Chemistry

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1962

SovietRxiv

Abstract

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Spectra of Derivatives of 2,4-Dinitroaniline
The Presence of Quasi-Autonomous Cochromophoric Systems

(Presented by Academician B. A. Kazanskii, 20 VI 1962)

The spectra of derivatives of 2,4-dinitroaniline (DNA) (I) and 2,4-dinitrodiphenylamine (2,4-$(NO_2)_2$-DPA) (II) were investigated. For analysis of structural effects, the principle of decomposing the structure of a molecule into polar chromophoric systems* was applied. It proved possible to assign individual $\lambda_{\max}$ values to definite systems: B^1KA^1, B^2KA^1, B^2K, A^1K, $A^1\Phi$, $A^1\Phi A^2$ (Tables 1 and 2). The quasi-autonomy of individual chromophoric systems upon excitation by light in molecules with complex cochromophoric systems was demonstrated experimentally.

(schemes I and II)

$B^1 = n\text{-}NO_2$; $B^2 = o\text{-}NO_2$; K —benzene nucleus a; $\Phi = n\text{-}C_6H_4$ —nucleus b;
A^1 in I: NH_2, $NHEt$, NMe_2, NEt_2; A^1 in II: NH; $A^2 = H$, OCH_3, NH_2, NMe_2.

Table 1

Genesis of the bands of derivatives of 2,4-dinitroaniline (I) and (II, $A^2 = H$) (in 95% ethanol. $C = 10^{-4}$)

No. of compound	Compound $R = 2,4\text{-}(O_2N)_2C_6H_3$—, —$C_6H_4$— and C_6H_5—	B^1KA^1 (nucleus a) $n\text{-}O_2NC_6H_4A^1$, 2_a-band λ	B^1KA^1 (nucleus a) 2_a-band ε	B^1KA^1 (nucleus a) $C_6H_5A^1$, $2'_a$-band λ	B^1KA^1 (nucleus a) $2'_a$-band ε	B^2KA^1 (nucleus a) $o\text{-}O_2NC_6H_4NH_2$, B^2KA^1, 1_a-band B^2KA^1 λ	1_a-band B^2KA^1 ε	B^2K, 2_a-band B^2K λ	2_a-band B^2K ε	KA^1, 2_a-band KA^1 λ	2_a-band KA^1 ε	$A^1\Phi$ (nucleus b) $NH\Phi$, 2_b-band $A^1\Phi$ λ	$A^1\Phi$, 2_b-band $A^1\Phi$ ε
1	$n\text{-}O_2NC_6H_4OH^*$	312	10600	225	7100	—	—	—	—	—	—	—	—
2	$o\text{-}O_2NC_6H_4OH^*$	—	—	—	—	346	3140	272	6000	—	—	—	—
3	$R—OH^*$	293	9200	overlapped	—	~ 330	~ 4000	253	10200	—	—	—	—
4	$n\text{-}O_2NC_6H_4NH_2$	375	15700	227	1150	—	—	—	—	—	—	—	—

No. of compound	Compound $R =$ 2,4-$(O_2N)_2C_6H_3$— and C_6H_5—	B^1KA^1 (nucleus a) 2_a-band λ	B^1KA^1 (nucleus a) 2_a-band ε	B^1KA^1 (nucleus a) $2'_a$-band λ	B^1KA^1 (nucleus a) $2'_a$-band ε	B^2KA^1 (nucleus a) o-$O_2NC_6H_4NH_2$, 1_a-band B^2KA^1 λ	B^2KA^1, 1_a-band B^2KA^1 ε	B^2K, 2_a-band B^2K λ	B^2K, 2_a-band B^2K ε	KA^1, 2_a-band KA^1 λ	KA^1, 2_a-band KA^1 ε	$A^1\Phi$ (nucleus b) $NH\Phi$, 2_b-band $A^1\Phi$ λ	$A^1\Phi$, 2_b-band $A^1\Phi$ ε
5	o-$O_2NC_6H_4NH_2$	—	—	—	—	403	5300	276	4900	231	16600	—	—
6	$R—NH_2$	335	13900	overlapped	—	~ 375	~ 7000	257	9160	225	9900	—	—
7	$R—NHEt_2^*$	347	16600	overlapped	—	375	6700	260	8900	—	—	—	—
8	$R—NMe_2$	361	16300	220	13000	—	—	—	—	—	—	—	—
9	$R—NEt_2$	375	16600	225	12350	—	—	—	—	—	—	—	—
10	$R—NH\Phi$	352	18000	overlapped	—	~ 385	~ 11600	overlapped	—	232	14200	257	11200
11	n-$O_2N\Phi NH\Phi^{**}$	395	29200	~ 225	~ 8560	—	—	—	—	—	—	257	13500
12	o-$O_2N\Phi$—$NH\Phi$	—	—	—	—	430	6500	~ 280	10800	220	13100	257	13900

