

Model to study Delocalization

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In order to gain insight into the nature of π delocalization and its role with regard to the geometry of a compound, we propose a simple model, M_n , to simulate the π -component of $(CH)_n$, where M is a hypothetical particle with virtual nuclear charge 3.18 and with only one electron in the atomic orbital $2p_\pi$. Test calculations on cyclobutadiene and benzene show that the σ -frame prefers a regular geometry while π electrons tend to be localized.

The delocalization of π electrons in conjugated systems is an important concept in chemistry. The resonance theory developed by Pauling and Wheland,^{1,2} very successfully illustrates electronic delocalization. However, there are still some controversies over the relationship between delocalization and stability. Several authors^{3–8} have argued that π electrons prefer localization and σ electrons prefer bond equalization. Others have claimed that π delocalization is, in part, responsible for the equilibrium symmetric structure.^{9–11} Shaik, Hiberty and co-workers^{12–16} studied the factors that cause instability toward a localizing distortion, and concluded that the π -component of benzene ought to be distortive. Subsequently, they devised a σ - π energy partition scheme which is based on constant nuclear repulsion during the distortion, and which demonstrated the validity of this conclusion for benzene and its heteroatomic analogues at the all-electron *ab initio* level. Later, Jug and Köster¹⁷ proposed a general σ - π separability criterion to discuss the different energy contributions of a σ component and a π component. Notably, Gerratt and co-workers¹⁸ produced six, essentially localized, non-orthogonal p_π orbitals on benzene by means of the spin-coupled valence bond (VB) method, and validated the resonating picture of two Kekulé structures.

In order to understand the properties of π electrons, calculation of the π component of the energy is essential. Nevertheless, the Coulomb and exchange interaction energy between σ - π electrons prevents a unique separation of the energy into two components and as an approximation it is usually divided into two equal parts. Another choice to study the π electrons in $(CH)_n$ is to use the $(H)_n$ model, but the difference between the two atomic orbitals (AOs) $C(2p_z)$ and $H(1s)$ is obvious, subsequently the results are very qualitative. In this paper, we have proposed a simple model to treat the π -component of $(CH)_n$ and performed π -configuration interaction (CI) calculations with a classical *ab initio* VB method.

Methodology

In this paper, π -CI calculations are performed using a simple spin-free VB method called the bonded tableau unitary group approach (BTUGA).^{19–23} Since this method involves adopting bonded tableaux (BTs) as state functions of a system, where these state functions can describe resonance structures, BTUGA is much closer to classical concepts and ideas than other many-body theories. For an N electron system, a BT $\psi(k)$ is defined as

$$\begin{aligned}\psi(k) &= A_k e^{[\lambda]} \psi_0(k) \\ &= A_k e^{[\lambda]} [u_1(1)u_2(2) \cdots u_n(n)]\end{aligned}\quad (1)$$

where A_k is a normalization constant, $e^{[\lambda]}$ is a standard projection operator and u_i is a one-electron basis function. Also,

if the spin quantum number of the system is S , $[\lambda] = [2^{1/2N-S} 1^{2S}]$ is an irreducible representation of permutation group S_N . In fact, the above BT corresponds to a VB resonance structure where two AOs u_{2i-1} and u_{2i} overlap to form a bond ($i \leq N/2 - S$ and if $u_{2i-1} = u_{2i}$, the 'bond' is a lone electron pair) and the last $2S$ AOs are unpaired. Thus the true wavefunction of the system can be expressed as a superimposition of all possible BTs, namely

$$\Psi_i = \sum_{k=1}^M C_{ik} \psi(k) \quad (2)$$

The structural weight of a BT $\psi(k)$ in the Ψ_i can be defined as

$$T_i(k) = \sum_{l=1}^M C_{il} C_{lk} S_{kl} \quad (3)$$

where S_{kl} is the overlap integral between BTs $\psi(k)$ and $\psi(l)$. The condition of normalization requires

