

Carbon-13 NMR Studies of Some ortho-substituted C-aryl-N-tert-butylimines

Salim S. Al-Showiman

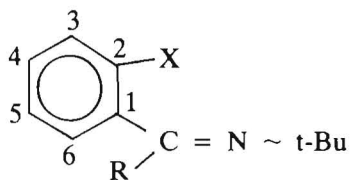
Department of Chemistry, College of Science,
King Saud University, P.O. Box 2455, Riyadh 11451,
Saudi Arabia

ABSTRACT. Carbon-13 chemical shift assignments are reported for some N-tert-butylimines bearing ortho-substituted C-phenyl rings. The influence of electronic and stereochemical effects on the ^{13}C signal positions were inspected. The variation of the ^{13}C chemical shifts allows calculation of the substituent chemical shift (SCS) effects. The results indicate that electron withdrawing substituents cause upfield shifts in the position of the C=N resonance.

In recent years many papers concerned with ^{13}C NMR spectra have appeared but relatively limited progress has been achieved in the development of unified criteria for data analyses (Echevarria *et al.* 1985 and Inouye *et al.* 1985). Accordingly, one of the main topics of interest today has been the transmission of substituent effects in order to get precise chemical shift assignments. The additivity of substituent effects, both steric and electronic, for some benzenoid aromatics are well documented in the literature (Ewing 1979).

Recently there has been considerable discussion regarding ^{13}C NMR spectra of imines and some related compounds (Jennings *et al.* 1983 and Inouye *et al.* 1985). However, much work remains to be carried out on the investigation of ^{13}C chemical shifts and SCS effects of aryl-substituted imines.

In the present work, a number of N-t-butylimines derived from ortho-substituted aldehydes or ketones have been prepared and their ^{13}C chemical shifts and SCS effects have been investigated (Tables 1 and 2). The relative electronic and stereochemical effects of various substituents have been inspected.

Table 1. ^{13}C chemical shifts in CDCl_3 at 28°

Compound	R	X	C=N	C-1 ^a	C-2 ^b	N-C-	Me ₃
1	H	H	155.05	137.16	128.51	57.13	29.37
2	H	NO ₂	151.94	133.50	151.94	58.30	29.47
3	CH ₃	H	162.39	140.96	127.69	54.20	30.13
4Z	CH ₃	OCH ₃	165.21	128.75	158.81	54.95	30.58
E			162.86	127.28	156.52	55.36	30.41
5Z	CH ₃	CH ₃	168.90	140.08	137.32	53.25	30.70
E			168.20	139.90	137.08	54.54	30.41
6Z	CH ₃	Br	167.55	144.83	120.12	53.31	30.65
E			166.38	141.07	119.19	55.48	30.15
7Z	CH ₃	Cl	164.21	144.25	131.86	55.23	30.59
E			160.98	141.72	130.52	56.89	30.25
8Z	CH ₃	NO ₂	162.51	139.40	147.01	51.02	30.86
E			161.57	135.80	145.48	52.31	30.17
9Z	CH ₃	ph	165.58	138.80	141.20	51.10	29.80
E			164.60	138.36	140.60	52.33	29.66

a) C-1 The ring carbon directly bonded to the C=N group.

b) C-2 The ring carbon bearing the ortho-substituent.

Table 2. SCS effect on C-1 and C-2 relative to (10)^a and (11)^a and additivity deviation, Δ

Compound		R	X	C-1	C-2
1	SCS Δ^b	H	H	0.34	0.69
				0.34	0.69
2		H	NO ₂	4.00	-22.74
				0.90	-2.84
3		CH ₃	H	-0.06	0.11
				0.60	0.07
4Z		CH ₃	OCH ₃	12.15	-34.01
				-2.27	0.39
E				13.80	-28.72
				-0.80	2.68
5Z		CH ₃	CH ₃	0.82	-9.52
				1.48	-0.03
E				1.00	-9.28
				1.66	0.06
6Z		CH ₃	Br	-3.93	7.68
				-0.73	1.88
E				-0.17	8.61
				3.03	2.81
7Z		CH ₃	Cl	-3.35	-4.06
				-2.95	2.24
E				-0.82	2.72
				-0.42	3.59
8Z		CH ₃	NO ₂	1.50	-19.21
				-3.40	0.69
E				-5.10	-17.68
				0.20	2.22
9Z		CH ₃	ph	2.10	-13.40
				1.00	-0.30
E				2.54	-12.80
				1.44	0.30

a) See text.

