more efficient line narrowing that leads to higher image resolution and less severe artifacts. Also, development of postprocessing techniques to correct for resonance offset effects is currently underway.

In addition to 3-D mapping of proton density, an immediate extension of this technique is the examination of polymer microstructure (such as cross-link density, homogeneity in blends, and crystallinity) utilizing relaxation[22] (T_1 and $T_{1\rho}$) and spin-diffusion-weighted image protocols. Direct experimental measurement of morphological changes affected by stress, physical aging, phase transitions, annealing, mechanical and thermal degradation, and oxidation is also possible.

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Ab Initio Calculations of the Relative Energies of Homocub-1(9)-ene and Homocub-9-ylidene. How Strong Is the Twisted "π" Bond in the Olefin? What Is the Ground State of the Carbene?

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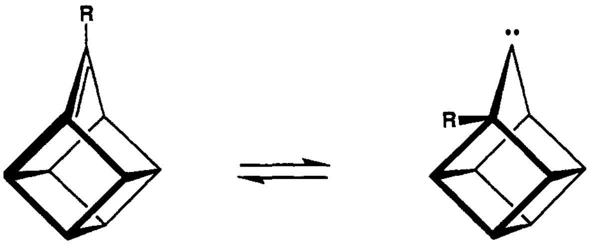
Rearrangements of carbenes to olefins are usually highly exothermic and, hence, irreversible reactions.[1] Nevertheless, bridgehead olefins with sufficient torsional strain are capable of undergoing reversion to carbenes.[2] The best and most recently studied example of the latter process was discovered by Eaton and Hoffmann in the rearrangement of 9-phenylhomocub-1(9)-ene (**1a**) to 1-phenylhomocub-9-ylidene (**2a**).[3] Subsequent investigations in the desphenyl series demonstrated that the olefin (**1b**) can also be formed from the carbene (**2b**),[4] and experiments by Jones, Platz, and co-workers have found the equilibrium constant for this reaction to be approximately unity at room temperature.[5]



1a, R = Ph
1b, R = H

2a, R = Ph
2b, R = H

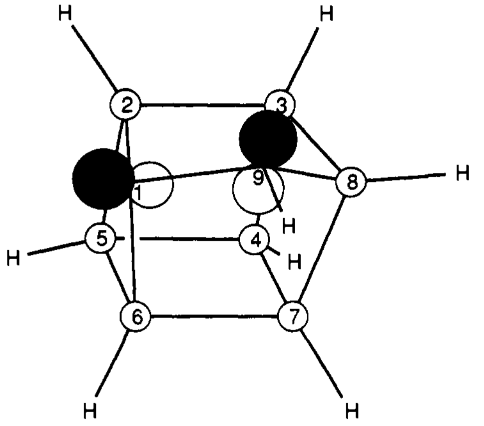


Figure 1. GVB/6-31G* optimized geometry for **1b**, depicting the alignment of the atomic orbitals at C_1 and C_9 that results from the pyramidalization at C_9.

Table I. Relative Energies Calculated at the GVB/6-31G* Level for Singlets and at the ROHF/6-31G* Level for Triplets

molecule, state, geometry, symmetry	energy (kcal/mol)
1b, singlet, equilibrium geometry, C_1	3.8
1b, singlet, C_9 planar, C_s	8.2
1b, triplet, equilibrium geometry, C_1[a]	5.0
2b, singlet, equilibrium geometry, C_s[b]	0[c]
2b, triplet, equilibrium geometry, C_{2v}	1.6

[a] This geometry, with the hydrogen at C_9 31.8° out of the plane defined by C_1, C_8, and C_9, is lower by 1.4 kcal/mol than the optimized C_s geometry in which the hydrogen at C_9 lies in this plane. [b] This geometry, in which C_9 is tilted 13.0° out of the plane defined by C_1, C_5, C_4, and C_8, is 0.2 kcal/mol lower in energy than the optimized C_{2v} structure, in which all five carbons lie in the same plane. [c] $E = -345.2291$ hartrees.

In this communication we report the results of ab initio calculations on the relative energies of **1b** and **2b**. Our calculations not only confirm that **1b** and **2b** are nearly isoenergetic but also they predict that only 4.4 kcal/mol is required to break the highly twisted "π" bond in olefin **1b**, and they indicate a singlet ground state for carbene **2b**.

