

appears in the second moment difference if the β_{ij} are not all set equal and also a more sizeable change in the third moment. **24** shows how the μ_4 difference curve needs to be modified as a result.

Acknowledgment. This research was supported by the National Science Foundation under NSF DMR 8019741 and DMR 8216892. We also thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for their partial support of this research and Dr. Z. G. Soos for bringing the work of ref 15 to our attention.

Appendix

Details of Numerical Calculations. The plots of Figures 2 and 3 were obtained via an extended Hückel based tight-binding method.⁸ The parameters for the two metals were single- ζ Slater

d orbitals with an exponent of 2.10 for both atoms and Coulomb integrals of 9.1 and 11.1 eV. A total of 40 symmetry inequivalent k points were used for a primitive tetragonal unit cell (bcc derivative structure doubled along c). The validity of the plots of **17** and **20** for S_2N_2 and the $(SN)_x$ polymer was checked by performing calculations on the observed structures by using the geometrical and orbital parameters of ref 20 and then reversing the S and N sites. The new structure has shorter S-S distances and longer N-N distances than might be expected for a molecule or solid of this type. We did not allow these to relax however, since we have little faith in the ability of extended Hückel calculations to correctly mimic the energetic changes associated with bond length variations.

Registry No. Cyclobutadiene, 1120-53-2.

When Does Electronic Delocalization Become a Driving Force of Molecular Shape and Stability? The "Aromatic" Sextet

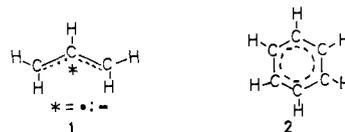
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Abstract: The conceptual grasp of electronic *delocalization vs. localization* is reexamined computationally by using "aromatic" 6-electron 6-center (X_6) model species as archetypal systems. It is shown that the character and weights of the resonance structures, which contribute to the "aromatic" sextet, *yield no differentiating information regarding the stabilities or geometries of the X_6 species*. A qualitative model is utilized to understand the physical basis behind the quantitative results. It is shown that the X_6 systems must "pay a price" for *electronic reorganization, while undergoing delocalization*. The "price" depends on the identity of X in X_6 . Thus, whenever the X-X two-electron bond is strong (e.g., H-H), the price for electronic reorganization is too high. Such systems (e.g., H_6) will prefer a geometry that *prohibits* delocalization of the electronic sextet. Among these systems is the suspended π system, $Li_6(\pi)$, that lacks a σ skeleton and shows no propensity for π delocalization. Only in a few cases will the price of electronic reorganization be low enough to afford delocalization of the electronic sextet. Such systems possess weak X-X two-electron bonds and will consequently tend to cluster in a regular hexagonal X_6 structure—where electronic delocalization takes place. In view of these trends, a question mark is cast over the propensity of the π system of benzene to remain delocalized without the buttressing effect of the σ framework.

The concepts of resonance theory and electronic delocalization occupy prime places in our conceptual thinking and chemical education.² Owing to their very nature, concepts must occasionally be examined. Following this philosophy of reexamination, it was recently proposed^{3,4} that electronic delocalization is neither the driving force nor the root cause of the geometric features of "resonating" systems such as **1** and **2**, etc.⁵ Rather, it was

suggested that electronic delocalization, in many organic species, *is forced*, and the "resonating" π systems may well be unstable transition states trapped in a stiff σ framework.^{3,4}



(1) Permanent address: Department of Chemistry, Ben-Gurion University, Beer Sheva 84105, Israel.

(2) (a) Resonance theory is summarized in many textbooks. The following is a casual selection showing the importance of the concept in different branches of chemical education. Pauling, L. "The Nature of the Chemical Bond", 3rd ed.; Cornell University Press: Ithaca, NY, 1960. Lowry, T. H.; Richardson, K. S. "Mechanism and Theory in Organic Chemistry"; Harper and Row Publishers: New York, 1976. Levine, I. N. "Quantum Chemistry"; Allyn and Bacon, Inc.: Boston, 1965. Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry"; Interscience Publishers: New York, 1966. (b) The concept of delocalization is common to resonance theory and MO theory. Although the concept is differently formulated, it occupies an important status in both theories. (c) The concept of "aromaticity" is thought to originate in the seminal works of Kekulé and Couper. See: Kekulé, A. *Bull. Soc. Chim. Fr.* **1865**, 3, 98. Couper, A. C. R. *Hebd. Seances Acad. Sci.* **1858**, 46, 1157. See also: Wotiz, J. H.; Rudofsky, S. *Chem. Br.* **1984**, 720.

(3) Epiotis, N. D. *Nouv. J. Chim.* **1984**, 8, 11. Epiotis, N. D. *Lecture Notes Chem.* **1983**, 34, 358-371. Epiotis, N. D. *Pure Appl. Chem.* **1983**, 55, 229.

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

Since such propositions constitute antitheses to current ways of *thinking and teaching*, we have decided to initiate a quantitative study which is directed at two aims. The specific aim is to in-

(5) (a) Similar ideas based on Nückel theory with a variable β were expressed in the following: Longuet-Higgins, H. C.; Salem, L. *Proc. R. Soc. London, Ser. A* **1959**, A251, 172. Salem, L. "The Molecular Orbital Theory of Conjugated Systems"; W. A. Benjamin, Inc.: Reading, MA, 1972, pp 103-106 and 494-505. (b) Electronic delocalization was shown not to be an important driving force in certain allyl-radical-type species: Feller, D.; Davidson, E. R.; Borden, W. T. *J. Am. Chem. Soc.* **1984**, 106, 2513. Feller, D.; Huyser, E. S.; Borden, W. T.; Davidson, E. R. *J. Am. Chem. Soc.* **1983**, 105, 1459. Feller, D.; Davidson, E. R.; Borden, W. T. *J. Am. Chem. Soc.* **1983**, 105, 3347. Explanations were couched in terms of second-order Jahn-Teller effect and in terms of resonance theory. (c) Localization in some polyenic radicals was found by VB computations to prevail. See: Said, M.; Malrieu, J. P.; Bach, M.-A. G. *J. Am. Chem. Soc.* **1984**, 106, 571.

investigate 6-electron 5-center X_6 systems, such as **2**, and to generate for them quantitative indicators which can test these ideas^{3,4} and thereby either *falsify* or *verify* the basic concepts of resonance and delocalization theories. The second and the more general aim is to explore the conditions under which an electronic system would be stabilized by resonance (delocalization), and when would such a system tend to prefer a localized electronic structure, and a *geometry that hinders electronic resonance*. Thus, our integrated aim is to gradually understand the problem of electronic delocalization vs. localization in its totality, and this is the first paper along these aims.

