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## FEATURE ARTICLE

## When Does Electronic Delocalization Become a Driving Force of Chemical Bonding?

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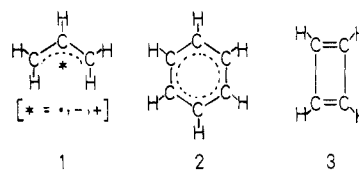
A curve-crossing diagram model is used to conceptualize the stability trends in delocalized clusters  $X_n^z$  ( $n = 3, 4, 6$ ;  $z = 0, -1$ ;  $X = H, Li, Na, K, F, Cl, Br, I$ ). The size of the diagram's gap ( $G$ ) appears to be the decisive stability factor. Large gaps result in *unstable (distortive) clusters with a high percentage of bond stretching and large quantum mechanical resonance energies (QMRE)*, e.g.,  $H_6$ . Since  $G$  is related to the strength of the two-center  $X-X$  bond it follows that only atoms which form very weak bonds will generate stable delocalized clusters. Such clusters will possess *slightly stretched bonds (on a percentage basis) and small QMRE's* (e.g.,  $Li_3, Li_6$ ). The strength of the  $\pi$ -bond between carbon atoms indicates that  $\pi$ -components, of conjugated  $\pi$ - $\sigma$ -systems, are distortive. This is confirmed by ab initio  $\sigma$ - $\pi$  energy partitions for benzene and allyl radical. The results show that the species involve distortive  $\pi$ -transition states which are forced to be delocalized by the  $\sigma$ -frames. In accord with the general trend, the distortive  $\pi$ -components also possess large QMRE. It is shown that the Hückel  $4n/(4n+2)$  dichotomy is reflected in the corresponding QMRE values but not in the  $\pi$ -distortivity, and that the connection between "aromaticity-antiaromaticity" and geometry is not necessary. These conclusions carry over to other  $\sigma$ - $\pi$ -systems,  $X_n$  ( $X = CH, SiH, N, P$ ;  $n = 4, 6$ ). The QMRE and the  $\pi$ -distortivities are *two distinct molecular properties which must be probed by different experiments*. Measurements of rotational barriers (in allyl) and thermochemical resonance energies are shown to be QMRE-related properties. Measurements of the  $\pi$ -distortivity are rare.

## Introduction

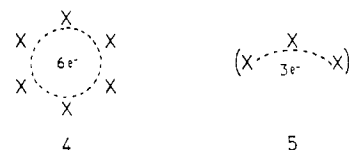
Electronic delocalization has become over the years an important concept which can rationalize and predict the structural and electronic features of a variety of organic species.<sup>2</sup> As a consequence of this success, the delocalization concept is now deeply rooted in our ways of thinking and teaching. A concept of this status requires reexamination and this is the essence of this Feature Article. Let us begin by reviewing a few basic facts and terms.

Experimental and theoretical investigations have demonstrated that certain modes of  $\pi$ -delocalization e.g., in **1** and **2** are favorable.<sup>2</sup> These species are symmetric and more stable than any  $\pi$ -localized model system. It is part of the conventional wisdom that in these systems (and analogues) there is an inherent propensity of the  $\pi$ -electrons to be delocalized<sup>3,4</sup> and that this is the source of both the stability and the symmetric geometry.

In contrast to **1** and **2**, cyclobutadiene (**3**) represents an unfavorable mode of  $\pi$ -delocalization, so-called "antiaromatic".<sup>2</sup> The rectangular geometry and instability of cyclobutadiene are ascribed to the tendency of the  $\pi$ -electrons to escape the unfavorable mode of delocalization. Furthermore, **2** and **3** represent  $4n+2$  and  $4n$   $\pi$ -electrons and are the prototypes of the Hückel  $(4n+2)/4n$  rule<sup>2,5,6</sup> that relates the stability of  $\pi$ -systems to their  $\pi$ -electron count, which is a topological property. There are not even a handful of facts, in organic chemistry, which seem to counter the foregoing conclusions in any obvious manner.<sup>2</sup>



Where is then the dilemma? This becomes apparent by using another topology argument, the isoelectronic (or isolobal<sup>7</sup>) analogy. Consider then, two families of isoelectronic and delocalized species. The family in **4** is made of 6-electron/6-center species which are isoelectronic and isostructural to the  $\pi$ -component of benzene, **2**. Similarly, the family in **5** possesses 3-electron/3-center delocalized species that are isoelectronic and isostructural to the  $\pi$ -component of allyl radical in **1**. The term  $\pi$ -component leaves out the  $\sigma$ -electrons (hereafter, the  $\sigma$ -frame) of **1** and **2** and of any other conjugated  $\sigma$ - $\pi$ -system.



A measure of the stability of the delocalized  $X_n$  species is  $\Delta E$ , which is the energy difference between  $X_n$  and its localized constituents, as exemplified in the equations

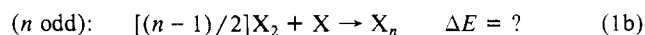
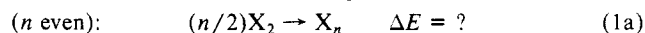
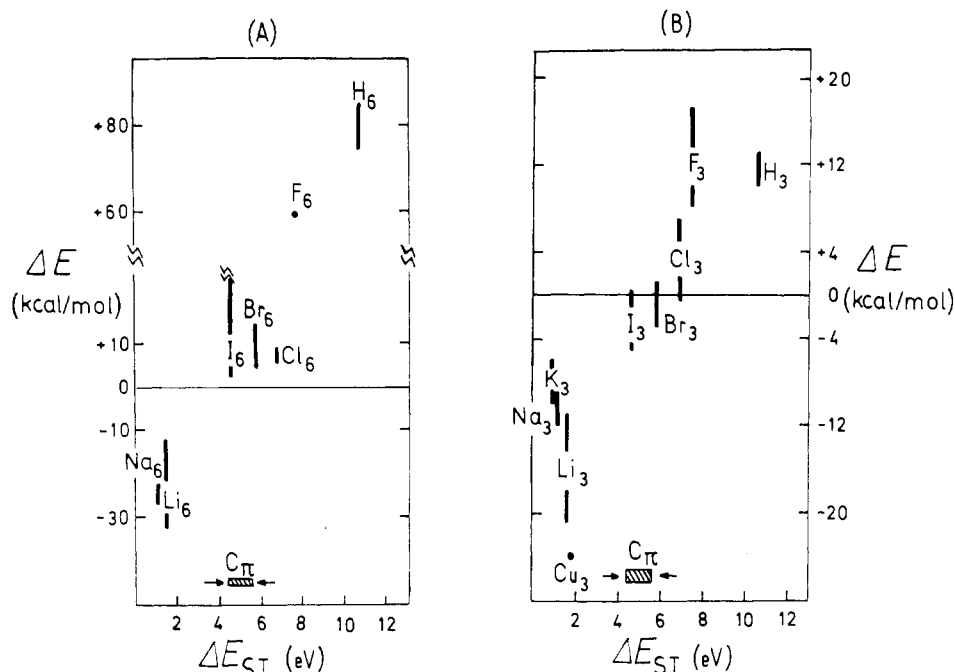


Figure 1 is a plot of  $\Delta E$  for  $X_6$  and  $X_3$  species<sup>8-25</sup> against

(1) (a) Ben-Gurion University. (b) Université De Paris-Sud.  
(2) An excellent summary of the concept in organic chemistry is given in: Garratt, J. P. *Aromaticity*; Wiley: New York, 1986.  
(3) See e.g.: (a) pp 297 in ref 2. (b) Garratt, P. *Endeavour* **1987**, *11*, 36.  
(4) Baird, N. C. *J. Org. Chem.* **1986**, *51*, 3907.  
(5) For Hückel's method and its applications see: Heilbronner, E.; Bock, H. *The HMO Model and Its Application*; Wiley-Interscience: New York, Vol. 1 (Engl. Transl.), 1976.  
(6) See e.g.: Roberts, J. D. *Notes on Molecular Orbital Calculations*; Benjamin: New York, 1962; pp 77-78.

(7) Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 711.  
(8)  $Li_6$ , theoretical  $\Delta E$  values: (a) Pickup, T. B. *Proc. R. Soc. London, A* **1973**, *339*, 69. (b) Dixon, D. A.; Stevens, R. M.; Herschbach, D. R. *Faraday Discuss. Chem. Soc.* **1977**, *62*, 110. (c) Förner, W.; Seel, M. *J. Chem. Phys.* **1987**, *87*, 443. (d) Plavšić, D.; Koutecký, J.; Pacchioni, G.; Bonačić-Koutecký, V. *J. Chem. Phys.* **1983**, *87*, 1096.

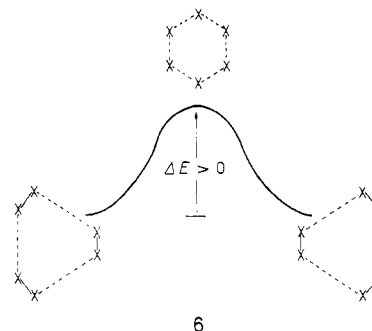


**Figure 1.** Plots of  $\Delta E$  (eq 1a and 1b) against  $\Delta E_{ST}$  of the X-X bond for delocalized species which are (A) isoelectronic and isostructural with the  $\pi$ -component of benzene (2, 4), and (B) isoelectronic and isostructural with the  $\pi$ -component of allyl radical (1, 5). The vertical bars represent the range of available  $\Delta E$  values (experimental and computational). The horizontal bar indicated by  $C_\pi$  shows the range of  $\Delta E_{ST}(\pi\pi^*)$  with model  $\pi$ -bonds being those of ethylene and acetylene.

$\Delta E_{ST}(X-X)$  which is the singlet to triplet excitation<sup>26</sup> energy of the localized bond in the dimer. For the moment, it is sufficient

to regard  $\Delta E_{ST}$  as simply representing some property of X, by which we can organize the data.

