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schematic structures I-IV

Figure 1: schematic structures I-IV

orbital/conjugation diagram V

Figure 2: orbital/conjugation diagram V

Abstract

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ABSORPTION SPECTRA OF 4-NO_2-DIPHENYLAMINE DERIVATIVES

ON THE EFFECT OF ELECTRON-DONOR GROUPS IN THE *m*-POSITION

AND ALKYLATION OF THE NH GROUP

(Presented by Academician B. A. Kazanskii, March 4, 1960)

The study of the spectra of 4-NO_2 derivatives of diphenylamine (DPA) of structure (1) ([1]), on the basis of the principle of decomposing the structure into separate chromophoric components ([2–4]), led to the conclusion that "a single conjugated system (with participation of the *p*-electrons of NH) with a single excitation vector along the π-system is absent."

There are two decoupled systems, BKA^1* and A^1KA^2 (I), each with its own laws of transition to the excited state. In the spectra of (I) we find the bands of these systems. The vectors intersecting at the central N atom (which is an isolator of conjugation) prove, in this way, to be mutually coupled, depending to a corresponding degree on one another ([1]). As a result of disturbance of the coplanarity (V)**, the N atom of the NH(NR) group may be conjugated either with *a* or with *b*. Thus, the existence of geometrical isomers of conjugation is possible ([7]), which may explain the chromoisomerism in NO_2-derivatives of DPA.

V

* B is an electrophilic chromophoric component (NO_2), K is a conjugated system; A, A^1, A^2 are electron-donor chromophoric components.
** The scheme V is constructed with allowance for standard sizes ([5]) under the condition of coplanarity. The H atom is indicated by the dotted circle. The

planes of the benzene nuclei a and b are rotated by $\sim 33^\circ$ ([6]). In the case of NMe the angle of deviation should be larger.

The principal chromophoric system is BKA^1 (I), modified by the degree of polar displacements in the ground and excited states as a result of the influence of A^2K. According to the rules relating the bathochromic effect to the degree of electronic displacements,* the greater the degree of electron displacement in

$$BKA \; n\text{-}O_2N\Phi N <$$

from the state expressed by the limiting valence structural formula (I), the lower the excitation energy by light and the greater the bathochromic effect. From this point of view, the cause of the bathochromic effect in the transition from n-$O_2N\Phi NH_2$, $\lambda_{max}371\,m\mu$, to n-$O_2N\Phi NHC_6H_5$, $\lambda_{max}395\,m\mu$ ($\Delta\lambda + 24\,m\mu$ in ethanol and $+34\,m\mu$ in cyclohexane) should be sought in the increase of electronic displacement and of the charge $\Delta+$ on the N atom in the system

$$O_2N\Phi N <$$

(II) as a result of the influence of the polar deformation of benzene nucleus b (II) ($\delta-$ enhances the deformation). The influence of phenyl is thus close to the influence of alkyls, which

Table 1

Spectra of compounds in 95% ethanol*

No. of compound	Structure** Φ = phenylene or C_6H_5	System BKA: band x*** $\lambda_{max}, m\mu$	ε_{max}	System BKA: band x*** $\lambda_{max}, m\mu$	ε_{max}	System BKA: band x'*** $\lambda_{max}, m\mu$	ε_{max}	System A^1KA^2 or KA^2: band β $\lambda_{max}, m\mu$	ε_{max}	System A^1KA^2 or KA^2: band β $\lambda_{max}, m\mu$	ε_{max}	System A^1KA^2 or KA^2: band γ $\lambda_{max}, m\mu$	ε_{max}	System A^1KA^2 or KA^2: band γ $\lambda_{max}, m\mu$	ε_{max}
1	$O_2N\Phi NHC_6H_5$	395	29220	–		–		257	13500	–		–			
2	$O_2N\Phi NHC_6H_4CH_3$-m	403	30430	–		–		257	17840	~ 220		~ 28240			
3	$O_2N\Phi NHC_6H_4CH_3$-o	395	28284	–		–		~ 260	~ 17720	245		29530			
4	$O_2N\Phi NHC_6H_3(CH_3)_2$-$m$	388	30230	–		–		254	18130	~ 220		~ 22300			
5	$O_2N\Phi NHC_6H_3(CH_3)_2$-$m$	399	28345	–		–		~ 260	~ 15760	235		31720			
6	$O_2N\Phi NHC_6H_2(CH_3)_3$-$m$	403	24110	–		–		–	–	247		28740			
7	$O_2N\Phi N(CH_3)\Phi$	387	21760	228.5		8425		250	5925	–		–			

