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[2.2.2]Propellane Isomerization by Grob Rearrangement: An Ab Initio MR-AQCC Study

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The multireference average quadratic couple cluster (MR-AQCC) method has been employed to explore isomerism in the [2.2.2]propellane **1** as well as the accompanying Grob-type fragmentation. It is shown that the open form **2** is more stable than the conventional closed propellane **1** by 3.6 kcal mol^{-1}. These two isomers are separated by a barrier as high as 22.7 kcal mol^{-1}, taking **1** as a reactant, a value that is in excellent agreement with experiment. However, system **2** is not a stable species because it is located in a very shallow energy minimum. Consequently, it undergoes almost barrierless cage-opening to the thermodynamically most stable 1,4-dimethylenecyclohexane (**3**). The singlet–triplet gap along the bond-stretch reaction coordinate has been calculated too. It is shown that intersystem crossing can be expected in the vicinity of the saddle point. It is concluded that photochemical closure of the bridgehead C–C bond yielding **1** has a lower probability than geometry relaxation leading to structure **2** and ultimately to the stable compound **3**. The structural features of the elusive systems **1** and **2** are discussed in some detail.

Introduction

Propellanes are an interesting family of compounds that illustrate the versatility of carbon atoms to form chemical bonds in many different ways. These molecules are characterized by inverted carbon atoms meaning that all four valences are directed towards just one half of the 3D space in small systems and with appreciable bond bending in large systems. Consequently, the valence electron density distribution around the bridgehead carbon atoms is strongly deformed leading to pronounced molecular strain. Not unexpectedly, propellanes are not easy to prepare and still provide a challenge to synthetic chemists. In spite of this, a number of propellane derivatives have been synthesized,[1–8] while others remain persistently elusive. They are the subject of unabated research interest owing to their unusual chemical properties and peculiar electronic structures. One of the protagonists is the cage [2.2.2]propellane system **1** (tetracyclo[2.2.2.0^{1,4}]octane), which was first theoretically studied by Stohrer and Hoffmann.[9] They put forward the hypothesis that **1** should exhibit bond-stretch isomerism leading to the diradical **2**, which might be jeopardized, however, by the Grob rearrangement[10–12] which yields 1,4-dimethylenecyclohexane (**3**). These predictions were essentially confirmed by Newton and Schulman[13] at a rather low level of theory according to present standards by using SCF/STO-3G calculations followed by two-configuration CI with very limited geometry optimization along the D_{3h} reaction coordinate for the bond-stretch isomerisation. Wiberg at al.[14] used a combination of the SCF method and molecular mechanics to find that **1** is more stable than **2** by around 10 kcal mol^{-1}. Subsequently, Feller and Davidson[15] reported the results of CASSCF(2,2)/6-31G(d)//CASSCF(2,2)/3-21G calculations, but these did not offer a clear cut conclusion. Two minima corresponding to **1** and **2** were identified, but it was not established beyond reasonable doubt that the latter is deep enough to prevent a spontaneous ring-opening reaction leading to 1,4-dimethylenecyclohexane (**3**). Later, Davidson improved upon these results by performing CASSCF(8,8)/6-31G(d) calculations[16] for ring-opening to the bicyclic diyl **2** or to dimethylenecyclohexane **3**. The open diyl form is lower in energy than **1**, but it possesses only a shallow energy well and ring-opens to give the stable system **3**. He also found, surprisingly enough, that the spin-unrestricted UB3LYP/6-31G(d) calculations produced results comparable to those offered by the more intricate CASSCF(8,8) method. It is important to mention that [2.2.2]propellane **1** has not been synthesized as yet, but its derivatives **4**, **5** and **6** have been prepared, the latter being the only compound stable as a crystalline material at room temperature. Eaton and Temme[17] synthesized

