SPECTROSCOPIC STUDY OF MOLECULAR COMPLEXES OF AROMATIC SCHIFF BASES WITH POLYNITRO COMPOUNDS

By

J. CSÁSZÁR and N. M. BIZONY

Institute of General and Physical Chemistry, József Attila University, P.O.B. 105, H-6701, Szeged, Hungary

(Received 1 October 1987.)

Schiff bases were formed from salicylaldehyde an aminopyridines and their methyl derivatives and molecular complexes of these Schiff bases with 2,4-dinitroaniline,. picric acid and dipicrylamine were prepared. The spectral behaviour of the parent Schiff bases and their molecular complexes was studied and discussed.

Introduction

Molecular complexes of polynitro compounds with Schiff bases as π-donor systems are an interesting group of compounds, which have recently been widely studied [1-5]. Issa and El-Essawey [6] found that the type and structure of these complexes may be studied well via UV, IR and ^{1}H NMR-spectroscopy.

As a continuation of our earlier work, we have prepared molecular complexes of Schiff bases as donors (formed from salicylaldehyde and 2-aminopyridine, its methyl derivatives

and 3-aminopyridine) with aromatic polynitro compounds as acceptors. The present paper reports a spectral study of the parent Schiff bases and their molecular complexes.

Experimental

The donors were Schiff bases having the general structures I and II.
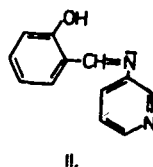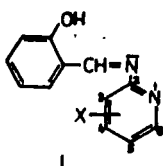
1 X = H   5 X = 5-CH$_3$
3 X = 3-CH$_3$ 6 X = 6-CH$_3$ 2
4 X = 4-CH$_3$

The acceptors used were 2,4-dinitroaniline (DNA), picric acid (PA) and dipicrylamine (DPA).

All chemicals were pure lab. grade BDH products. The preparation of the molecular complexes was described previously [4, 5]. The analytical data are listed in Table I; these data are in good agreement with the expected compositions for a donor:acceptor stoichiometric ratio of 1:1 (DNA and PA) or 1:2 (DPA).

The UV and visible spectra were recorded on a SPECORD UV-VIS spectrophotometer, using spectroscopically pure solvents. The IR spectra were measured on a ZEISS UR-20 spectrophotometer, in KBr discs; the ^{1}H NMR spectra were observed on

Table I

Analytical data on the molecular complexes studied

Acceptor	Donor	M.p.*		Colour**	C%		C%	
					Calcd.	Found	Calcd.	Found
DNA	1	178.5	(64.1)	LY	56.69	56.48	3.96	3.96
	2	120.5	(57.0)	LY		56.50		3.91
	3	113.5	(80.3)	O	57.72	57.66	4.33	4.30
	4	93.5	(99.4)	LY		57.69		4.28
	5	96.0	(100.5)	BY		57.71		4.30
	6	178.5	(65.8)	LY		57.66		4.26
PA	1	218.5		LY	50.59	50.50	3.07	3.01
	2	165.0		LY		50.52		3.05
	3	218.5		LY	51.71	51.66	3.43	3.40
	4	218.0		LY		51.61		3.38
	5	228.5		LY		51.65		3.41
	6	202.5		LY		51.60		3.37
DPA	1	177.5		R	40.16	40.01	1.87	1.77
	2	136.5		R		39.96		1.80
	3	197.5		BB	40.75	40.15	2.03	1.98
	4	196.5		O		40.33		2.00
	5	175.5		SC		40.51		1.88
	6	186.5		SC		40.55		1.78

* the data in parentheses are the m.p.s. of the Schiff bases

** LY: lemon-yellow; O: orange; BY: brownish-yellow; R: red; BB: bluish-brown; SC: scarlet

a JEOL 60 MHz instrument in CCl_4, with TMS as internal
standard.

