

## THE CONFORMATION OF BENZALANILINES STUDIED BY NMR

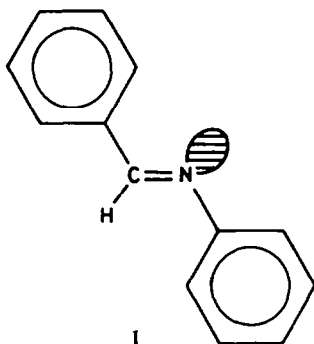
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**Abstract**—Proton chemical shifts for benzalaniline and some *p,p'*-derivatives in dilute solutions in cyclohexane were obtained and compared with those for the corresponding parent benzaldehydes and anilines. Discussion of these chemical shifts showed that there is rapid rotation of the phenyl rings about the C—C and C—N bonds at room temperature, and provided evidence of the averaged (effective) dihedral angles between the H—C=N nuclear plane and the ring planes; in particular, this was shown to be 45° at most for the aniline ring. Solvent effects, especially the effect of protonation, are also briefly investigated.

THE CONFORMATION of the *trans* isomer of benzalaniline (I) and its derivatives in solution has been the object of several papers in recent years.<sup>1–6</sup> Various physical and chemical properties, especially electronic spectra, have been investigated and lead to the conclusion that, contrary to the traditionally accepted view, I is not planar. This

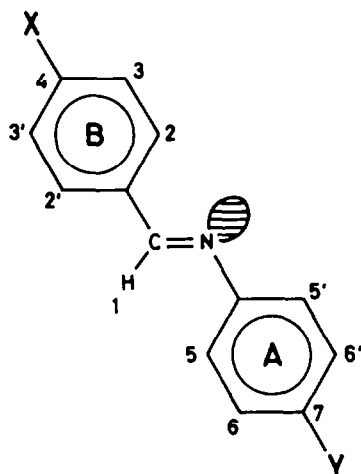


is reasonable because, although  $\pi$ - $\pi$  conjugation would be maximum for a planar situation, steric considerations (involving the olefinic H atom and the nearest H of the N-phenyl group) and the possibility of  $n$ - $\pi$  conjugation (involving the N lone pair and the adjacent aromatic ring, as in aniline) would favour a perpendicular arrangement of the H—C=N nuclear plane and the plane of the N-phenyl ring. Values of 40°–60°<sup>5</sup> and approx 90°<sup>6</sup> (perpendicular situation) have been proposed for the dihedral angle  $\psi$  between those planes.

In this paper, we apply proton magnetic resonance spectroscopy to the problem. In particular, proton chemical shifts of benzalaniline and some *p,p'*-derivatives have been obtained and are discussed in relation to the molecular geometry. Solvent effects are also investigated.

## RESULTS

Table 1 shows the  $\tau$ -values for dilute cyclohexane solutions (see Experimental) for the various compounds studied as well as the differences ( $\Delta$ ) observed with respect to



- I: X = H Y = H  
 II: X = Cl Y = Cl  
 III: X = Cl Y = CH<sub>3</sub>  
 IV: X = NO<sub>2</sub> Y = Cl  
 V: X = NO<sub>2</sub> Y = CH<sub>3</sub>

the corresponding parent compounds (*p*-X-benzaldehyde and *p*-Y-aniline) in similar conditions of solvent and concentration (positive  $\Delta$ -values correspond to shifts to high field.)

Table 2 shows the differences  $\Delta'$  observed on going from cyclohexane to other solvents: acetone, *d*-chloroform and trifluoroacetic acid (TFA).

Except in the case of I, all spectra were of the AA'BB' type. No detailed analysis of the spectrum of I was attempted. The  $\Delta'$ -values shown in parenthesis for the TFA solutions of IV and V result from an alternative assignment of signals in the TFA spectra. The various values quoted are thought to be accurate to  $\pm 0.01$  ppm.

## DISCUSSION

The first point to be noted is that the chemical shifts of protons 2 and 2' are the same, and so are those of protons 5 and 5'. This means that, at room temperature, there is rapid (in the NMR time scale) rotation of the phenyl rings B and A about the C-C and C-N bond directions, respectively, or, at least, rapid oscillation about a conformation in which the ring planes are perpendicular to the H-C=N plane. (The alternative explanation, i.e. the existence of a rigid perpendicular conformation, does not seem plausible). Therefore, we must consider (weighted) average dihedral angles instead of fixed angles.

