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# Theoretical investigations on bond enthalpy additivity deviations in the formation of triplet diradicals from hetero-substituted 1,3-dimethylenecyclobutanes

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ABSTRACT: In our continuing effort to understand better the cause of the large positive deviation from bond enthalpy additivity (BEA) observed in the formation of triplet 1,3-dimethylenecyclobutane-2,4-diyl (**1c**) from 1,3-dimethylenecyclobutane (**1a**), we performed B3LYP/6–31G* calculations on a series of 1,3-disubstituted cyclobutanes, where the methylene groups in **1a** are replaced by hetero groups, specifically O, NH, S, PH and $SiH_2$. The size of the deviation from BEA ($\Delta$BEA) is found to increase consistently with decreasing bond strength of the exocyclic $\pi$ bonds. DFT calculations were also carried out on related hydrocarbons and the $\Delta$BEA value in each case was found to be in close agreement with that predicted by simple Hückel theory. All of the computational results provide convincing evidence that antiaromaticity is absent in these diradicals, and the positive deviations from BEA, as large as 30.3 kcal $mol^{-1}$, are due to the more substantial increase in the $\pi$ electron delocalization in the monoradicals than that in the diradicals. Copyright © 2001 John Wiley & Sons, Ltd.

KEYWORDS: bond enthalpy additivity; B3LYP; hetero-substituted cyclobutanes; diradicals; antiaromaticity

## INTRODUCTION

C—H bond enthalpy additivity (BEA) is said to hold when the bond dissociation enthalpy for forming the diradical, $BDE_1 + BDE_2'$ (or $BDE_1' + BDE_2$), is equal to the sum of the enthalpy changes for forming the two monoradicals, $BDE_1 + BDE_1'$ (Fig. 1). In other words, BEA holds if $BDE_2' = BDE_1'$ (or $BDE_2 = BDE_1$). For molecules where the two C—H bonds are equivalent, deviation from BEA is simply the difference between the second and the first C—H bond dissociation enthalpies.

Negative deviations from BEA refer to situations where $BDE_2 < BDE_1$, which usually occur when the two radical centers interact with each other, either through-bond or through-space, such that the diradical is stabilized. The magnitude of the negative deviation provides a measure of the strength of such interactions.[1]

A positive deviation is observed when $BDE_2 > BDE_1$, which means that the BDE for a specific bond is larger in forming a diradical than a monoradical. In contrast to the negative deviations from BEA, positive deviations usually result from an unfavorable interaction between the two radical centers, which destabilizes the diradical. For example, in the formation of singlet trimethylene-methane (TMM) from isobutene, the strong electron repulsion between the two unpaired electrons destabilizes TMM, resulting in a positive deviation from BEA of 14.6 kcal $mol^{-1}$ (it is estimated from the $\Delta$BEA in forming triplet TMM[2] and the value of $\Delta E_{S\text{-}T}$[3]) (1 kcal = 4.184 kJ). On the other hand, in triplet TMM, the electron repulsion is dramatically reduced, and TMM is both predicted by theory (TMM calculations are reviewed by Borden[3]) and confirmed by experiments,[2] to have a triplet ground state. There is, however, a small $\Delta$BEA of ~1.5 kcal $mol^{-1}$ observed in forming triplet TMM.[2] Simple Hückel theory predicts $0.83\beta$ of $\pi$ system stabilization in forming the 2-methylallyl radical, which is more than half the total of $1.47\beta$ of stabilization in

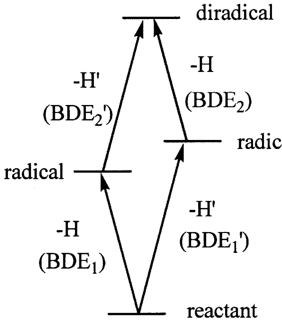

**Figure 1.** Energy diagram for the C—H bond dissociation reactions in forming the monoradical and the diradical

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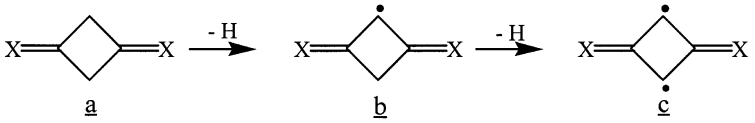


1. X = $CH_2$
2. X = O
3. X = NH
4. X = S
5. X = PH
6. X = $SiH_2$

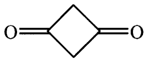
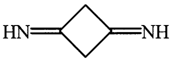
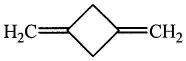
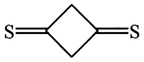
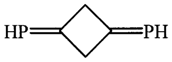
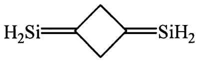
**Scheme 1**

triplet TMM. The relatively low-lying radical thus results in a less endothermic reaction for the first bond dissociation process, which consequently leads to a small positive deviation from BEA.

