Spectroscopic studies of the autocomplex type compounds
1. Use of spectrophotometry derivatives for interpretation of electronic spectra of autocomplexes of the picramide series

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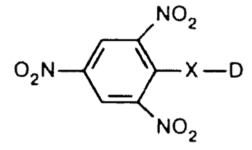
The complicated electronic absorption spectra of several picramide autocomplexes were interpreted by the second derivative spectrophotometric method. A linear correlation was established between the values of the intramolecular charge-transfer energy and the ionization potential of a donor fragment of molecules. The ionization potentials of several compounds were determined.

Key words: autocomplexes, electronic absorption spectra; spectrophotometry, derivatives; ionization potentials.

It is known that the main criterion of assignment of compounds to the type of autocomplexes is the existence of the long-wave absorption band in their electronic spectra, which is absent in spectra of simpler substances modeling individual donor and acceptor fragments. As a rule, the intramolecular charge-transfer (ICT) band undergoes a bathochromic shift as the donor component is enhanced. Its position on the frequency scale, ν_{CT} (or the corresponding energy, E_{CT}), is the experimental spectroscopic parameter of the autocomplex, which is used most frequently for the analysis of donor-acceptor interactions in such systems.

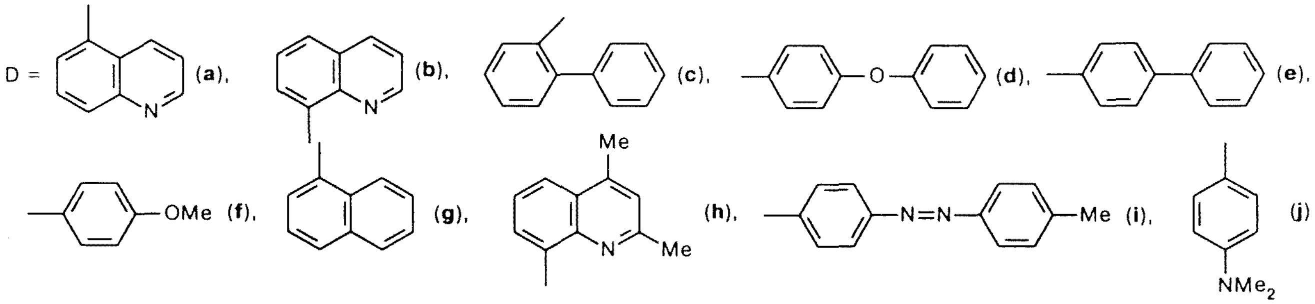
The linear dependence of the energy of the transition from ICT on the ionization potential of the donor fragment is usually observed in the electronic spectra of autocomplexes of the same type. However, in some cases, for example, for autocomplexes of the nitroaryl series,[1] no similar correlation is observed, because absorption bands overlap upon the usual spectrophotometric measurement.

These difficulties can be eliminated by the method of second derivatives of absorption spectra along the wavelength in narrow spectral regions.[2] The latter condition is necessary to exclude the possible distortion of symmetry of the initial absorption spectra and, hence, their derivatives, because in the comparatively narrow spectral ranges, the wavelength is almost linearly related to the frequency, and the forms of the derivatives by frequency and wavelength are the same.



1a,c—f,h,j, 2b,e—g,i,j

X = NH (**1**), O (**2**)



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The presence of two unresolved absorption bands in the electronic spectra is determined by the appearance of two negative maxima or satellites positive in asymmetry in the second derivatives.

This work presents the results of the studies of several autocomplexes of the picramide series (**1** and **2**) by spectrophotometry using the second derivative method.

Results and Discussion

The procedures of the syntheses of compounds **1** and **2** and the results of their spectral studies were presented in previous communications.[3—9] To interpret the absorption spectra, we used an empirical method that makes it possible to determine the number of bands and their origin in electronic spectra of polysubstituted benzene derivatives of the donor-acceptor (D—A) type.[10] According to this method, the spectra of the considered compounds **1** and **2** should exhibit (as the excitation energy decreases) bands corresponding to the charge-transfer transitions: from the donor XD fragment to the acceptor p-NO_2 group ($CT_{XD}{}^{p\text{-}NO_2}$); from the XD fragment to the planar o-NO_2 group ($CT_{XD}{}^{o\text{-}NO_2}$); and the band of the intramolecular charge transfer that occurs through the space between the donor fragment and the second o-NO_2 group shifted from the plane of the trinitrophenyl ring.

