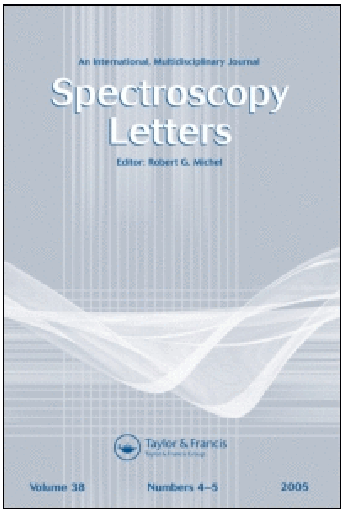

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Dependence of The Relative Location of the nπ - and ππ*- States of Molecules on their Structure

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DEPENDENCE OF THE RELATIVE LOCATION OF THE $n\pi^*$ - AND $\pi\pi^*$- STATES OF MOLECULES ON THEIR STRUCTURE

I. Unsaturated and Aromatic Carbonyl Compounds

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ABSTRACT

The effect of the length and topology of the conjugated bond system on the relative location of the $n\pi^*$- and $\pi\pi^*$-molecular states of the unsaturated and aromatic carbonyl molecules is theoretically investigated.

INTRODUCTION

Spectral, luminescent and photochemical properties of molecules with unsaturated bonds and heteroatoms containing the n- electrons are determinated to a considerable degree by the relative disposition of their $n\pi^*$- and $\pi\pi^*$- excited electronic states [I-4]. At present there are many works concerned with the experimental study of the effect of the molecular structure on the relative disposition of these states (see [3-4] and references therein).

Majority of theoretical investigations of the dependence of the relative $n\pi^*$-and $\pi\pi^*$- state dispositions on the molecular structure based on the one-electron, and one-configuration approximation, or even employed the Hückel method [1], [5-7]. The derived results are merely qualitative and some essential features of the problem at hand can not be described in such an approximation, as will be apparent below. There are several works [8,9] in which the calculation of the energies of the $n\pi^*$- and $\pi\pi^*$ - states have been performed with the use of more exact methods. However, the problem of the relation between the relative disposition of the $n\pi^*$- and $\pi\pi^*$- states and the structural characteristics of the molecule was not raised. Therefore in the present and in the forthcoming papers we reexamine the indicated problem as correctly as possible.

The length of the conjugated bond system of a molecule is the most important characteristic on which the relative disposition of the $n\pi^*$- and $\pi\pi^*$- states is dependent. Previously this point was considered in works [I,5]. In particular it was shown that the energy of the lowest $\pi\pi^*$- state in polyenaldehydes is decreasing more rapidly than the energy of the $n\pi^*$- state when increasing the length of conjugated chain. Thus the molecules with a highly developed system of conjugated bonds have the $\pi\pi^*$- state as their lowest singlet or triplet state. Experimental data agree with this conclusion. However, they indicate [3] that often the energy of the $n\pi^*$- states not only is not decreasing on growing the system of conjugated bonds but it is also increasing. Besides, it is known at present that the relative disposition of the $\pi\pi^*$- and $n\pi^*$-

states depends not only on the extent of the conjugated system, but also on its topology [3,11]. These questions can be studied theoretically in the approximation that evidently takes into account the interaction between electrons and configuration interaction.

In this paper we study the effect of the extent of the conjugated bond system and its topological properties on the relative disposition of the lowest excited ππ*- and nπ*- states for the molecules of the unsaturated and aromatic carbonyl compounds as a particular example.

METHOD OF CALCULATION

The PPP-method was used to calculate the energy levels and wave functions of the molecules. The calculation of the energy levels (ε_n) of n-electrons based on the employment of a model that does not take into account the delocalization of n-electrons. The arguments for such a choice of the model follow from the results of the calculations of molecules with n-electrons in which all the valent electrons have been taken into consideration [12]. These calculations indicate that the delocalization of the n-electrons in carbonyl compounds is small and, what is particularly important, the wave function of n-electrons is noticeably nonzero only for the atoms that are adjacent to C=O group. An experimental foundation of the model follows from the fact that the ionization potentials of the n-electrons in the molecules of the same kind do not change appreciably from molecule to molecule [13]. For example, when passing from the molecule $(CH_3)_2C{=}O$ to $C_4H_9{-}CH_3C{=}O$ - molecule the ionization potential is decreasing only by 0,3 ev.

