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Abstract

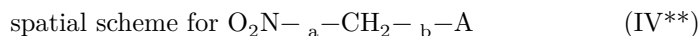
Full Text

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ABSORPTION SPECTRA OF DIPHENYLMETHANE AND DIPHENYLETHANE DERIVATIVES CONTAINING NITRO AND AMINO GROUPS IN DIFFERENT RINGS

(Presented by Academician B. A. Kazanskii, March 21, 1961)

We undertook a study of the absorption spectra of compounds constructed according to the scheme $O_2N- (CH_2)_n A^*$. The spectra were measured for derivatives of *n*-NO₂-diphenylmethane (*n*-NO₂-DPM) (I) and *n*-NO₂-diphenylethane (*n*-NO₂-DPE) (II), in which the electron-donor chromophoric component A₂-H is NHCOCH₃, OH, NH₂, NMe₂** (for the color, see Table 1). Compounds (II) were obtained analogously to (I) ⁽¹⁾.



Analysis of the spectra of the *n*-NO₂-DPM compounds (I) was carried out from the standpoint of the theory of inductively interacting systems ^(2,3), developed for analyzing the spectra of diphenylamine derivatives of the structure 4-O₂N NH A-4'.

In derivatives of 4-NO₂-diphenylamine the main chromophoric system is the system BKA' O₂N NH; in derivatives of *n*-NO₂-DPM and *n*-NO₂-DPE the main chromophoric system should be the system BKA' *n*-O₂N CH₂ (IV), the state of which is modified by inductive interaction with the system KA². The validity of this approach is confirmed by the fact that in the spectra of (I) and (II) we find bands of the systems of both rings: ring *a*, BKA' (bands *I^a* and *II^a*) and ring *b*, KA², more precisely A'KA² (bands *I^b* and *II^b*), Table 1.

Upon introduction of phenyl into O₂N CH₃ (No. 1) we observe a displacement of band *I^a* by +3 mμ, and of band *II^a* by +10 mμ. Bands *I^a* and *II^a*, relative to the calculated sum of the extinctions of the systems of rings *a* and *b* (No. 4),

are also shifted bathochromically by +3 $m\mu$ and +10 $m\mu$, respectively, but the absorption limit at $\lg \epsilon = 1$ is shifted by +15 $m\mu$ (Nos. 1-4, Table 1, Fig. 1). In agreement with ^(3,5), we regard this effect as a consequence of increased polarization in the ground state of the BKA' O₂N CH₂ system: as a result of mutual induction, in (III) there arises $\delta-$, which enhances $\Delta+$ in comparison with $\Delta+$ in the initial O₂N CH₃. The correctness of this approach is confirmed: 1) by the fact that the curve of O₂N CH₂CH₂ (No. 5) almost coincides with curve (No. 1) in Fig. 2: replacement of the CH₂ group by the CH₂CH₂ group leads to a fall in the polarization of ring *b*, to a decrease in inductive interaction, and to the approach of the spectrum to the calculated one (Nos. 4-5); 2) by the fact that a shift toward longer wavelengths occurs upon introduction into (I) and (II) of A² = NH₂, NMe₂.

Under the influence of A², a larger charge $\delta'-$ should arise in (I) than $\delta-$ in (III), which in turn should intensify the polarization in BKA'

* Φ = *n*-phenylene -C₆H₄; at the end of the chain -C₆H₅; Me = CH₃; *n* = 1, 2.

** Construction of scheme (IV) with allowance for standard dimensions shows the presence of spatial factors preventing coplanarity of the benzene rings *a* and *b*: according to ⁽⁴⁾ they are rotated by 52°; the angle of the vectors of *a* and *b* is 120°.

Table 1*

No.	Compound (m.p. and color)	Bands of nu-cleus <i>b</i> :		Bands of nu-cleus <i>b</i> :		Bands of nu-cleus <i>a</i> :		Bands of nu-cleus <i>a</i> :		Absorption edge at $\lg \epsilon$		
		Ib	IIb	Ib	IIb	Ia	IIa	Ia	IIa	Exoband	Endoband	
	Solvent	λ_{\max}	ϵ_{\max}	λ_{\max}	ϵ_{\max}	λ_{\max}	ϵ_{\max}	λ_{\max}	ϵ_{\max}	λ_{\max}	ϵ_{\max}	1
1	O ₂ N-C ₆ H ₄ -CH ₃	-	-	-	-	274	10850	320	830	-	-	385
2	O ₂ N-C ₆ H ₄ -CH ₃	-	-	-	-	277	10600	330	820	-	-	400
2a	O ₂ N-C ₆ H ₄ -CH ₂ - Φ	-	-	-	-	277	10400	330	500	-	-	385
2b	31°, G col- or- less	-	-	-	-	267	11300	310	330	-	-	385
3	H ₃ C-C ₆ H ₄ -C ₆ H ₅	-	-	255	360	-	-	-	-	-	-	-
3	H ₃ C-C ₆ H ₄ -C ₆ H ₅	-	-	262	340	-	-	-	-	-	-	-
4	(O ₂ N-C ₆ H ₄ -CH ₃ + H ₃ C- Φ) calc.	-	-	-	-	274	10800	320	830	-	-	385
5	O ₂ N-C ₆ H ₄ -CH ₂ -CH ₂ - Φ	-	-	-	-	277	8200	330	450	-	-	385

