Valence Bond Descriptions of Benzene and Cyclobutadiene and Their Counterparts with Localized Bonds

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ABSTRACT: Geometry optimizations have been performed for benzene and cyclobutadiene and for the corresponding moieties with nonresonating double bonds, viz. 1,3,5-cyclohexatriene and 1,3-cyclobutadiene. The calculations were done using the valence bond self-consistent field method including orbital optimization. Both strictly local and delocalized p-like orbitals were used for the π system, which influences the strengths of the π bonds. The calculations result in geometries and resonance and stabilization energies for benzene and cyclobutadiene, which are compared with theoretical models of aromaticity. The importance of resonance is discussed. Int J Quantum Chem 91: 566–574, 2003

Key words: benzene; cyclobutadiene; valence bond; aromaticity; cyclohexatriene

Introduction

The properties of aromatic and antiaromatic compounds have been studied for more than a century. An overview of the discussions and experimentally measurable effects can be found in textbooks like the one by Garratt [1], an article by Schleyer and Jiao [2], and reviews by Wiberg [3] and Krygowski et al. [4].

The theoretical models start with Kekulé's [5] description of benzene as having two structures. Later Hückel [6, 7] discovered his $4n+2$ and $4n$ rules and was able to account for the stability of benzene ($4n+2$) and the instability of cyclobutadiene and cyclooctatetraene (both $4n$). The $4n+2$ compounds were called aromatic after benzene, while the $4n$ compounds were given the designation antiaromatic.

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A natural way to study aromaticity would be to make use of the concept of two structures, as introduced by Kekulé. While it is not possible to do so experimentally because reference compounds like 1,3,5-cyclohexatriene cannot be made, the valence bond (VB) model makes it possible to create a wave function consisting of Kekulé structures. The first to use this view were Pauling and Wheland [8], who used an approximate form of the VB method developed by Heitler and London [9] for describing the aromaticity of benzene.

Classic VB calculations using fixed orbitals and containing all possible covalent and ionic structures for the π system were done by Norbeck and Gallup [10] and Tantardini et al. [11]. They both used σ orbitals from a self-consistent field (SCF) calculation. Their resonance energy is the energy difference between benzene and 1,3,5-cyclohexatriene at a certain geometry; in both cases, different sets of covalent and ionic structures were used with fixed orbitals. In these calculations, high-resonance energies of 61.4 and 67.4 kcal/mol were obtained for benzene.

More recently, Mo et al. [12] used this type of description for benzene and cyclobutadiene as well. They manually optimized the geometries of these molecules and of the ones with localized bonds. In this way, they not only obtained resonance but also stabilizsation energies. Another difference with the previous work is that they used a different set of structures for the description of the cyclohexatriene, which leads to another resonance energy.

The first calculations on benzene using optimized orbitals were done by Cooper et al. [13] using their spin-coupled VB [14] method. Recently, a review [15] appeared with an overview of their work on aromatic and antiaromatic compounds. For cyclobutadiene, they used branching diagram spin functions and obtained another representation for square geometries where the orbitals are + and − combinations of local orbitals. The problem with this description is that it loses the VB viewpoint by introducing completely delocalized orbitals and spin functions without a clear chemical significance.

Resonating generalized VB (GVB) calculations were performed on cyclobutadiene by Voter and Goddard [16], who found a resonance energy of 22 kcal/mol for this molecule. According to them, its geometry cannot easily be predicted and is determined by the interaction between resonance and bond strain.

In the last 15 years, new theories about aromaticity appeared. Originally, the symmetrical structure of benzene, which was always considered a key feature of aromaticity, was considered just an effect of the interacting π electrons. Shaik et al. [17–23] challenged that view and stated that the π system of benzene favors a distorted geometry with localized bonds. The σ system forces the molecule to be symmetrical. They draw this conclusion from several partition schemes for the σ and π energies, from calculations on H_6 and on benzene molecules with a septuplet spin state, and by looking at the energy of the so-called quasiclassic state of benzene. The partitioning schemes they used are arbitrary and incorporate a constant nuclear repulsion, which may have a large influence.