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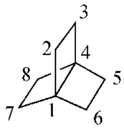
dimethylcarboxamide derivative **4** and measured the temperature dependence of the rate of disappearance of its NMR signal. An Arrhenius activation energy of 22 kcal mol^{-1} was deduced for the ring-opening reaction, resulting in the $CONMe_2$ derivative of **3**.[17] The heavily fluorinated molecules **5** and **6** have been prepared by Lemal and co-workers.[18,19] Unfortunately, the barriers to the ring-opening reactions leading to the corresponding substituted dimethylenecyclohexanes were not measured. We note in passing that Dannenberg and Prociv[20] performed INDO calculations of the lowest singlet and triplet energy hypersurfaces, which indicated that **1** was substantially more stable than **2** and that the former compound could be obtained photochemically via the first triplet state by intersystem crossing.[21] These results, however, are not conclusive. We note in passing that recently some propellanes including **1** were considered by the electron localization function (ELP) within the DFT framework.[22]



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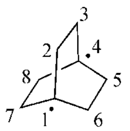

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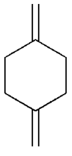

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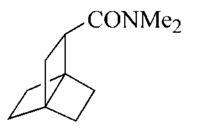

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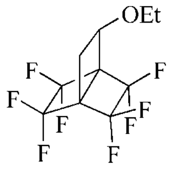

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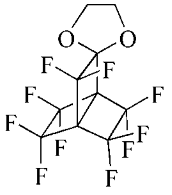

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The aim of this work was to provide a careful study of the [2.2.2]propellane system by using state-of-the-art theoretical methods. Particular attention will be focused on the existence of the singlet-state diradical **2**, the barrier between the isomer **1** and the expected bond-stretch isomer **2** and the Grob rearrangement to the undoubtedly most stable isomer **3**. The results should provide reliable information on this intriguing system and its reactivity as both geometries and total molecular energies of the ground state and the first triplet state have been treated at a very high theoretical level thus offering benchmark data.

Computational Procedures

Single-state and state-averaged multiconfiguration self-consistent field calculations[23–25] denoted as SS-CASSCF and SA-CASSCF, respectively, were carried out followed by multireference-averaged coupled cluster (MR-AQCC) computations.[26,27] A distinct advantage of the adopted method is a good combination of multireference and approximate size extensivity effects that ensures a balanced description of non-dynamic and dynamic electron correlation effects.[28,29] The availability of analytical gradients[30–32] for the MR-AQCC method allows geometry optimization of equilibrium structures and location of the transition states at a very high level of theory thus enabling reliable results to be obtained. The Pople 6-31G(d) basis set,[33] which represents a fair compromise between quality and flexibility,[34] was used in all the calculations reported herein.

Preliminary searches for energy minima were performed using the SS-CASSCF(2,2) method and enforced D_{3h} symmetry of the molecular structure. However, it was shown that the reduction of D_{3h} to D_3 symmetry was necessary to locate true saddle points and minima. Therefore D_3 symmetry was used in all subsequent calculations.[35] The preliminary SS-CASSCF(2,2) calculations were extended by investigations using the SA-CASSCF(8,8) method which serves as a basis for the MR-AQCC treatment used in the geometry optimizations. In the case of the CAS(2,2) approach, the active orbitals correspond to bonding and antibonding combinations of carbon 2p orbitals across the central C1–C4 bond with symmetry-allowed admixtures of 2p orbitals associated with vicinal C2–C3, C5–C6 and C7–C8 bonds. Their plots as well as the plots of other relevant active orbitals are shown in the Supporting Information. State-averaging was performed over the two lowest electronic singlet states of A_1 symmetry as isomer **1** has the dominating configuration $(...(7a_1)^2\ (6a_2)^0)$, which corresponds to the excited-state configuration $(...(6a_2)^2\ (7a_1)^0)$ in **2** and vice versa (Table 1). In other words, the leading configuration is exchanged between the two isomers.

Table 1. Weights of the leading configurations (in %) calculated by the CASSCF(8,8; SA) method for structures **1**, **SP1** and **2**.

