Accurate Calculation of Aromaticity of Benzene and Antiaromaticity of Cyclobutadiene: New Homodesmotic Reactions

Cherumuttathu H. Suresh and Nobuaki Koga*

Graduate School of Human Informatics, Nagoya University, Chikusa-ku, Nagoya 464-8601, Japan

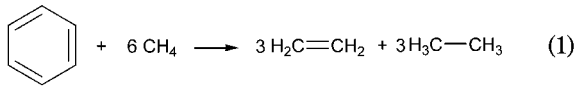
koga@info.human.nagoya-u.ac.jp

Received September 5, 2001

Abstract: Newly designed homodesmotic reactions based on radical systems predict an absolute aromaticity of 29.13 kcal/mol for benzene and an absolute antiaromaticity of 40.28 kcal/mol for cyclobutadiene at the MP4(SDQ)/6-31G-(d,p) level.

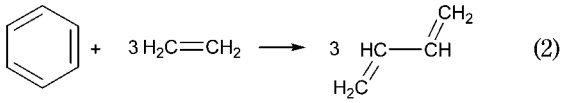
Aromaticity, a fundamental concept in chemistry, has multidimensional character.[1−4] For example, aromaticity in molecules is characterized by their high thermodynamic stability, magnetic properties, special reactivity, and special geometric features.[1−4] In general, all aromatic molecules contain several unsaturated carbon atoms and cyclic delocalized distribution of π-electrons. Undoubtedly, the root cause of aromaticity is the cyclic delocalized distribution of π-electrons. On the other hand, in the case of antiaromatic systems, the cyclic distribution of electrons is more localized and they are highly unstable. A perfect case of an aromatic system is benzene, and that of an antiaromatic system is cyclobutadiene. Both of these systems have been intensely studied by experimentalists and theorists for the past several years to determine their π-electron stabilization or destabilization.[1]

Isodesmic and homodesmotic reactions are frequently used for the study of aromaticity from the energetic point of view.[5,6] In isodesmic reactions (IDR), there is matching of the bonds in reactants and products species according to their formal type (single, double, or triple).[5] A typical IDR used for studying the stabilization of benzene is the bond separation reaction shown in eq 1. Although the formal type of single and double bonds are conserved in IDR, the bonding state of the carbon atoms in the CC



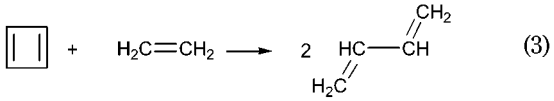
(1)

and CH bonds are not conserved. For instance, in eq 1, there is no $C_{sp3}-C_{sp3}$ bond in the reactant side. George et al.[6] used a subclass of IDR known as homodesmotic reaction (HDR) to evaluate the stabilization energies for cyclic conjugated hydrocarbons. In such reactions there are equal numbers of each type of carbon−carbon bond ($C_{sp3}-C_{sp3}$, $C_{sp2}-C_{sp3}$, $C_{sp2}-C_{sp2}$, $C_{sp2}=C_{sp2}$, etc.) as well as equal number of each type of carbon atom (C_{sp3}, C_{sp2}, etc) with zero, one, two, and three hydrogen atoms. For example, see the most commonly used HDR[6,7] for evaluating the stabilization energy of benzene due to the π-electron conjugation as given in eq 2. In this reaction,



(2)

a cyclically delocalized six π-electron system is combined with linearly localized 3 double bonds to produce linearly delocalized 3 four-π-electron systems. Because all of the bond types and hybridization types are conserved here, the energy change associated with this reaction is mainly accounted for by the stabilization of benzene due to the cyclic π-electron conjugation. Glukhovtsev and Schleyer[7a] have calculated this stabilization energy at the MP4SDTQ/6-31G(d,p)//MP2(full)/6-31G(d,p) level as 23.9 kcal/mol, and the corresponding experimental value was 21.4 kcal/mol.[8] In fact, this energy change is not really the classical resonance energy of benzene because the energy of this reaction does not correspond to the localization of six cyclically conjugated π-electrons to three localized π-bonds.[9] In other words, the energy of this reaction reflects only the relative aromaticity of benzene and not its absolute aromaticity. Similar to benzene, the homodesmotic reaction in eq 3 can be designed for cyclobutadiene. It is



(3)

obvious that the energy of this reaction cannot give the absolute or even the relative aromatic destabilization of cyclobutadiene because there is no way to describe the destabilization of it caused by the ring strain, a major contributor of its overall destabilization.

