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Why Does Benzene Possess a D_{6h} Symmetry? A Quasiclassical State Approach for Probing π-Bonding and Delocalization Energies

Philippe C. Hiberty,[*,†] **David Danovich,**[‡] **Avital Shurki,**[‡] **and Sason Shaik**[*,‡]

Contribution from the Laboratoire de Chimie Theorique, Universite de Paris-Sud, 91405 Orsay Cedex, France, and Department of Organic Chemistry and Fritz-Haber Research Center for Molecular Dynamics, The Hebrew University, 91904 Jerusalem, Israel

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Abstract: In response to a recent controversy over the issue of whether the π-electrons of benzene do or do not possess a distortive tendency away from a D_{6h} symmetry, we have developed a new approach based on the quasiclassical (QC) state, which is the spin-alternant state of a chemical species and which allows definition of the π-bonding energy in a manner which does not depend on energy partition and is free of the dilemma of assignment of the nuclear repulsion. The QC state concept is applied to probe bonding energies in H_2 and C_2H_4 and then used to quantify delocalization energies of H_6 and benzene. It is shown that the π-bonding energy of benzene is stabilized by a localizing B_{2u} distortion. As such, the π-system of benzene behaves precisely like the delocalized H_6 hexagon which is a transition state more stable in a distorted D_{3h} geometry. The analogy between the delocalized π-electrons of benzene and H_6 is further highlighted by demonstrating, computationally, that they both possess exalted diamagnetic susceptibilities associated with ring currents. While H_6 simply falls apart to three H_2 molecules, the π-electrons of benzene are held together by the σ-frame. Benzene is therefore the site of two opposing driving forces. The π driving force tends to distort the molecule while the stronger σ driving force of the QC state acts in the opposite direction and imposes a regular geometry. As such, benzene possesses a unique delocalized π-component which has a dual nature; at any geometry of the C_6H_6 structure, the π-electrons are strongly stabilized by the quantum mechanical resonance energy (QMRE), and at the same time, they possess a global distortive tendency toward a D_{3h} structure. It is demonstrated that this dual picture of benzene is in perfect agreement with the "aromatic" behavior of benzene. Applications are presented to the Stanger model of bent benzene, tricyclobutabenzene, and naphthalene.

Introduction

Benzene is not simply a molecule; it is a paradigm which has played a central role in the development of the theory of organic chemistry and of chemical epistemology.[1,2] As such, benzene merits repeated reexamination whenever there is an advance in the probing power of our scientific methods and whenever there develops a controversy over a key issue of the molecule. These two requirements have been recently met and are the subject of the present paper. Firstly, a key controversial issue exists[3−12] and is being vividly debated by several groups;[9] this is the question of whether the π-electrons of benzene do or do not possess a distortive tendency away from a D_{6h} symmetry. Secondly, in order to focus the scientific debate, and in response to the controversy, we have devised a new analysis which can probe electronic delocalization and bonding issues in a manner free from some limiting features of past analyses which, themselves, originate the controversy.[5b,12] This paper utilizes the new approach to provide a lucid insight into the question of π-electron distortivity. It will be shown that the π-electrons

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[†] Universite de Paris-Sud.

[‡] The Hebrew University.

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of benzene possess two distinct properties; distortivity and resonance stabilization. The isoelectronic analogy with H_6 and Li_6 will be explored, and the conclusions will be used to settle the properties of benzene into a single coherent picture.

The issue dates back to the early 1960s when Longuet-Higgins and Salem[3a,b] used Hückel theory with variable β[7] to argue that the distortivity of π-electrons in cycles "exists already in benzene".[3b] Two years later Berry[3c] used a similar approach to account for the low IR frequency associated with the B_{2u} mode and argued that the low frequency originates in the distortivity of π-electrons. Meanwhile, the same conclusions have been reaffirmed by Epiotis[4b] and by Shaik and Bar[5a] and have been put in a wider context of delocalization in isoelectronic species, using totally different reasonings based on qualitative valence bond analyses. It appears however, that these views have not gained much ground in organic chemistry which accumulated a tremendous amount of support for the special stability of benzene and the association of this stability with the "aromatic" behavior of the π-electrons as predicted by the original Hückel rules.[1,2] In this sense, the idea that the π-electronic system of benzene or other aromatic molecules might have an inherent tendency to distort is often felt as a paradox.

The present day controversy originated when the distortive behavior of the π-electrons was probed by us[5b] and subsequently by Jug and Köster[6] by use of modern all-electron methods. Thus, we have developed an integral partition scheme[5b-i] that allows us to obtain, from the total ab initio SCF (or π-CI) energy, the variation of the individual σ and π energy components along the B_{2u} mode. Note that the $\sigma-\pi$ partition deals with electronic energies and not with total energies which include the nuclear repulsions V_{nn} term. Thus, in order to associate variations of electronic energies with variations of σ or π bonding energies, it was deemed neccessary to eliminate the V_{nn} problem by choosing distortions that keep constant nuclear repulsions between carbons. Sometime later, Jug and Köster[6] proposed a $\sigma-\pi$ partition of the total energy, inclusive of nuclear repulsion, and investigated the distortivities of the σ- and π-components along the B_{2u} mode without the constraints of constant V_{nn}. The two methods led precisely to the same qualitative conclusion: that the π-component of benzene is distortive along the B_{2u} mode. An independent method, used by us,[5b-d,f,i] compared the resistance to distortion of the ground state of benzene with that of a high-spin excited state, with all π-electrons having parallel spins. By analogy with high-spin hydrogen chains, it was shown that the π-electrons of the high-spin state of benzene are nearly indifferent to distortion, so that the resistance to distortion of such a state is close to that of the σ-frame alone. Since the high-spin state was found to resist distortion *more* than the ground state, it was deduced that the force that is responsible for the D_{6h} symmetry of ground state benzene is composed of an overriding symmetrizing σ-component and a smaller distortive π-component. Thus, in the benzene picture that emerges from these all-electron studies, the π-component enjoys resonance stabilization, but is also distortive and prefers a D_{3h} symmetry, and it is the resistance of the σ-frame to the distortion that restores the D_{6h} structure.

This viewpoint of benzene has been criticized recently by Glendening et al.,[12] who have cautioned that the energy partition within all-electron calculations is arbitrary and possibly misleading because it may involve an inherent bias toward π-distortivity.[12a] Similarly, it was argued that the high-spin modeling of a localized π-component is not conclusive since the π-electrons in the high-spin state undergo exchange repulsions that are not present in the ground state.[12b] The stand point of Glendening et al.[12a] is that the treatment of delocalization should be restricted to the comparison of the behaviors of a Kekulé structure vs benzene, *without* attempting the separation of $\sigma-\pi$ contributions. However, if one is not allowed to consider separately the effect of the π-energy, the π-distortivity cannot be addressed and one loses thereby the relationship of the benzene molecule to the broader problem of electronic delocalization in the isoelectronic species[4b,5a,b,f,i] and in the general context of other species in organic chemistry and solid state chemistry.[10] On the contrary, if it is possible to establish the π-electronic behavior of benzene, then on the one hand added insight and broad unity are gained, and on the other hand a link can be drawn between the views derived from all-electron treatments and the views of Hückel theory. Since Hückel theory is the basis of the $\sigma-\pi$ separation view, of the π-electron-based intuition, and of the topological aromaticity concept,[1a] and since the β-variable version of this theory shows π-distortivity,[7a] then this latter issue calls for serious considerations and must definitely be addressed and be based on modern all-electron theories. All the above questions and issues ultimately depend on the question, *whether or not it is possible to define the π-energy behavior in an all-electron calculation.* The problem at hand is concerned then with layers of insight and with a search for a consistent foundation of the benzene paradigm.

