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# Theoretical Study of the Aromatic Character of the Transition States of Allowed and Forbidden Cycloadditions

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**Abstract:** It is demonstrated that the resonance and delocalization energies defined in the theory of aromaticity can be computed using a VB Hamiltonian obtained from a CASSCF wave function. The resonance and delocalization energies of benzene and cyclobutadiene computed in this way are in good agreement with the accepted empirical estimates. An application of this procedure to the transition structure of the $[2\pi_s + 2\pi_s]$ ethylene dimerization (as a prototype of a forbidden cycloaddition) and to the transition structure for the $[2\pi_s + 4\pi_s]$ addition of ethylene and butadiene (as a prototype of an allowed cycloaddition) shows that the concepts of aromaticity and antiaromaticity can be used to rationalize the stability of transition states of pericyclic reactions. The delocalization energy, which accounts for the large stability of benzene, also rationalizes the low reaction barrier for the $[2\pi_s + 4\pi_s]$ transition structure as well as the instability of square cyclobutadiene and the large reaction barrier for the $[2\pi_s + 2\pi_s]$ transition structure. The magnitude of the delocalization energy itself has been rationalized in terms of exchange integrals $K_{ij}$ and the related exchange density matrix elements $P_{ij}$. The 1,2 interactions give broadly similar stabilizing contributions in four- and six-electron systems. The small delocalization energy in four-electron systems (square cyclobutadiene and the $[2\pi_s + 2\pi_s]$ transition structure) arises from the destabilizing effect of the 1,3 interactions. In contrast, the 1,4 interactions have a significant additional stabilizing effect on the delocalization energy of six-electron systems, benzene and the $[2\pi_s + 4\pi_s]$ transition structure (while the effect of the destabilizing 1,3 interactions is smaller for geometric reasons).

## 1. Introduction

The concepts of aromaticity and antiaromaticity are cornerstones of organic chemistry.[1] Recently there has been a renewed interest both in the definition of the basic concepts[2–4] and in the application of these concepts to the study of chemical problems.[5,6] Of particular interest is the work of Schleyer et al.[6] which has addressed the aromatic character of transition states in an indirect way by computing the corresponding magnetic properties. Schleyer et al.[6] have computed the magnetic susceptibility, which is a magnetic property uniquely associated with systems with cyclic delocalization of electrons, and have shown that the calculated magnetic susceptibilities for aromatic transition states occurring in Diels–Alder reactions agree well with the corresponding value in benzene.

The purpose of the present paper is to show that the delocalization energy of transition states can also be evaluated directly, in the framework of a valence bond (VB) scheme. The procedure adopted in this work involves the computation of the resonance and delocalization energies, using an ab-initio VB model derived from CASSCF computations in which[7] the CASSCF wave function is rigorously transformed to a VB space of all covalent VB determinants. These covalent VB structures contain charge transfer effects through the use of delocalized atomic orbitals.

In this paper, we focus our attention on two prototype forbidden and allowed pericyclic reactions: the dimerization of ethylene and the cycloaddition of butadiene and ethylene. To rationalize the fact that the forbidden reaction has a much higher activation barrier than the allowed reaction, it has been suggested that the transition state of a forbidden reaction such as ethylene + ethylene has an antiaromatic character similar to that of square cyclobutadiene,[8] while the transition state of an allowed cycloaddition reaction, such as ethylene + butadiene,

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(1) For general reviews on this subject, see: (a) Streitwieser, A., Jr. *Molecular Orbital Theory for Organic Chemists*; Wiley: New York, 1961. (b) Badgor, G. M. *Aromatic Character and Aromaticity*; Cambridge University Press: London, 1969. (c) March, J. *Advanced Organic Chemistry*, 3rd ed.; Wiley: New York, 1985; Chapter 2. (d) Wheland, G. W. *Resonance in Organic Chemistry*; Wiley: New York, 1955. (e) Kolb, D. *J. Chem. Educ.* **1979**, *56*, 334. (f) Streitwieser, A., Jr.; Heathcock, C. H. *Introduction to Organic Chemistry*, 3rd ed.; Macmillan: New York, 1985; Chapters 20 and 21. (g) Garrat, J. P. *Aromaticity*; Wiley: New York, 1986. (h) Minkin, V. I.; Glukhovtsev, M. N.; Simkin, B. Y. *Aromaticity and Anti-Aromaticity*; Wiley: New York, 1994.

(2) (a) Shaik, S. S.; Hiberty, P. C.; Ohanessian, G.; Lefour, J. M. *J. Phys. Chem.* **1988**, *92*, 5086. (b) Shaik, S. S.; Hiberty, P. C.; Lefour, J. M.; Ohanessian, G. *J. Am. Chem. Soc.* **1987**, *109*, 363. (c) Shaik, S. S.; Hiberty, P. C.; Ohanessian, G.; Lefour, J. M. *Nouv. J. Chim.* **1985**, *9*, 385. (d) Hiberty, P. C.; Shaik, S. S.; Lefour, J. M.; Ohanessian, G. *J. Org. Chem.* **1985**, *50*, 4657. (e) Shaik, S. S.; Hiberty, P. C. *J. Am. Chem. Soc.* **1985**, *107*, 3089.

(3) Jug, K.; Koster, A. M. *J. Am. Chem. Soc.* **1990**, *112*, 6772.