Figure 1 displays a clear dichotomy.<sup>27</sup> Thus, when  $\Delta E_{ST}$  is very small ( $\leq 2$  eV), delocalized clusters ( $\Delta E < 0$ ) result. All other available  $X_n$  ( $n = 6, 3$ ) species with  $\Delta E_{ST} \geq 4.5$  eV are either unstable or have marginal stability, e.g.,  $Br_3$ ,  $Cl_3$ .<sup>19-22</sup> The unstable species may be viewed as transition states for the interconversion of their two localized and mirror image structures, as represented in 6 for  $X_6$ .



Precisely the same dichotomy as in Figure 1, appears in 4-electron-3-center species where, e.g.,  $H_3^-$  is an unstable<sup>28</sup> delocalized species whereas  $I_3^-$  is a stable one.<sup>29</sup> Even 4-electron/

(9)  $Na_6$ , theoretical  $\Delta E$  values estimated from: Gelb, A.; Jordan, K. D.; Silbey, R. *Chem. Phys. Lett.* **1975**, *9*, 175.

(10) (Halogen)<sub>6</sub>, theoretical  $\Delta E$  values: (a) ref 8b. (b) Thompson, D. L.; Suzukawa, H. H. Jr. *J. Am. Chem. Soc.* **1977**, *99*, 3614.

(11) (Halogen)<sub>6</sub>, experimental  $\Delta E$  values for postulated hexagonal transition states: (a) Schweitzer, P.; Noyes, R. M. *J. Am. Chem. Soc.* **1971**, *93*, 3561 ( $I_6Br_2$ ). (b) King, D. L.; Dixon, D. A.; Herschbach, D. R. *J. Am. Chem. Soc.* **1974**, *96*, 3328. Dixon, D. A.; Herschbach, D. R. *J. Am. Chem. Soc.* **1975**, *97*, 6268.

(12)  $H_6$ , theoretical values: (a) ref 8b. (b) Shaik, S. S.; Hiberty, P. C. *J. Am. Chem. Soc.* **1985**, *107*, 3089.

(13)  $Cu_3$ , experimental datum: Morse, M. D. *Chem. Rev.* **1986**, *86*, 1049.

(14)  $Li_3$ , experimental datum: Wu, C. H. *J. Chem. Phys.* **1976**, *65*, 3181 ( $\Delta E = -16 \pm 5$  kcal/mol).

(15)  $Li_3$ , theoretical values: (a) Companion, A. L. *Chem. Phys. Lett.* **1978**, *56*, 500. (b) Kendrick, J.; Hillier, I. H. *Mol. Phys.* **1977**, *33*, 635. (c) Beckmann, H. O. *Chem. Phys. Lett.* **1982**, *93*, 240.

(16)  $Na_3$ , experimental datum: Hayden, J. S.; Woodward, R.; Gole, J. L. *J. Phys. Chem.* **1986**, *90*, 1799 ( $\Delta E = -(8.7-12)$  kcal/mol).

(17)  $Na_3$ , theoretical values: (a) Thompson, T. C.; Izmirlan, G., Jr.; Lemon, S. J.; Truhlar, D. G.; Mead, C. A. *J. Chem. Phys.* **1985**, *82*, 5597. (b) Martin, R. L.; Davidson, E. R. *Mol. Phys.* **1978**, *35*, 1713. (c) Malrieu, J. P.; Maynau, D.; Daudey, J. P. *Phys. Rev. B* **1984**, *30*, 1817.

(18)  $K_3$ , experimental datum: (a) ref 16 ( $\Delta E = -(5.8-10.3)$  kcal/mol). (b) Lindsay, D. M.; Herschbach, D. R.; Kwiram, A. L. *Mol. Phys.* **1976**, *32*, 1199. (c) A theoretical datum in ref 17a.

(19)  $Cl_3$ , experimental values: range between  $\Delta E > 0$  and  $\Delta E \sim -1$  kcal/mol: (a) Boal, D. H.; Ozin, G. A. *J. Chem. Phys.* **1971**, *55*, 3598. (b) Nelson, L. Y.; Pimentel, G. C. *J. Chem. Phys.* **1967**, *47*, 3671. (c) Bunker, D. L.; Davidson, N. *J. Am. Chem. Soc.* **1958**, *80*, 5090. (d) Lee, Y. T.; LeBreton, P. R.; McDonald, J. D.; Herschbach, D. R. *J. Chem. Phys.* **1969**, *51*, 455.

(20)  $Cl_3$ , computational values are generally  $\Delta E > 0$ ; see e.g.: Duggan, J. J.; Grice, R. *J. Chem. Soc., Faraday Trans. 2* **1984**, *80*, 809 ( $\Delta E = 6.9$  kcal/mol).

(21)  $Br_3$ , experimental values are generally  $\Delta E < 0$ : a) ref 19c,d ( $\Delta E = -3$  kcal/mol). (b) Reference 19a.

(22)  $Br_3$ , theoretical values are generally  $\Delta E > 0$ : see e.g.: Koshi, M.; Ito, H.; Matsui, H. *Chem. Phys. Lett.* **1983**, *103*, 180.

(23)  $I_3$ , experimental values are generally  $\Delta E < 0$ : see ref 19c,d ( $\Delta E \sim -5$  kcal/mol).  $I_3$ , theoretical values are generally  $\Delta E > 0$ : see ref 22.

(24)  $F_3$ , theoretical datum: Duggan, J. J.; Grice, R. *J. Chem. Soc., Faraday Trans. 2* **1984**, *80*, 795.

(25)  $H_3$ ,  $\Delta E$  values: (a) Liu, B. *J. Chem. Phys.* **1973**, *58*, 1925. (b) Reference 8b. (c) Reference 12b. (d) Our recent VB calculations with a DZ + P basis give 15.1 kcal/mol, to be published.

(26)  $\Delta E_{ST}$  values of the  $\sigma \rightarrow \sigma^*$  variety are taken from (a) ref 13 ( $Cu_2$ ). (b) Konowalow, D. D.; Olson, M. L. *J. Chem. Phys.* **1979**, *71*, 450 ( $Li_2$ ). (c) Konowalow, D. D.; Rosenkrantz, M. E.; Olson, M. L. *J. Chem. Phys.* **1980**, *72*, 2612 ( $Na_2$ ). (d) Jeung, G. H.; Daudey, J. P.; Malrieu, J. P. *J. Phys. B* **1983**, *16*, 699 ( $K_2$ ). (e) Cartwright, D. C.; Hay, J. P. *J. Chem. Phys.* **70**, 3191 ( $F_2$ ). (f) Peyerimhoff, S. D.; Bunker, R. *J. Chem. Phys.* **1981**, *57*, 279 ( $Cl_2$ ). (g) Oldman, R. J.; Sander, R. K.; Wilson, K. R. *J. Chem. Phys.* **1975**, *63*, 4252 ( $Br_2$ ). (h) Das, G.; Wahl, A. C. *J. Chem. Phys.* **1978**, *69*, 53 ( $I_2$ ). (i) Reference 8b ( $H_2$ ). (j) Sunil, K. K.; Jordan, K. D.; Shepard, R. *Chem. Phys.* **1984**, *88*, 55. Dance, D. F.; Walker, I. C. *Chem. Phys.* **1973**, *18*, 601,  $\Delta E_{ST}(\pi\pi^*)$  for a  $\pi$ -bond modelled by  $C_2H_4$  and  $C_2H_2$ .

(27) For previous discussions see: (a) Shaik, S. S.; Bar, R. *Nouv. J. Chim.* **1984**, *8*, 411. (b) Shaik, S. S.; Hiberty, P. C.; Lefour, J.-M.; Ohanessian, G. *J. Am. Chem. Soc.* **1987**, *109*, 363. (c) Reference 12b. (d) Shaik, S. S.; Hiberty, P. C.; Ohanessian, G.; Lefour, J. M. *Nouv. J. Chim.* **1985**, *9*, 385. (e) Epitotis, N. D. *Nouv. J. Chim.* **1984**, *8*, 11. (f) Epitotis, N. D. *Lect. Notes. Chem.* **1983**, *34*, 358. (g) Malrieu, J. P. *Nouv. J. Chim.* **1986**, *10*, 61.

(28) Keil, F.; Ahlrichs, R. *J. Am. Chem. Soc.* **1976**, *96*, 4787 ( $\Delta E \sim 11$  kcal/mol).

4-center species exhibit this dichotomy, with unstable squares like  $H_4$  and  $Cl_4^{8b,11b}$  and a  $Li_4$  square that appears, both experimentally<sup>30a</sup> and computationally,<sup>30b</sup> to be more stable than its localized constituents,  $2Li_2$ .

It is important to recognize that the stable  $X_n$  clusters, e.g.,  $Li_6$ ,  $Li_4$ , have other geometries with a greater stability than those considered here. For example, the most stable form of  $Li_4$  appears in ab initio computations to be rhomboid rather than square.<sup>30b-d</sup> The structures of choice are used here in terms of the isoelectronic and isostructural analogies to the  $\pi$ -components of the organic species 1–3. In this respect, it is not apparent from Figure 1 that  $\pi$ -electrons should possess any inherent propensity to be delocalized by themselves (see horizontal bar for  $\Delta E_{ST}(\pi\pi^*)$  values).

The observations in Figure 1 and the following discussion create a few dilemmas. The general question is expressed in the title of this Feature Article and is related to understanding the properties that make delocalization a driving force of chemical bonding and hence, of structure. The particular questions concern the nature of the  $\pi$ -components in organic species. For example, does the  $\pi$ -component of benzene have a driving force to be delocalized like  $Li_6$ , or is the  $\pi$ -component distortive like  $H_6$ ? The seeds of this dilemma can be traced back to the 1950s,<sup>31</sup> but it persists to date as evidenced in recent controversies.<sup>32,33</sup> A case is made here which favors the assignment that  $\pi$ -delocalization is not a driving force but a byproduct phenomenon of the constraints of the  $\sigma$ -frame.<sup>27a-d</sup> This property of the  $\pi$ -components blends them naturally into their general isoelectronic families (e.g., Figure 1).

