

## Spectroscopic Studies of Some New (2'-Hydroxy- Substituted -N-Benzylidene Alkylamines

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ABSTRACT.  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR chemical shifts are reported for a series of 18 imines,  $\text{Ar}(\text{OH})(\text{Br})\text{CH}=\text{N}\sim\text{R}$ , and 18 amines,  $\text{Ar}(\text{OH})(\text{Br})\text{CH}_2\text{NH}\sim\text{R}$  ( $\text{R}=\text{CH}_3$ ,  $^1\text{Pr}$ ,  $^1\text{Bu}$ ,  $^3\text{Bu}$ ,  $^1\text{Bu}$  or  $\text{Ph}$ ). The amines were obtained by the reduction of the appropriate imine. The stereochemistry of imines was determined through their NMR spectral data. The imines were found to exist in solution as only a single E-isomer at ambient temperature. Interestingly, the carbon-13 chemical shifts for imino ( $\text{CH}=\text{N}$ ) and benzylic ( $\text{Ph}\text{CH}_2$ ) carbons are affected by alkyl groups (R), while the halo-substituted benzene ring has no effect on the chemical shift of the imine group. Substituent chemical shift (SCS) effects for - OH, - Br,  $\text{CH}=\text{N}$ -,  $\text{CH}_2\text{-NH}$ -, or - CHO are not additive at all positions.

In recent years several papers on  $^1\text{H}$  and  $^{13}\text{C}$ -NMR spectra of imines have been reported (Inamoto *et al.* 1974, Naulet *et al.* 1975, Ruxer *et al.* 1977, Solladie *et al.* 1977, Arrowsmith *et al.* 1978, Walter *et al.* 1978). One of the main topics of interest has been the transmission of substituent effects particularly in anils derived from substituted benzaldehydes which exist exclusively in the *anti* (E) conformation (Inamoto *et al.* 1974, Arrowsmith *et al.* 1978, Walter *et al.* 1978, Buchanan *et al.* 1980). In the present work, N-alkyl imines derived from bromo-substituted salicylaldehydes and primary amines or aniline have been prepared and thoroughly investigated by UV, IR,  $^1\text{H}$  and  $^{13}\text{C}$ -NMR spectroscopy. In addition, appropriate secondary amines were obtained by the reduction of the above mentioned imines.

### Results and Discussion

In the present work, the new (2'-hydroxy- substituted -N- benzylidene) alkylamines (Schiff's bases) were obtained from the reaction of bromo-substituted

salicylaldehydes with either primary aliphatic amines or with aniline to give (2'-hydroxy- substituted -N- benzylidene) alkylamine. The products were solids and the yields were reasonably high which indicates greater reactivity of these carbonyl compounds.

### The Stereochemistry of the Schiff's Bases

The stereochemistry of the free imines was determined on the basis of their  $^1\text{H}$  and  $^{13}\text{C}$ -NMR spectral data. In chloroform-d solution, the  $^1\text{H}$  spectrum shows that there is only one set of isomer signals [Table (5)], imine 13. Thus, N-CH<sub>3</sub> appears as a doublet at  $\delta$  3.49 ppm; = C-H as quartet at  $\delta$  8.26 ppm and the aromatic protons were at  $\delta$  6.89 to  $\delta$  7.37 as multiplets.

Similar observations were obtained in acetone-d<sub>6</sub>, benzene-d<sub>6</sub>, dimethyl-d<sub>6</sub> sulfoxide which confirm the existence of these imines as 100% as in one diastereomeric form. Further evidence come from  $^4\text{JHCNCH}$  where imine 13, shows a value of 1.47 Hz which is in good agreement with an earlier study concerning *E*-conformation of similar imines (Bjorgo *et al.* 1974). The *Z*-configuration of imine 2 requires the  $^4\text{JHCNCH}$  coupling constants to be larger than *E*-form (ca. 2.2 Hz) (Bjorgo *et al.* 1974). The  $^{13}\text{C}$ -NMR chemical shifts of imines 1-18 (Tables 3-5) lead to precise stereochemical assignments of these imines. Inspection of the spectra shows that each Carbon gave one signal in the completely decoupled spectra. No satellites or any other small signals which may arise due to other isomers have been observed. These observations confirm the existence of these imines in only one diastereomeric form (*E*-form). The UV spectra of the imines have a characteristic absorption bands for the C=N group (ca. 255-268 nm in CH<sub>2</sub> Cl<sub>2</sub>). The infrared data showed absorption of the C=N group for imines 1-18 in the region 1615-1650 cm<sup>-1</sup> as one band for each imine. The UV and IR results are in good agreement with an earlier study of imines derived from thiophene derivatives which have been reported to exist exclusively in the *E*-form (Andoye *et al.* 1982, Al-Showiman *et al.* 1987).

### $^1\text{H}$ and $^{13}\text{C}$ NMR Chemical Shifts

#### a) Schiff's Bases

The  $^1\text{H}$  NMR spectra of imine 13, derived from 5-bromo-substituted salicylaldehyde and methyl amine has been chosen as a model in order to simplify the  $^1\text{H}$  NMR spectrum (Table 5). The N-CH<sub>3</sub> and =C-H groups of this imine resonate apart from each other in chloroform at 25°C. The N-CH<sub>3</sub> signal appears as a doublet peak at  $\delta$  3.49, indicating that these protons are long-range coupled with =CH

proton,  $^4J_{\text{HCNCH}} = 1.47$  Hz. The =CH signal appears as a quartet peak at  $\delta$  8.26,  $^4J_{\text{HCNCH}} = 1.47$  Hz. The aromatic protons ( $H_3$  and  $H_4$ ) appear as a multiplets centered at  $\delta$  6.89 (assigned for  $H_3$ ) and at  $\delta$  7.33 assigned for  $H_4$ ; while  $H_6$  appears as a simple peak at  $\delta$  7.34. The OH proton appear as a broad peak at  $\delta$  13.25-14.36.

