can again be invoked to explain these observations. Hexane should be a poorer solvent for interaction with a vacant coordination site, and more nucleophilic methanol should form a stronger interaction. Similar behavior has been reported for the group 6 penta-carbonyls[31,41,42] in coordinating solvents. As a comparison of relative reactivities, the recombination rate of $Mo(CO)_2(PEt_3)_2Br_2$ in hexane is only a factor of 4 smaller than that observed for $Cr(CO)_5$ (7.0×10^5 M^{-1} s^{-1} vs 3×10^6 M^{-1} s^{-1}). This is surprisingly large given the isolability of the dicarbonyl in the absence of nucleophile.

Chromium, molybdenum, and tungsten pentacarbonyls have been observed to react with CO at nearly diffusion-controlled rates in perfluoromethylcyclohexane.[38–40] In contrast, stabilization of a coordinatively unsaturated compound occurring via interaction of a bridging carbonyl in $Mn_2(CO)_9$[14,43,44] does not permit a diffusion-controlled reaction rate. The reaction rate of $Mo(CO)_2(PEt_3)_2Br_2$ in noncoordinating perfluoroalkane solvent could not be measured because of the lack of solubility. The measured shift of the d–d absorbance band to low energy in Teflon does indicate there would be minimal solvent interaction. It is probable, though, that the rate constant in perfluoroalkane would not approach the diffusion-controlled encounter rate because the dicarbonyl is a stable isolable intermediate with a nonzero activation energy barrier.

(41) Dobson, G. R.; Awad, H. H.; Basson, S. S. *Inorg. Chem. Acta* **1986**, *118*, L5.

(42) Asali, K. J.; Basson, S. S.; Tucker, J. S.; Hester, B. C.; Cortes, J. E.; Awad, H. H.; Dobson, G. R. *J. Am. Chem. Soc.* **1987**, *109*, 5386.

(43) Hepp, A. F.; Wrighton, M. S. *J. Am. Chem. Soc.* **1983**, *105*, 5935.

(44) Church, S. P.; Hermann, H.; Grevels, F.-W.; Schaffner, K. *J. Chem. Soc., Chem. Commun.* **1984**, 785.

Is Delocalization a Driving Force in Chemistry? First- and Second-Row Heteroannulenes

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Conjugated squares and hexagons X_n ($n = 4, 6$; X = CH, N, SiH, P) are investigated computationally in the context of the title question. These species exhibit contrasting distortive behaviors with respect to a localizing distortion to bond-alternated structures. In contrast to the case for benzene, P_6 and Si_6H_6 are found to resist only weakly such a distortion, and the square rings Si_4H_4 and P_4 are indifferent to a distortion toward a rectangular geometry, at variance with the case for C_4H_4 and N_4. These trends are rationalized on the basis of valence bond (VB) correlation diagrams, leading to the following general features: (i) the adequate unified description of all conjugated molecules is in terms of a competition between symmetrizing σ frames and distortive π; (ii) the π singlet–triplet energy gap of the corresponding localized two-electron–two-center bonds is the very parameter that correlates with the π distortion energy; (iii) all molecules possess a sizable quantum-mechanical resonance energy (QMRE), but there is a large quantitative difference between "aromatic" and "antiaromatic" compounds. It follows that the Hückel rule cannot be a safe base for predicting geometries of molecules other than hydrocarbons. On the other hand, the VB approach allows an understanding of why the rule is successful for hydrocarbons and when contradictions to it should be expected. In such cases, new structural behaviors emerge that are potentially interesting for the synthesis of molecules with new properties.

Introduction

Electron delocalization and concepts devised to describe its effects, such as aromaticity, have a vital importance in the chemistry of conjugated organic molecules, their stability, and modes of reactivity. Quantum chemistry has produced a very simple means of accounting for much of these phenomena, the $4n/4n + 2$ Hückel rule.[1] As made clear by its very name, this rule states that the stability of π systems derives from their electron count. Several theoretical refinements have been subsequently developed,[2] but electron counting remains their essential building block.

This simple picture has, however, been questioned by recent advances in other areas of chemistry, in particular the synthesis of gas-phase clusters of monovalent atoms, which are isoelectronic analogues of organic π systems. A striking example is the stability of numerous alkali-metal clusters,[3] in contrast with the instability of hydrogen clusters.[4] Halogen[5] and noble-metal[6] trimers together with the former ones have in fact provided a whole spectrum of stability, the explanation of which requires one to go beyond the Hückel rule. In addition, this rule leads one to expect a sharp alternation of properties with cluster size, which is not observed. Thus, for example, despite their "antiaromatic" nature, planar

(1) Hückel, E. *Z. Phys.* **1932**, *76*, 628.

(2) Some leading references follow: (a) Longuet-Higgins, H. C.; Salem, L. *Proc. R. Soc. London, Ser. A* **1960**, *257*, 445. (b) Dewar, M. J. S.; Gleicher, G. J. *J. Am. Chem. Soc.* **1965**, *87*, 685. (c) Dewar, M. J. S.; deLlano, C. *J. Am. Chem. Soc.* **1969**, *91*, 789. (d) van der Hart, W. J.; Mulder, J. J. C.; Oosterhoff, L. J. *J. Am. Chem. Soc.* **1972**, *94*, 5724. (e) Hess, B. A., Jr.; Schaad, L. J. *J. Am. Chem. Soc.* **1971**, *93*, 305. (f) Randic, M. *J. Am. Chem. Soc.* **1977**, *99*, 44. (g) Gutman, I.; Milun, M.; Trinajstic, N. *J. Am. Chem. Soc.* **1977**, *99*, 1692. (h) Haddon, R. C. *J. Am. Chem. Soc.* **1979**, *101*, 1722. (i) Kollmar, H. *J. Am. Chem. Soc.* **1979**, *101*, 4832. (j) Malrieu, J. P.; Maynau, D. *J. Am. Chem. Soc.* **1982**, *104*, 3021. (k) Kuwajima, S. *J. Am. Chem. Soc.* **1984**, *106*, 6496. (l) Klein, D. J.; Trinajstic, N. *J. Am. Chem. Soc.* **1984**, *106*, 8050.