Note. The compound numbers correspond to the numbers of the curves in Figs. 1 and 2. $\lambda_{\max}$ and $\varepsilon_{\max}$ determined from the bend in the curve are denoted by the sign ~.

* Literature source ([8]). ** Literature source ([9]).

In the spectrum of DNA (I, $A^1 = NH_2$) we find bands of two systems: n-$O_2N\Phi NH_2$ (B^1KA^1) and o-$O_2NC_6H_4NH_2$ (B^2KA^1) (Nos. 4, 5, 6, Table 1, Fig. 1).

* This principle, advanced in ([1]), proved useful in the study of spectra of benzene derivatives ([2–6]).

The main 2_a-band at 375 mμ in the spectrum of n-$O_2N\Phi NH_2$ is associated with the $\pi \to \pi^*$ transition in a mesosystem of type BKA (in I B^1KA^1). The $2'_a$-band, $\lambda_{\max}$227 mμ, may be assigned chiefly to a $\pi \to \pi^*$ transition, but to the next higher excited state of the π-electron system ([7]). When an o-NO_2 group is introduced into n-$O_2N\Phi NH_2$ (B^2), the main 2-band* is retained, but is strongly shifted toward the ultraviolet ($\Delta\lambda = -40$ mμ) with a strong decrease in ε ($\Delta\varepsilon = -11\,800$). The o-NO_2 group removes the NH_2 group from coplanarity; the degree of conjugation of the p-electrons of the N atom with the benzene ring decreases. At the same time, three bands of the o-$O_2NC_6H_4NH_2$ system appear, also shifted toward the u.-v. part of the spectrum: the 1_a-band of the system B^2KA^1, $\Delta\lambda = -28$; the 2_a-band of the system KA^1 ($C_6H_3NH_2$), $\Delta\lambda = -6$; and the 2_a-band* of the system B^2K ($C_6H_3NO_2$), $\Delta\lambda = -19$ mμ.

(Figure: Fig. 1)

Fig. 1

A complete analogy is observed in the spectrum of 2,4-dinitrophenol (Table 1, No. 3). The introduction into n-$O_2N\Phi OH$ of a second NO_2 group, while the n-$O_2N\Phi OH$ (B^1KA^1) bands are retained, leads to the appearance of a system of o-$O_2N\Phi OH$ bands (B^2KA^1) (Table 1, Nos. 1-3). The smaller hypsochromic shift of the $\lambda_{\max}$ of the 2-band of the B^1KA^1 n-$O_2N\Phi OH$ system upon introduction of o-NO_2 ($\Delta\lambda = -19$ mμ) is apparently connected with stabilization of the spatial structure by the hydrogen bond of OH with o-NO_2 and with the smaller volume of the OH group. Hypsochromic shifts are also observed on passing from No. 2 to No. 3 for the system B^2KA^1: for the 2_a-band of the B^2K system $\Delta\lambda = -19$ mμ; for the 1-band of the system B^2KA^1, $\Delta\lambda = -16$ mμ.

