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$\sigma-\pi$ ENERGY DIAGRAMS FOR SUBSTITUTED RINGS

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The recently developed $\sigma-\pi$ energy separation technique was applied to substituted monocyclic ring systems. Modified correlation diagrams are presented which allow the influence of the substituent on the σ and π energies to be assessed. The slopes of the σ and π electron energy curves can be used to classify aromatic, non-aromatic and anti-aromatic compounds. A two-dimensional resonance coordinate representation shows a clustering of compounds of the three classes in distinctly different regions of this plane.

INTRODUCTION

The concept of aromaticity has been both widespread and fruitful in organic chemistry.[1] Much time and effort have been spent on establishing similarities of organic compounds with benzene, the prototype of aromatic compounds. The properties of benzene are attributed to the delocalized π electron system. From the many properties which were considered in the past,[2] four major categories of aromaticity criteria have emerged: geometric, energetic, magnetic and reactive criteria. A discussion of aromaticity as a multidimensional phenomenon[3–5] and its consequences for the analysis of compounds has contributed to a clarification of this complex topic. In this paper we shall only be concerned with the aspects of energetic criteria. π electron theories such as the Hückel method dwelt on the assumption that the delocalization of the π electron system has a stabilizing effect on the structure and is the reason for the D_{6h} symmetry of benzene. There were several indications in the past that the assumption of a stabilization effect of π electron delocalization may not be reconcilable with observed facts. These included large systems,[6] infrared spectra[7] and heats of formation.[8] However, only recently was the idea of delocalization stabilization of π electrons seriously challenged by Shaik *et al.*[9] on the basis of model *ab initio* calculations for benzene. They showed that the driving force for the structure of benzene are the σ electrons and that the π electrons would prefer the localized bonding of the Kekulé structures. We could generalize the idea of driving forces by a different $\sigma-\pi$ electron energy separation technique.[10] This new definition of σ and π electron energy included a $\sigma-\pi$ separation of nuclear repulsion and in consequence allowed arbitrary distortions. It was applied to a variety of compounds including six-, five-, four- and three-membered rings and open-chain systems. Nitrogen and oxygen were included as heteroatoms in the ring. In this paper we present the results of outer substitution in such ring systems on the σ and π electron energy curves. This should give some evidence of the modification of the aromatic properties of these rings under substitution.

$\sigma-\pi$ ENERGY SEPARATION

We first determine how many σ and π electrons each atom contributes to the molecule. This can be done by an analysis of an SCF calculation for the ground state of the considered system. For a closed-shell system the, total wave function can be written as

$$\Psi_0 = \frac{1}{\sqrt{n!}} \mid \psi_1\bar{\psi}_1 \ldots \psi_n\bar{\psi}_n \mid \qquad (1)$$

The molecular orbital (MOs) ψ_i are usually approximated as a linear combination of atomic orbitals (LCAO). In the following we refer to an expansion in symmetrically orthogonalized atomic orbitals (OAOs) λ_μ:[11]

$$\psi_i = \sum_\mu c_{\mu i}\lambda_\mu \qquad (2)$$

The total electronic density matrix P is then defined as

$$P_{\mu\nu} = 2\sum_i^{\text{occ}} c^*_{\mu i}c_{\nu i} \qquad (3)$$

where the $\mathbf{c}_i$ are column vectors of the occupied molecular orbitals. In order to achieve a $\sigma-\pi$ separation of the total energy we must subdivide the total density matrix into σ and π parts:

$$P_{\mu\nu} = P^\sigma_{\mu\nu} + P^\pi_{\mu\nu} \qquad (4)$$

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$P^{\sigma}_{\mu\nu}$ and $P^{\pi}_{\mu\nu}$ are obtained as similar sums analogous to equation (3) over occupied σ and π MOs, respectively. The total energy of the system can then be formulated as

$$E_{\text{total}} = E_{\sigma}^{\text{core}} + E_{\pi}^{\text{core}} + E_{\sigma\sigma} + E_{\pi\pi} + E_{\sigma\pi} + E_{NN} \quad (5)$$

