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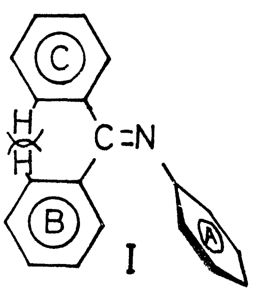
CONFORMATIONS OF N-(α-PHENYLBENZYLIDENE)ANILINES

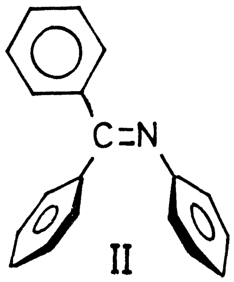
Masato YOSHIDA, Hiroshi MINATO, and Michio KOBAYASHI
Department of Chemistry, Tokyo Metropolitan University, Fukazawa, Setagaya,
Tokyo 158

PMR spectra of N-(α-phenylbenzylidene)anilines were analyzed by use of differences in spin-lattice relaxation times on a pulse-FT-NMR spectrometer. The results suggested that both the imino benzene ring and the benzene ring adjacent to the imino benzene ring are greatly rotated out of the molecular plane.

The UV spectra of N-(α-phenylbenzylidene)anilines suggested that the imino benzene ring (ring A) is rotated by about 90° around the Ar-N axis,[1] but conformations of the other two benzene rings have not been clarified.

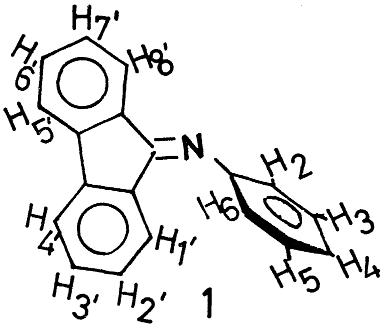
Conformations plausible for ring B and ring C are the following two (I and II). In (I), both ring B and ring C are slightly rotated out of the molecular plane owing to steric hindrance. In (II), ring B is rotated by about 90°, but ring C is not rotated.


I


II

The present study has been undertaken in order to find out the conformations of N-(α-phenylbenzylidene)aniline and its methyl derivatives by examining the effects of the C=N group and ring A on the chemical shifts of various hydrogen atoms.

In N-fluorenylideneaniline (1), owing to the anisotropic deshielding effect of the C=N group, H_8' is expected to resonate at a lower field in comparison with other protons, as suggested by a PMR study of N-benzylideneanilines.[2] Because of the ring current effect of ring A, H_1' is expected to resonate at a higher field in spite of the deshielding effect of the C=N group. Figure 1a is the PMR spectrum of 1, in which signals are too crowded to be assigned. Since spin-lattice relaxation times of these protons vary considerably, assignment was attempted by use of a partially-relaxed pulse-FT-NMR (PRFT) technique.[3,4] By determining the spectra at varying pulse intervals τ in the 180°-τ-90° pulse sequence, signals can be separated and assigned (see Fig. 1).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In order to differentiate the H_1' signal from the H_2 and H_6 signals which also appear at higher fields owing to the shielding effect of the C=N group, the spectra of **1**-2,4,6-d_3 synthesized were also examined (Fig. 2). In Fig. 2b, a multiplet at the lowest field (δ 7.90-8.00) is assigned to H_8', and a multiplet at the highest field (δ 6.48-6.61) is assigned to H_1'. Because of the ring current effects of ring A, the H_1' and H_8' signals separate by about 1.4 ppm.

Methyl derivatives of N-(α-phenylbenzylidene)aniline, **2**~**4**, were synthesized,[5] and their PMR chemical shifts are compared in the Table.

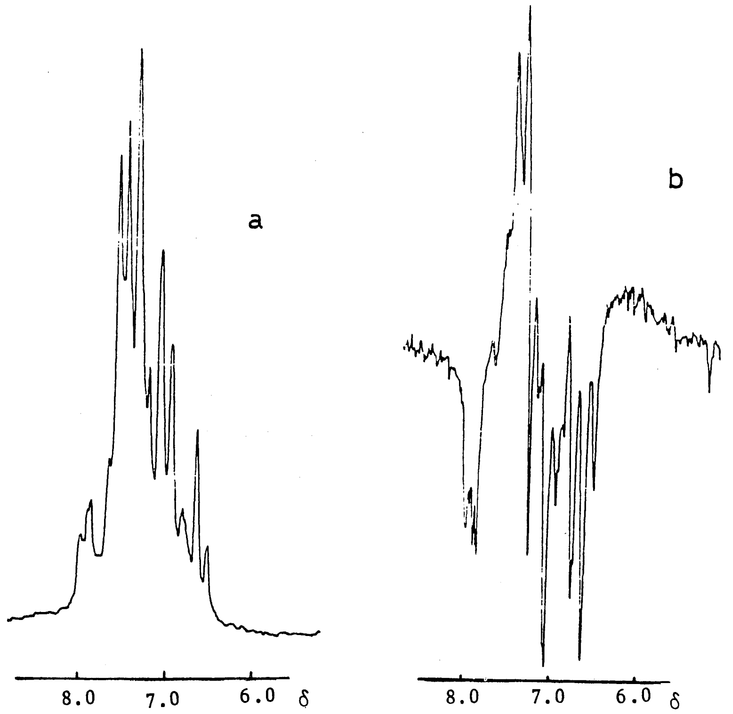


Fig. 1. a, Normal FT PMR Spectrum of **1**;
b, PRFT PMR Spectrum of **1** (τ = 1.4 sec in 180°-τ-90°).

