Study of electron structures of 3-(X-phenyl)iminoxindoles

[a]A. KOŠTURIAK, [b]S. STANKOVIANSKY, and [c]D. ZACHAROVÁ-KALAVSKÁ

[a]*Department of Experimental Physics, Faculty of Natural Sciences,*
P. J. Šafárik University, 041 54 Košice

[b]*Institute of Chemistry, Komenský University,*
816 31 Bratislava

[c]*Department of Analytical Chemistry, Faculty of Natural Sciences,*
Komenský University, 816 31 Bratislava

Electronic absorption spectra of ten 3- and 4-substituted 3-phenyliminoxindole derivatives in solvents of different permittivity were measured and discussed. Conclusions were drawn about the nature of interactions of the studied derivatives with the medium from relationships of the slope values of linear dependences of the molar absorptivities *vs.* absorption band position in dependence on the logarithm of the permittivity of the medium. The electron stucture of the studied compounds was concluded from the relationships of the spectral data *vs.* constants expressing the electronic effects of the substituents.

Были измерены и обсуждены электронные абсорбционные спектры десяти 3- и 4-замещенных производных 3-фенилиминоксиндола в раство-рителях разной диэлектрической проницаемости среды. Из отношения между величинами угловых коэффициентов линейных зависимостей мольных коэффициентов абсорбции и положение полосы поглощения в зависимости от логарифма диэлектрической проницаемости среды дела-лось заключение на характер взаимодействий изучаемых производных 3-фенилиминоксиндола с средой. В зависимости спектральных характе-ристик от постоянных выражающих электронные влияния заместителей, делалось заключение на электронную структуру изучаемых соединений.

It is known that 2,3-dioxindole can exist in several molecular, tautomeric, and ionic forms depending on the media [1—3]. The existence of these forms was proved by numerous physicochemical studies [4—11] as well as by the course of their syntheses [12, 14].

It was evident from the i.r. spectra of the studied 3-phenyliminoxindole derivatives that these compounds existed in solid state and in concentrated solutions in the form of cyclic dimers with intermolecular hydrogen bonds. Also

Table 1

Values of λ_{max} (nm) and ε (mol l^{-1} cm^{-1}) in dependence on the solvent and the substituent
for 3-phenyliminoxindole derivatives

Compound	Medium	Dioxan	Dioxan+ 11.1 M-H$_2$O	Dioxan+ 28.2 M-H$_2$O	Dioxan+ 44.3 M-H$_2$O	Benzene
	Permitivity	2.05	11.5	35.6	61.8	2.28
		λ_{max} (ε)	λ_{max} (ε)	λ_{max} (ε)	λ_{max} (ε)	λ_{max} (ε)
I	4'-N(CH$_3$)$_2$	500 (12 600)	518 (9 800)	526 (6 850)	526 (4 400)	504 (12 500)
II	4'-NH$_2$	482 (8 900)	488 (6 700)	484 (4 400)	477 (3 000)	479 (8 850)
III	4'-OH	454 (5 900)	448 (4 400)	442 (2 950)	439 (1 850)	*a*
IV	4'-OCH$_3$	449 (4 700)	444 (3 950)	437 (2 860)	435 (1 700)	458 (4 750)
V	4'-OC$_2$H$_5$	451 (4 500)	445 (3 650)	441 (3 010)	438 (1 780)	454 (4 600)
VI	4'-CH$_3$	426 (3 600)	423 (3 030)	420 (2 530)	418 (1 630)	429 (3 700)
VII	3'-CH$_3$	415 (2 900)	414 (2 500)	413 (2 050)	413 (1 500)	418 (2 850)
VIII	-H	413 (2 750)	413 (2 300)	412 (1 850)	412 (1 350)	413 (2 850)
IX	4'-Br	422 (3 300)	418 (2 820)	417 (2 490)	416 (1 760)	424 (3 300)
X	3'-Cl	415 (2 650)	414 (2 270)	412 (2 070)	412 (1 600)	415 (2 500)

a) The compound is insoluble in the used solvent; *b*) σ_M is not known in the literature;
c) without σ_M.

a strong mesomeric interaction was found between the substituted benzene ring and the system of bonds —N=C̦—C̦=O. It was proved in [15] that the studied compounds existed in keto forms in polar as well as non-polar solvents.

