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schemes of structures I-IV

Figure 1: schemes of structures I-IV

Abstract

Full Text

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THE EXO-INTERACTION BAND IN THE SPECTRA OF SALTS OF DIPHENYLALKANES WITH NO_2 AND OH GROUPS IN DIFFERENT NUCLEI

(Presented by Academician B. A. Kazanskii, 30 IX 1961)

Taking into account that the electron-donor properties and the influence on the spectrum of the phenolate $\overset{\times\times}{O}^-$ in chromophores of the VKA type* are very close to those of the NMe_2 group (2), we suggested, on the basis of a number of our works, for example (3,4), that phenolate chromophoric components of the type $C_6H_5O^-$, n-$CH_3C_6H_4O^-$ should form colored complexes of the type [VK···AK], for example $[C_6H_5NO_2 \ldots C_6H_5O^-]Na^+$, analogous to $[C_6H_5NO_2 \ldots C_6H_5NMe_2]$.

Further, proceeding from the fact established by us that the coloration of NMe_2 derivatives of n-NO_2-diphenylmethane (n-NO_2-DFM) (I, $A^2 = NMe_2$) and n-NO_2-diphenylethane (n-NO_2-DFE) (II, $A^2 = NMe_2$) is a consequence not of endomolecular (through CH_2 or CH_2CH_2), but of exomolecular interaction of the VK and AK systems (5), it could be expected that compounds of the type $O_2N—(CH_2)_n—OH$ would form colored salts of the type $[O_2N—(CH_2)_n—O^-]Na^+$ as a result of strengthening of the donor group OH upon conversion to O^- and of manifestation of exo-interaction with formation of a colored complex of structure III or, more probably, IV.

To test this, derivatives of n-NO_2-DFM (I) and n-NO_2-DFE (II) with $A^2 =$ OH were synthesized, and the spectra of solutions of their salts ($A^2 = O^-$) were compared with the spectrum of a solution of $[O_2N\ CH_3 + H_3C\ ONa]$, in which, according to what was stated above, formation of a colored complex $[O_2N\ CH_3 \ldots CH_3\ O^-]Na^+$ could be expected (Figs. 1, 2; the numbers of the curves correspond to the numbers in Table 1).

On addition to solutions No. 1 and No. 8 in alcohol of an equimolecular amount of caustic alkali, the pale-yellow coloration, as we expected, turns yellow. Bands I^a and II^a of the nucleus system a, on conversion to the salt, remain in the same place (No. 4 and No. 9); in the UV there appears band I^b of the salt of component H_3C ONa (No. 5). The deepening of the color is a consequence of the appearance of a new absorption region—the exo-band ~ 420 mμ (Figs. 1, 2), close to the exo-band (II, $A^2 = NMe_2$) (^{5}) λ_{max}430 mμ. For No. 9 II ($A^2 = O^-$) the band appears in the form of a distinct bend, and for No. 7 only in the form of a shoulder ($\varepsilon = 10^3$ at $\lambda \sim 420$ mμ).**

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* A conjugated cochromoform system (^{1}), constructed from an electrophilic chromophoric component B (for example NO_2), an electron-donor chromophoric component A (for example NMe_2), and a K-conjugated chromophoric component, for example n-C_6H_4—(designation Φ).

** With respect to the properties and spectra of I and II with $A^2 = NH_2$ and NMe_2, one should be guided by (^{5,6}), since (^{7}) contains a number of errors.

Table 1

No.*	Compound (m.p., °C, and color)	Concentration, mol/L	Solvent**	Nucleus **b** system, band I: λmax	Nucleus **b** system, band I: εmax	Nucleus **b** system, band II: λmax	Nucleus **b** system, band II: εmax	Nucleus **a** system, band I: λmax	Nucleus **a** system, band I: εmax	Nucleus **a** system, band II: λmax	Nucleus **a** system, band II: εmax	Exo-band: λmax	Exo-band: εmax	Absorption limit at lgε = 1, mμ
1	$O_2N\Phi CH_2\Phi OH$	10^{-2}	C	–	–	–	–	275	11360	330	1700	–	–	412
1a	(119°, pale yellow)	10^{-4}	C	–	–	–	–	275	13670	330	1900	–	–	400
1		10^{-2}		–	–	–	–	275	11600	330	1000	–	–	389
1		10^{-4}		–	–	–	–	275	12200	330	1000	–	–	387
1		10^{-4}		–	–	–	–	270	14400	330	430	–	–	387
2	$H_3C\Phi OH$	10^{-4}	C	222	8100	280	2340	–	–	–	–	–	–	–
3	($O_2N\Phi CH_3$ + $H_3C\Phi OH$), calculated	10^{-4}	C	–	–	–	–	274	12800	320	830	–	–	385
4	$[O_2N\Phi CH_2\Phi O^-]$ Na^+	10^{-2}	C + NaOH	250	10400	–	–	275	12400	330	1430	for 420	270	498
4a	(yellow)	10^{-4}	Same	–	–	–	–	275	12770	330	1600	for 420	112	477