Since the n-electron delocalization over σ-bonds is not negligibly small, it is taken into consideration when choosing the parameters for calculation.

In the described model the wave function of the n-electrons of carbonyl compounds is the non-hybridized 2px-orbital of the oxygen atom (the x-axis is perpendicular to the C=O bond and lies in the plane of a molecule) The n-orbital energy ε_n is equal to the diagonal matrix element F_{nn} of the Fock energy matrix for which one can write [6,8]:

$$F_{nn} = \varepsilon_n = U'_n + \sum_t (P_{tt} - Z_t^{\pi}) \gamma^{nt}_{2px\ 2pz} - 1/2\ P_{oo} æ^{On}_{2px2pz} \qquad (I)$$

where $U'_n = U_n + \gamma_{nn}$ is the one-center core integral for n-electron on the 2px-orbital at the oxygen atom; P_{tt} - the π-electron density on the atom t; Z_t^{π} - the core π-electron charge of the atom t; γ^{nt}_{2px2pz} - the integral of the Coulomb repulsion between two electrons one of which is on the 2px-orbit of the oxygen atom and the other one is on the 2pz orbit of the atom t (including the oxygen atom as well); P_{oo} - the π-electron density on the oxygen atom; $æ^{on}_{2px2pz}$ - one-center exchange integral of the oxygen atom [8].

The geometry of molecules were estimated from the data of the work [14]. One-center integrals $\gamma_{\mu\mu}$ were evaluated according to Julg [15]. The Mataga-Nishimoto formula [16] has been used for the calculation of the two-electron integrals. The resonance integrals $\beta_{\mu\nu}$ were calculated from the formula of the Wolfsberg-Helmholtz [17] with the parameter K= -1,17. The core potentials U_{μ} and U'_n were estimated with consideration for surroundings [18] and their values together with γ^{no}_{2px2pz} were varied to the best coincidence of the calculated values of the ionization potentials and the energies of the singlet-triplet and singlet-singlet transitions of the formaldehyde molecule with their experimental values. The magnitudes of all the employed parameters are listed in the table.

The energies of the mono-excited singlet and triplet configurations with respect to the ground state energy are given by the formulas

$$\Delta E^{S}_{i\rightarrow j} = E_j - E_i - I_{ij} + 2K_{ij} \qquad (2)$$

$$\Delta E^{T}_{i\rightarrow j} = E_j - E_i - I_{ij} \qquad (3)$$

where i any j are the MO between which the transition occurs; I_{ij} and K_{ij} - Coulomb and exchange integrals for electrons on i-th and j-th MO. Nondiagonal matrix elements of the configuration interaction matrix were calculated from the standard formulas (see, e.g.[8]). The interaction between all the mono-excited configurations for which $E_j - E_i < 10$ ev has been accounted for in the calculations. For aromatic molecules the calculation of the energies of the triplet $T_{\pi\pi^*}$ - states were performed in the limited basis (up to seven) of mono-excited configurations.

TABLE

The Parameters Employed in the Calculations (ev).

$U_c(C{=}O) = -9,10$	$\gamma_{oo} = \gamma_{nn} = 12,51$
$U_c(ph) = -9,50$	$\gamma^{no}_{2px2pz} = 10,20$
$U_o = -15,00$	$\varkappa^{no}_{2px2pz} = 0,90$
$U'_n(O) = -11,60$	$\beta_{cc} = -2,39$ ($R_{cc} = 1,4$A°)
$\gamma_{cc} = 9,87$	$\beta_{co} = -2,80$ ($R_{co} = 1,21$A°)

RESULTS AND DISCUSSION

Dependence of the lowest excited $S_{\pi\pi^*}$-, $S_{n\pi^*}$ -, $T_{\pi\pi^*}$- and $T_{n\pi^*}$- state energies on the length of the system of conjugated bonds in the molecules H-$(CH{=}CH)_N$ - CH=O and Ar-CH=O (Ar - phenyl, naphthyl, anthracene) is shown on Fig. 1, and 2.

It is seen from these figures that the coincidence between the calculated and experimental values of the excited state energies is satisfactory. This may be regarded as a confirmation of the applicability of the model employed in the calculation.