Glendening et al. [24], however, do not agree with their view because their calculations on benzene with localized bonds showed that the interaction between the two Kekulé structures is necessary for the molecule to have a symmetrical geometry. They, therefore, concluded that the symmetrical structure of benzene is caused by the resonance in the π system.

Recently, Zilberg and Haas [25] investigated the VB model from a fundamental perspective by examining the interaction between the Kekulé structures of systems with $4n$ and $4n+2$ electrons. Using this approach, they found that the sign and the absolute size of the interaction alternate between the systems. They concluded that the distorted geometric structure for $4n$ systems follows from the VB description.

It is clear that there is still discussion about the relation between aromaticity and geometry. Because our VB program TURTLE [26] is of a general nature, it allows for a more extensive description of benzene and cyclobutadiene than is available in the previous studies. This includes full or restricted orbital optimization as well as geometry optimization using recently added gradient capabilities [27, 28]. We make use of two models. The first has p-like (p_π) orbitals strictly localized on the carbon atoms; the second uses delocalized p_π orbitals with tails to neighboring atoms. In this way, we can adjust the strength of the π bonds, which gives more insight into the balance between contributions of the σ and π systems to the forces on the atoms.

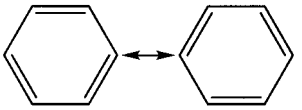

FIGURE 1. Two Kekulé resonance structures for benzene.

Method

We performed calculations on benzene and cyclobutadiene using the VBSCF method [29, 30], where the wave function is a linear combination of structures, which may for example be the Kekulé resonance structures.

The orbitals within the structures are completely optimized. We use doubly occupied SCF-like orbitals for the σ part and one singly occupied p_π orbital on every carbon atom for the π system. The σ orbitals are orthonormal and the p_π orbitals are orthogonal onto the σ system but not orthogonal onto each other.

To the structures, weights can be attributed using a formula given by Chirgwin and Coulson [31]:

$$W_i = \sum_j^N c_i c_j S_{ij}. \qquad (1)$$

The summation is over the number of structures N. The coefficients c of structures i and j are multiplied by their overlap S_{ij}, and added to obtain the weight W_i of structure i.

The benzene molecule is described using the two Kekulé resonance structures shown in Figure 1. The three Dewar structures, shown in Figure 2, were not taken into account. Previous calculations [13, 32] showed that they have a weight of about 6–7% each. Because these weights are relatively small compared to the total weight of the Kekulé structures of about 80%, and because they obscure the view of the resonance of the latter structures, they were left out. In our earlier calculations, we found a resonance energy of 20.3 kcal/mol with delocalized orbitals at a CASSCF geometry, in accordance with

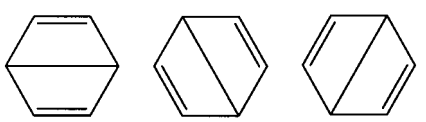

FIGURE 2. Three Dewar structures of benzene, not included in the wave function.

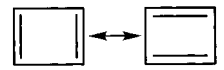

FIGURE 3. Two resonance structures for cyclobutadiene.

Cooper et al. [13, 15], compared to 19.8 kcal/mol in our present work with just the two Kekulé structures at their optimal geometry.

For the cyclobutadiene molecule, there are only two covalent structures possible. They are shown in Figure 3.

We also performed nonresonating calculations for benzene and cyclobutadiene using only one structure. These correspond to 1,3,5-cyclohexatriene and 1,3-cyclobutadiene. These molecules are shown in Figure 4. We will denote the cyclobutadiene with two structures as simply cyclobutadiene and the molecule with localized bonds (one structure) as 1,3-cyclobutadiene.