	1	**SP1**	**2**
Ground state (1^1A_1)			
$...(7a_1)^2\ (6a_2)^0$	69.1	77.8	17.3
$...(6a_2)^2\ (7a_1)^0$	0.6	17.2	76.5
First excited state (2^1A_1)			
$...(7a_1)^2\ (6a_2)^0$	0.9	15.9	54.3
$...(6a_2)^2\ (7a_1)^0$	91.4	78.3	14.1

In constructing the reference configurations, it turned out that the use of the entire CAS(8,8) as reference space for the MR-AQCC calculations resulted in final expansion spaces that are too large in terms of configuration state functions (CSFs). Therefore, CAS(8,8) was reduced by using the occupancy of the natural orbitals as selection criterion. Two orbitals possessing the largest (1.947, 1.947 for **1**, 1.951, 1.948 for **SP1** and 1.951, 1.944 for **3**) and the lowest (0.038, 0.031 for **1**, 0.030, 0.030 for **SP1** and 0.034, 0.031 for **3**) occupation numbers were transferred to the restricted active space (RAS) and the auxiliary space (AUX), respectively. Hence, the reference space in the MR-AQCC calculations was constructed by using all possible configurations generated by distributing four electrons among the remaining four CASSCF orbitals complemented by all single and double excitations from RAS to CAS and from CAS to AUX. This method is denoted hereafter as MR-AQCC(8,8*; SA). The final expansion space for the MR-AQCC calculation was obtained by allowing all single and double excitations from all reference configurations into all internal and virtual orbitals. The carbon 1s core electrons were kept frozen. Only reference configurations possessing the symmetry of the electronic state in question were selected and the interacting space restriction condition was imposed.[36] A total number of 112.3 and 134.5 million CFSs were obtained to describe the singlet and triplet states, respectively. State-averaging was not applied in the characterization of the triplet potential energy curve.

The structural parameters of all minima and TS geometries were computed in natural internal coordinates as defined by Fogarasi et al.[37] using the GDIIS method.[38] Zero-point vibrational energy (ZPVE) corrections were calculated at the MR-AQCC(2,2; SS) level for stationary points along the reaction path leading from **1** to **3**. Harmonic force constants were computed by using finite differences in the energy gradients. In describing the cage-opening of the [2.2.2]propellane by C–C vicinal bond scission, the CASSCF(2,2) approach was found to be inadequate. Instead, a CASSCF(4,4) scheme was utilized to compute the harmonic force constants. All computations were carried out using the COLUMBUS suite of codes.[29,39,40] The atomic orbital (AO) and gradient integrals were computed with program modules taken from the DALTON program package.[41] The harmonic vibrational frequencies were obtained using the SUSCAL program developed by Pongor and co-workers.[42]

Results and Discussion

The potential energy curve along the C1–C4 stretching reaction coordinate in [2.2.2]propellane was calculated using the MR-AQCC(8,8*; SA) method and is displayed in Figure 1. It was obtained from a preliminary optimization of the saddle point 1 (**SP1**) at the MR-AQCC(2,2; SS) level. Then consecutive steps along the bridgehead C1–C4 bond were made in both directions towards structures **1** and **2** reoptimizing all other independent structural parameters under the D_3 symmetry restriction using the MR-AQCC(8,8*; SA) method. Finally, the initial structures **1** and **2** as well as **SP1** were fully optimized. The same procedure for the calculation of the reaction coordinate was applied to calculate the potential energy curve of the first triplet state. In addition, vertical energies for the first triplet state were calculated on ground-state points, as indicated by the dashed curve in Figure 1.

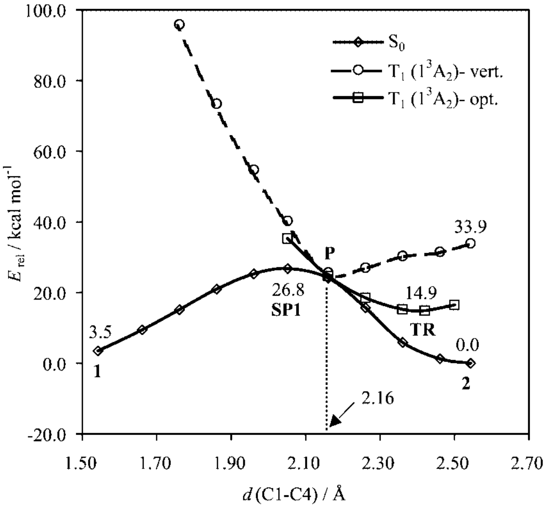

Figure 1. Potential energy curves along the C1–C4 stretching reaction coordinate calculated using the MR-AQCC(8,8*; SA)/6-31G(d) method. The relative energies have not been corrected for ZPVE contributions. Point **P** is the minimum on the vertical first triplet energy curve. The minimum of the adiabatic T_1 (1^3A_2) potential energy curve is denoted by **TR**.