I. The Concepts of Resonance Theory and Electronic Delocalization

Let us begin by briefly reviewing the basic concepts of resonance theory. It is common knowledge² that a chemical species tends to be more stabilized relative to its localized Kekulé versions, if we can describe such a species by two or more resonance structures. The availability of several resonance structures means that there are more ways, than just one, in which to distribute the electrons over the nuclei. Such a situation results in electronic delocalization which is usually considered to be a root cause of stability.⁶ Thus, there is a common notion that there should exist some relationship between the stability of a delocalized system and the valence bond (VB) makeup of its wave function (i.e., identity and weights of contributing resonance structures). Put differently, stability of a delocalized system is assumed to correlate with the extent of its electronic delocalization.

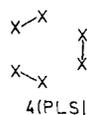
Since electronic delocalization is considered to be a stabilizing feature, it is further assumed that a chemical species will seek a geometry which maximizes the resonance interactions and that the optimum geometry will necessarily reflect the characters and weights of the contributing resonance structures, i.e., the VB composition of the wave function.

To summarize: resonance theory leads to the conclusion *that there is a relationship between the VB makeup of the electronic system, the stability, and the geometry of the species.*^{7a} And this relationship is based on the premise that electronic delocalization or resonance is an important driving force in the shaping of geometry and stability of a chemical species.

In what follows we shall present quantitative results which expose the fragility of these concepts, and in so doing, we shall begin to outline the domain of their sovereignty. To demonstrate our ideas we have selected the problem of the "aromatic sextet".

II. Strategy and Description of the Systems

Consider all the 6-electron 6-center X_6 systems. Among them we can find the π system of benzene, the H_6 system, the Li_6 system, etc. These species have, among other options, two structural possibilities: The systems can cluster in a regular hexagonal geometry in which six electrons can partake in resonance, as shown in **3**. Or else, these systems may choose a structure made up of three isolated dimers, X-X, as shown in **4**. In this second arrangement, the electrons are localized in their respective bonds, and therefore this system, **4**, is a perfectly localized system (PLS).

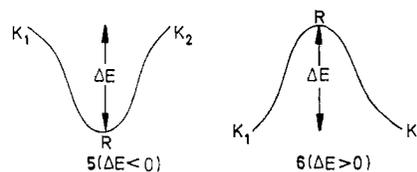


In terms of resonance theory, **3** and **4** are respectively the "resonating" state (R) and its localized Kekulé version (K)—the latter being in its own equilibrium geometry. One could imagine two types of energetic relationships between the Kekulé versions

(6) Only in antiaromatic systems is such a consideration known to be wrong. In other cases, the importance of delocalization is equally emphasized by both resonance and qualitative MO theories.

(7) (a) For accuracy's sake, resonance theory, in its original formulation, strictly considered localization vs. delocalization in a given fixed geometry. In the course of application through the years, a link has been made between delocalization (wave function composition)—geometrical choice—and stability. (b) See, e.g.: Firestone, R. F. *Tetrahedron* **1977**, *33*, 3009 (in particular pp 3015–3016).

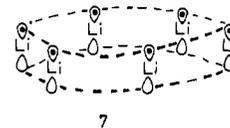
(two mirror-image structures K_1 and K_2) and the resonating state (R) as shown in **5** vs. **6**.



The situation in **5** describes a truly resonance stabilized system, while that in **6** describes a system in which electronic delocalization is energetically demanding. This latter type of species, **6**, is then unstable toward a "Kekulean distortion"⁴—preferring a distorted geometry, as in **4**, with a localized electronic system.

Resonance theory or any delocalization theory (on a qualitative level)^{2,6} is not equipped to predict whether a given X_6 system would belong to situation **5** or **6**. If anything at all, it is implicit in these qualitative concepts that X_6 molecules would tend to cluster in the regular hexagonal geometry (i.e., situation **5**) to enjoy maximal resonance interaction.^{7b} We are going to explore the plausibility of such a situation and to achieve some understanding into the factors that determine the distribution of the X_6 systems within the spectrum spanned by **5** to **6**. Simultaneously, we shall analyze the VB makeup of such X_6 systems to verify whether the characters and weights, of the contributing resonance structures, have any relationship to the stability and geometric features of the "resonating" X_6 state (R in **5** and **6**).

As representative test cases, we have selected five different 6-electron 6-center systems. Of course some of these systems are simply models for 6-electron 6-center resonance and should not be regarded as attempts to represent isolable species. The first one is H_6 which can potentially afford delocalization of six electrons over six 1s orbitals.⁸ The second system is denoted by $Li_6(s)$, where we have, *on purpose*, used only 2s orbitals in the valence shell of Li. This system allows delocalization over six 2s orbitals.⁹ The third and fourth systems are benzene, $(CH)_6$, and hexaazabenzene, N_6 —each of which possesses a delocalized π system buttressed by a σ framework.¹⁰ And finally, the fifth system is $Li_6(\pi)$ where we have removed the 2s orbitals of Li and allowed the six electrons to delocalize over six $2p^\pi$ atomic orbitals. Thus, this last system mimicks a suspended π system, *by itself*, without the σ framework, as shown in **7**.



These five systems were computed with the ab initio technique utilizing the STO-3G basis. The energies and optimized geometries were obtained both at the monodeterminantal SCF level and at the full CI level (for $(CH)_6$ and N_6 , only π -space CI was carried out).¹¹ The various geometries are tabulated in the Appendix.

To determine which resonance structures contribute to the wave function, each level of computation was followed by a VB analysis, using the mapping procedure that was developed by Hiberty and Leforestier.¹² The VB makeup will serve to assess the extent of

(8) For previous ab initio computations see: (a) Dixon, D. A.; Stevens, R. M.; Herschbach, D. R. *Faraday Discuss. Chem. Soc.* **1977**, *62*, 110. (b) Wright, J. S. *Chem. Phys. Lett.* **1970**, *6*, 476; *Can. J. Chem.* **1975**, *53*, 549. (c) Thompson, D. L.; Suzukawa, H. H., Jr. *J. Am. Chem. Soc.* **1977**, *99*, 3614. (d) Ichikawa, H. *J. Am. Chem. Soc.* **1983**, *105*, 7467.