Geometry optimizations were performed for all molecules shown in Figures 1, 3, and 4. We started the optimizations at asymmetrical geometries (i.e., D_{2h} and D_{3h} as opposed to D_{4h} and D_{6h}, respectively) to be sure that asymmetrical solutions were found if present. When a geometry had almost converged to a symmetrical one, symmetry was applied and we checked if a lower energy was obtained. The geometry optimizations were performed to within a maximum gradient of 10^{-4} a.u.

Pauling's [8] definition of the electronic resonance energy (E_{res}) is the difference between the total energy of the two-structure wave function and the energy of the structure with the lowest energy in the same calculation. The theoretical resonance energy (TRE [12]) is the difference between the energies of the molecule with two structures and of the molecule with one structure, both at their optimal geometry. For benzene this is the energy difference between benzene and 1,3,5-cyclohexatriene and for cyclobutadiene the energy difference between cyclobutadiene and 1,3-cyclobutadiene.

In the VB calculations, we made use of two models. The first uses p_π orbitals strictly localized on the carbon atoms. This corresponds to the classical Heitler–London model [9] but with optimal orbit-

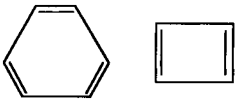

FIGURE 4. 1,3,5-Cyclohexatriene and 1,3-cyclobutadiene molecules.

TABLE I

Results for geometry optimizations for ethene and 1,3-*trans*-butadiene.

Calc.	p_π orbital model	CC_1 (Å)	CC_2 (Å)	E_{total} (a.u.)	E_{struc} (a.u.)	E_{res} (kcal/mol)	W_1	W_2
C_2H_4	Local	1.367	—	−78.004284	—	—	—	—
C_2H_4	Delocalized	1.343	—	−78.035206	—	—	—	—
C_4H_6	Local	1.505	1.366	−154.848591	—	—	1.000	—
C_4H_6	Local	1.484	1.371	−154.852240	−154.848259	−2.50	0.877	0.123
C_4H_6	Delocalized	1.469	1.347	−154.923257	—	—	1.000	—
C_4H_6	Delocalized	1.464	1.349	−154.924406	−154.922952	−0.91	0.904	0.096

CCs, carbon—carbon bond lengths; E_{struc}, energy of the structure with the lowest energy; E_{res}, resonance energy; Ws, weights of the structures.

als. The second model uses delocalized orbitals, centered on one atom but with tails to neighboring atoms. This model was first used by Coulson and Fischer for describing H_2 [33]. The main difference between them is that the delocalization of the orbitals introduces the effects of ionic structures, giving stronger bonds in the molecule. This allows us to study the effect of the bond strength in the π system on the geometry. Full geometry optimizations were performed for both models.

The calculations were performed using the TURTLE [26] program, which has been integrated into the GAMESS-UK [34] package to make use of the integral and geometry optimization routines therein. Details have been described in other work [27, 28]. We used the 6-31G basis set [35] in all calculations.

Results and Discussion

EFFECT OF DELOCALIZATION ON BOND STRENGTH

To investigate the effect of the delocalization of the p_π orbitals on the strength of the bonds, we studied the ethene (C_2H_4) and 1,3-*trans*-butadiene (C_4H_6) molecules using all covalent structures possible with, respectively, two and four singly occupied orbitals. The results are given in Table I. For ethane, the effects of switching from local to delocalized orbitals are an energy lowering of 19.4 kcal/mol and a shortening of the bond lengths by 0.024 Å. This shows that the π bonds are indeed stronger, as one would expect. Similar results are found for 1,3-*trans*-butadiene. Here, the energy lowering is 46.9 kcal/mol for the structure with two double bonds. This energy is more than twice the lowering for ethane because of, for instance, the enhanced delocalization possibilities and the resulting improved bond strength of the intervening single bond in the four-atom molecule.

BENZENE

The results for the calculations on the benzene molecule, using strictly local orbitals, are listed in Table II. The wave function is found to be the symmetrical combination of the two Kekulé structures.

