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THE GEOMETRY OF N-BENZALANILINE

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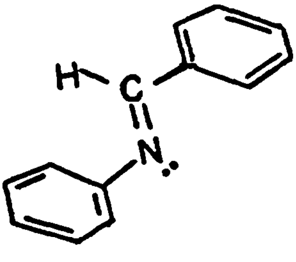
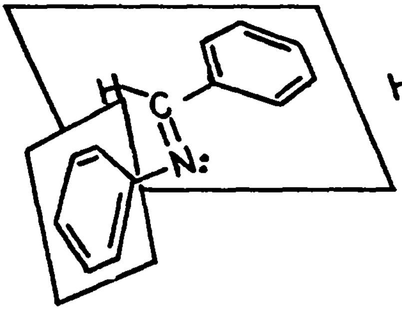
Abstract—The NMR spectra of N-benzalaniline, its six monomethylated and both *sym*-trimethylated derivatives have been recorded. These spectral results are consistent with a mean conformation for N-benzalaniline in which the aniline ring is twisted out of the plane of the benzalimino moiety.

INTRODUCTION

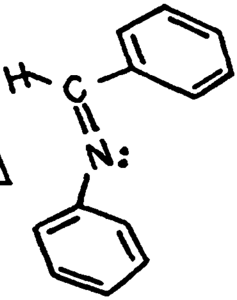
SPECTROSCOPIC,[2–5] theoretical,[6–9] and crystallographic[10] investigations of the geometry of N-benzalaniline **1** have been interpreted in terms of both planar **1a** and non-planar **1b** *anti*-geometries.[11, 12] In the latter case, the aniline ring is twisted out of the molecular plane. Most recently, theoretical studies have been interpreted in terms of conformation **1c** which, although planar, postulates an abnormally large C=N—Ph bond angle.[13]



1a



1b



1c

In view of the structural dichotomy of these results, it is somewhat surprising that almost no NMR analyses of N-benzalaniline and its derivatives have previously been undertaken. Since NMR seemed admirably suited to resolve these structural ambiguities, we presently report the results of such a study.

RESULTS AND DISCUSSION

N-*Benzalaniline.* In addition to a sharp methine proton singlet at δ 8·45 ppm, the NMR spectrum of N-benzalaniline **1** consists of two distinct aromatic multiplets. By comparison with the spectra of the various methylated derivatives (Table 1), the lower field two-proton multiplet in the spectrum of **1** was assigned to the *orthro*-protons in the benzal ring. Deshielding of these protons relative to the other aromatic hydrogens indicates a mean conformation in which the *ortho*- protons of the benzal ring are in the deshielding zone of the imine double bond (Fig 1).[14] Failure of the analogous protons in the aniline ring to be similarly deshielded suggests that these protons lie out of the plane of the imine double bond and thus out of the latter's deshielding zone.

TABLE 1. METHINE AND METHYL PROTON CHEMICAL SHIFTS

Compound	δH Methine	δo-CH_3	δm-CH_3	δp-CH_3
N-Benzalaniline 1	8·35	—	—	—
N-(*o*-Tolual)-aniline II	8·65	2·51	—	—
N-(*m*-Tolual)-aniline III	8·31	—	2·34	—
N-(*p*-Tolual)-aniline IV	8·32	—	—	2·31
N-(2,4,6-Mesital)-aniline V	8·72	2·51	—	2·24
N-Benzal-*o*-toluidine VI	8·26	2·35	—	—
N-Benzal-*m*-toluidine VII	8·35	—	2·35	—
N-Benzal-*p*-toluidine VIII	8·36	—	—	2·30
N-Benzal-2,4,6-mesidine IX	8·16	2·10	—	2·25
Benzaldehyde X	9·80	—	—	—
o-Tolualdehyde XI	10·10	2·62	—	—
m-Tolualdehyde XII	9·83	—	2·40	—
p-Tolualdehyde XIII	9·82	—	—	2·41

