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A Theoretical Study of Tricyclo[4.2.1.0^{2,5}]non-2(5)-ene, Tricyclo[4.2.2.0^{2,5}]dec-2(5)-ene and Related Pyramidalized Alkenes

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Dedicated to Professor Pelayo Camps

Keywords: Ab initio calculations / Density functional calculations / Hydrocarbons / Pyramidalized alkenes / Strained molecules

HF, MP2 and CAS ab initio theory and B3LYP, B3PW91, SVWN and MPW1PW91 density functional theory were used to study a series of cyclobutenyl-fused tricycles such as tricyclo[4.2.1.0^{2,5}]non-2(5)-ene, tricyclo[4.2.2.0^{2,5}]dec-2(5)-ene and related compounds. Examination of the stepwise torsional potentials for **5**–**8** and **10**–**11** by scanning of the cyclobutene butterfly angles at the B3LYP/6-31G(d) level revealed that there is only one minimum for each compound, with the cyclobutene bent in the *endo* direction in **5**, **6**, **10** and **11**, and in the *exo* direction in **8**. Examination of the stepwise heats of hydrogenation of **9** revealed that this compound, which displays a method-dependent ground state, is antiaromatic.

Introduction

Pyramidalized alkenes are molecules containing carbon–carbon double bonds in which one or both of the sp^2 carbon atoms do(es) not lie in the same plane as the attached atoms.[1] Alkenes of this kind are very interesting targets for both synthetically and theoretically oriented organic chemists, due to their intriguing physical properties and their fascinating reactivity.[2] In recent years, our research group has focused on the synthesis, chemical trapping and dimerization of several highly pyramidalized alkenes, such as tricyclo[3.3.0.0^{3,7}]oct-1(5)-ene and related compounds.[3] We and others have also applied ab initio and DFT calculations to several highly pyramidalized alkenes in order to understand and explain their structures, properties and reactivities.[4]

Our continuing interest in pyramidalized alkenes and the recent and very stimulating contributions by Margetić, Warrener, Williams and co-workers on theoretical studies of pyramidalized alkenes such as **1**–**4** and related compounds prompted us to carry out a theoretical study on the homologous compounds **5**–**9** (Figure 1).[5] Also, in recent papers, the effect of oxygen atoms on the degree of the double bond pyramidalization in norbornenes, sesquinorbornenes and related compounds has been addressed.[6] It was found that the position(s) of the oxygen atom(s) play(s) a very important role in the pyramidalization of the double bond. In order to explore the effects of oxygen atoms in pyramidalization further, here we have also carried out calculations on compounds **10** and **11**. Notably, in all these compounds, pyramidalization does not proceed from a structural constraint, as in our previous work in the series of tricyclo[3.3.0.0^{3,7}]oct-1(5)-ene derivatives, but from considerable ring strain in the molecules.

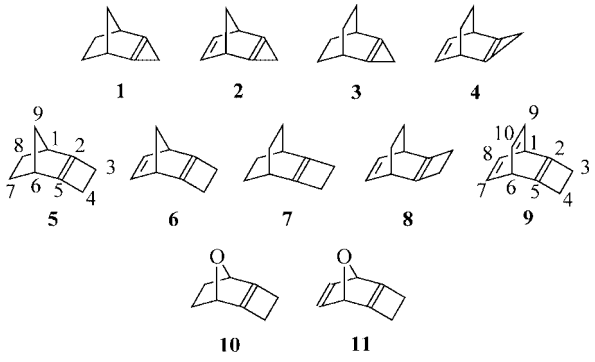

Figure 1. Pyramidalized olefins **1**–**11**.

