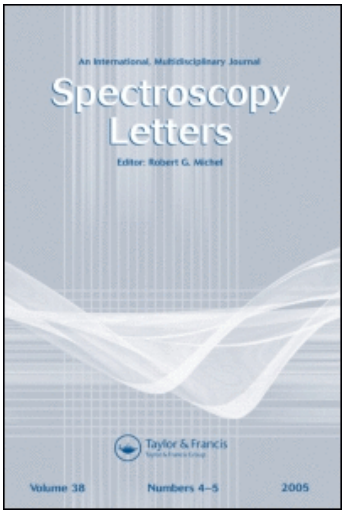

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^{1}H NMR Study of the Photoisomerization of Cinamylidene-2-Methyl-5-Chloro aniline

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ABSTRACT

Cinamylidene-2-methyl-5-chloro-aniline undergoes isomerization from the trans form to the cis form under irradiation with u.v. light at room temperature. The isomerization was studied in three solvents and the % cis was found to be in the following order: in DMSO $>$ $CDCl_3$ $>$ CCl_4. The rate of the process of isomerization was found to be a first order one.

Introduction

Cinamylideneanilines are known to be present in a high percentage ($>$ 99 %) in the stable trans form, and usually they give rise to a strongly overlapping complex patterns[1-3]. Cinamyl-

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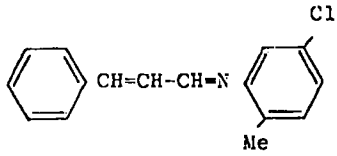
ideneanilines[4,5] with their benzylideneanilines analogues[6,7] can transform to the cis form by addition of lanthanide shift reagents. However, benzylideneanilines can also transform to the less stable cis form by irradiation[8] by u.v. light at low temperatures (-70° to -100°C), but the cis form obtained returns back to the trans on warming the sample to room temperature.

In the present work we would like to present the isomerization of cinamylidene 2-methyl-5-chloro-aniline (I) on irradiation by u.v. light at room temperature in three solvents by NMR spectroscopy.



(I)

Experimental:

Compound (I) was prepared by mixing an equimolar amounts of cinamaldehyde with the substituted aniline according to the procedure described by El-Bayoumi and coworkers[9].

The NMR measurements were performed on a 60 MHz Hitachi Perkin Elmer NMR spectrometer, except for the sample in $CDCl_3$ solvent which was measured on 90 MHz Brucker connected with an Aspect 2000 Computer (8K domain). The pulse width was 3 μs with zero delay. Spectra were recorded for substrates with concentration of (0.274 M) in $CDCl_3$, CCl_4 and DMSO. TMS was used as a standard reference.

Doublicate samples were prepared in each solvent and were exposed to u.v. light (Gallenkamp u.v. lamp) for various periods of time, and their NMR spectra were recorded after each exposure.

