

# SPECTRAL STUDIES OF SEVERAL AROMATIC SCHIFF BASES

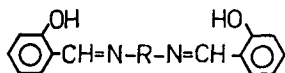
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The visible, <sup>1</sup>H NMR and infrared spectral properties of twenty aromatic Schiff bases have been studied and correlations have been detected between the spectral characteristics and the structures of the bases.

In previous papers [1] evidence was cited for the enol imine-keto amine tautomerism of a great number of aromatic Schiff bases which are potentially multidentate ligands of metal chelates. In the present work the ultraviolet, infrared and <sup>1</sup>H NMR spectra of the following aromatic Schiff bases from salicylaldehyde and aliphatic and aromatic diamines have been examined:



R =

Abbreviations\*

1	(CH <sub>2</sub> ) <sub>2</sub>	BHSAL-en
2	(CH <sub>2</sub> ) <sub>3</sub>	BHSAL-pda
3	(CH <sub>2</sub> ) <sub>4</sub>	BHSAL-bda
4	(CH <sub>2</sub> ) <sub>5</sub>	BHSAL-pmda
5	(CH <sub>2</sub> ) <sub>6</sub>	BHSAL-hxmda
6	(CH <sub>2</sub> ) <sub>7</sub>	BHSAL-hpmda
7	(CH <sub>2</sub> ) <sub>8</sub>	BHSAL-pmda
8	(CH <sub>2</sub> ) <sub>9</sub>	BHSAL-nmda
9	(CH <sub>2</sub> ) <sub>10</sub>	BHSAL-dmda
10	(CH <sub>2</sub> ) <sub>2</sub> NH(CH <sub>2</sub> ) <sub>2</sub>	BHSAL-deta
11	(CH <sub>2</sub> ) <sub>2</sub> NH(CH <sub>2</sub> ) <sub>2</sub> NH(CH <sub>2</sub> ) <sub>2</sub>	BHSAL-teta
12	(CH <sub>2</sub> ) <sub>2</sub> N(CH <sub>2</sub> ) <sub>2</sub> N(CH <sub>2</sub> ) <sub>2</sub>	
		THSAL-teta
13	N[(CH <sub>2</sub> ) <sub>2</sub> N=CH-C <sub>6</sub> H <sub>4</sub> OH] <sub>3</sub> **	THSAL-tatea
14	o-C <sub>6</sub> H <sub>4</sub>	BHSAL-ofda
15	m-C <sub>6</sub> H <sub>4</sub>	BHSAL-mfda

\* B: bis-; T: tris-; HSAL: salicylaldehyde anion; mda: methylenediamine; deta: diethylenetriamine; teta: triethylenetetramine; tatea: triaminotriethylamine; fda: phenylenediamine; nfda: naphthylenediamine.

\*\* Complete formula.

R =	Abbreviations
16 p-C <sub>6</sub> H <sub>4</sub>	BHSAL-pfda
17 C <sub>6</sub> H <sub>4</sub> -C <sub>6</sub> H <sub>4</sub>	BHSAL-bzd
18 1,2-C <sub>10</sub> H <sub>8</sub>	BHSAL-1,2-nfda
19 1,5-C <sub>10</sub> H <sub>8</sub>	BHSAL-1,5-nfda
20 1,8-C <sub>10</sub> H <sub>8</sub>	BHSAL-1,8-nfda

### Experimental

The Schiff bases studied were prepared by mixing stoichiometric quantities of salicylaldehyde and the diamines in methanolic solution. The mixtures were heated to about 50 °C; on cooling, crystalline products separated out. The crude products were recrystallized from methanol. BHSAL-deta was prepared by adding diethylenetriamine to HSAL (1:2 molecular equivalent) dissolved in methanol. After stirring for ~10 min, the volume of the solution was reduced until only oil remained. The compound was identified *via* NMR and C, H analysis.  $\beta$ ,  $\beta'$ ,  $\beta''$ -Triaminotriethylamine.3HCl (tatea.3HCl) was prepared according to JONASSEN and STRICKLAND [2]; THSAL-tatea was synthesized by a literature method [3]. The m.p. data are listed in Table I.

The u.v. absorption spectra were measured with a SPECORD UV-VIS spectrophotometer using quartz cells. The i.r. spectra were recorded in CHCl<sub>3</sub> solution on a Perkin-Elmer Infracord. The <sup>1</sup>H NMR spectra were measured in CDCl<sub>3</sub> on a JEOL 60 MHz instrument, using TMS as internal standard.