No.	Compound (m.p. and color)	Solvent	Bands of nu-cleus		Bands of nu-cleus		Bands of nu-cleus		Bands of nu-cleus		Absorption edge at lg ϵ	
			λ_{\max}	ϵ_{\max}	λ_{\max}	ϵ_{\max}	λ_{\max}	ϵ_{\max}	λ_{\max}	ϵ_{\max}	λ_{\max}	ϵ_{\max}
5a	70-71°, colorless	G	—	—	—	—	267	14000	370	470	—	—
6	$O_2N\Phi CH_2\Phi NH_2$	B	11600	—	—	—	275	9200	330	1530	420	40
6a	98°, orange-yellow	B	—	—	—	—	275	8100	320	1760	420	20
6b	98°, orange-yellow	G	230	9680	—	—	255	14700	320	1700	—	—
7	$H_3C\Phi NH_2$	B	235	11700	290	1800	—	—	—	—	—	—
8	$(O_2N\Phi CH_2\Phi NH_2 + H_3C\Phi NH_2)$ calc.	B	235	15900	—	—	274	11800	320	900	—	—
9	$O_2N\Phi CH_2\Phi NH_2$	B	—	—	—	—	—	—	330	2640	420	140
10	$O_2N\Phi CH_2\Phi NH_2$	B	12800	—	—	—	275	13400	330	1100	420	135
10a	138°, yellow-orange	G	—	—	—	—	255	19200	330	730	400	130
11	$O_2N\Phi CH_2\Phi NH_2$	B	—	—	—	—	—	—	330	2700	420	270
12	$O_2N\Phi CH_2\Phi NMe_2$	B	2200	—	—	—	270	20000	340	2235	420	190
12a	87°, yellow-orange	B	—	—	—	—	270	18900	340	1600	420	100
12b	87°, yellow-orange	G	262	25700	302	4000	—	—	340	1600	—	—
13	$H_3C\Phi NMe_2$	B	252	13300	302	1900	—	—	—	—	—	—
14	$O_2N\Phi CH_2\Phi NMe_2$	B	—	—	—	—	—	—	340	3400	420	670

No.	Compound (m.p. and color)	Solvent	Bands of nu-cleus		Bands of nu-cleus		Bands of nu-cleus		Bands of nu-cleus		Absorption edge at lg ϵ		
			λ_{\max}	ϵ_{\max}	λ_{\max}	ϵ_{\max}	λ_{\max}	ϵ_{\max}	λ_{\max}	ϵ_{\max}	Exoband	Endoband	
15	(O ₂ NΦCH ₂ + H ₃ CΦNMe ₂) calc.	C	252	19000	—	—	270	13900	330	800	—	—	385
16	O ₂ NΦCH ₂ CH ₂ ΦNMe ₂	C	260	19500	—	—	275	14400	340	1100	430	250	515
16	O ₂ NΦCH ₂ CH ₂ ΦNMe ₂	C	260	20600	302	3480	—	—	340	750	400	170	504
16a	147°, DMA yellow-orange	—	—	—	—	—	—	340	3400	430	830	530	
17	147°, yellow-orange	—	—	—	—	—	—	—	—	—	—	—	

* The numbers of the compounds and solutions in Table 1 correspond to the numbers in the text and in the figures. The concentration of the solutions is 10^{-4} mol/l.

