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REGULAR ARTICLE

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# Some answers to frequently asked questions about the distortive tendencies of $\pi$-electronic system

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**Abstract** The paper reviews briefly the various computational strategies, which have been devised by different groups to probe the symmetrizing vs distortive propensities of the $\pi$-bonding species of polyenes. All methods point to the same conclusion that the $\pi$-bonding components of benzene, allyl, aromatic annulenes and related species have intrinsic distortive tendencies; these species maintain bond-equalized geometries due to the symmetrizing driving force of the corresponding $\sigma$ frames. Some frequently asked questions, that deal with the compatibility of the $\pi$-distortivity scenario with the greater body of experimental data regarding aromatic stability and $\pi$-delocalization, are addressed. Many of these questions are immediately answered, once the notion is accepted that delocalized $\pi$-systems possess a duality: their $\pi$-component is distortive and at the same time resonance stabilized relative to the localized structure with the same geometry. The notion of distortive $\pi$-electronic components of polyenes is shown to find a natural place in the wider context of a unified model of electronic delocalization that is valid for both conjugated $\pi$- and $\sigma$-electronic systems.

## 1 Introduction

The idea that the $\pi$-system of benzene might be distortive dates back to the 1950s when Salem and Longuet-Higgins demonstrated that the Hückel energy of benzene, calculated with a distance-dependent $\beta$ parameter, *gets lower* when the ring is distorted along the $b_{2u}$ mode, that transforms the $D_{6h}$ regular geometry to a $D_{3h}$ geometry of a Kekulé type, with alternated bond lengths [1]. Two years after, Berry noted that the frequency of the $b_{2u}$ vibrational mode is surprisingly low compared to that of, for example, the breathing mode [2]. To explain this finding, Berry put forward the proposal that the $\pi$-system of benzene might possess an intrinsic distortive propensity. The analogy between $\pi$-electronic systems and the distortive chains or rings of hydrogens atoms was also known in the semi-empirical community [3].

Interestingly, these two works went generally unnoticed and gradually altogether forgotten, perhaps because of the qualitative or semi-empirical nature of the arguments or because the notion was expressed, but never really evolved into a model that enabled chemists to verify or refute this prediction. Thus, for lack of rigorous arguments in support of the distortivity of $\pi$ systems, it has long been assumed in chemistry that the regular geometry of benzene and analogous species (e.g. allyl radical and ions and so on) were imposed by the $\pi$-electronic component, which was considered to be more stable in a regular geometry than in a bond-alternated one. This widespread assumption, which, for convenience, we refer to as the "traditional view", was first challenged in 1984 by Shaik and Bar [4], using a general model of electronic delocalization based on valence bond state correlation diagrams (VBSCD), which showed: (1) how the $\pi$-components actually fitted within their respective isoelectronic series, and (2) why must they be unstable distortive entities. This work was followed by a series of studies, of the present two authors and their coworkers, which provided confirmatory evidence for $\pi$-distortivity, by separating the driving forces exerted by the $\pi$-bonds from those of the $\sigma$-bonds at the ab initio level [5]. In addition, the issue was addressed by quite a few other groups who used a variety of approaches leading to the same final conclusion [6–9]. Among them Karl Jug [10], the laureate of this volume, played a prominent role in devising an original method for separating $\sigma$- and $\pi$-energies within all-electron quantum chemical procedures. There were, of course, also opposing views [11], but after more than one decade of vivid debates and exchanges, it is fair to state that the idea that the $\pi$-components of benzene, allyl and other related species, are unstable electronic systems whose bond-equalized geometries are imposed by the $\sigma$ frame, is now

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accepted (or at least tolerated) by chemists [12]. As will be shown below, this new point of view is neither disturbing nor paradoxical, but on the contrary, it removes all the paradoxes that afflict the traditional view. The new description of $\pi$-systems leads to a single coherent picture of electronic delocalization, that applies to conjugated $\pi$- and $\sigma$-systems, all the way from benzene to reaction transition states.

Moreover, recent experimental spectroscopic results, on the excited states of benzene and other aromatic species [13], support the new picture, but cannot be accommodated by the traditional view. In fact, the story might have been considered as a finished chapter, had it not been for the recurring doubt; how does the distortivity concept actually fit within the greater body of experimental data on these conjugated systems? These recurrent questions, raised either in personal conversations or in the literature, have prompted us to write this manuscript that aims to answer these concerns. We find it especially fitting to dedicate this paper to our colleague and friend Karl Jug, on the occasion of his 65th birthday.

The paper is organized as follows. The following section will briefly review the various aspects of the $\pi$-distortivity of benzene and related species. The most frequently asked questions will then be addressed and answered, in turn, in the subsequent sections.

## 2 The distortive tendencies of $\pi$-electronic systems

The question of $\pi$-distortivity can most clearly be expressed in terms of bonds and bonding energies. Thus, considering that benzene and related species are held together by bonds, classified as $\sigma$- and $\pi$-types, and that these molecules resist the distortion along the Kekulé mode, it is legitimate to inquire which of the two sub-systems of bonds is responsible for the bond-equalized geometries; is it the $\pi$-system of electrons, the $\sigma$-system or maybe both? In this sense, the energy cost, $\Delta E$, of distorting a conjugated molecule away from its equilibrium regular geometry (equal C–C bond lengths) can be written as a sum of the respective contributions arising from the $\sigma$-bonds and $\pi$-bonds, as written in Eq. 1:

$$\Delta E = \Delta E_\sigma + \Delta E_\pi \,. \tag{1}$$

From now on, we shall use the term "driving force" to address the energy components in Eq. 1.

### 2.1 What is wrong with the traditional view? Isoelectronic paradoxes

According to the traditional view $\Delta E_\pi$ is positive in Eq. 1, that is, the $\pi$-system of bonds is more stable in a symmetrical geometry than in an alternated one, and hence the regular geometry is driven by the $\pi$-electrons. This point of view originated from an intuitive interpretation of Hückel theory of conjugated molecules, which entirely neglects the $\sigma$-bonding system. Hückel theory (with a single universal $\beta$parameter) finds $D_{6h}$ benzene to be more stable, by a quantity $2\beta$, compared with its $D_{3h}$ distorted structure; the latter is assumed to have the same energy as three separate ethylenic units (and hence, $\Delta E_\pi = -2\beta > 0$, in Eq. 1). It therefore seems natural to conclude that the $\pi$-bonds of benzene have an inherent tendency to prefer geometries that favor delocalization, and thereby constitute the driving force that restores the geometry of benzene, from a $D_{3h}$ Kekulean geometry to a regular $D_{6h}$ hexagon. Whereas this view may seem apparently convincing, it is wrong even at the level of Hückel theory [1,4,6], and it further leads to a number of disturbing paradoxes which have been largely overlooked in the chemical community.

As already noted, the first of these paradoxes originates from Hückel theory itself, since a logical improvement of the method, by introducing a distance-dependent $\beta$ parameter, suffices to reverse the sign of $\Delta E_\pi$ from positive to negative [1,4,6]. A more fundamental paradox concerns the seemingly disparate behaviors of conjugated systems of conjugated $\sigma$- and $\pi$-varieties, which according to the traditional view would seem to display completely different responses to the localization/delocalization alternatives. Some isoelectronic analogies between $\pi$-electronic components and hydrogen atom aggregates or organic transition states are displayed in Fig. 1. The $\pi$-electronic system of benzene is isoelectronic with the corresponding electronic structure of a ring of six hydrogen atoms arranged in a hexagon, and as such, both species will possess a six-orbital-six-electron array. Indeed, computations show that benzene and the $H_6$ ring share some important properties that are associated with aromaticity: comparable values of exalted diamagnetic susceptibilities, $\Lambda$ [5e, f], quasi-identical diamagnetic ring currents induced by a magnetic field [14,15], etc. Nevertheless, while benzene is most stable in its regular hexagonal structure, the $\sigma$-conjugated hexagonal $H_6$ is an unstable species that distorts to three isolated dihydrogen molecules. What is the reason for that ?