### Results and discussion

The methanolic solutions of 1–13 give very similar absorption spectra (Figs. 1 and 2); the main bands are to be found in the ranges 213–217, 253–257, 260–290, 310–320 and 390–410 nm (Table I). The band in the region of 250–260 nm can be considered a  $\pi \rightarrow \pi^*$  benzenoid band, in view of the assignment made by CHATTERJEE and DOUGLAS [4]. All these bases show a medium-intensity band in the visible which disappears in apolar solvents, e.g. in benzene. This behaviour can be interpreted by a benzoid/quinoid equilibrium [5, 6]. The structure of the spectra of CHCl<sub>3</sub> solutions is the same: two high-intensity bands appear at around 250 and 320 nm. The equilibrium constants (Table I) measured in methanol/benzene systems vary between 0.7 and 1.0, and no correlation can be found between the structures of the Schiff bases and the *K* values. Interpretation of the high *K* values of BHSAL-deta and THSAL-tatea is difficult. The visible band is absent from the spectra of 14–20 (Figs. 3 and 4) and it is probable that the above tautomeric equilibrium does not develop. The spectra of BHSAL-en, BHSAL-ofda and BHSAL-bzd exhibit an increase in intensity, which can be correlated with the number of double bonds in the molecule. Replacement of the CH<sub>2</sub>-CH<sub>2</sub> bridge by a phenyl ring or by a biphenyl ring system increases the number of double bonds.

The spectra of 1–13 in 98% sulphuric acid contain bands at around 220, 300 and 350 nm, similarly to the spectrum of salicylaldehyde in strongly acidic medium

Table I  
Melting points of Schiff bases and visible spectral data on their solutions in methanol\*

No.	m.p.**	nm and log $\epsilon$					$K \pm 0.05^{***}$
1	125.6	213(4.48)	257(4.33)	~286	319(3.88)	408(3.22)	0.76
2	51.6	215(4.42)	257(4.37)	~286	318(3.88)	404(3.55)	0.91
3	90.2	216(4.45)	255(4.22)	~284	317(3.88)	400(3.30)	1.00
4	60.7	216(4.77)	253(4.41)	277(3.97)	313(3.84)	398(3.52)	0.85
5	73.4	216(4.92)	253(4.54)	277(4.14)	313(3.99)	398(3.70)	0.81
6	49.5	217(4.79)	253(4.45)	277(4.06)	313(3.88)	398(3.63)	0.92
7	75.2	217(4.78)	253(4.38)	277(3.99)	313(3.80)	398(3.55)	0.79
8	57.2	217(4.81)	253(4.41)	277(4.04)	313(3.84)	398(3.61)	0.78
9	64.6	217(4.81)	253(4.40)	277(4.03)	313(3.83)	398(3.58)	0.79
10	105.2	215(4.64)	255(4.31)	~285	314(3.78)	400(2.81)	1.35
11	105.2	215(4.76)	254(4.41)	~280	315(3.87)	398(2.83)	0.85
12	105.6	215(4.68)	254(4.30)	~280	315(3.74)	400(2.81)	0.89
13	90.0	213(4.86)	252(4.40)	~275	314(3.97)	401(3.36)	1.30
14	163.8	215(5.09)	~230	264(4.35)	332(4.57)		
15	109.1	216(4.61)	230(4.59)	273(4.52)	343(4.48)		
16	213.4	209(4.55)	~233	274(4.02)	366(4.31)		
18	260.0		230(4.41)	273(4.13)	~330	395(3.78)	
19	220.1	216(4.70)		265(4.37)	363(4.15)		
20	188.0	~210	233(4.90)	276(3.71)	335(4.26)		

\* 17 is only very slightly soluble; \*\* uncorrected values; \*\*\* in  $\text{CH}_3\text{OH}/\text{C}_6\text{H}_6$  systems.