In the present work, a new type of radical-based HDR will be introduced for the accurate calculation of the absolute values of the aromatic stabilization and anti-

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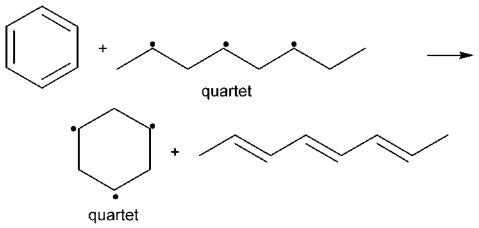
10.1021/jo010903q CCC: $22.00
Published on Web 02/19/2002

aromatic destabilization of benzene and cyclobutadiene, respectively.

Methodology

The radical-based reactions designed for benzene and cyclobutadiene are given in eqs 4 and 5, respectively. In these



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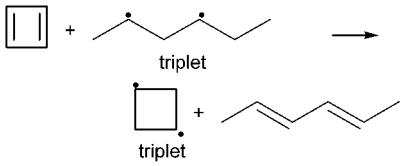
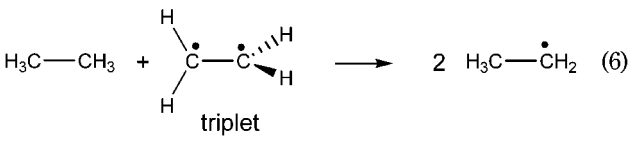


(5)

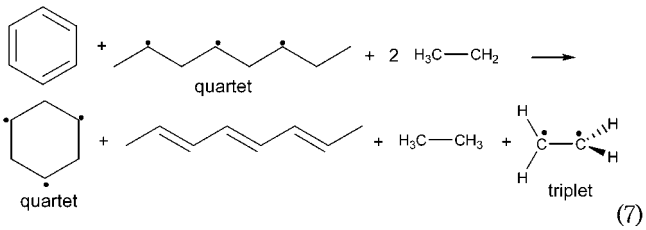
reactions, the cyclic π-electron system is converted to a cyclic polyradical system so that no two radical centers are at adjacent positions. At the same time, a linear polyradical system having no radical centers at adjacent positions is converted to a linear polyene. Further, the radical centers are on secondary carbon atoms at both sides of the reaction. In the calculation, we consider only the high spin state for the polyradical systems. This will help to minimize the spin contamination in the wave function. Such spin distribution will also eliminate any bonding interaction between two radical centers. Even if there is some radical−radical interaction, the energy of the reaction will be mostly unaffected by this as a result of the cancellation of such effects from both sides of the reaction. Further, the use of cyclic polyradical system is expected to balance the strain in both sides of the reactions. The energy of the reactions in eqs 4 and 5 will therefore mainly account for the change of cyclic π-electron distribution to a matching linear π-electron distribution. In other words, the energy of these reactions will be the aromatic stabilization/destabilization of the cyclic π-electron system as compared to the corresponding linear π-electron system.

