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Studies on the Configuration of *N*-Cyclohexylideneanilines with ^{13}C-NMR Spectroscopy

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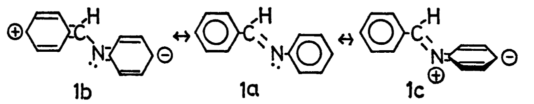
Synopsis. ^{13}C-NMR chemical shifts and the rates of thermal *E-Z* isomerizations of *N*-cyclohexylideneanilines have been determined and the substituent effects discussed.

In a previous paper the existence of two types of conjugation[1] in *N*-benzylideneanilines (**1a**) was reported. One is conjugation between the π-electrons of the carbon-nitrogen double bond and aromatic ring (**1b**), and the other is conjugation between the lone pair electrons of the nitrogen and aromatic ring (**1c**).

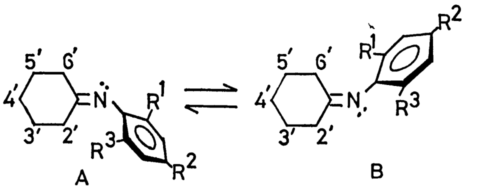


1b 1a 1c

There is no type **1c** conjugation when the dihedral angle between the >C=N– plane and imino benzene ring is 0°, whereas an angle of 90° represents the optimum conditions. *N*-Cyclohexylideneanilines appear to be suitable compounds to study this type of conjugation since the imino benzene rings are known to rotate by about 90° out of the >C=N– plane.[2] The ^{13}C-NMR spectra of substituted *N*-cyclohexylideneanilines (**2**—**6**) have been studied at several temperatures and the substituent effects discussed in connection with the thermal isomerism between the *E* and *Z* forms.

Results and Discussion

Thermal isomerization between the *E* and *Z* forms of the *N*-benzylideneanilines is known to readily occur. In *N*-cyclohexylideneaniline, thermal isomerization between the forms **A** and **B** shown below is expected.



	2	3	4	5	6
R^1	H	H	H	H	Me
R^2	NO$_2$	COOEt	H	OMe	NO$_2$
R^3	H	H	H	H	Me

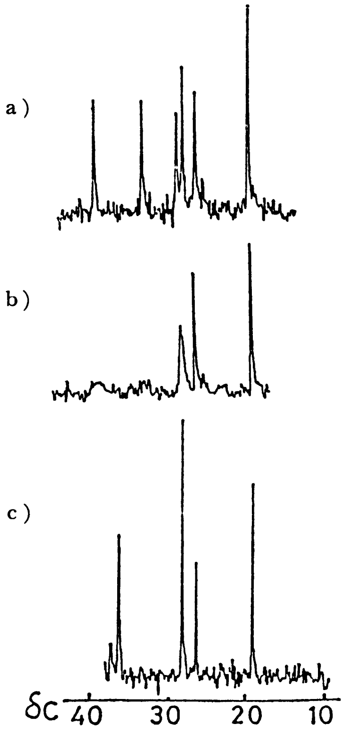


Fig. 1. ^{13}C-NMR spectra of compound **6** at a) −50 °C in CDCl$_3$, b) at room temperature in CDCl$_3$, and c) at 100 °C in DMSO-d_6.

TABLE 1. CARBON-13 CHEMICAL SHIFTS OF **2**—**6** AT ROOM TEMPERATURE

	2	3	4	5	6[a]
C-1	157.0	154.9	150.0	144.0	154.5
C-2,6	120.0	119.3	119.6	120.9	127.2
C-3,5	125.0	130.4	128.5	114.1	123.1
C-4	143.5	124.9	122.7	155.7	142.2
C-1'	176.4	175.2	174.5	175.2	175.6
C-2'	32.1	31.5	31.1	31.2	32.1
C-3'	27.8	27.4	27.4	27.7	26.9
C-4'	25.6	25.4	25.6	25.9	25.2
C-5'	27.8	27.6	27.7	27.9	27.7
C-6'	39.3	39.0	39.2	39.5	38.3

a) At −50 °C.