The  $^{13}\text{C}$ -NMR spectra of imine 13 has been chosen as a model in order to simplify the  $^{13}\text{C}$ -NMR spectra (Table 5). The quaternary carbons, C-1, C-2 and C-5 and the carbon of the imine group C=N, are readily identified since they are less intense compared with other signals as a result of long relaxation times of the quaternary carbons (Al-Najjar *et al.* 1987, Al Showiman *et al.* 1982). The  $^{13}\text{C}$  spectrum (in  $\text{CDCl}_3$ ) shows signals at  $\delta$  164.27 assigned to the C = N group and at  $\delta$  119.00 and 110.70 assigned to the C-1 and C-5 quaternary carbons and confirmed by using the NOE technique. N- $\text{CH}_3$  resonate at  $\delta$  45.67. Phenyl carbons C-3, C-4 and C-7 appear at  $\delta$  118.60,  $\delta$  134.28 and  $\delta$  132.23 respectively. The assignments of the chemical shifts of the backbone carbons are based either on spin-lattice relaxation, or on the study of substituent effects in benzene derivatives (Ewing 1979, Arrowsmith *et al.* 1978). Table (9) also shows the shift deviation from the value calculated due to additivity of chemical shifts of benzene substituents:  $\Delta = \delta$  (calc.) -  $\delta$  (exp.). The results obtained for some compounds (Table 9) indicate that, when the benzene ring is polysubstituted, there is a lack of additivity, particularly at  $\delta C_{\text{ipso}}$  and  $\delta C_{-2}$  positions.

The  $^{13}\text{C}$ -NMR chemical shift of other 5-bromo substituted salicylaldehyde imine derivatives are listed in Table (5). It is worthnoting that the  $^{13}\text{C}$  chemical shifts of both C-1 (C-iposo) and the C=N carbons are sensitive to the groups attached to the imine nitrogen (Tables 3-5). Interestingly, with t-butyl group, a considerable shift to high field occurs for the C=N, which appears at  $\delta$  158.52 (Table 5, compound 17) compared with N-methyl group (Table 3, compound 13) which appears at  $\delta$  164.27. The imine 17,  $\text{R}=(\text{CH}_3)_3\text{C}$ , donates more electrons to C=N (compared with  $\text{R}=\text{CH}_3$ , imine 13). Thus, there is a decrease in the polarization of  $\text{C}^+-\text{N}^-$  in the imine bond and the carbon resonance shifts to higher field when  $\text{R}=(\text{CH}_3)_3\text{C}$  group compared with  $\text{R}=\text{CH}_3$ .

#### b) $^1\text{H}$ - and $^{13}\text{C}$ - NMR Chemical Shifts of Amines

Amines were obtained by the reduction of the appropriate imine, (see experimental), and the  $^1\text{H}$  and  $^{13}\text{C}$ -NMR spectrum of amine 31, Table 8 has been chosen as a model in order to simplify the interpretation of NMR spectra. The  $\text{CH}_2\text{-N}$  and the  $\text{NH-CH}_3$  groups of this secondary amine resonate in the  $^1\text{H}$  NMR spectrum (DMSO at  $26^\circ\text{C}$ ) apart from each other. The spectrum shows two singlets for  $\text{CH}_2\text{-N}$  at  $\delta$  3.91 and for  $\text{NH-CH}_3$  at  $\delta$  2.44 (Table 8). The  $^1\text{H}$  chemical shifts of other protons are simply identified and listed in Tables (6-8).

The  $^{13}\text{C}$  chemical shifts for amines (19 - 36) are given in Tables (6-8). The quaternary carbons are readily identified, since they are less intense and almost invariant in position. The  $^{13}\text{C}$  chemical shifts of the  $\text{CH}_2\text{-N}$  and  $\text{NHCH}_3$  are readily identified and resonate at  $\delta$  51.39 and  $\delta$  34.18 respectively (Tables 6-8). These values were confirmed by using the NOE technique.

Interestingly, first, the  $^{13}\text{C}$ -1 (*ipso*) carbon of the amine derivatives, (Tables 6-8) resonates downfield compared with  $^{13}\text{C}$ -1 (*ipso*) of the corresponding imine (Tables 3-6) and the rest of the carbons resonate upfield compared with analogous carbons in the imines, This shift is due to substituent chemical shift effect (SCS) exerted by the  $\text{CH}_2$  group, which is derived from reduction of imine ( $\text{CH}=\text{N}$ ) group. Secondly, it is worthnoting that the resonance of the  $\text{CH}_2$  carbon in amines is sensitive to the nature of (R) group which is attached to the secondary nitrogen ( Tables 6-8).The NH and OH protons appear as broad peaks. It is of interest that when the attached group is t-butyl (*i.e.* Table 8), a considerable shift to higher field occurs for the Ph  $^{13}\text{CH}_2$ , which has a value of  $\delta$  51.45 for compound 35, as compared to compound 33,  $\delta$  Ph  $^{13}\text{CH}_2$ , which appears at  $\delta$  56.74 and compound 34, Ph  $^{13}\text{CH}_2$ , which resonates at  $\delta$  53.92 (Table 8). The upfield shift of R=  $^t\text{Bu}$ , in compound 35 may be due to increasing electron density on the  $\text{CH}_2$  group as a result of  $\sigma$ -donation of  $^t\text{Bu}$  group as compared to  $^i\text{Bu}$  and  $^s\text{Bu}$  groups in 33 and 34 respectively.