(3) The first prediction of the stability of the lithium trimer was in: (a) Companion, A. L.; Steible, A. J.; Starshak, J. *J. Chem. Phys.* **1968**, *49*, 3637. Numerous theoretical studies have subsequently been devoted to the structure and stability of alkali-metal oligomers. For a recent study and bibliography, see: (b) Koutecky, J.; Beckmann, H.-O.; Bonacic-Koutecky, V.; Fantucci, P.; Pacchioni, G.; Pewestorf, W. *J. Phys. B* **1986**, *19*, L451. The experimental literature is also abundant. A selection is as follows: (c) Foster, P. J.; Leckenby, R. E.; Robbins, E. J. *J. Phys. B* **1969**, *2*, 478. (d) Lindsay, D. M.; Herschbach, D. R.; Kwiram, A. L. *Mol. Phys.* **1976**, *32*, 1199. (e) Wu, C. H. *J. Chem. Phys.* **1976**, *65*, 3181. (f) Thompson, G. A.; Lindsay, D. M. *J. Chem. Phys.* **1981**, *74*, 959. (g) Howard, J. A.; Sutcliffe, R.; Mile, B. *Chem. Phys. Lett.* **1984**, *112*, 84 and references therein.

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alkali-metal tetramers are more stable than the corresponding pair of dimers.[7] This state of matters reveals a need for a new theoretical approach, encompassing these clusters and their isoelectronic π systems, to rationalize these seemingly contradictory tendencies.

We recently proposed such a model,[8,9] based on correlation diagrams of valence bond (VB) type. Its main outcome is the prediction that whenever a dimer X_2 possesses a large vertical singlet–triplet energy gap (ΔE_{ST}), no higher X_n aggregate of the same atom is expected to be stable. In contrast, a low ΔE_{ST} value in X_2 can generate stable X_n ($n > 2$) aggregates. The aggregation of alkali metals is therefore due to the low ΔE_{ST} value of Li_2 (30.5 kcal/mol),[10] Na_2 (22.9 kcal/mol),[11] etc., and the reason for the instability of H_n lies in the very high ΔE_{ST} value of H_2 (244.9 kcal/mol).[12] It is interesting to note that ΔE_{ST} values usually correlate with bond energies, so that a simple generalization emerges: only weak two-electron bonds can generate stable delocalized species.[8a,c]

A crucial point behind the above generalization is that bond lengths are significantly longer in clusters than in isolated bonds. Bringing two Kekulé-type structures into resonance therefore requires bond stretchings that become more costly as the localized bonds get stronger (isolated dimers may be viewed as forming one Kekulé structure, while the aggregate is a resonance hybrid). Resonance stabilization may then not be enough to overcome these local effects. There is a competition in each case, and only when local terms are small enough can delocalization be the most favorable alternative. The VB method is particularly appropriate for such a discussion because it relates molecular wave functions to local bonding properties between pairs of electrons in a simple manner. Drawing the VB correlation diagrams allows for a simple graphical illustration of the competition between local and nonlocal energy terms.

How do π-conjugated molecules fit in this picture? As is well-known, two-electron π bonds of carbon are rather strong and therefore fall in the range where delocalized aggregates are not expected to be stable. It is thus predicted that π systems, were they on their own, would tend to adopt "dimerized" geometries with localized full double bonds. This tendency is opposed, however, by the σ electrons, which always exert a driving force
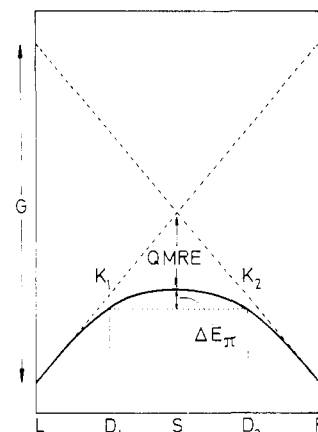

Figure 1. π electron valence bond diagram. The abscissa represents the geometric deformation of a system constituted of alternating short and infinitely long π bonds (L) to its mirror image (R) obtained by shortening the infinitely long bonds and stretching the short ones to infinity. S is the symmetric geometry with uniform bond lengths r_0, and D_1 and D_2 are distorted geometries generated from S by alternately lengthening and shortening r_0 by 0.06 Å. Each dotted line represents the energy of a single Kekulé structure (K_1 or K_2) as a function of the geometry. The thick solid line represents the ground-state energy, resulting from the mixing of the Kekulé structures. G is the diagram gap, which is equal to $^3/_4 n(\Delta E_{ST})$, where n is the number of localized bonds in a Kekulé structure and ΔE_{ST} is the $\pi\pi^*$ singlet–triplet promotion energy of a π bond.[9] ΔE_π is the distortion energy of the delocalized π system. The potential energies of σ bonds are not considered in this figure, for the sake of clarity.

toward symmetrization.[13] The outcome of this σ–π opposition does depend on electron count in organic π systems, since σ appears to win in aromatic and allylic compounds, while the π component imposes localizing distortions in antiaromatics and linear polyenes. When σ terms are stronger as in benzene, the π electrons are forced to adopt the delocalized structure; and even while they are not at their preferred arrangement, resonance does take place and endow them with typical properties of delocalized systems.

Computational experiments[9,14] in which the total deformation energy is partitioned into its σ and π components (ΔE_σ and ΔE_π, see next section) have confirmed this description: the π systems of benzene and allyl radical have been found to behave much like their isoelectronic and isostructural clusters H_3 and H_6 (D_{6h}) with $\Delta E_\pi < 0$, and the molecular geometry is eventually determined by the σ frames.

In the case of cyclobutadiene, the π distortive propensity ($\Delta E_\pi < 0$) is approximately the same as in benzene but the σ frame of the former resists the distortion to a much lesser extent than that of the latter, having four σ bonds instead of six.[9] The result is a rectangular cyclobutadiene, in contrast with a symmetrical, hexagonal benzene. It is concluded that these geometries are not derived in fact, from ΔE_π but rather from quantitative ΔE_σ differences.

All the above properties have been shown to be in full accord with the thermochemical stability of C_6H_6, $C_3H_5{}^\bullet$, and C_4H_4. For instance, a rotational barrier can exist in allyl radical despite, and in agreement with, the π distortive propensity. In a similar manner, benzene was shown to possess a positive resonance energy despite the distortive wills of the π electrons.