From the fig. 1 and 2 it follows that the energy of the $\pi\pi^*$ - states is appreciably decreasing on the lengthening of conjugated bond system. As for the energies of the $S_{n\pi^*}$- states they are at first lowering but then they increase. One can in-

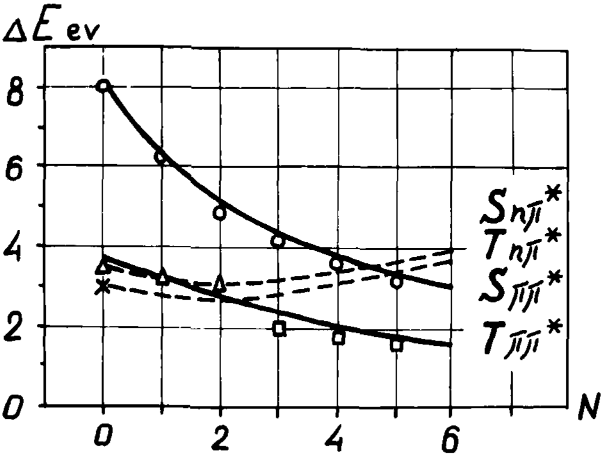

FIG. 1

The Energies of the Lowest Excited $\pi\pi^*$- and $n\pi^*$- states of the Molecule H-$(CH{=}CH)_N$-CH=O as a Function of the Length of the Conjugated Chain.

o-, Δ-, x-, □- experimental values of the $S_{\pi\pi}*$-, $S_{n\pi}*$-, $T_{n\pi}*$- and $T_{\pi\pi}*$- states respectively taken from the works [3,4,8].

(—) and (- - -) the results of our calculation.

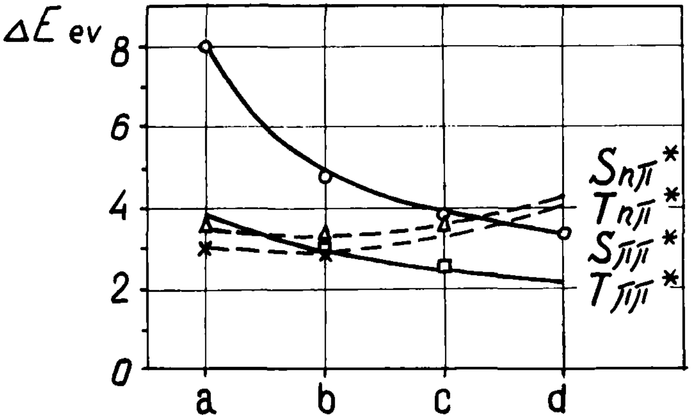

FIG. 2
The Energies of the Lowest Excited $\pi\pi^*$- and $n\pi^*$- states of the Molecule Ar-CH=O as a Function of the Extent of the Conjugated Bond System. (a)-Formaldehyde, (b)-Benzaldehyde, (c)-2-Naphthaldehyde , (d)-2-Anthraldehyde .
o-,Δ-,×-, □ -experimental values of the energies of the $S_{\pi\pi^*}$-, $S_{n\pi^*}$-, $T_{n\pi^*}$- and $T_{\pi\pi^*}$- states respectively taken from the works 3,4,8,11.
(—) and (- - -) - the results of our calculation.

fer from the formulas (2), (3) that the energy of the $n\pi^*$-configuration is determined mostly by two terms: $\mathcal{E}_{\pi^*}-\mathcal{E}_n$ and $I_{n\pi^*}$, for the magnitude of $K_{n\pi^*}$ is relatively small. For small conjugated systems, as they are growing, the first term $\mathcal{E}_{\pi^*}-\mathcal{E}_n$ (decreasing predominantly at the expence of the π^* - orbit energy lowering) dominates in the variation of the energy of the $n\pi^*$- configuration. For large systems, on the contrary, the delocalization of the π^* orbitals is crucial that leads to the predominant decreasing (asymptotically as N^{-1}) of the $I_{n\pi^*}$-integral as compared with $\mathcal{E}_{\pi^*}-\mathcal{E}_n$ when N increases.

This explains the different behaviour of the energy of the $n\pi^*$- states for small and long chains of conjugation when N grows.

When the conjugated bond system is growing a decreasing of the S-T splitting of the $n\pi^*$- states occurs that is caused by the increasing of the π^*- orbit delocalization. However, this splitting would be somewhat smaller if the calculations were perfomed with no regard for the configuration interaction.

