

R σ diagonalization: application to C_nH_n systems

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The application to the C_nH_n system entailed the crucial task of transforming the calculated eigenvectors to the symmetry-adapted molecular orbitals. Absent this step, one could be in a quandary to interpret the varying orbital coefficients generated by the three methods. Moreover, the application provides a good example of that well-known property regarding eigenfunctions belonging to degenerate eigenvalues. And while group theory may be used to generate symmetry-adapted orbitals for the other macrocyclic systems, it can be a lengthy exercise requiring the construction of the character tables for the rotational subgroups. In this case, algorithms such as those employed in this paper may be considered as useful alternatives.

Keywords: Diagonalization method, C_nH_n systems.

THE STUDY OF MOLECULAR STRUCTURE AND SIMILAR PROBLEMS IN chemistry often ends up in solving eigenvalue equations. For example, in molecular orbital theory, a molecular orbital ψ_k is approximated by a linear combination of basis orbitals ϕ_m centered on the constituent atoms of the molecule, i.e.,

$$\psi_k = \sum_{m=1}^n \phi_m c_{mk}$$

Using the linear variation method and assuming the overlap matrix elements are given by

$$S_{ij} = \int \phi_i \phi_j d\tau = \delta_{ij}$$

as in the Huckel approximation, the resulting eigenvalue equation is given by

$$\mathbf{HC} = \mathbf{CE}$$

where \mathbf{H} is the hamiltonian matrix in the ϕ basis, \mathbf{C} is the coefficient or eigenvector matrix and \mathbf{E} contains the orbital energies along its diagonal. Written as a similarity transformation, the eigenvalue equation becomes

$$\mathbf{C}^{-1}\mathbf{HC} = \mathbf{E}, \quad \mathbf{C}^{-1}\mathbf{C} = \mathbf{I} \quad (1)$$

where \mathbf{I} is the identity matrix. The solution of eq 1 entails finding the matrices \mathbf{C} and \mathbf{E} . In an earlier paper [1], we introduced the R σ diagonalization methods precisely to solve problems of this type.

Application

The diagonalization methods were employed to study the carbocyclic systems C_nH_n, $n = 1, 12$, within the Huckel framework. To a first approximation we consider them as belonging to the D_{nh} point group. Using the usual α, β no-

tation, the non-zero elements of the hamiltonian matrix are $H_{ii} = H_{1n} = H_{n1} = \alpha$, and $H_{ij} = H_{ji} = \beta$, where i and j refer to adjacent carbon atoms. We can further simplify the matrix by setting $\alpha = 0$ and $\beta = 1$. This is equivalent to having $\alpha = 0$ as the zero of the energy axis and expressing the energies in units of β . Note that n , which denotes the number of pi electrons, also indicates the dimension of the hamiltonian matrix and hence the number of eigenvalues and corresponding molecular orbitals to be determined.

We illustrate the results for C₅H₅ in Tables 1 to 4. The calculated energies agree to six decimal places. What appears alarming are the varying molecular orbital coefficients corresponding to the doubly degenerate levels. These observations also hold for all the other carbocyclic systems studied. It may be added that perhaps this fact, in addition to the absence of uniform correction factors mentioned earlier [1], provide the basis for suspecting the Jacobi method as unreliable when it comes to eigenvector calculation. This, of course, is not the case.

The varying coefficients may be explained by the fact that the diagonalization methods yield non-unique molecular orbitals, i.e., if ψ_1 and ψ_2 are molecular orbitals belonging to a degenerate eigenvalue, then the linear combinations

$$\psi_1' = c_1\psi_1 + c_2\psi_2, \quad \psi_2' = c_1\psi_1 - c_2\psi_2,$$

are also molecular orbitals or eigenfunctions belonging to the same eigenvalue. The coefficient c_1 and c_2 are completely arbitrary but are usually chosen so that ψ_1 and ψ_2 are orthonormal. To demonstrate this well-known property and in order to evaluate the accuracy of the coefficients shown in Tables 1 to 3, we consider the symmetry-adapted molecular orbitals for each carbocyclic system. These orbitals, including the energies, are given in Cotton(2) for $n = 3$ to 8. For $n = 9$ to 12, the character tables for the corresponding rotational subgroups C_n had to be

Table 1. Calculated molecular orbital energies and coefficients using the R σ /A method for C₅H₅.

