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1961

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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-NO_2-diphenylmethane (n-NO_2-DPM) (I) and n-NO_2-diphenylethane (n-NO_2-DPE) (II), in which the electron-donor chromophoric component A_2-H is $NHCOCH_3$, OH, NH_2, NMe_2** (for the color, see Table 1). Compounds (II) were obtained analogously to (1) ([1]).

$$O_2N-{}_a-CH_2-{}_b-A \qquad (I)$$

$$O_2N-{}_a-CH_2CH_2-{}_b-A \qquad (II)$$

$$O_2N-{}_a-CH_2-{}_b \qquad (III)$$

spatial scheme for $O_2N-{}_a-CH_2-{}_b-A$ (IV**)

Analysis of the spectra of the n-NO_2-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-O_2N NH A-4′.

In derivatives of 4-NO_2-diphenylamine the main chromophoric system is the system BKA′O_2N NH; in derivatives of n-NO_2-DPM and n-NO_2-DPE the main chromophoric system should be the system BKA′ n-O_2N CH_2 (IV), the state of which is modified by inductive interaction with the system KA^2. 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, KA^2, more precisely A′KA^2 (bands I^b and II^b), Table 1.

Upon introduction of phenyl into O_2N CH_3 (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),

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are also shifted bathochromically by +3 mμ and +10 mμ, respectively, but the absorption limit at $\lg \varepsilon = 1$ is shifted by +15 mμ (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′ O_2N CH_2 system: as a result of mutual induction, in (III) there arises $\delta-$, which enhances $\Delta+$ in comparison with $\Delta+$ in the initial O_2N CH_3. The correctness of this approach is confirmed: 1) by the fact that the curve of O_2N CH_2CH_2 (No. 5) almost coincides with curve (No. 1) in Fig. 2: replacement of the CH_2 group by the CH_2CH_2 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 $A^2 = NH_2, NMe_2$.

Under the influence of A^2, a larger charge $\delta'-$ should arise in (I) than $\delta-$ in (III), which in turn should intensify the polarization in BKA′

* $\Phi = n$-phenylene $-C_6H_4$; at the end of the chain $-C_6H_5$; Me = CH_3; $n = 1, 2$.

** 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)	Solvent	Bands of nucleus b: Ib λ_{max}	Ib ϵ_{max}	Bands of nucleus b: IIb λ_{max}	IIb ϵ_{max}	Bands of nucleus a: Ia λ_{max}	Ia ϵ_{max}	Bands of nucleus a: IIa λ_{max}	IIa ϵ_{max}	Exoband λ_{max}	Exoband ϵ_{max}	Absorption edge at lg ϵ = 1
1	$O_2N\Phi C CH_3$		–	–	–	–	274	10850	320	830	–	–	385
2	$O_2N\Phi C CH_3$		–	–	–	–	277	10600	330	820	–	–	400
2a	$O_2N\Phi CH_2\Phi$		–	–	–	–	277	10400	330	500	–	–	385
2b	31°, colorless	G	–	–	–	–	267	11300	310	330	–	–	385
3	$H_3C\Phi C$		–	–	255	360	–	–	–	–	–	–	–
3	$H_3C\Phi C$		–	–	262	340	–	–	–	–	–	–	–
4	$(O_2N\Phi C CH_3$ + $H_3C\Phi)$ calc.		–	–	–	–	274	10800	320	830	–	–	385
5	$O_2N\Phi CH_2CH_2\Phi$		–	–	–	–	277	8200	330	450	–	–	385

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No.	Compound (m.p. and color)	Solvent	Bands of nucleus *b*: Ib λmax	Ib ϵmax	Bands of nucleus *b*: IIb λmax	IIb ϵmax	Bands of nucleus *a*: Ia λmax	Ia ϵmax	Bands of nucleus *a*: IIa λmax	IIa ϵmax	Exoband λmax	Exoband ϵmax	Absorption edge at lg ϵ = 1
5a	70–71°, colorless	G	–	–	–	–	267	14000	370	470	–	–	–
6	$O_2NC_6H_4CH_2C_6H_4NH_2$	E	235	11600	–	–	275	9200	330	1530	420	40	440
6a	98°, orange-yellow	B	–	–	–	–	275	8100	320	1760	420	20	435
6b	98°, orange-yellow	G	230	9680	–	–	255	14700	320	1700	–	–	400
7	$H_3CC_6H_4NH_2$	E	235	11700	290	1800	–	–	–	–	–	–	–
8	($O_2NC_6H_4CH_3$ + $H_3CC_6H_4NH_2$) calc.	E	235	15900	–	–	274	11800	320	900	–	–	385
9	$O_2NC_6H_4CH_2C_6H_4NH_2$	A, 10^{-2}	–	–	–	–	–	–	330	2640	420	140	490
10	$O_2NC_6H_4CH_2CH_2 \cdot C_6H_4NH_2$	E	235	12800	–	–	275	13400	330	1100	420	135	475
10a	138°, yellow-orange	G	–	–	–	–	255	19200	330	730	400	130	437
11	$O_2NC_6H_4CH_2CH_2 \cdot C_6H_4NH_2$	A, 10^{-2}	–	–	–	–	–	–	330	2700	420	270	508
12	$O_2NC_6H_4CH_2C_6H_4NMe_2$	E	265	25200	–	–	270	20000	340	2235	420	190	480
12a	87°, yellow-orange	B	–	–	–	–	270	18900	340	1600	420	100	438
12b	87°, yellow-orange	G	262	25700	302	4000	–	–	340	1600	–	–	409
13	$H_3CC_6H_4NMe_2$	E	252	13300	302	1900	–	–	–	–	–	–	–
14	$O_2NC_6H_4CH_2C_6H_4NMe_2$	D	–	–	–	–	–	–	340	3400	420	670	500

