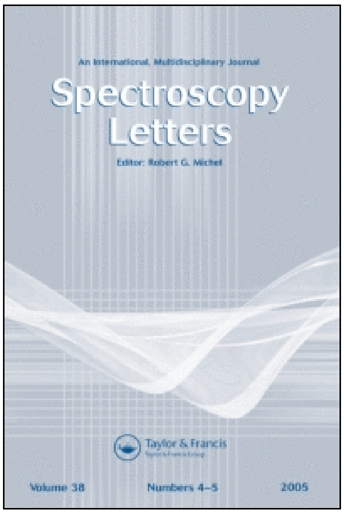

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The Studies of ^{13}C NMR Chemical Shifts and Induced Lanthanide Shift Reagent Cis-trans Isomerization of N-Cinamylidene-hexyl, t-butyl and Substituted Aryl-Amines

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The Studies of ^{13}C NMR Chemical Shifts and Induced Lanthanide Shift Reagent Cis-trans Isomerization of N-Cinamylidene-hexyl, t-butyl and Substituted Aryl-Amines.

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KEYWORDS ^{13}C NMR Chemical Shift and Cis/trans isomerization Cinamylideneanilines

Abstract: The Carbon-13 chemical shifts of N- Cinamylidene-hexyl, t-butyl and sixteen substituted aryl amines were analysed. The lanthanide induced carbon-13 chemical shifts of the cis and trans of four N-cinamylidene substituted anilines were analysed. The spectra N-cinamylidene hexylamine showed only the trans form. The cis/trans ratio of N-cinamylidene aryl amines increased as the LSR concentration increased.

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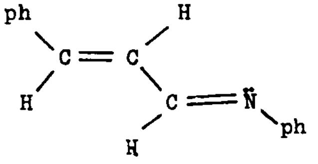
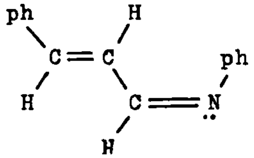
Introduction: Cis-trans isomerization of N-Benzylidene-alkyl or aryl amines induced by a Lanthanide Shift reagent (LSR) were previously reported using ^1H and ^{13}C NMR spectroscopy[1,2]. Two sets of carbon-13 signals appeared after the addition of Eu(fod)$_3$ and the cis/trans ratio depend on the molar ratio of LSR. The trans form showed very small lanthanide induced shifts (LIS) compaired with that of the cis form and the ratio of LSR/Cis form $\cong$ 3. Nitrogen inversion mechanism was suggested for the trans-cis isomerization[3].

Ultra violet spectroscopy was used in the study of lanthanide shift reagents induced cis/trans isomerization of cinamylidene-substitutedanilines and it was found that the substituents on the aniline have no effect on the isomerization process[4].

In this paper we report the carbon-13 NMR assignment and the lanthanide shift reagent induced isomerization of N-Cinamylidene-alkyl or aryl-amines using ^{13}C NMR spectroscopy.



trans (E) isomer



cis (Z) isomer

Experimental: N-cinamylidene-alkyl- or substituted anilines (1-18) were prepared according to a previously reported general method for schiff-base[5].

Equimolar of each of the alkyl amines or substituted aniline were dissolved in ethanol. The amine solution was added

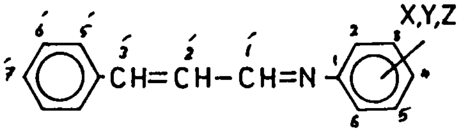
drope wise to the cinamaldehyde solution and the mixture was heated for few mints cooled, washed with cold ethanol and recrystallized from ethanol.

Note: For the ortho-substituted anilines the reaction mixture was refluxed for few hours to complete the reaction.

The products gave satisfactory CHN elemental analysis and checked by ^{1}H NMR spectroscopy, the yeild was always > 85% and the m.p or b.p as follows 1, 101°C, 2,88°C, 3,97°C, 8, 91, 9, 68°C, 10, 121°C, 11, 83°C, 12, 74°C, 13, 107°C, 14, 67°C, 16, 84°C.

The ^{13}C NMR spectra were recorded at ambient probe temperature (25°C) on a Bruker WH90DS spectrometer operating at 22.63 MHz. The broad-band proton-decoupled ^{13}C NMR spectra were run at a spectral width of 6KHz and an 8k data memory size, a pulse width of 6 µS, a line broadening of 0.6 and a pulse delay of 3s. chemical shifts were accurate to better than ± 0.06 ppm.