It can be noted that both reactions in eqs 4 and 5 are isodesmic. In fact, they are very close to a homodesmotic reaction because the number of C_{sp2} and C_{sp3} carbon atoms in the left-hand side (LHS) and the right-hand side (RHS) of the equations are equal. Further, they have equal number of CC and CH bonds as well as equal number of CCC, CCH, and HCH bond angles at the LHS and RHS. However, a close look at these reactions show that the number of $C_{sp2}-C_{sp2}$, $C_{sp2}-C_{sp3}$, and $C_{sp3}-C_{sp3}$ bonds is not balanced at the LHS and RHS. The LHS has one $C_{sp2}-C_{sp2}$ and one $C_{sp3}-C_{sp3}$ bond in excess as compared to the RHS; the RHS has two $C_{sp2}-C_{sp3}$ bond in excess as compared to the LHS. It means that in eqs 4 and 5, apart form the change in conjugation there is a change of one $C_{sp2}-C_{sp2}$ and one $C_{sp3}-C_{sp3}$ bond to two $C_{sp2}-C_{sp3}$ bonds. To find out the energy change associated with this bonding change, the reaction in eq 6 is used as a model. In eq 6, a perpendicular ethylene is used to avoid π



(6)

bonding between the two carbon atoms (a π bond is not needed in eq 6 because already the double bond description is matched in the LHS and RHS of eqs 4 and 5). Subtracting eq 6 from eqs 4 and 5 will give us homodesmotic reactions depicted in eqs 7 and 8. The energy change associated with reactions in eqs 7 and



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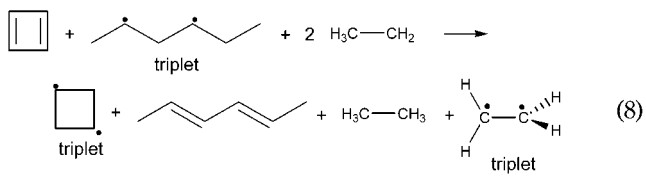

(8)

8 can be taken as the aromatic stabilization of benzene and antiaromatic destabilization of cyclobutadiene, respectively.

Geometries of all molecular systems involved in reactions in eqs 7 and 8 have been optimized first at B3LYP/6-31G(d,p) level (UB3LYP level for radical systems), and they were confirmed as minima by frequency calculations. The geometries thus obtained were further optimized at MP4(SDQ) levels (UMP4-(SDQ) level for radical systems) employing 6-31G(d,p) basis sets. Gaussian 98 suite of programs[10] was used for all the calculations. The maximum spin contamination of only 0.001 was found for octane-2,4,6-triyl triradical at MP4(SDQ) level of theory.

In Figure 1, the optimized geometries of benzene, 1,3-cyclobutadiene, ethane, 2,4-hexadiene, and 2,4,6-octatriene at the MP4(SDQ)/6-31G(d,p) level is given. These geometries are in excellent agreement with the corresponding experimental geometries. For instance, the MP4(SDQ)/6-31G(d,p) structure of benzene has D_{6h} symmetry with all of the C−C and C−H bond lengths equal to 1.396 and 1.082 Å, respectively (experimental geometry[11] determined using neutron diffraction at 15 K gives all the C−C bond length of benzene equal to 1.3983 Å). Nearly the same geometry parameters are obtained at B3LYP/6-31G-(d,p) level for all these molecules.

The geometries of radical systems, viz., cyclohexane-1,3,5-triyl triradical, cyclobutane-1,3-diyl diradical, hexane-2,4-diyl diradical, octane-2,4,6-triyl triradical, triplet state of perpendicular ethylene, and ethyl radical at MP4(SDQ)/6-31G(d,p) level are depicted in Figure 2. In the case of cyclobuta-1,3-diyl diradical, carbon atoms are all in the same plane. In other polyradical systems the carbon skeleton is not completely planar. However, in them the sum of the angles around the carbon atom having the unpaired electron (the radical site) is between 359° and 360°. This means that the radical site carbon atoms are mostly sp^2 hybridized and the unpaired electrons reside in the p atomic orbital. Further, the bond lengths of $C_{sp3}-C_{sp2}$ bonds are in the range of 1.493−1.502 Å, which is in fact very close to typical $C_{sp3}-C_{sp2}$ distances.[12] In eqs 7 and 8, the reactant and product sides have an equal number of CC and CH bonds as well as an equal number of CCC, CCH, and HCH bond angles. In the case of eq 7, the number of CC and CH bonds in the reactant or the product side of the reaction is equal to 15 and 31, respectively. The total sum of the CC bond lengths in the reactant side is

