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structural formulas I and II

Figure 1: structural formulas I and II

Abstract

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GENETICS OF THE SPECTRA OF DERIVATIVES OF BENZYLIDENEANILINE AND BENZYLIDENE-1-NAPHTHYLAMINE CONTAINING NO_2 AND NMe_2 GROUPS

(Presented by Academician A. N. Terenin, March 23, 1964)

Izmailskii and Smirnov ([1]) pointed out that, in discussing the spectra of benzylideneaniline (BA) and its derivatives (I) and (II), two types of participation of CH = N in conjugation should be taken into account: by means of the π-electrons of the double bond and by means of the free doublet of the N atom. In the latter case the coplanarity of nuclei *a* and *b* is disturbed. This was confirmed by the fact that in the case (II, B = NO_2) bands of the $H_2N\Phi NO_2$ system are observed.

K –the entire conjugated system; K_b –the conjugated system of nucleus *b* with a substituent and the CH = N group (the K_b band); K_a –bands of the system of the aniline nucleus *a* with a substituent; B = H, NO_2; A = H, NMe_2, OH, OCH_3.

In analyzing the spectra, account was taken of the possibility of manifestation in the spectrum of a band of a single conjugated system of the stilbene type (K-band) (Fig. 4 ([1]); Fig. 13 ([2])) and of bands of partial conjugated systems: nucleus *b* with CH = N (K_b –band of the $XC_6H_5CH = N$ system) and nucleus *a* with the N atom of the CH = N group (K_a –band) (I, II)*. The same hypothesis was put forward by Ebara ([3]), without mentioning priority ([1]), and with erroneous spectroscopic data**. Brocklehurst ([4]) confirmed the idea of noncoplanarity ([1]) and gave an interpretation of the spectral bands of BA at ~312 and 256 mμ. He assigned the 256 mμ band to the K_b system, comparing it with $C_6H_5CH{=}NMe$ (λ_max 246 mμ). The presence of the K_a band of the aniline $=NC_6H_5$ system has been observed ([3], [5]).

We undertook to check these conclusions on a series of BA and benzylidene-1-naphthylamine (BNph) derivatives (III) and (IV), and, in order to eliminate

structural formulas III and IV

Figure 2: structural formulas III and IV

possible decomposition in alcohol ([1]) of derivatives (II, IV, B = NO_2), we investigated the spectra in dichloroethane (DCE).

* In the present work we have used simplified designations of the chromophoric systems K, K_a, and K_b, without indicating all the constituent parts of the chromophoric system (BKA, BK, AK, etc.), as is customary in our papers.

** Ebara did not take into account the decomposition of compounds (II, B = NO_2) in alcohol ([1]) and even in mixtures of alcohol and conc. HCl. As a result, the conclusions lack an experimental basis and are sometimes clearly erroneous.

Table 1

Spectra of compounds in 1,2-dichloroethane, $C = 10^{-4}$ mol/l

No.	Compound, Φ = C_6H_5	K band λ_{max}	K band ε_{max}	K_b band λ_{max}	K_b band ε_{max}	K_a, 1-band λ_{max}	K_a, 1-band ε_{max}	K_a, 2-band λ_{max}	K_a, 2-band ε_{max}	K_a, 2′-band λ_{max}	K_a, 2′-band ε_{max}
1	ΦCH = NΦ	312	~8200	265	16450	overlap		~237	8730	–	–
2	ΦCH = NMe	–	–	246	19400	–	–	–	–	–	–
3	ΦCH = NΦNO_2	–	–	overlap	–	–	–	332	17700	226	16050
4	H_2NΦNO_2	–	–	–	–	–	–	350	14900	227	6580
5	O_2NΦCH = NΦ	347	16560	292	16120	overlap		overlap	–	–	–
6	O_2NΦCH = NMe	–	–	285	15700	–	–	–	–	–	–
7	O_2NΦCH = NNMe_2	410	18730	282	19200	overlap		overlap	–	–	–
8	H_2NΦNMe_2	–	–	–	–	313	2000	250	15850	–	–
9	ΦCH = NNMe_2	375	18250	255	18800	~320	6680	overlap		–	–
10	Me_2NΦCH = NΦ	385	35400	~320	17650	overlap		240	13970	–	–
11	Me_2NΦCH = NMe	–	–	305	24000	–	–	–	–	–	–
12	Me_2NΦCH = NNO_2	410	27500	312	11000	–	–	overlap		225	13470
	Nph = naphthyl, naphthylene					α-band [3]		p-band [3]		β-band [3]	