## Experimental

### 3-, 4- and 5-Bromosalicylaldehydes

These aldehydes were prepared (Casiraghi *et al.* 1978) by heating a mixture of the appropriate bromophenoxy magnesium bromide, hexamethylphosphoramide, and paraformaldehyde in anhydrous benzene under reflux for three hours. After cooling, the mixture was acidified with 10% aqueous hydrochloric acid and extracted with ether. Evaporation of the solvent under reduced pressure gave crude product which was purified by steam distillation and subsequent recrystallization or distillation under high vacuum to give the following products: 3-bromosalicylaldehyde (85%), b.p.  $65^\circ\text{C}$  at 0.5 mm Hg, m.p.  $52^\circ\text{C}$  (ethanol) lit.  $51^\circ\text{C}$  (Denton *et al.* 1963); 4-bromosalicylaldehyde (75%), b.p.  $70^\circ\text{C}$  at 0.5 mm Hg, m.p.  $51^\circ\text{C}$  (ethanol) lit.  $52^\circ\text{C}$  (Sen *et al.* 1932), 5-bromosalicylaldehyde (87%), m.p.  $106^\circ\text{C}$  (ethanol) lit.  $103^\circ\text{C}$  (Denton *et al.* 1963),  $104\text{-}105^\circ\text{C}$  (Czerwinska 1964)).

### Substituted Imines and Amines

The imines of 3-, 4-, and 5- bromosalicylaldehydes were made by refluxing 10 mmol of the corresponding bromosalicylaldehyde with 30 mmol of redistilled primary amine in 100 ml methanol for two hours. After cooling, the solvent was removed under reduced pressure and the product was recrystallized from ethanol, methanol or

benzene. In case of the reaction of methylamine with bromosalicylaldehydes, the methylamine gas was generated from 40% methylamine solution by the addition of sodium hydroxide pellets in parts to the warm (40-50°) methylamine solution (40ml) and the generated gas was passed immediately to a different flask containing bromosalicylaldehyde in methanol. Table (1) shows the physical and microanalytical properties of the prepared imines.

The appropriate secondary amines were made by reducing the above imines by the addition of anhydrous sodium borohydride (4 mmol) in portions to a solution of imine (4 mmol) in methanol (100 ml) with continuous stirring at room temperature for one hour, then at refluxing temperature for another hour. After cooling, the reaction mixture was poured into 200 ml of iced water then extracted with ether and the combined ether extracts were dried over anhydrous sodium sulphate. The ether was removed under reduced pressure and the product was recrystallized from ethanol or benzene. Table (2) shows the physical and microanalytical properties of the prepared secondary amines.

The NMR spectra was obtained on Jeol JNM FX-100 spectrometer operating in the Fourier Transform (FT) mode. All the spectra were recorded at ambient temperature 26°C, and the sample concentration was generally 0.2 M in the appropriate solvent. Chemical shifts were determined relative to the internal standard tetramethylsilane (TMS). The instrument conditions were as follows:

*i) <sup>13</sup>C-NMR Spectra*

<sup>13</sup>C observe frequency 25 MHz; pulse width 10 μs (45°); pulse delay 15 sec, acquisition time auto set; data points 8k; spectral width 5000 Hz, effective resolution 0.015 ppm, sample tube 10 mm; probe <sup>1</sup>H/<sup>13</sup>C dual probe, <sup>1</sup>H noise decoupling and internal lock on the deuterium signal of the solvent.

*ii) <sup>1</sup>H NMR Spectra*

<sup>1</sup>H observe frequency 100 MHz; pulse width 20 μs (45°); pulse delay auto set, acquisition time auto set; data points 8k; spectral width 1000 Hz, effective resolution 0.10 Hz, probe temperature 26°C, sample tubes 10 mm, probe <sup>1</sup>H/<sup>13</sup>C dual probe and deuterium internal lock.

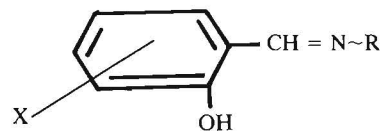
*iii) Nuclear Overhauser Enhancement (NOE) Measurements*  
(Al-Najjar *et al.* 1987)

The absolute NOE determined at 25 MHz was recorded after gating the decoupler to allow interrupted (pulse modulated)  $^1\text{H}$  decoupling. Using the technique of decoupling just before the short  $^{13}\text{C}$  pulses and during short ( $\mu\text{s}$ ) acquisitions of the free-induction decays, while leaving the decoupler off for the longer ( $\geq 4T_1$ ) pulse intervals, allowed direct measurements of the NOE values from the  $^1\text{H}$  decoupled spectra.

#### *Acknowledgements*

The author gratefully acknowledge the technical assistance of Mr. O. M. Farhan. I also thank the Research Centre, College of Science, King Saud University for financial support.

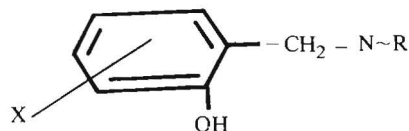
**Table 1.** Physical and Microanalytical Properties of Compounds