As expected, the C—C bond lengths are equal for the molecule with the two Kekulé structures (II.1). The TRE [the energy difference between this calculation and the optimal 1 structure calculation (II.3)] is −11.32 kcal/mol. Resonance at the geometry of

TABLE II

Results for geometry optimizations for the benzene molecule using local orbitals.

Calc.	No. of struc.	CC_1 (Å)	CC_2 (Å)	E_{total} (a.u.)	E_{struc} (a.u.)	E_{res} (kcal/mol)	W_1	W_2
II.1	2	1.426	1.426	−230.548734	−230.508318	−25.36	0.500	0.500
II.2	1	(II.1)	(II.1)	−230.508688	−230.508688	—	1.000	—
II.3	1	1.509	1.368	−230.530694	−230.530694	—	1.000	—
II.4	2	(II.2)	(II.2)	−230.542990	−230.530654	−7.74	0.788	0.212

CCs, two carbon—carbon bond lengths; E_{struc}, energy of the structure with the lowest energy; E_{res}, resonance energy; Ws, weights of the two structures.

TABLE III

Results for geometry optimizations for the benzene molecule using delocalized orbitals.

Calc.	No. of struc.	CC_1 (Å)	CC_2 (Å)	E_{total} (a.u.)	E_{struc} (a.u.)	E_{res} (kcal/mol)	W_1	W_2
III.1	2	1.399	1.399	−230.693447	−230.661873	−19.81	0.500	0.500
III.2	1	(III.1)	(III.1)	−230.678149	−230.678149	—	1.000	—
III.3	1	1.433	1.369	−230.681589	−230.681589	—	1.000	—
III.4	2	(III.2)	(III.2)	−230.691547	−230.678195	−8.38	0.742	0.258

CCs, two carbon—carbon bond lengths; E_{struc}, energy of the structure with the lowest energy; E_{res}, resonance energy; Ws, weights of the two structures.

II.3 as calculated in II.4 is smaller but still significant. It is also clear that the resonance is necessary for a symmetrical geometry. When there is no resonance (only one structure), the molecule prefers alternating bond lengths. These results show the importance of resonance, as suggested by Glendening et al. [24].

Table III shows the results for the calculations using delocalized orbitals. We find that the energy, bond lengths, and absolute size of the resonance energy decrease (III.1). The TRE with respect to III.3 is now −7.44 kcal/mol, which is also smaller than for the calculation with localized orbitals. The shortening of the bonds can be explained by the introduction of stronger π bonds. The decrease in resonance energy and TRE is related to the fact that the orbitals delocalize to both neighboring carbon atoms.

Some of the previous calculations stressed the importance of ionic configurations. They are indeed needed for a proper description of the bonding when the orbitals are not completely optimized, as shown, for example, by the results obtained by us with local orbitals. We then find bond lengths of 1.426 Å where the experimental value is 1.399 Å [36]. When an improved wave function with delocalized orbitals is used, our results for the bond lengths are in good agreement, however. Although the ionic structures are originally meant to mimic the effect of orbital relaxation, they also introduce extra correlation, thus giving huge resonance energies, due to the large number of ionic structures used in the description of benzene. The only reasonable definition for the resonance of benzene is the interaction between two Kekulé structures with optimal orbitals. Using ionic structures instead makes interpretation unclear and makes it difficult to construct a balanced description of both 1,3,5-cyclohexatriene and benzene. Different choices can be made for the description of the former. This is illustrated by comparing the choice for the number of structures for 1,3,5-cyclohexatriene of Norbeck and Gallup [10] to that of Mo and Wu [12]. The first use 7 structures where the last use 27.

CYCLOBUTADIENE

Table IV shows the results for the calculations on cyclobutadiene using local orbitals. The wave function found for cyclobutadiene is the minus combination (cf. [16]) of the two structures of Figure 3, in contrast to benzene.

The molecule has equal C—C bond lengths (IV.1), not in line with the generally accepted rect-

TABLE IV

Results for geometry optimizations for the cyclobutadiene molecule using local orbitals.