For the ground state two minima were located on the potential energy surface (PES) corresponding to the C1–C4 bond lengths 1.542 (**1**) and 2.543 Å (**2**). Structure **2** is more stable than structure **1** by 3.6 kcal mol^{-1} if ZPVE is taken into account (Figure 2). The saddle-point structure **SP1** for the interconversion of **1** into **2** lies 26.8 kcal mol^{-1} above **2**. We also note that the corrections reduce the barrier by 0.5 kcal mol^{-1} (Figure 2 and Table 2). This is in accordance with previous findings that the ZPVE has only a small effect on the energy barrier.[43] Importantly, the barrier height for the **1**→**2** interconversion taking **1** as the reactant is 22.7 kcal mol^{-1} if ZPVE is included, which is in excellent agreement with the value of 22 kcal mol^{-1} measured by Eaton and Temme.[17]

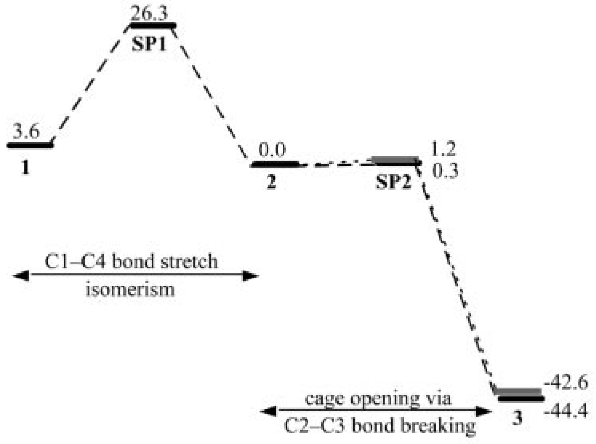

Figure 2. Relative energies as measured against the open-cage structure **2** (in kcal mol^{-1}) corrected for ZPVE contributions for two reaction paths calculated using the MR-AQCC(8,8*; SA)/6-31G(d) method and given as full lines. The uncorrected relative energies for cage-opening by breaking of the C2–C3 bond are given above the corrected ones.

Table 2. Comparison of the relative energies (in kcal mol^{-1}) of the initial system **1**, saddle points **SP1** and **SP2** and the most stable 1,4-dimethylenecyclohexane isomer **3** relative to the open virtual system **2** calculated by different theoretical approaches with the 6-31G(d) basis set.[a]

Method	1	SP1	SP2	3	Ref.
MR-AQCC(8,8*; SA)	3.5	26.8	1.2	–42.6	this work
MR-AQCC(8,8*; SA)+ZPVE	3.6	26.3	0.3	–44.4	this work
RHF	–16.5	37.5			[16]
UHF	19.1	37.1			[16]
CASSCF(2,2)	5.1	20.5			[15,16]
MP2/CASSCF(2,2)	5.7	21.6			[16]
MP2/CASSCF(2,2)+ZPVE	4.8	19.8			[16]
CASSCF(4,4)	5.2	21.3	0.6	–56.9	[16]
MP2/CASSCF(4,4)	8.4	25.2			[16]
CASSCF(8,8)	6.9	24.1	0.3		[16]
MP2/CASSCF(8,8)	15.1	33.5			[16]
MP2/CASSCF(8,8)+ZPVE	14.9	33.4			[16]
B3LYP (unrs, unpr)	3.9	28.7		–47.1	[16]
BLYP (REKS)	≈10	≈36			[47]

[a] The total electronic and ZPVE energies for our best calculation of the reference point **2** are –310.91434 and 0.18178 a.u., respectively. The unrestricted and unprojected B3LYP method is denoted by (unrs, unpr). The total electronic and ZPVE energies for **3** are –312.03801 and 0.17972 a.u., respectively, as calculated using UB3-LYP(unrs, unpr).