X	R	M.P. °C	Yield %	Molecular Formula	Calculated (%)			Found (%)		
					C	H	N	C	H	N
3-Br	Me	96.0	94	C <sub>8</sub> H <sub>8</sub> NOBr	44.90	3.77	6.54	44.77	3.42	6.45
	<sup>i</sup> Pr	35.0	85	C <sub>10</sub> H <sub>12</sub> NOBr	49.60	4.99	5.79	48.71	4.85	5.94
	<sup>i</sup> Bu	81.0	87	C <sub>11</sub> H <sub>14</sub> NOBr	51.88	5.51	5.47	50.13	5.32	5.05
	<sup>s</sup> Bu	31.0	85	C <sub>11</sub> H <sub>14</sub> NOBr	51.88	5.51	5.47	51.82	5.41	5.23
	<sup>t</sup> Bu	62.0	88	C <sub>11</sub> H <sub>14</sub> NOBr	51.88	5.51	5.47	50.93	5.23	4.91
	Ph	68.5	90	C <sub>13</sub> H <sub>10</sub> NOBr	56.54	3.65	5.07	55.75	3.60	4.67
4-Br	Me	65.0	95	C <sub>8</sub> H <sub>8</sub> NOBr	44.90	3.77	6.54	44.63	3.58	6.41
	<sup>i</sup> Pr	50.0	87	C <sub>10</sub> H <sub>12</sub> NOBr	49.60	4.99	5.79	49.50	4.75	5.85
	<sup>i</sup> Bu	46.0	75	C <sub>11</sub> H <sub>14</sub> NOBr	51.88	5.51	5.47	51.73	5.42	5.54
	<sup>s</sup> Bu	44.0	82	C <sub>11</sub> H <sub>14</sub> NOBr	51.88	5.51	5.47	51.85	5.32	5.56
	<sup>t</sup> Bu	62.0	85	C <sub>11</sub> H <sub>14</sub> NOBr	51.88	5.51	5.47	51.65	5.20	5.35
	Ph	122.0	90	C <sub>13</sub> H <sub>10</sub> NOBr	56.54	3.65	5.07	55.94	3.52	4.85
5-Br	Me	69.0	87	C <sub>8</sub> H <sub>8</sub> NOBr	44.90	3.77	6.54	44.67	3.96	6.19
	<sup>i</sup> Pr	74.0	82	C <sub>10</sub> H <sub>12</sub> NOBr	49.60	4.99	5.79	49.84	5.01	5.38
	<sup>i</sup> Bu	32.0	84	C <sub>11</sub> H <sub>14</sub> NOBr	51.88	5.51	5.47	51.97	5.41	5.31
	<sup>s</sup> Bu	47.0	90	C <sub>11</sub> H <sub>14</sub> NOBr	51.88	5.51	5.47	52.01	5.20	5.45
	<sup>t</sup> Bu	62.0	92	C <sub>11</sub> H <sub>14</sub> NOBr	51.88	5.51	5.47	52.73	5.57	5.33
	Ph	125.0	87	C <sub>13</sub> H <sub>10</sub> NOBr	56.54	3.65	5.07	56.10	3.81	4.79

X = Br (at position 3,4, or 5).

Table 2. Physical and Microanalytical Properties of Compounds



X	R	M.P. °C	Yield %	Molecular Formula	Calculated (%)			Found (%)		
					C	H	N	C	H	N
3-Br	Me	150.0	87	C <sub>8</sub> H <sub>10</sub> NOBr	44.47	4.67	6.48	44.24	4.34	6.42
	<sup>i</sup> Pr	127.0	85	C <sub>10</sub> H <sub>14</sub> NOBr	49.14	5.78	5.74	48.21	5.63	5.62
	<sup>t</sup> Bu	79.5	78	C <sub>11</sub> H <sub>16</sub> NOBr	51.17	6.25	5.43	50.93	6.15	5.22
	<sup>s</sup> Bu	99.0	80	C <sub>11</sub> H <sub>16</sub> NOBr	51.17	6.25	5.43	52.34	6.42	5.52
	<sup>t</sup> Bu	150.0	90	C <sub>11</sub> H <sub>16</sub> NOBr	51.17	6.25	5.43	50.81	6.33	5.65
	Ph	97.0	95	C <sub>13</sub> H <sub>12</sub> NOBr	56.13	4.35	5.04	55.82	4.12	4.85
4-Br	Me	129.0	82	C <sub>8</sub> H <sub>10</sub> NOBr	44.47	4.67	6.48	44.72	4.41	6.23
	<sup>i</sup> Pr	68.0	85	C <sub>10</sub> H <sub>14</sub> NOBr	49.14	5.78	5.74	48.81	5.88	5.67
	<sup>t</sup> Bu	67.0	87	C <sub>11</sub> H <sub>16</sub> NOBr	51.17	6.25	5.43	51.37	6.03	5.57
	<sup>s</sup> Bu	49.0	90	C <sub>11</sub> H <sub>16</sub> NOBr	51.17	6.25	5.43	50.82	6.11	5.72
	<sup>t</sup> Bu	94.0	95	C <sub>11</sub> H <sub>16</sub> NOBr	51.17	6.25	5.43	51.80	6.45	5.21
	Ph	136.5	90	C <sub>13</sub> H <sub>12</sub> NOBr	56.13	4.35	5.04	55.94	4.21	4.98
5-Br	Me	132.0	84	C <sub>8</sub> H <sub>10</sub> NOBr	44.47	4.67	6.48	44.31	4.71	6.52
	<sup>i</sup> Pr	68.0	80	C <sub>10</sub> H <sub>14</sub> NOBr	49.14	5.78	5.74	48.93	5.94	6.14
	<sup>t</sup> Bu	59.0	87	C <sub>11</sub> H <sub>16</sub> NOBr	51.17	6.25	5.43	51.41	6.26	5.14
	<sup>s</sup> Bu	52.0	90	C <sub>11</sub> H <sub>16</sub> NOBr	51.17	6.25	5.43	51.38	6.69	5.75
	<sup>t</sup> Bu	102.0	84	C <sub>11</sub> H <sub>16</sub> NOBr	51.17	6.25	5.43	51.01	6.39	5.12
	Ph	122.0	90	C <sub>13</sub> H <sub>12</sub> NOBr	56.13	4.35	5.04	56.10	4.27	5.25

X = Br (at position 3,4, or 5).



