Study of the effect of substituents on electronic structure of the silver and potassium salts of 3-(X-phenyl)iminoxindoles

[a]A. KOŠTURIAK, [b]M. ŠINGLIAR, and [c]A. NINČÁKOVÁ

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

[b]Research Institute for Petrochemistry,
972 71 Nováky

[c]Department of Inorganic Chemistry, Faculty of Natural Sciences,
P. J. Šafárik University, 041 54 Košice

The silver and potassium salts of 3-(X-phenyl)iminoxindole derived either from its enol or keto form were prepared.

In order to distinguish the salts with the bonds O—metal from those with the N—metal bonds the bands at the longest possible wavelengths of the visible region λ_{max} were used. A linear relationship between λ_{max} of these bands and the constants of substituent was revealed.

Были приготовлены соли серебра и калия 3-(X-фенил)иминоксиндолов, относящихся к энольной и кетонной формам 3-(X-фенил)иминоксиндолов.
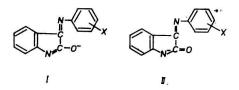
Для распознания солей O-металл и N-металл были использованы λ_{max} полос поглощения при наиболее удаленных длинах волн в видимой области спектра. Обнаружена линейная зависимость λ_{max} этих полос поглощения от констант заместителей.

As early as in 1882 *Bayer* concluded that isatin could exist either in keto or enol form [1, 2].

The studies concerned with the structure of the silver, sodium, and potassium salts of isatin demonstrate that the sodium and potassium salts of isatin are derived from the keto form [3, 4] whereas the silver salts are derived from the enol form of isatin [5, 6].

The sodium salt of isatin can be prepared very easily by the reaction of sodium ethoxide with isatin dissolved in absolute alcohol. Besides, a mixed aqueous-alcoholic solution of isatin with excess sodium acetate is formed. The silver salt is to be prepared by the reaction of silver acetate with the sodium or potassium salt of isatin. The silver salt which is used for the preparation of 2-methoxyisatin or 2-substituted isatin derivatives may be prepared from the sodium salt by adding an equivalent amount of $AgNO_3$ into aqueous alcoholic solution of this substance. On boiling, a red precipitate of the silver salt of isatin is separated almost in a quantitative yield. In light this precipitate changes colour and turns coffee-hued [7, 8].

The reactions between isatin and hydroxylamine, hydrazine or its derivatives always give rise nearly in quantitative yields to 3-substituted isatin derivatives [9—11] which can exist in two tautomeric forms, *i.e.* enol form (*I*) and keto form (*II*).

In our preceding study [12] we found that the λ_{max} value of the bands of 3-(X-phenyl)iminoxindoles was influenced not only by the substituent but also by the pH value of solutions. The intensity of absorption bands increased with the electron-donor ability of the substituent. Furthermore, we revealed that these compounds were able to exist in two tautomeric forms, the keto form (*II*) being much more stable than the enol form (*I*). We demonstrated that an increased alkalinity of medium brought about a reversible hydrolysis of 3-(X-phenyl)iminoxindoles into α-anilisatinic acids.

We synthesized compounds of the types for which either enol (*I*) or keto form (*II*) might be assumed and afterwards we studied these substances under equal conditions.

Experimental

The synthesis of 3-(X-phenyl)iminoxindoles from which we prepared the silver and potassium salts is described in [13].

For the preparation of the salts of 3-(X-phenyl)iminoxindoles which were not isolated from solutions we used the modified method according to *Hovorka* and *Diviš* elaborated for the preparation of the sodium and silver salts of isatin [7, 8].

For the preparation of the potassium salts of *II* one part of the 10^{-3}—10^{-4} M ethanolic stock solution of the required 3-(X-phenyl)iminoxindole (according to substituent) and three parts of the aqueous solution of KCl were mixed.

The silver salts of *I* were prepared by using one part of the ethanolic stock solution of the corresponding 3-(X-phenyl)iminoxindole and three parts of the aqueous 5×10^{-2} M solution of silver nitrate in 0.2 M sodium acetate. After the addition of silver nitrate the colour of the solution changed in case of electron-donating substituents in a moment, otherwise after a short space of time.

The electronic spectra were measured on a spectrometer Perkin—Elmer 402 after 20 hrs standing of the solutions prepared. For the measurements in the region between 210 and 270 nm quartz cells with the absorbing layer width of 0.5 cm were used. As the absorption maxima in the region of the longest wavelengths were rounded, the values were read accurate to ±3 nm.

The absorption bands at λ_{max} were correlated with the constants of substituents in the same manner as described in previous papers dealing with the structure of 3-(X-phenyl)iminoxindoles [12, 13]. As σ constants the values according to *McDaniel* and *Brown* [14], the σ constant of 4-OC$_2$H$_5$ according to [15], the σ^+ constants according to *Brown* and *Okomoto* [16], and the σ_M constants published by *Exner* [17] were used. In Table 1 the λ_{max} values as well as the constants of substituents are summarized.