In fact, properties such as molar extinctions<sup>4-6, 8</sup> or ring proton shifts due to  $\pi$ - $\pi$  or  $n$ - $\pi$  conjugation (see below) are not linear functions of the dihedral angle  $\psi$  but are approximately proportional to  $\cos^2\psi$ . Thus, rigorously, what one may get from studying such properties is a weighted averaged  $\cos^2\psi$ . However, it may be convenient to

TABLE I.  $\tau$ -VALUES FOR BENZALANILINES ( $C_6H_{12}$  SOLUTIONS) AND DIFFERENCES  $\Delta$  RELATIVE TO PARENT COMPOUNDS

Molecule	Proton	$\tau$ -values	$\Delta$ (ppm)
I	1	1.69	1.61
	2,2'	2.20	-0.05
	3,3'	2.7-3.0	0.1-0.4
	4	2.7-3.0	0.1-0.4
	5,5'	2.7-3.0	-0.8- -0.5
	6,6'	2.7-3.0	-0.3-0
	7	2.7-3.0	-0.8- -0.5
II	1	1.75	1.62
	2,2'	2.27	-0.06
	3,3'	2.69	0.07
	5,5'	2.99	-0.62
	6,6'	2.79	-0.27
III	1	1.72	1.59
	2,2'	2.28	-0.05
	3,3'	2.70	0.08
	5,5'	2.97	-0.66
	6,6'	2.97	-0.24
IV	1	1.61	1.61
	2,2'	2.06	-0.05
	3,3'	1.80	0.05
	5,5'	2.92	-0.69
	6,6'	2.74	-0.32
V	1	1.57	1.57
	2,2'	2.05	-0.06
	3,3'	1.79	0.04
	5,5'	2.91	-0.72
	6,6'	2.91	-0.30

define an effective average  $\psi$  such that  $\cos^2\psi_{eff} = av.(\cos^2\psi)$ ; this  $\psi_{eff}$  will not be the same as the averaged  $\psi$ , but they will change in the same direction. The values found in the literature for the dihedral angle between the H-C=N plane and the N-phenyl ring<sup>5, 6</sup> of I are in fact approximate  $\psi_{eff}$  values.

In this work we were trying to get some idea about  $\psi_{eff}$  for the compounds in  $C_6H_{12}$  (where specific solvent effects are minimum), from the differences  $\Delta$  between the  $\tau$ -values for the benzalanilines and those for the parent molecules, and compare the results with the  $\psi_{eff}$  values determined from electronic spectra.

(a) *Spectra in cyclohexane*

Table I shows that the proton 1 signal moves to high field by about 1.6 ppm on going from benzaldehydes to the corresponding benzalanilines. This is due to several factors. The most important one is the replacement of an oxygen atom having two lone-pair orbitals by a nitrogen atom not only less electronegative but also having only one electron lone-pair; the additional lone-pair orbital in the oxygen atom has a low-field effect (electric dipole and magnetic anisotropy effects<sup>9</sup>). This factor exceeds

TABLE 2. EFFECT OF SOLVENT ON THE PROTON CHEMICAL SHIFTS OF BENZANILINES ( $\Delta'$  ppm with respect to  $C_6H_{12}$ )

Molecule	Proton	Acetone	$CDCl_3$	TFA
I	1	-0.25	-0.11	-0.86
	2,2'	-0.11	-0.07	-0.41
	3,3'	—	—	—
	4	—	—	—
	5,5'	—	—	—
	6,6'	—	—	—
	7	—	—	—
II	1	-0.34	-0.13	-0.89
	2,2'	-0.23	-0.10	-0.43
	3,3'	-0.21	-0.12	-0.43
	5,5'	-0.26	-0.12	-0.63
	6,6'	-0.18	-0.14	-0.43
III	1	-0.30	-0.09	-0.83
	2,2'	-0.22	-0.06	-0.42
	3,3'	-0.20	-0.10	-0.46
	5,5'	-0.15	-0.09	-0.56
	6,6'	-0.15	-0.09	-0.44
IV	1	-0.40	-0.13	-1.05
	2,2'	-0.27	-0.12	-0.60
	3,3'	-0.15	-0.12	-0.34
	5,5'	-0.26	-0.12	-0.59 (-0.69)
	6,6'	-0.18	-0.12	-0.51 (-0.41)
V	1	-0.32	-0.12	-0.95
	2,2'	-0.24	-0.09	-0.51 (-0.61)
	3,3'	-0.12	-0.09	-0.35 (-0.25)
	5,5'	-0.14	-0.10	-0.59
	6,6'	-0.14	-0.10	-0.39

in magnitude the low-field contribution due to the presence of the additional phenyl ring A (steric compression involving protons 1 and 5, and ring current effects); in biphenyl this contribution is only  $-0.24$  ppm.<sup>10</sup> There may also be a small contribution arising from changes in the B-ring current effect due to possible alterations in the dihedral angle ( $\psi_B$ ) distribution.

