

A REKS Assessment of the Face-Diagonal Bond in 1,3-Didehydrocubane and a Comparison with Benzyne Biradicals

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The three isomeric cubane biradicals were studied using spin-restricted ensemble-referenced Kohn–Sham (REKS) density functional calculations at the B3LYP/6-31G(d) level of theory. The most stable biradical was found to be *ortho*-cubene with the *meta*-cubene and *para*-cubene biradicals 4.7 kcal mol⁻¹ and 17.8 kcal mol⁻¹ higher in energy, respectively. The singlet ground states are well separated from their lowest lying triplet states. These singlet-triplet energy differences mostly originate from through-space interactions for

the *ortho* and *meta* isomers, whereas these interactions are rather weak for the *para* isomer. In contrast to *para*-benzyne, which was also considered for comparison with an unsaturated system, the singlet-triplet energy gap remains large in *para*-cubadiyl, mainly as a result of its much stronger through-bond interactions.

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Introduction

Organic singlet open-shell (OS) biradicals (also referred to as diradicals) are important yet controversial reaction intermediates.^[1,2] The structures of the didehydrobenzene biradicals, **1–3**,^[3–5] constitute a particular case in point. While 1,2 (*ortho*)-didehydrobenzene (**1**) is generally viewed as having predominantly a closed-shell character,^[6–8] (i.e., a sensible representation would be **1c**, where “c” stands for closed-shell and “o” for open-shell), the opposite is true for 1,4 (*para*)-didehydrobenzene (*para*-benzyne, **3**) which is known for its DNA-cleaving ability by virtue of its pronounced biradical character.^[9–11] 1,3 (*meta*)-Benzyne (**2**) lies in-between **1** and **3** and its true nature was a highly controversial issue until a series of beautiful experiments in combination with high-level computational studies came to an agreement just recently.^[12–19] Although the biradical character of **2** varies (19–32%), depending upon the theoretical method employed, the geometry appears to be a σ -

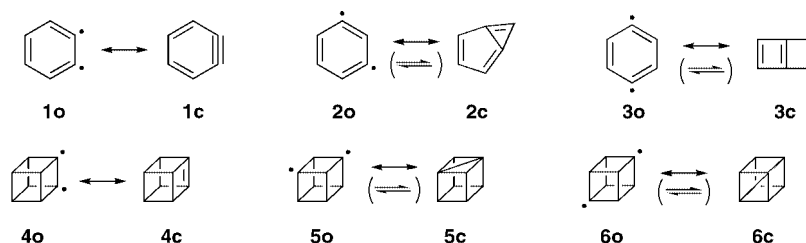
allylic hybrid between **2o** and **2c** with a rather long 1,3-C–C bond separation of around 2 Å.^[20]

Detailed computational analyses are, in principle, capable of answering questions regarding the “true” nature of these important intermediates.^[21–23] A key question, posed early on by R. W. Hoffmann, is the composition of through-bond versus through-space coupling.^[3] The availability of a coupling mechanism allows predictions about the biradical character to be made — strong coupling indicates the existence of a bond rather than two unpaired spin densities. While the biradical characters of **1–3** were exhaustively examined by means of high-level computations,^[6,7,16–19,24–33] it would also be instructive to compare these results for unsaturated systems — where unsaturation provides coupling mechanisms^[33] — to a suitable set of saturated molecules. This paper, therefore, discusses the question of the through-space versus through-bond coupling in **4–6**, where such a coupling mechanism is less apparent.^[34] 1,2 (*ortho*)-Didehydrocubane (**4**, cubene)^[35] has been investigated extensively,^[34,36–40] and as for **1**, the general consensus is that it is mostly closed-shell in nature, despite the anti-Bredt character of the incipient double bond in **4c**. Based on the singlet-triplet energy separation ΔE_{ST} , the double bond strength was estimated to be about 26 kcal mol⁻¹ (TCSCF/6-31G* and ROHF/6-31G* levels of theory for the singlet and the triplet respectively).^[34] The through-space single bond in **6c** was deemed experimentally unrealistic because it is too long (2.686 Å) and very weak ($\Delta E_{ST} = 10.3$ kcal mol⁻¹).^[34] Trapping products derived from **6o** or just its monoradical precursor were observed.^[41] Hence, while **4** is a closed-shell molecule and while it paral-