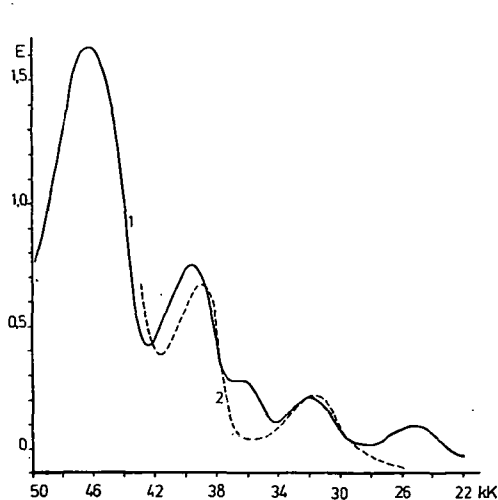


Fig. 1. Absorption spectra of BHSAL-pmda in methanol (1) and in chloroform (2). Concentration =  $2.9 \cdot 10^{-4}$  mol/dm<sup>3</sup>;  $d=0.1$  cm

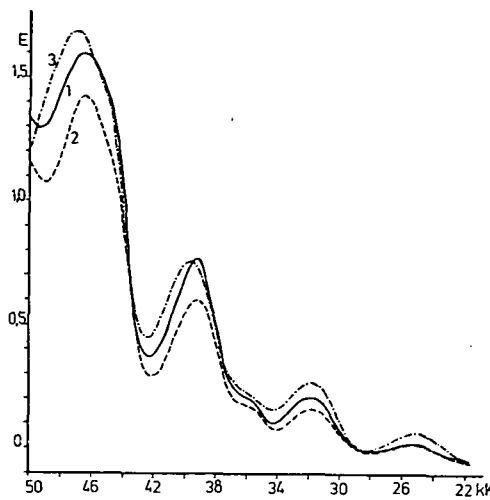


Fig. 2. Absorption spectra of BHSAL-teta (1); THSAL-teta (2); and THSAL-tatea (3). Solvent: ethanol; concentration =  $3.1 \cdot 10^{-4}$  mol/dm<sup>3</sup>;  $d=0.1$  cm

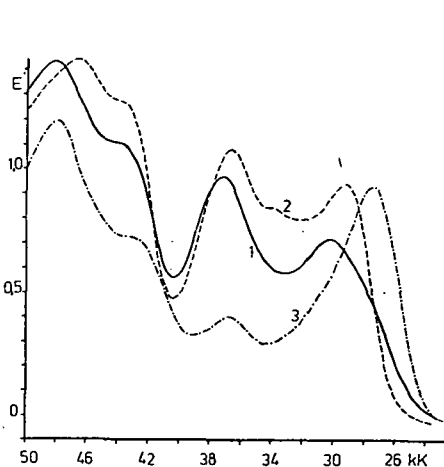


Fig. 3. Absorption spectra of ethanolic solutions. (1) BHSAL-ofda; (2) BHSAL-mfda; (3) BHSAL-pfda. Concentration =  $3.14 \cdot 10^{-4}$  mol/dm<sup>3</sup>;  $d=0.1$  cm

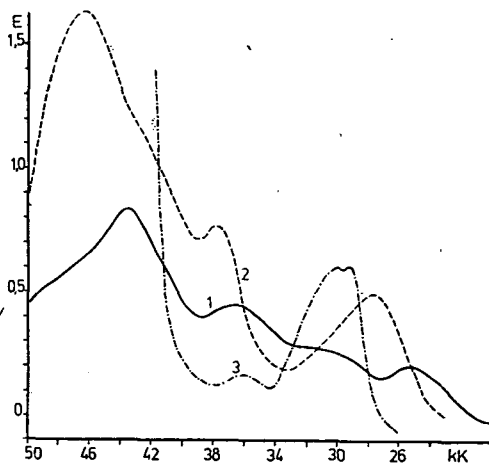


Fig. 4. Absorption spectra of naphthylenediamines. (1) BHSAL-1,2-nfda; (2) BHSAL-1,5-nfda; (3) BHSAL-1,8-nfda. Concentration =  $3.26 \cdot 10^{-4}$  mol/dm<sup>3</sup>;  $d=0.1$  cm

(Table II). It is important to note that the spectra of these bases change in time; kinetic investigations are in progress. The characteristic spectral range of the phenylenediamine derivatives in 98% H<sub>2</sub>SO<sub>4</sub> will be discussed in a subsequent paper.

The i.r. spectra of these compounds are very complex; the two main frequencies are given in Table III. The spectra show a broad band in the range 2800—3100 cm<sup>-1</sup>,

Table II  
Spectral data on sulphuric acid solutions

No.	nm and log $\epsilon$			
*	220(3.04)	292(4.02)	400(2.70)	—
1	226(4.24)	292(4.56)	357(3.91)	—
2	225(4.44)	283(4.66)	350(4.05)	—
3	225(4.43)	280(4.65)	350(3.94)	—
14	~225	308(4.48)	~380	—
15	~240	323(4.66)	387(4.47)	—
16	~240	266(3.95)	350(4.57)	403(4.62)
17	234(4.22)	282(4.30)	—	403(4.69)
18	223(4.68)	296(4.90)	329(4.43)	~355
19	219(4.89)	291(4.67)	—	394(4.54)
20	221(5.31)	292(4.59)	373(4.22)	—

\* salicylaldehyde.