b) Deviation from values calculated from additivity chemical shifts (ppm) of (10 and 11), $\Delta = \delta_{\text{calc.}} - \delta_{\text{exp.}}$

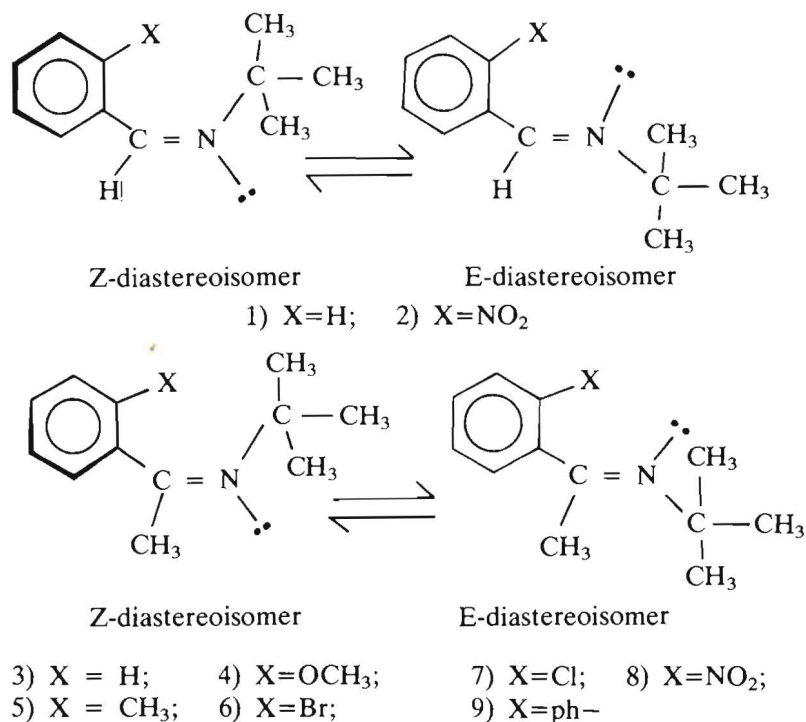
c) (+) shielding; (-) deshielding.

Results and Discussion

All the imines in this study were isolated in liquid form, characterized by their elemental analyses, IR, ^1H NMR and ^{13}C NMR spectra. However, the ^{13}C spectral analyses presented later are consistent with the structures of the material studies. These imines were found to exist in solution as E/Z isomeric mixtures (Al-Showiman 1985).

The stereochemistry of these imines (1-9) was assigned from their ^1H NMR spectra by analogy with some related imines in which the N-alkyl protons of the Z-isomer resonate at higher field as a result of increased shielding of the N-alkyl group due to the proximate aryl ring (Bjorgo *et al.* 1974).

The ^{13}C NMR spectra were recorded at ambient temperature. The signal assignment was straightforward in most cases as the N-alkyl, aromatics and imino carbons all resonate at characteristic positions (Jennings *et al.* 1983 and Inouye *et al.* 1985). Some of the imines (4-9) showed two unequal sets of ^{13}C signals due to the existence of an equilibrium mixture of E- and Z-diastereoisomers. The ^{13}C

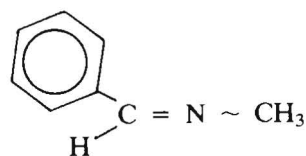


signals of the E- and Z-diastereoisomers were assigned according to their relative intensities in the spectra recorded with relatively long pulse intervals since the E/Z diastereoisomers ratio was not 1:1 (Jenning *et al.* 1983).