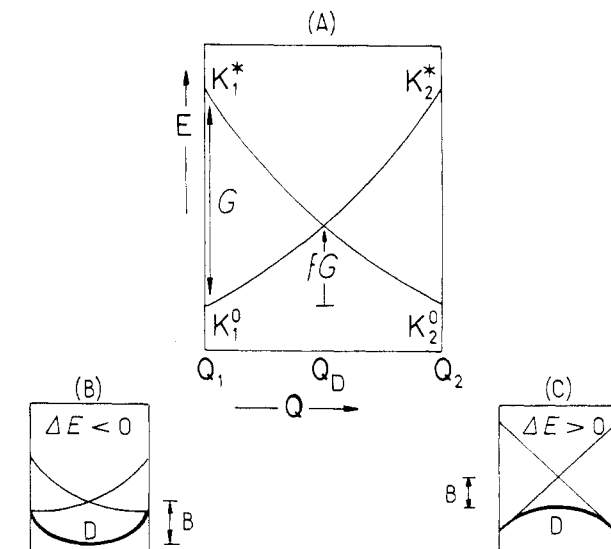
Figure 1, the datum on  $Li_4$ ,<sup>30</sup> and the instability of hexaaza-benzene<sup>34</sup> show that stability and structure are not topological properties of electron count and mode of delocalization. This creates a need to understand the origins and success of the Hückel rules in organic chemistry, and how we should go beyond these rules to understand data that do not fall within the theoretical confines.

The most curious dilemma arises from the conclusion that  $\pi$ -components are distortive species confined by their  $\sigma$ -frames to be delocalized.<sup>27a-d</sup> If this is so, we will have to understand how such species can exhibit thermochemical stability in various measurements.<sup>2,3</sup> In short, what properties of the  $\pi$ -components are being measured and what are those that are being missed by the methodology of organic chemistry?

The Feature Article is constructed around the above questions and summarizes previous works<sup>27a-d,35</sup> and more recent results.<sup>36</sup>

### When Does Delocalization Become a Stable Option? A Curve-Crossing Diagram Model

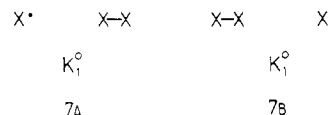
The curve-crossing diagram model<sup>27a-d</sup> provides qualitative



**Figure 2.** (A) A curve-crossing diagram of two "Kekulé curves". The diagram gap is  $G$ , while  $fG$  is the deformation energy (bond distortion and intermolecular exchange repulsion) required to achieve crossing. The diagram is appropriate also for  $\pi$ -components (devoid of  $\sigma$ -frames). (B, C) The diagrams with inclusion of avoided crossings. The states after avoided crossing are shown by dark lines. The avoided crossing resonance interaction is  $B$ .

insight into the factors which determine the relative stability of a delocalized  $X_n$  and its localized constituents (eq 1a, 1b). Figure 2a is such a diagram for a species whose electronic delocalization can be described by a resonance of two Kekulé structures.

The lower anchor points of the curves,  $K_1^0$  and  $K_2^0$ , refer to the two Kekulé structures at their optimum geometries. For example, 7a and 7b for the 3-electron/3-center problem. Thus, the optimum Kekulé structures have short two-electron bonds ( $X-X$ ) and infinitely long linkages between a dimer and a single atom, as in 7, or between dimers, in cases like  $X_n$  with  $n = 4, 6$ , and so on.



In accord, the abscissa of Figure 2 records the geometric changes involved in transmuting one Kekulé geometry into its mirror image ( $Q_1 \rightarrow Q_2$ ). The midpoint of the coordinate ( $Q_D$ ) corresponds to a symmetric geometry with uniform bond lengths and this is where delocalization takes place by avoided crossing. The avoided crossing is shown only in parts B and C of Figure 2.

The upper anchor points of the Kekulé curves are two excited forms  $K_1^*$  and  $K_2^*$ . Each of the excited forms has the geometry of the state directly below it, but the same bond-pairing pattern of the ground state with which it correlates. We have called these unique excited forms, the "electronic images" of the Kekulé states ( $K_1^0, K_2^0$ ).<sup>27a,b</sup> By this term we mean that each curve,  $K_1^0 \rightarrow K_2^*$  and  $K_1^* \rightarrow K_2^0$ , represents a single bond-pairing situation.<sup>37,38</sup>

The crossing point in Figure 2 can be regarded as the point where a pair of "states"  $K^0$  and  $K^*$  attain equal energy. Since the two "states" are initially separated by an energy gap  $G$ , the energy equality has to be achieved by bond distortion and intermolecular interactions, which destabilize  $K^0$  and stabilize  $K^*$ . The total deformation energy required to achieve resonance ( $\Delta E_{def}$ )

(29) (a)  $\Delta E = -(11-15)$  kcal/mol may be estimated from solvent effect on the  $I_3^- \rightarrow I_2 + I^-$  equilibrium constant. See: Parker, A. J. *J. Chem. Soc. A* **1966**, 221. (b) For solid-state data see: Dunitz, J. D. *X-Ray Analysis and Structure of Organic Molecules*; Cornell University Press: New York, 1979. Cotton, F. A.; Kibala, P. A. *J. Am. Chem. Soc.* **1987**, *109*, 3308.

(30) (a) Wu, C. H. *J. Phys. Chem.* **1983**, *87*, 1534. (b) Beckmann, H. O.; Koutecký, J.; Bonačić-Koutecký, V. *J. Chem. Phys.* **1980**, *73*, 5182. (c) 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.; Koutecký, J.; Botschwina, P.; Meyer, W. *Chem. Phys. Lett.* **1979**, *67*, 119. (d)  $Li_2$  (also  $Na_2$ ) exhibits unusual electron density maximum at the bond's midpoint. See, Gatti, C.; Piercarlo, F.; Pacchioni, G. *Theor. Chim. Acta* **1987**, *72*, 433. This, however, does not affect the argument. See discussion and ref 42 later on.

(31) (a) Longuet-Higgins, H. C.; Salem, L. *Proc. R. Soc. London, A* **1959**, *251*, 172. (b) Salem, L. *The Molecular Orbital Theory of Conjugated Systems*; Benjamin: Reading, MA, 1972; pp 103–106, 494–505. (c) Labhart, H. *J. Chem. Phys.* **1957**, *27*, 957. (d) Ooshika, Y. *J. Phys. Soc. Jpn.* **1957**, *12*, 1238, 1246. (e) Berry, R. S. *J. Chem. Phys.* **1961**, *35*, 29, 2253.

(32) (a) Ichikawa, H. *J. Am. Chem. Soc.* **1984**, *106*, 6249; **1983**, *105*, 7467, vs Haddon, R. C.; Raghavachari, K.; Whangbo, M. H. *J. Am. Chem. Soc.* **1984**, *106*, 5364.

(33) Reference 4 vs Hiberty, P. C.; Shaik, S. S.; Ohanessian, G.; Lefour, J.-M. *J. Org. Chem.* **1986**, *51*, 3908.

(34) Saxe, P.; Schaefer, H. F., III. *J. Am. Chem. Soc.* **1983**, *105*, 1760.

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

(36) (a) Ohanessian, G.; Hiberty, P. C.; Lefour, J.-M.; Flament, J.-P.; Shaik, S. S. *Inorg. Chem.*, in press. (b) Ohanessian, G. Ph.D. Thesis, Université de Paris-Sud, 1986.

(37) For recent computations of such VB curves see: (a) Sevin, A.; Hiberty, P. C.; Lefour, J.-M. *J. Am. Chem. Soc.* **1987**, *109*, 1845. (b) Hiberty, P. C.; Lefour, J.-M. *J. Chim. Phys.* **1987**, *84*, 607.

(38) For related diabatic curve crossing computations see: (a) Bernardi, F.; Robb, M. A. *J. Am. Chem. Soc.* **1984**, *106*, 54. (b) Bernardi, F.; Olivucci, M.; McDouall, J. J. W.; Robb, M. A. *J. Am. Chem. Soc.* **1987**, *109*, 544.

is then simply a fraction ( $f$ ) of the gap which has to be overcome,<sup>39</sup> as expressed in the equation

$$\Delta E_{\text{def}} = fG \quad (2)$$

As shown in parts B and C of 2, the crossing is avoided by quantum mechanical mixing, which lowers the delocalized state (D) by an amount  $B$  relative to the crossing point.  $B$  is then simply the quantum mechanical resonance energy (QMRE)<sup>40</sup> of the delocalized state. We emphasize that the QMRE and the empirical resonance energy are not identical quantities (see discussions later).

The energy of the delocalized state relative to  $K^0$  is set by a balance between the deformation energy and the QMRE, as expressed in eq 3. As shown in Figure 2, the avoided crossing

$$\Delta E(K^0 \rightarrow D) = fG - B; \quad (fG = \Delta E_{\text{def}}; B = \text{QMRE}) \quad (3)$$

may lead, in principle, to stable delocalized states ( $\Delta E < 0$ , Figure 2B) or unstable ones ( $\Delta E > 0$ , Figure 2C). Thus, irrespective of whether the delocalized state is distortive ( $\Delta E > 0$ ) or stable ( $\Delta E < 0$ ), the state is endowed with a QMRE.

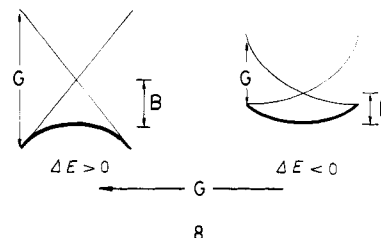
It is important to emphasize that QMRE is a property of a delocalized system regardless of the electron count and mode of delocalization. Thus, according to the model, antiaromatic 4-electron/4-center squares—like any delocalized species—have quantum mechanical resonance energies,  $B^{27b,41}$  (see later in Tables II and III).

