

SPECTRAL STUDIES OF MOLECULAR COMPLEXES OF AROMATIC
SCHIFF BASES WITH PICRIC ACID

By

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(Received 1 October 1987)

Twenty-six 1:1 molecular complexes of Schiff bases (formed from salicylaldehyde, ortho-vanillin, iso-vanillin and aniline derivatives) with picric acid were prepared and their UV, visible and IR spectral behaviour was investigated. The results suggested that the molecular complexes are formed via $\pi-\pi^*$ charge-transfer interactions.

Introduction

The formation of molecular complexes of aromatic hydrocarbons as donors with polynitrobenzenes as acceptors has been the subject of several studies [1-7]. It has been pointed out on the basis of visible, IR and ^1H NMR data that the following differentiation can be made: (a) charge-transfer ($\pi-\pi^*$) complexes, (b) proton-transfer interaction, and (c) molecular complexes involving $n-\pi^*$ or hydrogen-bonds besides a $\pi-\pi^*$ interaction [e.g. 6]. Similar derivatives of aromatic Schiff bases have received relatively little attention from this point of view [8, 9]. According to Issa [10], the aniline

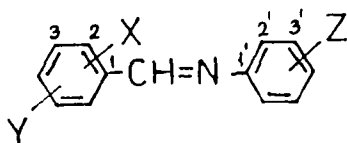
moiety of the Schiff bases is the donor centre, because the anilines have lower ionization potentials than the benzaldehyde derivatives.

In the present paper we discuss the preparation and the UV, visible and IR spectra of 1:1 molecular complexes of Schiff bases of salicylaldehyde, ortho-vanillin, iso-vanillin and aniline derivatives as donors (I) with picric acid as acceptor (Table I).

Experimental

The studied complexes were prepared by mixing hot methanolic solutions of the donor and the acceptor in a 1:1 mole ratio. On cooling, the complexes separated out as fine crystals having different colours. The products were recrystallized from a 1:1 acetone-methanol mixture. The m.p. and analytical data are listed in Table II. It is also possible to prepare 1:2 complexes, but the present paper discusses only the 1:1 complexes.

The visible and UV spectra were recorded on a SPECORD UV-VIS spectrophotometer; the solvents were spectroscopically pure. The reflection spectra were measured on a BECKMAN DU spectrophotometer against MgO standard. The IR spectra were measured on a ZEISS UR-10 instrument, in KBr discs.



I.

Table I.

Positions of the substituents in the donor molecules and the numbering of their molecular complexes in the text

No.	X	Y	Z	No.	X	Y	Z
<u>I</u>	2-OH	H	4'-N(CH ₃) ₂	<u>XIV</u>	2-OH	H	3'-OCH ₃
<u>II</u>	2-OH	H	4'-OH	<u>XV</u>	2-OH	H	4'-OCH ₃
<u>III</u>	2-OH	H	4'-OC ₄ H ₉	<u>XVI</u>	2-OH	H	3',4'-(OCH ₃) ₂
<u>IV</u>	2-OH	H	4'-CH ₃	<u>XVII</u>	2-OH	3-OCH ₃	H
<u>V</u>	2-OH	H	H	<u>XVIII</u>	2-OH	3-OCH ₃	2'-OCH ₃
<u>VI</u>	2-OH	H	4'-NHCOCH ₃	<u>XIX</u>	2-OH	3-OCH ₃	3'-OCH ₃
<u>VII</u>	2-OH	H	4'-Cl	<u>XX</u>	2-OH	3-OCH ₃	4'-OCH ₃
<u>VIII</u>	2-OH	H	4'-Br	<u>XXI</u>	2-OH	3-OCH ₃	3',4'-(OCH ₃) ₂
<u>IX</u>	2-OH	H	4'-I	<u>XXII</u>	4-OH	3-OCH ₃	H
<u>X</u>	2-OH	H	4'-COCH ₃	<u>XXIII</u>	4-OH	3-OCH ₃	2'-OCH ₃
<u>XI</u>	2-OH	H	4'-CN	<u>XXIV</u>	4-OH	3-OCH ₃	3'-OCH ₃
<u>XII</u>	2-OH	H	4'-NO ₂	<u>XXV</u>	4-OH	3-OCH ₃	4'-OCH ₃
<u>XIII</u>	2-OH	H	2'-OCH ₃	<u>XXVI</u>	4-OH	3-OCH ₃	3',4'-(OCH ₃) ₂