Such thermochemical properties were shown to derive mostly from the quantum-mechanical resonance energy (QMRE), which was itself found to follow the Hückel rules, being larger for aromatic than for antiaromatic systems. Thus, benzene possesses a distortive π component, which enjoys a large QMRE in the

(4) (a) Dixon, D. A.; Stevens, R. M.; Herschbach, D. R. *Faraday Discuss. Chem. Soc.* **1977**, *No. 62*, 110. (b) Ichikawa, H. *J. Am. Chem. Soc.* **1983**, *105*, 7467; **1984**, *106*, 6249. (c) Haddon, R. C.; Raghavachari, K.; Whangbo, M.-H. *J. Am. Chem. Soc.* **1984**, *106*, 5364. (d) Siegbahn, P.; Liu, B. *J. Chem. Phys.* **1978**, *68*, 2457.

(5) Some important experimental and theoretical references are as follows: (a) Lee, Y. T.; LeBreton, P. R.; Herschbach, D. R. *J. Chem. Phys.* **1969**, *51*, 455. (b) Mamantov, G.; Vasini, E. J.; Moulton, M. C.; Vickroy, D. G.; Maekawa, T. *J. Chem. Phys.* **1971**, *54*, 3419. (c) Valentini, J. J.; Coggiola, M. J.; Lee, Y. T. *J. Am. Chem. Soc.* **1976**, *98*, 853. (d) Parr, C. A.; Truhlar, D. G. *J. Phys. Chem.* **1971**, *75*, 1844. (e) Koshi, M.; Ito, H.; Matsui, H. *Chem. Phys. Lett.* **1983**, *103*, 180. (f) Sannigrahi, A. B.; Peyerimhoff, S. D. *Chem. Phys. Lett.* **1985**, *114*, 6; *Int. J. Quantum Chem.* **1986**, *30*, 413.

(6) Some important experimental and theoretical references are as follows: (a) Hilpert, K.; Gingerich, K. A. *Ber. Bunsen-Ges. Phys. Chem.* **1980**, *84*, 739. (b) Weltner, W., Jr.; Van Zee, R. J. *Annu. Rev. Phys. Chem.* **1984**, *35*, 291. (c) Morse, M. D. *Chem. Rev.* **1986**, *86*, 1049. (d) Walch, S. P.; Bauschlicher, C. W., Jr.; Langhoff, S. R. *J. Chem. Phys.* **1986**, *85*, 5900 and references therein.

(7) (a) Beckmann, H.-O.; Koutecky, J.; Bonacic-Koutecky, V. *J. Chem. Phys.* **1980**, *73*, 5182. (b) Richstmeier, S. C.; Dixon, D. A.; Gole, J. L. *J. Phys. Chem.* **1982**, *86*, 3942. (c) Martins, J. L.; Buttet, J.; Car, R. *Phys. Rev. B: Condens. Matter* **1985**, *31*, 1804. (d) Wu, C. H. *J. Phys. Chem.* **1983**, *87*, 1534. (e) The rhomboid structure of Li_4 appears to be strongly ionic and is different in this respect from the square Li_4. See: Beckmann, H.-O.; Botschwina, P.; Meyer, W. *Chem. Phys. Lett.* **1979**, *67*, 119.

(8) (a) Shaik, S. S.; Bar, R. *Nouv. J. Chim.* **1984**, *8*, 411. (b) Shaik, S. S.; Hiberty, P. C. *J. Am. Chem. Soc.* **1985**, *107*, 3089. (c) See also VB considerations in: Epiotis, N. D. *Nouv. J. Chim.* **1984**, *8*, 11.

(9) Shaik, S. S.; Hiberty, P. C.; Lefour, J.-M.; Ohanessian, G. *J. Am. Chem. Soc.* **1987**, *109*, 363.

(10) (a) Olson, M. L.; Konowalow, D. D. *Chem. Phys.* **1977**, *21*, 393. (b) Konowalow, D. D.; Olson, M. L. *J. Chem. Phys.* **1979**, *71*, 450.

(11) Konowalow, D. D.; Rosenkrantz, M. E.; Olson, M. L. *J. Chem. Phys.* **1980**, *72*, 6212.

(12) Kolos, W.; Wolniewicz, L. *J. Chem. Phys.* **1965**, *43*, 2429.

(13) With use of a simple harmonic potential, e.g. $0.5k(r - r_0)^2$, it can be shown that an asymmetric distortion (by $\pm\Delta r$) of a pair of bonds always raises the energy by a given increment, irrespective of the initial bond length.

(14) (a) Shaik, S. S.; Hiberty, P. C.; Ohanessian, G.; Lefour, J.-M. *Nouv. J. Chim.* **1985**, *9*, 385. (b) Hiberty, P. C.; Shaik, S. S.; Lefour, J.-M.; Ohanessian, G. *J. Org. Chem.* **1985**, *50*, 4657.

**Table I.** Structural Data (Å) for Four- and Six-Membered Rings[a]

X	X₆		X₄			
	hexagon	distorted	square	distorted	$(XH)_2$	$(XH_2)_2$
CH	1.40[b]	1.34/1.4627	1.453[c]	1.393/1.5162	1.315[d]	1.542[d]
N	1.322[e]	1.262/1.3848	1.3736[f]	1.3136/1.4370	1.239[d]	1.451[d]
SiH	2.223[g]	2.163/2.2847	2.2856[f]	2.2256/2.3476	2.143[h]	2.382[h]
P sv[i]	2.185[i,j]	2.125/2.2467	2.2674[f]	2.2074/2.3294	2.102[k]	2.357[k]
P svp[i]	2.096[l]		2.143[m]	2.083/2.2051	2.005[l]	2.214[l]

[a] The choice of distorted geometries is described in the text. [b] Experimental value of ref 37. The 6-31G value is 1.396 Å from ref 30. [c] Minimal basis plus π-CI value from ref 38. [d] 3-21G value from ref 39. [e] DZ value from ref 23. [f] 6-31G value from this work. [g] DZ value from ref 20b. [h] 3-21G value from ref 20a. [i] For P₄ and P₆, sv refers to split-valence geometries (see footnotes f and k), while svp stands for 6-31G* (see footnotes l and m). [j] The 3-21G value is 2.197 from ref 28. [k] 3-21G value from ref 28. [l] 6-31G* value from ref 28. [m] 6-31G* value from this work.

experimental geometry, while the equally distortive π part of cyclobutadiene possesses a much smaller QMRE. The situation can be summarized as in Figure 1, where a π electron valence bond diagram is displayed. It illustrates the energy difference between each individual Kekulé structure and the delocalized ground state resulting from their mixing. The stabilization brought by the mixing is maximal at the symmetric geometry, diminishes but does not vanish in the distorted geometries D_1 and D_2, and finally would vanish in a hypothetical system constituted of n local π bonds separated from each other by an infinite distance. Note that in real conjugated molecules, be they cyclic or open polyenes, the geometries are nearly confined between the limits D_1 and D_2 by the σ frame. Thus, the ground-state energy curve can exhibit a maximum; i.e., the π system can be distortive even though it enjoys a substantial QMRE as a result of delocalization.