(9) (a) Previous Li_6 computations are described: Beckmann, H.-O.; Koutecky, J. B.; Botschwina, P.; Meyer, W. *Chem. Phys. Lett.* **1979**, *67*, 119. (b) $Na_6(s)$ clusters were computed with the DIM technique (Gelb, A.; Jordan, K. D.; Silbey, R. *Chem. Phys.* **1975**, *9*, 175) and $Li_6(s)$ (Pickup, B. T. *Proc. R. Soc. London, Ser. A* **1973**, *A333*, 69).

(10) Previous ab initio computations of N_6 are described: (a) Huber, H. *Angew. Chem. Int. Ed. Engl.* **1982**, *21*, 64. (b) Ha, T.-K.; Cimbrigia, R.; Nguyen, M. T. *Chem. Phys. Lett.* **1981**, *83*, 317. (c) Saxe, P.; Schaefer H. F., III *J. Am. Chem. Soc.* **1983**, *105*, 1760.

(11) CI diagonalization was performed with the CIPSI program: Huron, B.; Malrieu, J. P.; Rancurel, P. *J. Chem. Phys.* **1973**, *58*, 5745.

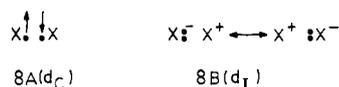
Table I. VB Contributions in PLS ($3X_2$)^a

X	VB wt (%), SCF ^b		VB wt (%), SCF + CI ^b	
	covalent	monoionic	covalent	monoionic
H	12.5	37.5	51.2	38.4
Li(π)	12.5	37.5	66.5	29.1
Li(s)	12.5	37.5	72.9	24.3
CH	12.5	37.5	51.2	38.4
N	12.5	37.5	59.7	33.6

^aThe model X_2 dimers in the PLS (4) of $X = N, CH$ are $HN=NH$ and $H_2C=CH_2$. ^bThe rest of the configurations, which complete the weights to 100%, are diionic and triionic. The ionic configuration of each X-X linkage is described by **8B**.

delocalization in the "resonating" state (R) and to compare it to its localized Kekulean version (see **5** vs. **6**).

The reference Kekulean version is the perfectly localized system (PLS) in **4**. Once one knows the weights (d_C, d_I) of the covalent (**8A**) and ionic (**8B**) forms in the X-X dimer, one can then very



easily obtain the covalent contribution (W_C) in the PLS (4). This contribution (W_C) is simply the product of the respective covalent weights (d_C in **8A**) of the three X-X dimers, i.e.¹³

$$W_C = (d_C)^3; 3 = \text{number of covalent bonds} \quad (1)$$

Likewise, the weight of a monoionic structure (W_I) in which one of the bonds of the PLS in **4** is described by the zwitterionic form **8B** reads

$$W_I = (d_C)^2 d_I \quad (2)$$

The results for the PLS (4) are summarized in Table I. At the SCF level, each X-X bond is described by 50% covalent (**8A**) and 50% ionic (**8B**) characters. Therefore, the weight of the covalent form is 12.5% according to eq 1 (0.5^3). This covalent form is a single Kekulé form which describes the pairing scheme of the PLS (4) at its equilibrium geometry. Similarly, any monoionic form, which has a zwitterionic character (defined by **8B**) across one X-X linkage (of the PLS), also contributes 12.5% according to eq 2. And since the PLS has three such linkages, then the total monoionic character sums up to 37.5%. The exact same process, delineated by eq 1 and 2, applies to the CI results in Table I. The main variation, relative to the SCF results, is the increase in the contribution of the covalent Kekulean form, which now becomes the dominant resonance structure of the PLS wave function. And this is, in brief terms, the VB description of the perfectly localized system, $3X_2$ (4) of X_6 .

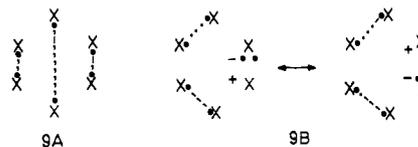
Let us now compare the above results to the various properties of the delocalized states in the regular hexagonal geometry, **3**. Table II summarizes these properties that were obtained at the SCF level. In addition to the weights of the resonance structures (VB weights), we report in Table II ΔE values. These values measure the energy difference between the delocalized hexagonal structures X_6 and their PLS Kekulean systems, as illustrated in **5** vs. **6** (see above). And finally, we also report a geometric index which measures the percentage of lengthening of the X...X bond in the delocalized state, X_6 , relative to $3X_2$, as follows

$$\begin{aligned} [\Delta r/r(X_2)] &= [r_{XX}(X_6) - r_{XX}(X_2)]/r_{XX}(X_2) \quad (3) \\ [\Delta r/r &= \text{distortion effort}] \end{aligned}$$

And this index is really a measure of the distortion effort of the system to achieve delocalization.

Comparison of the VB makeup of X_6 (Table II) with that of the $3X_2$ -PLS (Table I) illustrates what can be taken as the

meaning of delocalization in the language of resonance theory.^{2a} In the first place, X_6 is described by two covalent Kekulé structures in comparison with a single one in $3X_2$ -PLS. In addition, X_6 possesses three Dewar type (e.g., **9A**), thirty monoionic types (e.g., **9B**), and fifty multionic configurations (dionic and triply ionic). In this sense, X_6 indeed undergoes considerable delocalization relative to the PLS (4) above.



The most interesting feature in Table II is the fact that all of the X_6 species have exactly the same VB makeup, and in this sense, they exhibit a constant degree of electronic delocalization. Despite this constancy, the various X_6 species fall within a wide range of energetics. As the ΔE values show, $Li_6(s)$ is a truly resonance stabilized system, like the one described in **5**, with $\Delta E \cong -5$ kcal/mol. While on the other hand, $Li_6(\pi)$ and H_6 belong to the type described in **6** with $\Delta E > 0$. These two latter systems are, therefore, unstable with respect to a Kekulean distortion despite the "resonance stabilization" that is available to them in the hexagonal geometry.^{14a}

Thus, a clear-cut picture emerges from Table II: that there is no relationship between the degree of delocalization (indicated by the characters and weights of the VB structures) and the stability or instability of the X_6 system^{14b} toward a localizing distortion. In particular, the fact that X_6 species exhibit a resonance interaction of two Kekulé structures does not seem to have any important effect on the stability trends of these systems.