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

(5) (a) Sini, G.; Shaik, S. S.; Lefour, J. M.; Ohanessian, G.; Hiberty, P. C. *J. Phys. Chem.* **1989**, *93*, 5661. (b) Sini, G.; Shaik, S. S.; Hiberty, P. C. *J. Chem. Soc., Perkin Trans. 2* **1992**, 1019. (c) Ioffe, A.; Shaik, S. S. *J. Chem. Soc.. Perkin Trans. 2* **1992**, 2101.

(6) (a) Chandrasekhar, J.; Jemmis, E. D.; Schleyer, P. v. R. *Tetrahedron Lett.* **1979**, 3700. (b) McEwen, A. B.; Schleyer, P. v. R. *J. Org. Chem.* **1986**, *51*, 4357. (c) Bremer, M.; Schleyer, P. v. R.; Scholz, K.; Kausch, M.; Schnidler, M. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 761. (d) Jiao, H.; Schleyer, P. v. R. *Angew. Chem.. Int. Ed. Engl.* **1993**, *32*, 1763. (e) Jiao, H.; Schleyer, P. v. R. *J. Chem. Soc., Perkin Trans. 2* **1994**, 407. (f) Jiao, H.; Schleyer, P. v. R. *J. Chem. Soc.. Faraday Trans.* **1994**, *90*, 1559. (g) Jiao, H.; Schleyer, P. v. R. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1761.

(7) Bernardi, F.; Olivucci, M.; Mc Douall, J. J. W.; Robb, M. A. *J. Chem. Phys.* **1988**, *89*, 6365.

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has an aromatic character similar to that of benzene.[9] However, this idea has never been tested in a quantitative manner via ab-initio computations using optimized geometries. In this paper, we report the computation of the delocalization energy for the forbidden ethylene + ethylene and allowed ethylene + butadiene supra−supra transition states (denoted as $[2\pi_s + 2\pi_s]$ and $[2\pi_s + 4\pi_s]$, respectively). As a reference point, the energy cycles for the resonance energy of cyclobutadiene and benzene have also been computed.

## 2. Theoretical Model

The central practical difficulty in the computation of the resonance and delocalization energies arises from the fact that the precise definition of these quantities is intimately connected with the VB method, yet the VB method is seldom used in routine modern electronic structure computations. Further, geometry optimizations within the VB method are never performed.

Recently we have developed methods to circumvent these problems, by showing that it is possible to transform a CASSCF wave function to VB space[7,10] without loss of accuracy. In this scheme, the VB space consists of all the neutral valence (i.e., covalent) VB structures and the transformation is performed using an effective Hamiltonian.[7] Geometry and wave function optimization is carried out in a routine CASSCF computation. The VB wave function, obtained for each structure by transformation, is used to decompose the energy into the quantities needed to discuss the concepts of aromaticity (for a discussion of the use of effective Hamiltonians for this type of problem, see ref 11).

The matrix elements of the effective VB Hamiltonian, $(H_{\text{eff}})_{\text{KL}}$, where K and L denote the VB structures, can be written in terms of the parameters that are familiar from the Heitler−London (HL) treatment of $H_2$:

$$(H_{\text{eff}})_{\text{KK}} = Q + \sum_{ij} X_{ij}^{\text{KK}} K_{ij} \tag{1a}$$

$$(H_{\text{eff}})_{\text{KL}} = \sum_{ij} Y_{ij}^{\text{KL}} K_{ij} \tag{1b}$$

Here $Q$ is the Coulomb energy and the $K_{ij}$ are exchange integrals. The quantities $X_{ij}^{\text{KK}}$ and $Y_{ij}^{\text{KL}}$ are symbolic matrix elements that depend upon the details of the spin coupling, whose definitions are given in ref 12. The parameters $K_{ij}$ are assumed to have the form:

$$K_{ij} = [ij|ij] + 2s_{ij}\langle i|h|j\rangle \tag{2}$$

where the $[ij|ij]$ are the usual two-electron exchange repulsion integrals, the $\langle i|h|j\rangle$ are the kinetic plus nuclear attraction integrals, and the $s_{ij}$ are the overlap integrals. The $k_{ij}$ integrals are consistent with using a distorted nonorthogonal atomic orbital (AO) basis and therefore depend mainly upon the AO overlap $s_{ij}$.

The quantity $Q$ contains the effect of the repulsion of the closed-shell inactive orbitals and the nuclear repulsions, as well as the small effects arising from the singly occupied valence orbitals themselves. In an organic system, $Q$ mainly reflects the energy effects associated with deformations and steric repulsions in the skeleton which are not directly associated with the bond-breaking and bond-forming processes. The total energy of the system, which is obtained by diagonalization of this Hamiltonian in the space of any desired set of VB spin couplings, is

$$E = Q + \sum_{ij} P_{ij} K_{ij} \tag{3a}$$

where $P_{ij}$ denotes the exchange density matrix elements defined as

$$P_{ij} = \sum_{\text{KL}} C_{\text{K}} Y_{ij}^{\text{KL}} C_{\text{L}} \tag{3b}$$

where the $C_{\text{K}}$ are coefficients of VB structure K in the eigenvectors of $(H_{\text{eff}})_{\text{KL}}$. These density matrix elements have a simple physical interpretation which is related to the spin coupling between electrons in orbitals $i$ and $j$. As it is well known,[13] the $P_{ij}$ for a simple singlet VB spin pairing is just $+1$ for pairs that are spin coupled, $-\frac{1}{2}$ for uncoupled pairs, and $-1$ for triplet (parallel) spins. Thus the $P_{ij}$ indicates where bonding (positive $P_{ij}$) and antibonding (negative $P_{ij}$) interactions are located in a specific electronic state. This type of analysis has the advantage that it is independent of the basis of configurations used. Further, the trace of the exchange density matrix is related to the total spin by

$$S(S+1) = -\left(\frac{N(N-4)}{4}\right) + \sum_{ij} P_{ij} \tag{4}$$

where $S$ is the spin and $N$ is the number of active electrons.