GVB calculations that correlate one pair of electrons provide adequate wave functions for the weakly bonding pair of electrons in a deformed alkene[6] and also for the pair of nonbonding electrons in a singlet carbene.[7] Therefore the geometries of both **1b** and **2b** were optimized[8] with GVB-PP(1) calculations,[9] using both the 3-21G[10] and 6-31G* basis sets.[11] Vibrational analyses,[12] per-

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formed with the smaller basis set, found both **1b** and **2b** to be true minima. The geometries of the lowest triplet state of **1b** and **2b** were optimized[8] at the ROHF level,[9] using the same basis sets.

The optimized geometry of **1b** is shown in Figure 1, and the energies of the lowest singlet and triplet states of **1b** and **2b** are given in Table I. At the GVB level of theory, alkene **1b** is calculated to be 3.8 kcal/mol higher in energy than the carbene **2b**. This energy difference corresponds to an enthalpy difference of $\Delta\Delta H_f^{298}$ = 3.6 kcal/mol, after correction for the very small differences in zero-point energies and heat capacities.

Since CI calculations on **1b** and **2b** were beyond our computational resources, we performed multireference (MR) SDCI calculations[13] on ethylene and ethylidene models to investigate the probable effect of providing additional electron correlation for **1b** and **2b**. All the bond angles and C–C bond lengths in the C_2H_4 models were frozen at the values for C_1 and C_9 in **1b** and **2b**, and the C–H bond lengths in the models were optimized at the GVB/6-31G* level. SDCI calculations were performed, using three reference configurations for the twisted ethylene and two for the ethylidene.[14]

At the GVB level, the twisted ethylene model for **1b** is 4.9 kcal/mol higher in energy than the ethylidene model for **2b**. The good agreement of this GVB energy difference with that of 3.8 kcal/mol, computed between **1b** and **2b**, is indicative of the adequacy of the twisted ethylene/ethylidene model for **1b**/**2b**. At the MR-SDCI level of theory, the energy difference between the model alkene and carbene decreases to 2.1 kcal/mol. This finding suggests that a similar decrease of about 2.8 kcal/mol would be found in the energy difference between **1b** and **2b**, if the energies of these two isomers were recalculated at the MR-SDCI level.

After correction of the GVB/6-31G* energy difference of 3.8 kcal/mol between **1b** and **2b** for differences in zero-point energies, heat capacities, and estimated MR-SDCI correlation energies, our calculations predict that the ΔH_f^{298} of **1b** is higher than that of **2b** by 0.8 kcal/mol. The entropy of **2b** is calculated to be 1.1 eu greater than that of **1b**, resulting in a predicted free energy change of $\Delta G^{298} = -1.1$ kcal/mol for the conversion of **1b** to **2b**. This computational result is in excellent agreement with the experimental finding that the equilibrium constant between **1b** and **2b** is near unity.

Table I contains information about the electronic structure of each of these two isomers. At the GVB-ROHF/6-31G* level of theory, the singlet state of carbene **2b** is predicted to be the ground state by 1.6 kcal/mol. Since GVB-ROHF/6-31G* calculations *overestimate* the stability of triplet methylene, relative to the lowest singlet, by more than 5 kcal/mol,[7,15] confidence in the prediction that **2b** does, in fact, have a singlet ground state seems warranted. The chemistry observed for **2b**[4,5] is consistent with the singlet being the ground state or, at least, the reactive state.

Part of the reason for the finding of a singlet ground state for **2b** is the constrained C–C–C bond angle at C_9.[16] The GVB/6-31G* optimized bond angle in singlet **2b** of 97.5° is slightly smaller than that of 102.3° in singlet methylene. In contrast, the ROHF/6-31G* optimized bond angle of 101.1° in triplet **2b** is considerably smaller than the ROHF/6-31G* value of 128.5° in triplet methylene.

However, angle constraint is not wholly responsible for the singlet ground state predicted for **2b**. When GVB and ROHF/6-31G* calculations were performed on singlet and triplet methylene, with the bond angle in each state constrained to be the same as that predicted at C_9 in the appropriate state of **2b**, the singlet–triplet splitting was reduced from the 14.5 kcal/mol,[15] calculated at the equilibrium geometry for each state, to 4.6 kcal/mol; but the triplet was still found to be the ground state.