No. of compound	Structure** Φ = phenylene or C_6H_5	System BKA: band x*** $\lambda_{max}, m\mu\varepsilon_{max}$	System BKA: band x***	System BKA: band x'*** $\lambda_{max}, m\mu\varepsilon_{max}$	System BKA: band x'***	System A^1KA^2 or KA^2: band β $\lambda_{max}, m\mu\varepsilon_{max}$	System A^1KA^2 or KA^2: band β	System A^1KA^2 or KA^2: band γ $\lambda_{max}, m\mu\varepsilon_{max}$	System A^1KA^2 or KA^2: band γ
8	$O_2N\Phi N(388)\Phi$	22200		–	–	~ 250	~ 10430	222	17390
9	$O_2N\Phi N(391)\Phi$	26000	Ac	–	–	~ 275	~ 11595	236	21015
10	$O_2N\Phi N(397)\Phi$	NH_2		–	–	249	13720	235	13575
11	$O_2N\Phi N(397)\Phi$	18980	Me_2	~ 245	~ 11110	265	17592	–	–
12	$O_2N\Phi N(392)\Phi$	20694		228	8820	~ 250	~ 5880	–	–
13	$O_2N\Phi N(394)\Phi$	23300		–	–	~ 245	~ 7500	225	12950
14	$O_2N\Phi N(394)\Phi$	23710	Ac	(220)	(27310)	~ 260	~ 10196	~ 230	~ 20078
15	$O_2N\Phi N(400)\Phi$	21790	NH_2	(~ 220)	(~ 47410)	250	13242	–	–
16	$O_2N\Phi N(401)\Phi$	19450	Me_2	~ 240	~ 10650	265	16650	–	–
17	$O_2N\Phi N(391)\Phi$	20370		228	7450	~ 250	~ 5646	–	–
18	$O_2N\Phi N(392)\Phi$	21898		(~ 220)	(58750)	254	8524	–	–
19	$O_2N\Phi N(392)\Phi$	22430	Ac	–	–	~ 270	~ 8980	237	18050
20	$O_2N\Phi N(400)\Phi$	25700	NH_2	(~ 220)	(~ 51710)	~ 250	~ 15089	–	–
21	$O_2N\Phi N(400)\Phi$	20260	Me_2	~ 245	~ 11400	265	17700	–	–
22	$O_2N\Phi N(390\text{-}Pr_2^i)\Phi$	22990		230	8935	~ 250	~ 4635	–	–
23	$O_2N\Phi N(390\text{-}Pr_2^i)\Phi$	24630	Me	(~ 220)	(~ 62000)	~ 245	~ 9160	–	–
24	$O_2N\Phi N(390\text{-}Pr_2^i)\Phi$	22700	HAc	–	–	–	–	242	20810
25	$O_2N\Phi N(387\text{-}Pr_2^i)\Phi$	24950	NH_2	(~ 225)	(~ 29480)	~ 250	~ 13950	–	–
26	$O_2N\Phi N(400\text{-}Pr_2^i)\Phi$	25088	Me_2	~ 240	~ 11900	265	20410	–	–
27	$O_2N\Phi N(391)C_6H_4OMe$-m	23400		–	–	~ 245	~ 9150	225	23610

