

Influence of σ and π Electrons on Aromaticity

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Abstract: A new σ - π separability criterion is used to divide the total energy of planar ring systems into two parts, a σ part and a π part. The behavior of these parts under distortions toward resonance structures is investigated. The calculations show that the σ energy tends toward bond equalization, whereas the π energy tends to bond localization. The total structure depends on the relative dominance of σ versus π electron trends. The properties of benzene referred to as aromaticity are due to a forced π -electron delocalization.

1. Introduction

Since the introduction of Hückel theory on the π -electron level, the delocalization of π electrons in benzene and more generally in $4n + 2$ π -electron systems became a common belief among chemists. This viewpoint has recently been challenged by Shaik, Hiberty, and collaborators¹ in a paper on the question as to whether delocalization is a driving force in chemistry. These authors suggested that π -electron delocalization is the byproduct of geometric constraint and occurs despite the opposite inherent tendency of the π electrons. In ab initio calculations with different basis sets on benzene and cyclobutadiene, distortion energies with respect to equilibrium energies for σ and π electrons were calculated under two requirements. First, the bond compressing of one set of bonds is accompanied by a bond stretching of the other set of bonds. Secondly, the nuclear repulsion energy is kept constant under these distortions. It was concluded from these calculations that the bond distortion energies are positive for σ electrons and negative for π electrons in benzene and butadiene. This means that π electrons prefer localization and σ electrons prefer bond equalization. This leads to higher symmetry and forced π -electron delocalization. From these results, the stabilization of benzene by π -electron delocalization appears as pure fiction. A few years earlier, Shaik and Bar² had already qualitatively discussed some aspects of the possible π -instability problem. In this context, an older paper by Longuet-Higgins and Salem³ with a model distortion of the π system was brought to new attention. At the same time, Epiotis⁴ had reached the same conclusion of π -electron destabilization in benzene by qualitative arguments involving heats of hydrogenation and by comparison with H_6 . In 1961, Berry⁵ concluded, from estimates of a low distortion energy and large classical zero-point amplitude of motion, that the π electrons might well have lower energy if the rings approach cyclohexatriene-like shapes. This would imply, in Berry's opinion, that the π electrons are largely responsible for the ease of distortion and the σ electrons determine the regular hexagon structure. In the present paper, we wish to contribute to the present discussion by semiempirical SINDO1 calculations on six-, five-, and four-membered rings. The method was extensively tested⁶ and found reliable for first-row elements. It is amply documented for the molecules treated in the present work. Geometries are usually calculated at the SCF level, but configuration interaction (CI) can also be included. In the next section we shall introduce a new σ - π separability method. In the applications we shall demonstrate that there is agreement with Shaik, Hiberty,

and collaborators' conclusions. We shall introduce a more general criterion for distortion and extend the application to systems with heteroatoms and to nonaromatic systems.

2. σ - π Separation of Energy

Shaik, Hiberty, and collaborators¹ introduced three different kinds of distortion energies: the σ -electron distortion energy, the π -electron distortion energy, and the total σ - π distortion energy which are related by

$$E_{\text{dis}}^{\sigma-\pi} = E_{\text{dis}}^{\sigma} + E_{\text{dis}}^{\pi} \quad (2.1)$$

They used three different methods to calculate these quantities. One involves fictitious high-spin states, another one highly charged cations which are generated by the removal of π electrons. Both methods allow the calculation of E_{dis}^{σ} . The first can also be used for the calculation of $E_{\text{dis}}^{\sigma-\pi}$, which eventually allows the indirect calculation of E_{dis}^{π} . The most reliable one is a method which starts from the true ground-state energy expression.

$$E_{\text{total}}^{\sigma-\pi} = E_{\sigma}^{\text{core}} + E_{\sigma\sigma} + E_{\text{NN}} + E_{\pi}^{\text{core}} + E_{\pi\pi} + E_{\sigma\pi} \quad (2.2)$$