One of the predictions of the VB model is that π bonds which possess much lower ΔE_{ST} values than C=C would generate delocalized π systems that could be stable against a localizing distortion, much like alkali-metal clusters. Such molecules would be endowed with new properties; for instance it would be possible to design nondistortive "antiaromatic" square analogues of C_4H_4. Their study is expected to shed light on the two aspects of electron delocalization: π distortion propensity and QMRE.

It is the purpose of this paper to investigate a series of such molecules. A simple way to reduce bond energies and ΔE_{ST} is to go down the periodic table. The synthesis and chemistry of unsaturated compounds of silicon and phosphorus has been an active field of research in recent years,[15] and it has indeed been found that their properties are quite different from those of usual hydrocarbon compounds. The molecules studied here are π analogues of benzene and cyclobutadiene, made up of nitrogen, silicon, and phosphorus atoms, i.e. the planar, monocyclic N_6, Si_6H_6, and P_6 benzenoids **1** and N_4, Si_4H_4, and P_4 cyclobutadienoids **2**.

X = CH, N, SiH, P

1   **2**
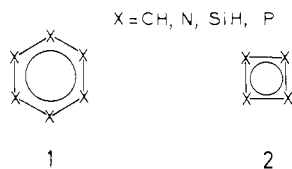
None of these molecules have been unambiguously characterized to date, even though N_6 has been reported as a fleeting product of the UV photolysis of $(PPh_3)_2Pt(N_3)_2$[16] and P_6 has been synthesized as a bridging central ligand in the triple-decker sandwich compound $Cp'Mo(\eta^6\text{-}P_6)MoCp'$, where Cp' is $\eta^5\text{-}C_5\text{-}(CH_3)_5$.[17] P_4 is, however, well-known in its tetrahedral geometry[18]

and is the molecular building block of white phosphorus. Recent computations by Clabo and Schaefer[19a] also suggested that tetrasilatetrahedrane is a true minimum on the Si_4H_4 potential energy surface but that a planar geometry of D_{2h} cyclobutadienoid type is more stable.[19b] This structure in turn may be stabilized by out-of-plane motions, probably leading to a low-symmetry nonplanar structure as the absolute minimum. Results for Si_6H_6[20] and P_6[21] indicated that these molecules may well be amenable to observation, in their D_{6h} conformation, with modern experimental techniques. Recent results, however, show quite a flat surface for Si_6H_6 with a puckered molecule being 1.7 kcal lower.[22]

As a whole, our models for aromatic and antiaromatic compounds are among the lowest structures in all cases and therefore could have been expected to display bonding properties analogous to those of hydrocarbons within the domain of planar, cyclic structures. A spectacular illustration that negates this expectation is given by the fact that N_6, which as recalled above is unstable or metastable, has an optimized[23] N–N length closer to a double bond than is the C–C bond in benzene compared to the bond length of ethylene.

In this context, our aim in this paper will be to answer the following questions: (i) Is the correlation between π instability and the ΔE_{ST} value of the dimer of general validity? (ii) Do low ΔE_{ST} values generate stable benzenic π systems? (iii) Can second-row analogues of cyclobutadiene be stable in a square geometry?

Before describing the results and the accompanying analysis, we first discuss in detail the computational aspects of this work.

Computational Details

Our strategy involves two steps. The first is the computation of the energy required to distort each symmetrical structure to a partially localized one and the decomposition of this energy into its σ and π components. The second one is the evaluation of the quantum-mechanical resonance energy (QMRE), a well-defined quantity that corresponds to the resonance stabilization in the symmetrical geometry. All definitions have been presented in a previous paper,[9] hereafter referred to as I, and we will therefore mainly focus here on the more specific computational details for the molecules under study.

1. Geometries. As recalled above, some of the molecules among the set chosen here have recently been subject to computations by several groups. We have therefore used their geometries when available and tried to pick up values at a common level of theory as far as possible. The other molecules were optimized at the Hartree–Fock level (as is the case in the literature), by using the standard closed-shell method for hexagons and Davidson's ROHF[24] method for squares. All calculations were

(15) See, e.g.: (a) Cowley, A. H. *Polyhedron* **1984**, *3*, 389; *Acc. Chem. Res.* **1984**, *17*, 386. (b) Raabe, G.; Michl, J. *Chem. Rev.* **1985**, *85*, 419.
(16) Vogler, A.; Wright, R. E.; Kunkely, H. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 717.
(17) (a) Scherer, O. J.; Sitzmann, H.; Wolmershaüser, G. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 351. See also: (b) Schmettow, W.; Lipka, A.; von Schnering, H. G. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 345. (c) Abicht, H.-P.; Hönle, W.; von Schnering, H. G. *Z. Anorg. Allg. Chem.* **1984**, *579*, 7.
(18) (a) Stoll, D. R., Prophet, H., Eds. *JANAF Thermochemical Tables*; NSRDS-NBS 37; Government Printing Office: Washington, DC, 1971. (b) Barin, I.; Knacke, O. *Thermochemical Properties of Inorganic Substances*; Springer: West Berlin, 1971.