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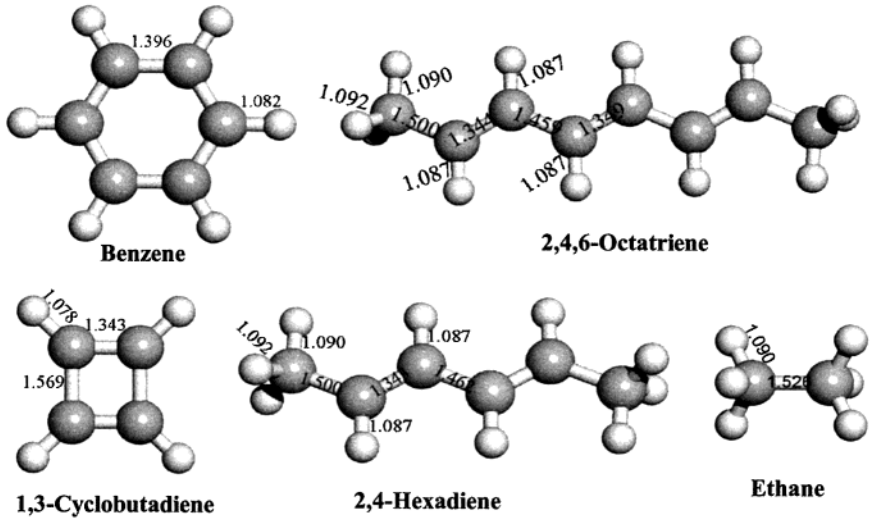

Figure 1. MP4(SDQ)/6-31G(d,p) level geometries of benzene, 1,3-cyclobutadiene, 2,4,6-octatriene, 2,4-hexadiene, and ethane.

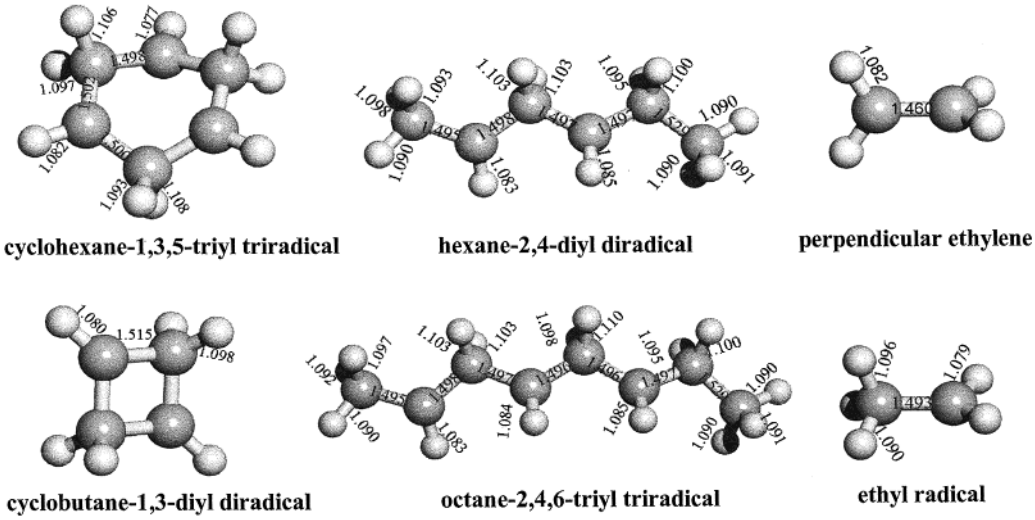

Figure 2. MP4(SDQ)/6-31G(d,p) level geometries of polyradical systems at their high spin state.