The ^{13}C-NMR spectra of **2**—**5** were measured at room temperature in CDCl$_3$, and the δ_C values for **2**—**5** are given in Table 1. The differences in value of $\delta_{C-2'}$ and $\delta_{C-6'}$ (or $\delta_{C-3'}$ and $\delta_{C-5'}$) for **2**—**5** indicates that the configurations of **2**—**5** are fixed within the NMR time scale at room temperature. As shown in Fig. 1b the ^{13}C-NMR of C-2'-6' of compound **6** could not be observed as a set of five signals. Five ^{13}C-NMR signals of each C-2'-6' were observed at −50 °C, while at 100 °C the signals of C-2' and C-6' (also C-3' and C-5') coalesced and the ^{13}C-NMR signals of C-2'-6' appeared as three signals. This indicates that the thermal isomerization between **6A** and **6B** is slower at −50 °C and faster at 100 °C than the

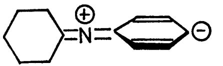
Table 2. Coalescence temperatures (T_c) of $C_{2'}$, $C_{6'}$ and ΔG^* values for **2**—**6**[a)]

	$\nu C_{2'}$–$\nu C_{6'}$	T_c/K[b)]	ΔG^*/kcal mol^{-1}
2	106.20	348	16.7
3	109.86	398	19.2
4	118.14	>413	>19.7
5	124.51	>413	>19.7
6	92.77	328	15.7

a) Solv. DMSO-d_6 for **2**—**5** and $CDCl_3$ for **6**. b) Accuracy: ±5 K.

NMR time scale. Consequently, at elevated temperatures, the thermal isomerizations in **2**—**5** are expected to be observable by NMR. The ^{13}C-NMR spectra of **2**—**6** were measured at several temperatures, and the coalescence temperatures (T_c) for C-2′ and C-6′ signals determined, and the ΔG^* values calculated. The results are summarized in Table 2.

Type **1b** conjugation should not be possible when the imino benzene ring is rotated out of the >C=N– plane by approximately 90°. Interaction between the *N*-lone pair and imino benzene ring however becomes important. Table 1 shows that $\delta_{C-1'}$ is very little affected by the substituents of the aromatic ring in comparison with $\delta_{C-\alpha}$ of *N*-benzylideneanilines ($PhCH{=}N{-}C_6H_4{-}R{-}p$) whose imino benzene rings are rotated approximately 50°.[3)] This suggests that the substituents of the aromatic ring do not affect the electron density on the carbon atom of >C=N– when the imino benzene ring is rotated out of the >C=N– plane by approximately 90°. As shown in Table 2, the ΔG^* of **2** and **3** having electron-withdrawing groups are smaller than those of **4** and **5**. This can be explained by assuming a linear transition state **C** for the thermal isomerization between forms **A** and **B**.[4)]



C

In this transition state, the hybridization of the N atom is of the sp type. The transition state (**C**) should be stabilized by the electron-withdrawing substituent on the imino benzene ring to a greater extent than in the ground state, since the delocalization of the *N*-lone pair into the imino benzene ring will be easier with a linear structure. Electron-withdrawing substituents on the imino benzene ring will assist this delocalization and decrease ΔG^*.

Experimental

N-Cyclohexylideneanilines[2)] were prepared by condensation between the corresponding anilines and cyclohexanone diethyl acetal:[5)] bp (mp): **2**; 176 °C/6 mmHg, **3**; 187 °C/5 mmHg, **4**; 140 °C/18 mmHg, (lit,[2)] 156 °C/30 mmHg), **5**; 76—77 °C (mp), **6**; 57—58 °C (mp).

^{13}C-NMR chemical shifts were determined at room temperature in $CDCl_3$ with a JEOL Fx-60 FT spectrometer. The accuracies of chemical shifts were approximately 0.1 ppm (data points; 4096, sampling time; 900 ms, pulse flipping angle; 45°). The coalescence temperatures were determined in DMSO-d_6 well-dried with molecular sieves, and the values of the activation free energy calculated using the following equation,[6)]

$$k = \pi\nu_{ab}/\sqrt{2} = (KT/h)\exp(-\Delta G^*/RT).$$

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