Samples for the ^{13}C NMR measurments were prepared by dissolving 120–180 mg of the substrate in 1.5 ml of $CDCl_3$containg 2% TMS as internal reference. The $Eu(fod)_3$ was weighed and added directly to the sample solution so that the desired molar ratio was obtained.



Y = z = H
1) X = H
2) X = 4-F
3) X = 4-Cl

Z = H
11) X =2-CH_3 , Y = 3-CH_3
12) X =2-CH_3 , Y = 4-CH_3
13) X =2-CH_3 , Y = 5-CH_3

4) X = 4-Br
5) X = 4-OH
6) X = 4-OCH_3
7) X = 4-CH_3
8) X =4-$CH(CH_3)_2$
9) X =2-CH_3
10) X =3-CH_3

14) X =3-Cl, Y = 5-Cl
15) X =2-CH_3 , Y = 5-Cl
16) X =2-CH_2CH_3, Y =6-Et
17) $phCH{=}CH{-}CH{=}N{-}(CH_2)_5CH_3$
18) $phCH{=}CH{-}CH{=}N{-}C(CH_3)_3$

Results and Discussion: The carbon-13 NMR spectra of 1A-18A showed 96-99% one isomer (Table 1). Both proton decoupled and coupled carbon-13 NMR spectra were used in the assignments. The cinamylidene moiety were assigned using the reported value of cinamic acid[6] , cinamaldehyde[7] in addition to comparison with the simple spectrum of N-cinamylidene hexyl and t-butylamine 17A and 18A. The arylamines part of compounds A(1-18) were assigned using the previously reported, value for the corresponding part of benzylidene arylamines[2], in addition to the substitution increments[8] and from the fluorine-^{13}C coupling patterns[9]. It is worth notting that the carbon-13 chemical shifts for the cinamyl moiety showed no or very small changes as a result of substitution on the aniline rings. However C-1 in 2A - 8A (Para substituted aniline) showed a small deshielding $\simeq$ 0.6 ppm on changing the substitution from H to P-F, Cl and Br, while shielding effect $\simeq$ -2.2 ppm for p.OCH_3 6A(similar effect was observed for the P-OH 5A in d_6DMSO as solvent). Further alkyl substitution [p-CH_3(7A) and $(CH_3)_2CH$] showed also shielding of - 0.5 ppm.

Table 1: Carbon-13 Chemical Shift assignment relative to TMS for N-Benzyllidene aryl amines (A, before the addition of LSR) in $CDCl_3$

Comp.	1A (JCH)	2A (JC-F)	3A	4A (JCH)	5A* (JCH)	6A	7A	8A	9A
C-1$^-$	161.4 (156.3)	161.3	161.9	161.9 (158.9)	158.4 (158.7)	159.5	160.7	160.9	161.4
C-2$^-$	128.5 (162.5)	128.3	128.4	128.4 (161.1)	128.8 (154.2)	128.4	128.9	128.9	128.9
C-3$^-$	143.8 (153.8)	144.1	144.6	144.7 (156.3)	142.3 (153.8)	142.9	143.5	143.5	143.6
C-4$^-$	135.5 (-)	135.5	135.5	135.5 (-)	135.7 (-)	135.9	136.0	135.8	135.5
C-5$^-$	127.4 (153.8)	127.5	127.5	127.6 (161.1)	127.3 (158.7)	127.4	127.5	127.5	127.5
C-6$^-$	129.1 (161.1)	129.0	129.0	128.8 (161.2)	128.9 (153.8)	128.9	128.9	128.9	128.9
C-7$^-$	129.5 (153.8)	129.7	129.7	129.8 (163.6)	129.1 (153.9)	129.4	129.4	129.5	129.5
C-1	151.7 (-)	147.8 (U)	150.3	150.8 (-)	142.8 (-)	144.7	149.2	149.5	151.4
C-2	120.8 (153.8)	122.4 (7.3)	122.2	122.7 (161.2)	122.3 (158.6)	122.2	120.9	120.9	131.7
C-3	128.8 (161.2)	115.9 (22.0)	129.3	132.3 (166.0)	115.8 (158.7)	114.5	129.4	127.5	130.5
C-4	126.0 (161.5)	161.4 (244.0)	131.7	119.5 (161.1)	156.3 (-)	158.5	136.0	147.2	125.7
C-5	128.8 (161.2)	115.9 (22.0)	129.3	132.3 (166.0)	115.8 (158.7)	114.5	129.4	127.5	126.8
C-6	120.8 (153.8)	122.4 (7.3)	122.2	122.7 (161.2)	122.3 (158.6)	122.2	120.9	120.0	117.8
X	-	-	-	-	-	55.4	20.9	33.8	17.9
Y,Z								24.1	