Calc.	No. of struc.	CC_1 (Å)	CC_2 (Å)	E_{total} (a.u.)	E_{struc} (a.u.)	E_{res} (kcal/mol)	W_1	W_2
IV.1	2	1.465	1.465	−153.601084	−153.572936	−17.66	0.500	0.500
IV.2	1	(IV.1)	(IV.1)	−153.573182	−153.573182	—	1.000	—
IV.3	1	1.556	1.395	−153.588567	−153.588567	—	1.000	—
IV.4	2	(IV2)	(IV.2)	−153.596619	−153.588525	−5.08	0.788	0.212
IV.5[a]	2	1.561	1.452	−153.498380	−153.486544	−7.43	0.713	0.287

CCs, two carbon—carbon bond lengths; E_{struc}, energy of the structure with the lowest energy; E_{res}, resonance energy; Ws, weights of the two structures.

[a] Calculation with local σ and π orbitals for the C—C bonds. This geometry optimization only converged to 10^{-3}.

TABLE V

Results for geometry optimizations for the cyclobutadiene molecule using delocalized orbitals.

Calc.	No. of struc.	CC_1 (Å)	CC_2 (Å)	E_{total} (a.u.)	E_{struc} (a.u.)	E_{res} (kcal/mol)	W_1	W_2
V.1	2	1.552	1.367	−153.649966	−153.648409	−0.98	0.896	0.104
V.2	1	V.1	V.1	−153.648540	−153.648540	—	1.000	—
V.3	1	1.561	1.361	−153.648659	−153.648659	—	1.000	—
V.4	2	(V.2)	(V.2)	−153.649871	−153.648554	−0.83	0.906	0.094
V.5	2	1.452	1.452	−153.642916	−153.625055	−11.21	0.500	0.500

CCs, two carbon—carbon bond lengths; E_{struc}, energy of the structure with the lowest energy; E_{res}, resonance energy; Ws, weights of the two structures.

angular geometry [37]. The resonance energy is large, as is the TRE of −7.85 kcal/mol with respect to IV.3. In this one-structure calculation, the molecule attains a rectangular geometry. This again shows the necessity of resonance for obtaining equal bond lengths.

To rationalize this apparent discrepancy, it should be stipulated that the π bonds are too weak in this system compared to the σ bonds due to the use of local orbitals for π and delocalized orbitals for σ. The square geometry can therefore be explained by a preference of the σ system for equal bond lengths. To restore the balance, we performed a second calculation that used local orbitals for the σ system as well. In this calculation, one perfect-pairing structure was used for the C—C bonds of the σ system. All orbitals were localized on the C—H fragments. Doubly occupied orbitals were used for the C—H bonds and local singly occupied orbitals for the C—C bonds. The results for this calculation (IV.5) are a rectangular geometry and a much lower resonance energy. The bond lengths are also longer than for calculation IV.3, which shows that the bonds are indeed weaker. Hence, the conclusion must be that weak bonds in the σ system again lead to alternating bond lengths.

Turning back to the model with strong (delocalized) σ bonds, we now allow the orbitals of the π system to delocalize, introducing stronger σ bonds. The results for these calculations are shown in Table V.

Now the molecule immediately attains the expected rectangular shape (V.1). The resonance energy is small, almost negligible. The geometry, therefore, does not change much when only one structure is taken into account (V.3), and the resonance at this geometry (V.4) is also almost zero. The TRE of V.1 with respect to V.2 is only −0.82 kcal/mol.

To find the maximum possible resonance, a calculation was performed forcing a square geometry while optimizing the other parameters. This results in a large resonance energy, although lower than that using local orbitals (IV.1). The TRE at this square configuration of V.5 compared to V.3 is now +3.60 kcal/mol, which means that the molecule is destabilized and prefers a rectangular geometry.