Diradical **1c** has received much attention both theoretically and experimentally.[4–10] Like TMM, **1c** has a triplet ground state, and belongs to the class of non-Kekulé molecules. Such molecules may be used as ferromagnetic coupling units in forming high-spin species,[4,5] which have potential applications in drug design[6] and material science.[7–10] Both experimental and theoretical thermochemistry have shown that **1c** has a large positive $\Delta$BEA of 13.1 kcal mol$^{-1}$.[11,12] The cause of such a large positive deviation has been controversial. Since a resonance structure which contains an antiaromatic 1,3-cyclobutadiene unit may be drawn for **1c**, it was suggested by Hill and Squires that **1c** is of higher energy owing to the electronic destabilization of the $\pi$ system from partial antiaromaticity.[11] In a recent paper,[12] however, we concluded that antiaromaticity does not contribute at all in **1c**. The large $\Delta$BEA is due to the smaller BDE in forming the first pentadienyl-like radical, **1b**, in which the $\pi$ system receives a much larger stabilization than that in forming the diradical where the second radical center is allyl-like instead (Scheme 1).

As an extension of our earlier study, we have investigated a series of derivatives of **1a**, where the methylene groups are replaced by heteroatomic groups. Based on our understanding of the nature of the radical centers in the hydrocarbons (**1b** and **c**), we expect BDE$_1$ to change dramatically upon substitution, since the $\pi$ electrons in both of the C=X $\pi$ bonds will be fully conjugated to the radical center. On the other hand, BDE$_2$ is predicted to be less sensitive to exocyclic substitution, since the second unpaired electron is allylic and conjugated to one of the C=C in the four-membered ring. The size of $\Delta$BEA, therefore, is expected to correlate closely with the C=X bond strength, provided that antiaromaticity is absent in all of the diradicals. In order to clarify further the contribution of antiaromaticity in these diradicals, we carried out density functional theory (DFT) calculations on these molecules, the results

**Table 1.** Bond dissociation enthalpies and $\Delta$BEA values, together with $\pi$ bond strength data[17]

| Molecule | $\pi$ bond strength (kcal mol$^{-1}$) | BDE$_1$ (kcal mol$^{-1}$) | BDE$_2$ (kcal mol$^{-1}$) | $\Delta$BEA (kcal mol$^{-1}$) |
|---|---|---|---|---|
|  O O<br>2 | 93.4 | 87.7 | 95.6 | 7.9 |
|  HN NH<br>3 | 80.8 | 81.5 | 89.7 | 8.2 |
|  $H_2C$ $CH_2$<br>1 | 69.6 | 73.5 | 86.6 | 13.1 |
|  S S<br>4 | 55.7 | 72.3 | 87.5 | 15.2 |
|  HP PH<br>5 | 49.4 | 62.2 | 85.7 | 23.5 |
|  $H_2Si$ $SiH_2$<br>6 | 36.1 | 54.6 | 84.9 | 30.3 |

of which, together with those for several related hydrocarbons, are presented in this paper.

## COMPUTATIONAL METHODOLOGY

DFT calculations were carried out with the 6–31G* basis set,[13] utilizing Becke's hybrid exchange functional[14] and the non-local correlation functional of Lee, Yang and Parr.[15] All of the calculations were performed using the Gaussian 98 suite of programs.[16]

A vibrational frequency analysis was carried out for each optimized geometry in order to verify it as a minimum on the potential energy surface. Zero-point energy corrections were included to compute the BDEs at 298 K. In order for correct comparison with the results in forming **1c**, the data for the diradicals refer to their triplet states, whether or not the triplet is the ground state for the particular species.

