Chem. Rev. **2001,** *101,* 1501–1539

A Different Story of π-Delocalization—The Distortivity of π-Electrons and Its Chemical Manifestations[†]

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

Department of Organic Chemistry and The Lise Meitner-Minerva Center for Computational Quantum Chemistry, The Hebrew University, 91904 Jerusalem, Israel, and Laboratoire de Chimie Physique, Groupe de Chimie Théorique, Université de Paris-Sud, 91405 ORSAY Cédex, France

Received August 28, 2000

Contents

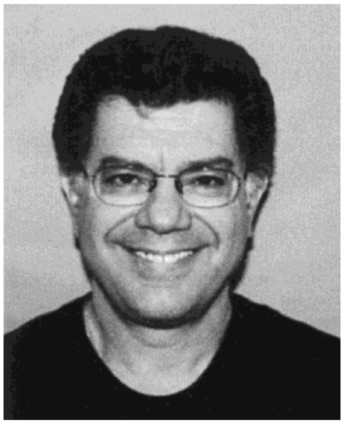
10.1021/cr990363l CCC: $36.00

I. Introduction

The delocalized π-electronic component of benzene is unstable toward a localizing distortion and is at the same time stabilized by resonance relative to a localized reference structure, Scheme 1. This dual property characterizes *most, if not all, delocalized species* in organic chemistry. This concept of dual character of conjugated delocalized molecules has been crystallized and demonstrated by us *using modern all-electron ab initio calculations* during the years 1984−1997.[1] This view and related work will be the main focus of the present review, which will emphasize its chemical manifestations in the ground and excited states of organic molecules and their isoelectronic analogues.

Such a review with a wide scope of this topic has never appeared before and is timely in view of the surge in interest in the concept of aromaticity. Earlier reviews covered subtopics. Thus, a Feature Article in 1988[2] covers literature up to 1987 and focuses on 'proving' the notion of π-distortivity in benzene and allyl radical within the context of isoelectronic species. A 1996 paper[3] reviews the "twin states" concept in relation to the properties of the first covalent excited state of benzene and linear acenes. Two proceedings have appeared in the years 1993 (Seventh International Symposium of Novel Aromatic Compounds)[4] and 1997 (WATOC 96)[1] and give a bird's eye view on the topic until 1996. The methodologies of partitioning π- and σ-energies were reviewed in the original work.[4−6] Related methods of energy partition were devised and reviewed by Jug and Köster[7−9] and by other groups using Hückel, semiempirical PPP, empirical VB, and modern VB methods.[10−26] In addition, several other brief descriptions of the work have appeared in monographs and textbooks by Minkin et al.,[27] Burdett,[28,29] and Carroll.[30] Two papers in *The Journal of Chemical Education* address the topic and show that π-distortivity of benzene and allyl radical is a property independent of the quality of the wave function used to describe the systems.[13,15]

In 1995, we decided to stop further research on this topic because it seemed a philosophical idea that engages primarily theoreticians with little or no impact on experimental chemistry. That this was a premature decision became obvious at the end of 1995, when we learned from Haas and Zilberg[31] about the frequency exaltation of the bond alternating vibrational mode in the 1^1B_{2u} excited state of benzene. This created a link of the purely theoretical notion to an experimental probe. The synthesis of Siegel's distorted benzene[32,33] demonstrated that a ground state "cyclohexatriene" has been finally achieved and that this may be a case where π-distortivity is at work. This was followed by a demonstration that, indeed, the bond-alternated feature of Siegel's molecule is due to the manifested π-distortivity.[34] The structural link of π-distortivity provided, in turn, insight into the nature of π-electronic delocalization when examined both in the ground and



Sason Shaik was born in 1948 in Iraq. His family emigrated to Israel in the Exodus of the Iraqi Jewry. Has received his B.Sc. and M.Sc. degrees in Chemistry from Bar-Ilan University. His M.Sc Thesis, under the supervision of Professor M. Albeck, involved experimental investigations of electrophilic mechanisms of organotellurium reagents. In 1974 he went to the United States as a Fulbright Scholar (1974–1979), where he earned his Ph.D. degree in Quantum Chemistry working with Professor N. D. Epiotis at the University of Washington. In 1978 Sason Shaik started his Postdoctoral research with Professor R. Hoffmann at Cornell University. He has felt fortunate ever since to have had these two great mentors in theory and to have experienced a taste of experimental chemistry. In 1980 he started his first academic position as a Lecturer at Ben-Gurion University, where he became Professor in 1988. He still misses these formative years where his only duty was to teach and carry out research with wonderful colleagues such as Addy Pross and Philippe Hiberty. In 1992 he received a call and moved to The Hebrew University, where he is currently the director of The Lise Meitner-Minerva Center for Computational Quantum Chemistry. Among the awards he received are the Lise-Meitner-Alexander von Humboldt Senior Award in 1996–1999 and the 2001 Israel Chemical Society Prize. His research interests are in the use of quantum chemistry to develop paradigms which can pattern data and lead to the generation and solution of new chemical problems. He loves valence bond theory.

Avital Shurki was born in 1970; after two years in the army, she began studying chemistry in 1990 at The Hebrew University, where she finished *summa cum laude* and was on the Dean's and Rector's Lists. In 1995 she received the Sara Wolf Prize for Graduate students. In 1994 she joined the group of S. Shaik and completed her Ph.D. degree in Quantum Chemistry in 1999. One of the main themes in her dissertation was the aromaticity, antiaromaticity, and π-delocalization. In 2000 she received the Rothchild Fellowship and joined the group of Professor A. Warshel at USC. Her research interests involve applications of VB ideas and calculations to chemical reactivity and bonding.

[†] Dedicated to Edgar Heilbronner, whose wise and humorous comments on the problem, starting with his first letter of Aug 5, 1985, were a source of inspiration and a motivation to follow this fundamental issue.

* Correspondence should be addressed to Professor S. Shaik. Phone: +972-2-6585909. Fax: +972-2-6584680. E-mail: sason@yfaat.ch.huji.ac.il.

[‡] The Hebrew University.

[§] Université de Paris-Sud.

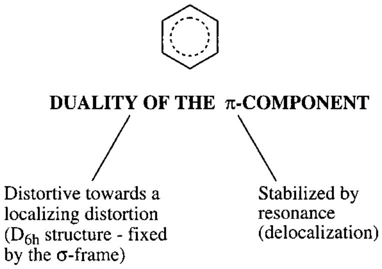
David Danovich was born in Russia in 1959. He graduated in physics from Irkutsk State University in Russia in 1982 and obtained his Ph.D. degree in Quantum Chemistry there in 1989 under the guidance of Dr. V. Zakrzevski and Prof. V. Voronov. He was a postdoctoral fellow with Professor Yitzhak Apeloig at Technion, Haifa, Israel, from 1990 to 1992. In 1992 he joined the group of Professor Sason Shaik at The Hebrew University, where he is now Computational Chemist at the Lise Meitner Minerva Center for Computational Quantum Chemistry. His major topics of interest are the design and implementation of codes for quantum mechanical computations and development of theoretical models for chemical systems.

Philippe C. Hiberty was born in 1948 in Paris. He studied Theoretical Chemistry at the University of Paris-Sud in Orsay. He prepared the French equivalent of an M.Sc. degree under the supervision of Professor W. J. Hehre; then he completed his Ph.D. degree under the supervision of Professor L. Salem in Orsay and got a research position at the Centre National de la Recherche Scientifique (CNRS). In 1979 he started his postdoctoral research with Professor J. Brauman at Stanford University and then with Professor H. F. Schaefer III at Berkeley. He went back to Orsay to join the Laboratoire de Chimie Théorique, where he started developing a research program based on valence bond theory. His main contribution to the latter field is the proposal of a new method, called "Breathing Orbital Valence Bond", that is aimed at giving the valence bond method the accuracy it lacked. He became Directeur de Recherche in 1986, and in addition to his research position in the Laboratoire de Chimie Théorique, he now teaches organic chemistry at the Ecole Polytechnique. He started a long-term collaboration with Sason Shaik as early as 1984. His research interest are, among others, in the application of quantum chemistry and valence bond theory to the fundamental concepts of organic chemistry.

excited states of the molecule.[34] These links to experimental probes reawakened the issue and now pose a real chance for changing a fundamental paradigm.

The present review is intended for the general reader, and hence, it avoids technical details (to be found elsewhere[4−6]). It outlines the π-distortivity scenario in Scheme 1 and addresses the possible manifestations of the π-distortivity, such as the new benzene derivatives with bond fixation,[35,36] the properties of twin excited states which are the counterparts of delocalized ground states,[3,37] the relation to transition states,[38] etc.

Scheme 1. Dual Character of the π-Electron Component of Benzene



A recent summary of the history and dynamics of the theoretical models of benzene[39] cites a view that even though the current molecular orbital (MO) view of benzene seems complete and ultimate while the valence bond (VB) view seems obsolete, the recent findings about π-distortivity in benzene indicate that the "benzene story" is likely to take additional twists and turns that will revive the VB viewpoint (see footnote 96 in ref 39). What the present review will show is that the notion of delocalized π-systems in Scheme 1 is an outcome of both VB and MO theories, and the chemical manifestations are reproduced at all levels. The use of VB theory leads, however, to a more natural appreciation of the π-distortivity, while the manifestations of this ground state's π-distortivity in the excited state of delocalized species provides *for the first time a physical probe of a "Kekulé structure"*.[3]

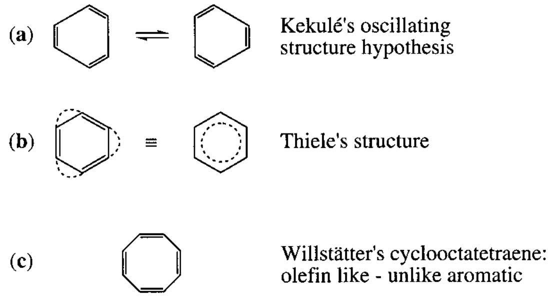
II. Background on π-Delocalization and π-Distortivity

The incubation and birth of a scientific concept is interesting. Therefore, we shall trace, even if with a personal taste, the development of the π-delocalization concept. Since much of the concept is connected with benzene, there will be a natural emphasis on this molecule. Subsequently, we shall describe the background related to π-distortivity.

A. Pre-electron Notions of π-Delocalization

The concept of electronic delocalization has germinated in the pre-electron period to Kekulé's 'structural theory' and its application to benzene as a prototype of a family of compounds so-called "aromatics". Kekulé had to address two major properties of benzene revealed from substitution experiments. The first was the empirical equivalence of all positions of benzene, what is called today the D_{6h} symmetry of both geometry and electronic structure, and second the persistence of the aromatic essence in chemical reactions, what we recognize today as "aromatic stability". Thus, Kekulé postulated that there is a C_6 nucleus and the four valences of the carbons are distributed to give *two oscillating structures*, which when cast in our contemporary molecular drawings look like part a in Scheme 2.[39−44] One of the many alternative hypotheses on the nature of

Scheme 2. Contemporary Representations of Kekulé's Hypothesis (a), Thiele's Structure (b), and Willstätter's Cyclooctatetraene (c)



benzene was due to Thiele, who invoked a single structure with "partial valences" that governs the properties of benzene.[45] In contemporary form, Thiele's structure shown in Scheme 2b is virtually identical to today's view of benzene.[46] However, it had not been at all obvious how to associate the stability of aromatics with such a picture nor how to distinguish between the oscillatory and single structure hypotheses.

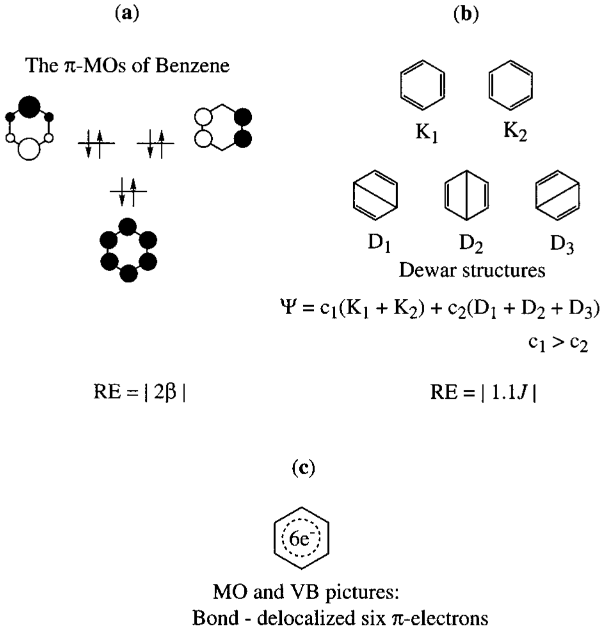
With the discovery of the electron[47] and the formulation of electron pair theory,[48] "valences" became electron pairs and the significance of Kekulé structures changed to today's electronic structure formulas. The notion of "delocalization" began to crystallize in terms of Ingold's theory of mesomerism (initially termed "intra-annular tautomerism"),[41,49,50] whereby benzene was represented by a few such electron pair structural formulas, dynamically interchanging much as in the Kekulé oscillatory picture (Scheme 2a). However, the newly synthesized cyclooctatetraene,[51] C_8H_8, shown in Scheme 2c that behaved like an olefin posed a serious difficulty to all concepts: Why was cyclooctatetraene "not aromatic" even though it could be described in mesomeric terms much like benzene? Armit and Robinson[52] postulated that the six electrons in benzene endow it with stability and that "six" is a magic number much like that of the Octet Rule. They coined the term "aromatic sextet"[52] to characterize the "aromatic" stability in benzene and other polynuclear aromatic compounds (e.g., naphthalene).

In the end of the 1920s, the structure of hexamethylbenzene was solved by Lonsdale[53] by means of X-ray diffraction and found to have identical CC bond lengths. Thus, a correspondence has been established between the "real" geometric structure and the empirical equivalence of the molecular positions deduced from the early experiments of the Kekulé era. Still, the difference between benzene and cyclooctatetraene defied all existing hypotheses. The concept of delocalization has been latent still, and its connection to stability is not at all apparent.

B. Quantum Chemical Notion of π-Delocalization

The recognition of electronic delocalization had to wait until the 1930s. The notion has gained a proper perspective with the development of quantum theory and with the recognition that electrons are also waves which are intrinsically delocalized. Heisenberg's theory of resonance,[54] which was applied by Heitler and London to the H_2 molecule,[55] demonstrated that the chemical bond found a home in the new theory. This treatment formed a basis for the VB method, which was developed by Slater[56] and Pauling.[57] Quite in parallel, MO theory was developed by Hund[58] and Mulliken[59] following London's suggestion to express a molecular orbital as a combination of atomic functions.[41] With these new theories, Hückel[60] initially tackled the question of restricted rotation in ethylene where he invoked the π-type and σ-type orbitals which differed in their symmetry with respect to the molecular plane.[61] Equipped with this facility of $\pi-\sigma$-separability, Hückel turned to solving the electronic structure of benzene using both VB (actually Heitler–London method) and MO approaches, the latter giving better "quantitative" results and hence being preferred. The MO picture, Scheme 3a, was quite unique in the sense that it viewed the molecule as a whole, with a σ-frame dressed by π-electrons which occupy three completely delocalized π-orbitals. The delocalized π-component which was closed shell was found to have a lower energy relative to three isolated π-bonds in ethylene. Thus, the MO picture resolved the stability issue, the empirical equivalence of all the positions, and the identical C–C bond lengths, all in a single structure shown in Schemes 3a,c which is analogous to the Thiele's picture (Scheme 2b) with partial valences or to Havréz formula.[46]

Scheme 3. Representations of π-Delocalization in Benzene: (a) Hückel's π-MO's. (b) Wheland–Pauling's Resonance Hybrid. (c) Symbolic Representation of π-Delocalization by a Dotted Circle[a]



[a] RE is resonance energy (β and J are energy parameters in the two theories).

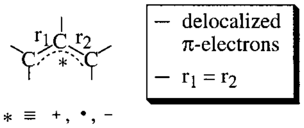
While Hückel favored the MO description because it appealed to his physical sense, looking like a vibration which is 'delocalized' over an entire string even though the perturbation that caused it is transmitted between 'close neighboring' elements,[61] the VB method has begun to flourish. Slater was the first to suggest that the "resonance" between the two forms of Kekulé (Scheme 2a) can lower the energy of benzene.[41] Subsequently, in 1933 Pauling and Wheland[62] adopted the $\pi-\sigma$-separability and presented a VB picture of benzene, part b in Scheme 3, as a resonating wave function made from the two Kekulé structures (K_1, K_2) and three additional minor structures (D_{1-3}), called Dewar structures (after the alternative structural proposition of James Dewar[50]). The superposition of these structures, so-called the "resonance hybrid", corresponded to a complete delocalization of the π-electrons in a single D_{6h} geometry much as in the MO treatment. Approximately 80% of the entire resonance energy of benzene was computed to arise from the resonating Kekulé structures.

Thus, the new electronic theories were converging on the same picture of benzene in Scheme 3c: a species that has identical CC bond lengths and a "π-sextet" of electrons which are "smeared" uniformly over the σ-skeleton and confer stability on the molecule. In 1937, following Lonsdale's work,[50,63] it was recognized that the exaltation of the diamagnetic susceptibility, found by Pascal[64] for benzene and other polynuclear aromatic species, could be associated with magnetic orbits which span the entire ring perimeter in benzene. Even larger circumferences were determined for naphthalene, anthracene, and graphite,[50] providing strong support of the delocalized picture of the π-electrons.

Hückel[65,66] used his MO theory to further study systems such as cyclopentadienyl anion, $C_5H_5^-$, and cycloheptatrienyl cation, $C_7H_7^+$, as well as "antiaromatic" ones such as cyclobutadiene, C_4H_4, etc. The former species were found to possess closed π-shells and to resemble benzene in their stability patterns, whereas the latter ones had open shells and zero resonance energy relative to the same number of isolated π-bonds. This lead Hückel to formulate his famous *aromaticity rule*, whereby *systems that possess $4N + 2$ π-electrons have a closed π-shell and special stability associated with delocalization*. In contrast, systems such as C_4H_4 which possess $4N$ electrons had no apparent resonance stabilization (but he did not call them antiaromatics). Quite differently, simple resonance theory which is a qualitative version of VB theory suggested that C_4H_4 should be resonance-stabilized like benzene. The fact that C_4H_4 could not be made at that time was already an advantage for MO theory over VB. This was a point of divergence of the two theories and marked the beginning of the downfall of VB theory, actually for no good reason other than the inadequate application of the theory.[67−70]

The appreciation of Hückel rules soared in 1950s when Doering and Knox[71] prepared $C_7H_7^+$ derivatives and Breslow et al.[72] synthesized the triphenyl cyclopropenium cation, all predicted to be stable by the Hückel rule. These examples were augmented by the aromatic [*n*]-annulenes that were made by Sondheimer[73] and by Vogel's bridged annulene systems.[74] A big stride was taken when Schröder and Oth prepared [16]-annulene[75] and showed that its NMR chemical shifts were precisely reversed relative to those of the [18]-annulene. A breakthrough was marked by the synthesis of cyclobutadiene and its derivatives.[44,76,77] These species were shown to be rectangular and spectacularly different from benzene in all respects.[78,79] This and the instability of cyclopropenium anion[80] led both Breslow and Dewar to coin the term "antiaromatic" for π-systems with $4N$ electrons.[81]

Scheme 4. Bond-Delocalized Allylic Species

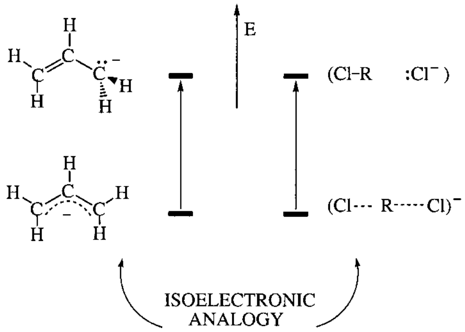


Since Hückel MO treatment does not predict "antiaromatic" behavior for cyclobutadiene, and in some cases such as pentalene the molecule is even predicted to have a resonance energy larger than benzene,[27,69] a different definition of resonance energy (delocalization energy) had to be devised. Quite independently, Breslow and Mohacsi[82] and Dewar and co-workers[83] related the resonance stabilization/destabilization of a cyclic system to an open-chain analogue possessing the same number of double bonds and being "isoconjugate" with the cycle[27,84] but having a degree of conjugation of an open-chain species. With this definition, systems with $4N + 2$ π-electrons are "aromatic", while those having $4N$ π-electrons are "*antiaromatic-destabilized by cyclic resonance*". A beautiful example of the $4N\backslash(4N + 2)$ dichotomy was provided by the conversion of C_8H_8, which has alternating single and double bonds and is tub-shaped, to a planar delocalized species by just adding two electrons to give $C_8H_8^{2-}$.[85,86] All this evidence has established the contemporary picture of aromatic species as having a bond-delocalized π-electronic component, uniform geometry, and special stability relative to an open-chain reference. In contrast, in antiaromatic systems the π-components are bond-localized, *destabilized by cyclic delocalization,* and their geometries are nonuniform exhibiting alternating C−C bonds. This classification has been supported throughout the years by modern quantum chemical calculations at various levels of sophistication.[87−89]

In the meantime, other π-delocalized systems were discovered among open-chain systems, notably the three allylic systems, Scheme 4. All of these systems showed a behavior akin to the aromatic systems; they are delocalized, have uniform geometries, and are more stable than saturated analogues.[90−93] Furthermore, they all possess rotational barriers with heights related to the resonance stabilization of the species.

The colossal edifice of evidence has created a very strong cause and effect link between π-delocalization and geometry, with a lot of emphasis on the preference of the π-electron energy. A consensus seemed to have been reached that the symmetric geometries (with uniform C−C bond lengths) in species such as benzene or allyl result from *the inherent tendency of π-electrons to undergo bond delocalization* in the absence of constraints by the σ-frame.[13,19] The extent of the consensus may be witnessed from papers[94,95] on barriers of identity S_N2 reactions such as $Cl^- +$ RCl. The authors reason that since the $(Cl-R-Cl)^-$ transition state is isoelectronic to allyl anion, which

Scheme 5. A Naive Isoelectronic Analogy that Leads to the Conclusion that the S_N2 Transition State Should Have Been a Stable Minimum



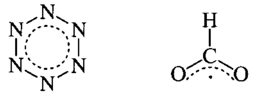
is more stable than its bond-twisted form (Scheme 5), it follows that the S_N2 transition state should also be more stable than its reactants had it not been for the steric congestion around the compact carbon atom. This analogy leads to wrong conclusions. In his most recent paper on the subject, Heilbronner[13] describes the roots of the consensus as the naive (as he calls them "meta-theoretical") application of both Hückel theory and Pauling's resonance theory. The popularity of these naive applications is with no doubt due to their immense success, which has formed what Hoffmann[96] calls a "credibility nexus" between simple theory and its experimental verification. Nevertheless, these naive applications are of course wrong as we shall immediately see.

C. π-Distortivity in HUckel-Type Theories

Despite this consensus on the inherent tendency of π-electrons to be delocalized and thus drive their molecules to adopt geometries with uniform C−C bond lengths, there were a few early studies which indicated that the situation is quite different. Thus, already in the 1950s Longuet-Higgins and Salem[16] used Hückel theory with a variable β parameter and σ-compression energy to treat the problem of bond alternation in long polyenes and cyclic annulenes. The σ-compression energy, which was composed of individual bond contributions taken as harmonic in the distortion from equilibrium, always preferred cycles with uniform C−C bond lengths. On the other hand, the π-electrons were found to be invariably distortive along a bond alternation mode. Theory predicted that in interplay of these two opposing tendencies, the π-distortivity will overcome the σ-compression energy starting with $C_{34}H_{34}$, where an actual distortion will set in. In his monograph, Salem states that the π-distortivity "exists already in benzene".[97,98] Subsequently, Berry[99] focused on the IR frequency and the force constant for the bond alternating vibrational mode (b_{2u}, ω_{14}) of benzene. He deduced that the mode is unusually soft due to the π-distortivity which thereby causes benzene to spend 15% of its time as a cyclohexatriene. Other Hückel-type and semiempirical MO and VB treatments which followed[20−25] reached similar conclusions about benzene and stressed the role of the σ-compression energy as the factor that determines the uniform bond length in benzene.

In 1966, Binsch and Heilbronner[100] examined the question of bond fixation using Hückel theory and showed that the bond−bond π-polarizability terms (which prefer a variable β parameter) can induce bond fixation if the first eigenvalue of the bond−bond π-polarizability matrix, λ_1, is larger than a critical value determined by the ratio $k|\beta_o|/\beta'^2_o$, where k is the stretching force constant of a σ-bond and β_0 is the value of the Hückel parameter while β'_o is the first derivative of β_o with respect to the bond alternating mode. An amusing exchange between Heilbronner and Binsch in the 1971 Jerusalem Aromaticity Symposium[101] projects the unease with the emphasis of π-bond delocalization in conjugated systems without the constraints of the σ-compression energy. Nevertheless, all these studies were largely overlooked by the experimental community.

Scheme 6. Examples of Species with Distortive π-Components


1 **2**

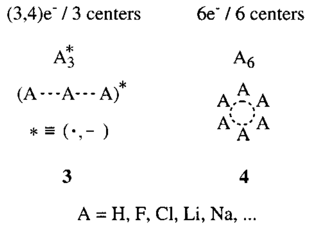
III. π-Distortivity—A Conclusion from a Broad Chemical Perspective

In the early 1980s, the problem was tackled again from an entirely different perspective, that of the wider context of chemistry. As noted by Shaik and Bar[102] in 1984, delocalized species such as benzene and allyl radical are rare among other nonmetallic elements. Hexazine, **1** (Scheme 6), which is isoelectronic with benzene and could have a perfectly "aromatic" structure with π-sextet and a σ-frame, has never been made.[103] Its calculations in a D_{6h} symmetry by Saxe and Schaefer[103c] show that it distorts easily to a D_{3h} structure. Similarly, the π-state of formyloxy radical, **2** (Scheme 6), that is isoelectronic with allyl radical has been shown by Davidson and Borden[104] to distort easily to a bond-alternated localized structure. Clearly, in these species the distortive π-electron component overcomes the σ-constraints and distorts the structure despite the availability of "aromatic stabilization" in hexazine and allylic stabilization in the π-formyloxy radical. It was further noted by Shaik and Bar[102] that Hückel rules did not seem useful or applicable to predict the behavior in nonmetallic elements other than carbon. A natural question then followed: Is there anything special about carbon species which render them delocalized?

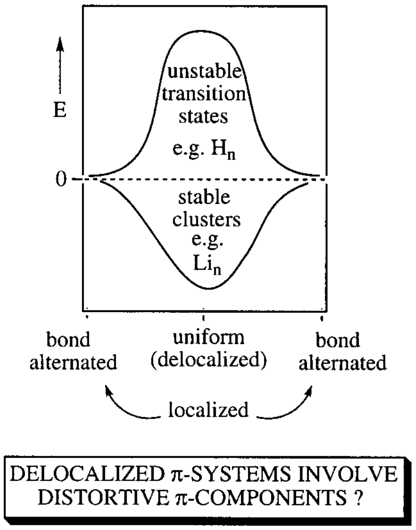
A. To Be or Not To Be Delocalized Is the Question

With this question as a guide it became apparent that delocalization in systems such as benzene and allyl must be examined within a broader family of isoelectronic species. This was done in 1984 by Shaik and Bar[102] and by Epiotis,[105] and in 1985 it was demonstrated by computational means by Shaik and Hiberty.[106] Thus, one can, for example, assemble the isoelectronic A_n clusters of monovalent atoms with different electron counts, e.g., **3** and **4** in Scheme 7.

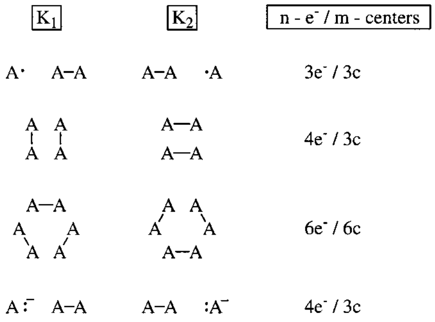
Scheme 7. Bond-Delocalized *n*-Electron−*m*-Center Species Isoelectronic to the π-Components of Allyl and Benzene



Scheme 8. Stability Patterns of Bond-Delocalized A_n Species



Scheme 9. Kekulé Structures for *n*-Electron−*m*-Center Species



All these systems are isoelectronic with π-benzene and π-allyl and have topologically identical orbital manifolds.

The stability patterns of the uniform delocalized species relative to the corresponding bond-alternated structures fall into two broad families shown in Scheme 8. The first family exhibits delocalized bond-uniform clusters that are transition states, falling apart into the corresponding diatomics, e.g., the hydrogenic clusters H_n. In the second group, e.g., Li_n, the delocalized bond-uniform cluster is stable with respect to a localizing distortion which alternates the bond lengths. This second group generally involves clusters of metallic atoms and a few delocalized clusters of nonmetallic elements which are analogues of allyl anion e.g., Cl_3^-, I_3^-, etc.[107] A similar division exists for squares, isoelectronic of π-cyclobutadiene, where the square Li_4 is stable relative to its dimers, while all other squares, e.g., cyclobutadiene, H_4, etc., are distortive.[5,107]

The division is apparent: Atoms which form strong bonds disfavor aggregation in geometries with uniform bond distances which confer delocalization.[102,105,106] Only very weak binders, like Li, mildly prefer uniform bond lengths and delocalization. Indeed, this is a natural division in the Periodic Table, where bond delocalization is ubiquitous in metals but not among the strong binding nonmetallic elements. Carbon must then find itself within this general division, and there is nothing that suggests that it is mysteriously "a special element". In fact, projecting from the strength of the π_{CC} bond (which is significant, ca. 70 kcal/mol), one would tend to conclude that π-electron components are distortive transition states, and therefore, π-bond delocalization must be a byproduct of the constraints applied by the σ-frame which prefers geometries with uniform C−C bonds. However, to affirm such a conjecture, a new model was needed that accounts for the existence of the dichotomy in Scheme 8 in a systematic manner. Here, Hückel theory with a variable β parameter is not very helpful because it would predict that all delocalized A_n clusters are distortive.

