

ULTRAVIOLET, INFRARED AND NMR SPECTRAL STUDIES OF AROMATIC SCHIFF BASES

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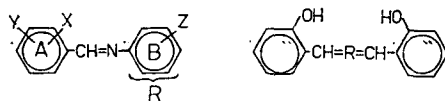
The authors have investigated Schiff-bases derived from 2-, 3- and 4-OH-benzaldehyde and aliphatic, aromatic amines and pyridine derivatives, resp. On the basis of ultraviolet, infrared and NMR spectra, conclusions are drawn regarding the behaviour of chelate-forming ligands in solution.

1. Introduction

It is known that the aromatic Schiff bases form chelate compounds of different stereochemistry with transition metal ions [1—3]. The physico-chemical properties and stereochemistry of these chelates are strongly depending on the character, number and position of substituents of ligand molecules [4—10].

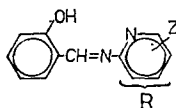
The spectroscopical investigations of Schiff bases tend first of all to the 200—400 nm spectral range [11—17] and relatively fewer data can be obtained from the region above 400 nm.

In this paper we are discussing the visible, infrared and NMR spectra of Schiff bases derived from 2-, 3-, 4-OH-benzaldehyde, aliphatic and aromatic amines and pyridines [Structure I—III], and pay special attention to the spectral region above 400 nm.



I.

II.



III.

2. Experimental

2.1. *Preparation.* The Schiff bases under study were prepared by mixing alcoholic or benzene solutions of appropriate aldehydes and amines in mole ratios 1:1 and 1:2, *resp.* The crude product was recrystallized from methanol; composition and purity were checked by N analysis and m.p. measurements. Table I contains the compounds and their symbols.

Table I
Composition and assignment of Schiff bases

X	Y	R	No.				
			orto	meta	para		
2-OH	H	-C ₆ H ₄ OH	I	II	III		
		-C ₆ H ₄ OCH ₃	IV	V	VI		
		-C ₆ H ₄ CH ₃	VII	VIII	IX		
		-C ₆ H ₅		X			
		-C ₆ H ₄ F	XI	XII	XIII		
		-C ₆ H ₄ Cl	XIV	XV	XVI		
		-C ₆ H ₄ NO ₂	XVII	XVIII	XIX		
		-C ₆ H ₄ N		XX			
		-C ₆ H ₃ N-3-CH ₃		XXI			
		-C ₆ H ₃ N-4-CH ₃		XXII			
		-C ₆ H ₃ N-5-CH ₃		XXIII			
		-C ₆ H ₃ N-6-CH ₃		XXIV			
		=N-N=		XXV			
		=N-(CH ₂) ₂ -N=		XXVI			
		=N-(CH ₂) ₃ -N=		XXVII			
		=N-(CH ₂) ₄ -N=		XXVIII			
		-C ₆ H ₅	3-OCH ₃		XXIX		
		-C ₆ H ₄ OCH ₃		XXX	XXXI	XXXII	
		3-OH	H	-C ₆ H ₅		XXXIII	
				-C ₆ H ₄ OCH ₃	XXXIV	XXXV	XXXVI
4-OH	H	-C ₆ H ₅		XXXVII			
		-C ₆ H ₄ OCH ₃	XXXVIII	XXXIX	XL		
	3-OCH ₃	-C ₆ H ₅		XLI			
		-C ₆ H ₄ OCH ₃	XLII	XLIII	XLIV		

2.2. *Spectra.** The u.v. and visible spectra were measured with Beckman DU and SPECORD UV-VIS spectrophotometer; the solvents were purified according to the literature [18].

The infrared spectra were recorded on a UNICAM SP-100 spectrophotometer in the 675—2100 cm⁻¹ region, in KBr pellets.

The ¹H NMR spectra were recorded on a JEOL 60 MHz instrument at 25 °C, in CDCl₃, CDCl₃+DMSO and CD₃OD solutions, using TMS as internal standard.

* We wish to thank dr. J. KISS and dr. Gy. DOMBI for the infrared and NMR spectral measurements.

3. Discussion

3.1. *Ultraviolet and visible spectra.* The maximum data of methanolic and benzene solutions are listed in Table II; Figures 1—3 presents some typical spectra.

In the u. v. spectra three or four group of bands can be found. According to JAFFE et al. [19, 20] the spectra of benzal-anilines can be treated as perturbed stilbene spectra. As regards the band-assignments the opinions are differing [11, 15, 21—23].

