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EFFECT OF THE HETEROATOM ON THE ENERGIES OF THE BOUNDARY MOLECULAR ORBITALS OF DIBENZO DERIVATIVES OF FIVE-MEMBERED HETEROCYCLES

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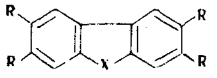
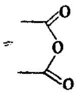
The effect of the heteroatom on the energy characteristics of their boundary molecular orbitals was studied by investigation of the charge-transfer complexes (CTC) of the dibenzo derivatives of five-membered heterocycles. Tetramethyl-substituted dibenzo derivatives of five-membered heterocycles were investigated as electron donors, and their corresponding dianhydrides were investigated as electron acceptors. Their ionization potentials and electron affinities, respectively, were determined. From the regularities in the change in these characteristics it was concluded that replacement of one heteroatom by another leads to approximately identical energy shifts of both boundary molecular orbitals.

The energy characteristics of the boundary molecular orbitals (BMO) for a number of similar compounds are directly related to their properties, such as, for example, their ability to undergo oxidation and reduction. The establishment of the regularities in the change in the BMO therefore makes it possible to predict certain properties of an unknown compound of a given series. In this connection, the problem of the effect of the heteroatom on the energy characteristics of the BMO of dibenzo derivatives of five-membered heterocycles (I) is extremely interesting since many practically important substances contain this fragment:



I–III

a X = SO_2, b O, c S, d $NCOCH_3$, e NH;

I R = H; II R = CH_3; III RR =


The energies of the BMO can be characterized by the ionization potentials (IP) and the electron affinities (EA). The latter can be determined by a study of the charge-transfer complexes (CTC) of the investigated compounds both with electron-donor and electron-acceptor components. Since the principles of the effect of the heteroatom on the IP and EA of the I system should not change in the case of a certain modification of the system itself, stronger donors — tetramethyl-substituted dibenzo derivatives (II) — were investigated in the determination of the IP, and the corresponding dianhydrides (III) were investigated in the determination of the EA. For comparison, we investigated the properties of the corresponding sulfones IIa and IIIa.

Except for IIa, all electron donors II readily form CTC with such electron-acceptors as p-chloranil (HA) and tetracyanoethylene (TCNE). New long-wave bands associated with intermolecular charge transfer appear in the absorption spectra of mixed solutions of the compo-

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TABLE 1. Maxima of the Charge-Transfer Bands in Chloroform Solutions and Ionization Potentials (IP) of I and II

No.	Donor	λ_{max}, nm		IP*, eV	IP, eV, literature data
		HA	TCNE		
1	Ib	475	530	8,1	7,9[2]
2	Ic	500	572	7,9	7,9[2]
3	Ie	555	623, ~370†	7,7, ~9,1†	7,68; 8,08, 9,09[3]
4	IIa	465	520	8,15	—
5	IIb	563	630	7,65; 8,7, ~9,3	—
6	IIc	580, ~385	647, ~420, ~355	7,55; ~8,6; 9,1	—
7	IId	577, ~385	650, ~420, ~360	7,55; ~8,6; 9,1	—
8	IIe	641, ~400	727, ~435, ~370	7,35; ~8,5; ~9,0	—

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*Rounded off to 0.05.

†The second and third ionization potentials are approximate because of the fact that the precise maxima of the charge-transfer bands are difficult to determine.

TABLE 2. Maxima of the Charge-Transfer Bands for the Charge-Transfer Complexes

No.	Acceptor	λ_{max}, nm				EA*, eV
		pyrene	anthracene	BTTF	MTTF	
1	HA	600	615	880	—	2,45
2	IIIa	497	505	670	860	2,0
3	IIIb	~420	—	550	650	1,55†
4	IIIc	—	—	—	640	1,5†
5	IIId	—	—	—	640	1,5†
6	IIIe	—	—	—	580	1,3†

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*Rounded off to 0.05 eV.

†Compound IIIa was a comparison acceptor.

nents (Table 1). The results of a study of the CTC of Ib, Ic, and Ie are also included in Table 1, although some of these complexes have already been described [1]. Since the first ionization potentials in the Ib, Ic, and Ie and IIb, IIc, and IIe series are interrelated by a linear dependence, the assumption that a certain degree of modification of the I system will not distort the effect of the heteroatom should be considered to be fully justified.