B. Valence Bond Model for Electronic Delocalization

The VB diagram model[37,102,106] provides the necessary insight into this dichotomy of delocalized systems and enables one to develop a more precise means to think about π-components by themselves within their isoelectronic families.

1. Kekulé Structures Always Cross along the Bond Alternating Coordinate

For the sake of clarity, we apply the model for cases where two principal VB structures exist that can describe the delocalized state. The structures labeled as K_1 and K_2 are referred to hereafter as the Kekulé structures. Scheme 9 displays these structure pairs for a few generic situations of delocalization for A_n species: A being a univalent atom (e.g., H, Li, Cl, C_π, etc.). The behavior of these Kekulé pairs *along the bond alternating mode* is general; they interchange in energy forming a VB correlation diagram with two state curves.

Figure 1 exemplifies the VB correlation diagram

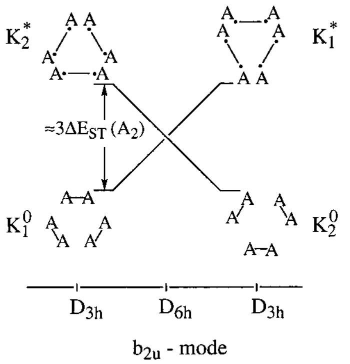


Figure 1. VB correlation diagram for the Kekulé structures of 6-electron−6-center A_6 species, along the bond alternating coordinate (b_{2u} mode).

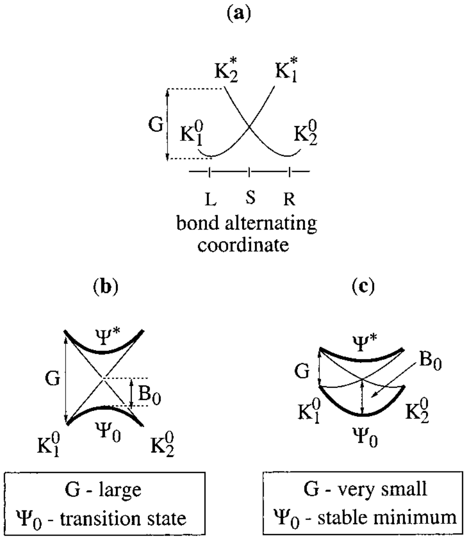


Figure 2. (a) Generalized VB correlation diagram for two Kekulé structures, along the bond alternating coordinate. *R* and *L* represent extremes of the coordinate when one bond is short and the other is infinitely long. The symmetric structure with uniform distances is indicated by S. Diagrams b and c describe avoided crossing (resonance mixing) of the Kekulé structures. B_0 is the vertical resonance energy. The resulting states are the bold curves. Ψ_0 and Ψ^* are the twin states at the symmetric geometry.

for species which are isoelectronic with π-benzene, having six electrons delocalized over six centers, along the b_{2u} coordinate that alternates the bond lengths passing through a hexagon with D_{6h} symmetry. Stretching of the A–A bonds and shortening the nonbonded A- -A linkages of K_1° along the b_{2u} coordinate raises the energy of K_1° and converts it to K_1^*. In this excited state, the nonbonded interaction between the electrons on the nonpaired A• atoms is like in a triplet situation.[5] Therefore, K_1^* (a vertical excited state of K_2°) can be viewed as a state in which all the bonds of the ground-state A_2 molecules are approximately unpaired to triplets and the electrons are paired anew across the infinitely long linkages. A similar description is equally valid for the $K_2^\circ \rightarrow K_2^*$ transformation in the reverse direction of the b_{2u} coordinate. Consequently, the state curves cross each other and interchange along the b_{2u} coordinate.

VB correlation diagrams of this type have been computed for the other generic systems in Scheme 9 using ab initio VB methods.[37,108–112] For 3-electron–3-center A_3 species, which are analogues of allyl radical, and for 4-electron–4-center A_4 species analogous to square singlet cyclobutadiene, the excited states in the diagram involve, much as in Figure 1, singlet–triplet promotion energies due to unpairing of the ground state's bonds to triplet pairs. For the 4-electron–3-center A_3^- species, analogues of allyl anion, the excited states in the VB diagram, $K_1^*$and K_2^*, are charge-transfer states involving a transfer of an electron from the $A:^-$ terminus to the short A–A bond. In fact, the same diagrams can be drawn for all *n*-electron–*n*-center species, analogues of [*n*]-annulenes, as well as for other species which potentially possess delocalized states described by more than one Kekulé structure. This general situation is depicted in part a of Figure 2, which shows the interchange of two Kekulé structures along the bond alternating mode and the correlation of K_1° and K_2° to $K_1^*$and K_2^*, respectively, the latter states being the excited states of the Kekulé structures at the extremes left (L) and right (R) of the bond alternation coordinate.

In cases where the symmetry of the ground-state electronic wave function belongs to a degenerate irreducible representation of the point group, e.g., H_3^- (D_{3h}), $H_3^\bullet$ (D_{3h}), etc., the wave functions cannot mix for symmetry reasons and, thus, the crossing point describes a Jahn–Teller situation which is always distortive.[113] However, in all other cases, the two VB structures can mix and lead to a pair of bonding and antibonding states—the twin states (Ψ_0, Ψ^*) made from the Kekulé structures. The avoided crossing interaction, measured relative to the crossing point, is the quantum mechanical resonance energy[114] which we label as B_0 in Figure 2 parts b and c. The relationship between the twin states is deferred to a later section, while here we discuss the ground state only by reference to the significance of the two situations shown in Figure 2 parts b and c.

The bonding combination of the Kekulé structures is a delocalized electronic state and can be described by the resonating linear combination of the two structures, eq 1.

$$\Psi_0 = N[K_1 + (-1)^p K_2]; \qquad N = \text{normalization constant} \quad (1)$$

Here, the sign of the ground-state combination depends on the parity (*p*) of the systems and is determined by the sign of matrix elements between the Kekulé structures.[113,115,116] As a rule, whenever the ground state behaves as the totally symmetric representation of the respective point group, the parity is even and the combination is positive, while when the ground state is not totally symmetric, the parity is odd and the wave function is the negative combination. For example, for H_6, Li_6, π-benzene, etc., with totally symmetric ground states, the positive combination is the ground state and the same applies to all A_n species which fall into the aromatic category ($n = 4N + 2$). In contrast, in all antiaromatic situations ($n = 4N$) and in 3-electron systems, like $H_3^\bullet$, π-allyl, etc., where the ground state is not totally symmetric, the wave function is the negative combination of the two Kekulé structures.[113,115]

The stability of the delocalized state depends on whether, after avoided crossing, the resulting state Ψ_0 is either more or less stable than K_1° and K_2°. Parts b and c of Figure 2 show that the answer to this question depends on the size of the promotion energy, *G*, between the ground and excited states at the diagram's extremes. When the gap is large, as in Figure 2b, the delocalized state is expected to be a transition state for the bond exchange process of the A–A molecules. However, when the promotion gap *is very small*, the avoided crossing will lead to a stable delocalized cluster, as shown in Figure 2c. VB ab initio calculations by Maitre et al.[117] for H_3 and Li_3 reproduced the two situations and thereby provided a proof of principle. The calculations presented

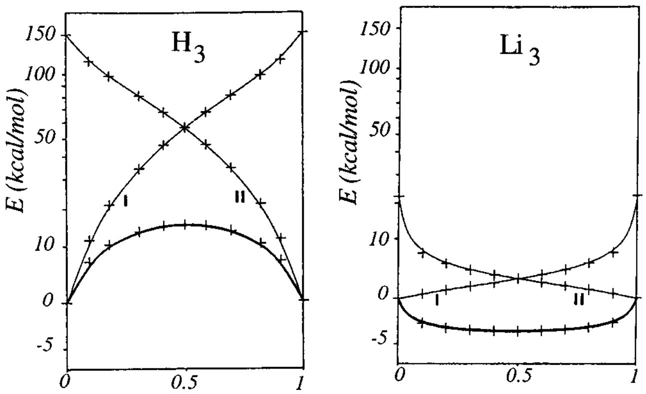


Figure 3. Computed VB diagrams (ref 117) for H_3 and Li_3. I and II are the Kekulé curves. Energies in kcal/mol. The reaction coordinate is dimensionless. Only ground states are shown.

in Figure 3 show clearly that H_3, which possesses a larger promotion energy, produces a transition state structure, while for Li_3, which possesses a tiny promotion energy, the avoided crossing leads to a stable delocalized cluster. Note that even though B_0(H_3) is much larger than B_0(Li_3), the decisive quantity which determines the stability of the delocalized species is the promotion gap.

The promotion gap is determined by two basic excitations. For k-electron pairs, the promotion energy is k-fold singlet−triplet excitation of the A−A dimer, while for mixed-valence cases where the number of electrons exceeds the number of centers (e.g., H_3^-) and vice versa, the promotion energy is a charge-transfer excitation, (e.g., from H:$^-$ to H_2 in H_3^-). Let us now use the promotion gap quantity to pattern the data concerning delocalized species.

For the 6-electron−6-center problem, the promotion energy is given by the sum of the singlet−triplet excitations which are required to unpair the electrons in the A−A dimers in the ground state (Figure 1) and to prepare them in the excited state for the bond interchange. Thus, the large singlet−triplet gap of 10.5 eV for H_2 makes H_6 a highly unstable transition state with $\Delta E^{\ddagger} \geq 74$ kcal/mol for the bond exchange reaction. In contrast, Li_6, with a very small Li−Li singlet−triplet gap of ∼1.5 eV, is a stable delocalized species.[5,106] The promotion gap for the six π-electrons of benzene can be obtained by looking at the $^3\pi\pi^*$ excitation energy of a short π-bond. Depending on the model for a π-bond, values of the corresponding promotion energy are 4.6−5.2 eV, between the two extremes of H_2 and Li_2. Since the stability of the delocalized state requires *very small promotion gaps* and since the stability of the D_{6h} hexagon of Li_6 relative to $3Li_2$ molecules is in any case not overwhelming,[106] it follows that the π-sextet of benzene must behave like the H_6 species, as a transition state that has a distortive propensity along the localizing coordinate.

For 3-electron−3-center delocalized species, A_3, which are analogues of allyl radical, the excited states in the diagram involve singlet−triplet promotion energies due to unpairing of the ground state's bonds to a triplet. Much the same as in the six-electron problem, here too the $^3\pi\pi^*$ energy of a short π-bond places the delocalized species in the unstable region, among the distortive species of the respective isoelectronic series, as in Figure 2b. The same trend applies for 4-electron−4-center A_4 species, analogues of square singlet cyclobutadiene. Thus, here too the square Li_4 is more stable than its dimers, $2Li_2$, while square H_4 is highly unstable with respect to its dimer products. The π-component of square C_4H_4 is also distortive, and while for this species the distortivity is expected and observed, it is mentioned only as a demonstration of the coherence of the predictions.

For the 4-electron−3-center A_3^- species that are analogues of the π-component of allyl anion, the excited state in the VB diagram is a charge-transfer state involving a transfer of an electron from the A:$^-$ terminus to the short A−A bond. Species with small promotion energies such as I_3^- are stable delocalized states, while species such as H_3^- with a large promotion energy are unstable transition states. Here too the promotion energy for the π-component of allyl anion places it among the 4-electron−3-center transition states, analogues of H_3^- (and of S_N2 transition states).[1,2,4,102]

Therefore, the promotion energy that determines the energy expense needed to bring the Kekulé forms into resonance clearly serves as an organizing quantity[117] and determines the global stability trends of the isoelectronic series, as summarized in Figures 2b and 2c. The promotion gap is generally related to the binding strength of the constituent atoms. Since carbon is a strong π-binder, this leads to large promotion energies for delocalization and consequently the π-delocalized components must behave as distortive transition states. *The observed π-bond delocalization in benzene and the allylic species must, therefore, be a byproduct of the σ-constraints to prefer uniform C−C bond lengths.*

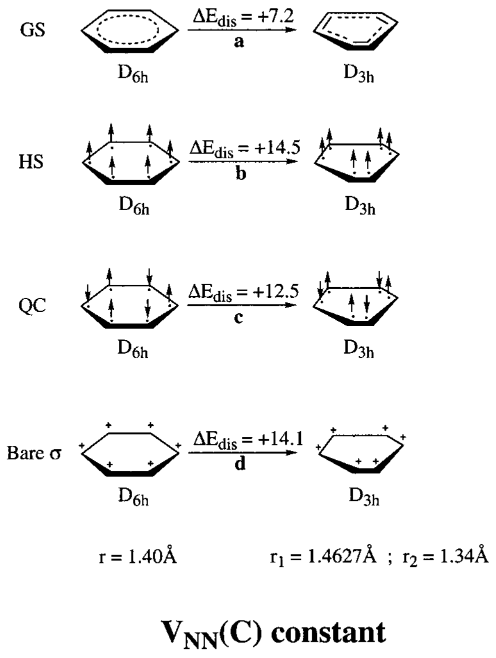
Other trends could be explained in the same manner.[1,2,4] For example, hexaazabenzene, **1** (Scheme 6), should have a much more distortive π-component than benzene, simply because the $^3\pi\pi^*$ promotion energy for π_{NN} is larger than that for π_{CC}. Similarly, the π-state of formyloxy radical, **2** (Scheme 6), which is an analogue of allyl, easily distorts to a C_s structure[104] because the $^3\pi\pi^*$ energy of the π_{CO} bond is larger than that of the π_{CC} bond. Conversely, manipulations which reduce the π-distortivity may generate analogues of cyclobutadiene which maintain a square geometry. Therefore, the VB correlation diagram serves an important role because it demonstrates that the behavior of the π-components is part of a general trend associated with a fundamental property of the constituent atoms.

C. Computational Evidence for π-Distortivity

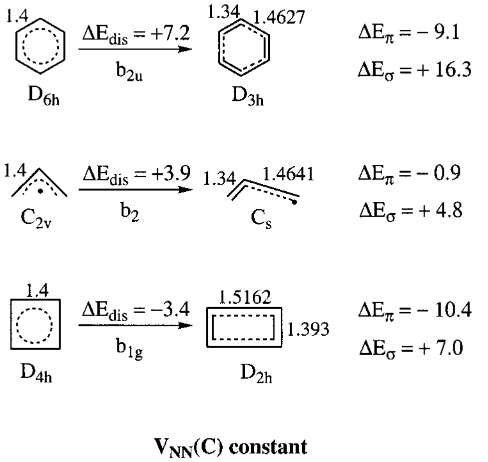
1. π-Distortivity in ab Initio All-Electron Calculations

The methodology for obtaining the π-and σ-energies for π-systems is reviewed elsewhere,[2,4−6,118] and hence, this section presents some of the computational evidence without going into the computational details. The interested reader is advised to consult the above references. The evidence comes from two types of 'computational experiments', shown in Schemes

Scheme 10. Distortion Energies in kcal/mol (Refs 5 and 6) for Benzene (a), Its Models with Unpaired π-Electrons (b,c), and Its Bare σ-Frame (d)

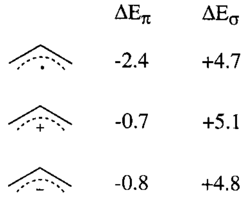


Scheme 11. π- and σ-Distortion Energies, in kcal/mol (from Ref 5) for Benzene, Ally Radical, and Square Cyclobutadiene[a]



[a] Total distortion energy is given above the arrows.

Scheme 12. Distortion Energies in kcal/mol (from Ref 93) for the Allylic Species



10−12 and designed to answer the question what causes delocalized species such as benzene and allylic species to assume symmetric structures?

Scheme 10 shows the distortion energies of the ground state (GS) of benzene in part a in comparison with situations where π-delocalization is 'turned off' in parts b−d. All the distortions are carried out along the localizing b_{2u} mode with a small correction which keeps a constant total nuclear repulsion between carbon atoms; all values for distortion energies, ΔE_{dis}, in Scheme 10 correspond to the π-CI/6-31G level (MRMP and CISD).[5,6] In Scheme 10b we show the high-spin (HS) species in which all π-electrons are unpaired to the high-spin situation where π-bonding and delocalization are *completely absent*. In Scheme 10c we show the quasiclassical state (QC) in which π-electrons are unpaired to a spin alternant arrangement (known also as antiferromagnetic). As shown elsewhere,[6,118−120] the uncoupled p_π electrons in both the HS and QC states do not contribute to the energy change along the bond alternating b_{2u} distortion. Since the π-electrons are strictly uncoupled from each other in the QC state, this state turns off all π-bonding and π-resonance without affecting the σ-frame. Finally, in Scheme 10d we show the distortion energy of the 'bare σ-frame' where all p_π electrons are removed. It is apparent from the calculated ΔE_{dis} values in Scheme 10 that the distortion energy of parts b−d is significantly larger than the distortion energy of the ground state, Scheme 10a. *It follows, therefore, that when resonance and π-bonding are turned off, the energy required to distort the 6-fold hexagon into a D_{3h} structure increases significantly compared with the ground state where both resonance and π-bonding are present.* The conclusion applies also to allyl radical which is not shown in the scheme, and the reader is referred to the original literature.[2,5,6,118]

The second type of computational experiment is concerned with the σ−π-energy partitions of the ground state, and the results are given in Scheme 11 for benzene, allyl radical, and cyclobutadiene, all at the π-CI/6-31G level (MRMP). Since the total nuclear repulsion energy between carbon atoms is held constant during the distortion, the resulting distortion energy given above the arrow is an electronic energy change which can be partitioned into σ- and π-contributions.[2,5,6,118] Inspection of the data in Scheme 11 shows that ΔE_π is a negative quantity, and as such, all π-components behave as distortive transition states. In contrast, all the ΔE_σ quantities are positive, showing that the σ-frames prefer geometries with uniform C−C distances. Scheme 12 shows the results of a slightly modified energy partitioning method for the three allylic species by Gobbi and Frenking,[93] where the same picture of a σ−π-opposition emerges.

2. The σ-Frame: Why Does It Behave the Way It Does?

The behavior of the π-electrons is explicable by the VB diagram model (Figure 2b). The energy expense required to bring the Kekulé structures into resonance at the crossing point is sufficiently large to create a distortive species analogous to a transition state of a chemical reaction. However, what is the root of the different behavior of the σ-frame which itself is highly delocalized?[121−124] Despite the highly delocalized nature of σ-electrons, the energy of the σ-frame is known to behave in an additive manner as a collection of localized single bonds, each having its own "independent" bond energy contribution. Each carbon atom in a planar σ-frame utilizes three of its valence atomic orbitals for bonding, and while the resulting wave function is highly delocalized, it can be transformed to a set of localized bond functions directed at the ligand atoms of each carbon. It is clear that such a set of equivalent C−C bonds would always prefer a symmetric structure with identical bond lengths.[2,4,5,125]

A simple proof of principle[13,16] which has been used by most workers is to represent the energy of a σ_{CC} bond as a quadratic function of the C−C distance, r_i, as in eq 2 where k_σ is the stretching force constant.

$$E_\sigma = \Sigma_i 0.5 k_\sigma r_i^2 \tag{2}$$

Equation 2 is not a poor representation of the energy function because it can be shown that a Morse potential in real distances assumes a simple quadratic form if one uses a dimensionless bond order coordinate.[126a] In any event, minimization of this function leads to the conclusion that the minimum energy is attained when all bonds have the same length. Furthermore, a bond alternating distortion that lengthens and shortens a pair of adjacent bonds by ±Δr can be shown to raise the σ-energy as in eq 3a.

$$\Delta E_\sigma = n_p E_p;\ E_p = k_\sigma[\Delta r]^2 \tag{3a}$$

$$E_p \sim 5 \text{ kcal/mol for } \Delta r = \pm 0.06 \text{ Å} \tag{3b}$$

where n_p is the number of adjacent pairs and E_p is the pair distortion energy. In this sense, it is instructive to inspect the ΔE_σ quantities in Schemes 11 and 12. It is seen that the allylic species which have one pair of adjacent σ-bonds have a σ-distortion energy of approximately 5 kcal/mol. For benzene, with three adjacent pairs, the ΔE_σ quantity is approximately three times the pair energy for allyl. In cyclobutadiene, with two pairs, the ΔE_σ quantity is somewhat less than twice the pair distortion energy, presumably due to the severe angle strain which modifies the σ-force constant (eq 3b) compared with a strain-free case. All in all, the σ-energy behaves as a collection of localized C−C bonds which resist bond alternation and eq 3b can be used as an approximate estimate of this resistance.[126b]

3. The Geometries of Conjugated Systems–A Balance of σ–π Opposition

The actual geometry of a conjugated system is determined by a fine balance of the distortive π-component and the symmetrizing force of the σ-frame.[1,2,4] This σ−π-balance and opposition is summarized schematically in Figure 4. In allylic species and in benzene, the σ-frames win and the species remain symmetric, with equal C−C distances and with delocalized π-electrons. In contrast, in cyclobutadiene the σ-resistance is insufficient and the structure relaxes to a rectangular geometry.

D. Evidence of π-Distortivity Deduced from Other Methods

The π-distortivity has been proven by a variety of methods which we shall mention in brief, while a more detailed treatment can be found elsewhere.[4−9,118] These methods fall into a few categories: (i) Hückel methods; (ii) semiempirical Dewar π-type methods (PPP with σ-compression energy); (iii) all-electron semiempirical and ab initio methods; (iv) indirect methods, e.g., Walsh diagram arguments.

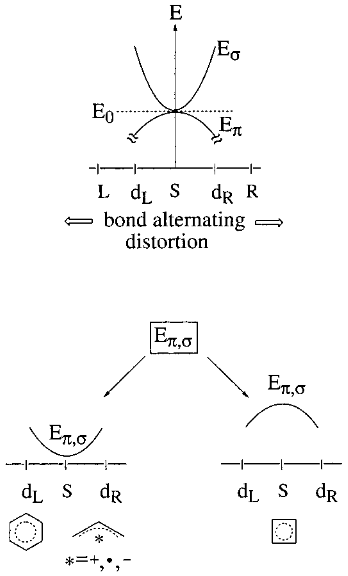
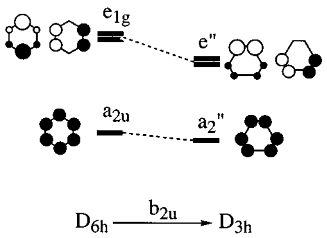


Figure 4. The σ- and π-curves for a bond-delocalized species. The d_R and d_L on the bond alternating coordinate represent small distortions (smaller than the extremes *R* and *L*) permitted by the σ-frame. The bottom two diagrams show the total energy curves for archetypal species.

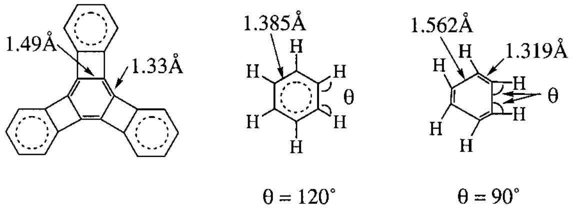
Hückel methods which utilize a variable β-parameter date back to the 1950s and have already been mentioned in Section II.C. A few new treatments appeared more recently. Thus, Heilbronner[13] and Mulder[15] have shown that the Hückel π-electron energy is invariably lowered if the Hückel β-parameter is allowed to assume alternating values, $\beta(1 + \delta)$ and $\beta(1 - \delta)$, and they concluded that the σ-frame must be responsible for the observed symmetric geometries of allyl and benzene. A similar conclusion was reached by Nakajima and Kataoka[17] based on the same approach. More recently, Buk[10] used σ-compression energies calibrated to the ab initio values of the QC state method[6] and Hückel π-electron theory. He applied the methods to aromatic and antiaromatic [*n*]-annulenes and reached the same conclusion that π-components are distortive and this distortivity is opposed by the σ-frame. Glukhovtsev et al.[14] applied Hückel theory to benzene and noted that the π-energy is distortive. They point out, however, that contrary to the total π-energy which prefers to distort, the topological resonance energy of benzene favors a symmetric geometry. As we shall see later, the topological resonance energy is simply the quantum mechanical resonance energy, B_0, in the VB diagram model (Figure 2).

Semiempirical methods which involve an explicit quantum mechanical treatment of the π-electrons by PPP-type theories, coupled with a classical σ-compression energy, have been employed by Paldus et al. to investigate the general question of Peierls distortion in polyenes and in large [*n*]-annulenes.[22−25] The results show that the π-energy tends to be

Scheme 13. Walsh Diagram for the π-MOs of Benzene along the b_{2u} Mode



Scheme 14. Starphenylene, 5, and the Distortion of Benzene 6 → 7 Used To Understand (Ref 129) Bond Alternation in 5



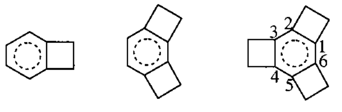
5 **6** **7**

lowered along a bond alternating distortion and is opposed by the σ-compression energy. Paldus and Chin[22] concluded that the π-energy behaves like the total energy of H_n cycles. Jenneskens et al.[11] applied a Dewar parametrized PPP method to benzene and supported the same conclusion. Their ΔE_π and ΔE_σ values are in fact very close to the values deduced from our ab initio calculations in Scheme 11.

Jug and Köster[7−9] devised an energy partitioning scheme within semiempirical all-electron theory (the SINDO1 method) in a manner that enables partitioning of the σ−π-electron repulsion as well as the nuclear repulsion equally between the σ- and π-components. With this method they were able to extend the treatment to many systems, including odd-membered rings, in a general manner. Their treatment supports the π-distortivity scenario in delocalized species. The only species where the π-energy is not distortive and prefers a symmetric geometry was found by Jug and Köster[7−9] to be the $C_4H_4^{2+}$ species. Finally, Bernardi et al.[127] deduced the π-distortivity in benzene from a CASSCF calculation.

Another way to deduce the opposing effects of σ- and π-electrons involves a Walsh diagram type approach which allows one to look separately at the π- and σ-orbital energies along a given distortion. While this is quite risky, since orbital energies and total energies are not the same, it is nevertheless important to discuss this approach. Thus, Janoschek[128] used for benzene a Walsh diagram along the b_{2u} mode, Scheme 13, and showed that the sum of π-orbital energies is lowered by the distortion and that it is the σ-MO block energy that rises during the distortion and forces a symmetric D_{6h} hexagon. Stanger and Vollhardt[129] hypothesized that the bond-alternated structure of starphenylene,[130] **5** in Scheme 14, is determined by the angular strain on the σ-frame while the π-electrons follow the trend imposed by the σ-behavior. To test their hypothesis, they applied angular distortion on the HCC angles of benzene, **6** → **7**, Scheme 14, and optimized the structure under the angular constraints. The strained benzene was found to undergo bond alternation (**7**) in a manner similar to starphenylene. Following the orbital energies, the authors concluded that the π-orbital energy of benzene is lowered while the σ-orbital energy is raised during the distortion.

Scheme 15. Cyclobuta-Annelated Benzene Derivatives, 8-10, Studied in Ref 131 for understanding the Origins of Bond Alternation[a]



8 **9** **10**

$$\Delta R = (R_{12} + R_{34} + R_{56}) - (R_{23} + R_{45} + R_{61})$$

[a] ΔR quantifies the degree of bond alternation.

Ou and Chu[131] considered the cyclobuta-annealated benzene derivatives, **8**−**10**, in Scheme 15, relative to the corresponding methylated derivatives. They defined ΔR as a bond-alternation function and found that all the test systems **8**−**10** exhibit significantly larger bond alternation relative to the reference methylated systems. Along with the increased bond alternation, it was observed that the π-energies of the test systems are lowered with respect to the reference systems. This last trend was substantiated by the corresponding ionization potential data from photoelectron spectroscopy of the molecules. Thus, the bond alternating distortion was found to endow the test molecules, **8**−**10**, with higher π-ionization potentials compared with the reference molecules, in accord with the conclusion from the energy lowering of the π-orbitals.

A related but at the same time more rigorous approach was taken by Gobbi et al.,[12] who sought a method that does not rely on energy partition. They used a force constant formalism to investigate the σ- and π-tendencies along the bond alternating modes of benzene and the allylic species. They derived the conditions under which the second derivative of the energy can be expressed as a sum of the corresponding derivatives of the SCF orbital energies, ϵ_i, eq 4

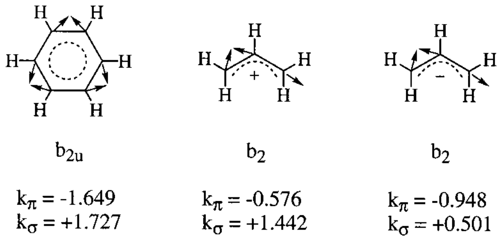
$$\partial^2 E/\partial^2 Q_k = \Sigma_i[\partial^2 \epsilon_i/\partial^2 Q_k] \tag{4}$$

It turns out that the localizing distortions ($Q_k = b_{2u}$ for benzene and b_2 for allyl) fulfill these conditions, and therefore, one is able to separate the π- and σ-force constants for these modes as follows

$$\partial^2 E/\partial^2 Q_k = \Sigma_{i,\pi}[\partial^2 \epsilon_{i,\pi}/\partial^2 Q_k] + \Sigma_{i,\sigma}[\partial^2 \epsilon_{i,\sigma}/\partial^2 Q_k] = k_\pi + k_\sigma \tag{5}$$

Scheme 16 shows the results for benzene and the allylic systems. It is seen that in all cases the π-force constant is negative while the σ-force constant is positive. This is an extremely important conclusion since it is connected to physical observables discussed later in this review. Note that Gobbi et al.[12] make it very clear that eq 5 holds for bond localizing distortions but cannot be applied to arbitrary distortions which do not meet the condition of eq 4.