The present paper takes up the challenge and employs a novel theoretical analysis based on the concept of a "quasiclassical state" which leads to a definition of the π-bonding energy in a manner which is general, clear, and independent of nuclear–nuclear repulsion and does not call for any $\sigma-\pi$ integral partitions. The first section of the discussion presents the quasiclassical state concept and uses it to define the bonding energy of H_2 and the π-bonding energy of C_2H_4. The second part of the discussion section follows with applications of the concept to the problem of electronic delocalization in benzene and isoelectronic hexagons. Applications are presented also to benzene derivatives in which the σ-frames are made slightly distortive by ring-strain effects, as in Stanger's model of benzene,[9c] in tricyclobutabenzene, and in naphthalene. The results of the quasiclassical state concept are then compared with those of the integral partition scheme, and a coherent picture emerges concerning the title question.

Methods and Computational Details

All MO and CI computations were performed with the GAUSSIAN-92 and GAMESS-93 series of programs[13,14] on IBM/RS6000 workstations of the Hebrew University and the University of Paris-Sud.

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Table 1. Optimized Geometries of Diatomic and Hexagonal Species

entry	species	basis set	theoretical level	optimized geometry[a]
1a	H_2	6-31G	RHF	R(HH) = 0.730
1b	H_2	6-31G	CISD	R(HH) = 0.746
2	C_2H_4	6-31G	RHF	R(CC) = 1.322; R(CH) = 1.074 ∠(HCH) = 121.93
3	H_6 (D_{6h})	6-31G	RHF	R(HH) = 0.99
4	Li_6 (D_{6h})	6-31G	RHF	R(LiLi) = 3.065
5	Li_6 (D_{6h})	6-31G	CISD[b]	R(LiLi) = 3.0215
6a	C_6H_6	6-31G	RHF	R(CC) = 1.3883; R(CH) = 1.074
6b	C_6H_6	6-31G	CISD(π)[b,c]	R(CC) = 1.395;[d] R(CH) = 1.074

[a] Bond lengths in Å units and angles in deg. The ∠ symbolizes an angle. [b] With size consistency correction. [c] With Davidson correction. [d] Optimization at this level is performed by a stepwise procedure within a D_{6h} constraint. For comparison, a full optimization at the MP2/6-31G** level gave a value of 1.394 79 Å.

Magnetic susceptibilities were computed with the IGLO package using Basis Set II.[15] The geometries of all the species were optimized by gradient methods and checked by frequency calculations using the 6-31G basis set[13] at the restricted Hartree–Fock (RHF) level. Single-point energies were determined at the CISD level with size consistency correction. For π-systems, the CISD (π-only) calculations were performed using GAMESS,[14] which allows specification of the window for the CISD calculations. The $VEC section of the GAMESS input is taken from the RHF wave function of the corresponding species. The only requirement is the reorganization of the $VEC input to group all the π-type orbitals as an active space. The CI-type is specified in the $DRT section (e.g., for benzene in the 6-31G basis set; $DRT GROUP = C1 IEXCIT = 2 NDOC = 3 NVAL = 9 NEXT = 0 NFZV = 0 $END). The optimized geometries of the various species in this study are listed in Table 1. It is seen that the effect of CISD (π-only) on the geometry of benzene is very small, and we therefore decided to utilize a CC distance of 1.39 Å in all further investigations. The geometries of the Stanger[9c] model for benzene and tricyclobutabenzene were optimized using the 6-31G* basis set.[13] The geometry of naphthalene was optimized with the 6-31G basis set.

Quasiclassical Energies. The quasiclassical state (QC) was computed by inputting a guess wave function in a UHF option, using the appropriate singly occupied atomic orbitals (AO's) on alternating atoms. To obtain a spin-alternant determinant, i.e. a spin-wave state, we input equal numbers of α and β spin orbitals defined over alternating atoms. The option consists of orthogonalizing the orbitals without changing the Slater determinant, then computing the expectation energy by use of Slater's rules. The expectation energy of this wave function at iteration zero defines the quasiclassical energy of the spin-alternant determinant. In the case of a ring of hydrogens, the AO is the optimized 1s orbital obtained from a UHF calculation on a single H atom. In the case of π-systems, the AO is the corresponding $2p_\pi$ orbital of carbon, obtained from an UHF calculation of planar CH_3. In the case of ethylene we tried also a $2p_\pi$ AO taken from the calculation of triplet CH_2. The results based on the two guesses were virtually identical, and therefore, all other calculations were performed with an optimized $2p_\pi$ AO taken from the planar CH_3 calculation. The sensitivity of the QC energy to the choice of a UHF or an ROHF AO was also found to be negligible (less than 1 kcal/mol). In the case of ethylene and benzene the QC state is associated only with the π-electrons, while the σ-orbitals are used as a doubly occupied core identical to that of the ground state.

Results and Discussion

The Purely Electronic Definition of Bonding Energies in Valence Bond Theory. The exact definition of bonding energy for two interacting fragments is the difference in total energy between the molecule at equilibrium geometry and at the separated fragments limit. This definition is, however, of no use for calculating π-bonding energy, since the total energy includes the nuclear repulsion V_{nn}, which cannot be partitioned in a physically meaningful sense into σ- and π-components (see however Jug and Köster's ingenious partition[6]). Valence bond (VB) theory offers a solution to the problem by allowing formulation of a reference nonbonding electronic state which permits *a definition of the bonding energy* of a given species, independent of the nuclear repulsion. This state is the spin-alternant determinant of an electronic system which is referred to hereafter as the "quasiclassical" (QC) state because its energy is concerned with the classical energy terms. This quasiclassical energy has been used already by Kutzelnigg[16] to obtain a lucid picture of the physical origins of the chemical bond in the H_2 molecule. Malrieu[17] has emphasized the special status of the QC state (called there the spin-wave state or the Neel state) and used it extensively in his VB treatment of conjugated hydrocarbons. Hereafter we wish to apply the QC state to elucidate the behavior of the bonding energy which is associated with the π-electrons in benzene.

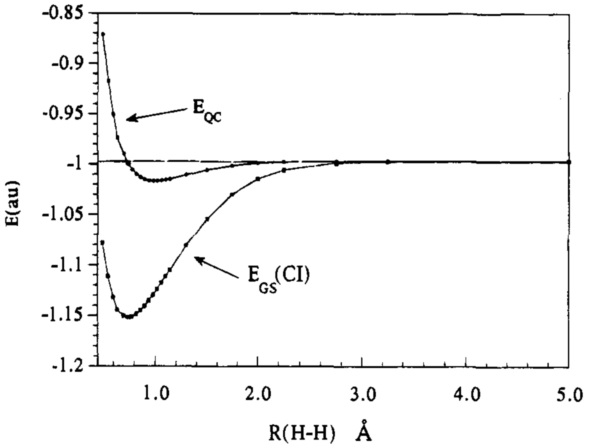

Figure 1. Quasiclassical (QC) and full CI energy curves for H_2 using the 6-31G basis set.