The electronic spectra of 3-phenyliminoxindole derivatives are very similar to those of their potassium salts (enol form) and differ from those of their silver salts (keto form) [16].

The aim of the present work is to study the nature of interactions of the lone electron pair on nitrogen in the phenylimino group with the solvent.

Table 1 (Continued)

Pyridine	Acetone	Acetonitrile	Isoamyl alcohol	Ethanol	Methanol			
12.3	21.5	37.5	16.0	25.8	33.0	σ	σ_M	σ^+
λ_{max} (ε)	λ_{max} (ε)	λ_{max} (ε)	λ_{max} (ε)	λ_{max} (ε)	λ_{max} (ε)			
516 (11 600)	504 (10 200)	506 (9 050)	517 (11 400)	520 (9 450)	517 (9 120)	−0.83	−0.93	−1.70
495 (7 600)	483 (6 650)	484 (6 200)	495 (7 250)	490 (6 300)	489 (5 760)	−0.66	−0.76	−1.30
457 (5 050)	450 (4 700)	442 (5 050)	452 (4 700)	449 (4 700)	447 (4 300)	−0.37	−0.62	−0.92
450 (4 700)	446 (4 600)	436 (4 250)	446 (4 600)	440 (4 550)	438 (4 280)	−0.27	−0.52	−0.78
448 (4 600)	445 (4 300)	440 (4 750)	445 (4 600)	441 (4 300)	436 (4 120)	−0.25	b	−0.72
430 (3 200)	419 (3 200)	418 (3 250)	420 (3 500)	420 (3 400)	419 (3 470)	−0.17	−0.12	−0.31
422 (2 650)	413 (2 700)	412 (2 750)	415 (2 800)	415 (2 650)	412 (3 500)	−0.07	c	−0.07
415 (2 600)	410 (2 650)	408 (2 700)	412 (2 750)	413 (2 600)	410 (2 680)	0.00	0.00	0.00
426 (3 150)	418 (3 050)	416 (2 800)	420 (3 050)	417 (3 000)	415 (2 820)	0.23	−0.22	0.15
417 (2 500)	409 (2 500)	408 (2 400)	415 (2 500)	410 (2 450)	408 (2 300)	0.37	c	0.40

Experimental

Preparation and identification of the 3-(X-phenyl)iminoxindole derivatives are described in [17].

Electronic absorption spectra of the studied compounds in 2×10^{-4}—4×10^{-5} M solutions were measured on a Perkin—Elmer 402 spectrophotometer in the region 200—650 nm using silica cells of 0.5, 1.0, and 2.0 cm thickness. The solvents used were of spectral grade or were purified according to the procedures mentioned in [18]. The permittivities (DC) of the used solvents were taken from [19] and the permittivity of the mixture dioxan—water from [20]. σ Constants were taken from [21], the σ constant for 4-OC_2H_5 from [22], σ_M constants from [23], and the σ^+ from [24]. The statistical parameters of the regression analysis were obtained on a Minsk 21 computer using the standard programme.

Results and discussion

The electronic spectra of 3-phenyliminoxindole derivatives, similarly as those of 2,3-dioxindole [11], showed four well distinguished absorption bands. Only the position (λ_{max}) and the intensity of the band in the region 410—530 nm depended on the substituent and on the permittivity of the solvent (Table 1). It is evident from the data in Table 1 that the electron-donating substituents caused a bathochromic shift of the absorption bands with a hyperchromic effect. The above-mentioned absorption band was attributed to n—π^* electron transfer in [17] which was proved also in [25].

The statistical parameters of linear correlations of the spectral data with the substituent constants are presented in Table 2. The values of slopes, obtained from the relationship ε vs. λ_{max}, are plotted against permittivities of the solvents in Fig. 1. The values from those relationships where mainly intermolecular forces acted between the studied compounds and the solvents are presented on the straight line 1. The dependence is linear and can be expressed by the following equation

$$\varrho = -51.6(\pm 0.69) \log DC + 119.2(\pm 0.81); \ n = 5, \ r = 0.999$$

The values of slopes against the values of permittivities of those solvents which affected the lone electron pair on nitrogen in the phenylimino group by electrostatic forces are plotted on the straight line 3. This dependence can be expressed by the equation of the straight line 3

$$\varrho = -31.0(\pm 0.81) \log DC + 112.2(\pm 0.86); \ n = 5, \ r = 0.995$$

The curve 2 represents the above-mentioned relationship with those solvents which affected the lone electron pair on nitrogen in the phenylimino group by electrostatic forces and were able to form also intermolecular hydrogen bonds with the studied compounds.

