Tetrahedron. Vol. 27, pp. 3301 to 3306. Pergamon Press 1971 Printed in Great Britain

THE STRUCTURE OF N-BENZALANILINIUM IONS

J. W. PAVLIK
Department of Chemistry, Wisconsin State University, River Falls, Wisconsin 54022

and

A. VAN PUTTEN[1]
Department of Chemistry, McMaster University, Hamilton, Ontario

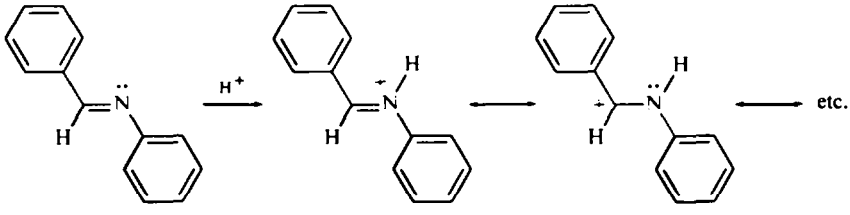
(*Received in the USA* 4 *November* 1970; *Received in the UK for publication* 11 *November* 1970)

Abstract—The NMR spectra of protonated N-benzalaniline, its six monoethylated and both *sym*-trimethylated derivatives in 96% sulfuric acid indicate limited but detectable positive charge delocalization into the benzal ring. The spectra are consistent with an ion in which the aniline ring is twisted out of the molecular plane.

INTRODUCTION

KINETIC data concerning the rates of acid catalyzed hydrolysis of variously substituted N-benzalanilines have been shown to deviate significantly from a Hammett free-energy relationship.[2,3] Lack of a linear relationship between the rates of reaction and σ_{para} suggests lack of resonance interaction between the substituent position and the reaction center in the protonated N-benzalanilines, or more correctly, in the transition state leading to the first intermediate ion.

Because of the stability resulting from charge delocalization throughout the adjacent benzal ring, one might expect *a priori* a delocalized ion to result from



I Ia Ib

protonation of N-benzalaniline I. However, although contribution of aminocarbonium ion forms (Ib, etc.) has been suggested,[4] available spectroscopic evidence indicates the predominance of the immonium ion form Ia.[5]

To further elucidate the structure of these ions in order to explain the anomalous acid catalyzed rate data,[2,3] we presently report the results of an NMR study of the ions derived from protonation of N-benzalaniline I, its six monomethylated isomers II–VII, and both *sym*-trimethylated isomers VIII and IX.[6] Measuring the effect that a Me group's relative position has on the rate of a chemical reaction[7] as well as observing the substituents magnetic deshielding brought about by conversion of the

neutral molecule to the corresponding ion[8–11] have been shown to be two effective methods of probing the extent of positive charge delocalization in organic cations.

RESULTS AND DISCUSSION

Charge delocalization in N-*benzalanilinium ions.* N-Benzalaniline, as well as its monomethylated derivatives, were found to dissolve in 96% H_2SO_4 at room temperature to yield stable ions which gave well-resolved NMR spectra. No N-H signal was observed in H_2SO_4 most likely because of broadening due to the quadrupole interaction of the N^{14}.[12] Rapid exchange was not responsible for this since splitting of the adjacent methine proton into a doublet was observed in all cases. As expected, splitting did not occur in D_2SO_4 and in this solvent the methine proton appeared as a one-proton singlet. The proton chemical shifts and coupling constants for the methyl and methine protons in the neutral and protonated imines in $CDCl_3$ and H_2SO_4 respectively are tabulated in Table 1.

In order to assess the extent of charge delocalization into the aromatic rings, it is of interest to compare the deshielding, $\Delta\delta_{CH_3}$, experienced by the various Me substituents upon N-protonation. Fig 1 summarizes the deshielding in ppm at 60 Mc observed for each of the Me groups in the monomethylated N-benzalanilines on

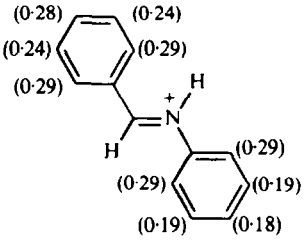


FIG 1. Deshielding of methyl groups upon N-protonation

going from $CDCl_3$ to 96% sulfuric acid solvent. From the magnitudes of the methyl group deshielding values, it can be seen that the greatest electron deficiency (i.e., greatest deshielding) in the aniline ring is located at the *ortho*-ring positions. Furthermore, the electron deficiency decreases rapidly to an essentially constant value at the *meta* and *para* ring positions. This order of magnitude, $o > m = p$, is consistent with charge transfer via an inductive mechanism.[13] Such results are in accord with resonance theory which precludes resonance interaction between the positive charge and the aniline ring.