Scheme 16. π- and σ-Force Constants (hartree/Å^2) along the Bond Alternating Modes (Ref 12)



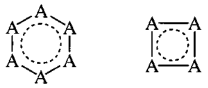
However, the idea of π-distortivity also encountered criticism. Replies to the criticism have been given.[6,118,132,133] The technical aspects of the criticism are discussed in detail elsewhere,[118] and here we focus on the principal nontechnical issues. The major criticism expressed by a few researchers[18,19,134,135] concerns the choice of the distortion coordinate. For example, it has been argued that π-distortivity depends on the choice of the distortion, and a "more realistic" distortion than the b_{2u} mode used by us[133] would lead to the conclusion that π-electronic energy prefers a uniform delocalized structure while the σ-frame is indifferent to the distortion. This argument overlooks an important point, namely, that the π-electron component behaves like a transition state. As such it has *one and only one* mode along which its energy descends while along all other modes the energy increases.[132] Therefore, the question of a more appropriate or a less appropriate distortion is entirely invalid. *To prove π-distortivity, one needs to find one mode which lowers the π-energy. This happens to be the localizing distortion of the respective molecules (b_{2u} for benzene and b_2 for allyl), all other modes or combinations thereof are immaterial for this question.*

Another critical view by Glendening et al.[134] was based on computational findings that a single Kekulé structure of, e.g., benzene prefers a bond-alternated structure while the resonance of the two structures restores the symmetric geometry (a similar conclusion was reached by Glukhovtsev et al.[14] based on Hückel calculation of the topological resonance energy of benzene). It must be remembered, however, *that it is the total π-energy that exhibits the distortivity and not the resonance energy component which by itself acts as a symmetrizing factor*.[4,6] As shown in Section IV, the π-distortivity and the resonance energy are two coexisting properties of the π-electrons. Thus, the rather evident result of comparing a single Kekulé structure with the resonating two Kekulé species does not at all counter the π-distortivity scenario.

E. π-Distortivity in Analogues of Benzene and Cyclobutadiene

To establish trends of the π-distortivity in systems which involve both π- and σ-electrons, we applied the σ−π-partition method to delocalized hexagons (**11**) and squares (**12**), in Scheme 17. Even though some of these systems are unrealistic (e.g., N_4), others have different geometries than those used in Scheme 17 (e.g., Si_4H_4,[136] P_4[137]), and others are nonplanar (Si_6H_6,[138] P_6[103d,139,140−142]), the investigation of these species is worthwhile because they are isoelectronic to benzene and cyclobutadiene and may therefore provide insight into the factors which govern the π-distortivity in analogous systems made from different atoms. Tables 1 and 2 show the ΔE_π and ΔE_σ data.[2,4,143] It is apparent that in all cases the π-component is distortive. Furthermore, the π-distortivity is related to the magnitude of the $^3\pi\pi^*$ excitation (ΔE_{ST}) of a short π-bond; the larger the excitation the more distortive the delocalized π-component, be it of the aromatic or antiaromatic variety. This trend follows the predictions of the VB correlation diagram in Figure 2 and establishes the ΔE_{ST} quantity as a reliable predictor of the trend in π-distortivity.

Scheme 17. Analogous Species to Benzene (11) and Square Cyclobutadiene (12)



11, D_{6h} **12**, D_{4h}

A = CH, SiH, N, P

Table 1. π- and σ- Distortion Energies (ΔE_π, ΔE_σ) of Analogues of Benzene, and $^3\pi\pi^*$ Excitation Energies of a π-Bond (ΔE_{ST})[a,b]

	N_6	C_6H_6	P_6	Si_6H_6
ΔE_σ	+13.7	+16.3	+3.8	+5.3
ΔE_π	−13.3	−9.1	−2.8	−2.1
ΔE_{ST}	108	99	47	40

[a] The distortion is ±0.06 Å with appropriate amendments to keep constant nuclear repulsion. All energies are in kcal/mol at the MRMP(π-CI)/6-31G level. [b] ΔE_{ST} values for X_2 (X = N, CH, SiH) at the MRMP(π-CI)/6-31G//HF/3-21G level. For X = P the geometry was optimized with 6-31G*. From ref 143.

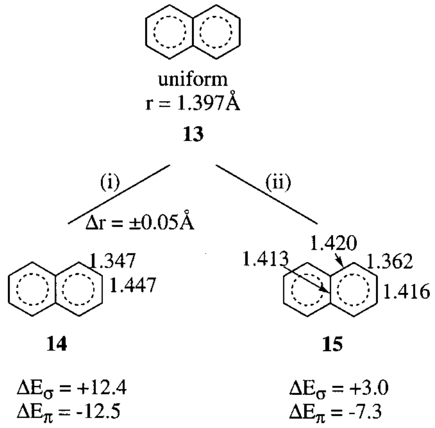
Table 2. π- and σ- Distortion Energies (ΔE_π, ΔE_σ) of Analogues of Cyclobutadiene, and $^3\pi\pi^*$ Excitation Energies of a π-Bond (ΔE_{ST})[a,b]

	N_4	C_4H_4[c]	P_4[d]	Si_4H_4
ΔE_σ	+9.2	+7.6 (+7.0)[c]	+3.7(+2.9)[d]	+2.7
ΔE_π	−14.7	−11.0 (−10.4)[c]	−3.6(−2.6)[d]	−2.1
ΔE_{ST}	108	99	47	40

[a] The distortion is ±0.06 Å with appropriate amendments to keep constant nuclear repulsion. All energies are in kcal/mol at the MRMP(π-CI)/6-31G level. All ΔE_σ values out of parentheses were obtained with the quintet HS species (see e.g., Scheme 10). [b] See comment b in Table 1. [c] The values in parentheses in the case of C_4H_4 are obtained by energy partition in the singlet state species.[5] [d] Out of parentheses are the distortion energies calculated with the 6-31G* basis set.

Another trend which is apparent from the data is that the final geometry is obtained as a fine balance between the σ-resistance to distortion and the π-distortivity. Thus, hexagonal benzene is a D_{6h} hexagon because its σ-resistance exceeds the π-distortivity by a significant margin. In contrast, N_6 is almost indifferent to the distortion because its π-component is more distortive while its σ-frame is less resistant to the distortion than those of benzene. No doubt, the σ-lone pair repulsion affects the force constants of the σ-frame in N_6. Similarly, while cyclobutadiene and N_4 are clearly distortive as a whole, the P_4 and Si_4H_4 squares are pretty indifferent to distortion. This is because the π-distortivity gets very small and the

Scheme 18. Distortion Energies, in kcal/mol (Ref 6), of Naphthalene with a Uniform C−C Distance along the b_{2u} Mode (i) and along the Mode that Leads to the Optimized (HF/6-31G) Structure (ii)

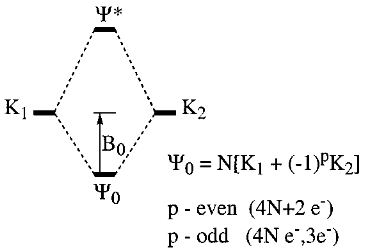


σ-resistance becomes competitive.

The fine balance between π-distortivity and σ-resistance can be further appreciated by the data in Scheme 18 for naphthalene (**15** is the HF/6-31G optimized structure).[6] This molecule, **15**, has a bond alternating structure, but the alternating pattern is not uniform. Since *trans*- and *cis*-decaline, which possess the same σ-frame, have virtually uniform C−C distances, it is clear that the π-component distorts the naphthalene framework. In this case, unlike benzene, the bond alternation mode is not a pure b_{2u} distortion but must be a compromise between the three available Kekulé structures (see $K_{1,2}$ and K_c later in Scheme 36), one of which is totally symmetric and the other two account for the π-resonance along the perimeter of the molecule. The final distortion is a consequence of the π- and σ-force constants for the distortion modes i and ii in Scheme 18. Starting from a symmetric structure (**13**), we find (by application of the QC state method[6]) that distortion (mode i) along a pure b_{2u} mode, leading to a bond-alternated structure **14**, has a significant σ-resistance (for the same distortion of 0.05 Å in benzene, $\Delta E_\sigma(\mathrm{QC}) = +7.5$ kcal/mol) and an almost equal π-distortivity. In contrast, the distortion to the optimized structure **15** (mode ii) involves a much smaller σ-resistance and a comparatively larger π-distortivity. Thus, wherever possible, the molecule finds a path of small σ-resistance whereby its π-distortivity can manifest itself.

Clearly, as already summarized in Figure 4, benzene and allyl radical are quite special in having a combination of strong σ-resistance which overcomes a moderately distortive π-component. On the contrary, in cyclobutadiene the fine balance is tipped in favor of the π-distortivity. However, this balance is fragile and can be tampered with. Even substituted cyclobutadienes have been considered at times to be effectively square.[144−146] As we shall see later, manipulation of the σ-resistance by proper substitution of benzene enables its π-distortivity to become manifest. Heilbronner's expression[13] of the fragility of the π−σ-balance for benzene and allyl radical is perhaps a most appropriate one: *"If by an act of God all the sp^2−sp^2 σ-bond force constants were reduced to half their values..., then benzene would have the [Kekulé] structure **2A** or **2B** and allyl radical the [Kekulé] structure **3A** or **3B**."*

Scheme 19. A VB Mixing Diagram Showing the Splitting of the Kekulé Structures into the Twin States, Ψ_0 and Ψ^*[a]



[a] B_0 Is the vertical resonance energy.

IV. Resonance Energies of Delocalized Species

The topic of resonance energy dates back to the treatments of benzene by Hückel and Pauling and Wheland.[61,62,65,70] The amount of literature devoted to this topic is vast, and the reader may consult a few review sources.[27,76,86,147] The monograph by Minkin et al.[27] summarizes in one chapter the types of models of resonance energy which have been used and are acceptable in contemporary research. We shall focus in this section on the resonance energy quantity as defined by VB theory. We shall then relate this resonance energy quantity to the widely accepted definition of resonance energy (Dewar resonance energy[27]) and show how the π-distortivity and the resonance energy stabilization coexist in harmony.

A. Vertical Resonance Energies of Delocalized Species

Delocalized species generally enjoy stabilization relative to their localized Kekulé (or Lewis) structures at a given geometry. This stabilization is measured by the vertical resonance energy which in Figure 2b,c is denoted as B_0, where the subscript indicates that this is the quantity at the symmetric geometry (this term will be used hereafter to describe the geometry with uniform bond distances). Previously we termed this quantity[5] the quantum mechanical resonance energy. For convenience of the discussion, Scheme 19 depicts the vertical resonance interaction at the crossing point of Figure 2 as a VB mixing diagram of the participating Kekulé structures.

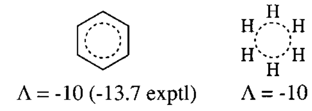
From Figure 2 parts b and c, it is clear that B_0 is an intrinsic property of delocalized states, whether they are stable ones or transition states which are unstable toward a localizing distortion. Table 3 demonstrates precisely this feature by showing B_0 values for a few species, among which quite a few transition states.[111,117,148−158] Most of the B_0 values are calculated with VB methods of different varieties, while some, entries 9−13, are calculated also by means of MO methods (with or without CI) using Kollmar's method.[157] All species are seen to have substantial vertical resonance energies. In fact, even square cyclobutadiene and octagonal cyclooctatetraene have appreciable vertical resonance energies.

Table 3. Vertical Resonance Energies (B_0) for Delocalized Species

		B_0 values, kcal/mol			
entry	species	VB value	ref	MO(CI) value	ref
1	Li_3	7^a	117		
2	H_3	43^a	117		
3	FHF	43^a	112		
4	CH_3-H-CH_3	41^a	111		
5	C_3H_5(allyl radical)	$10-14^b$	148		
5a	C_3H_5(allyl radical)	$23^c(20)^c$	$111^d(149)$		
6	H_3^-	28^e	150		
7	$(X-CH_3-X)^-$	20 ± 3^e	110(a) 151		
8	$C_3H_5^-$ (allyl anion)	50^c	149		
9	H_6			119^g	5
10	C_6H_6(benzene)	$65^c(62^f)$ $[74^a]$	$111^d(127)[153]$	$85^g(112^h)$	2(154)
11	C_6H_6(benzene); *exptl*	55^1 $(65)^j$	155(156)		
12	N_6(hexazine)			103^g	5
13	C_4H_4(cyclobutadiene)	$21^b(22^c)[15^f]$	$158(111)^d[127]$	30^g	5
14	C_8H_8(cyclooctatetraene)	$49^{c,k}$	111^d		

[a] Using classical VB with localized AOs and a mixture of covalent and ionic structures. [b] Using RGVB (semidelocalized AOs). [c] Using bond-distorted orbitals where semidelocalization is permitted only to the centers that are formally bonded in the Kekulé structure. This method leads to more realistic B_0 values than those produced by removing the constraints over the sites of semidelocalization. [d] B_0 values from ref 111 are variational VBSCF/6-31G quantities (i.e., the energies of the delocalized state as well as of the single structure are variationally determined). [e] Using extended Hückel, calibrated to reproduce VB results as in *a*. [f] Using CASSCF projection into the space of Kekulé structures. [g] Using an input of a localized guess (following ref 157) and getting B_0 as $B_0 = E(\text{guess}) - E(\text{SCF})$. [h] Using the same method as in *g*, but with SINDO1 and with guess optimization. [i] Experimental value, estimated from the transition energy to the excited state; $B_0 = \Delta E(S_0 - S_1)/2$. [j] Experimental value, estimated by use of thermochemistry and empirical force constants. [k] Planar structure with $r_{C=C} = 1.4016$ Å from ref 164a.

Scheme 20. Diamagnetic Exaltations, Λ (in ppm cgs units), for Benzene and H_6 ($R_{HH} = 1.4$ Å)[a]



16 **17**

[a] Taken from ref 6 (see also ref 162).

It is further seen that unstable transition states such as H_6 have large B_0, whereas stable delocalized species such as Li_3 have a small one. There is nothing unusual about benzene which possesses a vertical resonance energy somewhat smaller than H_6 and N_6, which are unstable with respect to a localizing distortion. The vertical resonance energy does not indicate the distortivity of the species (or stability toward a localizing distortion). We can conclude that *the vertical resonance energy is a property that coexists with the π-distortivity of the delocalized state, provided the species does not fall apart* like H_6, but can be held together by the σ-frame.

1. Dual Property of Delocalized π-Components

To further appreciate this view, we present in Scheme 20 the computed Λ quantity of H_6 and benzene.[6] This quantity is the difference between the diamagnetic susceptibilities (χ) of the molecule and a suitable localized reference, defined in eq 6

$$\Lambda = \chi_{\text{del}} - \chi_{\text{loc}}; \chi < 0 \qquad (6)$$

As shown by Pascal,[64] Lonsdale,[63] and Dauben,[159] the Λ quantity for aromatic molecules is exalted, namely, the delocalized molecule is more diamagnetic than the localized reference; Λ is a negative quantity. The exalted diamagnetism was interpreted to result from the ring currents carried by the delocalized electrons which circulate under the influence of the external magnetic field in orbits with radii that are determined by the path of delocalization.[50] Aihara[160] used graph theory to show that the exalted Λ quantity is associated directly with the cyclic delocalization and is correlated with the cyclic resonance energy (topological resonance energy), which itself is precisely analogous to the vertical resonance energy quantity, B_0. Schleyer et al.[161] established that the exalted Λ quantity is a probe of 'aromatic delocalization'. Subsequently, Jiao and Schleyer[162] demonstrated that highly unstable transition states for cycloadditions which involve $4N + 2$ electrons, e.g., the trimerization of acetylene, etc., possess magnetic properties like benzene. A similar observation has been made by Galbraith et al.[152] for the transition state of the Bergman cyclization. As may be seen from Scheme 20, the highly unstable transition state, H_6, and the stable molecule, benzene, have equally exalted diamagnetic susceptibilities. Thus, a magnetic property which corresponds to 'aromatic' species is not synonymous with absolute stability.

Scheme 21. NICS (π-only) and Λ Values (Ref 141) for Benzene and Its Analogs

	C_6H_6	Si_6H_6	N_6
Λ	-13.9	-32.8	–
$NICS_\pi$	-16.8	-14.1	-15.9

Another index of delocalization, devised and widely applied by Schleyer et al.,[163] is the nuclear-independent chemical shielding (NICS) value. When calculated above the ring, this value corresponds to the π-contribution which is a significantly negative quantity for situations with 'aromatic delocalization'. Scheme 21 shows the Λ and $NICS_\pi$ values computed by Schleyer et al.[141] for benzene, hexasilabenzene, and hexazine. The three species are seen to possess equally aromatic electron sextets, as indeed anticipated from the appreciable vertical resonance ener-

Table 4. Vertical Resonance Energies (B_0) for Aromatic and Antiaromatic Species[a]

R	B_0, kcal/mol R_6	 R_4
N	103	45
CH	85	30
P	44	25
SiH	42	18

[a] HF/6-31G calculations from ref 2 and 143. Using the method in ref 157.

gies of these species in Table 3 (see also Table 4). We recall that N_6 is a nonexistent species with a highly distortive π-component. Thus, the necessary condition for aromaticity is only the capability of the species to enforce π-delocalization. For benzene and allyl, this is the role of the σ-frame that keeps the structure intact and in the symmetric geometry.

2. Vertical Resonance Energies of Aromatic and Antiaromatic Species

Table 4 shows B_0 values calculated for hexagons and squares using Kollmar's method.[157] Comparison of entries 1−4 to entries 5−8 reveals that the benzene analogues, with the $4N + 2$ electrons, have considerably larger B_0 values than the $4N$ analogues of square cyclobutadiene. This trend is related to the accepted view that cyclic delocalization of $4N + 2$ electrons possesses a higher resonance energy than cyclic delocalization of $4N$ electrons.

There is, however, another feature of B_0 for n-electron−n-center species ($n = 4N$, $4N + 2$) that is different in $4N$ compared with $4N + 2$ situations. Thus, in the $4N + 2$ situations the resonance interaction between the two Kekulé structures is mainly due to the monoelectronic part of the Hamiltonian. On the other hand, in the $4N$ situations, it is the bielectronic term of the Hamiltonian that dominates the resonance interaction of the two Kekulé structures.[113] This means that *delocalization of the 4N + 2 electrons is supported by overlap of the atomic orbitals, while for 4N electrons the resonance energy is due to the lowering of the Coulomb correlation energy.*[164] *The latter factor in fact keeps the electrons apart*, even if at the same time the mixing of the Kekulé structures scrambles the *4N* electron density uniformly over the ring (for a more technical explanation, consult ref 164b). A detailed VB analysis[164a] of the problem, which is beyond the scope of the present review, shows that this difference in the mode of delocalization in $4N$ vs $4N + 2$ cases is manifested in the $4N$ cases *as a discontinuity of the electron flow in the ring*, and this may be in the roots of the striking difference in the magnetic properties of the two classes. A related explanation was given long ago by Goddard, who classified allowed and forbidden reactions in terms of the orbital phase continuity principle.[165] According to this principle, aromatic situations would be typified by a phase continuity between the orbitals of the interchanging Kekulé structures, whereas in antiaromatic cases there will be a discontinuity in the orbital phases.

The largest difference in vertical resonance energy occurs for aromatic and antiaromatic species with an odd number of atoms and mixed-valence situations, e.g., $C_3H_3^+$ (D_{3h}) vs $C_3H_3^-$ (D_{3h}), $C_5H_5^-$ (D_{5h}) vs $C_5H_5^+$ (D_{5h}), etc. In these cases, the species which possess $4N$ electrons have an electronic state which belongs to degenerate representations of the corresponding point groups. A VB treatment shows[113,166] that the energy of this degenerate state remains as that of a single Kekulé structure due to antibonding interactions in the VB wave function, and hence, their vertical resonance energy is zero, $B_0 = 0$. In contrast, the corresponding molecules with $4N + 2$ electrons have appreciable resonance energies.

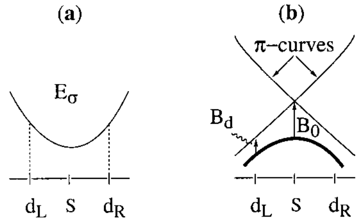


Figure 5. The σ-energy curve (a) and the π-avoided crossing VB diagram (b) in conjugated n-electron−n-center species. Note that in the narrow range of the permitted distortion, $d_R \leftrightarrow d_L$, the vertical resonance energy is significant.

The corresponding radicals with $4N + 1$ and/or $4N + 3$ electrons possess also a degenerate electronic state with a zero vertical resonance energy.[113,166] In fact, the odd-nonalternant rings with $4N$, $4N + 1$, and $4N + 3$ electrons are truly "antiaromatic", even though not all of them are referred to as such. We shall not dwell on these cases anymore, and hereafter we shall focus on n-electron−n-center systems ($n = 4N$, $4N + 2$ electrons).

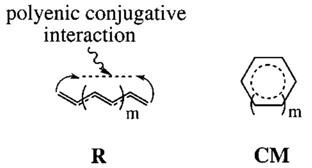
B. Thermochemical Properties of Delocalized Species: Their Relation to Vertical Resonance Energies and π-Distortivity

Benzene and other aromatics alike are stable molecules, while cyclobutadiene and other antiaromatic molecules are unstable molecules.[27,76] Similarly, allylic species are stable intermediates and possess significant rotational barriers. It may appear as a contradiction that, for example, the π-component of benzene can be distortive but it still endows the molecule with special stability or that the distortive π-component of allyl radical can lead to a rotational barrier. We would like to show in this section that these stability *patterns derive from the vertical resonance energy which is expressed as a special stability because for most experimental probes (including substitution reactions) the σ-frame restricts the molecule to small distortion*[167] in which the vertical resonance energy is still appreciable, as shown schematically in Figure 5.

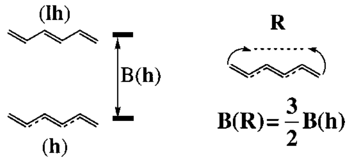
1. Resonance Energies in Benzene and Its π-Distortivity

Dewar et al.[83] showed that the energy of linear polyenes is an additive quantity of bond energy increments. This enabled Dewar to quantify the thermochemical stability or instability of a cyclic molecule relative to a reference molecule. The reference molecule **R** for a conjugated cyclic molecule

Scheme 22. Definition of a Reference Structure, R, Which Is a π-Isoconjugate to a Cyclic Molecule (CM) but with a Degree of Conjugation of an Open-Chain Polyene



Scheme 23. Vertical Resonance Energy of the Reference Structure, B(R), for Benzene and Its Relation to the Vertical Energy of Hexatriene, B(h)



(**CM**) is shown in Scheme 22, and it is seen to involve cyclic conjugation, but all the interactions between the π-bond units have a polyenic character. The relative energy of the two structures, as in eq 7, is defined as the Dewar resonance energy (DRE) of the cyclic molecule.

$$\mathrm{DRE}(\mathbf{CM}) = \mathrm{E}(\mathbf{R}) - \mathrm{E}(\mathbf{CM}) \qquad (7)$$

The DRE is accepted now, albeit with some modifications, as the standard measure of the thermochemical stability or instability of the cyclic molecule.[27,168] DREs are determined routinely by use of homodesmic processes, which provide reproducible estimates, but are indirect measurements of the DRE quantity. Since the polyene's conjugative interactions are additive, it is possible to use a VB method[111] or Kollmar's MO method[157] to derive the DRE directly from the vertical π-resonance energies, as exemplified in Scheme 23. Thus, to construct a reference molecule for benzene, one determines the vertical resonance energy of hexatriene, B(**h**), as the difference between the ground state of hexatriene (**h**) and the strictly localized structure (**lh**). Since B(**h**) is composed of two conjugative interactions, the reference molecule, which is a hexatriene tied unto itself by an additional conjugative interaction, will have a vertical resonance energy given by 1.5 B(**h**). Alternatively, the vertical resonance energy of the reference structure will be three times that of butadiene, which has a single conjugative interaction.

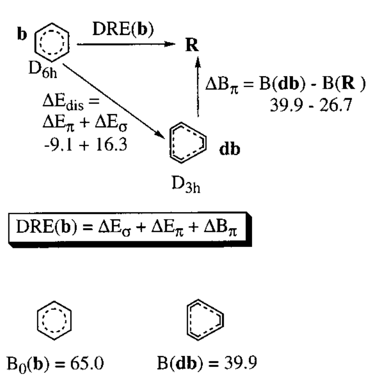


Figure 6. Hess cycle used to relate the Dewar resonance energy of benzene, DRE(**b**), to the vertical resonance energy, B_0. Vertical resonance energy values for benzene and distorted benzene (calculated in this study[111]) are shown below the cycle. All energies are given in kcal/mol.

Figure 6 shows a Hess cycle which links benzene (**b**) to its reference molecule (**R**), such that the energies of the steps sum up to the Dewar resonance energy of benzene, DRE(**b**). At the VBSCF/6-31G level,[111] the DRE(**b**) value is 20.4 kcal/mol, which is within 1 kcal/mol of the experimentally derived value[27] based on heats of formation of benzene and cyclohexatriene (the latter value is determined from an additivity scheme). Our older value in the original literature,[5] DRE(**b**) = 31 kcal/mol, was determined with the Kollmar method,[157] which is less accurate than the VBSCF method[111] used here. Since, our VB-derived DRE(**b**) value matches the unanimously accepted value,[27] we can turn back to Figure 6 to see the link between DRE(**b**) and the vertical resonance energy $B_0(\mathbf{b})$. Thus, initially benzene is distorted to give the distorted benzene species, **db**, which possesses a vertical resonance energy B(**db**). Subsequently, the conjugation of **db** is allowed to assume its value B(**R**) in the reference structure. Since the $\Delta E_{\mathrm{dis}}(\mathbf{b})$ quantity is a sum of the opposing σ- and π-component energies, the quantity is intrinsically small and the thermochemical stability of benzene is dominated by the more favorable vertical resonance energy of distorted benzene compared with the reference molecule. Indeed, a large resonance energy for distorted benzene is computed by a variety of methods, e.g., by direct VB calculations of Mo et al.[153] and here[111] using an improved Kollmar method by Jug et al.,[154] Kollmar's method with NBOs[134], etc. Furthermore, a simple testimony of the large B(**db**) is provided by calculated[169,170] magnetic properties, e.g., Λ, of distorted benzene which are found to be very similar to those of benzene. The same is observed experimentally for the distorted Siegel molecule,[36,171] which exhibits NMR and UV properties characteristic of delocalized benzene. Figure 6 shows side by side the B(**db**) and $B_0(\mathbf{b})$ quantities, and it is apparent that distorted benzene maintains a degree of delocalization which borrows its largeness from the large vertical resonance energy of D_{6h} benzene, B_0(**b**).

Why does distorted benzene possess such a large resonance energy? Because it is restricted by its σ-frame to geometries which are very close to the perfect hexagon, as discussed by reference to Figure 5. In this neighborhood, the resonance energy is significant, reflecting the aromatic mode of delocalization of benzene. It is for this reason that D_{6h} benzene can have a distortive π-component but at the same time behave as a stable species, lower in energy than a corresponding cyclic polyene. Indeed, some experiments, such as heats of hydrogenation, reactivity, UV spectroscopy, magnetism, etc., derive from the vertical resonance energy of benzene, while other experiments, such as the IR frequency of the b_{2u} mode,[99] probe the π-distortivity. We will see more of these latter experiments in the next section. In contrast, hexagonal H_6 and N_6, which possess equally large if not larger vertical resonance energies than

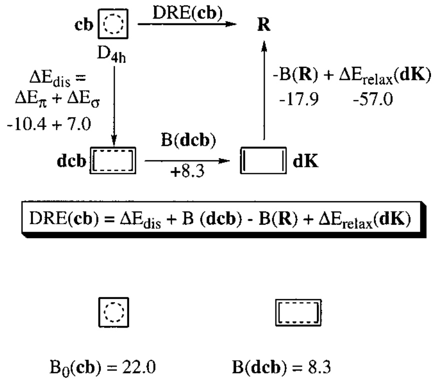


Figure 7. Hess cycle used to relate the Dewar resonance energy of cyclobutadiene, DRE(**cb**), to the vertical resonance energy, B_0 (calculated in this study[111]). All energies are given in kcal/mol.

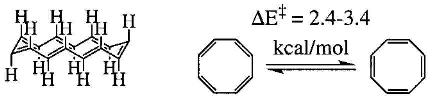
benzene, lack a buttressing σ-frame, as in H_6, or have a fragile σ-frame, as in N_6, and cannot present us with this interesting duality.

2. Resonance Energies in Cyclobutadiene and Its Antiaromaticity

Figure 7 shows a Hess cycle which links cyclobutadiene (**cb**) to its reference molecule (**R**), such that the energies of the steps formally sum up as the Dewar resonance energy, DRE(**cb**), which is estimated to be −70.0 kcal/mol using VBSCF/6-31G computed *B* values. This value is in accord with a recent measurement of the antiaromaticity of cyclobutadiene by Deniz et al.[172] An important reason for the very large negative quantity is the large negative relaxation term, ΔE_{relax}(**dK**). Part of it is due to ring strain difference between the distorted Kekulé structure compared with the reference **R**. Using data in Deniz et al.,[172] the strain release can be estimated as −32 kcal/mol. The other part of ΔE_{relax}(**dK**), estimated as −25 kcal/mol,[173] is the π−π-overlap repulsion in the Kekulé structure (**dK**) that places the π-bonds face to face, unlike the reference molecule where this repulsive interaction is not taken into account. If these terms are left aside, the DRE(**cb**) portion which is associated only with delocalization is −13 kcal/mol. This negative value is due to the smallness of the vertical resonance energy of distorted cyclobutadiene (B(**dcb**) = 8.3 kcal/mol) in comparison with the reference structure (B(**R**) = 17.9 kcal/mol).