The second interesting feature in Table II is the behavior of the suspended π system (7) of $Li_6(\pi)$. This system is unstable, toward a Kekulean distortion ($\Delta E \cong +35$ kcal/mol), and it shows no propensity to enjoy the "resonance stabilization" of the "aromatic sextet". This instability of $Li_6(\pi)$ does not originate in the reluctance of the $2p\pi$ orbitals of Li to form bonds. And in fact $Li_2(\pi)$ is bound, having a bond energy of 13.4 kcal/mol (see Table III). Thus, the instability of $Li_6(\pi)$ toward a Kekulean distortion is an inherent property of its delocalized π system.

With this in mind, we can turn to N_6 and benzene (Table II). As we have seen, the fact that X_6 systems can be represented by two resonating Kekulé structures, as well as others, has no consequence on the stability of these systems toward a localizing distortion ($X_6 \rightarrow 3X_2$). The example of $Li_6(\pi)$ further illustrates that a " π -aromatic sextet" may not be endowed with any special stability. Therefore, while the π system of benzene may still be a stable species, it may well be, with the same probability, an unstable transition state trapped in a stiff hexagonal σ framework.^{3-5a}

Further inspection of Table II shows that the geometric index ($\Delta r/r(X_2)$, eq 3) varies considerably (6.2–35%) while the wave functions of X_6 and the PLS are constant. Thus, there is no clear relationship between geometric preference and the VB makeup (or degree of delocalization) of the delocalized system.^{7,14b}

There is, though, one meaningful correlation in Table II. This is the relationship between the geometric index ($\Delta r/r(X_2)$) and the ΔE value. Thus, Table II shows a clear-cut correlation between the instability of the delocalized state and the distortion effort ($\Delta r/r(X_2)$, see eq 3) of the system to achieve the delocalized state.¹⁵ This is an important trend which will become clear in section III.

The process of CI is known to generate "more correct" wave functions in comparison with those obtained from a SCF procedure

(14) (a) Consideration of nuclear repulsion (V_{NN}) shows that ΔV_{NN} does not account for the ΔE trends (Table III). (b) Similar conclusions for CH_2CN^+ , CH_2CN^- , C_2CCH^+ and C_2CCH^- , were reached: Delbecq, F. J. *Org. Chem.*, to be published.

(15) Houk et al. have performed an analysis of related systems, reaching an equivalent conclusion. See: Houk, K. N.; Gandour, R. W.; Strozier, R. W.; Rondan, N. G.; Paquette, L. A. *J. Am. Chem. Soc.* **1979**, *101*, 6797.

(12) (a) Hiberty, P. C.; Leforestier, C. *J. Am. Chem. Soc.* **1978**, *100*, 2012. (b) Hiberty, P. C. *Int. J. Quantum Chem.* **1981**, *19*, 259.

(13) Hiberty, P. C.; Ohanessian, G. *Int. J. Quantum Chem.* **1985**, *27*, 245 and 249.

Table II. Properties of Delocalized X_6 Systems (SCF Level)

X_6	VB weights (%) ^{a,b}				$\Delta E(3X_2 \rightarrow X_6)$ (kcal/mol)	[$\Delta r/r$] $\times 100\%$
	Kekulé	Dewar	monoionic	multiionic		
H ₆	4.86 (2)	2.08 (3)	30.79 (30)	62.27 (50)	+120.5	34.7
Li ₆ (π)	4.86 (2)	2.08 (3)	30.79 (30)	62.27 (50)	+34.8	25.4
Li ₆ (s)	4.86 (2)	2.08 (3)	30.79 (30)	62.27 (50)	-4.8	9.0
N ₆	4.86 (2)	2.08 (3)	30.79 (30)	62.27 (50)	>0 ($\sigma + \pi$)	8.7
(CH) ₆	4.86 (2)	2.08 (3)	30.79 (30)	62.27 (50)	<0 ($\sigma + \pi$)	6.2

^aThe number of corresponding VB forms is shown in parentheses. An ionic situation is defined by **8B**. ^bThe weight of the covalent and ionic forms in X_2 is 50%–50% for any X .

Table III. Properties of Delocalized X_6 Systems (CI Level)

X_6	VB wt (%) ^a				$\Delta E(3X_2 \rightarrow X_6)$ (kcal/mol)	[$\Delta r/r(X_2)$] 100%	$\Delta E_T(X_2)^b$	$D(X_2)$
	Kekulé	Dewar	monoionic	multiionic				
H ₆	21.82	11.15	49.20	17.83	+109.3	34.5	384.4	128.1
Li ₆ (π)	34.26	17.79	39.52	8.43	+27.4	26.6	47.7	13.4
Li ₆ (s)	36.86	19.61	33.63	9.90	+0.04 ^e	7.0	25.2	11.0
N ₆	29.32	15.03	43.75	11.90	>0($\sigma + \pi$)	7.6	98.5 ^c	
(CH) ₆	22.20	10.99	47.90	18.80	<0($\sigma + \pi$)	4.8	110.3 ^c	73.0 ^d

^aNote, the ionicity (in **8B** sense) of each bond is not so large as may be implied by the dominance of the wave function by ionic configurations. For example, the leading ionic term with a symmetrized zwitterionic character (**8B**) across an adjacent linkage has a weight of about 4%. ^bTriplet excitation energies are computed as the energy of the triplet state (RHF level) less the singlet energy (CI level). ^cThese are triplet excitation energies ($\pi\pi^*$) for HN=NH and H₂C=CH₂, respectively. ^dThe π -bond energy computed from rotational barrier (optimized geometries at the CI level). ^eLi₆ becomes a stable species ($\Delta E < 0$) only after adding the 2p σ atomic orbitals to the basis set.

alone. We may therefore expect to extract more reliable information from the CI wave functions of the various X_6 systems. The full CI results are summarized in Table III.

Inspection of the VB weights in Table III reveals, however that still there is no correlation between the nature and weights of the contributing resonance structures, on the one hand, and the stability or instability of the delocalized state (ΔE values), on the other hand. For example, the Li₆(s) system is the most stable one against a localizing distortion ($\Delta E \sim 0$). This relative stability could have been attributed to the higher contribution of the resonating Kekulé and Dewar structures relative to, e.g., H₆ which is very unstable ($\Delta E = +109.3$ kcal/mol). However, Li₆(π), which is an unstable delocalized system ($\Delta E = +27.4$ kcal/mol), has almost the same wave function as Li₆(s) has. Thus, two systems which vary greatly in stability against a localizing distortion possess almost the same degree of delocalization.