No.*	Compound (m.p., °C, and color)	Concentration, mol/l	Solvent***	Nucleus **b** system, band I: λmax	Nucleus **b** system, band I: εmax	Nucleus **b** system, band II: λmax	Nucleus **b** system, band II: εmax	Nucleus **a** system, band I: λmax	Nucleus **a** system, band I: εmax	Nucleus **a** system, band II: λmax	Nucleus **a** system, band II: εmax	Exo-band: λmax	Exo-band: εmax	Absorption limit at lgε = 1, mμ
5	$[H_3C\Phi O^-]$ Na^+	10^{-2}	» »	225 (242)	5300 (5900)	290	1700	–	–	–	–	–	–	–
5a		10^{-4}	» »	225	6000	280	1700	–	–	–	–	–	–	–
6	$O_2N\Phi CH_3$ + $[H_3C\Phi O^-]Na^+$, calculated	10^{-2}	» »	245	10400	–	–	274	13850	330	550	–	–	392
6a		10^{-4}	» »	–	–	–	–	274	12300	320	830	–	–	385
7	» », found	10^{-2}	» »	245	7840	–	–	275	10200	330	500	420	10	412
7a		10^{-4}	» »	–	–	–	–	275	11800	330	450	390	12	391
8	$O_2N\Phi CH_2CH_2OH$	10^{-2}	C	225	11700	–	–	275	9900	330	1000	–	–	431
8a	(118°, pale yellow)	10^{-4}	C	225	17370	–	–	275	13500	330	980	–	–	402
8		10^{-4}		–	–	–	–	270	15600	310	700	–	–	402
9	$[O_2N\Phi CH_2CH_2O^-]$ Na^+	10^{-2}	C + NaOH	247	10400	–	–	277	12100	330	1200	420	210	522
9a	(yellow)	10^{-4}	Same	–	–	–	–	277	12700	330	1100	420	160	514
10	$O_2N\Phi CH_2\Phi NHCOCH_3$	10^{-2}	C	255	16900	–	–	270	12760	330	1260	–	–	415
10a	(162°, pale yellow)	10^{-4}	C	255	24450	–	–	270	15570	330	1550	–	–	405
10		10^{-4}		–	–	–	–	270	13300	330	1100	–	–	395
10		10^{-4}		250	30100	–	–	270	13300	320	1600	–	–	395
11	$H_3C\Phi NHCOCH_3$	10^{-4}	C	245	19700	–	–	–	–	–	–	–	–	–

No.*	Compound (m.p., °C, and color)	Concentration, mol/l	Solvent**	Nucleus **b** system, band I: λmax	Nucleus **b** system, band I: ϵmax	Nucleus **b** system, band II: λmax	Nucleus **b** system, band II: ϵmax	Nucleus **a** system, band I: λmax	Nucleus **a** system, band I: ϵmax	Nucleus **a** system, band II: λmax	Nucleus **a** system, band II: ϵmax	Exo-band: λmax	Exo-band: ϵmax	Absorption limit at lgϵ = 1, mμ
12	($O_2N\Phi CH_3$ + $H_3C\Phi NHCOCH_3$), calculated	10^{-4}	C	245	24900	–	–	270	13450	320	830	–	–	385
13	$O_2N\Phi CH_2CH_2\Phi NHCOCH_3$	10^{-2}	C	247	20360	–	–	265	16100	330	1000	–	–	430
13a	(189°, pale yellow)	10^{-4}	C	247	22200	–	–	265	16200	330	1000	–	–	396
13		10^{-4}		245	27360	–	–	–	–	320	850	–	–	396

* The numbers of compounds and solutions in Table 1 correspond to the numbers in Figs. 1 and 2. For comparison, see the spectra of the parent compounds ($O_2N\Phi CH_3$; $O_2N\Phi CH_2\Phi$; $O_2N\Phi CH_2CH_2\Phi$) in the table in [5].

** C –alcohol, –benzene, –*n*-hexane. The NaOH concentration is equimolecular with the corresponding phenol.

That these bands are of the same origin and are a consequence of the exomolecular interaction of the systems of nucleus *a* (BK(A′)) and nucleus *b* (A′KA^2) is confirmed by the following: 1) its position coincides with the exo-band of a solution of the complex $C = 10^{-2}$ mole/liter [O_2N CH_3 + CH_3 ONa] (7, 9, Fig. 2); 2) when the concentration is increased from 10^{-4} to 10^{-2} mole/liter, owing to the shift of the equilibrium

$$\mathrm{BK} + \mathrm{AK} \rightleftarrows [\mathrm{BK} \ldots \mathrm{AK}]$$

to the right, ε at 420 mμ increases (4, 4a, 9, 9a), and the absorption edge shifts toward longer wavelengths.