The two higher energy bands of the spectra are assigned to the excitation of the aromatic ring [24] ($\sigma \rightarrow \sigma^*$ transition); the substituents of the *B* ring and the solvent-effect are hardly influencing the energy of these bands. The band of $\pi \rightarrow \pi^*$ transition, at about 310—360 nm, is even more sensitive for the change in the structure. The position of these bands changes considerably, for instance, by the substitution of $-\text{OCH}_3$ groups of the *B* ring (No. IV—VI, XXX—XXXII, XXXIV—XXXVI, XXXVIII—XL, XLII—XLIV). The direction and the extent of the changes are mainly depending on the mutual effect of the substituents of *A* and *B* ring, *resp.*

In polar solvents, depending mainly on the structure of amine-component, a band with medium intensity may appear above 400 nm. The appearance of this band has been interpreted by the formation of intramolecular hydrogen-bridge [25, 26], benzoid-quinoid system [27], and solvent-Schiff base associates [28, 29]. It can be stated that this phenomenon at the 2-OH-derivatives is in connection

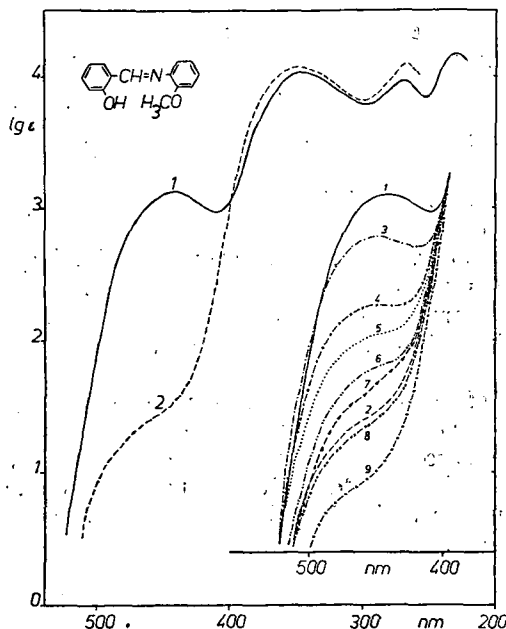


Fig. 1. Spectra of IV. 1: methanol, 2: benzene, 3: cyclohexanol, 4: chloroform, 5: dichlormethane, 6: acetone, 7: dioxane, 8: *p*-xylene, 9: cyclohexane.

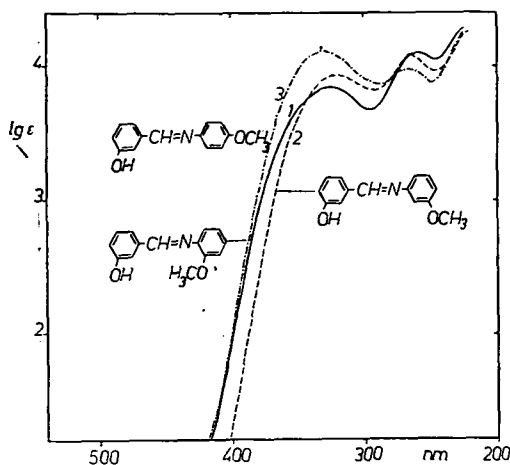


Fig. 2. Spectra of methanolic solution of XXXIV, XXXV and XXXVI.

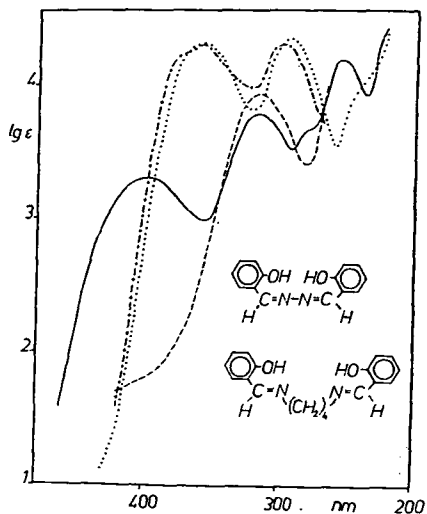


Fig. 3. Spectra of XXV (..... in ethanol, -+--+ in benzene) and XXVIII (— in ethanol, - - - in benzene)

with the benzoid/quinoid equilibrium of the intramolecular hydrogen-chelate [30—32]. This is supported by the following facts:

a) Band is appearing only at the derivatives of 2-, *or*/and 4-OH-benzaldehyde; where quinoid structure may be formed.

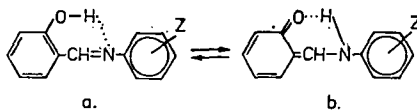
b) Since there is a band at the 4-OH-derivatives, it is evident, that the intramolecular hydrogen-bridge is not, or at least not firstly responsible for the appearance of the band.

c) The intensity of the band is increasing with the polarity of the solvent, while its position is slightly changing only.

d) NMR investigations [33] have also showed enol-imine/keto-amine tautomer equilibrium; the ORD measurements have proved the same.

e) Analogous phenomenon can be observed at the thermochromic and photochromic transformation of some Schiff bases, too, when *cis*- and *trans*-keto-amine are forming [34].

