THE JOURNAL OF PHYSICAL CHEMISTRY A LETTERS

2008, *112,* 2131−2133

Ab Initio Structures for 90°-Twisted *s-trans*-1,3-Butadiene and Cyclooctatetraene: The Naked sp^2−sp^2 Bond

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Received: October 4, 2007; In Final Form: November 26, 2007

The bond length of a carbon−carbon sp^2−sp^2 σ-bond without the perturbing effects of π-interactions has been estimated by high level calculations on two prototypical systems: a 90°-twisted form of butadiene and the tub conformer of cyclooctatetraene. The former system yields a value of 1.4818 Å, considerably longer than previous estimates. The corresponding bond length in the latter is slightly shorter due to some π-electron delocalization.

A longstanding issue in structural chemistry is the length of a naked C−C sp^2−sp^2 σ-bond, i.e., this bond without the clothing of some π-electron contribution. No simple molecule presents an example of such a bond. In 1959, Dewar and Schmeising estimated the sp^2−sp^2 bond length to be 1.471−1.479 Å by comparing bond lengths in various small hydrocarbons with differently hybridized carbon atoms and by energy/bond length arguments.[1] Recently, Craig et al. used another argument to arrive at a bond length of 1.470 Å from the modern, near-equilibrium bond lengths in propene and ethane.[2,3] The shrinkage in bond length from ethane (sp^3−sp^3) to propene (sp^2−sp^3) was applied to the sp^2−sp^3 bond length in propene to estimate the desired sp^2−sp^2 bond length. This estimate of the naked sp^2−sp^2 σ-bond length was used to demonstrate the structural consequences of π-electron delocalization in *s-trans*-1,3-butadiene.[2]

Because of the approximations involved in deriving the previous estimates of the sp^2−sp^2 bond length, we have reexamined the issue through a series of high level calculations of prototypical systems. One limitation in our previously reported estimate was that only *near*-equilibrium structures of propene and ethane were available. Another assumption was that the shrinkage in the bond length is linear in going from sp^3−sp^3 in ethane and sp^2−sp^3 in propene over to sp^2−sp^2 in similar molecules. A third approximation was neglecting the role of additional atoms in propene compared to ethane. We now report the results of highly correlated ab initio structural calculations addressing the question of the naked sp^2−sp^2 bond length. The first structure is that of the 90°-twisted form of butadiene. The other is the tub conformer of cyclooctatetraene. In twisted butadiene, which is close to a transition state on the internal rotation potential surface, the π-electron clouds are nearly orthogonal and thus not subject to delocalization. For comparison with the ab initio and semiexperimental structures of *s-trans*-butadiene, we computed the structure of 90°-twisted butadiene at the same high level of theory. The optimizations were performed with the MOLPRO program package at the CCSD(T)(FC)/aug-cc-pV*n*Z (n = D,T,Q) levels of theory, followed by extrapolation to the complete basis set (CBS) limit and corrections for core/valence electron correlation and scalar relativistic effects.[4−6] Figure 1 shows the two forms of butadiene with the p orbitals indicated.

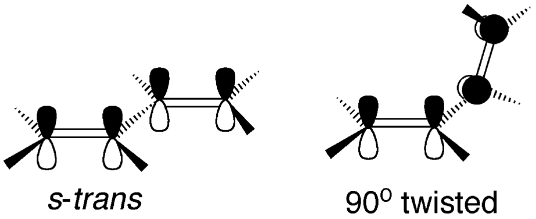

Figure 1. Sketches of *s-trans* and 90°-twisted butadiene emphasizing p orbitals.

Table 1 compares the calculated CC and CH bond lengths for *s-trans*-butadiene,[4] 90°-twisted butadiene, and the tub conformer of cyclooctatetraene. This table also contains the values for the semiexperimental equilibrium structure of *s-trans*-butadiene,[2] the X-ray structure for cyclooctatetraene,[7] and the electron diffraction structure for cyclooctatetraene.[8] The excellent agreement between the semiexperimental equilibrium structure and the ab initio structure for *s-trans*-butadiene, as well as the comparisons on a much larger collection of molecules,[4] supports the conclusion that calculations at this level should be capable of accurate structural predictions.

The C═C and C−C bond lengths in 90°-twisted butadiene are the lengths for isolated bonds. (In the discussion in this paper, we use C═C and C−C as labels for bonds that are localized or participate in some delocalization.) The calculated C═C bond length of 1.3329 Å in 90°-twisted butadiene is close to the C═C bond length of 1.3305 Å obtained for the semiexperimental structure of ethylene.[2] We believe that the C−C bond length of 1.4818 Å is the first accurate value for a pure sp^2−sp^2 σ-bond length. This value is longer than the previous estimate of 1.470 Å. The greater length may reflect on some of the approximations in the earlier estimates. The slight

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10.1021/jp7097334 CCC: $40.75

TABLE 1: Equilibrium Structures for Butadiene and Cyclooctatetraene

	butadiene			cyclooctatetraene (tub)		
	s-trans semiexptl[a]	*s-trans* ab initio[b]	90°-twist ab initio	ab initio	X-ray[c]	electron diffract.[d]
$r_{C=C}$/Å	1.3376	1.3377	1.3329	1.3407	1.333	1.334(1)
r_{C-C}/Å	1.4539	1.4548	1.4818	1.4668	1.469	1.462(1)
$r_{C-H\alpha}{}^{e}$/Å	1.0847	1.0846	1.0852	1.0879		1.090(5)
$r_{C-Hc}{}^{e}$/Å	1.0819	1.0823	1.0819			
$r_{C-Ht}{}^{e}$/Å	1.0793	1.0799	1.0808			
dihedr angle[f]	0	0	90	57.8	57.2	

[a] Reference 2. [b] Reference 4. [c] Average values. Reference 7. [d] Reference 8. Uncertainty in last place given in parentheses. [e] α for interior hydrogen atoms; c for hydrogen atoms cis to the C−C bond; t for hydrogen atoms trans to the C−C bond. [f] C═C−C═C dihedral angle.