Table 3.  $^1\text{H}$  and  $^{13}\text{C}$ -NMR Spectra of Imines (1-6)<sup>a</sup>

Compound No.	$\delta_{\text{HC=N}}$	$\delta_{\text{C}_{\text{ipso}}}$	$\delta_{\text{C-2}}$	$\delta_{\text{C-3}}$	$\delta_{\text{C-4}}$	$\delta_{\text{C-5}}$	$\delta_{\text{C-6}}$	$\delta_{\text{C}}$	$\delta_{\text{CH}}$	$\delta_{\text{CH}_2}$	$\delta_{\text{CH}_3}$	$\delta_{\text{CH}_3}$	$\delta_{\text{OH}}$	$\delta_{\text{NH}}$
A	$^1\text{H}$ 9.83 <sub>s</sub> (CHO)				7.54dd 7.7Hz 1.5Hz	6.92t 7.7Hz	7.75dd 7.7Hz 1.5Hz						11.57b	
	$^{13}\text{C}$ 195.94 (CHO)	121.28	157.99	111.06	139.90	120.7c	132.91							
1	$^1\text{H}$ 8.29b				7.58dd	6.50t	6.75dd					3.50d <sup>4</sup> J 1.22 44.00		
	$^{13}\text{C}$ 165.65	119.00	160.70	111.16	135.68	118.53	130.39							
2	$^1\text{H}$ 8.25b				7.57dd	6.68t	7.14dd		3.64m		1.32d		15.05b	
	$^{13}\text{C}$ 161.57	118.82	160.52	112.18	135.73	118.23	130.56		58.44		23.90			
3	$^1\text{H}$ 8.21b				7.53dd	6.75t	7.19d		1.98m	3.43d	0.99d			
	$^{13}\text{C}$ 164.22	118.70	160.63	112.18	135.84	118.23	130.56		29.48	65.66	20.32			
4	$^1\text{H}$ 8.23b				7.57dd	6.67t	7.19d		3.30m	1.63m	0.89t	1.29d	13.13b	
	$^{13}\text{C}$ 162.22	118.58	160.70	112.18	135.73	118.11	130.62		64.78	30.54	10.57	21.85		
5	$^1\text{H}$ 8.19b				7.58dd	6.60t	7.16dd				1.39s			
	$^{13}\text{C}$ 159.22	119.00	165.47	112.64	130.56	121.70	132.56	56.30			30.50			
6	$^1\text{H}$ 8.59b				7.54dd	6.94t	7.38b	(Ph N=C)			7.38 Co	7.37 Cm	7.38 Cp	14.41b
	$^{13}\text{C}$ 161.46	119.93	157.70	111.24	136.32	119.70	131.39		Cipso 146.78		121.17	129.57	127.45	

a =  $\delta$  ppm relative to TMS.

A = 3-Bromosalicylaldehyde.

Table 4.  $^1\text{H}$  and  $^{13}\text{C}$ -NMR Spectra of Imines (7-12).a

Compound No.	$\delta_{\text{HC=N}}$	$\delta_{\text{C}_{\text{ipso}}}$	$\delta_{\text{C-2}}$	$\delta_{\text{C-3}}$	$\delta_{\text{C-4}}$	$\delta_{\text{C-5}}$	$\delta_{\text{C-6}}$	$\delta_{\text{C}}$	$\delta_{\text{CH}}$	$\delta_{\text{CH}_2}$	$\delta_{\text{CH}_3}$	$\delta_{\text{CH}_3}$	$\delta_{\text{OH}}$	$\delta_{\text{NH}}$
B $^1\text{H}$ $^{13}\text{C}$	9.32b (CHO) 195.81 (CHO)	119.47	161.81	7.16s 120.99	130.74	7.05d 123.52	7.38d 134.50							
7 $^1\text{H}$ $^{13}\text{C}$	8.23b 165.63	117.35	163.00	7.01s 120.93	126.84	6.96d 121.49	7.11d 132.09					3.45d $^4\text{J}$ 1.22 44.99		
8 $^1\text{H}$ $^{13}\text{C}$	8.24b 161.51	118.93	164.23	7.01s 121.17	130.62	6.95d 121.17	7.10d 132.27		3.56m 58.85		1.31d 23.90			
9 $^1\text{H}$ $^{13}\text{C}$	8.18b 164.15	117.05	164.15	7.02s 121.23	127.27	6.95d 121.23	7.11d 132.33		2.00m 29.48	3.40dd 0.73 Hz 66.13	0.98d 20.38		13.28b	
10 $^1\text{H}$ $^{13}\text{C}$	8.23b 161.98	118.93	163.92	7.01s 121.05	130.62	7.00d 121.28	7.12d 132.21		3.27m 65.55	1.60q 30.60	0.89t 10.63	1.29d 21.91	13.13b	
11 $^1\text{H}$ $^{13}\text{C}$	8.21b 159.22	119.00	165.74	7.01s 120.64	127.51	6.91b 121.70	7.09b 132.56	56.00			1.36s 29.48			
12 $^1\text{H}$ $^{13}\text{C}$	8.54 161.51	123.48	161.93	7.08s 120.64	130.69	7.00b 127.39	7.18b 133.09	(Ph-N=C)	Cipso 147.83	7.38 Co 121.05	7.37 Cm 129.45	7.38 Cp 127.22	13.23b	

a =  $\delta$  ppm relative to TMS.

B = 4-Bromosalicylaldehyde.