The Quasiclassical State of H_2. Let us consider first briefly, the H_2 molecule, with χ_a and χ_b being the atomic orbitals of the two hydrogen atoms, H_a and H_b. The corresponding QC state is defined then as the spin-alternant determinant in eq 1,

$$\Psi_{QC} = |\bar{\chi}_a\chi_b| \quad (\text{or } |\chi_a\bar{\chi}_b|) \tag{1}$$

where the two electrons in the spin orbitals, χ_a and χ_b, have opposite spins without being coupled into a singlet spin. The corresponding QC energy is given by,

$$E_{QC} = \epsilon_a + \epsilon_b + V_{nn} + J_{ab} + (V_{en})_{ab} + (V_{en})_{ba} \tag{2}$$

Here $\epsilon_a + \epsilon_b$ is a constant quantity that accounts for the sum of the 1s orbital energies of the isolated atoms, V_{nn} is the nuclear repulsion, J_{ab} is the Coulombic electron–electron repulsion, while the last two terms in eq 2 correspond to the electron–nuclear attractions of an electron on atom A with nucleus B and vice versa.

For a truly classical system, these energy terms will fully compensate each other and the energy curve will be flat throughout the internuclear distances. In chemical species, however, the electrons are described by wave functions, and their asymptotic behavior at $R = 0$ is not classical, while the nuclear repulsion energy term V_{nn}, which is expressed classically, goes to infinity at $R = 0$. We therefore expect that the QC energy will behave approximately classically for a range of distances larger than R_{eq} of the bond but will rise sharply at shorter distances. This is indeed the case as might be seen from

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the energy of the QC state in Figure 1. The curve is relatively flat and of nearly constant energy in the region $R = 0.86-1.14$ Å, with a shallow minimum near 1.0 Å. Furthermore, the QC energy at the ground state's equilibrium distance, R_{eq}, differs from the energy at 5.0 Å by only 1.4 kcal/mol. It follows therefore that, for any distance $\geq R_{eq}$, the classical terms nearly compensate each other and lead to *a flat energy curve for the QC state.*

This flatness of the QC energy eliminates altogether the problem of how to handle the V_{nn} term and enables the calculation of a decent approximation for the bonding energy of H_2. The bonding energy becomes then simply the difference between the energies of the ground state and the QC state, at any given internuclear distance. Moreover, the ground state (GS) can be taken at any desired level, RHF, CI, VB, etc., and provide thereby the bonding energy (E_B) and bond dissociation energy (D_e) appropriate to that level, as generalized in eq 3.

$$E_B = E_{GS} - E_{QC} \quad (D_e = -E_B) \tag{3}$$

Figure 1 shows the full CI curve (with the 6-31G basis set) and the dissociation energy at the full CI level is 97.4 kcal/mol, while the value defined by eq 3 relative to the QC state is 95.3 kcal/mol. It is apparent therefore that the QC state is a convenient reference for defining bonding energies, at a good range of internuclear distances, for any computational level and with fair accuracy.

The Quasiclassical State of C_2H_4. A similar definition of the QC state for ethylene can be used for the calculation of a π-bonding energy. Here the QC state possesses a filled σ-core of MO's which are kept intact precisely as in ethylene. On the other hand, the π-system is replaced by two spin-alternant $2p_\pi$ spin orbitals, χ_a and χ_b, as expressed by eq 4, where a and b refer to the corresponding carbon atoms.

$$\Psi_{QC} = |(...\sigma_i\bar{\sigma}_i...)\chi_a\bar{\chi}_b| \tag{4}$$

The energy of this π-QC state was found to lie in between the ground state and the triplet state and close to the energy of the twisted triplet. This intermediate energy location of the QC state confirms that its π-interaction behaves indeed quasiclassically, similar to the H_2 example. Another confirmation of this quasiclassical behavior is the use of the QC state for calculating the π-bonding energy with good accuracy, by use of eq 3 for $R_{eq} = 1.322$ Å. Thus, for MCSCF(π) and CISD(π) ground state wave functions, the so-calculated π-bond dissociation energies are 60.9 and 61.8 kcal/mol, respectively, which is in good agreement with most estimations of π-bond energy.[18,19]

The energy curve of the π-QC state of ethylene has a minimum at $R = 1.44$ Å, which is close to the accepted value (~1.46 Å) for a single σ-bond between sp^2 carbons.[20] This is again an indication that the π-QC state is indifferent to the total interaction of the spin-alternant p_π-electrons. When the two p_π-electrons "condense" into a π-bond, the equilibrium distance of the ground state shifts from 1.44 Å to a shorter distance of 1.322 Å, as might be expected from a compromise between the σ-preference and the π-bonding. It follows therefore that the π-QC state provides a reliable π-nonbonding reference state, that may serve to calculate realistic π-bonding energies without resort to integral partitioning and independent of nuclear repulsion.

Table 2. Distortion Energies of Hydrogen Rings and Their Quasiclassical States[a]

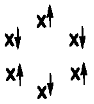
	σ-bonded H_6 (1s AO's)		π-suspended H_6 ($2p_\pi$ AO's)
bond lengths	ΔE_{QC}	ΔE_{GS}[b]	ΔE_{QC}
(1.39/1.39)	0.0	0.0	−0.0
(1.40/1.38)	−0.01	−0.11	−0.02
(1.41/1.37)	−0.03	−0.42	−0.06
(1.42/1.36)	−0.06	−0.95	−0.14
(1.43/1.35)	−0.11	−1.67	−0.24
(1.44/1.34)	−0.18	−2.59	−0.38
(1.45/1.33)	−0.26	−3.71	−0.55
(1.46/1.32)	−0.35	−5.00	−0.74
(1.47/1.31)	−0.45	−6.47	−0.96
(1.48/1.30)	−0.57	−8.10	−1.21
(1.49/1.29)	−0.70	−9.88	−1.49
(1.50/1.28)	−0.84	−11.80	−1.78

[a] Bond lengths are in Å units and energies in kcal/mol units. [b] Calculated at the CISD level with size consistency correction.

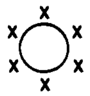
The Quasiclassical States of X_6 Hexagons. In order to study the delocalization problem in a hexagonal six-electron, six-orbital electronic system X_6, we must first establish a proper behavior of the QC state of these many-electron systems. The QC state is shown in **1** and its wave function is given by eq 5,

$$\Psi_{QC} = |(...\mathrm{core}...)\bar{\chi}_a\chi_b\bar{\chi}_c\chi_d\bar{\chi}_e\chi_f| \tag{5}$$

for a general case where there exist also core orbitals. Thus, the AO's, χ, can be the 1s orbitals of H or the $2p_\pi$ orbitals of C, with the appropriate core orbitals whenever present. The ground state in **2** is the familiar delocalized state which is also traditionally represented as a resonance between two Kekulé structures.



1



2

It is apparent from **1** and eq 5 that, unlike the two-electron case, in this six-electron spin-wave state, there are six through-space triplet repulsions due to identical spins across all the 1−3 positions of the hexagon. Therefore we might expect that along distortions which describe breathing of the hexagon, at D_{6h} symmetry, the energy of **1** will vary significantly because the through-space repulsions will vary with the breathing mode of the hexagon especially at short X- -X distances. Indeed, the energy curve for the QC state of H_6 exhibits a minimum at $R = 1.34$ Å, and this minimum species is 56.3 kcal/mol more stable than the QC state species at $R = 0.99$ Å. Since the corresponding QC energy for H_2 is flat, this energy difference does not arise from the adjacent H- -H interactions and reflects the change in 1−3 triplet repulsions upon the breathing motion of the ring. This was verified by us by independent calculations of the triplet repulsions at the corresponding distances. This means that the QC has repulsive walls along the symmetry-conserving A_{1g} mode.