Pursuing the analogy between $\pi$-systems and hydrogen chains, the $\pi$-component of allyl radical is isoelectronic with the linear $\sigma$-conjugated $H_3$ radical. $H_3$ is an unstable transition state en route of the hydrogen-exchange reaction (2), and lying some 10 kcal/mol over $H_2$ + $H^\bullet$ [16]. By contrast, allyl radical is stable at its regular $C_{2v}$ geometry. The same paradox juxtaposes the $C_{2v}$ stable allyl anion and the $\sigma$-conjugated linear $H_3^-$ species, the latter being an unstable delocalized species and a transition state during the exchange reaction (3). Why are the systems seemingly so different?

$$H_2 + H^\bullet \rightarrow [H\text{–}H\text{–}H]^\bullet \rightarrow H^\bullet + H_2 \tag{2}$$

$$H_2 + H^- \rightarrow [H\text{–}H\text{–}H]^- \rightarrow H^- + H_2 \,. \tag{3}$$

One might have argued that the above reactions, which involve clusters of hydrogens, are not chemically interesting, and that therefore the questions that these systems raise are merely academic. However, these isoelectronic paradoxes, generated by the traditional view, prevade the whole of chemistry. For example, as noted some time ago by Dewar [17], the $\pi$-electronic system of allyl anion is isoelectronic with the active system of the transition state for a general class of reactions, the $S_N2$ nucleophilic displacements (4):

$$X^- + CR_3Y \rightarrow [X\text{–}CR_3\text{–}Y]^- \rightarrow XCR_3 + Y^- \,. \tag{4}$$

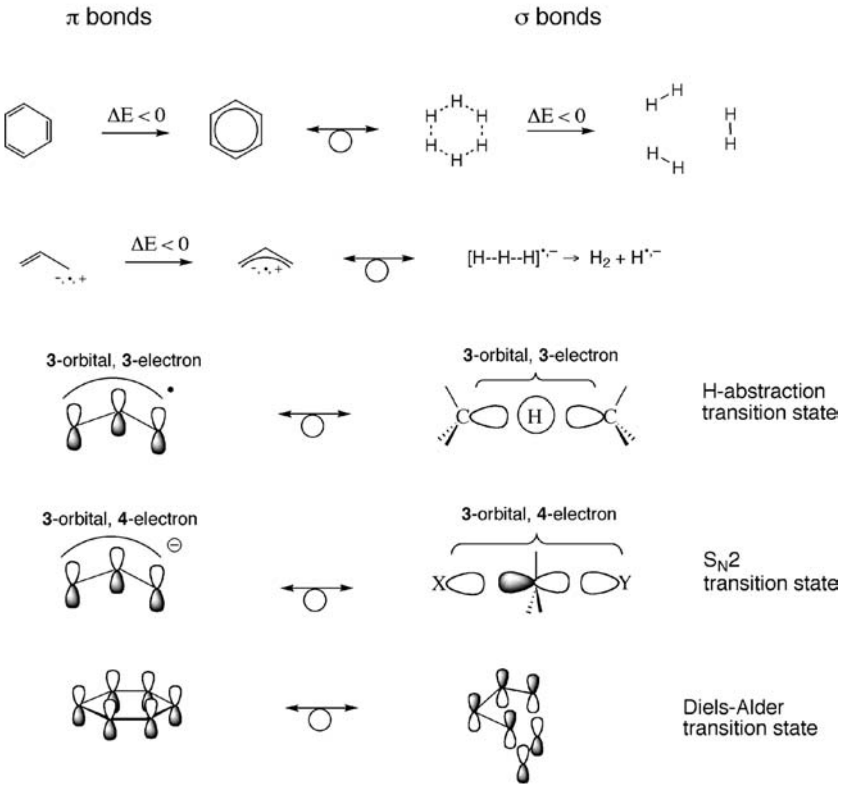


**Fig. 1** Some isoelectronic analogies between $\pi$-delocalized components of conjugated species and hydrogen clusters or organic transition states. Adapted from Ref. [32] with permission of the PCCP Owner Societies

Disregarding the C–R bonds, which do not participate in the reaction, the active moiety of the transition state in reaction (4) is no more than a 4-electron-3-orbital species (see Fig. 1) analogous to the $\pi$-component of allyl anion. Yet, $S_N2$ species are unstable transition states, whereas allyl anion is a stable $C_{2v}$ structure that favors a delocalized $\pi$-electronic component [18].

Turning to radical reactions, the transition state of the hydrogen-abstraction reaction-like reaction (5) has an active moiety composed of a 3-orbital 3-electron system:

$$CH_4 + {}^{\bullet}CH_3 \rightarrow [CH_3\text{–}H\text{–}CH_3]^{\bullet} \rightarrow\rightarrow CH_3^{\bullet} + CH_4 \,. \qquad (5)$$

It is in fact analogous to the $\pi$-system of allyl radical. Here too, the delocalized C–H–C species is an unstable transition state, whereas the isoelectronic allyl radical is delocalized and stable. In the same vein, the aromatic transition state of the Woodward–Hoffmann allowed Diels–Alder reaction (6) is unstable and higher lying (ca. > 20 kcal/mol) than its reactants. It requires no elaboration to see that the active bonds of this transition state are isolectronic to the $\pi$-electronic system of benzene (Fig. 1).

$$\text{butadiene} + \text{ethylene} \rightarrow [\text{transition state}] \rightarrow \text{cyclohexene} \,. \qquad (6)$$

In fact, the very existence of organic transition states is a nagging paradox hanging over the traditional view of $\pi$-delocalization in conjugated molecules. If indeed the $\pi$-electronic components had the inherent tendency to be stable in regular geometries, whereas at the same time the active moieties of organic transition states obey an opposite trend, then one would have been forced to conclude that $\pi$-bonds and $\sigma$-bonds follow fundamentally different bonding principles, a statement that can hardly be justified by any known principle of quantum mechanics.

## 2.2 A valence bond model for electron delocalization in isoelectronic species

In order to remove the above paradoxes and to obtain a coherent picture of electronic delocalization, it is necessary to use a general model that is equally valid for $\pi$-systems as well as hydrogen rings or organic transition states. Such a model exists and is based on VBSCD that have been used for some time to analyze the problem [4,5]. The VBSCD model has been discussed in details elsewhere [19] and will only be briefly described here, in a simplified form that is sufficient to deal with the problem at hand.

Valence bond state correlation diagrams apply to the general category of processes that can be described as the interplay of two major VB structures; one for the reactants and of the other, for the products. The subsequent VB mixing of the two structures generates the delocalized state, which in a case of a chemical reaction would be the corresponding tran-

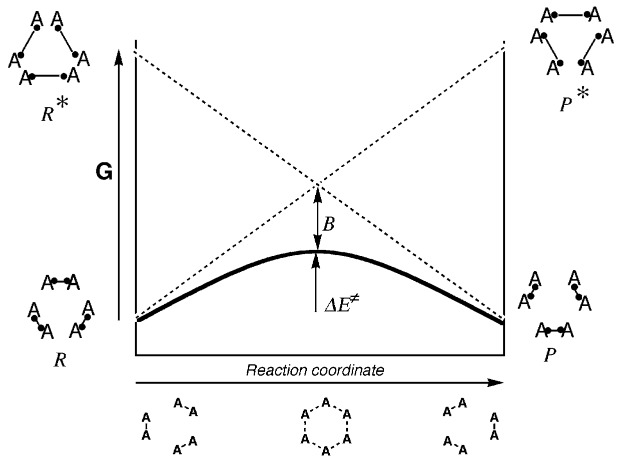
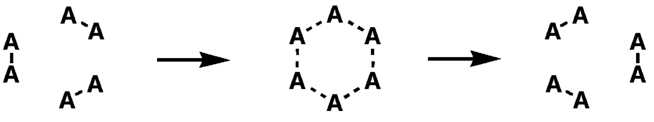