(continued)

Table 1 (continued)

Comp.	10A	11A	12A	13A	14A	15A	16A	17A	18A
C-1'	161.3	161.1	160.5	161.1	163.6	161.5	164.1	161.9	156.8
C-2'	128.9	128.9	128.9	128.9	129.0	128.5	128.5	128.2	128.4
C-3'	143.7	143.2	142.9	143.3	146.0	144.0	143.7	140.7	140.6
C-4'	135.6	135.7	135.8	135.7	133.4	135.0	135.5	135.7	135.7
C-5'	127.5	127.4	127.4	127.4	127.8	127.0	127.5	126.9	126.8
C-6'	128.9	128.9	128.9	128.9	129.0	129.0	128.9	128.5	128.4
C-7'	129.5	129.4	129.4	129.5	130.1	129.7	129.6	128.7	129.1
C-1	151.8	141.9	148.0	151.1	154.0	149.7	150.6	61.6	56.0
C-2	121.6	130.2	131.8	126.3	119.8	130.9	133.1	31.7	29.0
C-3	139.0	137.4	131.2	130.2	135.4	130.2	126.2	31.0	-
C-4	126.6	126.0	135.9	126.3	125.7	126.7	124.1	27.0	-
C-5	128.7	128.9	127.2	136.1	135.4	133.8	126.2	22.6	-
C-6	117.9	115.5	117.4	118.5	119.8	118.8	138.1	14.1	-
X,Y,	21.4	13.7	17.8	17.4	-	17.8	24.6	-	-
Z	-	20.1	20.8	20.9	-	-	14.8		

* Sdvent d_6 DMSO

The 2-substituted compounds A (9, 11-13) and (15-16) (increased the steric hindered around the nitrogen lone -pair) showed very small changes in the chemical shift of the cinamyl moiety (Table 1).

Systematic ^{1}H NMR study was carried out on 13 and 15 which revealed that the cis form is present in 2% for compound 15. The ^{1}H NMR spectra of 13 and 15 showed two sets of signal correspondence the trans and cis forms after the addition of LSR. The cis and trans

Table 2: Carbon-13 Chemical Shift assignment relative to TMS in $CDCl_3$ (B) trand form and (C) Cis form after LSR addition

Comp.	2B (JCF)	2C (JCF)	3B	3C	6B	6C	8B	8C	17B
C-1^{-}	175.5	231.0	176.9	232.0	174.9	230.0	172.1	232.0	173.0
C-2^{-}	129.8	131.8	129.7	132.0	129.7	132.0	130.4	133.2	128.2
C-3^{-}	149.9	157.6	150.1	164.0	149.5	160.0	149.7	163.0	145.2
C-4^{-}	135.0	136.0	135.1	135.0	135.4	135.0	135.0	135.6	134.1
C-5^{-}	127.4	127.4	127.4	127.8	127.8	127.8	128.6	128.0	127.5
C-6^{-}	128.7	127.8	128.8	129.7	128.7	128.7	129.7	128.6	128.2
C-7^{-}	130.0	130.0	130.0	(a)	130.0	130.0	130.4	130.4	128.2
C-1	161.3 (U)	183.3 (U)	163.8	185.0	160.0	(a)	164.1	182.6	73.4
C-2	135.0 (7.3)	133.0 (9.0)	130.4	133.4	135.4	132.0	134.3	132.0	62.4
C-3	118.6 (24.9)	131.8 (19.9)	131.8	137.7	117.6	126.0	131.1	138.2	35.4
C-4	162.9 (246.0)	(a)	132.0	133.4	161.0	163.7	149.7	151.7	32.4
C-5	118.6 (24.9)	131.8 (19.8)	131.8	137.7	117.6	126.0	131.4	138.0	23.0
C-6	135.0 (7.3)	133.0 (9.0)	130.4	133.4	135.4	132.0	134.3	132.0	14.2
X	-	-	-	-	56.4	56.7	35.1	36.5	-
Y,Z						24.4	23.5		
LSR molar ratio	0.91		1.01		1.221		1.28		0.28
%	64	36	70	30	71	29	58	42	

proton chemical shifts showed increased LIS with the increase in the LSR molar ratio (up to 1.2 mol). Furthermore cis/trans ratio increased linearly with LSR mole ratio.