The interaction of solvent molecules, capable of strongly polar hydrogen-bridge, with the phenolic oxygen, decreases the charge-density on the oxygen atom. If there is no strong electron-withdrawing group on the *B* ring, the hydrogen atom bound covalently to the nitrogen atom of the azomethine group, which is an excellent proton-acceptor by means of its free electron-pair and the quinoid structure can be formed (Structure IV).



IV.

Table II
Ultraviolet spectral data of methanolic and benzene solutions of Schiff bases [10, 35, 36]
 (The wavelengths are in nm; lge values in parantheses)

No	In methanol				In benzene	
I	442(3.28)	347(4.08)	269(4.00)	~ 230	357(4.03)	270(3.99)
II	425(2.50)	338(3.98)	267(3.98)	~ 225	342(4.07)	268(4.05)
III	430(2.60)	348(4.20)	270(3.91)	~ 230	350(4.14)	268(3.93)
IV	440(3.12)	344(4.04)	273(3.97)	~ 229	347(4.07)	274(4.05)
V	432(2.31)	337(4.02)	268(4.04)	~ 216	343(3.97)	270(3.99)
VI	430(2.48)	347(4.21)	274(3.95)	~ 224	351(4.09)	274(3.89)
VII	434(2.50)	338(4.03)	268(4.08)	~ 220	362(4.00)	270(4.06)
VIII	430(2.45)	335(4.04)	270(4.06)	~ 225	342(4.00)	270(3.98)
IX	430(2.40)	340(4.33)	269(4.32)	~ 228	345(4.06)	269(4.00)
X	435(2.26)	340(4.00)	269(4.11)	~ 224	342(3.76)	276(3.86)
XI	440(2.02)	340(4.05)	271(4.10)	~ 228	343(3.96)	268(4.04)
XII	445(1.96)	337(4.09)	271(4.17)	~ 225	344(3.96)	~ 265
XIII	432(2.16)	337(4.05)	272(4.05)	~ 220	342(4.04)	270(4.04)
XIV	450(1.86)	340(4.00)	273(4.08)	~ 228	347(4.01)	272(4.08)
XV	450(1.85)	340(4.08)	270(4.16)	~ 230	343(4.03)	270(4.11)
XVI	436(2.04)	342(4.38)	272(4.40)	~ 230	345(4.07)	271(4.06)
XVII	402(3.89)	376(3.90)	~ 250	~ 230	390(3.87)	267(3.09)
XVIII		346(4.02)	276(4.31)	~ 220	345(3.97)	276(4.00)
XIX		358(4.30)	~ 320	~ 220	350(4.17)*	

Table II
(Continued)

No	In methanol					In benzene		
XX	450(2.10)	345(4.02)	303(4.07)	270(4.03)	~222	352(4.04)	307(4.07)	270(4.00)
XXI	445(2.47)	346(4.08)	315(4.06)	271(4.04)	~220	356(4.22)	320(4.18)	270(4.12)
XXII	440(2.20)	345(4.01)	302(4.06)	272(4.04)	~224	353(4.06)	305(4.10)	272(3.95)
XXIII	450(2.20)	347(4.06)	310(4.08)	269(4.04)	~226	355(4.13)	315(4.09)	273(4.07)
XXIV	444(2.30)	343(4.09)	310(4.10)	269(4.07)	~222	353(4.10)	312(4.06)	275(3.94)
XXV		358(4.33)	293(4.38)			360(4.30)	300(4.33)	
XXVI	408(3.22)		319(3.88)	257(4.33)			323(3.98)	259(4.37)
XXVII	404(3.35)		318(3.88)	257(4.37)			322(3.99)	259(4.41)
XXVIII	400(3.30)		317(3.80)	255(4.22)			317(3.96)	
XXIX	455(2.72)	352(3.76)	316(4.12)	276(4.06)	226(4.33)	357(3.70)	318(3.98)	282(3.94)
XXX	461(3.46)	344(4.07)		280(3.92)	230(4.22)	342(3.98)		282(3.98)
XXXI	450(2.77)	357(3.80)	316(4.07)	278(4.05)	230(4.24)	357(3.84)	323(4.08)	280(4.12)
XXXII	444(2.90)	368(3.90)	333(4.20)	276(3.98)	227(4.26)	362(3.98)	338(4.15)	279(3.98)
XXXIII			315(3.96)	287(4.08)	~220			
XXXIV			325(3.84)	261(4.10)	~220			
XXXV			321(3.93)	265(4.07)	~222			
XXXVI			331(4.11)	267(3.98)	~220			
XXXVII	414(2.16)		314(4.12)	280(4.10)	~220		320(4.00)	282(4.14)
XXXVIII	420(2.14)		324(3.97)	283(4.11)	~220		333(3.84)	279(4.16)
XXXIX	416(2.19)		314(4.13)	285(4.10)	~220		344(3.97)	278(4.15)
XL	420(2.24)		330(4.20)	286(4.13)	~224			
XLI	433(2.70)		328(4.19)	278(3.90)	~233(4.10)		322(4.10)	281(4.01)
XLII	422(2.54)		327(3.92)	282(3.86)	~232(4.01)		322(3.80)	277(3.92)
XLIII	434(2.82)		327(4.25)	284(4.04)	~230(4.19)		322(3.95)	279(3.88)
XLIV	431(2.76)		337(4.30)	282(4.06)	~234(4.18)		339(4.15)	282(4.04)