The relationships λ_{max} vs. σ and vs. σ_M were used to study the excited state of 3-phenyliminoxindole derivatives similarly as in [26, 27]. The derivatives IX and X showed evident deviations from linearity, therefore, they were omitted from the relationships λ_{max} vs. σ. Analogous deviations of these electron-accepting substituents were reported in [14, 17, 28]. On the basis of different statistical significance of the presented correlations, it can be assumed that the structure of the excited state of the studied compounds is well expressed by the structure 1.

240

Table 2

Statistical parameters of correlations between spectral data and substituent constants for the substituted 3-(X-phenyl)iminoxindole derivatives (*I*)

No.	Dependence	Medium	n	ϱ	s_ϱ	q	s_q	S	r	Excluded
1	$\varepsilon=f(\lambda_{max})$	Dioxan	10	102.0	0.68	−39 940	300.4	901.5	0.960	
2	$\varepsilon=f(\lambda_{max})$	Dioxan+11.1 M-H_2O	10	67.0	0.30	−25 490	132.6	398.0	0.986	
3	$\varepsilon=f(\lambda_{max})$	Dioxan+28.2 M-H_2O	10	39.6	0.19	−14 641	84.5	253.6	0.986	
4	$\varepsilon=f(\lambda_{max})$	Dioxan+44.3 M-H_2O	10	25.0	0.15	− 8 900	66.7	200.1	0.977	
5	$\varepsilon=f(\lambda_{max})$	Benzene	9	100.4	0.81	−34 470	360.3	1019.4	0.953	*III*
6	$\varepsilon=f(\lambda_{max})$	Pyridine	10	82.4	0.45	−32 100	202.1	606.4	0.977	
7	$\varepsilon=f(\lambda_{max})$	Acetone	10	71.1	0.44	−26 810	192.5	577.5	0.970	
8	$\varepsilon=f(\lambda_{max})$	Acetonitrile	10	61.6	0.29	−22 622	141.3	423.0	0.976	
9	$\varepsilon=f(\lambda_{max})$	Isoamyl alcohol	10	73.3	0.51	−27 790	227.4	682.4	0.969	
10	$\varepsilon=f(\lambda_{max})$	Ethanol	10	58.2	0.28	−21 340	126.2	378.9	0.985	
11	$\varepsilon=f(\lambda_{max})$	Methanol	10	54.2	0.78	−19 670	342.4	1027	0.891	
12	$\lambda_{max}=f(\sigma)$	Dioxan	8	−107.2	5.05	413.8	2.12	5.78	0.982	*IX, X*
13	$\lambda_{max}=f(\sigma)$	Dioxan+11.1 M-H_2O	8	−128.7	4.70	407.1	1.98	5.38	0.989	*IX, X*
14	$\lambda_{max}=f(\sigma)$	Dioxan+28.2 M-H_2O	8	−135.4	7.36	402.8	3.10	8.42	0.977	*IX, X*
15	$\lambda_{max}=f(\sigma)$	Dioxan+44.3 M-H_2O	8	−127.7	9.03	402.1	3.80	10.33	0.962	*IX, X*
16	$\lambda_{max}=f(\sigma)$	Benzene	7	−104.6	7.66	417.1	3.29	8.36	0.968	*IX, X*
17	$\lambda_{max}=f(\sigma)$	Pyridine	8	−123.0	2.32	413.8	0.98	2.67	0.997	*IX, X*
18	$\lambda_{max}=f(\sigma)$	Acetone	8	−115.7	4.66	408.4	1.97	5.36	0.987	*IX, X*
19	$\lambda_{max}=f(\sigma)$	Acetonitrile	8	−124.5	4.19	403.0	1.77	4.82	0.991	*IX, X*
20	$\lambda_{max}=f(\sigma)$	Isoamyl alcohol	8	−132.0	4.17	407.2	1.76	4.79	0.992	*IX, X*
21	$\lambda_{max}=f(\sigma)$	Ethanol	8	−132.0	4.48	405.3	1.90	5.16	0.991	*IX, X*
22	$\lambda_{max}=f(\sigma)$	Methanol	8	−133.8	4.15	402.1	1.74	4.20	0.993	*IX, X*
23	$\lambda_{max}=f(\sigma_M)$	Dioxan	7	− 90.5	5.36	408.5	2.98	7.49	0.973	*V, VII, X*
24	$\lambda_{max}=f(\sigma_M)$	Dioxan+11.1 M-H_2O	7	−105.7	9.84	402.4	5.47	13.8	0.936	*V, VII, X*
25	$\lambda_{max}=f(\sigma_M)$	Dioxan+28.2 M-H_2O	7	−108.9	12.76	399.1	7.09	17.84	0.905	*V, VII, X*