Table 5.  $^1\text{H}$  and  $^{13}\text{C}$ -NMR Spectra of Imines (13-18).<sup>a</sup>

Compound No.	$\delta_{\text{HC=N}}$	$\delta_{\text{C}_{\text{ipso}}}$	$\delta_{\text{C-2}}$	$\delta_{\text{C-3}}$	$\delta_{\text{C-4}}$	$\delta_{\text{C-5}}$	$\delta_{\text{C-6}}$	$\delta_{\text{C}}$	$\delta_{\text{CH}}$	$\delta_{\text{CH}_2}$	$\delta_{\text{CH}_3}$	$\delta_{\text{CH}_3}$	$\delta_{\text{OH}}$	$\delta_{\text{NH}}$
C $^1\text{H}$ $^{13}\text{C}$	9.84d (CHO) $^4J$ 1.59 195.35 (CHO)	121.31	160.57	119.32	139.67	111.36	135.61						10.92	
13 $^1\text{H}$ $^{13}\text{C}$	8.26q	119.00	158.14	118.60	134.28	110.70	132.23				3.49d $^4J$ 1.47 45.67		13.80	
14 $^1\text{H}$ $^{13}\text{C}$	8.20b	119.05	159.00	119.05	134.62	110.78	133.27		3.56m		1.29d		13.67b	
15 $^1\text{H}$ $^{13}\text{C}$	8.18b	120.05	160.63	119.05	134.67	109.65	133.22		1.89m	3.39d	0.96d		13.61	
16 $^1\text{H}$ $^{13}\text{C}$	8.21b	120.11	160.52	119.00	134.56	109.65	133.21		3.2m	1.58q	0.86t	1.25d	14.33	
17 $^1\text{H}$ $^{13}\text{C}$	8.25b	120.11	161.34	119.4	134.47	109.56	133.44	56.80			1.34s		14.36	
18 $^1\text{H}$ $^{13}\text{C}$	8.50b	120.58	160.16	119.2	135.61	110.48	134.20	(Ph-N=C)	$\text{C}_{\text{ipso}}$ 147.90	7.38 Co 121.17	7.37 Cm 129.45	7.38 Cp 127.34	13.25b	

a =  $\delta$  ppm relative to TMS.  
C = 5-Bromosalicylaldehyde.

Table 6.  $^1\text{H}$  and  $^{13}\text{C}$ -NMR Spectra of Amines (19-24)<sup>a</sup>

Compound No.	$\delta$ $\text{pHCH}_2$	$\delta\text{C}_{\text{ipso}}$	$\delta\text{C-2}$	$\delta\text{C-3}$	$\delta\text{C-4}$	$\delta\text{C-5}$	$\delta\text{C-6}$	$\delta\text{C}$	$\delta\text{CH}$	$\delta\text{CH}_2$	$\delta\text{CH}_3$	$\delta\text{CH}_3$	$\delta\text{OH}$ b	$\delta\text{NH}$ b
$^{19}\text{F}$ 19	4.03				7.46dd	6.70t	7.24dd				2.49			
$^{13}\text{C}$	50.80	122.48	154.29	110.00	132.62	120.00	129.21				33.42			
$^1\text{H}$ 20	3.99s				7.44d	6.63t	6.85dd		2.91m		1.16d			
$^{13}\text{C}$	50.10	123.40	154.83	110.62	131.97	119.70	127.04		48.40		22.38			
$^1\text{H}$ 21	3.97				7.28dd	6.60t	6.87dd		1.82m	2.5d	0.95d			
$^{13}\text{C}$	56.74	123.81	155.29	110.54	132.03	119.70	127.22		28.02	52.92	20.49			
$^1\text{H}$ 22	4.02s				7.35dd	6.77t	7.20dd		2.80m	1.62m	1.28d	0.92t	6.20b	6.20b
$^{13}\text{C}$	54.80	123.95	155.30	111.00	133.21	121.58	130.77		36.90	26.90	16.68	9.98		
$^1\text{H}$ 23	3.95s				7.35dd	6.63t	7.13dd				1.23s			
$^{13}\text{C}$	52.39	124.16	155.29	111.59	128.21	119.87	127.57	45.52			27.96			
$^1\text{H}$ 24	4.42									7.36 Co	7.38 Cm	7.36 Cp		
$^{13}\text{C}$	47.05	124.00	155.30	111.21	131.80	119.93	127.98	$\text{C}_6\text{H}_5^-$	$\text{C}_{\text{ipso}}$ 146.78	121.17	129.57	127.45		

a =  $\delta$  ppm relative to TMS.b =  $\delta$  of OH and NH recorded when observed.

Table 7.  $^1\text{H}$  and  $^{13}\text{C}$ -NMR Spectra of Amines (25-30)<sup>a</sup>.

Compound No.	$\delta$ $\text{phCH}_2$	$\delta\text{C}_{\text{ipso}}$	$\delta\text{C-2}$	$\delta\text{C-3}$	$\delta\text{C-4}$	$\delta\text{C-5}$	$\delta\text{C-6}$	$\delta\text{C}$	$\delta\text{CH}$	$\delta\text{CH}_2$	$\delta\text{CH}_3$	$\delta\text{CH}_3$	$\delta\text{OH}_b$	$\delta\text{NH}_b$
25 $^1\text{H}$ $^{13}\text{C}$	3.91 50.75	 122.64	 157.86	7.10 123.90	— 131.27	6.97 120.40	7.10 130.33				2.36 38.06			6.03b
26 $^1\text{H}$ $^{13}\text{C}$	3.63s 49.63	 122.28	 158.36	6.92s 118.88	 130.04	6.88b 121.87	7.19b 131.15		3.00m 47.87		1.13d 22.78			
27 $^1\text{H}$ $^{13}\text{C}$	3.95 56.70	 122.28	 159.28	7.12 118.92	 131.56	6.86 121.80	7.20 131.00		1.82m 28.40	2.50d 52.42	0.94d 21.03			
28 $^1\text{H}$ $^{13}\text{C}$	3.94 52.34	 122.16	 159.20	7.20 119.01	 130.80	6.74 121.87	7.22 130.60		2.6dm 49.45	1.48m 28.96	1.13d 19.03	0.92t 9.93		
29 $^1\text{H}$ $^{13}\text{C}$	3.90 52.63	 122.10	 159.28	7.11 119.47	 130.70	6.88 121.70	7.18 130.09	44.23			1.25 27.73			
30 $^1\text{H}$ $^{13}\text{C}$	4.34s 49.04	 122.28	 157.58	7.23 119.87	 130.22	6.84 121.98	7.18 129.98	$\text{C}_6\text{H}_5$	$\text{C}_{\text{ipso}}$ 146.60	7.36 Co 121.17	7.38 Cm 129.57	7.36 Cp 12.45		

a =  $\delta$  ppm relative to TMS.

b =  $\delta$  of OH and NH recorded when observed.