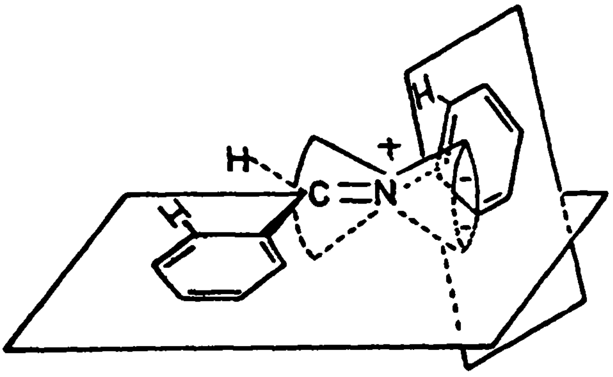


FIG 1. Shielding (+) and deshielding (−) zones

These observations tend to support conformation **1b** in which the aniline ring is twisted out of the molecular plane but do not necessarily preclude wide angle conformation **1c**.* Such a conformation, however, seems unlikely. Whereas the lone pair of electrons on nitrogen may not be sterically able to maintain normal sp^2 bond angles, N-protonation should result in an ion with more normal trigonal angles at nitrogen. Thus, although N-protonation of **1c** should result in a coplanar ion, the spectrum of **1** in conc H_2SO_4 is inconsistent with this interpretation.[15] Furthermore, no evidence for abnormally wide valence angles at sp^2 hybridized nitrogen was observed in the NMR spectrum of isoelectronic *anti*-azobenzene. Significantly, the coplanarity of the phenyl rings in this latter compound[16, 17] was clearly reflected in its NMR spectrum which shows all four *ortho*-ring protons deshielded.[18]

Methylated derivatives of N-*benzalaniline* (Table 1). Further support for conformation **1b** was obtained by an analysis of the NMR spectra of the six monomethylated (II–IV and VI–VIII) and two *sym*-trimethylated (V and IX) derivatives of **1**. Accordingly, it is of interest to examine the chemical shifts of the Me substituents as a function of their relative ring positions and to observe how these latter structural changes affect the position of the methine absorption.

In the benzal ring, the chemical shift of the Me substituent is dependent upon its relative ring position. Thus, as expected for a planar benzal moiety, an *ortho*-Me group is significantly deshielded relative to the nearly equivalent *meta* and *para*-Me groups. The single *ortho*-Me signal in the spectrum of trimethylated derivative V, which is identical in position with the analogous signal in mono-*ortho*-methylated II, indicates not only the equivalence of the two *ortho*-substituents but also that introduction of a second *ortho*-Me group is not accompanied by a significant mean conformational change. Such a change in the mean relative spatial distribution of the *ortho*-Me groups and the imine double bond caused by successive *ortho*-substitution would be accompanied by corresponding changes in the deshielding of these Me groups.

In contrast to these observations, Table 1 shows that for mono-substitution in the aniline ring the chemical shift of the Me group is independent of relative ring position. Thus, lack of deshielding at the *ortho*-position of the aniline ring is again observed and is further evidence for an out-of-plane aniline ring. Introduction of a second *ortho*-methyl group into the aniline ring as in trimethylated derivative IX again shows the equivalence of the *ortho*-ring positions. The observed shielding of the *ortho*-Me groups in IX relative to the analogous substituent in mono-*ortho*-methylated VI, however, indicates that successive *ortho*-substitution in the aniline ring is accompanied by a significant mean conformational change. Thus, it appears that introduction of a second *ortho*-Me group forces the aniline ring further out of the molecular plane into a mean conformation in which the Me groups are located more directly in the shielding zone of the imine bond.

This observed conformational sensitivity to *ortho*-substitution in the aniline ring provides further evidence against wide angle conformation **1c**. Thus, whereas molecular models containing normal bond angles at nitrogen substantiate steric interference between the methine proton and the *ortho*-substituents in the aniline ring, this interaction becomes negligible with an increasing C=N—Ph angle.

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* An alternative deshielding mechanism might involve the nitrogen lone pair. This mechanism seems unlikely, however, since the *ortho*-benzal ring protons were similarly deshielded in the N-benzalanilinium ion.[15]

An examination of the methine proton chemical shift as a function of the relative Me group position in the aniline ring leads to similar structural conclusions. Thus, whereas the observed additive methine proton shielding as a result of successive *ortho*-Me substitution (~0·1 ppm per o-Me_3 group) may be largely due to the inductive effect of the Me groups[19] rendering the methine C atom more negative, it may also reflect the position this proton assumes above the plane of the aniline ring[20] as the latter is rotated out of the molecular plane.

