The delocalization of π electronic systems as a destabilizing constraint imposed by the σ frame. Allyl, benzene, cyclobutadiene and related heteroannulenes

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Abstract

A valence bond model of electronic delocalization, including aggregates of monovalent atoms as well as reaction transition states or π systems, predicts that the π bonding energies of benzene or allyl radical are weaker in the regular geometry than they are in a distorted geometry typical of a Kekuké structure. This prediction is verified by accurate ab initio calculations applied to allyl radical, benzene, cyclobutadiene and isoelectronic heteroannulenes, in which the driving force responsible for the regular geometry is decomposed into its σ and π components. It is found that the π systems of these conjugated molecules are indeed unstable in the regular geometry, and stabilized by a kekuléan distortion leading to alternate long and short bonds. On the other hand, the σ frame always favor equal bond lengths.Thus, the regular geometry of benzene or allyl is the by-product of two opposing driving forces: a distortive π system and a symmetrizing σ frame. This latter driving force is the strongest of the two, and forces π electronic delocalization. It is shown, through appropriate thermodynamic cycle, that this finding is not contradictory with the known empirical resonance energy of allyl, benzene and other aromatic molecules

INTRODUCTION

The special stability and the regular geometry of aromatic hydrocarbons are generally well accounted for by Hückel theory. This simple model, applied to π electrons, and featuring nearest neighbours interactions with a unique parameter β whatever their atomic distances, predicts that the π-electronic system of benzene gains some stability because delocalization is favored by a regular geometry, relative to the set of three localized π bonds that characterize a Kekulé structure. The same rationalization is extended to other aromatic hydrocarbons, or to allyl radical or ions, and the so-calculated π-electron resonance energies are often associated, if not identified, with the empirical special stabilities of these compounds relative to linear polyenes displaying alternated geometries. This looks fine, but some problems are encountered when one tries to extend this simple concept to isoelectronic, non-hydrocarbon, systems. For example, H_3 and H_6, isoelectronic to the π systems of allyl radical and benzene, are unstable (ref. 1). Li_3, on the other hand, is stable (ref. 2), as is Li_4 (ref. 3), however

isoelectronic to the antiaromatic cyclobutadiene. The transition states of S_N2 reactions are generally unstable, yet being of the 4-electron, 3-center type, just like allyl anion's π-electronic system. Worse, the isoelectronic analogy fails to explain why cyclic N_6, although isoelectronic to benzene, is unknown.

Things become even worse when one tries to improve the Hückel model by varying the ß parameter as a function of the interatomic distances. If, for example, one distorts a benzene ring from the D_{6h} geometry to a D_{3h} one, it seems natural to ascribe a resonance integral of the type ß(1+∂) to the short bond, and ß(1-∂) to the long one. But, as has been shown by Salem and Longuet-Higgins (ref. 4a,b) and by Heilbronner (ref. 5), the so-calculated Hückel total π energy is a decreasing function of ∂, so that the π-electronic system is *stabilized* by a Kekulean distortion from D_{6h} to D_{3h}. Thus, even at the Hückel level, the role of the aromatic π-electronic systems as a driving force leading to symmetric geometries is unclear.

A VALENCE BOND MODEL FOR ELECTRONIC DELOCALIZATION

It is clear that another theory, more general than the Hückel model, is needed to lift the above-noted paradoxes and to understand, in the general case, why electrons either tend to delocalize or, on the contrary, tend to form separate bonds. Shaik and Bar have proposed such a theory (ref. 6), based on the general model of curve-crossing valence bond diagrams. The model can be applied indifferently to conjugated molecules or X_n planar clusters (X= hydrogen, alkali, halogen, or any monovalent atom or group), and is aimed at predicting whether or not a delocalized electronic system is more stable than the corresponding set of local two-electron bonds. Consider an X_3 system as an example. In valence bond theory, this system can be described by the resonance between two Lewis structures (X-X X• <—> X• X-X), also called Kekulé structures if one is dealing with a conjugated molecule. In what follows we will use the generic term "Kekulé structures" for any case. In the symmetrical geometry with equal X-X bond lengths (middle of the diagram in Fig. 1), both Kekulé structures have the same energy. If one distorts this geometry by shortening one bond and lengthening the other (left-hand side or right-hand side of the diagram), one Kekulé structure is stabilized while the other one is destabilized (dotted curves in Fig. 1), so that an energy gap G separates the
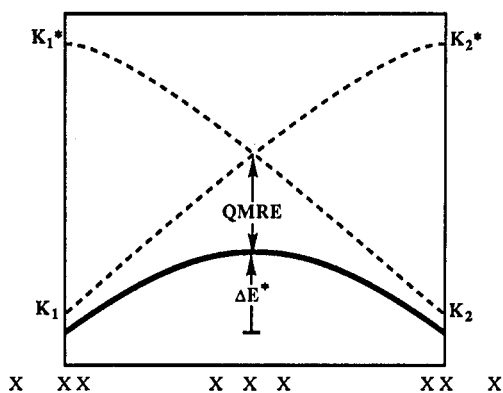