The first ionization potentials obatined for I are in good agreement with the data from photoelectronic spectroscopy. It is interesting that it is possible in many cases to record not only the long-wave charge-transfer bands but also one or even two short-wave charge-transfer bands. In those cases for which several bands can be recorded for the CTC of both acceptors their relative energy shift does not depend on the acceptor. It is also known that the appearance of several charge-transfer bands in the case of complexes of the HA and TCNE acceptors is usually associated with the fact that the donor uses several occupied orbitals [4]. Consequently, from the position of the second and third charge-transfer bands one can roughly determine the values of the successive IP [5]. The data from photoelectronic spectroscopy for Ie and the corresponding benzo derivatives [6] confirm this.

The first ionization potentials decrease in the following order for substituent X: SO_2 > O > S > $NCOCH_3$ ∿ NH. By taking X = O as the reckoning point [6], one can obtain the quantitative characteristics (Y) of the heteroatoms and the X groupings from the equation $Y_X = IP_X - IP_O$: Y_{SO_2} = 0,5, Y_O + 0, Y_S = Y_{NCOCH_3} = −0.1, and Y_{NH} = −0.3.

The acceptor properties of dianhydrides III were determined by a study of the CTC in absolute dioxane with such electron donors as pyrene, anthracene, dibenzotetrathiofulvalene (BTTF), and tetramethyltetrathiofulvalene (MTTF). The results of these studies are presented in Table 2.

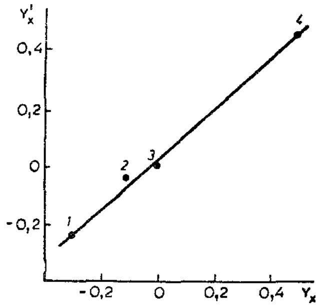

Fig. 1. Relationship between the effect of the heteroatom on the energy of the higher occupied MO of II and the lower vacant MO of III. Compounds II and III contain the following heteroatoms and groupings: 1) NH; 2) $NCOCH_3$ and S; 3) O; 4) SO_2.

Except for IIIa, all of the remaining dianhydrides are relatively weak electron acceptors [7]. Their electron affinities are lower than that of pyromellitic dianhydride (1.9 eV) and are found in the range of the EA of maleic anhydride (1.4 eV). Only the strongly electron-withdrawing SO_2 grouping increases the electron affinity to 2.0 eV. It should be noted that the determination of the EA values for the IIIb-e acceptors in practice reduced to a study of the CTC of one donor (MTTF), and this makes the EA values obtained for these acceptors less reliable than those obtained for the IIIa acceptor.

Using the EA values in analogy with Y, one can determine new quantitative characteristics of heteratom Y' from the equation

$$Y' = EA_O - EA_X:$$

$$Y'_{SO_2} = 0.45;\ Y'_O = 0;\ Y'_S = Y'_{NCOCH_3} = -0.05;\ Y'_{NH} = -0.25$$

It was found that Y'_X depends approximately linearly on Y_X (see Fig. 1), i.e., a change in X in the given π-electron systems leads to a simultaneous decrease or increase in both frontal MO, and the magnitudes of these shifts are proportional to the characteristics of Y_X. The lower vacant MO of III is less sensitive to a change in the heteroatom or the X grouping than the occupied MO of II; this is evidently associated with the more developed π-electron system of the former. It may therefore be assumed that a change in the heteroatom in the starting I systems leads to approximately identical shifts of both BMO.

EXPERIMENTAL

The electronic absorption spectra of solutions of the compounds in chloroform containing 3% by volume ethanol and in absolute dioxane [8] were recorded with a Specord UV-vis spectrophotometer. The ionization potentials were calculated from the equations $h\nu = 0.87\ IP - 4.46$ eV and $h\nu = 0.82\ IP - 4.31$ eV for the CTC of the HA and TCNE acceptors, respectively. The electron affinities were calculated from the equation $h\nu_{HA} - h\nu_X = EA_X - EA_{HA}$, where $h\nu_{HA}$ and $h\nu_X$ are the charge-transfer energies for the CTC of a given donor with the HA acceptor and the investigated acceptor, respectively, and EA_X and EA_{HA} are the corresponding electron affinities for the investigated acceptor and p-chloranil.

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