Protons 2,2' and 3,3' experience opposite though small shifts  $\Delta$ . The high-field shift for protons 3,3' reflect the smaller  $\pi$  inductive effect of N as compared with O. This should cause an even more marked high-field shift for 2,2'. The fact that a low-field shift is observed instead may be attributed to the larger N lone-pair effect. This seems to indicate that the average  $\psi_B$  has not increased (note that the low-field effect of the lone-pair decreases on increasing  $\psi^{11}$ ). It should be about the same as in benzaldehyde, probably very nearly  $0^\circ$ . In fact,  $(\psi_B)_{eff}$  is expected to be less than  $\psi_{eff}$  for 2-phenylpyridine because in this latter, besides an N...H—C interaction (attraction) similar to that in benzanilines, there is an *ortho* C—H...H—C repulsion; for that compound  $\psi_{eff}$  is much less than  $45^\circ$ .<sup>11</sup>

The  $\Delta$ -values for ring A are much more pronounced. Let us firstly consider the protons 6,6'; the corresponding  $\Delta$ -values vary from  $-0.24$  to  $-0.32$ . These differences

result essentially from changes in the  $\pi$ -electron density at the positions 6,6' on going from the *p*-Y-aniline to the benzaniline. In turn, these changes arise primarily because of the  $\pi$  inductive effect of N (absent in the anilines) upon ring A, as well as alterations in the  $n$ - $\pi$  conjugation. Both contributions depend on the angle  $\psi_A$  distribution. The latter is also caused by changes of the N lone-pair orbital on going from anilines to benzanilines.

If  $(\psi_A)_{eff}$  were approx  $90^\circ$  as suggested by Haselbach and Heilbronner,<sup>6</sup> then we would have to consider only the conjugation between the essentially  $sp^2$ -nitrogen lone-pair orbital and the aromatic  $\pi$  system. We may get an indication of how much this effect would be from a comparison with aniline. Here the corresponding effect is 0.21 ppm.<sup>12\*</sup> The  $n$  orbital in this case is either a  $p$  or an  $sp^3$  orbital, or one of intermediate character; on the other hand,  $\psi_{eff}$  for aniline does not seem to be  $90^\circ$ .<sup>13</sup> If it were, instead of 0.21 ppm one would have a larger effect. Therefore, for  $(\psi_A)_{eff} = 90^\circ$  we would have an effect of at least 0.2 ppm if it were not for the different nature of the lone-pair orbital. For the same  $\psi$ , an  $sp^2$  lone-pair orbital has an effect which is about 75% of that of an  $sp^3$  orbital and 50% of that of a  $p$  lone-pair orbital. This is because  $\pi$  density changes are approximately proportional to the square of the overlap integral between the orbital  $n$  and the nearest  $p$  atomic orbital in the ring.† In conclusion, the effect of an  $sp^2$  lone-pair on the  $\tau$ -values of 6,6' for  $(\psi_A)_{eff} = 90^\circ$  should be at least  $0.2 \times 0.5 = 0.1$  ppm. Since the corresponding effect observed in aniline is 0.2, this would imply a  $\Delta$ -value of  $-0.1$  at the most. The observed  $\Delta$ -values are in the range of  $-0.25$  to  $-0.30$ ‡ therefore, we are led to conclude that  $(\psi_A)_{eff}$  must be appreciably less than  $90^\circ$ . A similar discussion of the 5,5' proton shifts leads to the same conclusion. In particular, the expected  $\Delta$ -value for 5,5' would be  $-0.35$  ppm at the maximum (note that the  $NH_2$  effect on the *ortho* proton shifts is 0.69 ppm),§ whereas the observed values are much bigger.