Fig. 1. A valence bond diagram for the deformation of an X_3 system, from one Kekuléan geometry to the other. The abcissa is the geometric deformation supersystem. The left-hand side corresponds to alternate long and short X-X bonds, the middle to equal bond lengths, and the right-hand side to short and long bonds.The energy of each Kekulé structure is plotted in dotted lines. The ground state energy is in dark full line.
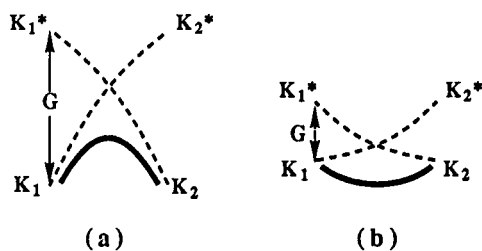
Fig. 2. Two limiting cases for the valence bond diagram displayed in Fig. 1.
(a) G is large. The X_3 system is most stable in a geometry of Kekulé type.
The symmetrical conformation is a transition state for the interchange of the two Kekulé structures K_1 and K_2.
(b) G is small. The symmetrical conformation is the most stable.

two Kekulé structures, e.g. K_1 and K_1^*, in the distorted geometry, and the diagram displays a crossing between the two Kekulé energy curves. Now the total energy of the electronic system (dark full curve) is the result of the interaction between the two Kekulé structures, leading to a stabilization that we call, following Coulson, "Quantum Mechanical Resonance Energy" (QMRE). This resonance is weak in the distorted geometries (both ends of the diagram), and much bigger in the symmetric geometry (middle of the diagram). Thus the symmetric geometry may or may not be preferred over the distorted one, depending on two opposing factors: (i) a single Kekulé structure would be most stable in a distorted geometry (its energy at the symmetric geometry is that of the crossing point); (ii) the QMRE stabilizes the symmetrical geometry relative to the localized ones. Two possibilities can then occur: If the crossing point is high, the QMRE may not be large enough to make the symmetrical geometry stable (part (a) of Fig. 2), and the delocalized electronic system is a transition state in the interconversion of the two Kekulé structures. If on the contrary the crossing point is low, then the QMRE has a chance to make the delocalized geometry stable (part (b) of Fig. 2). In a qualitative model, it is intuitively reasonable to correlate the height of the crossing point with the gap G between K_1 and K_1^*, and it has been shown that this gap is proportional to the singlet-triplet energy gap of the X-X two-electron system, or nearly equivalently to the strength of the X-X bond. Thus, weak binders like alkali metals should form stable trimers while strong binders should not, X_3 being then a transition state in the interconversion $X_2 + X \rightarrow X + X_2$. The reasoning can obviously be extended to 6-membered rings.

Shaik and Bar's theory has been shown to be quite successful for the series X = alkali metals, halogens, Cu, H (ref. 7,8). Thus, Li_3, Na_3 and K_3 are stable, while H, a strong binder, has an unstable H_3 transition state, and Br_3 and Cl_3 are in-between. Now the π C-C bonds, in the framework of this model, fall in the range of rather strong bonds, leading to unstable delocalized electronic systems! Note that this prediction does not automatically contradict the known regular geometry of benzene, since the σ bonds, as a harmonic model potential shows, tend to favor equal C-C bond lengths. Thus, Shaik and Bar's model predicts that the resistance of benzene towards a Kekulean distortion is the result of two opposing driving forces, one coming from the π bonds, tending to distort the molecule, and a stronger one coming from the σ framework, which imposes a D_{6h} geometry and forces the π electron to delocalize. If this is true, then the π systems find their natural place in a general model for delocalization which also includes clusters of heteroatoms, and can be used for predicting properties of conjugated molecules containing heteroatoms. If not, then one has to assume that the valence bond model, though successful for the interactions between monovalent atoms, breaks down when π bonds are considered. Thus, the VB model adresses a fundamental question regarding all aromatic compounds: What is the nature of the driving force that makes benzene more stable in a D_{6h} geometry than in an alternated D_{3h} geometry of Kekulé type, and does the π-electronic system act in favor or against this tendency? The aim of the present work is to provide an answer to this question, based on quantitative ab initio calculations. The same type of question may be invoked to understand the regular geometry of allyl radical or the rectangular geometry of cyclobutadiene, or more generally their isoelectronic analogs of the first and second rows of the periodic tables. All these compounds will also be investigated here.