In contrast with benzene where the resonance energy decreases slowly upon bond alternation, in cyclobutadiene the resonance energy is reduced quite sharply by bond alternation. Thus, square cyclobutadiene has a vertical resonance energy of the same order of magnitude as that of the reference structure, while the rectangular molecule has a small residual vertical resonance energy.[111,153,158] Cyclobutadiene is a unique molecule where the factors which contribute to instability of the square structure are not associated with a lack of resonance energy or with the π-distortivity.[174] A similar explanation was given by Voter and Goddard.[158] In fact, the negative DRE(**cb**) conceals the fact that the square species has significant resonance energy. As we shall see later, the excited state of cyclobutadiene and other antiaromatic species can reveal the mixing of the two Kekulé structures.

Scheme 24. Example of [*n*]-transannulenes, 18. The Bond Shift Process in Planar Cyclooctatetraene, 19



18 **19**

3. Trends in [n]-Annulenes and Related Species

Longuet-Higgins and Salem[16] used Hückel theory to predict that aromatic C_nH_n [*n*]-annulenes ($n = 4N + 2$) will exhibit a distortion starting with $n = 34$. Semiempirical theories predict that a distortion will set in at a much smaller annulene.[22] Recent treatments by Choi and Kertesz[87] using density functional theory show that aromatic C_nH_n annulene ($n = 4N + 2$) remains delocalized, albeit with small fluctuations from bond-length uniformity, up to $n = 30$. Larger aromatic annulenes undergo an increasing bond alternation which converges to 0.06 Å. Antiaromatic annulenes ($n = 4N$), on the other hand, have bond-alternated structures from $n = 4$ throughout the series. Schleyer et al.[88] showed that a new family of [*n*]-transannulenes, **18** Scheme 24, exhibits all the characteristics expected from the $4N + 2$, $4N$ dichotomy. The antiaromatic transannulenes have bond-alternated structures and typical magnetic properties, while the aromatic ones have uniform C−C bond lengths and appropriate magnetic properties. Bond alternation in the latter starts to set in for $n = 30$.

Using the recipe for the σ-frame, in eqs 3a and 3b, we can rationalize the behavior of larger annulenes. Thus, the barrier for bond shift in planar cyclooctatetraene, **19** Scheme 24, has been measured[175−177] and is approximately 2.4−3.4 kcal/mol. With four adjacent pairs of σ-bonds, eq 3b predicts for the σ-frame of planar cyclooctatetraene $\Delta E_\sigma = +20$ kcal/mol. Consequently, the π-distortivity must exceed this value by 2.4−3.4 kcal/mol, i.e., $\Delta E_\pi = -(22-24)$ kcal/mol (which is approximately twice the value for cyclobutadiene, Scheme 11 and Table 2). For the sake of simplicity, let us assume that the next annulene $C_{10}H_{10}$ has the same value of π-distortivity, −(22−24) kcal/mol. Then with five pairs of adjacent σ-bonds, $C_{10}H_{10}$ has a larger σ-resistance, $\Delta E_\sigma = +25$ kcal/mol, and the annulene will not be distortive (recall though that the molecule is nonplanar due to angular strain and H- -H repulsion in the σ-frame).

Let us continue with this assumption that the π-components of the antiaromatic and the successive aromatic annulene (e.g., C_4 vs C_6, C_8 vs C_{10}, etc.) have the same π-distortivity. Thus, we can use the π-distortivity value calculated for cyclobutadiene (see Table 2, from −10.4 to −11.0 kcal/mol) and assume that in antiaromatic annulenes, C_nH_n ($n = 4N$), the π-distortivity is a linear function of the annulene size, *n* (its number of π-bonds is *n*/2), and that the successive aromatic annulene ($n = 4N + 2$) has precisely the same π-distortivity, as specified in eqs 8 and 9:

$$\Delta E_{\pi}\,(n = 4N) = -5.4(n/2)\ \text{kcal/mol} \qquad \Delta r = \pm 0.06\ \text{Å} \quad (8)$$

$$\Delta E_{\pi}\,(n = 4N) = \Delta E_{\pi}\,(n = 4N + 2); \quad \text{for a given } N \quad (9)$$

The σ-frame follows the recipe in eq 3 and exhibits a resistance which is simply proportional to the number of adjacent σ-bonds

$$\Delta E_{\sigma} = +5.0(n/2)\ \text{kcal/mol} \quad \Delta r = \pm 0.06\ \text{Å} \qquad (10)$$

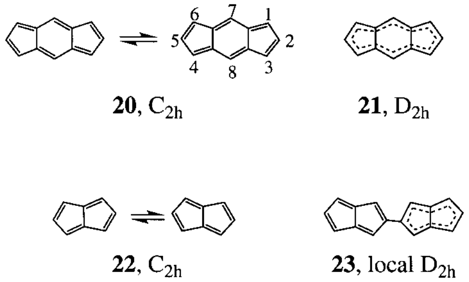
Using these values it is easy to reproduce the computed data on annulenes and see that while all antiaromatics are distortive, in aromatic annulenes distortivity sets in at $n = 30$ and increases thereafter. This π-distortivity behavior is in harmony with the fact that the aromatic species enjoy larger vertical resonance energy compared with the antiaromatic annulenes. As the annulene grows, VB as well as MO theory show that the vertical resonance energy of the aromatic species decreases and at the "polyenic asymptote" (large enough n) the vertical resonance energy of the annulene becomes polyenic and the molecule distorts. In conclusion, π-distortivity of aromatic annulenes is a property that coexists in harmony with the resonance stabilization of these species.

The fine balance of σ-resistance and π-distortivity can be further appreciated by looking at some antiaromatic hydrocarbons which can be made delocalized and symmetric by tinkering with the σ-frame. For example, s-indacene, **20** in Scheme 25 is an antiaromatic molecule which exists as a bond-shift equilibrium of two C_{2h} structures.[13] Hafner and Dunitz demonstrated by means of X-ray diffraction that substitution of electropositive groups on the symmetry equivalent positions (7,8-diamino or 1,3,4,6-tetra-*tert*-butyl) converts **20** to a single D_{2h} structure, **21**.[145b,178] Heilbronner and Yang[179] offered a rationale of the symmetrization effect in terms of the delicate π–σ-balance. Computations by Koch et al.[180] show that even in the unsubstituted molecule, the energy difference between a single delocalized D_{2h} structure and two fluctuating C_{2h} structures is very small. Recent computations by Choi and Kertesz[181] affirm the flatness of the surface for **20** and the delocalized D_{2h} structure, **21**, for the 1,3,4,6-tetra-*tert*-butyl-substituted s-indacene.

Pentalene, **22**, is another antiaromatic molecule known to undergo bond-shift equilibrium with a barrier of approximately 4 kcal/mol.[182] A second-order perturbation Hückel treatment[100] by Heilbronner and Shaik[183] indicated that linking pentalene into bipentalene, **23**, should cause one of the moieties to undergo delocalization or at least lower the barrier for achievement of the local D_{2h} situation. Many antiaromatic species seem to behave in the same manner.[184]

The *very delicate* π–σ-balance poses an opportunity to study delocalized antiaromatic species and to gain new insight into the resonance energy of antiaromatics and its manifestations, e.g., in the magnetic properties. The calculations of van Wüllen and Kutzelnigg[185] show that D_{4h} cyclobutadiene has a positive Λ value as opposed to aromatic species which possess negative Λ values.[161] While this value changes upon distortion to D_{2h} the change is small, indicating that the electronic structure still reflects the typical pattern of square cyclobutadiene. *The paratropic chemical shift of antiaromatic molecules does not reflect that resonance is destabilizing because it is always stabilizing in the sense that it is an outcome of configuration mixing.* As mentioned already, the aromatic/antiaromatic difference is associated with the sign problem of the wave function (eq 1 and Scheme 19) and with the nature of the antiaromatic resonance energy that prevents a concerted electronic movement around the ring and bars a sustained diamagnetic ring current.[164]

Scheme 25. s-Indacene (20, 21), Pentalene (22), and Bipentalene (23)



a. Origins of "Instability" of Antiaromatic Molecules. Antiaromatic molecules are "unstable" and when formed react instantly, either by dimerizing or with other available molecules.[78,186] While the instability of cyclobutadiene can be related to a great deal of angular strain and overlap repulsion, in other antiaromatic species such as pentalene, heptalene, etc., these factors do not appear to be so severe. One might wonder, therefore, whether the "instability" is not in fact a kinetic lability of these compounds.

Molecular reactivity can be understood by application of VB diagrams as amply[37] reviewed in the literature. According to this model, *a molecule is very reactive if it possesses low-lying excited states with spin-unpaired electrons which can be paired into new bonds*. Triplet states of a conjugated molecule prepare the molecule to react by cyclodimerization or cycloaddition with another molecule in its own appropriate triplet state.[37] This is illustrated in Figure 8 for the cyclodimerization of cyclobutadiene. The barrier for the reaction is some fraction of the triplet promotion energy (G), which is extremely low for cyclobutadiene. Consequently, the dimerization will be very facile and *cyclobutadiene will be a highly reactive molecule because it possesses a very low-lying triplet state*.

Antiaromatic molecules have, as a rule, very low-lying triplet states, ca. 10 kcal/mol or less above the ground state.[89,187] Furthermore, since the σ-frame limits the distortivity of the antiaromatic molecule, the triplet excitation is constrained to remain small. Consequently, the "instability" of antiaromatic species is a kinetic instability associated with availability of low-lying triplet states. A related argument has been used recently by Zilberg and Haas.[188]

The heightened reactivity of an antiaromatic molecule, with n-electrons on n-centers, is not rooted in

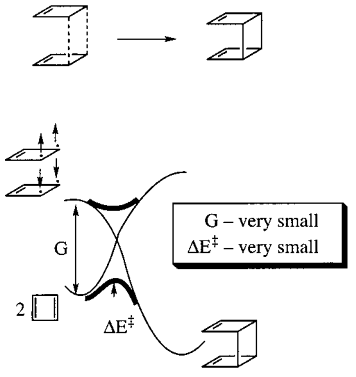


Figure 8. VB diagram (ref 37) describing the barrier for dimerization of cyclobutadiene. The barrier is small since the excitation gap, *G*, is small.

a lack of resonance stabilization of the symmetric species because the vertical resonance is appreciable (see Table 3) nor is the kinetic instability a direct consequence of the π-distortivity. In fact, it is the appreciable vertical resonance energy that reduces the π-distortivity of an antiaromatic species sufficiently to make the symmetric geometry easily accessible. In this geometry the triplet state is invariably very low lying, *for its own specific reasons*, making the molecule kinetically unstable. Of course, the low-lying triplet state reflects the type of delocalization in the singlet antiaromatic species, which in some of the cases, but not all, is a diradicaloid (as in cyclobutadiene but not in pentalene, etc.). However, low-lying triplet states do not require an antiaromatic electronic structure, but whenever such as situation is present, the molecule is always reactive. We have shown previously that even formally "forbidden" reactions become facile due to low-lying triplet states, e.g., in dimerization of disilenes.[37,110a]

4. The Rotational Barrier of Allyl Is Not in Conflict with the π-Distortivity

Shaik and Bar[102] demonstrated that allyl anion has a distortive π-component but at the same time exhibits a rotational barrier. This analysis was reaffirmed later for allyl radical.[5] Subsequently, Gobbi and Frenking[93] pointed out that the total distortion energy of allylic species is very small because it reflects the balance of π-distortivity opposed by the σ-symmetrizing propensity. They further argued that along with this π-distortivity, the allylic species enjoys resonance stabilization which is the source of the rotational barrier. A detailed VB analysis by Mo et al.[149] established the same tendency.

Figure 9 is a Hess cycle that relates the 'special stability' of allyl radical to its rotational barrier, $\Delta E_{\mathrm{ROT}}(\mathbf{a})$, using data of Gobbi and Frenking[93] which are very close to our own data[5] for this species. It is seen from the data that since the distortion energy is small, the rotational barrier is dominated by the vertical resonance energy of distorted allyl radical, $B(\mathbf{da})$. The values of the vertical resonance energies of the symmetric allyl radical and its distorted form are shown too (VBSCF/6-31G data). It is seen that the largeness of $B(\mathbf{da})$ draws from the corresponding $B_0(\mathbf{a})$ value for the symmetric species. As concluded repeatedly, here too the σ-frame constrains the allylic species to perform the rotation in the region where the vertical resonance energy is significant. *The rotational barrier experiment measures, therefore, the resonance energy of a distortive π-transition state.*

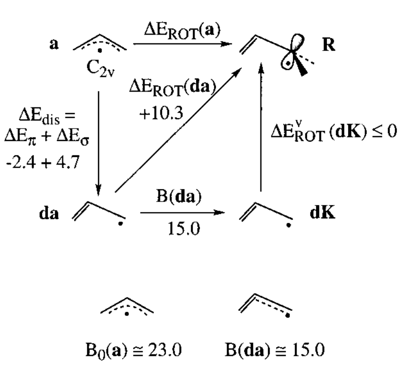


Figure 9. Hess cycle used to relate the rotational barrier of allyl radical to its resonance energy. All energies are given in kcal/mol (data for the cycle is taken from ref 93; *B* values from ref 111).

C. Probes of π-Delocalization Are Independent of π-Distortivity

The generality of Scheme 1 is apparent by now; π-distortivity and resonance stabilization are two coexisting properties of delocalized species which are constrained to relatively small distortions around a symmetric geometry. This situation that typifies conjugated π-systems of carbon allows one to measure the two properties independently of each other.

A beautiful demonstration of this virtual independence comes from the experimental[189] and theoretical[190,191] work on [*n*]-paracyclophanes which lose the intrinsic stability of the benzene nucleus because of the very severe strain applied on the para positions. For example, [4]-paracyclophane is less stable than its Dewar benzene isomer[190,191] because it possesses 85 kcal/mol of strain energy.[191] Nevertheless, the molecule and its [5]-cyclophane kin retain ring currents and have electronic spectra reminiscent of delocalized π-electrons.[189] Moreover, despite the constraints and the ensuing instability of the π-component, the C−C bond lengths of the six-membered ring exhibit only a small degree of bond alternations. Thus, even though the thermochemical stability (defined relative to reference structure) of the benzene nucleus is lost by the distortion, the vertical resonance energy remains and is probed by NMR and electronic spectroscopy. The ability to probe π-delocalization in this highly distorted molecule highlights the strong resistance of the σ-frame of hydrocarbons to bond alternate and its ability to buttress the π-component within a close range where delocalization is still appreciable.

A simple consequence of the above is the large vertical resonance energy of the distorted benzene in Figure 6 and its aromatic magnetic behavior both computed and measured.[32,169−171] In fact, as emphasized by Choi and Kertesz,[87] even when the aromatic [*n*]-annulenes undergo bond alternating distortion, their magnetic properties are still those of an aromatic species. In fact, Choi and Kertesz conclude that a symmetric geometry is not a necessary condition for an "aromatic" behavior. A similar conclusion was reached by Mendel et al.[192] in their study of bismethano[14]annulenes. We fully agree with this conclusion and reiterate what we have said all along: that the stiff σ-frame of conjugated hydrocarbons restricts the distortions of the molecules to geometries where the Kekulé structures still mix strongly, as supported by calculations[5] and indicated in Figure 5.

V. Structural Manifestations of π-Distortivity: Ground States

How can π-distortivity be induced in species which do not normally exhibit bond alternation, e.g., benzene? What are the possible manifestations of a latent π-distortivity? We already mentioned a few spectroscopic probes of distortivity.[99,131] This section analyzes structural probes of π-distortivity in the ground states of delocalized molecules.

A. Bond Alternation in the Ground State of Substituted Benzene

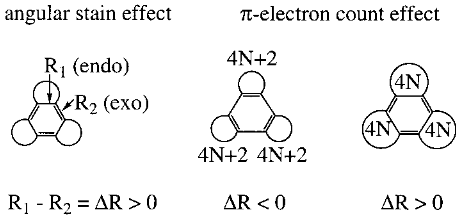
The notion of bond fixation dates back to Mills and Nixon,[193a] who used the Kekulé oscillating picture of benzene, Scheme 2a, to predict that annelation by small rings will favor one of the Kekulé forms, leading to double-bond localization (bond fixation). While the model used by Mills and Nixon is now considered to be obsolete,[193b] the idea of bond fixation is still valid and very much alive.[194] The long search for the Holy Grail of converting benzene to "cyclohexatriene" has finally been completed with the synthesis of tris-bicyclo[2.1.1]benzene (**30** in Scheme 27) by Siegel et al.[32,33,36,171] Let us first briefly summarize the story of the search for the cyclohexatriene motif and of the attempts to rationalize the observed patterns. Subsequently, we shall demonstrate that "Siegel-cyclohexatriene" and other bond-fixated benzene derivatives are the children of π-distortivity.

1. Modes of Bond Alternation Induced by Strain and π-Electron Count

At the simplest level of Mills−Nixon-type argumentation, annelation of benzene by small saturated rings should favor the Kekulé structure that places the double bond outside (exo) of the strained small ring. Thus, angular strain is expected to lead to *normal bond alternation*, $\Delta R > 0$, where the endo bond, R_1, is longer than the exo bond, R_2, as shown in **24,** Scheme 26.

Another expected factor is related on the classical π-aromaticity/antiaromaticity electron count.[36,194,195] This is illustrated using the drawings **25** vs **26** in which unsaturated rings are employed for annelation. The case in **25** shows that an unsaturated annelating ring will cause *a reversed bond alternation*, $\Delta R < 0$, if by incorporating the double bonds into the endo positions, the annelating rings would count $4N + 2$ electrons. The case in **26** describes the situation where $\Delta R > 0$ is induced because the annelating rings try to avoid having antiaromatic $4N$ electrons by preferring the Kekulé structure with double bonds in the exo positions.

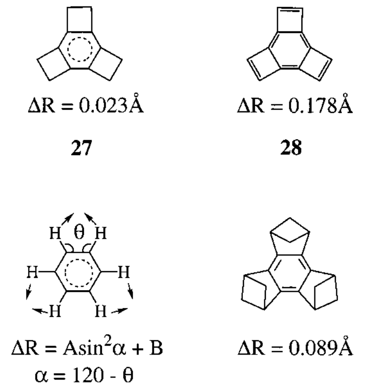
Scheme 26. Types of Mills−Nixon (MN) Effects[a]



24 **25** **26**

[a] **24** Defines the "normal" MN-effect, $\Delta R > 0$, which occurs due to angular strain. **25** and **26** define the dependence of the MN effect on the π-electron count in the annelating rings. **25** shows an inverse MN effect, $\Delta R < 0$, which occurs whenever incorporation of the π-bonds of benzene into the endocyclic positions leads to an aromatic π-electron count in the annelating rings. **26** shows a normal MN effect, which occurs whenever the π-bonds of benzene are placed in the exocyclic positions to avoid antiaromaticity of the annelating rings.

Scheme 27. Observed MN Effects in 27−30

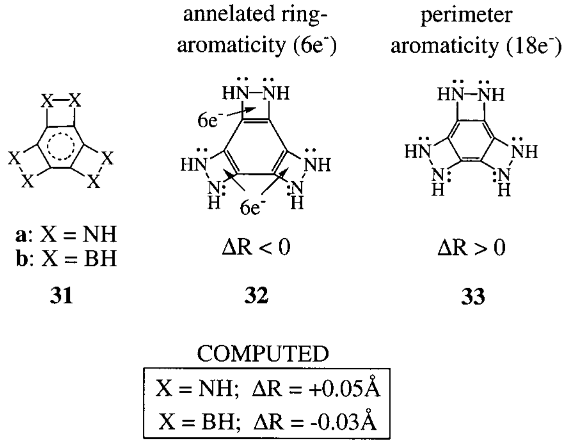


29 **30**

The hopes to achieve the "cyclohexatriene" motif by annelation of small rings proved disappointing, as shown in tris-cyclobutabenzene **27**,[196] Scheme 27, which possesses only a moderate bond alternation. An even smaller one was found computationally by the tris-cyclopropabenzene.[195,197] The hopes rose again when Diercks and Vollhardt[130] synthesized starphenylene, **5**, shown before in Scheme 14. This molecule and its derivatives exhibit a significant positive Mills−Nixon effect that is modeled quite well by **28**.[129,198] Both these molecules appear to follow the classical π-electron count argument and undergo bond alternation to avoid the antiaromaticity in the annelating rings (as in **26** in Scheme 26).

While the π-aromaticity/antiaromaticity argument seemed sound for **5** and **28**, Stanger and Vollhardt[129] nevertheless argued that angular strain, *by itself*, can cause the observed bond alternation. By constraining the angles of benzene as in **29** to deviate from 120°, the molecule underwent a significant bond alternation which correlated with the deviation of the HCC angles from 120°. No π-antiaromaticity was needed to achieve this bond alternation. Stanger and Vollhardt argued that in tris-cyclobutabenzene, **27**, the C−C bonds of the annelating cyclobutano rings undergo bending (bent bonding−banana bonding) so

Scheme 28. Ambiguity of the π-Electron Count Argument for 31a and 31b (Ref 35)



that the "real" CCC angle is significantly larger than the 90° implicated by the four-membered ring geometry. Consequently, α is small in **27**, resulting in a small degree of bond alternation. Electron density determination by low-temperature X-ray diffraction of **27** by Boese et al.[196] showed that the σ_{C-C} bonds of the annelating rings are indeed curved and thus affirmed Stanger's model of ring strain. Subsequently, Siegel et al.[32] made tris-bicyclo[2.1.1]benzene, **30**, which seemingly involves only σ-strain and was found to exhibit a significant bond alternation. Siegel et al.[32,36] reasoned that the rigid bicyclic moiety cannot relax by bent bonding and hence should induce an appreciable bond alternation in the benzene nucleus.

In the meantime, Stanger critically examined the classical argument of electron counting as an explanation for bond alternation (**25** vs **26**).[35] He showed that counting electrons can lead to ambiguous conclusions whenever the π-electron count in the annelating ring clashes with the perimeter's π-count. In such a case it is not clear which of the effects should be the more important one. Stanger's argument can be illustrated, as in Scheme 28, with the imino and borohydrido derivatives in **31**. As exemplified in **32** vs **33**, for the imino derivative, a dominant aromaticity of the annelating rings would 'fix' the benzene's double bond as in **32**, thereby predicting bond alternation in the inverse sense, $\Delta R < 0$. In contrast, a dominant perimeter aromaticity as in **33** would fix the benzene double bonds in the endo positions and lead to $\Delta R > 0$. The same ambiguity can be demonstrated for the borohydrido derivative. As shown in the box in Scheme 28, the two molecules undergo bond alternation in opposite senses, thus rendering the electron count argument unhelpful. Accordingly, Stanger judged that bond localization is induced mainly by angular strain, namely, by the behavior of the σ-frame under ring strain.

Indeed, application of ring strain using Siegel's bicyclic annelation strategy[32,36,199,200] has proven to be a very fruitful way of achieving the cyclohexatriene motif. However, in a recent work, Jemmis and Kiran[201] compared the effect of annelation on cyclohexane and benzene. Their results showed that while the annealated cyclohexanes and benzenes exhibit the same patterns of bond alternation, the effect on the "pure" σ-system is much smaller than that on benzene. Thus, Jemmis and Kiran concluded that bond alternation seems to be *enhanced* by the π-electrons and must, therefore, involve an interplay of σ- and π-effects. We shall now show that a σ-strain, small as it may be, causes the latent π-distortivity to manifest and thereby magnify the bond alternation in the ground state.

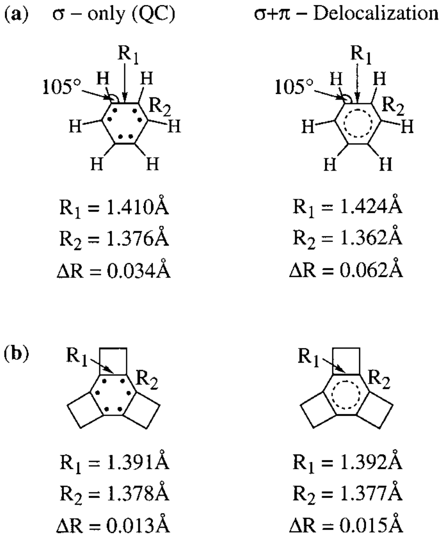


Figure 10. Angular strain effect on optimized geometries of benzene species and their σ-frames (from ref 6). The σ-frame is the QC state (see Scheme 10). (a) Stanger-benzene. (b) Triscyclobutabenzene.

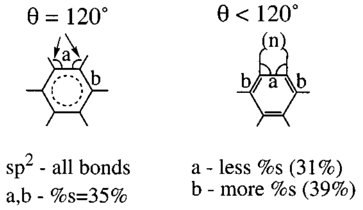
B. σ-Strain and How It Causes π-Distortivity to Manifest

The σ–π-interplay in bond fixation has been analyzed by using the QC state technique to study separately the σ- and π-effects.[6] Figure 10 shows the structures of Stanger-benzene in part a (fixing $\theta = 105°$) and of tris-cyclobutabenzene in part b with and without π-delocalization. Initially the molecules were optimized (HF/6-31G) and the minima found to exhibit some bond alternation as shown in the right-hand side structures. Subsequently, the π-electrons were unpaired into the nonbonding QC state, which describes the effective σ-frame, and the new minima were found along the bond alternation mode. These σ-minima results are shown on the left-hand side structures. It is seen that in both cases the angular strain induces bond alternation as anticipated by Stanger and others. However, it is also apparent that when π-bonding and delocalization is allowed to take place, the extent of the distortion is magnified, even if very little as in tris-cyclobutabenzene. *Thus, a small bond alternation caused by the σ-frame enables the π-distortivity to manifest and magnify the bond alternation.*

1. Origins of Bond Alternation of the σ-Frame

It is interesting to note that the σ-frame of tris-cyclobutabenzene, in Figure 10, appears to be less strained than the σ-frame of the Stanger-benzene, in accord with Stanger's prediction.[129,198] As such, a brief discussion of the σ-frame follows based on the work

Scheme 29. Rehybridization σ-Effects Induced by Angular Strain



of Stanger[35] and identical explanations in Ou-Chu[131] and Maksic et al.[194] Scheme 29 shows the rehybridization expected when the endocyclic angle of benzene, θ, changes from 120° to a smaller value. The values in Scheme 29 are obtained from an NBO analysis by Ou and Chu[131] for tris-cyclobutabenzene. At 120°, all carbon atoms are exactly sp^2-hybridized. As the endocyclic angle shrinks, the carbon atoms of the strained C$-$C bond (bond a) undergo rehybridization closer to sp^3 and s-character is "drained" from bond a. Since the percentage of s-character must be conserved, the adjacent bond (bond b), for which the exocyclic angle is larger than 120°, undergoes a complementary rehybridization closer to sp and is enriched with s-character. Consequently, bond a gets longer while bond b gets shorter. The effect may be transmitted further but in a much weaker manner. Three such constraints distributed as in the molecules in Scheme 27 would cause, therefore, bond alternation in the σ-frame. Another factor which is invoked[201] to induce σ-bond alternation is the steric effect between the substituents of the strained bond. No doubt, the two effects are present in the strained σ-frame.

However, as shown by Jemmis and Kiran[201] and as our data in Figure 10 reveal, the σ-bond alternation is weak[202] since the σ-frame is rather stiff in this mode (see also the k_σ value of the b_{2u} mode in Scheme 16). What makes the bond alternation more significant is the distortive π-component as revealed by the data in Figure 10. The patterns of this π-enhancement of bond alternation are elaborated below.

C. π-Enhanced Bond Alternation of Strained Benzene

Let us consider the interplay of a π-component and a hexagonal σ-frame for a case with angular strain.[1,6,34] Figure 11 shows a few diagrams drawn along the bond alternation coordinate and describes different $\pi-\sigma$-scenarios. The zero of the bond alternation coordinate corresponds to the symmetric geometry with a local D_{6h} symmetry, while the $\Delta R > 0$ and $\Delta R < 0$ describe the two modes of bond alternation in terms of the relative bond lengths of the endo (R_1) and exo (R_2) bonds. In all the parts of the figure the σ-frame's minimum is displaced slightly from the origin in the $\Delta R > 0$ direction to reflect the strain-induced alternation of the σ-frame discussed above.

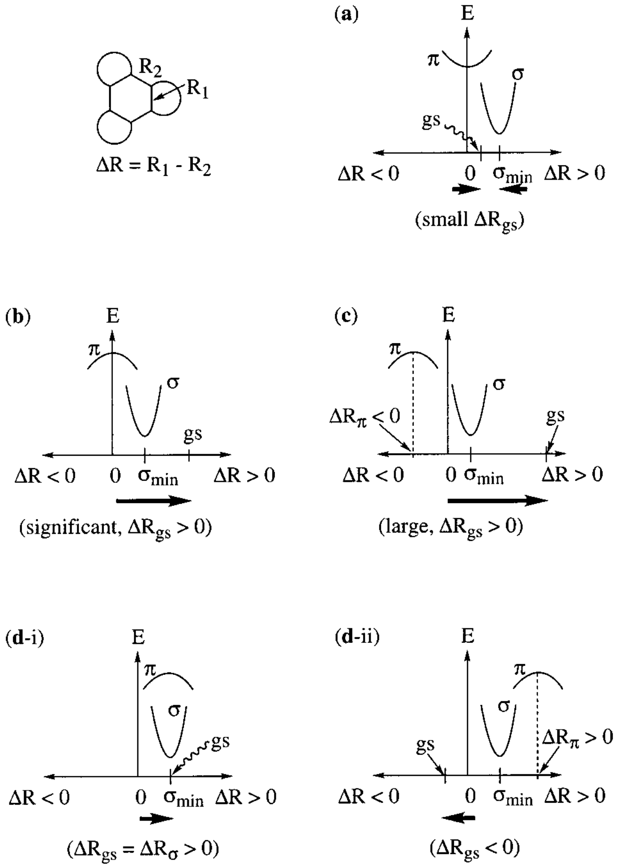


Figure 11. Interplay patterns of π- and σ-curves along the bond alternation coordinate, ΔR, in annelated benzene. Cases a$-$d depict the situations in eqs 11$-$14. The degree of bond alternation in the ground state, ΔR_{gs}, is indicated by the bold arrows underneath the ΔR coordinate.