Table 2 (Continued)

No.	Dependence	Medium	n	ϱ	s_ϱ	q	s_q	S	r	Excluded
26	$\lambda_{max}=f(\sigma_M)$	Dioxan+44.3 M-H_2O	7	-102.5	12.34	398.6	7.41	18.66	0.886	*V, VII, X*
27	$\lambda_{max}=f(\sigma_M)$	Benzene	6	-94.2	4.40	411.1	2.39	5.56	0.988	*III, V, VII, X*
28	$\lambda_{max}=f(\sigma_M)$	Pyridine	7	-102.9	7.93	409.0	4.40	11.08	0.955	*V, VII, X*
29	$\lambda_{max}=f(\sigma_M)$	Acetone	7	-98.7	6.46	402.4	3.59	9.03	0.967	*V, VII, X*
30	$\lambda_{max}=f(\sigma_M)$	Acetonitrile	7	-101.0	9.64	398.6	5.35	13.47	0.933	*V, VII, X*
31	$\lambda_{max}=f(\sigma_M)$	Isoamyl alcohol	7	-110.7	8.67	401.7	4.81	12.12	0.954	*V, VII, X*
32	$\lambda_{max}=f(\sigma_M)$	Ethanol	7	-109.4	10.47	400.3	5.81	14.64	0.933	*V, VII, X*
33	$\lambda_{max}=f(\sigma_M)$	Methanol	7	-109.3	10.34	398.3	5.74	14.46	0.935	*V, VII, X*
34	$\lambda_{max}=f(\sigma)$	Dioxan	8	-52.1	1.12	411.0	1.02	2.77	0.996	*IX, X*
35	$\lambda_{max}=f(\sigma^+)$	Dioxan+11.1 M-H_2O	8	-60.9	3.23	405.0	2.95	8.00	0.976	*IX, X*
36	$\lambda_{max}=f(\sigma^+)$	Dioxan+28.2 M-H_2O	8	-63.3	4.86	401.1	4.43	12.02	0.952	*IX, X*
37	$\lambda_{max}=f(\sigma^+)$	Dioxan+44.3 M-H_2O	8	-62.0	5.30	399.8	4.83	13.12	0.941	*IX, X*
38	$\lambda_{max}=f(\sigma^+)$	Benzene	7	-52.5	0.93	414.1	0.85	2.16	0.998	*III, IX, X*
39	$\lambda_{max}=f(\sigma^+)$	Pyridine	8	-58.6	2.58	411.6	2.35	6.39	0.983	*IX, X*
40	$\lambda_{max}=f(\sigma^+)$	Acetone	8	-56.1	1.81	405.5	1.65	4.48	0.991	*IX, X*
41	$\lambda_{max}=f(\sigma^+)$	Acetonitrile	8	-58.0	3.36	401.2	3.06	8.32	0.972	*IX, X*
42	$\lambda_{max}=f(\sigma^+)$	Isoamyl alcohol	8	-63.1	2.99	404.6	2.73	7.40	0.981	*IX, X*
43	$\lambda_{max}=f(\sigma^+)$	Ethanol	8	-62.4	3.84	403.3	3.50	9.50	0.968	*IX, X*
44	$\lambda_{max}=f(\sigma^+)$	Methanol	8	-62.5	3.85	400.6	3.51	9.54	0.968	*IX, X*

n — number of experimental points; ϱ — line slope; s_ϱ — slope error; q — intercept on y axis; s_q — intercept error; S — standard deviation; r — correlation coefficient.