The first three terms are considered as E^{σ} and the last three terms as E^{π} . In all cases the nuclear repulsion E_{NN} is kept constant for distortions. This allows a physical explanation for their partitioning.⁷ Our approach is somewhat different. We define

$$\begin{aligned} E^{\sigma} &= E_{\sigma}^{\text{core}} + E_{\sigma\sigma} + \frac{1}{2}E_{\sigma\pi} + E_{\text{NN}}^{\sigma} \\ E^{\pi} &= E_{\pi}^{\text{core}} + E_{\pi\pi} + \frac{1}{2}E_{\sigma\pi} + E_{\text{NN}}^{\pi} \end{aligned} \quad (2.3)$$

with $E_{\text{NN}} = E_{\text{NN}}^{\sigma} + E_{\text{NN}}^{\pi}$

To understand the separation for nuclear repulsion energy, we go by the following steps. The nuclear repulsion energy can be written explicitly as

$$E_{\text{NN}} = \sum_A \sum_{B>A} \frac{Z_A Z_B}{R_{AB}} \quad (2.4)$$

In neutral molecules the number n^{σ} of σ electrons plus the number n^{π} of π electrons equals the nuclear charge Z .

$$Z_A = n_A^{\sigma} + n_A^{\pi} \quad (2.5)$$

Insertion of (2.5) into (2.4) results in

$$\begin{aligned} E_{\text{NN}} &= \sum_A \sum_{B>A} \frac{(n_A^{\sigma} + n_A^{\pi})(n_B^{\sigma} + n_B^{\pi})}{R_{AB}} \\ &= \sum_A \sum_{B>A} \left(\frac{n_A^{\sigma} n_B^{\sigma}}{R_{AB}} + \frac{n_A^{\sigma} n_B^{\pi} + n_B^{\sigma} n_A^{\pi}}{R_{AB}} + \frac{n_A^{\pi} n_B^{\pi}}{R_{AB}} \right) \end{aligned} \quad (2.6)$$

Analogous to the separation of the electronic repulsion energy $E_{\sigma\pi}$ in two equal parts for σ and π electrons, we partition the second

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term of the nuclear repulsion energy equally among the σ and π part. So we define

$$E_{\text{NN}}^{\sigma} = \sum_A \sum_{B>A} \left(\frac{n_A^{\sigma} n_B^{\sigma}}{R_{AB}} + \frac{1}{2} \frac{n_A^{\sigma} n_B^{\pi} + n_B^{\sigma} n_A^{\pi}}{R_{AB}} \right) \quad (2.7)$$

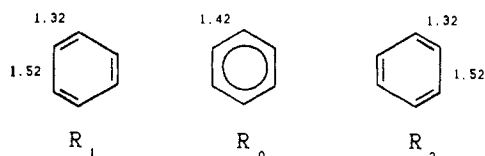
$$E_{\text{NN}}^{\pi} = \sum_A \sum_{B>A} \left(\frac{n_A^{\pi} n_B^{\pi}}{R_{AB}} + \frac{1}{2} \frac{n_A^{\sigma} n_B^{\pi} + n_B^{\sigma} n_A^{\pi}}{R_{AB}} \right)$$

A physical interpretation for this partitioning is given by the fact that the removal of an electron, classified as σ or π , generates a corresponding single nuclear charge. The classical interaction of this nuclear charge parallels the quantum mechanical interaction of the electron. In consequence we use the same partitioning scheme for electrons and nuclei. The procedure allows us to deviate from distortions which keep the nuclear repulsion constant. Beyond this procedure, the calculation of E^{σ} and E^{π} of (2.3) involves then only the separation of the total density matrix $P_{\mu\nu}$ in σ and π parts for the electrons.

$$P_{\mu\nu} = P_{\mu\nu}^{\sigma} + P_{\mu\nu}^{\pi} \quad (2.8)$$

3. Six-Membered Rings

In order to demonstrate the effect of distortion in an illustrative way, we have constructed correlation diagrams. For this purpose we take the equilibrium structure as the reference and define resonance structures for distortion from equilibrium in the following way. We use Kekulé structures with formally localized double and single bond lengths. In practice, the equilibrium structures were fully optimized with the SINDO1 method.⁴ For the resonance structures single and double bond lengths were taken from optimized reference structures. For CC bonds, we take the single bond length of ethane and the double bond length of ethylene. The other angular coordinates of the reference structures were optimized with SINDO1. The bond lengths involving hydrogen were kept constant. Since the effects we investigate are of basic nature, we expect no qualitative differences compared to ab initio calculations. For benzene the following structures are taken.



