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STRUCTURES OF THE MONO-ACID CATIONS OF 4-AMINOAZOBENZENE AND ITS DERIVATIVES

G. E. Lewis
Organic Chemistry Department, University of Adelaide, South Australia

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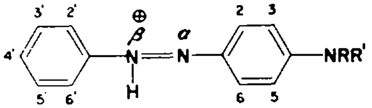
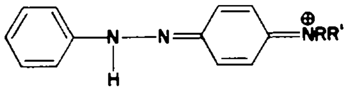
Abstract—Conflicting views exist on the structures of the mono-acid cations of 4-aminoazobenzene and its derivatives. The azonium structure (I) and the ammonium structure (II) have been separately upheld as correct, but detailed examination of spectroscopic data shows that both forms exist in solution as tautomeric equilibrium mixtures (I ⇌ II).

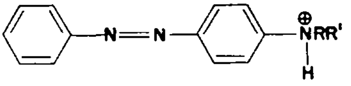
VARIOUS conclusions have been published concerning the structures of the mono-acid cations of 4-aminoazobenzene and its derivatives in solution. It has been generally accepted for a long time that the proton in these cations is attached to the β-azo nitrogen atom, forming the resonance-stabilized azonium ion (Ia ↔ Ib).[1-5]



Ia



Ib



II

In recent years some authors[6-9] have discredited this view and advanced arguments in favour of the ammonium structure (II).

It is clear, however, from careful examination of the ultra-violet and visible spectra in solutions of different acidities that both forms are present as a tautomeric equilibrium mixture (I ⇋ II) in nearly every case.[10-17]

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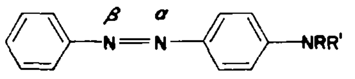
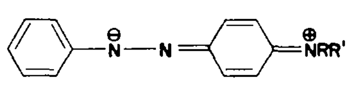
[1] A. Hantzsch and F. Hilscher, *Ber. Dtsch. Chem. Ges.* **41**, 1171 (1908).
[2] F. Kehrmann, *Ber. Dtsch. Chem. Ges.* **48**, 1933 (1915).
[3] A. Hantzsch, *Ber. Dtsch. Chem. Ges.* **52**, 509 (1919).
[4] C. R. Bury, *J. Amer. Chem. Soc.* **57**, 2115 (1935).
[5] M. T. Rogers, T. W. Campbell and R. W. Maatman, *J. Amer. Chem. Soc.* **73**, 5122 (1951).
[6] H. H. Jaffé, *J. Chem. Phys.* **21**, 415 (1953).
[7] I. M. Klotz, H. A. Fiess, J. Y. Chen Ho and M. Mellody, *J. Amer. Chem. Soc.* **76**, 5136 (1954).
[8] W. S. McGuire, T. F. Izzo and S. Zuffanti, *J. Org. Chem.* **21**, 632 (1956).
[9] L. Pentimalli, *Tetrahedron* **5**, 27 (1959).
[10] A. Hantzsch and A. Burawoy, *Ber. Dtsch. Chem. Ges.* **63**, 1760 (1930).
[11] G. M. Badger, R. G. Buttery and G. E. Lewis, *J. Chem. Soc.* 1888 (1954).
[12] G. Cilento, E. C. Miller and J. A. Miller, *J. Amer. Chem. Soc.* **78**, 1718 (1956).
[13] E. Sawicki, *J. Org. Chem.* **21**, 605 (1956).
[14] E. Sawicki, *J. Org. Chem.* **22**, 365 (1957).
[15] E. Sawicki, *J. Org. Chem.* **22**, 621 (1957).
[16] E. Sawicki, *J. Org. Chem.* **22**, 1084 (1957).
[17] H. H. Jaffé and Si-Jung Yeh, *J. Org. Chem.* **22**, 1281 (1957).

In the present review an account of the main experimental data and interpretations leading to these diverse conclusions is given. A suggestion that the proton could be bonded preferentially to the α-azo nitrogen in the mono-acid cations[18] is considered too untenable from theoretical argument and spectroscopic evidence[5,11] to warrant detailed discussion.

It is obvious from electronic theory[19,20] that structures such as IIIb contribute significantly to resonance in 4-aminoazobenzene and its derivatives (IIIa↔IIIb), so that the electronic charge at the β-azo nitrogen atom must be considerably greater than at the nitrogen atoms of azobenzene. The electron density at the amino group, on the other hand, should be much lower than normal due to electron-attraction by the azo nitrogen.



IIIa



IIIb

It might be expected, therefore, that a proton should attack either the amino group or the β-azo nitrogen with more or less comparable case, but not the α-azo nitrogen.