Alternatively, one could have been tempted to attribute the thermodynamic stability of benzene to the fact that its π wave function contains high contribution of the 80 different ionic structures. This temptation would be based on the idea that whenever more resonance structures contribute to the wave function, this must necessarily mean improved stability. However, such a temptation is certainly quenched by the fact that the unstable H₆ species involves exactly the same amount of ionic structures, as does the π system of benzene. In fact, no other feature in the wave functions seems to be a reliable pointer of stability against a localizing distortion.

Further comparison of the wave function of the PLS (Table I, CI level) with those of the delocalized X_6 systems (Table III) buttresses the conclusion that the wave function carries no information on stability. Thus, as the species are transformed from the $3X_2$ -PLS to X_6 , they undergo approximately a constant change, in their wave function, in achieving electronic delocalization (compare the changes in covalent and ionic characters). Therefore, the X_6 systems can be considered to possess a *constant degree of delocalization* (relative to their respective $3X_2$ -PLS), and yet these species are endowed with different degrees of stabilization (ΔE) against a localizing distortion. Thus, once again, the delocalization of the wave function cannot guarantee that the π system (by itself) of benzene is not an unstable transition state trapped in a stiff hexagonal σ framework.

An initial clue is provided by considering the correlation between the ΔE values, the distortion effort, $\Delta r/r(X_2)$, and the $\Delta E_T(X_2)$ values (Table III). These latter values are the triplet excitation energies of the localized X–X moiety. As can be seen, H₆, Li₆(π), and Li₆(s) exhibit a very clear behavior. The ΔE values, in this

series, vary in proportion to $\Delta E_T(X_2)$. As $\Delta E_T(X_2)$ increases, the instability of the delocalized X_6 system increases,^{14a} and at the same time the distortion effort to achieve delocalization also increases. Thus, H₆, which has the largest value of $\Delta E_T(X_2)$, is the most unstable delocalized sextet with the largest distortion effort (34.5%). The Li₆(π) system possesses the second *largest* $\Delta E_T(X_2)$ and hence it is ranked second in instability and second in distortion effort. On the other hand, Li₆(s), which has the lowest $\Delta E_T(X_2)$, is the X_6 which is the most stable “aromatic system” against a localizing distortion.

While we still have to establish the physical meaning of this correlation, it clearly stands as the only informative trend in Table III. If we follow this trend, we reach the conclusion that the $\Delta E_T(X_2)$ values of π -N₆ and π -benzene are high enough to place them close to H₆ and the unstable suspended π system of Li₆(π).

To summarize: Our findings at this point show that the intuitive concepts of our chemical education may be flawed and that, at least for the X_6 model systems studied here, the extent of electronic delocalization—as measured by the identities and weights of the contributing resonance structures—does not affect the stability of the “resonating state” toward a localizing distortion. We have also shown that the tendency to form a delocalized state depends on the identity of the atom X, in a manner that is not predictable by resonance theory or by any other qualitative concepts of delocalization. This exploration of concepts completes the first section of our paper. We shall now turn to the next part and try to establish the physical basis of the correlation which we have just noted in Table III.

III. State Correlation Diagrams for $3X_2 \rightarrow X_6$

In a recent publication, Shaik and Bar⁴ have presented a general model which describes the energetic relationship between the delocalized “resonating” state (R) and its two localized Kekuléan versions (K_1 , K_2) in their equilibrium mirror-image geometries. This model is shown in Figure 1.

Figure 1 is a state correlation diagram that is composed of two intersecting curves along a coordinate that interchanges the geometries of the two Kekulé forms ($S_1 \rightarrow S_2$) and passes through the regular geometry (S_R) of the delocalized state. The curves are anchored, at each end, at the ground state and a specific excited configuration of the Kekulé structures (e.g., K_1 and K_1^*).

The specific excited configurations are those that prepare the ground Kekulé forms for bond shift. For example, K_1^* is obtained, from K_1 , by a specific electronic promotion which prepares K_1 for the requisite electronic reshuffle to become K_2 . Thus, K_1^* is the electronic template (or “image”) of K_2 , and therefore K_1^*

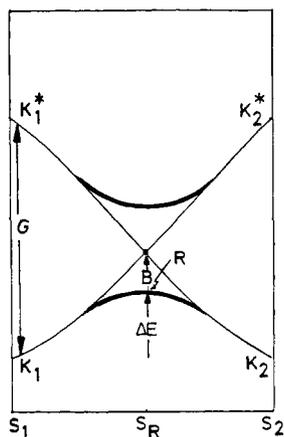


Figure 1. A state correlation diagram for the transformation of two mirror-image Kekulé forms (K_1 , K_2) through the delocalized state (R). S_1 and S_2 signify equilibrium geometries of the two ground-state Kekulé forms. S_R signifies the geometry of the "resonating" delocalized state (R). K_1^* and K_2^* are the specific excited configurations. G is the K_1 - K_1^* (K_2 - K_2^*) energy gap. ΔE is the energy of R relative to K_1 and K_2 . B is the resonance interaction. For $\sigma + \pi$ systems (e.g., N_6 , $(CH)_6$) the diagram is limited to π electrons only (σ framework is removed).

will correlate with K_2 along the interchange coordinate ($S_1 \rightarrow S_2$). And symmetric arguments apply to the $K_2^* \rightarrow K_1$ correlation.

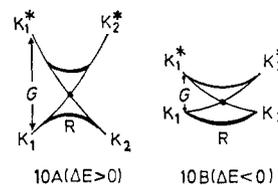
The two energy curves intersect at the regular geometry, S_R , and avoid the crossing by interacting with each other.^{16,17} The avoided crossing, which is shown by the heavy lines in Figure 1, generates the delocalized "resonating" state, R . And this state is stabilized, relative to the crossing point, by the resonance interaction B . Let us now briefly develop the conclusions of the model.