Discussion

Spectra of Schiff bases. The absorption spectra were
similar to those of other Schiff bases of salicylaldehyde and
aromatic amines [7-10]. Three main bands appear, at 270-280,
300-320 and 320-360 nm (Fig. 1, curves a,c), which may be as-
signed to $\pi^* \leftarrow \pi$ transitions of the aromatic systems. The
positions and intensities of the bands measured in chloroform,
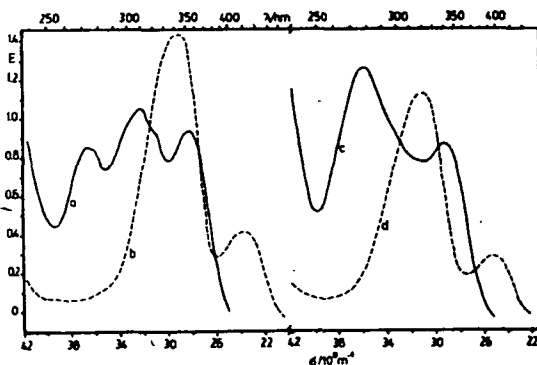benzene, hexane, etc. did not vary considerably (Table II).

Figure 1: UV spectra. a: 1 in $CHCl_3$, $c=8.07.10^{-4}$, b: 1 in
conc. H_2SO_4, $c=7.57.10^{-4}$; c: 2 in $CHCl_3$,
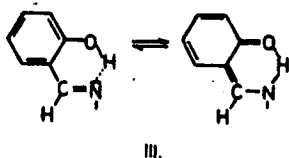$c=8.58.10^{-4}$; d: 2 in conc. H_2SO_4, $c=8.07.10^{-4}$
mol/dm^3. d=0.1 cm.

Table II
UV and visible spectral data on the Schiff bases, measured in different solvents

No.	Solvent*	λ/nm (log ε)			
1	M	270(4.03)	303(4.07)	345(4.02)	450(2.10)
	Chl	270(4.03)	310(4.12)**	353(4.06)	~460
	B	270(4.00)	307(4.07)	352(4.04)	---
	S	---	---	341(4.26)	419(3.74)
2	M	276(4.06)	---	340(3.88)	---
	Chl	279(4.17)	---	344(4.01)	---
	B	281(4.04)	---	343(3.92)	---
	S	---	---	322(4.14)	398(3.56)
3	M	271(4.04)	315(4.06)	346(4.08)	445(2.47)
	Chl	274(4.01)	313(4.05)**	355(4.08)	~460
	B	270(4.12)	320(4.18)	356(4.22)	---
	S	---	---	329(4.07)	412(3.60)
4	M	272(4.04)	302(4.06)	345(4.01)	440(2.20)
	Chl	274(4.06)	309(4.16)**	352(4.13)	~460
	B	272(3.95)	305(4.10)	353(4.06)	---
	S	---	---	331(4.18)	414(3.72)
5	M	269(4.04)	310(4.08)	347(4.06)	450(2.20)
	Chl	272(4.09)	320(4.15)**	351(4.17)	~460
	B	275(3.94)	312(4.06)	353(4.10)	---
	S	---	---	342(4.26)	414(3.74)
6	M	269(4.07)	310(4.10)	343(4.09)	444(2.30)
	Chl	273(4.11)	319(4.14)**	354(4.16)	~460
	B	275(3.94)	312(4.06)	353(4.10)	---
	S	---	---	341(4.29)	415(3.76)

* M: methanol; Chl: chloroform; B: benzene; S: concentrated sulphuric acid

** double band

We presume that the same transitions are involved in the
spectra of all the Schiff bases studied; the wavelength ra-
tios ν_3/ν_2 are between 1.10 and 1.16, and the solvent effect
does not appreciably influence the relative energies of the
ground and excited states of the chromophores. However, in
methanol, or in other hydrogen-bond forming solvents, a band
can be detected between 400 and 450 nm, which is absent from
the spectra of the benzene or hexane solutions. These medium-
-intensity bands can be interpreted in terms of a ben-
zoid/quinoid tautomeric
equilibrium (Structure III)
[10]. Similar phenomena can be
observed in the photochromic
[11, 12] and thermochromic
[e.g. 13-15] transformations
of the Schiff bases in the
solid state.

III.

Totally different spectral behaviour can be observed for
2; the visible band disappears almost completely. The nitro-
gen atom in the "meta" position decreases the charge density
on the azomethine nitrogen to nearly the same extent as a
nitro group; the probability of the above equilibrium is very
small. The K values calculated for the methyl derivatives 3-6
vary in the sequence 3 < 6 < 4 < 5; owing to its steric ef-
fect, the methyl group in position 3 twists the pyridine ring
out of the plane and thereby hinders extension of the quino-
idal structure over the entire molecule; the value of K is
the lowest. The different behaviour of 2 is also well seen
from the low δCHN and high νCHN frequencies (Table III).