(19) (a) Clabo, D. A., Jr.; Schaefer, H. F., III. *J. Am. Chem. Soc.* **1986**, *108*, 4344. (b) It has recently been reported that a C_{2v} bis(siladiyl), (SiSi-H₂)₂, is the most stable structure: Sax, A. F.; Kalcher, J. *J. Chem. Soc., Chem. Commun.* **1987**, 809.
(20) (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. (d) See, however, the recent results of: Nagase, S.; Teramae, H.; Kudo, T. *J. Chem. Phys.* **1987**, *86*, 4513. (e) For an earlier, semiempirical calculation, see: Dewar, M. J. S.; Lo, D. H.; Ramsden, C. A. *J. Am. Chem. Soc.* **1975**, *97*, 1311.
(21) (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. (c) For an earlier, semiempirical calculation, see: Baird, N. C. *Can. J. Chem.* **1984**, *62*, 341.
(22) Sax, A. F.; Kalcher, J.; Janoschek, R. *J. Comput. Chem.*, in press.
(23) Saxe, P.; Schaefer, H. F., III. *J. Am. Chem. Soc.* **1983**, *105*, 1760.

carried out with the MONSTERGAUSS series of programs;[25] the results are displayed in Table I and will be discussed in the next section.

The distortion that brings each symmetrical geometry to a localized one has been chosen as in paper I. Standard C–C values of 1.40 and 1.34 Å were used to mimic benzene and ethylene, respectively. This is just our criterion for calibrating the bond compression for all types of bonds. A value of 0.06 Å is therefore quite close to the aromatic–nonaromatic bond length difference for carbon and reasonably close to the same quantity for the other atoms, as may be judged from the pure double-bond lengths listed in Table I. Localized geometries were chosen so as to be close to the B_{2u} path, which allows one C–C distance to contract and the adjacent ones to expand, thereby connecting the symmetrical molecule to three identical dimers. This is crucial since B_{2u} is the only mode along which the π systems may be distortive (in particular, mixing of a significant amount of A_{1g} leads to erroneous conclusions[26]). As appears in Table I, bond compressions and elongations are, however, not strictly equal in each molecule. This is due to a second requirement that in order to perform a meaningful σ/π energy partition, the localized and delocalized structures must have equal nuclear repulsions between heavy atoms. Each bond compression was therefore optimized so as to match the nuclear repulsion of the corresponding symmetrical structure. The "single" bond of distorted benzene is thus 1.4627 Å long, so that the increment is in fact quite close to 0.06 Å, corresponding to a typical value for a conjugated C_{sp^2}–C_{sp^2} single bond. In any case, it should be noted that the B_{2u} mode is defined at the symmetrical point and that larger lengthenings than shortenings are eventually required to lead to three dimers at infinity.

2. Basis Sets and Electron Correlation. While it is now well established that calculations at a moderate level of theory, e.g. split-valence SCF, are reasonably accurate for structural studies on conjugated hydrocarbons, recent work on heteroannulenes has led to a much less clear situation. It seems quite certain that at least split-valence bases should be used, all the more as second-row atoms are involved, but much debate has centered on the role of polarization functions on heavy atoms and that of configuration interaction (CI).

The existence of a difficulty has been highlighted by the work of Saxe and Schaefer on the N_6 potential surface.[23] Double-ζ calculations found the optimum hexagon to be a transition state on the B_{2u} dissociation mode, surrounded by two slightly distorted minima of very close energy, and then two transition states in which bond stretches and shrinkages are much more extensive, with an activation barrier of only 1.3 kcal/mol. Upon addition of polarization functions, the D_{6h} structure became a true minimum, separated from 3 N_2 by an activation barrier of 10.3 kcal/mol. Inclusion of electron correlation via singles and doubles CI on the same geometries led however to a reduction of this barrier to 1.3 kcal/mol and even to a negative value of -3.8 kcal/mol when Davidson's correction[27] for unlinked clusters was included. It is therefore not clear whether cyclic N_6 would be a stable species if geometry optimizations had been carried out at the correlated level.

A similar effect was found by Nagase and Ito for P_6,[28] with a double minimum at the split-valence 3-21G SCF level and a single hexagonal well with the polarized 6-31G* basis. Inclusion of CI at the MP2/6-31G* and MP3/6-31G* levels led to a decrease of the barrier, which however remained substantially larger than in the N_6 case (20.2 kcal/mol with MP3/6-31G*). This quantitative difference was attributed to the fact that the $P_6 \rightarrow 3P_2$ reaction is slightly endoergic ($+4.8$ kcal/mol) while $N_6 \rightarrow 3N_2$ is strongly exoergic (-227.6 kcal/mol).

In the case of benzene, the activation energy is much higher (ca. 60 kcal/mol) and, in contrast to the case for N_6 and P_6, no distorted minimum was found at the SCF 3-21G level. The results of Bach et al.[29] indicated similar computational trends since polarization functions tend to increase the SCF barrier while it is decreased by CI. Here again, it was noted that reliable relative energies demand a careful treatment of electron correlation. More specifically, the important lowering of the activation barrier was found to arise from the correlation of the σ electrons. No such study has been reported to date for hexasilabenzene, Si_6H_6.

What conclusions can be drawn from these results? It has been argued in the case of hydrocarbons that both polarization functions and

CI should act in favor of the most delocalized species.[30] because the electrons are more mobile and should therefore execute a more complicated motion. This applies to the above molecules as well and explains why distorted minima are most probably an artifact of DZ and split-valence bases for particularly flat surfaces and disappear at higher levels. When the surface is not flat as in benzene, such minima do not exist. This discussion does not apply, however, to highly distorted structures which have to be considered as transition states for chemical reactions. In particular, CI is much more important for structures involving highly stretched bonds than in normal closed-shell molecules and therefore lowers the activation barriers.

It appears that a highly precise determination of structures is not available at present but that this may not be a severe handicap with regard to our specific aims in this study. This idea stems from our previous results for two surfaces of very different flatness, viz. C_6H_6 and N_6, that yielded separated σ and π energy variations of much larger amplitudes than for the total energy. The *trends* for these energy components are likely to be much less sensitive to small structural changes than is the total potential energy, especially when the corresponding surface is very flat as in N_6. This is also reinforced by the fact that the high sensitivity of the activation barrier height to the level of computation is most probably due to the difficulty of describing several highly stretched σ bonds. This is not of concern for the present study since our interest is limited, as may be seen in Table I, to small distortions. In this geometry range, we know that π electron correlation will tend to stabilize more the hexagon and to stretch its bonds.