Similarly carbon-13 NMR spectra of 2 showed two sets of signals after the addition of Eu(fod)$_3$. The major set 2B (64% at 0.911 LSR mole ratio) showed the exact number of ^{13}C chemical shifts and were assigned using the carbon - fluorine coupling patterns[9] in addition to the comparison with the simple form (trans) of the N-cinamylidene hexyl amine 17B.

The minor form (36.0%) 2C was assigned in a similar way with the aid of the intensity (The minor signals). The ^{13}C - signals of the p-fluoroaniline of 2C resemble the corresponding part previously reported for the cis form of the N-benzylidene p-fluoroaniline after the addition of LSR[2]. Similarly the assignment of the trans form (B) and cis form (C) of 3,6 and 8 were acheived and checked using X , Y and Z substitution increments[8] and by comparison throughout the series. The trans form 2B experience a low-field LIS after the addition of LSR by 14.2 (C-T) , 5.8 (C-$\bar{3}$), 13.5(C-$\bar{1}$), 12.6 (C-2,6), 2.7 (C-3,5) and 1.5 ppm (C-4) (Table 3). Similar pattern and value of effect were observed for the trans form B of 3,6,8 and the cinamylidene part of 17 while C-1, C-2, C-3 , C-4, C-5 and C-6 of the hexylamine part suffer deshielding of 11.8, 30.7, 4.4, 1.0 and 1.0 ppm respectively.

The somehow large LIS for trans form B in the cinamylidene substituted arylamine compared with the corres-

Table 3: Lanthanide-induced shift effect on the ^{13}C chemical shifts of the trans (B) and Cis(C) forms.

Compound	C-$\bar{1}$	C-$\bar{2}$	C-$\bar{3}$	C-$\bar{4}$	C-$\bar{5}$	C-$\bar{6}$	C-$\bar{7}$	C-1	C-2	C-3	C-4	C-5	C-6	X	Y,Z
2B-2A	14.2	1.5	5.8	-0.5	-0.1	-0.3	+0.3	13.5	12.6	2.7	1.5	2.7	12.6	-	-
2C-2A	69.7	3.6	13.5	0.5	-0.1	-1.2	0.3	35.5	10.6	15.9	-	15.9	10.6	-	-
3B-3A	15.0	1.3	5.5	-0.4	-0.1	-0.2	0.3	13.5	8.2	2.5	0.3	2.5	8.2	-	-
3C-3A	70.1	3.6	19.4	-0.5	0.3	0.7	-	34.7	11.2	8.4	1.7	8.4	11.2	-	-
6B-6A	15.4	1.3	6.6	-0.5	0.4	-0.2	-0.6	15.3	13.2	3.1	2.5	3.1	3.2	1.0	-
6C-6A	70.5	3.6	17.1	-0.9	0.4	-0.2	0.6	-	9.8	11.5	3.2	11.5	9.8	1.3	-
8B-8A	11.2	1.5	6.2	-0.8	1.4	0.8	0.9	14.6	13.4	3.6	2.5	3.9	14.3	1.3	0.3
8C-8A	71.1	4.2	17.5	-0.8	0.8	-0.3	0.9	33.0	11.1	10.8	3.5	10.5	12.0	2.7	-0.6
17B-17A	12.1	0	4.5	-1.6	0.6	-0.3	-0.3	11.8	30.7	4.4	5.4	1.0	0.1	-	-

ponding trans form of the N-benzylidene substituted arylamines[2] could be attributed to the fact that the nitrogen lone-pair (the only complex formation site in the compounds) is less sterically hindered and form a more stable complex with the bulky[10] Eu(fod)3 in the cinnamylidene schiff-base compared with that of benzylidene schiff-base. The cis form (C) of 2,3,6 and 8 experience rather large deshielding effect for $C-\bar{1}$ and $C-\bar{1}$ by 69.7 and 35.5 ppm (for 2C Table 3) while $C-\bar{2}$, $C-\bar{3}$, C-2,6, and C-3,5 showed deshielding of 3.6, 13.5, 10.6 and 15.9 ppm respectively (Table 3). These LIS are similar to those were found for the same parts in the cis form of N-benzylidene aryl amines.

The same approach was used to explaine the LIS cis-trans isomerization that found in N-benzylidene arylamines[2] i.e trans-cis isomerization favors the nitrogen inversion mechanism. This indicate that the less sterically hindered nitrogen lone-pair in the cis forms a more stable complex than that for trans isomer with the bulky Eu(fod)3.

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