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Thermal Behavior of [2.1.1]Propellane: A DFT/ab Initio Study

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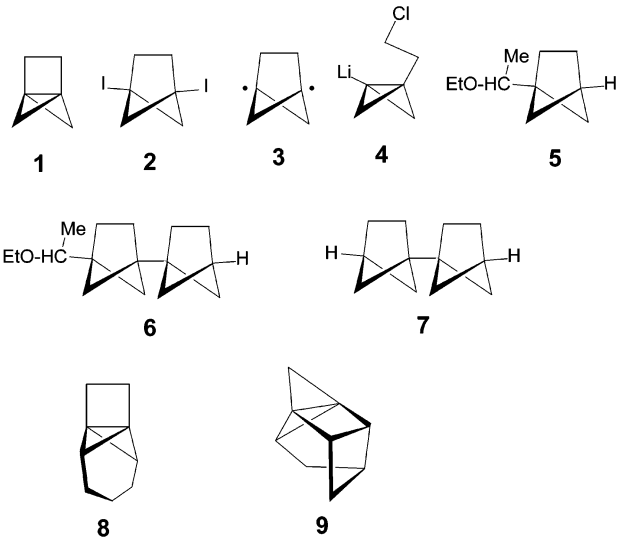
Density functional and ab initio molecular orbital calculations have been used to search for the low energy path of the thermal isomerization of [2.1.1]propellane **1**. Three reaction modes were considered: ring opening of the bicyclo[1.1.0]butane unit in **1** to give 1,2-dimethylenecyclobutane **21**, opening of the four-membered ring of **1** to afford 1,3-dimethylenecyclobutane **20**, and breaking of the [2.1.1]propellane central bond and one of the bicyclo[1.1.0]butane side bonds to form carbene **17**. At the CAS(12,12)PT2N/6-31G(d) level of theory, the activation barrier of the latter route was lowest in energy. Further investigation of this process at the QCISD(T)/6-311G(d,p)//QCISD/6-31G(d) and B3PW91/6-311G(d,p)// B3PW91/6-311G(d,p) level of theory indicated that the barrier of isomerization of **1** → **17** amounts to 29 kcal/mol and that **17** is stabilized by hydrogen migration to give dienes **18** and **19**.

Introduction

Within the family of [*n*.1.1]propellanes,[1] [2.1.1]propellane **1** is the only member that cannot be isolated at room temperature as a stable molecule. Its existence has been proven by IR spectroscopy of a sample of **1**, generated in the gas phase in a nitrogen atmosphere by reaction of potassium atoms with 1,4-diiodobicyclo[2.1.1]hexane **2** and trapping of **1** into a nitrogen matrix at about 30 K.[2] At 50 K, the IR spectrum disappeared, apparently because **1** polymerized.[1] Ab initio calculations at the HF/6-31G* level of theory showed that **1** is a local minimum on the C_6H_8 energy hypersurface. In addition, the strain energy of **1** was computed as 106 kcal/mol,[3] and the central bond dissociation energy of **1** to the hypothetical diyl **3** as approximately 30 kcal/mol.[4] Later experimental efforts to obtain **1** as an isolable molecule were unsuccessful: the cyclization of **4** afforded a mixture of **5**, **6**, and **7**;[5] **5** and **6** could be explained by radical chain processes, but the formation of **7** is not well understood. Efforts to synthesize derivatives of **1**, the tetracyclic compound **8** or the pentacyclic compound **9**, led to products that indicated that the [2.1.1]propellane derivatives **8** and **9** were formed as fleeting intermediates, which reacted quickly by bimolecular processes with rupture of the central propellane bond.[6,7]

These results indicate that propellane **1** and its derivatives show an enhanced reactivity toward addition of organometalic reagents and radicals, which add across the central CC bond. However, little information is available concerning the thermal stability of **1** with respect to unimolecular rearrangements. Therefore we have used computational methods to search for low energy paths of the thermal isomerizations of **1**.