Table 8.  $^1\text{H}$  and  $^{13}\text{C}$ -NMR Spectra of Amines (31-36)<sup>a</sup>

Compound No.	$\delta$ phCH <sub>2</sub>	$\delta$ C <sub>ipso</sub>	$\delta$ C-2	$\delta$ C-3	$\delta$ C-4	$\delta$ C-5	$\delta$ C-6	$\delta$ C	$\delta$ CH	$\delta$ CH <sub>2</sub>	$\delta$ CH <sub>3</sub>	$\delta$ CH <sub>3</sub>	$\delta$ OH b	$\delta$ NH b
31 $^1\text{H}$	3.91			6.70	6.68		7.24b				2.44			6.03b
31 $^{13}\text{C}$	51.39	123.75	156.87	117.64	131.74	110.01	131.33				34.18			
32 $^1\text{H}$	3.95s			6.70d	7.12b		7.11b		2.90m		1.11d			
32 $^{13}\text{C}$	51.24	123.30	155.86	118.20	131.27	110.41	130.62		47.20		23.04			
33 $^1\text{H}$	3.94s			6.70d	7.26dd		7.14b		1.80m	2.48d	0.93d		6.18b	6.18b
33 $^{13}\text{C}$	56.74	124.57	157.58	118.17	131.33	110.59	130.80		28.07	52.45	20.44			
34 $^1\text{H}$	3.95s			6.72d	7.18b		7.12b		2.6dm	1.48m	1.13d	0.92t		
34 $^{13}\text{C}$	53.92	123.82	157.63	118.29	131.39	110.54	130.74	45.46	49.45	28.96	19.03	9.93		
35 $^1\text{H}$	3.91			6.70d	7.20b		7.11b				1.21s		5.60b	5.60b
35 $^{13}\text{C}$	51.45	122.80	157.70	118.41	131.15	110.47	130.51	51.45			28.37			
36 $^1\text{H}$	4.36s			6.87dd	6.87dd		7.20b	C <sub>6</sub> H <sub>5</sub>	C <sub>ipso</sub>	7.34 Co	7.36 Cm	7.34 Cp		
36 $^{13}\text{C}$	49.22	122.52	157.58	118.41	132.15	110.60	131.50		146.78	121.17	129.60	127.46		

a =  $\delta$  ppm relative to TMS.b =  $\delta$  of OH and NH recorded when observed.

Table 9. Substituent Chemical Shift (SCS) Effects

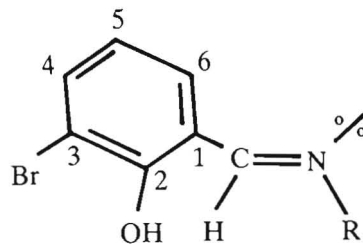
Compound No.	$\delta^{C_{ipso}}$	$\delta^{C-2}$	$\delta^{C-3}$	$\delta^{C-4}$	$\delta^{C-5}$	$\delta^{C-6}$
A	$\delta^a$ 121.28 $\delta^b$ 125.70 $\Delta$ 4.42	157.99 159.80 1.81	111.06 110.40 -0.66	139.90 138.75 -1.40	120.70 123.20 2.50	132.91 132.65 -0.41
B	$\delta^a$ 119.47 $\delta^b$ 134.50 $\Delta$ 15.03	161.81 158.20 -3.61	120.09 119.40 -1.59	130.74 129.75 -0.72	123.52 124.80 1.28	134.50 132.65 -1.85
C	$\delta^a$ 121.31 $\delta^b$ 125.70 $\Delta$ 4.39	160.57 155.00 -5.57	119.32 117.80 -1.52	139.67 138.75 -0.92	111.36 115.80 4.44	135.61 134.75 -0.86
1	$\delta^a$ 119.00 $\delta^b$ 126.10 $\Delta$ 7.10	160.70 159.10 -1.60	111.16 110.00 -1.16	135.68 135.35 -0.33	118.53 122.80 4.27	130.39 128.75 -1.64
7	$\delta^a$ 117.35 $\delta^b$ 122.90 $\Delta$ 5.55	163.00 157.50 -5.50	120.93 119.00 -1.93	126.84 126.35 -0.49	121.49 124.40 2.91	132.09 131.95 -0.14
13	$\delta^a$ 119.00 $\delta^b$ 126.10 $\Delta$ 7.10	158.24 154.30 -3.84	118.60 117.40 -1.20	134.28 135.35 1.07	110.70 115.40 4.70	132.23 133.55 1.32
19	$\delta^a$ 122.48 $\delta^b$ 130.40 $\Delta$ 7.92	154.29 158.25 3.96	110.00 109.55 -0.45	132.62 134.85 2.23	120.00 122.35 2.50	129.21 127.90 -1.31
25	$\delta^a$ 122.64 $\delta^b$ 127.20 $\Delta$ 4.56	157.86 156.65 -0.95	123.90 118.55 -5.35	131.27 125.85 -5.42	120.40 123.95 3.55	130.33 131.10 0.77
31	$\delta^a$ 123.75 $\delta^b$ 130.40 $\Delta$ 6.65	156.87 153.45 -3.42	117.64 116.95 -1.14	131.74 134.85 -3.45	110.01 114.95 4.94	131.33 132.47 1.14

$\delta^a$  = ppm from TMS ( $\delta(\text{exp.})$ ).