Table 1. Electronic absorption spectra of autocomplexes **1a,c—f,h,j** in chloroform, the results of the second derivative method; ionization potentials (*IP*) of donor fragments, and the values of ICT energies (E_{ICT})

Compound	IP/eV[11,12]	$CT_{NHD}{}^{p\text{-}NO_2}$	$CT_{NHD}{}^{o\text{-}NO_2}$	ICT	E_{ICT}/eV
		λ_{max}/nm (ε)			
1a	9.28		365[a] (15300)		
		305—310[b]	335[b]	372[b]	3.33
1c	8.78[c]		374[a] (13410)		
		325[b]	374[b]	384[b]	3.23
1d	8.50		378[a] (13650)		
		325[b]	372[b]	385[b]	3.22
1e	8.27		360 (12600)	390 (14400)	3.18
1f	8.22		385[a] (11900)		
		335[b]	376[b]	395[b]	3.14
1h	8.10[c]		416[a] (14680)		
		315[b]	350[b]	408[b]	3.04
1j	7.14	312 (11280)	390 (7400)	468 (9600)	2.65

[a] The band has a complex character.

[b] The λ_{max} value of the negative peak of the second derivative of the absorption spectrum.

[c] The *IP* value was determined experimentally by line *A* (see Fig. 1).

Table 2. Electronic absorption spectra of autocomplexes **2b,e—g,i,j** in chloroform, the results of the second derivative method; ionization potentials (*IP*) of donor fragments, and the values of ICT energies (E_{ICT})

Compound	IP/eV[11,12]	$CT_{OD}{}^{p\text{-}NO_2}$	$CT_{OD}{}^{o\text{-}NO_2}$	ICT	E_{ICT}/eV
		λ_{max}/nm (ε)			
2b	8.67		294[a] (15300)		
		276—300[b]	314[b]	345[b]	3.59
2e	8.27	250—260 (20000)	335—340[a] (3250)		3.48
			326[b]	356[b]	
2f	8.22	250—260 (15000)	340[a] (2900)		3.42
			330[b]	362[b]	
2g	8.14	270 (14000)	330—340[a] (2200)		3.42
			340[b]	362[b]	
2i	7.85[c]		336[a] (20000)		3.30
		320[b]	335[b]	376[b]	
2j	7.14	265—270 (15840)	355[a] (3800)		3.10
			340[b]	400[b]	

[a] The band has a complex character.

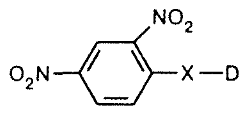
[b] The λ_{max} value of the negative peak of the second derivative of the absorption spectrum.

[c] The *IP* value was determined experimentally by line *B* (see Fig. 1).

However, the analysis of the absorption spectra of compounds **1** and **2** shows that all of them contain only one broad long-wave maximum, which undergoes some bathochromic shift as the donor component is enhanced. The supposition that this broad long-wave maximum is complex and conceals several transitions was confirmed by the results of the studies by the second derivative method. The application of the latter makes it possible to distinguish three independent transitions in one broad maximum in each particular case.

Tables 1 and 2 present the values of wavelengths of absorption maxima (λ_{max}/nm) and extinction coefficients (ε/L mol^{-1} cm^{-1}) of charge-transfer bands of the studied compounds obtained experimentally; the results of their assignment (see Ref. 10), the values of wavelengths of the negative peaks of the second derivatives of the absorption spectra, the values of ionization potentials (*IP*/eV)[11,12] of the donor fragments, and the calculated values of ICT energies (E_{ICT}). The comparison of the absorption spectra and the second derivatives in the series of compounds **1** and **2e,f,j** studied allows one to estimate the effect of the nature of the bridge group X on the extent of charge transfer in the autocomplexes, which increases from X = O to X = NH.

To confirm the validity of the assignments in the electronic spectra of the autocomplexes studied, some of their dinitro-analogs **3e,j** and **4e,f,j** were synthesized and studied by spectrophotometry.