Consideration of the deshielding of the Me groups in the benzal ring brought about by N-protonation shows that the electron deficiency at the *ortho* and *para* ring positions is essentially equal and of somewhat larger value than at the *meta* position. Although this order of magnitude, $o = p > m$, is consistent with resonance delocalization of the positive charge into the benzal ring,[14] the difference in deshielding between the *ortho* or *para* and *meta*-Me groups, 0·05 ppm, approaches the limits of uncertainty in the spectrometer measurement and cannot be taken to unambiguously

TABLE 1. NMR CHEMICAL SHIFTS

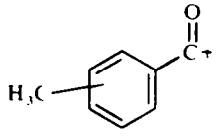
	$\delta = C\overset{\prime}{\underset{H}{\backslash}}$	$\delta^+ = C\overset{\prime}{\underset{H}{\backslash}}$	$\Delta\delta$	$J_{CH,NH}$	$\delta_{o\text{-}CH_3}$	$\delta^+_{o\text{-}CH_3}$	$\delta_{o\text{-}CH_3}$	$\delta^+_{m\ CH_3}$	$\delta_{p\text{-}CH_3}$	$\delta^+_{p\text{-}CH_3}$
N-Benzalaniline (I)	8·35	9·09	0·74	17·4						
N-Benzal-*o*-toluidine (II)	8·27	8·95	0·68	17·4	2·35	2·64				
N-Benzal-*m*-toluidine (III)	8·35	9·01	0·66	17·4			2·35	2·54		
N-Benzal-*p*-toluidine (IV)	8·36	9·00	0·64	17·4					2·29	2·47
N-(*o*-Tolual)-aniline (V)	8·65	9·31	0·66	17·4	2·51	2·80				
N-(*m*-Tolual)-aniline (VI)	8·31	9·03	0·72	17·4			2·34	2·61		
N-(*p*-Tolual)-aniline (VII)	8·32	8·95	0·63	17·4					2·31	2·59
N-Benzal-2,4,6-mesidine (VIII)[c]	8·16	8·70	0·54	17·4	2·10	2·40			2·25	2·45
N-(2,4,6-Mesital)-aniline (IX)[c]	8·72	9·25	0·53	17·4	2·50	2·80			2·25	2·50

[a] δ values represent chemical shifts of neutral N-benzalanilines in $CDCl_3$ in ppm downfield from internal TMS.

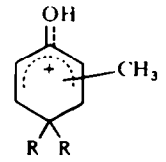
[b] δ^+ values represent chemical shifts of N-benzalanilinium ions in 96% H_2SO_4 in ppm relative to TMS (calculated from CH_2Cl_2 used as an internal secondary standard; δ = 5·30 ppm downfield from TMS)

[c] Ions are disulfonated.

support delocalization. In contrast to the deshielding observed in the aniline ring, however, the order of the deshielding in the benzal ring is totally inconsistent with an inductive mechanism which does not predict the same extent of deshielding at both *ortho* and *para* positions. This latter fact may suggest a very limited resonance



X



XI

interaction between the positive nitrogen and the benzal ring. A difference in deshielding of 0·16 ppm in both aryl oxocarbonium ions X[10] and protonated cyclohexadienones XI[8] for $\Delta\delta_{o,\,p\text{-}CH_3} - \Delta\delta_{m\text{-}CH_3}$ and $\Delta\delta_{3\text{-}CH_3} - \Delta\delta_{2\text{-}CH_3}$ respectively has recently been reported and reflects the greater extent of delocalization in these ions as compared to the N-benzalanilinium ions presently under consideration.

