Tetrahedron. Vol. 25, pp. 741 to 746. Pergamon Press 1969. Printed in Great Britain

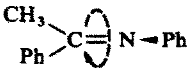
EFFECT OF COMPLEX FORMATION ON *CIS–TRANS* ISOMERIZATION IN N-(α-METHYLBENZYLIDENE)ANILINE

E. A. Jeffery, A. Meisters and T. Mole
Division of Applied Chemistry, C.S.I.R.O., Chemical Research Laboratories, P.O. Box 4331,
Melbourne, Australia, 3001

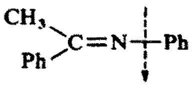
(*Received in the UK* 6 *August* 1968; *Accepted for publication* 10 *September* 1968)

Abstract—*cis-trans* Isomerization in N-(α-methylbenzylidene)aniline has been studied by PMR spectroscopy in the presence of trimethylaluminium, which complexes with the anil. Both the position of equilibrium and the rate of isomerization are affected by the trimethylaluminium. The complexed anil does not isomerize; this confirms that the uncomplexed anil isomerizes by inversion of the nitrogen lone-pair, rather than by rotation about the C=N double bond.

Unimolecular *cis–trans* isomerization about the C=N double bond of N-(α-methylbenzylidene)aniline may take place either (a) by rotation of the N—Ph group through 180° about the C=N double bond, as shown in structure A, or (b) by a vibrational movement in the >C=N plane through transition state B.



A



B

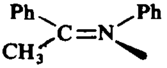
Earlier workers[1, 2] have regarded mechanism (b) as more likely than mechanism (a), firstly because Schiff bases are more easily isomerized than compounds with C=C double bonds, and secondly from a consideration of the effect of substituents in the Schiff base upon the rate of isomerization.[2–4]

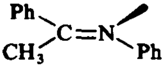
The crucial test distinguishing the two mechanisms is the effect of complex formation upon the rate of isomerization. If the lone-pair of the N atom is bound to a Lewis acid, transition state B should no longer be accessible. However transition state A should be attained more easily, since the C=N bond order is likely to be reduced on complex formation and since the relief of steric strain on twisting the N—Ph group out of the >C=N plane is probably greater in the complex than in the free anil.

In this paper it will be shown that the anil stops isomerizing when complexed with trimethylaluminium. Thus the anil isomerizes by mechanism (b), i.e. by inversion of the lone pair of electrons of the N atom.

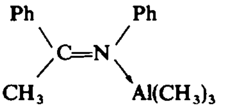
RESULTS AND DISCUSSION

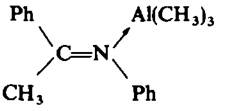
N-(α-methylbenzylidene)aniline in chlorobenzene shows only one sharp methyl resonance, 1·96 ppm to low field of TMS, although both *cis* and *trans* isomers are possible (*cis*-I and *trans*-I, respectively). *cis-trans* Isomerization in anils is not particularly sensitive to the nature of substituents on the C atom of the double bond$^{1-4}$ and normally has a half-life of about 1 second at room temperature.$^{1-3}$ Hence the 1·96 ppm peak is thought to represent the more stable of the isomers of I. On steric grounds *trans*-I should be more stable than *cis*-I. Further the more stable isomer of a Schiff base normally has the bulkier group on the C atom *trans* to the organic group on the N atom.$^{1-3}$ Therefore the 1·96 ppm peak is assigned to *trans*-I. The alternative possibility that the 1·96 ppm peak represents a rapidly isomerizing mixture of *cis*-I and *trans*-I may be rejected because there is no broadening of the peak down to $-35°$ in chlorobenzene or to $-60°$ in toluene.