In concentrated sulphuric acid solution, the $>$C=$\overset{\oplus}{N}$H-
protonated forms of the Schiff bases are present, and the
molecules have a planar or nearly planar conformation [16,
17]. Table II shows that the intensity of the third band is

)

increased considerably compared, for example, to the spectra
of the methanolic solutions (Fig. 1, curves b, d). Ont the
basis of the intensity differences, the twist angle θ_N of
the aniline ring can be calculated [18-20] (Table III); the
values differ only slightly, and the different positions of
the methyl group scarcely influence the conformation.

The OH proton signals are in the interval 12.4-13.7 ppm;
the lowest value is observed for 2. We found that the ppm
values and the intensities of the advanced visible bands
change in parallel. The 6.5-9.5 ppm region is extremely com-
plicated, the signals of the aldehyde and pyridine ring
protons appear with significant couplings in this range.

Spectra of the molecular complexes. DNA, PA and DPA dif-
fer considerably in their acidic character (pK_a = 15.0, 2.68
and 1.0, respectively). The donors have a basic character,
and thus their behaviour towards the acceptors used differs.
In the case of DNA and DPA, only a charge-transfer (CT) in-
teraction is expected, but in the case of PA proton-transfer
is also possible theoretically.

The three groups of molecular complexes studied show
different spectral behaviour; characteristic data on the com-
plexes DNA/1-6 and PA/1-6 are presented in Table IV.

The absorption spectra of DNA/1-6 display two high-in-
tensity bands, at around 260-265 and 330-335 nm; in the
longer-wavelength region, an inflection is also found. On the
basis of the positions and intensities of the main bands, we
assigned these to $\pi^* \leftarrow \pi$ transitions in the aromatic systems,
while the inflection is due to CT° processes between the
aromatic rings of the donor and acceptor. Table IV shows that
the solvent effect is not so important.

It is remarkable that the spectra of DNA and its com-
plexes are practically the same. However, the formation of
molecular complexes is supported by the facts that the inten-

Table III

Characteristics of the Schiff bases

No.	δOH^a	δCHN^a	δCH_3^a	νCHN^b	K^c	θ_N^d
1	13.11	9.47		1618s	4.0	81
2	12.46	8.60		1629s	-	-
3	13.69	9.40	2.49	1620s	2.0	74
4	13.23	9.50	2.38	1603s	5.7	80
5	13.19	9.43	2.33	1619s	8.6	80
6	13.26	9.47	2.55	1619s	4.6	79

a: measured in CCl$_4$; b: in KBr discs; c: in methanol/benzene mixtures see e.g.[8,9]; d: calculated via the intensity of the protonated form.

sities are higher than that of DNA and the predicted one, and the analytical data also correspond to the formation of 1:1 complexes.

Ross and Labes [21] suggested that in the molecular complexes of aniline with 1,3,5-trinitrobenzene the two aromatic rings are parallel to each other. We propose an analogous structure (Structure IV), in which the DNA mole-cule and the pyridine ring of the Schiff base lie parallel, and only a $\pi - \pi^*$ interaction need be taken into account.

IV
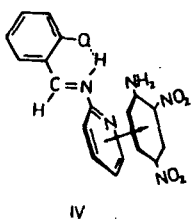
The high similarity of the meas-ured spectra to the one calcu-lated on the basis of the ad-ditivity suggests that in solu-tions corresponding to the equilibrium D.A $\rightleftharpoons$ D$^+$ + A$^-$ the sum of the spectra of the donor and acceptor is measurable (Fig.2).