The statistical parameters of regression analysis were calculated by means of a standard program on a computer Minsk and they served as a test for the significance of correlations.

The numerical values of the correlation coefficients were used as a major criterion of the probability of the suggested structure.
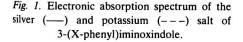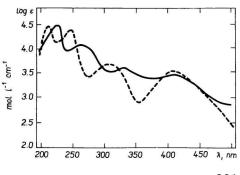
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Table 1

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Ultraviolet spectral data (λ_{max} in nm) and the constants of substituents for the silver (*I*) and potassium (*II*) salts of 3-(X-phenyl)iminoxindoles

No.	X	*I* λ_{max}	*II* in 2.5×10^{-2} M-KCl λ_{max}	*II* in 2 M-KCl λ_{max}	σ_M	σ^+
1	4-N(CH$_3$)$_2$	528	514	520	−0.83	−0.93	−1.70
2	4-NH$_2$	512	463	468	−0.66	−0.76	−1.30
3	4-OH	476	437	435	−0.37	−0.62	−0.92
4	4-OCH$_3$	462	430	432	−0.27	−0.52	−0.78
5	4-OC$_2$H$_5$	460	430	434	−0.25		−0.72
6	4-CH$_3$	428	420	418	−0.17	−0.12	−0.31
7	3-CH$_3$	420	414	412	−0.07		−0.07
8	H	412	407	410	0.00	0.00	0.00
9	3-Cl	392	405	405	0.37		0.40

Results and discussion

Fig. 1 shows the dependence of log ε on the wavelength of the potassium and silver salt of 3-(X-phenyl)iminoxindole. The shape of the electronic spectra as well as the position of absorption bands is different. These differences were observed with the salts of all compounds studied and they are caused by different structure of the silver and potassium salts of 3-(X-phenyl)iminoxindoles.

A comparison of the plot log ε *vs.* λ measured for 2-methoxyisatin by *Mangini* and *Passerini* [19] with that found for the silver salts of 3-(X-phenyl)iminoxindole in this work shows that the character of the relationship is in both cases identical. On the other hand, the course of this relationship for the potassium salts is again similar to that found for 3-(X-phenyl)iminoxindoles [12, 13] in which the presence of carbonyl groups has been proved by infrared spectrophotometry [18]. On the basis of these observations it may be stated that the potassium salts contain a carbonyl group in their molecules and occur in keto form while the silver salts occur in enol form. As the original conjugated systems existing in

Fig. 1. Electronic absorption spectrum of the silver (——) and potassium (– – –) salt of 3-(X-phenyl)iminoxindole.

3-(X-phenyl)iminoxindoles are preserved in the potassium salts, it may be expected that the correlations between λ_{max} and the σ, σ_M, or σ^+ constants will show a similar character as found for 3-(X-phenyl)iminoxindoles [12, 13]. On the other hand, some changes in these relationships are to be expected for the silver salts because of the change in structure of the oxindole system.
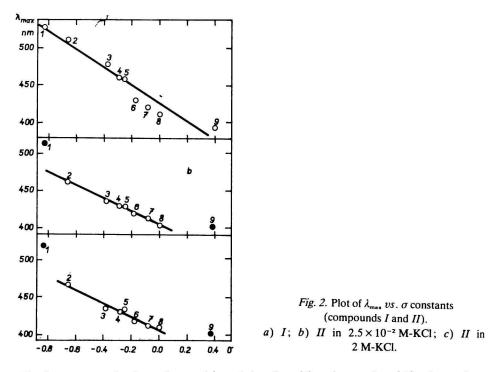

Fig. 2. Plot of λ_{max} *vs.* σ constants (compounds *I* and *II*).
a) I; b) II in 2.5×10^{-2} M-KCl; *c) II* in 2 M-KCl.

Fig. 2 represents the dependence of λ_{max} of the silver (*I*) and potassium (*II*) salts on the σ constants of substituents.

As obvious (Fig. 2a), the relationship between λ_{max} of all silver salts and the σ constants is linear and may be expressed by the straight line equation (*1*)