cis-I


trans-I

On step-wise addition of trimethylaluminium to N-(α-methylbenzylidene)aniline in chlorobenzene, the peak (T) attributed to *trans*-I moves progressively to high field, remaining sharp but decreasing in intensity. At the same time a new peak (C) appears at 2·65 ppm. The sum of the intensities of peaks C and T is equal to the original intensity of peak T. When an equivalent of trimethylaluminium has been added (i.e. ½ mole of trimethylaluminium dimer per mole of anil), C (2·65 ppm) and T (1·87 ppm) have comparable intensities. Any further increase in the ratio of trimethylaluminium to anil does not change the position or intensities of peaks C and T. The addition of enough pyridine to complex with the trimethylaluminium reverses the spectral change; peak C disappears, and peak T regains its intensity and reverts to 1·96 ppm. Therefore the changes just described are attributed to the formation of complexed anils, *cis*-II and *trans*-II, from *trans*-I.


cis-II


trans-II

Since the changes are complete upon addition of only one equivalent of trimethylaluminium, it appears that complex formation is quantitative.

When at least an equivalent of trimethylaluminium is present, one of the two peaks must be assigned to *cis*-II and the other to *trans*-II. Since the 1·87 ppm (peak T) results from a continuous shift of the peak attributed to *trans*-I to high field, it is assigned to *trans*-II. When less than an equivalent of trimethylaluminium is present, peak T appears between 1·96 and 1·87 ppm; the peak then represents a mixture of *trans*-I and *trans*-II, in which trimethylaluminium groups are being rapidly transferred from the latter to the former.

Peak C then must be assigned to *cis*-II. Its chemical shift does not change with the ratio of trimethylaluminium to anil. Presumably *cis*-I and *cis*-II are in rapid equilibrium, in the same way as *trans*-I and *trans*-II are. The constancy in chemical shift of peak *C* is consistent with the presence of *cis*-I in only very low concentrations.

By contrast with the rapid appearance of peak C in the presence of less than an equivalent of trimethylaluminium, several days at room temperature are required for its appearance after a large excess of trimethylaluminium is added rapidly to the anil. It appears, therefore, that *trans*- to *cis*-isomerization occurs rapidly only when free *trans*-anil (*trans*-I) is present.

The hypothesis that *trans*-I isomerizes much faster than *trans*-II was tested kinetically by a study of the line broadening (due to isomerization) of peaks *C* and *T* under equilibrium conditions in chlorobenzene at 85°.

The data obtained was handled using Eqns (1)–(13) given in the Experimental, below. Reciprocal pre-isomerization lifetimes, τ_C^{-1} and τ_T^{-1}, defined by Eqs (3) and (4), were derived from the measured linewidths using Eqs (1) and (2). Values of τ_C^{-1} and τ_T^{-1} over a range of concentrations of trimethylaluminium and anil are given in Table 1. The concentrations of these two reactants give the concentrations of *trans*-I, *trans*-II and *cis*-II by use of Eqs (11) to (13).

Fig. 1 shows a plot of τ_C^{-1} [*cis*-II] against [*trans*-I]. The plot is linear, and so confirms Eq. (8) and the hypothesis that *trans* to *cis* isomerization is a first-order reaction of *trans*-I alone. Eq. (8) was used in conjunction with values of τ_C^{-1} to derive values of the first order rate constant, *k*. Eq. (10) and values of τ_T^{-1} were used similarly, and the values of *k* obtained by both methods are shown in Table 1. These are considered to be self-consistent within experimental error. The average value of the first-order rate constant for isomerization of *trans*-I to *cis*-I at 85° in chlorobenzene is 5 sec.$^{-1}$ The rate constant for the reverse process must be higher than this by a factor of at least 10^2.

The full mechanism for isomerization in the presence of trimethylaluminium is:

$$\begin{array}{lll} \textit{trans}\text{-II} \rightleftharpoons \textit{trans}\text{-I} + \tfrac{1}{2}(\mathrm{CH_3})_6\mathrm{Al_2} & & \text{rapid} \\ \textit{trans}\ \text{I} \rightleftharpoons \textit{cis}\text{-I} & & \text{slow} \\ \textit{cis}\text{-II} \rightleftharpoons \textit{cis}\text{-I} + \tfrac{1}{2}(\mathrm{CH_3})_6\mathrm{Al_2} & & \text{rapid} \end{array}$$

If *cis*- and *trans*-II isomerize directly, they do so much more slowly than *cis*- and *trans*-I. This result is that predicted for a vibrational mechanism for isomerization (mechanism b), but is the opposite of what would be expected if isomerization took place by hindered rotation about the C=N double bond (mechanism a). Therefore it is concluded that isomerization occurs by the vibrational mechanism, i.e. by lone pair inversion.