Table IV

UV and visible spectral data on the molecular complexes

of DNA *and* PA

Acceptor	Donor	Solvent*	λ/nm (log ε)		
DNA	1	Chl	262(4.34)	331(4.47)	~380
		AcCN	261(4.30)	333(4.49)	~380
	2	Chl	263(4.47)	334(4.48)	~380
		AcCN	263(4.42)	335(4.43)	~370
	3	Chl	262(4.43)	333(4.53)	~380
		AcCN	264(4.44)	331(4.50)	~380
	4	Chl	263(4.42)	334(4.52)	~370
		AcCN	263(4.43)	333(4.53)	~380
	5	Chl	263(4.42)	333(4.54)	~380
		AcCN	261(4.42)	335(4.50)	~380
	6	Chl	262(4.42)	331(4.53)	~380
		AcCN	261(4.45)	330(4.51)	~380
PA	1	MeOH	~315	354(4.41)	~390
		Chl	~318	344(4.28)	411(4.01)
		AcCN	310(4.06)	369(4.29)	~410
	2	MeOH	252(4.47)	349(4.44)	~400
		Chl	252(4.08)	341(3.94)	~410
		AcCN	243(4.49)	374(4.45)	~420
	3	MeOH	314(4.28)	357(4.40)	~410
		Chl	323(4.30)	346(4.32)	412(4.02)
		AcCN	307(4.11)	367(4.34)	~420
	4	MeOH	311(4.11)	358(4.32)	~420
		Chl	~315	350(4.28)	414(4.01)
		AcCN	303(4.01)	369(4.34)	~410
	5	MeOH	~325	357(4.33)	~400
		Chl	338(4.25)	~350	414(3.93)
		AcCN	~318	369(4.33)	~415
	6	MeOH	320(4.24)	358(4.30)	~400
		Chl	326(4.29)	~340	406(4.06)
		AcCN	313(4.12)	372(4.35)	~420

*MeOH: methanol; Chl: chloroform; AcCN: acetonitrile.

It must be mentioned that the possibility for intermolecular n - π* bonding between the amino and nitro groups should not be excluded [22], but our results do not support this possibility.
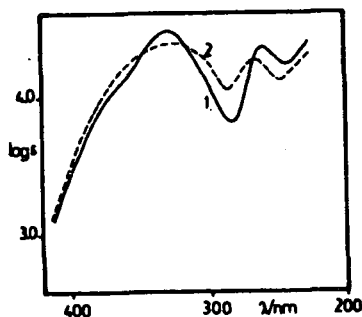

Figure 2: UV spectra of DNA/1 in CHCl₃. 1: measured, 2: calculated spectrum.

The chloroform solutions of complexes PA/1-6 also show two intense bands; a well-defined band appears at around 400 nm (Fig. 3). This band corresponds unambigously to the molecular complex, and is also due with high probability to π - π* processes. In methanol or in acetonitrile, the long-wavelength band disappears and an inflection is observed in the same region. If the spectral data and the changes are taken into account, it may be presumed that the structures of the molecular complexes are similar to those discussed above; only the π - π* CT process is possible; the intramolecular hydrogen-bond in the Schiff bases prevents intermolecular proton-transfer [e.g. 1-3]; the characteristic frequencies of the ⟩C=NH- group are absent from the solid-state IR spectra.

It has long been known that DPA yields slightly-soluble compounds with, for example, quaternary ammonium compounds [23] and different organic bases [24, 25]. While the complexes discussed above are yellow or orange, the molecular complexes of DPA are brick-red, scarlet or violet. Since it is obvious from the structure of DPA that donor ← acceptor proton trans-
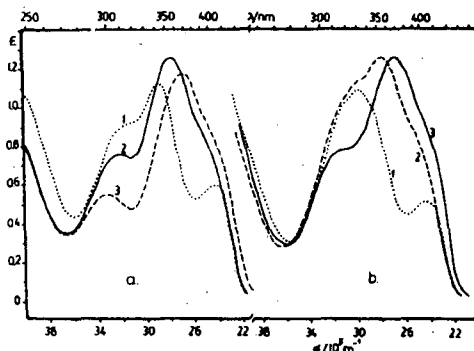
Figure 3: UV and visible spectra. a) PA/4 in 1: CHCl$_3$, c=5.89.10^{-4}; 2: CH$_3$OH, c=5.89.10^{-4}; 3: AcCN, c=5.44.10^{-4}. b) PA/5 in 1: CHCl$_3$, c=6.12.10^{-4}; 2: CH$_3$OH, c=5.89.10^{-4}; 3: AcCN, c=5.89.10^{-4} mol/dm^3. d=0.1 cm.

fer is impossible, in this case only CT processes need be taken into account; typical spectra are shown in Fig. 4.