In studying pyramidalized alkenes, it is convenient to use a geometrical parameter to measure pyramidalization. Although in our previous work the degree of pyramidalization was measured using the pyramidalization angle (ϕ) as defined by Borden,[7] it has to be taken into account that strictly speaking, the ϕ angle is applicable only to those cases involving C_{2v} symmetry. For this reason, in this work we have used the butterfly bending angle (Ψ) recently intro-

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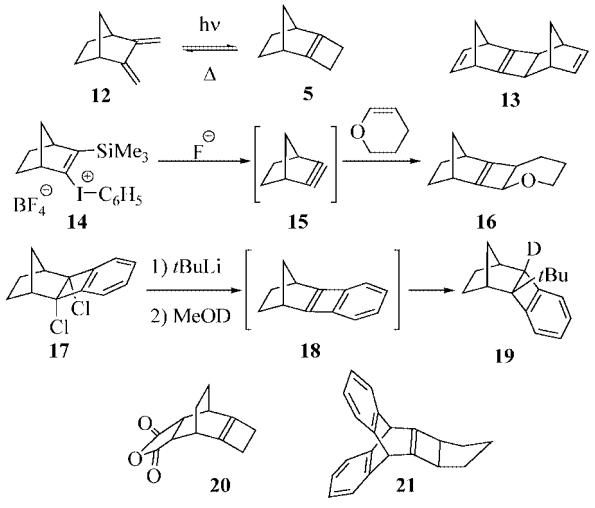
duced by Margetić, Williams and Warrener for compounds of at least C_s symmetry, with a mirror plane bisecting and perpendicular to the double bond, because all the compounds studied here are of at least C_s symmetry.[5b] The angle Ψ can be calculated from the dihedral angle (D) defined by the bonding sequence 1–2–3–4 shown in Figure 2, by the formula $\Psi = 180 - |D|$. This approach allows easier comparison with the calculations reported on similar compounds.[5,6]

Figure 2. Definitions of the pyramidalization angle (ϕ) and the butterfly bending angle (Ψ).

It should be noted that there are a small number of literature reports involving tricyclo[4.2.1.0^{2,5}]non-2(5)-ene (**5**) and the related compounds shown in Figure 1. Aue and Reynolds synthesized the air-sensitive **5** by photochemical ring-closure of 2,3-dimethylenebicyclo[2.2.1]heptane (**12**).[8] They found that, in solution, **5** tends to polymerize, a fact that complicated the study of the activation energy for the ring-opening reaction to **12**. Later on, Houk and co-workers theoretically studied the cyclobutene ring-opening process from **5** to **12** and found that polymerization of **5** did not occur in the gas phase.[9] On the other hand, Roth and co-workers found a heat of hydrogenation of 44.9 kcal mol^{-1} for **5**.[10] More recently, **5**, **6**, **10** and **11** were theoretically studied in connection with a DFT study on the cycloaddition reactions of cyclobutano[*c*]cyclopentadiene and cyclobutano[*c*]furan with ethylene and acetylene,[11] and Gilbert and co-workers have reported that treatment of bicyclo[2.2.1]hept-2-yne (norbornyne, **15**) with 2,3-dihydropyran gave a mixture containing **16**.[12] On the other hand, dehalogenation of dichloride **17** with *tert*-butyllithium followed by quenching with [D$_1$]methanol led to **19**, probably through the intermediacy of **18**, a benzo derivative



Scheme 1. Synthesis of several pyramidalized olefins related to **5**–**8**.

of **5**.[13] Finally, **13** seems to be the only derivative related to diene **6** so far reported in the literature.[14] To the best of our knowledge, compounds **20** and **21** are the only tricyclo[4.2.2.0^{2,5}]dec-2(5)-ene derivatives so far described in the literature,[15] although the parent compound, **7**, has been studied theoretically.[16] Notably, pyramidalization-related issues were not addressed in these papers (Scheme 1).[17]

