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BONDING IN SMALL RING PADDLANES†

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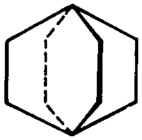
Summary: The geometries of [1.1.1.1]paddlane and [2.2.2.2]paddlane have been calculated via ab initio mo theory. In both cases, a short bridgehead-bridgehead distance and a relatively large bond order was found, indicating a bonding interaction between these formally non-bonded atoms. The energies of conversion to more stable compounds were estimated.

[2.2.2.2]Paddlane (1)[1-5] has been of interest for some time because of its unusual mode of distortion at the bridgehead carbons. Some related compounds, the [n.2.2.2]paddlanes (2) have been prepared. Benzo derivatives of 2 with n=12[2] and 14[3] have been reported and Eaton and Leipzig have obtained 2 with n = 10, 12 and 14.[5] As *n* is reduced, it would be expected that the energy would rise rapidly, and for 1, a strain energy in excess of 300 kcal/mol was predicted.[4]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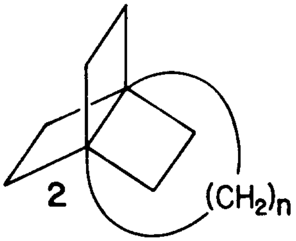

The high energy of 1 is related to the large strain energy associated with a near-planar carbon.[6-8] Here, the central carbon may interact with the four attached groups mainly via the *s* and the two in-plane *p* orbitals, leaving an essentially unbound out-of-plane *p*-orbital at the central carbon.[6] This might be stabilized by suitable substituents which could interact with the orbital.[7] Another possibility for stabilizing the carbon would be to introduce a similar carbon at a bonding distance from the first. A way to accomplish this is illustrated by [1.1.1.1]paddlane (3). Semi-empirical mo calculations for [2.2.2.2]paddlane suggest that this is an important interaction.[4] In view of the difficulties in estimating energies of some small ring compounds via semi-empirical methods,[9] and in order to obtain better estimates of

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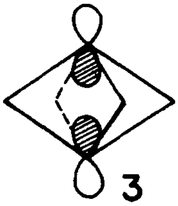
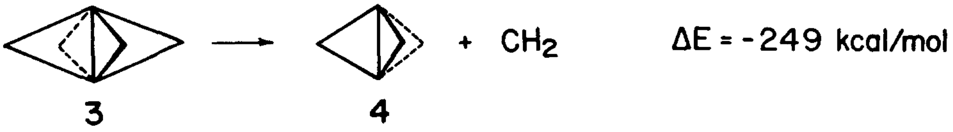
†Dedicated to Professor Harry H. Wasserman on the occasion of his 65th birthday.

the bond orders, we have carried out an ab initio geometry optimization for 3 using the 4-31G and 6-31G* basis sets.[10] The latter, which includes polarization functions at carbon (d-orbitals) was included because they have been found to be important for the proper description of highly strained cyclopropane derivatives.[11] The results are shown in Table I.



3

The calculated geometry for the structure having D_{4h} symmetry (i.e. with the methylene hydrogens in a plane) had a non-bonded H-H distance of only 1.807 Å. In order to relieve this steric strain, the calculation was repeated using D_4 symmetry which allows the CH_2 groups to twist. This allowed the H-H distance to increase to 2.158 Å, and reduced the energy significantly. The calculated distance between the bridgehead carbons was 1.575 Å as compared with the bridgehead-methylene distance of 1.668 Å. Thus, the interaction between the bridgehead carbons can only be described as a bond. The compound is still highly strained, the the calculated change in energy on cleavage to [1.1.1]propellane (4) and methylene is -249 kcal/mol using the 6-31G* energies.[12] The ΔH_f is estimated to be 438 kcal/mol[13] corresponding to a strain energy of 456 kcal/mol!



We were interested in seeing if greater stabilization might be achieved with larger rings, and so the structure and energy of [2.2.2.2]paddlane (1) also was calculated using the 4-31G basis set. It was impractical to optimize the geometry of such a large molecule using the 6-31G* basis set. It is known that the 4-31G and 6-31G* basis sets give essentially the same geometry for most cycloalkanes,[14] and therefore the 6-31G* energy was calculated at the former geometry. The results are summarized in Table I. The calculated bridgehead-bridgehead distance is 1.525 Å, and the distance between the methylene groups is 1.489 Å. Thus, the bridgehead carbon is calculated to be essentially planar. Since in the absence of the bridgehead-bridgehead interaction, the geometry at the bridgeheads would be expected to be pyramidal,[8] it is clear that the bridgehead-bridgehead interaction must be described as a bond in this case also. The bridgehead-methylene distances is 1.787 Å, corresponding to what one might expect for a bond order of 0.75 (i.e. three bonding orbitals distributed over four bonds). The above geometry is similar to that derived from the semi-empirical calculation.[4]

Again, despite what stabilization might be achieved in this fashion, the compound is highly strained. The calculated change in energy on going to [2.2.2]propellane (5) and ethylene is −230 kcal/mol.[13] The estimated ΔH_f is 311 kcal/mol corresponding to a strain energy of 349 kcal/mol.

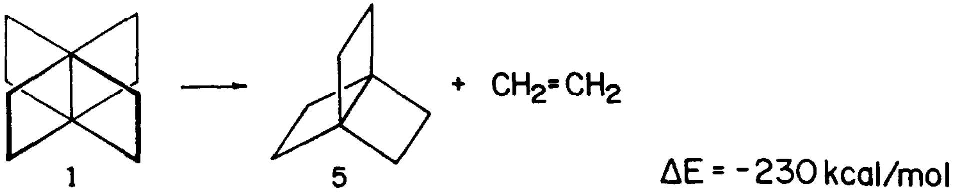
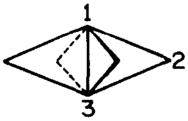


Table I

Energies and Structures of Paddlanes



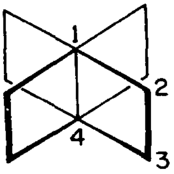
E = −230.77171 Hartree (D_{4h})(4-31G)

E = −230.77434 Hartree (D_4)(4-31G)

E = −231.16622 Hartree (D_4)(6-31G*)

$r(C_1-C_3) = 1.575$, $r(C_1-C_2) = 1.668$, $r(C_2-H) = 1.059$

$C_1C_2C_3 = 56.4°$, $HC_2H = 117.1°$



E = −386.91658 Hartree (D_{4h})(4-31G)

E = −387.47471 Hartree (D_{4h})(6-31G*/4-31G)

$r(C_1-C_4) = 1.525$, $r(C_1-C_2) = 1.787$, $r(C_2-C_3) = 1.489$

$C_1C_2C_3 = 90.6°$, $HC_2H = 108.7°$

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