The first two terms are the core attraction energy and the next three terms the repulsion energy of the electrons. The last term contains the nuclear repulsion energy

$$E_{NN} = \sum_{A<B} \frac{Z_A Z_B}{R_{AB}} \quad (6)$$

The nuclear repulsion energy is now separated into a σ and a π part in the following way. In neutral molecules the number n^{σ} of σ electrons plus the number n^{π} of π electrons equals the nuclear charge Z:

$$\begin{aligned} E_{NN} &= \sum_{A<B} \frac{(n_A^{\sigma} + n_A^{\pi})(n_B^{\sigma} + n_B^{\pi})}{R_{AB}} \\ &= \sum_{A<B} \left(\frac{n_A^{\sigma} n_B^{\sigma}}{R_{AB}} + \frac{n_A^{\sigma} n_B^{\pi} + n_B^{\sigma} n_A^{\pi}}{R_{AB}} + \frac{n_A^{\pi} n_B^{\pi}}{R_{AB}} \right) \\ &= \sum_{A<B} \left(\frac{n_A^{\sigma} n_B^{\sigma}}{R_{AB}} + \frac{1}{2} \frac{n_A^{\sigma} n_B^{\pi} + n_B^{\sigma} n_A^{\pi}}{R_{AB}} + \frac{n_A^{\pi} n_B^{\pi}}{R_{AB}} \right. \\ &\quad \left. + \frac{1}{2} \frac{n_A^{\sigma} n_B^{\pi} + n_B^{\sigma} n_A^{\pi}}{R_{AB}} \right) \\ &= E_{NN}^{\sigma} + E_{NN}^{\pi} \end{aligned} \quad (7)$$

Here we have also used the fact that the effect of the σ electrons on the π electrons is the same as that of the π electrons on the σ electrons. In the same way, the fifth term on the right-hand side of equation (5) is partitioned into two equal parts for the σ and π electron energies. We finally obtain

$$E_{\text{total}} = E^{\sigma} + E^{\pi}$$

with

$$\begin{aligned} E^{\sigma} &= E_{\sigma}^{\text{core}} + E_{\sigma\sigma} + \tfrac{1}{2} E_{\sigma\pi} + E_{NN}^{\sigma} \\ E^{\pi} &= E_{\pi}^{\text{core}} + E_{\pi\pi} + \tfrac{1}{2} E_{\sigma\pi} + E_{NN}^{\pi} \end{aligned} \quad (8)$$

This procedure allows more general distortions of the structure than the energy separation by Shaik *et al.*[9] and can be used to generate σ and π electron potential curves. The merits of the new procedure are apparent from a comprehensive set of calculations already published.[10]

CORRELATION DIAGRAMS

In the following we present energy correlation diagrams between the fully optimized structure (M) and the so-called localized structure (L) or delocalized structure (D). The localized structure is obtained from the minimum structure by replacing the ring bond lengths by single and double bond lengths and by keeping the inner bond angles and the rest of the framework concerning hydrogens and substituents fixed. The delocalized structure is the average structure of several localized structures. In the case of benzene, M and D are the same. In cyclobutadiene, D is a square structure with averaged single and double lengths. A resonance coordinate is now defined as

$$\begin{aligned} r &= \sum_{i}^{\text{atoms}} |\mathbf{r}_i - \mathbf{r}_i(\text{M})| = \sum_{i}^{\text{atoms}} |\Delta \mathbf{r}_i| \\ &= \sum_{i}^{\text{atoms}} (\Delta x_i^2 + \Delta y_i^2 + \Delta z_i^2)^{1/2} \end{aligned} \quad (9)$$

where $\mathbf{r}_i$ is the position vector of atom i and the origin of the coordinate system is in the centre of mass; $r = r(\text{M})$ is zero for the minimum structure M, $r = r(\text{L})$ is larger than zero for the localized structure L and $r = r(\text{D})$ is larger or equal to zero for the delocalized structure D. The changes from M to L or D are expected to cause the least necessary motion. We use the resonance coordinate r_{L} for linear interpolation between M and L and r_{D} for linear interpolation between M and D. In a previous paper[10] we used positive and negative values for the resonance coordinate to indicate the two different directions of change in the benzene ring to the two Kekulé structures. In this paper we shall use only the positive resonance coordinates. This is half of the symmetric picture[10] and the least motion pathway in cases of asymmetry.