21.869 Å and that at the product side is 21.941 Å. The total sum of the CH bond lengths in the reactant and products sides are, respectively, 33.771 and 33.786 Å. Almost complete matching of the CCC, CCH, and HCH bond angles can also be seen at both sides of the reaction. There are 46 CCH bond angles in the reactant side. Of these, 22 angles are in the range of 116.6−121.6° and the remaining 24 are in the range of 108.8−111.9°. The same numbers and figures for CCH angles are found at the product side as well. Similarly, among the 12 CCC bond angles found at both the reactant and product sides, 9 are between 120.0° and 124.7° and the remaining are between 111.8° and 114.1°. There are 17 HCH bond angles at both sides of the reaction, in which 3 are between 103.8° and 105.3°, 12 are between 106.8° and 108.2°, and the remaining 2 are between 116.8° and 117.4°. For the reaction in eq 8, similar matching of the bond lengths and bond angles is seen (cf. Figures 1 and 2). It is also mentioned that only a very negligible amount of spin contamination is present in the wave functions corresponding to the radical systems and there is also the matching of the radical centers (all radical centers are on secondary carbon atoms) at the reactant and product sides. All of these results thus suggest that eqs 7 and 8 describe truly homodesmotic reactions. We also note that the geometry parameters of all the above-mentioned systems at B3LYP/6-31G(d,p) level are almost completely matched with the MP4(SDQ)/6-31G(d,p) level and therefore they will not be discussed in detail.

The reaction in eq 7 can be visualized as the transformation of a cyclic 6π-electron conjugated system to a linear 6π-electron conjugated system. Generally, the linear 6π-electron conjugated system is considered as a nonaromatic system, and benzene is the ideal aromatic system.[13] Therefore, the energy change accompanying the reaction in eq 7 accounts for the transformation of an 6π-electron aromatic system to a matching 6π-electron nonaromatic linear system. In other words, the energy of the reaction in eq 7 gives the absolute aromatic stability of benzene. At MP4(SDQ)/6-31G(d,p) level, this energy value is calculated as 29.13 kcal/mol. At B3LYP/6-31G(d,p) level, it is 28.91 kcal/mol.

Similarly, the reaction in eq 8 describes the transformation of the antiaromatic cyclobutadiene to the matching nonaromatic 4π-electron linear conjugated system. The energy of this reaction at MP4(SDQ)/6-31G(d,p) and B3LYP/6-31G(d,p) levels is −45.74 and −47.88 kcal/mol, respectively. If we consider that the ring strain of cyclobutadiene is almost the same as that of cyclobutane-1,3-diyl diradical, these values would represent a very good estimate of the absolute value of the antiaromatic destabilization of cyclobutadiene. However, the actual antiaromatic destabilization of cyclobutadiene would be less negative than the energy of the reaction in eq 8 because cyclobutadiene with 4 sp^2 carbon atoms is expected to show a higher ring strain than cyclobutane-1,3-diyl diradical with 2 sp^2 and 2 sp^3 carbon atoms. To estimate the amount of ring strain incorporated via the cyclobutane-1,3-diyl diradical, a ring opening homodesmotic reaction as given in eq 9 is designed. The energy of this reaction is a direct

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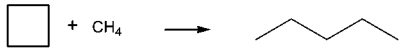
(9)

estimate of the ring strain, which is −29.20 and −28.03 kcal/mol at MP4(SDQ)/6-31G(d,p) and B3LYP/6-31G(d,p) levels, respectively. Because the ring strain and antiaromaticity are combined in cyclobutadiene, it is almost impossible to accurately calculate only the ring strain of it by a ring opening reaction. However, the following indirect method is suggested for this purpose. In this method, first we calculate the ring strain of cyclobutane (−28.40 kcal/mol at MP4(SDQ)/6-31G(d,p) and −25.98 kcal/mol at B3LYP/6-31G(d,p)) and cyclobutene (−31.53 kcal/mol at MP4(SDQ)/6-31G(d,p) and −30.41 kcal/mol at B3LYP/6-31G(d,p)) from the simple homodesmotic reactions depicted in eqs 10 and 11. The higher value of ring strain in cyclobutene as