Computational Methodology

We employed methodology that has been validated in calculations on related systems.[4–6] Initial geometries, which were further optimized using the Gaussian 03 suite of programs,[18] were obtained using the PCMODEL program.[19] Geometries were optimized using the 6-31G(d) basis set[20] with a series of ab initio methods: Hartree–Fock (HF), second-order Möller–Plesset perturbation theory (MP2)[21] and Complete Active Space Self Consistent Field calculations with two, four or six active orbitals [CASSCF(2,2), CASSCF(4,4) and CASSCF(6,6), respectively], corresponding to the π and π* orbitals of each of the double bonds.[22] Geometries were also optimized using the 6-31G(d) basis set with a series of DFT methods, together with a local functional SVWN (Slater exchange with Vosko, Wilk and Nusair correlation),[23] as well as three nonlocal functionals [B3LYP (Becke's three-parameter hybrid exchange[24] with Lee, Yang and Parr correlation),[25] B3PW91 (Becke three-parameter hybrid exchange[24] with Perdew–Wang 1991 gradient corrected correlation functional),[26] and MPW1PW91 (Barone–Adamo one-parameter functional with Perdew–Wang 1991 gradient corrected correlation functional)].[27] For compound **9**, additional calculations were carried out using the 6-311+G(d,p) basis set. Analytical energy second derivatives were calculated at all stationary points to obtain zero-point and thermal corrections to the electronic energies and to ensure that the structures were true minima. Transition state structures were verified to be true first-order saddle points using analytic energy second derivatives. The vibrational frequencies were not scaled. Potential energy surfaces were carried out at B3LYP/6-31G(d) and found a single minimum when scanning the cyclobutene butterfly bending angle.

Results and Discussion

It is known that while the norbornene and norbornadiene double bonds are pyramidal by ca. 7° and ca. 4°, respectively, fusion with a cyclopropene ring, as in **1** and **2**, increases pyramidalization to ca. 45°. Similarly, while bicyclo[2.2.2]octene is only slightly pyramidalized (Ψ = 3°), compounds **3** and **4** showed $\Psi \approx 45°$.[5a] We have now found that fusion of a cyclobutene ring to norbornene, norbornadiene, bicyclo[2.2.2]octene and bicyclo[2.2.2]octadiene rings also increases pyramidalization.

Table 1 collects the butterfly bending angles for compounds **5**–**11** obtained by using ab initio (HF, MP2) and DFT (B3LYP, B3PW91, SVWN, MPW1PW91) methods,

Table 1. Butterfly bending angles for compounds **5**–**11** calculated with the 6-31G(d) basis set.

Compound	Angle	HF	MP2	B3LYP	B3PW91	SVWN	MPW1PW91
5	Ψ[a]	15.7	22.7	18.5	18.8	23.4	19.1
6	Ψ[a]	14.0	22.4	17.5	17.5	21.4	17.6
6	Ψ'[b]	1.6	2.1	1.9	2.1	2.4	2.1
7	Ψ[a]	0.0	0.0	0.0	0.0	0.0	0.0
8	Ψ[a]	4.8	10.6	6.5	6.5	8.7	6.6
8	Ψ'[b]	2.6	2.7	2.9	2.9	3.2	2.9
9	Ψ[a]	0.0	6.0	0.0	0.0	1.9	0.0
9	Ψ'[b]	0.4	0.4	0.4	0.4	0.2	0.4
9	Ψ''[c]	0.4	0.9	0.4	0.4	0.6	0.4
10	Ψ[a]	16.0	24.0	19.8	19.9	24.5	20.2
11	Ψ[a]	18.1	28.4	22.4	22.4	27.7	22.5
11	Ψ'[b]	2.0	2.4	2.3	2.4	2.5	2.3

[a] Butterfly bending angle (C2=C5 double bond). [b] Butterfly bending angle (C7=C8 double bond). [c] Butterfly bending angle (C9=C10).

while Table 2 shows the results for compounds **6**, **8**, **9** and **11** obtained by using CASSCF methods. Inspection of these tables reveals that, for a given compound, the calculated butterfly bending angles (Ψ) are the smallest for the HF method, with the MP2 values significantly larger and those calculated using B3LYP, B3PW91 and MPW1PW91 intermediate between the HF and MP2 values. The SVWN functional gives butterfly bending angles similar to those obtained using MP2, and the CASSCF method results in the largest butterfly bending angles.