Selected structural parameters for the structures considered so far are displayed in Figure 3, while the Cartesian coordinates of all the optimized structures are given in the electronic supporting information. In structure **1** all the C–C bond lengths, including the central C1–C4 bond, are very similar and comparable to the C–C bond length in cyclobutane (1.548 Å).[44] The C1–C4 distance of 1.573 Å[19] measured for structure **6** is longer than the calculated value of 1.542 Å in **1**. This difference is not unexpected since the [2.2.2]propellane cage in **6** is strongly affected by the fluorine and acetal substituents. Going from structure **1** to structure **2**, the changes in, for example, the vicinal C2–C3 and geminal C1–C2 distances are substantially smaller (<0.12 Å) than the changes in the central C1–C4 bond (Δd(C1–C4) = 1.001 Å). Contrary to all previous theoretical calculations, for which the existence of a mirror plane perpendicular to the C1–C4 axis was assumed, leading to D_{3h} symmetry, and imposed from the outset, rotation of the C2,C6,C7 subunit with respect to the C3,C5,C8 one was found in our MR-AQCC optimizations for propellane **1** and **SP1**. The dihedral angles are 7.3 and 9.1°, respectively (Figure 4). However, note that the energy differences between the D_{3h} structures are extremely small (0.1 and 0.2 kcal mol^{-1}, respectively) as computed at the MR-AQCC(2,2; SS)/6-31G(d) level of theory. Note also that structure **2** and the saddle point **SP2** possess a symmetry plane, as evidenced by &πηι; = 0°, thus resulting in D_{3h} symmetry. The dihedral angles &πηι; are 18.0 and 4.2° for **3** and the adiabatic first triplet minimum structure **TR**, respectively.

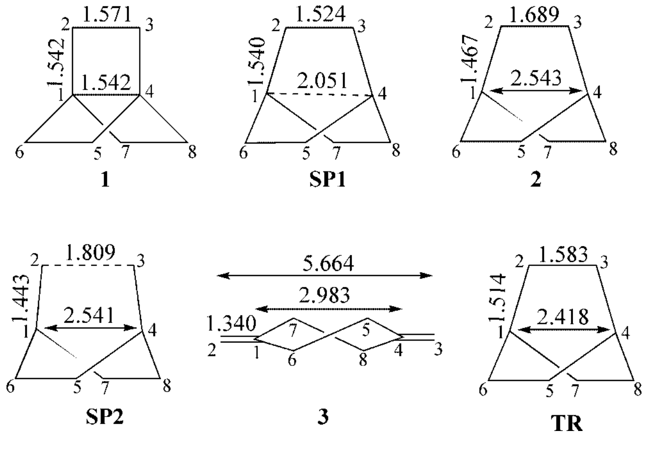

Figure 3. Selected geometry parameters calculated using the MR-AQCC(8,8*; SA)/6-31G(d) method.

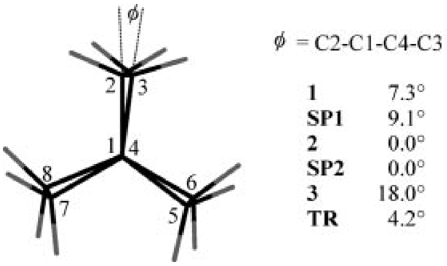

Figure 4. Dihedral angles ϕ (C2–C1–C4–C3) calculated using the MR-AQCC(8,8*; SA)/6-31G(d) method.

Note that the C2–C3 bond length increases by 0.17 Å on going from **SP1** to **2**, whereas the C1–C2 bond is compressed by 0.7 Å. It is conceivable that through-space coupling is replaced by through-bond coupling[45] in **2**, contributing to this variation in bond lengths. However, this question lies outside the scope of this paper.