A SIMPLE COMPUTATIONAL EXPERIMENT

Any standard ab initio computational method is able to reproduce the resistance to distortion of benzene or allyl radical, even at a low level of theory. Thus, if one distorts benzene as in Fig. 3, by alternately compressing one bond by 0.06 Å and stretching the adjacent bond by nearly the same quantity (the exact distortion mode used will be

specified and vindicated below), the total energy of benzene goes up by 6.6 kcal/mol (6-31G/SCF) and 7.2 kcal/mol (6-31G + full π-CI) (ref. 7). Similarly, the distortion energy of allyl radical is in the range 3.8-4.4 kcal/mol, depending on the computational level (ref. 7). These values correspond to total energies, in which both σ and π components are included. Now there is a very simple way to compute the σ component alone, by computing the distortion energy of a state in which the σ bonds still experience the field of the π electrons, the latter being nearly indifferent to a localizing distortion. In the case of allyl radical, such a state exists, it is the quartet state in which the σ frame is left unchanged relative to the ground state but the π electrons all have parallel spins.[a] Even without accurate calculations, one can roughly estimate the effect of a localizing distortion on the π electrons of this excited state, by analogy with a hydrogen chain having the same multiplicity and the same bond lengths as allyl's C-C bonds. Thus, the energy of the quartet H_3 rises, upon distortion, by only 0.48 kcal/mol (ref. 9) at the level of 6-311G + full CI, and this value constitutes a higher limit for the π interactions of quartet allyl, since two hydrogenoid atomic orbitals overlap more than two parallel p atomic orbitals of carbon at the same interatomic distance. It follows that the high spin state of allyl can be used as a probe for estimating the σ component to the distortion energy of the ground state, as it represents a species in which the π driving force has been nearly eliminated.
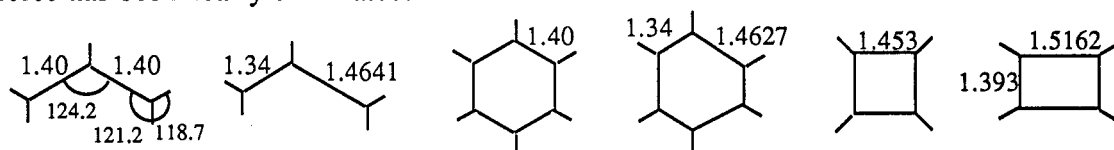

Fig. 3. Symmetric and distorted geometries of allyl radical, benzene, and singlet cyclobutadiene. The distortion keeps constant nuclear repulsions between carbons. Bond angles are the same for the distorted and symmetric structures.

The distortion energies of the quartet state of allyl are reported in Table 1 side by side with those of allyl's ground state. These energies (referred to as ΔE^{tot}) are calculated at various levels, the highest of which using a triple-zeta basis set and electron correlation in the ($\sigma + \pi$) space. It first appears that the distortion energy of the high spin state is rather insensitive to electron correlation; but the striking result is that, at all levels, the quartet allyl resists *more* the distortion than the ground state, by some 0.6-1.0 kcal/mol. Even assuming that the π electrons with parallel spins resist the distortion by 0.5 kcal/mol like the analogous hydrogen chain, which would certainly be an overestimation, it remains that the σ component of the distortion energy ranges from 4.4 to 4.5 kcal/mol, and is slightly larger than the total ($\sigma + \pi$) distortion energy of allyl's ground state. The same computational experiment can be made with the analogous heptet state of benzene, whose distortion energy is about three times that of quartet allyl, and is now much larger than the ground state's resistance to distortion (see Table 1). These computational results support the predictions that have been ventured above; the geometries of allyl and benzene are governed by two opposing driving forces: the σ bonds which favor a regular geometry, and the π bonds which act in an opposite way by favoring an alternated Kekuléan geometry. The latter driving force is rather weak in the case of allyl, and stronger in benzene, but in both cases it is outweighed by the σ driving force and a symmetrical geometry results, not because but in spite of the π electrons.