$$\sum_{k=1}^M T_i(k) = 1 \quad (4)$$

To treat the π -component of $(CH)_n$, we suppose that in the hypothetical system $(M)_n$, without σ frame, there are only n electrons occupying p_π AOs, and the forces of the virtual nuclear charges Z^* of M acting on these electrons are very similar to those of the nuclear charges and σ electrons in the real systems $(CH)_n$. For a single atom, the effective charge in an AO can be determined by the well known Slater rules for effective nuclear charges, thus the value for $C(2p)$ is *ca.* 3.0. As a simple model to study the behaviour of π electrons, we here define a hypothetical particle, M , whose virtual nuclear charge is *ca.* 3.0, while there is only one electron on the specific AO $C(2p_\pi)$. Obviously, it should be noted that M is neutral and its true nuclear charge Z , equal to one, is used exclusively in determining the nuclear repulsion in $(M)_n$.

To optimize further the virtual nuclear charge, Z^* , of $C(2p_\pi)$ in $(CH)_n$ and to perform subsequent π -CI calculations, we apply the classical *ab initio* VB method to $(CH)_n$ and $(M)_n$ ($n = 4, 6$), where the σ electrons in $(CH)_n$ are confined in the molecular orbitals (MOs).^{24,25} When a minimal basis set is used, there are a total of 175 and 20 resonance structures for $n = 6$ and 4, respectively.²⁶ A detailed comparison between the individual structural weights of $(CH)_n$ and $(M)_n$ shows that the optimal value of the effective charge Z^* of $C(2p_\pi)$ in $(CH)_n$ is 3.18.²⁷ Simultaneously, the excitation energies of several low-lying excited states of $(M)_n$ are almost identical with those of $(CH)_n$. Note that the forms of $C(2p_\pi)$ in $(CH)_n$ and $(M)_n$ are the same, thus the method can be applied with large basis sets. In the calculations, GAUSSIAN-80²⁸ program and the internal STO-6G basis set are used to obtain the AO integrals and MOs, while an *ab initio* VB program has been prepared by ourselves.

Results and Discussion

Since H_6 and C_4H_4 vibrate with B_{2u} and B_{1g} modes, we calculate the distortion energies of C_6H_6 , C_4H_4 , M_6 and M_4 from the regular geometries with the same bond length, R , to alternative geometries whose short-bond and long-bond lengths are $R_1 = R - \Delta r$ and $R_2 = R + \Delta r$, respectively, where Δr is a measure of the degree of alteration in the structure. In such a way, the centre of mass is kept fixed for all distortions from equilibrium. The R value for C_6H_6 and M_6 is 1.397 Å while the value for C_4H_4 and M_4 is 1.453 Å.²⁶ Table 1 lists the results.

From Table 1 we find that when C_6H_6 and C_4H_4 distort, the π component of the energies, which are taken as the electronic energies of M_6 and M_4 , will decrease according to the extent of the distortion. This result confirms that the π electrons prefer a localized structure, or a bond-alternating geometry. Interestingly, the distortion energy of M_6 is almost coincident with that of M_4 if the variations in bond lengths are the same.

We also consider distortions that keep the nuclear repulsions constant. The conformations are slightly different from the values of Shaik *et al.*¹⁴

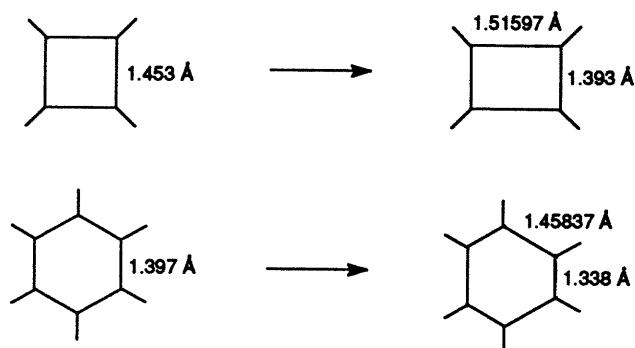


Table 2 gives the total energies of regular and distorted structures, where the data for M_6 and M_4 are their electronic energies. $E_{\sigma}(\text{MO})$ is the σ -component energy defined by Shaik *et al.*¹⁴ as

$$E_{\sigma}(\text{MO}) = \sum h_{\sigma} + R_{\sigma\sigma} + V_{NN}$$

Thus if we use the formula $\Delta E_{\pi} = \Delta E_{\text{tot}} - \Delta E_{\sigma}(\text{MO})$, the variations in the π component of the energy of benzene and

