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Orthogonene Redux: A Nearly Orthogonal Alkene Predicted to Exhibit Considerable Stability. A Computational Study

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A strongly twisted, as yet unknown, alkene, orthogonene (tetracyclo[8,2,2,$0^{2,7}$,$0^{3,10}$]tetradecene-2(3)), was computationally reinvestigated: earlier work had indicated that the stereoisomer with the pair of bridgehead hydrogens on the methine group at one end of the double bond *syn* to the pair at the other end (C−H/C−H "up−up/up−up", C_2 symmetry, B3LYP/6-31G* double bond angle 83°) is at best of low stability, rearranging with a very small barrier to a carbene or possibly a cyclopropane. Here it is shown that the *anti* ("up−up/down−down") stereoisomer (ideally D_2 symmetry, CASSCF(4,4)/6-31G* double bond torsional dihedral angle 88°) is much more stable: the barrier to rearrangement to a carbene is calculated to be ca. 200 kJ mol^{-1} (CASSCF(4,4)/6-31G*), indicating this compound to be a realistic synthetic objective. The vertical ionization energy of this molecule is predicted to be ca. 5.3 eV, comparable to that of the alkali metals and similar to that predicted by others for a hypothetical planar tetracoordinate carbon molecule.

1. Introduction

Orthogonene (tetracyclo[8,2,2,$0^{2,7}$,$0^{3,10}$]tetradecene-2(3), **1**) (Figure 1) is the ingenious brainchild of Jeffrey and Maier, who two decades ago reported an attempted synthesis[1] and semiempirical calculations[2] on this highly twisted alkene. Orthogonene can in principle exist as several stereoisomers, differing in the relative orientations of the bridgehead C−H bonds (the methine groups) at the ends of the double bond, for example, C−H/C−H-*syn* ("up−up/up−up") and C−H/C−H-*anti* ("up−up/down−down") (**1-s** and **1-a**, respectively, Figure 2. A recent publication[3] concluded that **1-s** would rearrange with a very low barrier to the carbene **c1-s** (rather than to the carbene **c2-s**, which was not a stationary point on the B3LYP potential energy surface; **s** and **a** are used here to distinguish molecules in the *syn* and *anti* series when members of both series are relevant) and that this in turn would form the cyclopropane **cy1** or the alkene **a1-s**, the formation of the alkenes **a2-s** and **a3−3** being calculated to be much higher energy processes (Figure 3, from ref 3). Here I show that the *anti*-orthogonene stereoisomer **1-a** is in fact likely to be far more stable than the *syn* isomer **1-s**. These results indicate that **1-a**, a molecule of great interest from the viewpoint of the experimental and theoretical challenges associated with strongly twisted carbon−carbon double bonds,[4] is a realistic synthetic objective. This is a remarkable conclusion, considering how close the molecule is to being orthogonally twisted (calculated, 88.2°).

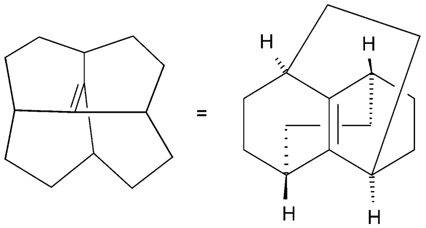
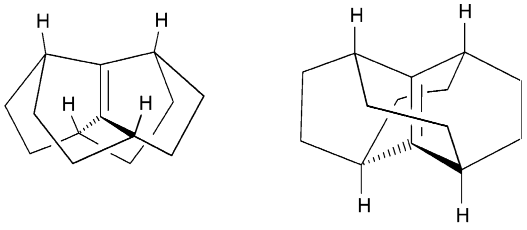
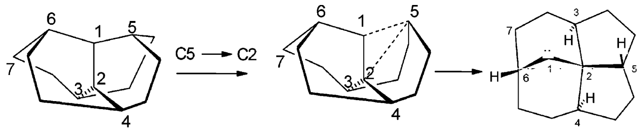


Figure 1. Orthogonene. Several stereoisomers are possible (see the text).



1-s C_2 **1-a** D_2

Figure 2. Orthogonene, the *syn* (**1-s**) and *anti* (**1-a**) stereoisomers. The symmetry designation of **1-a** refers to an idealized symmetric structure (see the text).



1-a **2t** **3c**

Figure 3. Rearrangement of orthogonene **1-a** through transition state **2t** to carbene **3c**.

2. Computational Methods

Calculations were done on Pentium 4 machines running under XP with the Gaussian03 program package,[5] and the structures and vibrational frequencies were visualized with GaussView 3.0.[6] Ab initio,[7] complete active space[8] CASSCF(4,4)/6-31G* (CASSCF = complete active space self-consistent field) geometry optimizations were followed by frequency calculations at the same level to confirm the nature (local minimum or saddle point) of the optimized structure and to obtain its zero-point energy (ZPE);[9] the (uncorrected) ZPE was added to the raw ab initio energy to give the corrected energy. The vertical ionization energy was obtained by comparing the neutral with the radical cation at the same geometry, and here a ZPE correction was not used.