Table 2. Butterfly bending angles for compounds **5**–**11** calculated with CASSCF(2,2), CASSCF(4,4) and CASSCF(6,6) and the 6-31G(d) basis set.

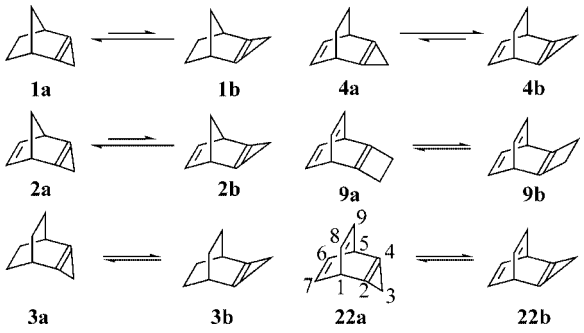
Compound	Ψ[a]	Diradical character[b]	Ψ'[c]	Ψ''[d]
5[e]	23.8	4.7	–	–
6[e]	26.2	5.2	1.6	–
6[f]	25.6	5.5	2.9	–
7[e]	0.0	3.9	–	–
8[e]	17.7	4.3	1.6	–
8[f]	25.5	4.5	2.2	–
9[e]	23.1	5.0	1.6	1.6
9[f][g]	21.7	4.9	1.7	2.2
9[f][h]	21.7	5.2	2.4	1.7
9[i]	20.1	5.1	1.9	2.4
10[e]	25.5	4.9	–	–
11[e]	30.2	5.8	1.9	–
11[f]	29.6	6.0	2.9	–

[a] Butterfly bending angle (C2=C5 double bond). [b] Diradical character in C2=C5 bonds. [c] Butterfly bending angle (C7=C8 double bond). [d] Butterfly bending angle (C9=C10). [e] Calculated with CASSCF(2,2)/6-31G(d). [f] Calculated with CASSCF(4,4)/6-31G(d). [g] The π and π* orbitals of C2=C5 and π and π* orbitals of C9=C10 were regarded as the active space for the CASSCF(4,4)/6-31G(d). [h] The π and π* orbitals of C2=C5 and π and π* orbitals of C7=C8 were regarded as the active space for the CASSCF(4,4)/6-31G(d). [i] Calculated with CASSCF(6,6)/6-31G(d).

Interestingly, while a slight decrease in the pyramidalization is observed on going from **5** to **6** (e.g., Ψ = 18.5° and 17.5° for **5** and **6**, respectively, B3LYP), probably as a consequence of hyperconjugative interactions, the reverse is true in the corresponding oxygen derivatives **10** and **11** (e.g., Ψ = 19.8° and 22.4° for **10** and **11**, respectively, B3LYP). Thus, although in the pair **5**/**10**, the pyramidalization is little affected by substitution of the methylene bridge with an oxygen bridge, as previously observed in related systems,[6] an important increase (ca. 5°) is observed, irrespective of the method, on going from **6** to **11**. As first noticed by Balci and Brickmann,[6c] this increase may be related to the interactions between the double bond orbitals and the antibonding orbitals of C1–O9 and C6–O9, which are not found in the carbocyclic compounds.

Some diradical character has previously been found in highly pyramidalized alkenes. Since HF does not include electron correlation and DFT does not treat electron correlation fully, in pyramidalized alkenes the diradical character is usually estimated from CASSCF calculations.[2b,4a,28] In this way, the diradical character can be estimated from the squares of the coefficients of the CASSCF states. As shown in Table 2, alkenes **5**–**11** indeed have some diradical character, although lower than those previously calculated for **1**–**4**.[5a]

Williams et al. found that compounds **1**–**4** had double minimum surfaces with both *endo* (**1a**–**4a**) and *exo* (**1b**–**4b**) bent optimized structures. In the norbornyl systems (**1** and **2**), the *endo* bent isomers were more stable than the *exo* bent isomers, whereas in the diene **4** the reverse was true, with the *exo* bent isomer being the lower energy form. In the case of **3**, the two isomers were degenerate (Scheme 2).[4c,5a,29]



Scheme 2. The *exo* and *endo* isomers of compounds **1**–**4**, **9** and **22**.