3e,j, 4e,f,j
X = NH (**3**), O (**4**)

Compounds **3e,j** have been obtained previously.[8] Derivative **4e** has been synthesized for the first time, and compounds **4f,j** are described in the literature.[13]

Table 3. Absorption spectra of autocomplexes **3e,j** and **4e,f,j** in chloroform, the results of the second derivative method; ionization potentials (*IP*) of donor fragments

Compound	*IP*/eV[11,12]	$CT_{XD}^{p\text{-}NO_2}$	$CT_{XD}^{o\text{-}NO_2}$
		λ_{max}/nm (ε)	
3e	8.27	350[a] (16600)	
3j	7.14	350 (10100)	380 (9900)
4e	8.27	252 (23300)	312 (11400) 310[b]
4f	8.22	255 (10360)	285 (12800)
4j	7.14	255 (18000) 250[b]	276 (16800) 274—292[b]

[a] The band has a complex character.

[b] The λ_{max} value of the negative peak of the second derivative of the absorption spectrum.

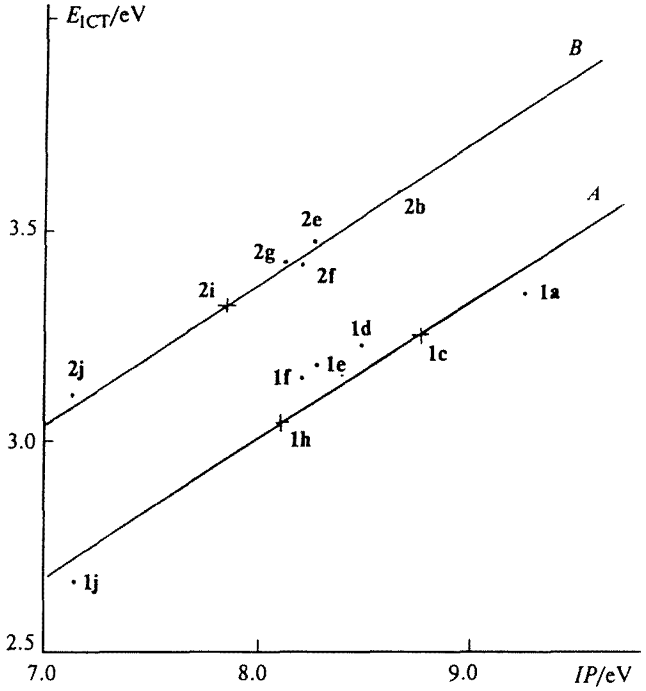


Fig. 1. Dependence of the ICT energy (E_{ICT}) on the ionization potential (*IP*) of the donor fragment. Line *A*, for compounds **1**; line *B*, for compounds **2** (the numeration of the points corresponds to the numbers of compounds in Tables 1 and 2).

Table 3 presents the experimental values of λ_{max}/nm and ε/L mol^{-1} cm^{-1} of the charge-transfer bands of the dinitro-analogs mentioned, the results of their assignment (see Ref. 10), the values of wavelengths of the negative peaks of the second derivatives of the absorption spectra, and the *IP*/eV values for the donor fragments.

The fact that the electronic spectra of the dinitro-analogs contain only two absorption bands related to the *ortho-* and *para*-substituents, respectively, and do not contain the third, long-wave maximum, which was not also determined by the method of second derivatives of the absorption spectrum, confirms the validity of the previous conclusions about the nature of the long-wave maximum in the spectra of trinitro-analogs as the ICT band.

The nature of long-wave transitions as ICT is proved by the existence of the linear dependence (Fig. 1) between E_{ICT} and *IP* according to Eqs. (1) and (2) for autocomplexes **1** and **2** obtained by the statistical processing of the spectral parameters by the least-squares method.

$$E_{ICT} = 0.4 + 0.33IP,\ r = 0.948 \qquad (1)$$

$$E_{ICT} = 0.8 + 0.32IP,\ r = 0.996 \qquad (2)$$

At the same time, the use of the spectral data without the expansion of the absorption bands by the second derivative method for compounds **2** gives the equation of the form $E_{ICT} = 0.68 + 0.38IP$ with the very low correlation coefficient (r = 0.777), which does not allow one to judge about the existence of a statistically significant linear dependence between these values.

Using the correlations obtained (or straight lines A and B in Fig. 1) as calibration ones, the unknown ionization potentials of several compounds can be estimated. Thus, we have determined the ionization potentials of the donor fragments of autocomplexes **1c** (8.78 eV), **1h** (8.10 eV), and **2i** (7.85 eV).