E	2	.6180342	.6180341	-1.618034	-1.618034
	ψ_1	ψ_2	ψ_3	ψ_4	ψ_5
c ₁	.4472136	-.6307411	4.653777E-02	-.512743	-.370263
c ₂	.4472136	-.2391698	-.5854891	.6324529	-1.833721E-03
c ₃	.4472137	.482926	-.4083902	-.5105874	.3732301
c ₄	.4472136	.5376343	.3330904	.1936947	-.602065
c ₅	.4472136	-.1506496	.6142511	.1971826	.6009316

Table 2. Calculated molecular orbital energies and coefficients using the R σ /B method for C₅H₅.

E	2	.6180343	.6180341	-1.618034	-1.618034
	ψ_1	ψ_2	ψ_3	ψ_4	ψ_5
c ₁	.4472136	-.6279685	7.520549E-02	-.5598758	-.2941753
c ₂	.4472136	-.1225282	-.620473	.6258609	-9.109385E-02
c ₃	.4472136	.5522418	-.3082681	-.4527887	.4415083
c ₄	.4472137	.4638323	.4299529	.1067663	-.6233785
c ₅	.4472136	-.2655775	.5739935	.2800371	.5670795

Table 3. Calculated molecular orbital energies and coefficients using the Jacobi method for C₅H₅.

E	2	.6180342	.6180339	-1.618034	-1.618034
	ψ_1	ψ_2	ψ_3	ψ_4	ψ_5
c ₁	.4472136	.2289218	-.5895717	9.904171E-02	.6246525
c ₂	.4472137	-.4899752	-.3999051	-.447288	-.4471392
c ₃	.4472137	-.5317431	.3424167	.6246855	9.883391E-02
c ₄	.4472136	.1613401	.6115304	-.5634743	-.2872225
c ₅	.4472135	.6314568	3.552972E-02	.287035	.5635697

Table 4. Symmetry-adapted molecular orbitals calculated from Table 1. The three methods yield identical results (to six decimal places) in complete agreement with symmetry-adapted orbitals obtained using group theory.

E	2	.6180342	.6180341	-1.618034	-1.618034
	ψ_A	ψ_{E_1a}	ψ_{E_1b}	ψ_{E_2a}	ψ_{E_2b}
c ₁	.4472136	.6324556	0	.6324556	0
c ₂	.4472136	.1954396	-.6015008	-.5116673	-.371748
c ₃	.4472137	-.5116673	-.3717482	.1954395	.6015011
c ₄	.4472136	-.5116672	.371748	.1954395	-.601501
c ₅	.4472137	.1954394	.6015008	.5116672	.371748

constructed. Only the molecular orbital energies and coefficient for $C_{10}H_{10}$ are shown in Table 5 for purposes of brevity. The objective is to show that the figures in Tables 1 to 3, as well as those for the other systems, lead to symmetry-adapted coefficients that are in complete agreement with those in Tables 4, 5 and the above-mentioned reference.

Inspection of the molecular orbitals of the type ψ_{Ea} and ψ_{Eb} , reveals the following: the coefficient of the basis orbital ϕ_1 in ψ_{Ea} is equal to $\sqrt{2/n}$; whereas it is equal to zero for molecular orbitals of the type ψ_{Eb} . We may therefore do the following transformation: let ψ_k and ψ_l be the orthonormal molecular orbitals corresponding to a doubly degenerate eigenvalue as calculated by any of the diagonalization methods.

$$\psi_k = \sum_m \phi_m c_{mk}, \quad \psi_l = \sum_m \phi_m c_{ml} \quad (2)$$

We then form the linear combinations

$$\psi_{Ea}(k) = \frac{b\psi_k + \psi_l}{\sqrt{1+b^2}}, \quad \psi_{Eb}(l) = \frac{\psi_k + b\psi_l}{\sqrt{1+b^2}} \quad (3)$$

The constant b is chosen so that ψ_{Ea} and ψ_{Eb} orthonormal. Using eq 2 and considering only the coefficient of ϕ_1 in ψ_{Eb} , we obtain

$$b = c_{1k}/c_{1l}$$

The coefficient of ϕ_1 in ψ_{Ea} is

$$\frac{bc_{1k} + c_{1l}}{\sqrt{1+b^2}} = \sqrt{\frac{2}{n}}$$

which may be written as

$$\frac{1}{\sqrt{c_{1k}^2 + c_{1l}^2}} = \sqrt{\frac{2}{n}}$$

With these results, the symmetry-adapted molecular orbitals are given by

$$\psi_{Ea}^{(k)} = \sqrt{\frac{n}{2}} (c_{1k} \psi_k + c_{1l} \psi_l) \quad (4)$$

$$\psi_{Eb}^{(l)} = \sqrt{\frac{n}{2}} (c_{1l} \psi_k + c_{1k} \psi_l) \quad (5)$$