By way of contrast, examination of the stepwise torsional potentials for **5**–**8** and **10**–**11** by scanning of the cyclobutene butterfly angle with B3LYP/6-31G(d) in each case reveals a

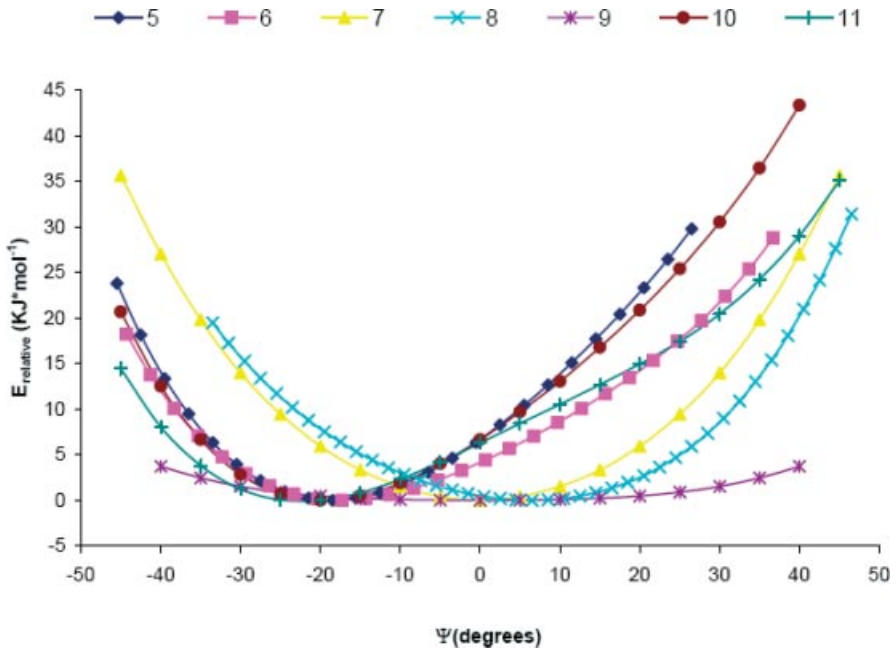


Figure 3. Torsional energy surfaces for molecules **5**–**11**. $E_{relative}$ = total $E(\Psi)$ – total E(optimized geometry).

single minimum surface, with the cyclobutene bent in the *endo* direction in **5**, **6**, **10** and **11** and in the *exo* direction in **8** (Figure 3).

A particularly interesting feature of this work is the determination of the ground state geometries of the C2=C5 double bonds of the symmetrical **7** and **9**. The two faces of the C2=C5 double bonds in **7** and **9** are identical and, on symmetry grounds, planar geometries might be predicted. Williams et al. found that, in spite of its symmetry, **3** was highly pyramidalized [Ψ = 43.1; B3LYP/6-31G(d)], probably as a consequence of the substantial ring strain. They also found that conformers **3a** and **3b** are degenerate and that interconversion is facile, proceeding through a transition state with a planar double bond and an activation barrier [B3LYP/6-31G(d)] of only 6.41 kcal mol^{-1}. HF, TCSCF, MP2, B3PW91 and SVWN calculations also predicted two degenerate pyramidalized ground states. In contrast, we have now found that **7** displays, irrespective of the calculation method, a planar geometry.