Every effect that is favourable for the formation of quinoid structure is increasing the intensity of the visible band. The most important ones are the electron-donating and -withdrawing effects of the substituents. The increase of the electron-donating properties of the substituents of *B* ring, the probability of Structure IV/b and the intensity of the long-wave band is increasing (Fig. 4). In the presence of strong electron-withdrawing group (e.g. NO_2) the band does not appear. In the case of *p*-X-aniline-derivatives, the intensity of visible band may be calculated by the

$$\lg \varepsilon = -0.98\sigma_p + 2.24$$

relation.

The appearance of long-wave band depends only on the substituents of *B* ring. It is proved by the fact, that independently of the substitution of *A* ring the visible band appears, if there is no strong electron-withdrawing group on the *B* ring (e.g. 5- NO_2 -salicylidene-4-OH-aniline, or 5-Br-salicylidene-4- CH_3 -aniline). Besides this qualitative statement it can be observed that, for instance, $-\text{OCH}_3$ group in the *A* ring causes extinction-increase and red-shift of the band (see Table II, compd. IV—VI, XXX—XXXII, XXXVIII—XL, XLII—XLIV, resp.). If there are more equal substituents on the *B* ring, the spectral data are scarcely changing (e.g. 3,4-dimethoxy- or 3,4,5-trimethoxy-derivatives).

There are three conditions of the appearance of visible band:

- strongly polar solvent, capable of hydrogen-bonding;
- the presence of OH group on the *A* ring in *o*- or/and *p*-position;
- a required charge-density on the nitrogen atom.

Some authors [13] assigned this band to the $n \rightarrow \pi^*$ transition. According to their calculations, the intensity of the visible band is so much the greater as the *s* character of *n* orbital is greater. In the case of 2-OH-derivatives, the excitation energy of the long-wave band is always higher (10—20 nm, 0.3—0.5 kcal/mole) than in that of 4-OH-compounds. This indicates that the hydrogen-chelate is stabilizing the molecule. Similar results were obtained in the case of $\pi \rightarrow \pi^*$ band, around 340 nm, too.

The intensity of visible band depends on the dielectric constant of the solvent. In alcoholic solutions the band-intensity increases by the increase in the dielectric constant of solvents. The behaviour of *i*-alcoholic solution is completely different. In the case of strongly electron-donating groups the band intensity, measured in *n*- and *i*-alcohols, considerably vary, while in the case of electron-withdrawing groups it changes only slightly (Fig. 5). The electron-withdrawing groups decrease the charge-density on the nitrogen atom to such an extent, that the IV/a form is the dominant and the solvent effect scarcely appears. Naturally, it cannot be excluded, that in the interaction of Schiff base — solvent steric factors take part, too.

In mixture of polar and apolar solvents (e.g. methanol/benzene) the IV/a \rightleftharpoons IV/b equilibrium may form; the equilibrium constant of the system can easily be cal-

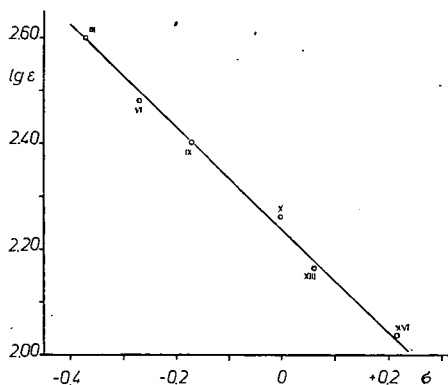


Fig. 4. Change in the intensity with the σ_p constants.

culated on the basis of the spectrum-change (e.g.[35]). It can be stated again, that every effects, which is decreasing the charge-density on the oxygen atom and increasing it on the nitrogen atom, increases the value of equilibrium constant. At the 2-OH-derivatives (IV—VI, X) the value of equilibrium constant is always higher than at the derivatives of 4-OH-benzaldehyde (XXXVII—XL).