No. of compound	Structure** Φ = phenylene or C_6H_5	System BKA: band x*** $\lambda_{max}, m\mu\varepsilon_{max}$	System BKA: band x*** $\lambda_{max}, m\mu\varepsilon_{max}$	System BKA: band x'*** $\lambda_{max}, m\mu\varepsilon_{max}$	System BKA: band x'*** $\lambda_{max}, m\mu\varepsilon_{max}$	System A^1KA^2 or KA^2: band β $\lambda_{max}, m\mu\varepsilon_{max}$	System A^1KA^2 or KA^2: band β $\lambda_{max}, m\mu\varepsilon_{max}$	System A^1KA^2 or KA^2: band γ $\lambda_{max}, m\mu\varepsilon_{max}$	System A^1KA^2 or KA^2: band γ $\lambda_{max}, m\mu\varepsilon_{max}$
28	$O_2N\Phi NH(Ac)$-m	390	25750	–	–	–	–	242	26130
29	$O_2N\Phi NH_2$-m	395	27760	–	–	–	–	235	24070
30	$O_2N\Phi NMe_2$-m	395	26080	–	–	–	–	255	23620

* Nos. 1-6 and 27-30 were measured at $C = 10^{-4}$. The remaining spectra at $C = 10^{-3}$. $\sim \lambda_{max}$ was determined approximately from the bend of the curve; in parentheses are given λ and ε of a band whose origin is still unclear.
** $Me = CH_3$; $Et = CH_2CH_3$; $Pr = CH_2CH_2CH_3$; iso-Pr = $CH(CH_3)_2$; $Ac = CH_3CO$.
*** The subdivisions of the bands of the BKA system into x and x' are given in the sense of ([9,11]).

appears in the transition from n-$O_2N\Phi NH_2$ to n-$O_2N\Phi NMe_2$ (λ_{max}390 $m\mu$) and n-$O_2N\Phi NE_2$ (λ_{max}400 $m\mu$). Hence one could expect that the greater the electron-donor activity of group A^2 in (III), the greater the polarization of the system A^2K, the greater will be δ'-(III), and hence the greater will be $\Delta'+$ on NH and the greater will be the bathochromic effect: $H < NHCOCH_3 < OCH_3 < NH_2 < NMe_2$ ($\Delta\lambda = 0,\ +2,\ +5,\ +10,\ +15$) ([1]). Thus were

* This rule was stated by Izmail' skii as a consequence of the hypothesis of the relation between color and mesomeric structure as early as 1915 ([7,8]), and later by Lewis and Calvin ([9]).

the previous conclusions were confirmed [(10)]. These effects $\Delta\lambda$ are considerably smaller than those values (+40 to +120 mμ) which would have occurred if the conjugated chain had in fact been lengthened by 4π-electrons. The conjugation of n-A^2 with NO_2 is disrupted by the absence of coplanarity [(5)]. The aim of the present study is to test the influence on the spectrum of A^2 in the m-position (IV) and to determine the effect on the spectra of n-A^2- and m-A^2-substituted compounds (V) of a further disruption of coplanarity by introducing an alkyl group into NH (Table 1).

According to calculations of molecular diagrams for $C_6H_5NH_2$, the electronic charges at m-C are lower than at n-C and at the C atoms of the unsubstituted benzene

Fig. 1. 1, 2, 8, 27—see Table 1; I—n-O_2N NH OCH_3-n'

Fig. 1

Figure 3: Fig. 1

Fig. 2

Figure 4: Fig. 2

nucleus [12]. It could therefore be expected that, in the case of m-derivatives (IV), hypsochromic effects would be observed, since $\delta'''^{-} < \delta^{-} < \delta a'^{-}$. Indeed, for m-A^2 = $\mathrm{H}, \mathrm{OCH_3}, \mathrm{NHCOCH_3}, \mathrm{N(COCH_3)_2}, \mathrm{NH_2}, \mathrm{NMe_2}$, $\Delta\lambda = 0, -2, 0, -7, +4, +8$ mμ (Table 1, Nos. 1-6). The presence of a negative effect thus appeared clearly for m-$\mathrm{OCH_3}$ and m-$\mathrm{N(COCH_3)_2}$. However, for strong donors (m-$\mathrm{NH_2}$ and m-$\mathrm{NMe_2}$) the effects were positive in character $(+4, +8)$, although according to the molecular diagrams by the molecular-orbital method a negative effect could have been expected here as well [12].