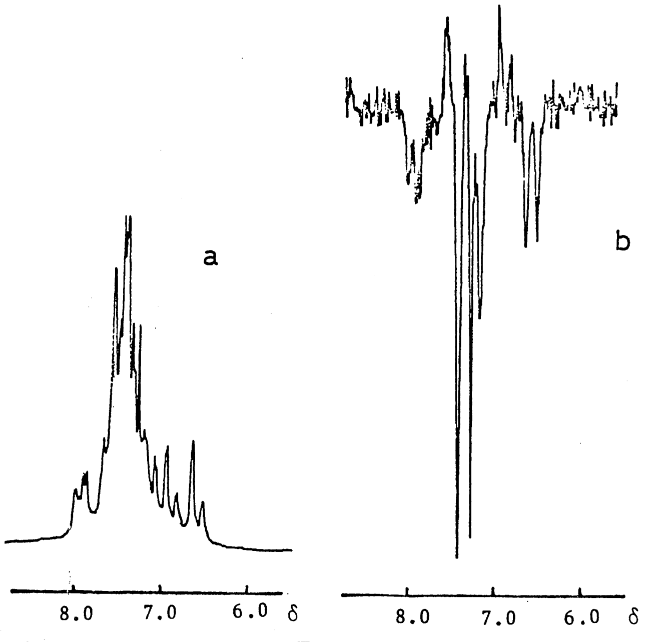
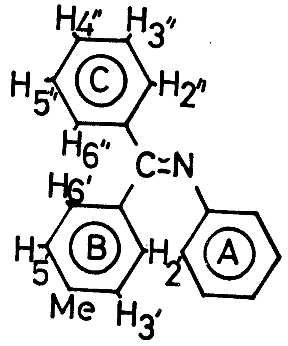
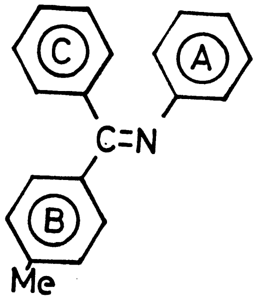


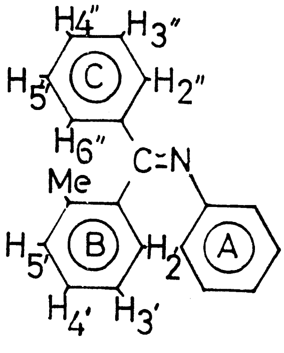
Fig. 2. a, Normal FT NMR Spectrum of **1**-2,4,6-d_3;
b, PRFT PMR Spectrum of **1**-2,4,6-d_3 (τ=1.4 sec in 180°-τ-90°).



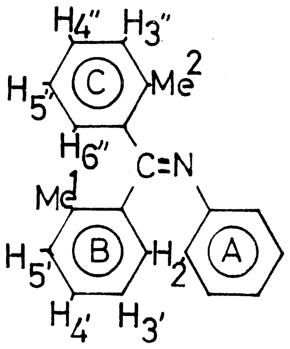
2 (Z)



2 (E)



3 (Z)



4

Table PMR Chemical Shifts of **2**~**4**[a]

	δ_{Me}	$\delta_{H_2'(H_6')}$	$\delta_{H_2''(H_6'')}$
2	2.40(s), 2.31(s)	6.65-6.75(m)	7.57-7.70(m)
3	2.04(s)	6.69-6.79(m)	7.54-7.70(m)
4	2.01(s), 2.51(s)	6.66-6.76(m)	b

[a] See ref. 3; δ in $CDCl_3$ at 25°.

[b] No signals influenced by the deshielding effect of the C=N group were observed.

The spectrum of **2** shows two Me signals, and suggests that both conformations **2**(Z) and **2**(E) are present in an approximately 1:1 ratio. The spectrum of **3** shows only one Me signal, and indicates that either of the Z or E isomer is present.[8] The spectrum of **4** has two Me signals at δ 2.01 and 2.51. The signal at δ 2.51 is assigned to Me^2 influenced by the deshielding effect of the C=N group, and that at δ 2.01 is assigned to Me^1 influenced by the shielding effects of the C=N group and of the ring current of ring A which is greatly rotated out of the moleuclar plane. Since the Me protons in **3** and the Me^1 protons in **4** resonate at almost the same field, the Me in **3** and the Me^1 in **4** are in a similar environment, and **3** probably has the Z structure shown.