However, whereas for a solution of the components the formation of the complex at $C = 10^{-4}$ mole/liter almost disappears (7, 7a, Table 1), in the case when the components AK and BK are connected with one another by the group $Q = CH_2CH_2$ and CH_2, the exo-interaction is manifested to a considerably greater extent; the band lies at considerably larger values of ε, and lowering the concentration causes a greater decrease in the value of ε (9, 9a, Fig. 2). This

Fig. 1

Figure 2: Fig. 1

Fig. 2

Figure 3: Fig. 2

indicates that, in the case when the components of the complex are connected with one another in the molecule by the group Q, the conditions for formation of complex (IV) are more favorable ($CH_2CH_2 > CH_2$) than in the case when the components are two independent molecules.

Fig. 1

In the case of weak donors $A^2 = \mathrm{OH}, \mathrm{NHCOCH_3}$ in alcohol, even at $C = 10^{-2}$ mole/liter, almost complete coincidence is observed with the spectrum calculated for the sum of the components (3 and 1, 8; 12 and 10, 13): $\varepsilon_{\max}$ of band I^b for Nos. 10, 13 is a consequence of the superposition of the component bands (12, Table 1). Exo-interaction in an incipient form is manifested here only in a small shift of the absorption edge relative to the calculated curve, more clearly when the concentration is increased from 10^{-4} to 10^{-2} mole/liter. That the indicated effect is a consequence of exomolecular interaction is evident from the fact that the magnitude of the bathochromic shift of the absorption edge increases 1) when the concentration is increased from 10^{-4} to 10^{-2} mole/liter and 2) when the CH_2 group is replaced by CH_2CH_2.

A small effect of endomolecular interaction is manifested only in insignificant bathochromic shifts of bands I^b and II^a with some increase in ε. This effect was explained from the standpoint of the theory of inductively interacting systems (5). The assumptions (8) concerning the presence of a single conjugated system are erroneous; the influence of NO_2 on the decrease in the reactivity of NH_2 has other causes. If conjugation existed between BKA' and $\mathrm{A}'\mathrm{KA}^2$ (I), then, in view of the considerable increase of the π-system and the presence of a single vector of electron displacement upon excitation by light, we should have observed a significant shift of the principal band I^a.

Thus, the ability of phenolate components to form colored donor-acceptor complexes of the type of aminocomponent complexes with nitro compounds has been established. The ability has been established for phenols of the structure $O_2N\Phi$—Q—ΦOH with $Q = (CH_2)_n$ to form colored salts with the appearance of an exo band as a result of extramolecular interaction. It may be assumed that, for a large value of n, exo–

Fig. 2

interaction may arise not only by an intermolecular route, but also intramolecularly, through bending of the chain. By the term "exomolecular" (^{9,10}) we include interactions between the A K and B K systems, carried out not only intermolecularly but also intramolecularly through bending of the chain when structural possibilities are present.

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CITED LITERATURE

1. V. A. Izmail' skii, *Khim. nauka i prom.*, **3**, No. 2, 232 (1958).
2. V. A. Izmail' skii, E. E. Miliaresi, *DAN*, **141**, No. 4, 875 (1961).
3. V. A. Izmail' skii, A. N. Guseva, *ZhOKh*, **24**, 1403 (1954).
4. V. A. Izmail' skii, S. V. Dmitrienko, *ZhOKh*, **29**, 1843 (1959).
5. V. A. Izmail' skii, V. A. Glushenkov, *DAN*, **139**, No. 2, 361 (1961).
6. V. A. Izmail' skii, V. A. Glushenkov, *Zhurn. Vsesoyuzn. khim. obshch. im. Mendeleeva*, **6**, No. 1, 111 (1961).
7. V. A. Izmail' skii, G. V. Alekseeva, R. S. Tsekhanskii, in: *Some Questions of the Synthesis and Application of Dyes* (Scientific-Technical Conference, 1954), 1956, p. 76.
8. L. M. Litvinenko, N. F. Levchenko, *ZhOKh*, **29**, issue 5, 1673 (1960).
9. V. A. Izmail' skii, P. A. Soldov, *DAN*, **60**, No. 4, 587 (1948).
10. V. A. Izmail' skii, *Proceedings of the 8th Conference on Aniline-Dye Chemistry*, 1947, Publishing House of the Academy of Sciences of the USSR, 1950, p. 110.

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