We found that structure **2** has only very little diradical character, as evidenced by the natural orbital occupation numbers being 0.212 and 1.780 |e| for the frontier 7a$_1$ and 6a$_2$ orbitals, respectively. This is presumably a consequence of the through-bond interaction, as conjectured by Hoffmann and co-worker.[9,45] Going from [2.2.2]propellane **2** to [2.2.2]propellane **1**, the natural orbital occupation numbers of the frontier orbitals of **1** are reversed, being 1.934 and 0.048 |e|, thus causing highly pronounced diradical character in the **SP1** structure (1.600 and 0.384 |e|, respectively) relative to **2**. It is, however, still far from the expected singly occupied frontier MOs. Note that the most pronounced diradical character is found approximately at point **P** (1.203 and 0.780 |e|, respectively) located in the vicinity of **SP1**. Note that in both frontier MOs the unpaired spin density is approximately the same, being 0.8. Point **P** is the minimum energy point on the vertically calculated first triplet potential energy curve. The corresponding singlet–triplet gap is very small (1.5 kcal mol^{-1}). If the geometry of the triplet state at point **P** is optimized (keeping the distance C1–C4 fixed at 2.16 Å), the singlet–triplet gap drops to only 0.6 kcal mol^{-1}, thus maximizing singlet–triplet coupling and enhancing the probability of intersystem crossing. Full geometry optimization shifts the triplet minimum to the right side of the singlet potential energy curve in the direction of the opened structure **2** (Figure 1). This finding explains the very low yields of [2.2.2]propellane produced by the photochemical experiments as reported by Dannenberg at al.[21] and contrary to their previous semiempirical predictions.[20]

The complete picture of the [2.2.2]propellane reaction channel requires consideration of the possible breaking of one of the vicinal C–C bonds, leading to 1,4-dimethylenecyclohexane (**3**). This reaction is known as Grob-type fragmentation.[10–12] This rearrangement is a symmetry-allowed process[12] and consequently it is thermodynamically favoured with respect to suspected bond-stretch isomerism leading to [2.2.2]propellane **1**. Indeed, structure **3** is 44.4 kcal mol^{-1} lower in energy than [2.2.2]propellane **2**. This huge energy difference in stability is in accord with chemical intuition because a large amount of angular strain energy is released. What is more important, the saddle-point structure for the cage-opening is only 1.2 kcal mol^{-1} higher in energy than **2**. The ZPVE correction decreases the barrier height to only 0.3 kcal mol^{-1}, thus corroborating the conjecture derived by considering symmetry arguments alone. It is fair to say that the open form of the [2.2.2]propellane **2** is expected to collapse to **3** in a barrierless process. Thus it is safe to conclude that the open system **2** is nonexistent! The geometry of the second saddle point **SP2** resembles the geometry of the [2.2.2]propellane form **2** with a C2–C3 bond length elongated by only 0.12 Å. As could be expected, the equivalent C1–C2 and C3–C4 bonds are shortened by 0.02 Å as double bonds are formed in the final product **3** [*d*(C1–C2 and C3–C4) = 1.340 Å].

It follows as a corollary that, if bond-stretch isomerism is desired in the [2.2.2]propellane system, then some new structural features must be incorporated into the system that will prevent Grob-type fragmentation. It also has to be taken for granted that a sufficiently high barrier along the bond-stretch coordinate is preserved. The synthesis of the thermodynamically stable and heavily fluorinated derivative propellane **6** (unchanged after 10 h at 100 °C) supports this conclusion.[19] It is not clear at present whether its existence is a consequence of an increased stability of **1** over **2**, a substantial barrier height for bond-stretch isomerism and/or because of hindered Grob-type fragmentation.

These results on the fragmentation of the [2.2.2]propellane system represent the most accurate description of this reaction to date. Therefore, it would be interesting to compare them with other ab initio data on the bond-stretch barrier height and relative stability of the starting material and product: the relevant data are presented in Table 2.