(Figure: Fig. 2)

Fig. 2

As we assumed, replacement of NH_2 by the groups NHEt, NMe_2, NEt_2 causes a gradual increase in $\lambda_{\max}$ of the 2_a-band of the system B^2KA^1: $\Delta\lambda = +12, +32, +40$ mμ (Table 1, Nos. 6-9; Fig. 1). All three bands of the system B^2KA^1 disappear, and the previously overlapped $2'_a$-band of the system n-$O_2N\Phi NH_2$ B^1KA^1 appears. However, such a considerable shift of the 2-band of the system B^1KA^1 upon replacement of NH_2 by the groups NMe_2, NEt_2 cannot be explained only by an increase in the donor character of the amino group ($\Delta\lambda$ in the transition $O_2N\Phi NH_2 \rightarrow O_2N\Phi NEt_2$ is only $+23$ mμ). Dialkylation of the NH_2 group leads not only to strengthening of conjugation of the N atom with the benzene nucleus a, but also to restoration of its coplanarity with the benzene nucleus owing to an increase in the volume of the amino group and destruction of the hydrogen bond and complete disruption of the coplanarity of the o-NO_2 group. As a result of the destruction of the interaction of o-NO_2 with the benzene ring in Nos. 8, 9, the spectrum returns to the spectrum of No. 4 n-$O_2N\Phi NH_2$ (system B^1KA^1).

The study of the genetics of the bands of 2,4-$(NO_2)_2$-DPA (II, $A^2 = H$) on the basis of comparison of spectrum No. 10 with the spectra of Nos. 6, 11, and 12 (Table 1, Fig. 2) confirmed the conclusions from the study of the spectra of 4-NO_2-DPA (^{6}). The spectrum contains bands not only of the systems of nucleus a, B^1KA^1 and B^2KA^1, but also of the system of nucleus b ($A^1\Phi$). A single conjugated system is absent. Owing to the noncoplanarity of the benzene nuclei a and b, normal conjugation of the p-electrons of the N atom simultaneously with

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* In accordance with (^{2,4,7}) we consider the 1_a band as the shifted 1-band of benzene ($\lambda_{\max} = 255$ mμ, $\varepsilon_{\max} = 205$), and the 2_a bands as shifted 2-bands of benzene ($\lambda_{\max} = 200$ mμ, $\varepsilon_{\max} \sim 7000$). The signs a and b, added to the designation of the band type, indicate affiliation with nucleus a or b.

both nuclei is impossible. The existence of geometrical isomers of conjugation (³) IIIa and IIIb, as in (⁶)*, is possible.

[[structural schemes IIIa and IIIb]]

The band of nucleus *b*, NHΦ, appears at the same λ_{max}, 257 mμ (Fig. 2), in all three DPA derivatives Nos. 10, 11, and 12. This indicates the identical

Table 2

Genetics of the bands of derivatives of 2,4-dinitro-DPA (II). Comparison of compounds R^1A^2 and R^2A^2*
($R^1 = 4\text{-}O_2NC_6H_4NH-$; $R^2 = 2,4\text{-}(NO_2)_2C_6H_3NH-$)

No. of compound	A^2	2_a-bands of nucleus *a*: R^1-A^2 (B^1KA^1)			2_a-bands of nucleus *a*: R^2-A^2 (B^1KA^1)						2_b-bands of nucleus *b*: R^1-A^2 ($A^1\Phi A^2$)			2_b-bands of nucleus *b*: R^2-A^2 ($A^1\Phi A^2$)				$Me_2N\Phi A^2$, for comparison	
		λ	ε	$\Delta\lambda$ to No. 1	λ	ε	$\Delta\lambda$ to No. 1	$\Delta\lambda$ to R^1A^2	λ	ε	λ	ε	$\Delta\lambda$ to No. 1	λ	ε	$\Delta\lambda$ to No. 1	$\Delta\lambda$ to R^1A^2	λ	ε
1	H	395	29220	0	352	18000	0	−43	232	14200	257	13500	0	257	11200	0	0	250	14150
2	CH_3	—	—	—	352	17100	0	—	232	13000	—	—	—	260	10500	+3	—	253	14150
3	OCH_3	400	25800	+5	355	14800	+3	−45	225	14600	257	12300	0	255, 260	11600 11000	0,	0	250	13490
4	NH_2	405	21100	+10	360*	12750	+8	−45	overlapped		260	13780	+3	247	16150	−10	−13	250	12020
5	NMe_2	410	22650	+15	365**	12340	+13	−45	overlapped		265	19220	+8	260	21000	+?	[[unclear]]	26[[?]]	16220