The absorption spectra of 4-aminoazobenzene and its N,N-diethyl and N,N-dimethyl derivatives in acidic solution led Hantzsch and Burawoy[10] to propose that the mono-acid cations of these compounds exist as tautomers. Such tautomerism was confirmed by Badger *et al.*[11] after extension of spectroscopic studies to other azo-compounds. The rationale underlying the conclusions in this work is summarized as follows with reference to Table 1.

Table 1. Absorption maxima of azobenzene derivatives and their mono-acid cations in aqueous ethanol

Compound	References	Free base		Mono-acid cation			
		K band		K′ band		Q band	
		λ_{max} (mμ)	ε_{max} ($\times 10^{-3}$)	λ_{max} (mμ)	ε_{max} ($\times 10^{-3}$)	λ_{max} (mμ)	ε_{max} ($\times 10^{-3}$)
Azobenzene	11	320	21	—	—	—	—
4,4′-Azoanisole	11	350	16	—	—	500	43
4-Phenylaminoazobenzene	11	420	28	—	—	540	61
4-Methylaminoazobenzene	11	410	23	320	8	510	39
4-Dimethylaminoazobenzene	10, 11	420	24	320	10	520	34
4-Ethylaminoazobenzene	11	410	24	320	13	510	29
4-Ethylmethylaminoazobenzene	11	430	25	320	15	530	22
4-Aminoazobenzene	10, 11	380	22	320	18	500	11
4-Diethylaminoazobenzene	10, 11	440	29	320	20	520	10
4-Dimethylamino-3-methylazobenzene	25	375	18	320	22	—	—
4-Dimethylamino-2-methylazobenzene	25	420	27	326	4	520	50
4-Dimethylamino-2′-methylazobenzene	25	410	27	326	16	520	10

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[18] S. E. Sheppard and P. T. Newsome, *J. Amer. Chem. Soc.* **64**, 2937 (1942).

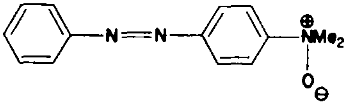
[19] B. Pullman and J. Baudet, *C. R. Acad. Sci., Paris* **238**, 2529 (1954).

[20] A. Pullman and B. Pullman, *C. R. Acad. Sci., Paris* **243**, 1322 (1956).

Azobenzene in aqueous ethanolic solution displays a strong absorption peak at 320 mμ. This has been assigned to a transition of the $\pi \rightarrow \pi^*$ type[21] and designated the K band.[22] The K band of 4-aminoazobenzene arises in the 380 mμ region in the same solvent. The K bands of the N-substituted compounds have their maxima at even longer wavelengths, 410–440 mμ, bathochromic displacement being a result of the conjugating power of the amino-group with the azo linkage. In solution of sufficient acidic strength to ensure in each case that the compound is present entirely as the mono-acid salt, no absorption maximum appears in the 400 mμ region. There is instead one band in the 500–540 mμ region and another at approximately 320 mμ. The intensities of the bands, designated Q and K′ bands respectively,[11] were found to vary inversely as substituents were introduced or changed.

The Q bands, being at long wavelengths, have been attributed to the azonium ions in which high degrees of resonance-stabilization are apparent (Ia ↔ Ib).[1–5] On the other hand, the K′ bands are associated with the ammonium cations (II), essentially for the reason that they lie in the same region as the K band of azobenzene.

It is well known that aniline and N-substituted anilines in neutral solutions absorb at longer wavelengths and higher intensities than benzene, whereas the absorption characteristics of the anilinium ions are very similar to those of benzene.[23] If II were the structure of a 4-aminoazobenzene mono-acid cation its absorption should be similar to that of azobenzene in neutral solution. This reasoning is augmented by the following facts. 4-Dimethylaminostilbene in acidic solution has an absorption spectrum almost identical with that of stilbene in neutral solution, as expected from proton-addition to the dimethylamino group.[24] 4-Dimethylaminoazobenzene methiodide,[10] assigned the quaternary ammonium structure, and 4-phenylazodimethylaniline N-oxide (IV)[9] show very similar spectra to azobenzene.



IV

Furthermore, 4,4′-azoanisole as the free base shows a K band at 350 mμ and its mono-acid cation, presumably existing only in the azonium form, exhibits a strong Q band at 500 mμ, but no K′ band.

The inverse relationship between the intensities of the Q and K′ bands shows that the cations exist in equilibrium mixtures (I $\rightleftharpoons$ II) and the relative intensities of the peaks measure the proportions of the tautomers present.[11,12]

Effects of substitution in various positions of the aromatic nuclei of 4-dialkylaminoazobenzenes provide additional support for the tautomeric equilibrium theory and clearly indicate that the β-azo nitrogen is the atom bonding the proton in the azonium ion.