We now define the various quantities that we will use for our discussion of aromaticity. The energy, $E(Q,K,P)$, of the molecular system is a function of $Q$, the $K_{ij}$, and the $P_{ij}$ computed at a given geometry. We shall define a reference geometry and use $Q_0,K_0$ to denote the Coulomb and exchange parameters computed at this reference geometry. In addition, we will use a reference spin coupling (e.g., the Kekulé spin coupling in benzene) and we use $P^{\text{R}}$ to represent the corresponding fixed (i.e., geometry independent) reference exchange density.

The energy cycle that can be used to describe the change in spin coupling and geometry from a suitable reference is shown in Scheme 1. In the vertical direction the variable is the spin coupling ($P^{\text{R}} \rightarrow P$). The energy relative to any reference spin pairing is a delocalization energy. At the optimum geometry the delocalization energy D−B is defined as

$$E_{\text{del}} = E(Q,K,P) - E(Q,K,P^{\text{R}}) \tag{5}$$

while at the reference geometry we have $E_{\text{del}}^{0}$ C−A defined as

$$E_{\text{del}}^{0} = E(Q_0,K_0,P) - E(Q_0,K_0,P^{\text{R}}) \tag{6}$$

In the horizontal direction in Scheme 1, the variable is the geometry change ($Q$ and the $K_{ij}$ change as the geometry of the

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[8] (a) Zimmerman, H. E. *J. Am. Chem. Soc.* **1966**, *88*, 1564. (b) Zimmerman, H. E. *Tetrahedron* **1982**, *38*, 753.

[9] (a) Dewar, M. J. S. *Orbital Symmetry Papers*; American Chemical Society: Washington, DC, 1974. (b) Evans, M. G.; Warhurst, E. *Trans. Faraday Soc.* **1938**, *34*, 614.

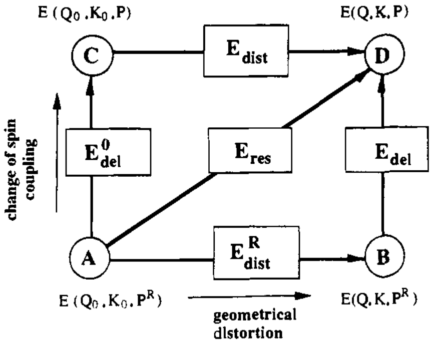
[10] (a) Robb, M. A.; Bernardi, F. *New Theoretical Concepts for Understanding Organic Reactions*; Bertran, J., Czismadia, I. G., Eds.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1989; p 101. (b) Bernardi, F.; Olivucci, M.; Robb, M. A. *Res. Chem. Intermed.* **1989**, 217. (c) Bernardi, F.; Olivucci, M.; Robb, M. A. *Acc. Chem. Res.* **1990**, *23*, 405.

[11] (a) Kabbaj, O. K.; Volatron, F.; Malrieu, J. P. *Chem. Phys. Lett.* **1988**, *147*, 353. (b) Kabbaj, O. K.; Lepetit, M. B.; Malrieu, J. P.; Sini, G.; Hiberty, P. C. *J. Am. Chem. Soc.* **1991**, *113*, 5619.

[12] Bearpark, M. J.; Robb, M. A.; Bernardi, F.; Olivucci, M. *Chem. Phys. Lett.* **1994**, *217*, 513.

[13] Eyring, H.; Walter, J.; Kimball, G. *Quantum Chemistry*; Wiley: New York, 1944.

**Scheme 1**



system changes). The distortion energy $E_{\text{dist}}$ D−C is

$$E_{\text{dist}} = E(Q,K,P) - E(Q_0,K_0,P) \tag{7}$$

The distortion energy $E^{\text{R}}_{\text{dist}}$ B−A, if one keeps the reference spin coupling fixed and allows only the geometry to change, is

$$E^{\text{R}}_{\text{dist}} = E(Q,K,P^{\text{R}}) - E(Q_0,K_0,P^{\text{R}}) \tag{8}$$

The resonance energy D−A is now defined either as

$$E_{\text{res}} = E^{\text{R}}_{\text{dist}} + E_{\text{del}} \tag{9a}$$

or

$$E_{\text{res}} = E_{\text{dist}} + E^{0}_{\text{del}} \tag{9b}$$

Each of the energy components above can be decomposed into a contribution from $Q$ and $K$. Clearly, from Scheme 1, $E_{\text{dist}}$ and $E^{\text{R}}_{\text{dist}}$ will be a function of $Q$ and of the $K_{ij}$ while $E_{\text{del}}$ and $E^{0}_{\text{del}}$ depend only on the $P_{ij}$.