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lels the findings for **1** in terms of electronic coupling, the singlet-triplet gap for the 1,4 derivative **6** is still substantial, unlike the results for its aromatic cousin **3**. Again, the most critical structure is **5**, for which we now have a method of preparation at hand starting from 1,3-diiodocubane,^[42] which itself can be synthesized by our recently introduced phase-transfer catalytic alkane halogenation protocol that is described in detail elsewhere.^[43] Amongst other issues, the present computational study reassesses^[34] the feasibility of making the face-diagonal bond in **5c**, utilizing the spin-restricted ensemble-referenced Kohn–Sham (REKS) method. Comparisons with the benzyne radicals will be made to assess the biradical coupling mechanisms. It is well beyond the scope of this paper to include the preparation and thorough characterization of **5**, and the present work rather serves as a computational prediction of its properties.

Methods

We showed recently that the REKS method is an extremely powerful tool for the calculation of biradicals.^[44–54] Our results showed excellent agreement between REKS calculations and experiment. Furthermore, our calculations used a fraction of the CPU time and were found to be on par with, or better than, sophisticated high-level *ab initio* methods. Hence, this methodology is also expected to work very well for the low-lying states of the cubane biradicals **4–6**, as it does for the aromatic benzyne **1–3**.^[48,52]

The molecular structures of all singlet species were optimized using the REKS approach^[50] which is implemented in a development version of the Gaussian98 program package.^[55] Triplet states were calculated using the spin-restricted open-shell Kohn–Sham method (ROKS).^[53,54]

To understand the basic idea of REKS, consider two electrons sharing two degenerate or nearly degenerate orbitals, ϕ_r and ϕ_s . The occupations in ϕ_r and ϕ_s can be expressed in terms of the weighted sum of the following quasidegenerate Kohn–Sham determinants [Equation (1)]:

$$\begin{aligned}\Psi_{\text{cov}} &= \frac{1}{\sqrt{2}} (|\phi_r \bar{\phi}_r| - |\phi_s \bar{\phi}_s|) \\ \Psi_{\text{ion}} &= \frac{1}{\sqrt{2}} (|\phi_r \bar{\phi}_r| + |\phi_s \bar{\phi}_s|)\end{aligned}\quad (1)$$

The density for such a strongly correlated system is represented in terms of Kohn–Sham orbitals with fractional

occupations n_r and n_s of the active orbitals ϕ_r and ϕ_s , Equation (2). The doubly occupied core orbitals are ϕ_k .

$$\rho(\mathbf{r}) = 2|\phi_k(\mathbf{r})|^2 + n_r|\phi_r(\mathbf{r})|^2 + n_s|\phi_s(\mathbf{r})|^2 \quad (2)$$

The ground state REKS energy ($E_{\text{gs}}^{\text{REKS}}$) gives then the following expression [Equation (3)]:

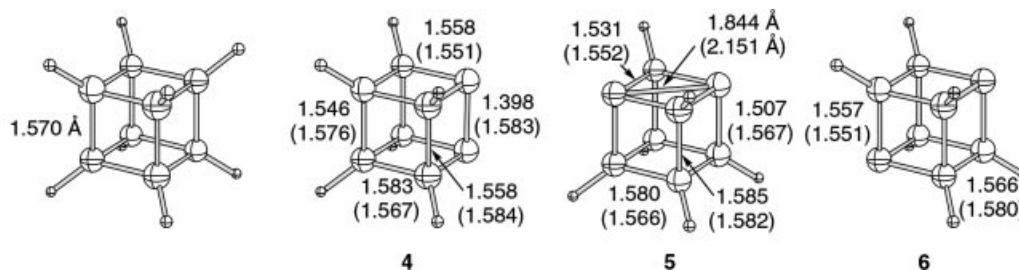
$$E_{\text{gs}}^{\text{REKS}} = \frac{n_r}{2} E(\phi_r \bar{\phi}_r) + \frac{n_s}{2} E(\phi_s \bar{\phi}_s) + (n_r n_s)^{3/4} \left[E(\phi_r \phi_s) - \frac{1}{2} E(\phi_r \bar{\phi}_s) - \frac{1}{2} E(\phi_s \bar{\phi}_r) \right] \quad (3)$$

The one-electron orbitals and fractional occupation numbers are obtained by self-consistent minimization of the energy with respect to the density. All calculations were performed with a 6-31G(d) basis set with the B3LYP hybrid density functional,^[56–58] all geometries were fully optimized and were identified as minima by vibrational frequency analyses.