As in the case of the aniline ring, *meta* or *para* Me-substitution in the benzal ring has almost no effect on the position of the methine proton signal. Substitution in the *ortho*-position of the benzal ring, however, is accompanied by distinct methine proton deshielding. Being inconsistent with either an inductive or resonance electronic effect, this deshielding is more likely due to the close spatial proximity of the methine proton and methyl group when the latter is in the *ortho*-ring position. An exactly identical trend is observed for the aldehyde proton in benzaldehyde X and its methylated derivatives XI–XIII (Table 1). Variable temperature experiments have confirmed a mean planar conformation for benzaldehyde[21] and by comparison support a similar conclusion for the benzal ring in the compounds presently under consideration.

These NMR results are thus consistent with conformation **1b** in which the aniline ring is distorted from the molecular plane by an angle unequal to 90°. This conclusion is in agreement with dipole moment studies,[22, 23] with most reported studies of the angle of distortion,[4, 7–10] and with the observation that the properties of N-benzalaniline can be considered as resulting from non-interacting benzalimino and phenyl moieties.[2, 5, 7, 24, 25]

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.

NMR spectra. All spectra were recorded with a Hitachi–Perkin Elmer R-20 High Resolution Spectrometer at 60 Mc on samples containing 50 mg solute in 0·5 ml $CDCl_3$ with TMS as internal standard.

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REFERENCES

[1] Pre-doctoral Graduate Assistant, 1970–1971
[2] E. Haselbach and E. Heilbronner, *Helv. Chim. Acta* **51**, 16 (1968)
[3] O. H. Wheeler and P. H. Gore, *J. Org. Chem.* **26**, 3298 (1961)
[4] P. Brocklehurst, *Tetrahedron* **18**, 299 (1962)
[5] W. Krauss and C. G. J. Wagner, *Z. Naturforsch.* **A22**, 746 (1967)
[6] H. H. Jaffé, S. Yeh and R. W. Gardner, *J. Mol. Spectr.* **2**, 120 (1958)
[7] W. F. Smith, *Tetrahedron* **19**, 445 (1963)
[8] V. I. Minkin, Yu. A. Zhadanov, E. A. Medyantzeva and Yu. A. Ostroumor, *Ibid.* **23**, 3651 (1967)
[9] G. Favini and A. Gamba, *J. Chim. Phys.* **62**, 995 (1965)
[10] H. B. Buergie and J. D. Dunitz, *J. Chem. Soc.* D 472 (1969)
[11] E. Fischer and Y. Frei, *J. Chem. Phys.* **27**, 808 (1957)

[12] D. G. Anderson and G. Wettermark, *J. Am. Chem. Soc.* **87**, 1433 (1965)

[13] S. A. Houlden and I. G. Csizmadia, *Tetrahedron* **25**, 1137 (1969)

[14] G. J. Karabatsos, G. C. Sonnichsen, N. Hsi and D. J. Fenoglio, *J. Am. Chem. Soc.* **89**, 5067 (1967)

[15] J. W. Pavlik and A. van Putten, recently submitted for publication

[16] J. J. de Lange, J. M. Robertson and I. Woodward, *Proc. Roy. Soc.* **A171**, 398 (1939)

[17] C. J. Brown, *Acta Cryst.* **21**, 146 (1966)

[18] Sadtler *NMR Spectra Catalog* No. 1208

[19] L. M. Jackman and S. Sternhell, *Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry* p. 79. Pergamon Press, New York, N.Y.

[20] C. E. Johnson and F. A. Bovey, *J. Chem. Phys.* **29**, 1012 (1958)

[21] F. A. L. Anet and M. Ahmad, *J. Am. Chem. Soc.* **86**, 119 (1964)

[22] V. Gaouck and R. J. W. LeFèvre, *J. Chem. Soc.* 741 (1938)

[23] C. Curran and E. P. Chaput, *J. Am. Chem. Soc.* **69**, 1134 (1947)

[24] J. D. Margerum and J. A. Sousa, *J. Appl. Spectry.* **10**, 91 (1955)

[25] L. E. Clougherty, J. A. Sousa, and J. M. Wyman, *J. Org. Chem.* **22**, 462 (1957)