A. KOŠTURIAK, S. STANKOVIANSKY, D. ZACHAROVÁ-KALAVSKÁ

This structure is stabilized better by solvents of higher permittivities. Correlations of λ_{max} with σ^+ were utilized in identification of the significant conjugated systems in molecular compounds. These correlations are statistically significant. The derivatives with the most electron-accepting effects (*IX* and *X*) were omitted for evident deviations from linearity. In the case when all compounds were included, the linear relationships λ_{max} *vs.* σ^+ were still statistically significant. For instance, when all compounds ($n = 10$) were included, the following values of correlation coefficients were obtained in dioxan with the increasing concentration of water: $r_{dioxan} = 0.968$, $r_{dioxan+11.1\ M\text{-}H_2O} = 0.944$, $r_{dioxan+28.2\ M\text{-}H_2O} = 0.918$, $r_{dioxan+44.3\ M\text{-}H_2O} = 0.906$. The correlation coefficient decreased with the increasing concentration of water in dioxan, *i.e.* with the increasing hydration ability of the solvent. It can be seen from the relationship λ_{max} *vs.* σ^+ (Fig. 2) that in dioxan itself, all derivatives filled the requirements of linearity (line *1* in Fig. 2). In dioxan containing water (44.3 M) the derivatives *I* and *II* behaved differently than the derivatives *III—X*. The relationships with these derivatives formed two different lines (*2a* and *2b*; Fig. 2) with significantly distinct slopes. The transition of the relationship λ_{max} *vs.* σ^+ from the line *1* to the line *2* was continuous for all derivatives at continual change of solvation abilities of the solvents. The above-mentioned relationship for silver salts (enol form; [16]) of all derivatives was linear also in strongly hydrating media with similar slope as with 3-phenyliminoxindoles in dioxan. With potassium salts of 3-phenyliminoxindole derivatives (keto form), the mentioned dependences in the system dioxan—water were analogous to those with 3-phenyliminoxindole derivatives themselves. These relationships indicated that two significant conjugated
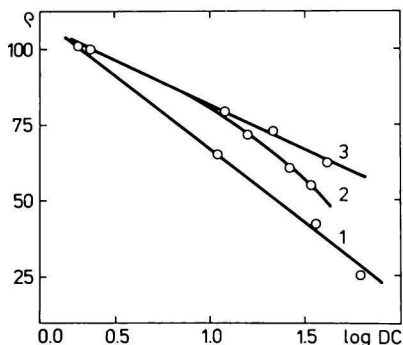

Fig. 1. Dependence of slopes ϱ of the linear relationship ε *vs.* λ_{max} on log *DC*.

1. Solvents forming intermolecular hydrogen bonds; *2.* solvents forming intermolecular hydrogen bonds and acting by electrostatic forces; *3.* solvents acting by electrostatic forces.
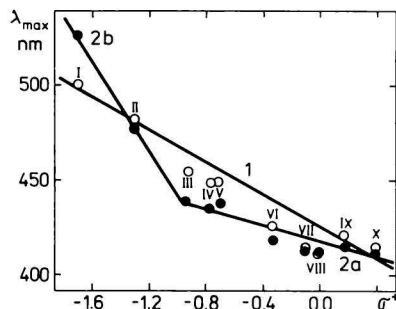
Fig. 2. Dependence of λ_{max} on the substituent constants σ^+ for 3-(X-phenyl)iminoxindoles.
○ Dioxan; ● dioxan + 44.3 M-H_2O.

systems A and B were present in the molecules of the studied compounds. With the electron-accepting substituents in solvents of low solvation ability, the substitution effect was transferred by both systems A and B. With the electron-accepting substituents in polar solvents these effects were transferred only by the system A. In the solvents of high solvation or hydration abilities the substitution effect was transferred by the system B only in the case of strongly electron-donating substituents; with other derivatives the transfer vanished (Fig. 2).