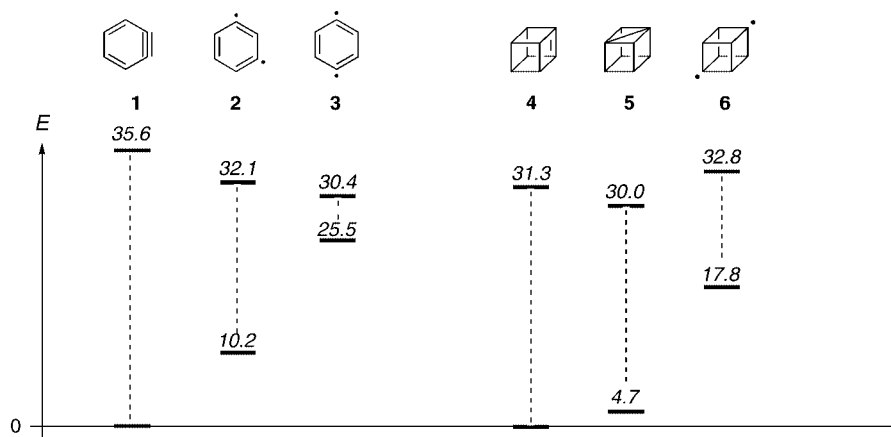
Results and Discussion

As noted before,^[34] the geometry of singlet-**4** is characterized by a short C–C bond of 1.398 Å between the two radical centers; this is indicative of and in agreement with the notion of an anti-Bredt double bond (Scheme 1). As expected for the uncoupled triplet state, this distance is much longer and characteristic of a single bond (1.583 Å). The 1,3-C–C distance in singlet-**5** is quite long (1.844 Å) and would constitute the longest single bond ever observed. The 2.635 Å for the 1,4-C–C distance of singlet-**6** is clearly too long to call it a bond;^[34] this is in agreement with the unsuccessful attempts in preparing **6c**.^[41] All other C–C bond lengths in the three isomers (in either spin state) are quite normal single bonds (compared to the parent cubane) and lie between 1.5–1.6 Å.

The relative energies of the computed isomers of the cubane biradicals are depicted in Scheme 2. Remarkably, singlet-**5** is only 4.7 kcal mol^{−1} above singlet-**4** at the level of theory used here. Earlier computations, however, not including dynamic electron correlation (TCSCF/6-31G*) give an energy difference of 8.1 kcal mol^{−1}.^[34] In contrast, singlet-**6** is substantially higher in energy (17.8 kcal mol^{−1}). In all cases the singlet state is well separated from the triplet state. The smallest singlet-triplet gap is obtained for **6** (15.0 kcal mol^{−1}; 10.5 kcal mol^{−1} (one-pair GVB-ROHF/6-31G*)



Scheme 1. Optimized molecular structures of parent cubane, 1,2-cubane (**4**), 1,3-cubane (**5**), and 1,4-cubane (**6**) in their singlet and triplet (in parentheses) spin states



Scheme 2. Relative energies (without ZPVE in kcal mol⁻¹) between the singlet and triplet spin states of **1–6**; the ground states are invariably singlets

and 12.1 kcal mol⁻¹ using a multi-reference second order CI expansion of 6 electrons in 36 GVB natural orbitals without further geometry optimization^[41]). Our value is substantially higher than the computed singlet-triplet gap of *para*-benzyne of 4.9 kcal mol⁻¹. For comparison, the relative energies of **1–3** are also shown in Scheme 2. Although cubane is a saturated hydrocarbon, whereas the benzyne is unsaturated, there are striking similarities between the relative energies of the different biradicals. That is, the through-space interaction must dominate the biradical coupling mechanism because the correlation between distance (of the radical sites) and the ΔE_{ST} values is obvious. This conclusion is based on the fact that there is no apparent through-bond coupling mechanism in **4–6** due to unfavorable orbital overlap (90° angles). Despite proper orbital alignment (co-planar) in **6**, its ΔE_{ST} is the lowest for the didehydrocubanes.