For the sake of argument, we will assume that both the π- and the σ-energies are quadratic in the distortion coordinate, with respective force constants k_π and k_σ.[34] This leads to the following expression for the displacement of the ground state (ΔR_{gs}) relative to the zero of the bond alternation coordinate

$$\Delta R_{gs} = \Delta R_\sigma + K(\Delta R_\pi - \Delta R_\sigma);\ K = [k_\pi/(k_\pi + k_\sigma)]$$

$$K > 0\ (\pi\text{-attractive}),\ K < 0\ (\pi\text{-distortive}) \qquad (11)$$

The above equation predicts that the total displacement of the ground state will be a sum of the intrinsic σ-strain effect (ΔR_σ) and an additional term which is proportional to the difference between the π- and σ-displacements, scaled by K which itself is a function of the π- and σ-force constants. Consider the two curves which exhibit minima (henceforth, "attractive") in Figure 11a. For these attractive curves, both k_π and k_σ are positive and the factor K is *positive and small*. However, if the π-curve has a maximum (i.e., it is "distortive") whereas the σ-curve is "attractive" as in Figure 11b$-$d, then $k_\pi < 0$ and $k_\sigma > 0$. Since in absolute magnitude the π-force constant is smaller than the σ-force constant, i.e., $|k_\pi| < k_\sigma$, *the factor K in eq 11 will be negative and large* for a distortive π-component. With these ideas in mind let us analyze the different scenarios in Figure 11.

Figure 11a shows a hypothetical situation where both π- and σ-curves resist the bond alternating distortions from their respective minima; the π-minimum is unperturbed and located at $\Delta R = 0$. Since the two curves are attractive, the ground-state minimum will be located between the two curve minima, with a smaller bond alternation relative to the

σ-frame. That this cannot be the correct scenario is apparent from our results in Figure 10, as well as from the results of Jemmis and Kiran.[201] Clearly, *the π-component must be distortive.*

Parts b and c of Figure 11 describe the scenarios where the π-component is distortive and the σ-frame is shifted to $\Delta R > 0$ due to strain. In part b we show a situation where the distortive π-component is unperturbed by the annelation, $\Delta R_\pi = 0$. It is seen from the figure that even though the π-component is unperturbed, the fact that it is distortive *causes an amplification of the ground-state displacement farther away from the σ-frame's minimum*. Equation 11 shows that the amplification is due to the fact that the second term, now being eq 12, is positive for a distortive π-component.

$$K(\Delta R_\pi - \Delta R_\sigma) = -K\Delta R_\sigma = |K|\Delta R_\sigma > 0;\ \Delta R_\pi = 0 \tag{12}$$

For benzene itself, $|K| > 1$ (since $|k_\pi| < k_\sigma$, see Scheme 16). This scenario corresponds to the case where the annelating ring has no interaction with the π-electrons, or only a weak one, and fits beautifully the results of Stanger-benzene in Figure 10.

Part c of Figure 11 shows a case where in addition to the σ-displacement the π-component is also displaced by π-interaction with the annelating ring but in the opposite $\Delta R < 0$ direction. With a negative π-displacement, $\Delta R_\pi < 0$, *the π- and σ-effects will be strongly amplified* due to the second term in eq 11. This term is now positive and proportional to the distance between the two displacements ($|\Delta R_\pi| + \Delta R_\sigma$), as shown in eq 13.

$$\Delta R_\pi < 0 \text{ and } K < 0 \Rightarrow K(\Delta R_\pi - \Delta R_\sigma) = |K|(|\Delta R_\pi| + \Delta R_\sigma) \tag{13}$$

The more distant the two extrema, the greater the final ground state's displacement and the larger its bond alternation! This scenario corresponds to starphenylene, **5**, and the model system **28** (Schemes 14 and 27) where the π–π-interaction between the annelating ring and the benzene nucleus is obviously present. The reason the π-maximum exhibits a negative displacement $\Delta r_\pi < 0$ is explained later.

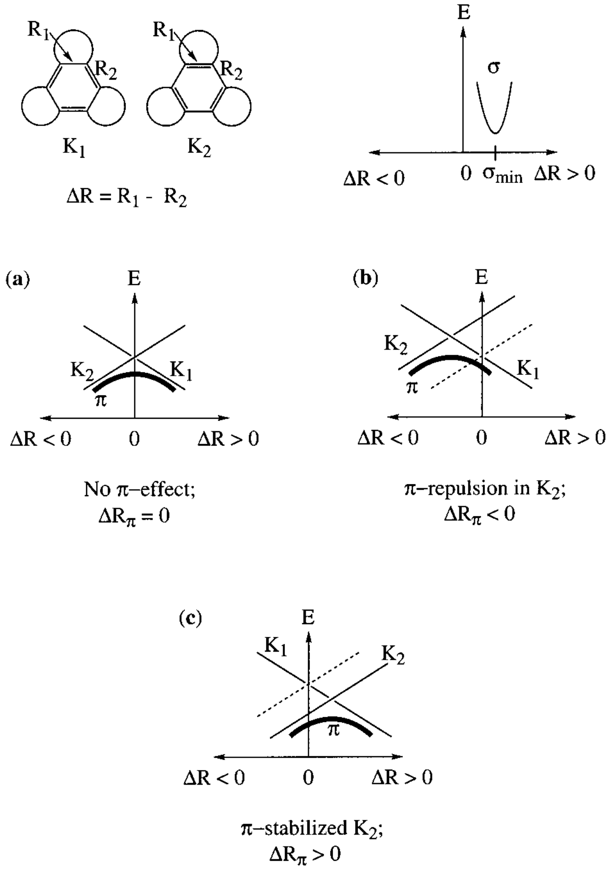
If, however, the π-maximum shifts in the same direction as the σ-minimum, with $\Delta R_\pi > 0$, the second term in eq 11 will involve a difference of the π- and σ-displacements. As shown in eq 14, this term can either be a small positive quantity or a negative quantity, depending on the relative magnitudes of the displacements.

$$-|K|(\Delta R_\pi - \Delta R_\sigma) > 0, \text{ if } \Delta R_\pi < \Delta R_\sigma \tag{14a}$$

$$-|K|(\Delta R_\pi - \Delta R_\sigma) < 0, \text{ if } \Delta R_\pi > \Delta R_\sigma \tag{14b}$$

$$-|K|(\Delta R_\pi - \Delta R_\sigma) = 0, \text{ if } \Delta R_\pi = \Delta R_\sigma \tag{14c}$$

Consequently, for a π-displacement equal to the σ-displacement, the final ground-state minimum stays put (eq 14c). The latter case is shown in part d of Figure 11 (diagram i). Whenever the π-interaction is strong enough, then the π-displacement will *exceed* the corresponding σ-one, i.e., $\Delta R_\pi > \Delta R_\sigma$ (eq 14b). In this case the minimum of the ground state will shift to ΔR smaller than the σ-minimum. An inverted Mills–Nixon effect, in the $\Delta R < 0$ direction, can also be obtained, depending on the difference ($\Delta R_\pi - \Delta R_\sigma$) between the displacements as shown in diagram ii in Figure 11d. Inverted Mills–Nixon effects are small since the π-effect has to work generally against the σ-induced bond alternation.



No π–effect; $\Delta R_\pi = 0$

π–repulsion in K2; $\Delta R_\pi < 0$

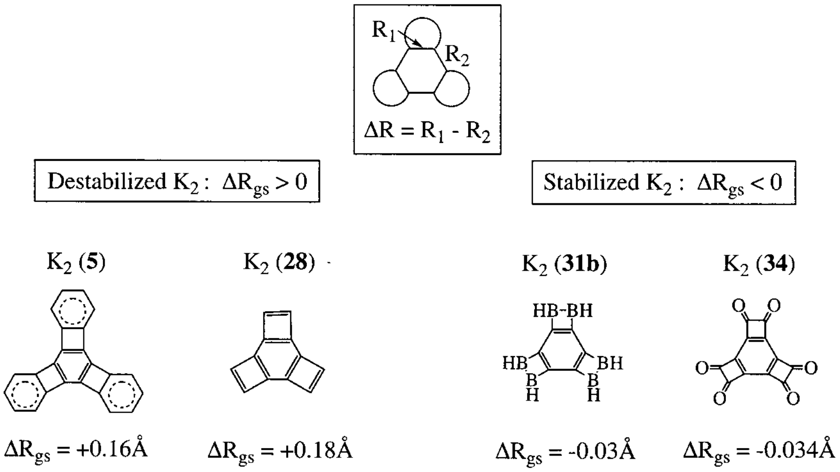
π–stabilized K2; $\Delta R_\pi > 0$

Figure 12. Pattern of the π-displacement due to a differential interaction of the π-electrons of the annelator with the π-bonds in K_1 and K_2. Note that here and in all subsequent diagrams, K_2 rises in energy in the $\Delta R > 0$ direction since, in this direction, the double bonds across R_1 undergo stretching. K_1 rises in the opposite direction since in this direction the double bonds across R_2 undergo stretching. The state π-curves arise from avoided crossing of these two structures and are drawn in bold lines. The σ-curve is displaced to $\Delta R > 0$ due to angular strain. (a) The situation in cases where the annelator has no π-electrons. (b) K_2 is destabilized by the π-electrons of the annelator and rises vertically compared to the dashed line of an unperturbed curve. The avoided crossing generates a π-curve with a maximum displaced in the $\Delta R < 0$ direction. (c) Stabilization of K_2 by π-acceptor groups in the annelator results in a π-curve displaced in the $\Delta R > 0$ direction.

1. Annelation π-Effects on the Distortive π-Component of Benzene

To understand the directionality of the π-displacement, we now consider the effect of an annelating ring that maintains π–π-interaction with the Kekulé structures of benzene, shown in Figure 12. At its top, the figure shows the Kekulé structures, K_2 with the double bonds in the endo-positions and K_1 with the

Scheme 30. Cases in Which π-Repulsion Destabilizes K_2 (see Figure 12b) and the Observed MN Effects, $\Delta R_{gs} > 0$. Cases in Which K_2 Is Stabilized by Interaction with the π-Acceptors in the Annelating Rings and Their Inverse MN Effects, $\Delta R_{gs} < 0$



double bonds in the exo positions, along with the displaced σ-curve due to angular strain. Parts a–c of the figure describe VB correlation diagrams for the π-Kekulé structures along the bond alternating ΔR coordinate. Schemes 30 and 31 provide examples which illustrate the arguments.

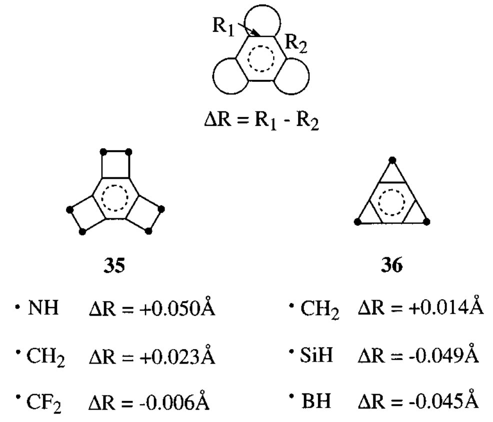
Part a of Figure 12 shows the situation in benzene, where the Kekulé structures cross and establish a distortive π-curve with a maximum at the D_{6h} symmetry (the origin of the ΔR coordinate). Parts b and c describe two opposite effects of π-interaction between the annelating ring and the endo-double bonds in K_2.

Part b describes a case where K_2 is destabilized by π-overlap repulsion with the annelating ring and is vertically raised relative to the unperturbed Kekulé structure (dashed line). The avoided crossing will create a π-curve with a maximum displaced in the $\Delta R < 0$ direction. As discussed already (Figure 11c), such a negative π-displacement will greatly magnify the small bond alternation in the σ-frame. Scheme 30 shows the destabilized K_2 structure of starphenylene, **5**, and its model system **28** and projects the strong effect of a negative π-displacement.

Part c of Figure 12 describes a case where K_2 is stabilized by interaction with π-acceptor groups in the annelating ring and is thereby lowered relative to the unperturbed Kekulé structure (dashed line). The avoided crossing will create a π-curve with a maximum shifted in the $\Delta R_\pi > 0$ direction, namely, a positive π-displacement. The resulting positive π-displacement will now push the bond alternation *against the σ-effect* and may result in an inverted Mills–Nixon region ($\Delta R < 0$). Two model systems that involve a stabilized K_2 structure due to the presence of π-acceptor groups in the annelating rings are **31b** and **34** in Scheme 30, which exhibit the inverted Mills–Nixon effect.[195]

Scheme 31 provides a few examples of the positive and negative π-displacements. Thus, in **35** are shown cases of annelation with four-membered rings,[35,198,203] whereas in **36** are shown cases of annelation with three-membered rings.[35,203] In both cases the annelating rings can undergo π-interactions with the benzene ring via either pseudo-π- or pseudo-π^*-orbitals (e.g, in CH_2, SiH_2), the lone pairs (in NH), or vacant p-orbitals (in BH). It is seen that as the annelating groups change from π-donors to π-acceptors, the bond alternation changes from a normal to an inverted Mills–Nixon effect, precisely as predicted by the model. Note that what counts is not the number of π-electrons in the annelating rings, but whether these electrons destabilize or stabilize the Kekulé structure with the endo π-bonds, designated as K_2.

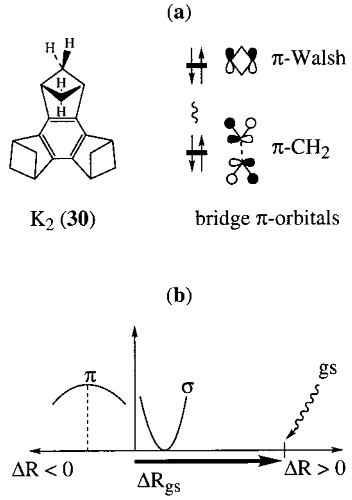
Scheme 31. Variable MN Effect in 35 and 36 (Refs 35, 198, and 203)



2. Manifestations of π-Distortivity in Siegel-Cyclohexatriene

Scheme 32 illustrates that the reason for the significant effect in Siegel-cyclohexatriene is the magnification exerted by the distortive π-component, along the same lines discussed above. The scheme shows that the bicycle annelator possesses pseudo-π-orbitals that can interact with and destabilize the π-bonds of the Kekulé structure, K_2. The secondary orbital is made from the methylene groups above and below the plane of the benzene ring. The primary and most important one is the π-type Walsh orbital of the bridged cyclobutano moiety. This Walsh π-orbital overlaps well with the π-bond of K_2 and destabilizes it considerably.[204] An analogous destabilization has

Scheme 32. π-Repulsion between the Pseudo-π-orbitals of the Abridged Bicycle of 30 and K_2. (a) Pseudo-π-orbitals. (b) $\pi-\sigma$ Interplay between the Displaced π-Curve and the σ-Curve Causes a Significant Bond Alternation Indicated by the Arrow on the ΔR Coordinate (consult Eq 13)



been discussed by Jorgensen and Borden[205] for bicyclo-[2.1.1]hexene. As reasoned above, the destabilization of K_2 will lead to a negative π-displacement and will therefore magnify the bond alternation in the positive Mills−Nixon sense. This is illustrated in in Scheme 32b.

To further illustrate the point, consider the trend in the bond alternation exhibited by the tris-bicyclic-substituted benzene derivatives[32,36,206−208] in Figure 13. As indicated by the angle, θ, the angular strain exerted by the bicyclic moiety decreases along the series. Consequently, the σ-induced bond alternation diminishes along the series **a** → **c**, as indicated in diagram i by the σ-minimum which gradually approaches the origin of the bond alternation coordinate. Even if we assume, as in diagram i, that the π-interaction of the bicycle with benzene's Kekulé structure, K_2, produces a constant π-displacement, still the distance between the displacements $((|\Delta R_\pi| + \Delta R_\sigma)$, eq 12) shrinks along the series **a** → **c** with a concomitant decrease of the bond alternation. In fact, as the annelating ring gets larger in **a** → **c**, its pseudo-π-orbitals become less and less effective to overlap with π-bonds of the Kekulé structure, K_2, resulting in a decreasing displacement of the π-curves as in diagram ii. It is the combined σ- and π-effects which cause a fast decrease of bond alternation from 0.089 to 0.015 Å.

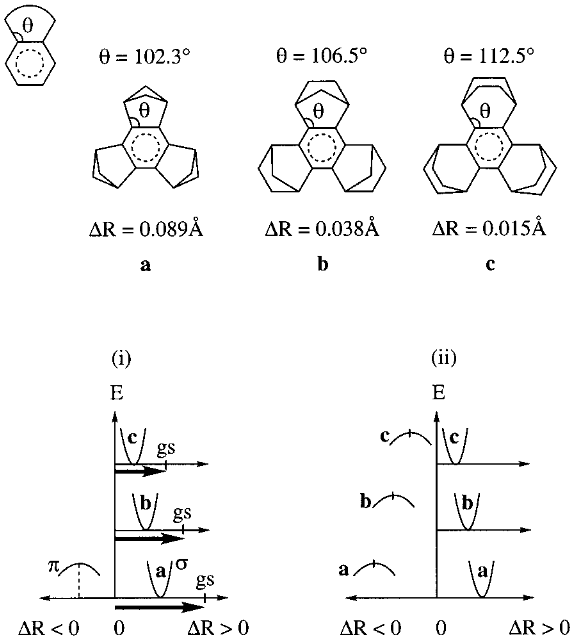


Figure 13. Bond alternation in a−c (from refs 32 and 206−208). Diagrams i and ii describe the $\pi-\sigma$-interplay that governs the bond alternation trends.

Before moving to the next topic, it is important to recall that ultimately all the distortions discussed above are rather small and the annealated benzenes have UV, NMR, and other properties which still typify an aromatic mode of electron delocalization.[36,171]

VI. Structural Manifestations of Ground State's π-Distortivity: The Twin Excited State

This section considers structural manifestations of the ground state's π-distortivity by its comparison with the excited state that can be constructed from the same VB structures as the ground state, henceforth called the twin excited state.[1,3,37,113,150,188,209]

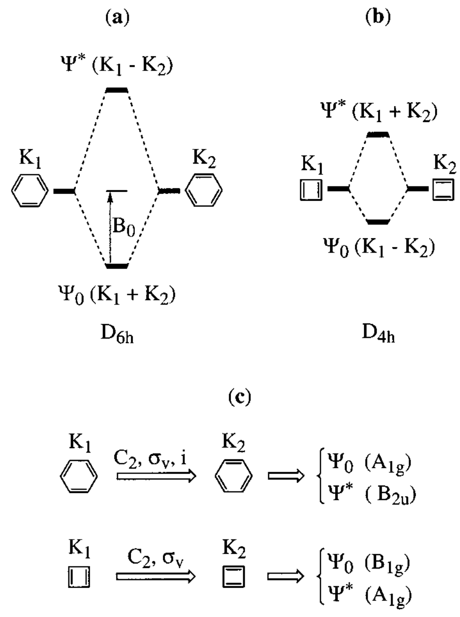
A. The Concept of Twin States

Referring to Figure 2 and to Scheme 19, the avoided crossing of the Kekulé structures leads to their resonance mixing and a formation of bonding and antibonding pair of states,[3,150,209] which we refer to as the twin states, thus denoting their common Kekulé parenthood. The twin states are unique since they are the only states which arise from the fundamental Kekulé structures of the molecule which interchange along the bond alternation mode. Scheme 33 shows the twin-state pairs for benzene and cyclobutadiene as prototypical examples of aromatic and antiaromatic *n*-electron−*n*-center species. The two VB mixing diagrams illustrate that the vertical resonance energy (B_0) is significantly larger for the aromatic species, as already discussed in Tables 3 and 4 (Section IV.A.2).

Another feature of the resonance mixing, already alluded to, is the sign inversion which is caused by the different nature of the matrix elements that mix the Kekulé structures for aromatics and antiaromatics. Thus, in the case of benzene (part a), the ground state is the positive combination of the two Kekulé structures, while in cyclobutadiene (part b), the ground state is the negative combination.[15,116,158,210−214] Consequently, the twin excited states are the negative and positive linear combintions, respectively, for aromatics and antiaromatics.[1,3,15,115,209−212] This relationship of the ground and excited states to the fundamental Kekulé structures has been derived early on by the pioneers of VB theory.[211,214]

The symmetry assignment of the twin states can be made using the information in Scheme 33c. For

Scheme 33. Generation of the Twin States by Mixing of the Kekulé Structures for Benzene (a) and Cyclobutadiene (b) as Archetypal Aromatic and Antiaromatic Species. (c) Transformation Properties of K_1 and K_2 with Respect to Symmetry Operations of the D_{6h} and D_{4h} Point Groups



benzene, the Kekulé structures are mutually transformable by the point group, D_{6h}, operations i, C_2, and σ_v. Consequently, the ground state which is the in-phase combination is the totally symmetric A_{1g} state, while the twin excited state which is the out of-phase combination is B_{2u}. [1,3,209,212,214] In the case of D_{4h} cyclobutadiene, the two Kekulé structures are mutually transformable via C_2, and σ_v (both structures are symmetric with respect to i), and hence, the ground-state combination is B_{1g} whereas the twin excited state which is the in-phase combination is A_{1g}.[115,158,164a,188,210,211,214]

The twin excited state is low lying and generally the first excited state of the molecules. A recent extensive calculation using spin-coupled VB theory[212] verifies that the $^1B_{2u}$ state is indeed made from the negative combination of the two Kekulé structures. Similarly, VB and CASSCF calculations for square cyclobutadiene[158,188,210] affirm the nature of the twin excited state for this molecule. A similar treatment[164a,188,213] verifies the twin-state assignment for cyclooctatetraene. Since the twin states are connected via their avoided crossing along the bond alternation mode, the twin excited state will contain information associated with the π-distortivity in the ground state.[209]

1. The Twin Excited State of Benzene

As illustrated in Figure 14, the $^1B_{2u}$ excited state of benzene[31,164a,209,214,215] retains the D_{6h} geometry of the ground state,[216] with a slight expansion of the ring. The consequences of the avoided crossing of the two Kekulé structures are shown in parts a and b of Figure 15, computed with the VB method.[164a,209] Figure 15a shows the behavior of the total energies of the two Kekulé structures along the b_{2u} coordinate. Figure 15b traces only the π-energy along the same b_{2u} mode (using the QC state technique[6] to separate the π- and σ-contributions). In accord with the qualitative analysis, the quantitative calculation of the VB correlation diagram shows that the $^1A_{1g}(\pi)$ ground state is distortive whereas the twin excited state $^1B_{2u}(\pi)$ is "attractive", having a minimum at the D_{6h} symmetry.

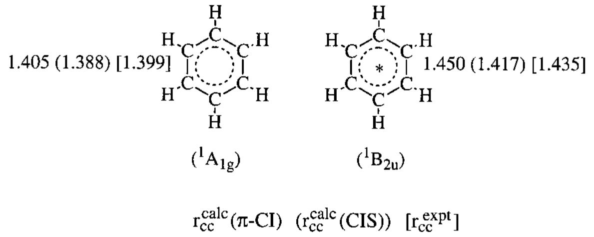


Figure 14. Experimental and theoretical C−C bond lengths of benzene in the ground state (ref 216a,b) and in the twin excited state (ref 215; refs 164a, 188, and 209).

2. Twin Excited States of "Siegel-Cyclohexatriene" and of Benzene Derivatives with Expressed Mills–Nixon Effect

Let us return to Siegel-cyclohexatriene (**30**) and inspect the relationship between the geometries of the ground state and the twin excited states. The model in Figure 11a (also eq 11) predicts that an "attractive" π-curve, displaced to the left of the σ-minimum, will reduce the bond alternation induced by the σ-strain. Since the π-curve of the twin excited state is attractive, this state will lose the bond alternation of the ground state and the benzene nucleus will regain its local D_{6h} symmetry.

Figure 16 shows the results of calculations by Shurki et al.[34,164a] for the twin states of Siegel-cyclohexatriene. It is seen that the significant bond alternation in the ground state, $\Delta R = 0.099$ Å, becomes negligible in the twin excited state, which virtually regains bond uniformity in the benzene nucleus. The diagrams below each structure show the $\pi-\sigma$-interplay, following the model in Figure 11 above. Thus, the negative displacement of the repulsive π-curve of the ground state causes a significant and positive Mills−Nixon bond alternation. In contrast, the "attractive" π-curve of the twin excited state almost cancels out the strain-induced bond alternation of the σ-frame and produces a ring with local D_{6h} symmetry.

Figure 17 shows another case where now the ground state exhibits a significant and negative Mills−Nixon effect while the twin excited state exhibits a negligible positive effect and virtually restores a D_{6h} symmetry in the benzene nucleus. The $\sigma-\pi$-interplay diagrams show that in this molecule the σ-strain is negligible,[217] and hence, the σ-curve is virtually undisplaced and located at the origins. On the other hand, the π-curves show a positive displacement due to repulsive $\pi-\pi$-interaction exerted on K_1 by the substituents. The negative Mills−Nixon effect in the ground state arises from a positive π-displacement of the distortive π-curve. In contrast, the twin excited state which possesses an attractive π-curve with a positive displacement establishes a minimum very near the origin.[34]

The mirror image behavior of the two states is the result of their complementarity through the avoided

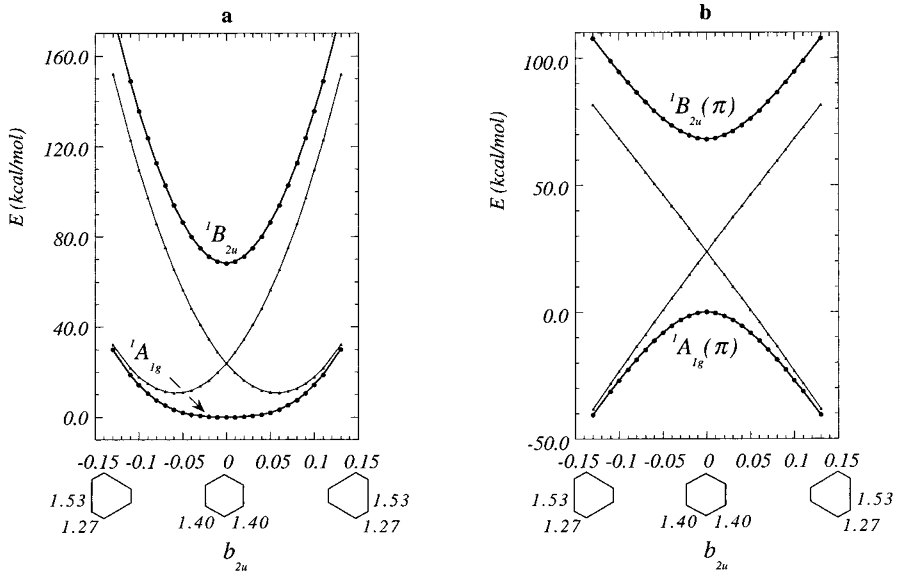


Figure 15. VB computed (ref 164a, 209) avoided crossing diagrams for benzene along the b_{2u} mode. The regular lines are the Kekulé structures. The bold lines refer to the resulting ground and excited states.

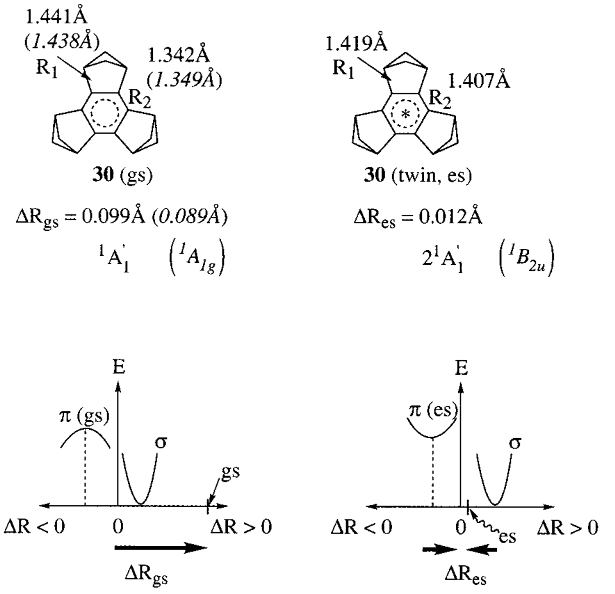


Figure 16. Calculated (refs 34 and 164a) and experimental geometries (in italics, from ref 32) for the ground state and twin excited state of Siegel-cyclohexatriene. The diagrams at the bottom show the σ–π-interplay in the two states. The key difference is the attractive π-curve in the excited state.