Table 1 Distortion energies for C_6H_6 , C_4H_4 , M_6 and M_4 (kcal mol⁻¹)

$r/\text{Å}$	C_4H_4	M_4	C_6H_6	M_6
0.00	0.0	0.0	0.0	0.0
0.025	-0.68	-3.43	0.94	-3.19
0.050	-2.49	-12.76	3.98	-12.55
0.075	-3.82	-26.22	9.66	-27.49
0.100	-3.58	-42.58		

Table 2 Total energies for C_6H_6 , C_4H_4 , M_6 and M_4

	regular $/E_h$	distorted $/E_h$	ΔE_{tot} $/\text{kcal mol}^{-1}$	$\Delta E_{\sigma}(\text{MO})$ $/\text{kcal mol}^{-1}$
C_4H_4	-153.338 028	-153.343 159	-3.22	10.39
M_4	-17.369 628	-17.388 882	-12.08	
C_6H_6	-230.238 402	-230.229 167	5.79	16.90
M_6	-33.452 664	-33.462 545	-6.20	

cyclobutadiene will be $-11.11 \text{ kcal mol}^{-1}$ and $-13.61 \text{ kcal mol}^{-1}$, respectively. However, in the above evaluation the interaction between σ and π electrons is totally ascribed to the π component. If we take the model M_n to represent the π -component of $(\text{CH})_n$, the variations in the π component of the energy of benzene and cyclobutadiene will be $-6.20 \text{ kcal mol}^{-1}$ and $-11.34 \text{ kcal mol}^{-1}$, respectively. These values are quite surprising to us and they were originally supposed to be almost equal since the distortions are almost the same for M_4 and M_6 . Careful analyses found that this abnormal phenomenon results from the violation of vibration modes. When M_4 and M_6 vibrate with the B_{2u} and B_{1g} modes, the distorted geometries may be (1.393 Å and 1.513 Å) for M_4 and (1.337 Å and 1.457 Å) for M_6 . However, small differences in the long-bond lengths are needed to achieve the requirement of constancy in the nuclear repulsion. Such violation of the vibration mode will lead to a sharp rise in energy. For M_4 , when the structure changes from (1.393 Å and 1.513 Å) to (1.393 Å and 1.51597 Å), the variation of the electronic energy will be $5.18 \text{ kcal mol}^{-1}$, while for M_6 the variation of electronic energy will be as high as $10.75 \text{ kcal mol}^{-1}$ from (1.337 Å and 1.457 Å) to (1.337 Å and 1.45837 Å). In fact, Shaik *et al.*¹⁴ had pointed out that the selected distortion is very crucial and a wrong distortion will lead to a wrong conclusion. However, it is still unexpected that these small variations in the geometries will result in such big energy changes. Consequently, it can be concluded that the σ - π energy partition scheme which is based on constant nuclear repulsion during the distortion seems to be too rough an approximation.

Conclusions

We have defined a hypothetical particle M whose virtual nuclear charge, Z^* is 3.18, while there is only one electron on the specific AO $C(2p_n)$ and the true nuclear charge Z of M is one. The difference between Z^* and Z is that the former determines the forces acting on electrons and the latter determines the nuclear repulsion in $(M)_n$. Classical *ab initio* VB calculations on $(\text{CH})_n$ and $(M)_n$ ($n = 4, 6$) have been performed. Numerical results indicated that, in benzene and cyclobutadiene, the π electrons are distortive to almost the same degree, while the σ -frame prefers a regular geometry. The competition between the above two factors determines whether a system takes a regular (*e.g.* benzene) or an alternant geometry (*e.g.* cyclobutadiene).

We thank the National Natural Science Foundation of China for its financial support. This work is also a State Major Key Project for Basic Researches. We thank the referee for his helpful and critical suggestions to update the manuscript.

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Paper 4/04404E; Received 18th July, 1994