Along the B_{2u} mode the situation is entirely different because the changes in the 1−3 triplet repulsions are expected to be mutually compensating. That this is indeed the case is apparent from Table 2, which shows, in the first energy column, the energy changes of the QC state upon a B_{2u} distortion for an H_6 hexagon made of six hydrogen atoms, initially arranged to match the positions of the six carbons in benzene. The QC state was calculated with the 6-31G basis set, in various geometries ranging from the D_{6h} hexagon with R(HH) equal to 1.39 Å all

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(18) A value of 60 kcal/mol appears in the following: Benson, S. W. *J. Chem. Educ.* **1965**, *42*, 502.

(19) A calculated value of 69 kcal/mol along with other calculated values of 63-66 kcal/mol appear in the following: Schleyer, P. v. R.; Kost, D. *J. Am. Chem. Soc.* **1988**, *110*, 2105.

(20) Hess, B. A.; Schaad, L. J. *J. Am. Chem. Soc.* **1983**, *105*, 7500.

the way to a highly distorted D_{3h} hexagon with alternating bond lengths of 1.50 and 1.28 Å. It is seen that the energy ΔE_{QC} of the quasiclassical state is extremely flat, along the B_{2u} distortion, relative to the variation of the ground state energy (ΔE_{GS}) of this system, which is calculated at the CISD level. It is apparent therefore that the QC state of H_6 (1s) behaves quasiclassically along a B_{2u} distortion, and that the energy difference between the ground state and its corresponding QC state along the B_{2u} distortion, i.e. $\Delta E_{GS} - \Delta E_{QC}$, will be reasonably close to the exact values of the actual distortion energy (ΔE_{GS}). It follows therefore that *the problem of delocalization can be studied safely along the B_{2u} mode, which is also the traditional localizing mode for hexagons.*

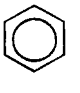
An even closer model for benzene is the "suspended" H_6 (π) six-membered ring, where each hydrogen atom bears a p_π atomic orbital perpendicular to the H_6 plane instead of a 1s orbital. For making the model as close as possible to the π-bonding system of benzene, the π atomic orbitals are exact $2p_\pi$ orbitals of carbon, arising from an UHF calculation on the planar methyl radical, in the 6-31G basis set. The distortive behavior of the QC state of H_6 (π) is displayed in the third energy column of Table 2. It is seen that the energy of this π-type QC state remains nearly constant under the effect of the distortion, varying by only −1.78 kcal/mol for the maximum distortion. This small figure can be compared with the distortion energy of −18.3 kcal/mol that will be calculated below for the π-system of benzene (Figure 2). Moreover, the negative ΔE_{QC} values for the two H_6 model systems, in Table 2, show that these QC states themselves are slightly distortive, and consequently, our definition of the bonding energy based on the QC state (eqs 3 above and 6 below) cannot be biased toward strong distortivities. On the contrary, the errors, if any, inherent to this approximation will in fact *underestimate* the distortive tendency of a bonding system.

The foregoing tests serve as models for the π-QC state of benzene and serve to ascertain that the actual π-QC state of benzene will behave quasiclassically along the B_{2u} mode and whatever energy variation exhibited by the state will be due to the σ-frame. As a further confirmation, the actual π-QC state of benzene exhibits a minimum at R(CC) = 1.45 Å, which is very close to the corresponding distance in the minimum of the QC state of ethylene (1.44 Å) and to the standard single σ-bond distance between sp^2 carbons.[20] We may therefore feel confident to use the QC state to explore the behavior of the π-bonding energy of benzene along the B_{2u} mode.

Application to the π-Bonding System of Benzene. Let us now consider the benzene molecule itself. The approximate π-bonding energy $E_B{}^\pi$ is given by eq 6 and is defined as the

$$E_B{}^{\pi} = E_{GS}(\mathbf{3}) - E_{QC}(\mathbf{4}) \qquad (6)$$

energy difference between the ground state **3**, calculated at the level of CISD (size) among π-electrons, and the quasiclassical state **4**, described by the spin-wave determinant which involves a doubly occupied σ-core and spin-alternated p_π-electrons. Note that the π-bonding energy defined by eq 6 accounts for the full π-bonding energy including the delocalization effect due to the resonance of the two Kekulé structures in the ground state **3**.



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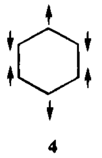

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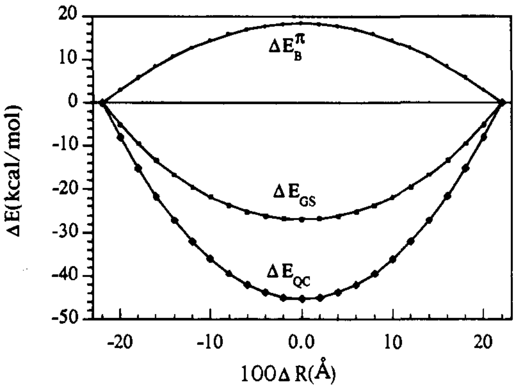
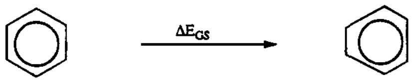


Figure 2. Energy changes due to the distortion of benzene from D_{6h} to D_{3h}. The CC-bond lengths are 1.39 Å in the D_{6h} geometry, and the distortion keeps constant the sum of CC-bond lengths. ΔR is the difference between the long and short CC bonds in the hexagon. All the energies are arbitrarily anchored at the zero of the energy scale. The $\Delta E_B{}^\pi$ corresponds to the bonding energy change (eq 6 and drawings **5** and **6**) of the π-component. The other curves are the ground state (GS) and the QC state curves.

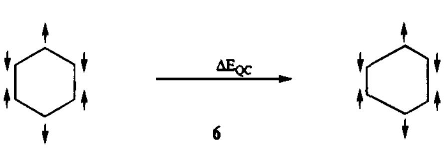
Thus, the change of this bonding energy along the B_{2u} mode will define the propensity or lack thereof of the π-bonding energy to undergo partial localization.

It is important to emphasize at the outset that the QC state approach for calculating the contribution of the π-bonding to the distortion energy is *independent of any σ–π* partitioning of integrals or of the V_{nn} problem. Therefore, the criticism expressed in ref 12 regarding the energy partition is initially inapplicable to the conclusion derived from the computational experiment based on the QC state concept.

The computational experiment is driven as follows in **5** and **6**. In a first step, **5**, we compute the resistance to distortion, ΔE_{GS}, of the D_{6h} ground state (itself with R_{eq}(CC) = 1.39 Å) under a localizing B_{2u} distortion that changes the D_{6h} equilibrium geometry of benzene to a D_{3h} structure which is less delocalized.