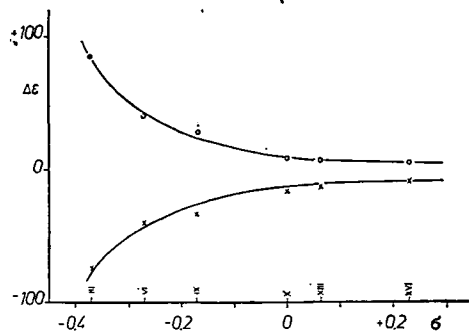


Fig. 5. Correlation between the intensity-difference of the visible band measured in normal- and *iso*-alcohols and the values of σ_p . (o) propanol, (x) butanol.

and the assignment of the bands — due to the extensive couplings — is difficult (Fig. 6. Table III).

On the basis of ^{15}N substitution, the assignment of the main bands can be carried out with great probability [37—40]. The intensive bands around 1610—1630 and 1550—1580 cm^{-1} correspond to the coupled $\nu\text{C}=\text{N}$ vibration.

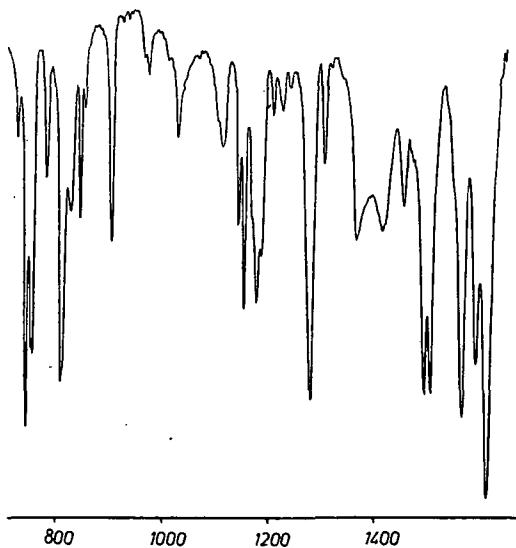


Fig. 6. Infrared spectrum of VI.

The long-wave band does not appear at the 2-OH-derivatives neither, if there is no possibility for the formation of quinoid structure. Besides the XVII—XIX compounds, as an example, compound XXV may be mentioned, where we suppose that the position of the two molecule parts are not in the same plane and so prevents the formation of a quinoid structure ranging over the whole molecule. At the 2-amino-pyridine derivative of the 2-OH-benzaldehyde the visible band appears [36], at that of the 3-amino-pyridine derivative it cannot be detected.

3.2. *Infrared spectra.* The infrared spectra of compounds are very complex,

and the assignment of the bands — due to the extensive couplings — is difficult (Fig. 6. Table III). Between the two limits, at about 1600 cm^{-1} , the band is not sensitive for ^{15}N substitution, this may be ordered to the stretching vibration of the aromatic ring. The band of the $\nu\text{C}=\text{N}$ vibration is at about 1350 cm^{-1} , and that of the $\nu\text{C}-\text{O}(\text{H})$ vibration is at about 1380 cm^{-1} . It stands by the assignment of the latter one, that its position is not changing for the effect of ^{15}N substitution, and the frequency increases at the complex-formation [41].

From the tables it can be seen that the $\nu\text{C}=\text{N}$ frequency is markedly changing depending on the substituents. We suppose, that the substituents — besides other effect — influence the vibration energy of $\nu\text{C}=\text{N}$, mainly by changing the charge-density on the nitrogen atom.

Table III
The main infrared frequencies of Schiff bases (in cm⁻¹)