**Fig. 2** A model VBSCD for the reaction exchanging three $A_2$ diatomic molecules through a hexagonal transition state. The ground state is the bold curve. The thin dotted curves describe the diabatic states. The VB coupling of the diabatic curves, indicated by •—•, is conserved along the reaction coordinate. Adapted from Ref. [32] with permission of the PCCP Owner Societies

sition states. The model further projects the root causes of the barrier, and allows making qualitative and semi-quantitative predictions about barrier heights. Let us exemplify such diagrams with the general exchange reaction below where A is a monovalent atom (H, halogen, alkali, etc. . . ):



(7)

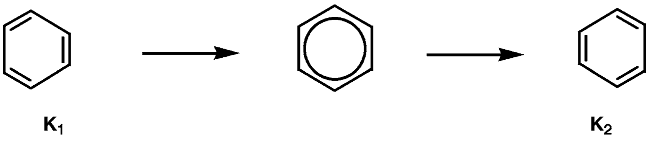
The diagram, depicted in Fig. 2 displays the ground state energy profile of the reacting system (bold curve), as well as the energy profiles of the VB structures (dotted lines) as a function of the reaction coordinate. Thus, starting from the reactant's geometry on the left, the VB structure that represents the reactant's electronic state, $R$, has the lowest energy and it merges with the ground state of the supersystem. Then, as one deforms the supersystem toward the products' geometry, $R$ gradually rises in energy and finally reaches an excited state $P^*$ that represents the VB structure of the reactants in the products' geometry. A similar diabatic curve can be traced from $P$, the VB structure of the products in their optimal geometry, to $R^*$, the same VB structure but now in the reactants' geometry. Consequently, the two curves cross in the middle of the diagram, which corresponds to a regular geometry with uniform A–A distances. The crossing is of course avoided in the adiabatic ground state, owing to the resonance energy $B$ that results from the mixing of the two VB structures. The barrier $\Delta E^{\neq}$ is thus interpreted as arising from avoided crossing between the two diabatic curves that represent the energy profiles of the VB structures of the reactants and products.

The barrier depends on the magnitude of the gap $G$, the curvature of the diabatic curves, and on the size of the resonance energy, $B$. However, in reaction-families of related reactions, it can be assumed that the explicite influence of the two latter parameters can be ignored because they are either quasi-constants or vary in proportion to $G$ [4,19,20]. As such, the crucial parameter that governs the energy barrier in reaction-families is the gap $G$. It has been demonstrated [5], and it appears by inspection of the excited states $R^*$ and $P^*$ which display stretched A–A bonds, that $G$ is proportional to the bonding energy of the dimer $A_2$:

$$G \propto D_e(\mathrm{A-A})\,. \tag{8}$$

Equation 8 draws a direct relationship between the strength of the A–A bond and the magnitude of the barrier in the exchange reaction (7), and hence, it defines the status of the delocalized state as a transition state or a stable cluster. This relationship is displayed in Fig. 3, and shows that the barrier is high for strong binders like hydrogen atoms ($D_e = 110$ kcal/mol), smaller for medium binders like halogens ($D_e = 58$ kcal/mol for A = Cl), and eventually becomes negative for weak binders like alkali ($D_e = 17$, 25 kcal/mol for A = Na and Li) [21]. It follows that while $Li_6$ and $Na_6$ hexagonal clusters are stable (even if not the most stable conformers) against dissociation toward three dimers, $A_6$ species composed of medium to strong binders are unstable. This is a general trend in the periodic table that only weak binders (generally metallic elements) form "sticky" delocalized clusters.

Let us now apply the VBSCD model to $\pi$-electronic systems. Consider $\pi$-bonds alone, in a hypothetical reaction that exchanges the two Kekule structures $K_1$ and $K_2$, as shown in Eq. 9:



(9)

The delocalized $D_{6h}$ structure of benzene can in principle behave either as a transtion state or as a stable cluster. However, since $\pi$ carbon–carbon bonds are fairly strong, with a bonding energy estimated to be in the range 65–71 kcal/mol [22–24], the VBSCD model predicts that the $\pi$-electronic system would be more stable in the bond alternated localized situations in Eq. 9. The $\pi$-component of benzene should then be viewed as an unstable transition state that is forced by the $\sigma$ frame to remain in a $D_{6h}$ geometry with equalized C–C bonds. The VBSCD model can be applied to allyl radical and ions as well and lead to similar conclusions, which unify the responses of conjugated $\sigma$- and $\pi$-electronic systems to the localization vis-à-vis delocalization alternatives. Clearly, as has been already concluded by Burdett in his beautiful book, "Chemical Bonds: a Dialogue" [25], the VBSCD is a general model that unifies stable clusters and pseudo Jahn–Teller unstable ones, including $\pi$-electronic components.

It remains now to demonstrate that these qualitative conclusions are confirmed by means of accurate ab initio calculations.

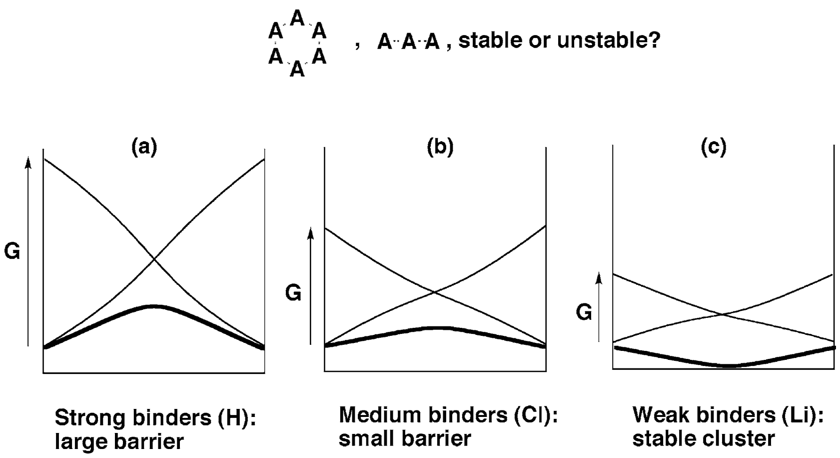


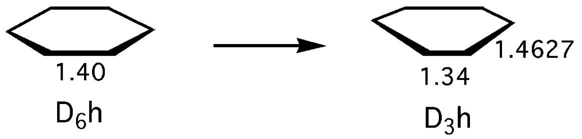
**Fig. 3** Schematic VBSCD for the reaction $3A_2 \rightarrow A_6 \rightarrow 3A_2$. This diagram is a prototype for other problems of the same nature (e.g. $A_3^-$, $A_3^\bullet$, $A_4$, etc). Adapted from Ref. [32] with permission of the PCCP owner societies

## 2.3 Some ab initio tests of the distortivity of π-systems

Returning to Eq. 1, it is of course easy to calculate the total distortion energy $\Delta E$ for a $b_{2u}$ type distortion. The problem, however, is the division of this energy into σ- and π-components, $\Delta E_\sigma$ and $\Delta E_\pi$. This problem has been solved long ago in semi-empirical π-electron methods (e.g. PPP), where the π-system was defined as a set of π electrons moving in the field of a σ skeleton bearing effective positive charges on carbon [26]. In this representation, the π-system is analogous and isoelectronic to a corresponding species of hydrogen atoms, wherein the electrons move in the field of a real set of nuclei, each bearing unit positive charge. In the mid-1980s, we decided [5a] to extend this separation to all-electron ab initio methods, by defining the *electronic* energy of the π-system as the three first terms of Eq. 10:

$$E = \sum_{\pi}^{\mathrm{occ}} h_\pi + R_{\pi\sigma} + R_{\pi\pi} + \sum_{\sigma}^{\mathrm{occ}} h_\sigma + R_{\sigma\sigma} + V_{NN}\,. \qquad (10)$$