The origins of the coupling mechanism in the biradicals **4–6** can be analyzed in terms of through-space and through-bond effects. Table 1 shows the occupation numbers in the biradical orbitals for the two spin states. One orbital is the in-phase bonding combination, labelled as $\sigma(C\cdots C)$, and the other is the out-of phase antibonding

combination, labelled as $\sigma^*(C\cdots C)$, where $C\cdots C$ refers to the through-space $C\cdots C$ bond. Although in the triplet state the REKS density places a single electron in each orbital, the population of one of these orbitals is larger than one, while that of the other is smaller than one in the singlet biradical. In the case of **4** and **5**, the σ orbital has the greater population, while in **6** it is the σ^* orbital that is more highly populated. This population pattern is obtained

Table 1. Orbital populations extracted from REKS

Isomer ^[a]	Orbital population $\sigma(C\cdots C)$	$\sigma^*(C\cdots C)$
³ 4, ³ 5, ³ 6	1.00	1.00
¹ 4 (T)	1.78	0.22
¹ 5 (T)	1.72	0.28
¹ 6 (T)	0.25	1.75
¹ 4 (S)	1.97	0.03
¹ 5 (S)	1.97	0.03
¹ 6 (S)	0.20	1.80

^[a] In parentheses we indicate the geometry. For example ¹4 (T) is a singlet state with triplet geometry, while ¹4 (S) is a singlet state with a singlet geometry.

irrespective of whether the singlet biradical is calculated with the geometry and orbitals of the triplet or with its own relaxed orbitals and geometry. As such, we can immediately conclude that the singlet-triplet gap in **4** and **5** originates mostly from through-space coupling, while in **6** the dominant factor must apparently be the residual through-bond coupling. An estimate of this effect (without including geometric and orbital relaxations) can be obtained by calculating the singlet biradicals with the orbitals and geometries of the triplet species.

This dissection for **4–6** is depicted in Scheme 3. On the left we show the vertical effects, namely when both states are calculated at the geometry of the triplet biradical. The through-space interaction ($\Delta E_{\text{through-space}}$, ΔE_{ts}) is the dominant factor for the preferred singlet state stability, no matter how the evaluation is performed. The energy difference between the zero-iteration and the fully converged singlet wavefunction at the fixed triplet geometry gives the effect of orbital relaxation ($\Delta E_{\text{orb-relax}}$) of the singlet biradicals. On the right we show the two spin-states at their own optimized geometries (i.e., adiabatic), and also where the singlet is calculated, once with the triplet orbitals and subsequently with its own optimized orbitals — in this case, the adiabatic $\Delta E_{\text{through-space}}$ term does include geometry relaxation effects, which reflect the bond shortening of the “through-space bond.” It is apparent that **6** is much less affected by geometric changes compared with the through-space effect in the other biradicals; the effect of orbital relaxation remains small and rather similar to the vertical value. Notably, the orbital relaxation terms for **4–6** are also almost unchanged and similar to the evaluations in the vertical regime. The results depicted in Scheme 3 show that the through-space coupling in the singlet state of **4** and **5** becomes more important when the geometries are allowed to relax. This is not the case for **6** where the through-bond (ΔE_{tb}) interactions are hampered by improper bond alignment and where the through-space component involves occupation of an antibonding orbital. Hence, geometric changes cannot alter this picture significantly. This is also in perfect agreement with our experimental findings that

the 1,4-dihalogen substituted cubanes form in only very minor (<10%) quantities in the dihalogenation of cubane, where 1,2- as well as 1,3-products dominate.⁴² The origin of this selectivity must be the lack of proper stabilization of the halogen-substituted intermediate radical in the 1,4-case.