No	ν C=N	ν C-O	γ (=CH)	Other bands
I	1625 s, 1586 s	1274 s, 1222 s	736 s, 758 s	1508 s, 1522 s, 1460 s, 1304 m, 1138 s
II	1612 s, 1587 s	1285 s, 1234 s	749 s, 770 m, 838 m	1454 s, 1160 v, 1142 v, 952 v, 898 v
III	1613 s	1278 s, 1258 s	747 s, 833 s	1504 s, 1455 v, 1210 v, 1184 v, 1149 v
IV	1611 s, 1566 s	1280 s, 1247 s	750 s	1581 s, 1480 s, 1453 m, 1146 m, 1113 m
V	1596 s, 1568 s	1283 s, 1257 s	746 m, 791 m, 863 m	1479 m, 1137 s, 1045 m
VI	1616 s, 1565 s	1276 s, 1245 s	733 m, 832 m	1596 m, 1506 s, 1185 m, 1146 v, 1026 m
VII	1611 s, 1564 s	1275 s	748 s	1588 m, 1480 m, 1437 m, 1147 m, 1110 m
VIII	1611 s, 1565 s	1274 s	749 s, 794 m, 831 v	1590 m, 1477 v, 1204 v, 1146 m, 904 m
IX	1612 s, 1562 s	1279 s	744 s, 809 s	1590 m, ~1500 s, 1177 m, 1153 m, 1145 m
X	1611 s, 1567 s	1275 s	750 s, 775 m	1584 m, 1480 m, 1389 m, 1181 m, 1145 m
XI	1616 s, 1570 s	1280 s	748 s, 801 m	1592 m, 1486 s, 1225 m, 1175 v, 1101 v
XII	1618 s, 1586 s	1280 s	752 s, 796 m, 867 m	1458 m, 1215 m, 1125 m, 948 v
XIII	1609 s, 1565 s	1269 s	749 s, 833 s	1587 m, 1501 s, 1454 m, 1227 m, 1179 m
XIV	1609 s, 1567 s	1275 s	750 s, 779 m	1580 m, 1471 s, 1395 s, 1183 m, 1052 m
XV	1614 s, 1566 s	1276 s	748 s, 770 s, 874 m	1583 m, 1454 m, 1182 m, 1146 v, 1074 v
XVI	1606 s, 1563 s	1269 s	753 s, 833 s	1580 m, 1482 s, 1454 s, 1398 s, 1179 m
XVII	1623 s, 1564 s	1278 s	736 s, 771 v	1588 m, 1506 s, 1427 m, 1341 m, 1240 s
XVIII	1612 s, 1566 s	1276 s	743 s, 777 m, 890 m	1591 m, 1516 s, 1488 m, 1347 s, 1184 v
XIX	1607 s, 1561 s	1267 s	760 s, 847 m	1594 m, 1504 s, 1479 m, 1337 s, 1172 m
XX	1604 s, 1551 s	1276 s	753 s, 785 s	1583 s, 1494 m, 1463 s, 1185 s, 1146 m
XXI	1605 s, 1560 s	1275 s	751 s, 785 m	1451 m, 1416 m, 1203 m, 1151 m, 1109 m
XXII	1593 s, 1541 s	1271 s	754 s, 823 m, 885 v	1562 m, 1449 m, 1405 m, 1205 m, 1141 s

Table III
(Continued)

No	ν C=N	ν C-O	ν (=CH)	Other bands
XXIII	1604 s, 1558 s	1275 s	761 s, 833 s, 910 m	1583 s, 1489 m, 1460 s, 1406 m, 1181 s
XXIV	1608 s, 1549 s	1278 s	753 s, 791 s	1518 m, 1494 m, 1452 s, 1184 s, 1138 m
XXV	1618 s, 1566 m	1274 s	744 s	1482 m, 1203 m, 1152 v, 887 m, 778 m
XXVI	1631 s, 1573 m	1280 s	744 s	1602 m, 1493 m, 1018 m, 853 m, 849 m
XXVII	1630 s, 1577 m	1279 m	749 s	1606 m, 1495 m, 1208 m, 878 m, 851 m
XXVIII	1626 s, 1573 m	1281 m	746 s	1605 m, 1492 m, 1041 v, 1007 v, 851 m
XXIX	1617 m, 1590 s	1274 s	688 s, 781 s, 859 m	1452 m, 1207 s, 1154 v, 1079 v, 990 v
XXX	1620 m, 1587 s	1293 s	760 s, 786 m, 870 m	1488 m, 1455 m, 1245 s, 1211 s, 970 v
XXXI	1586 s	1285 m	774 m, 850 m	1486 m, 1440 m, 1257 m, 1220 m, 1139 s
XXXII	1622 m, 1586 m	1277 s	778 m, 830 m, 864 v	1505 m, 1455 m, 1245 s, 1167 m, 1110 v
XXXIII	1596 m, 1576 s	1284 s	686 m, 755 s	1515 m, 1450 m, 1240 m, 1164 s, 837 s
XXXIV	1600 s, 1580 s	1282 s	744 s, 835 m	1494 m, 1463 m, 1250 s, 1163 s, 1113 m
XXXV	1589 s	1281 s	776 m, 824 m, 846 v	1478 m, 1180 m, 1146 s, 938 m, 871 vw
XXXVI	1603 s, 1574 s	1283 s	840 s	1510 m, 1249 s, 1189 m, 1161 s, 1032 m
XXXVII	1610 s, 1584 s	1254 s	687 s, 780 s	1467 s, 1195 s, 1075 m, 965 s, 734 m
XXXVIII	1610 s, 1584 s	1257 s	728 m, 776 m	1569 v, 1464 s, 1176 m, 1116 m, 967 m
XXXIX	1590 s, 1570 m	1244 s	728 m, 774 m, 862 m	1460 s, 1138 s, 1039 m, 965 m, 675 m
XL	1610 s, 1572 m	1248 s	822 m	1504 m, 1467 s, 1193 m, 961 m, 725 m
XLI	1612 v, 1580 s	1284 s	689 m, 763 m, 869 m	1518 s, 1456 v, 1158 s, 1027 v, 734 v
XLII	1616 m, 1578 s	1293 s	746 m, 821 v, 864 v	1516 s, 1460 v, 1293 s, 1154 m, 1029 m
XLIII	1576 s	1278 s	677 m, 720 v, 836 v	1511 s, 1163 m, 1147 m, 1035 m, 940 m
XLIV	1617 m, 1587 m	1290 s	829 m, 858 v	1513 s, 1450 m, 1246 s, 1210 m, 1147 m

We have not found correlation between the main frequencies and the σ -values. We have not succeeded in detecting $\nu\text{C}=\text{O}$ band characteristic of the quinoid form.

