Theoretical Studies on Radialenes and Related Molecules

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For certain classes of molecules it is possible to obtain a general solution
of the Hückel problem, *i. e.* to derive expressions for the orbital energy, orbital
coefficients, total π-electron energy, *etc.* in a closed analytical form[1-5]. General
solutions are important because a large amount of numerical labour can be
saved. Besides, they show the dependence of HMO quantities on the molecular
topology, which has been recently investigated by various authors.[6-8]

We have investigated molecules denoted by Q_n^m (see Fig. 1a). Atoms are
numbered by two indexes for simplicity. AO's are labelled by the same two
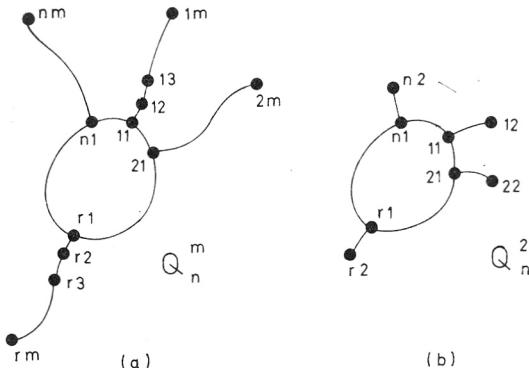
Fig. 1.

indexes. The special case where m = 2 (see Fig. 1b) represents [n] radialenes.
They have been investigated previously by various authors[9-13]. Q_n^1 are the [n]
annulenes, which are considered in detail elsewhere[14-17].

Although the molecules Q_n^m are *not claimed to possess any definite geo-
metry*, we can treat them as if they belong to the D_{nh} symmetry group. This is
a proper consequence of the fact that the symmetry of the Hückel Hamiltonian
is determined by the group of automorphisms of the graph corresponding to
the given molecule[18-21].

Orbital coefficients for Q_n^1 can be easily obtained using symmetry con-
siderations,[1] and are well known[22,23]. Thus,

$$\Psi_{t1} = (n)^{-1/2} \sum_{r=1}^{n} \exp\left(i \frac{2\pi t r}{n} \right) \chi_{11} \tag{1}$$

are the HMO's for [n] annulene.

Any symmetry operation of the D_{nh} group transforms the sets of atoms

$$\{1p,\ 2p,\ 3p,\ \ldots,\ np\} \qquad p = 1,\ 2,\ \ldots,\ m$$

into itself. Therefore they form different symmetry classes and the MO of the whole molecule is of the form[24]

$$\Psi_t = \sum_{p=1}^{m} c_{tp}\,\Psi_{tp} \tag{2}$$

From the topology of the molecule Q_n^m it can be deduced that the action of the Hückel Hamiltonian on atomic orbitals χ_{rp} is given by

$$H\,\chi_{r1} = \alpha\,\chi_{r1} + \beta\,(\chi_{r-1,1} + \chi_{r+1,1} + \chi_{r,2})$$
$$H\,\chi_{rp} = \alpha\,\chi_{rp} + \beta\,(\chi_{r,p-1} + \chi_{r,p+1}) \quad p = 2,\ 3,\ \ldots,\ m-1$$
$$H\,\chi_{rm} = \alpha\,\chi_{rm} + \beta\,\chi_{r,m-1} \tag{3}$$

where by definition,

$$\chi_{01} \equiv \chi_{n1}$$
$$\chi_{n+1,1} \equiv \chi_{11}$$

From eqs. (3) it follows that:

$$H\,\Psi_{t1} = \left(\alpha + 2\beta \cos \frac{2\pi t}{n}\right)\Psi_{t1} + \beta\,\Psi_{t2}$$
$$H\,\Psi_{tp} = \alpha\,\Psi_{tp} + \beta\,(\Psi_{t,p-1} + \Psi_{t,p+1}) \quad p = 2,\ 3,\ \ldots,\ m-1$$
$$H\,\Psi_{tm} = \alpha\,\Psi_{tm} + \beta\,\Psi_{t,m-1} \tag{4}$$

and hence the equation

$$H\,\Psi_t = E\,\Psi_t \tag{5}$$

can be written in the form

$$c_{t1}\left[(\alpha + 2\beta \cos \frac{2\pi t}{n} - E)\,\Psi_{t1} + \beta\,\Psi_{t2}\right] + \sum_{p=2}^{m-1} c_{tp}\,[(\alpha - E)\,\Psi_{tp} +$$
$$\beta\,(\Psi_{t,p-1} + \Psi_{t,p+1})] + c_{tm}\,[(\alpha - E)\,\Psi_{tm} + \beta\,\Psi_{t,m-1}] = 0 \tag{6}$$

Formally, the above relation corresponds to a Hückel problem for a chain of m atoms with a perturbation $\alpha \to \alpha + 2\beta \cos \dfrac{2\pi t}{n}$ on the first one.