Is there one factor which, more than others, governs the stability of the delocalized state? In previous publications<sup>27a-d</sup> it was concluded that  $G$  is the organizing quantity in an isoelectronic series. This conclusion requires further clarification.

Our recent VB ab initio computations of curve-crossing diagrams<sup>42,43</sup> show that in isoelectronic series ( $X_n$ ) where the atomic identity of  $X$  is changed, the value of  $B$  is proportional to  $G$  (see also Tables II and III later).<sup>43</sup> So if  $f$  were to be a constant, throughout the series, all diagrams would differ from each other by only a scaling factor, and the decrease of  $G$  would have, in turn, corresponded to unstable species,  $X_n$ , with a decreasing barrier. But, one can show by use of semiempirical VB arguments, based on a DIM Hamiltonian,<sup>42</sup> that  $f$  is also related to  $G$ . For example, when  $G$  varies considerably as for  $H_3$  and  $Li_3$  (157 vs 21 kcal/mol) there results a corresponding decrease of the  $f$  factor.<sup>42</sup> Therefore, as  $G$  decreases considerably in an isoelectronic series, the deformation energy term  $fG$  (in eq 2 and 3) which has a double dependence on  $G$  will decrease drastically. At small  $G$ , the deformation energy term will become small enough to be dominated by the QMRE term,  $B$ . This is the reason why stable  $X_n$  species (with  $\Delta E < 0$ ) are eventually reached in an isoelectronic series.

A generalization can be made that each isoelectronic series will exhibit a spectrum of stability whose organizing quantity is  $G$ . The spectrum is shown schematically in 8 which also conveys the information discussed above on how  $f$  and  $B$  vary with  $G$  at the extremes.

**A. Energy Gaps for Different Delocalization Problems.** Expressions for  $G$  can be generalized for two distinct cases: (a)  $X_n$  species with an average of 1 electron/center (1e/c), and (b)  $X_n$



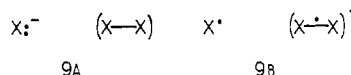
species with a noninteger number of electrons per center (mixed-valent species). The two classes differ in the elementary electronic excitation which is involved in the gap between  $K^0$  and  $K^*$  (Figure 2).

To obtain  $K^*$  from  $K^0$  for the class of 1e/c cases, each infinitely long linkage has to be singlet-coupled. As a result, each of the short X-X linkages will acquire an electronic configuration which is 75% triplet and 25% singlet (see Appendix 1 in ref 27b). We may therefore say that the elementary excitation for the 1e/c class is approximately a singlet  $\rightarrow$  triplet promotion<sup>27a,b</sup> of each of the electron-pair bonds of the ground state. The corresponding expression for  $G$  becomes as follows

$$G = n(3/4)\Delta E_{ST} \quad (4)$$

where  $\Delta E_{ST}$  is the singlet-triplet excitation energy of X-X and  $n$  is the number of X-X dimeric units in a Kekulé ground state.<sup>43</sup>

For the mixed-valent cases, the  $K^*$  states in the diagram are charge-transfer states of the Kekulé states below them.<sup>27a</sup> For example, 9a and 9b describe a  $K^0$ - $K^*$  pair for a 4-electron/3-center problem of delocalized  $\sigma$ -type  $X_3^-$ .<sup>27a</sup> Thus, in 9a there are an anion  $X_3^-$  and a dimer. The anion has an electron pair (dark circles in 9a) in an atomic orbital or a hybrid orbital, while the dimer is described by a  $\sigma$ -bond. In 9b, an electron is transferred from  $X_3^-$  to  $X_2$  to generate a radical and a radical anion, and the two odd electrons (dark circles) are spin-paired.<sup>27a,39</sup>



In general, the  $K^*$  states, of all other mixed-valent problems (e.g.,  $X_3^+$ ,  $X_3^-$ , etc.), are charge-transfer states which involve an electron transfer from a donor (D) moiety to an acceptor moiety (A). The gap expression is accordingly the vertical electron-transfer energy

$$G = I_D - A_A \quad (5)$$

where  $I$  is the ionization potential and  $A$  is an electron affinity.

**B. General Trends in Delocalized  $X_n$  Species.** In both series of  $X_3$  (3e/3c) and  $X_6$  (6e/6c) species<sup>8-25</sup> the general order of stability is dominated by the singlet-triplet excitation,<sup>26</sup>  $\Delta E_{ST}$ , as shown in Figure 1. Stable  $X_3$  and  $X_6$  clusters are found only for quite small  $\Delta E_{ST}$  values ( $\leq 2$  eV). Beyond this small value, clusters are either unstable or have a marginal stability. Thus, the general behavior across the board is in accord with the description in 8.

In fact, in each of the series there appear to be also species with  $\Delta E \sim 0$ , just in the boundary between the extremes. Thus,  $Cl_3$  is either unstable<sup>19a</sup> or indifferent to a localizing distortion to a  $C_{\infty v}$  structure.<sup>19b</sup> Similarly, a hexagonal  $I_4Br_2$  species was invoked<sup>11a</sup> as a possible transition state with  $\Delta E < 2$  kcal/mol, for the exchange reaction of  $Br_2$  and  $I_2$ .

A stability spectrum like 8 also typifies  $X_4$  squares. Here too squares with  $\Delta E \leq 0$  are found only when  $\Delta E_{ST}$  is very small, as for  $Li_4$ .<sup>30</sup>

The series  $X_3^-$  with 4-electrons/3-centers correlates nicely with the quantity  $I_{X-X} - A_{X-X}$ .<sup>27a</sup> Thus,  $H_3^-$  which possesses the largest  $I_{X-X} - A_{X-X}$  quantity ( $\geq 4$  eV) is unstable with  $\Delta E \cong +11$  kcal/mol.<sup>28</sup> On the other hand,  $I_3^-$ ,  $F_3^-$ , and  $Br_3^-$  for which  $I_{X-X} - A_{X-X}$  is  $\sim 0.3$ – $0.8$  eV are stable delocalized species.<sup>29,44,45</sup> In between these

(39) For such arguments see e.g.: Shaik, S. S. *Prog. Phys. Org. Chem.* **1985**, *15*, 197. Mitchell, D. J.; Schlegel, H. B.; Shaik, S. S.; Wolfe, S. *Can. J. Chem.* **1985**, *63*, 1642.

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

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

(42) Hiberty, P. C.; Ohanessian, G., unpublished results from DEA Thesis of Maitre, P. A., manuscript is in preparation.

(43) These values have been derived for the  $X_3$  cases for which  $G = 0.75\Delta E_{ST}$ .<sup>27b</sup> Using a Heisenberg Hamiltonian with neglect of overlap (e.g., of ref 17c) we obtain  $B = 0.25\Delta E_{ST}$  (at  $Q_D$ ), while employing the DIM Hamiltonian (e.g., in Companion, A. L. *J. Chem. Phys.* **1968**, *48*, 1186) and including overlap in the  $2 \times 2$  solution at the crossing point, one obtains  $B = 0.25\Delta E_{ST}[(1 - s^2)/(1 + 0.5s^2)]$  (at  $Q_D$ ).  $\Delta E_{ST}$  is the singlet-triplet excitation of X-X at the bond length that corresponds to the crossing point ( $Q_D$ ). Thus,  $B$  is proportional to  $G$ . Since X-X is longer at  $Q_D$  than at the equilibrium distance, the corresponding  $\Delta E_{ST}$  is smaller than the  $\Delta E_{ST}$  value which determines the gap at  $Q_1$  and  $Q_2$ .

(44)  $F_3^-$ , experimental and theoretical data: (a) Ault, B. S.; Andrews, L. *Inorg. Chem.* **1977**, *16*, 2024. (b) Cahill, P. A.; Dykstra, C. E.; Martin, J. C. *J. Am. Chem. Soc.* **1985**, *107*, 6359 ( $\Delta E = -11$  kcal/mol).

extremes there exist species, such as  $\text{Cl}_3^-$ , which appear to be indifferent to distortion ( $\Delta E \sim 0$ )<sup>44a,46</sup> in accord with their intermediate gap value of  $\sim 1.2$  eV.<sup>27a</sup>

It is apparent that in a broad range of isoelectronic and isostructural species, the gap  $G$  is an organizing quantity. It is only when  $G$  is very small that electronic delocalization becomes a significantly favored option and, hence, a driving force of chemical bonding and structure. Breakdowns in the order of stability are expected and known, when the differences in  $G$  are not large.

Generally, the quantity  $G$  is related to the bond strength of the dimer  $\text{X}-\text{X}$ .<sup>27a</sup> When this bond is strong both triplet excitation and charge-transfer energies are high, with some exceptions.<sup>47</sup> A rule of thumb may be used that, as the bond strength of the dimer ( $\text{X}-\text{X}$ ) increases, delocalized  $\text{X}_n$  species are expected (a) to become more unstable, (b) to have more stretched (on percentage basis)  $\text{X}\cdots\text{X}$  bonds,<sup>12b,39</sup> and (c) to possess higher QMRE ( $B$ ).

The relationship between stability and bond strength in delocalized species has been derived by using other approaches within VB theory by Epiotis<sup>27e,f</sup> and Malrieu.<sup>27g</sup>

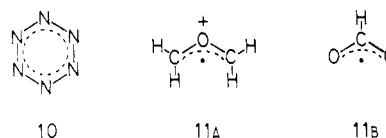
**C. General Expectations for the Distortive Behavior of  $\pi$ -Components.** In  $\sigma$ - $\pi$ -systems, the  $\pi$ -distortivity may be latent as the  $\pi$ -electrons are confined to the  $\sigma$ -frame. The correlation diagram model provides a criterion,  $G$ , by which one can think about  $\pi$ -components by themselves.