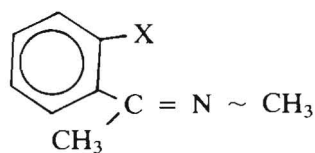
The upfield quaternary N-t-butyl ^{13}C signal was assigned to the E-isomer by analogy with some related N-alkylimines (Al-Showiman 1985 and Jennings *et al.* 1983). The assignment of the aromatic ^{13}C signals was often difficult due to the presence of diastereoisomer mixtures, overlapping in some cases and nonequivalence of the ring carbons. However, the quaternary C-1 and C-2 (Table 1) signals were easily identified by their low intensities.

In Table 1, the results indicate that the ^{13}C signal of the Me_3 of the t-butyl group was not markedly affected by changing the ortho-substituent. On the other hand, the N- ^{13}C signal was somewhat variable indicating that the inductive field effect of the ortho-substituent influences distant chemical shifts in a poorly understood manner. The results also show that the ^{13}C chemical shifts of C-1 and C-2 suffered pronounced differences due to changes in the size and the electronic structure of the ortho-substituent. The values for C-1 and C-2 are listed in Table 1. As one might expect, the large variation between C-1 shifts (ca. 17.5 ppm) and C-2 shifts (ca. 37.6 ppm) reflects the influence of larger inductive and resonance effects of the substituents on the electronic environment of substituted carbon nuclei.

The values for SCS (Table 2) were calculated from (10) for the first two imines and from (11) for the other imines, as a parent molecules, using the SCS_x values in



10



X = H 11

chloroform-d solution tabulated by Ewing (Ewing 1979). Accordingly, ^{13}C chemical shifts of C-1 and C-2 in (10) were found to be 137.50 and 129.20 ppm respectively while C-1 and C-2 in (11) were 140.90 and 127.80 ppm respectively relative to benzene (δ 128.7). The SCS effect of the different substituents (X) of the title compounds were obtained (Al-Showiman *et al.* 1982) as follows:

$$\delta \text{SCS} = \delta(\text{parent imine 10 or 11}) - \delta(\text{substituted imine, Table 1}).$$

The shielding of the C-1 and C-2 of the aryl carbons relative to the parent imines (10 and 11) is affected by SCS of both $\text{C} = \text{N-t-but.}$ and the

ortho-substituent (X). Accordingly, the deviation, Δ , was calculated (Al-Showiman *et al.* 1982) from additivity of chemical shifts and can be used to check the C-1, C-2 assignments (Table 2) using SCS_x values in chloroform-d solution reported by Ewing (1979), and C-1, C-2 chemical shift of the parent imine (10) and (11) respectively.

The results presented in Table 2 show that the SCS effect of C-1 and C-2 in imine (1) and (3) was very small as a result of similarity with compounds (10) and (11) respectively. The small observed SCS effect may be due to changing the N-methyl with N-t-butyl group. On the other hand, pronounced SCS effect on C-1 and C-2 was observed for the rest of the series (Table 2). The SCS effect can be attributed to changes in the σ and π electron densities of the aryl ring (Ewing 1979).

The $^{13}\text{C}=\text{N}$ signal was characteristic and was found to be relatively sensitive (ca. 8 ppm) to changing the ortho-substituent since such changes affect the electron density of the aryl ring which leads to a direct influence on the imino group (Jennings *et al.* 1983). The present data indicate that electron withdrawing substituents cause an upfield shift in the position of the $\text{C}=\text{N}$ group as a result of changing polarization. (Jones and Wilkins 1978). It has been reported (Boyd *et al.* 1978) that the steric interaction between the N-alkyl group and the neighbouring ring ortho-substituent forces the ring to twist out of the $\text{C}=\text{N}$ plane which may also explain the variations in the $^{13}\text{C}=\text{N}$ position as a result of the size differences of the ortho-substituents (Hirsch 1967).