4-Dimethylamino-3-methylazobenzene[25] in acidic solution shows no absorption in the 500 mμ region, but a very intense band at 320 mμ. In this case it is obvious that the 3-methyl group prevents the dimethylamino group from assuming coplanarity

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[21] P. P. Birnbaum, J. H. Linford and D. W. G. Style, *Trans. Faraday Soc.* **49**, 735 (1953).

[22] A. Burawoy, *J. Chem. Soc.* 1865 (1937).

[23] A. Wohl, *Bull. Soc. Chim.* [5], **6**, 1312 (1939).

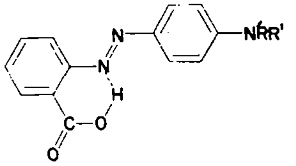
[24] G. E. Lewis, *J. Org. Chem.* In press.

[25] J. A. Miller, R. W. Sapp and E. C. Miller, *J. Amer. Chem. Soc.* **70**, 3458 (1948).

with the aromatic nucleus, thereby restricting its mesomeric effect. Addition of the proton in these circumstances appears to occur only at the dimethylamino group. 3,5-Dimethyl-4-dimethylaminoazobenzene behaves similarly.[26]

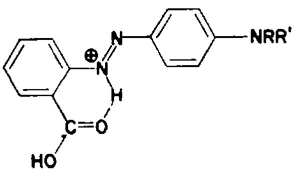
Comparison of the spectra of the 2-methyl and 2′-methyl derivatives of 4-dimethylaminoazobenzene under acidic conditions[25] indicates that the proton does not attack the α-azo nitrogen atom. The cation of the 2-methyl compound displays an intense Q band and a weak K′ band. A strong K′ band and weak Q band are shown by the 2′-methyl compound. A methyl group substituted in the 2-position of azobenzene is known to sterically hinder reactions preferentially at the nearer azo nitrogen atom.[27,28] This accounts for restriction of proton-addition at the β-azo nitrogen in 4-dimethylamino-2′-methylazobenzene, whereas in 4-dimethylamino-2-methylazobenzene the β-azo nitrogen is not hindered and the proton attaches itself almost exclusively to this position.

According to Ross and Warwick[29] a variety of substituents in the 2′-position of 4-dialkylaminoazobenzenes markedly oppose protonation at the azo linkage. A 2′-carboxy group, however, behaves anomalously due to strong intramolecular hydrogen bonding to the β-azo nitrogen atom (V).[29,30] The hydrogen bond appears to actually aid formation of the azonium ion.

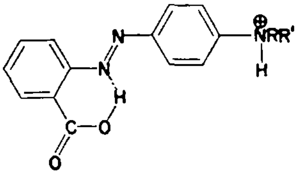


V

In acidic solution such derivatives display intense Q bands; a very weak K′ band is shown by the 4-dimethylamino compound (VI; $R = R' = Me$) and no K′ band at all in the case of the di(2-chloroethyl)amino compound (VI; $R = R' = CH_2CH_2Cl$).[29] The equilibrium (VIa $\rightleftharpoons$ VIb) is therefore displaced almost completely to the left.



VIa



VIb

The foregoing discussion recounts the main evidence in support of the tautomeric equilibrium theory. Additional support has come from other sources.[13-17]

The arguments advanced in favour of proton-addition solely at the β-azo nitrogen or the amino nitrogen atom are not so consistently logical. In many cases the interpretations are unsound because insufficient experimental data have been considered. Those workers who have maintained that the mono-acid cations possess only the

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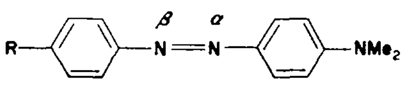
[26] L. Horner and H. Müller, *Ber. Dtsch. Chem. Ges.* **89**, 2756 (1956).
[27] G. M. Badger and G. E. Lewis, *J. Chem. Soc.* 2147 (1953).
[28] G. M. Badger and G. E. Lewis, *J. Chem. Soc.* 2156 (1953).
[29] W. C. J. Ross and G. P. Warwick, *J. Chem. Soc.* 1719 (1956).
[30] I. N. Zhmurova, *J. Gen. Chem. U.S.S.R.* **27**, 2745 (1957).

azonium structure have failed to recognize the significance of absorption in the 320 mμ region.[5]

Exponents of the opposite view have based their conclusions on various types of experimental data. McGuire *et al.*[8] proposed, after comparing the absorption spectra of azobenzene, 4-dimethylaminoazobenzene and Methyl Orange in neutral and acidic solutions, that protonation occurs only at the dimethylamino group. It is clear, however, from the incomplete absorption curves published by these workers that the critical peaks in the 500 mμ region were ignored. Their interpretations may therefore be disregarded.

