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MICROSTRUCTURE AND SPECTRA OF DERIVATIVES OF BENZYLIDENEANILINE AND AZOBENZENE AND OF THEIR SALTS

Table 1

1961

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Abstract

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CHEMISTRY

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MICROSTRUCTURE AND SPECTRA OF DERIVATIVES OF BENZYLIDENEANILINE AND AZOBENZENE AND OF THEIR SALTS

(Presented by Academician B. A. Kazanskii, 19 V 1961)

To establish the cause of the deepening of the color of *n*-dimethylaminoazobenzene (∗*n* ∗ -Me_2N—AB) upon addition of H^+, it is necessary to compare it with the spectra of *n*-Me_2N-benzylideneaniline (∗*n* ∗ -Me_2N—BA) and its analogues ([2,3]). The correct approach ([1,4,5]), from the standpoint of the connection between color and "mesostructure," "mesostate," was first developed as early as 1913-1918. It was substantiated by criticism of the quinonoid structure, by establishment of the principle of the gradual shift of the spectrum when the structure is changed, and by the analogy in spectral shifts under the action of acid on *n*-Me_2N–BA, *n*-Me_2N–AB and under the action of alkali on *n*-$O_2N\Phi OH$* ([2]). The genesis of the spectra has been investigated (Table 1).

Table 1

Absorption spectra of derivatives of benzylideneaniline and azobenzene in $CHCl_3$ at $C = 10^{-3}$ mol/l

No.	Compound, where Φ —*n*-phenylene or C_6H_5	K-band λ_{max}	K-band ε_{max}	K-band $\Delta\lambda$	$[HCl]^2$ mol/l
1	Φ– N CH– Φ	265	16600	0	
2	Φ– N CH– Φ– OCH_3	284	18200	+19	
2	Φ– N CH– Φ– OCH_3	(~317)	(~15000)		

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No.	Compound, where Φ —*n*-phenylene or C_6H_5	K-band λ_{max}	K-band ε_{max}	K-band $\Delta\lambda$	$[HCl]^2$ mol/l
3	Φ–N CH–Φ–OH	285	17250	+20	
3	Φ–N CH–Φ–OH	(315)	(14350)		
4	[Φ–N CH–Φ–O^-]$^-K^+$	360	38400	+95	$[KOH] \cdot 10^{-1}$ mol/l
5	Φ–N CH–Φ–NMe_2	356	34100	+91	
6	[Φ–NH^+ CH–Φ–OCH_3]$^+Cl^-$	365	15400	+100	10^{-2}
7	[Φ–NH^+ CH–Φ–OH]$^+Cl^-$	375	16800	+110	10^{-1}
7	[Φ–NH^+ CH–Φ–OH]$^+Cl^-$	(390)	(15900)		
8	[Φ–NH^+ CH–Φ–NMe_2]$^+Cl^-$	436	54200	+171	$2 \cdot 10^{-3}$
9	Φ–N=N–Φ	317	16350	0	
9	Φ–N=N–Φ	(~324)	(~15200)		
10	Φ–N=N–Φ–OCH_3	350	24400	+33	
11	Φ–N=N–Φ–OH	345	21700	+28	

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No.	Compound, where Φ —*n*-phenylene or C_6H_5	K-band λ_{max}	K-band ε_{max}	K-band $\Delta\lambda$	$[HCl]^2$ mol/l
12	[Φ–N=N–Φ–O^-]$^-K^+$	407	27600	+90	[KOH] · 10^{-1} mol/l
12	[Φ–N=N–Φ–O^-]$^-K^+$	(~404)	(~26500)		
13	Φ–N=N–Φ–NMe_2	407	28600	+90	
13	Φ–N=N–Φ–NMe_2	(~416)	(~28100)		
14	[Φ–NH^+=N–Φ–OCH_3]$^+Cl^-$	462	28300	+145	10^{-1}
15	[Φ–NH^+=N–Φ–OH]$^+Cl^-$	465	41200	+148	10^{-1}
16	[Φ–NH^+=N–Φ–NMe_2]$^+Cl^-$	535[3]	51400	+218[3]	10^{-1}
16	[Φ–NH^+=N–Φ–NMe_2]$^+Cl^-$	(525 and 545)	51000		

[1] Side bands appearing as inflections are marked with the sign ~.
[2] We used solutions of HCl in $CHCl_3$ instead of $(CH_3CO)_2O$ ([2,3]). The use of HCl in EtOH gives, for azo dyes, abnormal spectra ([11]).
[3] λ_{max} by the half-width of the band. Two peaks are indicated below.