Experimental

IR spectra (in Vaseline oil) were recorded on a UR-20 instrument. UV spectra (in chloroform) were recorded on a Cary-219 spectrophotometer at the concentration of solutions from 10^{-3} to $5 \cdot 10^{-4}$ mol L^{-1}. The second derivative, $d^2A/d\lambda^2$, was recorded in the automatic regime.

Compounds **4f,j** were obtained by the known procedures, and the constants of the compounds synthesized corresponded to the literature data.[13]

2,4-Dinitro-4′-phenyldiphenyloxide (4e). A mixture of 4-hydroxydiphenyl (0.17 g), 2,4-dinitrofluorobenzene (0.372 g), and triethylamine (0.222 g) in DMF (10 mL) were heated for 5 min at 80—100 °C, an aqueous solution (5 mL) of ammonia was added dropwise until the solution became turbid, and the mixture was left for crystallization. The yellow precipitate formed was filtered off, washed with water, and recrystallized from alcohol. The yield was 0.287 g (88 %), m.p. 220—223 °C. IR, ν/cm^{-1}: 1350 (NO_2); 1260 (—O—). Found (%): C, 63.95 and 63.70; H, 3.55 and 3.57; N, 8.01 and 7.98. $C_{18}H_{12}N_2O_5$. Calculated (%): C, 64.29; H, 3.57; N, 8.33.

References

1. O. V. Mikhalev, Ph. D. Thesis (Chem.), M. V. Lomonosov Moscow State University, Moscow, 1988 (in Russian).
2. I. Ya. Bershtein and Yu. L. Kaminskii, *Spektrofotometricheskii analiz v organicheskoi khimii* [*Spectrophotometric Analysis in Organic Chemistry*], Khimiya, Leningrad, 1975, 230 pp. (in Russian).
3. I. G. Il'ina, O. V. Mikhalev, and V. M. Potapov, in *Organicheskie poluprovodnikovye materialy* [*Organic Semiconducting Materials*], Perm' Gos. Univ., Perm', 1986, part 7, 42 (in Russian).
4. I. G. Il'ina, E. V. Ivanova, O. V. Mikhalev, and V. M. Potapov, in *Elektronika organicheskikh materialov* [*Electronics of Organic Materials*], Nauka, Moscow, 1985, 228 (in Russian).
5. I. G. Il'ina, O. V. Mikhalev, and V. M. Potapov, in *Organicheskie poluprovodnikovye materialy* [*Organic Semiconducting Materials*], Perm' Gos. Univ., Perm', 1984, part 9, 102 (in Russian).
6. V. V. Redchenko, S. G. Semenov, O. V. Mikhalev, and I. G. Il'ina, *Zh. Obshch. Khim.*, 1987, **57**, 2599 [*J. Gen. Chem. USSR*, 1987, **57** (Engl. Transl.)].
7. G. V. Gridunova, V. N. Petrov, I. G. Il'ina, Yu. T. Struchkov, and O. V. Mikhalev, *Kristallografiya*, 1990, **35**, 54 [*Sov. Phys.-Crystallogr.*, 1990, **35** (Engl. Transl.)].
8. K. P. Butin, I. G. Il'ina, A. A. Moiseeva, and O. A. Reutov, *Zh. Obshch. Khim.*, 1992, **62**, 188 [*J. Gen. Chem. USSR*, 1992, **62** (Engl. Transl.)].
9. I. G. Il'ina, S. V. Zabaznova, E. V. Ivanova, and K. P. Butin, *Zh. Org. Khim.*, 1994, **30**, 281 [*Russ. J. Org. Chem.*, 1994, **30** (Engl. Transl.)].
10. E. E. Milliaresi, V. E. Ruchkin, T. I. Orlova, and V. V. Efremov, *Dokl. Akad. Nauk SSSR*, 1972, **205**, 353 [*Dokl. Chem.*, 1972, **205** (Engl. Transl.)].
11. F. Gutman and L. E. Lyons, in *Organic Semiconductors*, New York, 1967.
12. V. I. Vedeneev and L. V. Gurvich, in *Energii razryva khimicheskikh svyazei. Potentsialy ionizatsii i srodstvo k elektronu* [*Energies of Chemical Bond Cleavage. Ionization Potentials and Electron Affinity*], Nauka, Moscow, 1974, 229 (in Russian).
13. A. L. Beckwith and J. Miller, *J. Org. Chem.*, 1954, **19**, 1708.

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