5



6

The second step, **6**, consists of subjecting the QC state to the same B_{2u} distortion as above. Furthermore, the QC state is calculated with the same σ orbitals as in the ground state at any point along the B_{2u} distortion. Since the π-electrons of the QC state behave quasiclassically and are indifferent to the distortion, then the energetic cost of the distortion, ΔE_{QC}, will reflect the σ-frame's resistance to distort in the field of a nonbonding p_π-electronic system. Consequently, the difference $\Delta E_B{}^\pi$ between the ΔE_{GS} and the ΔE_{QC} quantities will provide the energy change due to bonding of the π-electrons only.

The results of the computational experiment are displayed in Figure 2. As expected, the distortion of the ground state is endothermic and the ground state energy rises smoothly as ΔR increases, reaching a final value of 27.0 kcal/mol above the D_{6h} minimum. Similarly, the QC state having a σ-system and nonbonding p_π-electrons, is also seen to be destabilized by the localizing distortion, an expected tendency since a set of six

Table 3. Distortion Energies of C_6H_6 along B_{2u} Distortion Modes

	distortion[a]		energy[a,b]		
entry	R (D_{6h})	R_1; R_2 (D_{3h})	ΔE_{QC}	ΔE_{GS}	$\Delta E_B{}^{\pi}$
1	1.39	1.33; 1.45	+13.2	+7.5	−5.7
2	1.39	1.28; 1.50	+45.3	+27.0	−18.3
3	1.45[c]	1.39; 1.51	+9.5	+4.2	−5.3
4	1.45[b]	1.36; 1.54	+21.6	+9.9	−11.7
5	1.40[d]	1.34; 1.4627	+12.5	+7.1	−5.4
6	1.40[e]	1.34; 1.4627	+16.3 (ΔE_σ)	+7.2	−9.1 (ΔE_π)[f]
7	1.35	1.33; 1.37	+1.8	+1.2	−0.6
8	1.50	1.48; 1.52	+0.8	+0.2	−0.6

[a] All distortions are in Å, and energies are in kcal/mol units. [b] All values of $\Delta E_B{}^{\pi}$ are determined at the CISD (π) level with Davidson correction, using eq 6. [c] This distance corresponds to the energy minimum of the QC state. [d] This entry corresponds to the distortion used in ref 5b. [e] This entry corresponds to the integral partition scheme used in ref 5b. [f] This value is from ref 5b and corresponds to a multireference π-CI (the CIPSI algorithm).

equivalent σ-bonds can only prefer a regular structure over an alternated one. The striking feature, in Figure 2, is that ΔE_{QC} is larger in absolute value than ΔE_{GS}, at any point of the distortion coordinate. Thus, *turning off the bonding and delocalization of the π-electronic system of benzene results in an increase of the reluctance of the C_6H_6 hexagon to undergo the B_{2u} distortion.* Accordingly, as can be seen from the Figure, the π-bonding energy curve, as calculated by means of eq 6, displays an curvature opposite to that of ΔE_{QC} and ΔE_{GS} and exhibits a maximum at the D_{6h} structure, the total π-distortivity amounting to −18.3 kcal/mol.

To ascertain that this behavior does not depend on the initial geometry used for benzene, we have employed the same computational experiment starting from other geometries of the D_{6h} hexagon at different R(CC) distances. These results are collected in Table 3 and demonstrate that, *irrespective of the initial geometry of the D_{6h} hexagon, the delocalized π-bonding system of benzene is distortive and prefers a D_{3h} structure.* This is an important result that shows that the π-distortivity is a quality of the delocalized π-electrons and not an artifact of the chosen geometry, as was implied by Glendening et al.[12]

It is instructive to compare, in this sense, the results of the QC state method for benzene with those of the integral partition approach of ref 5b. First we must emphasize that the nuclear repulsion V_{nn} cannot be partitioned into σ- and π-components in a physically meaningful way, and this is the reason why we have considered, in our previous work[5b] as well as in entry 6 in Table 3, only variations along distortions that *keep constant nuclear repulsion between carbon atoms.*[21] In this and only this manner the variation of the π- and σ-electronic energies may be meaningfully equated with changes in the corresponding bonding energies. It is therefore misleading to model the behavior of benzene, as was done by Glendening et al.,[12a,c] by applying the partition to the compression of a single π-bond, a case in which the condition of constant V_{nn} could not be satisfied.

It is apparent from entries 5 and 6 in Table 3 that the σ- and π-bonding components, obtained from the application of the QC state concept (entry 5) and those obtained from the integral partition scheme (entry 6), exhibit the same qualitative behavior. The same picture, in fact, emerges also from yet another computational experiment, the one that is based on the high-spin state of benzene.[5b,d] Clearly, three methods independent of one another provide a consistent and qualitatively identical picture of the π-electrons of benzene. It is apparent therefore that, no matter how we approach the problem of benzene at the all-electron level, we reach the same conclusion that *the delocalized π-electrons of benzene possess a propensity to distort to a localized structure, but this propensity is overcome by the σ-frame which restores a hexagonal D_{6h} geometry.*

Key Features of Delocalized Species. What kind of a driving force is electronic delocalization in chemical systems? This is a fundamental question in chemistry, with relevance to molecular aggregates, hypervalent compounds, transition states of reactions, and aromatic or antiaromatic conjugated hydrocarbons,[5] as well as conductivity in solids.[10] Before examining this question it is important to define lucidly what specific feature is really meant by invoking the single word "delocalization". This elucidation will be done by appeal to two model systems, the H_6 and Li_6 *planar rings.*

Delocalized states can belong to two different varieties, the distortive and the nondistortive, depending on the relative energy of the electronic species at the regular geometry relative to the alternated geometry. The Li_6 (D_{6h}) hexagon belongs to the nondistortive category; it is more stable than a set of three Li_2 units.[22] Thus, our calculated distortion energy at the CISD (corr) level is +6.46 kcal/mol, when Li_6 (D_{6h}, R = 3.0210 Å) is distorted to a D_{3h} structure (R_1 = 3.4215 Å, R_2 = 2.6681 Å). In this sense, delocalization is a stabilizing factor and a driving force that leads to the aggregation of Li_6. In contrast, the delocalized H_6 species belongs to the distortive category; it is an unstable transition state[5b,f,i,8] which distorts from a D_{6h} geometry along a D_{3h} pathway toward three separated H_2 molecules, as indeed appears from the negative distortion energies ΔE_{GS} in Table 2. In that sense, delocalization is not a factor that can keep the H_6 aggregate intact (under ambient pressures). All transition states of chemical reactions are distortive delocalized states which belong to the same category as H_6. As such, it is sufficient to find one localizing mode which lowers the energy of a delocalized species in order to prove the distortivity of the species.[11b]

A feature which is shared by all the delocalized species is the vertical resonance energy[23] which following Coulson[24] we called the "quantum mechanical resonance energy" (QMRE). The QMRE of a delocalized system in a given geometry is the difference between the energy of the true ground state, composed of a set of resonating Kekulé structures, and the energy of a single Kekulé structure taken at the *same geometry.* It is obvious, from simple properties of the variational theorem, that QMRE is always stabilizing, even in highly unstable systems like H_6 or in any chemical transition state. Moreover, it is apparent that the QMRE peaks at the regular geometry and gets smaller at distorted geometries. Thus, there exist distortive and nondistortive delocalized species and all of them possess QMRE stabilization relative to a localized reference. It follows that the distortivity of a delocalized species does not mean that the species does not possess QMRE stabilization. In fact, the very distortive H_6 possesses a very large QMRE[5b] and is more stable than its localized reference at any given geometry.

