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ORTHOGONENE

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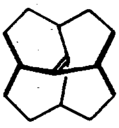
Abstract: Orthogonene is a symmetrical polycyclic olefin with a highly twisted double bond. Semiempirical calculations predict the orthogonal structure to be lower in energy than the twisted form which makes it the first symmetrically substituted orthogonal olefin.

For atoms with a degenerate set of orbitals to be occupied by two electrons Hund's multiplicity rule predicts the triplet state to be lower in energy than the corresponding singlet. This rule applied to molecules is generally accepted in organic chemistry. Several ab initio calculations on pure hydrocarbons indicate violations of Hund's rule; planar cyclobutadiene[1] and orthogonal ethylene[2] are predicted to have singlet states lower in energy than the triplet.[3] We are interested in the electronic nature of orthogonal olefins which are related to bridgehead olefins.[4] Orthogonal ethylene itself is the transition state for rotation around the double bond and as such defies experimental investigation. The design and synthesis of an orthogonal olefin with a sufficient lifetime to allow detailed characterization of its electronic nature is a challenge of basic importance for our understanding of bonding concepts.

Schleyer, in his unorthodox attempts to violate classical bonding concepts, has found by quantum mechanical calculations that 1,1-dilithioethylene[5] and diboraalkenes violate van't Hoff's stereo-chemical rules.[6] These molecules, although orthogonal, do not have degenerate sets of highest occupied molecular orbitals and are thus not directly related to the problem of twisted hydrocarbon alkenes and the violation of Hund's rule. With the help of force field[7] and semiempirical calculations,[8] we have designed a novel polycyclic olefin with an orthogonal double bond in its ground state. The systematic name of this olefin is tetracyclo-[8,2,2,$0^{2,7}$,$0^{3,10}$]tetradecene-2(3) but due to its symmetrical structure and its predicted properties and ground state structure we refer to it as 'orthogonene' (1).



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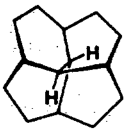

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According to molecular mechanics calculations, orthogonene is a twisted olefin with a heat of formation of 83.4 kcal/mol and an internal strain energy of 118 kcal/mol. The double bond is calculated to be twisted in a way to maintain at least some of the π-overlap the force field has been parameterized for (see scheme 1, structure A). The parent hydrocarbon (2) is calculated to have a ΔH_f^o of 41.2 kcal/mol corresponding to a strain energy of 99.6 kcal/mol. This results in an olefinic strain energy (OS) of 18.4 kcal/mol which classifies orthogonene as a borderline case between isolable and observable bridgehead olefins.[4] The calculations indicate that the parent hydrocarbon is highly strained mainly due to transannular interactions resulting from the internal hydrogen atoms on carbons 1 and 2. This unfavorable interaction may be an important factor which should increase the kinetic stability of orthogonene. Unfortunately, the absolute values calculated must be regarded as trends rather than predictions.

Force fields are parameterized from data derived from stable compounds which provide reliability within the framework of the parameterization set. The numbers calculated for highly strained molecules represent extrapolations which are meaningful with respect to their relative changes within a given set of similarly distorted compounds but may be in error with respect to the absolute value obtained. Although the force field approach generally handles strain effects well it can not treat or recognize electronic effects.

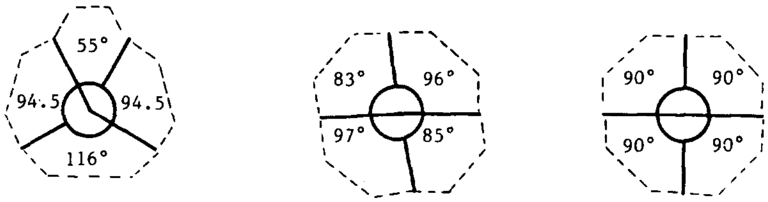
Table 1: ΔH_f° (kcal/mol) calculated for orthogonen

Computational level	Triplet	Orthogonal singlet	Twisted singlet
MM2	-	-	83.4
MINDO/3	89.6[a]	112.9[a]	112.6[a]
MNDO	52.0	83.7	79.8
MNDO-UHF	46.1[a]	44.6[c]	50.0[a]
MNDO 2x2CI		53.3	56.0
MNDO 3x3CI		52.0[b]	55.1[b]

[a] single point calculations on the MNDO optimized geometries
[b] single point calculations on the 2x2 CI opt. geometries
[c] single point calculation on the MNDO triplet optimized geometry

More information about the electronic structure of orthogonene is obtained with semiempirical calculations (see table 1). Starting with the MM2 geometry, orthogonene was completely optimized on the closed shell level with MNDO.[9] It was surprising to find a considerable relaxation of the double bond as indicated by structure B (see scheme 1). The heat of formation of 79.8 kcal/mol is surprisingly close to the force field energy. Most surprising, however, was to find another global minimum with a heat of formation of 83.7 kcal/mol corresponding to the orthogonal structure C. Careful investigation however showed that this minimum was due to the high symmetry of the molecule which led to a faulty satisfaction of the optimization tests in the Fletcher-Powell optimization. Stepwise geometry optimization at dihedral angles between 90 and 85 degrees revealed the absence of an activation barrier establishing the twisted structure as the only minimum on the closed shell surface.

