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Molecules in Molecules Calculations on Decacyclene

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The "molecules in molecules" method has been used to calculate the energies of the lowest four excited states of the decacyclene molecule which has been regarded as composed of three acenaphtylene biradicals. Comparison with experimental data and previous theoretical results shows that the results obtained with the present method are satisfactory.

The transition energy of the infrared electronic absorption band of the mononegative ion of decacyclene has been calculated with this method, and is in reasonable agreement with the experimental value.

Because of the small energy difference (approximately 600 cm^{-1}) between the lowest excited singlet states of acenaphtylene and decacyclene it might be profitable to discuss the latter molecule in terms of the molecules in molecules (MIM) method rather than the conventional MO method.

The MIM method developed by Longuet-Higgins and Murrell [1] has been applied to acenaphtylene and fluoranthene [2] and more recently to five groups of hydrocarbon molecules or ions [3].

For the present problem the obvious reason for using the MIM method is the idea, that decacyclene may be regarded as a structure, composed of three acenaphtylene biradiacals.

If the molecular orbitals of the individual acenaphtylenes are denoted by λ_i, μ_i and ν_i, a local excited singlet configuration e.g. $\lambda_{+1}\lambda_{-1}$, as obtained by the promotion of an electron from the highest bonding λ_{+1} to the lowest antibonding orbital λ_{-1}, can be described as:

$$\lambda_{+1}\lambda_{-1} = 2^{-\frac{1}{2}}\{|\ldots \lambda_i\bar{\lambda}_i \ldots \lambda_{+1}\bar{\lambda}_{-1} \ldots| - |\ldots \lambda_i\bar{\lambda}_i \ldots \bar{\lambda}_{+1}\lambda_{-1} \ldots|\}$$

Electron transfer configurations like $\lambda_{+1}\mu_{-1}$ may be formulated in a similar way.

Limiting ourselves to the singly excited configurations, arising from the two highest bonding and two lowest antibonding orbitals of acenaphtylene, we find that according to the covering symmetry D_{3h}, the electronic states of decacyclene can be described in terms of the following functions (the appropriate normalisation factors have been omitted).

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States A_1'

Closed shell ground state configuration

$$\{\lambda_{+1}\lambda_{-2}+\mu_{+1}\mu_{-2}+\nu_{+1}\nu_{-2}\}$$
$$\{\lambda_{+2}\lambda_{-1}+\mu_{+2}\mu_{-1}+\nu_{+2}\nu_{-1}\}$$
$$\{\lambda_{+1}\mu_{-1}-\mu_{+1}\lambda_{-1}+\nu_{+1}\lambda_{-1}-\lambda_{+1}\nu_{-1}+\mu_{+1}\nu_{-1}-\nu_{+1}\mu_{-1}\}$$
$$\{\lambda_{+2}\mu_{-1}+\lambda_{+2}\nu_{-1}+\mu_{+2}\lambda_{-1}+\mu_{+2}\nu_{-1}+\nu_{+2}\lambda_{-1}+\nu_{+2}\mu_{-1}\}$$

States A_2'

$$\{\lambda_{+1}\lambda_{-1}+\mu_{+1}\mu_{-1}+\nu_{+1}\nu_{-1}\}$$
$$\{\lambda_{+2}\lambda_{-2}+\mu_{+2}\mu_{-2}+\nu_{+2}\nu_{-2}\}$$
$$\{\lambda_{+1}\mu_{-1}+\mu_{+1}\lambda_{-1}+\nu_{+1}\lambda_{-1}+\lambda_{+1}\nu_{-1}+\mu_{+1}\nu_{-1}+\nu_{+1}\mu_{-1}\}$$
$$\{\lambda_{+2}\mu_{-1}-\lambda_{+2}\nu_{-1}-\mu_{+2}\lambda_{-1}+\mu_{+2}\nu_{-1}+\nu_{+2}\lambda_{-1}-\nu_{+2}\mu_{-1}\}$$

States E'

$$\begin{cases}\{\mu_{+1}\mu_{-1}-\nu_{+1}\nu_{-1}\}\\ \{2\lambda_{+1}\lambda_{-1}-\mu_{+1}\mu_{-1}-\nu_{+1}\nu_{-1}\}\end{cases}$$

$$\begin{cases}\{\mu_{+1}\mu_{-2}-\nu_{+1}\nu_{-2}\}\\ \{2\lambda_{1}\lambda_{-2}-\mu_{+1}\mu_{-2}-\nu_{+1}\nu_{-2}\}\end{cases}$$

$$\begin{cases}\{\mu_{+2}\mu_{-2}-\nu_{+2}\nu_{-2}\}\\ \{2\lambda_{+2}\lambda_{-2}-\mu_{+2}\mu_{-2}-\nu_{+2}\nu_{-2}\}\end{cases}$$