No.	Compound, Φ = C_6H_5	K λ_{max}	K ε_{max}	K_b λ_{max}	K_b ε_{max}	K_a, 1-band λ_{max}	K_a, 1-band ε_{max}	K_a, 2-band λ_{max}	K_a, 2-band ε_{max}	K_a, 2′-band λ_{max}	K_a, 2′-band ε_{max}
13	ΦCH = N—Nph—1	347	8400	257	20200	–	–	290	10700	232	44600
14	H_2N—Nph—1	–	–	–	–	–	–	322	6700	245	27500
15	ΦCH = N—Nph—NO_2—2,4	362	18800	–	–	–	–	380	13600	230	26000
16	H_2N—Nph—NO_2—1, 4	–	–	–	–	–	–	402	14750	257	13280
17	O_2NΦCH = N—Nph—2	390	8610	282	21200	–	–	overlap		230	45300
18	O_2NΦCH = N—Nph—NO_2—2,4	412	17200	280	19500	–	–	overlap		257	18000
19	H_2N—Nph—NMe_2—1, 4	–	–	–	–	–	–	342	8980	255	16900
20	O_2NΦCH = N—Nph—NO_2—2,4	382	20630	–	–	–	–	392	13450	–	–
21	ΦCH = N—Nph—NMe_2—2,4	380	16000	257[4]	25600	–	–	overlap		257[4]	25600
22	Me_2NΦCH = N—Nph—1	387	30800	overlap		–	–	overlap		230	33700
23	Me_2NΦCH = N—Nph—NMe_2—2,4	428	28600	340	18350	–	–	overlap		247	29200
24	Me_2NΦCH = N—Nph—NO_2—2,4	422	27400	342 322	11600 10700	–	–	overlap		255	16350
25	ΦCH = N—Nph—2	325	12200	267	30700	overlap		overlap		225	38200
26	H_2N—Nph—2	–	–	–	–	345	2240	282	6810	240	37920
27	O_2NΦCH = N—Nph—2	370	17000	282	23700	overlap		260	21800	222	71000
28	Me_2NΦCH = N—Nph—2	362	37200	~ 320	14850	overlap		290	10180	232	32000
29	ΦCH = N—Antr[5]	397	10200	overlap		–	–	overlap		260	109000
30	H_2NAntr	–	–	–	–	–	–	390	4790	262 242	56600 59100
31	O_2NΦCH = N—Antr	427	7450	~ 280	24500	–	–	~ 390	5800	255	120000
32	Me_2NΦCH = N—Antr	410	28900	350	20300	–	–	overlap		260	85300

[1] The numbers of the compounds in Table 1 correspond to the numbers in the figures.
[2] Classification of the bands of the *a* nucleus according to [11].
[3] Classification of the bands of Nph derivatives (Nos. 13-28) and anthracene (Antr) derivatives (Nos. 29-32) according to [9].
[4] Superposition of bands.
[5] Antr = α-anthranyl.

In the spectrum of BNph (IV, $A = B = H$, Table 1, No. 13) four bands were found: the K-band λ_{max} = 347 mμ; the small ε (8400) is caused by violation of coplanarity; the K_b-band at 257 mμ of the ΦCH = N system; and the bands of the K_a system at 290 and 233 mμ—both bands of the α-naphthylamine system, shifted toward the UV because of replacement of the H_2N group by the

Figure 1

Figure 3: Figure 1

Fig. 2

Figure 4: Fig. 2

CH = N group and partial disturbance of conjugation of the N atom with the Nph nucleus.

Spectra of ΦCH = NArNO$_2$. Upon introduction into BA of the strong electron-acceptor group NO$_2$ in the *n*-position to the N atom of nucleus *a*, conjugation of the N-atom doublet is enhanced. The K_a band at 322 mμ of BA-NO$_2$-4 is a hypsochromically shifted band of the *n*-NO$_2$-aniline system (Nos. 3, 4, Fig. 1, Table 1). Even a χ'-band is observed

Fig. 1

~226 mμ, typical for cochromophores of the BKA type ([6]). The angle of rotation of ring *a* with respect to ring *b* should approach 90°. However, the increase in ϵ ($\Delta\epsilon$ 2800) in comparison with 4-NO$_2$-aniline indicates the possibility of superposition of a stilbene-type K band (4-NO$_2$-stilbene 350 mμ). The hypsochromic shift of the λ_max band of the O$_2$NΦNH$_2$ system ($\Delta\lambda = -18$ mμ) is explained by replacement of the H$_2$N group by CH=N. The K_b band (O$_2$NΦCH=N) is overlapped.

Fig. 2

Similarly, for BNph-NO$_2$-4 (No. 15), λ_max = 380 mμ is a hypsochromically shifted band of 4-nitro-1-naphthylamine ($\Delta\lambda = -22$ mμ). The 262 mμ band belongs mainly to ring *b* (probably with some superposition of the *β*-band of NO$_2$NphNH$_2$-1,4, 257 mμ) (Fig. 1, Nos. 15, 16, 2). This is confirmed by the observation that in O$_2$NΦCH=NNphNO$_2$-1,4 (No. 20) the 262 mμ band is shifted to 282 mμ, which is close to 285 mμ for O$_2$NΦCH=NCH$_3$ (No. 6, Table 1). Such a shift would not have been observed if the 262 mμ band belonged to ring *a*. The 230 mμ band belongs to the naphthalene system.

