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Inverted Carbon Geometries: Challenges to Experiment and Theory

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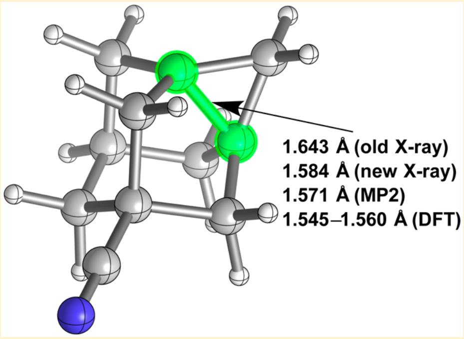
S *Supporting Information*

ABSTRACT: Disproving a long C−C-bond textbook example: The reported 1.643 Å C−C bond in 5-cyano-1,3-dehydroadamantane was redetermined and "only" amounts to 1.584 Å. While this value is well reproduced with *ab initio* methods, some common DFT approaches perform poorly and are only consistent with CCSD(T)/cc-pVTZ optimizations for noninverted carbons. Large deviations from experiment were also found for other molecules with atypical electron density distributions, e.g., cubane, bicyclo[2.2.0]hexane, and bicyclo[2.1.0]- and bicyclo[1.1.1]pentane, thereby presenting challenging structures for some DFT implementations.



Highly strained small-ring polycyclic molecules such as cubanes,[1] tetrahedranes,[2] staffanes,[2] fenestranes,[2] triangulanes,[3] and many others[4] often display highly unusual bonding arrangements. One of the most intriguing and long-standing discussions is associated with the structures and bonding in small-ring propellanes and, especially, with their smallest representative [1.1.1]propellane[5] (**1**, Figure 1). The poor orbital overlap between the two inverted carbon atoms on the concave face in combination with high strain (estimated to be 98−103 kcal mol^{-1})[6] rendered the preparation of **1** "problematic".[7] Since its first preparation,[8,9] the nature of the central C−C bond in **1** has been puzzling theoreticians and experimentalists alike.[10,11] The bonding situation in this molecule is clearly unusual, as it does not display a bond critical point (based on the theory of atoms in molecules[12]) between the inverted carbons, which would be characteristic for a covalent bond. Although "charge-shift" bonding was suggested for **1**,[13] the "nonbonding"[14,15] situation is in line with the observation that its central bond *shortens* upon ionization of **1** to the radical cation.[16] Despite the high rigidity of **1**, the computed distance between two inverted carbons strongly depends on the computational method (Figure 1).

The best match with the experimental 1.594(5) Å C−C bond distance determined through gas electron diffraction[17] and 1.60 Å from single crystal X-ray diffraction[18] thus far was achieved at CASPT2/6-31(d) (1.596 Å),[13] which is identical to our MP2/cc-pVTZ and CCSD(T)/cc-pVTZ data (Figure 1). While MP2/cc-pVDZ overestimates the C−C bond distance relative to MP2/cc-pVTZ, further basis set extension to cc-pVQZ and cc-pV5Z has little effect on the geometry of **1**.

Several commonly used DFT methods, especially M06-2X, underestimate the central C−C bond distance of **1**, likely due to unusual electron localization.[19] Basis set extensions, which M06-2X is somewhat sensitive to,[20] have only minimal effect on the geometry of **1** as the C−C distance remains constant within ±0.002 Å with aug-cc-pVXZ (X = 2−5) basis sets. To probe the DFT computations for the descriptions of the inverted geometry of carbon, we optimized several [*n.n.n*]propellanes (*n* = 1−3) ranging from the extreme case of **1** to [3.3.3]propellane with an almost normal tetrahedral geometry around the quaternary carbons (Figure 2).

To judge the degree of inversion we chose the deviation of the angle sum around the central carbons from the idealized tetrahedral arrangement. For the [1.1.1], [2.1.1], and [2.2.1]-propellanes with inverted carbon atom geometries the B3LYP, B3PW91, and M06-2X functionals systematically underestimate the central C−C distance relative to MP2/cc-pVQZ and CCSD(T)/cc-pVTZ. The situation changes for larger propellanes that comprise "normal" tetrahedral carbon geometries where both DFT and *ab initio* results agree very well. We conclude that the DFT methods under consideration are not able to describe the interactions between the inverted carbons possibly due to overestimation of medium-range correlation between the electron densities outside the central C−C axis. This observation is in line with the fact that M06-2X, which was parametrized to include medium-range electron correlation,[21] displays even shorter central CC distances than B3LYP and B3PW91.