$$\begin{cases}\{\mu_{+2}\mu_{-1}-\nu_{+2}\nu_{-1}\}\\ \{2\lambda_{+2}\lambda_{-1}-\mu_{+2}\mu_{-1}-\nu_{+2}\nu_{-1}\}\end{cases}$$

$$\begin{cases}\{\mu_{+1}\lambda_{-1}-\nu_{+1}\mu_{-1}+\nu_{+1}\lambda_{-1}-\mu_{+1}\nu_{-1}\}\\ \{2\lambda_{+1}\mu_{-1}-2\lambda_{+1}\nu_{-1}-\nu_{+1}\lambda_{-1}-\mu_{+1}\nu_{-1}+\mu_{+1}\lambda_{-1}+\nu_{+1}\mu_{-1}\}\end{cases}$$

$$\begin{cases}\{\mu_{+1}\lambda_{-1}-\nu_{+1}\mu_{-1}-\nu_{+1}\lambda_{-1}+\mu_{+1}\nu_{-1}\}\\ \{2\lambda_{+1}\mu_{-1}+2\lambda_{+1}\nu_{-1}-\nu_{+1}\lambda_{-1}-\mu_{+1}\lambda_{-1}-\mu_{+1}\lambda_{-1}-\nu_{+1}\mu_{-1}\}\end{cases}$$

$$\begin{cases}\{\mu_{+2}\nu_{-1}-\nu_{+2}\lambda_{-1}+\mu_{+2}\lambda_{-1}-\nu_{+2}\mu_{-1}\}\\ \{2\lambda_{+2}\mu_{-1}+2\lambda_{+2}\nu_{-1}-\mu_{+2}\nu_{-1}-\nu_{+2}\lambda_{-1}-\mu_{+2}\lambda_{-1}-\nu_{+2}\mu_{-1}\}\end{cases}$$

$$\begin{cases}\{\mu_{+2}\nu_{-1}-\nu_{+2}\lambda_{-1}-\mu_{+2}\lambda_{-1}+\nu_{+2}\mu_{-1}\}\\ \{2\lambda_{+2}\mu_{-1}-2\lambda_{+2}\nu_{-1}-\mu_{+2}\nu_{-1}-\nu_{+2}\lambda_{-1}+\mu_{+2}\lambda_{-1}+\nu_{+2}\mu_{-1}\}\,.\end{cases}$$

In order to formulate and to solve the secular equations, resulting from these functions we make use of:

- an idealized decacyclene frame *i.e.* equal distances between neighbouring carbonatoms (1.39 Å), see Fig. 1.
- Hückel molecular orbitals for the acenaphtylenes [4].
- The value -2.371 eV for the resonance integral β_{pq} in case p and q are neighbouring atoms, otherwise $\beta_{pq}=0$.

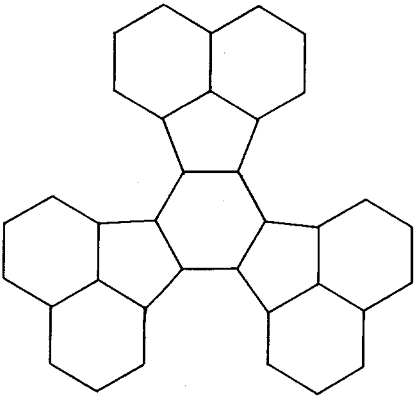

Fig. 1. Model of decacyclene

— Values for the Coulomb electronic repulsion γ_{pq}, based on reference [5].

— The transition energies of the acenaphtylene for substitution in the diagonal elements as collected by Heilbronner *et al.* [2], especially:

transition	E (eV)
1, -1	2.730
1, -2	4.788
2, -1	3.775
2, -2	5.718

values for the energies of the charge transfer configurations, calculated on the basis of reference [6].

The series of transitions found by this procedure agrees, so far as the lower excited states are concerned, reasonably well with the Pariser-Parr-Pople type calculations and matches the one, deduced from the absorption spectrum in 2-MTHF (Table 1) [7].

The question of interest is whether this procedure, when applied to the mononegative ion of decacyclene, is able to predict the very characteristic infrared electronic absorption band at 4950 cm^{-1} which is due to a transition from the ground state to the first excited doublet state [7].

Table 1. *Transition energies in decacyclene*

State	Representation	ΔE_{MIM} (eV)	$\Delta E_{\mathrm{P.P.P.}}$ (eV)[a]	ΔE_{exp} (eV)[a]
N	A_1'	—	—	—
V_1	A_2'	2.49	3.04	2.64
V_2	E'	2.84	3.12	2.76
V_3	E'	3.78	3.55	3.27
V_4	A_1'	3.81	3.59	—

[a] Taken from [7].

In these calculations only those doublet configurations which arise from the highest bonding and the lowest antibonding molecular orbitals of acenaphtylene have been used. The calculated value of the energy separation between the lowest excited doublet state and the ground state of the ion is 0.45 eV, which may be compared with the experimental value of 0.61 eV.

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