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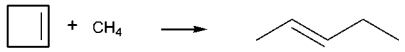

(11)

compared to cyclobutane can be considered as the effect of changing one CC single bond to one CC double bond in a tetragonal system. Assuming this effect is additive, the increase in the ring strain on going from cyclobutane to cyclobutadiene can be estimated as at least two times higher than the increase in the ring strain on going from cyclobutane to cyclobutene. Therefore, the ring strain of cyclobutadiene can be assigned as −34.66 and −34.84 kcal/mol at MP4(SDQ)/6-31G(d,p) and B3LYP/6-31G(d,p) levels, respectively. It means that the difference between the ring strain energies of cyclobutadiene and cyclobutane-1,3-diyl diradical must be subtracted from the energy of the reaction in eq 8 to obtain a very good estimate of the absolute antiaromatic destabilization of cyclobutadiene (the corrected value is −40.28 and −41.08 kcal/mol at MP4(SDQ)/6-31G(d,p) and B3LYP/6-31G(d,p) levels, respectively).

It was mentioned earlier that the energy of the homodesmotic reaction given in eq 3 is sometimes used as a measure of the antiaromatic character of cyclobutadiene. At B3LYP/6-31G(d,p) level, the energy of this reaction is estimated as −83.56 kcal/mol. Such a high negative value is mainly due to the neglect of strain effect in this homodesmotic reaction. Further, the improper balancing of the delocalized π-electrons in both sides of this reaction will also contribute to this cause.

In a recent work, Deniz, Peters, and Snyder[14] have carried out the experimental determination of the antiaromaticity of cyclobutadiene from a cleverly designed experimental method. In their method, photoacoustic calorimetry has used for measuring the enthalpy change accompanying the formation of cyclobutadiene by pulsed-laser photolysis of a polycyclic precursor. However, this enthalpy change was used in combination with the heats of formation of the photochemical reactant and byproducts of the reactions calculated at semiempirical AM1 and PM3 level of theories to finally arrive at the antiaromaticity of cyclobutadiene (55 ± 11 kcal/mol). This value is therefore not completely an experimental one. In fact, there is still ambiguity in this value because of the use of semiempirical theory, as well as a rather large error factor of 11 kcal/mol. It is to be noted that the absolute value of the antiaromaticity of cyclobutadiene obtained in the present work is nearly at the lower end of the error limit proposed in the experimental work.[14]

The new homodesmotic reactions studied in the present paper predict an absolute aromatic stability of 29.13 kcal/mol for benzene, which is about 5.23 kcal/mol higher than the relative aromatic stability calculated from the homodesmotic reaction of benzene + 3 ethylene giving 3 butadiene.[7a] The smaller aromatic stability from the later reaction is due to comparing the delocalization energy of one benzene molecule (represents one set of 6 delocalized π-electrons) with 3 butadiene molecules (represent three sets of 4 delocalized π-electrons). The homodesmotic reactions designed for cyclobutadiene predict a value of 40.28 kcal/mol for its absolute antiaromatic destabilization and 34.66 kcal/mol for its ring strain destabilization.

Acknowledgment. The research was supported by the Grant-In Aid for Scientific Research on Priority Areas "Molecular Physical Chemistry" from the Ministry of Education, Culture, Sports, Science, and Technology. Part of the calculations was carried out at the Research Center for Computational Science of Okazaki National Research Institutes, Japan. C.H.S. gratefully acknowledge the Japan Society for the Promotion of Science (JSPS) for the award of a fellowship.

Supporting Information Available: Cartesian coordinates of the optimized geometries and total energies at MP4(SDQ)/6-31G(d,p) and B3LYP/6-31G(d,p) levels. This material is available free of charge via the Internet at http://pubs.acs.org.

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