Figure 3 shows the PRFT spectrum of **2** determined by the 180°-τ-90° pulse sequence with τ = 1.3 sec. A multiplet at a lower field (δ 7.57-7.70) and that at higher field (δ 6.65-6.75) can easily be distinguished from other signals since these two multiplets have much longer spin-lattice relaxation times. The spectrum of **3** has similar two sets of multiplets at δ 6.69-6.79 and δ 7.54-7.70, whereas that of **4** has only the multiplet at a higher field and no multiplet at lower fields. These data together with the chemical shifts of H_1' and H_8' of **1** indicate that the multiplet at the higher field is assigned to H_2' (or H_6') and that at the lower field is assigned to H_2''(or H_6'').

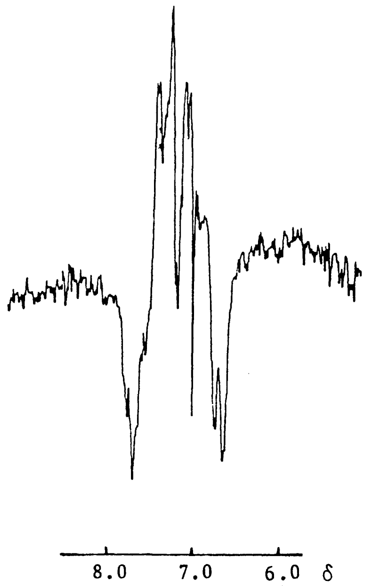
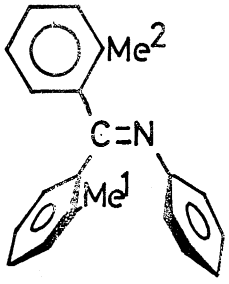


Fig.3. PRFT PMR Spectrum of **2**. (τ=1.3 sec in 180°-τ-90°).

The facts that $\delta_{H_2'(H_6')}(\mathbf{2})$ and $\delta_{H_2'(H_6')}(\mathbf{3})$ have similar[6] values and that $\delta_{H_2''(H_6'')}(\mathbf{2})$ and $\delta_{H_2''(H_6'')}(\mathbf{3})$ have similar values suggest that N-(α-phenylbenzylidene)anilines have conformation II. If they have conformation I, $\delta_{H_2''}(\mathbf{3})$ is expected to have a smaller value than $\delta_{H_2''}(\mathbf{2})$, since ring B and ring C in **3** would greatly be rotated out of the molecular plane owing to the presence of the Me group. If one assumes that **2**, **3**, and **4** have conformation II and ring B is rotated by about 90° out of the molecular plane, one can reasonably explain all the data including the facts that $\delta_{H_2''}$(**2**) and $\delta_{H_2''}$(**3**) have similar values and that δ_{Me}(**3**) and δ_{Me^1} (**4**) have similar values.

The fact that $\delta_{H_2''}$(**2**) has a smaller value than $\delta_{H_8'}$(**1**) can be ascribed to the equilibration of H_2'' and H_6'' in **2** due to the rapid rotation of ring C on the NMR time scale. In **4**, such free rotation of ring C must be inhibited and **4** keeps the conformation shown below, since its PMR spectrum has no signals of the protons influenced by the deshielding effect of the C=N group.



The observation that **3** has only the Z structure can be explained as follows. Although the rotation of ring B is restricted both in the Z and E structures owing to the presence of the Me group, the rotation of ring C is possible in the Z structure but not in the E structure. Thus the Z structure is favored from the aspect of entropy.

REFERENCES AND NOTES

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2) A. van Putten and J. W. Pavlik, Tetrahedron, 27, 3007 (1971).
3) R. Freeman and H. D. W. Hill, J. Chem. Phys., 53, 4103 (1970).
4) Solvent, $CDCl_3$; spectral width, 1 kHz; data points, 4096; 90° pulse = 43 μsec. In PRFT $-(180°-\tau-90°-T)_n-$, T = 8 sec and n = 10 - 15. A JEOL-FX60 spectrometer was used.
5) **1**, **1**-2,4,6-d_3, **2**, **3**, and **4** were prepared by condensation of the corresponding ketones and aniline. Melting points are: **1**, 84-85.5° (lit.,[6] 88-89°); **1**-2,4,6-d_3, 84-86°; **2**, oil (lit.,[7] bp 238°/16 mm); **3**, 107-109° (lit.,[7] 104.5°); **4**, 86-88°. The results of elemental analysis of **4** were satisfactory.
6) M. E. Taylor and T. L. Fletcher, J. Org. Chem., 21, 523 (1956).
7) G. Reddelien, Ber., 48, 1470 (1915).
8) N-(α-Phenylbenzylidene)anilines exist as equilibrium mixtures of Z and E structures, which tautomerize readily each other. For instance, the activation energy for thermal isomerization of p-$MeOC_6H_4(Ph)C=N-C_6H_4$-p-Cl was found to be 19.7 ± 0.4 kcal/mol.[9] Therefore, if the E and Z structures of **3** have similar stabilities, the PMR spectrum of the solution should show the signals of both structures. Although it is possible that one isomer was selectively formed or selectively isolated by recrystallization, the fact that the PMR spectrum of the solution of the product showed only one Me signal is best explained by assuming that the equilibrium lies far to one side.
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