The electronic systems of the azo group or azomethine group in derivatives of types I, II, IV, V are *chromophoric components* that participate with other chromophoric components in the formation of a unified electronic system of a complex chromophore, a *cochromophore* ([6]). The starting derivatives BA, AB

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and their HCl salts may be regarded as compounds whose cochromophore is constructed according to the type B–K–A of our classification of chromophoric systems, where K is the conjugated system n-C_6H_4–; B is an electrophilic chromophoric component: ΦN=CH, ΦN=N, ΦNH^+=CH, ΦNH^+=N, NO_2; A is an electron-donor chromophoric component ([6]): NMe_2, O^-, OH. The question reduces to comparing I, II, IV, V with the structure and spectra of simpler benzene derivatives of the type B–Φ–A, for example III (Table 1, 4).

* Φ–n-phenylene; at the end of the chain–phenyl.

The spectrum of the bases BA and AB is connected with the mesomeric structure. The microstructure formulas Iv, IIv are analogous to IIIv. They are a simplified transcription of the ideas concerning the mixed structure that follows from consideration of the schemes Ia Ib, IIa IIb, IIIa IIIb*.

$$\mathrm{Ph{-}N{=}CH{-}\langle C_6H_4\rangle{-}NMe_2} \leftrightarrow \mathrm{Ph{-}\overline{N}{-}CH{=}\langle C_6H_4\rangle{=}\overset{+}{N}Me_2}$$

(Ia) (Ib)

$$\mathrm{Ph{-}N{=}N{-}\langle C_6H_4\rangle{-}NMe_2} \leftrightarrow \mathrm{Ph{-}\overline{N}{-}N{=}\langle C_6H_4\rangle{=}\overset{+}{N}Me_2}$$

(IIa) (IIb)

$$\mathrm{Ph{-}\overset{-}{N}{=}CH{=}\langle C_6H_4\rangle{=}\overset{+}{N}Me_2} \qquad \mathrm{Ph{-}\overset{-}{N}{=}N{=}\langle C_6H_4\rangle{=}\overset{+}{N}Me_2}$$

(Iv) (IIv)

$$\mathrm{O_2N{-}\langle C_6H_4\rangle{-}NMe_2} \leftrightarrow \mathrm{\overline{O_2N}{=}\langle C_6H_4\rangle{=}\overset{+}{N}Me_2}$$

(IIIa) (IIIb)

$$\mathrm{O_2\overset{-}{N}{=}\langle C_6H_4\rangle{=}\overset{+}{N}Me_2}$$

(IIIv)

The magnitude of the bathochromic shift of the K-band maximum λ_{max} ($\pi \rightarrow \pi^*$ transition), according to the rule relating the bathochromic effect to the degree of electronic displacements in the ground state ([8]), is the greater, the greater the electrophilicity of B and the electron-donor power of A. The bathochromic effect upon addition of H^+ to I and II can be explained by an increase in the electrophilicity of B when the groups PhN=CH, PhN=N are replaced by the groups $PhNH^+$=CH, $PhNH^+$=N. The degree of electronic displacements expressed by the microstructure formulas IVv, Vv can be evaluated only by

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comparing IVa IVb, Va Vb. In Figs. 1, 2 and Table 1 we see that the actual gradual shifts of the K-band upon strengthening the groups A and B very much resemble the shifts observed for compounds of the type B–Ph–A (Tables 2, 3, 4).

$$\left[\mathrm{Ph{-}\overset{+}{N}H{=}CH{-}\langle C_6H_4\rangle{-}NMe_2} \leftrightarrow \mathrm{Ph{-}NH{-}CH{=}\langle C_6H_4\rangle{=}\overset{+}{N}Me_2}\right]^+$$

(IVa) (IVb)

$$\left[\mathrm{Ph{-}\overset{+}{N}H{=}N{-}\langle C_6H_4\rangle{-}NMe_2} \leftrightarrow \mathrm{Ph{-}NH{-}N{=}\langle C_6H_4\rangle{=}\overset{+}{N}Me_2}\right]^+$$

(Va) (Vb)

$$\left[\mathrm{Ph{-}\overset{+}{N}H{=}CH{=}\langle C_6H_4\rangle{=}\overset{+}{N}Me_2}\right]^+ \qquad \left[\mathrm{Ph{-}\overset{+}{N}H{=}N{=}\langle C_6H_4\rangle{=}\overset{+}{N}Me_2}\right]^+$$

(IVv) (Vv)

The schemes IVa IVb, Va Vb make it possible to approach an explanation of the increase in ε upon transition to the cation (Figs. 1, 2) in comparison with Nos. 2, 6; 10, 14 (Table 1) from the point of view of approximation of the structure to a symmetrical one ([12]) owing to the presence at the periphery of groups with similar electron-withdrawing effect: the action of NMe_2 (IVb, Vb), according to ([13]), lies close to the action of NHPh (IVa, Va).