Our objective is to demonstrate, numerically, that one can apply the concepts of aromaticity, as they are traditionally used, to a model reactivity problem. We will proceed as follows. In section 3 we will describe the details about the computations carried out in this study. Then in section 4 we will present the different components of the energy cycles of benzene and cyclobutadiene extracted from CASSCF ab-initio results as well as the delocalization energies computed for the $[2\pi_s + 4\pi_s]$ and $[2\pi_s + 2\pi_s]$ transition states. In particular, we shall show that a forbidden transition structure is characterized by a small value of $E_{\text{del}}$ and an allowed transition structure by a larger one. To conclude we will give an analysis of the delocalization energy using the exchange integrals $K_{ij}$ and the exchange density matrix elements $P_{ij}$. Using this scheme we will demonstrate that the magnitude of $E_{\text{del}}$ is directly related to geometrical or spin-coupling factors of the system under investigation.

## 3. Computational Details

All calculations reported in this paper have been performed with the Gaussian 92 suite of programs[14] at the CASSCF/4-31G[15] level. The orbitals included in the active space correspond to the $\pi$-orbitals of the systems under investigation. Thus we have used a six-electron/six-orbital active space for benzene and for the $[2\pi_s + 4\pi_s]$ reaction and a four-orbital/four-electron active space for cyclobutadiene and for the $[2\pi_s + 2\pi_s]$ reaction.

The determination of the $K_{ij}$ in eq 1 requires some comment. The procedure has been described in detail in refs 7 and 10a, where the background to the method is also given. The CASSCF wave function can be rigorously transformed (using the techniques described in ref 7) to a VB space of all neutral (covalent) VB determinants that can be built from $n$ orbitals and $n$ electrons with a Hamiltonian of the form given in eq 1. This transformation is accomplished via this effective Hamiltonian whose eigenvalues reproduce the CASSCF eigenvalues *exactly*. One simply solves eq 1 for the $K_{ij}$ and $Q$ as unknowns, given the matrix elements of the effective Hamiltonian $(H_{\text{eff}})_{\text{KL}}$ which are obtained from the ab-initio CASSCF computation. The resulting $K_{ij}$ and $Q$ are assembled into an ab-initio VB Hamiltonian, the eigenvalues of which reproduce the CASSCF energies. For more than four orbitals and four electrons, the equation system 1 is overdetermined and a fitting procedure must be used. Thus diagonalization of the Hamiltonian of eq 1 with the $K_{ij}$ determined in this way will reproduce the eigenvalue spectrum in an averaged fashion. The raw energy values computed in this way, i.e. via eq 3, are listed in Table 1, together with the ab-initio CASSCF/4-31G energies. The error in the lowest eigenvalue in benzene is about 8 kcal mol$^{-1}$; however, this error is independent of geometry and thus does not affect the results to be discussed subsequently.

## 4. Results and Discussion

We begin with a discussion of the energy cycles[16] for benzene and cyclobutadiene. From Scheme 1 we need to define a reference geometry and a reference spin coupling ($P^{\text{R}}$). Benzene provides an example that illustrates the general approach. In a VB treatment, the electronic structure of benzene is described in terms of five linearly independent Rumer spin couplings, i.e. two Kekulé and three Dewar bond eigenfunctions.[13] The Kekulé structure provides a natural way to define and evaluate a reference structure and supplies the reference spin coupling (i.e., $P^{\text{R}}$). The reference energy (i.e., $E(Q_0,K_0,P^{\text{R}})$) and geometry corresponding to a distorted Kekulé benzene can be rigorously determined by finding the minimum of $E(Q,K,P^{\text{R}})$ with respect to geometry. This procedure was used numerically to optimize the two different C−C bond lengths in $D_{3h}$ Kekulé benzene. The same type of procedure can be applied to the location of a $D_{2h}$ reference structure of cyclobutadiene. However, in this case, the structure found actually coincides with the fully optimized structure of cyclobutadiene (a minimum on the adiabatic CASSCF potential energy surface). Thus, in the region of the $D_{2h}$ cyclobutadiene minimum, only one of the two possible Kekulé bond eigenfunctions makes a contribution. The resulting geometric parameters for the optimized $D_{3h}$ Kekulé benzene and $D_{2h}$ cyclobutadiene are given in Figure 1 together with the fully optimized $D_{6h}$ benzene which is a minimum and $D_{4h}$ cyclobutadiene structure which is a transition state.

The computed benzene and cyclobutadiene energy cycles, defined in Scheme 1, are shown in Figures 2 and 3. The partition of the distortion energies $E_{\text{dist}}$ and $E^{0}_{\text{dist}}$ into Coulomb and exchange contributions is shown as *[Q,K]*. At the bottom of Figure 2 the structure labeled $D_{3h}$ Kekulé Benzene corresponds to the optimized reference structure while the structure labeled $D_{6h}$ Kekulé Benzene has the geometry of $D_{6h}$ benzene but the bonds are not allowed to resonate. At the top of the figure, the structure labeled $D_{3h}$ Benzene has the same geometry as $D_{3h}$ Kekulé benzene but the bonds are allowed to resonate.

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[14] Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. *Gaussian 92*, Revision B; Gaussian, Inc.: Pittsburgh, PA, 1992.

[15] Ditchfield, R.; Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* **1971**, *54*, 724−728.

[16] As discussed in ref 1a (p 237), the vertical resonance or delocalization energy (which we define as $E_{\text{del}}$ in Scheme 1) of benzene should not be referred to a cyclohexatriene with alternating bond lengths. Rather, the reference point should be a geometry which is the same as benzene but with $\pi$-interactions only between alternating bonds. In order to relate this to the empirical resonance energy (which we define as $E_{\text{res}}$ in Scheme 1) derived from heats of hydrogenation of cyclohexatriene, one neeeds the energy ($E_{\text{dist}}$ in Scheme 1) required to deform cyclohexatriene to the benzene geometry (stretching the double bonds and compressing the single bonds).