The rate constant for *trans* to *cis* isomerization cannot be measured under equilibrium conditions in the absence of Lewis acid because there is negligible free *cis*-anil present. It is only the displacement of equilibrium upon addition of trimethylaluminium that allows a rate constant to be derived. Equilibrium between the complexed anils favours the *cis*-anil much more than does equilibrium in the absence of trimethylaluminium. This suggests that it may be possible to prepare the thermodynamically less stable isomer of a Schiff base by allowing equilibrium to be attained in the presence of slightly less than one equivalent of a Lewis acid, and then removing the Lewis acid. This procedure would not be applicable for anils, which isomerize rapidly in the absence of Lewis acids, but might be useful for Schiff bases derived from alkyl amines.

The relatively high rate of inversion of anils may be understood in terms of the

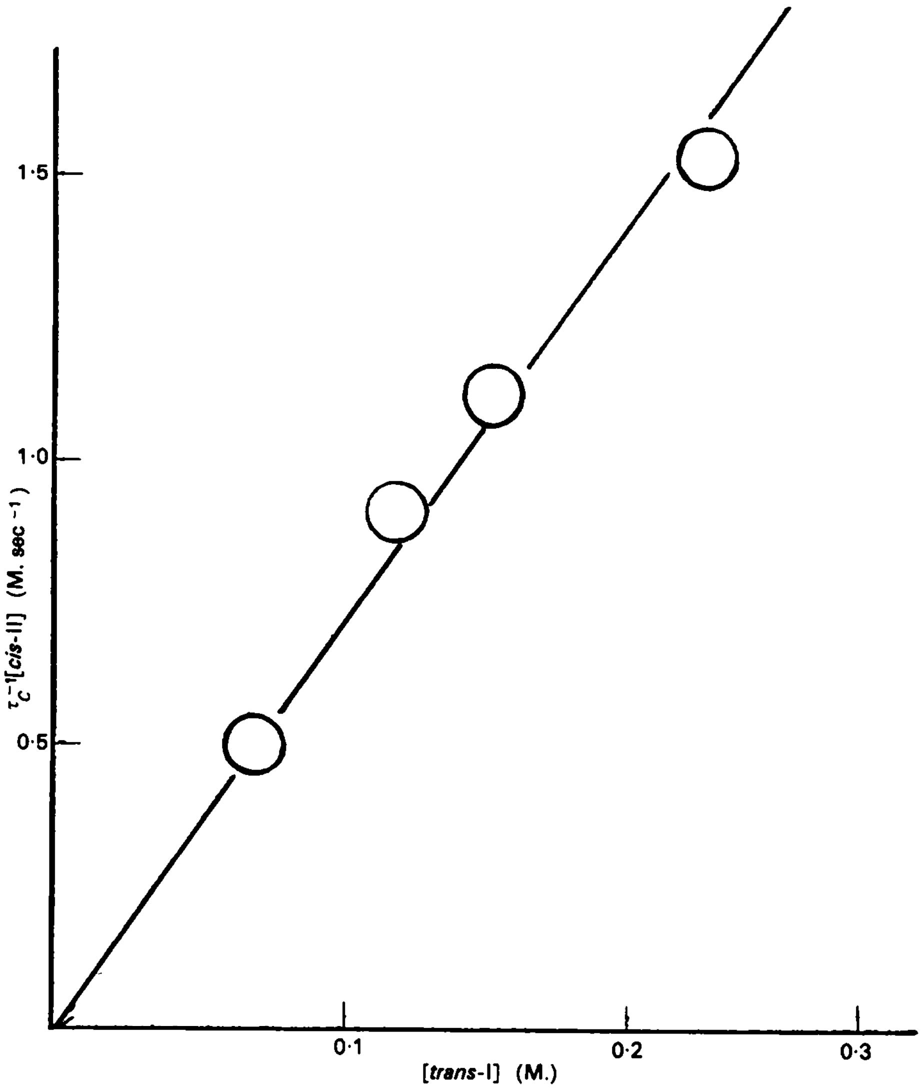
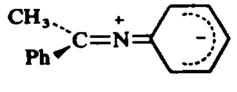