If the concept set forth above—of the influence of the magnitude of the charge δ'''^{-} on the magnitude of the charge Δ''^{+} (IV) and on the spectrum—is correct, then it must be admitted: 1) in the case of such strong donor groups as $\mathrm{NH_2}$, $\mathrm{NMe_2}$, the total electron density in benzene nucleus b is increased so much that in the m-position to $\mathrm{NH_2}$, $\mathrm{NMe_2}$ there is a greater electronic charge than in the unsubstituted benzene nucleus e(III), i.e., in the case of $\mathrm{NH_2}$, $\mathrm{NMe_2}$, $\delta'''^{-} > \delta^{-}$; 2) according to our spectroscopic data, calculations of electronic charges in the molecular diagrams of $\mathrm{C_6H_5NH_2}$ are not sufficiently accurate (the discrepancy between values calculated by the molecular-orbital method and by the mesomeric method [12] says the same). On the other hand, the spectroscopic data obtained by us, indicating definite differences in the effects of groups on the electronic charge at the m-C atom for groups of the type $\mathrm{NHCOCH_3}$, $\mathrm{OCH_3}$ and groups of the type $\mathrm{NH_2}$, $\mathrm{NMe_2}$, are in agreement with values of the electron-density estimate based on the magnetic parameter [13].

Upon alkylation of NH for H, Me, Et, $\mathrm{C_3H_7}$, iso-$\mathrm{C_3H_7}$, $\Delta\lambda = 0, -8, -3, -4, -5$ mμ (Table 1, Nos. 1, 7, 12, 17, 22). Such a strong hypsochromic effect of $\mathrm{CH_3}$ (1, 7) is explained by disruption of coplanarity of nuclei a and b and by withdrawal from conjugation of the N atom of the NR group with nucleus a (as na-

was observed for $\mathrm{NMe_2}$ [14]). The action of other alkyls was analogous in character, but it varied depending on the competing inductive and steric influences. On introducing n'-A^2 into n'-$\mathrm{O_2N}$ N(Me) , a bathochromic effect was observed: for n-A^2 = $\mathrm{H}, \mathrm{OCH_3}, \mathrm{NHCOCH_3}, \mathrm{NH_2}, \mathrm{NMe_2}$, $\Delta\lambda = 0, +1, +4, +10, +10$ mμ (Table 1, Nos. 7-11). This confirms the hypothesis that here, as in the case of (III), there is only inductive interaction of BKA and A^2K. If $\lambda_{\max}$ for Nos. 8-11 is compared with $\lambda_{\max}$ of the parent No. 1, then the effect of n-$\mathrm{OCH_3}$ and n-$\mathrm{NHCOCH_3}$ is clearly hypsochromic, $\Delta\lambda = -4, -4$ mμ, and only for n-$\mathrm{NH_2}$ and n-$\mathrm{NMe_2}$ is $\Delta\lambda =$

Fig. 2. 1, 5, 10, 29—see Table 1; II—n-$\mathrm{O_2N}$ NH $\mathrm{NH_2}$-n'

$= +2, +2$ mμ. Unexpectedly, on introducing into No. 7 m-A^2 = $OCH_3, NHCOCH_3, NH_2, NMe_2$ (Nos. 26–30), instead of a hypsochromic effect a bathochromic effect was observed ($\Delta\lambda = +3, +3, +7, +7$ mμ), the origin of which requires explanation. However, simultaneous introduction of m-A^2 and CH_3 gave, in comparison with the parent No. 1, a hypsochromic effect: for m-OCH_3 and m-$NHCOCH_3$, $\Delta\lambda = -5, -5$ mμ; for m-NH_2 and m-NMe_2, in both cases $\Delta\lambda = 0$ and 0 mμ (Table 1, Nos. 1, 27–30).

Compounds Nos. 2–30 have been described previously ([15]).

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Note: Figure translations are in progress. See original paper for figures.