## RESULTS AND DISCUSSION

The $\mathrm{BDE}_1$ and $\mathrm{BDE}_2$ values for the hydrocarbons (**1a–c**) and their hetero-substituted derivatives are presented in Table 1. The molecules are listed in order of decreasing C═X $\pi$ bond strength.

The first bond dissociation enthalpy, $\mathrm{BDE}_1$, ranges from 54.6 to 87.7 kcal $\mathrm{mol}^{-1}$, with the largest in forming cyclobutane-1,3-dione-2-yl (**2b**) and the smallest in forming 1,3-disilylenecyclobutan-2-yl (**6b**). $\mathrm{BDE}_1$ decreases consistently as the $\pi$ bond strength of the exocyclic C═X bond decreases. The calculated $\pi$ bond strengths reported by Schleyer and Kost[17] are also included in Table 1 for analysis.

In a previous paper,[12] it was shown that resonance structures give excellent qualitative descriptions of the stabilities of the radical as well as the diradical, and hence are extremely helpful in explaining the magnitudes of the BDEs. Figure 2 displays all the possible resonance contributors to the monoradicals (A–C) and the diradicals (A′–C′). As is shown, on forming the radical, the original unconjugated exocyclic C═X $\pi$ bonds in the reactant become conjugated in the pentadienyl-like radical which has a total of three resonance structures. The diradical has a total of five resonance structures. The structures which contain a 1,3-cyclobutadiene unit with the two unpaired electrons outside the ring have been excluded as resonance contributors in the diradical, because the symmetry of one of the singly occupied MOs forbids such structures to contribute.[12] By comparing the two sets of the resonance structures, it can be seen that the second radical center is allylic and is confined inside the ring.

Structures A and C in Fig. 2 would contribute less if the exocyclic $\pi$ bonds were stronger than the C═C $\pi$ bond. Such is the case in cyclobutane-1,3-dione, where the carbonyl groups have strong C═O $\pi$ bonds, with a $\pi$ bond strength of 93 kcal $\mathrm{mol}^{-1}$. The radical center in **2b** is, therefore, more localized on the ring carbon than in **1b**, in order not to exchange the strong C═O bonds for weaker C═C bonds. The unpaired electron receives less stability from conjugation, which results in a much higher $\mathrm{BDE}_1$ with a value 14.2 kcal $\mathrm{mol}^{-1}$ higher than that in forming **1b**. Conversely, the $\mathrm{BDE}_1$ in forming **6b** is 16.6 kcal $\mathrm{mol}^{-1}$ smaller than that in hydrocarbon **1a**. The C═Si $\pi$ bond in **6a** is much weaker, with a bond strength of only half that of the C═C $\pi$ bond. On forming the radical, the unpaired electron is more localized on the heteroatom so as to take the advantage of forming stronger C═C bonds. As a result, the monoradical, **6b**, is much more stabilized so the first C—H bond dissociation reaction is much less endothermic.

So far, resonance structure theory has successfully explained the trend of the $\mathrm{BDE}_1$ values in this series of molecules. However, it is apparent that the BDE for forming the thionyl radical, **4b**, is much larger than expected from the relative C═S $\pi$ bond strength.

Behaving much differently from the $\mathrm{BDE}_1$ values, the $\mathrm{BDE}_2$ values do not vary as dramatically throughout the series. They stay more or less constant, close to that of 88.0 kcal $\mathrm{mol}^{-1}$ in forming the allylic radical of 1-methylcyclobuten-4-yl from 1-methylcyclobutene, except for that from **2b** (95.6 kcal $\mathrm{mol}^{-1}$), which is 7.6 kcal $\mathrm{mol}^{-1}$ higher. The $\mathrm{BDE}_2$ value is the smallest in forming **6c** and the largest in forming **2c**, displaying a trend similar to that in the $\mathrm{BDE}_1$ values, such as the values for $\mathrm{BDE}_2$ decrease as the $\pi$ bond strength decreases, except for the thionyl radical, **4b**, which is