Here $E$ is the total energy of the molecule, $h_\pi$ and $h_\sigma$ are the corresponding monoelectronic integrals of the occupied π- and σ-spinorbitals. The $R$ terms stand for electron–electron repulsion of a type specified by the subscript, while $V_{\mathrm{NN}}$ accounts for nuclear repulsion. Equation 10 is valid at the Hartree–Fock level, but can be extended to higher levels provided the σ electrons are left uncorrelated. In such a case, the expression of the energy of the σ frame remains simple and involves the last three terms of Eq. 10. Substracting this quantity from $E$ gives the π-electronic energy. Of course, electronic energies as such are of limited utility, and we are more interested in *bonding* energies. This is why we applied a distortion of a particular type that is defined in Eqs. 11 and 12 for benzene and allyl, respectively:



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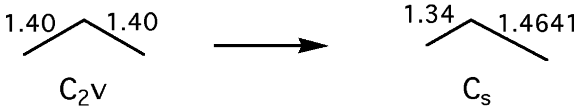


(12)

The distortion in Eq. 11 is seen to be extremely close to a $b_{2u}$ distortion, and the residual deviation (in the third and fourth digits) serves to keep constant nuclear–nuclear repulsion between carbons. Thus, the so-defined $b_{2u}$-almost distortion rids us of the thorny issue of the variation of electrostatic repulsion between the formal positive charges on the carbon atoms that constitute the framework over which the π-electrons are moving. The advantage of this special distortion is that the variations of π-electronic energy, in Eq. 10, is now identical to the change in the π-bonding energies. This identity solves the question of how to separate σ- from π-bonding energies at least for the problem at hand. The same reasoning applies to the $b_2$-almost distortion of allylic species in Eq. 12.

The total distortion energies $\Delta E$ for benzene and allyl radical, were calculated at the π-CI/6-31G level [5c], and the $\Delta E_\sigma$ values were quantified by means of Eq. 10. The results are displayed in Table 1 (entries 1 and 4). It is seen that $\Delta E_\sigma$ is significantly *larger* than the total distortion energy $\Delta E$, as such leading to the conclusion that benzene, as a whole, has a weaker resistance to distortion than its σ frame alone. Similarly, the bare σ frame of allyl resists distortion more than the full allyl radical species. Using these $\Delta E_\sigma$ quantities in Eq. 1 leads to negative $\Delta E_\pi$ values (−9.1 kcal/mol for benzene and −0.9 kcal/mol for allyl radical), which mean that the π-components of benzene and allyl are distortive species.

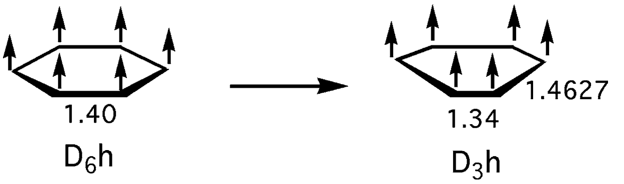
Another, more intuitive, computational experiment consists of estimating $\Delta E_\sigma$ as the distortion energy of benzene in a particular state in which the π-electronic system is practically indifferent to a $b_{2u}$ distortion. Such a state exists; it is the sextuplet spin-state of benzene (or quadruplet spin-state in the case of allyl radical), in which all π-electrons have parallel spins. Since one may worry whether the π-electrons with the parallel spins, of this sextuplet state, may or may not play a role in the final conclusion, one can test the dis-

**Table 1** Distortion energies for the ground states, high-spin states and bare $\sigma$ frames of benzene and allyl radical

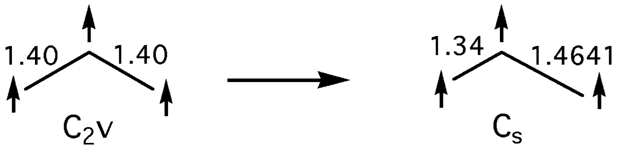
| | $\Delta E$ | $\Delta E_\sigma$ | $\Delta E_\pi$ |
|---|---|---|---|
| Benzene | | | |
| Ground state[a] | 7.2 | 16.3 | −9.1 |
| High-spin state[b] | 14.5 | 13.7 | 0.8 |
| Bare $\sigma$ frame[b] | | 14.5 | |
| Allyl radical | | | |
| Ground state[a] | 3.9 | 4.8 | −0.9 |
| High-spin state[b] | 4.9 | 4.8 | 0.1 |
| Bare $\sigma$ frame[b] | | 4.8 | |

[a] $\pi$-CI/6-31G level
[b] SCF/6-31G level

tortive propensity of this state by calculating $\Delta E_\pi$ through Eq. 10. The result in Table 1, entry 2, shows clearly that the spin-parallel $\pi$-electrons are indifferent to the distortion. An additional verification is obtained by calculating the distortion energy of the analogous ${}^6H_6$ state; the results show again that the high-spin species is indifferent to the distortion [27]. The same is true for the corresponding quartet state of allyl radical (see entry 5 in Table 1). Thus, whichever way we calculate these $\pi$-distortion energies for the high-spin states, the values are found to be negligible. Therefore, in such high-spin states, the $\Delta E_\pi$ contribution to the overall distortion energy is close to zero, so that the distortion energies calculated for reactions (13) and (14) should give us a reliable measure of $\Delta E_\sigma$.



(13)



(14)

The computational results, displayed in Table 1, show that benzene (entry 2) and allyl (entry 5) resist a Kekulean distortion more strongly in their high-spin states, which are devoid of $\pi$-bonds, than in their ground states where $\pi$-bonding is present and causes delocalization. Applying the so-obtained $\Delta E_\sigma$ values to the total distortion energy expression in Eq. 10 leads once again to negative value for the $\Delta E_\pi$ quantities of the ground state, in good agreement with the preceding set of calculated data. A further confirmation of the soundness of the $\Delta E_\sigma$ values, obtained from the above procedures, is provided by the direct calculation of these quantities as the distortion energies of the naked $\sigma$ frames of benzene and allyl, that is, the distortion energies of $(C_6H_6)^{6+}$ and $C_3H_3)^{3+}$, both cations being devoid of $\pi$ electrons. The data in Table 1 (entries 3 and 6) show notable consistency with the other values and lead thereby to the same conclusion regarding the distortive propensity of the $\pi$-electronic component.

To summarize, benzene and allyl radical resist a localizing distortion more when the $\pi$ electrons are absent as in the cationic states, or uncoupled as in the high-spin states. In agreement with this finding, the $\pi$-component of the ground state, as calculated through an integral partitioning (Eq. 10) is found to favor the distortion, unlike the $\sigma$ frame that strongly favors the $D_{6h}$ and $C_{2v}$ structures. Clearly therefore, these simple computational experiments verify the qualitative conclusion that the $\pi$-components of benzene and allyl radical have distortive tendencies, and that the bond-equalized geometries are imposed by the $\sigma$ frame. Qualitatively speaking, *the $\pi$-components of benzene and allyl behave exactly like rings or chains of hydrogen atoms*, namely as transition states with a distortive propensity.

## 3 Can a $\sigma - \pi$ partition be valid?

This question has been fervently debated. The definition of $\pi$-electronic energy that is displayed in Eq. 10 is chemically appealing, as it rests on the comparison between a set of $\pi$-electrons moving in the field of a $\sigma$ skeleton bearing effective positive charges, and a set of electrons moving over some protons to form a chain or a ring of hydrogen atoms. Actually, it is a fact that this definition yields $\pi$-electronic energies that are of the same orders of magnitude as electronic energies of H rings, which is what one would expect from electrons moving in the field of carbon moieties with a unit of positive charge. Yet, Eq. 10 is not fully satisfactory from the mathematical or aesthetical points of view. The problem originates from the $R_{\sigma\pi}$ integrals, which represent the mutual repulsions between the electrons of the $\sigma$ frame and those of the $\pi$-electronic system. In Eq. 10, those integrals are entirely ascribed to the $\pi$-electronic energy, which may appear arbitrary even though it is fully justified from the model point of view. The philosophy of this definition is that the $\sigma$ electrons are considered as being part of the $\sigma$ frame over which the $\pi$ electrons are moving. As such, the repulsive effect of these $\sigma$-electrons is nothing more than a simple screening effect between the actual $C^{6+}$ nuclei and the $\pi$ electrons. Nevertheless, it is true that this partition lacks a formal physically required equivalence of the $\sigma$- and $\pi$-components.