It appears that all ab initio methods give the same relative ordering of the critical points on the PES (**1** and **SP1**) with RHF being the only exception. This is not surprising since this method is incapable of a correct description of diradicals; it gives completely unrealistic results for all structures with a C1–C4 distance longer than 1.71 Å. The situation is much improved by using the UHF method, but the energy barrier and relative destabilization energy of **1** are overestimated greatly. The CASSCF approach as a multireference method should be capable of describing diradicals as well as non-dynamic correlation energy contributions connected with the change in configuration along the reaction coordinate, which is crucial for the [2.2.2]propellane system. However, the performance of the CASSCF method strongly depends on the size of the active space. For instance, the CASSCF(2,2), CASSCF(4,4) and CASSCF(8,8) **SP1** saddle-point energies are 20.5, 21.3 and 24.1 kcal mol^{-1}, respectively, thus being in fair-to-good agreement with the present most accurate value of 26.3 kcal mol^{-1}. The relative energies between isomers **1** and **2** are reasonable too. The problem with the CASSCF methods is that they tend to exaggerate the stability of the open-cage isomer **3**. Further, MP2 correction of the CASSCF energies at the CASSCF(2,2) and CASSCF(4,4) levels slightly improves the barrier height of the **SP1** structure, but worsens the relative stability of isomers **1** and **2**. The MP2/CASSCF(8,8) results are quite unrealistic. One is inclined to conclude that the relatively good results for the barrier height obtained by the CASSCF method are somewhat fortuitous. It seems that the same holds for the unrestricted and unprojected B3LYP(unrs, unpr) method. Although the relative stability of the isomers **1** and **2** is reproduced correctly with a very small error of only 0.3 kcal mol^{-1} and the barrier height of **SP1** deviates by a qualitatively acceptable 2.4 kcal mol^{-1}, the B3LYP(unrs, unpr) method is unable to locate the **SP2** critical point and **2** is not a true minimum. Moreover, the UB3LYP approach fails to describe the Diels–Alder reaction of ethene and 1,3-butadiene.[46] Furthermore, the spin-restricted ensemble-referenced Kohn–Sham (REKS) method[47] yields unacceptably high *E*(**1**)–*E*(**2**) and **SP1** barrier height values (Table 2). Hence, caution has to be exercised in using and interpreting B3LYP(unrs, unpr) results. It appears that reliable predictions of the chemical reactivity of propellanes can only currently be provided by the MR-AQCC method. Having said this, note that Thatcher Borden and co-workers.[48] found the UB3LYP method useful in discussing the dimerization of bicyclo[2.2.0]hex-1(4)-ene and its perfluoro derivative. The activation enthalpy was in fair agreement with the measured value. Clearly, the UB3LYP method should be employed only if the results can be tested against some experimental check points.

Conclusions

The high level post-HF MR-AQCC method, which is capable of optimizing the geometric parameters and describing both dynamic and non-dynamic electronic correlation energies on an equal footing, has been applied to the problem of possible [2.2.2]propellane isomerism as well as the Grob-type fragmentation. It follows beyond any reasonable doubt that the alleged open form of the [2.2.2]propellane is an artefact as its stability is negligible. It undergoes barrierless cage-opening resulting in the thermodynamically more stable 1,4-dimethylenecyclohexane (**3**). Therefore, bond-stretch isomerism does not occur in this system. The present results indicate that [2.2.2]propellane **1** is a potentially stable compound in spite of a high energy content because it is protected by a high barrier of 22.7 kcal mol^{-1} from the Grob fragmentation process. However, once this barrier is overcome, system **1** interconverts into 1,4-dimethylenecyclohexane (**3**), which is more stable by 48 kcal mol^{-1}. Note that the barrier height is in excellent agreement with the experimental results of Eaton and Temme.[17] The singlet–triplet energy gap along the bond-stretch reaction coordinate has been calculated. It was found that intersystem crossing can be expected in the vicinity of the saddle point **SP1**, but at a longer C1–C4 bond length (2.161 Å), on the [2.2.2]propellane **2** side of the potential energy curve. Therefore, photochemical closure of the bridgehead C–C bond has a lower probability than the relaxation of the system on the singlet ground-state PES leading to structure **3**. These results explain the difficulties in attaining photochemical C1–C4 bond closure to yield the conceivable, but elusive system **1**. The minimum on the first triplet T_1 (1^3A_2) potential energy curve is located 11.4 and 59.3 kcal mol^{-1} above the ground-state energies of the equilibrium structures **1** and **3**, respectively.

Supporting Information (see also the footnote on the first page of this article): Total electronic energies (a.u.) and Cartesian coordinates (Bohr) of structures **1**–**3**, **SP1**, **SP2** and **TR** calculated by the

MR-AQCC(8,8*; SA)/6-31G(d) method. Natural orbital occupation numbers of active molecular orbitals (|e|) calculated at the CASSCF(8,8; SA) level for structures **1**, **SP1** and **2**.

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