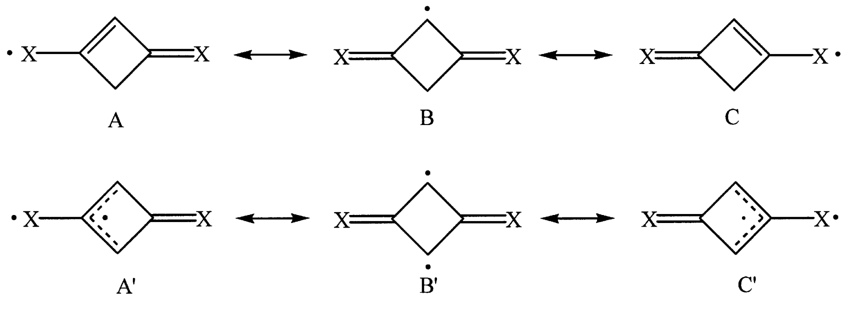


**Figure 2.** Resonance structures in the monoradical (A–C) and the diradical (A′–C′)

**Table 2.** Bond length data for $C_1$—$C_2$ and the change in $C_1$—X bond length in forming the monoradicals and the diradicals

| Molecule | $r(C_1—C_2)$ (Å) | $\Delta r(C_1—X)$ (Å) |
|---|---|---|
| 2a | 1.545 | 0 |
| 2b | 1.475 | 0.014 |
| 2c | 1.489 | 0.025 |
| 3a | 1.536 | 0 |
| 3b | 1.444 | 0.024 |
| 3c | 1.470 | 0.035 |
| 1a | 1.530 | 0 |
| 1b | 1.427 | 0.029 |
| 1c | 1.460 | 0.036 |
| 4a | 1.529 | 0 |
| 4b | 1.424 | 0.039 |
| 4c | 1.460 | 0.048 |
| 5a | 1.530 | 0 |
| 5b | 1.414 | 0.048 |
| 5c | 1.456 | 0.054 |
| 6a | 1.533 | 0 |
| 6b | 1.410 | 0.062 |
| 6c | 1.454 | 0.066 |

slightly out of the pattern. (It is not clear, at this point, why the thionyl radical **4b** is relatively more unstable. The calculation results have shown that the filled–filled interaction between the exocyclic $\pi$ orbitals and the two $C_3$—H $\sigma$ orbitals in **4b** is the strongest in comparison with **1b**, **5b** or **6b**, which could be one of the contributors to the instability of **4b**.) The small changes in $BDE_2$ among the various heteroatom substituents reflect the allylic nature of the second radical center, which has the unpaired electron confined inside the ring and in conjugation with the C=C $\pi$ electrons.

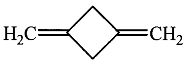
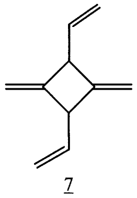
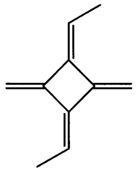
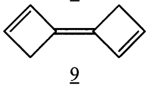
The dramatic decrease in $BDE_1$ coupled with the essentially constant values for $BDE_2$, results in positive ΔBEA values which correlate very closely with the C=X $\pi$ bond strength throughout the series. These ΔBEAs cover a very large range, between 7.9 and 30.3 kcal mol$^{-1}$.

Additional insight may be gained from the geometries of the stationary points, especially from the $C_1$—$C_2$ bond length and the change in the $C_1$—X bond length ($\Delta C_1$—X) during each bond dissociation step. These data, presented in Table 2, provide a good indication of the degree of $\pi$-electron delocalization in the radical and diradical species.

The $C_1$—$C_2$ bond shortens on forming the radical in all of the molecules. Consistent with the degree of conjugation, the $C_1$—$C_2$ bond is the shortest in **6b** and the longest in **2b**. The amount of shortening increases down the rows, from 0.070 to 0.123 Å. On forming the diradical, the $C_1$—$C_2$ bond lengthens. The amount of lengthening also increases down the column, covering a much smaller range, between 0.014 and 0.044 Å.