In contrast to **1**, which is very reactive toward oxygen and other electrophiles,[22] the relatively stable polycyclic [1.1.1]-

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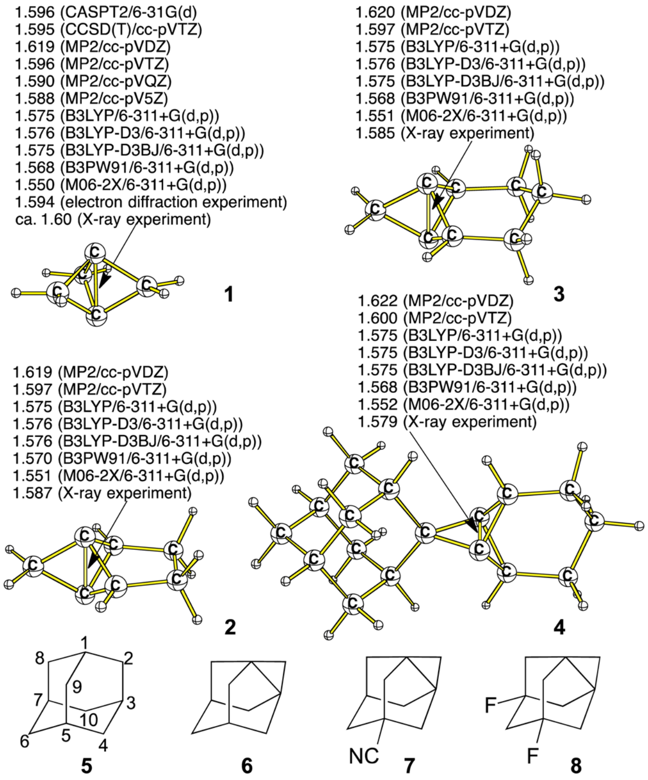


Figure 1. Computed and experimental central C−C bond distances (in Å) of [*n*.*n*.1]propellanes (**1**−**4**); adamantane (**5**) with numbering of carbon atoms, and selected derivatives (**7** and **8**) of 1,3-didehydroadamantane (**6**).

propellane derivatives **2**−**4** (Figure 1) do not react with oxygen under ambient conditions. They were characterized through X-ray crystal structure analyses,[23] indicating that the propellanic C−C distances are shorter than that of **1**. As stated above, the DFT methods underestimate the experimental bond length in **2**−**4** (1.575−1.576 Å at B3LYP, B3LYP-D3[24] and B3LYP with Becke-Johnson damping (B3LYP-D3(BJ)),[25] and 1.551−1.552 Å at M06-2X[26] with a 6-311+G(d,p) basis set); the latter shows again the largest deviation. As in the case of **1**, the basis set size influences the MP2 geometries of **2**−**4** considerably (1.619 Å vs 1.597 Å for **2** and 1.622 Å vs 1.600 Å for **4** with cc-pVDZ and cc-pVTZ, respectively). The MP2 method with the cc-pVTZ basis set describes the geometry of the inverted carbons in the [1.1.1]propellanic system well. However, the relevance of this approach to the larger [*n*.*n*.1]propellanic systems with inverted carbons ($n \leq 3$) still is questionable.

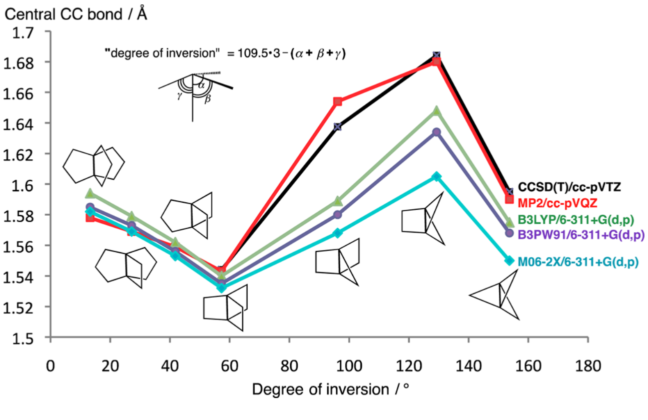
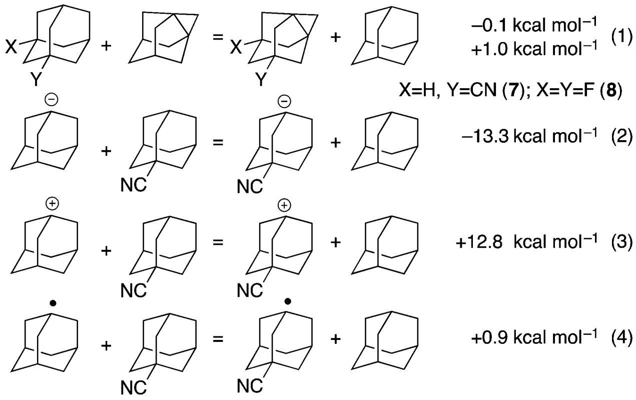


Figure 2. Central CC bond distances in the [*n*.*n*.*n*]propellane series (n = 1−3) at various DFT and *ab initio* levels.