The diagram reveals that both electron reorganization as well as bond distortions are required to bring the Kekulé forms into "resonance".¹⁷ The energy gap of the diagram, G , measures the cost of electronic reorganization—as the energy required to prepare a Kekulé structure (at a frozen geometry) for bond shift. As can be seen from the figure, this energy gap sets the stability limits of the resonating state (R) relative to its Kekulé forms (K_1 , K_2) at their equilibrium geometries. Thus the relative energy, ΔE , is a fraction f of the energy gap less the resonance energy, B , i.e.,^{18a,b}

$$\Delta E = fG - B; f < 1 \quad (4)$$

From basic principles⁴ the model and its offspring equation predict that an ensemble of *isoelectronic* delocalized "resonating" states (R) will fall into the two extremes which are schematically described in **10A** vs. **10B**.^{18c} Accordingly, cases with large gaps (G) will exhibit unstable delocalized states ($\Delta E > 0$), while cases with small gaps will exhibit stable delocalized states ($\Delta E < 0$). Thus, the model predicts that the cost of electronic

reorganization—measured by G —will determine the stability of the delocalized state toward a localizing distortion.^{18d}

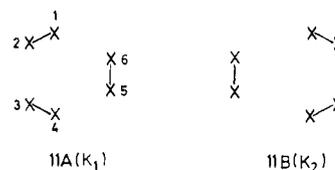


Consider now the geometric features of the delocalized state (R) relative to its Kekuléan versions (K_1 , K_2). As can be seen from Figure 1, the delocalized state is achieved at the crossing point of K_1 and K_1^* (or K_2 - K_2^*). Since the two states are initially separated by an energy gap G , geometric distortions will be required to overcome and close this gap. The "reactive" distortions are those that destabilize K_1 and simultaneously stabilize K_1^* , so that the gap is thereby closed and the system reaches the crossing point (Figure 1). The extent of the requisite distortion effort will depend then on the size of the gap (G) that is to be overcome by the distortions. Thus a general correlation will exist between the extent of the distortion effort (e.g., $\Delta r/r$ in Table III) and the size of the energy gap, such that:

$$\text{distortion effort} \propto G \quad (5)$$

Note that distortion effort will be required for either one of the classes that are described by **10A** and **10B**. Moreover, the distortion should not be, in principle, related to the VB makeup of the wave function. Or put differently, the nature and weights of the contributing resonance structures are predicted by the model to have a minor influence on the features of the delocalized state.^{18d}

As we shall show now, these general conclusions of the model form the physical basis for the quantitative trends that are exhibited by the X_6 species in Table III. Each one of the two Kekulé forms of the X_6 species is described by the perfectly localized system PLS (see **4** and Table I). Each PLS possesses three short and localized bonds as shown in **11A** and **11B**. The X-X bonds of the PLS are composed of two spin paired electrons: within a mixture of the Heitler-London and the zwitterionic forms (**8A**, **8B**). And these are the two-electron bonds which are denoted by lines connecting the atoms in **11A** and **11B**:



The two PLS in **11A** and **11B** define the ground anchor states of the correlation diagram in Figure 1 (K_1 and K_2). To obtain the excited anchor configurations of the diagram (K_1^* , K_2^*), we must recall that each one of these excited configurations prepares its respective ground Kekulé structure for a bond shift. Let us take for example K_1^* . This excited configuration is generated by an electronic promotion so that K_1^* becomes an electronic template of K_2 . Such an electronic promotion must *unpair* the bonds of K_1 , in **11A**, and *repair* them across the X_2 - X_3 , X_4 - X_5 , and X_6 - X_1 linkages. In this manner, we obtain the electron pairing scheme of K_2 , but in a structure whose geometry is that of K_1 , and this pairing scheme is the requisite K_1^* . One of the ways to achieve this electronic reorganization is described in **12**, where dashes signify spin paired electrons and arrows signify spins of electrons (electrons denoted by dots).



(16) For a theoretical analysis of such avoided crossings see: Shaik, S. S. *J. Am. Chem. Soc.* **1981**, *103*, 3692. See also ref 4.

(17) (a) That there should be an *avoided orbital crossing* in this problem has been concluded in ref 15 above. (b) The avoided crossing in Figure 1 can also be deduced on the basis of MO theory with "natural orbital correlations". See: Devaquet, A.; Sevin, A.; Bigot, B. *J. Am. Chem. Soc.* **1978**, *100*, 2009. The authors are grateful to J. M. Lefour and A. Sevin for revealing discussions.

(18) (a) The value of f depends on the curvature of the two intersecting curves. For example, two intersecting parabolae lead to $f = 0.25$, while two straight lines lead to $f = 0.5$, etc.... The size of f is related to various interactions such as nuclear-nuclear (V_{NN}) repulsions, overlap repulsion, interaction of covalent and ionic configurations, etc.... These interactions control the ascent and descent of the curves in Figure 1, and they will thereby determine the curvature and the size of f . For details see Appendix 1 in ref 4. (b) The resonance energy B depends on the interaction between two Kekulé forms and the interaction of those with the ionic forms (Table III) that mix into the intersection point (and into the two curves in general). (c) Our assumption is that in an isoelectronic series (e.g., X_6), f and B vary slowly with atomic identity, while variations in G dominate the trend. (d) Our model is unable to distinguish whether **10A** will be a *local* minimum (as a result of secondary mixings into the crossing point) or a saddle point.

If we compare **12** to **11A** we find that the X_1 - X_2 and X_3 - X_4 bonds of **11A** are excited to a total triplet (note the triplet pair at X_1 and X_4 in **12**).¹⁹ At the same time the X_5 - X_6 bond of **11A** is also excited to a triplet, and the entire X_1 ... X_6 system is coupled to a total singlet. In this manner, the electron pairing, in **12**, takes place across X_2 - X_3 , X_4 - X_5 , and X_6 - X_1 . And this pairing scheme is the template of the ground Kekulé form K_2 (in **11B**).¹⁹ By applying the exact same reasoning we can obtain K_2^* from K_2 , and this K_2^* will be the electronic template of K_1 (**11A**), but at the geometry of K_2 (only π electrons are considered for benzene and N_6).

