V. A. GLUSHENKOV, V. A. IZMAILSKII, Yu. Sh. MOSHKOVSKII

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Abstract

Full Text

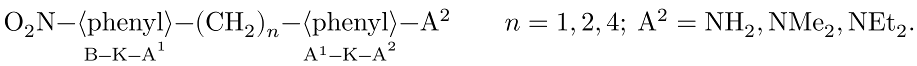
PHYSICAL CHEMISTRY

V. A. GLUSHENKOV, V. A. IZMAILSKII, Yu. Sh. MOSHKOVSKII

SPECTRA OF E.D.A. COMPLEXES OF 4-NITRODIPHENYLALKANES CONTAINING A DONOR GROUP IN THE OTHER RING. E.P.R. EFFECT

(Presented by Academician A. N. Terenin, 19 VII 1963)

The coloration and the long-wavelength part of the spectrum of derivatives of *p*-nitrodiphenylalkanes (I) are a consequence not of endomolecular but of exomolecular interactions, i.e., of the formation of electron-donor-acceptor complexes (e.d.a. complexes (^{4})) through interaction of the electron-donor component A^1KA^2 with the acceptor BKA^1 (I) ($^{1-3}$):

I. 

$$O_2N\text{–}\underbrace{\langle\text{phenyl}\rangle}_{B\text{–}K\text{–}A^1}\text{–}(CH_2)_n\text{–}\underbrace{\langle\text{phenyl}\rangle}_{A^1\text{–}K\text{–}A^2}\text{–}A^2 \qquad n = 1, 2, 4;\ A^2 = NH_2, NMe_2, NEt_2.$$

This supposition was confirmed by the observation that the long-wavelength branch of the spectral curve shifts toward longer wavelengths: 1) upon increasing the concentration and 2) upon adding to a solution of compounds of type (I) an excess of one of the components*: BKA^1 in the form of* p*-nitrotoluene or nitrobenzene, A^1KA^2 in the form of *p*-CH_3—C_6H_4—NH_2, *p*-CH_3—C_6H_4—NR_2, or C_6H_5—NH_2, C_6H_5—NR_2 (^{2}). Of particular interest is the use as BKA^1 of a simplified model in the form of nitrobenzene (NB), and as A^1KA^2 of aniline (AN), dimethylaniline (DMA), and diethylaniline (DEA) as solvent, i.e., in the form of a large excess in order to shift the equilibrium toward the e.d.a. complex.

Fig. 1. Absorption spectrum of 4-nitro-4^1-aminodiphenylethane.
I –calculated sum, $C = 10^{-4}$ mol/l; *II* –in *n*-hexane, $C = 10^{-4}$ mol/l; *III* –in alcohol, $C = 10^{-4}$ mol/l; 3 –in NB, $C = 10^{-2}$ mol/l; 3*a* –in NB, $C = 10^{-4}$ mol/l; 3*b* –in AN, $C = 10^{-2}$ mol/l; 3*v* –in AN, $C = 10^{-4}$ mol/l.

For derivatives (I), at $C = 10^{-2}$ mol/l in NB solution, as compared with spectra in *n*-hexane, benzene, and alcohol, there is not only a bathochromic shift of the absorption boundary at $\lg\varepsilon = 1$, but also a significant increase in $\varepsilon_{\max}$ of the e.d.a. band (Figs. 1 and 2). At $C = 10^{-4}$ mol/l, besides preservation of the e.d.a. α-band with a peak at 420 mµ, a clearly pronounced e.d.a. β-band appears with $\lambda_{\max}$ 440–445 mµ (Table 1, Nos. 6a, 7a, 8a, 9a).

* Method for proving the connection of the spectrum with formation of an e.d.a. complex, proposed by V. A. Izmailskii and V. E. Limanov (5).