Very interestingly, triene **9** behaves quite differently. As would be expected on symmetry grounds, HF, B3LYP, B3PW91 and MPW1PW91 methods indicate that **9** has a ground-state planar geometry. However, the planar geometry of **9** is a transition state for the degenerate butterfly bending **9a**–**9b**, when SVWN, MP2 and CAS calculations are used (Scheme 2). While Ψ for C2=C5 is moderate for SVWN and MP2 calculations (Ψ = 1.9 and 6.0, respectively) it reaches Ψ = 20.1 when CASSCF(6,6) is used. In spite of the pyramidalization, the double-minimum torsional energy surface for the butterfly bending **9a**–**9b** shows an extreme flatness, regardless of the method, with less than 1 kcal mol^{-1} difference between the pyramidal ground states and the planar transition state. We also reoptimized **9** with HF, MP2, B3LYP, B3PW91, MPW1PW91 and SVWN using the 6-311+G(d,p) basis set and found results consistent with the 6-31G(d) ones. Thus, only SVWN/6-311+G(d,p) and MP2/6-311+G(d,p) predict pyramidal ground states (Ψ = 12.4° and 13.6°, respectively), 0.9 kcal mol^{-1} lower than the planar transition states.

Taking into account the different behaviour of symmetrical **3** and **7** (pyramidalized and planar, respectively, regardless of the calculation method) and of **9** (planar or pyramidalized depending on the calculation method), we optimized the not previously studied symmetrical triene **22**, which contains a cyclopropene ring. All the methods used [HF, B3LYP, B3PW91, MPW1PW91, SVWN, MP2 and CASSCF(2,2), CASSCF(4,4) and CASSCF(6,6)] indicate that the C2=C4 double bond of **22** is strongly pyramidalized (ranging from Ψ = 44°, using the HF method up to Ψ = 48° using CAS methods). As expected, the two conformers **22a** and **22b** are degenerate, and interconversion proceeds through a transition state with a planar double bond and an activation barrier [B3LYP/6-31G(d)] of 9.29 kcal mol^{-1}, higher than that previously calculated by Williams et al. for the interconversion of **3a** and **3b** (6.41 kcal mol^{-1}).[5a] Interestingly, of all the aforementioned compounds, triene **9** is the only one that features a method-dependent ground state.

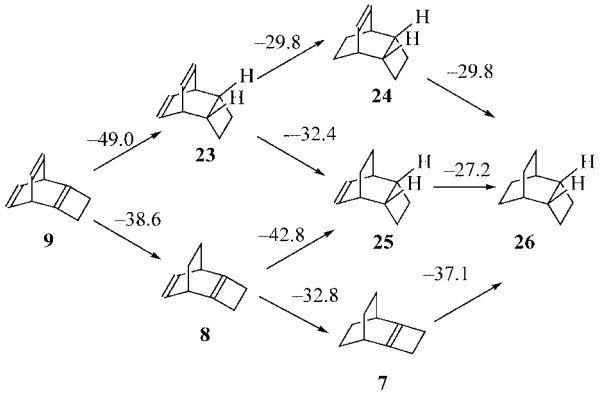
It has not escaped our attention that **9** features a bicyclo[2.2.2]octa-2,5,7-triene ("barrelene") unit, itself a very interesting compound because the unique arrangement of the double bonds in barrelene makes it impossible to select a set of π orbitals in which the overlap of all π orbitals is bonding, and so it can be considered a Möbius-like molecule.[30]

Allinger and co-workers studied the stepwise heats of hydrogenation of barrelene to bicyclo[2.2.2]octane, using the HF/6-31G(d) method and found the sequential heats of hy-

drogenation to be 38.1, 31.8 and 28.4 kcal mol^{-1}.[31] Their results agreed very well with the available experimental data (37.6 and 28.6 kcal mol^{-1} for the hydrogenation of barrelene to bicyclo[2.2.2]octa-2,5-diene and of bicyclo[2.2.2]oct-2-ene to bicyclo[2.2.2]octane, respectively).[32] The unusually large heat of hydrogenation of the first step confirms that the three double bonds of barrelene form an antiaromatic system.