These geometries are taken as starting point for linear interpolation. The center of mass is kept fixed for all distortions from equilibrium. The distortions consist of bond stretching and contraction, but no rotations. A resonance coordinate is defined which measures the amount of distortion from equilibrium. It is zero for the equilibrium structure R_0 . The minimal resonance coordinate corresponds to R_1 , the maximal resonance coordinate to R_2 . The absolute magnitude is a measure for the geometry distortion compared with equilibrium geometry. It is calculated as the sum of deviations from equilibrium bond lengths for all ring bonds. The explicit definition of the resonance coordinate r is

$$r = \sum_i^{\text{atoms}} |\Delta \bar{r}_i| = \sum_i^{\text{atoms}} (\Delta x_i^2 + \Delta y_i^2 + \Delta z_i^2)^{1/2}$$

The results for benzene are shown in Figure 1. It shows the dependence of the σ and π parts of the total energy in dependence on the resonance coordinate. The total σ energy is on the left side; the total π energy is on the right side. The left end of the potential curves refers to R_1 , the right end to R_2 , and zero to the equilibrium structure R_0 . The π potential curve has a maximum and σ potential curve a minimum at the equilibrium structure. This means that the σ electrons prefer the highly symmetric D_{6h} structure with equal bond lengths, whereas the π electrons prefer a localized structure. This agrees fully with the conclusions reached by Shaik, Hiberty, and collaborators.¹ Also the numerical values of σ and π distortion energies in benzene are similar to these of Shaik,

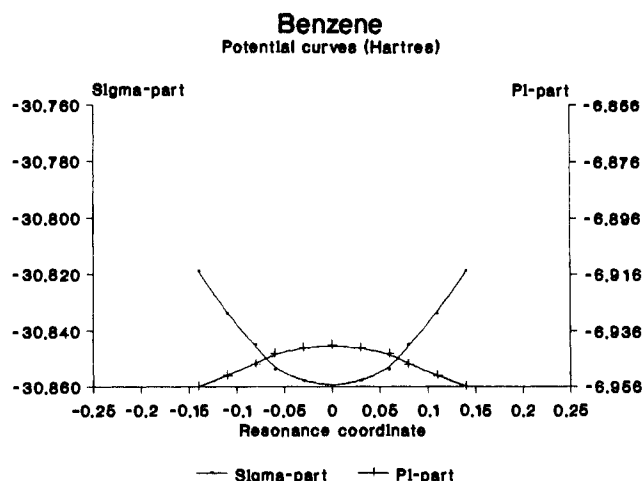
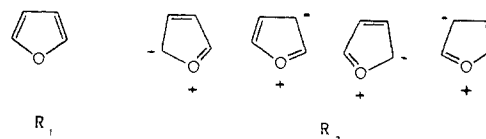


Figure 1. Dependence of σ and π parts of the total energy of benzene on the resonance coordinate.

Hiberty, and collaborators. Our results are at variance with conclusions reached by Baird⁸ that the chosen values for the reference single and double bond lengths influence the quality of the curvature of π -electron potential curves. We found that the negative curvature of the π curves is rather insensitive with respect to variations of the relative values of 1.32 and 1.52 Å. So the delocalization of π electrons and bond equalization is enforced by the σ electrons which dominate over the π electrons. In order to see the general impact of this conclusion more clearly, we have calculated the corresponding potential curves for the following sequence of nitrogen-containing ring compounds: pyridine, pyrimidine, 1,3,5-triazine, 1,2,3,5-tetraazine, pentaazine, and hexaazine. Here one to six nitrogen atoms are sequentially substituted in the benzene ring. The results are given in Figure 2. In all compounds the behavior of σ and π electrons is qualitatively the same as in benzene. In all cases the σ electrons dominate over the π electrons. There is an interesting observation if we compare the curves for benzene and hexaazine. The curves for the σ part are almost the same in both cases. However, the curvature of the π part of N_6 is much larger than for benzene. This means that the π electrons in N_6 have a much higher tendency to localize than the π electrons in benzene. In consequence, the total potential curve for N_6 is quite flat and little energy is needed to distort it. This agrees very well with the fact that N_6 is only metastable on the potential surface and will dissociate easily in $3N_2$ with a small barrier for the transition structure.