Table III  
 $^1\text{H}$  NMR and i.r. data on the Schiff bases

No.	$\delta$ ppm <sup>a)</sup>				cm <sup>-1</sup> <sup>b)</sup>	
	CH <sub>2</sub> <sup>c)</sup>	CH <sub>2</sub> <sup>c)</sup> *	CH=N	OH	$\nu$ C—O	$\nu$ C=N
1		3.97	8.55	13.23	1274s	1631s
2	2.13	3.76	8.48	13.45	1276s	1622s
3	1.87	2.68	8.43	13.58	1276s	1632s
4	1.83	3.54	8.35	13.74	1277s	1633s
5	1.50	3.53	8.33	13.73	1278s	1632s
6	1.43	3.51	8.33	13.66	1277s	1633s
7	1.36	3.51	8.31	13.81	1275s	1634s
8	1.35	3.51	8.33	13.84	1276s	1633s
9	1.33	3.52	8.35	13.66	1279s	1637s
10	2.94	3.64	8.36	?	1276s	1633s
11	2.63	3.59	8.26	13.10	1277s	1633s
12	2.80	3.55	8.25	13.15	1278s	1636s
13	2.78	3.48	7.83	12.66	1277s	1637s
14			8.61	13.12	1280s	1622s
15			8.66	13.18	1280s	1624s
16			8.63	13.26	1279s	1617s
18 <sup>d)</sup>			8.69	13.20	1272s	1604s
19			8.71	13.35	1263s	1605s
20			8.54	13.22	1250s	1609s

<sup>a)</sup> in CDCl<sub>3</sub>; <sup>b)</sup> in CHCl<sub>3</sub>; <sup>c)</sup> the mean peak of multiplets; <sup>d)</sup> 17 is only very slightly soluble.

which is assigned to intramolecularly hydrogen bonded OH. The strong band around 1600—1640 cm<sup>-1</sup> is attributed to the  $\nu$ C=N stretch, in view of previous assignments [7, 8]. The position of this band is almost independent of the methylene chain length. The strong band around 1250—1280 cm<sup>-1</sup> is ascribed to the phenolic C—O

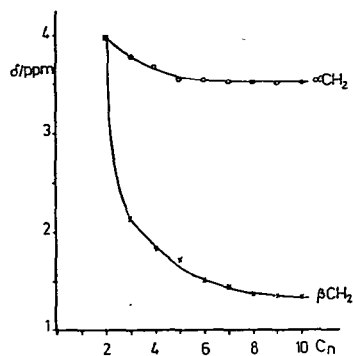


Fig. 5. Plots of ppm values of  $\alpha\text{CH}_2$  and  $\beta\text{CH}_2$  signals against number of carbon atoms in alkyl chains of compounds 1—9

(Table III) stretching vibration, in analogy with the assignments of MARVEL ET AL. [9] and KOVACIC [10]. The i.r. spectra of 14—20 in KBr and in chloroformic solution show no marked differences.

The  $^1\text{H}$  NMR spectra of the Schiff bases studied contain a sharp singlet at around 8.30—8.70 ppm, which corresponds to the methine proton; the broad signal of the OH can be found between 13.10 and 13.90 ppm (Table III). The  $\alpha\text{CH}_2$  signals of compounds 2—9 vary between 3.80 and 3.50 ppm. This triplet system is shifted towards lower ppm values with increase of the chain length; a similar tendency can also be seen for the  $\beta\text{CH}_2$  signals (of Fig. 5). In the spectra of BHSAL-deta and BHSAL-teta the  $\alpha\text{CH}_2$  signals are well distinguishable; however, the  $\beta\text{CH}_2$  and the NH signals generally overlap.

#### References

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#### СПЕКТРОСКОПИЧЕСКОЕ ИЗУЧЕНИЕ РЯДА АРОМАТИЧЕСКИХ ШИФФОВЫХ ОСНОВАНИЙ

Й. Часар

Изучены  $^1\text{H}$  ЯМР, электронного возбуждения и ИК спектроскопические свойства двадцати ароматических Шиффовых оснований и определены корреляции между спектральными характеристиками и структурой изученных соединений.