Substituting eq 2 into eqs 4-5 yields the orbital coefficients for the ψ_{Ea} and ψ_{Eb} -type molecular orbitals,

$$\psi_{Ea}^{(k)} = \sum_m \phi_m s_{mk}, \quad s_{mk} = \sqrt{\frac{n}{2}} (c_{1k} c_{mk} + c_{1l} c_{ml}) \quad (6)$$

$$\psi_{Eb}^{(l)} = \sum_m \phi_m t_{ml}, \quad t_{ml} = \sqrt{\frac{n}{2}} (c_{1l} c_{mk} - c_{1k} c_{ml}) \quad (7)$$

Table 4 gives the symmetry-adapted coefficients for C_5H_5 calculated according to eqs 6-7. Except for a multiplicative factor of -1 for some molecular orbitals, the fig-

Table 5. Symmetry-adapted molecular orbital energies and coefficients for $C_{10}H_{10}$ obtained using group theory.

E	2	ϵ_1^1	ϵ_1	ϵ_2	ϵ_2	ϵ_3	ϵ_3	ϵ_4	ϵ_4	-2
	ψ_A^2	ψ_{E1a}	ψ_{E1b}	ψ_{E2a}	ψ_{E2b}	ψ_{E3a}	ψ_{E3b}	ψ_{E4a}	ψ_{E4b}	ψ_B
c_1^3	1	1	0	1	0	1	0	1	0	1
c_2	1	c_1	s_1	c_2	s_2	c_3	s_3	c_4	s_4	-1
c_3	1	c_2	s_2	c_4	$-s_4$	c_4	$-s_4$	c_2	$-s_2$	1
c_4	1	c_3	s_3	c_4	$-s_4$	c_1	$-s_1$	c_2	s_2	-1
c_5	1	c_4	s_4	c_2	s_2	c_2	s_2	c_4	$-s_4$	1
c_6	1	-1	0	1	0	-1	0	1	0	-1
c_7	1	c_4	$-s_4$	c_2	s_2	c_2	$-s_2$	c_4	s_4	1
c_8	1	c_3	$-s_3$	c_4	s_4	c_1	s_1	c_2	$-s_2$	-1
c_9	1	c_2	$-s_2$	c_4	$-s_4$	c_4	s_4	c_2	s_2	1
c_{10}	1	c_1	$-s_1$	c_2	$-s_2$	c_3	$-s_3$	c_4	$-s_4$	-1

¹ $\epsilon_k = 2 \cos k\omega$, $\omega = 2\pi/10$.

² The normalization constant for ψ_A and ψ_B is $\sqrt{1/10}$; it is equal to $\sqrt{2/10}$ for all the ψ_E -type molecular orbitals.

³ c_1 in the first column refers to the expansion coefficients c_{mi} in $\psi_i = \sum_m \phi_m c_{mi}$. In the inner columns, $c_k = \cos k\omega$ and $s_k = \sin k\omega$. To obtain the numerical values of c_{mi} multiply the entries in a given column by the appropriate normalization constant.

ures are in complete accord with the orbital coefficients obtained using group theory. The same agreement is obtained for all the carocyclic systems studied, including $C_{10}H_{10}$ as shown in Table 5. We may therefore conclude that the eigenvectors calculated by the R diagonalization methods, the Jacobi scheme as well, are accurate.

Examples of eqs 4-5, using results for C_5H_5 in Table 1, are given by the following equations,

$$\psi_{E_{1a}} = -0.9972892 \psi_2 + 7.358268E-02 \psi_3$$

$$\psi_{E_{1b}} = 7.358268E-02 \psi_2 + 0.9972892 \psi_3$$

$$\psi_{E_{2a}} = -0.8107179 \psi_4 - 0.5854372 \psi_5$$

$$\psi_{E_{2b}} = -0.5854372 \psi_4 + 0.8107179 \psi_5$$

Orbital, Total and Delocalization Energies

Figure 1 illustrates a summary of the orbital energies in units of β for the C_nH_n systems. The following observations are noted:

1. The lowest energy for any system is 2. This is associated with a strongly bonding orbital ψ_A .

2. For n odd, there are $(n-1)/2$ doubly degenerate energy levels.
3. For n even, the highest energy is -2, associated with a strongly anti-bonding orbital ψ_B . There are $(n-2)/2$ doubly degenerate energy levels.
4. The energy levels are ordered as follows:

$$A < E_1 < E_2 < \dots < B.$$

From group theory, it can be shown that the energy of a doubly degenerate level E_k is given by [3,4]

$$\varepsilon(E_k) = 2 \cos k\omega, \quad \omega = 2\pi/n \quad (8)$$

The numerical results obtained from any of the diagonalization methods agree with eq 8 for all the C_nH_n systems. This further establishes the accuracy of the R and Jacobi algorithms.

The total and the delocalization energies are given in Table 6. The total energy E_T is given by

$$E_T = 2\varepsilon(A) + n_1\varepsilon(E_1) + n_2\varepsilon(E_2) + n_3\varepsilon(E_3)$$

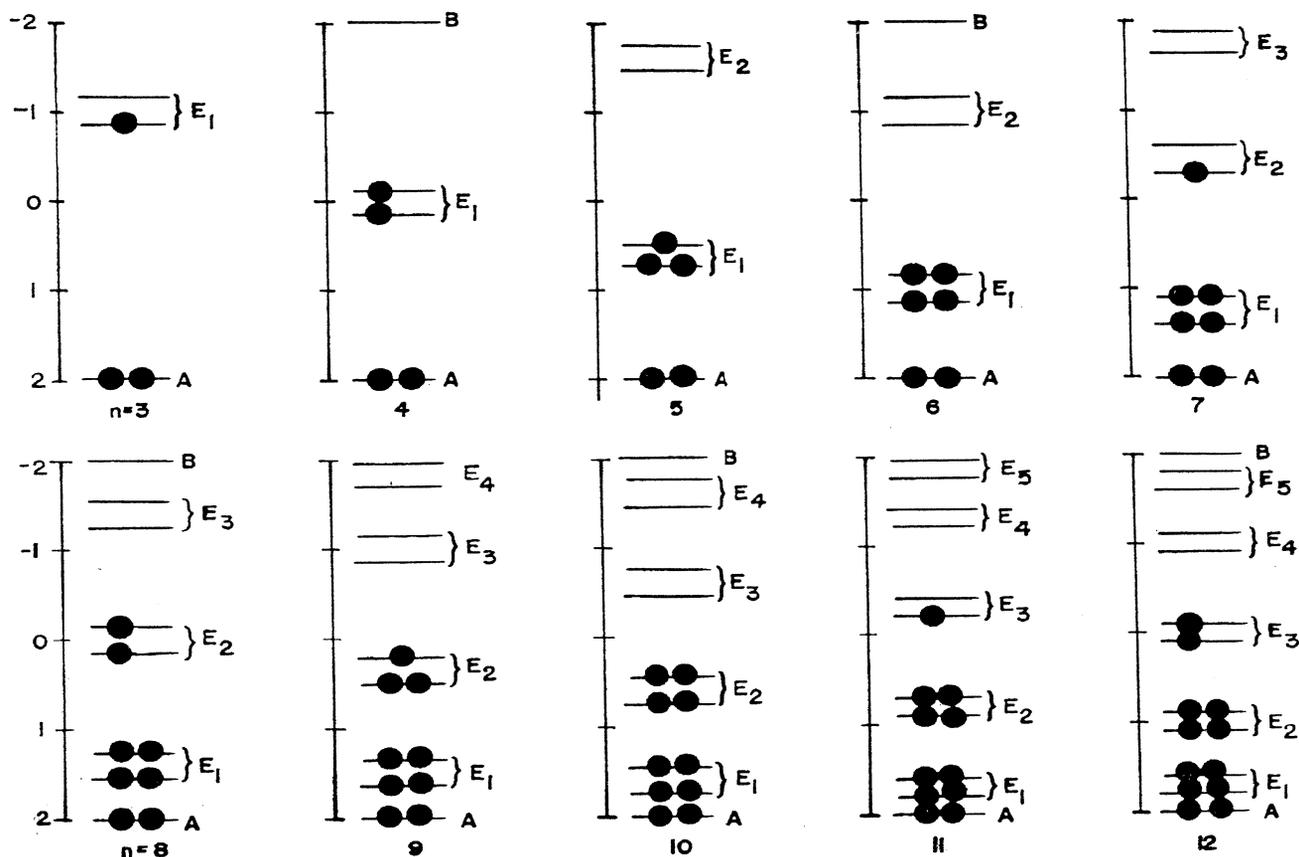


Figure 1. Energy level diagrams for the C_nH_n systems.