The  $G$  quantity for  $\pi$ -components is large, because of the strength of  $\pi$ -bonds formed by first-row elements (e.g., C, N, O, etc.). For example,  $\Delta E_{\text{ST}}(\pi\pi^*)$  values for most such  $\pi$ -bonds are in the range of  $\sim 4.5$ – $6.2$  eV.<sup>48,49</sup> Turning back to Figure 1, it is seen that, in this range of  $\Delta E_{\text{ST}}$ , the delocalized species are either marginally stable or unstable–distortive systems. This means that the  $\pi$ -components of benzene and of allyl radical should be also either distortive or marginally stable toward a localizing distortion.

Similarly, owing to their strength,  $\pi$ -bonds of first-row elements are generally poor acceptors, so that the electron-transfer energy gaps for anionic delocalization are generally high. For example, the  $I_D-A_A$  quantity for the  $\pi$ -component of allyl anion can be estimated<sup>50</sup> at  $\sim 2$ – $3.7$  eV. Recalling that  $\text{Cl}_3^-$ , with a gap of 1.2 eV, may already be at the borderline of stability,<sup>44a,46</sup> we again have to conclude that the  $\pi$ -component of allyl anion should either be distortive like  $\text{H}_3^-$ , or possess a marginal stability toward a localizing distortion.

Similar conclusions can be extended to analogous  $\pi$ -compounds of other first-row elements (i.e., C, N, O). The largeness of the  $G$  quantity, which originates in the strength of the  $\pi$ -bond, generally makes  $\pi$ -delocalization a disfavored option which has to be forced by the  $\sigma$ -frame. Indeed, some cases show this distortive propensity quite clearly. These are the hexaaza analogue of benzene,<sup>10</sup> and the allylic type systems,<sup>51</sup> **11a,b**, all of which distort easily to partially localized geometries (i.e., to  $D_{3h}$  and  $C_3$ ).

Exceptional cases are expected among the electron-deficient situations such as allyl cation, and so on. In these cases, the charge-transfer energy gaps are not large because the acceptor



moiety is a positive carbon center. Thus,  $\pi$ -delocalization may be a favored option in some cases but not in many. This may be witnessed from the marginal stability of nonclassical and delocalized carbonium ions over their classical localized analogues. In some cases, this relative stability has not been established unequivocally,<sup>52</sup> while in other cases the localized carbonium ion is the most stable species.<sup>53</sup>

Conclusions about the distortive behavior of  $\pi$ -components have been derived from different approaches and throughout the last three decades. In 1959 Longuet-Higgins and Salem,<sup>31a</sup> following Labhart<sup>31c</sup> and Ooshika,<sup>31d</sup> proposed on the basis of a variable- $\beta$ -Hückel treatment and pseudo-Jahn-Teller arguments, that the tendency of a  $(4n+2)\pi$ -electronic system to distort<sup>31b</sup> "exists already in benzene". Similar arguments, coupled with an analysis of the experimental  $B_{2u}$  vibration, were subsequently used by Berry.<sup>31e</sup> This distortive propensity in  $\text{C}_6\text{H}_6$  is predicted also by semiempirical calculations of Paldus and Chin<sup>54a</sup> and by arguments used by Heilbronner.<sup>54b</sup> Using a VB analysis Epiotis<sup>27e,f</sup> has reasoned that the  $\pi$ -components of benzene and allyl radical must be distortive like their isoelectronic  $\text{H}_n$  analogues. The ease of distortion of allyl radical species (**11**) has recently been discussed by Borden<sup>51</sup> and collaborators, using a second-order Jahn-Teller approach.

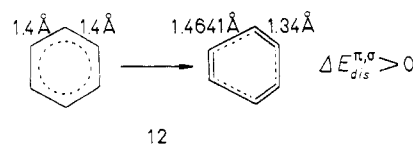
Let us turn to review the quantitative analysis of the  $\sigma$ - $\pi$  behavior in organic species.

### Is There a Driving Force for $\pi$ -Electrons To Be Delocalized? Computational Tests

The basic strategy consists of applying a localizing distortion on a  $\sigma$ - $\pi$ -species, and partitioning the total distortion energy  $\Delta E^{\pi,\sigma}_{\text{dis}}$  into its individual components,  $\Delta E^{\pi}_{\text{dis}}$  and  $\Delta E^{\sigma}_{\text{dis}}$ . To get both reliable and meaningful results, one has to define a correct distortion<sup>27b,33,35</sup> and to devise a meaningful  $\sigma$ - $\pi$ -energy partition in an all-electron ab initio computational scheme.<sup>27b,d,35</sup>

Consider, for example, benzene. If its  $\pi$ -component is indeed an unstable transition state, there should then exist *only one nontotally symmetric mode* (within constraints of planarity) which lowers the energy of the delocalized  $\pi$ -component. In order not to miss this mode,<sup>33</sup> the choice localizing distortion is a  $B_{2u}$  mode, which is the distortion which has a negative force constant<sup>8b</sup> for the  $\text{H}_6$  transition state.

The actual localizing distortion for benzene is **12** which is nearly identical with the  $B_{2u}$  mode and involves alternately, compressing one bond by 0.06 Å and stretching the other by nearly the same amount. The small difference in the third figure of the stretched bond is required for getting a meaningful electronic energy partition, as this difference conserves constant nuclear repulsion (between carbons) in the distortion (vide infra).<sup>27b,d,35</sup>



Equation 6 expresses the total SCF energy of a  $\sigma$ - $\pi$ -system.

$$E_{\text{tot}} = \sum h_{\pi} + R_{\pi\pi} + R_{\pi\sigma} + \sum h_{\sigma} + R_{\sigma\sigma} + V_{\text{NN}} \quad (6)$$

Here,  $h_{\pi}$  and  $h_{\sigma}$  are the corresponding mono-electronic integrals of the occupied  $\pi$ - and  $\sigma$ -spin orbitals. The  $R$  terms stand for

(52) See the recent whole issue devoted to the 2-norbornyl cation problem: *Acc. Chem. Res.* **1983**, *16*, 426–454.

(53) See e.g.: Lipkowitz, K. B.; Larter, R. M.; Boyd, D. B. *J. Am. Chem. Soc.* **1980**, *102*, 85.

(54) (a) Paldus, J.; Chin, E. *Int. J. Quantum Chem.* **1983**, *24*, 373. (b) Heilbronner, E., private communication to P.C.H. and S.S.S.

(45)  $\text{Br}_3^-$  and other data are reviewed in Gabes, W.; Elst, R. *J. Mol. Struct.* **1974**, *21*, 1. Using their criteria of the force constants  $k_{\text{sym}}$  and  $k_{\text{asym}}$  for the stretching vibrations, the relative stability may be inferred to vary as follows:  $\text{F}_3^- \sim \text{I}_3^- > \text{Br}_3^- > \text{Cl}_3^-$  ( $\text{F}_3^-$  data from ref 44).

(46) Ault, B. S.; Andrews, L. *J. Chem. Phys.* **1976**, *64*, 4853. See, however, data in benzene solutions: Evans, J. C.; Lo, G. Y.-S. *J. Chem. Phys.* **1966**, *44*, 3638.

(47)  $\text{F}_2$  is an exception with a very weak bond but a very large  $\Delta E_{\text{ST}}$  (see ref 26e).

(48) Reference 26j;  $\Delta E_{\text{ST}}(\pi\pi^*) \cong 4.5$ – $5.4$  eV depending on the model  $\pi(\text{CC})$  bond.

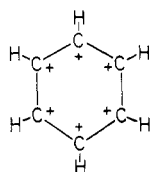
(49) (a) Clouthier, O. J.; Ramsay, D. A. *Annu. Rev. Phys. Chem.* **1983**, *34*, 31;  $\Delta E_{\text{ST}}(\pi\pi^*) = 5.53$  eV for  $\text{H}_2\text{CO}$ . (b) Lofthus, A.; Krupenie, P. H. *J. Phys. Chem. Ref. Data* **1977**, *6*, 113;  $\Delta E_{\text{ST}}(\pi\pi^*) = 6.2$  eV for  $\text{N}_2$ .

(50) (a) Vertical electron affinities of  $\pi$ -bonds are  $-(2$ – $2.6)$  eV using ethylene and acetylene as model  $\pi(\text{CC})$  bonds: Jordan, K. D.; Burrow, P. D. *Acc. Chem. Res.* **1978**, *11*, 341. (b) Model  $\pi(\text{C}^-)$  can be taken as  $\text{CH}_2^{-(2B_1)}$  whose  $\pi$ -ionization potential is 1.1 eV: Leopold, D. G.; Murray, K. K.; Lineberger, W. C. *J. Chem. Phys.* **1984**, *81*, 1084. Using  $\text{CH}_3^-$  as a model gives a value of 0.08 eV: Ellison, G. B.; Engelking, P. C.; Lineberger, W. C. *J. Am. Chem. Soc.* **1978**, *100*, 2556.

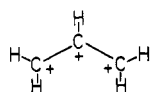
(51) Feller, D.; Davidson, E. R.; Borden, W. T. *J. Am. Chem. Soc.* **1984**, *106*, 2513.

electron-electron repulsion of a type that is specified by the subscript, and  $V_{NN}$  accounts for nuclear repulsion.

The first two terms describe the energy of the  $\pi$ -electrons in the field of the bare nuclei. For benzene, for example, the first two terms correspond to the  $\pi$ -electronic energy in a field of  $(C^6+H^1+)_6$ . By addition of the third term,  $R_{\pi\sigma}$ , to the first two, part of the positive field  $(C^6+H^1+)_6$ , felt by the  $\pi$ -electrons, is screened by electron-electron repulsion which is exerted by the  $\sigma$ -electrons, five effectively on each carbon and one effectively on each hydrogen. The net result is that the first three terms in eq 6, for the case of benzene, describe the energy of the six  $\pi$ -electrons in the field of the effective  $\sigma$ - $(C^1+H)_6$  framework in 13. Further accuracy of the  $\pi$ -energy can be achieved by inclusion of  $\pi$ -space correlation ( $\pi$ -CI).