Table 1*

No.	Compound	Solvent**	Conc., mol/l	e.d.a. bands, $\lambda_{\max}$	e.d.a. bands, $\varepsilon_{\max}$	Long-wavelength limit at $\lg\varepsilon = 1$
1	$C_6H_5—NH_2$ (5)	NB	10^{-2}	430	54	
2	$O_2NC_6H_4—CH_2—C_6H_4—NH_2$	NB	10^{-2}	425	120	485
2a		NB	10^{-4}	α 420 β 445	30190	494
2		AN	10^{-2}	~ 420	160	490
2		AN	10^{-4}	~ 420	1580	485
3	$O_2N—C_6H_4—(CH_2)_2—C_6H_4—NH_2$	NB	10^{-2}	425	255	501
3a		NB	10^{-4}	α 420 β 440	58210	492
3		AN	10^{-2}	~ 420	270	508
3		AN	10^{-4}	445	1320	507
4	$O_2N—C_6H_4—(CH_2)_4—C_6H_4—NH_2$	NB	10^{-2}	425	195	521
4a		NB	10^{-4}	α 420 β 445	50235	512
4		AN	10^{-2}	420	160	520
5	$C_6H_5—NMe_2$ (5)	NB	10^{-2}	427	232	
6	$O_2N—C_6H_4—CH_2—C_6H_4—NMe_2$	NB	10^{-2}	420	875	514
6a		NB	10^{-4}	442	620	516
6		DMA	10^{-2}	~ 420	470	510
6		DMA	10^{-4}	~ 420	670	501
7	$O_2N—C_6H_4—(CH_2)_2—C_6H_4—NMe_2$	NB	10^{-2}	420	840	550
7a		NB	10^{-4}	α 420 β 442	320850	547
7		DMA	10^{-2}	430	530	557
7		DMA	10^{-4}	430	830	530
8	$O_2N—C_6H_4—CH_2—C_6H_4—NEt_2$	NB	10^{-2}	420	900	530
8a		NB	10^{-4}	α 420 β 435	9001000	527
8		DEA	10^{-2}	~ 420	680	533
8		DEA	10^{-4}	~ 420	700	527
9	$O_2N—C_6H_4—(CH_2)_2—C_6H_4—NEt_2$	NB	10^{-2}	420	660	530
9a		NB	10^{-4}	α 420 β 440	175500	524
9		DEA	10^{-2}	430	155	527

Fig. 2

Figure 2: Fig. 2

No.	Compound Solvent**	Conc., mol/l	e.d.a. bands, $\lambda_{\max}$	e.d.a. bands, $\varepsilon_{\max}$	Long-wavelength limit at $\lg\varepsilon = 1$
9	DEA	10^{-4}	430	575	520

* The numbers of compounds and solutions in the table correspond to the numbers of the curves in Figs. 1 and 2.
** AN–aniline, NB–nitrobenzene, DMA–dimethylaniline, DEA–diethylaniline.

A similar picture is observed with an excess of A^1KA^2, i.e., for solutions in aniline (Nos. 2 , 2 , 3 , 3 , 4) and in dimethylaniline (Nos. 6 , 6 , 7 , 7 , Figs. 1 and 2) or in diethylaniline (8 , 8 , 9 , 9).

The close position of the observed maxima in the indicated solutions to the maxima of the e.d.a. complexes $[C_6H_5$—$NMe_2 + C_6H_5$—$NO_2]$, $[C_6H_5$—$NH_2 + C_6H_5$—$NO_2]$ according to (5) (Table 1, Nos. 1, 5) confirms the correctness of explaining their origin as the result not of endo-, but of exo-interaction of the systems A^1KA^2 and BKA^1 (I).