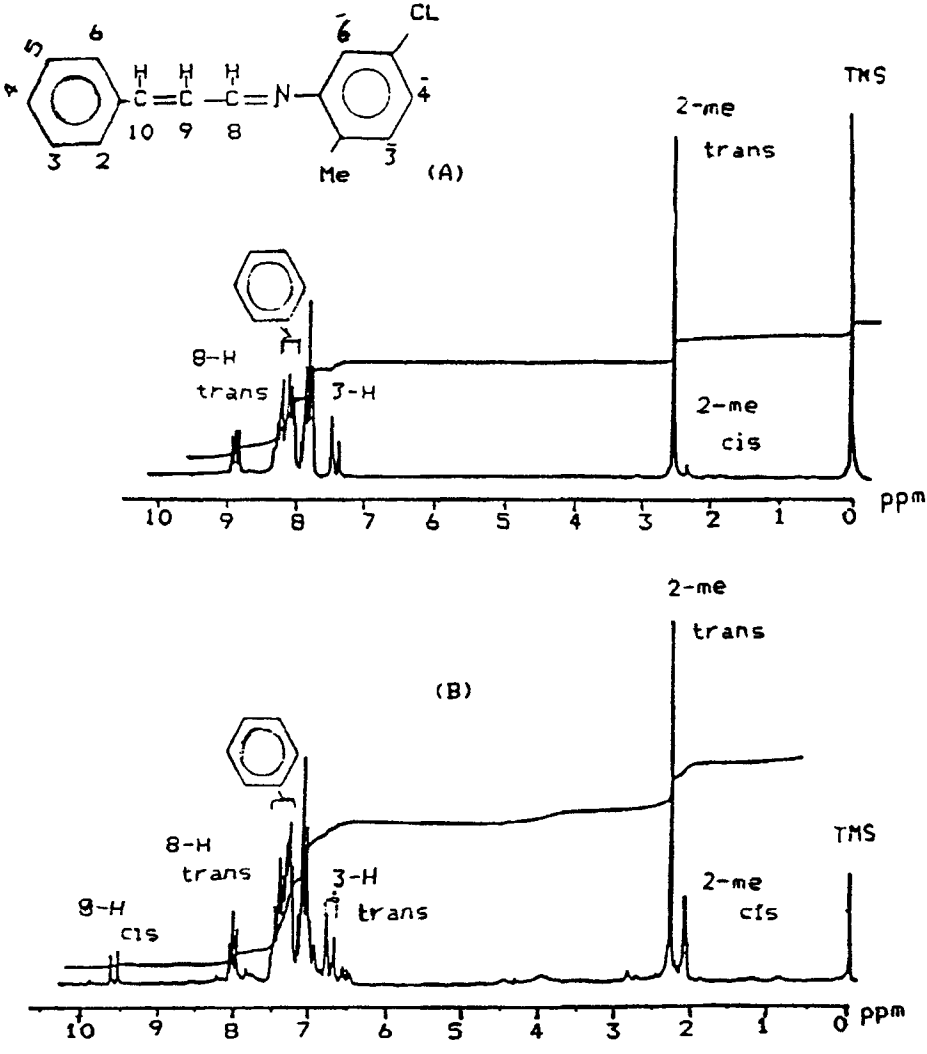


Fig. 1. The ^{1}H NMR spectrum of cinamylidene-2-methyl-5-chloro-aniline in $CDCl_3$ (0.1 M) measured at 90 MHz (A) before irradiation (B) after irradiation with u.v. light.

Table (1). The calculated % cis of cinamylidene-2-methyl-5-chloro aniline in $CDCl_3$, CCl_4 and DMSO after irradiation with u.v. light.

CCl_4		$CDCl_3$		DMSO	
Time (hours)	% cis	Time (hours)	% cis	Time (hours)	% cis
0	3.0	0	3.0	0	3.0
36.5	3.8	39.5	5.3	36.3	5.3
164.3	5.1	55.0	6.0	103.3	9.0
234.3	6.4	96.0	8.6	122.3	11.0
317.8	7.0	112.1	9.3	234.3	17.4
361.8	8.4	193.0	13.0	279.3	18.0
415.0	8.7	235.5	16.0	317.8	21.4
518.4	11.1	305.5	19.0	361.8	24.0
552.4	9.8	342.0	20.6	415.8	28.0
687.3	12.0	366.0	22.5	518.3	33.0
		450.0	25.0		

For the decay experiment of the cis, a sample (in $CDCl_3$) was immersed in a thermostat which was afixed at 50°C, and the disappearance of the cis was followed by measuring the NMR spectra after different intervals of time.

Results and Discussions:

The ^1H NMR spectrum of cinamylidene-2-methyl-5-chloro aniline in $CDCl_3$ measured at 90 MHz (Fig. 1 A) show that it is present in a large extent in the trans form. A small signal (2.35 ppm) integrating 3 % corresponding to the cis isomer was observed near the methyl resonance signal (2.55 ppm). Chemical

