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CHARGE-TRANSFER SPECTRA OF CONJUGATED HYDROCARBONS, THEIR HETERO-ANALOGUES, AND DERIVATIVES

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IT is well known that there exists a relationship between the energy of the highest occupied π-molecular orbital (HOMO) of donors and the energy of the first absorption charge-transfer band ($\tilde{\nu}$) belonging to their complexes with various acceptors.[1-5]

Hitherto, however, most interest has been devoted to the relation of the energy $\tilde{\nu}$ to the ionization potentials of donors.[6] The correlations between the energies $\tilde{\nu}$ and HOMO as already studied are not very close. For the sake of clearness let us begin with the examination of hydrocarbons, which represent the simplest compounds among those under investiga-

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tion (hydrocarbons, hetero-analogues, substituted derivatives). First of all we shall treat the dependence for the complexes with 1,3,5-trinitrobenzene because these data are most complete. In Fig.1 the energies of charge-transfer bands[2,7,8] are plotted against the energies of HOMO calculated by means of the simple MO-LCAO method. The set of data includes three types of compounds: benzenoid hydrocarbons, α,ω-diphenylpolyenes and a polyene. Evidently, the correlation of the whole set of data is far from being close. It appears, however, that the data concerning the benzenoid hydrocarbons satisfy fairly well a linear dependence except several hydrocarbons. We suppose that in the case of benzene, triphenylene, and coronene the deviations are caused by the degeneracy of the highest occupied molecular orbitals. In the cases of other acceptors (tetracyanoquinodimethane, tetracyanoethylene, chloranil, p-benzoquinone, and iodine) the data for these three hydrocarbons lie also on a straight line which is parallel to the regression line for benzenoid hydrocarbons but has a significantly smaller value of interception (the constants b, cf. Table I). The deviations of some other data are probably due to experimental errors. The data for polyenes are very limited, nevertheless, it seems that they will satisfy another straight line which is characterized by a higher value of the interception. The data for α,ω-diphenylpolyenes fit a sigmoidal curve (Fig.1). This can be explained by the fact that these compounds pass in the limiting cases into the above-mentioned classes of compounds, i.e. benzenoid hydrocarbons (biphenyl) and polyenes. Evidently, this situation resembles that recently found in the case of the p-bands of

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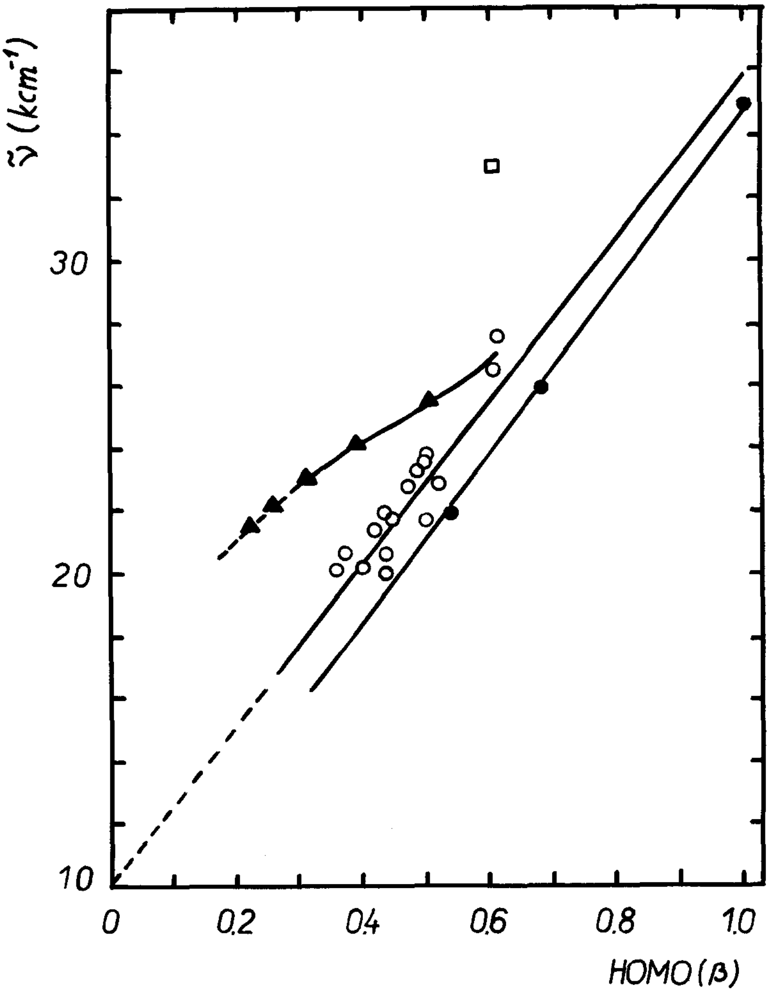

FIG. 1. Energy of the first charge-transfer bands of the complexes of hydrocarbons with 1,3,5-trinitrobenzene plotted against the energies of HOMO. Designation: ○ benzenoid hydrocarbons, ● benzenoid hydrocarbons with degenerate energy of HOMO (benzene, triphenylene, coronene) (both taken from Ref. 2), △ α,ω-diphylpolyenes (taken from Ref. 9), □ 1,3-butadiene.

TABLE I

Constants a and b of Regression Lines of the Dependences $\tilde{\nu}(\mathrm{kcm}^{-1}) =$ $= a \cdot \mathrm{HOMO}\ (\beta) + b$ and Correlation Coefficients r

Donor	Acceptor	n [a]	a	b	r
Benzenoid hydrocarbons	1,3,5-Trinitrobenzene	16	26.551	10.130	0.903
	Tetracyanoethylene	20	26.275	2.202	0.961
	Chloranil	9	25.966	5.080	0.993
	Tetrachlorophthalic anhydride	5	22.614	13.620	0.992
	Tetracyanoquinodimethane	9	26.319	1.581	0.991
	p-Benzoquinone	6	27.215	10.409	0.985
	Iodine	6	20.872	14.583	0.989
Aromatic amines	Tetracyanoethylene	9	23.654	4.351	0.957
	Chloranil	11	25.020	5.893	0.911

[a] Number of compounds.

the electronic spectra of conjugated hydrocarbons.[9] The treatment of the values of the ionization potentials leads to an analogous result. The reasons for such a behaviour are under study.

From Table I it is obvious that for hydrocarbons the slopes of the five straight lines are approximately the same (26.0 - 27.2 kcm^{-1}/β). The values of the slopes of the dependences for tetrachlorophthalicanhydride and especially iodine complexes are markedly smaller. The significance of these slopes should not be overestimated, since the respective sets have relatively few members; besides, in the case of iodine another type of complex

(π - n)is concerned. The magnitude of the interceptions is probably a measure of the electron affinity of acceptors; this view is supported by MO-LCAO calculations.

Moreover, we have studied the energies of the charge-transfer bands of pyridine-like polynuclear compounds and of derivatives of benzenoid hydrocarbons (amines, phenols, halogeno compounds). The complexes of these derivatives with tetracyanoethylene and chloranil exhibit charge-transfer maxima giving a close correlation with the appropriate energies of HOMO.[10] The slopes of the regression lines for amines are similar to those for benzenoid hydrocarbons (Tab.I) but the lines are somewhat shifted. A similar situation exists with heterocyclic compounds and the other above-mentioned derivatives. In both these classes of substances, i.e. derivatives and heterocyclic compounds, the situation is complicated by the reactivity of some compounds.

Further details about these studies will be published in Coll. Czech. Chem. Comm.

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