These two features of delocalization which may seem fairly obvious for the H_6 and Li_6 models become for some reason controversial when benzene is addressed.[9,11,12] To avoid further confusion we should address the question of the π driving force in benzene in the most straightforward way: does the π-bonding system of benzene resemble that of the H_6 or the Li_6 system?

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[21] For a recent discussion of π-electronic delocalization in allyl radical, cation, and anion and the application of the integral scheme to them, see: Gobbi, A.; Frenking, G. *J. Am. Chem. Soc.* **1994**, *116*, 9275.

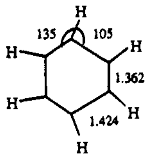
[22] Note though that the planar Li_6 (D_{6h}) structure is used here and elsewhere[5b] as a model, but the global minimum of Li_6 is not D_{6h}. In any event, the model Li_6 (D_{6h}) hexagon is more stable than three isolated Li_2 molecules. See, for example: Bonacic-Koutecky, V.; Patucci, P.; Koutecky, J. *Chem. Rev.* **1991**, *91*, 1035.

[23] Kollmar, H. *J. Am. Chem. Soc.* **1979**, *101*, 4832.

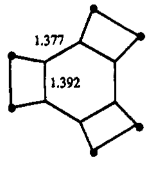
[24] Coulson, C. A.; Altman, S. L. *Trans. Faraday Soc.* **1952**, *48*, 293.

Obviously, from the above results, in Table 3, it is apparent that the π-electrons of benzene belong to the distortive category of H_6. To further appreciate the analogy of H_6 and the π-electrons of benzene, we can look at the magnetic properties of the two rings. It had been shown by Dauben and coworkers[25] in the 1960's that benzene and other "aromatic" species exhibit exaltation of the diamagnetic susceptibility, χ, relative to a localized reference. This exaltation was shown to be a mark of $4n + 2$ cyclic delocalization in the molecule. Recently, Jiao and Schleyer[26a] have demonstrated by means of IGLO[15] calculations that the same magnetic susceptibility exaltation is exhibited by transition states which are classified as "aromatic" and have argued that *the exaltation constitutes a topological property associated with the "aromatic" mode of electronic delocalization*, be the species a stable molecule or an unstable transition state. Our own IGLO calculations of H_6 show that the D_{6h} hexagon possesses an exalted diamagnetic susceptibility ($\chi = -21.3$ ppm cm^3 mol^{-1})[26b] with an exaltation of about 10 units relative to that of an open chain H_6 or 5−6 units relative to those of distorted D_{3h} hexagons. This value of the exaltation in H_6 is quite close to the experimental and theoretical values determined[25,27] for benzene (13.7 and 9 units, respectively) and the values calculated[26] for quite a few of the six-electrons, six-center transition states. Thus, following Jiao and Schleyer,[26] *the delocalization in the D_{6h} H_6 species is perfectly aromatic and this species is a very good analog of the π-delocalization in benzene.* The analogy stops here because, while H_6 simply falls apart to three H_2 molecules, the π-electrons of benzene are held together by the σ-frame. Benzene is therefore the site of two opposing driving forces; the π driving force tends to distort the molecule while the stronger σ driving force of the QC state acts in the opposite direction and imposes a regular geometry. As such, benzene possesses a unique delocalized π-component which has a dual nature; *at any geometry of the C_6H_6 structure, the π-electrons are strongly stabilized by the QMRE and, at the same time, they possess a global distortive tendency toward a D_{3h} structure.*

Expressions of π-Distortivity in Some Benzene Derivatives and in Naphthalene. To further test the π-distortivity we applied the QC state method to investigate the origins of bond alternation in 7 and 8. These molecules serve as probes for the Mills-Nixon effect[9c,28] and are typified by angular constraints which are exerted on the σ-frame while not affecting the π-electrons directly.[28c] Thus, 7, which is the Stanger model[9c] for a strained σ-system with an external HCC angle of 105° (taken as a midway value between the range of angles 90°−120° investigated by Stanger), exhibits a significant bond alternation. In 8, the σ-strain is exerted by the cyclobutano-fused rings while the π-effect is negligible as shown by a VB analysis by Hiberty et al.[28c] This molecule exhibits a rather weak, though still observable, bond alternation.[28a,b]

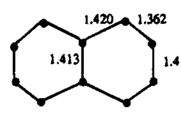


7



(• =CH_2)

8



(• =CH)

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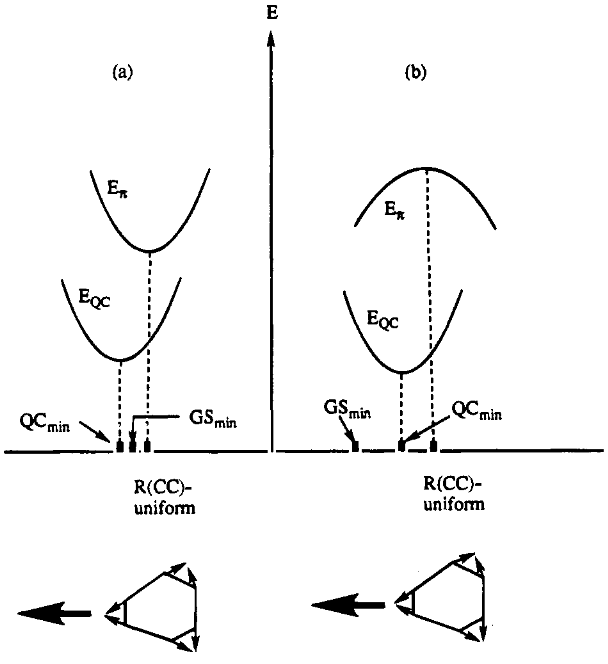

Figure 3. Possible σ−π scenarios for 7 and 8. The abscissa of the diagram refers to a distortion mode which causes bond alternation as shown by the arrows in the drawing (in analogy with the B_{2u} mode in benzene). The center of the diagram refers to a structure with uniform R(CC) distances in the benzenic nucleus. The minimum of the σ-frame (represented by the QC state's energy) is displaced in each case to a bond-alternated geometry. Part a shows the expectation if the π-bonding and delocalization energy is nondistortive (attractive). Then the minimum of the ground state (GS_{min}) will be located closer to the R(CC)-uniform structure in comparison with the QC_{min}. Part b shows the expectation if the π-bonding and delocalization energy is distortive. Then the GS_{min} will be located at a more bond-alternated structure in comparison with the QC_{min}. The molecules in 7 and 8 follow the π-behavior in b.

In both of the test systems, the constraints apply on the σ-frame (the QC state) a bond-alternation distortion which, in the point group symmetry of 7 and 8, is labeled as A_2' and is the mode analogous to B_{2u} in benzene. The question is, does or does not the π-bonding reinforce this distortivity? Without assuming anything about the π-distortivity or lack thereof, we present in Figure 3a,b the possible σ-π scenarios which may be encountered for 7 and 8. In both cases, the QC state (σ-frame) is displaced from the uniform-R(CC) structure (midpoint of the abscissa) due to the angular strain which acts on the σ-frame. In Figure 3a, the π-bonding is portrayed as a nondistortive species, and if this were the case, the ground state (GS) minimum would have been located in between the uniform R(CC)-structure and the minimum of the QC state. However, if indeed the π-bonding is distortive as in Figure 3b, then the π-electrons should reinforce the CC-bond alternation and the GS minimum should be more distorted than the QC minimum.