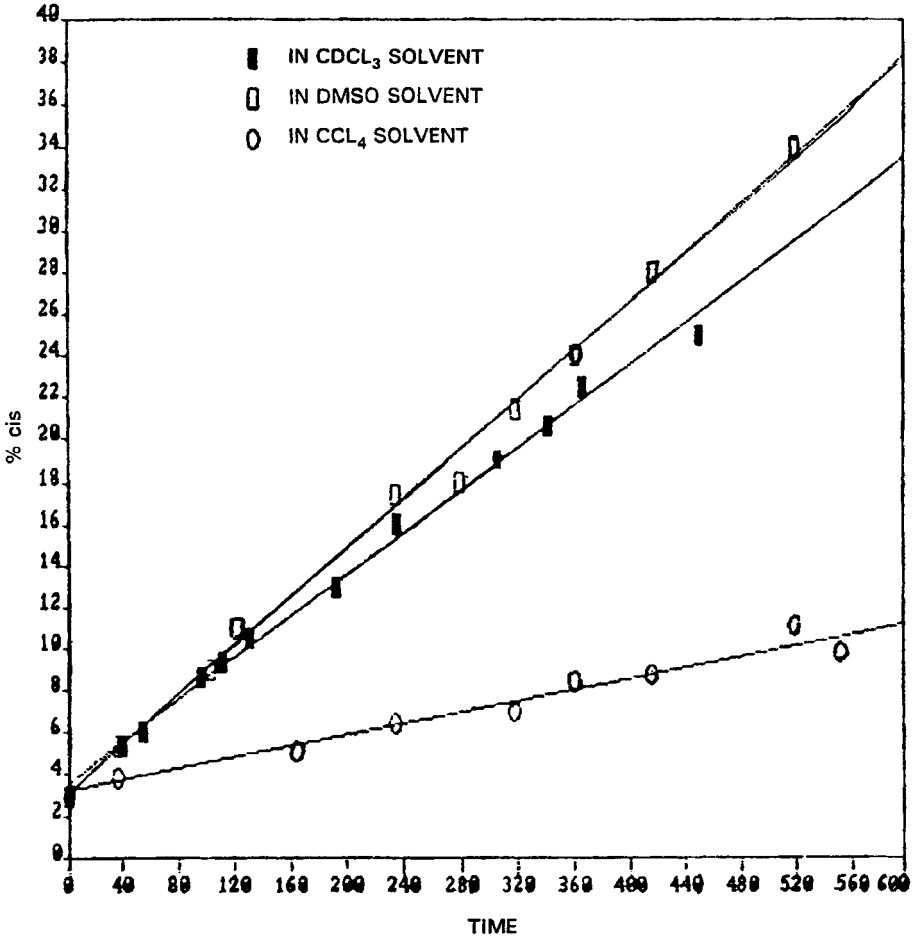


Fig. 2. Plot of the % cis of cinamylidene-2-methyl-5-chloro aniline at different times of irradiation in different solvents.

shifts for the other protons in the spectrum are 8-H (8.00 ppm), 4-H (6.70 ppm), the aromatic protons (7.21 - 7.54 ppm) and the olefinic protons (6.98 - 7.17 ppm).

Compound (I) in $CDCl_3$ was irradiated by u.v. light at room temperature, for different times. Its NMR spectrum show that the

Table (2). ln(a-x)* values for cinamylidene-2-methyl-5-chloro aniline calculated at different times in CCl_4, $CDCl_3$ and DMSO.

CCl_4		$CDCl_3$		DMSO	
Time (hours)	ln(a-x)	Time (hours)	ln(a-x)	Time (hours	ln(a-x)
0	4.574	0	4.574	0	4.574
36.5	4.534	39.5	4.518	36.3	4.518
164.3	4.520	55.0	4.510	103.3	4.477
234.3	4.506	96.0	4.481	122.3	4.454
317.8	4.499	112.1	4.473	234.3	4.377
361.8	4.484	193.0	4.430	279.3	4.369
415.0	4.480	235.5	4.394	317.8	4.325
518.4	4.453	305.5	4.356	361.8	4.290
552.4	4.468	342.0	4.335	415.8	4.234
687.3	4.442	366.0	4.310	518.3	4.158
		450.0	4.276		

(*) ln(a-x) represent the % trans before irradiation (97 %) - % cis obtained.

small signal which was identified as the cis (the minor component, 2.35 ppm) increased in its intensity with increasing periods of irradiation. It was also noticed that a new signal was observed to the low field (a doublet, 9.55 ppm, J = 8 Hz) (See Fig. 1 B), which was attributed to 8-H (cis). This signal was accompanying the spectra of all the irradiated samples. Other signals in the spectrum were not possible to identify due to the collapsing of the signals of the two forms. It is worth to notify that 8-H (cis)