In order to circumvent the problem, Jug [10a] proposed a more aesthetic $\sigma$-$\pi$ partition, in which the $R_{\sigma\pi}$ integrals are equally divided between $\sigma$- and $\pi$-electronic energies. Thus, in Jug's definition, just as the $\pi$-electrons may be regarded as moving in the field of a core of bare nuclei plus $\sigma$-electrons, so should the $\sigma$ electrons be regarded as moving in the field of the bare nuclei plus the $\pi$-electrons. Moreover, Jug also proposed a way to partition the nuclear repulsion into $\sigma$- and $\pi$-components. This separation has the advantage that it allows studying any arbitrary distortion of the molecule. Importantly, however, irrespective of how different Jug's $\sigma$-$\pi$ partition is from the one in Eq. 10, it still fully confirms the preceding conclusion that the $\pi$-system of bonds is distortive. Thus, using Jug's partition scheme along a resonance coordinate that interpolates the situation between the equilibrium structure of benzene and the two Kekulé structures, the energy curve for the $\sigma$-energy is found to have a minimum at the equilibrium uniform geometry, whereas the $\pi$-energy curve exhibits a maximum at the same geometry. The same picture was found for benzene and other aromatic molecules [10a, d].

Another vindication of the soundness of Eq. 10 emerges from an application to another type of integral partitioning where the answer is known at the outset: the core-valence partition in a ring of lithium atoms. Let us consider a planar hexagonal ring of six lithium atoms with uniform Li–Li distances of 3.065 Å at the RHF/6-31G* level. This hexagon is stable against a localizing distortion (even if the planar form is not the most stable one). Applying a localizing Kekulean distortion, for example, alternating the bond lengths of the ring to 2.549 and 3.6857 Å, raises the total energy by 5.77 kcal/mol (note that this distortion keeps the nuclear–nuclear repulsion constant). Since the interaction between the electronic $1s^2$ cores of the lithium atoms is totally negligible at such interatomic distances, and since anyway the core–core repulsion is made constant by the $b_{2u}$-almost distortion, the resistance to distortion obviously reflects the structural preference of the valence electronic system alone.

Equation 15 which is analogous to Eq. 10 (and derived from it by replacing the subscripts $\sigma$ and $\pi$ by core and valence, respectively), can be used to separate the valence from core electronic energies and calculate the contribution of the valence electrons to the distortion:

$$E = \sum_{v}^{\mathrm{occ}} h_v + R_{cv} + R_{vv} + \sum_{c}^{\mathrm{occ}} h_c + R_{cc} + V_{NN}\,. \tag{15}$$

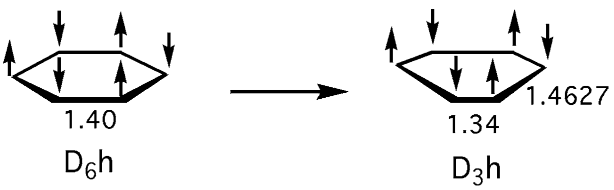
Since the distortion keeps the $1s^2$ core repulsion constant, the variation of valence bonding energy is strictly equal to the variation of valence electronic energy. Using Eq. 15 this amounts to 5.61 kcal/mol at the RHF/6-31G* level, a value that agrees very well with the "exact" all-electron value (at this level) of 5.77 kcal/mol. Clearly, the energy partition reproduces the chemically expected trend that the distortion energy is dominated entirely by the valence electrons. Thus, validity of the partition in Eq. 10 is confirmed by yet another method.

### 3.1 A general method for studying $\sigma$ and $\pi$ distortion energies

Still another way to demonstrate that the phenomenon of $\pi$-distortivity is real and not an artefact of a specific type of $\sigma$–$\pi$ integral partitioning is by the use of an approach that avoids integral partition altogether. Let us turn back to the simple question originally posed above in terms of bonds: since benzene is a composite system of bonds of the $\sigma$ or $\pi$ type, which one of these sets of bonds is responsible for the bond-equalized geometry? A straightforward way to answer this question, without any consideration of integral partitioning, would be to undo the pairing of the $\pi$-bonds while leaving the $\pi$-electrons in place and without introducing any special interactions between the spins of the unpaired $\pi$-electrons. The resistance to distort, of this "structure" that is devoid of $\pi$-bonding, is then simply the resistance of the $\sigma$ frame in the field of uncoupled $\pi$-electrons. Valence bond theory provides the means to do so using a well-defined reference nonbonding electronic state in the equilibrium geometry of the bonded species. This state is the "quasiclassical (QC) state," which in the case of the hydrogen molecule is a normalized spin-alternant determinant where the two atomic spin-orbitals $\chi_{\mathrm{a}}$ and $\chi_{\mathrm{b}}$ are, respectively, spin-up and spin-down and do not exchange their spins, as in Eq. 16:

$$\Psi_{QC} = |\bar{\chi}_a \chi_b| \; (or\; |\chi_a \bar{\chi}_b|) \tag{16}$$

The energy of this state is nearly constant all the way from the bonding distance to infinite distance [5e], and hence, it can serve as a reference nonbonding state (i.e. with zero-bonding energy), even when the atoms are close together. In the case of benzene the QC state in which the $\pi$-bonds have been unpaired is the spin-alternant determinant schematically represented in reaction (17).



(17)

Applying the same Kekulean distortion as in Eqs. (11) or (13) to the QC state of benzene, the energy is raised by 12.5 kcal/mol, compared with only 7.2 kcal/mol for the delocalized ground state of benzene. This result is clear-cut; the driving force exerted by the $\pi$ electronic component of benzene is to distort the bond-equalized geometry toward a bond-alternated one.

### 3.2 Additional methods for studying $\sigma$- and $\pi$-distortion energies

Finally, still another way to get rid of the integral partitioning problem is to reason in terms of orbital energies. While this is quite risky in general, since orbital energies and total energies are not the same, Gobbi et al. [9b] derived the conditions under which the second derivatives of the total energies can be expressed as the second derivatives of the orbital energies. It turns out that the Kekulean distortion ($b_{2u}$ for benzene and $b_2$ for allyl) fulfill these conditions, so that one may separate the $\sigma$ and $\pi$ force constants for these modes as follows:

$$\begin{aligned} \partial^2 E/\partial^2 Q_k &= \sum_{i,\pi}[\partial^2 \varepsilon_{i,\pi}/\partial^2 Q_k] \\ &\quad + \sum_{i,\sigma}[\partial^2 \varepsilon_{i,\sigma}/\partial^2 Q_k] = k_\pi + k_\sigma \end{aligned} \tag{18}$$

The $\pi$ and $\sigma$ force constants of benzene, allyl cation and allyl anions were calculated by this procedure, and the results nicely confirm the $\pi$-distortivity of allyl and benzene: in all cases the $\pi$ force constants are negative for the Kekulean mode, while the $\sigma$ force constants are positive [9b].

## 4 Is the conclusion that the $\pi$-system is distortive really dependent on the choice of the distortion ?

Baird criticized our challenging of the traditional view, by showing that the distortive nature of the $\pi$-electronic component depends critically on the choice of the bond distances used to calculate the distorted structures [28]. While the distances we used above for distorted benzene are 1.34 and 1.4627 Å, Baird proposed another set of values, 1.368 and 1.4627 Å. To get rid of the problem of the non-constancy of carbon nuclear–nuclear repulsions with these distances, he estimated the distortion energy $\Delta E_\sigma$ of the $\sigma$ frame by means of a Morse function potential with parameters established by Dewar and deLano [29]. With Baird's bond distances, the resistance of the $\sigma$ frame to the localizing distortion was found to be slightly *negative*; namely, the $\sigma$ frame is stabilized by the distortion, while the $\pi$-component actually resists the distortion and exerts a symmetrizing driving force, in agreement with the traditional view. Based on this result, Baird concluded that the results showing $\pi$-distortivity are invalid since the outcome depends on the choice of the distortion.