4. Five-Membered Rings

The treatment of five-membered rings is interesting because these systems are considered less aromatic than six-membered rings. In order to understand their behavior in more detail, we must subject them to the same treatment as the six-membered rings. The procedure is slightly more complicated because the definition of resonance structures is no longer so straightforward. We define them for furan as



The formally neutral localized structure R_1 is confronted with the average R_2 of four formally ionic structures. R_2 represents here a delocalized structure. The equilibrium structure R_0 is again between R_1 and R_2 . The behavior of potential curves of the σ part, π part, and total energy between R_1 and R_2 is depicted in Figure 3 for oxygen- and nitrogen-containing five-membered heterocycles. These curves look different from those for the

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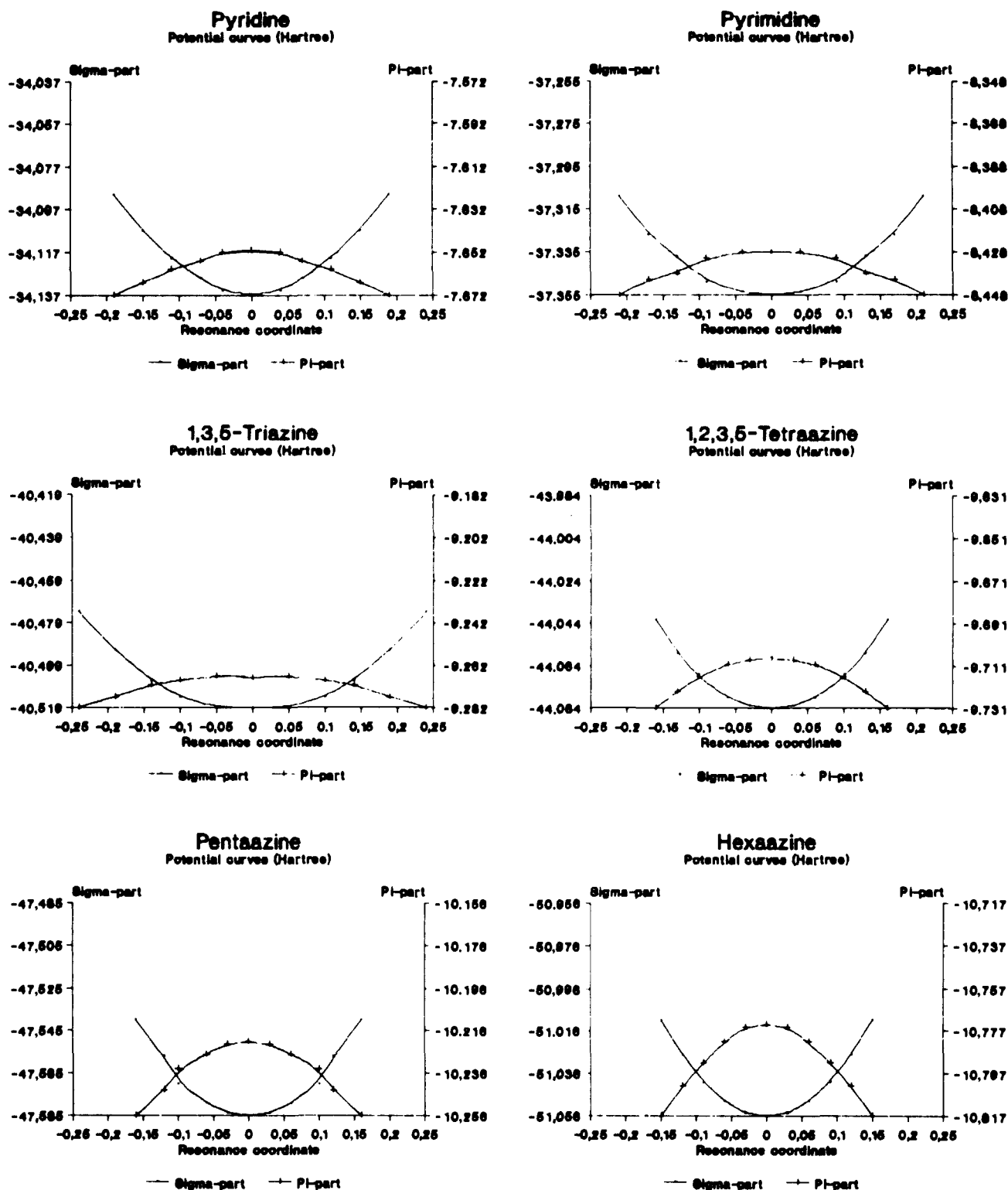