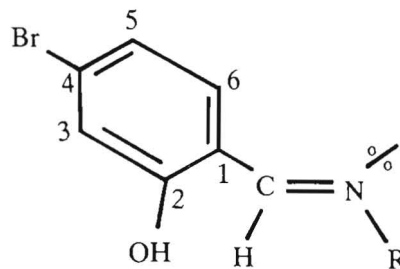
$\delta^b$  = SCS, ppm calculated from the substituent Br, OH and C= N (or CH-NH, CHO) groups ( $\delta(\text{calc.})$ ).

$\Delta$  = Deviation from value calculated from additivity of chemical shifts of benzene.

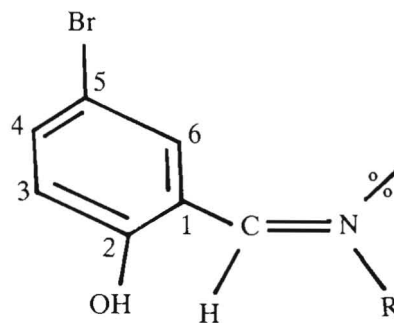
1.  $R = \text{CH}_3$
2.  $R = \text{CH}(\text{CH}_3)_2$
3.  $R = \text{CH}_2\text{CH}(\text{CH}_3)_2$
4.  $R = \text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_3$
5.  $R = \text{C}(\text{CH}_3)_3$
6.  $R = \text{C}_6\text{H}_5$



7.  $R = \text{CH}_3$
8.  $R = \text{CH}(\text{CH}_3)_2$
9.  $R = \text{CH}_2\text{CH}(\text{CH}_3)_2$
10.  $R = \text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_3$
11.  $R = \text{C}(\text{CH}_3)_3$
12.  $R = \text{C}_6\text{H}_5$

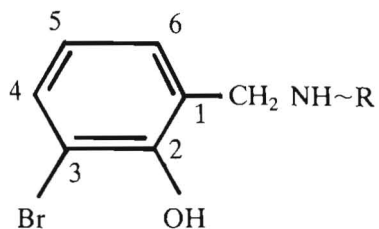


13.  $R = \text{CH}_3$
14.  $R = \text{CH}(\text{CH}_3)_2$
15.  $R = \text{CH}_2\text{CH}(\text{CH}_3)_2$
16.  $R = \text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_3$
17.  $R = \text{C}(\text{CH}_3)_3$
18.  $R = \text{C}_6\text{H}_5$

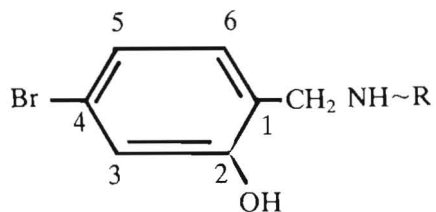




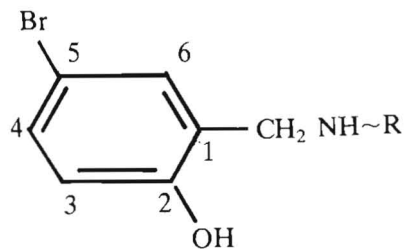
19.  $R = \text{CH}_3$   
 20.  $R = \text{CH}(\text{CH}_3)_2$   
 21.  $R = \text{CH}_2\text{CH}(\text{CH}_3)_2$   
 22.  $R = \text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_3$   
 23.  $R = \text{C}(\text{CH}_3)_3$   
 24.  $R = \text{C}_6\text{H}_5$



25.  $R = \text{CH}_3$   
 26.  $R = \text{CH}(\text{CH}_3)_2$   
 27.  $R = \text{CH}_2\text{CH}(\text{CH}_3)_2$   
 28.  $R = \text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_3$   
 29.  $R = \text{C}(\text{CH}_3)_3$   
 30.  $R = \text{C}_6\text{H}_5$



31.  $R = \text{CH}_3$   
 32.  $R = \text{CH}(\text{CH}_3)_2$   
 33.  $R = \text{CH}_2\text{CH}(\text{CH}_3)_2$   
 34.  $R = \text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_3$   
 35.  $R = \text{C}(\text{CH}_3)_3$   
 36.  $R = \text{C}_6\text{H}_5$



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(Received 05/10/1993;  
in revised form 21/01/1994)

## دراسات طيفية لبعض الأمينات الألكيلية الجديدة من نوع (٢) - هيدروكسي - بديل - ن - بنزليدين

حسان بكر أمين

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

تم في هذا البحث التعرف على الازاحة الكيميائية للكربون - ١٣ والبروتون لثمانية عشر أمينا وثمانية عشر أمينا حيث تم تحضير الأمينات من اختزال الأيمينات . كما تم تحديد الكيمياء الفراغية للأيمينات من نتائج الطيف النووي المغناطيسي لها حيث وجد أنها توجد في المحلول على هيئة مماكب واحد فقط (E-isomer) عند درجة حرارة الغرفة .

وقد وجد أن الازاحة الكيميائية لذرة كربون المجموعة الأيمينية (CH = N) والمجموعة البنزلية (-CH<sub>2</sub>-) تتأثر بوجود المجموعة الألكيلية المرتبطة بذرة النيتروجين في حين أن الهالوجين البديل على الحلقة البنزينية ليس له تأثير على الازاحة الكيميائية لمجموعة الأيمن .

كذلك وجد أن تأثير الازاحة الكيميائية للبديل غير اضافي للمجموعات -OH ، - Br ، - CH = N- ، - NH- ، - CH<sub>2</sub> - ، - CHO - في جميع المواضع .