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[a] In the high spin state where all π electrons have the same spin, delocalization is switched off. The π system can be described as a superposition of local triplets on each C-C bond. Bond compression (stretch) leads to an energy rise (lowering). In the range of distortions considered here (approximately +- 0.06 Å) the energy variation of the two-electron triplet is nearly linear. Thus a sum of bond compressions and elongations leaves the total π energy nearly unchanged in the high spin state.

TABLE 1. Distortion energies (kcal/mol) of allyl radical, benzene, and cyclobutadiene, and their π and σ components separated by means of eq. (1). A negative value means a distortive species.

I. High spin states, all π e⁻ having parallel spins.

Species, Method	ΔE^{tot}	ΔE^{π}	ΔE^{σ}
Allyl, 6-31G/SCF	4.9	0.1	4.8
Allyl, 6-311G/SCF	4.8	0.1	4.7
Allyl, 6-311G/π-CI	4.8	0.1	4.7
Allyl, 6-311G/(π+σ)-CI	5.0		
Benzene, 6-31G/SCF	14.5	0.8	13.7
C_4H_4, 6-31G/π-CI	7.7	0.1	7.6

II. Ground states.

Species, Method	ΔE^{tot}	ΔE^{π}	ΔE^{σ}
Allyl, 6-31G/π-CI	3.9	-0.9	4.8
Allyl, 6-311G/π-CI	3.8	-0.9	4.7
Allyl, 6-311G/(π+σ)-CI	4.4		
Benzene, 6-31G/SCF	6.6	-9.7	16.3
Benzene, 6-31G/π-CI	7.2	-9.1	16.3
C_4H_4, 6-31G/π-CI	-3.4	-10.4	7.0

The above computational experiment rests on two assumptions: (i) The interactions between π electrons in the high spin states are not more sensitive to the distortions than analogous interactions in hydrogen chains; (ii) the force constants of the σ bonds do not much depend on the way π electrons are coupled, and can be considered as similar in the ground states and in the high spin states. Both these assumptions will be accurately verified in the following section.

DIRECT SEPARATION OF σ AND π DRIVING FORCES

The total energy, E, of a conjugated molecule can always be decomposed as in Eq. 1, which is routinely used in π electron calculations (ref. 10):

$$E = \sum_{\pi} h_{\pi} + R_{\pi\sigma} + R_{\pi\pi} + \sum_{\sigma} h_{\sigma} + R_{\sigma\sigma} + V_{NN} \qquad (1)$$

Here, h_{σ} and h_{π} are the corresponding one-electron integrals of the occupied π- and σ-spinorbitals. The R terms stand for electron-electron repulsion of a type that is specified by the subscript, and V_{NN} accounts for nuclear repulsion. The π electronic energy is defined as the energy of π electrons in the field of a σ frame constituted of the nuclei and the σ electrons. It involves the first two terms of Eq. (1) (attraction between π electrons and nuclei, and repulsion between π and σ electrons), and $R_{\pi\pi}$ (repulsion between π electrons).[b] But the π electronic energy alone does not reflect the energy of a π bond, which is constituted of the interaction between two parallel p orbitals borne by two effective positive charges repelling each other, and includes part of the V_{NN} term. To circumvent this difficulty, we have chosen to define the distortion mode so as to keep exactly constant the nuclear repulsion between carbon atoms (see Fig. 3). In this manner, the repulsion between positive centers is annihilated in the π component ΔE^{π} of the resistance to distortion, which can now be defined without ambiguity as the variation of the π *electronic* energy throughout the distortion. The σ component, ΔE^{σ}, of the total distortion energy ΔE_{tot} is defined by Eq. (2):

$$\Delta E_{tot} = \Delta E^{\sigma} + \Delta E^{\pi} \qquad (2)$$

So defined, ΔE^{σ} is the distortion energy of a bare σ frame devoid of π electrons, whose σ orbitals would have been optimized in the field of the π electrons. The distortion mode of interest is the b_{2u} mode, leading to alternated geometries. We have fixed the short bonds at 1.34 Å to make it close to ethylene, and the long ones have been obtained such that the nuclear repulsion between carbons be the same as in the hexagon, as explained above.

b   There are several ways of partitioning the total energy into σ and π components, since $R_{\pi\sigma}$ can be entirely included in $E\pi$ as we have done here, or partitioned into σ and π in various ways. The qualitative conclusions remain unchanged (see ref. 11 for details).