3.3. *NMR spectra.* Table IV. contains the NMR data (δ , ppm) of the compounds; the spectrum of XXVII can be seen in Fig. 7. For compounds I—III, due to the rapid exchange, the signals of OH-proton disappear; probably similar reasons influence compounds XXXVII—XL, too. The concentration dependence of chemical shifts can be neglected. We are not discussing the 6.5—7.5 ppm region of the spectra.

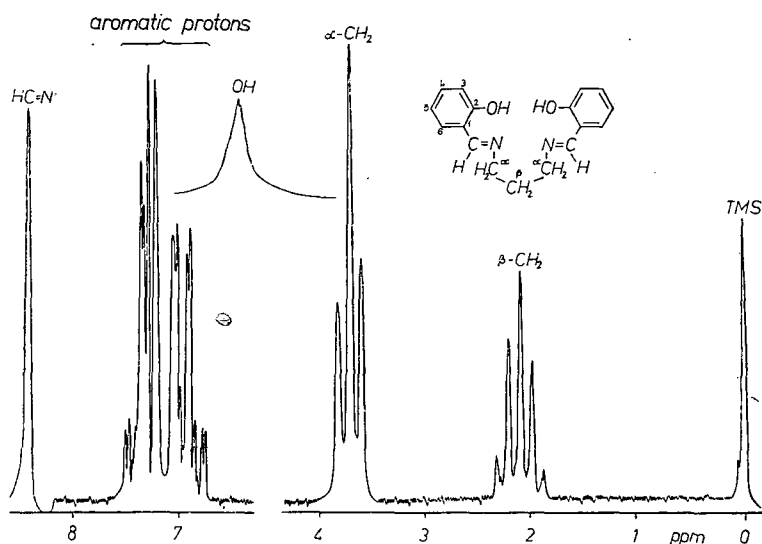


Fig. 7. NMR spectrum of XXVIII measured in CDCl_3 .

NMR investigations [32, 42—44] have shown, that at room temperature, in non-hydroxylic solvent, compound X is mostly present in phenol-imine form. In the presence of keto-amine form the splitting of $\delta\text{CH}=\text{N}$ proton signal may be expected; in CDCl_3 solution the shift of neither that, nor the shift of aromatic proton signal cannot be observed (Table IV, Fig. 7).

It can be stated — in contradiction to other authors [37] — that the $\delta\text{CH}=\text{N}$ — σ_p relation is linear at the *p*-X-aniline derivatives (Fig. 8); the chemical shift of methine-proton can be calculated by the

$$\delta(\text{CH}=\text{N}) = -0.154\sigma_p + 8.55$$

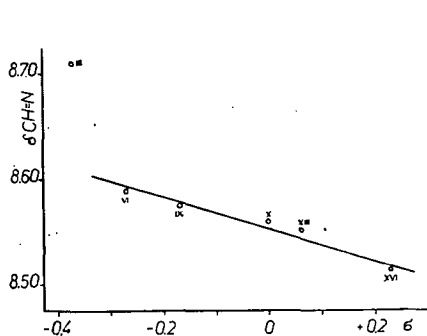
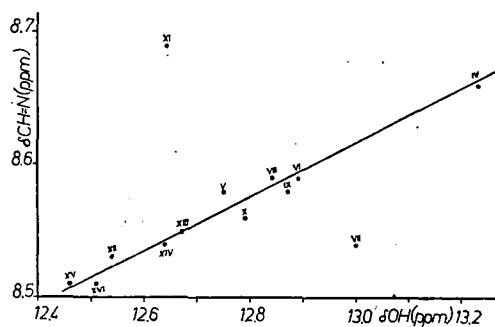
relation.