$$
\begin{array}{cccc}
\alpha + 2\beta \cos \dfrac{2\pi t}{n} & \alpha & \alpha & \alpha \\
\text{O}\!-\!\!-\!\!-\!\!-\!\!-\!\!-\!\!\text{O}\!-\!\!-\!\!-\!\!-\!\!-\!\!\text{O}\!-\cdots-\!\!\text{O} & & & \\
1 & 2 & 3 & m \\
\Psi_{t1} & \Psi_{t2} & \Psi_{t3} & \Psi_{tm}
\end{array} \tag{7}
$$
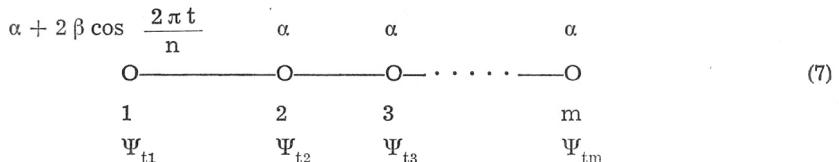
Here the Ψ_{tp}'s play the role of AO's. The secular equation to be solved is of the form:

$$D_m(w) \equiv \begin{vmatrix} w + 2\cos\dfrac{2\pi t}{n} & 1 & 0 & 0 & \cdot & \cdot & \cdot & \cdot & 0 \\ 1 & & w & 1 & 0 & \cdot & \cdot & \cdot & 0 \\ 0 & & 1 & w & 1 & \cdot & \cdot & \cdot & 0 \\ \cdot & & & & & & & & \cdot \\ \cdot & & & & & & & & \cdot \\ \cdot & & & & & & w & 1 \\ 0 & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & 1 & w \end{vmatrix} = 0 \tag{8}$$

where

$$w = \frac{\alpha - E}{\beta}$$

A. For $m = 1$ eq. (8) represents [n] annulenes with

$$w = -2\cos\frac{2\pi t}{n} \tag{9}$$

B. For $m = 2$ it describes [n]radialenes with

$$w = \begin{cases} -\cos\dfrac{2\pi t}{n} - \sqrt{1 + \cos^2\dfrac{2\pi t}{n}} & \text{bonding levels} \\[2mm] -\cos\dfrac{2\pi t}{n} + \sqrt{1 + \cos^2\dfrac{2\pi t}{n}} & \text{antibonding levels} \end{cases} \tag{10}$$

Therefore, radialenes cannot possess NBMO's and have always singlet ground states.

The total π-electron energy (in β units) can be approximated by an integral[25]:

$$E_\pi = 2\sum_{t=1}^{n}\left[\cos\frac{2\pi t}{n} + \sqrt{1 + \cos^2\frac{2\pi t}{n}}\right] = 2\sum_{t=1}^{n}\sqrt{1 + \cos^2\frac{2\pi t}{n}}$$

$$\approx 2\,\frac{n}{2\pi}\int_0^{2\pi}\sqrt{1 + \cos^2 t}\,dt = 2.43201\,n \tag{11}$$

Note that E_π is linearly proportional to the number of carbon atoms. Hence there is no change in stability of the π-electron system when the number of atoms is increased. Radialenes are typical examples of nonaromatic compounds[26,27]. Steric effects will be of major influence for large n.

Charge densities are given by the formulae:

$$q(\text{inner}) = 1 + \frac{1}{n}\sum_{t=1}^{n}\frac{\cos\dfrac{2\pi t}{n}}{\sqrt{1 + \cos^2\dfrac{2\pi t}{n}}} \tag{12}$$

$$q(\text{outer}) = 1 - \frac{1}{n}\sum_{t=1}^{n}\frac{\cos\dfrac{2\pi t}{n}}{\sqrt{1 + \cos^2\dfrac{2\pi t}{n}}}$$

Because

$$\int_0^{2\pi} \frac{\cos t}{\sqrt{1 + \cos^2 t}} \, dt = 0 \tag{13}$$

the charge density distribution is nearly uniform, deviations being considerable only for small (odd) n.

(4 m + 3) rings show a tendency to become positively charged, while (4 m + + 1) rings have electron affinity. This property seems to have a topological background and it is presently being investigated by us.

C. Generally $D_m(w)$ can be evaluated in the form

$$D_m(w) = P_m(w) + 2 \cos \frac{2\pi t}{n} P_{m-1}(w) \tag{14}$$

where P_m is the characteristic polynomial for the chain of m atoms

$$P_0 = 1$$
$$P_1 = w$$
$$P_m = w P_{m-1} - P_{m-2}$$

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IZVOD

Teorijski studij radijalena i srodnih molekula

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Prikazano je opće rješenje Hückelovog problema za klasu molekula Q_n^m , kojih su specijalni slučajevi [n] anuleni (m = 1) i [n] radijaleni (m = 2). Pokazano je također da se opće rješenje može dobiti i promatranjem lanca od m atoma kod kojega se smetnja ($2\beta \cos \dfrac{2\pi t}{n}$) javlja na prvom atomu.