HIGH SPIN STATES

Let us first use Eq. (1) to estimate the resistance to distortion, ΔE^π arising from π interactions in the high spin states. The results are displayed in Table 1, and show a remarkable constancy at the three levels of computation used in the case of allyl. Note that when CI is performed in the π space, the π component ΔE^π of the distortion energy is not any more given by the three first terms in Eq. (1), but one can still compute it as the difference between the total distortion energy and its σ component, calculated from the last three terms of Eq. (1). It turns out that ΔE^π in the quartet allyl is effectively smaller than our higher limit of 0.5 kcal/mol, and does not appear to be sensitive to CI or basis set extension. Similar results are also observed in benzene and cyclobutadiene, in which the π systems of the high spin states also prove to be rather insensitive to the distortion.

GROUND STATES

The $\sigma-\pi$ partition in the ground states will be used for two aims: (i) to verify that ΔE^σ is roughly constant from high spin states to ground states, and (ii) to directly compute ΔE^π in the ground states whenever possible.

As postulated, the values of ΔE^σ, in the case of allyl, are the same in the high spin states and in the ground states: 4.7-4.8 kcal/mol. Projecting allyl's value of 2.4 kcal/mol per σ bond to the benzene σ frame, which involves six σ bonds, one would predict the value 14.1-14.4 kcal/mol for ΔE^σ which is calculated to be 13.7 kcal/mol in the heptet state, vs. 16.3 in the ground state and 14.1 in the $(C_6H_6)^{6+}$ cation, at the 6-31G/SCF level. Here the dependence of ΔE^σ on the status of π electrons is not nil, yet it remains too small to alter our previous finding of an unstable π system, all the more as ΔE^σ is larger in the ground state than it is in the high spin state, indicating that the π system is even more distortive, in benzene, than previously predicted.

In the case of cyclobutadiene, there is a good constancy of ΔE^σ. On the other hand, the value of ΔE^σ per bond cannot be compared with those of allyl and benzene, because the equilibrium bond lengths, in our calculations, are 1.40 Å in the latter vs. 1.453 Å in square cyclobutadiene.

The values of ΔE^π, as directly computed in the ground states via the $\sigma-\pi$ partition of Eq. (1), confirm the previous conclusions drawn from the high spin states: A localizing distortion leading to an alternated geometry of Kekulé type stabilizes the π bonds of benzene by 9.1-9.7 kcal/mol, and those of allyl radical by 0.9 kcal/mol.

An important point to note is that the π system of cyclobutadiene is the most distortive of the three, especially on a per-electron basis. This reflects the well-accepted idea that four-center resonance is less stabilizing than the six-center one, a point that will be developed in detail below.

EFFECT OF σ-ELECTRON CORRELATION

Do the above results depend on the computational level? To answer this question we computed the distortion energy of both the quartet and ground states of allyl radical at the level of triple-zeta basis set and correlation of π and σ electrons, by the CIPSI algorithm (ref. 12), more than $6*10^6$ Slater determinants being included in the multireference MP2 treatment. At this level, the $\sigma-\pi$ partition cannot be performed (since there are σ to π and π to σ excitations), but one may observe that the resistance to distortion is still larger in the quartet than in the ground state, 5.0 vs. 4.4 kcal/mol.

Assuming the value 0.1 kcal/mol for ΔE^π in the quartet state, one deduces the value 4.9 kcal/mol for ΔE^σ. If one now neglects the dependency of ΔE^σ on the type of coupling between the π electrons, one gets the value -0.5 kcal/mol for ΔE^π. If, on the other hand, one assumes that ΔE^σ increases from the high spin state to the ground state as it does in benzene, one may estimate ΔE^σ to be 5.8 kcal/mol, and thus ΔE^π to be -1.4 kcal/mol. Therefore, the high computational level confirms the previous conclusions of the respective roles of σ and π driving forces in allyl.