13



14

This is the commonly used  $\sigma$ - $\pi$ -partition in the effective  $\pi$ -electron calculations.<sup>55</sup> However, in ab initio calculations it is meaningless to partition  $V_{NN}$  into  $\sigma$ - and  $\pi$ -components. The problem is to be able to identify the variation of *electronic* energy in the  $\pi$ -component. In an  $H_n$  system the variation of the electronic energy would be determined by devising a distortion that keeps the nuclear repulsion constant. By analogy, in the  $\sigma$ - $\pi$ -molecules, a distortion is used which keeps constant the nuclear repulsion between carbon centers, since these play the same role as the nuclei in the  $H_n$  system. This constancy is achieved in 12 by the small difference between bond stretching and compression. In this manner, the total distortion energy following a localizing distortion, e.g., 12, can be partitioned into a sum of  $\pi$ - and  $\sigma$ -contributions as shown below in eq 7. The same strategy is used for all the species that are described in the following space.<sup>27b,d;35,36</sup>

$$\Delta E^{\pi,\sigma}_{dis} = \Delta E^{\pi}_{dis} + \Delta E^{\sigma}_{dis} \quad (7)$$

The consistency of the partition scheme is checked by calculating  $\Delta E^{\sigma}_{dis}$  directly from the  $\sigma$ -frames, e.g., 13 and 14, and from the highest spin species (i.e., septuplet benzene and quadruplet allyl).<sup>27b</sup> The resulting  $\Delta E^{\sigma}_{dis}$  values are equal or nearly so.<sup>27b</sup> Other partition schemes that have been proposed to us,<sup>56</sup> such as equally dividing  $R_{\pi\sigma}$ , have led to the same qualitative conclusions.

To ensure independence of the results on the quality of the computations, the current methodology of molecular calculations is followed of a gradual upgrading of the level of sophistication. In the case of allyl radical a very high level has been reached, using a triple- $\zeta$  basis set with  $\sigma$ - and  $\pi$ -correlations amounting to more than  $6 \times 10^6$  determinants.<sup>27b,d</sup> In no instance have we observed a change in the conclusions regarding the relative roles of  $\sigma$  and  $\pi$ . In retrospect, some of the extra caution may not have been necessary because most of the properties, for example of benzene, are reproduced even with small basis sets and without  $\pi$ -CI.<sup>57</sup>

Table I summarizes the results at the highest common level.<sup>27b</sup> The  $\Delta E^{\sigma}_{dis}$  values are consistently negative and show a clear tendency of the delocalized  $\pi$ -components to fall apart to the corresponding localized constituents. In this sense, the delocalized  $\pi$ -components fit nicely into their isoelectronic series and behave qualitatively like the corresponding  $H_n$  species. In close accord, the  $\pi$ -sextet is much more distortive than the  $\pi$ -components of the allylic species, the same as  $H_6$  vs  $H_3$ .

The  $\Delta E^{\sigma}_{dis}$  values are all positive, thus indicating the reluctance of the  $\sigma$ -frame to distort away from a uniform symmetric geometry. The  $\Delta E^{\sigma}_{dis}$  values are approximately proportional to the

TABLE I: Distortion Energies of  $\pi$ - $\sigma$  Organic Systems<sup>a</sup>

entry	species	method <sup>c</sup>	$\Delta E^{\pi,\sigma}_{dis}$	$\Delta E^{\pi}_{dis}$	$\Delta E^{\sigma}_{dis}$
1	$C_3H_5^b$	6-31G/ $\pi$ -CI	3.9	4.8	-0.9
2	$C_6H_6^c$	6-31G/ $\pi$ -CI	7.2	16.3	-9.1
3	$C_4H_4$ (singlet) <sup>d</sup>	6-31G/ $\pi$ -CI	-3.4	7.6	-11.0

<sup>a</sup>  $\Delta E_{dis}$  in kcal/mol. A distortive species is indicated by  $\Delta E_{dis} < 0$  and vice versa. <sup>b</sup> The distortion is  $r = 1.4$  Å (all C-C bond lengths) to  $r_1 = 1.34$  Å;  $r_2 = 1.4641$  Å. <sup>c</sup> The distortion is  $r = 1.4$  Å (all C-C bond lengths) to  $r_1 = 1.34$  Å;  $r_2 = 1.4627$  Å. <sup>d</sup> The distortion is  $r = 1.463$  Å (all C-C bond lengths) to  $r_1 = 1.393$  Å;  $r_2 = 1.5162$  Å. <sup>e</sup>  $\pi$ -CI refers to  $\pi$ -space electron correlation calculation.<sup>27b</sup>

number of adjacent pairs of  $\sigma$ -bonds. This means that the  $\sigma$ -frame can be considered *effectively* as a sum of localized electron-pair  $\sigma$ -bonds, as is usually assumed. Using a simple harmonic potential for each  $\sigma$ -bond, e.g.,  $0.5k(r - r_0)^2$ , it may be shown that an asymmetric distortion (by  $\pm \Delta r$ ) of a pair of bonds raises their energy by a given increment *irrespective* of the initial bond length. Using such a rough picture, the total  $\Delta E^{\sigma}_{dis}$  is proportional to the number of pairs which are undergoing an asymmetric distortion. Taking  $\sim 5$  kcal/mol as a pair distortion energy (for  $\Delta r \sim 0.06$  Å), the total  $\Delta E^{\sigma}_{dis}$  for  $n$  pairs can be roughly approximated as  $5n$  kcal/mol, which is in accord with empirical fits.<sup>4</sup>

It should be noted that the  $\pi$ -electrons of the high-spin states (e.g., septuplet benzene) are nearly indifferent to distortion,<sup>27b</sup> and therefore the total distortion energy of these, high-spin, species comes from their  $\sigma$ -frames. The clear-cut finding<sup>27b,35</sup> is that the high-spin states, of both allyl radical and benzene, resist the distortion *more* than their corresponding ground states. This result, by itself, demonstrates the distortive character of the  $\pi$ -components of the ground states of benzene and allyl radical, independently of any  $\sigma$ - $\pi$ -partition scheme.

Two main conclusions follow accordingly from the  $\sigma$ - $\pi$ -opposition in Table I. The first conclusion concerns benzene and allyl. It is seen that in these species  $\pi$ -delocalization is not a driving force of chemical bonding but rather a byproduct of the tendency of the  $\sigma$ -frame to maintain symmetric structures (at any given bond length). The second conclusion concerns the comparison of benzene and cyclobutadiene. As may be seen from the  $\Delta E^{\sigma}_{dis}$  values, both  $\pi$ -components are almost equally reluctant to be delocalized. The dominant factor of the structural choices is the number of bonds in the  $\sigma$ -frame, whose  $\Delta E^{\sigma}_{dis}$  values determine the final symmetric hexagonal shape of benzene and the rectangular shape of cyclobutadiene.

Thus, by seeking the driving force to maintain a symmetric geometry, we are led to conclude that many of the properties that are adapted by  $\pi$ -electrons depend on the constraints imposed by the  $\sigma$ -frame. Such  $\sigma$ -effects have been pointed out in several instances, and two examples follow. Thus, the puckered geometry of "aromatic" cyclobutadienide dication ( $C_4H_4^{2+}$ ) was ascribed, by Schleyer a co-workers,<sup>58</sup> to  $\sigma$ -effects. Similarly, Allinger and co-workers<sup>59a</sup> have shown that the tub shape of the "antiaromatic" cyclooctatetraene (COT) is imposed by the tendency of the  $\sigma$ -frame to relieve cyclic strain and H...H repulsion. The total distortivity ( $\Delta E^{\pi,\sigma}_{dis}$ ) of  $\pi$ -delocalized COT from  $D_{8h}$  to a  $D_{4h}$  structure was estimated as  $\sim -4$  kcal/mol by Paquette and co-workers,<sup>59b</sup> who also warned against the tendency to equate antiaromaticity with the nonplanarity of COT.

Using the approximation of  $5n$  kcal/mol ( $n = 4$ ) as an estimate of  $\Delta E^{\sigma}_{dis}$  and Paquette's result ( $\Delta E^{\pi,\sigma}_{dis} \sim -4$  kcal/mol), one obtains  $\Delta E^{\pi}_{dis} \sim -24$  kcal/mol for planar COT. This latter value is larger than the corresponding values for benzene and cyclobutadiene and is in qualitative agreement with the expectation based on the energy gap criterion in eq 4. Using the same value,  $\Delta E^{\pi}_{dis} = -24$  kcal/mol, for the next member,  $C_{10}H_{10}$ , in its planar

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**TABLE II: Computed Quantum Mechanical Resonance Energies,  $B$ , for Delocalized Species**

entry	species	$B$ , kcal/mol	basic set <sup>a</sup>	method	ref
1	H <sub>3</sub>	43	DZ + P	VB	42
1a	H <sub>3</sub>	47	STO-3G	VB	42
2	Li <sub>3</sub>	6	DZ + P	VB	42
3	C <sub>3</sub> H <sub>3</sub>	12; 14	DZ	GVB	61a,b
3a	C <sub>3</sub> H <sub>3</sub>	10	DZ	RGVB	61c
4	C <sub>4</sub> H <sub>4</sub>	21; 22	DZ	RGVB; GRVB	41
4a	C <sub>4</sub> H <sub>4</sub>	30	6-31G	SCF	27b
5	N <sub>4</sub>	47	6-31G	SCF	36a
6	H <sub>6</sub>	119	6-31G	SCF	27b
7	C <sub>6</sub> H <sub>6</sub>	85	6-31G	SCF	27b
8	N <sub>6</sub>	103	6-31G	SCF	27b

<sup>a</sup>DZ + P is a double- $\zeta$  + polarization basis set. A 6-31G basis set is roughly of a double- $\zeta$  quality.

conformation, one finds as expected that  $\Delta E^{\pi,\sigma}_{\text{dis}} > 0$  for this "aromatic" 10-annulene. Thus, the commonly accepted structural dichotomy for *planar* C<sub>4n</sub>H<sub>4n</sub> and C<sub>4n+2</sub>H<sub>4n+2</sub> systems can be qualitatively understood by considering the  $\pi$ -components, of the "antiaromatic" and the successive "aromatic" members, to be equally reluctant to achieve delocalization while the number of the  $\sigma$ -bonds determines whether the geometry has a uniform or an alternating bond length.