This criticism is interesting in the sense that it poses the question: what is the "correct" localizing distortion for probing the distortivity or lack thereof of the $\pi$-component? In answering such a question, one must remember that a transition state is characterized as such by being distortive along a single mode. Therefore, there is a single answer to the question and one is not free to check arbitrary distortions. To understand Baird's result, let us consider the benzene case and for simplicity restrict the reasoning to only two vibrational modes: the $a_{1g}$ "breathing mode," which elongates all C–C bonds simultaneously, and the $b_{2u}$ "Kekulean mode." As we have seen, the $b_{2u}$ mode is distortive (imaginary frequency), while the breathing mode is obviously symmetrizing (real frequency). Taking now arbitrary linear combinations of these two normal modes will give an infinite number of "distortion modes" which span a range of frequencies in-between those of the $a_{1g}$ and $b_{2u}$ modes; some will be real and some imaginary. As a matter of fact, even an intrinsically distortive transition state [30] like the $H_6$ ring system raises its energy if Baird's distortion is applied: that is, going from a uniform hexagon with all bonds being equal to 1.40 Å, to a distorted hexagon with the bond alternation defined by the bond lengths, 1.4624 and 1.368 Å. Thus, the fact that one given distortion raises the energy of the system does not prove that the system is stable. In order to get rid of any ambiguity, regarding the nature of the $\pi$-component, the question of the $\pi$-distortivity of for example, benzene and related systems should be formulated the same as for a transtion state. In this way, the question is uniquely answered in a non-ambiguous way: it is sufficient to find one localizing mode that lowers the energy of the delocalized structure to prove that the system is unstable toward localization and structural relaxation. In the benzene case, this mode is the $b_{2u}$ mode or a mode that is very close to it, like the "quasi-$b_{2u}$" mode displayed above in Eq. 11.

## 5 What is the role of resonance energy in the bond length equalization?

The title question is expressed in the following few versions: "Benzene has a bond-equalized geometry while antiaromatic systems and linear polyenes have bond-alternated ones. Since all these systems only differ by the resonance energy within the $\pi$ system, isn't this sufficient evidence that the $\pi$-system actually governs the geometry of polyenes? How then can one state that the $\pi$-bonding system of benzene exerts a distortive driving force?" Or, differently expressed: "since the $\pi$-electronic resonance energy of benzene is obviously larger in a bond-equalized geometry than in a distorted one, how can the $\pi$-bonding system prefer a bond-alternated geometry?"

Before answering the questions, it is important to note that the expression "resonance energy" has been employed in the literature with different meanings, which are sometimes mixed up. The thermochemical resonance energy (TRE), also called "aromatic stabilization energy," refers to the special stability of, for example, aromatic species relative to the conjugation of open-chain polyenes, and is estimated through energies of isodesmic reactions, or from thermochemical data and a group additivity scheme for the putative reference structure (e.g. "cyclohexatriene" as reference for estimating the TRE of benzene). On the other hand, the quantum mechanical resonance energy (QMRE) is the stabilization that arises from the mixing of two Kekulé structures, in a given geometry. The TRE and QMRE quantities are related to each other (a large QMRE implies a large and positive TRE), but are quantitatively different. For example, the TRE is positive for benzene and negative for cyclobutadiene, whereas both QMREs are positive, albeit much smaller in antiaromatic situations than in aromatic ones [5f]. In fact, since QMREs are always positive, it is clearer to use them, and this is the basis of the following discussion. To set the definitions straight, we note that QMRE corresponds to the quantity $B$ in Fig. 2.

The energy of a polyene, may it be aromatic, antiaromatic or linear, can always be expressed by reference to Fig. 4 in terms of two quantities. The first is $E^K$, the energy of the lowest of the two Kekulé structures $K_1$ and $K_2$ in a given geometry, while the second one is $B$, the QMRE in the same geometry:

$$E = E^K - B; B > 0 \tag{19}$$

$$E^K = \min[E(K_1) - E(K_2)]\,. \tag{20}$$

Note that Eqs. (19) and (20) are equally applicable to $\pi$ energies or to total $(\sigma + \pi)$ energies. Let us consider first the $\pi$-bonding system alone, and deal with its distortion energy

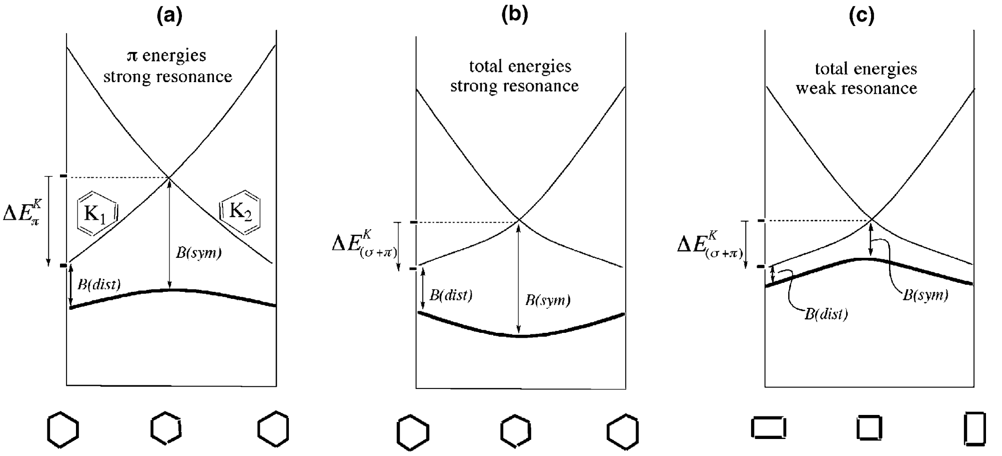


**Fig. 4** Energy as a function of the deformation coordinate along a $b_{2u}$ mode. Thin curves: energies of the Kekulé structures. Bold curves: energy of the resonating mixture of the two Kekulé structures. The deformation coordinate displays a bond-equalized geometry in the middle of the abcissa, and a bond-alternated one on the left-hand and right-hand sides. **a** Energy of the $\pi$-component, strongly resonating situation (benzene); **b** Total energy, strongly resonating situation; the situations in parts (**a**) and (**b**) correspond also to other strongly resonating species, for example, allylic ones. **c** Total energy for a weakly resonating situation (linear polyenes, antiaromatic molecules). By reference to Eq. 21, $\Delta B = B(\mathrm{sym})B(\mathrm{dist})$

$\Delta E_\pi$, which can be expressed as follows by reference to Eq. (19):

$$\Delta E_\pi = \Delta E_\pi^K - \Delta B\,, \qquad (21)$$

where $E_\pi^K$ is the energy of the $\pi$ component of the lowest Kekulé structure.

Starting from the crossing point, and applying a Kekulean distortion (moving either to the right or left from the midpoint of Fig. 4a) lowers the energy $E_\pi^K$. The Kekulé term $\Delta E_\pi^K$ is therefore always negative, and is a driving force for bond-alternation. On the other hand, since the QMRE term $B$ is larger in a symmetrical geometry than in a distorted one, the term $\Delta B$ is a driving force for symmetrization ($\Delta B < 0$). The distortivity of $\pi$-electronic systems, be they linear, antiaromatic or aromatic, is a consequence of the fact that $\Delta E_\pi^K$ is always larger, in absolute value, than $\Delta B$. As far as the energies of the $\pi$-components are considered, the Kekulé term always wins over the resonance term!