The ppm values of $\delta\text{CH}=\text{N}$ and of the δOH signals are changing parallel (Fig. 9). It is clear from the tables, that with increasing $\nu\text{C}=\text{N}$ values the $\delta\text{CH}=\text{N}$ values are decreasing (see [37], too). Since the chemical shift of ^1H signal is proportional to the density of p-electron of the supporting atom, it can be expected, that the increasing shielding of the methine-proton accompanies the increase in the $\nu\text{C}=\text{N}$ frequency, caused by the substituent. This tendency is well recognizable

Table IV
NMR data (δ , ppm) of Schiff bases (see [10,35])

No	OH	CH=N	OCH ₃	CH ₂	CH ₃
I ^c		8.89			
II ^c		8.68			
III ^c	13.23	8.71			
IV ^a	13.23	8.66	3.83		
V ^a	12.76	8.58	3.79		
VI ^a	12.89	8.59	3.81		
VII ^a	13.00	8.54			2.40
VIII ^a	12.84	8.59			2.38
IX ^a	12.87	8.58			2.35
X ^a	12.79	8.56			
XI ^a	12.64	8.69			
XII ^a	12.54	8.59			
XIII	12.67	8.55			
XIV ^a	12.64	8.54			
XV ^a	12.46	8.51			
XVI ^a	12.51	8.51			
XVII ^a	12.17	8.63			
XVIII ^a	12.23	8.68			
XIX ^b	12.58	8.68			
XX ^a	13.11	9.47			
XXI ^a	13.69	9.46			2.49
XXII ^a	13.23	9.50			2.38
XXIII ^a	13.19	9.43			2.33
XXIV ^a	13.26	9.47			2.55
XXV ^b	11.58	8.94			
XXVI ^b	13.23	8.45		3.97	
XXVII ^b	13.45	8.48		1.91—2.36	
XXVIII ^b	13.58	8.43		3.64—3.87	
XXIX ^a	12.98	8.63	3.89	1.71—1.97	
XXX ^a	13.46	8.66	3.87	3.58—3.77	
XXXI ^b	13.61	8.66	3.85+3.93		
XXXII ^a	13.10	8.59	3.81+3.89		
XXXIII ^a	13.08	8.21			
XXXIV ^a	13.17	8.23	3.76		
XXXV ^a	13.31	8.21	3.71		
XXXVI ^a	13.12	8.35	3.81		
XXXVII ^c		8.43			
XXXVIII ^c		8.41	3.83		
XXXIX ^c		8.41	3.81		
XL ^c		8.50	3.84		
XLI ^b	13.21	8.36	3.91		
XLII ^b	13.30	8.36	3.84		
XLIII ^b	13.42	8.36	3.81+3.84		
XLIV ^b	13.38	8.40	3.81+3.87		

a: in CCl₄, b: in CDCl₃, c: in CD₃OD.


 Fig. 8. $\delta\text{CH}=\text{N}$ as a function of σ_p values.

 Fig. 9. $\delta\text{CH}=\text{N}$ as a function of δOH at the 2-oxy-derivatives.

for the $\nu\text{C}=\text{N}$ frequencies around 1580 cm^{-1} . The chemical shift of methine and OH-proton signals, *resp.*, can be calculated by the

$$\delta(\text{CH}=\text{N}) = 0.188\delta(\text{OH}) + 6.16$$

relation.

There is a relation between the intensity of absorption band measured for instance in alcohol and that of the δOH values (Fig. 10). By the decrease in the shielding of OH-proton, the degree of chemical shift increases. If the shielding decreases, there is a greater possibility of the formation of IV/b quinoid structure, and the intensity of the long-wave band increases. We have found relation between the $\lg \epsilon$ and $\delta(\text{OH})$ values: at the aniline derivatives

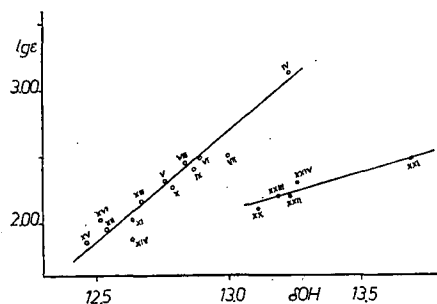
$$\lg \epsilon = 1.66\delta(\text{OH}) - 18.88$$

in the case of pyridine derivatives:

$$\lg \epsilon = 0.56\delta(\text{OH}) - 5.18.$$

The fact that by infrared and NMR techniques the quinoid structure cannot be proved, does not exclude its possibility; however, the solvents applicable for this two methods are not favourable to the formation of this structure.

The establishments discussed in this paper are valid only for a certain group of compounds, having analogous structure (see *e.g.* Fig. 10); but they cannot be generalized for every Schiff base.


 Fig. 10. Correlation between $\lg \epsilon$ and δOH values.

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**УЛЬТРАФИОЛЕТОВОЕ, ИНФРАКРАСНОЕ И ЯМР. СПЕКТРОСКОПИЧЕСКОЕ
ИЗУЧЕНИЕ АРОМАТИЧЕСКИХ ШИФОВЫХ ОСНОВАНИЙ**

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Изучены Шифовые основания полученные из 2-, 3-, и 4-ОН-бензальдегидов и алифатических и ароматических аминов, а также производных пиридина, соответственно. На основании ультрафиолетовых, инфракрасных и ЯМР спектров сделаны заключения относительно свойств хелатообразующих лигандов в растворах.