Having defined the four anchor states for the correlation diagram $3X_2 \rightarrow X_6$, some physical insight can now be extracted. The relative energies of K_1^* and K_1 (or K_2^* and K_2) define the energy gap of the diagram, G (see Figure 1). As can be seen from **12** vs. **11A**, the K_1^* - K_1 energy gap is related to the triplet excitation energy, $\Delta E_T(X_2)$, of the localized X-X bonds of K_1 . An estimate for G is given in eq 6, where $D(X_2)$ is the X-X bond energy.

$$G(K_1^* - K_1) \cong 2\Delta E_T(X_2) + D(X_2) \quad (6)$$

Therefore the cost of electronic reorganization, G , for the X_6 problem is measured by the sum of the triplet excitation energy and the bond energy of the localized X-X moiety. Using our reasonings that generated before eq 4 and 5, we can rationalize the physical basis of the data in Table III. Thus the stability (ΔE) of the delocalized state relative to the PLS (**11**) is given by eq 7 in analogy with eq 4:

$$\Delta E(3X_2 \rightarrow X_6) = f[2\Delta E_T(X_2) + D(X_2)] - B; f < 1 \quad (7)$$

Similarly, $\Delta r/r(X_2)$ measures the distortion effort that the PLS (in **11**) must invest to achieve delocalization. This distortion effort is required to overcome the K_1^* - K_1 energy gap and thus bring the X_6 system to the crossing point (Figure 1). Hence, in analogy with eq 5, $\Delta r/r(X_2)$ will correlate with the size of the gap that has to be overcome, i.e.,

$$[\Delta r/r(X_2)] \propto [2\Delta E_T(X_2) + D(X_2)] \quad (8)$$

In accord with eq 7 and 8, we can understand now that H_6 , which possesses the largest $\Delta E_T(X_2)$ and $D(X_2)$, exhibits the most unstable delocalized state with the greatest distortion effort, in the series H_6 , $Li_6(\pi)$, and $Li_6(s)$, in Table III. The second species, $Li_6(\pi)$, is second in instability and distortion effort, owing to the large values of $\Delta E_T(X_2)$ and $D(X_2)$. On the other hand, $Li_6(s)$, which has small $\Delta E_T(X_2)$ and $D(X_2)$ values, forms a distortion-indifferent delocalized state with the smallest distortion effort (7.0%) in the series.

Thus, the series H_6 , $Li_6(\pi)$, and $Li_6(s)$ generates a spectrum between the two extremes **10A** vs. **10B** that are predicted by the model. And the principal determinant of the stability and geometry of X_6 is seen to be the cost of electronic reorganization, G (eq 7). The features of the delocalized state originate then in a distortion effort which is required in order to perform the electronic reorganization that is necessary for achieving delocalization.¹⁵

The nature of the wave function and its contributing resonance structures are seen not to play a decisive role in determining the stability and geometry of the delocalized state.^{18c} In fact, we have already concluded that as the species are transformed, from the PLS- $3X_2$ to X_6 , they undergo approximately a constant change, in their wave function, by achieving delocalization (compare Table III to Table I CI results). We can, therefore, say that the stability and geometry of the delocalized state, X_6 , are determined by the distortion effort that is required in order to achieve a constant degree of electronic reorganization (relative to the PLS- $3X_2$).

(19) The X_1 ... X_4 portion is described by the following spin pairing scheme $\alpha(1)\alpha(4)[\alpha(2)\beta(3) - \beta(2)\alpha(3)]$. This pairing scheme is coupled to the triplet X_5X_6 to a total singlet. There are two other equivalent ways: couple triplet X_1X_2 with triplet X_3 ... X_6 and triplet X_3X_4 with triplet $X_1X_2X_5X_6$. The linear combination of the three forms generates K_1^* . Using MO language each one of the forms is described by a triplet HOMO-LUMO excitation of the two fragments (e.g., X_1 ... X_4 and X_5X_6). This will correspond to the crossing proposed in ref 15.

Benzene and Hexaazabenzene—A Revisit. Now that we have rationalized the physical basis behind the trends in the series H_6 , $Li_6(\pi)$, and $Li_6(s)$, we can turn to a more delicate problem: Are the π systems of benzene and N_6 stable aromatic sextets? While the answer to this problem may be thought to have only an academic value, we feel that such an inquiry is important, for it will serve to refine our conceptual grasp of the role played by electronic delocalization. The model, in Figure 1, provides initially two criteria of stability: the cost of electronic reorganization that opposes delocalization (eq 6 and 7), and the distortion effort of the delocalized sextet (eq 8). The actual distortion effort of N_6 and $(CH)_6$ is a combined $\sigma + \pi$ effect, and it cannot be compared with the distortion efforts of H_6 , $Li_6(\pi)$, and $Li_6(s)$. On the other hand, the factor that opposes delocalization, G (eq 6), is the direct measure of the reluctance of the π system (*by itself*) to undergo delocalization. And therefore, this latter factor will serve as our indicator.

With N_6 the problem is not so serious. Firstly, there is no tradition of viewing this molecule as a stable aromatic species. And secondly, the molecule is thermodynamically unstable¹⁰ (decomposes to $3N_2$), and therefore we can make new rationalizations without opposing previous established notions. Examining the $\Delta E_T(X_2)$ value for the π system of N_6 (Table III), we find that the factor that opposes π delocalization will be quite large for this case. Such a large opposition (eq 6) places N_6 on the unstable side of the spectrum (**10A**), as can be judged from $\Delta E_T(X_2)$ values of the H_6 , $Li_6(\pi)$, $Li_6(s)$ series. Therefore we may conclude that, by itself, the π system of N_6 should be unstable with respect to a Kekuléan distortion. Since the $\sigma(N-N)$ bonds are weak they will not be able to sustain the unstable π system, and the N_6 species will tend to disintegrate.¹⁰

The benzene problem is much more difficult. Firstly, the molecule, as a whole, possesses a special stability.²⁰ And secondly, there is a long tradition² of viewing the stability of this molecule as a consequence of the "resonating" π system. Therefore we must make our rationalizations, in this case, against established tradition. However, since our VB results in Tables II and III do not establish the delocalization phenomenon (e.g., the two Kekulé forms, etc.) as a sure endowment of stability, we must feel free to abandon tradition. Our model shows that there is a cost of electronic reorganization (G in eq 6) that opposes delocalization (ΔE in eq 7). Since the ΔE_T value (Table III) for the π system of benzene is very large, then the cost of electronic reorganization will also be very large. In fact, the ΔE_T factor will place the π system of benzene near the unstable regime (**10A**) of $Li_6(\pi)$ and H_6 . This, together with the fact that there is at least one π system which is not stable (in $Li_6(\pi)$), must cast some doubt on the stability of the π system (*by itself*) of benzene in the regular hexagonal array.^{3,5a} Be it as it may, the model suggests that the propensity of the π sextet, of benzene, toward delocalization will not be significant. Thus, much of what we think about benzene may well originate in its stiff hexagonal σ framework,^{3-5a} that buttresses the delocalized π system.

