

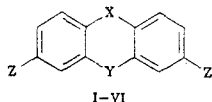
M. B. Ryzhikov, A. N. Rodionov, S. A. Serov,
and D. N. Shigorin

UDC 547.672.2'816'127.3:543.422.6:
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The electron donor and electron acceptor properties of some mono- and dihetero derivatives of 9,10-dihydroanthracene were studied by means of UV spectroscopy and quantum chemistry. Changes in the electronic absorption spectra of these compounds on formation of complexes with π -electron donors and acceptors were investigated. Donor-acceptor amphoterism of phenaza- and phenoxaborines is established experimentally.

The spectral luminescent properties of molecules are determined by the relative position of the interacting electronically excited states of different orbital nature and multiplicity [1]. The electronic states are formed from molecular orbitals, the nature and energy of which depend on the electronic structure of the molecule, the heteroatoms it contains, and its functional groups. In the case of monoheteroderivatives of benzene, naphthalene, fluorene, and dihydroanthracene [2], it has been shown that unshared pairs of electrons located in ℓ -AOs [atomic orbitals] of heteroatoms take part primarily in the formation of occupied MOs [molecular orbitals] and the ground state of the molecular system. In a number of cases, the contribution of the ℓ -AO of the heteroatom can determine the energy of the UOMO (upper occupied MO). In its turn, the vacant v_p - or v_d -AOs of the heteroatoms participate in the formation of the LUMO (lowest unoccupied MO) and the orbital nature and energy of the LUMO depends on the contribution of the v -AO of the heteroatoms. The introduction of two heteroatoms of different electronic structure into the molecule must lead to intramolecular charge transfer, the efficiency of which depends on the nature of the heteroatoms and their positions relative to each other. In the absence of direct overlap of the AOs of the heteroatoms, one expects that the autonomy of the electron acceptor (v -AO) and electron donor (ℓ -AO) properties of the segments containing the heteroatoms will be preserved to some degree or other and, as a consequence, the donor-acceptor amphoterism of the molecules.

Some heteroderivatives of dihydroanthracene can serve as examples of molecules of this kind. In the present work, we have studied donor-acceptor interactions of compounds I-VI with the π -acceptor, tetracyanoethylene, and with the π -electron donors pyridine, phenothiazine, and acridine. For comparison in this work we have also studied the complexes of diphenylamine (VII) and diphenyl oxide (VIII) with tetracyanoethylene.



The starting compounds were purified by vacuum distillation and the purity of the materials was checked by the absorption and mass spectra. The donor-acceptor complexes were prepared by simply mixing equal volumes of chloroform or petroleum ether solutions of the compounds investigated ($c = 10^{-6}$ M) and the donors or acceptors ($c = 10^{-3}$ - 10^{-2} M). This ensured that the equilibrium was shifted almost completely to the side of the complexes. The absorption spectra were measured on a Shimadzu MPS-50 spectrophotometer (see Fig. 1). The energies and nature of the UOMO and LUMO were calculated by the LCAO MO method in the CNDO/S-CI approximation [3, 4].

The formation of charge-transfer complexes (CTC) leads to a substantial drop in the intensity of absorption in the UV spectra and the appearance of additional absorption bands that are absent in the electronic spectra of the initial compounds: 855 (I), 544 (II), 848

L. Ya. Karpov Scientific-Research Institute of Physical Chemistry, Moscow 107120. Translated from *Khimiya Geterotsiklicheskikh Soedinenii*, No. 12, pp. 1676-1679, December, 1989. Original article submitted November 9, 1987; revision submitted May 3, 1988.

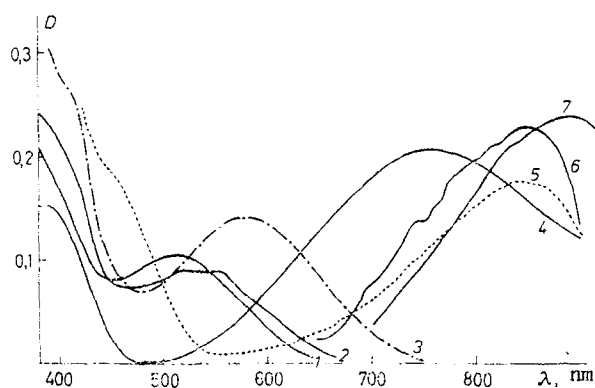


Fig. 1. Electronic absorption spectra of complexes of tetracyanoethylene with the compounds (chloroform, 293 K): 1) diphenyl oxide; 2) phenoxaborine; 3) xanthene; 4) diphenylamine; 5) phenazasiline; 6) phenazaborine; 7) acridine.

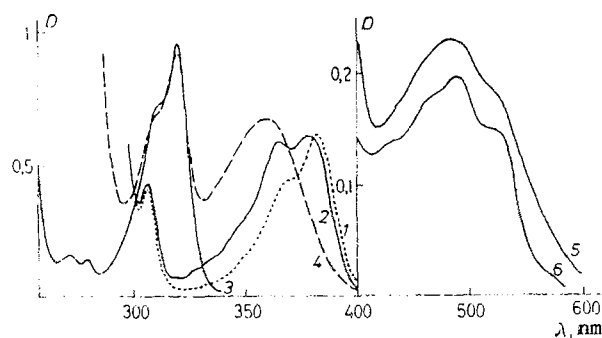


Fig. 2. Electronic absorption spectra (petroleum ether, 293 K): 1) phenazaborine; 2) complex of phenazaborine with pyridine; 3) phenoxaborine; 4) complex of phenoxaborine with pyridine; 5) complex of phenazaborine with phenothiazine; 6) complex of phenoxaborine with phenothiazine.