Substituted benzene

We first investigated monosubstituted benzenes by full structure optimization and subsequent distortion of a Kekulé resonance structure L along a resonance coordinate r_{L}. All calculations were performed with the SINDO1 method.[12] In Figure 1 the σ and π electron energies of benzene are plotted together with two representative substituted benzenes, nitrobenzene and phenol. The energy E^{σ}_{rel} is plotted relative to the minimum structure M and the energy E^{π}_{rel} relative to the localized structure L:

$$\begin{aligned} E^{\sigma}_{\text{rel}} &= E^{\sigma} - E^{\sigma}(\text{M}) \\ E^{\pi}_{\text{rel}} &= E^{\pi} - E^{\pi}(\text{L}) \end{aligned} \quad (10)$$

The minimum structure M coincides with the delocalized structure D in benzene and is very close to D in substituted benzene. Therefore, D is not considered in this case. We see that NO_2 substitution decreases and OH substitution increases the slope of the curves with respect to benzene. Several other substituted benzenes were tried and gave curvatures in between these two. The sequence of curvatures for E^{σ}_{rel} is $NO_2 < CN \approx BF_2 < NC < NH_2 \approx H < BH_2 \approx Li < OH$ and for E^{π}_{rel} it is $NO_2 < BF_2 < CN < H < NC < NH_2 < BH_2 < Li < OH$. The two important observations from these

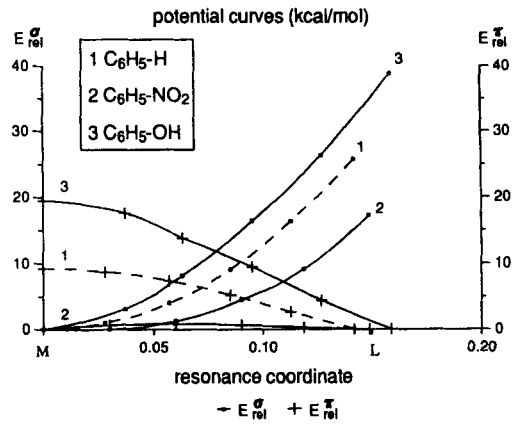

Figure 1. Dependence of σ and π parts of the total energy of benzene, nitrobenzene and phenol on the resonance coordinate r_L (Å) for the localized structure L

sequences are that π donors have on average larger curvatures than π acceptors and that an increase in the σ energy curvature is accompanied by an increase in the π energy curvature.

We then investigated polysubstituted benzenes, with fluorine as a representative substituent. The whole series of mono-, di-, tri-, tetra-, penta- and hexafluorobenzenes was fully optimized. Since fluorine is a π donor, all the curves are on the same side as phenol compared to benzene. No systematic trend from mono- to hexafluorobenzene was found in the σ and π electron energy curves. However, if the total energies are considered, the energy difference in kcal mol^{-1} between L and M increases systematically in the sequence H (16·3) < F (17·5) < 2 F (18·7) < 3 F (20·1) < 4 F (20·7) < 5 F (23·2) < 6 F (23·8) (1 kcal = 4·184 kJ). Here 1,4-difluorobenzene, 1,2,3-trifluorobenzene and 1,2,4,5-tetrafluorobenzene are included. It is also possible to consider distortions of 1,2-difluorobenzene or 1,2,3,4-tetrafluorobenzene, but the two Kekulé structures are no longer equivalent. In these cases distortion plots with positive and negative resonance coordinates must be included and the energy curves show minima for σ curves and maxima for π curves shifted from the $r = 0$ value to positive and negative r values, respectively.

Substituted cyclobutadiene

It is now interesting to see how substitution affects a typical antiaromatic system such as cyclobutadiene. Here we have to distinguish the minimum structure M from the localized structure L and the delocalized structure D:

$$E^{\sigma}_{rel} = E^{\sigma} - E^{\sigma}(M)$$
$$E^{\pi}_{rel} = E^{\pi} - E^{\pi}(M) \qquad (11)$$

We now compare the σ and π energy curves of cyclobutadiene with two typical substituted cyclobutadienes, cyclobutadienylborondifluoride and aminocyclobutadiene. The former has a π acceptor and the latter a π donor substituent. Organic chemists have used such properties to stabilize cyclobutadiene with sets of push–pull substituents. This stabilization is accompanied by an increased HOMO–LUMO distance in cyclobutadiene.[13]

The energy curves along the two resonance coordinates r_L and r_D are plotted in the same diagram. Starting from M in Figure 2, we see that the σ energy curves show a negative slope and the π energy curves a positive slope for cyclobutadiene. The BF_2-substituted molecule shows essentially the same behaviour for small changes in the resonance coordinate. For NH_2 substitution, the pathway along r_D to the delocalized structure is again similar to that in cyclobutadiene, but an inversion of slopes is observed along r_L. In addition to these two substituents, substitution by F, CHO and CFO was studied. The result is that the dominance of the π electron system is decreased with increasing positive or negative mesomeric effect[14] of the substituent. This means that the more pronounced the donor or acceptor quality of the π system of the substituent, the less antiaromatic is the substituted ring system. We find for the π electron system the sequence F < NH_2 for the positive mesomeric effect and CHO < CFO < BF_2 for the negative mesomeric effect along the resonance coordinate r_D. The first two are π donors and the other three are π acceptors.