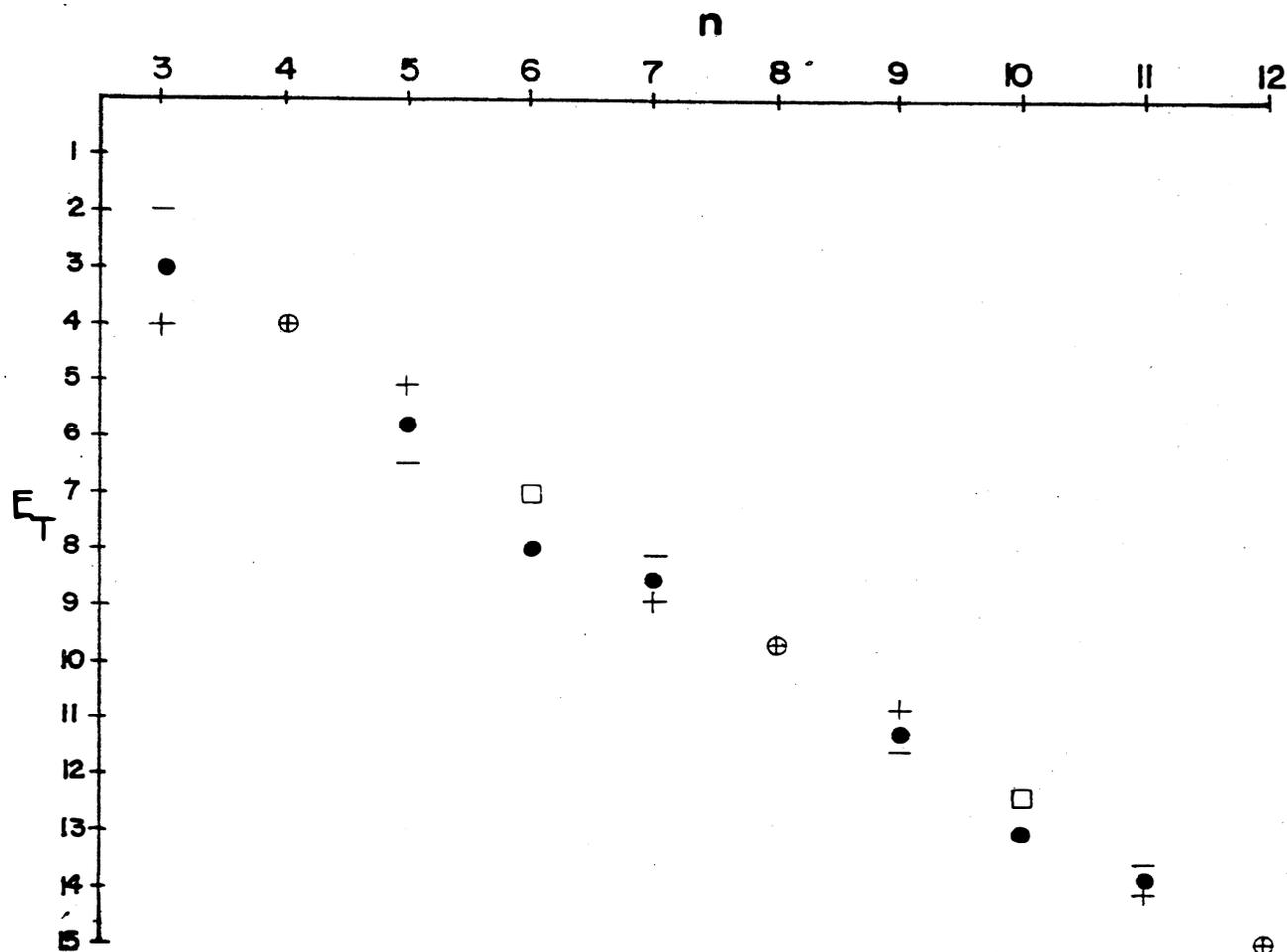


Figure 2. Total energy of the $C_n H_n$ systems including the molecular ions: + denotes $C_n H_n^+$; -, $C_n H_n^-$; o, $C_n H_n$, o, refers to both cation and anion; \oplus , refers to molecular ions and neutral species together.