A comparison of our results with other VB calculations shows that our data are in agreement with those of Voter and Goddard [16] and support their suggestion that the geometry of cyclobutadiene cannot be predicted beforehand. They stated that it results from a balance between bond strain and resonance. The balance is more complex, however, and involves π bond strengths as well. In comparison with benzene, the σ bonds of cyclobutadiene are weaker due to ring strain, which gives a larger influence of the π system on the geometry.

EFFECT OF DELOCALIZATION ON RESONANCE ENERGY

The effect of delocalization on the energy of the Kekulé structures is shown by the single-structure calculations. The energy lowering for ethene, when going from local to delocalized orbitals, is 19.4 kcal/mol. Considering that we obtained an extra lowering for butadiene of about 8 kcal/mol and that the effect is bigger in benzene because of the shorter intervening bond, we expect a delocalization energy for benzene of around 100 kcal/mol for one of the Kekulé structures of benzene. As seen from the tables, the lowering for benzene is 94.7 kcal/mol. Indeed, the bond length of the formal single bonds is shortened significantly by delocalization of the π bonds, showing that the strengths of these bonds are increased as well, with the associated energy effect.

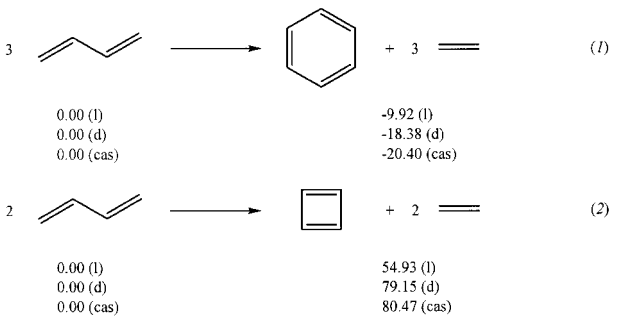

FIGURE 5. Homodesmotic reactions for benzene and cyclobutadiene.

Because the orbitals were optimized for the single structures, their energy is lower than that of the structures in the corresponding two-structure calculations. These energy lowerings are 0.3 and 10.2 kcal/mol for the local and delocalized cases, respectively. This difference can be explained by the extra degrees of freedom in the delocalized orbital case, where the orbitals are now allowed to become asymmetrical.

It is clear that the orbital model chosen has an effect on the resonance energy. It is hard to tell, however, which model is best. The choice is a matter of interpretability and accuracy. The local orbital model is clearly interpretable. Using delocalized orbitals improves the accuracy of the total energy but makes the orbital picture more fuzzy. Ultimately, the delocalized model is the only sustainable picture when the basis set nears completeness.

The effect of orbital delocalization on the structure energies of cyclobutadiene is an energy lowering of -37.7 kcal/mol when the optimal geometries for the one-structure molecules are used. This is close to twice the ethene value. In this case, the single bond actually gets slightly longer, as the double bond is shortened due to the delocalization. This must be an effect of the bond strain in this molecule. The effect on the resonance of orbital delocalization is similar to that in benzene when the totally symmetrical geometries are compared.

HOMODESMOTIC REACTIONS

The reaction energy of the homodesmotic reaction for the formation of benzene indicates that with both models benzene is stabilized in contrast to 1,3-butadiene. However, the reaction energy obtained with the use of local orbitals is too low compared to the CASSCF value and that obtained by using delocalised p_π orbitals (see Fig. 5). This can be attributed to the weaker bond strength due to the use of localized p-orbitals. Cyclobutadiene is destabilized with respect to 1,3-butadiene. Again, the value obtained by using delocalized orbitals is in agreement with the CASSCF data. Hence, delocalized orbitals should be used to obtain quantitative data.

Analysis

Using the option to have either local or delocalized orbitals in our VB wave functions, we are able to define an enhanced model for the influences of the σ and the π systems on the geometry of aromatic systems.

From the calculations on benzene, it is clear that the symmetrical structure is due to the resonance of the two Kekulé structures. When a calculation is done using only one structure, the molecule becomes asymmetrical, consistent with the findings of Glendening et al. [24], who state that the resonance between the structures is the key factor for delocalization.