In order to check whether **9** is also an antiaromatic compound, we calculated its stepwise heats of hydrogenation. First of all, we evaluated whether B3LYP/6-31G(d) would be well suited for theoretically calculating the heats of hydrogenation of this kind of polycyclic compounds, as well as of barrelene. For compound **5** we found a heat of hydrogenation of 43.5 kcal mol^{-1}, which fits well with the experimentally determined one (44.9 kcal mol^{-1}).[10] Moreover, our results for the stepwise hydrogenation of barrelene (37.4, 32.0 and 29.2 kcal mol^{-1}) are in very good agreement with the available experimentally measured values (see above).

Having observed that B3LYP/6-31G(d) is suitable for predicting the heats of hydrogenation of these compounds, we calculated the stepwise hydrogenation of **9**. As expected, the hydrogenation of the strained C2=C5 double bond in **9** to diene **23** is the most exothermic process (49.0 kcal mol^{-1}), being 11.6 kcal mol^{-1} and 10.4 kcal mol^{-1} more exothermic than that of the hydrogenation of barrelene to bicyclo[2.2.2]oct-2,5-diene (37.4 kcal mol^{-1}) and that of the hydrogenation of **9** to diene **8** (38.6 kcal mol^{-1}), respectively, the difference in both cases being a consequence of the strain of **9** (Scheme 3). Taking account of these values and of the fact that the heats of hydrogenation of pyramidalized alkene **8** to **25** and to **7** are 42.8 and 32.8 kcal mol^{-1}, respectively, we can therefore accept that the antiaromaticity of **9** roughly accounts for 6 kcal mol^{-1}.



Scheme 3. Heats of hydrogenation (kcal mol^{-1}) of triene **9**.

Conclusions

Fusion of a cyclobutene ring to norbornene and norbornadiene, such as in tricyclo[4.2.1.0^{2,5}]non-2(5)-ene (**5**), tricyclo[4.2.1.0^{2,5}]non-2(5),7-diene(**6**), 9-oxatricyclo[4.2.1.0^{2,5}]-non-2(5)-ene (**10**) and 9-oxatricyclo[4.2.1.0^{2,5}]non-2(5),7-diene (**11**), increases the pyramidalization up to $\Psi \approx 20°$. While the pyramidalization is little affected on going from **5** to its oxa derivative **10**, an important increase in pyramidalization is observed on going from diene **6** to its oxa derivative **11**, probably as result of interactions between the double bond orbitals and the antibonding orbitals of C1–O9 and C6–O9.

In sharp contrast with the fusion of a cyclopropene ring to bicyclo[2.2.2]octene, which led to a highly pyramidalized alkene, fusion of a cyclobutene ring, as in tricyclo-[4.2.2.0^{2,5}]dec-2(5)-ene (**7**), gave a compound with a planar ground state. Moreover, the increase in pyramidalization produced by fusion of a cyclobutene ring to bicyclo[2.2.2]-octa-2,4-diene ($\Psi \approx 3°$), as in tricyclo[4.2.2.0^{2,5}]deca-2(5),7-diene (**8**), is very modest (e.g., $\Psi \approx 6°$, DFT methods).

Very interestingly, while HF, B3LYP, B3PW91 and MPW1PW91 predict a planar ground state for tricyclo[4.2.2.0^{2,5}]deca-2(5),7,9-triene (**9**), SVWN, MP2 and CAS calculations predict that the planar conformation is a transition state between two degenerate pyramidalized ground states, with less than 1 kcal mol^{-1} energy difference between the pyramidal minima and the planar transition state. Examination of the stepwise heats of hydrogenation of **9** reveals that this compound is antiaromatic.

Supporting Information (see footnote on the first page of this article): Cartesian coordinates and energies for all calculated structures.

Acknowledgments

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