In methanol or acetonitrile the molecular complexes DPA/1-6 show a broad high-intensity band between 420 and 430 nm; this band corresponds to the characteristic 383 nm band of DPA (Table V) [26]. The longer-wavelength side of this band is asymmetric, which indicates the presence of a covered band. In chloroform or dioxane solutions, the maximum is situated at around 380 nm, with an inflection in the interval 440-460 nm. The higher-energy band appears at 290-320 nm.
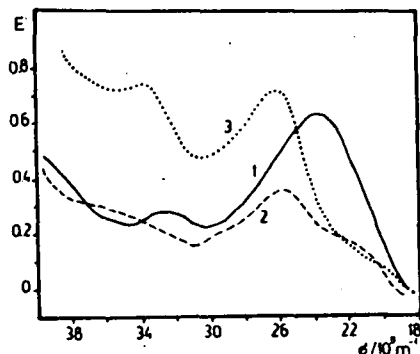
Figure 4: UV spectra of DPA/2 in 1: CH$_3$OH, c=1.02.10^{-4};
2: CHCl$_3$, c=8.82.10^{-5}; 3: 1,4-dioxane,
c=1.10.10^{-4} mol/dm^3, d=0.1 cm.

We presume that the inflection appearing next to the
383 nm band (logε ≈ 3.5-4.0) corresponds to π - π* proces-
ses; the CT bands occur in a similar range in the spectra of
molecular complexes of other Schiff bases [1, 2].

According to Issa [27], the aniline ring is primarily
the centre contributing to the intermolecular CT interaction,
but in the case of 1:2 donor:acceptor complexes the aldehyde
ring, takes also part in the formation of complexes. On the
basis of these findings, the analytical data, the intensity
relations and the intense colours, we assume that 1:2
donor:acceptor complexes are formed, i.e. the aniline and
aldehyde rings of the Schiff bases bind two acceptor molecules
via π - π* CT (Structure V). The formation of a 2:1 donor:ac-
ceptor complex is improbable, because of the steric inhibition.
The structural considerations are very problematic, because

Table .V

*Spectral data on the molecular complexes of* DPA

Donor	Solvent*	λ/nm	(log ε)	
1	MeOH	310(4.62)	---	421(4.92)
	Chl	~280	384(a)	~460
	Diox	295(4.58)	380(4.51)	~460
	AcCN	298(4.43)	---	423(4.84)
2	MeOH	305(4.45)	---	419(4.79)
	Chl	~280	386(4.60)	~460
	Diox	294(4.82)	383(4.81)	~460
	AcCN	300(4.26)	---	423(4.70)
3	MeOH	315(4.46)	---	422(4.74)
	Chl	~280	389(4.42)	~440
	Diox	297(4.64)	380(4.58)	~460
	AcCN	304(4.32)	---	426(4.72)
4	MeOH	318(4.41)	---	420(4.73)
	Chl	~280	385(4.33)	~460
	Diox	300(4.52)	381(4.49)	~480
	AcCN	313(4.34)	---	425(4.79)
5	MeOH	311(4.68)	---	420(5.02)
	Chl	~280	384(a)	~470
	Diox	296(4.62)	382(4.57)	~460
	AcCN	302(4.26)	---	425(4.72)
6	MeOH	261(4.72)	350(4.59)	420(4.58)
	Chl	278(4.78)	350(4.66)	~390
	Diox	278(4.80)	346(4.69)	~390
	AcCN	273(4.69)	347(4.63)	423(4.60)

*
*
MeOH: methanol; Chl: chloroform; Diox: 1,4-dioxane; AcCN:
Acetonitrile; a) very low solubility

the DPA acceptor molecule, as discussed previously [22], is
a twisted one due to the high steric interference of the
nitro groups in the 2,2', 6,6' positions.

    Detailed investigations of DPA complexes by means of
different physico-chemical methods are in progress.

V.
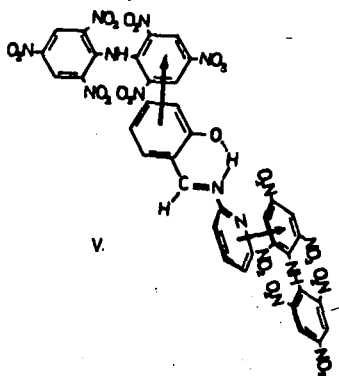
References

[1] *Issa, R.M., M. Gaber, A.I. El-Ansary, H.F. Rizk*: Bull. Soc. Chim. France, No.2., 173 (1985).