$$\lambda_{max} = -126.0(\pm 8.7)\,\sigma + 422.9(\pm 3.6), \tag{1}$$

$$r = 0.973; \quad n = 9$$

where r is the coefficient of correlation and n is the number of experimental points.
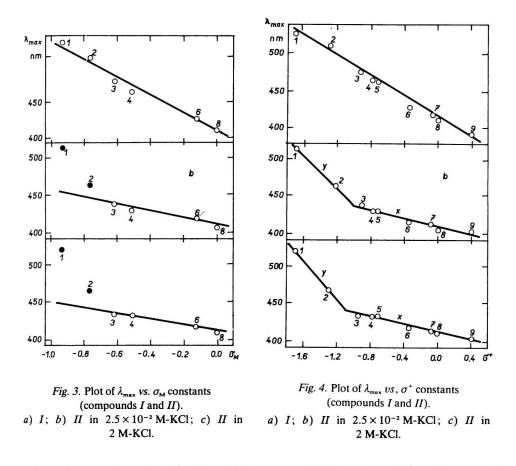
The linear relationship between λ_{max} and the σ constants found for the potassium salts in 2.5×10^{-2} M-KCl and 2 M-KCl (Fig. 2b and 2c) may be described by eqns (*2*) and (*3*)

$$\lambda_{max} = -84.0(\pm 1.4)\,\sigma + 407.2(\pm 0.6), \tag{2}$$

$$r = 0.999; \quad n = 7; \quad 2.5 \times 10^{-2}\ \text{M-KCl}$$

$$\lambda_{max} = -89.5(\pm 4.4)\,\sigma + 407.0(\pm 4.4). \tag{3}$$

$$r = 0.993; \quad n = 7; \quad 2\ \text{M-KCl}$$

Fig. 3. Plot of λ_{max} *vs.* σ_M constants (compounds *I* and *II*).

a) *I*; *b)* *II* in 2.5×10^{-2} M-KCl; *c)* *II* in 2 M-KCl.

Fig. 4. Plot of λ_{max} *vs,* σ^+ constants (compounds *I* and *II*).

a) *I*; *b)* *II* in 2.5×10^{-2} M-KCl; *c)* *II* in 2 M-KCl.

As to the potassium salts (Fig. 2*b* and 2*c*), compounds *1* and *9* were left out because of evident deviations from the linearity of the plot λ_{max} *vs. σ*.

In compound *1* the electron-donating substituent is responsible for the entering of the free-electron pair of nitrogen in the phenylimino group into conjugation with π electrons of the oxindole system. Owing to this strong n—π interaction the free-electron pair of compound *1* is relatively the least solvated by the polar medium.

On the other hand, compound *9* contains an electron-withdrawing substituent in its molecule and this substituent does not allow the free-electron pair of phenylimino group to enter into conjugation with the whole oxindole system.

Fig. 3 shows the dependence of λ_{max} on σ_M for compounds *I* and *II*. For the construction of this plot the data corresponding to compounds *5, 7, 10* were not used. This is due to the fact that no σ_M value was found for compound *5* containging the 4-OC$_2$H$_5$ substituent and compounds *7* and *10* do not possess σ_M constants. The λ_{max} values of all silver salts lie on a straight line (Fig. 3*a*) which may be expressed by eqn (*4*)

$$\lambda_{max} = -123.0(\pm 6.7)\,\sigma_M + 409.2(\pm 3.6). \tag{4}$$

$$r = 0.983; \quad n = 6$$

It is obvious (Fig. 3*b* and 3*c*) that the potassium salts of compounds *1* and *2* exhibit deviations from the linear plot of λ_{max} vs. σ_M. The cause of these deviations is the same as stated for the correlations between λ_{max} and σ^+ The dependence of λ_{max} on σ_M for the alkali salts of the substituted derivatives of 3-phenyliminoxindole may be described by eqns (*5, 6*)

$$\lambda_{max} = -41.6(\pm 4.69)\ \sigma_M + 410.4(\pm 1.92), \tag{5}$$
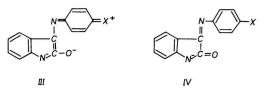
$$r = 0.962; \quad n = 4; \quad 2.5 \times 10^{-2}\ \text{M-KCl}$$

$$\lambda_{max} = -38.8(\pm 2.88)\ \sigma_M + 411.5(\pm 0.77). \tag{6}$$

$$r = 0.973; \quad n = 4; \quad 2\ \text{M-KCl}$$

Regardless of the two compounds (*1* and *2*) which have been omitted in the series of potassium salts, the correlation coefficients of silver salts are higher than those of potassium salts.

As to the correlations between λ_{max} and σ, the situation in the series of silver and potassium salts is just opposite (Fig. 2*a—c*). It ensues from these observations that the silver salts have structure *III* whereas the potassium salts have structure *IV*

III   IV

This conclusion is in agreement with the results of structural research of the silver and potassium salts of isatin [3—6].

We used the correlations between λ_{max} and the σ^+ constants for the identification of some more marked conjugated systems in molecules of the silver and potassium salts of 3-(X-phenyl)iminoxindoles following the different structure of these salts. The results of these correlations are represented in Fig. 4.