Measurement of the electron paramagnetic resonance (e.p.r.) spectra showed that charge transfer can occur only for the substance in the solid crystalline state, whereas ionization in solution does not occur. The e.p.r. effect for the solution [nitrobenzene + dimethylaniline]

is absent at room temperature in the liquid state and upon cooling. *No appreciable EPR effect was also found for derivatives of* p*-nitrodiphenylmethane in the region corresponding to absorption of a free electron with a g-factor equal to ~ 2.000. This can be explained as the result

Fig. 2. Absorption spectra of 4-nitro-4′-dimethylaminodiphenylethane. I–calculated sum, $C = 10^{-4}$ mol/l; II–in n-hexane, $C = 10^{-4}$ mol/l; III–in alcohol, $C = 10^{-4}$ mol/l; 7–in NB, $C = 10^{-2}$ mol/l; 7a–in NB, $C = 10^{-4}$ mol/l; 7b–in DMA, $C = 10^{-2}$ mol/l; 7–in DMA, $C = 10^{-4}$ mol/l.

of the inductive interaction of the CH_2 group-separated electron-acceptor (BK^{A^1}) and electron-donor $(A^1K^{A^2})$ systems. In a single molecule there is an equalization of the ionization potential of the indicated components, thereby reducing the ability to form EDA complexes (^{1,2}) and hindering charge transfer.

With lengthening of the polymethylene chain separating the benzene nuclei, the inductive interactions weaken sharply, and the ionization potential of the electron-donor system should decrease, while the electron-affinity energy of

Fig. 3

Figure 3: Fig. 3

the nitro system should increase; consequently, the appearance of an EPR signal could be expected. In a series of derivatives of *p*-nitrodiphenylethane (I. $A^2 = \mathrm{NH_2}$, $\mathrm{NMe_2}$ and $\mathrm{NEt_2}$), only very weak absorption at the noise level was observed. However, for 4-nitro-4′-aminodiphenylbutane with $(\mathrm{CH_2})_4$ in the crystalline state, a distinct absorption line appeared with a width of ~ 11 oersted and a *g*-factor coinciding with the *g*-factor of the standard (diphenylpicrylhydrazyl) (Fig. 3). Thus, with lengthening of the chain separating the benzene nuclei in derivatives (I), a spin density appears in the crystalline state, which is undoubtedly associated with transfer of an electron from the electron-donor to the electron-acceptor system.

Fig. 3. EPR spectra. *a*—diphenylpicrylhydrazyl, *b*—4-nitro-4′-aminodiphenylbutane.

* Upon cooling with liquid nitrogen, the light-red liquid turns into colorless crystals, which indicates decomposition of the complex (analogously to (^{6})).

An unexpected increase of ε in the region of the EDA band is observed when the concentration of solutions in AN, DMA, DEA, and NB is decreased, and at the same time there is a considerable broadening of the band; on the other hand, there is a considerable decrease of ε of the EDA α-band in NB with a hypsochromic shift from 425 to 420 mμ ($\Delta\lambda = -5$ mμ) and the appearance of a new maximum in the region 440–445 mμ (Table 1, Figs. 1 and 2, Nos. 2a, 3a, 4a, 6a, 7a, 8a, 9a), the intensity of the peak of the EDA α-band varying in the order $\mathrm{NH_2} > \mathrm{NEt_2} > \mathrm{NMe_2}$ (Figs. 1 and 2).

On the basis of the work of Briegleb and Czekalla (^{7}), we put forward the hypothesis that in our case, too, EDA complexes of two types are formed in NB solution: an EDA α-complex as a result of layered association of molecules of type (I) without participation of solvent molecules (EDA α band); and an EDA β-complex as a result of layered association of molecules of type (I) with participation of solvent molecules (EDA β band). With decreasing concentration, the EDA α complex decomposes to a considerable extent as a result of a shift of the equilibrium toward nonassociated molecules. As a consequence, the relative fraction of the EDA β complex increases because of the very large excess of one of the components (the solvent). In this process the absolute absorption decreases, while the molar absorption increases.

State Scientific Research Institute
of Organic Intermediates and Dyes

Institute of Chemical Physics
Academy of Sciences of the USSR

Moscow State Pedagogical Institute
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Note: Figure translations are in progress. See original paper for figures.