Since the dominance of the π system is characteristic for the antiaromaticity of cyclobutadiene, consideration of the bond orders of the ring bonds of the differently substituted systems was suggested. Bond orders[15] for single and double bonds of the ring are listed in Table 1. The data show an increase in σ bonding and a decrease in localized π bonding in all substituted systems. The most pronounced effect is for NH_2.

Another criterion could be the energy difference between structures D and M. Here the sequence in kcal mol^{-1} is found to be NH_2 (19) < BF_2 (28) < F (29) < CFO ≈ CHO (32) < H (33).

Substituted trimethylencyclopropane

Trimethylencyclopropane, $C_3(CH_2)_3$, is a radialene of non-aromatic character. The derivative with fluorine substitution $C_3(CF_2)_3$ was considered for comparison. The relevant structures are shown in Figure 3. The σ and π potential curves are plotted in Figure 4. E^{σ}_{rel} and E^{π}_{rel} are defined as in equation (11). These non-aromatic compounds show characteristics of both aromatic and

anti-aromatic compounds. Distortions from M to L correspond to the curves of aromatic compounds, whereas distortions from M to D resemble the curves found for anti-aromatic compounds. Fluorine substitution of the radialene causes a decrease in the slope with the π electron system dominating. For the substituted system the delocalized structure is closer to the minimum structure than for the unsubstituted structure.

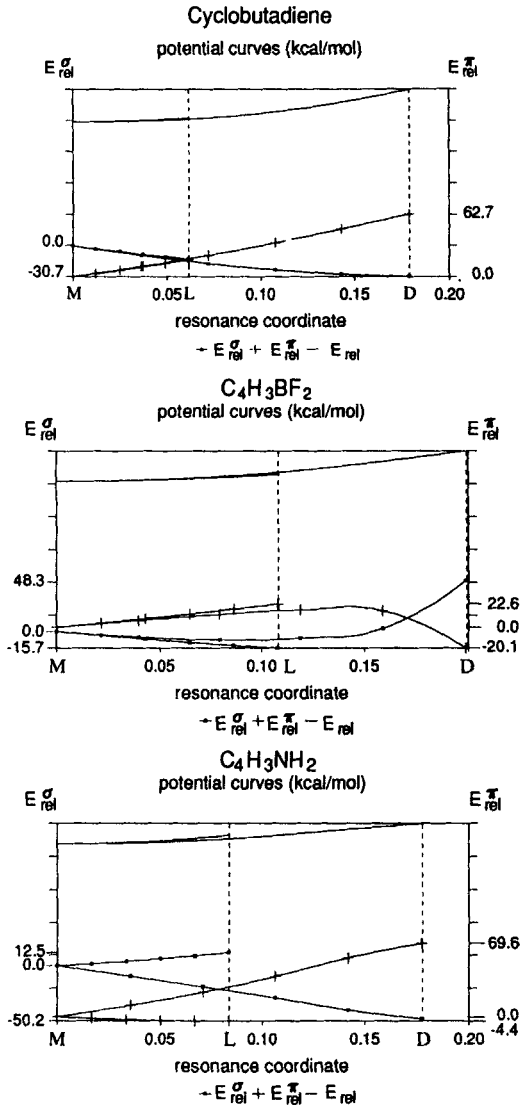

Figure 2. Dependence of σ and π parts of the total energy of cyclobutadiene, cyclobutadienylborondifluoride and aminocyclobutadiene on the resonance coordinates r_L and r_D (Å) for the localized structure L and the delocalized structure D

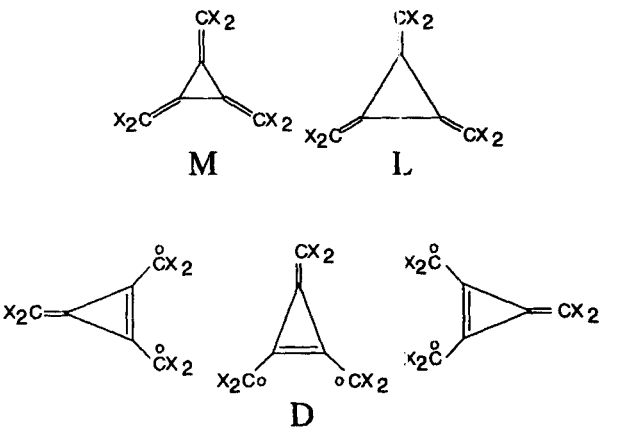

Figure 3. Minimum (M), localized (L) and delocalized structure (D) of substituted trimethylenecyclopropanes