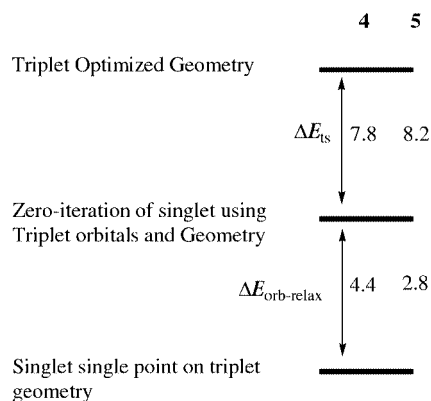
Apparently, the through-bond interactions in the didehydrocubane systems are more efficient than in the benzynes, because the C–C bonds in the former have higher-lying bonding and lower-lying antibonding orbital combinations that can couple more efficiently with the biradical.

The strain energy of **5** has not been evaluated but is necessary to judge the feasibility of making this peculiar alkane. As the heat of formation of **5** is unknown, but required to properly estimate the strain energy, we first determined ΔH_f° utilizing homodesmotic Equation (4).

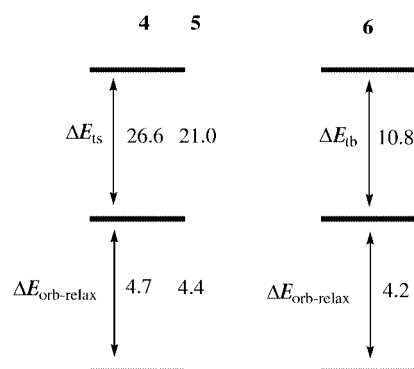


The heats of formation of cubane (148.7 ± 1.0 kcal mol^{−1}), [1.1.0]bicyclobutane (51.9 ± 0.2 kcal mol^{−1}) and cyclobutane (6.78 ± 0.02 kcal mol^{−1}) are known.^[59] At the B3LYP/6-311G* level of theory, we compute $\Delta H_f^\circ = 241.0 \pm 1.0$ kcal mol^{−1} for **5**, a value which compares well with the experimentally determined heat of formation of 236 ± 5 kcal mol^{−1} for the slightly more stable **4**.^[60] The energy difference of 5 kcal mol^{−1} also matches perfectly our computed energy difference of 4.7 kcal mol^{−1} between **4** and **5** (despite the considerably larger experimental error bars) and lends confidence to the theoretical approach used here. Utilizing Schleyer single-conformation strain-free increments^[61] of -2.2 kcal mol^{−1} for C–H groups and -0.3 for C for determining the theoretically unstrained heat of formation of **5** (-13.8 kcal mol^{−1}), we calculate a strain energy of 255 kcal mol^{−1}. The same approach gives 166 kcal mol^{−1} for cubane, in excellent agreement with another recent high-level computational estimate (165.4 kcal mol^{−1}

(a) Vertical:



(b) Adiabatic



Scheme 3. The separation of the energy differences between the triplet and singlet optimized geometries in through-space (ΔE_{ts}) and through-bond (ΔE_{tb}) interactions; $\Delta E_{\text{orb-relax}}$ is the orbital relaxation term; part (a) shows the vertical excitation energy, while part (b) shows the adiabatic one; all values are in kcal mol^{−1}

at MP2/6-311G**) and the available experimental values (157,^[62] 162.7,^[63] and 181 kcal mol⁻¹ ^[64]).

Conclusion

Spin restricted ensemble referenced Kohn–Sham (REKS) calculations have been performed on a series of cubane biradicals (**4**–**6**). As with the biradicals of benzyne (*ortho*-, *meta*-, and *para*-, **1**–**3**, respectively), the most stable one is the 1,2-isomer, **4**. Whereas the singlet–triplet energy separations depend more on through-space than on through-bond coupling in **4** and **5**; the relative importance of these two types of coupling is reversed in **6**.

With respect to making **5**, we estimate the strain energy to be huge (255 kcal mol⁻¹), although the biradicals couple as singlets and hence constitute a “face-diagonal” bond that would, however, be exceedingly long (1.844 Å). Notwithstanding these findings, we hope to be able to prepare **5** under low temperature matrix conditions (4–6 K), where it is expected to be kinetically stabilized — as cubane derivatives typically are — due to the rigid hydrocarbon framework. Work in this direction is underway and will be reported in due course.

Acknowledgments

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