In the other extreme situation, that is  $(\psi_A)_{eff} = 0^\circ$ , there would be no  $n$ - $\pi$  conjugation. This would result in  $\Delta$ -values for 6,6' and 5,5' of  $-0.2$  and  $-0.7$  ppm, respectively. In addition, there will be the  $\pi$  inductive effect making  $\Delta$  even more negative. On the other hand, the electric dipole and magnetic anisotropy effects associated with the N lone-pair will also help to shift 5,5' to a lower field, the smaller is the angle  $\psi$ . We would then have  $\Delta$ -values appreciably more negative than the observed ones. This shows that  $(\psi_A)_{eff}$  must be appreciably larger than  $0^\circ$ .

Let us assume that the maximum low-field shift of protons 6,6' due to the  $\pi$  inductive effect is  $-0.2$  ppm for  $\psi_A = 0$ , which seems reasonable in view of the corresponding effect in nitrobenzene ( $-0.3$  ppm<sup>12</sup>). On the other hand, the minimum high-field shift due to  $n$ - $\pi$  conjugation for  $\psi_A = 90^\circ$  is, as we have seen, 0.1 ppm. Thus, the maximum low-field shift (or a lower limit for a high-field shift) for any angle  $\psi_A$  is

$$\Delta_{6,6'} = -0.2 - 0.2 \cos^2 \psi_A + 0.1 \sin^2 \psi_A$$

\* About the same value as for *p*-toluidine and *p*-chloroaniline.

†  $n$ - $\pi$  conjugation of a  $sp^2$  orbital is likely to be slightly less because the energy of this orbital is less than that of  $p$  or  $sp^3$  orbitals.

‡ The  $\Delta$ -values for IV and V are more negative than those for II and III probably due to the electron withdrawing effect of the nitro-group on the B ring.

§ 0.76 ppm for  $CCl_4$  solutions<sup>12</sup>.

For  $(\psi_A)_{eff} = 45^\circ$ , we have a maximum low-field shift of  $-0.25$  ppm. Comparison with the observed values suggests therefore that  $(\psi_A)_{eff} \leq 45^\circ$ , in qualitative agreement with the work of Minkin *et al.*<sup>5</sup> A similar application of the 5,5' proton shifts is not so easy, mainly because of the electric dipole and magnetic anisotropy effects due to N which are important for those protons.

### (b) Solvent effects

Changing from cyclohexane to acetone or chloroform as solvents affects the chemical shifts in a manner very similar to that found for the parent compounds. In spite of this observation, we find it difficult to deduce any changes in the molecular geometry from such solvent effects.

Bigger differences are found for the TFA solutions of I-V with respect to the parent molecules. In fact,  $\Delta'$ -values (difference between  $\tau$ -values for TFA and  $C_6H_{12}$  solutions) for the *p*-X-aldehydes are only of the order of  $-0.1$ ,  $-0.3$  and  $-0.2$  for protons 1,2(2') and 3(3'), respectively. This clearly shows that the nitrogen atom in I-V is protonated to a larger extent than the oxygen atom in the benzaldehydes. Evidence for this protonation comes also from an observed splitting of the H-C=N proton signal ( $J = 18$  Hz, see also ref 14).

Protonation of the nitrogen lone-pair removes the  $n-\pi$  conjugation effect and greatly enhances the  $\pi$  inductive effect of N. In spite of the former effect being less important in I-V than in anilines, larger  $\Delta'$ -values would be expected for the benzalanilines. This is not so, however. The corresponding  $\Delta'$ -values for the *p*-Y-aniline are of the order of  $-1.0$  and  $-0.5$  ppm respectively for 5(5') and 6(6'). This discrepancy may be due to several factors, namely, the removal (on protonation) of a low-field effect\* on 5(5') arising from the electric dipole and magnetic anisotropy associated with the N lone-pair, less extensive protonation of benzalanilines compared to anilines, and increase of  $(\psi_A)_{eff}$ , thus tending to reduce the  $\pi$  inductive effect of the nitrogen atom on the A ring.

## EXPERIMENTAL

The various benzalanilines were prepared by refluxing equimolar amounts of the corresponding anilines and benzaldehydes in MeOH,<sup>7</sup> and recrystallizing from the same solvent.

The NMR spectra were obtained at room temp, on a Varian HA-100 spectrometer. Solns containing 5 mg/ml for the parent comps and 10 mg/ml for the benzalanilines were used throughout, except for *p*-nitrobenzaldehyde and IV and V in cyclohexane, in which cases the concentration was less for reasons of solubility.

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\* This being more marked in I-V than in anilines, because of a larger  $(\psi_A)_{eff}$  in the latter.

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