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THE INFLUENCE OF 1,3-π-TYPE ELECTRONIC INTERACTION ON THE SPECTRA OF CYCLOBUTANE DERIVATIVES

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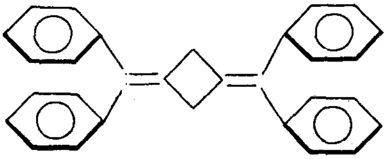
Two methods have been envisaged for the theoretical description of the electronic spectra of organic molecules built from two or more separate fragments, each being a conjugate systems (1, 2, 3).

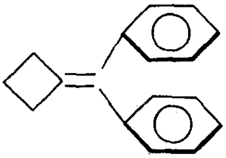
In the first one, due to Davydov, the excited states are described by linear combinations of the wave functions in which the excitation is localized on each fragment.

The second one, developed by Longuet-Higgins and Murrel, is particularly useful for the treatment of molecules in which two or more conjugated systems are connected by one or more non essential double bonds (4).

The 1,3-derivatives of cyclobutane in which the substituents are conjugate systems represent an interesting situation: there is no direct bond between π-electron centers in different fragments but their distance is well below the distance between the molecules in organic crystals. An example of such compound is the 1,3bis-diphenylmethylenecyclobutane molecule (I). The spectra of (I) and of diphenylmethylenecyclobutane (II) have been described by Griffin and Vellturo (5, 6).



(I)



(II)

Both spectra show an intense absorption band due to an allowed π-π electronic transition: λ_{max} = 267 mμ , ε = 31.760 for (I), λ_{max} = 255 , ε = 16.130 for (II) (room temperature, solvent ethanol).

Both the previously mentioned theoretical methods have been used in this work for an interpretation of the bathochromic shift of 11 mμ on going from (II) to (I).

No experimental data are available for the geometry of either compound (I) or (II): the assumed geometry for compound I and II was one with a square cyclobutane ring (C-C distance equal to 1.56 Å), double bonds in the same plane (C=C equal to 1.34 Å), twisting of the phenyl groups of 33°, $C_{arom}-C_{ethyl}$ = 1.48 Å and standard values for the other bond distances and angles.

To provide a suitable basis, standard H.M.O.'s for the 1,1-diphenyl-ethylene fragment were calculated, with β for benzene as reference and taking care of variations with distance and orientation through proportionality to overlap integrals (7, 8). The zero differential overlap approximation was adopted throughout the calculations.

According to Davydov (1), in a molecule that is described as the unification of two equal fragments, each excited state in the fragment, with excitation energy $\Delta E'_i$, is split in two excited states. The excitation energy, owing to the assumed geometry, is given by:

$$\Delta E''_{i\pm} = \Delta E'_i \pm \left(- \frac{2\, e^2 \mu^2}{R^3} - \frac{e^2\, S^2}{R_{\alpha\beta}} - C + 2\, SJ \right)$$

Transition from the ground state to the plus excited states are allowed, and to the minus excited states are forbidden. R is the distance between the midpoints of the transition moments (R = 5.74 Å), $R_{\alpha\beta}$ is the distance between the two closest π-electron centers in different fragments ($R_{\alpha\beta}$ = 2.20 Å), S is the overlap integral between the π-orbitals in these centers, C and J are the exchange and the nuclear attraction integrals for these same orbitals (Slater 2p atomic orbitals with effective nuclear charge z = 3.18 were used). The modulus of the dipole transition moment μ for the fragment was evaluated by an empirical procedure from the first band in the U.V. spectrum (9).

In the L.M. method, interaction was considered between ground configuration, locally excited configurations, and electron transfer configurations. The energy of a locally excited configuration, is taken from experiment, the energy of an electron transfer configuration, is calculated as I - A - Q where I and A are the ionization potential and the electron affinity of the fragments and Q is the coulomb attraction of the transferred electron and the positive hole left in the donating fragment. In the absence of experimental values for I and A , empirical values were obtained from the relations (10):

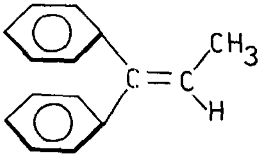
$$A = 2.991 - 0.700\ \Delta E' \qquad \text{and}$$

$$I + A = 8.14\ \text{eV}$$

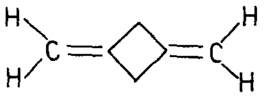
The matrix elements were obtained by standard procedures. The values for the integrals over atomic orbitals were calculated in two different ways: in the first one (w_1) taking care of the different orientations of the orbitals, using the usual semiempirical values of the integrals in the range of distances up to 2.80 Å , the theoretical values from 2.80 Å to 4.85 Å and the point charge approximation for distances larger than 4.85 Å (11, 12); in the second one (w_2) using the last approximation for all distances.