Figure 2. The same dependence as in Figure 1 for pyridine, pyrimidine, 1,3,5-triazine, 1,2,3,5-tetraazine, pentaazine, and hexaazine.

six-membered rings. However, a closer inspection reveals that σ electrons prefer the delocalized structure R_2 , whereas the π electrons prefer the localized structure R_1 . The equilibrium is determined by relative dominance of σ and π parts. From the six cases presented it appears that the equilibrium is closer to the localized structure R_1 . This means that the π electrons in the five-membered rings have a more important role in the structure determination than in the six-membered rings. The final structure is not given by the dominance of σ or π part, but rather is a compromise from the behavior of these two potential curves. The sudden curvature change at the equilibrium R_0 is due to the two linear interpolations between R_1 and R_0 which is different from the one between R_0 and R_2 .

5. Nonaromatic and Antiaromatic Rings

To complete this study we present also calculations on the representative nonaromatic compounds cyclopentadiene and fulvene together with butadiene. The distortions are analogous to those for the five-membered rings, where averages of ionic resonance structures are used. Delocalization of π electrons in cyclopentadiene and butadiene is possible only by inclusion of ionic structures. The results are given in Figure 4. There is a similarity in the curves for cyclopentadiene and butadiene. The lowest total energy is found in both cases close to the localized resonance structure R_1 on the left. The behavior described here seems to be typical for nonaromatic compounds. The σ potential generates a minimum for a partially delocalized structure, but in the total