Results and Discussion

The first series of complexes studied involves 4-X-N(2-hydroxybenzylidene)aniline derivatives (I-XII); the compounds are yellow in colour, except for I and X, which are brown and reddish-brown, respectively. The m.p.'s of the molecular complexes are higher than those of the parent components, except for XII, which has a lower m.p., similarly as for the molecular complexes of the aniline derivatives [7]. Relatively low m.p.'s were measured for the molecular complexes of benzylideneanilines with trinitrotoluene, for example, where

Table II
Analytical data on the molecular complexes

No	M.p.	Colour	C%		H%	
			Calcd.	Found	Calcd.	Found
<u>I</u>	154.0	P	53.73	53.70	4.08	4.02
<u>II</u>	184.9	GY	51.59	51.49	3.19	3.16
<u>III</u>	142.0	GY	55.42	55.40	4.45	4.40
<u>IV</u>	179.6	LY	54.55	54.49	3.66	3.65
<u>V</u>	157.8	LY	53.53	53.48	3.31	3.26
<u>VI</u>	205.7	LY	52.18	52.13	3.54	3.55
<u>VII</u>	169.7	LY	49.53	49.49	2.84	2.80
<u>VIII</u>	167.1	LY	45.17	45.11	2.59	2.55
<u>IX</u>	166.1	LY	41.33	41.25	2.37	2.38
<u>X</u>	141.0	BR	53.85	53.77	3.44	3.38
<u>XI</u>	145.2	GY	53.22	53.21	2.90	2.81
<u>XII</u>	136.8	OY	49.70	48.36	2.71	2.71
<u>XIII</u>	184.0	LY	52.64	52.47	3.53	3.50
<u>XIV</u>	175.5	GY		52.51		3.45
<u>XV</u>	172.0	LY		52.44		3.49
<u>XVI</u>	165.0	BY	51.86	51.77	3.73	3.68
<u>XVII</u>	176.5	O	52.64	52.60	3.53	3.50
<u>XVIII</u>	190.5	LY	51.86	51.74	3.73	3.69
<u>XIX</u>	137.0	BY		51.75		3.70
<u>XX</u>	121.0	BY		51.80		3.68
<u>XXI</u>	118.0	BR	51.17	51.08	3.90	3.88
<u>XXII</u>	201.0	LY	52.64	52.55	3.53	3.47
<u>XXIII</u>	171.5	BR	51.86	51.77	3.73	3.66
<u>XXIV</u>	167.0	OY		51.69		3.68
<u>XXV</u>	212.0	OY		51.71		3.61
<u>XXVI</u>	182.5	O	51.17	51.06	3.90	3.90

P: purple; GY: greenish-yellow; LY: lemon-yellow; BR: brick-red; OY: orange-yellow; BY: brownish-yellow; O: orange;

neither $n-\pi^*$ interaction nor proton-transfer is possible, and only $\pi-\pi^*$ charge-transfer takes place [7, 9]. The interaction between the studied Schiff bases and picric acid in solution is weak, and thus considerable changes in the UV and visible spectra are not probable; however, a comparison of the spectral behaviour of the components with that of their molecular complexes is of interest.

The solution spectra of the yellow compounds in chloroform show a sharp band at about 340 nm, with a small bathochromic shift relative to the spectra of the corresponding Schiff base, and a well-defined inflection ($\log \epsilon \sim 2-2.5$) in the range 420-440 nm. Salicylideneanilines give a band at around 420 nm in hydrogen-bond forming solvents (e.g. methanol), due to the formation of an intermolecular six-membered ring with guinoidal structure [11]. However, in chloroform this band is absent, and the inflection is therefore assigned to the molecular complexes formed (Table III).

In the spectra of I and X, a well-defined band occurs in the visible range (Fig. 1). The spectral data measured in different solvents are presented in Table IV. It can be seen that the intensities of the main band (520-540 nm) do not vary considerably, whereas the structures and positions of the bands do. In solvents with low (< 10) permittivity, well-defined inflections are observed on both the long and short-wavelength sides of the main band, but in higher-permittivity solvents only a single band can be observed between 510 and 520 nm (Fig. 2). No correlation can be found between the characteristics of the solvents and the spectral data; this problem necessitates further investigations. The reflection spectrum of X contains only one inflection, at about 545 nm.