TABLE 1. Energies of the UOMO and LUMO and the Ionization Potentials (I^*) of Compounds I-VIII (eV)

Compound	x	y	z	E_{UOMO}	E_{LUMO}	$h\nu_{CTC}$	I_{theor}	I_{calc}	I_{exp}
I	N-CH ₃	B-OH	CH ₃	-8.21	-1.16	1.45	7.77	6.67	—
II	O	B-OH	H	-8.44	-1.14	2.28	7.93	8.12	—
III**	N-CH ₃	Si-(CH ₃) ₂	H	-8.73	-1.35	1.46	8.14	6.69	7.17
IV**	O	Si-(CH ₃) ₂	H	-9.37	-1.25	2.22	8.60	7.98	7.79
V	N-H	CH ₂	H	-7.83	0.04	1.38	7.49	6.55	7.24
VI	O	CH ₂	H	-8.40	-0.07	2.10	7.90	7.78	—
VII	—	—	—	-8.70	—	1.63	8.12	6.98	7.33
VIII	—	—	—	-9.42	—	2.41	8.64	8.30	8.10

* I_{theor} were obtained by quantum mechanical calculations;
 I_{calc} from UV spectral data for the CTC; I_{exp} from PE spectral data.

**Data calculated by the PPDP method from [7].

(III), 560 (IV), 900 (V), 582 (VI), 760 (VII), and 514 (VIII) nm. The compounds investigated clearly divide into two groups according to the energy of the long-wavelength absorption band of the CTCs: nitrogen derivatives (I, III, V, VII) and oxygen derivatives (II, IV, VI, VIII). The closeness of the values of λ_{max} of the CTC with tetracyanoethylene within each group and the marked difference of λ_{max} between the groups indicate a definite contribution in the CTC of molecular orbitals of the Ph-O-Ph and Ph-N-Ph segments containing π -AOs of nitrogen and oxygen. The presence in compounds I-VI of the electron acceptor segments

Ph-B-Ph and Ph-Si-Ph does not substantially affect the energy of the CTC. This regularity is confirmed by the pairwise comparison of the λ_{\max} values of the CTC of compounds I, II, III, and IV and compounds V, VI, VII, and VIII. Nevertheless, the differences observed in the λ_{\max} values within each group can be related to the change in the donor strength of the ℓ -AO of oxygen and nitrogen as a result of their participation in the formation of intramolecular charge transfers. From quantum chemical calculations, it follows that the contribution of the p_z -AO of the heteroatoms to the UOMO of molecules of compounds I-VI depends on the nature of the heteroatom and is 16% (IV) and 14.5% (II) for oxygen, 29% (III) and 25% (I) for nitrogen, and 1-3% (I-IV) for boron and silicon.

Analysis of the functional constitution and structure of the UOMO of compounds I-VI confirmed that their nature is formed by Ph-N-Ph (II, VI, IV) and Ph-O-Ph (I-III) segments. Hence, one should expect a similarity in the UOMO energies and ionization potentials in each group of compounds investigated. In fact, the UOMO energies and ionization potentials calculated in the CNDO/S-CI approximation as well as those obtained by the procedure in [6] based on spectral data for the CTC with tetracyanoethylene and the data in [5, 6] for PE [photoelectron] spectra confirm this rule (Table 1).

On the other hand, the presence of a heteroatom with a vacant v -AO (boron, silicon) has to lead to differences in the strength of the electron acceptor properties of compounds I-IV (Fig. 2). The formation of the complexes is accompanied by the appearance of additional bands, the λ_{\max} of which are dependent on the nature of the acceptor segment Ph-B-Ph and donor molecule and virtually independent of the Ph-N-Ph and Ph-O-Ph segments of the compound studied. Thus, λ_{\max} of the CTC in the UV spectra of compounds I and II are observed in one and the same region, depending on the donor molecule: 360 nm for pyridine, 380 nm for acridine, and 500 nm for phenothiazine.

The lack of marked changes in the UV region investigated of the spectra of mixtures of phenazasiline, III, and phenoxasiline, IV, with the donor molecules used, confirms that the electron-accepting ability of the vacant v_d -AO of silicon is substantially less than that of the v_p -AO of boron. An analysis of the quantum chemical data shows that, unlike the UOMO, the functional structure of the LUMO in the compounds investigated is formed with the substantial participation of the boron v_p -AO (35-45%) and the silicon v_d -AO (8-10%), while the contributions of the oxygen and nitrogen ℓ -AO do not exceed 2-3%. The LUMO is fundamentally localized on the Ph-Y-Ph segment; this also causes the LUMO characteristics to depend on the properties of this segment. In fact, the energies of the LUMOs of compounds I and II, III and IV, and V and VI are pairwise similar (Table 1).

Thus, phenaza- and phenoxaborines display both π -donor and π -acceptor properties. The ionization potentials (UOMO energies) depend basically on the structure of the donor fragment and the contribution of the ℓ -AO to the UOMO. In turn, the electron affinities (LUMO energies) are determined by the contribution of the boron v_p -AO to the LUMO and are weakly dependent on the structure of the donor fragment of the molecules.

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