For the silver salts (Fig. 4*a*) the values of λ_{max} of all compounds obey the linear dependence on σ^+ and may be expressed by eqn (*7*)

$$\lambda_{max} = -68.3(\pm 2.0)\ \sigma^+ + 413.5(\pm 1.8). \tag{7}$$

$$r = 0.994; \quad n = 9$$

This relationship also indicates a different electronic structure of the silver and potassium salts of 3-(X-phenyl)iminoxindoles.

As to the potassium salts (Fig. 4*b* and 4*c*), compounds *1* and *2* show evident deviations from linearity. The dependence of λ_{max} on the σ^+ constants of substituents of other compounds may be expressed by eqns (*8, 9*)
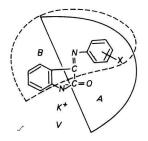
$$\lambda_{max} = -24.9(\pm 1.8)\ \sigma^+ + 411.9(\pm 1.0), \tag{8}$$

$$r = 0.978; \quad n = 7; \quad 2.5 \times 10^{-2}\ \text{M-KCl}$$

$$\lambda_{max} = -25.5(\pm 1.6)\ \sigma^+ + 412.1(\pm 0.9). \tag{9}$$

$$r = 0.982; \quad n = 7; \quad 2\ \text{M-KCl}$$

From the qualitative agreement of the electronic absorption spectra of isatin [19], 3-(X-phenyl)iminoxindoles, and potassium salts of 3-(X-phenyl)iminoxindoles it is possible to infer that two conjugated systems (*VA* and *VB*) are present in the molecules of the potassium salts of 3-(X-phenyl)iminoxindoles as well as 3-(X-phenyl)iminoxindoles [12].

Provided sufficiently efficacious electron-donating substituents (compounds *1* and *2*) are present, the free-electron pair of nitrogen in the phenylimino group is delocalized over the system *VA* as well as *VB*. In other compounds the free-electron pair of the phenylimino group is delocalized merely over system *A*. A carbonyl group with strong $-I_{eff}$ and $-M_{eff}$ occurs in this system. This extinguishment of delocalization of the free-electron pair in system *B* manifests itself in the correlation between λ_{max} and the σ^+ constants by two straight lines with different slopes.

In Figs. 4*b* and 4*c* the straight lines designated by *y* correspond to the distribution of that free-electron pair over both systems *A* and *B* of structure *V* whereas the straight lines *x* correspond to the distribution of the free-electron pair of nitrogen in the phenylimino group caused by substituents merely over system *A* of structure *V*.

On the other hand, the silver salts appear as one conjugated system in which the electron pair of nitrogen in the phenylimino group is uniformly delocalized by the effect of substituents. This difference in the distribution of electrons of nitrogen in the phenylimino group of the silver salts in comparison with the potassium salts is due to a shift of the double bond $>C=O$ in the structure of potassium salts to the heterocyclic nitrogen. In the structure of the silver salts of 3-(X-phenyl)iminoxindoles this shift results in an extinguishment of the strong $-I_{eff}$ and $-M_{eff}$ effects in the silver salts and a uniform distribution of the free-electron pair of nitrogen in the phenylimino group over whole molecule is established by the effect of substituents.

References

1. Bayer, A., *Ber.* **15,** 2093 (1882).
2. Bayer, A., *Ber.* **16,** 2188 (1883).
3. Cleacz, M., *Ber.* **50,** 511 (1917).
4. Heller, G., *Ber.* **40,** 1291 (1907).
5. Hantzsch, A., *Ber.* **54B,** 1221 (1921).
6. Hantzsch, A., *Ber.* **55B,** 3180 (1922).
7. Hovorka, V. and Diviš, L., *Rozpravy Čs. akademie věd.* (Discussion of the Czechoslovak Academy of Sciences.) **59,** 1 (1949).
8. Hovorka, V. and Diviš, L., *Collect. Czech. Chem. Commun.* **13,** 589 (1948).

9. Eckschlager, K., *Chem. Listy 56,* 489 (1962).
10. Gabriel, S., *Ber. 16,* 518 (1883).
11. Hovorka, V. and Sýkora, V., *Chem. Listy 32,* 241 (1938).
12. Košturiak, A. and Šingliar, M., *Petrochémia 13,* 120 (1973).
13. Košturiak, A. and Ninčáková, A. *Petrochémia 13,* 30 (1974).
14. McDaniel, D. M. and Brown, H. C., *J. Org. Chem. 23,* 420 (1938).
15. Tiee, B. B., Lee, J., and Hendal, F. H., *J. Amer. Chem. Soc. 83,* 329 (1963).
16. Brown, H. C. and Okomoto, V., *J. Amer. Chem. Soc. 80,* 4979 (1958).
17. Exner, O., *Chem. Listy 53,* 1302 (1959).
18. Košturiak, A. and Perjéssy, A., *Collect. Czech. Chem. Commun. 41,* 410 (1976).
19. Mangini, A. and Passerini, R., *Gazz. Chim. Ital. 85,* 840 (1951).

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