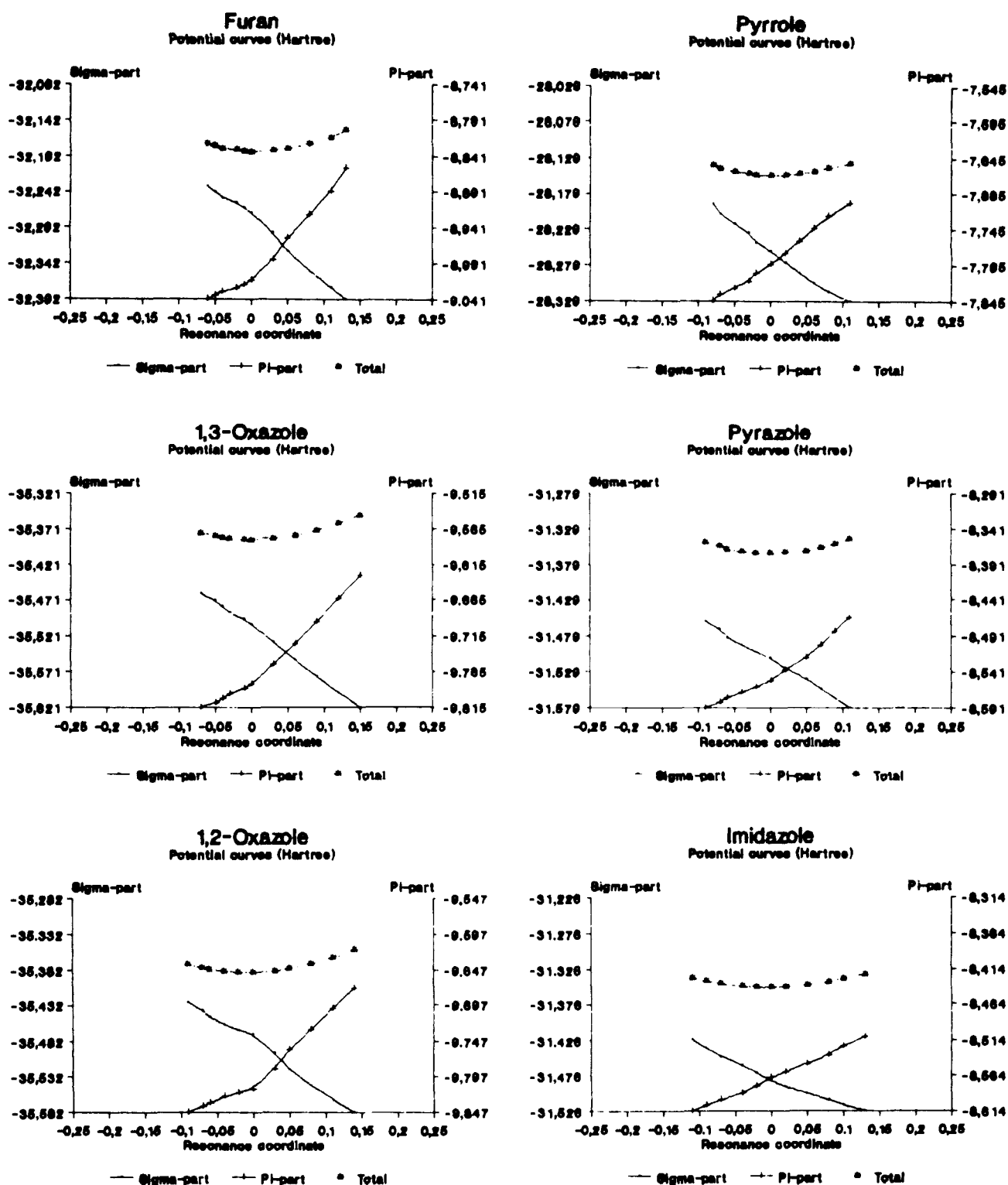


Figure 3. Dependence of σ part, π part, and total energy of furan, pyrrole, 1,3-oxazole, pyrazole, 1,2-oxazole, and imidazole on the resonance coordinate.

energy potential this minimum is shifted to the left owing to the dominating influence of the π electrons. Fulvene is a more complicated case. Different from other systems already discussed, the π curve has a minimum at the equilibrium structure R_0 and the σ curve has a maximum. But the energy differences are not very pronounced at the equilibrium; again σ electrons tend toward delocalized structures and π electrons toward localized structures. A similar behavior to that in fulvene is found in oxirene. Here the behavior of σ and π parts is more pronounced. There is one possible interpretation for the behavior of these curves, namely, that the resonance structure R_1 is more delocalized than the equilibrium structure R_0 . Such a conclusion was drawn already from the ring current criterion of aromaticity.⁹ Here it was found

that weakening of σ bonds compared to normal single bonds is the reason for antiaromaticity. This would also classify fulvene as antiaromatic. Because of the flat potential curves more sophisticated calculations are needed to describe fulvene properly. The behavior of cyclobutadiene is very illuminating for the behavior of antiaromatic compounds. For convenience we have modified the presentation of the potential curves. R_0 and R_0' are the two equivalent rectangular equilibrium structures. R_3 is the quadratic form. It is clear that the dominating influence of the π curve is responsible for the rectangular structure. The distortion from a quadratic form which is preferred by the σ electrons goes