When the spectra of our molecular complexes are compared

Table III
UV and visible data on the complexes, measured in
chloroform

No.	λ/nm ($\log \epsilon$)			
Picric acid	~260	336(3.66)		
<u>I</u>	---	~340	387(4.26)	485(3.72)
<u>II</u>	274(4.32)	~320	348(4.30)	~430
<u>III</u>	265(4.28)	~325	350(4.27)	~420
<u>IV</u>	270(4.31)	~320	343(4.26)	~430
<u>V</u>	270(4.36)	~320	338(4.21)	~420
<u>VI</u>	271(4.55)	~330	348(4.51)	~430
<u>VII</u>	272(4.43)	~325	344(4.30)	~420
<u>VIII</u>	272(4.40)	~325	343(4.28)	~420
<u>IX</u>	---	~330	346(4.34)	~430
<u>X</u>	280(4.44)	---	340(4.33)	530(2.94)
<u>XI</u>	275(4.47)	~325	346(4.26)	~430
<u>XII</u>	---	---	335(4.33)	---

with those of complexes containing dipicrylamine as acceptor, the similarity is obvious; for I and X, a visible band appears. In the latter case, proton-transfer is improbable, and consequently the band above 500 nm must be due to $\pi-\pi^*$ charge-transfer. In the case of 4-nitro-N-(2-aminobenzylidene)aniline, for example, the formation of an intramolecular hydrogenbond is impossible. The molecular complexes of these compounds with picric acid have intense colour and considerable absorbancy above 400 nm, and the ν_{NH} band is absent from the IR spectra.

The second series comprises the molecular complexes of Schiff bases containing a methoxy group(s) on the aldehyde

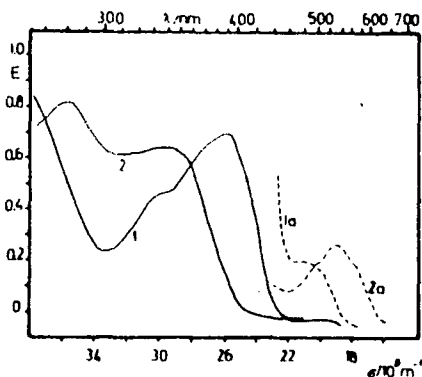


Figure 1: UV and visible spectra in chloroform of I (1, 1a), $c=3.8 \cdot 10^{-4}$, and X (2, 2a), $c=3 \cdot 10^{-4}$ mol/dm³; $d=0.1$ cm (1, 2) and 1.0 cm (1a, 2a).

Table IV

Visible spectral data on X, measured in different solvents

Solvent	λ/nm ($\log \epsilon$)		
1,4-Dioxane	500(2.83)	536(2.91)	~570
Benzene	~500	534(2.98)	~575
Chloroform	500(2.96)	526(3.09)	558(2.95)
Chlorobenzene	~500	529(3.02)	~562
Dichloroethane	~505	532(3.05)	---
Benzyl alcohol	---	530(3.00)	~560
Cyclohexanol	~495	521(2.99)	~550
Acetone	---	513(3.02)	---
Methanol	---	515(3.03)	---
Acetonitrile	---	511(3.03)	---
DMSO	---	523(2.96)	---

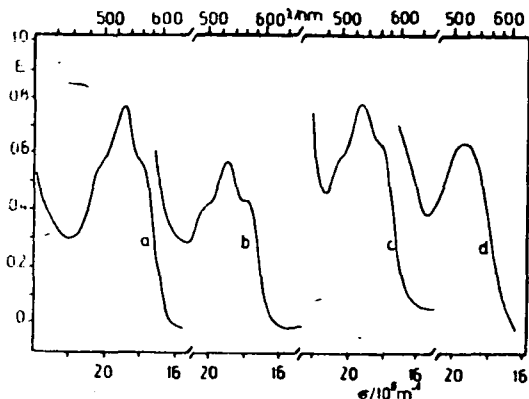


Figure 2: Visible spectra of X, measured in a: chloroform; b: chlorobenzene; c: cyclohexanol; d: acetone; $c = 6.4 \cdot 10^{-4} \text{ mol/dm}^3$, $d = 1.0 \text{ cm}$.

or/and on the aniline rings (XIII-XXVI). The data in Table V reveal that the spectra in chloroform solution are characterized by two high-intensity bands; the structures of the spectra are very similar to those of the parent Schiff bases (see e.g. Figs 3 and 4). The two main bands appear between 268-280 and 310-350 nm, respectively, but these bands have higher intensities than in the case of the Schiff bases. The wavelength ratios do not change considerably: they vary between 1.15 and 1.35.