To ascertain the actual behavior of 7 and 8, we have started from their GS minima and have stepped along the A_2' mode (the analog of B_{2u} in benzene) and examined the energies of the QC state and of the π-bonding. Our analysis shows that the minimum of the QC state along this mode is located at the bond-alternated geometries with R(CC) bond lengths of 1.4096 and 1.3764 for 7 and 1.3907 and 1.3784 Å for 8. Comparing

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(25) Dauben, H. J., Jr.; Wilson, J. D.; Laity, J. L. *J. Am. Chem. Soc.* **1968**, *90*, 811.

(26) (a) Jiao, H.; Schleyer, P. v. R. *J. Chem. Soc., Faraday Trans.* **1994**, *90*, 1559. (b) Preliminary results for H_6 and Li_6 were presented by Schleyer during the discussion of ref 26a (to be reported in *Chem Phys. Lett*).

(27) (a) Katritzky, A. R.; Barczynski. P.; Musumarra, G.; Pisano, D.; Szafran, M. *J. Am. Chem. Soc.* **1989**, *111*, 7. (b) Fleischer, U.; Kutzelnigg, W.; Lazzaretti, P.; Muhlenkamp, V. *J. Am. Chem. Soc.* **1994**, *116*, 5298.

(28) (a) Balridge, K. K.; Siegel, J. S. *J. Am. Chem. Soc.* **1992**, *114*, 9583. (b) Boese, R.; Bläser, D.; Billup, W. E.; Haley, M. M.; Maulitz, A. H.; Mohler, D. L.; Volhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 313. (c) Hiberty, P. C.; Ohanessian, G.; Delbecq, F. *J. Am. Chem. Soc.* **1985**, *107*, 3095.

Table 4. Driving Forces of the σ- and π-Components in Benzene, Open-Chain Polyene, and Cyclobutadiene

		symmetrizing or distortive driving forces		
polyene	QMRE	π-component	σ-frame	total ($\sigma + \pi$)
benzene	large[a]	weakly distortive	symmetrizing	symmetrizing
polyene chain	small[b]	strongly distortive	symmetrizing	distortive
cyclobutadiene	small[c]	strongly distortive	symmetrizing	distortive

[a] 85.2 kcal/mol in ref 5b. An empirical value of 66 kcal/mol can be estimated (see ref 30). [b] The QMRE is additive and is calculated in ref 5b to be ~9.5 kcal/mol per one conjugative interaction. See also refs 20 and 23. [c] 30 kcal/mol (ref 5b). 21 kcal/mol in ref 31.

these QC minima to the optimum geometries for the corresponding GS's in **7** (1.4238 and 1.3622 Å) and **8** (1.3922 and 1.3769 Å) shows that, in both cases, the GS is more bond-alternated than the corresponding σ-frame. *It follows therefore, that the π-bonding energy behaves in a distortive manner and reinforces the distortion of the σ-frame* according to the scenario in Figure 3b. The π-distortivity in **7** and **8** was further ascertained for a variety of initial geometries. Thus, for these cases *where the strain on the σ-frame is of the bond-alternating type, the molecule finds an assisting σ-pathway to undergo distortion in the direction dictated by the π-propensity along the same mode.*

While the above conclusion applies to **7** and **8** and their analogs, it is apparent that, in the general case where the σ-constraints are not of the bond-alternating type, the molecule will seek distortive pathways along which the σ-frame is quite soft, softer than the bond-alternating pathway which is expensive for these molecules. While an exhaustive treatment of the distortive patterns of conjugated systems is beyond the focus of the present paper, still a case in point is the distortive mode of naphthalene, **9**, which we analyzed by use of the QC state method. Thus, naphthalene does not utilize the uniform B_{2u} distortion pathway ($\Delta E_{QC} = +12.4$ kcal/mol; $\Delta E_{\pi} = -12.5$ kcal/mol for a ±0.05 Å distortion from a uniform $R(CC) = 1.3972$ Å structure). Instead, naphthalene finds a mode which mostly shortens the $C_{\alpha}-C_{\beta}$ bond (to 1.362 Å) while applying a nonuniform lengthening of the other C−C bonds (see **9**). This mode which is quite soft in the σ-frame ($\Delta E_{QC} = +3.0$ kcal/mol) takes better advantage of the π-distortivity ($\Delta E_{\pi} = -7.3$ kcal/mol) than the B_{2u}, which is very expensive in the σ-frame. Thus, the π-distortivity takes different expressions which ultimately depend on the strain applied on the σ-frame.

Benzene, Open-Chain Polyene, and Cyclobutadiene. For further elucidation we present in Table 4 a summary of the opposing driving forces for three classical models of organic chemistry: benzene, open-chain polyene, and cyclobutadiene. All of these species possess a distortive π-component with QMRE and a geometry-symmetrizing σ-frame. The magnitude of QMRE obeys the classical Huckel $(4n + 2)/4n$ rules, being large for benzene and small for open-chain polyene and for cyclobutadiene. For any one of the two cyclic compounds, the QMRE is larger at the uniform geometry than in the bond-alternated structure. Thus, *considered by itself*, the QMRE *is* always a driving force for symmetrization of the structure. However this driving force, by itself, is too weak to compensate for the huge π-destabilization that a Kekulé structure undergoes by passing from an alternated to a regular geometry[5b,12a] and, consequently, the π-component as a whole remains distortive. This distortivity is opposed by the σ−frame which tends to equalize bond lengths, and the tendency increases as the number of pairs of σ-bonds increase, being the largest in benzene and the smallest in cyclobutadiene.[29]

In benzene, with the largest QMRE (85.2,[5b] 66[30] kcal/mol), the π-distortivity is the weakest and, consequently, the σ-frame with the largest symmetrizing force wins out and restores a D_{6h} structure. On the contrary, in open-chain polyene, with only one Kekulé structure, the QMRE is very weak (e.g., ~19 kcal/mol for the hexatriene[5b]) and the π-system is strongly distortive and overcomes the σ restoring force, leading thereby to bond alternation. Finally, in cyclobutadiene, the QMRE is weak (ca. 21−22 kcal/mol[5f,31]), significantly less stabilizing than the six-electron QMRE[5b,f,31,32] and, therefore, the combination of a strong distortive π driving force and a weaker σ restoring force results in a rectangular structure.

The QMRE being stronger in benzene than in open-chain polyenes is also the root cause for the special stability of benzene.[1a] It is due to the σ-framing that the QMRE is manifested as "aromatic stability", which is a general characteristic of benzene in chemical reactions. Consider a competition between two chemical reactions of benzene, one of which destroys its cyclic π-delocalization, while the other one restores the delocalization in the end. Clearly, the destructive reaction will always be at disadvantage because the excess QMRE stability which is gained by restoring the π-electron delocalization will favor the latter reaction type. This is the reason why substitution, which regenerates the benzene nucleus, is the most common reaction of benzene, while addition is a rare process.[1] Thus, the observed "aromatic" behavior is due to the QMRE of the six π-electrons, and its observation, despite the distortivity of the π-electrons, originates in the constraints of the σ-frame that preserves π-electron delocalization.