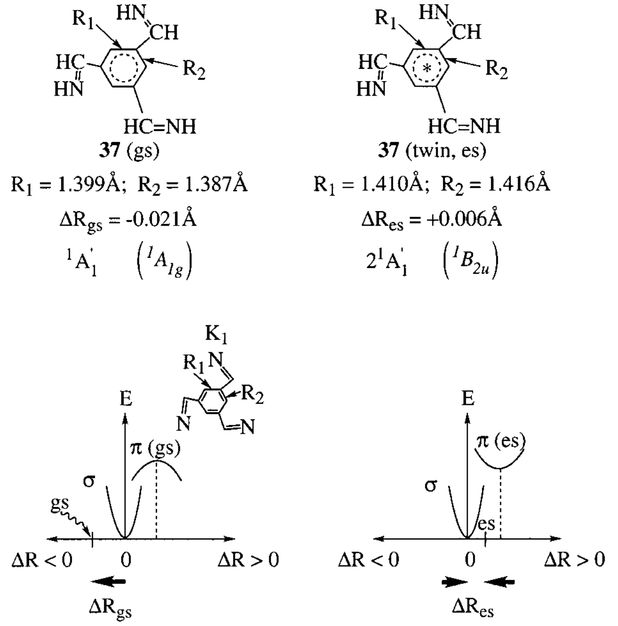


Figure 17. Calculated (refs 34 and 164a) geometries for the twin states of **37**. The diagrams at the bottom show the σ–π-interplay in the two states. The ground state exhibits an inverse Mills–Nixon effect since, due to repulsion of the substituents with the π-bonds of K_1, the π-curve is displaced in the $\Delta R > 0$ direction.

crossing mechanism. Thus, looking at the geometries of the twin states reveals that the most consistent way to understand the patterns in both states is with the π-distortivity scenario of the ground state.

3. Twin Excited States of Cyclobutadiene, Cyclooctatetraene, and Antiaromatic Annulenes

The avoided crossing of the Kekulé structures along the bond alternation coordinate for pristine antiaromatic hydrocarbons[5,37,102,106] produces a π-distortive ground state and a π-attractive twin excited state, much like in aromatic molecules. The σ–π-interplay along the bond alternating mode is shown in Figure 18a. Now, both the π- and σ-curves possess their extrema at the origin of the coordinate. The π-distortivity of the ground state is expressed since it overcomes the resistance of the σ-frame. In contrast, the "attractive" π-curve of the twin excited state would drive this state toward regaining the symmetric geometry. This restoration of the symmetric geometry in the singlet excited state of cylcobutadiene was indeed discussed some time ago by Bally and Masamune.[78] In more recent work, Bally et al.[218] invoked the same phenomenon for the twin excited state of pentalene.

Parts b and c of Figure 18 show the results of a recent computational study by Zilberg and Haas[188,210] aimed at probing the properties of the ground $^1B_{1g}$ and excited $^1A_{1g}$ twin states of cyclobutadiene and

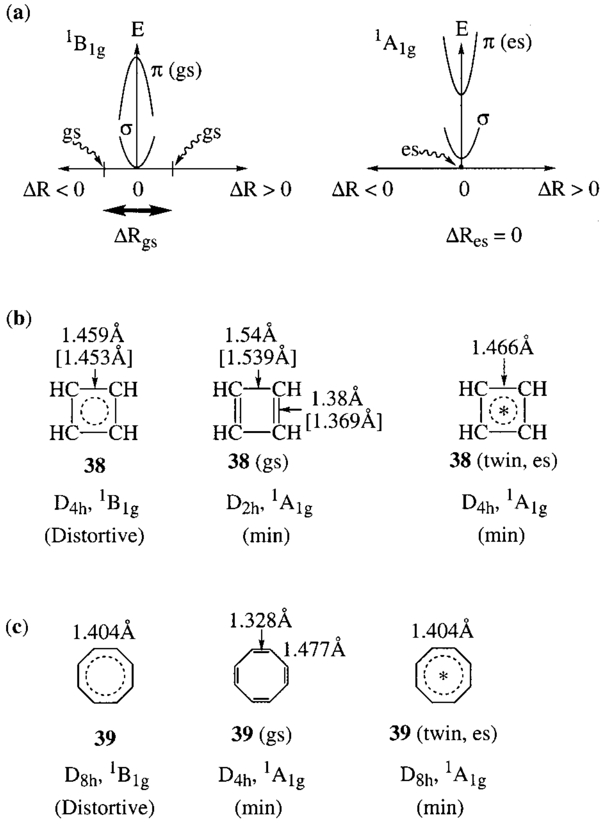


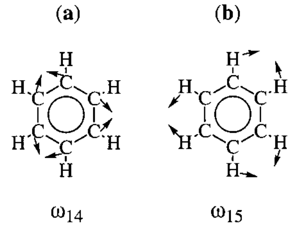
Figure 18. (a) $\pi-\sigma$-Interplay diagrams for the twin states of n-electron$-n$-center antiaromatic species. (b,c) Calculated geometries for the twin states of cyclobutadiene and cyclooctatetraene (from refs 164a, 177, 188, and 219).

cyclooctatetraene. The data are displayed along with complementary data of Borden et al.[89,219,220] The results project the structural manifestations of the avoided crossing. It is seen that in both cases a bond-alternated $D_{(n/2)h}$ ground state becomes a symmetric D_{nh} species in the $^1A_{1g}$ twin excited state. In cyclooctatetraene, the effect in the twin excited state is apparently strong enough to overcome the inherent tendency of the σ-frame for nonplanar geometries which relieve H- -H repulsions.

Clearly, the $\pi-\sigma$-interplay for antiaromatic species in their twin states resembles the above scenario for Siegel-cyclohexatriene. The difference is that the bond alternation in the ground state of benzene needs the constraints of σ-strain and π-repulsion that displace the π- and σ-curves in opposite directions along the bond-alternating coordinate and induces the manifestation of the π-distortivity. In contrast, in the antiaromatic species where the σ-resistance is weaker than the π-distortivity, the bond alternation manifests in the pristine molecule. The twin excited state of the two classes of π-systems behaves in fact the same; in both cases the π-curve is “attractive” and adds to an “attractive” σ-curve to stabilize a symmetric geometry. The $\sigma-\pi$-delicate balance in the ground state becomes a strong symmetrizing force in the excited state.[187,221−223]

The above arguments are quite general and applicable to other bond-alternated ground states in aromatic molecules (e.g., the distorted [18]-annulene produced with the bicyclic annelations[224] as well as in other antiaromatic annulenes and other species such as pentalene, s-indacene, etc.), where the $\pi-\sigma$-interplay in their twin states can reveal essential insight on the π-distortivity in the ground state. Tinkering with the σ-resistance and with the π-distortivity in the twin states offers creative opportunities. Applications to transition states and their twin excited states follow precisely the same principles.[225]

Scheme 34. b_{2u} Modes of Benzene and Their Frequencies in the Ground and $^1B_{2u}$ Excited States of Benzene (Refs 227, 232, and 233)



	ω_{14}	ω_{15}
1^1A_{1g}	1310 cm^{-1}	1149 cm^{-1}
1^1B_{2u}	1571 cm^{-1}	1150 cm^{-1}

VII. Spectroscopic Manifestations of π-Distortivity: The Twin Excited State

The avoided crossing of the Kekulé structures has unique consequences in the spectroscopy of the twin states. Since the twin states are the only two states made from the Kekulé structures and since the bond alternating mode is the only one that causes avoided crossing of Kekulé structures, we expect to find state- and mode-selective manifestations of the avoided crossing in the spectroscopic properties of the twin states. The bond alternating mode is called, in the spectroscopic community,[226−241] the Kekulé mode, and we shall be using this term hereafter. In brief, *the avoided crossing of the Kekulé structures and π-distortivity in the ground state will be manifested as a low-frequency Kekulé mode (lower than for a C=C stretch) in the ground state and a high frequency for the same mode in the twin excited state.* This is expected to be a general signature of the Kekulé avoided crossing and π-distortivity.

As we are about to tell now, the theme of the Kekulé modes involves stories within stories. The longer and fascinating one is that of the Kekulé modes of benzene and aromatics.[1,3,209] The complementary story deals with Kekulé modes in antiaromatic molecules[188,210] and is likely to continue in the future with further advances in spectroscopic techniques.[218,222] Finally, another off-shoot of the main theme relates to the twin states in the case of aromatic transition states.[225]

A. The Kekulé Modes in the Twin State of Benzene

The Kekulé mode of benzene is the skeletal b_{2u} mode ω_{14}, which has been discussed all along and is shown in Scheme 34a. Another b_{2u} mode is the hydrogenic movement shown in in Scheme 34b and is labeled as ω_{15}. These modes are both IR and Raman inactive for D_{6h} benzene in the ground state. The electronic transition to the 1^1B_{2u} excited state is disallowed, and hence, the observations of the b_{2u}

modes in the excited state not only posed enormous difficulties, but had also been delayed to the early 1970s with the advent of two-photon spectroscopy that enabled the study of the 1^1B_{2u} excited state.

A long debate over the ground state's Kekulé mode had started in 1936 when Ingold assigned a very high frequency of 1850 cm^{-1} to ω_{14}.[50] Subsequently, in 1946 Bailey et al.[226] studied the IR frequencies of isotopomers of benzene in the gas phase where the b_{2u} modes are not observable. From the observed spectra, Ingold et al. calibrated a force field and thereby assigned 1649 cm^{-1} to ω_{14} and 1110 cm^{-1} to ω_{15}. Three years later, Mair and Hornig[227] studied the vibrational spectra of benzene in the solid state, where slight perturbation made ω_{14} weakly allowed and hence observable. Their assignment of the skeletal mode ω_{14} was to a much lower frequency of 1310 cm^{-1}. In 1960 Califano and Crawford[228] used an updated force field (Urey−Bradley force field, UBFF) to which they added a resonance term to account for the delocalized nature of benzene. Since both Ingold's and Mair-Hornig's assignments gave essentially good fits, Califano and Crawford concluded that applying Ockham's Razor led to a preference of Ingold's assignment, because presumably there was no evidence against this assignment which seemed coherent with other data. A year later, Scherer and Overend,[229] intrigued by the conclusion of their predecessors, used the UBFF to which they now added a Kekulé term to account for the stabilization of the Kekulé forms during the vibration. This led to a perfect fit to the Mair-Horning assignment, and the frequency of the Kekulé mode was fixed at 1310 cm^{-1}, as shown Scheme 34 underneath the appropriate modes. In the same year, Berry[99] addressed the same problem and ascribed the low frequency of the skeletal Kekulé mode to the distortivity of the π-electrons. His conclusions seem to have been largely ignored in mainstream chemistry.

The story of the Kekulé mode in the 1^1B_{2u} state of benzene had to wait almost 30 years to unfold, when in 1973 Hochstrasser et al.[230] observed the "green" two-photon band in benzene and triggered a revolution in spectroscopy. Early assignments of the corresponding ω_{14} mode met with difficulties which were gradually resolved.[231] In 1977, Robey and Schlag[232] made the assignment in Scheme 34. This assignment was finalized in the early 1990s, when Goodman et al.[233] established the entire set of frequencies for the ground and excited state and demonstrated that the excited state's ω_{14} mode is virtually a pure skeletal mode consisting of carbon atom movements, as shown in the scheme. Clearly, the striking feature is the frequency of the Kekulé mode which was found to undergo exaltation by 261 cm^{-1} in comparison with the ground state's mode. This feature was unexpected and remained a source of puzzlement in the literature. To quote from the 1977 paper by Robey and Schlag, "The remarkable upshift in frequency... of the dominant coupling mode [ω_{14}] was unexpected".[232]

Explanations of the frequency upshift were given by Ohno,[236a,b] Orlandi et al.,[236c] and Mikami and Ito[239] in terms of a vibronic coupling model. While the model was quantitatively successful, it did not give a clear qualitative explanation of the state specificity of the phenomenon.[237] In 1989, Michl and co-workers[238] observed frequency upshift in the excited state of a bridged [14]-annulene and explained it in terms of crossing of Kekulé structures but did not relate their finding to the phenomenon in benzene. The status of the phenomenon, expressed in the paper by Robey and Schlag[232] as being puzzling and unexpected, persisted well into the 1990s. In 1995, Zilberg and Haas[234] investigated β-methyl styrene and found that a vibrational frequency of a mode, essentially looking like the Kekulé mode of benzene, undergoes exaltation in the first excited state. In the same year, they[31] performed HF and CIS calculations on the ground state and the 1^1B_{2u} state of benzene and interpreted the frequency shift in terms of the π-distortivity of benzene. Thus, according to this interpretation, the $\pi-\pi^*$ excitation weakens the π-distortive propensity and thereby reveals "more clearly the influence of the σ-potential on the b_{2u} mode", leading to a frequency exaltation of this vibrational mode. The Zilberg−Haas[31] articulation of the π-distortivity scenario has shown that the effect is linked to experimental facts that can be interpreted reasonably if the distortive nature of the π-electrons is admitted.

Despite our natural satisfaction with this explanation, we noted that it nevertheless does not provide a clear physical mechanism for the effect. For example, it was not evident why the frequency exaltation is state selective, i.e., it is not observed in any other state, and the frequency of all other modes are reduced upon excitation. It was deemed necessary, therefore, to articulate the avoided crossing model, derive a clear physical origin of the frequency exaltation of the Kekulé mode, its state, and mode specificity, and establish the connection of the phenomenon to the π-distortivity in the ground state. This was achieved in 1996.[209]

1. Origins of the Exalted Frequency of Kekulé Modes in the 1^1B_{2u} State of Benzene

Using the computed VB diagrams in Figure 15, it is apparent that the π-force constant of benzene is negative in the ground state and positive in the twin excited state, eq 15.

$$k_\pi(^1A_{1g}) < 0,\ k_\pi(^1B_{2u}) > 0 \qquad (15)$$

The total force constant of the two states is then the sum and difference of the σ- and π-force constants, eqs 16a and 16b

$$k(^1A_{1g}) = k_\sigma - |k_\pi(^1A_{1g})| \qquad (16a)$$

$$k(^1B_{2u}) = k_\sigma + k_\pi(^1B_{2u}) \qquad (16b)$$

It follows that the excited state will have a Kekulé mode with a larger force constant and therefore also an exalted frequency, as expressed in eq 17

$$k(^1B_{2u})/k(^1A_{1g}) > 1 \Rightarrow \omega(^1B_{2u})/\omega(^1A_{1g}) > 1 \qquad (17)$$

This effect is illustrated in the total energy curve of the two states in Figure 19 (computed with full

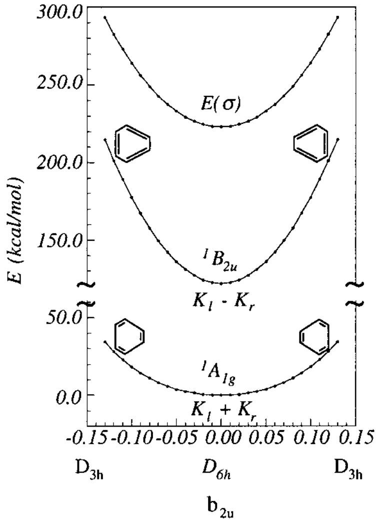


Figure 19. Computed (full-πCI/STO-3G data from refs 164a and 209) σ-curve and total energy curves for the twin states of benzene along the b_{2u} mode.

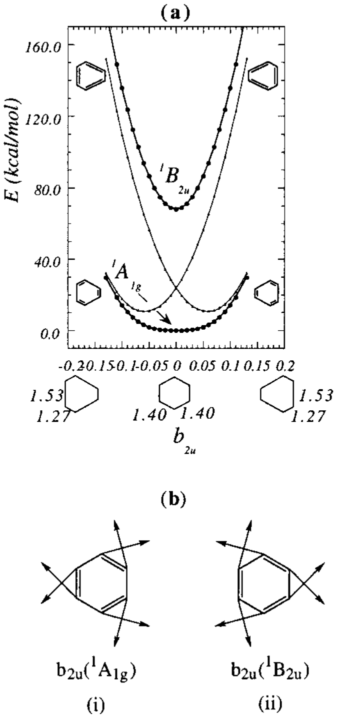
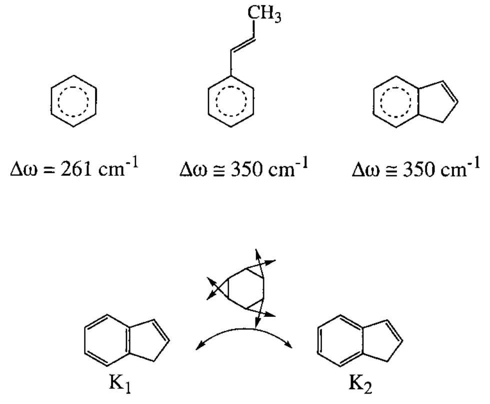


Figure 20. (a) Avoided crossing of the Kekulé structures of benzene (ref 164a, 209). The state curves are in bold lines. The b_{2u} oscillation in the ground state is dominated by the Kekulé structures drawn at the bottom ends, near the ground-state curve, whereas in the excited state the b_{2u} oscillation is dominated by the Kekulé structures drawn at the upper part of the diagram. (b) In the ground state, the b_{2u} oscillation (i) occurs in harmony with the bonding preference of the Kekulé structures. In the excited state, the oscillation occurs in mismatch with the bonding features of the Kekulé structures (ii).

Scheme 35. Frequency Up-Shifts of the Kekulé Mode in Benzene and Its Derivatives (Refs 3, 234, and 235)[a]



[a] The Kekulé mode that interchanges the Kekulé structures of indene is illustrated below.

π-CI/ STO-3G).[209] Thus, adding to the common σ-curve, a repulsive π-curve leads to a flat potential in the ground state, along the skeletal Kekulé mode. In contrast, adding to the σ-curve the attractive π-curve for the twin excited state leads to a steep potential, along the Kekulé mode.

Let us complement the argument by shifting to a language of electronic structure. Inspection of Figure 20 shows that each of the Kekulé structures undergoes destabilization along the Kekulé mode and eventually correlates with an excited-state structure that has *stretched double bonds and short single bonds*. Due to the avoided crossing of the curves, the ground-state energy curve now correlates to the ground-state Kekulé structures and its energy variation is dominated by them. In contrast, the excited-state energy curve correlates to the excited-state Kekulé structures, and its energy is dominated by these higher lying strained structures.

Consider now a b_{2u} oscillation starting from the ground state's D_{6h} structure (drawing i in Figure 20). As the vibration sets in, the double bonds shorten while the weak single bonds elongate. This happens in both directions of the b_{2u} coordinate since the ground state correlates to the two Kekulé structures with the lower energy at the diagram's extreme. This is illustrated schematically in the left-hand drawing (i) in Figure 20b using *one of the Kekulé structures*. Thus, the nuclear motion in the ground state is performed in harmony with the bonding preference of the Kekulé structures for short double bonds and longer single bonds. Consider now the same vibration starting from the D_{6h} structure of the $^1B_{2u}$ excited state (drawing ii in Figure 20). The excited state's potential energy surface correlates to the Kekulé structures with the stretched double bonds. Consequently, motion of the nuclei stretches the double bond and shortens the single bonds. Thus, the b_{2u} mode is forced to occur now in a mismatch with the bonding preference of the Kekulé constituents, as shown in the right-hand drawing (ii) in Figure 20b using *one of Kekulé structures*. In this way, the VB model shows quite vividly how the Kekulé constituents of the electronic structure dictate the motion of the atoms in a complementary fashion in the ground state and its twin excited state.

One might have thought that the state- and mode-specificity of the frequency exaltation is dictated by the symmetry of the states and vibrational mode. Scheme 35 shows, however, that benzene derivatives where the D_{6h} symmetry is clearly absent exhibit this frequency upshift of Kekulé mode.[3,234,235] Moreover, in all these systems, no other state and no other mode seem to exhibit the frequency exaltation. The simplest rationale for the state and mode selectivity is the avoided crossing mechanism which is promoted by the Kekulé mode, as depicted in the scheme for indene. The twin states are the only states that are nascent from the Kekulé structures, and the Kekulé mode is the only mode that leads to the interchange and avoided crossing of the Kekulé structures. *This is the origin of the specificity.*

The frequency exaltation of the Kekulé mode is mirrored by the structural manifestations in the twin states, discussed with reference to Figures 16 and 17. Thus, the repulsive π-curve in the ground state softens the potential and thereby enables the ground-state molecule to distort along the Kekulé mode when angular strain is exerted. In contrast, the "attractive" π-curve in the twin excited state stiffens the potential and restores the local D_{6h} symmetry of the benzene nucleus. The two physical effects are in perfect harmony and find a natural reflection in the VB model.

B. The Kekulé Modes in the Twin States of Acenes

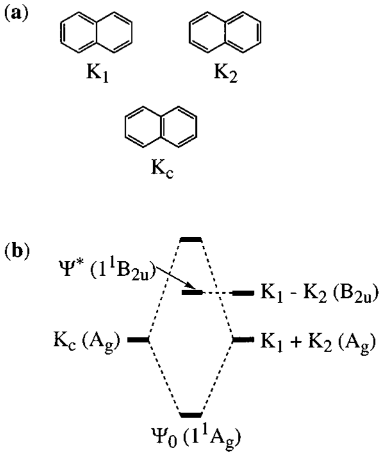
The frequency exaltation of the Kekulé-type b_{2u} modes of the electronically excited 1^1B_{2u} state is not limited to benzene and its derivatives. A similar observation was made by Michl and co-workers[238] for [14]-annulene, who explained the phenomenon in terms of the avoided crossing of the Kekulé structures similar to the above. Other hydrocarbons such as naphthalene, anthracene, etc. have been reported to exhibit the same phenomenon. Thus, in naphthalene,[239,240] the Kekulé-type mode undergoes a frequency exaltation of 189 cm^{-1} in the 1^1B_{2u} state relative to the ground state. In anthracene, two Kekulé-type modes exist. One was assigned and undergoes an upshift of 231 cm^{-1}.[241−243] The second anthracene mode has not been definitely assigned yet. It is calculated to be exalted by 96 cm^{-1}.[243]

The arguments presented in the case of benzene can be extended to other acenes, provided the excited state and the ground state may be described as Kekulé pairs along a suitable coordinate. In the case of naphthalene, a SCVB computation[244] showed that the ground state is very well represented by the three Kekulé structures. Taking the naphthalene computation as a proof of principle, we have adopted the Kekulé model for higher acenes.[3]

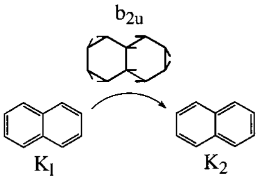
1. The Kekulé Modes in the Twin State of Naphthalene

The three classical Kekulé structures (already alluded to in section III.E) of naphthalene are shown in Scheme 36a. Two of them are designated as K_1 and K_2 and represent the annulenic resonance along the perimeter of the naphthalene, while the third one, K_c, has a double bond in the center and transforms as the totally symmetric irreducible representation, A_g of the D_{2h} group. The K_1 and K_2 structures are mutually interchangeable by the *i*, C_2, and σ_v symmetry operations of the point group, much as in the case of benzene. An in-phase combination transforms, therefore, as A_g, whereas an out-of-phase one transforms as B_{2u}. These symmetry adapted wave functions can now be mixed with the K_c structure to yield the final states as shown schematically in Scheme 36b. Due to symmetry, K_c can mix only with the in-phase combination, leading to the ground state Ψ_0-(^1A_g) and a high-energy state of the same symmetry (unlabeled in the scheme) which is hereafter abandoned. The out-of-phase combination K_1-K_2 that has no symmetry match remains unchanged and is the first excited 1^1B_{2u} state.

Scheme 36. (a) Kekulé Structures for Naphthalene. (b) A VB Mixing Diagram Which Shows the Twin States Generated from the A_g and B_{2u} Combinations of the Kekulé Structures

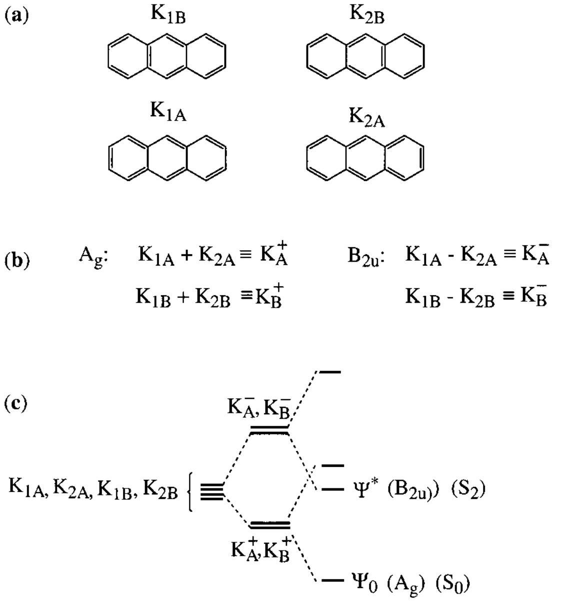


Scheme 37. Kekulé Mode that Interchanges the Kekulé (K_1, K_2) Structures of Naphthalene and Is Predicted To Possess an Exalted Frequency in the Twin Excited State (Ref 3)



Scheme 37 shows that a b_{2u} -type vibration interchanges the K_1 and K_2 structures by alternating the lengths of the C−C bonds, much as in the case of benzene and its derivatives (Scheme 35). On the basis of the foregoing discussions, the K_1 and K_2 structures undergo avoided crossing along this Kekulé mode. The $\pi-\sigma$-energy partition presented for naphthalene[6] in Scheme 18 shows that the contribution of K_c to the ground state does not cancel the π-distortivity along the b_{2u} mode. The twin excited state is made only from the Kekulé forms, which perform annulenic resonance, and since it is the negative combination, it is expected to possess an "attractive" π-curve along the b_{2u} mode. Thus, we expect the b_{2u} mode to be soft and have a low frequency in the ground state, whereas in the twin excited state it is expected to be stiff and have exalted frequency. The fact that frequency exaltation is experimentally observed[239] appears to justify this description. Finally, we note that the ab initio computed mode[3,240] whose frequency is exalted in the 1^1B_{2u} state is *annulenic*, not involving motion across the central bond, precisely as predicted by the Kekulé-crossing model.

Scheme 38. (a) Four Kekulé Structures for Anthracene and (b) Their Symmetry Adapted Combinations. (c) Generation of the Twin States (Ψ_0, Ψ^*) from These Combinations

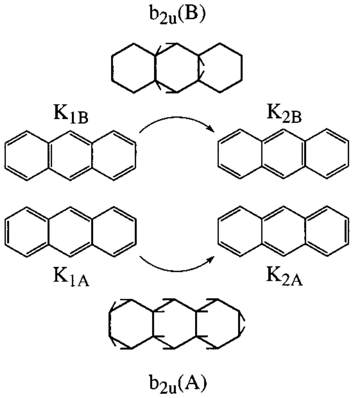


2. The Kekulé Modes in the Twin State of Anthracene

The four classical Kekulé structures for anthracene are shown in Scheme 38a. Two of them involve resonance within the central ring, as in benzene, and are designated as K_{1B} and K_{2B}. The other two, K_{1A} and K_{2A}, are annulenic and involve resonance along the perimeter of the molecule. These $K_{1B,2B}$ and $K_{1A,2A}$ couples are pairwise interchangeable by the D_{2h} symmetry elements (i, C_2, and σ_v); their in-phase and out-of-phase combinations are therefore symmetry adapted and transform as A_g and B_{2u}, respectively, as shown in Scheme 38b. The state diagram is obtained by considering the interaction between the symmetry adapted combinations, as shown in part c of Scheme 38. The ground state is constructed from the A_g Kekulé combinations. The twin excited state is made from the B_{2u} combinations. This excited state turns out to be the second excited state (S_2) of anthracene and has been recently studied using two-photon spectroscopy by Wolf and Hohlneicher[241] and ab initio calculations by Zilberg et al.[242,243] The S_1 state of anthracene is of B_{1u} symmetry and has a predominantly ionic character in the VB representation.

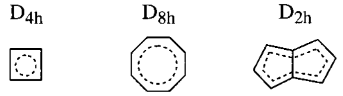
As shown in Scheme 39 the K_B and K_A pairs are interchanged by b_{2u}-type Kekulé modes. One alternates the bonds of the central benzene unit while the other is an annulenic mode alternating the bond length around the molecular perimeter. As such, the positive and negative combinations of each structural type are related by an avoided crossing along the suitable b_{2u} coordinate. The avoided crossing means in turn that the π-curve for the ground state will be distortive along the two modes while the excited state's π-curve will be attractive in the same modes. The vibrations associated with these modes are thereby expected to have a higher frequency in the S_2 state than in the S_0 one. This prediction was verified recently computationally by Zilberg et al.[243] and appears to be confirmed experimentally by Wolf and Hohlneicher[241] for the K_{1B} and K_{2B} pair switching mode, b_{2u} (B). The exaltation of the other mode b_{2u} (A) is not yet definitely assigned.

Scheme 39. Kekulé Modes that Interchange the Benzenic (B) and Annulenic (A) Kekulé Structures of Anthracene (Ref 3)[a]



[a] These modes are predicted to undergo frequency exaltation in the twin excited state (S_2).

Scheme 40. Frequencies of the b_{1g} Kekulé Mode in the Ground and Twin Excited States of Antiaromatic Species (Ref 188)



	D_{4h}	D_{8h}	D_{2h}
$\omega_{b_{1g}}(^1B_{1g})$	i1278 cm^{-1}	i1970 cm^{-1}	i2375 cm^{-1}
$\omega_{b_{1g}}(^1A_{1g})$	2098 cm^{-1}	2491 cm^{-1}	2506 cm^{-1}

C. The Kekulé Mode in the Twin States of Antiaromatic Molecules

We recall that in antiaromatic molecules the ground state in the symmetric geometry is ^1B_g while its twin excited state is 1^1A_g. Moreover, the two states are related by an avoided crossing along the b_{1g} coordinate, which is the corresponding Kekulé mode. In their study of pentalene excited states, Bally et al.[218] postulated that the frequency of the bond alternating mode will be exalted in the 1^1A_g excited state. A theoretical study (π-CASSCF/3-21G) of the twin states for antiaromatic species was performed by Zilberg and Haas,[188,210] who articulated the VB model[209] and demonstrated the presence of a frequency exaltation for the b_{1g} mode in the twin excited state. Their data for three antiaromatic species is shown in Scheme 40, which demonstrates a spectacular effect. The imaginary frequencies of the b_{1g} mode in the ground states become high real frequencies in the twin excited states. Even though all the frequencies are overestimated, the impressive effect is still apparent and exceeds the one discussed above for the aromatic species. This much higher exaltation in the antiaromatic species is rooted in the much smaller vertical resonance energy, B_0 for these species. Indeed, if we compare the B_0 values in Table 4, we find that they are 2−3 times smaller for the antiaromatic species (R_4) compared to the successive aromatic species (R_6). The same conclusion emerges from the excitation energy data of Zilberg and Haas[188] and of Schleyer and co-workers;[187] this excitation from the ground state to the twin state is much larger for aromatics than for antiaromatics. Thus, it is the smaller avoided crossing in the antiaromatic species that renders the curves much steeper in the avoided crossing region, causing a spectacular frequency exaltation of the Kekulé mode.[245]

Despite the quantitative difference between aromatics and antiaromatics, the qualitative picture is the same: The combination of a π-distortive ground state and a π-attractive excited state along the Kekulé modes is manifested in soft potentials in the ground state and steep ones in the twin excited state. This in turn is expressed as exalted frequencies and symmetrized geometries in the twin excited state.