Notes. The numbers of the compounds R^2A^2 correspond to the numbers of the curves in Fig. 3. Color of the crystals: R^2A^2: No. 1 —orange, No. 3 —red, No. 4 —reddish-brown, No. 5 —brown-black; R^1A^2: No. 1 —yellow, No. 3 —brown-yellow, No. 4 —reddish-brown, No. 5 —red-orange. For compound R^3A^3 the long-wave 1_a-band of the system B^1KA^1 of nucleus *a*, which appears as a bend in compounds Nos. 1, 2 at 400 mμ, has not been entered; in compounds Nos. 3-5 this band is apparently overlapped by the $2'_a$-band of the system B^1KA^1; the bands of the B^2K system of nucleus *a* are overlapped. In compounds R^1A^2 the 2_a-bands of the system B^1KA^1 of nucleus *a* are overlapped.

* λ_{max} by the half-width of the band, since there are 2 peaks: λ_{max} 257, 362 mμ (ε_{max} 12700, 12800).

** λ_{max} by the half-width of the band, since there are 4 peaks: λ_{max} 355, 362, 367, 375 mμ (ε_{max} 12350, 12400, 12350, 12250).

origin of the band and the independence of NHΦ in IIIb from the system of nucleus *a*. Since in DNA the NHΦ system is absent, the band at 257 mμ in No. 6, by analogy—

* In connection with this, the phenomena of chromoisomerism may perhaps be found.

apparently may be assigned, by analogy with No. 5, to the band of the system *o*-$O_2NC_6H_3NH$ (B^2KA^1), namely to the 2-band $B^2K\,O_2N$ (λ_{max} of nitrobenzene ~ 260 $m\mu$).

A study of the influence of A^2 (II) on the spectrum of 2,4-$(NO_2)_2$-DPA showed the following. Introduction of the *o*-NO_2 group causes shifts of λ_{max} toward the ultraviolet part of the spectrum by the same amount $\Delta\lambda = -45$ $m\mu$ (Table 2, Nos. 1-5); in the case of groups $A^2 = H, CH_3, OCH_3$, the spectrum contains the bands of all three systems B^1KA^1, B^2KA^1 (nucleus *a*) and A^1 A^2 (nucleus *b*) (Table 2, Nos. 1, 2, 3; Fig. 3); with an increase in the donor character of A^2 (NH_2, NMe_2), the spectrum shows bands of only two systems, B^1KA^1 (nucleus *a*) and A^1 A^2 (nucleus *b*), as in the case of the derivatives of 4-NO_2-DPA (Table 2, Nos. 4, 5; Fig. 3). The short-wavelength bands of the B^2KA^1 system of nucleus *a* are overlapped; strengthening of the donor character of A^2 ($H < OCH_3 < NH_2 < NMe_2$) causes an insignificant shift of λ_{max} of the 2*a*-band toward the infrared part of the spectrum of the B^1KA^1 system (of the same order as in 4-NO_2-DPA). This is explained only by the inductive effect of A^2 (cf. [6] and $\Delta\lambda$ for No. 1 for the bands of nucleus *a*, Table 2, Nos. 1-5); the shift of bands of type 2 of the A^1 A^2 system of nucleus *b* in (II) Nos. 4, 5 (Table 2) is not amenable to explanation, since in the ultraviolet part of the spectrum we have a complex system of overlapping bands.

(Figure: Fig. 3)

Fig. 3

The deeper color of the crystals of the derivatives of 2,4-(NO_2)-DPA (Table 2, Nos. 1-5), in comparison with 4-NO_2-DPA, is due to enhancement of intermolecular interactions in the solid state. In the case of $A^2 = NH_2, NMe_2$, exo-interaction also occurs in solutions (see the strong shifts of the long-wavelength branches of the curves toward the infrared part of the spectrum, Nos. 4, 5, Fig. 3, as also in [10]).

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Received
17 IV 1962

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