** C = alcohol, B = benzene, G = *n*-hexane, A = aniline, DMA = dimethylaniline.

($\Delta' + > \Delta +$), and, according to the rule relating the bathochromic effect to the degree of electron displacements in the ground state (^{2,5,6}), the spectrum should shift to the red. The influence of A²—NH₂ in No. 6 (I) on $\lambda_{\max}^{II^a}$ is still not large: $\lambda_{\max}^{II^a}$ remained at 330 m μ , but $\epsilon_{\max}^{II^a}$ increased to 1530 (Nos. 1, 2, 6). However, for No. 6 a strong bathochromic displacement of the absorption boundary is observed: at lg $\epsilon = 1$, +40 and +55 m μ (in comparison with No. 2 and No. 1, Fig. 1), and a new band at 420 m μ appears in the form of an inflection. It is a consequence not of endomolecular, but of exomolecular interactions of the external field of the electrophilic system *BKA'O₂NΦCH₂* with the electron-donor system *A'KA²CH₂ΦNH₂* (IV), with formation of a donor-acceptor complex as a result of association (see the analogous association (7)).

The presence of exomolecular interaction in solution No. 6 is confirmed by the observed increase in the bathochromic displacement of the spectral curve in the region of the exoband: 1) when the concentration is increased from $C = 10^{-4}$ to $C = 10^{-2}$ mol/l; 2) on going from *CH₂* to *CH₂CH₂*, i.e., to the DPE derivative No. 10; 3) when an excess of the *A'KA²* component is added to the alcoholic

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

solution in the form of $CH_3\Phi NH_2$ or $C_6H_5NH_2$ (No. 9, Fig. 1, Table 1); 4) for spectrum No. 10 in aniline (No. 11, Fig. 1). This conclusion is confirmed by the considerably stronger endo- and exo-effect for (I, $A^2 = NMe_2$). Since NMe_2 is stronger than NH_2 (No. 12, Table 1, Fig. 2), band II^a shifted bathochromically by $+10 m\mu$ and considerably

increased, while for the exopole the shift of the absorption edge at $\lg \varepsilon = 1$ is already $+95$ and $+80 m\mu$ relative to Nos. 1 and 2. That this effect is a consequence of the appearance of an exopole as a result of exomolecular interactions of the type of interaction in donor-acceptor complexes of nitrorel with arylamines is demonstrated by: the presence in Nos. 12 and

Fig. 1

Fig. 2

14 of stronger shifts than in Nos. 6 and 9 and in comparison with the spectrum of No. 15, calculated for the sum of the components ($O_2N CH_3 + CH_3 NMe_2$); the appearance, for the DPE derivative (II, $A^2 - NMe_2$), of a clearly expressed maximum of the exopole $\lambda_{\max}^{\text{exo}} = 430 m\mu$ ($\varepsilon = 250$), despite the low concentration $C = 10^{-4}$ M/l, and, finally, by an increase of ε_{\max} of the exopole to 800 (Fig. 2) with a shift of the absorption edge at $\lg \varepsilon = 1$ to $+130 m\mu$ and $+145 m\mu$ relative to Nos. 2 and 1 (Table 1) for solution No. 17 in $C_6H_5NMe_2$ (i.e., when using component \overline{KA}_2 in excess to shift the equilibrium toward a higher concentration of the complex).

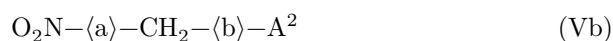
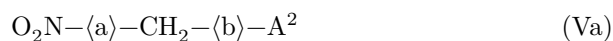
We see (Table 1, Fig. 3) that in the spectrum of No. 12, $O_2N\Phi CH_2\Phi NMe_2$, in the region of bands I and II there is a considerable deviation from curve No. 15, calculated for the sum of the components, and an even greater deviation from Nos. 1 and 2, which indicates a significant effect of endomolecular mutual influences of the NMe_2 and NO_2 groups: λ_{\max}^{16} for No. 15 (252 $m\mu$) is shifted to the red by $+13 m\mu$, with a considerable increase in ε from 19000 to 25200. For No. 16 this effect decreases ($\Delta\lambda + 8 m\mu$ and ε_{\max} 19500), i.e., in No. 16 the endomolecular interactions weaken: as a result of the greater separation of the charges $\Delta' +$ from $\delta' -$ in (II), the polarization of the nucleus a system decreases.

Fig. 3

Figure 3: Fig. 3

Fig. 3

Since in *n*-NO₂-DPM the planes of both nuclei *a* and *b* are rotated by 52°⁽⁴⁾, the conditions for conjugation of the nuclei by means of CH₂ are disturbed. As a result, the CH₂ group can interact, depending on the rotation of the benzene nuclei, now with nucleus *a*, now with nucleus *b*. This may be explained by the existence of two rotational states (conformations) and may be represented by schemes (Va) and (Vb) with different positions of conjugation of CH₂ with one of the two nuclei *a* or *b* (σ, π -conjugation). Owing to the polar opposition of NO₂ and CH₂, position (Va)



is more favorable (a larger value of the conjugation energy) and therefore predominates.

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