The effect of polarization functions seems much more difficult to predict on qualitative grounds, for both types of distortions, since no general trend seems to emerge from the various studies cited above. In the absence of computational information at the correlated level, we note that Haddon and Raghavachari,[30] using symmetrical and distorted geometries for benzene very similar to ours, found that d orbitals give opposite contributions to the distortion energy at the SCF and CI levels, largely canceling each other. We have therefore performed all computations at the 6-31G split valence level,[31] unless otherwise stated. As far as geometry is concerned, the situation is not clearer. While polarization functions always work at length shortening, their quantitative effect on D_{6h} geometries does not follow the expected pattern, numerical values being -0.01 Å (C_6H_6), -0.034 Å (N_6), -0.018 Å (Si_6H_6), and -0.101 Å (P_6). It is generally believed that d orbitals are more important for third-row than for second-row atoms, even in nonhypervalent molecules. Here, it seems that they discriminate between columns instead of rows of the periodic table. The growing importance of d orbitals with increasing electronegativity has already been observed in several cases (see, e.g., ref 29b), but such a gap seems very unusual. Since the geometries of P-based molecules seem particularly sensitive to d orbitals, test calculations with the polarized 6-31G* (5d) basis set have been performed.

Correlation corrections on π energetics were evaluated by CI calculations, which were carried out with the CIPSI algorithm,[32] as implemented by the Toulouse group.[33] This method may be described as multireference Moller–Plesset perturbation theory. The variational subspace includes all determinants whose coefficients are larger than a threshold τ, from which all single and double electron promotions to virtual orbitals are generated and treated to second order. In this study, a value of 0.01 has been used for τ. CI was restricted to the valence π space, therefore involving twelve orbitals and six electrons for six-membered rings and eight orbitals and four electrons for four-membered rings. For silicon and phosphorus compounds, the occupied core π SCF orbitals were kept frozen. Since these doubly occupied orbitals may be considered as localized electron pairs, it is expected that they would bring a negligible contribution to the energy change corresponding to a distortion that preserves the sum of nuclear repulsions. At this level, 90% or more of the correlation energy obtained is within diagonalization in all cases. We note that higher excitations, in particular quadruples, make a significant contribution and must be included for reliable results to be obtained.

3. Computation of Distortion and Quantum-Mechanical Resonance Energies. As discussed in paper I, the total distortion energy can be partitioned into σ and π components. This can be achieved by following the formal decomposition of π electron theories.[34] In this manner, the π energy gathers the pure π terms and σ–π repulsions, while the σ energy

(24) Davidson, E. R. *Chem. Phys. Lett.* **1973**, *21*, 565.
(25) Peterson, M. R.; Poirier, R. A. *MONSTERGAUSS*; Department of Chemistry, University of Toronto: Toronto, Ontario, Canada, 1981.
(26) (a) Baird, N. C. *J. Org. Chem.* **1986**, *51*, 3907. (b) Hiberty, P. C.; Shaik, S. S.; Ohanessian, G.; Lefour, J.-M. *J. Org. Chem.* **1986**, *51*, 3908.
(27) Davidson, E. R. In *The World of Quantum Chemistry*; Daudel, R., Pullman, B., Eds.; D. Reidel: Dordrecht, Holland, 1974; pp 17–30.
(28) Nagase, S.; Ito, K. *Chem. Phys. Lett.* **1986**, *126*, 43.
(29) Bach, R. D.; Wolber, G. J.; Schlegel, H. B. *J. Am. Chem. Soc.* **1985**, *107*, 2837.

(30) Haddon, R. C.; Raghavachari, K. *J. Am. Chem. Soc.* **1985**, *107*, 289.
(31) (a) For C and N: Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257. (b) For Si and P: Francl, M. M.; Pietro, W. J.; Hehre, W. J.; Binkley, J. S.; Gordon, M. S.; DeFrees, D. J.; Pople, J. A. *J. Chem. Phys.* **1982**, *77*, 3654.
(32) Huron, B.; Malrieu, J.-P.; Rancurel, P. *J. Chem. Phys.* **1973**, *58*, 5745.
(33) Pélissier, M. Thèse d'Etat, Toulouse, France, 1980.
(34) Parr, R. G. *Quantum Theory of Molecular Electronic Structure*; W. A. Benjamin: New York, 1963.

is made up of the pure σ terms. We have shown that such a σ energy is reasonable in that it is in good agreement with those computed when π resonance is "turned off" and when there are no π electrons at all.[35] This partition is performed at the SCF level, and π-CI is subsequently used to refine the π energy variation. The situation is somewhat more complicated for four-membered rings, since distorted structures are best calculated with the closed-shell Hartree–Fock method, while the square structures need the restricted open-shell formalism. As a consequence, the energies of both geometries cannot be compared directly, and numerical values are of interest at the CI level only. For the same reason, the σ distortion energies ΔE_σ that are computed at the SCF level are not reliable. Our previous experience[9] with the various computation schemes recalled above has shown that the most adequate method is to extract ΔE_σ from high π-spin quintet states, which treat both square and rectangular structures on equal footing. The $\Delta E_\sigma^{\text{quint}}$ values reported in Table III are therefore such values, along the lines detailed in paper I.

The energy gain due to the resonance interaction of the two Kekulé forms may be evaluated from various quantities. The one corresponding exactly to the π resonance stabilization at the experimental geometry is referred to as the quantum-mechanical resonance energy (QMRE). The computation of QMRE, as first devised by Kollmar,[2i] involves the calculation of a reference molecule conceived to mimic a pure Kekulé structure at the same geometry. Its σ orbitals are identical with those of the real molecule under study, while each π orbital is that of ethylene at the same geometry, localized on each formal double bond. The energy at the first SCF cycle is that of this set of orbitals (the π orbitals being only orthogonalized) and is therefore the energy of the reference structure. At the end of the SCF process, the mixings between localized π orbitals are optimal and the canonical, delocalized MOs result. It should be emphasized that such SCF calculations do not strictly correspond to the resonance energy between covalent functions such as those appearing in the VB diagram (Figure 1), because of the presence of an excess of ionic terms inherent to the SCF theory. Voter and Goddard have recently computed the resonance energy of cyclobutadiene using the GRVB method,[36] which amounts to optimizing the role of these ionic functions in the resonance hybrid. With the same square geometry as ours, a value of 22 kcal/mol was obtained, rather similar to our 30 kcal/mol result. We are thus confident that SCF calculations will yield a reasonable evaluation of QMREs. It is also felt that basis set extension would not bring important changes to the values reported here. Comparison with minimal basis calculations (paper I; ref 22 of the paper by Voter and Goddard;[36] ref 2i) showed a limited reduction of QMRE in all cases on going to the double-ζ level.