FIG. 1 First order plot for isomerization of N-(α-methylbenzylidene)aniline

stability of the transition state B for isomerization by lone pair inversion. In the transition state the valence electrons of the nitrogen atom are sp-hybridized, and one of the *p*-orbitals is used for the C=N double bond. The other *p*-orbital is free to overlap with the *p*-orbitals of the phenyl ring, as depicted in structure C.



C

Table 1. First-order rate constants and (pre-isomerization life-times)$^{-1}$ for isomerization of *trans* N-(α-methylbenzylidene)aniline in chlorobenzene at 85°

$[(CH_3)_6Al_2]$* (M.)	[Anil] (M.)	τ_C^{-1} (sec^{-1})	τ_T^{-1} (sec^{-1})	k from τ_C^{-1} (sec^{-1})	k from τ_T^{-1} (sec^{-1})
0·106	0·505	12·7 ± 0·6	3·7 ± 0·6	5·1 ± 0·5	4·8 ± 1·2
0·154	0·505	6·8 ± 0·3	3·1 ± 0·3	5·5 ± 0·6	5·2 ± 0·8
0·175	0·505	4·8 ± 0·3	2·1 ± 0·3	5·8 ± 0·6	4·4 ± 0·7
0·207	0·505	2·2 ± 0·3	1·3 ± 0·3	5·4 ± 1·2	4·0 ± 1·7
0·271	0·505	very small	very small		
0·350	1·01	4·3 ± 0·3	1·9 ± 0·3	5·5 ± 0·8	3·9 ± 0·8
0·175	0·505	4·8 ± 0·3	2·1 ± 0·3	5·8 ± 0·6	4·4 ± 0·7
0·088	0·253	4·8 ± 0·6	2·2 ± 0·6	6·0 ± 1·1	4·5 ± 1·5

* One mole of trimethylaluminium dimer complexes with two moles of anil.

Layer and Carman[5] have recently examined *cis-trans* isomerization about the carbon-nitrogen double bonds in quinonediimines and the derived N-oxides. By contrast with the present work, they concluded that isomerization occurs by a rotational mechanism. This suggests that neither the inversion mechanism nor the rotational mechanism of imine isomerism is universally applicable.

EXPERIMENTAL

Commercial trimethylaluminium, shown by PMR spectroscopy to contain no significant amount of dimethylaluminium methoxide, was used without purification. N-(α-methylbenzylidene)aniline was recrystallized from light petroleum. Chlorobenzene was fractionally distilled and stored over 4A molecular sieve under an atmosphere of N_2. All air-sensitive solns were handled under an atmosphere of dry, oxygen-free N_2 by glove-box techniques.

PMR spectra were measured using a Varian A60 spectrometer fitted with a variable temp probe. Solns for kinetic study were prepared by mixing a soln of trimethylaluminium in chlorobenzene with a soln of anil in chlorobenzene in a pyrex sample tube, which was then sealed. The total volume of soln in each tube was 0·6 ml, so as to minimize errors due to the vertical temp gradient in the spectrometer probe. Spectra were measured at 85°.