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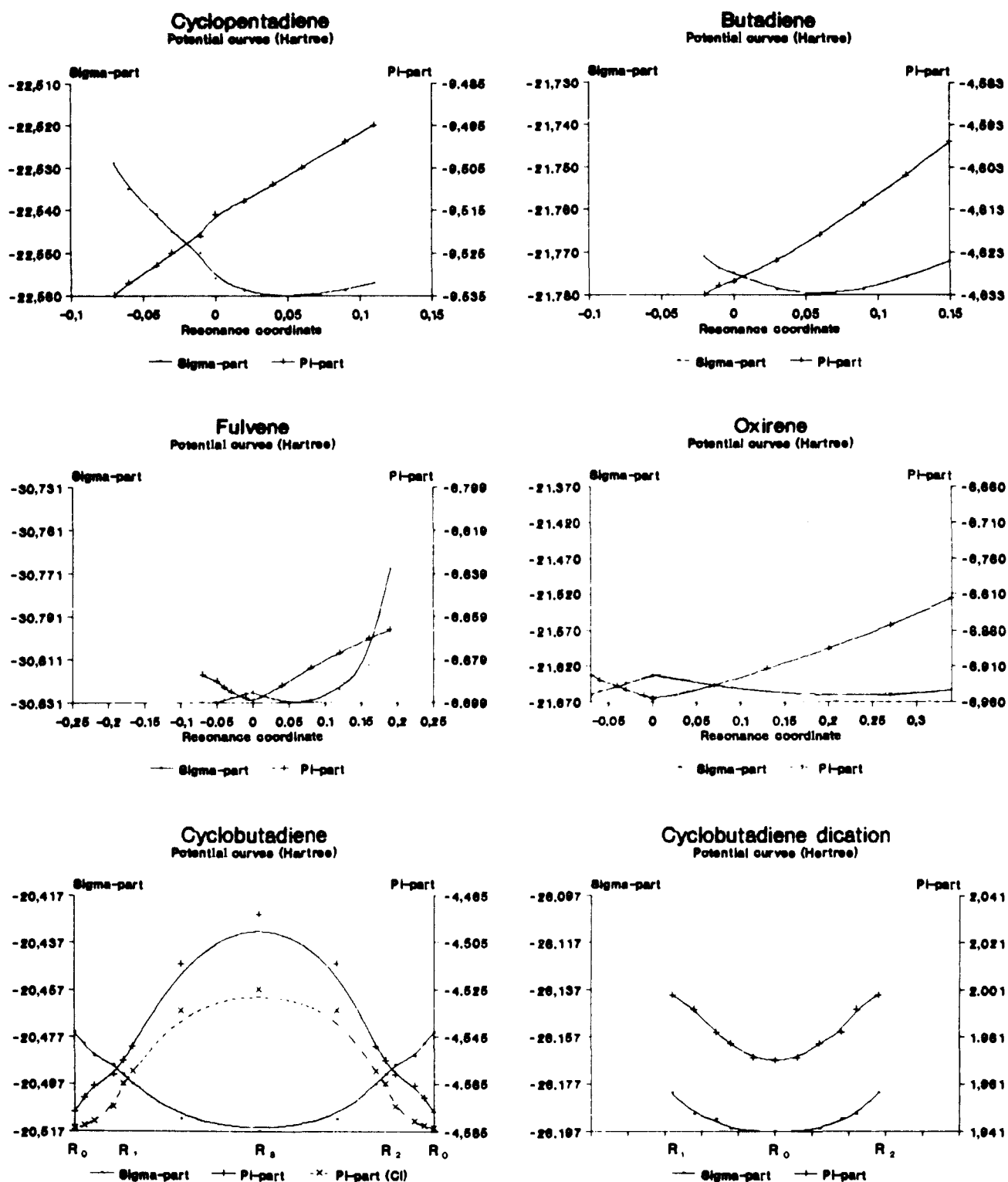


Figure 4. The same dependence as in Figure 1 for cyclopentadiene, butadiene, fulvene, oxirene, cyclobutadiene, and cyclobutadiene dication.