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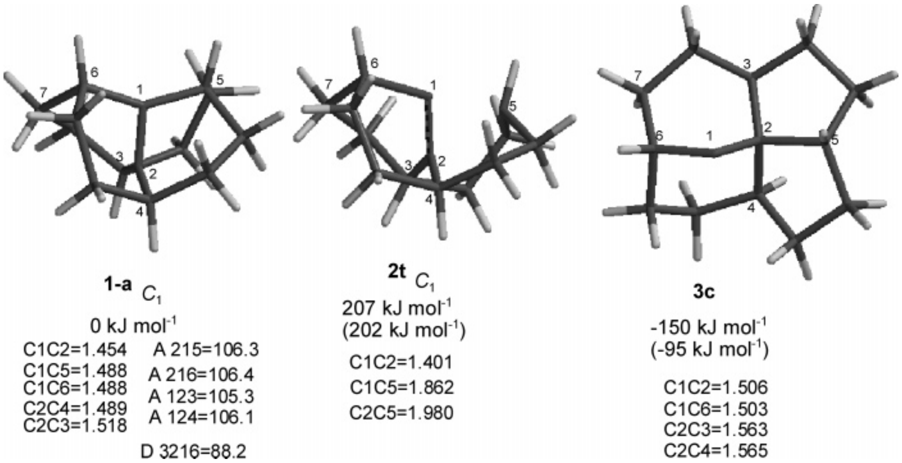

Figure 4. Computed structures of orthogonene **1-a**, transition state **2t**, and carbene **3c**. Bond lengths are in angstroms and bond angles and dihedral angle in degrees. Relative energies (kJ mol^{-1}) include ZPE and are CASSCF(4,4)/6-31G* or (in parentheses) CAS-MP2(4,4)/6-31G*//CASSCF-(4,4)/6-31G* values.

TABLE 1: Energies of 1-a, 2t, and 3c[a]

	relative energy, with ZPE			
	CASSCF	CASMP2	CASSCF/6-31G*	CASMP2/6-31G*//CASSCF/6-31G*
1-a	0	0	without ZPE, −541.66681 with ZPE, −541.33563	without ZPE, −543.49996 with ZPE, −543.16878
2t	207.9	202.0	without ZPE, −541.58590 with ZPE, −541.25644	without ZPE, −543.42131 with ZPE, −543.09185
3c	−150.1	−95.1	without ZPE, −541.72510 with ZPE, −541.39279	without ZPE, −543.53732 with ZPE, −543.20501

[a] Relative energies are in kilojoules per mole, and CAS(4,4) energies are in atomic units.

TABLE 2: Energies of Singlet and Triplet 1-a[a]

	relative energy, with ZPE			
	CASSCF	CASMP2	CASSCF/6-31G*	CASMP2/6-31G*//CASSCF/6-31G*
S	0	0	without ZPE, −541.66681 with ZPE, −541.33563	without ZPE, −543.49996 with ZPE, −543.16878
T	−0.18	−1.2	without ZPE, −541.66698 with ZPE, −541.33570	without ZPE, −543.50052 with ZPE, −543.16924

[a] Relative energies are in kilojoules per mole, and CAS(4,4) energies are in atomic units.

Because **1-a** is strongly twisted (naively a torsional angle of 90° might be expected, as implied by the name), straightforward "model chemistry" [10] methods such as standard ab initio[7] or DFT[11] calculations may not give reliable results. This is because these methods construct the wave function from a single determinant composed of spin orbitals that are in turn derived from spatial orbitals containing paired electrons;[12] they therefore work best for closed-shell molecules. Twisting a double bond toward a dihedral angle of 90° will in the limit uncouple the electrons of the π bond, giving a singlet diradical, and these open-shell species cannot be reliably handled by a one-determinant method. The point at which the transition from a conventional closed-shell to an open-shell molecule will occur cannot be confidently predicted beforehand; therefore, a method appropriate for the latter was applied here. The method chosen was the standard one for treating singlet diradicals, namely, the CASSCF method.[8] Recently, DFT methods of studying singlet diradicals have been investigated;[13,14] we explored some of these[14] but obtained chemically unrealistic results, i.e., an activation energy of ca. 1000 kJ mol^{-1} for the isomerization (see below) of orthogonene. To better correct the CASSCF energies for dynamic electron correlation, single-point energy calculations were done on the CASSCF geometries with Gaussian's CASSCF-MP2 procedure (it is recognized that this can be unreliable in some cases[15] compared to the more common CASPT2N[16] method, but it was found here to give realistic results for the ethene torsional barrier[17] and for the rearrangement of the twisted alkene bicyclo[2.1.1]hex-1(2)-ene to 2-carbenabicyclo[2.1.1]hexane[18a]). Another ambiguity in the electronic structure of orthogonene, the question of the relative energies of the singlet and triplet states, is addressed below.