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No.	Compound (m.p. and color)	Solvent	Bands of nucleus *b*: Ib λ_{max}	Ib ϵ_{max}	IIb λ_{max}	IIb ϵ_{max}	Ia λ_{max}	Ia ϵ_{max}	IIa λ_{max}	IIa ϵ_{max}	Exoband λ_{max}	Exoband ϵ_{max}	Absorption edge at lg ϵ = 1
15	($O_2N\Phi CH_3$ + $H_3C\Phi NMe_2$) calc.	C	252	19000	–	–	270	13900	330	800	–	–	385
16	$O_2N\Phi CH_2$ $CH_2\Phi NMe_2$	C	260	19500	–	–	275	14400	340	1100	430	250	515
16	$O_2N\Phi CH_2$ $CH_2\Phi NMe_2$	G	260	20600	302	3480	–	–	340	750	400	170	504
16a	147°, yellow-orange	DMA	–	–	–	–	–	–	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 A^2—NH_2 in No. 6 (I) on $\lambda_{max}^{II^a}$ is still not large: $\lambda_{max}^{II^a}$ remained at 330 mμ, but $\varepsilon_{max}^{II^a}$ increased to 1530 (Nos. 1, 2, 6). However, for No. 6 a strong bathochromic displacement of the absorption boundary is observed: at $\lg \varepsilon = 1$, +40 and +55 mμ (in comparison with No. 2 and No. 1, Fig. 1), and a new band at 420 mμ 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 $BKA'O_2N\Phi CH_2$ with the electron-donor system $A'KA^2CH_2\Phi NH_2$ (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 CH_2 to CH_2CH_2, i.e., to the DPE derivative No. 10; 3) when an excess of the $A'KA^2$ component is added to the alcoholic

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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, $A^2 = \mathrm{NMe_2}$). Since $\mathrm{NMe_2}$ is stronger than $\mathrm{NH_2}$ (No. 12, Table 1, Fig. 2), band II^a shifted bathochromically by +10 mμ and considerably

increased, while for the exopole the shift of the absorption edge at $\lg\varepsilon = 1$ is already +95 and +80 mμ 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 nitrotel 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 ($\mathrm{O_2N\ CH_3 + CH_3\ NMe_2}$); the appearance, for the DPE derivative (II, A^2—$\mathrm{NMe_2}$), of a clearly expressed maximum of the exopole $\lambda_{\max}^{\mathrm{exo}} = 430$ mμ ($\varepsilon = 250$), despite the low concentration $C = 10^{-4}$ M/l, and, finally, by an increase of $\varepsilon_{\max}$ of the exopole to 800 (Fig. 2) with a shift of the absorption edge at $\lg\varepsilon = 1$ to +130 mμ and +145 mμ relative to Nos. 2 and 1 (Table 1) for solution No. 17 in $\mathrm{C_6H_5NMe_2}$ (i.e., when using component $\overline{K}A_2$ 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, $\mathrm{O_2N\Phi CH_2\Phi NMe_2}$, 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 $\mathrm{NMe_2}$ and $\mathrm{NO_2}$ groups: $\lambda_{\max}^{16}$ for No. 15 (252 mμ) is shifted to the red by +13 mμ, with a considerable increase in ε from 19000 to 25200. For No. 16 this effect decreases ($\Delta\lambda + 8$ mμ and $\varepsilon_{\max}$ 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

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Fig. 3

Since in n-NO_2-DPM the planes of both nuclei a and b are rotated by 52° ([4]), the conditions for conjugation of the nuclei by means of CH_2 are disturbed. As a result, the CH_2 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 CH_2 with one of the two nuclei a or b (σ, π-conjugation). Owing to the polar opposition of NO_2 and CH_2, position (Va)

$$O_2N{-}\langle a\rangle{-}CH_2{-}\langle b\rangle{-}A^2 \qquad \text{(Va)}$$

$$O_2N{-}\langle a\rangle{-}CH_2{-}\langle b\rangle{-}A^2 \qquad \text{(Vb)}$$

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

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Received
21 III 1961

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