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The Stability of the Hartree Fock Solutions of Pentalene and Heptalene*

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The closed shell HF solutions for the π-electrons in pentalene and heptalene are found to exhibit singlet instabilities for values of the core integral β close to the standard value.

Recent calculations [1] on pentalene and heptalene molecules have suggested that the most stable structure is the one for which the nuclear framework is represented by the C_{2h} symmetry point group rather than what might be expected, the D_{2h} group. These conclusions are based on the results of an "iterative" SCF calculation for the π electron energy and an assessment of the effect of the nuclear displacement on the σ electron energy. As such the instability of the D_{2h} symmetry adapted solution is a so-called "lattice" instability [2]. Rather than comment further on the aforementioned instability we wish to draw attention to the instability of the symmetry adapted (D_{2h}) Hartree Fock (HF) solution, Φ_0^{HF}, for the π electrons of these same systems, i.e., we intend to deal with the possibility that the stationary point $E^\pi(\Phi_0^{\mathrm{HF}})$ may not be even a local minimum, much less a global minimum [3].

Paldus and Čižek have recently [4, 5] directed attention to the occurrence of closed shell single determinant symmetry adapted HF solutions for which $E^\pi(\Phi_0^{\mathrm{HF}})$ does not represent a local minima. In such cases the HF solution is said to be unstable and the lower energy solutions are said to exhibit broken (lower) symmetry. In those instances where the solution is "singlet unstable" the broken symmetry solution is normally found [4] to have broken space symmetry. In view of this an investigation of the stability of the HF solution of pentalene and heptalene has been undertaken and preliminary results show that the HF solutions for these systems exhibit instability for much larger values of $|\beta|$ than comparable closed-shell systems studied heretofore.

The method for determining the stability of a HF solution, given first by Thouless [6], and particularized by Čižek and Paldus [4] has been employed. The procedure involves writing the second variation in energy about the stationary point $E^\pi(\Phi_0^{\mathrm{HF}})$ as

$$\delta^{(2)} E_0^\pi = \sum_{U_2 U_1} \left\{ a_{U_1 U_2} \bar{d}_{U_1} d_{U_2} + \tfrac{1}{2} b_{U_1 U_2} \bar{d}_{U_1} \bar{d}_{U_2} + \tfrac{1}{2} \bar{b}_{U_1 U_2} d_{U_1} d_{U_2} \right\}, \qquad (1)$$

where the $a_{U_1 U_2}$ and $b_{U_1 U_2}$ are simply the matrix elements of the operator $\hat{Q} = \hat{H} - E_0^\pi$ ($\hat{H}$ is the π-electron Hamiltonian) between mono excited states U_1 and U_2

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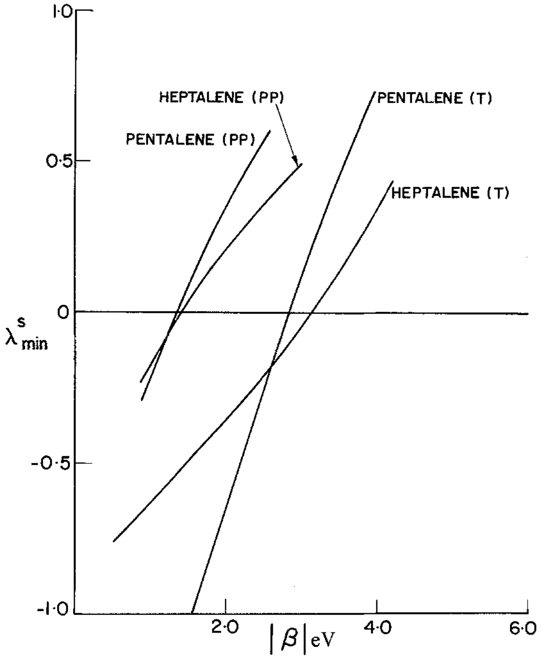
[*] Based on work contained in a Ph. D. Thesis by K. Vasudevan, University of Calgary, Calgary, Alberta.



as $a_{U_1U_2} = \langle U_1|\hat{Q}|U_2\rangle$ and between ground and "biexcited" states as $b_{U_1U_2} = \langle U_1 U_2|\hat{Q}|0\rangle$; the d_{U_i} are mixing coefficients for the admixture of the virtual orbitals with occupied orbitals. As a preliminary investigation we considered only those excitations involving transitions between the two lowest unoccupied and two highest occupied orbitals. The characteristic equation for the matrix of the quadratic form (1) can be written as

$$\begin{pmatrix} A & B \\ \bar{B} & \bar{A} \end{pmatrix} \begin{pmatrix} D \\ \bar{D} \end{pmatrix} = \lambda \begin{pmatrix} D \\ \bar{D} \end{pmatrix} .$$

Positive eigenvalues λ indicate that $\delta^{(2)} E_0^{\pi} > 0$, i.e., the stationary point is a local minimum whereas negative λ indicate $\delta^{(2)} E_0^{\pi} < 0$, i.e. that the HF solution is unstable.

It is well known [4, 5] that the aforementioned instability of the single determinant solution is dependent on the parametrization scheme adopted for the integrals defining the elements of A and B. For example the Pariser-Parr [7] (PP) scheme reduces the values for the two electron integrals from those values given by the "Theoretical" [8] (T) scheme, in an attempt to introduce some measure of "correlation" into the procedure. In our investigation we have employed the tight binding approximation, the zero differential overlap approximation and, to illustrate the relative effects of the PP and T scheme we present the results of the instability calculations for both parametrizations.

The results shown in the figure indicate that both the systems are singlet stable for standard values of the integrals (i.e. λ is positive). However decreasing the value of $|\beta|$, thereby increasing the relative importance of correlation effects, rapidly decreases the value of λ and as the figure shows the HF solution is unstable in the T parametrization at $\beta = -3.1$ eV for heptalene and at $\beta = -2.8$ eV for pentalene. These values[1] of the critical β are respectively 85% and 75% of the standard value of -3.72 eV and suggest that single determinant HF solutions for these systems are quite inapropriate. The results for the PP scheme are less dramatic but the value of $|\beta_{\mathrm{crit}}| = 1.4$ eV for pentalene is still relatively high and is to be compared [4, 5] to those found in the polyacene series (for example $|\beta_{\mathrm{crit}}| = 0.3$ eV for benzene and for the much larger pentacene $|\beta_{\mathrm{crit}}|$ is still only 0.7 eV).

This rather marked tendency to instability in the HF solutions deserves a fuller investigation of these systems, in particular the number of possible excitations could be increased and the study extended to include other small non-alternant systems. In the interim these results suggest that considerable caution should be exercised in the application to this type of system of those procedures (such as RPA, CPMET etc.) known [9] to be sensitive to such instabilities.

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[1] These values are upper bounds to β_{crit} (or lower bounds to $|\beta_{\mathrm{crit}}|$) which would be obtained for the full set of excitations.