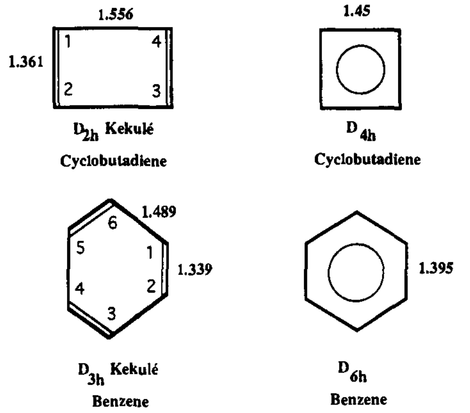


**Figure 1.** 4-31G-optimized geometrical parameters (Å) for the structures involved in the energy cycles for benzene and cyclobutadiene.

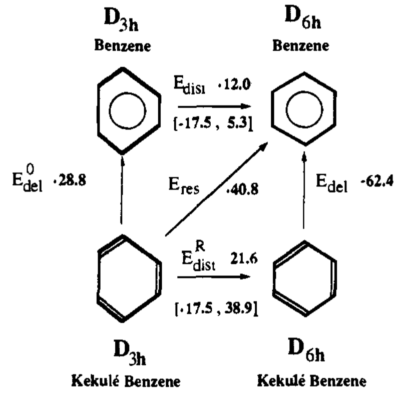


**Figure 2.** Energy cycle of benzene (kcal $mol^{-1}$). The partition of the distortion energies $E_{dist}$ and $E^0_{dist}$ into Coulomb and exchange contributions is shown as *[Q,K]*.

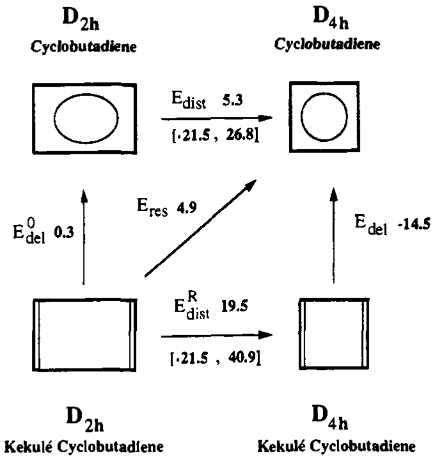
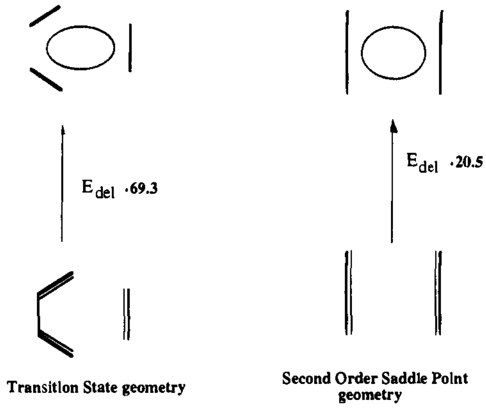


**Figure 3.** Energy cycle of cyclobutadiene (kcal $mol^{-1}$). The partition of the distortion energies $E_{dist}$ and $E^0_{dist}$ into Coulomb and exchange contributions is shown as *[Q,K]*.

Thus the left–right change in the figure corresponds to the change in geometry from $D_{3h}$ Kekulé benzene to $D_{6h}$ benzene and the bottom–top change corresponds to allowing for delocalization (i.e., $P^R \rightarrow P$). The results for cyclobutadiene are presented in an analogous fashion.

The computed values for the energy cycle of benzene are shown in Figure 2 and lie within the range of values estimated empirically.[1a,f] In particular, the distortion energy $E^R_{dist}$ is positive (i.e., destabilizing), while the delocalization energy $E_{del}$ and the resonance energy $E_{res}$ are negative (i.e., stabilizing). Obviously, the overall distortion energy $E_{dist}$ of $D_{6h}$ benzene relative to $D_{3h}$ benzene is also negative. It must be pointed out that the value of $E_{del}$ computed here is significantly larger than the values computed by Cooper et al. ranging between 21 and 25 kcal $mol^{-1}$ obtained using spin-coupled VB computations.[17]



(a) (b)

**Figure 4.** Delocalization energy for (a) the transition state for the [$2\pi_s + 4\pi_s$] cycloaddition (kcal $mol^{-1}$) and (b) the transition state (second-order saddle point[18]) for the [$2\pi_s + 2\pi_s$] cycloaddition (kcal $mol^{-1}$).

In Figure 3 it can be seen that, analogous to benzene, the distortion energy $E^R_{dist}$ of cyclobutadiene is positive and the delocalization energy $E_{del}$ is negative. However, while the distortion energy $E^R_{dist}$ remains of the same order of magnitude as in benzene, the delocalization energy $E_{del}$ of square-cyclobutadiene is much smaller with the result that the resonance energy $E_{res}$ becomes positive (i.e., destabilizing) in accord with its antiaromatic character. The $E_{del}$ value of cyclobutadiene agrees well with the value of 21–22 kcal $mol^{-1}$ computed by Voter and Goddard.[18] Note that for cyclobutadiene the overall distortion energy $E_{dist}$ of $D_{4h}$ cyclobutadiene relative to $D_{2h}$ cyclobutadiene is positive since $D_{4h}$ cyclobutadiene is a transition state. Finally, the partition of the distortion energies $E^R_{dist}$ and $E_{dist}$ in terms of the Coulomb and exchange contributions (given as *[Q,K]* in Figures 2 and 3) shows that the Coulomb term is negative and favors the symmetric structure while the exchange term is positive and favors the distorted reference structure. This result is in agreement with the results of $\sigma$–$\pi$ energy partition calculations published by Shaik, Hiberty, and co-workers[2] and Jug et al.,[3] since the Coulomb contribution can be taken to correspond to the $\sigma$ energy.