3. Results and Discussion

3.1. Structure of Orthogonene. On the assumption that the most likely path for isomerization of orthogonene would be that followed by other alkenes with severely twisted double bonds, namely, isomerization to a carbene,[18] the CASSCF calculations used a (4,4) active space with occupied orbitals (Figure 3) C1−C5 (σ) and C1−C2 (π) and unoccupied orbitals for electron excitation C1−C5 (σ*) and C1−C2 (π*). A CASSCF(4,4)/6-31G* wave function of this kind was used to investigate the reaction **1-a** → transition state **2t** → carbene **3c** (Figure 3). The computed structures and their relative energies are given in Figure 4.

Surprisingly, **1-a** was found to be distorted from ideal D_2 symmetry; this is most obvious from the fact that the lengths of the C−C bonds to the formal (see below) double bond are not equal. The calculated dipole moment is 0.02 D. If the distortion is not an artifact of the optimization method, it may be due to singlet diradical character imposing a Jahn−Teller-type distortion, a phenomenon that is known for nonlinear molecules with degenerate electronic states.[19] Orthogonene is predicted by these calculations to have little more than a merely formal double bond: the C1−C2 length of 1.454 Å is only a little shorter than the sp^2 C−sp^2 C length of 1.48 Å for the central bond of 1,3-butadiene, which is now regarded as being essentially a pure single bond.[20] This is expected from the large dihedral angle: the “double bond” is twisted through 88.2°, greatly reducing p−p overlap. This bond has calculated stretching vibrational frequencies at 1499, 1507, 1509, 1516, and 1519 cm^{-1}, coupled in various ways to C−H bending motions. By comparison, the double bond length of tetramethylethylene was calculated (CASSCF(2,2)/6-31G*, C−C π and π^*) to be 1.350 Å and the stretching frequency 1815 cm^{-1}. Tetraalkyl-substituted alkenes are known[21] from experiment to absorb near 1650 cm^{-1}, so a correction factor of $1650/1815 = 0.91$ may be applied to **1-a** to predict a double bond stretch of ca. $0.91 \times 1510 = 1374$ cm^{-1}; this may be hard to detect in view of the near symmetry of the molecule. The calculated values of the sp^2 C−sp^3 C stretches were ca. 1240−1280 cm^{-1} and those of the sp^3 C−sp^3 C stretches ca. 800−1100 cm^{-1}; a framework breathing mode at 746 cm^{-1} also stretches the double bond.

One consequence of the large degree of uncoupling of the p atomic orbitals of the formal double bond of **1-a** is a rather low ionization energy for a hydrocarbon: the difference between the CASSCF(4,4)/6-31G* energy of the neutral (−541.66681) and the CASSCF(3,4)/6-31G* energy of the cation at the geometry of the neutral (−541.47317) yields an ionization energy of 0.19364 hartrees or 5.3 eV. This is similar to that predicted for a hypothetical molecule with a planar tetracoordinate carbon atom[22] and similar to those of lithium and sodium; alkenes typically have ionization energies of ca. 8.3−8.8 eV.[23]

3.2. Stability of Orthogonene. The favored reaction of alkenes with highly twisted double bonds is known to be isomerization to a carbene by a 1,2-alkyl shift.[18] I assumed this was likely to be the lowest-energy reaction mode of **1-a** and calculated the activation energy of this process as a measure of the stability of orthogonene. The results are summarized in Figure 3, which illustrates the process, and Figure 4, which shows the computed structures and their relative energies (also see Table 1), **1-a** (0 kJ mol^{-1}), transition state **2t** (207.9 kJ mol^{-1}), and carbene **3c** (−150.1 kJ mol^{-1}). Orthogonene is predicted to isomerize with a barrier of ca. 200 kJ mol^{-1} to the carbene **3c**, which is calculated to lie ca. 95−150 kJ mol^{-1} below **1-a**. This is a remarkably high barrier for an ostensibly so strained molecule, although an alkene with a 66° twist has been isolated.[24] From experience the threshold for isolation at room temperature is about 100 kJ mol^{-1}.[25]

For a closed-shell singlet molecule the singlet is normally lower in energy than the triplet, but this is not necessarily true for an open-shell singlet.[26] The results of CASSCF and CASSCF-MP2 (Gaussian’s CASSCF-MP2 method has been reported to give reasonable results for singlet−triplet separations in diradicals[27]) calculations on orthogonene are shown in Table 2. The two states are predicted to have very similar energies, and it is not possible to decide from these results which is really lower.

Conclusions

The *anti*-orthogonene stereoisomer (with the bridgehead C−H bonds up−up/down−down) is predicted by CASSCF calculations to isomerize to a carbene with a barrier of ca. 200 kJ mol^{-1}, which is remarkably high for such a highly strained molecule (double bond twist 88°) and indicates that orthogonene is a reasonable synthetic objective and may even be stable at room temperature.

Supporting Information Available: Tables of Cartesian coordinates of the molecules discussed here. This material is available free of charge via the Internet at http://pubs.acs.org.

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