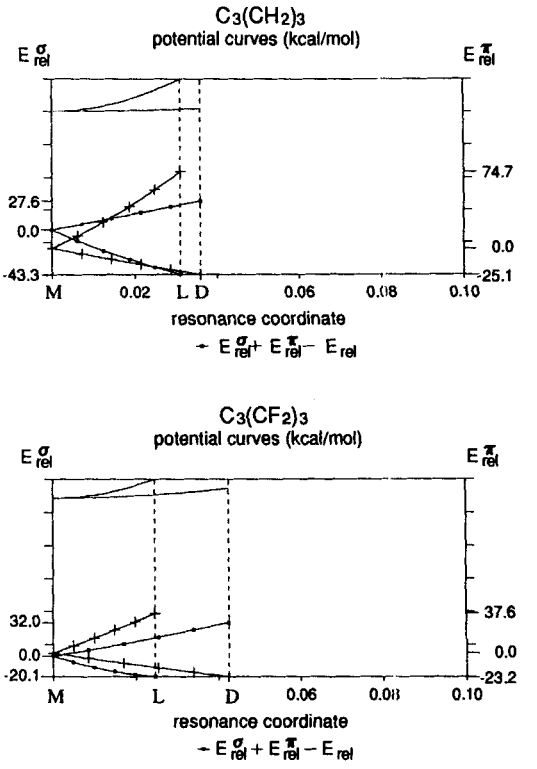

Figure 4. Dependence of σ and π parts of the total energy of trimethylenecyclopropane and perfluorotrimethylenecyclopropane on the resonance coordinates r_L and r_D (Å) for the localized structure L and the delocalized structure D

Table 1. Average single (P_{C-C}) and double ($P_{C=C}$) ring bond orders in cyclobutadienes

Substituent	P_{C-C}	$P_{C=C}$
H	0·980	2·040
CFO	0·979	2·017
CHO	0·980	2·015
BF_2	0·993	1·998
F	0·992	2·010
NH_2	1·028	1·947

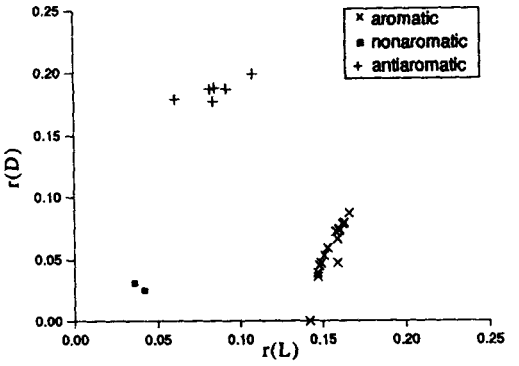

Figure 5. Grouping of aromatic, non-aromatic and anti-aromatic compounds in the $r(L)r(D)$ plane of localized (L) and delocalized (D) structure

CLASSIFICATION CHARACTERISTICS

From the three previous subsections, the following trends became apparent. Distortions from the minimum structure M are either to a localized structure L or to both localized structure L and delocalized structure D. The slopes of σ and π electron energy curves are characteristic for aromatic, non-aromatic and anti-aromatic systems. Table 2 shows these features. The minima of these curves are different for the three different classes. The total energy curve can be dominated by the σ or the π electrons, or a balance between these two opposing effects can be found.

For aromatic systems the minimum structure M coincides with or is very close to the delocalized structure D. The localized structure is distinctly different. For anti-aromatic systems a localized structure L and a delocalized structure D are distinctly different from minimum structure M. Here M is closer to L than to D. For non-aromatic structures the localized and delocalized structure are very close to each other. This suggests a clustering of the different classes in different regions of the $r(L)r(D)$ plane. We present these results in Figure 5, which shows that substitution affects the geometric properties of both aromatic and anti-aromatic compounds.

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Table 2. Aromaticity characteristics from σ–π energy diagrams

Characteristic	Aromatic	Non-aromatic		Anti-aromatic	
Distortion	M–L	M–L	M–D	M–L	M–D
σ slope	Positive	Positive	Negative	Negative	Negative
π slope	Negative	Negative	Positive	Positive	Positive
σ minimum	M	M	D	L	D
π minimum	L	L	M	M	M
Dominance	σ	none	π	none	π

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