13C-NMR SPECTRA OF N-BENZYLIDENEANILINES. EVIDENCE FOR DELOCALIZATION OF N-LONE-PAIR ELECTRONS TO ANILINE BENZENE RING

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Several N-benzylideneanilines were synthesized which possess anilino benzene rings rotated out of the Ar-C=N plane by various degrees due to steric hindrance. Their 13C-NMR spectra indicated that the N lone pair electrons are delocalized to ring A especially in the compounds in which ring A is forced to rotate out of the molecular plane.

In the trans form of N-benzylideneanilines, the anilino benzene ring (ring A) is rotated around the Ar-N= axis by about 50°, whereas the benzylidene benzene ring (ring B) and the -CH=N- group are on the same plane.[1] In the cis form of N-benzylideneanilines, ring A is rotated around the Ar-N= axis by about 90°, and ring B and the CH=N group are on the same plane.[2,3] This is in quite a contrast with the structures of cis-stilbenes and cis-azobenzenes, in which both of the benzene rings are rotated from the C=C and N=N planes, respectively, because of the steric repulsion between the two benzene rings. Such ease of rotation of ring A alone (and not ring B) in benzylideneanilines were ascribed to the energy gain by delocalization of the N lone pair electrons to ring A upon the rotation of the ring.[4,5] However, no experimental evidence has been presented on this point.

We have synthesized the following benzylideneanilines possessing ring A rotated out of the Ar-C=N plane by various degrees due to steric hindrance, and determined their 13C-NMR spectra. We have compared the chemical shifts of C-4 of ring A, and examined whether or not the electron density of ring A are increased when ring A is rotated.
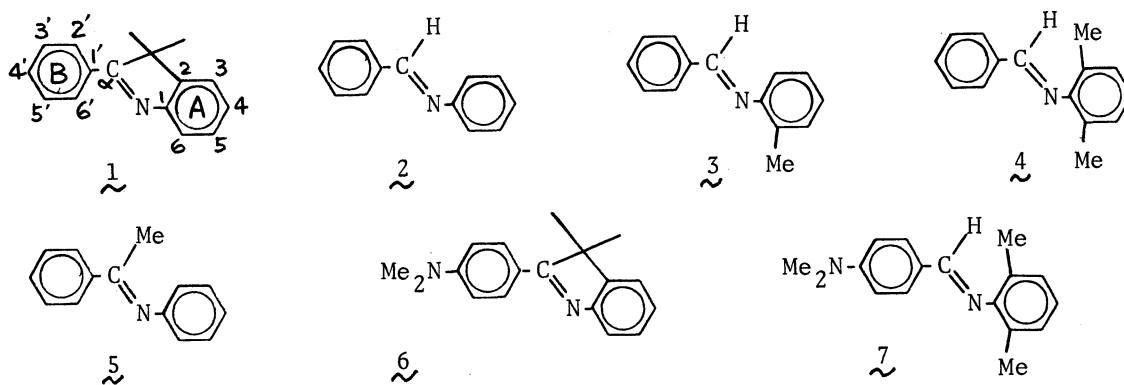
^{13}C-NMR spectra were determined in CDCl$_3$ with a JEOL FX-60 Spectrometer. The accuracies of chemical shifts δ were about ± 0.08 ppm. Signals were assigned on the basis of the off-resonance proton decoupling experiments, deuterium substitution experiments, and the data described in the literature.[6] The results are summarized in the Table.

Table.   Carbon-13 Chemical Shifts of 1~7[a]

	1	2[b]	3	4	5	6	7
C-1	152.99	151.94	151.04	151.13	151.68	151.61	151.78
C-2,6	147.47 120.77	120.77	117.52 131.73	126.69	119.21	147.39 119.80	127.43
C-3,5	120.77 127.66	c	130.19 126.62	d	e	120.61 127.43	f
C-4	125.72	125.80	125.56	123.53	123.11	124.50	122.96
C-α	183.10	159.97	159.24	162.16	165.18	182.86	161.84
C-1'	133.27	136.11	136.36	136.03	139.47	120.61	124.18
C-2',6'	g	c	}128.64	d	e	129.86	f
C-3',5'	g	c		d	e	111.36	111.52
C-4'	130.43	131.16	131.08	131.08	130.28	153.56	152.43

[a] In ppm downfield from internal TMS. Spectral width 2.5 kHz; pulse flipping angle
    45°; pulse width 9 μsec.; sampling time 900 msec.; data points 4096;
    accumulation 500-1000; pulse interval 3-5 sec.

[b] Carbon-13 chemical shifts of 2 were reported by Inamoto et al.,[o] but they were
    measured again in order to compare the data on 1-7 on the same instrument.