Let us now turn to total ($\sigma + \pi$) distortion energies, Eq. (22).

$$\Delta E_{(\sigma+\pi)} = \Delta E^K_{(\sigma+\pi)} - \Delta B \qquad (22)$$

$$\Delta E^K_{(\sigma+\pi)} = \Delta E_\pi^K + \Delta E_\sigma\,. \qquad (23)$$

The resonance term $\Delta B$ is $\pi$-only and is the same as in Eq. (21). But the Kekulé term now incorporates a symmetrizing driving force, $\Delta E_\sigma$, arising from the $\sigma$ frame. Combining Eqs. (22) and (23) into Eq. (24) shows that the distortive driving force of $\Delta E_\pi^K$ is now opposed by two

$$\Delta E_{(\sigma+\pi)} = \Delta E_\pi^K - \Delta B + \Delta E_\sigma\,, \qquad (24)$$

symmetrizing driving forces, $\Delta B$ and $\Delta E_\sigma$, which, so to speak, combine forces. As a result, a symmetrical geometry follows when the resonance term $\Delta B$ is large, like in benzene, allyl or related systems (Fig. 4b). On the other hand, when the resonance term is weak like in linear polyene or antiaromatic systems [31], the distortive driving force is the largest one, resulting in a bond-alternated geometry (Fig. 4c).

What is then the role played by the resonance energy ($B$) in bond equalization of allyl and benzene ? In fact, since the resonance energy $B$ is due to the $\pi$-electrons, Eq. 24 can be rewritten as Eq. 25:

$$\Delta E_{(\sigma+\pi)} = \Delta E_\pi + \Delta E_\sigma\,, \qquad (25)$$

where

$$\Delta E_\pi = \Delta E_\pi^K - \Delta B < 0 \qquad (26)$$

Equations 25 and 26 make a connection between all the elements. Thus, the $\pi$ component remains distortive in all cases, $\Delta E_\pi < 0$ in Eq. 26, but the role of resonance in benzene and allyl is to weaken the distortive propensity of the $\pi$-bonding system enough to allow the $\sigma$ frame to win over and impose a bond-equalized geometry. Clearly then, a strong resonance energy in the $\pi$-electronic system, and the fact that this resonance is stronger in a bond-equalized geometry than in an alternated one, can coexist with an overall preference of the $\pi$-bonding system for a Kekulean geometry. In the past [5f], this duality of $\pi$-systems was demonstrated by showing that one can numerically reproduce the empirical TRE quantities using thermochemical cycles which incorporate the $\pi$-distortivity. For space economy we refrain from repeating these cycles in the present paper. But once again, these demonstrate that from whichever way one approaches the problem, one is led to the same conclusion, namely that delocalized $\pi$-systems like benzene and allyl are simultaneously distorive and resonance stabilized.

## 6 Why does allyl radical have a barrier to rotation?

Put differently, the question can be phrased as follows: "since the $\pi$-electronic system of allyl is unstable in a bond-equalized geometry that favors resonance, why does it not rotate one of its terminal methylene group so as to disrupt resonance and adopt a bond-alternated geometry?" This question is related to the previous one, both depending on the relationship between resonance energy and $\pi$-distortivity.

While this question was answered before [4, 5f, 32], herein we treat it along the same lines as in the previous section. Consider first an allyl radical in its bond-equalized equilibrium geometry undergoing a 90° rotation of one methylene group without changing the C–C bond lengths. In the planar geometry allyl radical enjoys the stabilizing resonance energy $B$ (Eq. 19), rotating, however, one methylene group turns off $B$ to zero. Therefore, simply rotating one methylene group without relaxing the C–C bond lengths is obviously destabilizing ("vertical" rotational barrier), measuring the $B$ term. Let us now allow the C–C bond lengths to relax after methylene rotation, leading to a bond-alternated geometry at the 90° conformation. The rotational barrier will then be close to $B$ with a small correction due to the relaxation of the 90° rotated structure (the relaxation energy has contributions of steric release and some hyperconjugative interactions).

Alternatively, the entire process that starts from symmetrical planar allyl and ends up to relaxed rotated allyl can be divided into two other imaginary steps, represented in Fig. 5, corresponding to reactions (27) and (28):

$$\begin{aligned}&\text{Planar bond-equalized allyl}\\&\quad\rightarrow \text{planar bond-alternated allyl;}\\&\quad\Delta E_{(\sigma+\pi)} > 0;\ \Delta E_{\pi} < 0 \qquad (27)\\&\text{Planar bond-alternated allyl}\\&\quad\rightarrow \text{ rotated bond-alternated allyl;}\\&\quad\sim B(\text{dist}) > 0 \qquad (28)\end{aligned}$$

The first step is endothermic, since the ground state of allyl resists a $b_2$ distortion. However, as demonstrated above, its component analysis shows a distortive $\pi$-component with $\Delta E_{\pi} < 0$. Note that at the end of this first step, the planar bond-alternated allyl radical still enjoys resonance stabilization, referred to as $B$(dist) in Fig. 5. As such, the second step is also endothermic, since it corresponds to a loss of this resonance energy $B$(dist) at the distorted geometry (with contributions of steric release and some hyperconjugative interactions). Thus, the whole process of twisting allyl radical from its equilibrium planar conformation to its relaxed 90° conformation (sum of Eqs. 27 and 28) is obviously endothermic. At the same time, though, the planar Kekulean distorted structure (Fig. 5, Eq. 27) involves a distortive contribution of the $\pi$ component ($\Delta E_{\pi} < 0$) to the whole process. It follows that the preferred planar geometry of allyl radical and its significant barrier to methylene rotation are not contradictory with the distortive driving force of its $\pi$-bonding component. By the same reasoning, this conclusion readily extends to allyl cation and anion [4].

## 7 Why do aromatic systems have low reactivity?

One of the most frequently raised questions is: "If indeed the $\pi$-system of benzene is unstable and held in an unfavorable geometry by the $\sigma$ frame, why does this system have a low reactivity toward addition or substitution, and how can one explain the preference for substitution over addition?" The Hückel theory-based explanation for these well-known chemical facts is that anything that destroys the magical cyclic six-electron $\pi$-system is energetically "bad." Now, since Hückel theory makes a wrong prediction on the distortive/symmetrizing tendency of the $\pi$-bonding system, one might be tempted to think that all Hückel theory's predictions are wrong, including predictions on reactivity. This is certainly not so due to the fact that the $\pi$-distortivity coexists with resonance stabilization [5c–f, 27], and while Hückel theory misses the first feature due to the assumption of a universal $\beta$, this assumption leads the theory to capture the resonance stabilization feature.

Take benzene for example; benzene has a TRE of about 21 kcal/mol [33], according to experimentally derived heats of formation of benzene and estimated ones for hexatriene (the value is determined from an additivity scheme). As we showed [5f] the same value of TRE can be obtained by our model, and it coexists with $\pi$-distortivity. This duality is simply explained by the interplay between the resonance energy, $B$, and the distortive propensity. As shown above, the effect of the large resonance energy $B$ is to slightly weaken the distortive driving force of the $\pi$-bonding system. The same $B$ term endows the molecule with some thermodynamic stability that is reflected in a significant TRE [5f]. An addition reaction, which disrupts resonance and annihilate $B$, would of course be thermodynamically unfavorable. On the other hand, a linear polyene has a weak QMRE and a strongly distortive $\pi$-bonding component, leading to a bond-alternated geometry and appreciable reactivity toward addition reaction. The Hückel-based explanation holds, as far as reactivity is concerned, and does not contradict the distortive property of the $\pi$-component. An experiment based on reactivity probes only the resonance energy but not the distortivity of the $\pi$-electronic component. In this sense, and in the modern context, we are reminded of the well-known admonition of Walter Hückel [34] regarding the futility of the attempts to deduce the detailed bonding and structure of benzene from the nature of its reactivity. Experimental probes for different properties must normally be different from one another. *Testing of the* $\pi$-distortivity requires spectroscopic probes as amply discussed before [5f].