In contrast to the extreme cases of **1**−**4**, the tricyclic hydrocarbon adamantane (**5**) is a molecule with little strain[27] where removal of two of the four bridgehead hydrogens results in sensitive but isolable 1,3-didehydroadamantane (**6**), a [3.3.1]propellane with two inverted carbons.[28] Derivatives of **6** have been synthesized,[29] with 5-cyano-1,3-didehydroadamantane (**7**) being the first relatively stable one;[30] it was characterized by NMR[31] and X-ray crystal structure analysis.[32] Another known derivative in this series is 1,3-didehydro-5,7-difluoroadamantane (**8**).[33] The parent didehydroadamantane **6** and the substituted derivatives **7** and **8** are reactive but isolable compounds. The role of the substituent in the thermodynamic stabilization of **7** and **8** is negligible: homodesmotic[34] eq 1 reflecting the influence of the cyano group in **7** is thermoneutral (−0.4 kcal mol^{-1} at B3LYP/6-311+G(d,p) and −0.1 mol^{-1} at MP2/cc-pVTZ, ΔH_0). The analogous equation for **8** is even slightly endothermic (+1.0 kcal mol^{-1} at MP2/cc-pVTZ). While the electron-withdrawing properties of the substituents have virtually no effect on the neutrals (eq 1), the situation changes for the charged species (eqs 2 and 3), which show high exothermicity and endothermicity at MP2/cc-pVTZ, respectively. In line with eq 1 for the closed shell neutrals, eq 4 for the radicals is also thermoneutral.



Partial withdrawal of the electronic density from the inverted carbon atoms to the antibonding orbital of an electron-withdrawing cyano group leads to slight elongation of the CN bond in **7**. This effect is more pronounced in the 1-cyanoadamant-3-yl anion **7a**$^{-}$ due to effective 1,4-hyperconjugation through the adamantyl moiety. The fact that the same types of interactions are present in **7** and **7a**$^{-}$ is corroborated through the shapes of their highest occupied molecular orbitals (HOMOs, Figure 3).

The electronic density shift increases the propellanic C−C "bond" length in **7** vs parent **6** (1.571 vs. 1.568 Å, MP2/cc-pVTZ), indicating that the bonding situation in **6** and **7** must be similar to that of **1**. The reported experimental value for the central C−C distance in **7** of 1.643(4) Å was determined at room temperature and solved by direct methods with least-squares refinement to an *R*-value of 4.8%.[32] This long bond has been a textbook example for many years,[35] but it is much longer than our computed values at the MP2/cc-pVTZ as well as at various DFT levels (Table 1). To resolve this large discrepancy between experiment and theory, we resynthesized **7** using the previously published protocol[30] and solved its X-ray crystal structure (see Supporting Information (SI) for details) at 200 K

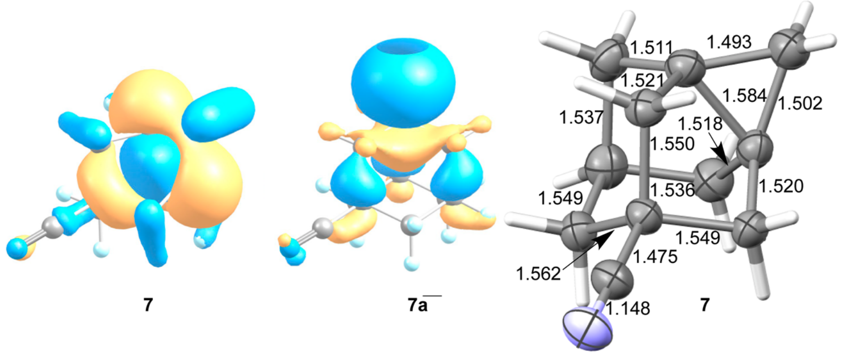


Figure 3. HOMOs of 7 and its **7a**$^-$ and the X-ray crystal structure geometry of 7 with interatomic distances in Å (right, ellipsoid contour probability level = 65%).