DISTORTIVE π-PROPENSITY AND RESONANCE ENERGY

The above computational results show that the π systems of benzene, allyl and cyclobutadiene are stabilized in an alternated geometry of Kekulé type, with respect to fully delocalized systems in symmetrical geometry. This finding may seem to be contradictory with the well-established stability of benzene with respect to linear polyenes, or with the known rotational barrier around the C-C bonds in allyl. What then is the role of π-electron delocalization in the stability of benzene and allyl and in the relative instability of cyclobutadiene? To answer this question, one must investigate in detail the phenomenon of resonance and, first of all, clarify the distinction between three concepts:

(i) The distortive propensity of π-electronic systems.

(ii) The stabilization resulting from the mixing of several Kekulé structures, *at a given geometry*. Following Coulson (ref. 13), we will call this quantity "Quantum Mechanical Resonance Energy" (QMRE).

(iii) The modern definition (ref. 14,15) of the resonance energy, aiming at reproducing the experimental stability of cyclic polyenes with respect to linear ones. Hereafter, we will call this quantity "Thermochemical Resonance Energy" (TRE).

QUANTUM MECHANICAL RESONANCE ENERGY

Kollmar (ref. 16) has developed a procedure to estimate, at the SCF level, the energy of one Kekulé structure of a cyclic polyene. Thus, the QMRE is simply the difference between the latter energy and the energy of the molecule as calculated by the regular SCF method, which allows for electron delocalization.
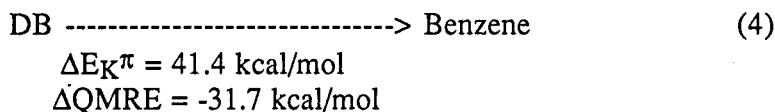
The QMRE's of a number of four- and six-membered cyclic polyenes, involving carbons as well as heteroatoms, are collected in Table 2. Several points are noteworthy:

(i) All QMRE's are positive and significant, even in the four-membered rings. This reflects the obvious fact that the mixing of two Kekulé structures, *at a given geometry*, is always stabilizing. Thus, although QMRE and TRE are occasionally confused with each other in the literature, these concepts are entirely different since the TRE can be negative as, e.g., in cyclobutadiene.

(ii) The QMRE of distorted benzene, i.e. benzene in a geometry of Kekulé type, is lower than that of hexagonal benzene, by 31.7 kcal/mol. Therefore, the QMRE is a driving force which *resists* the localizing distortion and tends to impose the symmetric geometry.

(iii) The QMRE's of four-membered rings are smaller than their six-membered analogues, even on a per-electron basis. This is the root of the Hückel rule, and is in agreement with the VB theory of aromaticity (ref. 17), showing that six-center interactions are more stabilizing than four-center ones.

Now how can these large QMRE's coexist with the distortive propensities of the π system? This becomes clear by considering in detail how a π system is affected by the geometric transformation of an alternated geometry to a regular one, and can be illustrated with the example of benzene. The π energy can be considered as the π energy E_K^π of a single Kekulé structure, lowered by the QMRE due to mixing with the other one, as in Eq. (3), where the variation of π energy upon distortion is decomposed.

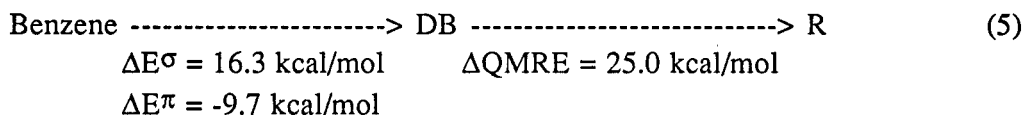$$\Delta E^\pi = \Delta E_K^\pi + \Delta QMRE \qquad (3)$$

Going from the Kekuléan geometry of the distorted benzene (DB) to the symmetric one inevitably raises the energy of the most stable Kekulé structure, by an amount $\Delta E_K^\pi = 41.4$ kcal/mol,[c] at the 6-31G/SCF level.

$$DB \text{ -----------------------------> Benzene} \qquad (4)$$
$$\Delta E_K^\pi = 41.4 \text{ kcal/mol}$$
$$\Delta QMRE = -31.7 \text{ kcal/mol}$$

This is only *partly* compensated for by a gain of 31.7 kcal/mol in QMRE. So the net result is that the π system is more stable in the alternated geometry, despite the stabilizing effect of electron delocalization.