This does not mean, however, that resonance is the only factor contributing to the symmetrical form of benzene. When the results for cyclobutadiene are considered, decreasing the strength of the π bonds by having local orbitals gives a symmetrical structure. Restoring the balance by decreasing the strengths of both π and σ bonds returns the geometry back to an asymmetrical structure. This suggests that the σ system is an important factor in the determination of the geometry, which can be understood in terms of the model given by Shaik et al. [17–23]. Zilberg and Haas [25] stated that the geometric distortion of cyclobutadiene is a fundamental property of $4n$ electron ring systems. This is not the case according to our calculations.

We can therefore now conclude that there are three contributions that determine the geometry of benzene and cyclobutadiene. The first is that of the

FIGURE 6. Energy curves for the σ system for two bond strengths. The axis gives the difference in the two C—C bond lengths.

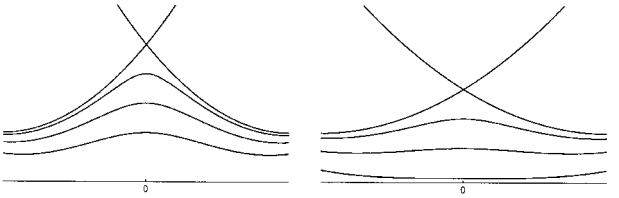

FIGURE 7. Resonance in the π system. The axis gives the difference in the two C—C bond lengths. Two crossing Kekule-like states are shown with curves with increasing (constant) resonance interaction drawn below them. The lowest curve has the largest resonance interaction. The first graph shows a system with strong π bonds and the second with weaker π bonds.

σ system, which prefers equal bond lengths. When we use the differences between the bond lengths as coordinates for the x-axis and keep the sum of the bond lengths fixed, we can describe the energy of the σ system with a symmetrical curve with a minimum at zero as shown in Figure 6.

The other two contributions are caused by the π bonds and π resonance, illustrated in Figure 7. The π bonds give rise to two states with a minimum at one of the geometries with alternating bond lengths, right and left in the graphs. The states cross at geometries with equal bond lengths. When there is an interaction between the states, the crossing disappears and the energy decreases. This energy lowering is the largest for equal bond lengths and gets smaller when the difference in bond length increases.

The total energy is obtained by adding the contributions from the σ and π systems. Both have a gradient of zero at equal bond lengths, as illustrated in the figures. The preferred geometry is determined by the curvatures of the π and σ energy curves at the equal bond length situation. The curvature for the σ system is always positive, while the curvature for the π system may also be negative. When these curvatures are added, the geometry will be symmetrical if the result is positive and asymmetrical when it is negative.

This shows that resonance is a necessary condition for a symmetrical geometry. When the resonance is small, the second derivative of the energy of the π system becomes negative for equal bond lengths and therefore the geometry will distort.

When we now apply this model to benzene, the character of the π system can be found by comparing the total energy and the structure energy for the symmetrical and asymmetrical geometries. For the local orbital model, the total energy increases by only 3.61 kcal/mol when going from the symmetrical to the asymmetrical geometry, while the structure energy is lowered by 14.02 kcal/mol. This suggests that the curve for the total energy is flat and has a small curvature.

Conclusions

Our calculations show that there are three important contributions to the geometry of benzene and cyclobutadiene. The first is that of the σ system, which prefers equal bond lengths. The second is that of the π bonds, which introduce alternating bond lengths. The last contribution is that of the resonance. This contribution makes it possible to obtain equal bond lengths by coupling the two Kekulé-like states of the π system with localized π bonds. The crossing between the states then disappears. Depending on the size of the interaction, the resulting energy curve for the π system has either one minimum at equal bond lengths or minima at the two alternating bond length geometries and a maximum in between at equal bond lengths. The contributions from the σ and π systems have to be added to obtain the final geometry. Its symmetry depends on the sum of the curvatures of the energy curves for the σ and the π systems at the point with equal bond lengths.

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