D. The Kekulé Modes in the Twin States: A Generalization

In fact, any twin pair of states related by avoided crossing along a normal mode is likely to exhibit the frequency exaltation and the symmetrization of geometry in the twin excited state. Thus, the model can be extended easily to higher acenes, as done recently,[3] or to other aromatic annulenes and to transition states of chemical reactions as well. Keeping the terminology of Kekulé structures (for general naming of VB structures) and Kekulé modes, the following generalization can be stated: *Any pair of Kekulé structures that are interchangeable along a suitable normal coordinate will give rise to states corresponding to in-phase and out-of-phase combinations of the Kekulé structures. These two structures are related by avoided crossing along the Kekulé coordinate. The frequency of the interchanging Kekulé mode will be exalted in the excited state compared to that in the ground state. For cases with many Kekulé structures, one has to subdivide these structures into interchangeable pairs by appropriate Kekulé modes. All these Kekulé modes will be exalted in the twin excited state.*

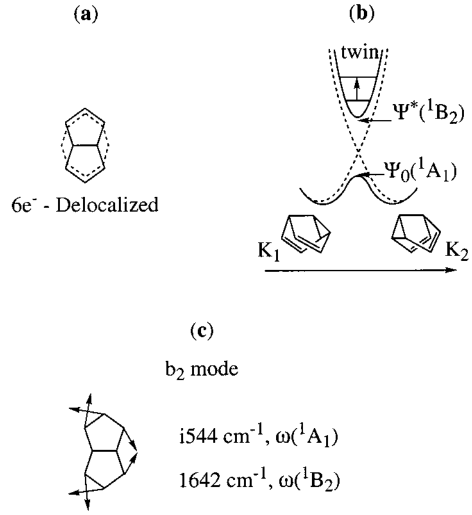
An application of this simple rule to transition states of chemical reactions is within the general theme of the present review, which regards the delocalized π-components as some kind of "transition states" trapped within their symmetrizing σ-frames. Such an application follows.

1. The Kekulé Modes in Twin States of Chemical Transition States

Throughout the review we have made the point that delocalized π-components have properties of transition states. Now we would like to reverse the argument and show that transition states can behave like delocalized π-components and exhibit frequency exaltation.

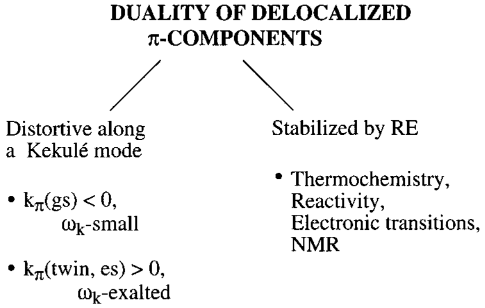
An isoelectronic analogue of the π-component of benzene is the transition state for the degenerate semibullvalene rearrangement in Scheme 41a. The VB correlation diagram,[37] in Scheme 41b, for this process is also analogous to that of benzene and involves two curves which correspond to the VB structures describing the reactants and products. It is expected that much like in benzene, here too the transition state will possess a twin state which is bound along the interchange coordinate and has an exalted frequency in this mode. The calculations of Zilberg et al.[225] show that the transition state 1^1A_1 has an imaginary mode of i554 cm^{-1} corresponding to the reaction mode, b_2. Above the transition state, there is a bound state with the expected symmetry, B_2, for a twin excited state. The frequency of the b_2 mode (Scheme 41c) in this state is seen to be highly exalted, 1642 cm^{-1}. Both the twin-state frequency and the energy gap between the transition state and its twin excited state (5.16 eV) have similar magnitudes to the corresponding properties of benzene.[3,209] The analogy is nearly perfect.

Scheme 41. (a) Transition State for the Degenerate Semibullvalene Rearrangement. (b) Avoided Crossing of the Corresponding "Kekulé Structures" Along the Reaction Coordinate Mode (b_2), and the Generation of the Twin States by Avoided Crossing. (c) Frequencies of the b_2 Mode in the Two States (Ref 225). Delocalized Bonds in c Are Removed for Clarity



Quast et al.[38,246,247] showed that by appropriate substitution of the semibullvalene, the barrier for valence tautomerism drops drastically, though it never really disappears. Interestingly, some derivatives exhibit thermochromism—they are colorless at low temperatures and colored when warmed. Quast[246] interpreted this phenomenon in terms of a two-state situation similar to the one shown in Scheme 41. The twin-state concept supports his interpretation and provides a simple rationale for the thermochromism. Thus, since the barrier in the ground state is very low, the transition state becomes vibrationally accessible at ambient temperatures. In the transition-state region, the energy gap to the twin excited state is the lowest and with appropriate substitution the transition energy shifts to the visible. As temperature decreases, the system now resides in the minima of either valence isomer where the energy gap between the ground and excited states is large, in the UV region, resulting in a colorless compound. A recent publication of Quast and Seefelder[248] discusses the potential of this system as a paradigm for direct observation of transition states.

Scheme 42. Duality of π-Components and Experimental Probes



This analogy of delocalized π-components and transition states is far reaching, and many potential applications exist,[37] which are beyond the scope of the present review.

VIII. Concluding Remarks

We have stated at the outset (Scheme 1) the duality of the π-component of benzene and we have taken our readers through a long journey to prove this duality. Having done so, a general picture of π-delocalization emerges as articulated in Scheme 42. Thus, the duality characterizes all delocalized π-components. They are, on one hand, distortive along the Kekulé mode and, on the other hand, stabilized by resonance energy. The resonance energy is expressed in thermochemical experiments, in reactivity, in electronic transitions, and in NMR spectroscopy. The distortivity is expressed as a negative π-force constant ($k_\pi < 0$) which endows the ground state with a soft surface and a low frequency along this Kekulé mode. The delocalized state possesses a twin excited state in which these properties are the mirror image of the ground state's. The π-force constant of the Kekulé mode is positive, the potential energy is stiff along this mode, and its frequency is exalted.

The duality is not a figment of VB theory or MO theory. It is rather an observable which emerges from all theories including density functional theory (DFT)[249] at almost any level of sophistication. Nonetheless, it is VB theory that provides the simplest way to conceptualize this duality of delocalization.

While this part of the story is complete, there remain many important problems to pursue in the topic of delocalization. For example, while there is a good model which explains the diamagnetic exaltation of aromatic molecules, there is no equally lucid model which explains the paratropism of antiaromatic molecules.[250] Even less understood are these properties in the excited states of these molecules; why, for example, are the triplet states of antiaromatics diamagnetically exalted?[187] The paradigm of delocalization is older than any electronic theory of the chemical bond, and ever since its recognition it posed a problem to grapple with. We expect that it will continue to do so, and it is perhaps appropriate to end the review with the famous citation[13] from Samuel Beckett, "*Hamm: J'aime les vielles questions. Ah les vieilles questions, les vieilles réponses, il n'y a que ça!*" Or succinctly, Old problems are good problems that never die out.

IX. Glossary of Abbreviations

B	vertical resonance energy
CASSCF	complete active space self-consistent field calculations
CI	configuration interaction
CIS	configuration interaction with singly excited determinants only
CISD	configuration interaction with singly and doubly excited determinants only
DRE	Dewar resonance energy
DFT	density functional theory
HF	Hartree–Fock (level of theory)
HS	high-spin
IR	infrared
MO	molecular orbital
MN	Mills–Nixon (effect)
MRMP (π-CI)	multireference Moller–Plesset perturbation theory (with π-configuration interaction)
NBO	natural bond orbital (analysis)
NICS	nuclear-independent chemical shift
NMR	nuclear magnetic resonance
PPP	Pariser–Parr–Pople method for π-electrons
QC	quasi-classical (state). A state with alternating spins on the p_π atomic orbitals
RE	resonance energy
RGVB	resonating generalized valence bond method
SCVB	spin-coupled valence bond method
SINDO	spectroscopic INDO (Intermediate neglect of differential overlap) method
UBFF	Urey–Bradley force field
UV	ultraviolet
VB	valence bond (theory, structure, etc.)

X. Acknowledgments

We are indebted to the following collaborators whose contributions throughout the years made it possible to write this review: R. Bar, J.-M. Lefour, P. Maitre, G. Ohanessian, G. Sini, J.-P. Flament, Y. Haas, and S. Zilberg. An enlightening dialogue with P. v. R. Schleyer helped the planning of this manuscript. We are thankful to T. Bally for critical reading of the manuscript and for exacting and constructive comments. The research at the Hebrew University was supported by the Volkswagen Stiftung, the Robert Szold Fund, and the Israel Science Foundation (ISF). We thank the ACS for permission to use in modified forms Schemes 3 and 4 from ref 3, Figures 1 and 3 from ref 209, and Figure 2 from ref 117. We thank Elsevier Science for permission to use in modified forms Schemes 10 and 11 from ref 1.

XI. References

(1) Shaik, S.; Shurki, A.; Danovich, D.; Hiberty, P. C. *J. Mol. Struct. (THEOCHEM)* **1997**, *398–399*, 155.
(2) Shaik, S. S.; Hiberty, P. C.; Ohanessian, G.; Lefour, J. M. *J. Phys. Chem.* **1988**, *92*, 5086.
(3) Shaik, S.; Zilberg, S.; Haas, Y. *Acc. Chem. Res.* **1996**, *29*, 211.
(4) Hiberty, P. C.; Ohanessian, G.; Shaik, S. S.; Flament, J. P. *Pure Appl. Chem.* **1993**, *65*, 35.
(5) Shaik, S. S.; Hiberty, P. C.; Lefour, J. M.; Ohanessian, G. *J. Am. Chem. Soc.* **1987**, *109*, 363.
(6) Hiberty, P. C.; Danovich, D.; Shurki, A.; Shaik, S. *J. Am. Chem. Soc.* **1995**, 117, 7760.
(7) Jug., K.; Köster, A. M. *J. Am. Chem. Soc.* **1990**, *112*, 6772.
(8) Jug., K.; Matuschewski, M.; Köster, A. M. *J. Phys. Org. Chem.* **1993**, *6*, 645.
(9) Jug., K.; Matuschewski, M. *Int. J. Quantum Chem.* **1994,** *49*, 197.
(10) Buck, H. *Int. J. Quantum Chem.* **2000**, *77*, 641.
(11) Jenneskens, L. W.; van Eenige, E. N.; Vliestra, E. J. *Nouv. J. Chim.* **1994**, *18*, 553.

(12) Gobbi, A.; Yamaguchi, Y. Frenking, G.; Schaefer, H. F., III *Chem. Phys. Lett.* **1995**, *244*, 27.
(13) Heilbronner, E. *J. Chem. Educ.* **1989**, *66*, 471.
(14) Glukhovtsev, M. N.; Simkin, B. Ya.; Minkin, V. I. *Zh. Org. Khim. Engl. Ed.* **1989**, *25*, 603.
(15) Mulder, J. J. C. *J. Chem. Educ.* **1998**, *75*, 594.
(16) Longuet-Higgins, H. C.; Salem, L. *Proc. R. Soc. London* **1959**, *A251*, 172.
(17) Nakajima, T.; Kataoka, M. *Theor. Chim. Acta* **1993**, *85*, 27.
(18) Aihara, J. I. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 1956.
(19) Baird, N. C. *J. Org. Chem.* **1986**, *51*, 3907.
(20) Kutzelnigg, W. *Einfuehrung in die Theoretische Chemie. Band 2, Die Chemische Bindung*, 1st ed.; VCH: Weinheim, 1978; pp 308−317.
(21) Coulson, C. A.; Dixon, W. T. *Tetrahedron* **1962**, *17*, 215.
(22) Paldus, J.; Chin, E. *Int. J. Quantum Chem.* **1983**, *24*, 373.
(23) Paldus, J.; Chin, E.; Grey, M. G. *Int. J. Quantum Chem.* **1983**, *24*, 395.
(24) Paldus, J.; Takahashi. M. *Int. J. Quantum Chem.* **1984**, *25*, 423.
(25) Takahashi, M.; Paldus, J. *Int. J. Quantum Chem.* **1984**, *26*, 349.
(26) Dijkstra, F. Valence Bond Theory; Ph.D. Dissertation, The University of Utrecht, The Netherlands, 2000; p 119.
(27) Minkin, V. I.; Glukhovtsev, M. N.; Simkin, B. Ya. *Aromaticity and Antiaromaticity*; Wiley: New York, 1994; Chapter 2.
(28) Burdett, J. K. *Chemical Bonds. A Dialog*; Wiley: New York, 1997; p 113−120.
(29) Burdett, J. K. *Chemtracts: Inorg. Chem.* **1991**, *3*, 57.
(30) Carroll, F. A. *Perspectives on Structure and Mechanism in Organic Chemistry*; Brooks/Cole Publishing Company: 1998; p 213.
(31) Haas, Y.; Zilberg, S. *J. Am. Chem. Soc.* **1995**, *117*, 5387.
(32) Bürgi, H.-B.; Baldridge, K. K.; Hardcastle, K.; Frank, N. L.; Gantzel, P.; Siegel, J. S.; Ziller, J. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1454; *Angew. Chem.* **1995**, *107*, 1575.
(33) Rouhi, A. M. *Chem. Eng. News* **1996**, *74* (Apr 1), 27.
(34) Shurki, A.; Shaik, S. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2205; *Chem. Eng. News* **1997**, *75* (Nov 3), 21.
(35) Stanger, A. *J. Am. Chem. Soc.* **1998**, *120*, 12034.
(36) Frank, N. L.; Siegel, J. S. *Advances in Theoretically Interesting Molecules*; JAI Press: London, 1995; Vol. 3, p209.
(37) Shaik, S.; Shurki, A. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 586; *Angew. Chem.* **1999**, *111*, 616.
(38) Quast, H.; Knoll, K.; Peters, E.-M.; Peters, K.; von Schnering, H. G. *Chem ber.* **1993**, *126*, 1047.
(39) Brush, S. G. *Stud. Hist. Philos. Sci.* **1999**, *30*, 263.
(40) Kekulé, A. *Bull. Soc. Chim. Paris,* **1865**, *3*, 98; *Bull. Acad. R. Belg.* **1865**, *19*, 551; *Ann. Chem. Pharm.* **1872**, *CLXII*, 77. In recent years, it has been repeatedly stated that much credit should go to J. J. Loschmidt as the originator of the structure of benzene (see, e.g., Wiswesser, W. J. *Aldrichchimica Acta* **1989**, *22*, 17; Noe, C. R.; Bader, A. *Chem. Br.* **1993**, 126). Indeed, Loschmidt's drawings with a circle representing the C_6 nucleus surrounded by six circles representing the hydrogen atoms looks like a perfectly modern representation of benzene. This, however, is not a unanimous view. For example, E. Heilbronner who read Loschmidt's pamphlet ("*Constitutions-Formulen der organischen Chemie in geographischer Darstellung*") maintains (in a private communication to S. Shaik) that Loschmidt referred to his circles as "spheres of influence" of the atoms and did not intend to convey a structure, as did Kekulé.
(41) Brush, S. G. *Stud. Hist. Philos. Sci.* **1999**, *30*, 21.
(42) Hafner, K. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 641.
(43) Kikuchi, S. *J. Chem. Educ.* **1997**, *74*, 194.
(44) Garratt J. P. *Endeavour* **1987**, *11*, 36.
(45) Thiele, J. *Liebigs Ann. Chem.* **1899**, *306*, 87.
(46) Heibronner et al. ascribe the first notion of a "delocalized benzene" to Havréz, see: (a) Heilbronner, E.; Dunitz, J. D. *Reflection on Symmetry*; VCH: New York, 1993; p 49. (b) Heilbronner, E.; Jacques, J. *Chem. Unserer Zeit* **1998**, *32*, 256.
(47) Thomson, J. J. *Philos. Mag.* **1899**, *48*, 547. See also: Chayut, M. *Ann. Sci.* **1991**, *48*, 527.
(48) Lewis, G. N. *J. Am. Chem. Soc.* **1916**, *38*, 762.
(49) Ingold, C. K. *J. Chem. Soc.* **1922,** *121*, 1133.
(50) Ingold, C. K. *Structure and Mechanism in Organic Chemistry*; Cornell University Press: Ithaca, NY, 1953; Chapter IV.
(51) Willstätter, R.; Waser, E. *Ber.* **1911**, *44*, 3423.
(52) Armit, J. W.; Robinson, R. *J. Chem. Soc.* **1925**, *127*, 1604.
(53) Lonsdale, K. *Trans. Faraday Soc.* **1929**, *25*, 352; Lonsdale, K. *Proc. R. Soc. London* **1929**, *A123*, 494.
(54) Heisenberg, W. *Z. Phys.* **1926**, *38*, 411; *38*, 499; **1926**, *38*, 239.
(55) Heitler, W.; London, F. *Z. Phys.* **1927**, *44*, 455.
(56) (a) Slater, J. C. *Phys. Rev.* **1931**, *37*, 481. Slater, J. C. *Phys. Rev.* **1931**, *38*, 325. Slater, J. C. *Phys. Rev.* **1931**, *38*, 1109. Slater, J. C. *Phys. Rev.* **1932**, *41*, 255. (b) Slater, J. C. *Quantum Theory of Molecules and Solids*; McGraw-Hill: New York, 1963; Vol. 1, Chapters 3, 10, and 12.
(57) (a) Pauling, L. *Proc. Natl. Acad. Sci.* **1928**, *14*, 359. Pauling, L. *J. Am. Chem. Soc.* **1931**, *53*, 1367. Pauling, L. *J. Am. Chem. Soc.* **1931**, *53*, 3225. (b) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960.
(58) Hund, F. *Z. Phys.* **1927**, *40*, 742; *42*, 93.
(59) Mulliken, R. S. *Phys. Rev.* **1928**, *32*, 186. Mulliken, R. S. *Phys. Rev.* **1928**, *32*, 761. Mulliken, R. S. *Phys. Rev.* **1929**, *33*, 730.
(60) Hückel, E. *Z. Phys.* **1930**, *60*, 423.
(61) For an interview with Hückel, in *Chem. Unserer Zeit* **1970**, *4*, 18, see the English translation in Gilde, W.-G. *J. Chem. Educ.* **1972**, *49*, 2. See also: Berson, J. A. *Chemical Creativity*; Wiley-VCH, NY, 1999.
(62) Pauling, L.; Wheland, G. W. *J. Chem. Phys.* **1933**, *1*, 362.
(63) Lonsdale, K. *Proc. R. Soc. London* **1937,** *A159***,** 149.
(64) Pascal, P. *Ann. Chim. Phys.* **1910**, *19*, 5. Pascal, P. *Ann. Chim. Phys.* **1912**, *25*, 289. Pascal, P. *Ann. Chim. Phys.* **1913**, *29*, 218.
(65) (a) Hückel, E. *Z. Phys.* **1931**, *70*, 204. (b) Hückel, E. *Z. Phys.* **1931**, *72*, 310.
(66) Hückel, von E. *Z. Phys.* **1932**, *76*, 628. Hückel, E. *Z. Elektrochem.* **1937**, *43*, 752. Hückel, E. *Z. Elektrochem.* **1937**, *43*, 827.
(67) Another VB-type application to antiaromatics is the Craig Rule. His rule, based on symmetry properties of the electronic state, distinguished for the first time between the aromatic $(4N + 2)$ species and the $(4N)$ ones which Craig called "pseudoaromatic". See: Craig, D. P. *J. Chem. Soc.* **1951,** 3175.
(68) See discussion of the sign of the VB matrix element on page 274 of ref. 39.
(69) For the VB-based Craig Rules, see: Streitweiser, A., Jr. *Molecular Orbital Theory for Organic Chemists*; Wiley: New York, 1961; Chapter 10.
(70) For a lucid explanation of the difference between MO and VB representations of cyclobutadiene and benzene, see: Wheland, G. W. *Proc. R. Soc. London* **1938**, *A159*, 397.
(71) Doering, W. v. E.; Knox, L. H. *J. Am. Chem. Soc.* **1954**, *76*, 3203.
(72) Breslow, R.; Höver, H.; Chang, H. W. *J. Am. Chem. Soc.* **1962**, *84*, 3168.
(73) (a) Sondheimer, F.; Wolovsky, R. *J. Am. Chem. Soc.* **1962**, *84*, 260. (b) Sondheimer, F. *Acc. Chem. Res.* **1972**, 5, *81*.
(74) Vogel, E. *Pure Appl. Chem.* **1969**, *20*, 237.
(75) Schröder, G.; Oth, J. F. M. *Tetrahedron Lett.* **1966**, *34*, 4083. Schröder, G.; Martin, W.; Oth, J. F. M. *Angew. Chem.* **1967**, *79*, 861.
(76) Garratt, P. J. *Aromaticity*; Wiley: New York, 1986.
(77) Chapman, O. L.; McIntosh, C. L.; Pacansky, J. *J. Am. Chem. Soc.* **1973**, *95*, 614. (b) Lin, C. Y.; Kranz, A. *Chem. Commun.* 1972, 1111. Kranz, A.; Lin, C. Y.; Newton, M. D. *J. Am. Chem. Soc.* **1973**, *95*, 2774. (c) Maier, G.; Sauer, W. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 51. Maier, G. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 425. Maier, G.; Pfriem, S.; Schaefer, U.; Matusch, R. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 520. (e) Kimling, H.; Krebs, A. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 932. (f) Delbaere, L. T. J.; James, M. N. G.; Nakamura, N.; Masamune, S. *J. Am. Chem. Soc.* **1975**, *97*, 1973.
(78) For a review of most aspects of cyclobutadiene, see: Bally, T.; Masamune, S. *Tetrahedron* **1980**, *36*, 343.
(79) The first unequivocal assignment of rectangular singlet cyclobutadiene by theory was reported by Buenker and Peyerimhoff, see: Buenker, R. J.; Peyerimhoff, S. D. *J. Chem. Phys.* **1968**, *48*, 354.
(80) Breslow, R.; Chu, W. *J. Am. Chem. Soc.* ***1970***, 92, *2165*.
(81) Breslow, R. *Acc. Chem. Res.* **1973**, *6*, 393.
(82) Breslow, R.; Mohacsi, E. *J. Am. Chem. Soc.* **1963**, 85, 431.
(83) (a) Dewar, M. J. S.; Gleicher, G. J. *J. Am. Chem. Soc.* **1965**, *87*, 685. (b) Dewar, M. J. S. *Tetrahedron Suppl.* **1965**, *8*, 75. (c) Dewar, M. J. S.; DeLlano, C. *J. Am. Chem. Soc.***1969**, *91*, 789.
(84) Schaad, L. J.; Hess, B. A., Jr. *J. Chem. Educ.* **1974**, *51*, 640.
(85) See page 145 of ref 76 here.
(86) Lloyd, D. *The Chemistry of Conjugated Cyclic Compounds*; Wiley: New York, 1989; Chapter 3.
(87) Choi, C. H.; Kertesz, M. *J. Chem. Phys.* **1998**, *108*, 6681.
(88) Fokin, A. A.; Jiao, H.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1998**, *120*, 9364.
(89) Hrovat, D. A.; Borden, W. T. *J. Mol. Struct. (THEOCHEM)* **1997**, *398*−*399*, 211.
(90) (a) Olah, G. A.; Comisarow, M. B. *J. Am. Chem. Soc.* **1964**, *86*, 5682. (b) Schleyer, P. v. R.; Su, T. M.; Saunders: M.; Rosenfeld, J. C. *J. Am. Chem. Soc.* **1969**, *91*, 5174. (c) Deno, N. C.; Haddon, R. C.; Nowak, E. N. *J. Am. Chem. Soc.* **1970**, *92*, 6691. (d) Raghavachari, K.; Whiteside, R. A.; Pople, J. A.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1981**, *103*, 5649.
(91) (a) Thompson, T. B.; Ford, W. T. *J. Am. Chem. Soc.* **1979**, *101*, 5459. (b) Brownstein, S.; Baywater, S.; Worsfold, D. *J. Organomet. Chem.* **1980**, *199*, 1. (c) Clark, T.; Rhode, C.; Schleyer, P. v. R. *Organometallics* **1983**, *2*, 1344. (d) Schleyer, P.v. R. *J. Am. Chem. Soc.*, **1985**, *107*, 4793.
(92) (a) Vajda, E.; Tremmel, J.; Rozsondai, B.; Hargittai, I.; Maltsev, A. K.; Kagramanov, N. D.; Nefedov, O. M. *J. Am. Chem. Soc.* **1986**, *108*, 4352. (b) Takada, T.; Dupuis, M. *J. Am. Chem. Soc.* **1983**, *105*, 1713. (c) Korth, H.-G.; Trill, H.; Sustmann, R. *J. Am. Chem. Soc.* **1981**, *103*, 4483.
(93) Gobbi, A.; Frenking, G. *J. Am. Chem. Soc.* **1994**, *116*, 9275.

(94) Dewar, M. J. S.; Healy, E. *Organometallics* **1982**, *1*, 1705.

(95) Carrion, F.; Dewar, M. J. S. *J. Am. Chem. Soc.* **1984**, *106*, 3531.

(96) Hoffmann, R. *Chem. Eng. News* **1974**, *52* (July 29), 32.

(97) Salem, L. *The Molecular Orbital Theory of Conjugated Systems*; Benjamin: Reading, MA, 1966; pp 103−106, 494−505.

(98) Longuet-Higgins expresses, however, surprise at the startling result that the distortion actually sets in for $C_{34}H_{34}$, see: Longuet-Higgins, H. C. International Union of Pure and Applied Chemistry—Theoretical Organic Chemistry. *The Kekulé Symposium*; The Chemical Society: London, Bullerworths, 1958 (Sept); p 9.

(99) Berry, R. S. *J. Chem. Phys.* **1961**, *35*, 2253.

(100) Binsch, G.; Heilbronner, E. *J. Mol. Phys.* **1966**, *11*, 305.

(101) Jerusalem Symposia on Quantum Chemistry and Biochemistry. *Aromaticity, Pseudoaromaticity, Antiaromaticity*; Israel Academy of Sciences and Humanities: 1971; Vol. 3: E. Heilbronner: On Mr Binsch's slide the following definition is proposed: "A conjugated π-electron system is called aromatic if it shows neither strong first-order nor second-order double bond fixation". Now, could you point out a molecule, except benzene, which classifies as "aromatic"? G. Binsch: Benzene is a perfect example! E. Heilbronner: Name a second one.

(102) Shaik, S. S.; Bar, R. *Nouv. J. Chim.* **1984**, *8*, 411.

(103) (a) Huber, H.; *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 64; *Angew. Chem.* **1982**, *94*, 69. (b) Ha, T. K.; Cimiraglia, R.; Nguyen, M. T. *Chem. Phys. Lett.* **1981**, *83*, 317. (c) Saxe, P.; Schaefer, H. F., III *J. Am. Chem. Soc.* **1983**, *105*, 1760. (d) Glukhovtsev, M. N.; Schleyer, P. v. R. *Chem. Phys. Lett.* **1992**, *198*, 547.

(104) (a) Feller, D.; Huyser, E. S. Borden, W. T.; Davidson, E. R. *J. Am. Chem. Soc.* **1983**, *105*, 1459. Note that our argument refers to the π-state of formyloxy radical and not to the ground state which is a σ-type radical. (b) For an explanation based on pseudo-Jahn−Teller argument, see: Feller, D.; Davidson, E. R.; Borden, W. T. *J. Am. Chem. Soc.* **1983**, *105*, 3347. Feller, D.; Davidson, E. R.; Borden, W. T. *J. Am. Chem. Soc.* **1984**, *106*, 2513. (c) For a related phenomenon, see: Ayala, P. Y.; Schlegel, H. B. *J. Chem. Phys.* **1998**, *108*, 7560.

(105) Epiotis, N. D. *Nouv. J. Chim.* **1984**, *8*, 11.

(106) Shaik, S. S.; Hiberty, P. C. *J. Am. Chem. Soc.* **1985**, *107*, 3089.

(107) (a) For a collection of references for clusters, see refs 2 and 5. (b) Note that the most stable form of Li_6 is not planar D_{6h}. The planar form is used as a model isoelectronic with the π-component of benzene. (c) For some recent calculations on Li clusters, see: Boustani, L.; Pewestorf, W.; Fantucci, P.; Bonacic-Koutecky, V.; Koutecky, J. *Phys. Rev. B* **1987**, *35*, 9437. (d) For trihalogen anionic clusters, see: Ault, B. S.; Andrews, L. *Inorg. Chem.* **1977**, *16*, 2024. Cahill, P. A.; Dykstra, C. E.; Martin, J. C. *J. Am. Chem. Soc.* **1985**, *107*, 6359. Gabes, W.; Elst, R. *J. Mol. Struct.* **1974**, *21*, 1.

(108) Sini, G. Ph.D. Thesis, Universite de Paris-Sud, Orsay, France, 1991.

(109) Maitre, P. Ph.D. Thesis, Universite de Paris-Sud, Orsay, France, 1991.