### Thermochemical Properties and the Quantum Mechanical Resonance Energies of Organic Species

The above  $\sigma$ - $\pi$ -picture calls for some clarifications concerning the general properties of  $\pi$ -systems and their relation to the Hückel rules. These are all connected to the quantum mechanical resonance energy (QMRE) which is designated by  $B$  in Figure 2.

**A. Quantum Mechanical Resonance Energies.** In the original literature<sup>27b</sup> we have used Kollmar's method<sup>60</sup> to calculate this quantity, at the SCF level. In the meantime, we have developed a VB program<sup>37</sup> to quantify  $B$  values.<sup>37a,42</sup> These values along with those reported by Goddard and collaborators<sup>41,61</sup> using GVB-related methods are summarized in Table II.

The SCF values are seen to be larger than the VB values (e.g., entries 4a vs 4) and some scaling down of the former values is required for making qualitative comparisons across the table. A few observations follow from these data. Firstly, all modes of delocalization possess significant QMRE, including the antiaromatic ones (entries 4, 5).

Another observation is related to the Hückel rules. These are reflected in the QMRE ( $B$ ) values of the "antiaromatic" squares and the "aromatic" hexagons. Thus, the "aromatic" species possess significantly larger QMRE values, even on a per electron basis. The model then contains and complements Hückel rules.

The most interesting observation in the table is the fact that the most distortive species possess the largest QMRE's. Thus for example, H<sub>3</sub> which is unstable possesses a resonance energy of 43 kcal/mol, while the stable Li<sub>3</sub> has a value of only 6 kcal/mol. Similarly, among the "aromatic" hexagons, H<sub>6</sub> which is highly unstable has the highest QMRE, and the fleeting N<sub>6</sub> species<sup>34</sup> has the second highest QMRE. *Large QMRE's seem to be then a mark of unstable species.*

**B. The Relationship between  $B$ ,  $\Delta E^{\pi}_{\text{dis}}$ , and  $\Delta E^{\sigma}_{\text{dis}}$ .** The above observations require some elaboration. Table III shows a few model  $\sigma$ - $\pi$ -systems with six and four  $\pi$ -electrons, respectively. The geometries of all the systems were optimized and constrained to be planar for the purpose of using them as models for planar  $\sigma$ - $\pi$ -systems with a chemical variable.<sup>36a</sup>

The first column shows the singlet-triplet  $\pi\pi^*$  transition energy of a model dimer. These values determine the variation of the energy gap according to eq 4. As predicted, the  $\pi$ -distortivity, measured by  $\Delta E^{\pi}_{\text{dis}}$ , increases with the size of  $\Delta E_{\text{ST}}$  in each of the two series in entries 1-4 and 5-8. As in Table II, here too

**TABLE III: Computed  $\Delta E_{\text{ST}}(\pi\pi^*)$ ,  $\Delta E_{\text{dis}}$ , and  $B$  (QMRE) Values (all in kcal/mol) for Some  $\sigma$ - $\pi$  Species<sup>a</sup>**

entry	species	$\Delta E_{\text{ST}}(\pi\pi^*)^b$	$\Delta E^{\pi}_{\text{dis}}$	$\Delta E^{\sigma}_{\text{dis}}$	$\Delta E^{\pi,\sigma}_{\text{dis}}$	$B$
1	N <sub>6</sub>	108	-13.7	13.7	0.4	103
2	C <sub>6</sub> H <sub>6</sub>	99	-9.1	16.3	7.2	85
3	P <sub>6</sub>	47 <sup>c</sup>	-2.8	3.8	1.0	44
4	Si <sub>6</sub> H <sub>6</sub>	42	-2.1	5.3	3.2	42
5	N <sub>4</sub>	108	-14.7	9.2	-5.5	45
6	C <sub>4</sub> H <sub>4</sub>	99	-11.0	7.6	-3.4	30
7	P <sub>4</sub>	47 <sup>c</sup>	-2.6	2.9	0.4	25
8	Si <sub>4</sub> H <sub>4</sub>	42	-2.1	2.7	0.6	18

<sup>a</sup>Data from ref 27b (entries 2, 6) and 36a (the rest). All the  $B$  data are 6-31G SCF values. All the  $\Delta E_{\text{dis}}$  values involve  $\pi$ -space CI.<sup>27b</sup>

<sup>b</sup>These are 3-21G values for model dimers (e.g., C<sub>2</sub>H<sub>4</sub>, N<sub>2</sub>H<sub>2</sub>, etc.).

<sup>c</sup>This value is calculated with a 3-21G\* basis.

the  $\Delta E^{\pi}_{\text{dis}}$  values for X<sub>6</sub> and X<sub>4</sub> are almost identical, for the same X (X = N, CH, P, SiH).

In turn,  $\Delta E^{\sigma}_{\text{dis}}$  values are all positive and oppose the distortive  $\pi$ -propensity. This  $\sigma$ -opposition is proportional to the number of  $\sigma$ -bonds and, in each series, also to the strength of the  $\sigma$ -bonds. Thus, for example, a combination of higher  $\pi$ -distortivity and lower  $\sigma$ -resistance causes N<sub>6</sub> to be an easily distortive species, in comparison with benzene.

An interesting consequence of the reduction of  $\Delta E_{\text{ST}}$  down a column of the Periodic Table is the distortive behavior of some "antiaromatic" squares (entries 5-8). Thus, as a result of the decrease of  $\Delta E^{\pi}_{\text{dis}}$ , the second-row squares P<sub>4</sub> and Si<sub>4</sub>H<sub>4</sub> do not have a tendency to distort to a rectangular structure. This reminds the behavior of the 4-electron/4-center isoelectronic family, where by moving from, e.g., H<sub>4</sub> to Li<sub>4</sub>, the square geometry becomes preferable over the rectangular.

Thus, once again the conclusion emerges that the geometry of a  $\sigma$ - $\pi$ -system should not be attached to its "aromaticity" or "antiaromaticity". In this respect, benzene is a *unique case* in Table III. Despite its high distortive  $\pi$ -propensity, benzene remains a delocalized uniform hexagon, owing to the  $\sigma$ -frame which exhibits the highest resistance to an asymmetric distortion. All the other analogues of benzene are almost indifferent to the distortion ( $\Delta E^{\pi,\sigma}_{\text{dis}} = 0.4$ -3.2 kcal/mol) and the second-row ones have stabler alternatives (e.g., hexasilaprismane).<sup>62</sup> These alternatives appear to be driven by the  $\sigma$ -frame's tendency to go out of planarity<sup>62b</sup> and by the general weakness of  $\pi$ -bonding in second-row elements.

The variation of the  $B$  values in Table III is in line with the trend in Table II. In each series in Table III (entries 1-4; 5-8) the  $\pi$ -component which is the most reluctant to be delocalized is the very one with the highest gain in delocalization energy. This trend is discussed above in light of the general model, namely that large  $G(\Delta E_{\text{ST}})$  generates *unstable species which possess large QMRE*.

It follows that in organic species the  $\pi$ -distortivity and the QMRE have to be treated as *two distinct molecular properties which must be probed by different sets of experiments*.

**C. Thermochemical Properties of C<sub>6</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>3</sub>, and C<sub>4</sub>H<sub>4</sub>. What Do They Represent?** It seems curious that distortive  $\pi$ -components should show signs of extra stability in some measurements. Thus, for example, if the  $\pi$ -component of allyl radical is a distortive transition state, how is it that allyl radical (or anion) exhibits a barrier to rotation? Or differently put, what property of allyl is being measured by the rotational barrier experiment?<sup>63</sup>

Owing to the bond length constraints of the  $\sigma$ -frame, allyl radical is *confined* to the avoided crossing region where the  $\pi$ -QMRE is significant. During the rotational process this  $\pi$ -interaction is lost and this accounts for the most part of the rotational

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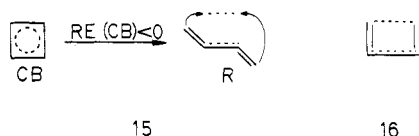


barrier. Thus, in accord with the classical view, the rotational barrier reflects the excess resonance stabilization of allyl relative to a  $\pi$ -localized situation. Viewed through the curve-crossing model, we can appreciate in addition that this is an approximate measurement of the delocalization energy of a *distortive but a confined  $\pi$ -transition state*.

In a similar manner, the positive empirical resonance energy (hereafter RE) of benzene "measures" its extra delocalization energy relative to a more localized reference structure ("cyclohexatriene").<sup>27b</sup> While we fully agree with the view, we simply clarify that the RE "experiment"<sup>57,60,64-66</sup> "measures" a QMRE-related property of a *distortive but a confined  $\pi$ -transition state*.

In contrast, the negative RE of cyclobutadiene means that this empirical estimate does not pick up the QMRE of  $C_4H_4$ .<sup>27b,41</sup> This result originates in the definition of the reference localized structure for  $C_4H_4$ .