We now apply the same type of analysis to the supra–supra [$2\pi_s + 2\pi_s$] transition state for the dimerization of ethylene (which actually is a second-order saddle point[19] with two imaginary frequencies) and to the supra–supra [$2\pi_s + 4\pi_s$] transition state of the cycloaddition between ethylene and butadiene. Since the analysis for benzene and cyclobutadiene has shown that $E_{del}$ represents the critical quantity which determines the aromatic/antiaromatic character, for the case of the transition states, we have limited the computational study only to $E_{del}$. The values of $E_{del}$ for the [$4\pi_s + 2\pi_s$] butadiene and ethylene addition and for the [$2\pi_s + 2\pi_s$] ethylene dimerization are reported in Figure 4, while the values of the main geometrical parameters for the two transition states optimized at the CAS-SCF/4-31G level are reported in Figure 5 (the values for the supra–supra [$2\pi_s + 2\pi_s$] transition state are taken from ref 19). The combupted energy values for the transition structures are listed in Table 1.

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

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

(19) Bernardi, F.; Bottoni, A.; Robb, M. A.; Schlegel, H. B.; Tonachini, G. *J. Am. Chem. Soc.* **1985**, *107*, 2260–2264.

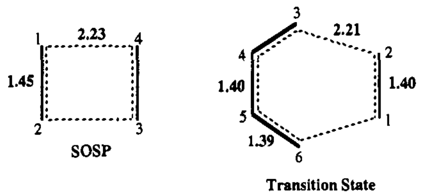


**Figure 5.** 4-31G-optimized geometrical parameters (in Å) for the transition structures of the $[2\pi_s + 2\pi_s]$ and $[2\pi_s + 4\pi_s]$ cycloadditions.

**Table 1.** Raw Energies Computed via Eq 3 of the Species Involved in the Energy Cycles A−D, Together with the Corresponding Coulomb $Q$ and Exchange $\Sigma_{ij}P_{ij}K_{ij}$ Contributions (All Values in au)

| | $E$ (eq 3) | $E$ (CASSCF) | Coulomb $Q$ | exchange $\sum_{ij}P_{ij}K_{ij}$ |
|---|---|---|---|---|
| | | Benzene | | |
| D | −230.468 83 | (−230.454 27) | −230.288 33 | −0.180 51 |
| C | −230.449 75 | (−230.438 36) | −230.260 67 | −0.189 08 |
| B | −230.369 39 | | −230.288 33 | −0.081 07 |
| A | −230.403 80 | | −230.260 67 | −0.143 14 |
| | | Cyclobutadiene | | |
| D | −153.476 17 | (−153.476 17) | −153.429 82 | −0.046 35 |
| C | −153.484 56 | (−153.484 56) | −153.395 54 | −0.089 02 |
| B | −153.453 02 | | −153.429 82 | −0.023 18 |
| A | −153.484 04 | | −153.395 54 | −0.088 42 |
| | | Butadiene + Ethylene $[4\pi_s + 2\pi_s]$ | | |
| D | −232.633 58 | (−232.643 61) | −232.493 18 | −0.140 40 |
| C | −232.710 12 | (−232.708 77) | −232.485 76 | −0.224 37 |
| B | −232.523 15 | | −232.493 18 | −0.029 97 |
| A | −232.705 04 | | −232.485 76 | −0.219 28 |
| | | Ethylene + Ethylene $[2\pi_s + 2\pi_s]$ | | |
| D | −155.782 99 | (−155.782 99) | −155.735 79 | −0.047 19 |
| C | −155.906 09 | (−155.906 09) | −155.730 56 | −0.175 53 |
| B | −155.750 37 | | −155.735 79 | −0.014 58 |
| A | −155.906 09 | | −155.730 56 | −0.175 53 |

Referring to Figure 4, we note that $E_{\mathrm{del}}$ is a negative quantity whose absolute magnitude is much larger in the $[2\pi_s + 4\pi_s]$ than in the $[2\pi_s + 2\pi_s]$ reaction. Thus it is the magnitude of the delocalization energy $E_{\mathrm{del}}$ that discriminates between the activation energies. We also note that the delocalization energy $E_{\mathrm{del}}$ for benzene and for the $[2\pi_s + 4\pi_s]$ reaction are almost identical. A similar comment applies to cyclobutadiene and the $[2\pi_s + 2\pi_s]$ reaction where the two delocalization energies are also similar. Thus, the larger stability of benzene relative to cyclobutadiene and the smaller activation energy of the $[2\pi_s + 4\pi_s]$ process relative to the $[2\pi_s + 2\pi_s]$ process correlate with the value of the delocalization energy $E_{\mathrm{del}}$.