Table 2

Comparison of the effects of bathochromic shift of the K-band ($\Delta\lambda^k_{max}$ in compounds of the type B–$\langle C_6H_4\rangle$–A upon strengthening of the electrophilic chromophoric component B (λ_{max} in mμ))

B	No. 1: *B* PhN=CH	No. 2: NO_2	No. 2: Δλ to No. 1	No. 3: *B* PhN=N	No. 3: Δλ to No. 1	No. 4: *B* PhNH⁺=CH	No. 4: Δλ to No. 1	No. 5: *B* PhNH⁺=N	No. 5: Δλ to No. 1	No. 6: Δλ to No. 3
OCH_3	284	305	+21	350	+66	365	+81	462	+178	+112
OH	285	314	+29	345	+60	375	+90	465	+180	+120
NMe_2	356	387	+31	407	+51	436	+80	535	+179	+128

The effects of bathochromic shifts upon transition to the cation when the PhN=CH group is replaced by the $PhNH^+$=CH group proved to be analogous

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Fig. 1. Absorption spectra of benzylideneaniline derivatives. Curve numbers correspond to the numbers in Table 1

Figure 1: Fig. 1. Absorption spectra of benzylideneaniline derivatives. Curve numbers correspond to the numbers in Table 1

Fig. 2. Absorption spectra of azobenzene derivatives. Curve numbers correspond to the numbers in Table 1

Figure 2: Fig. 2. Absorption spectra of azobenzene derivatives. Curve numbers correspond to the numbers in Table 1

to the shifts upon strengthening B without introducing a (+) charge and to be of approximately the same order as upon

* The symbol , proposed in ([9]), is intended to indicate a lowering of the energy of the molecule as a result of conjugation and mesomerism in comparison with the energy values calculated on the basis of possible limiting ("extreme") structural formulas.

strengthening of donor groups A. Thus, when the ΦN=CH group is replaced by the ΦNH^+=CH group, for compounds with different $A = OCH_3$, OH, NMe_2, $\Delta\lambda^k_{max}$ is 81, 90, 80 mμ, while when the ΦN=CH group is replaced by the ΦN=N group, $\Delta\lambda^k_{max}$ is +66, +60, +51 (Nos. 3, 4,

Fig. 1. Absorption spectra of benzylideneaniline derivatives. Curve numbers correspond to the numbers in Table 1

Fig. 2. Absorption spectra of azobenzene derivatives. Curve numbers correspond to the numbers in Table 1

Table 2). With strengthening of A: both for compounds with a (+) charge (B : ΦNH^+=N, ΦNH^+=CH), and without it (B : ΦN=CH, NO_2, ΦN=N), $\Delta\lambda^k_{max}$ is +72, +71, +82, +57, +73 (Table 3, No. 2). Similarly close to one another

Table 3

Comparison of the effects of bathochromic shift of the K-band ($\Delta\lambda^k_{max}$)

in compounds of the type $B-\overset{\ominus}{\underset{\ominus}{}}-A$ upon strengthening of the electron-donor chromophoric component A (λ_{max} in mμ)

B	No. 1 A: OCH_3	No. 2 A: NMe_2	No. 2 $\Delta\lambda$ to No. 1	No. 3 A: OH	No. 4 A: O^-	No. 4 $\Delta\lambda$ to No. 3	No. 5 $\Delta\lambda$ to No. 2
ΦN=CH	284	356	+72	285	360	+75	+4
ΦNH^+=CH	365	436	+71	–	–	–	–

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B	No. 1 A: OCH_3	No. 2 A: NMe_2	No. 2 $\Delta\lambda$ to No. 1	No. 3 A: OH	No. 4 A: O^-	No. 4 $\Delta\lambda$ to No. 3	No. 5 $\Delta\lambda$ to No. 2
NO_2 ([14])	305	387	+82	314	402.5	+88.5	+15.5
ΦN=N	350	407	+57	345	407	+62	0
ΦNH^+=N	462	535	+73	–	–	–	–

effects are observed when the ΦN=N group is replaced by the ΦNH^+=N group for compounds with different $A = OCH_3$, OH, NMe_2 : $\Delta\lambda^k_{max}$ is +112, +120, +128. The spectra of co-

compounds with $A = O^-$ and with $A = NMe_2$ (Nos. 4, 5 and 12, 13, Table 1; Figs. 1 and 2) almost coincided: $\Delta\lambda = +4$ and 0.