By continuous change of solvents with low solvation ability to those with high solvation ability the transfer by the system B vanished continually as well (structure *1*).
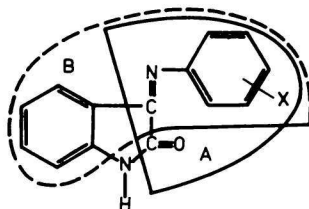
Structure 1

In the dependences λ_{max} *vs.* σ^+ (Fig. 2) the line *2b* expresses the degree of delocalization of the electron pair on nitrogen in the phenylimino group by the effect of the substituent transferred by the systems A and B; the line *2a* expresses the transfer only by the system A. Similar conclusions can be drawn also from the correlations of $\log \varepsilon$ with σ, σ_M, and σ^+.

References

1. Julien, P., Meyer, E., and Printi, E., *Geterotsyklicheskie soedineniya*, Tom 3, p. 151. Izd. inostr. lit., Moscow, 1954.
2. Sumpter, W. C. and Miller, F. M., *Heterocyclic Compounds with Indole and Carbazole Systems*, p. 115. Interscience, New York, 1954.
3. Sumpter, W. C., *Chem. Rev. 34,* 393 (1944).
4. Shigorin, D. N., *Zh. Fiz. Khim. 29,* 1033 (1955).
5. Kelie, A. E., O'Sullivan, D. G., and Sadler, P. W., *J. Chem. Soc. 1956,* 3809.
6. O'Sullivan, D. G. and Sadler, P. W., *J. Chem. Soc. 1956,* 2202.
7. Cowlay, B. and Partington, L., *J. Chem. Soc. 1936,* 47.
8. Sumpter, W. C., Williams, J. L., Wilken, P. H., and Willoughby, B. L., *J. Org. Chem. 14,* 713 (1949).
9. Menczel, C., *Z. Phys. Chem. 125,* 161 (1927).
10. Aulh, R. G., Hirst, E. L., and Morton, L. A., *J. Chem. Soc. 1935,* 1653.
11. Mangini, A. and Passerini, R., *Gazz. Chim. Ital. 85,* 840 (1955).
12. Heller, G., *Über Isatin, Isatyd, Dioxindol und Indophenin.* Ahrens Sammlung V, Leipzig, 1931.

13. Eckschlager, K., *Chem. Listy 56,* 489 (1962).
14. Košturiak, A., *Thesis.* Faculty of Natural Sciences, Komenský University, Bratislava, 1975.
15. Košturiak, A. and Perjéssy, A., *Collect. Czech. Chem. Commun. 41,* 410 (1976).
16. Košturiak, A., Šingliar, M., and Ninčáková, A., *Chem. Zvesti 30,* 229 (1976).
17. Košturiak, A. and Ninčáková, A., *Petrochémia 13,* 30 (1973).
18. Keil, B., *et al., Laboratorní technika organické chemie.* (Laboratory Technique of Organic Chemistry.) Pp. 725—753. Nakladatelství ČSAV. (Publishing House of Czechoslovak Academy of Sciences.) Prague, 1963.
19. Maryott, A. A. and Smith, E. R., *Table of Dielectric Constants of Pure Lignids.* National Bureau of Standards Circular 514, 1951.
20. Zýka, J., *et al., Analytická příručka.* (Analytical Handbook.) Second Enlarged Edition, p. 450. Státní nakladatelství technické literatury. (State Publishing House of Technical Literature.) Prague, 1972.
21. McDaniel, D. M. and Brown, H. C., *J. Org. Chem. 23,* 420 (1958).
22. Tice, B. B., Lee, J., and Hendal, F. H., *J. Amer. Chem. Soc. 83,* 329 (1963).
23. Exner, O., *Chem. Listy 53,* 1302 (1959).
24. Brown, H. C. and Okomoto, V., *J. Amer. Chem. Soc. 80,* 4979 (1958).
25. Košturiak, A. and Zacharová-Kalavská, D., *Collect. Czech. Chem. Commun. 41,* 712 (1976).
26. Kristian, P., Dzurilla, M., and Kováč, Š., *Chem. Zvesti 23,* 173 (1969).
27. Dzurilla, M. and Kristian, P., *Collect. Czech. Chem. Commun. 35,* 417 (1970).
28. Košturiak, A. and Zacharová-Kalavská, D., *Acta Facult. Rer. Natur. Univ. Comenianae (Chimia) 23,* 45 (1977).