The case of square four-membered rings is peculiar in that there is a second way of computing their QMRE. Indeed, the closed-shell SCF wave function corresponds to a single Kekulé structure for its covalent part. Such a wave function is identical with the former, with an ethylene π bond, when a minimal AO basis set is used. This no longer holds with a more flexible basis since this flexibility is used to optimize two different bonding situations. In what follows, the QMRE is always computed as the difference between closed- and open-shell SCF energies.

Results and Discussion

1. Six-Membered Rings. Hexagonal geometries are given in the second column of Table I. All bond lengths are seen to be intermediate between pure single- and double-bond values (see last two columns of Table I) as is typical of delocalized molecules. As discussed above, it is difficult to assess the strength of delocalization from these geometries as electron correlation and polarization functions are expected to bring changes to the hexagonal geometries. Nevertheless, a striking feature is that even those hexamers that are nearly indifferent to a B_{2u} distortion have a relatively short bond length. As discussed below, these geometries are best analyzed in terms of superposed σ and π energies.

Total distortion energies are reported at the SCF and CI levels as the third and fifth rows, respectively, of Table II. In agreement with previous computations, benzene, hexasilabenzene, and hexaphosphabenzene are found to be stable against a B_{2u} distortion while hexaazabenzene is slightly unstable at the SCF level and

Table II. Energy Quantities (kcal/mol) for Six-Membered Rings[a]

	N_6	C_6H_6	P_6	Si_6H_6
$\Delta E_\sigma^{\text{SCF}}$	+13.7	+16.3	+3.8	+5.3
$\Delta E_\pi^{\text{SCF}}$	−14.5	−9.7	−3.3	−2.4
ΔE_T^{SCF}	−0.8	+6.6	+0.5	+2.9
ΔE_π^{CI}	−13.3	−9.1	−2.8	−2.1
ΔE_T^{CI}	+0.4	+7.2	+1.0	+3.2
QMRE	102.5	85.2	44.1	41.6
ΔE_{ST}[b]	108.3[c]	99.0[c]	37.6[d] 47.3[f]	40.0[e]

[a] All the values are at the 6-31G level. [b] ΔE_{ST} stands for the singlet–triplet energy gaps of the dimers. [c] 3-21G geometry.[39] [d] 3-21G geometry.[41] [e] 3-21G geometry.[42] [f] 6-31G** geometry.[43]

stable when π-CI is included. As expected, benzene is by far the most reluctant to distort in the series. Correlation corrections are found to be rather limited, the largest value being 1.2 kcal/mol in the N_6 case.

Decomposition of the total deformation energies into σ and π components at the SCF level leads to $\Delta E_\sigma^{\text{SCF}}$ and $\Delta E_\pi^{\text{SCF}}$ quantities, the first two rows in Table II. It is seen that the general conclusion of paper I receives full confirmation: the total distortion energies are the results of a competition between unstable π systems and resisting σ frames. Even more, all π systems are found to be distortive, even though second-row atoms generate much weaker bonds than do first-row ones. The numerical values of ΔE_π are slightly lowered by π-CI as expected (fourth row of Table II), but the resulting energies remain significantly negative. π-Instability therefore seems established as a general phenomenon for conjugated molecules.

A clear trend emerges from the ΔE_π^{CI} values listed: first-row atoms generate π systems that are more unstable than those of the second row, and within each row, the more electronegative the atom, the more unstable the π hexagon. This is fully consistent with the listed vertical singlet to triplet transition energies ΔE_{ST},[40] except for a nonsignificant reversal between the ΔE_{ST} values of Si=Si and P=P double bonds that is due to the inaccuracy of the 3-21G geometry (see the ΔE_{ST} value calculated at the 6-31G** geometry). This is another confirmation of our previous results, that the ΔE_{ST} value is the very parameter that correlates the trend of π instability, though no causality is necessarily meant here.

The statement that second-row atoms generate less distortive π systems than first-row atoms may seem paradoxical, considering that multiple bonds between second-row atoms are rare compared to the particularly rich variety of unsaturated molecules containing C, N, and O. It is a strange outcome of facts that the lower distortive propensity of Si and P π systems is not materialized by stable conjugated molecules. This is due to different and stronger structural preferences of the σ electrons to form nonplanar molecules, e.g. tetrahedral P_4 or hexasilaprismane, Si_6H_6.

Let us now turn to the resonance stabilization, that is, the QMRE values appearing as the sixth row in Table II. The values obtained range from 102.5 to 41.6 kcal/mol, thus underlining the fact that QMRE is quantitatively very significant even for unstable molecules and also undergoes large variations. A striking result is that the largest QMRE is that of N_6, a molecule whose stability will be marginal even if it is established. This is in line with our previous results that the unstable H_6 hexagon has the largest resonance interaction among the delocalized hexagons, including

(35) Moreover, we have checked that an equal attribution of σ–π interactions in the σ and π energies, while of course changing absolute values, leaves the conclusion of stability or instability unchanged.
(36) Voter, A. F.; Goddard, W. A. *J. Am. Chem. Soc.* **1986**, *108*, 2830.
(37) Tamagawa, K.; Iijima, T.; Kimura, M. *J. Mol. Struct.* **1976**, *30*, 243.
(38) Borden, W. T.; Davidson, E. R.; Hart, P. *J. Am. Chem. Soc.* **1978**, *100*, 388.
(39) Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 939.

(40) These values are for doubly bonded species. Strictly speaking, however, the energy gap of the VB correlation diagram refers to the ΔE_{ST} values of the dissociation products, that is, the triple bonds of acetylene, dinitrogen, etc. The ordering is the same as that of double bonds. It seems, however, more adequate to use the ΔE_{ST} values of the double bonds, which closely correspond to the short bonds in the distorted hexamers that we calculate (see Table I).
(41) Ha, T.-K.; Nguyen, M. T.; Ruelle, P. *Chem. Phys.* **1984**, *87*, 23.
(42) Poirier, R. A.; Goddard, J. D. *Chem. Phys. Lett.* **1981**, *80*, 37. The Si=Si length in ref 20a is 2.143 Å.
(43) Yoshifuji, M.; Hashida, T.; Inamoto, N.; Hirotsu, K.; Horiuchi, T.; Higuchi, T.; Ito, K.; Nagase, S. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 211.