Table 4

Parallel bathochromic shift of the K-band in systems B—phenylene–A with a change in the polarity of one of the chromophoric components (λ_{max} in mμ)

With constant $B = NO_2$, A varies

	$A = H$	OCH_3	OH	NH_2	$NHCH_3$	NMe_2	NEt_2	O^-
λ_{max}	268	305	314	375([7])	386([7])	387([14])	390([7])	400([7])
ε_{max}	7800	13000	13000	15800	18430	18300	19020	21550

With constant $A = NMe_2$, B varies

	$B = COOH$	CH_3COCHO		$\Phi N = CH$	NO_2	$\Phi N = N$	NO	$\Phi NH^+ = CH$	$\Phi NH^+ = N$
λ_{max}	308([7])	337([7])	342([7])	356	390([7])	407	423([7])	436	540
ε_{max}	25400	25600	29200	34100	19020	28600	29400	54200	49100

In summary, we obtain confirmation that auxochromophores can have an analogous microstructure and an analogous spectral band irrespective of whether they are anions VII, cations VIII, or neutral compounds VI (Table 4) ([2], [6], [10]), where, for example, $K = n$-phenylene; A—OCH_3, OH, NMe_2, O^-; B—$\Phi N = CH$, NO_2, $N = N$, $\Phi NH^+ = CH$, NO, $\Phi NH^+ = N$.

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VI. $B-K-\overset{\times\times}{A} \rightleftarrows \overset{\times\times}{B}=K=A^{+}$ or $\overset{\delta-}{B} \rightleftharpoons K \rightleftharpoons \overset{\delta+}{A}$

VII. $[B-K-\overset{\times\times}{A} \rightleftarrows \overset{\times\times}{B}=K=A]^{-}$ or $[\overset{\delta-}{B} \rightleftharpoons K \rightleftharpoons \overset{\delta-}{A}]^{-}$

VIII. $[B-K-\overset{\times\times}{A} \rightleftarrows [\overset{\times\times}{B}=K=A]^{+}]^{+}$ or $[\overset{\delta+}{B} \rightleftharpoons K \rightleftharpoons \overset{\delta+}{A}]^{+}$

We express our gratitude to the management of the Derbenev Chemical Plant for assistance in carrying out the work.

Laboratory of Dye Chemistry and the Problem of Color
at the Moscow Pedagogical Institute
named after V. I. Lenin

Received
17 VI 1961

CITED LITERATURE

1. H. Zollinger, *Chemie der Azofarbstoffe*, Basel, 1958, p. 220.

2. V. A. Izmail' skii, ZhRKhO, **47**, 63, 80 (1915); Chem. Zbl., **1**, 701 (1916) –the term meso is omitted; ZhRKhO, **45**, 1866 (1913); **46**, 183 (1914).

3. V. A. Izmail' skii, ZhRKhO, a) **47**, 1626 (1915); b) **48**, part 11, 1 (1916); c) **50**, 167 (1918); d) **52**, 303 (1920).

4. A. I. Kiprianov, I. N. Zhmurova, ZhOKh, **23**, 626 (1953); **27**, 2704 (1957).

5. E. Sawicki, J. Org. Chem., **19**, 1868 (1954); **21**, 410 (1956).

6. V. A. Izmail' skii, *Khim. nauka i prom.*, **3**, 232 (1958).

7. W. D. Kumler, J. Am. Chem. Soc., **68**, 1184 (1946).

8. V. A. Izmail' skii, E. A. Smirnov, ZhOKh, **26**, 3051 (1956).

9. H. Staab, *Einführung in die theoretische organische Chemie*, Verlag Chemie, Weinheim, 1959, p. 96.

10. V. A. Izmail' skii, *Proceedings of the IV Conference on Aniline-Dye Chemistry in 1939*, Publishing House of the Academy of Sciences of the USSR, 1941, p. 53.

11. G. Smets, A. Delivaux, Bull. Soc. Chim. Belg., **56**, 106 (1947).

SovietRxiv

12. V. A. Izmail' skii, K. A. Nuridzhanian, Yu. Sh. Moshkovskii, *Proceedings of the XIII Conference on Spectroscopy in 1960*, Publishing House of the Academy of Sciences of the USSR (in press).

13. V. A. Izmail' skii, K. A. Nuridzhanian, DAN, **133**, No. 3 (1960).

14. W. F. Forbes, Canad. J. Chem., **36**, 1350 (1958).

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