THE ORIGIN OF THE THERMOCHEMICAL RESONANCE ENERGY

In modern definitions of the resonance energy (ref. 14,15) the linear polyenes are taken as the reference of resonance energy, as their π-energies are nearly additive. Their QMRE is assumed to be 9.5 kcal/mol per interaction between ethylenic units, i.e. 9.5 kcal/mol in butadiene, twice as much in hexatriene, and so on. Thus, the TRE of benzene is calculated by comparing its energy with that of a reference state R, a hypothetical cyclohexatriene with a QMRE of 28.5 kcal/mol. Such a reference state has a geometry very close to that of our distorted benzene, but its QMRE is smaller, by 25.0 kcal/mol (see Table 2). Thus, we can decompose the TRE of benzene by a thermodynamic cycle as in Eq. (5):

$$\text{Benzene -----------------------> DB ----------------------------> R} \qquad (5)$$
$$\Delta E^\sigma = 16.3 \text{ kcal/mol} \qquad \Delta QMRE = 25.0 \text{ kcal/mol}$$
$$\Delta E^\pi = -9.7 \text{ kcal/mol}$$

On going from benzene to DB, the σ frame is destabilized by 16.3 kcal/mol while the π system is stabilized by 9.7 kcal/mol. Now DB has still some significant QMRE and for this reason is more stable than R, by 25.0 kcal/mol. The final balance of Eq. 5 yields a TRE of 31.6 kcal/mol, in excellent agreement with other estimates by Hess and Schaad (ref. 15c). Thus, the thermodynamic cycle (5) shows that a sizeable TRE can coexist with the distortive tendency of the π bonds, and a similar reasoning (ref. 7) shows that the slightly distortive π system of allyl can coexist with the rotational barrier around the C-C bonds.

Often confused with each other, the TRE and QMRE are two distincts, though not independent, concepts. Their relationship can be quantified by combining eqs. 4 and 5.

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[c] This value is simply estimated by applying eq. 3.

On going from the reference structure (R) to the hexagonal geometry of benzene, two opposing effects take place:

(i) The total $(\sigma + \pi)$ energy of the lowest Kekulé structure raises, by 25.1 kcal/mol (41.4 - 16.3).

(ii) The stabilization due to QMRE increases, by 56.7 kcal/mol (31.7 + 25.0).

In other annulenes, including four-membered rings, a similar competition between these two opposing factors also takes place, and the balance between them either leads to aromaticity (positive TRE) or to antiaromaticity (negative TRE), according to which of the two factors wins. Thus, in benzene the QMRE gain overcomes the Kekulé destabilization, leading to a TRE of 31.6 kcal/mol, while an inverse balance is observed in cyclobutadiene. It follows that the QMRE is the root cause for the TRE, the empirical "resonance energy", in the sense that aromaticity is associated with large QMRE, while antiaromaticity is due to the QMRE being too small to overcome the instability of a Kekulé structure in a regular geometry.

HETEROANNULENES

A surprising outcome of the Valence Bond model is that the balance between $\Delta E_K{}^\pi$ and $\Delta QMRE$ may favor either regular or distorted structure, for any electron count.

To test the occurrence of such unexpected cases, it is of interest to apply the σ-π partition to conjugated molecules other than hydrocarbons, e.g. containing nitrogen, silicon or phosphorus atoms. Only the planar structures are of interest to us here. Although they are not the lowest energy minima, they are reasonably low in energy and correspond to local minima. The total distortion energies, as well as their σ and π components are displayed in Table 2, as calculated at the 6-31G/π-CI level.

TABLE 2. Computed distortion energies with their π and σ components, QMRE values for a series of planar annulenes, and singlet-triplet gaps ΔE_{ST} of the corresponding 2e-2c π bonds. The ΔE^σ values arise from the direct σ-π separation of eq. (1) in the ground states of the annulenes. The total distortion energies ΔE^{tot} are all calculated at the 6-31G/π-CI level. For all species, the distortion keeps constant nuclear repulsion between the atoms of the ring. The geometries of the hetero-annulenes are described in ref. 18. All energies are in kcal/mol.