The 400-450 nm range is characteristic of the spectra of the complexes studied. In every spectrum, a well-defined medium-intensity inflection appears at about 430-450 nm. On the basis of our results and literature data [8, 12], this band is assigned to $\pi-\pi^*$ charge-transfer processes from the higher occupied state of the donor to the lowest unfilled state of the acceptor ($\pi_{\text{HOMO}_D} - \pi_{\text{LUMO}_A}$).

Table V
Spectral data on XIII-XXVI, measured in chloroform

No	λ/nm ($\log \epsilon$)		
<u>XIII</u>	268(4.27)	345(4.22)	~440
<u>XIV</u>	270(4.38)	344(4.28)	~430
<u>XV</u>	269(4.19)	353(4.32)	~430
<u>XVI</u>	~265	352(4.29)	~430
<u>XVII</u>	276(4.35)	319(4.25) ^a	~470
<u>XVIII</u>	270(4.24)	342(4.14)	~480
<u>XIX</u>	275(4.38)	336(4.23)	~470
<u>XX</u>	273(4.34)	339(4.24)	~470
<u>XXI</u>	273(4.29)	337(4.32)	~460
<u>XXII</u>	275(4.26)	315(4.12)	~380
<u>XXIII</u>	~270	338(4.22)	~450
<u>XXIV</u>	277(4.27)	335(4.25) ^a	~380
<u>XXV</u>	~280	350(4.30)	396(4.23)
<u>XXVI</u>	~270	350(4.31)	405(4.13)

a: broad band

The IR data on I-XII are listed in Table VI. In the range $3000-3200 \text{ cm}^{-1}$, a diffuse band system appears which is assigned to the stretching vibration of the OH group on the aldehyde part of the schiff base. The range of appearance and the diffuse structure of this band suggest that an intra-molecular hydrogen-bond is also formed in the molecular complexes, similarly to the former observation in connection with the interaction between Schiff bases with p-nitrophenol [13].

No band can be observed in the range $2500-2900 \text{ cm}^{-1}$. In the IR spectra of the molecular complexes, e.g. benzyl-

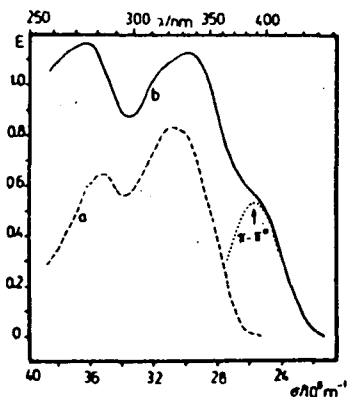


Figure 3: Spectra of the Schiff base (a), $c=6.05 \cdot 10^{-4}$, and its complex XXIV (b), $c=6.17 \cdot 10^{-4}$ mol/dm³, in CHCl₃, $d=0.1$ cm.

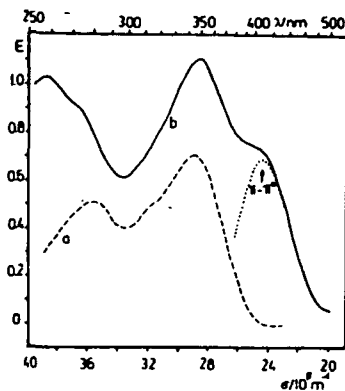


Figure 4: Spectra of the Schiff base (a), $c=4.55 \cdot 10^{-4}$, and its complex XXVI (b), $c=5.42 \cdot 10^{-4}$ mol/dm³ in CHCl₃; $d=0.1$ cm.

ideneanilines with picric acid, a characteristic band is found in this range, due to the $\nu=\overset{\oplus}{\text{N}}\text{H}$ vibration, as a consequence of a proton-transfer from the phenolic OH group to the basic centre >C=N- of the donor. On the basis of the above data, we presume that the formation of the intramolecular six-membered ring prevents the intermolecular proton-transfer.