Table III. Energy Quantities (kcal/mol) for Four-Membered Rings[a]

	N_4	C_4H_4	P_4		Si_4H_4
			sv^b	svp^b	
ΔE_σ^{quint}	+9.2	+7.6	+2.9	+3.7	+2.7
ΔE_π^{CI}	−14.7	−11.0	−2.6	−3.6	−2.1
ΔE_T^{CI}	−5.5	−3.4	+0.4	+0.1	+0.6
QMRE	44.6	30.2	24.8	23.8	17.7
ΔE_{ST}^c	108.3	99.0	37.6	47.3	40.0

[a] All quantities are at the 6-31G level unless otherwise noted. [b] For P_4, sv stands for 6-31G//6-31G calculations, while svp stands for 6-31G//6-31G*. [c] ΔE_{ST} values are, as in Table II, at the 6-31G//3-21G level, except for P_4 svp, which is at the 6-31G//6-31G** level.

benzene itself. The whole series of QMRE uncovers an even more intriguing trend: large QMRE values accompany large distortive tendencies, while lower values correspond to the less unstable π frames. Indeed, we can see from Table II that both orderings are the same. The paradox is in fact only an apparent one. The role of resonance stabilization should, in a more precise manner, be stated as follows: *all other things being equal*, a larger resonance interaction leads to a more stable molecule. However, our results show that when two cases are compared, both the resonance interaction and the energy that is necessary to bring a Kekulé structure to the hexagonal geometry do change. It turns out that the variation of QMRE is not enough to reverse the π distortive tendency set up by the ΔE_{ST} ordering.

2. Four-Membered Rings. Geometry optimization has been done for four-membered rings at the SCF ROHF level. The results reported in Table I show that the optimum bond lengths are consistently longer than in six-membered rings. While the difference amounts to 0.05 Å for C and for N, it is only slightly more for Si and P (0.06 and 0.08 Å, respectively), which is a relatively lesser lengthening. All are still shorter than the corresponding single bonds.

Since d orbitals have been previously found to affect the geometry of hexagonal P_6 in a significant manner, the geometry of P_4 has been reoptimized at the 6-31G* level. In a manner completely analogous to that for P_6, the P–P bond length was reduced (−0.125 Å for P_4, −0.101 Å for P_6). The distortion energy has then been recomputed with 6-31G at the 6-31G* geometry (such values are referred to as 6-31G//6-31G*).

Total distortion energies are reported in Table III. It appears that C_4H_4 and N_4 are, as expected, significantly distortive. The results for P_4 and Si_4H_4 sharply contrast with the former since *the distortion energies are computed to be very small* and even positive for both. The smallness of these ΔE_T values does not allow the definite conclusion that such squares resist a localizing distortion. Recent results[19] indicate that a complete search on the potential surface for Si_4H_4 would have possibly led to a small and negative ΔE_T value. Be the value as it may, the results of Table III show that the "antiaromatic" P_4 and Si_4H_4 squares do not possess any marked tendency to undergo a distortion to rectangular structures.

As predicted, it can be seen from Table III that the π components of the squares become less distortive as the ΔE_{ST} gap decreases. The σ components are seen to resist the distortion, as expected, and in the Si and P cases the two opposite driving forces are almost equal. It is apparent that the geometry of the cyclobutadienoids is a quantitative outcome of the σ–π opposition rather than a qualitative outcome of the Hückel rule. We note that, just

as was found for six-membered rings, large QMRE values in squares go along with large distortion energies of the π frames.

A final point concerns the relation between the hexagons and the squares; what is the difference between the two families? As can be seen from Tables II and III, the π distortion energies (ΔE_π^{CI}) are approximately the same, while the σ resistance values are consistently much smaller for the squares owing to their smaller number of bonds. The overall outcome is that the squares are more distortive than the hexagons and that this quantitative difference is σ dominated. The property that marks a distinct difference between the two families is the QMRE, which is approximately twice as large for the hexagons. QMRE is then dominated by electron count, as has been previously established in the framework of VB theory,[2d,j,k] and this is where the Hückel rule comes to the fore.

Conclusion

The conjugated molecules here investigated exhibit very different properties as far as their distortive propensity is concerned: while benzene strongly resists distortion, the isoelectronic species do not, and while four-membered rings of the first row avoid a square geometry, those of the second row show no such tendency. These trends, which may seem at first glance quite puzzling, are in fact simply rationalized in the framework of the VB diagrams. Thus, the tendency to adopt a symmetric or a distorted geometry is the result of a competition between two opposite driving forces: that of the σ skeleton, which is by nature always symmetrizing, and that of the π electrons, which, in all the cases investigated here, favors localized structures.

In accord with the VB diagram model, the distortive propensity of the π component becomes weaker with a decrease of the singlet–triplet energy gap of the corresponding two-electron π bond. As a result, the π distortion energy becomes very small in second-row compounds such as P_6, Si_6H_6, P_4, and Si_4H_4.

A consequence of the σ–π competition is that second-row squares have properties very different from those of first-row ones. As we move to second-row compounds, both the π distortion tendency and the σ resistance are weakened, but the former is weakened proportionally more. The result is that squares such as Si_4H_4 and P_4 do not wish any more to distort to rectangular structures.

These results clearly show that the $4n/4n + 2$ Hückel rule cannot safely be used to predict the shape of conjugated molecules other than hydrocarbons. On the other hand, the VB diagram model appears to rationalize the tendencies observed in delocalized systems as different as conjugated molecules of the first and second rows and monovalent aggregates, be they composed of three, four, or six centers.

A property that is common to all delocalized systems is the QMRE that is the resonance interaction between the Kekulé forms at the symmetric geometry (Figure 1). As is shown in this paper, the QMRE and the π distortive propensity are competing properties. Thus, some molecules possess a very large QMRE and at the same time a very distortive π component. Such a molecule is N_6, and its antipode is Si_4H_4, which possesses a weakly distortive π component with a rather small QMRE.

Unlike the π distortion energy, the QMRE follows the Hückel rule. It would be interesting to devise an experimental way to discriminate between these two properties.