To conclude, it remains to rationalize the various exchange contributions in terms of the $K_{ij}$ and $P_{ij}$ which are collected in Table 2. We have two objectives: (a) to explain the large positive contribution of the exchange to the distortion energy $E^{\mathrm{R}}_{\mathrm{dist}}$ in benzene and cyclobutadiene and (b) to give the origin of the large delocalization energies in benzene and in the $[2\pi_s + 4\pi_s]$ transition state and thus to rationalize the larger stability of benzene and the different barriers in the $[2\pi_s + 4\pi_s]$ and $[2\pi_s + 2\pi_s]$ reactions.

**Table 2.** Computed Values of $K_{ij}$ (au) and $P_{ij}$ (in parentheses)

Benzene CAS(6,6)/4-31G

| | $D_{6h}$ (aromatic benzene) | | $D_{3h}$(cyclohexatriene) | |
|---|---|---|---|---|
| $i,j$ | $K_{ij}$ | $P_{ij}$ | $K^0_{ij}$ | $P^{\mathrm{R}}_{ij}$ |
| 1,2 | −0.0726 | (0.432) | −0.0846 | (1.000) |
| 1,3 | −0.0015 | (−0.940) | −0.0018 | (0.500) |
| 1,4 | −0.0156 | (0.020) | −0.0126 | (0.500) |
| 2,3 | −0.0726 | (0.432) | −0.0576 | (0.500) |

Cyclobutadiene CAS(4,4)/4-31G

| | square | | rectangular | |
|---|---|---|---|---|
| $i,j$ | $K_{ij}$ | $P_{ij}$ | $K^0_{ij}$ | $P^{\mathrm{R}}_{ij}$ |
| 1,2 | −0.0486 | (0.500) | −0.0703 | (1.000) |
| 1,3 | −0.0254 | (−1.000) | −0.0231 | (−0.500) |
| 1,4 | −0.0486 | (0.500) | −0.0290 | (−0.500) |

$[4\pi_s + 2\pi_s]$ CAS(6,6)/4-31G Transition State

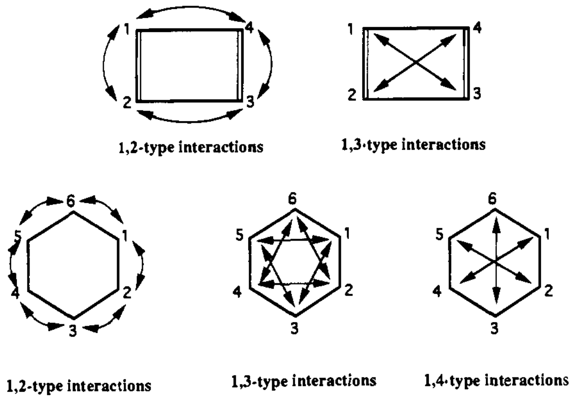
| $i,j$ | $K_{ij}$ | $P_{ij}$ | $i,j$ | $K_{ij}$ | $P_{ij}$ |
|---|---|---|---|---|---|
| 1,2 | −0.0507 | (0.402) | 3,4 | −0.0545 | (0.386) |
| 1,3 | −0.0004 | (−0.980) | 3,5 | −0.0018 | (−0.980) |
| 1,4 | −0.0306 | (0.136) | 3,6 | −0.0292 | (0.154) |
| 2,3 | −0.0516 | (0.420) | 4,5 | −0.0613 | (0.434) |
| 2,4 | −0.0002 | (−0.976) | | | |

$[2\pi_s + 2\pi_s]$ CAS(4,4)/4-31G SOSP[a]

| $i,j$ | $K_{ij}$ | $P_{ij}$ |
|---|---|---|
| 1,2 | −0.0416 | (0.308) |
| 1,3 | −0.0217 | (−0.978) |
| 1,4 | −0.0473 | (0.670) |

[a] Second-order saddle point. See ref 18.

**Scheme 2**



The $K_{ij}$ values are simply proportional to orbital overlap (and thus to the distance between the orbitals $i$ and $j$), while the $P_{ij}$ values provide information about the spin coupling that is independent of any particular choice of VB expansion. It is convenient to subdivide the $K_{ij}$ and the $P_{ij}$ into three groups (see Scheme 2): (a) 1,2 type interactions where the interacting centers are adjacent, (b) 1,3 type interactions where the interacting centers are separated by one bond, and (c) 1,4 type interactions where the interacting centers are separated by two bonds. In benzene, the $P_{12}$ type terms are positive, corresponding to singlet spin coupling, while the $P_{13}$ are negative and correspond to triplet spin coupling (i.e., nearly −1). In contrast, the $P_{14}$ are small and positive as a result of the small contribution of the Dewar VB structures. The fact that $K_{14}$ is non-zero in spite of the large 1−4 distance is due to charge transfer resulting from orbital delocalization. It is remarkable that the $P_{ij}$ for $D_{6h}$ benzene and for the $[2\pi_s + 4\pi_s]$ transition state are very similar. (Note that because of the reduction in symmetry there are more tabulated $P_{ij}$ for the $[2\pi_s + 4\pi_s]$ transition state.) Further, the $P_{13}$ type exchange density elements are always negative and thus destabilizing.

The behavior of the $K_{ij}$ and $P_{ij}$ provides a remarkably simple rationalization of the large positive contribution of the exchange to the distortion energy $E^{\mathrm{R}}_{\mathrm{dist}}$ and of the origin of the large delocalization energies in aromatic systems and allowed transition states. We begin with a discussion of the positive exchange contribution to the distortion energy $E^{\mathrm{R}}$ dist. For the geometric distortion A to B in Scheme 1, the $P_{ij}$ terms remain fixed (column 4 in Table 2) while the $K_{ij}$ terms change from $K_{ij}{}^0$ (column 3) to $K_{ij}$ (column 1). The large positive exchange contribution arises almost exclusively from the behavior of the 1,2 type interactions on distorting the geometry from A to B. This arises from the fact that on the passage from A to B the 1,2 type bond distances associated with spin-coupled pairs (i.e., positive $P_{ij}$) increase while those associated with uncoupled pairs (negative $P_{ij}$) decrease, causing a large positive contribution of the exchange to the distortion energy.