The $\nu_{\text{as}}\text{NO}_2$ band of picric acid contains two components, but for the complexes only a single, very intense band occurs, probably due to the destruction of the intramolecular hydrogen-bond in picric acid. The band generally shifts to higher frequencies. The $\nu_{\text{s}}\text{NO}_2$ band shifts in the opposite direction, as a result of the increased π -electron density

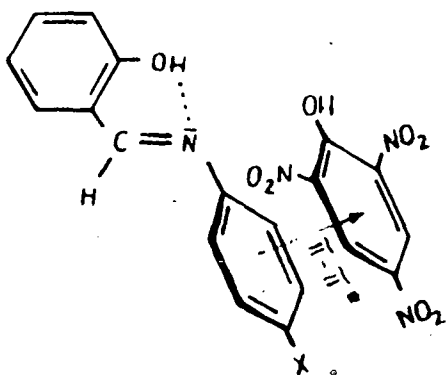
Table VI
IR data on complexes I-XII

No.	ν_{OH}	$\nu_{as} NO_2$	$\nu_s NO_2$	γ_{CH}	$\gamma_s NO_2$
Picric acid	3122s	1570s, 1550s	1352s	790m	735m, 712m
<u>I</u>	3140m	1588s	1340s, 1328s	776m, 758m	715m
<u>II</u>	3120m	1572s	1328s	778m, 756m	712s
<u>III</u>	3090m	1572s	1332s	780m, 772m	720s
<u>IV</u>	3090m	1578s	1321s	770m, 749m	710s
<u>V</u>	3080m	1577s	1330s	772m, 760m	718s
<u>VI</u>	3110m	1578s	1335s	778m, 766m	715s
<u>VII</u>	3100m	1570s	1338s	770m, 759m	718s
<u>VIII</u>	3100m	1570s	1338s	770m, 758m	718s
<u>IX</u>	3080m	1572s	1336s	772m, 756m	716s
<u>X</u>	3100m	1581s	1344s, 1328s	760m, 748m	719s
<u>XI</u>	3060m	1575s	1341s	769m, 758m	722s
<u>XII</u>	3120m	1575s	1350s	777m, 728m	728s

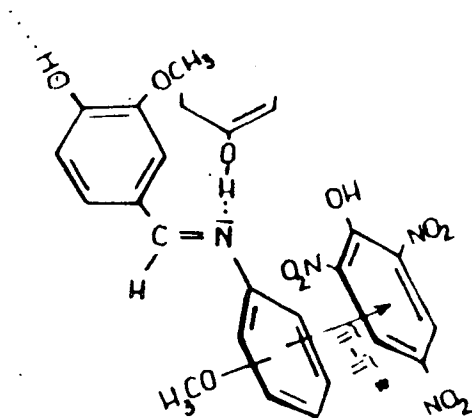
m: medium, s: strong

on the acceptor. It is noteworthy that in the case of IV and X the $\nu_s NO_2$ band splits.

The γ_{CH} bands of the acceptor are shifted to lower wavenumbers. Issa et al. [9] suggested that the shift of this band of the anilino moiety is higher than that of the aldehyde moiety, because the former is more the center contributing to the intermolecular charge-transfer, which takes place from the HOMO state of the donor to the LUMO state of the acceptor. An $n-\pi^*$ interaction is improbable, due to the blocking of the nitrogen lone pair through the intramolecular hydrogen-bond.



II.



III.

It was earlier discussed [e.g. 14] that the aniline ring is twisted out from the plane of the molecule. On the other hand, Ross and Labes [15] have suggested that in the case of molecular complexes of anilines with 1,3,5-trinitrobenzene the two aromatic rings are parallel to each other. On the basis of these statements and the above experimental findings, we propose Structure II. for the complexes of the 2-hydroxy derivatives (I-XXI). The problem is more complicated in the case of the 4-hydroxy derivatives (XXII-XXVI). We presume that an intermolecular interaction may be possible with the neighbouring molecules via the 4-OH group and the azomethine nitrogen atom (Structure III).

Further investigations of our molecular complexes are in progress by means of ^1H NMR and electrochemical methods.

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СПЕКТРАЛЬНОЕ ИЗУЧЕНИЕ МОЛЕКУЛЯРНЫХ
КОМПЛЕКСОВ АРОМАТИЧЕСКИХ ШИФФОВЫХ ОСНОВАНИЙ С ПИКРИ-
НОВОЙ КИСЛОТОЙ

И. Часар

Синтезированы и изучены ультрафиолетовые, видимые и инфракрасные спектры двадцати шести комплексов Шиффовых оснований, образованных из салицилальдегидных, орто-ванилиновых, изо-ванилиновых и анилиновых производных и пикриновой кислоты, состава 1 : 1. Результаты показывают, что эти молекулярные комплексы, вероятно, образовались при взаимодействиях $\pi - \pi^*$ переходов заряда.