Spectra of O$_2$NΦCH=NArX. The concept of disturbance of coplanarity ([1]) and the possibility of manifestation of three quasiautonomous* systems is also confirmed for derivatives of types (I, B = NO$_2$, A = H) and (III, B = NO$_2$, A = H), as well as in the presence in them of an additional 4-NMe$_2$ group in ring *a*. In all compounds 5, 17 and 7, 18 we find a K band and also a K_b band corresponding to the O$_2$NΦCH=N system (No. 6) (Fig. 2, Table 1). The system of ring *b* thus reveals its quasiautonomy, which is a consequence of the absence of coplanarity. In the naphthalene 4-nitrobenzylidene derivatives the *β*-bands of the amino system of ring *a* are also clearly visible: for No. 17 (III, B = NO$_2$, A = H) 230 mμ (ϵ = 45,300) (Fig. 2, Table 1). For No. 18 (III, B = NO$_2$, A = NMe$_2$) the band 257 mμ (ϵ = 18,000) is very close to the band 255

mμ (ϵ = 16,900) of N,N-dimethylnaphthylenediamine-1,4 (No. 19).

Spectra of 4′-Me_2NΦCH=NArX. The high intensity of the K bands of 4′-Me_2NBA and 4′-Me_2NBNph (Table 1, Nos. 10, 22) (ϵ = 35,300, 30,500) indicates their genetic relationship with the K band of 4-Me_2NΦCH=NCH_3 (λ_max = 305 mμ, ϵ = 24,000). The increase in ϵ simultaneously with λ_max from 305 to 355 and 367 mμ is a consequence of addition to the conjugated

* In the translation ([12]) of article ([11]), the term "quasiautonomous" was translated incorrectly: instead of *quasiautonomic*, *quasiatomic* was given.

system of the benzene or naphthalene nucleus and by approximation to the system 4-Me_2NΦCH = CHΦ. Complete coplanarity, however, is absent, as is evident from the presence of the K_b band, which appears in the lg $\varepsilon(\lambda)$ curve as an inflection in the region of 320 mμ, and also of the K_a band of the system = NC_6H_5 (240 mμ) (Table 1, Nos. 10, 10a). When 4-NO_2 is added to nucleus a, as might be expected, a considerable further bathochromic shift of the K band is observed to 405 (No. 12) and 425 mμ (No. 24); however, ε in both cases decreases somewhat (Table 1), and, in addition, bands appear in the region of 312 (No. 12), 322 and 342 mμ (No. 24), which we regard as bands of the K_b system with superposition of the system of nucleus a. This indicates that in both cases there are deviations from coplanarity.

Spectra of XΦCH = NArNMe_2**.** Of considerable theoretical interest is the observation [1] that NMe_2 in nucleus a on the side of the N atom in BA produces a substantially larger bathochromic effect than in nucleus b: in BA-NMe_2-4 and BNph-NMe_2-4 (Nos. 9, 21) λ_{max} is 375 and 380 mμ; for 4′-Me_2N-BA and 4′-Me_2N-BNph (Nos. 10, 22) λ_{max} is 355 and 367 mμ (Table 1). The 4-NMe_2 group creates a δ^- charge on the carbon of nucleus c bonded to the N atom of the CH = N group and thereby reduces the capacity of the N-atom doublet for conjugation with nucleus a and promotes the formation of a more coplanar conjugated K system of the type 4-Me_2NΦCH = CHΦ (λ_{max} 340 mμ, ε 29 500 in alcohol). That the disturbance of coplanarity in No. 9 is nevertheless considerable is evident from the small value of ε, 18 250, and also from the presence of bands of the K_b and K_a components. As a result of steric hindrance and the withdrawal of 4-NMe_2 from the plane of the naphthalene nucleus, the intensity of the K band for BNph-NMe_2-4 (No. 21) is greatly reduced, ε = 11 600 instead of 18 250 for No. 9. An analogous decrease in λ_{max} and ε_{max} of the K band as a consequence of steric hindrance is found for No. 18 in comparison with No. 7 (Fig. 2, Table 1).

The explanation set forth for the stronger influence on the magnitude of the shift of λ_{max} of NMe_2 in nucleus a than in b differs from Smith' s explanation [10], based on LCAO-MO calculations, by transitions to an excited state associated with electron migration toward the structures

$$\Phi - \overline{CH} - N = \ +$$

and

$$- \quad = \mathrm{CH} - \mathrm{N} = \quad + .$$

The author did not take into account that the transition to the excited state depends not so much on the microstructure of the initial BA system as on the ground state and the steric conditions in the microstructure of the substituted derivative. The substituent may introduce changes into the electron distribution in the ground and excited states. Our investigations provide an approach to explaining the genetics of the spectra from the standpoint of the possibility of manifestation in the spectra of separate quasi-autonomous chromophoric systems connected with different conditions for electron migration upon transition to the excited state.

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