This result suggests that interaction of the nominally empty p orbital at C_9 in **2b** with the strained C–C bonds of the homocubyl skeleton provides an additional 6.0 kcal/mol of selective stabilization for the singlet.[17] Qualitatively consistent with this inference is our finding that GVB-ROHF/6-31G* calculations on 2-propylidene give a singlet–triplet splitting of 7.6 kcal/mol for the unconstrained carbene, −1.8 kcal/mol when each state is constrained to have the same C–C–C bond angle as the corresponding state in **2b**, and −6.5 kcal/mol when the bond angles at the methyl hydrogens are also constrained to mimic the bond angles at the bridgehead carbons in **2b**.

The rigid constraints of the homocubyl skeleton are also responsible for weakness of the "π" bond between C_1 and C_9 in **1b**. Were it not for the dramatic pyramidalization of C_9,[19] which, as depicted in Figure 1, allows some overlap between the atomic orbitals on these two carbons, the two orbitals would be orthogonal by symmetry. Even at the equilibrium geometry of **1b**, the occupation number of only 1.42 for the bonding combination of these two orbitals is indicative of a large amount of diradical character[6] in the GVB wave function for **1b**. Planarizing C_9, which breaks the "π" bond to C_1, is calculated to require only 4.4 kcal/mol at the GVB/6-31G* level and to increase the C_1–C_9 bond length of 1.451 Å in **1b** by only 0.036 Å.

As shown in Figure 1, the predicted pyramidalization of C_9 results in none of the nine carbons being equivalent by symmetry at the equilibrium geometry of **1b**. Inversion of C_9 leads to site exchange between two sets of two carbons each and should result in the nine lines, predicted for the ^{13}C NMR spectrum of **1b** when inversion is slow, coalescing to seven lines, when inversion is fast. Thus, provided that tunneling does not provide the major pathway for inversion at C_9 and that inversion occurs faster than rearrangement to **2b**,[20] the temperature dependence of the ^{13}C NMR spectrum of **1b** should provide an experimental estimate of the energy required to planarize C_9 and, hence, break the very weak "π" bond in this torsionally strained, bridgehead olefin.

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Supplementary Material Available: Listing of optimized geometries for **1b** and **2b** (17 pages). Ordering information is given on any current masthead page.

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[13] MR-SDCI calculations were carried out using MELDF: McMurchie, L.; Elbert, S.; Langhoff, S.; Davidson, E. R.; Feller, D.; Rawlings, D.

[14] The C_1 symmetry of **1b** and, hence, of the ethylene model for it requires that a third configuration be included in the CI wave function for the two "π" electrons.[6] However, omitting this third configuration from the reference space gave an SDCI energy that was only 0.5 kcal/mol higher than when this configuration was included. The MR-SDCI wave function for the ethylene model consisted of 107 113 spin-adapted configurations, whereas the C_s symmetry of the ethylidene model reduced the number of configurations in its MR-SDCI wave function to 30 961.

[15] Very large basis sets are required in order to obtain a calculated singlet–triplet splitting in methylene that is within 1 kcal/mol of the experimental value of 9.1 kcal/mol.[7]

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[17] The findings that 9-homocubyl tosylate solvolyzes faster than expected[18a] and that the carbocation formed undergoes rapid degenerate rearrangements[18a,b] are consistent with the existence of such an interaction.

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[19] The angle between the C_9–H bond and the plane defined by C_1, C_8, and C_9 is 43.2°. Pyramidalization of the carbons in torsionally strained alkenes, in order to maximize overlap, has been previously discussed: Mock, W. L. *Tetrahedron Lett.* **1972**, 475. Radom, L.; Pople, J. A.; Mock, W. L. *Tetrahedron Lett.* **1972**, 479. Haddon, R. C. *Acc. Chem. Res.* **1988**, *21*, 243.

[20] Reversible rearrangement to **2b** eventually results in site exchange of all eight C–H groups in **2a**.[4b] Thus, it should be easy experimentally to distinguish this process from inversion of C_9, because of the very different effects that these two processes should have on the ^{13}C NMR spectrum of **2a**.