We must emphasize that our present results *do not, in any way*, establish the instability of the π system of benzene. Our results merely raise educated doubts about this stability, and about the importance of delocalization as a driving force of molecular stability and geometry. Thus, in our view, the problems of benzene and other delocalized systems are far from being established. Research trend should perhaps be reversed now and aimed at the new possibility of quantifying the potential instability of delocalized π systems (by themselves). The occurrence of stable as well as unstable isoelectronic species (Table II and III) may help to devise criteria for quantifying the actual propensity of such π systems to be delocalized by themselves.^{21,22}

(20) From thermochemical data the heat of hydrogenation of benzene is smaller by 20-30 kcal/mol than any localized analogue having three double bonds. See details, e.g., in: Hess, B. A., Jr.; Schaad, L. J. *J. Am. Chem. Soc.* **1983**, *105*, 7500. Wheland, G. W. "Resonance in Organic Chemistry"; Wiley: New York, 1955.

(21) For intriguing discussions of experimental data along similar lines see: Labarre, J.-F.; Crasnier, F. *Top. Curr. Chem.* **1971**, *24*, 45.

Table IV

X	CI results ^a		SCF results ^a	
	$r_{XX}(X_6)$, Å	$r_{XX}(X_2)$, Å	$r_{XX}(X_6)$, Å	$r_{XX}(X_2)$, Å
H	0.9886	0.7351	0.9593	0.7122
Li(π)	2.7718	2.1925	2.5095	2.0025
Li(s)	3.0717	2.8720	2.9093	2.6690
CH	1.4051	1.3407	1.3868	1.3060
N	1.3913	1.2928	1.3558	1.2475

^aThe X_2 models for X = N, CH are HN=NH(t) and H₂C=CH₂, respectively.

IV. Conclusions

The extent of delocalization in 6-electron 6-center systems cannot serve as a criterion of stability of the delocalized state against a localizing distortion. The composition of the wave function, in terms of the character and weights of the contributing resonance structures, was found to yield no information regarding the stability or the preferred geometry of the delocalized electronic sextet. Extreme care must be exercised not to attach special importance to the contribution of a certain resonance structure or another, at least in these types of systems.

While undergoing delocalization, an electronic system must pay the price of electronic reshuffle or reorganization (G in Figure

(22) Virial theorem analysis leads to some surprising conclusions regarding the delocalization in benzene, see: Blaise, P.; Henri-Rousseau, O. *C. R. Hebd. Seance Acad. Sci., Ser. C* 1980, 1290, 69.

1, eq 6). Whenever this price is costly, the system would prefer to remain localized in a geometry that hinders electronic delocalization (10A). Only in certain systems with weak two-electron bonds (low $\Delta E_T(X_2)$ and $D(X_2)$) will the price of electronic reshuffle be low enough to afford delocalization. In such cases, delocalization of the electronic sextet would indeed be a driving force that will shape the molecular stability and geometry.^{3,4} Our conceptual grasp of the role of electronic delocalization must accordingly be modified.

While there is no denying that benzene possesses a special stability,²⁰ our present studies raise the question whether it is really the π system that drives benzene to be a symmetric hexagonal species. Our preliminary calculations²³ show that indeed the π system, were it by itself, would have preferred a distorted localized structure. These results and others will be reported in future publications.²³

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Appendix

Table IV gives the geometric parameters which were obtained by optimization.

(23) Hiberty, P. C.; Shaik, S. S.; Lefour, J. M.; Ohanessian, G., submitted for publication.

The Valence-Bond Description of Conjugated Molecules. 4. Theoretical Study of the Mills–Nixon Effect, a Phenomenon of π -Bond Localization in Small Ring Annelated Aromatics

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Abstract: The so-called Mills–Nixon effect, a phenomenon of π -bond localization in aromatic rings annelated by strained saturated rings, is studied by means of ab initio calculations of valence-bond type on benzocyclopropene and benzocyclobutene, in their equilibrium geometries calculated by using a gradient technique. In apparent discrepancy with an experimental work, recently published in this journal,¹ dealing with cyclobutane-annelated dihydropyrenes, our results evidence a significant Mills–Nixon effect. To understand its origin, additional calculations have been performed on benzocyclopropene and benzocyclobutene in standard geometries and in distorted benzenes, showing that the influences of cyclopropene and cyclobutene on aromatic rings are of different natures. Tendencies arising from these calculations and additional ones on naphtho[b]cyclopropene and naphtho[b]cyclobutene suggest a possible explanation for the absence of sizable Mills–Nixon effect in cyclobutane-annelated dihydropyrene.

I. Introduction

Over 50 years ago, Mills and Nixon² postulated that the fusion of a small-ring compound on a benzene molecule induces a reorganization of the resonance between the two Kekulé structures, i.e., causes a partial π -bond localization as shown in the following scheme:



Their aim was to rationalize certain differences in the chemical reactivities in indan and tetralin. However, the experimental data

on which the effect was based were subsequently shown to be ambiguous,³ and the proposal of Mills and Nixon initiated a long series of experimental and theoretical studies on related molecules, trying to prove or disprove the effect.

While benzocyclopropene and benzocyclobutene still remain difficult to observe, an extensive series of large annelated aromatics have now been synthesized.⁴ A number of experimental techniques have been used to study their properties, such as X-ray crystallography and NMR and UV spectroscopies. Both the physical and chemical properties of many of these compounds were found to be sensitive to annelation, still no definite answer to the question of double-bond localization could be given.

(3) Badger, G. M. *Q. Rev. Chem. Soc.* 1951, 5, 147.

(1) Mitchell, R. H.; Slowey, P. D.; Kamada, T.; Williams, R. V.; Garratt, P. J. *J. Am. Chem. Soc.* 1984, 106, 2431.

(2) Mills, W. H.; Nixon, I. G. *J. Chem. Soc.* 1930, 2510.

(4) (a) Korp, J. D.; Bernal, I. *J. Am. Chem. Soc.* 1979, 101, 4273 and references therein. (b) A review of earlier work can be found: Halton, B. *Chem. Rev.* 1973, 73, 113.