It is seen, therefore, that our picture of distortive π-electrons conserves much of the conventional picture associated with π-systems, while adding a feature that places the organic species within a broader context of isoelectronic chemical species.[5b,f,i,10]

Is the π-Distortivity of Benzene a Paradoxical Result? The distortive tendency of π-systems has been demonstrated not only for benzene but also for other conjugated molecules and in particular in allyl radical[5b,c,f] and allyl anion and cation.[21] Thus, much like in benzene, the allyl species is the site of two driving forces, one arising from the σ-bonds and the other from the π-bonds. Generally, the σ-bonds constitute a symmetrizing driving force. This is demonstrated beautifully in the recent calculations of Koch et al.,[33] which show that even a formally *antiaromatic* system like *s*-indacene can be forced to adopt a regular geometry, once the σ-bonds are properly accounted for through extensive CI. It follows therefore, that a strong σ driving force is sufficient, by itself, to account for the symmetrical geometries of benzene or allyl. This of course is *a priori* coherent with either a symmetrizing or a weakly distortive

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(29) A referee asked about the distortivity of C_5H_5 and C_7H_7. These, as well as all odd-membered ring radicals have degenerate electronic states, which means that for them QMRE = 0. Such systems will of course be very distortive. This, however, is well recongnized from a Jahn−Teller argument. See analysis in the following: Shaik, S. S. In *New Theoretical Concepts for Understanding Organic Reactions*; NATO ASI Series, Vol. C267; Bertran, J. Csizmadia, I. G., Eds.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1986; pp 165−217 (especially p 197).

(30) Adding the compression energy of cyclohexatriene (~30 kcal/mol) to the thermochemical resonance energy (~36 kcal/mol) results in an empirical QMRE value of 66 kcal/mol.

(31) Voter, A. F.; Goddard, W. A., III *J. Am. Chem. Soc.* **1986**, *108*, 2830.

(32) (a) van der Hart, W. J.; Mulder, J. J. C.; Oosterhoff, L. J. *J. Am. Chem. Soc.* **1972**, *94*, 5724. (b) Malrieu, J. P.; Maynau, D. *J. Am. Chem. Soc.* **1982**, *104*, 3021. (c) Kuwajima, S. *J. Am. Chem. Soc.* **1984**, *106*, 6496. (d) Cooper, D. L.; Gerratt, J.; Raimondi, M. *Nature* **1986**, *323*, 699.

(33) Hertwig, R. H.; Holthausen, M. C.; Koch, W.; Maksic, Z. B. *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1192.

π driving force. Our computational tests of benzene and allyl species reveal that the corresponding π-components are all weakly distortive. In fact, the π-components of all heteroatomic analogs of benzene, like N_6, Si_6H_6, etc., were found to exhibit precisely the same behavior as in benzene.[5f,g] The π-distortivity appears then to be a general quality of π-electrons in organic and related main element species.

What is then the key factor that makes a bonding system symmetrizing or distortive? As far as aggregates of monovalent atoms are concerned (i.e., alkali atom, halogens, hydrogen, noble metals) some trends are well-known and have been rationalized by means of a VB model,[5a,b,f,i] itself supported by ab initio calculations.[34] Thus, in the case of atoms which form strong bonds like H, the delocalized aggregates are expected to be unstable toward a localizing distortion. On the other hand, atoms which form weak bonds like Li form delocalized clusters which resist a localizing distortion. In between these extremes, atoms like halogens with medium bond strengths form very weakly stable or unstable aggregates. The π-bonds fall in the range of relatively strong bonds, with a bonding energy of 60–70 kcal/mol in ethylene,[18,19] intermediate between the bond strengths of dihalogens and of dihydrogen. Therefore, it is only logical to deduce that delocalized π-bonding systems are distortive. Were it not so, the π-bonds would constitute an inexplicable exception in a model for delocalization which is otherwise successful and unifying. *The paradox, if any, would have been, in fact, if the delocalized π-bonding system were found to be symmetrizing.*

Concluding Remarks

The concept of a quasiclassical (QC) state shows that the π-bonding energy of benzene is stabilized by a localizing B_{2u} distortion. As such, the π-system of benzene behaves precisely like the delocalized H_6 hexagon which is a transition state, unstable relative to a distorted D_{3h} geometry. The analogy between the delocalized π-electrons of benzene and H_6 is further highlighted by inspecting their exalted diamagnetic susceptibility which results from ring currents.[25–27] Thus, the six π-electrons of benzene as well as the six electrons of H_6 endow their respective systems by large vertical resonance stabilization (QMRE). In fact, in both cases, the bonding energy tends to shrink the size of the D_{6h} hexagons along the respective A_{1g} modes[35] in an attempt to optimize the QMRE. At the same time, the bonding energy of both H_6 and the π-system of C_6H_6 is distortive along a localizing B_{2u} mode. While H_6 simply falls apart to three H_2 molecules, the π-electrons of benzene are held together by the σ-frame and, thereby, the QMRE of benzene gains expression in a variety of chemical phenomena. While H_6 simply falls apart to three H_2 molecules, the π-electrons of benzene are held together by the σ-frame.

Benzene is therefore the site of two opposing driving forces, σ and π; the π driving force tends to distort the molecule while the stronger σ driving force acts in the opposite direction and imposes a regular geometry. This conclusion has been most beautifully expressed by Heilbronner[7a] based on a Hückel treatment with variable β: "The highly symmetrical structure of benzene, allyl and similar systems is a consequence of the stiffness of their σ frame. If by an act of God all the sp^2-sp^2 σ-bonds force constants were reduced to half their values, i.e., $k = 250$ N m^{-1}, then benzene and allyl would have localized Kekulé structures." As such, *benzene possesses a unique delocalized π-component which has a dual nature; at any geometry of the C_6H_6 structure, the π-electrons are strongly stabilized by the QMRE, and at the same time, they possess a global distortive tendency toward a D_{3h} structure.*

Since Huckel theory,[3,7] VB analyses,[4b,5a] energy partitions of various kinds,[5b–i,6] and the application of the QC state concept, in the present work, all lead to the same conclusion, it seems inevitable that the classical view ought to make place for the distortivity of the π-electrons. Far from being paradoxical, this property allows inclusion of the π-electronic systems, alongside with molecular aggregates and reaction transition states, into a coherent and unifying model for delocalization. Furthermore, as shown by the analyses of **7** and **8**, the π-distortivity is expressed in the geometries of benzene derivatives with strained σ-frames. The π-distortivity is mode selective and will manifest only for the B_{2u} mode in benzene or the B_2 mode in allyl. It is along these modes that the distortivity should be probed and may eventually be verified. Recent results of Haas and Zilberg[36] on the spectroscopy of benzene suggests that π-distortivity may manifest itself afterall as a strikingly large spectral shift of the B_{2u} vibration in the $^1B_{2u}$ excited state of benzene.

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[34] For example, see the quantitative computations of VB curve-crossing diagrams for H_3 and Li_3, in the following: Maitre, P.; Hiberty, P. C.; Ohanessian, G.; Shaik, S. S. *J. Phys. Chem.* **1990**, *94*, 4089.

[35] The bonding energy for H_6 and the π-system of benzene are stabilizing upon bond shortening along the A_{1g} mode (even in the presence of the 1−3 triplet repulsions).

[36] Haas, Y.; Zilberg, S. *J. Am. Chem. Soc.* **1995**, *117*, 5387.