Species	ΔE^{tot}	ΔE^π	ΔE^σ	QMRE	QMRE per e⁻	ΔE_{ST}[a]
N_6	0.4	-13.3	13.7	102.5	17.1	108
C_6H_6	7.2	-9.1	16.3	85.2	14.2	99
DB[b]				53.5	8.9	
P_6	1.0	-2.8	3.8	44.1	7.4	47[c]
Si_6H_6	3.2	-2.1	5.3	41.6	6.9	42
N_4	-5.5	-14.7	9.2	44.6	11.2	108
C_4H_4	-3.4	-11.0	7.6	30.2	7.6	99
P_4	0.4	-2.6	2.9	24.8	6.2	47[c]
Si_4H_4	0.6	-2.1	2.7	17.7	4.4	42

[a]These are 3-21G values for model dimers (e.g. C_2H_4, N_2H_2, etc.).
[b]DB stands for Distorted Benzene
[c]This value is calculated with a 3-21G* basis set.

SIX-MEMBERED RINGS

The qualitative VB model predicts that the propensity of the π system to distort varies like the singlet-triplet gap ΔE_{ST} of the two-electron-two-center (2e-2c) π bond. This latter value increases from column 14 to column 15 of the periodic table, and decreases from first row to second row. In accord with the VB model, the calculated ΔE_{π} values follow the same tendency. Now the σ driving force also decreases from first to second row, and from column 15 to 16. As a consequence, the π distortivity of N_6 is larger than that of benzene while its σ driving force is weaker and opposes little resistance to distortion. The result is that hexagonal N_6 is rather indifferent to distortion (ref. 19), despite its isoelectronic analogy with benzene.

The same phenomenon can be observed in the second row, where now both σ and π driving forces are smaller than in the first row: the total resistance of Si_6H_6 to distortion is smaller than that of benzene, but larger than that of P_6.

FOUR-MEMBERED RINGS

Again the π-distortivities follow the variations of the ΔE_{ST} values of the 2e-2c π bonds. On the other hand, the σ driving forces of four-membered rings increase from column 15 to column 16, unlike six-membered rings. As a consequence, the tendency of N_4 to distort to a rectangular structure is not very much larger than that of cyclobutadiene. Both σ and π bonds are weaker in the second row than in the first, and this fact alone would lead to the prediction that Si_4H_4 and P_4 have a lesser tendency to distort than their first-row analogues. In addition, because of the rather long bonds, the overlap repulsions between the π bonds in the Kekulé structures of square Si_4H_4 and P_4 must not be very large. The striking result is that these two species are nearly indifferent to distortion, despite their expected antiaromatic character.

CONCLUSION

The alternated vs. regular geometry of six-membered, four-membered and linear polyenes is the result of a competition between two opposing driving forces: The σ bonds, which always tend to impose equal bond lengths, and the π bonds, which tend to impose an alternated geometry in all examples investigated here. The distortive propensity of the π systems is shown to vary like the strength of the corresponding 2e-2c π bond, or nearly equivalently like its singlet-triplet energy gap. This property is not contradictory with the known stability of, e.g., benzene, or the instability of cyclobutadiene (aromaticity vs. antiaromaticity) with respect to open chain polyenes, nor the rotational barrier around C-C bonds in allyl.

The electronic delocalization, *at a given geometry*, is always stabilizing (QMRE), and acts in favor of a regular geometry. In six-membered rings, the QMRE is not sufficient for preventing the π system to be distortive, but it weakens the π driving force enough to allow the σ to win, and a D_{6h} geometry results. Thus, the π system is forced by the σ frame to adopt a regular hexagonal geometry. As has been beautifully expressed by Heilbronner (ref. 5), *"The highly symmetrical structure of benzene, allyl and similar sytem 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. $k \approx 250\ Nm^{-1}$, then benzene and allyl would have localized Kekulé structures."*

In four-membered rings, the QMRE is rather weak as a consequence of the Hückel rule. It results that the π driving force wins over the σ and imposes an alternated geometry.

An additional driving force for distortion is the exchange repulsion energy between the two π bonds of a Kekulé structure and is rather important in C_4H_4 and N_4, but is expected to be weaker in their second row analogues, which are indifferent to distortion.

Thus, the π systems of hydrocarbons and their analogues appear to be similar in nature to aggregates of monovalent atoms like hydrogen, alkali metals, halogens, etc. and they find their place into a general model for delocalization based on valence bond diagrams. In this model, the key parameter is the singlet-triplet gap ΔE_{ST}, or nearly equivalently the strength of the bond, in the related dimer. The π systems of hydrocarbons fall in the range of fairly high ΔE_{ST} and strong bonds, and in that sense the analogy with hydrogen chains, already suggested by others (ref.1c), is entirely sound.

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