Experimental

The imines were prepared by standard methods (Morreti *et al.* 1970) and microanalytical data are as follows:

1. (b.p. 115-118/5 Torr) lit. 91-92/11 Torr (Emmons 1957).
2. (b.p. 130-131/4 Torr) calc. for $\text{C}_{11}\text{H}_{14}\text{N}_2\text{O}_2$, C 64.06, H 6.84, N 13.58%; found, C 64.10, H 6.70, N 13.4%.
3. (b.p. 158-160/4 Torr) calc. for $\text{C}_{12}\text{H}_{17}\text{N}$, C 82.35, H 9.70, N 7.93%; found, C 82.50, H 9.60, N 7.80%.
4. (b.p. 81-83/5 Torr) calc. for $\text{C}_{13}\text{H}_{19}\text{NO}$, C 76.14, H 9.32, N 6.82%; found, C 76.20, H 9.50, N 6.60%.
5. (b.p. 153-155/5 Torr) calc. for $\text{C}_{13}\text{H}_{19}\text{N}$, C 82.48, H 10.11, N 7.39%; found, C 82.70, H 10.00, N 7.20%.
6. (b.p. 96-98/1 Torr) calc. for $\text{C}_{12}\text{H}_{16}\text{NBr}$, C 56.70, H 6.34, N 5.51%, Br 31.43; found, C 56.80, H 6.40, N 5.40%, Br 31.20%.

7. (b.p. 115-118/12 Torr) calc. for $C_{12}H_{16}NCl$, C 68.73, H 7.68, N 6.67, Cl 16.91%; found, C 68.50, H 7.50, N 6.50%, Cl 16.70%.
8. (b.p. 100-103/2 Torr) calc. for $C_{12}H_{16}N_2O_2$, C 65.44, H 7.32, N 12.72%, found, C 65.60, H 7.30, N 12.60%.
9. (b.p. 150-152/4 Torr) calc. for $C_{18}H_{21}N$, C 86.01, H 8.42, N 5.57%, found, C 86.20, H 8.30, N 5.40%.

The NMR spectra were obtained on a JEOL JNM FX-100 spectrometer, operating at 25 MHz and with a 10 mm $^1H/^13C$ dual probe. Computation was made using JC 980B computer with 16K memory. The deuterium resonance of the solvent was used for internal lock; data were collected over a 5000 Hz sweep width using 8 K data points; proton noise decoupling and with 10 μs pulse width (45°) repeated at 15 s intervals. The ^{13}C chemical shifts were reproducible within the effective computer digital resolution of 0.05 ppm. The ^{13}C chemical shifts were obtained relative to an internal standard of tetramethylsilane (TMS). All the spectra were recorded at ambient temperature, $28^\circ C$ and the sample concentration was 0.5 M in $CDCl_3$.

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دراسة أطياف الرنين النووي المغناطيسي للكربون - ١٣ لبعض ايمينات البيوتيل الثالثي العطرية المستبدلة في الموضع - أرثو

سالم شويمان الشويمان

قسم الكيمياء - كلية العلوم - جامعة الملك سعود - ص . ب ٢٤٥٥
الرياض ١١٤٥١ - المملكة العربية السعودية

درست مواقع خطوط الطيف للكربون - ١٣ لبعض الايمينات الحاوية على مجموعة بيوتيل ثالثي والمستبدلة في الموضع أرثو على الحلقة العطرية . ولقد ركزت الدراسة على فحص التأثيرات الالكترونية والتأثيرات الفراغية للبدائل المختلفة على مواقع خطوط الطيف للكربون - ١٣ . دلت الدراسة على أن هناك تغيراً في مواقع الطيف للكربون - ١٣ نتيجة لتباين التأثيرات الإلكترونية والتأثيرات الفراغية للبدائل المختلفة في الموضع - أرثو . وتبين النتائج في جدول ١ أن للبدائل الساحبة للإلكترونات تسبب إزاحة خط طيف الكربون - ١٣ للمجموعة $C=N$ إلى مجال مغناطيسي أعلى نسبة للمجاميع المانحة للإلكترونات .