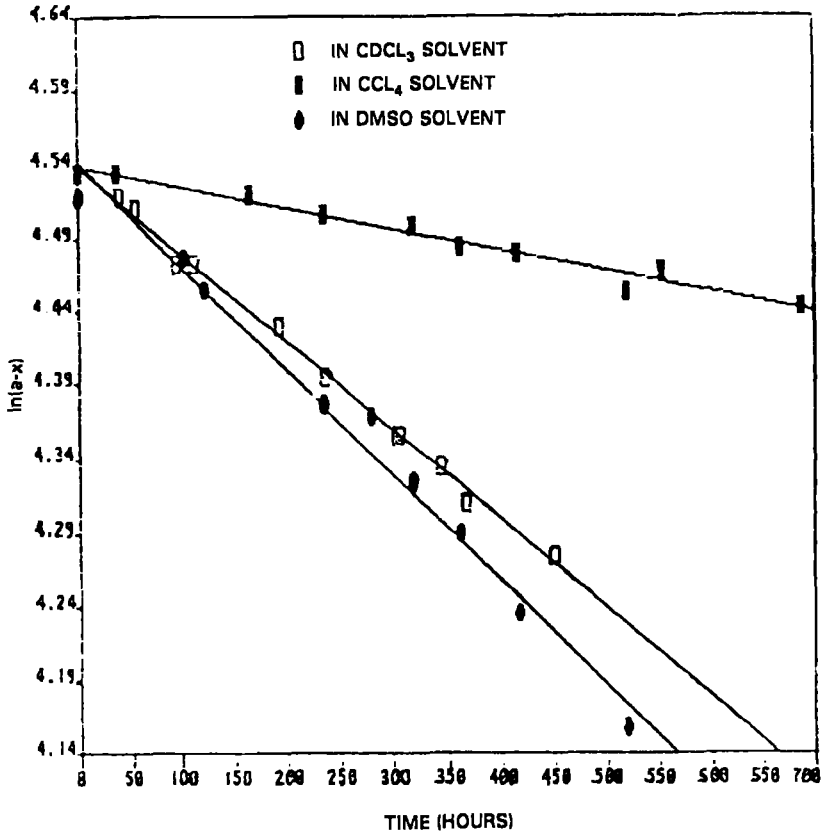


Fig. 3. Plot of ln(a-x) vs. time in different solvents for cinamylidene-2-methyl-5-chloroaniline.

signal was observed in our previous work of the isomerization with LSR[4].

The % cis values obtained as a result of the irradiation of (I) in $CDCl_3$ are given in Table 1.

Other irradiation experiments were performed for (I) in CCl_4 and DMSO and similar observations as those observed in $CDCl_3$ were obtained, and the results are also given in (Table 1).

Table (3). The values of % cis for cinamylidene-2-methyl-5-chloroaniline (in $CDCl_3$) after heating at 50°C for different times.

Time (hours)	% cis	Time (hours)	% cis
0	25.0	172.0	19.1
29.0	23.2	243.0	17.0
45.0	22.5	267.0	14.2
60.0	22.0	353.0	13.0
97.0	20.6	381.0	11.5
112.3	20.8	423.0	12.0
131.1	30.45	634.0	6.0

The % cis values were plotted vs. time of irradiation for the three solvents, linear plots were obtained (See fig. 2) with slopes given as: $(1.32 \times 10^{-2} \pm 0.214)$, $(4.97 \times 10^{-2} \pm 0.361)$ and $(5.88 \times 10^{-2} \pm 0.384)$ in CCl_4, $CDCl_3$ and DMSO, respectively. These values, as can be seen, are in the order of increasing polarity of the three solvents.

It can be seen from the above results that cinamylideneaniline (unlike benzylideneanilines[8]) can isomerize at normal temperature. This can be explained due to the presence of conjugation in the former one which results in the delocalization of the electrons, this will lower or decrease the double bond character which make the rotation freer and hence the formation of the cis will be more easier.