beyond resonance structure R_1 . The reason is again that the weakening of the σ bonds is more than compensated by the increased stabilization of localized π systems. Whereas small rest conjugation is present in nonaromatic systems, this is removed in cyclobutadiene. Because of the HOMO-LUMO degeneracy of the square structure in the ground state, the SCF curve for the π part is too high in the neighborhood of the square. In a 2×2 CI with HOMO-LUMO double excitation, the barrier is substantially reduced (Figure 4). A final consideration was now given to the removal of two electrons in cyclobutadiene. Cyclobutadiene dication was calculated with the same nuclear repulsion as cyclobutadiene to model the effect of the electron removal. The σ curve is quite similar to that of cyclobutadiene, but the π curve

now tends to stabilize the quadratic form also. This means that the aromatic behavior of pure hydrocarbons is determined mainly by the number of π electrons. This is the reason why the $4n + 2$ Hückel rule works. It should be emphasized here that the true SINDO1 structure of $C_4H_4^{2+}$ has a puckered form, in agreement with ab initio calculations.

6. Conclusion

We have investigated a large number of representative aromatic, nonaromatic, and antiaromatic monocyclic rings with respect to the behavior of σ and π electrons. In neutral systems the π electrons prefer localized structures, whereas the σ electrons prefer delocalized structures. In six-membered rings with six π electrons,

the σ electrons dominate and generate delocalized structures. The enforced delocalization of π electrons is the origin of the aromatic properties of such ring systems. In five-membered heterocycles with six π electrons, the general trends are similar, but no dominance of either σ or π part can be found. The equilibrium structure is a compromise between localized and delocalized structures, but some delocalization remains. The aromaticity is consequently less pronounced. Nonaromatic and antiaromatic rings prefer localized structures, where the antiaromatic compounds are more localized than the nonaromatic compounds. This

is expressed in a minimum of the π curve and a maximum of the σ curve at equilibrium. Finally, the removal of π electrons can cause the π curve to revert its trend from a preference for a localized to a preference for a delocalized structure. The properties attributed to aromaticity definitely depend on the π electrons and their delocalization, but the origin of delocalized structures in neutral ring compounds is due to the σ electrons.

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Projection Operator Hückel Method and Antiferromagnetism

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Abstract: We present a simple molecular orbital method by which the antiferromagnetism of KCuF_3 , La_2CuO_4 , and other one electron per atom or one hole per atom systems can be understood. The roles of alternancy and nonalternancy and of spatial distortions in producing the observed antiferromagnetic ordering are shown to be important. This simple molecular orbital method is also shown to be reliable in understanding the energetics of a model spin-Peierls system.

The extended Hückel (eH) method¹ has been shown to be successful in rationalizing many structural features found in solid-state chemistry. Questions of unusual coordination environments, metal-metal bonding, patterns of bond breaking or bond formation, and site preferences in materials that range from intermetallic alloys to halides have been studied by eH methods. There are several good review articles that summarize these results.²

In this paper we show that a technique which incorporates Hückel or eH calculations can be used in understanding strong antiferromagnetic spin-spin correlations. This approach is based on the work of many groups who have found a remarkable coincidence between molecular orbitals models and the spin Hamiltonians generally used in studies of ferromagnetic and antiferromagnetic systems.³ The methods that have been used vary from Lie group and quasi-spin approaches, Rumer diagram techniques,⁴ Pariser-Parr-Pople or Hubbard models and quantum Monte Carlo simulations,⁵ effective Heisenberg Hamiltonians,⁶ and the

Gutzwiller approximation.⁷ Although these models are technically involved, the results we will use in this work are quite simple. Indeed, one of the goals of this article is to recast the findings of these various workers in a form that can readily be used by chemists who are familiar with molecular orbital (MO) theory but who have never performed, for example, a quantum Monte Carlo simulation. We illustrate the utility of our technique by studying the antiferromagnetic (AF) ordering of KCuF_3 ⁸ and La_2CuO_4 ⁹ and the spin-Peierls distortion.¹⁰

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