All the possible cases of the dependence of the relative position of the $\pi\pi^*$ and $n\pi^*$- states on the structure of the conjugated bond system are not exhausted by the described above. Fig. 3 presents the position of the lowest excited states of p-benzoquinone, 1,4-naphthaquinone and 9,10-anthraquinone (In these cases the splitting of the $n\pi^*$- states was ignored).

One can see from this figure that the decreasing of the energy difference between the $n\pi^*$- and $\pi\pi^*$- states at the lengthening of the conjugated bond system occurs. Nevertheless, the lowest excited singlet state is the $n\pi^*$- state even for 9,10 - anthraquinone having highly developed conjugated system. This

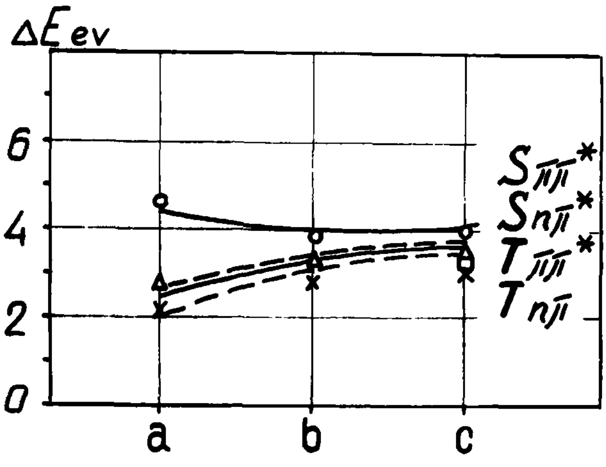

FIG. 3
The Energies of the Lowest Excited States: (a)-p-Benzoquinone, (b)-1,4-Naphthaquinone, (c)-9,10-Anthraquinone.
o-,Δ-,X-,□ -experimental values of the energies of the $S_{\pi\pi^*}$-, $S_{n\pi^*}$-, $T_{n\pi^*}$- and $T_{\pi\pi^*}$- states, taken from [3].
(—) and (- - -) - the results of our calculation.

means that the relative position of the $\pi\pi^*$- and $n\pi^*$- states depends not only on the length of the system of conjugated bonds, but also on its particular type.

As an example confirming this conclusion we display on Fig. 4 the results of the calculation of the lowest excited state energies of 7,8-benz-2-naphthaldehyde and 2-anthraldehyde.

Thus, from the analysis performed it is apparent that a various behaviour of the energies of the $n\pi^*$- and $\pi\pi^*$- states at the changing of the type and length of the conjugated bond system of the carbonyl compounds can be described within the framework of the model that does not incorporates the delocalization of the n-electrons patently. And the interesting thing is that though the intersection of the $n\pi^*$ and $\pi\pi^*$ states at the lengthening of the conjugated chain may occur, the relative position of these states strongly depends on the details of the conjugated system structure as well as on the extent of the conjugation of the C=O group with the rest of the molecule.

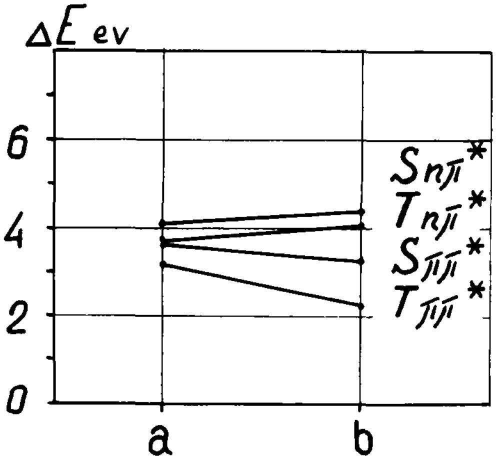

FIG. 4
The Calculated Energies of the Lowest Excited Electronic States of 7,8-benz-2-naphthaldehyde (a) and 2-anthraldehyde (b).

However the applicability of a localized n-electron model to arbitrary molecules does not follow from the present results. In particular, it may turn out that n-electrons are appreciably delocalized in molecules having weak σ-bonds with energy close to the energy of the 2px-electrons of the oxygen atom.

It should be also emphasized that a disaccount of a partial delocalization of the n-electrons in carbonyl molecules with a large conjugation system may lead to the overestimated theoretical values of the $n\pi^*$- state energies as compared with the experimental data. Particularly this may be seen from the Fig. 3.

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