The rate of isomerization was followed by plotting ln(a-x) vs. time (Table 2), straight lines were obtained for each experiment (See fig. 3) with slopes given as $(6.004 \times 10^{-4} \pm 0.029)$,

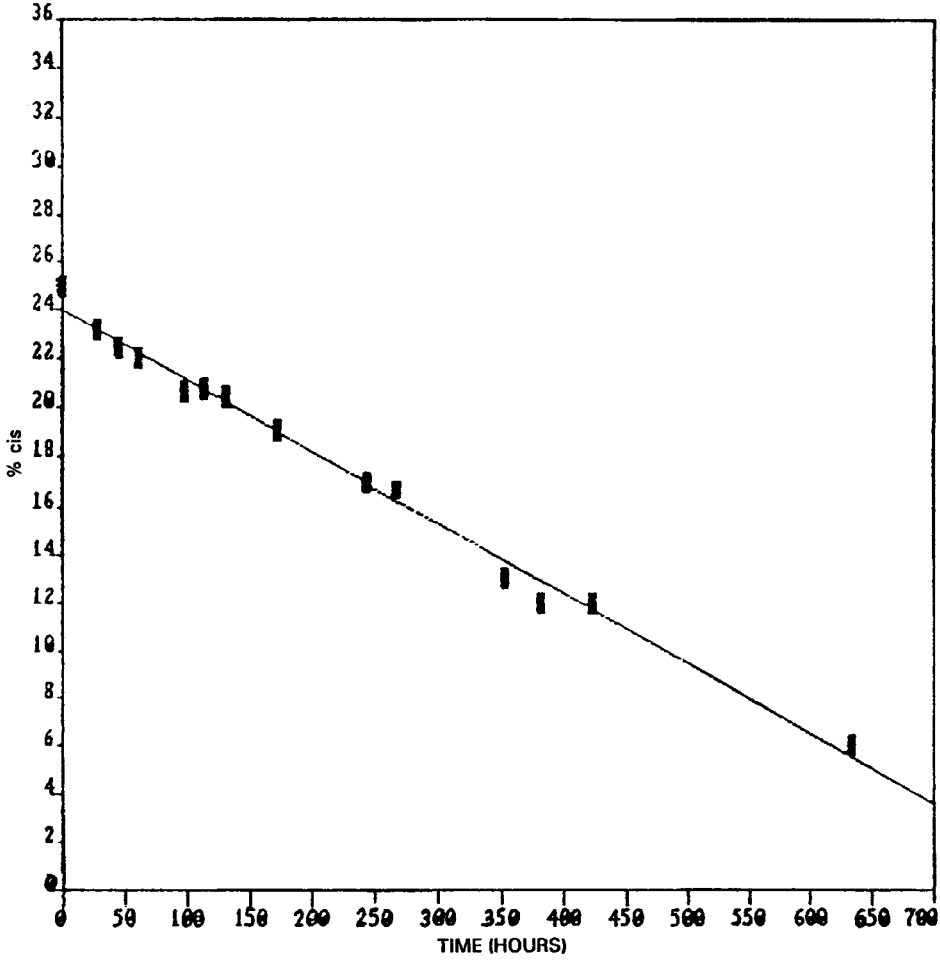


Fig. 4. Plot of % cis vs. time of cinamylidene-2-methyl-5-chloroaniline in $CDCl_3$ after heating the sample at 50°C.

($1.411 \times 10^{-4} \pm 0.029$) and ($7.07 \times 10^{-4} \pm 0.0197$) for CCl_4, $CDCl_3$ and DMSO, respectively, indicating a first order process.

The process of photoisomerization leads to the formation of the cis which remains stable for a long period. The stability of the cis was checked by measuring the NMR spectra of the sample after leaving it at N.T. for long times (more than six months), and it was found that the % cis value was almost the same.

The effect of temperature on the stability of cis isomer was studied by heating the sample (in $CDCl_3$) at 50^oC for various periods and measuring its NMR spectrum each time. The % cis began to decrease as the time of heating increases (Table 3), until the compound returns back to its original form.

A plot was performed between % cis vs. time, a linear relation was obtained (Fig. 4).

These results indicate that the process is a reversible photoisomerization process (and no other process can be detected) since the sample returns back to its original form and its NMR is identical to that before irradiation.

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