[c] 128.97, 128.97, 128.64.   [d] 128.48, 128.32, 127.99.

[e] 128.82, 128.30, 127.13.   [f] 129.86, 127.75.

[g] 128.48, 128.24.

The UV absorption maxima and extinction coefficients are : 1, λ_{max}= 309 nm, ϵ= 16600;[7] 2, λ_{max}= 314, ϵ=6940;[8] 3, λ_{max}= 325, ϵ=4230;[8] 4, λ_{max}= 331, ϵ=1740;[8] 5, λ_{max}= 320, ϵ=1840.[8] These UV data clearly show that in the case of 1, ring A and the C=N group lie in a plane, whereas an X-ray diffraction study has shown that in the case of 2, ring A is rotated about 50° around the Ar-N axis,[1,9] The smaller extinction coefficients in 4 and 5 in comparison with that in 2 have been ascribed to greater rotation of ring A around the Ar-N axis because of the steric hindrance involving methyl groups ,and ortho or alpha hydrogens.[8] The extinction coefficient of 3 is not much different from that of 2, and this suggests that the extents of rotation of ring A are similar in 2 and 3.[8] This is reasonable because the methyl group of 3 can be situated far from the methine hydrogen and no interaction between them may take place.

The Table shows that δ_{C-4} of 4 and 5 are observed at a much higher field than that in 1 ($\delta_{C-4}(1)$ - $\delta_{C-4}(4)$ = 2.19, and $\delta_{C-4}(1)$ - $\delta_{C-4}(5)$ = 2.61 ppm). This difference cannot be ascribed to the presence of electron-donating methyl groups, since methyl substituents do not affect δ_{C-meta} greatly,[10] and $\delta_{C-4}(2)$ and $\delta_{C-4}(3)$ are similar. The fact that δ_{C-4} of 5 possessing a methyl group on the methine carbon is similar to that of 4 possessing methyl groups on ring A suggests that the rotation of ring A around the Ar-N axis causes the upfield shift observed in 4 and 5.

If the fact that the C-4 signal of 1 resonates at a field higher than that in benzene (δ= 128.5) is due to the resonance shown in (1), rotation of ring A around the Ar-N axis is expected to decrease such resonance, and downfield shifts of the C-4 signals are expected.

(1)
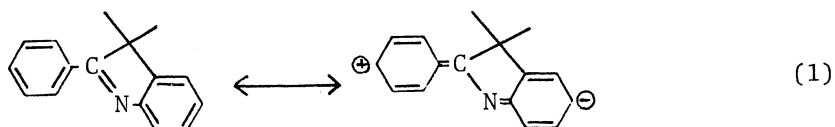
The upfield shift observed for the C-4 signals of 4 and 5 in comparison with that of 1 indicates the existence of the delocalization of N lone pair electrons to ring A by the resonance shown in (2), inaccord with the hypothesis described in the first paragraph.

(2)
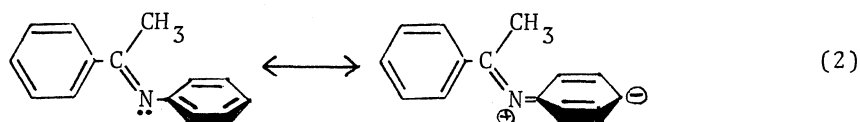
In 4 or 5, in which ring A is rotated from the Ar-C=N plane by about 90°, the resonance shown in (1) should not be possible and the resonance shown in (2) must be important. The greater electron density on C-4 of 4 and 5 in comparison with that of 1 suggests that the increased contribution of resonance (2) outweighs the decreased contribution of resonance (1). In 2 or 3, in which ring A is rotated by about 50°, the electron density on C-4 is about the same as that of 1, and these results indicate that increased contribution of resonance (2) is approximately equal to decreased contribution of resonance (1).

Our hypothesis is further supported by the results of the ^{13}C-NMR measurements on compounds 6 and 7. The C-4 of 6 resonates at a field higher than that of 1 ($\delta_{C-4}(1)$ - $\delta_{C-4}(6)$ = 1.22 ppm). This is ascribable to the resonance (1) donating electrons from the dimethylaminobenzene ring to ring A. The difference between $\delta_{C-4}(4)$ and $\delta_{C-4}(7)$ is smaller (= 0.57 ppm) than that between 1 and 6. This means that in 4 or 7 the contribution of resonance (1) is very small, and supports the hypothesis that the greater electron density on C-4 of 4 and 7 in comparison with those of 1 and 6 is due to the delocalization of the N lone pair electrons to ring A as expressed in (2).

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