In a different approach, Jaffé[6] concluded that the Hammett reaction constants (ρ)[31] relating to the primary and secondary ionizations of 4′-substituted 4-dimethylaminoazobenzenes (VII)[5] constituted evidence for the first proton becoming attached to the dimethylamino group and the second proton to the azo-linkage. The primary and secondary reaction constants found were $\rho_1 = 0\cdot55$ and $\rho_2 = 4\cdot35$ respectively.



VII

It was assumed that the reaction constant for protonation at the β-azo nitrogen should be of comparable value to that for the dimethylamino group in *p*-substituted dimethylanilines ($\rho = 4\cdot19$), and hence the above conclusion was reached. This is quite dubious because it may be just as reasonably assumed that the reaction constants for the dimethylanilines and the amino group of the azo-compounds should be quantitatively similar in view of the unrestricted conjugation between the substituent and the amino group in both cases.

Klotz *et al.*[7] claim to have proved unequivocally that the first proton adds to 4-dimethylaminoazobenzene exclusively at the dimethylamino group from a comparison of the p*Ka* values for azobenzene ($-2\cdot5$), 4-dimethylaminoazobenzene ($3\cdot5$) and dimethylaniline ($5\cdot1$) determined in aqueous media. It was estimated, on the assumption that the electronic effects of azo and nitro groups are roughly comparable, that the *p*-phenylazo group in 4-dimethylaminoazobenzene should lower the basicity of the dimethylamino group from 5·1 to approximately 3, the latter value being given as correct for *p*-nitrodimethylaniline. Using the reverse approach, these authors supposed that the electron-donating dimethylamino group in the 4-position of azobenzene might be expected to raise the p*Ka* of the azo linkage from —2·5 to 0·0. The observed value for 4-dimethylaminoazobenzene therefore led them to conclude that the mono-acid cation has the proton attached solely to the dimethylamino group.

It cannot be conceded that this is an unequivocal conclusion. In the reasoning process, whereby 4-dimethylaminoazobenzene is treated alternately as a *p*-substituted dimethylaniline and a 4-substituted azobenzene, the very nature of the resonance hybrid (IIIa$\leftrightarrow$IIIb) is overlooked. Furthermore, the respective p*Ka* values of 3 and 0·0 so suggested are approximations of insufficient accuracy to permit any comparison of the type attempted. No evidence was given to support the proposal that 0·0 should be the upper limit of the basicity of the azo linkage, and the value of 3 suggested as the lower limit of the basicity of the dimethylamino group appears to be too high because

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[31] L. P. Hammett, *Physical Organic Chemistry* p. 186. McGraw-Hill, New York (1940).

Hall[32] estimated the p*Ka* of *p*-nitrodimethylaniline in aqueous solution to be 0·8, an appreciably lower figure than that stated.

In an attempt to reinforce their argument, Klotz *et al.* erroneously contended that absorption in the 500 mμ region could be attributed to the amonium ion (II). Their interpretations of spectra have been already criticized.[12–14,24,30]

Pentimalli[9] has stated that the formation of 4-phenylazodimethylaniline N-oxide (IV), when 4-dimethylaminoazobenzene is oxidized by perbenzoic acid, is in agreement with the conclusions reached by Klotz *et al.*[7] Attack by the peracid at the dimethylamino-nitrogen atom, however, is not necessarily an indication of highest electron-density at that position. It could well be that there is greater steric resistance to oxidation at the azo linkage. Pentimalli's absorption curve for 4-phenylazodimethylaniline N-oxide, on the other hand, is in disagreement with the spectral interpretations advanced by Klotz *et al.*

Apart from studies of the mono-acid cations in solution, the solid hydrochlorides of 4-aminoazobenzene and 1-phenylazo-4-naphthylamine have been examined by infra-red spectroscopy.[34] As the free bases, aniline, 1-naphthylamine, 4-aminoazobenzene and 1-phenylazo-4-naphthylamine have absorption bands in the 3250–3400 cm^{-1} region due to the free amino groups.[33] Aniline hydrochloride and 1-naphthylamine hydrochloride display no absorption above 3100 cm^{-1}, but 4-aminoazobenzene hydrochloride and 1-phenylazo-4-naphthylamine hydrochloride both show three bands in the 3100–3350 cm^{-1} region.[34] It is clear from these observations that the proton is not attached exclusively to the amino group in the salts of the azo-compounds.

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[32] N. F. Hall, *J. Amer. Chem. Soc.* **52**, 5115 (1930).

[33] G. D. Bagratishvili, *Dokl. Akad. Nauk SSSR* **96**, 753 (1954).

[34] G. D. Bagratishvili, *Soobshcheniya Akad. Nauk Gruzin. SSR* **17**, 615 (1957).