In modern theories,<sup>57,60,64-66</sup> the reference is defined as a cyclic structure which possesses the same interbond  $\pi$ -conjugation as in open-chain polyenes. Since  $\pi$ -energies in polyenes are additive,<sup>65</sup> the reference molecule is taken to be simply butadiene tied unto itself, so as to afford one additional  $\pi$ -conjugative interaction and one additional  $\sigma$ -bond (see R in 15). A more representative localized reference, as in 16, should possess two localized  $\pi$ -bonds facing one another, which is the situation in cyclobutadiene. The commonly defined reference in 15, which lacks this feature, underestimates the  $\pi$ - $\pi$  repulsive interactions by at least 40 kcal/mol.<sup>27b</sup> This, in turn, is the cause of the negative RE (CB) value.<sup>57,60</sup> It follows that the RE "experiment" measures the repulsive  $\pi$ - $\pi$  interactions of cyclobutadiene but not its QMRE.



An example, which demonstrates how contradictory can the RE "experiment" be, was recently discussed in an *ab initio* study of [5]paracyclophane which has a boat-shaped benzene ring.<sup>67</sup> On the one hand, the computed RE of this molecule is negative, approximately -50 kcal/mol. On the other hand, the same ring shows, in other measurements and criteria, an "aromatic" behavior which indicates a highly delocalized species.

Clearly, as pointed out also by Schaefer et al.,<sup>67</sup> there are two different aspects here. The definition of a standard reference localized structure for the cyclophane reveals instabilities which are not related to delocalization. At the same time the confinement of the  $\pi$ -component of the cyclophane by its  $\sigma$ -frame imposes  $\pi$ -delocalization. Had it been possible to define a localized reference at the same boatlike geometry of the cyclophane, the resulting RE would have been positive and reflecting the QMRE.

Thus, while there cannot be any denying of the practical stability of benzene, it is still important to recognize the source of the stability. The essence is that all the reasonable localized reference structures, which may be *confined to a planar geometry by the  $\sigma$ -frame*, have less delocalization energy than benzene. At the same time, both *benzene and its reference localized structures possess distortive  $\pi$ -components* which prefer to segregate, to three isolated and very short  $\pi$ -bonds, but are confined "to stay" by the respective  $\sigma$ -frames.

Clearly, there is no contradiction between the distortivity ( $\Delta E^*_{dis}$ ) of  $\pi$ -components and their "measured" positive RE or rotational barrier. The two quantities refer to two distinct properties of the molecule. The RE or rotational barrier experiments use a localized reference to probe a property which is

related to the  $\pi$ -QMRE. This property is probed as global stabilization regardless of the instability of the delocalized  $\pi$ -components relative to a reference with short isolated suspended  $\pi$ -constituents.

All the organic chemical research which deals with "aromaticity" and related aspects probes QMRE-related properties of delocalized  $\pi$ -components. Indeed, much of the properties of benzene, including its regenerability<sup>2</sup> and tempered reactivity in chemical reactions, can be related to its large QMRE. This property is expressed only because of the confinement imposed by the  $\sigma$ -frame. On the other hand, experiments which probe the  $\pi$ -distortivity are rare. An exception that we are aware of is Berry's<sup>31e</sup> approach to deduce the  $\pi$ -distortive property of benzene from its  $B_{2u}$  vibrational frequency.

### Summary and Future Directions

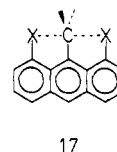
"To be or not to be" delocalized is a question even if large resonance energy is available to you. This summarizes the essence of the Feature Article. The curve-crossing model shows that the energy gap quantity,  $G$ , is the decisive factor in the above question.

The emerging trend is that atoms X which form strong bonds (large  $G$ ) generate *unstable* delocalized species, with highly *stretched* X...X bonds (on a percentage basis) and *large* QMRE's. On the other hand, atoms X which form very weak bonds (small  $G$ ) generate *stable* delocalized species, with only *marginally stretched* X...X bonds and *small* QMRE's. Thus, electronic delocalization is a driving force of chemical structure only for atoms which are weak binders.<sup>27</sup> The latter are typically metallic elements, though main elements in the lower part of the Periodic Table may also exhibit the same tendency.

Delocalized organic species, like allyl and benzene, fit into their isoelectronic families. Thus, the curve-crossing diagram rationalizes the tendencies of systems as different as  $H_n$ ,  $Li_n$ , or  $\pi$ -components into a uniform model. Since the  $\pi$ -bond is strong, the model indicates and computational tests affirm that the  $\pi$ -components are distortive transition states which are forced by the  $\sigma$ -frames to be delocalized. In accord with the above general observations, the distortive  $\pi$ -components also possess large QMRE,  $B$  in Figure 2. The Hückel  $4n/(4n+2)$  dichotomy is reflected in the corresponding  $B$  (QMRE) values but *not* in the  $\pi$ -distortivities. In accord, the connection between "aromaticity-antiaromaticity" and geometry is not meaningful in a broad sense.

The distortive  $\pi$ -propensity ( $\Delta E^*_{dis}$ ) and the QMRE ( $B$ ) are two distinct properties which require different experimental methodologies. Organic chemistry's research has focused on the QMRE property. In contrast, experiments which probe  $\Delta E^*_{dis}$  are rare.<sup>31e</sup> This is an area where physical chemistry's methodologies may become very useful.

While the idea of distortive  $\pi$ -transition states trapped by  $\sigma$ -cores may seem to some a theoretical curiosity, still the implications are practical. The seminal idea is to devise stiff cores which can trap transition-state analogues. In fact, J. C. Martin and collaborators have been doing just that for quite some time. Structure 17 is one example<sup>68</sup> where the rigid core of anthracene was employed to confine a 4-electron/3-center  $S_N2$  transition state. Further development of the seminal idea holds interesting prospects.<sup>69</sup>



17

Extension of the analogy of  $\pi$ -components to transition states indicates another future direction: the measurement of QMRE's for transition states of chemical reactions. Some progress in this

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direction has already been reported.<sup>70</sup> Accurate VB calculations of avoided crossing diagrams and QMRE's should be very useful to this end, and are currently in progress.

Finally, the model (Figure 2, eq 3) opens some new avenues to think about organic reagents. For example, why should radicals be "free"? Is it not possible to design organic radicals which will

cluster in analogy with, e.g.,  $\text{Li}_3$ ? Good prospects may lie beyond first-row elements. Other examples are the new "hyper-iodo" reagents,  $(\text{R}_f)_2\text{I}^-$  ( $\text{R}_f$  = fluoroalkyl),<sup>71</sup> which are simple analogues of  $\text{I}_3^-$ . Why not think then about other ways to stabilize suspended delocalized species relative to their normal-valent localized situations?

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## ARTICLES

### Conformations and Charge Distributions in 1,2-Dinitrosoethylene and Furoxan. 1. An ab Initio Molecular Orbital Study

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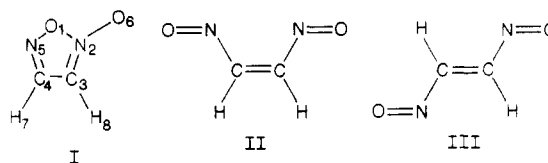
A computational analysis of the structures and electronic charge density distributions of the transoid *cis*- and *trans*-1,2-dinitrosoethylene has been carried out by means of an ab initio self-consistent-field molecular orbital method. Complete geometry optimization was carried out within the 4-31G and 4-31G\* basis sets, and the 6-31G\*\*//4-31G\* single-point calculations were carried out to improve energy calculations, charge distributions, and other properties. The calculations demonstrate that the electronic structures of both *cis*- and *trans*-1,2-dinitrosoethylene isomers are mainly determined by the cooperative enhanced charge withdrawal of the two nitroso groups. The overall result is a strengthening of the two C—N bonds and a weakening of the C=C bond (relative to nitrosoethylene). The 4-31G\* optimized geometry of furoxan has been found to compare quite well with available experimental data on related molecules. We observe that the furoxan extraannular oxygen induces a strong charge withdrawal effect and should be regarded as a very reactive site toward electrophiles.

#### Introduction

The interest in the chemistry of conjugated nitroso compounds has been renewed in recent years. Thus, Gilchrist<sup>1</sup> has reviewed the methods of generation and characteristic physical and chemical properties of the vinyl-nitroso compounds. Politzer et al.<sup>2</sup> have analyzed the effect of the nitroso and nitro groups upon aromatic reactive properties both with and without an additional  $\text{NH}_2$  substituent and upon the C=C bond.<sup>5</sup> They found that the nitroso group deactivates the aromatic ring toward nucleophilic attack, this being the overall result even in the presence of the resonance-donor  $\text{NH}_2$  substituent; however, it was found that the degree of deactivation was less than for the nitro group<sup>3,4</sup> and that the presence of the nitro group, in itself, strengthens the C=C bond; NO substitution, on the other hand, weakens it.<sup>5</sup>

Vinyl-dinitroso compounds have long ago been identified as transient species<sup>6,7</sup> in furoxan ring isomerizations. Recently, Willer and Moore<sup>8</sup> have suggested that ring isomerization in furoxano-[3,4-*b*]piperazines undergoes through a vinyl-dinitroso intermediate. Also, the synthetic interest in the nucleophilic opening of annelated furoxans to dinitroso products has been pointed out.<sup>9</sup>

This paper reports the results of a study using ab initio molecular orbital theory of 1,2-dinitrosoethylene and furoxan (I). Only the transoid structures of both the *cis* (II) and the *trans* (III) isomers of 1,2-dinitrosoethylene were found to be stable.



Of some relevance to the present study is the work of Bhujle et al.,<sup>10</sup> who determined by a CNDO calculation that the transoid structure of the nitrosoethylene is of slightly lower energy than the cisoid, and the work of Calleri et al.,<sup>11</sup> who carried out HF-SCF ab initio (IBMOL program) calculations using a minimal Gaussian basis set and CNDO/2 calculations for furoxan and several di-

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