Considerable resonance delocalization of the positive charge into the benzal ring is furthermore not reflected in the coupling constants, $J_{CH,\,\overset{+}{N}H}$. A significant contribution from aminocarbonium ion forms (Ib, etc.) would lower the carbon–nitrogen bond order and would not be expected to result in a normal *trans* coupling constant.[15–18] The value of 17·4 Hz observed in the present series does not reflect large changes from a normal double bond. Coupling constants do not appear, however, to be particularly sensitive to small changes in bond order. Protonation of the cyclohexadienone precursor of XI, for example, is accompanied by a change in the vinyl-proton coupling constants of no more than 1 Hz.[8] The much smaller change anticipated in the present case may not be detectable.

It is of further interest to compare the changes in the shielding of the methine proton in the monomethylated N-benzalanilinium ions of II–VII relative to Ia as a function of substituent position. The ability of the methyl group to enhance the electronic charge on the methine carbon atom and thus result in a diamagnetic shift of the methine proton was observed in all cases.

Moreover, in the aniline ring, as expected for an inductive effect, the magnitude of the shielding is a function of the distance between the methine proton and the methyl group and decreases in a regular manner *ortho* > *meta* > *para*. In contrast, shielding of the methine proton by methyl substituents in the benzal ring is not a function of distance but rather of relative substituent position. Thus, it can be seen (Table 1) that the shielding values are 0·11, 0·02, and 0·08 ppm for *ortho*, *meta*, and *para* Me substituents respectively. This order of magnitude $o \sim p > m$ reflects some degree of resonance interaction with the benzal ring. Moreover, these values are well within the reproducibility of the spectrometer and must be regarded as significant.

Because of rapid sulfonation at both *meta* positions in the trimethylated rings in the ions of VIII and IX, it was not possible to obtain the spectra of the unsulfonated trimethylated N-benzalanilinium ions.[10, 19] In spite of this, an inspection of Table 1 shows that the Me proton deshielding brought about by N-protonation, as well as

the shielding of the methine proton by the Me substituents, are consistent with the values observed for the monomethylated ions.

We conclude from these data that protonation of N-benzalaniline and its methylated derivatives results in immonium ions (e.g. 1a) in which aminocarbonium ion resonance forms (e.g. Ib, etc) make small but detectable contributions. Although resonance interaction between the positive charge and the aniline ring is not expected in terms of resonance theory, limited delocalization of the positive charge into the benzal ring is surprising in view of the added stability that would accompany such delocalization. In view of these conclusions, a nonlinear Hammett free-energy relationship for the acid catalyzed reactions is understandable.

Geometrical considerations. Because of only limited delocalization of the positive charge into the benzal ring, it is tempting to suggest a molecular geometry in which the benzal ring lies somewhat out of the plane of the imine double bond thus allowing only limited overlap of the ring and methine carbon 2p atomic orbitals. Such a suggestion, however is not supported by the aromatic proton resonance signals for the N-benzalanilinium ion. This portion of the spectrum clearly show two protons deshielded relative to the main aromatic complex. Fig 2 shows the NMR spectrum of N-(*p*-tolual)-anilinium ion in 96% H_2SO_4.* The two proton doublet (J = 8·4 Hz) centered at 8·08 ppm–0·45 ppm downfield from the main aromatic complex—was

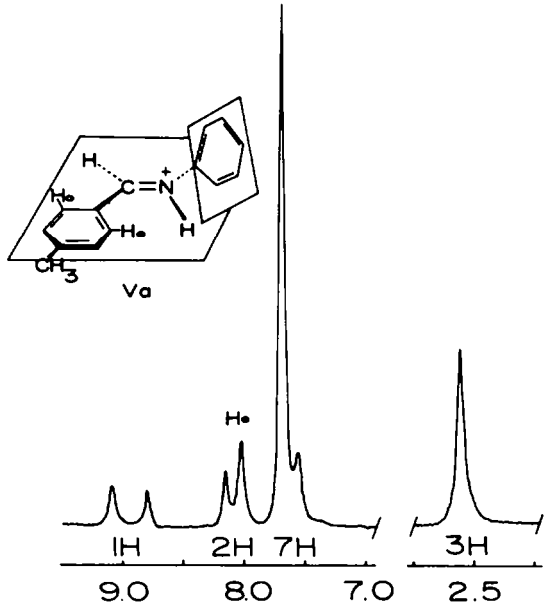


FIG 2. NMR spectrum of N-(*p*-tolual)-anilinium ion in 96% H_2SO_4. The scale is in ppm, zero at TMS