where n_k is the population of the $\varepsilon(E_k)$ energy level. Note that the highest occupied energy level is $\varepsilon(E_3)$ for $n = 11, 12$. The delocalization energy is

$$E_D = E_T - E_L$$

where E_L is the total energy corresponding to a cyclic structure where no resonance is allowed to occur. The hamiltonian matrix corresponding to such a structure is block-diagonal with nonvanishing elements $H_{i,i+1} = H_{i+1,i} = 1$, $i = 1, 3, 5, \dots$. For n even, there are $n/2$ block matrices of dimension 2×2 . For n odd, there are $(n-1)/2$ block 2×2 matrices, the remaining 1×1 matrix being the diagonal element $H_{nn} = 0$. The diagonalization of these matrices can be done by inspection as discussed in ref. 1 (Rσ/A, case 1) since $H_{pp} = H_{qq} = 0$. Thus, for n odd, the energies are 1, 0 and -1 with degeneracies $(n-1)/2$, 1 and $(n-1)/2$ respectively. For n even, the energies are 1 and -1, the degeneracy

of each of which is $n/2$. For n odd, a pi electron occupies the zero energy level (a non-bonding orbital) while the rest are in the lowest $(n-1)/2$ degenerate levels. E_L therefore for this case is $2 \times ((n-1)/2) \times 1$ or $E_L = n-1$. For n even, all the pi electrons are paired in the lowest $n/2$ degenerate levels. This gives $E_L = 2 \times (n/2) \times 1 = n$.

It is instructive to plot the total energies E_T as a function of the ring size as shown in Figure 2. It is immediately apparent that the carbocyclic systems group themselves according to what we may call an $n + 4$ rule, $n = 3, 4, 5, \dots$. Thus, C_3H_3 , C_7H_7 and $C_{11}H_{11}$ have the same energy distribution among their neutral and ionic species. The same can be said about C_4H_4 , C_8H_8 and $C_{12}H_{12}$, the group C_5H_5 and C_9H_9 , and still another group C_6H_6 and $C_{10}H_{10}$. That such grouping occur can be best understood by referring to Figure 1. It is clear that each group is characterized by similar energy level diagram. For instance, following the $n + 4$ rule with $n = 3$, a single pi electron occupies an anti-bonding orbital, while the rest are held in strongly bonding orbitals; this also obtains for $n = 7$ and 11. We

Table 6. Total and delocalization energies in units of .

System	E_T	E_D
$C_3H_3^+$	4	2
C_3H_3	3	1
C_3H_3	2	0
$C_4H_4^+$	4	0
C_4H_4	4	0
C_4H_4	4	0
$C_5H_5^+$	5.236	1.236
C_5H_5	5.854	1.854
C_5H_5	6.472	2.472
$C_6H_6^+$	7	1
C_6H_6	8	2
C_6H_6	7	1
$C_7H_7^+$	8.988	2.988
C_7H_7	8.543	2.543
C_7H_7	8.098	2.098
$C_8H_8^+$	9.657	1.657
C_8H_8	9.657	1.657
C_8H_8	9.657	1.657
$C_9H_9^+$	10.823	2.823
C_9H_9	11.170	3.170
C_9H_9	11.518	3.518
$C_{10}H_{10}^+$	12.326	2.326
$C_{10}H_{10}$	12.944	2.944
$C_{10}H_{10}$	12.326	2.326
$C_{11}H_{11}^+$	14.053	4.053
$C_{11}H_{11}$	13.769	3.769
$C_{11}H_{11}$	13.484	3.484
$C_{12}H_{12}^+$	14.928	2.928
$C_{12}H_{12}^+$	14.928	2.928
$C_{12}H_{12}$	14.928	2.928

also note the $n = 4x + 2$, $x = 1, 2, 3, \dots$ rule, where x refers to the number of fully occupied E_k levels, as indeed operative for the group that includes benzene. This indicates that carbocyclic systems with $n = 6, 10, \dots$ possess aromatic character.

The more stable species of the various C_nH_n systems are also clear from Figure 2. Because E_L is the same for a given C_nH_n system, the species with the lowest energy is thus most stable. For n odd, the stable species are $C_3H_3^+$, $C_5H_5^-$, $C_7H_7^+$, $C_9H_9^-$ and $C_{11}H_{11}^+$. Note the alternating ionic forms. For n even, the neutral species are the more stable structures. These results are also indicated by the values of E_D in Table 6.

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