Why are the $C_1$—$C_2$ bonds in the monoradicals shorter than those in the diradicals? In the monoradical, one out of the three resonance structures has a full double bond, whereas only one out of five in the diradical has a full double bond. To a first approximation, if all the resonance structures contribute equally to the overall structure of hydrocarbons, **1b** and **1c**, there will be 33% and 20%

**Table 3.** Bond dissociation energies and Hückel stabilization energies in **1a**–**c** and related hydrocarbons (**7**–**9**)

| Molecules | $BDE_1$ (kcal mol$^{-1}$) (ΔHückel) | $BDE_2$ (kcal mol$^{-1}$) (ΔHückel) | ΔBEA (kcal mol$^{-1}$) (ΔΔHückel) |
|---|---|---|---|
| <br>1a | 73.5(1.46$\beta$) | 86.6 (1.01$\beta$) | 13.1 (−0.45$\beta$) |
| <br>7 | 62.9 (2.0$\beta$) | 70.3 (1.73$\beta$) | 7.4 (−0.27$\beta$) |
| <br>8 | 74.7 (1.07$\beta$) | 76.4 (1.00$\beta$) | 1.7 (−0.07$\beta$) |
| <br>9 | 86.4 (1.13$\beta$) | 86.7 (1.13$\beta$) | 0.3 (0.0$\beta$) |

double bond character in the $C_1$—$C_2$ bonds in them, leading to a reduction of 0.103 and 0.070 Å in the bond length, respectively. In molecules with strong C═X $\pi$ bonds, such as **2a–c**, resonance structures A (A′) and C (C′) contribute less to the overall structure, resulting in smaller changes in the $C_1$—$C_2$ bond length. The opposite is observed in molecules with weak C═X $\pi$ bonds.

Resonance structure theory also accounts for the lengthening of the $C_1$—X bond during each C—H bond dissociation step. Specifically, the fully double bonded C═X in the reactant is reduced to only two out of the three in the monoradical, and is further reduced to three out of five in the diradical. The changes in the $C_1$—X bond length are more significant in molecules where the C═X $\pi$ bonds are weak, which is consistent with the differences in the contribution of each resonance structure to the overall structure of the molecule as discussed earlier.

Additional DFT calculations were performed on several hydrocarbons that are related to **1a**. Table 3 presents the calculated BDEs and the ΔBEA values for these hydrocarbons, together with the $\pi$ stabilization energy (ΔHückel) calculated based on simple Hückel theory for comparison. Substitution of the ethylidene groups at the 2- and 4-positions in **1a** to give **7** results in more conjugation for the radical center(s). This increased conjugation stabilizes both the monoradical and the diradical, lowering both the BDEs relative to those for **1a–c**. Furthermore, ΔBEA reduces to just over half of that in **1a**, which can be understood as the second unpaired electron in the diradical of **7** is allowed to delocalize much more extensively (i.e. out of the ring), rather than being confined to the ring as in **1c**.

The diradical formed from **8** is identical with that from **7**. However, since the four $\pi$ bonds are already in conjugation in **8**, it is of lower energy. This evidently makes both of the C—H bond dissociation reactions more endothermic and, hence, increases the values for both $BDE_1$ and $BDE_2$. Simple Hückel theory predicts a $\pi$ stabilization energy of $1.07\beta$ and $1.00\beta$ for the monoradical and diradical, respectively. Corresponding to the small difference in Hückel energies of $0.07\beta$, the DFT results show a ΔBEA of only 1.7 kcal $mol^{-1}$.

Molecule **9** serves as a model to test further if antiaromaticity exists at all in a four-membered ring where a 1,3-cyclobutadiene may be drawn as one of the resonance structures, since, if it did, it would add an arbitrary amount to $BDE_1$, owing to the instability introduced by partial antiaromaticity. As the partial antiaromatic radical would remove the possibility for the diradical to suffer further from any additional antiaromaticity, a more ‘normal’ size of $BDE_2$ would be expected, which should be smaller than $BDE_1$. The DFT calculation results, however, invalidate the assumption by producing two essentially identical BDEs. This shows that the two allylic radical centers are truly confined inside the ring, and antiaromatic structures are not involved.

## CONCLUSIONS

Our theoretical studies have shown that antiaromaticity does not contribute at all in diradicals where a 1,3-cyclobutadienyl unit may be drawn in one of the resonance structures.

Evidence comes from the excellent agreement between the structural data and the resonance structure analyses where the participation of the antiaromatic structures as resonance contributors has been excluded. Additional support is given by the BDE calculation results for related hydrocarbons (**7–9**), which show that the sizes of the deviations from BEA are in very close agreement with those predicted by simple Hückel theory, which, as is known, does not take antiaromaticity into account. The positive deviation from BEA is found to be solely caused by the more substantial $\pi$ system stabilization available to the monoradical than to the diradical.

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