The pre-isomerization lifetime, τ_C, of the *cis*-molecules responsible for peak C (i.e. *cis*-II) is related to the width (c/s) of peak C at half height, w_C, by Eq. (1):[6]

$$\tau_C^{-1} = \pi(w_C - w_C^{\circ}), \tag{1}$$

where w_C°, the width of line C in the absence of exchange, is obtained by measuring the width of the peak at 85° in the presence of excess trimethylaluminium. Similarly the pre-isomerization lifetime, τ_T, of the *trans*-molecules responsible for peak T (i.e. *trans*-I and *trans*-II) is given by Eq. (2):

$$\tau_T^{-1} = \pi(w_T - w_T^{\circ}), \tag{2}$$

where w_T is the width of line T, and w_T° is the corresponding width in the presence of excess trimethylaluminium.

τ_C^{-1} is related to the rate of isomerization of *cis*-molecules, $-\mathrm{d}[C]/\mathrm{d}t$, by:

$$\tau_C^{-1}[C] = -\mathrm{d}[C]/\mathrm{d}t, \tag{3}$$

and τ_T^{-1} is related to the rate of isomerization of *trans*-molecules $-\mathrm{d}[T]/\mathrm{d}t$, by:

$$\tau_T^{-1}[T] = -\mathrm{d}[T]/\mathrm{d}t \tag{4}$$

Since the rate of isomerization is measured at equilibrium,

$$\mathrm{d}[C]/\mathrm{d}t = \mathrm{d}[T]/\mathrm{d}t \tag{5}$$

Hence from Eqs (3) and (5),

$$\tau_C^{-1}[C] = -\mathrm{d}[T]/\mathrm{d}t \tag{6}$$

If isomerization of *trans*-I and *trans*-II molecules occurs by first order isomerization of *trans*-I, then $-\mathrm{d}[T]/\mathrm{d}t = k[trans\text{-I}]$, where k is the first order rate constant. Eq. (6) thus becomes:

$$\tau_C^{-1}[C] = k[trans\text{-I}], \tag{7}$$

Since $[cis\text{-I}]$ is negligibly small, $[C] \simeq [cis\text{-II}]$, therefore

$$k = \tau_C^{-1}[cis\text{-II}]/[trans\text{-I}] \tag{8}$$

Similarly Eq. (4) becomes:

$$\tau_T^{-1}[T] = k[trans\text{-I}], \tag{9}$$

and since $[T] = [trans\text{-I}] + [trans\text{-II}]$,

$$k = \tau_T^{-1}\{[trans\text{-I}] + [trans\text{-II}]\}/[trans\text{-I}] \tag{10}$$

Reaction of anil with trimethylaluminium to give a mixture of *cis*-II and *trans*-II is quantitative. Further the ratio $[trans\text{-II}]/\{[trans\text{-II}] + [cis\text{-II}]\} = 0{\cdot}44$ was obtained by integration of the PMR spectrum at 85° when more than one equivalent of trimethylaluminium was present. This ratio should be the same when less than one equivalent of trimethylaluminium is present. Hence, under the latter conditions:

$$[trans\text{-I}] = [\text{Anil}] - 2[(\text{CH}_3)_6\text{Al}_2] \tag{11}$$

$$[trans\text{-II}] = 0{\cdot}88\,[(\text{CH}_3)_6\text{Al}_2] \tag{12}$$

$$[cis\text{-II}] = 1{\cdot}12\,[(\text{CH}_3)_6\text{Al}_2] \tag{13}$$

REFERENCES

[1] D. Y. Curtin, E. J. Grubbs and C. G. McCarty, *J. Am. Chem. Soc.* **88**, 2775 (1966).

[2] D. Wurmb-Gerlich, F. Vögtle, A. Mannschreck and H. A. Staab, *Liebigs Ann.* **708**, 36 (1967).

[3] G. Wettermark, *Svensk kem. Tidskr.* **79**, 249 (1967).

[4] G. Wettermark, J. Weinstein, J. Sousa and L. Dogliotti, *J. Phys. Chem.* **69**, 1584 (1965).

[5] R. W. Layer and C. J. Carman, *Tetrahedron Letters* 1285 (1968).

[6] C. S. Johnson, *Advances in Nuclear Magnetic Resonance* (Edited by J. S. Waugh) Vol. 1; p. 33. Academic Press, New York (1966).