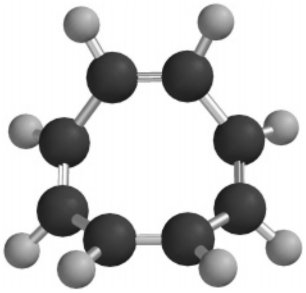

Figure 2. Tub rotamer of cyclooctatetraene.

lengthening of the isolated C═C bond in 90°-twisted butadiene relative to ethylene can be attributed to steric effects caused by the greater number of atoms in the former. This observation suggests that the sp^2-sp^2 σ-bond in 90°-twisted butadiene may also be somewhat longer than the σ-bond length in ethylene without the contribution of π-bonding. However, the present sp^2-sp^2 bond length in 90°-twisted butadiene is the best reference value. It confirms that the C−C bond in *s-trans*-butadiene is shortened significantly compared to a naked sp^2-sp^2 bond. In summary, comparison of bond lengths in *s-trans*-butadiene with those in 90°-twisted butadiene confirms that π-electron delocalization in butadiene lengthens the C═C bonds and shortens the C−C bond in accord with theory.

At the CCSD(T) CBS limit, the 90°-twisted form of butadiene lies 25.5 kJ/mol higher in energy than the s-trans conformer, ignoring zero point vibrational energies. When zero point energies are included, the energy difference decreases to 23.7 kJ/mol. The nearby transition state at approximately 77°,[9] separating the s-trans and s-gauche minima on the rotational potential surface, is ∼1.8 kJ/mol higher in energy, leading to a barrier of 25.5 kJ/mol when zero point energies are included. This result is in good agreement with an approximate experimental value of 25 kJ/mol.[9] Compared to the s-trans form, the s-gauche form is estimated from the potential function, obtained from the Raman spectrum of the torsional mode, to be 12 kJ/mol higher in energy.[9] Another value is 12.24 kJ/mol from the analysis of the temperature dependence of the electronic spectrum.[10]

Seeking a stable molecule, as distinct from a near transition state, to evaluate the length of an isolated sp^2-sp^2 σ-bond length, we computed the structure of the favored tub conformer of cyclooctatetraene, which is shown in Figure 2. The bond lengths from this calculation are given in Table 1 in comparison with those reported in the X-ray[7] and electron diffraction[8] investigations. The optimized ab initio structure for cyclooctatetraene deviates slightly from the expected D_{2d} symmetry. Thus, the C═C bond length in Table 1 is an average of two values that differ by 0.0003 Å. In the X-ray investigation of a crystal at 129 K with calculated corrections for thermal contributions from vibrations, differences were found in the C−C and C═C bond lengths, which could be attributed to uncertainties in the determinations of bond lengths or to some twisting due to crystal packing. Average values from the X-ray investigation for the C═C and C−C bond lengths are given in Table 1. Although the electron diffraction results (no corrections for vibrations) and the X-ray results are in reasonable agreement with the ab initio calculations, we regard the latter as a better characterization of isolated cyclooctatetraene molecules.

Compared to the C═C and C−C bond lengths in 90°-twisted butadiene, the corresponding bond lengths in cyclooctatetraene were surprising. The C═C bond seems too long, and the C−C bond, too short. In cyclooctatetraene, despite expectations from simple models, the dihedral angle between two C═C bonds and the connecting C−C bond is only 58°. The π-bonds are not orthogonal, and some π-electron delocalization presumably occurs. Because of the continuous, cyclic conjugation in cyclooctatetraene, π-electron delocalization should be enhanced (cf. benzene and hexatriene). Thus, despite our original expectation that cyclooctatetraene would provide another example of isolated C═C and C−C bonds in a conjugated system, we now have structural evidence for some π-electron delocalization in this molecule.

The theoretical CH bond length in cyclooctatetraene of 1.0879 Å is about 0.003 Å longer than the interior CH bond in the two forms of butadiene. This increased length is consistent with the dihedral angle of 48° for the H−C−C−H bond system, implying that the CH bond in cyclooctatetraene has some added p character even though the H−C═C−H dihedral angle is 0°.

In conclusion, a high level ab initio determination of the structure of 90°-twisted butadiene gives 1.4818 Å for an isolated sp^2-sp^2 σ-bond and 1.3329 Å for an isolated C═C bond in a C_4 hydrocarbon molecule. The zero point inclusive energy of the 90°-twisted form of butadiene is 23.7 kJ/mol higher than the energy of the s-trans conformer.

Acknowledgment. The calculations were done on the Beowulf cluster at Oberlin College. A National Science Foundation Grant (0420717) and Oberlin College supported this installation. Colleagues Manish A. Mehta, Matthew J. Elrod, and Nathaniel E. Daniels provided invaluable assistance in the computations. N.C.C. was supported by a Senior Scientist Mentor Grant from the Dreyfus Foundation.

Supporting Information Available: Tables containing the Cartesian coordinates and internal coordinates for 90°-twisted butadiene and the tub conformer of cyclooctatetraene. This material is available free of charge via the Internet at http://pubs.acs.org.

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