Table 1. C1−C3 Bond Lengths Computed for 1 and 6−8 at MP2 and DFT Levels with the cc-pVTZ Basis Set

compd	MP2	B3LYP	B3LYP-D3	B3LYP-D3(BJ)	M06-2X	expt
1	1.596	1.568	1.568	1.568	1.546	1.594[a]
6	1.568	1.554	1.557	1.556	1.546	n.a.
7	1.571	1.560	1.556	1.555	1.545	1.643[b] 1.584[c]
8	1.611	1.595	1.593	1.593	1.574	n.a.

[a]From electron diffraction.[17] [b]X-ray structure diffraction.[32] [c]X-ray structure diffraction, this work.

(Figure 3). Our X-ray structure solution provides a value of 1.5838(18) Å for the C1−C3 distance, in reasonable agreement with the MP2/cc-pVTZ (1.571 Å) computations for 7 (Table 1), but at variance with the earlier structure determination (1.643 Å).[32] Taking into account that the bond lengths in hydrocarbons determined through X-ray diffraction often are shorter[36,37] than in the gas phase,[38] we find that the B3LYP-D3 (1.555 Å), B3LYP-D3(BJ) (1.555 Å), and M06-2X functionals (1.545 Å) deviate substantially from experiment (Table S1) and suggest an even shorter propellanic central C−C distance. This is not merely a basis set effect as the B3LYP computed values deviate only by ±0.005 Å with cc-pVDZ (1.565 Å), 6-311+G(d,p) (1.562 Å), 6-311+G(3df,2p) (1.557 Å), and aug-cc-pVTZ (1.556 Å) basis sets. Similarly, relatively short bond distances were obtained for parent **6** and difluoride **8** at various levels of theory.

Apparently, several of the DFT methods utilized here, in contrast to MP2, are not able to reproduce the bonding between the inverted carbons properly. In order to make a comparison of the structures of **6**−**8** present in solution and various theoretical as well as experimental geometries, we computed the ^{13}C NMR chemical shifts[39] using the GIAO-MP2/cc-pVTZ-method.[40] For parent **6** and difluoro derivative **8** experimental ^{13}C NMR chemical shifts are available and our computations for the MP2/cc-pVTZ-geometries yield correlation coefficients R^2 between experiment and theory of greater than 0.99. Table S1 (SI) compiles experimental and theoretical values for **7** employing various geometries. NMR data for the X-ray diffraction geometries were computed for the experimentally found C_1 point group (using the Cartesian coordinates for the heavy atoms from the crystal structure and adding the hydrogens in idealized positions) and were averaged according to C_s-symmetry constraints. Although the computed values are systematically too large, the overall agreement for the computed geometries is excellent, apparently implying a very similar geometry for **7** in solution and in the gas phase (cf. SI). The computed shifts for the experimental X-ray geometry determined previously[32] deviate much more from the measured values in solution, especially for C1 and C2 of the three-membered ring. To probe the sensitivity of the ^{13}C NMR shift with respect to geometry changes, we scanned the potential energy surface of **7** by varying the C1−C3 distance but found that the GIAO-MP2//cc-pVTZ//MP2/cc-pVTZ computed shifts do not change much and the potential well around the equilibrium bond length is quite flat. The energy difference of **7** with a propellanic C−C bond of 1.571 or 1.640 Å is only 0.6 kcal mol^{-1} at MP2/cc-pVTZ//MP2/cc-pVTZ and 0.9 kcal mol^{-1} at CCSD(T)/cc-pVTZ//MP2/cc-pVTZ. This is in full agreement with the energy profile computed for **1**, where elongation of this bond within the 1.6−1.8 Å interval causes only little changes (Figure S1).[13] The scan also shows that the ^{13}C NMR shifts are not sensitive to geometric changes in the propellanic bonds implying that the electronic structure of the C1−C3 bond does not change dramatically upon elongation. This explains the apparently good agreement of ^{13}C NMR chemical shifts for the otherwise poorly performing M06-2X functional.

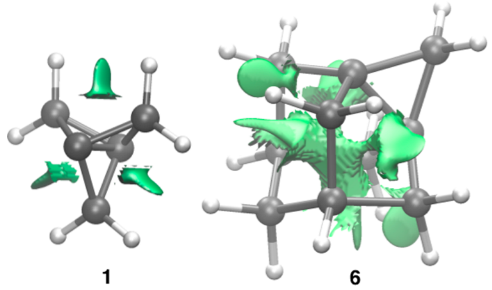


Figure 4. NCI isosurfaces for [1.1.1]propellane (**1**) and 1,3-dehydroadamantane (**6**).