Single point calculations on these geometries on the MINDO/3[10] level resulted in energies of 112.6 kcal/mol for the twisted and 112.9 kcal/mol for the orthogonal structure. For the orthogonal triplet state (complete geometry optimization) MNDO predicts a heat of formation of only 52.0 kcal/mol and MINDO/3 of 89.6 kcal/mol. Both methods predict the orthogonal triplet to be substantially lower in energy than the lowest closed shell singlet structure: 29.1 kcal/mol by MNDO and 23.0 kcal/mol by MINDO/3. Since orthogonal olefins have degenerate HOMO-LUMO sets, the closed shell wave function is insufficient for an adequate description of the electronic structure, although the methods have been parameterized to reproduce the experimental energy difference between planar and orthogonal ethylene.[9] A better description of the twisted and orthogonal structures of orthogonene and their relative energies was obtained by UHF calculations. Single point MNDO-UHF calculations on the optimized twisted and orthogonal singlet structures as well as on the triplet structures resulted in energies of 50.0, 44.6, and 46.1 kcal/mol respectively. MNDO-UHF predicts the orthogonal singlet to be lower in energy by 1.4 kcal/mol than the triplet which is 4 kcal/mol more stable than the twisted singlet structure. This result reverses the classical order of olefinic states and predicts that orthogonene will violate Hund's rule.



Scheme 1: double bond geometry of orthogonene optimized on various computational levels (dihedral angles are indicated).

Another approach to obtain an adequate electronic description of the highly twisted olefin is the inclusion of limited configuration interaction. With 2x2 CI MNDO predicts the orthogonal singlet, with 53.3 kcal/mol, to be less stable than the triplet and more stable than the twisted singlet (56.0 kcal/mol). On the 3x3 CI level the orthogonal singlet is calculated to be degenerate in energy with the triplet and more stable by 3.1 kcal/mol than the twisted singlet. Since these were single point calculations, it is safe to assume that geometry optimization on the 3x3 CI level will result in additional reduction of the energy of the orthogonal singlet state and thus predicts it to be more stable than the completely optimized triplet in agreement with the UHF calculations.

Although the absolute energies derived by these calculations may be in error, the trends predicted are unusual. Important are not the small energy differences calculated (especially since the immense computational effort required that we include several single point calculations) but the gross result, which at various levels consistently predicts this olefin to be an orthogonal ground state structure with the singlet and the triplet states close in energy and with surprisingly low total energy.

Table 2: ΔH_f° for D_{2h} and D_{2d} ethylene with MNDO in kcal/mol

ethylene	experimental	closed shell	3x3 CI	UHF	triplet	UHF-triplet
D_{2h}	12.5	15.3	6.3	15.4		
D_{2d}		77.8	45.1	39.7	45.1	41.7
rotational barrier	65.0	62.5	38.9	23.7	29.8	26.3
error		2.5	26.1	41.3	34.2	28.7

To calibrate the behavior of MNDO with orthogonal olefins we have included the following test calculations on ethylene (see table 2). Closed shell MNDO gives an energy difference of 62.5 kcal/mol between D_{2d} and D_{2h}. However, triplet ethylene on the half-electron level is, with 45 kcal/mol, considerably lower than the singlet state. The best 'ab initio' calculations consistently predict the orthogonal singlet to be lower in energy than the triplet by about 1-3 kcal/mol.[2] The energy calculated with 3x3 CI for the D_{2d} ethylene is identical with the triplet energy and thus in reasonable agreement with the 'ab initio' predictions on the relative energies of singlet and triplet states in twisted olefins. The UHF method assigns an energy of 39.7 kcal/mol to the orthogonal singlet and 41.7 kcal/mol to the triplet predicting the same state order as the sophisticated 'ab initio' calculations. Both the 3x3 CI and the UHF treatment considerably overestimate the stablility of the orthogonal structure. It is interesting to note that a correction of the orthogonene energies by the error found for orthogonal ethylene results in 78.4 kcal.mol for 3x3 CI and 85.4 kcal/mol for UHF, values very close to the 84 kcal/mol predicted by MM2 and the MNDO closed shell procedure.

These calculations show that it may be possible to violate classical bonding concepts by appropriately deformed structures. The most impressive example of structural violations achieved recently is the 1,1,1-propellane prepared by Wiberg et.al., where the bridgehead carbons are completely pyramidalized.[12] With orthogonene we have designed a polycyclic skeleton in which the strain produced in the peripheral cyclododecyl chain prevents the internal double bond to acquire the usual π-overlap. In addition, the polycyclic structure forces the vinyl bond angles to 107°, 13° smaller than in a regular olefin. This increases the hyperconjugation of the decoupled p-orbitals with the C-C sigma-bonds and thus provides additional stabilization of the orthogonal form. Our intensive efforts to synthesize this exciting molecule are only aggravated by a lack of funding.

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