* The *para*-Me group would not alter the relative spatial orientation of the benzal ring. It's presence, however, simplifies the spectrum and is more illustrative than the unsubstituted ion.

unambiguously assigned to the ortho-protons in the benzal ring by a comparison of the spectra of the various monomethylated isomers. Coplanarity of the benzalimino moiety places the *ortho*-benzal ring protons in the deshielding zone of the imine double bond and is thus a prerequisite for such *ortho*-proton deshielding.[20] Failure to observe similar deshielding of the *ortho*-protons in the aniline ring of the ions places these protons out of the deshielding zone of the imine double bond and suggests a conformation in which the aniline ring is rotated out of the plane of the benzalimino moiety (Fig 2).

EXPERIMENTAL

Preparation of N-*benzalanilines.* Equimolar quantities of the appropriate aniline and benzaldehyde derivatives were heated on a steam bath for 30 min and distilled at *ca* 0·5 mm Hg through a 15 cm Vigreux column. Their physical constants were consistent with literature values as reported elsewhere.

NMR spectra. All spectra were recorded on a Hitachi–Perkin–Elmer R-20 High Resolution Spectrometer at 60 Mc. Spectra of neutral N-benzalanilines were recorded on samples containing 50 mg solute in 0·5 ml $CDCl_3$ with TMS as internal standard. Spectra of N-benzalanilinium ions were recorded on samples containing 35 mg solute in 0·5 ml 96% H_2SO_4 with CH_2Cl_2 (δ = 5·30 ppm downfield from TMS) as a secondary internal standard. Spectra in 96% H_2SO_4 were recorded immediately upon solution preparation.

Acknowledgement—We wish to acknowledge the Chemical Laboratory of the Haile Selassie I University, Addis Ababa, Ethiopia where a portion of this work was carried out during our tenure there in the Department of Chemistry. One of us (JWP) would like to acknowledge The George Washington University, Washington, D.C. in whose Chemical Laboratory the NMR spectra were recorded.

REFERENCES

[1] Pre-doctoral Graduate Assistant, 1970–1971
[2] A. V. Willi and R. E. Robertson, *Canad. J. Chem.* **31**, 361 (1953)
[3] H. H. Jaffé, *Chem. Revs* **53**, 191 (1953)
[4] N. C. Deno, *Prog. Phys. Org. Chem.* **2**, 129 (1963)
[5] G. A. Olah and P. Kreienbuhl, *J. Am. Chem. Soc.* **89**, 4756 (1967)
[6] For an analogous study of the neutral N-benzalanilines, see A. van Putten and J. W. Pavlik, *Tetrahedron* in press
[7] P. von R. Schleyer and G. W. Van Dine, *J. Am. Chem. Soc.* **88**, 2321 (1966)
[8] E. C. Friedrich, *J. Org. Chem.* **33**, 413 (1968)
[9] V. P. Vitullo, *Ibid.* **34**, 224 (1969)
[10] D. A. Tomalia, *Ibid.* **34**, 2583 (1969)
[11] G. Fraenkel, R. E. Carter, A. McLachlan and J. H. Richards, *J. Am. Chem. Soc.* **82**, 5846 (1960)
[12] *Nuclear Magnetic Resonance Applications to Organic Chemistry* (Edited by J. D. Roberts), p. 80. McGraw-Hill, New York, N.Y. (1959)
[13] *Mechanism and Structure in Organic Chemistry* (Edited by E. S. Gould), p. 200. Holt, Rinehart and Winston, New York, N.Y. (1959)
[14] D. G. Farnum, *J. Am. Chem. Soc.* **89**, 2970 (1967)
[15] W. B. Smith and T. J. Kinet, *J. Phys. Chem.* **70**, 4084 (1966)
[16] N. Jonathan, S. Gordon and B. P. Dailey, *J. Chem. Phys.* **36**, 2443 (1962)
[17] K. Tori and T. Nakagawa, *J. Phys. Chem.* **68**, 3163 (1964)
[18] P. Lasslo, Thesis, Université de Paris (1965)
[19] H. Hart and T. Sulzberg, *J. Org. Chem.* **28**, 1159 (1963)
[20] J. Karabatsos, G. C. Sonnichsea, N. Hsi and D. J. Fenoglio, *J. Am. Chem. Soc.* **89**, 5067 (1967)