We conclude that MP2 computations with a polarized TZ basis set, in contrast to M06-2X, reproduce the experimental distances between the inverted carbons in propellanes well. Including *a posteriori* dispersion corrections for the DFT methods does not change the situation, reflecting a negligible influence of dispersion to the central C−C bonds in

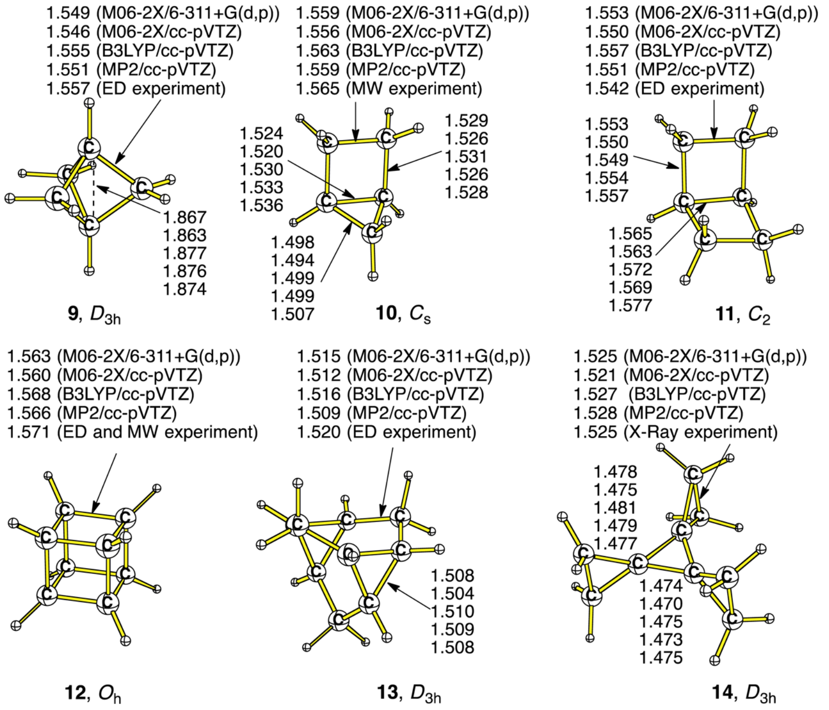


Figure 5. Bond distances (Å) in hydrocarbons **9**−**14** optimized at various levels of theory vs microwave (MW), electron diffraction (ED), and X-ray experimental data.

propellanes. This is seen from the noncovalent interaction (NCI)[41] surface plots for **1** and **6** where such types of interaction are observed between the CH and CH_2 moieties but not around the central C−C bond (Figure 4).

The shortening of the central C−C bonds at M06-2X possibly is due to overestimating the interaction between the electron densities *outside the inverted carbons* because this method is parametrized to capture medium range electron correlation rather than explicit van der Waals effects.[26] In a similar vein, we note that the experimental bond length in F_2 (1.412 Å,[42] and 1.401 Å at MP2/aug-cc-pVTZ) also is not well reproduced with M06-2X/aug-cc-pVTZ (1.365 Å). The question arises whether this is also found for other strained small-ring structures with M06-2X. We thus optimized a number of rigid hydrocarbons that comprise distorted tetrahedral carbon geometries and whose structures are experimentally known, namely bicyclo[1.1.1]pentane (**9**),[43] housane (**10**),[44] bicyclo[2.2.2]hexane (**11**),[45] cubane (**12**),[46] triasterane (**13**),[47] and [3]rotane (**14**)[48] (Figure 5).

While all our reference methods are able to reproduce the geometries of **13** and **14** satisfactorily, the situation with highly distorted molecules **9**−**12** is similar to that found for small-ring propellanes: The M06-2X method underestimates the bond distances between the carbons with highly distorted tetrahedral arrangements in **9** (53°), **10** (47°), **11** (30°), and **12** (48°).

Generally, heavily parametrized DFT methods such as M06-2X perform very well for molecules whose structures are strongly affected by noncovalent interactions;[49] however, this is not the case for structures **1**−**4** and **5**−**12** where geometrical distortions cause uncommon electron density distributions. Such molecules keep challenging DFT implementations.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Crystallographic information framework file for CCDC 1043567. Cartesian coordinates and absolute energies of all optimized geometries; NMR chemical shift comparisons; and X-ray data. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b00845.

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Notes

The authors declare no competing financial interest.

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■ DEDICATION

In memoriam of Paul von Ragué Schleyer for his seminal contributions to chemistry.

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