[2] *Hindawey, A.M., Y.M. Issa, R.M. Issa, H.F. Rizk*: Acta Acad. Sci. Hung., *112*, 415 (1983).

[3] *Issa, Y.M., A.E. El-Viholy, A.L. El-Ansary*: Acta Acad. Sci. Hung., *118*, 43 (1985).

[4] *Csáezár, J.*: Acta Phys. Chem. Szeged, in press.

[5] *Dale, B., R. Foster, D. LL. Hammick*: J. Chem. Soc., 3986 (1954); *R. Foster, D. LL. Hammick, P.J. Placito*: J. Chem. Soc., 3881 (1956).

[6] *Issa, R.M., M.M. El-Essawey*: Z. physik. Chem., *253*, 96 (1973).

[7] *Csáezár, J.*: Acta Phys. Chem., Szeged, *28*, 135 (1982).

[8] *Csáezár, J.*: Acta Phys. Chem., Szeged, *27*, 47 (1981).

[9] *Csáezár, J.*: Acta Phys. Chem., Szeged, *25*, 137 (1979).

[10] *Csáezár, J., J. Balog, A. Makáry*: Acta Phys. Chem., Szeged, *24*, 473 (1978).

[11] *Lewis, J.W., C. Sándorfy*: Canad. J. Chem., *60*, 1738 (1982).

[12] *Yoshida, M., M. Kobayashi*: Bull. Chem. Soc. Japan, *54*, 2395 (1981).
[13] *Cohen, M.D., G.M.T. Schmidt*: J. Phys. Chem., *66*, 2442 (1962).
[14] *Cohen, M.D., G.M.T. Schmidt, S. Flavian*: J. Chem. Soc., 2041 (1964).
[15] *Cohen, M.D., G.M.T. Schmidt*: In Reactivity of Solids., Ed. J.H. de Boer, Elsevier, Amsterdam, 1961. p. 556.
[16] *Brocklehurst, P.*: Tetrahedron, *18*, 299 (1961).
[17] *Minkin, V.I., Yu. A. Zhdanov, E.A. Megyantzeva, Yu. A. Ostroumov*: Tetrahedron, *23*, 3651 (1967).
[18] *Braude, E.A., F. Sondheimer*: J. Chem. Soc., 3754 (1955).
[19] *Kraszovickij, B.M., B.M. Bolomin, R.N. Nurmahatmetev*: Zh. Obsch. Khim., *34*, 3786 (1964).
[20] *Császár, J.*: Acta Phys. Chem. Szeged, *29*, 133 (1983); *32*, 17 (1986).
[21] *Ross, S., M. Labes*: J. Amer. Chem. Soc., *77*, 4916 (1955).
[22] *Hindawey, A.M., A.M.G. Nassar, R.M. Issa*: Acta Acad. Sci., Hung., *88*, 341 (1976).
[23] *Ackerman, D., H. Maner*: Z. physik. Chem., *279*, 114 (1943).
[24] *Kertes, S.*: Anal. Chim. Acta, *15*, 73 (1956).
[25] *Kertes, S., V. Kertes*: Anal. Chim. Acta, *15*, 154 (1956)
[26] *Császár, J.*: Acta Phys. Chem., Szeged, *33*, 11 (1987).
[27] *Issa, Y.M.*: Spectrochim. Acta, *40A*, 137 (1984).

СПЕКТРОСКОПИЧЕСКОЕ ИЗУЧЕНИЕ МОЛЕКУЛЯРНЫХ КОМПЛЕКСОВ АРОМАТИЧЕСКИХ ШИФФОВЫХ ОСНОВАНИЙ С ПОЛИНИТРОСОЕДИНЕНИЯМИ

Й. Часар и Н.М. Бизонь

Синтезированы молекулярные комплексы Шиффовых оснований образованные из салицилальдегида, амино пиридонов, а также их метиловых производных с 2,4-динитроанилином, пикриновой кислотой и дипикриламином. Изучены и обсуждены спектральные свойства исходных оснований и их молекулярных комплексов.