Assessment of the numerical value of the resonance integral β is rather difficult. According to Pariser Parr formula for the variation of β with the distance (13) we obtain $\beta_1 = - 0.043$ eV; the assumption of proportionality of β to the overlap integral gives $\beta_2 = - 0.58$ eV.

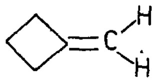
In the case of molecular crystals and of molecules with the fragments connected by non essential double bonds, the choice of the reference molecule for evaluation of transition energies and moments in the fragment is easily made. In our case two possibilities arise: to take (II) as a reference compound or to choose (III), from which molecule (I) can be formally derived following the prescription of Longuet-Higgins and Murrell.



(III)



(IV)



(V)

The former alternative is more suitable to include the effects of the cyclobutane ring on π-electron system; this model takes care of straining and steric effects but hyperconjugative effects are not properly accounted for. Such effects are perhaps better evaluated with the latter reference. Results with both methods and both reference compounds are collected in Table I. From the numerical values of the table, it can be seen that the L.M. method gives better agreement with the experiment. This is most probably due to the fact that the distance between the two fragments is such that the interaction term in the hamiltonian can not be safely expressed as a dipole-dipole interaction.

Therefore the splitting is not completely accounted for and the $\Delta E''_{+}$ values are too high.

TABLE 1

Compound (I) Compound (IV)

A) D Method

Reference compound	$\Delta E''$ (eV)	Reference compound	$\Delta E''$ (eV)
(II)	4.78	(V)	6.06
(III)	4.92	(VI)	6.89

B) L-M Method

Reference compound		$\Delta E''$ (eV)		Reference compound		$\Delta E''$ (eV)	
		β_1	β_2			β_1	β_2
(II)	w_1	4.48	4.43	(IV)	w_1	5.84	5.62
	w_2	4.39	4.34		w_2	5.62	5.40
(III)	w_1	4.62	4.58	(VI)	w_1	6.70	6.32
	w_2	4.52	4.48		w_2	6.48	6.11

$\Delta E''_{exp} = 4.64$ $\Delta E''_{exp} = 6.55$

Giving the preference to L.M. method, from Table I it can be seen that the theoretical evaluation of the electronic repulsion integrals (w_1) gives better results. Such results are not particularly sensitive to the β values, the best of which appears to lie in the explored range. The most appropriate choice of the reference fragment is (III); however the difference is rather small. This is connected with the fact that the maxima of the first absorption band in 1,1-diphenylethylene, 1,1-diphenylpropene and 2-methyl-1,1-diphenylpropene have the same position ($\Delta E' = 5.0$ eV (8)). This indipendence from the number of methyl groups in the molecules is in sharp contrast with the evidence from U.V. spectra of olefins (14): (ethylene 7.7 eV , propene 7.2 eV , isobutene 6.6 eV). These results suggest that in the olefins, with aromatic substituents, steric effects can counterbalance hyperconjugative effects. On this basis it can be forseen that propene should definetely be a better reference than methylenecyclobutane (V) for compound (IV). Spectra of both (IV) and (V) in n-heptane are now available (15, 16) : the first one shows a strong absorption band ($\varepsilon_{max} = 16.000$) in the 180-200 m$\mu$ region with $\Delta E = 6.55$ eV.

A second maximum with almost the same intensity appears at $\Delta E = 6.29$ eV and it is probably due to the vibrational structure of the spectrum. The spectrum for compound (V) shows an absorption band with ε_{max} half that of (IV) and a single maximum at 6.29 eV. Theoretical results for molecule (IV) are shown in Table I. The μ value for absorption of propene in n-heptane solution was evaluated from the theoretical oscillator strength corrected by the ratio f_t/f_{exp} for (III). The frequency was taken from vapour spectrum, with no correction. Again the L.M. method results are better and it is clearly shown that propene, as a reference molecule for the fragment, is the correct choice.

Calculations on a series of compounds to test the difference of results between the two methods and the importance of the reference are in progress.

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