## 8 How good is the analogy between $\pi$-systems and hydrogen chains or rings?

We already noted that it would be very surprising if the analogy did not hold. Quantum mechanically, there is no

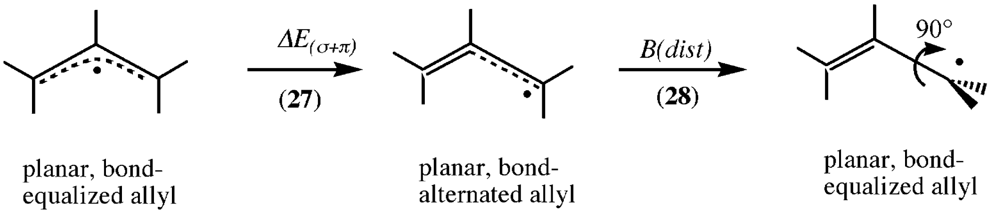
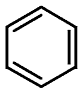


**Fig. 5** The rotational process of allyl radical divided in two imaginary steps: Step 1 (Eq. 27) involves distortion of the planar structure from bond-equalized to bond-alternated geometry; Step 2 (Eq. 28) consists of 90° rotation of the methylene group

fundamental difference between conjugated systems, be they $\sigma$ or $\pi$ types. In valence bond terms, in both cases the bond is made of a major covalent component [24] which owes its stability to spin exchange between the pairs of centers, augmented with a minor ionic component that further stabilizes the bonding interaction. It is therefore logical to expect that conjugated $\sigma$ and $\pi$-bonds obey the same laws regarding their behaviors toward localization and delocalization. The VBSCD model, described above [4,5], anchors this analogy in a fundamental property of the two-center bond, and shows how an entire series of isoelectronic species fits nicely with the predictions of the model. More quantitatively, the analogy between a hexagonal ring of hydrogens atoms and the $\pi$-system of benzene has been demonstrated from several points of view:

The main VB structures that describe the ground state of benzene are the Kekulé structures (e.g. 1), Dewar structures (e.g. 2), monoionic structures (e.g. 3) and other ionic structures (e.g. 4, etc). The cumulative weights for each category of structure, as calculated at the ab initio VB level, amount to 22.2, 11.0, 47.9 and 18.8%, respectively, for benzene, versus 21.8, 11.2, 49.2 and 17.8% for $H_6$ [35]. The weights of the various VB structures of benzene are modified when the geometry is deformed for any reason, as has been found in a computational study of Mills-Nixon systems [36]. In fact, when the $H_6$ ring was deformed in the same way as benzene, the structural weights of the valence bond structures in the two species followed almost exactly the same variations as a function of the geometrical deformation [37]. Clearly then, the two delocalized electronic species are comparable in terms of valence bond electronic structure. Moreover, the $B$ (QMRE) of both systems have been shown to be of the same order of magnitude, as estimated using Kollmar's MO-based method [38], respectively 85 kcal/mol for benzene vs 119 kcal/mol for $H_6$. Incidentally, the latter QMRE value for the distortive $H_6$ species demonstrates that a large QMRE is not at all in conflict with the distortivity of an electronic system.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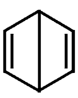
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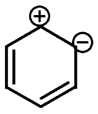
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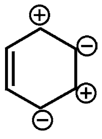
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Another point of comparison concerns the magnetic properties of delocalized systems. The exalted diamagnetism, as measured by a computed index $\Lambda$, is interpreted as a property of aromatic delocalized systems as opposed to non-aromatic or antiaromatic ones [39]. The $\Lambda$ value for benzene and for a ring of hydrogen atoms with H–H bond lengths of 1.40 Å was found to be exactly the same ($\Lambda = -10$) [5e].

From yet another point of view, an ab initio study of the $H_3^+$, $H_4$, $H_5^+$, $H_5^-$, $H_6$, $H_7^+$ and $H_8$ hydrogen rings by Wright and DiLabio [40] showed that each of these systems share the same MO energy pattern as the $\pi$-MOs of the isoelectronic ring of carbons, and that the hydrogen rings obey the $(4n/4n+2)$ rule. The $H_n$–$C_n(\pi)$ analogy is virtually perfect!

## 9 A unified picture for σ- and π- electronic delocalization

The distortivity of $\pi$-bonding systems of conjugated molecules has been probed by various computational means, ranging from semi-empirical to various strategies at the ab initio level. All computational results, irrespective of the variegated methods from which they derive, reach the same conclusions: the $\pi$-bonding species are unstable systems in the bond-equalized geometries; when such symmetrized structures are found, for example, in the case of benzene, allyl or aromatic annulenes, these are imposed by the $\sigma$ frame. In each case, the bond-equalized geometry is therefore the outcome of two opposing driving forces: a distortive driving force arising from the $\pi$-system, and a stronger, symmetrizing driving force arising from the $\sigma$ frame. In cases of antiaromatic or linear polyenes, the distortive driving force of the $\pi$-species is stronger than the $\sigma$ resistance and it imposes a bond-alternated geometry. Other conjugated molecules, which are neither annulenes nor linear polyenes (e.g. naphthalene) have intermediate geometries, as a result of a more complex interplay of several VB structures [5f].

The question, "to bond-alternate or not?" depends on a very delicate balance between the two opposing driving forces. As we have shown recently [5f, 32], a tiny change in one of the factors causes the nesting of bond-localization in $C_{4n+2}H_{4n+2}$ annulenes to switch from $n = 7$ (i.e. $C_{30}H_{30}$) to $n = 3$ (i.e. to $C_{14}H_{14}$). Recent results of Schleyer and his coworkers indeed show that the preference for bond-alternating structures in the $(4n + 2)$ $\pi$-electron series begins with the [14] annulene [41]; benzene appears to be almost unique.

Moreover, the bond-localized structure itself retains a significant resonance energy (see $B$(dist) in Fig. 4; for distorted benzene this value is 50 kcal/mol or so). As we have said all along, distortivity and resonance coexist, and must be taken as a fundamental double feature of delocalized species.

The distortive propensity of $\pi$-systems is not solely an academic concept. It is also related to physical and observable properties, that are summarized in a recent review paper [5f]. As striking examples, let us mention the frequency exaltation of the $b_{2u}$ vibrational mode of benzene and its derivatives, [14]-annulene, naphthalene, $\beta$-methyl styrene and so on [13], upon $\pi \rightarrow \pi^*$ excitation to the first excited singlet state. This frequency upshift shows that weakening the $\pi$-bonding system by excitation reinforces the symmetrizing driving force. In addition to spectroscopic manifestations, some structural manifestations are also observed. Thus, the tris-bicyclo[2.1.1] benzene, the first synthetic example of the "cyclohexatriene motif," is a benzene derivative that displays strong bond alternation ($\Delta R = 0.099$ Å) owing to appropriate cyclic substituents [42,43]. Remarkably, excitation of this molecule to its ${}^1B_{2u}$ state dramatically reduces the bond alternation ($\Delta R = 0.012$ Å). This almost bond equalization, achieved in the excited state, shows that disruption of the conjugation in the distorted benzene derivative indeed reinforces the symmetrizing driving force and almost restores the $D_{6h}$ symmetry [44].

Far from being paradoxical, the distortivity of $\pi$-electronic components fits nicely into a unified model for delocalization that is valid for $\pi$- and $\sigma$-systems as well. In this valence-bond-based model, and its confirmatory ab initio calculations, delocalized electronic species are unstable for strong and medium binders, but become stable intermediates for weak binders. Thus, the $\pi$-electronic system of benzene is unstable like the hexagonal $H_6$ species or the Diels-Alder transition state, that of allyl radical behaves like $H_3^{\bullet}$, and that of allyl anion like $H_3^-$ or the isoelectronic $S_N2$ transition states. As such, the distortivity of $\pi$-electronic components of conjugated molecules shows that electronic delocalization and resonance stabilization obey the rules of the same unifying picture irrespective of the nature, $\sigma$ or $\pi$, of the conjugated system [45]. This unified model, which is free of the paradoxes that afflict the traditional view, is fully compatible with the concept of aromaticity with all its structural, energetic and chemical implications like ($4n/4n+2$) rule, stability and low reactivity of aromatic polyenes, Hückel vs Möbius arrays in Woodward-Hoffmann rules and so on. Finally, it is rather amazing that the traditional view survived for a long time, despite the early appearance of fissures in its edifice. This is probably a question to be answered by philosophers of science.

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