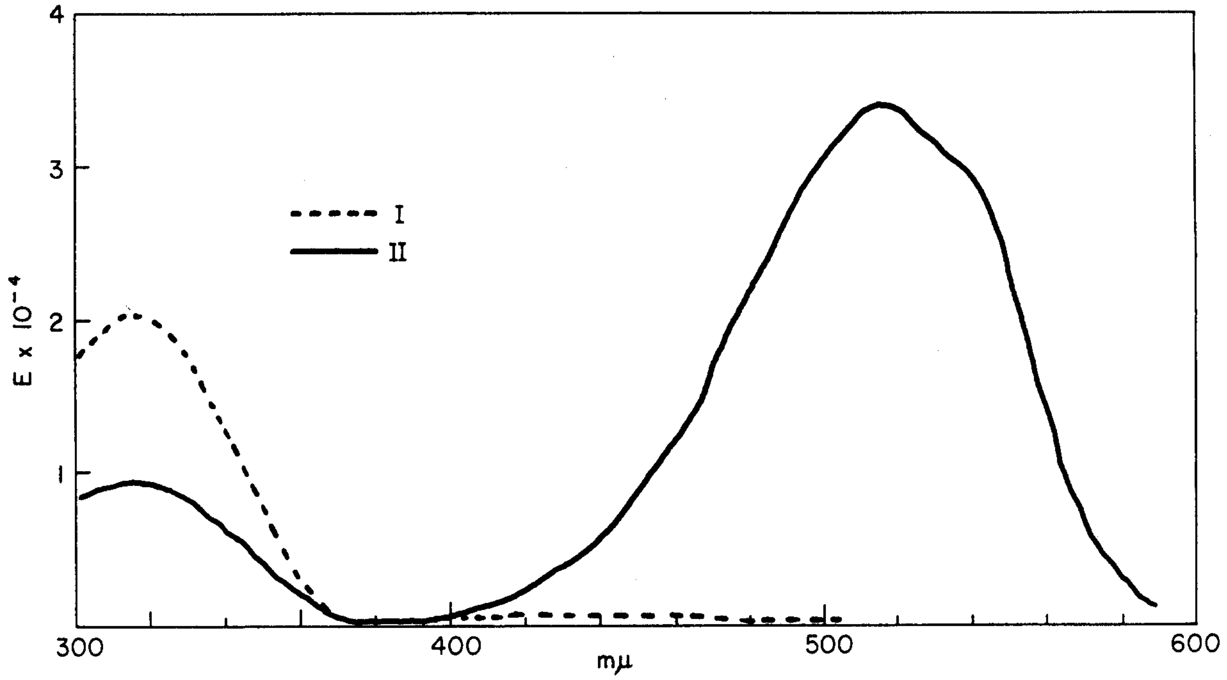

FIG. 1. SPECTRA OF *p*-PHENYLAZO-*N,N,N*-TRIMETHYLAMMONIUM METHYL SULFATE AND OF THE FIRST CONJUGATE ACID OF *p*-DIMETHYLAMINOAZOBENZENE.

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Reaction of Dialkyl Phosphites with Quinones[1]

Sir:

Dialkyl phosphites $(RO)_2P(O)H$ are known to add to unconjugated *olefins* in the presence of peroxides[2]. These have been regarded as radical chain processes propagated by the radical $(RO)_2\dot{P}(O)$. Benzaldehyde and *chloranil* combine photochemically with formation of the monobenzoate of tetrachlorohydroquinone[3]. For this reaction, Moore and Waters[3] postulated: (1) a photo-activation of the quinone to a diradical (or triplet state), $\cdot O\text{-}C_6Cl_4\text{-}O\text{-}O\cdot$, (2) a chain initiation step involving hydrogen abstraction from the aldehyde by the diradical and (3) a chain propagation sequence in which (a) the benzoyl radical added to unactivated quinone molecules giving aryloxy-radicals, $\cdot O\text{-}C_6Cl_4\text{-}O\text{-}COC_6H_5$ and (b) the latter reacted with benzaldehyde forming the product and regenerating benzoyl radicals.

During our studies on the mechanism of action of oxidizing agents on organophosphorus compounds,[4] we have related the two sets of observations described above. It was found that dialkyl phosphites and chloranil reacted smoothly with formation of the mono-dialkoxyphosphinyl derivatives of tetrachlorohydroquinone, I and II. The results obtained under several conditions are summarized in Table I.

TABLE I

REACTION OF DIALKYL PHOSPHITES, $(RO)_2P(O)H$ WITH CHLORANIL[a]

Temp., ° C.	Conditions	Time	Yield,[b] %	
			R=CH_3	R=C_2H_5
25	Dark	4.5 hr.	26(I)	24(II)
25	360–370 mμ[c]	4.5 hr.	64(I)[d]	66(II)[d]
25	Dark	3 days	100(I)	97(II)
100	Dark	1 hr.	95(I)	91(II)

[a] All reactions were carried out in an excess of freshly distilled dialkyl phosphites, in a nitrogen atmosphere. [b] Of dialkoxyphosphinyl derivatives of tetrachlorohydroquinone (I and II), based on chloranil. The material balance was unreacted chloranil. [c] Irradiation in quartz flask with a Hanovia 100-w Utility Model ultraviolet lamp and filter. [d] Quantitative yield in about 15–20 hr.

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(1) This work was carried out under Public Health Service Grant CY-3250.

(2) (a) R. L. McConnell and H. W. Coover, Jr., *J. Am. Chem. Soc.*, **79**, 1961 (1957); (b) W. E. Hanford and R. M. Joyce, U.S. Patent 2,478,390; (c) J. A. Bittles, Jr. and R. M. Joyce, U.S. Patent 2,559,754; (d) E. C. Ladd and M. P. Harvey, U.S. Patent 2,664,438; (e) N.V. de Bataafsche Petroleum Maatschappij, Brit. Patent 660,918; (f) A. R. Stiles and F. F. Rust, U.S. Patent, 2,724,718.

(3) R. F. Moore and W. A. Waters, *J. Chem. Soc.*, 238 (1953).

(4) (a) F. Ramirez and S. Dershowitz, *J. Am. Chem. Soc.*, **78**, 5614 (1956); (b) F. Ramirez and S. Dershowitz *J. Org. Chem.* (in press).