The differences in delocalization energies in aromatic/antiaromatic systems and in allowed/forbidden transition states are controlled by the balance between stabilizing (i.e., positive $P_{ij}$) 1,2 and 1,4 interactions and destabilizing (negative $P_{ij}$) 1,3 interactions. In $D_{6h}$ benzene and in the $[2\pi_s + 4\pi_s]$ transition state of the cycloaddition between ethylene and butadiene, the $K_{13}$ integrals are very small. However, in $D_{4h}$ cyclobutadiene and in the $[2\pi_s + 2\pi_s]$ transition state, the $K_{13}$ interactions are about 50% of the $K_{12}$ interactions so $E_{\text{del}}$ is much smaller. There is an additional effect that increases $E_{\text{del}}$ in $D_{6h}$ benzene and in the $[2\pi_s + 4\pi_s]$ transition state. While the 1,4 interactions are often assumed to be small, inspection of Table 2 shows that the $K_{14}$ interactions in the aromatic examples are quite large, due to charge transfer. $P_{14}$ is positive because of the interaction of the Dewar structures, and thus this term makes a stabilizing contribution to $E_{\text{del}}$.

Using the data in Table 2 and eq 5, one can partition the delocalization energy into the contributions from 1,2, 1,3, and 1,4 type interactions as shown below (kcal mol$^{-1}$)

$$E_{\text{del}}^{\text{benzene}} = (-49.7)_{12} + (2.5)_{13} + (-15.3)_{14}$$

$$E_{\text{del}}^{2\pi_s+4\pi_s} = (-34.5)_{12} + (1.4)_{13} + (-36.4)_{14}$$

$$E_{\text{del}}^{\text{cyclobutadiene}} = (-30.5)_{12} + (15.9)_{13}$$

$$E_{\text{del}}^{2\pi_s+2\pi_s} = (-33.3)_{12} + (13.0)_{13}$$

Notice that the 1,2 type contributions are broadly similar. This decomposition provides a strikingly simple rationalization of the reason why a $[2\pi_s + 2\pi_s]$ reaction barrier is larger than a $[2\pi_s + 4\pi_s]$ barrier. Our analysis shows (since the 1,2 contributions are broadly similar) that the difference in barriers is caused by two factors:

(i) A *geometric factor*, that originates from the destabilizing 1,3 interactions (i.e., $P_{ij}$ are negative), which favors the $[2\pi_s + 4\pi_s]$ cycloaddition because of the larger distance (and smaller overlap) between the interacting centers.

(ii) An *electronic factor*, that originates from the stabilizing 1,4 interactions arising from the following two effects: (a) the presence in the $[2\pi_s + 4\pi_s]$ reaction of three low-lying Dewar configurations which stabilize the $[2\pi_s + 4\pi_s]$ transition state (i.e., $P_{14}$ are positive) and (b) the effects of charge trnasfer which manifests itself in orbital delocalization and non-zero $K_{ij}$.

Our results show that the comparison between allowed and forbidden reactions is mainly controlled by the electronic factor. However, in the comparison between different types of $[2\pi_s + 4\pi_s]$ reactions (e.g., substituent effects), the geometric factor will play an important role.

Previous work[20] has suggested that electron transfer between the donor and the acceptor components of the $[2\pi_s + 4\pi_s]$ transition state has an important role to play. In our study, the charge transfer configurations are included in the covalent configurations through the use of "delocalized AO". Thus these effects are completely accounted for and manifest themselves in the "effective" exchange integrals $K_{ij}$.

## 5. Conclusions

In this paper, we have shown that the numerical computation of the energy cycles used in the theoretical definition of the resonance and delocalization energies can be performed using a VB Hamiltonian obtained from a CASSCF wave function. For the $[2\pi_s + 2\pi_s]$ ethylene dimerization (a prototype of a forbidden cycloaddition) and for the $[2\pi_s + 4\pi_s]$ addition of ethylene and butadiene (a prototype of an allowed cycloaddition), it is the magnitude of the delocalization energy that discriminates between the activation energies. Thus the delocalization energy, which accounts for the large stability of benzene, also rationalizes the low reaction barrier for the $[2\pi_s + 4\pi_s]$ transition structure as well as the instability of square cyclobutadiene and the large reaction barrier for the $[2\pi_s + 2\pi_s]$ transition structure.

The delocalization energy itself is easily rationalized in terms of exchange integrals $K_{ij}$ and related exchange density matrix elements $P_{ij}$. While the 1,2 interactions are broadly similar, the 1,3 interactions have been shown to have a significant destabilizing effect on the delocalization energy in four-electron systems (square cyclobutadiene and the $[2\pi_s + 2\pi_s]$ transition structure) while the 1,4 interactions have a stabilizing effect on the delocalization energy of six-electron systems (benzene and the $[2\pi_s + 4\pi_s]$ transition structure).

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[20] For a discussion, see: Pross, A. *Adv. Phys. Org. Chem.* **1985**, *15*, 197.