(110) (a) Shaik, S.; Hiberty, P. C. *Adv. Quantum Chem.* **1995**, *26*, 99. (b) Shaik, S. S.; Hiberty, P. C. In *Theoretical Models of Chemical Bonding*; Maksic, Z. B., Ed.; Springer-Verlag: Heidelberg, 1991; Vol 4, p 269−322.

(111) Shaik, S.; Hiberty, P. C.; Shurki, A.; Wu, W.; Danovich, D. Unpublished VB calculations on 3-electron−3-center, 4-electron−4-center, and 6-electron−6-center species. These VB calculations which are cited in this study were performed at the VBSCF/6-31G level. A bond in a localized structure is expressed with bond-distorted orbitals as explained by Mo et al.[149]

(112) Benneyworth, P. R.; Balint-Kurti, G. G.; Davies, M. J.; Williams, I. H. *J. Phys. Chem.* **1992**, *96*, 4346.

(113) Shaik, S. S. In *New Concepts for Understanding Chemical reactions*; Bertran, J., Csizmadia, I. G., Eds.; ASI NATO Series C267; Kluwer Publishers: Dordrecht, 1989; pp 165−218.

(114) Coulson, C. A.; Altmann, S. L. *Trans. Faraday Soc.* **1952**, *48*, 293.

(115) Hiberty, P. C. *J. Mol. Struct. (THEOCHEM)* **1998**, *451*, 237.

(116) (a) Mulder, J. J.; Oosterhoff, L. J. *Chem. Commun.* **1970**, 305. Mulder, J. J.; Oosterhoff, L. J. *Chem. Commun.* **1970**, 307. (b) Van Der Hart W. J.; Mulder, J. J.; Oosterhoff, L. J. *J. Am. Chem. Soc.* **1972**, *94*, 5742.

(117) Maitre, P.; Hiberty, P. C.; Ohanessian, G.; Shaik, S. S. *J. Phys. Chem.* **1990**, *94*, 4089. Note that B_0 and the curvature of the curves depend also on the promotion gap. In this manner, the gap becomes the organizing quantity.

(118) Jug, K.; Hiberty, P. C.; Shaik, S. *Chem. Rev.* **2001**, *101*, 1477.

(119) Kutzelnigg, W. in *Theoretical Models of Chemical Bonding*; Maksic, Z. B., Ed.; Springer-Verlag: Heidelberg, 1991; Vol. 2, p 1.

(120) Malrieu, J. P. In *Theoretical Models of Chemical Bonding*; Maksic, Z. B., Ed.: Springer-Verlag: Heidelberg, 1991; Vol. 2, p 107.

(121) Dewar, M. J. S. *J. Am. Chem. Soc.* **1984**, *106*, 669.

(122) Honegger, E.; Heilbronner, E. In *Theoretical Models for Chemical Bonding*; Maksic, Z. B., Ed.; Springer-Verlag: Heidelberg, 1991; Vol. 3, p 99.

(123) Minkin, V. I.; Glukhovtsev, M. N.; Simkin, B. Ya. *J. Mol. Struct. (THEOCHEM)* **1988**, *181*, 93.

(124) Cremer, D. *Tetrahedron* **1988**, *44*, 7427.

(125) Shaik, S. S.; Hiberty, P. C.; Ohanessian, G.; Lefour, J.-M. *Nouv. J. Chim.* **1985**, *9*, 386.

(126) (a) The exponential part of a Morse function, $\exp[-b(r - r_0)]$, varies between unity and zero as r changes from r_o to ∞. This exponential part can be replaced by a dimensionless coordinate, x, which varies also within the same limits, and is simply a bond order coordinate. The Morse function in this latter coordinate becomes $E = D(1 - x)^2$, D being the bond energy. (b) Note though that the relation bond energy-force constant is not universal due to "hybridization effects", see: Kaupp, M.; Metz, B.; Stoll, H. *Angew. Chem. Int. Ed.* **2000**, *39*, 4607.

(127) Bernardi, F.; Celani, P.; Olivucci, M.; Robb, M. A.; Suzzi-Valli, G. *J. Am. Chem. Soc.* **1995**, *117*, 10531.

(128) Janoschek, R. *J. Mol. Struct. (THEOCHEM)* **1991**, *229*, 197.

(129) Stanger, A.; Vollhardt, K. P. C. *J. Org. Chem.* **1988**, *53*, 4889.

(130) (a) Diercks, R.; Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 266. (b) Diercks, R.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1986**, *108*, 3150.

(131) Ou, M.-C.; Chu, S.-Y. *J. Phys. Chem.* **1994**, *98*, 1087.

(132) Hiberty, P. C.; Shaik, S. S.; Ohanessian, G.; Lefour, J.-M. *J. Org. Chem.* **1986**, *51*, 3908.

(133) Hiberty, P. C.; Shaik, S. S.; Lefour, J.-M.; Ohanessian, G. *J. Org. Chem.* **1985**, *50*, 4657.

(134) Glendening, E. D.; Faust, R.; Streitwieser, A.; Vollhardt, K. P. C.; Weinhold, F. *J. Am. Chem. Soc.* **1993**, *115*, 10952.

(135) Ichikawa, H.; Kagawa, H. *J. Phys. Chem.* **1995**, *99*, 2307.

(136) (a) Clabo, D. A., Jr.; Schaefer, H. F., III *J. Am. Chem. Soc.* **1986**, *108*, 4344. (b) Sax, A. F.; Kalcher, J. *J. Chem. Soc., Chem. Commun.* **1987**, 809.

(137) (a) Glukhovtsev, M. N.; Schleyer, P. v. R.; Maerker, C. *J. Phys. Chem.* **1993**, *97*, 8200. (b) See also ref 27, pp 44 and 62. (c) Reference 103d.

(138) (a) Nagase, S.; Kudo, T.; Aoki, M. *J. Chem. Soc. Chem. Commun.* **1985**, 1121. (b) Clabo, D. A., Jr.; Schaefer, H. F., III *J. Chem. Phys.* **1986**, *84*, 1664. (c) Sax, A.; Janoschek, R. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 651; *Angew. Chem.* **1986**, *98*, 634. (d) Nagase, S.; Terame, H.; Kudo, T. *J. Chem. Phys.* **1987**, *86*, 4513.

(139) (a) Nagase, S.; Ito, K. *Chem. Phys. Lett.* **1986**, *126*, 43. (b) Nguyen, M. T.; Hegarty, A. F. *J. Chem. Soc., Chem. Commun.* **1986**, 383.

(140) Reference 27, page 44.

(141) Schleyer, P. v. R.; Jiao, H.; van Eikema Hommes, N. J. R.; Malkin, V. G.; Malkina, O. L. *J. Am. Chem. Soc.* **1997**, *119*, 12669.

(142) P_6 was also reported as a ligand in Mo complexes, see: Scherer, O. J.; Sitzmann, H.; Wolmershäuser, G. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 351; *Angew. Chem.* **1985**, *97*, 358.

(143) Ohanessian, G.; Hiberty, P. C.; Lefour, J.-M.; Flament J.-P.; Shaik, S. S. *Inorg. Chem.* **1988**, *27*, 2219.

(144) (a) Borden, W. T.; Davidson, E. R. *J. Am. Chem. Soc.* **1980**, *102*, 7958; Borden, W. T. *J. Am. Chem. Soc.* **1975**, *97*, 5968. (b) Irngartinger, H.; Rodewald, H. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 740; *Angew. Chem.* **1974**, *86*, 783.

(145) See, however: (a) Ermer, O.; Heilbronner, E. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 402; *Angew. Chem.* **1983**, *95*, 414. (b) Dunitz, J. D.; Krüger, C.; Irngartinger, H.; Maverick, E. F.; Wang, Y.; Nixdorf, M. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 387; *Angew. Chem.* **1988**, *100*, 415.

(146) McKay, S. E.; Kiprof, P.; Brown, A. B. *J. Mol. Struct. (THEOCHEM)* **1996**, *368*, 197.

(147) George, P. *Chem. Rev.* **1975**, *75*, 85.

(148) (a) Levin, G.; Goddard, W. A., III *Theor. Chim. Acta* **1975**, *37*, 253. (b) Levin, G.; Goddard, W. A., III *J. Am. Chem. Soc.* **1975**, *97*, 1649. (c) Voter, A. F.; Goddard, W. A., III *Chem. Phys.* **1981**, *57*, 253.

(149) Mo, Y.; Lin, Z.; Wu. W.; Zhang, Q. *J. Phys. Chem.* **1996**, *100*, 6469.

(150) Shaik, S. S.; Duzy, E.; Bartuv, A. *J. Phys. Chem.* **1990**, *94*, 6574.

(151) Shaik, S.; Reddy, A. C. *J. Chem. Soc., Faraday Trans.* **1994**, *90*, 1631.

(152) Galbraith, J. M.; Schreiner, P. R.; Harris, N.; Wu, W.; Wittkopp, A.; Shaik, S. *Chem. Eur. J.* **2000**, *6*, 1446.

(153) Mo, Y.; Wu. W.; Zhang, Q. *J. Phys. Chem.* **1994**, *98*, 10048.

(154) Behrens, S.; Köster, A. M.; Jug, K. *J. Org. Chem.* **1994**, *59*, 2546.

(155) Wiberg, K. B.; Nakaji, D.; Breneman, C. M. *J. Am. Chem. Soc.* **1989**, *111*, 4178.

(156) (a) Hornig, D. F. *J. Am. Chem. Soc.* **1950**, *72*, 5772. (b) See also: Streitweiser, A., Jr. *Molecular Orbital Theory for Organic Chemists*; Wiley: New York, 1961; p 245.

(157) Kollmar, H. *J. Am. Chem. Soc.* **1979**, *101*, 4832.

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

(159) Dauben, H. J., Jr.; Wilson, J. D.; Laity, J. L. *J. Am. Chem. Soc.* **1969**, *91*, 1993.

(160) Aihara, J.-i. *Pure Appl. Chem.* **1982**, *54*, 1115.

(161) Schleyer, P. v. R.; Jiao, H. *Pure Appl. Chem.* **1996**, *68*, 209.

(162) Jiao, H.; Schleyer, P. v. R. *J. Phys. Org. Chem.* **1998**, *11*, 655.

(163) Schleyer, P. v. R.; Maerker, C.; Dransfeld, A.; Jiao, H.; van Eikema Hommes, N. J. R. *J. Am. Chem. Soc.* **1996**, *118*, 6317.

(164) (a) Shurki, A. Ph.D. Dissertation, Hebrew University, Jerusalem, Israel, 1999. (b) Consider, for example, CDB (C_4H_4) and benzene (C_6H_6). In MO terms, one needs two configurations to describe the π-system of CBD. Using Hückel MOs, these configurations are $\psi_1^2\psi_2^2$ and $\psi_1^2\psi_3^2$ and their matrix element is the corresponding MO exchange integral K_{23} that is a bielectronic matrix element.[113,158] Since each one of the MO configurations corresponds to one of the Kekulé structures of CBD,[70] the matrix element between the two Kekulé structures is also bielectronic. The exchange integral brings in Coulomb correlation that causes the electrons to avoid each other. This is much like the effect of Coulomb correlation on the electrons of a bond when the doubly excited configuration is mixed with the fundamental Hartree–Fock determinant. This mixing decreases the Coulomb repulsion of the bonding electrons by keeping them apart. In benzene, the situation is different and the matrix element between the Kekulé structures is due to the monoelectronic part of the Hamiltonian and is proportional to the AO overlap. This effect increases the probability of the electrons to "meet". A detailed VB analysis in ref 164a shows that in CBD a few of the ionic structures cannot mix into the covalent structures due to symmetry mismatch, while in benzene all the 170 ionic structures mix into the covalent structures. As such, the circular flow of the electrons is interrupted in CBD but not in benzene.

(165) Goddard, W. A., III *J. Am. Chem. Soc.* **1972**, *94*, 793.

(166) Epiotis, N. D. *Lect. Notes. Chem.* **1982**, *29*, 73–104.

(167) For the smallness of these distortions, see the thought-provoking paper on the structure of benzene: Ermer, O. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 782; *Angew. Chem.* **1987**, *99*, 791.

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

(169) Fleischer, U.; Kutzelnigg, W.; Lazzeretti, P.; Mühlenkamp, V. *J. Am. Chem. Soc.* **1994**, *116*, 5298.

(170) Schleyer, P. v. R. Unpublished calculations. Personal communication to S.S.

(171) Frank, N. L.; Baldridge, K. K.; Siegel, J. S. *J. Am. Chem. Soc.* **1995**, *117*, 2102.

(172) Deniz, A. A.; Peters, K. S.; Snyder, G. J. *Science* **1999**, *286*, 1119.

(173) Determined by use of VBDFT(s), see: (a) Wu, W.; Zhong, S.-J.; Shaik, S. *Chem. Phys. Lett.* **1998**, *292*, 7–14. (b) Wu. W.; Danovich, D.; Shurki, A.; Shaik, S. *J. Phys. Chem. A.* **2000**, *104*, 8744.

(174) For an illuminating discussion of the negative DRE(**cb**) and its critique, see ref 78. See also: Bauld, N. L.; Welsher, T. L.; Cessac, J.; Holloway, R. L. *J. Am. Chem. Soc.* **1978**, *100*, 6920.

(175) Garratt, P. J. *Aromaticity*; Wiley: New York, 1986. Page 41 reports a value of $\Delta G^{\ddagger} = 2.4$ kcal/mol for the bond shift in the planar COT.

(176) $\Delta G^{\ddagger} = 3.4$ kcal/mol for the bond shift in the planar COT. See: Paquette, L. A.; Hanzawa, Y.; McCulough, K. J.; Tagle, B.; Swenson, W.; Clardy, J. *J. Am. Chem. Soc.* **1981**, *103*, 2262.

(177) Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **1992**, *114*, 5879.

(178) Hafner, K.; Stowasser, B.; Krimmer, H.-P.; Fischer, S.; Böhm, M. C.; Lindner, H. J. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 630; *Angew. Chem.* **1986**, *98*, 646.

(179) Heilbronner, E.; Yang, Z.-Z. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 360; *Angew. Chem.* **1987**, *99*, 369.

(180) Hertwig, R. H.; Holthausen, M. C.; Koch, W.; Maksic, Z. B. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1192; *Angew. Chem.* **1994**, *106*, 1252.

(181) Choi, C. H.; Kertesz, M. Personal communication.

(182) (a) Jean, Y. *Nouv. J. Chim.* **1980**, *4*, 11. (b) Bloch, R.; Marty, R. A.; De Mayo, P. *J. Am. Chem. Soc.* **1971**, *93*, 3071.

(183) Heilbronner, E.; Shaik, S. *Helv. Chim. Acta* **1992**, *75*, 539.

(184) Heibronner, E., Shaik, S. Unpublished results.

(185) van Wüllen, C.; Kutzelnigg, W. *Chem Phys. Lett.* **1993**, *205*, 563.

(186) Garratt, P. J. *Aromaticity*; Wiley: New York, 1986; pp 46, 240, and 269.

(187) Gogonea, V.; Schleyer, P. v. R.; Schreiner, P. R. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 1945; *Angew. Chem.* **1998**, *110*, 2045.

(188) Zilberg, S.; Haas, Y. *J. Phys. Chem. A* **1998**, *102*, 10843.

(189) (a) van Straten, J. W.; Landheer, I. J.; de Wolf, W. H.; Bickelhaupt, F. *Tetrahedron Lett.* **1975**, 4499. (b) Jenneskens, L. W.; de Kanter, F. J. J.; Kraakman, P. A.; Turkenburg, L. A. M.; Koolhaas, W. E.; de Wolf, W. H.; Bickelhaupt, F.; Tobe, Y.; Kakiuchi, K.; Odaira, Y. *J. Am. Chem. Soc.* **1985**, *107*, 3716. (c) Kostermans, G. B. M.; Bobeldijk, M.; de Wolf, W. H.; Bickelhaupt, F. *J. Am. Chem. Soc.* **1987**, *109*, 2471.

(190) Grimme, S. *J. Am. Chem. Soc.* **1992**, *114*, 10542.

(191) Ma, B.; Sulzbach, H. M.; Remington, R. B.; Schaefer, H. F., III *J. Am. Chem. Soc.* **1995**, *117*, 8392.

(192) Nendel, M.; Houk, K. N.; Tolbert, L. M.; Vogel, E.; Jiao, H.; Schleyer, P. v. R. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 748; *Angew. Chem.* **1997**, *109*, 768.

(193) (a) Mills, W. H.; Nixon, I. G. *J. Am. Chem. Soc.* **1930**, 2510. (b) Siegel, J. S. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1721; *Angew. Chem.* **1994**, *106*, 1808.

(194) Maksic, Z. B.; Eckert-Maksic, M.; Mó, O.; Yáñez, M. Modern Medeling of the Chemical Bond. In *Theoretical and Computational Chemistry*; Maksic, Z. B., Orville-Thomas, W. J., Eds.; Elsevier: Amsterdam, 1999; Vol. 6, p 47.

(195) Baldridge, K. K.; Siegel, J. S. *J. Am. Chem. Soc.* **1992**, *114*, 9583.

(196) Boese, R.; Bläser, D.; Billups, W. E.; Haley, M. M.; Maulitz, A. H.; Mohler, D. L.; Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 313; *Angew. Chem.* **1994**, *106*, 321.

(197) Apeloig, Y.; Arad, D. *J. Am. Chem. Soc.* **1986**, *108*, 3241.

(198) Stanger, A. *J. Am. Chem. Soc.* **1991**, *113*, 8277.

(199) Mitchell, R. H.; Chen, Y.; Iyer, V. S.; Lau, D. Y. K.; Baldridge, K. K.; Siegel, J. S. *J. Am. Chem. Soc.* **1996**, *118*, 2907.

(200) Cardullo, F.; Giuffrida, D.; Kohnke, F. H.; Raymo, F. M.; Stoddart, J. F.; Williams, D. J. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 339; *Angew. Chem.* **1996**, *108*, 347.

(201) Jemmis, E. D.; Kiran, B. *J. Org. Chem.* **1996**, *61*, 9006.

(202) Mohler, D. L.; Vollhardt, K. P. C.; Wolff, S. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1151; *Angew. Chem.* **1990**, *102*, 1200. The authors show that tris(benzocyclobuta)cyclohexane exhibits a strong bond alternation ($\Delta R = 0.09$ Å) and a very long endo-σ-bond. This has been used as evidence for significant bond alternation of the σ-frame due to angular strain. However, the effect is in fact due to the interaction of the central σ-bonds of the cyclohexane with the π-orbitals of the benzo-rings. This interaction elongates the bonds considerably, so that the molecule is part-way along the ring opening process which is found indeed to occur and to possess a relatively small barrier.

(203) Eckert-Maksic, M.; Glasovac, Z.; Maksic, Z. B. *J. Organomet. Chem.* **1998**, *571*, 65.

(204) Hückel calculations of Siegel-cyclohexatriene with inclusion of β-parameters between the bridge π-orbital and the π-orbitals of the benzene moiety change the bond orders and predict the direction of bond alternation observed in the molecule. Heilbronner, E. Personal communication to S.S.

(205) Jorgensen, W. L.; Borden, W. T. *J. Am. Chem. Soc.* **1973**, *95*, 6649. Jorgensen, W. L.; Borden, W. T. *Tetrahedron Lett.* **1975**, 223.

(206) Frank, N. L.; Baldridge, K. K.; Gantzel, P.; Siegel, J. S. *Tetrahedron Lett.* **1995**, *36*, 4389.

(207) Rathore, R.; Lindeman, S. V.; Kumar, A. S.; Kochi, J. K. *J. Am. Chem. Soc.* **1998**, *120*, 6012.

(208) Komatsu, K.; Aonuma, S.; Jinbu, Y.; Tsuji, R.; Hirosawa, C.; Takeuchi, K. *J. Org. Chem.* **1991**, *56*, 195. Komatsu, K.; Jinbu, Y.; Gillette, G. R.; West, R. *Chem. Lett.* **1988**, 2029.

(209) Shaik, S.; Shurki, A.; Danovich, D.; Hiberty, P. C. *J. Am. Chem. Soc.* **1996**, *118*, 666.

(210) Zilberg, S.; Haas, Y. *Int. J. Quantum Chem.* **1999**, *71*, 133.

(211) (a) McWeeny, R. *Theor. Chim. Acta* **1988**, *73*, 115. (b) McWeeny, R. *Proc. R. Soc. London* **1954**, *A227*, 288.

(212) da Silva, E. C.; Gerratt, J.; Cooper, D. L.; Raimondi, M. *J. Chem. Phys.* **1994**, *101*, 3866.

(213) (a) Karadakov, P. B.; Gerratt, J.; Cooper, D. L.; Raimondi, M. *J. Phys. Chem.* **1995,** *99*, 10186. (b) Wright, S. C.; Cooper, D. L.; Gerratt, J.; Raimondi, M. *J. Phys. Chem.* **1992**, *96*, 7943.

(214) (a) Sklar, A. L. *J. Chem. Phys.* **1937**, *5*, 669. (b) Craig, D. P. *Proc. R. Soc. (London)* **1950**, *A202*, 498. Sklar, A. L. *J. Chem. Phys.* **1950**, *A200*, 401. (c) For a lucid summary of the VB method and its applications to excited states, see: *Electronic Spectra and Quantum Chemistry*; Prentice-Hall: Englewood Cliffs, NJ, 1964; pp 228–237.

(215) Callomon, J. H.; Dunn, T. M.; Mills, I. M. *Philos. Trans. R. Soc. London* **1966,** *A259*, 499.

(216) (a) For a theoretical determination of the structure of benzene at the highest current level, see: Gauss, J.; Stanton, J. F. *J. Phys. Chem. A* **2000**, *104*, 2865. (b) For a refined experimental structure (neutron diffraction) see: Jeffrey, G. A.; Ruble, J. R.; McMullan, R. K.; Pople, J. A. *Proc. R. Soc. London* **1987**, *A414*, 47.

(217) Krygowski, T. M.; Anulewicz, R.; Hiberty, P. C. *J. Org. Chem.* **1996**, *61*, 8533. The authors test the σ-effect using the all-perpendicular conformation of the substituents. Using this approach, our molecule **37** shows negligible positive σ-displacement.

(218) Bally, T.; Chai, S.; Neuenschwander, M.; Zhu, Z. *J. Am. Chem. Soc.* **1997**, *119*, 1869.

(219) Borden, W. T.; Davidson, E. R.; Hart, P. *J. Am. Chem. Soc.* **1978**, *100*, 388.

(220) Borden, W. T. In *Encyclopedia of Computational Chemistry*; Schleyer, P. v. R., Allinger, N. L., Clark, T., Gasteiger, J., Kollman, P. A., Schaefer, H. F., III, Schreiner, P. R., Eds.; Wiley: Chichester, 1998; Vol. 1, p 708.

(221) A few papers show that the triplet excited state of antiaromatic species have minima in symmetric geometries. This uniformity

of the C−C distances arises from an interplay of attractive σ- and π-curves. The attractive π-triplet curve does not originate in avoided crossing as described for the singlet Kekulé structures. This feature as well as the magnetic properties of triplet states will be discussed in a forthcoming publication.

(222) Wenthold, P. G.; Hrovat, D. A.; Borden, W. T.; Lineberger, W. C. *Science* **1996**, *272*, 1456.

(223) A simple explanation of the uniformity in the ${}^3A_{2g}$ state of C_4H_4 appears in ref 13.

(224) Baldridge, K. K.; Siegel, J. S. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 745; *Angew. Chem.* **1997**, *109*, 765.

(225) Zilberg, S.; Haas, Y.; Danovich, D.; Shaik, S. *Angew. Chem., Int. Ed.* **1998**, *37*, 1394; *Angew. Chem.* **1998**, *110*, 1470.

(226) Bailey, C. R.; Ingold, C. K.; Poole, H. G.; Wilson, C. L. *J. Chem. Soc.* **1946**, 222.

(227) Mair, R. D.; Hornig, D. F. *J. Chem. Phys.* **1949**, *17*, 1236.

(228) Califano, S.; Crawford, B., Jr. *Spectrochim. Acta* **1960**, *16*, 889.

(229) Scherer, J. R.; Overend, J. *Spectrochim. Acta* **1961**, *17*, 719.

(230) (a) Hochstrasser, R. M.; Sung, H. N.; Wessel, J. E. *Chem. Phys. Lett.* **1974**, *24*, 168. (b) Hochstrasser, R. M.; Wessell, J. E. *Chem. Phys. Lett.* **1974**, *24*, 1.

(231) Wunsch, L.; Metz, F.; Neusser, H. J.; Schlag, E. W. *J. Chem. Phys.* **1977**, *66*, 386.

(232) Robey, M. J.; Schlag, E. W. *J. Chem. Phys.* **1977**, *67*, 2775.

(233) (a) Ozkabak, A. G.; Goodman, L.; Berman, J. M. *Chem. Phys. Lett.* **1990**, *168*, 253. (b) Krogh-Jespersen, K.; Rava, R. P.; Goodman, L. *J. Phys. Chem.* **1984**, *88*, 5503. (c) Goodman, L.; Berman, J. M.; Ozkabak, A. G. *J. Chem. Phys.* **1989**, *90*, 2544. (d) Ozkabak, A. G.; Goodman, L.; Wiberg, K. B. *J. Chem. Phys.* **1990**, *92*, 4115.

(234) Zilberg, S.; Haas, Y. *J. Chem. Phys.* **1995**, 103, 20.

(235) Zilberg, S.; Kendler, S.; Haas, Y. *J. Phys. Chem.* **1996**, *100*, 10869.

(236) (a) Ohno, K. *Chem. Phys. Lett.* **1979**, *64*, 560. (b) Ohno, K. *J. Chem. Phys.* **1991**, *95*, 5524. (c) Orlandi, G.; Palmieri, P.; Tarroni, R.; Zerbetto, F.; Zgierski, M. Z. *J. Chem. Phys.* **1994**, *100*, 2458.

(237) The vibronic coupling effect depends on the energy gap between the zero-order states (at the geometry with uniform distances) and their coupling matrix elements. While the model reproduces the experimental results, it does not provide a clear explanation for the selectivity of the effect. There are several b_{2u}-type vibrations in large molecules (two in benzene but many more in naphthalene, anthracene, etc.); why is the upshift effect is so strong only for the skeletal Kekulé mode? Also, vibronic coupling is strong when the two electronic states are near each other. Why then, is the frequency exaltation in anthracene (and larger acenes) selective for the B_{2u} state, even though the B_{1u} state is lower in energy? Moreover, in benzene the B_{2u} state is ∼5 eV above the ground state and much closer to other excited states, while in naphthalene and other acenes an excited state exists with the same symmetry as the ground state and in proximity to the B_{2u} state. Nevertheless, the major vibronic coupling is between the B_{2u} state and the ground state, which are energetically far from each other (see comment in Brenner, L. J.; Senekowitsch, J.; Wyatt, R. E. *Chem. Phys. Lett.* **1993**, *215*, 63). The major effect is state and mode selective in all systems investigated so far (see e.g., ref 173b for the same phenomenon in polyenes). The vibronic coupling model can reproduce that, but it does not give the qualitative tools to make predictions.

(238) Klingensmith, K. A.; Dewey, H. J.; Vogel, E.; Michl, J. *J. Am. Chem. Soc.* **1989**, *111*, 1539.

(239) (a) Mikami, N.; Ito, M. *J. Chem. Phys.* **1976**, *64*, 3077. (b) Mikami, N.; Ito, M. *Chem. Phys.* **1977**, 23, 141.

(240) Swiderek, P.; Hohlneicher, G.; Maluendes, S. A.; Dupuis, M. *J. Chem. Phys.* **1993**, *98*, 974.

(241) Wolf, J., Hohlneicher, G. *Chem. Phys.*, **1994**, 181, 185.

(242) Zilberg, S., Samuni, U., Fraenkel, R., Haas, Y. *Chem. Phys.*, **1994**, 186, 303.

(243) Zilberg, S.; Haas, Y.; Shaik, S. *J. Phys. Chem.* **1995**, *99*, 16558.

(244) Sironi, M.; Cooper, D. L.; Gerratt, J.; Raimondi, M. *J. Chem. Soc., Chem. Commun.* **1989**, 675.

(245) Consider the excitation gap in the VB diagram in Figure 5 with π-curves only. For an antiaromatic case with $4N$ electrons, the gap is $(2N)\Delta E_{ST}$, where ΔE_{ST} is the singlet−triplet excitation energy of a π-bond. For a $4N + 2$ aromatic species, the gap is $(2N + 1)\Delta E_{ST}$. The ratio between the gaps is then $(2N + 1)/(2N)$. This ratio is smaller than the ratio (≥ 2) between the energy difference between the twin states at the symmetric geometry. This is due to the fact that the vertical resonance energy is much larger for the aromatic species. It follows, therefore, that the curvatures of the twin states at the symmetric geometry will be significantly larger for the antiaromatic species.

(246) Quast, H.; Christ, J. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 631; *Angew. Chem.* **1984**, *96*, 606.

(247) Quast, H.; Herkert, T.; Witzel, A.; Peters, E.-M.; Peters, K.; von Schnering, H. G. *Chem. Ber.* **1994**, *127*, 921.

(248) Quast, H.; Seefelder, M. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 1064; *Angew. Chem.* **1999**, *111*, 1132.

(249) Using the QC state approach (ref 6), we find that B3LYP calculations of benzene give virtually the same distortivity as the π-CISD level used in ref 6.

(250) Shurki, A.; Dijkstra, F.; Shaik, S. Submitted for publication. The paper shows that in C_4H_4, the ionic structures with a diagonal ion pair have B_{2g} symmetry and cannot mix with the ground state which has B_{1g} symmetry, and therefore, the circular flow of the electrons is interrupted. The mixing occurs, however, in the presence of an external magnetic field and induces the paramagnetic ring currents.

CR990363L