One could expect that the course of the thermal isomerization of **1** might be similar to those of [1.1.1]-propellane **10** and [3.1.1]propellane **11**. The latter has been subjected to a flash vacuum pyrolysis experiment, which was carried out at 380 °C/6 × 10^{-6} Torr and afforded a 2:1 mixture of the dienes **12** and **13**. Formation of carbene **14** from **11** and hydrogen migration from the adjacent methylene groups to the carbenic carbon would seem to be a logical interpretation of these results. [5] Our recent investigation of the thermal isomerization of **10**, which leads to diene **16**, proceeds according to DFT computational results via puckered carbene **15**.[8]

(1) Wiberg, K. B. *Chem. Rev.* **1989**, *89*, 975−983.
(2) Wiberg, K. B.; Walker, F. H.; Pratt, W. E.; Michl, J. *J. Am. Chem. Soc.* **1983**, *105*, 3638−3641.
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(5) Fuchs, J.; Szeimies, G. *Chem. Ber.* **1992**, *125*, 2517−2522.
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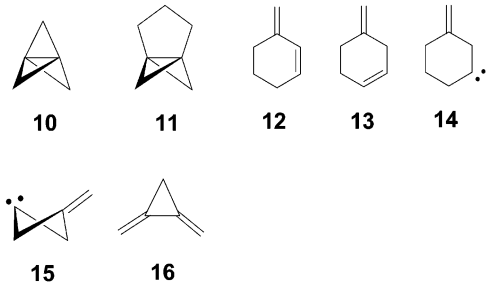
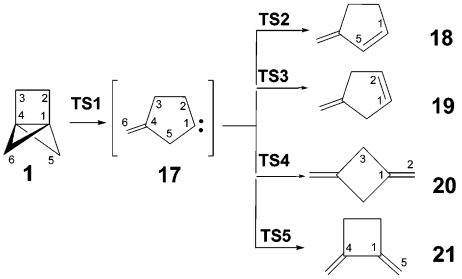


Therefore, a reasonable choice for the mechanism of the thermal isomerization of **1** would be the reaction path depicted in Scheme 1. Here, the central propellane bond

SCHEME 1 Retro-Carbene Path (Numbering of C Atoms as in 1)

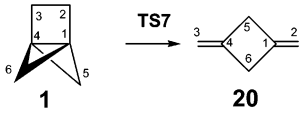


C1C4 and one of the four equivalent side bonds (C1C6) are broken in a retro-carbene reaction, leading to carbene **17** as an intermediate, which could be stabilized by four consecutive reactions: (a) hydrogen migration from C5 to give 3-methylenecyclopentene **18**; (b) hydrogen migration from C2 of **17** to afford 4-methylenecyclpentene **19**; (c) ring contraction by migration of C3 to the carbenic carbon C1 to form 1,3-dimethylenecyclobutane **20**; (d) ring contraction by migration of the vinylic carbon C4 to C1 leading to 1,2-dimethylenecyclobutane **21**.

Two alternative reaction paths have been considered, which are depicted in Schemes 2 and 3. The conversion

SCHEME 2. "Disrotatory" Bicyclo[1.1.0]butane Ring Opening of 1

SCHEME 3. Cyclobutane Ring Opening



of **1** → **21** may be viewed as a special case of the bicyclo-[1.1.0]butane/1,3-butadiene isomerization. This reaction has been thoroughly studied by computational methods by Nguyen and Gordon,[9] who describe a low energy ("concerted conrotatory TS") barrier and a high energy ("concerted disrotatory TS") process, which show strongly different transition state structures. In their latter transition state, the dihedral angle of methin-H, tert-C, tert-C, -methin-H has been computed to be very small (15.6°), whereas this value amounts to 128° in the low energy transition state. As the four-membered ring of **1** is completely retained in the conversion of Scheme 2, it seems obvious that only the high energy transition state of Nguyen and Gordon can be operative in this case.

The conversion of **1** → **20** in Scheme 3 is guided by the relief of considerable ring strain, which might provide this orbital-symmetry forbidden cyclobutane ring opening reaction with a sufficiently low barrier to make it energetically comparable to the other routes.

On the basis of our computational results concerning the thermal isomerization of [1.1.1]propellane **10**,[8] transition states or intermediates of Scheme 1 should not show any significant diradical character. Therefore, single determinant based methods should be adequate to investigate this process. This is certainly not true for the reaction paths depicted in Schemes 2 and 3, where in both cases a large diradical character is to be expected in the transition states. As a consequence, multiconfigurational techniques had to be applied here. To be able to compare the computational results of the three schemes, multiconfigurational calculations had also to be carried out for some stationary points of Scheme 1.

Methods of Calculation

The thermal rearrangements considered in this investigation proceed by breaking of the C1−C4 and C1−C6 bonds of **1** in Scheme 1, of the C1−C4 and C5−C5 bonds in Scheme 2, and of the C2−C3 and C1−C4 bonds in Scheme 3. To retain the symmetry of propellane **1**, the multiconfigurational wave function requires an active space containing the MOs associated with the four side-bonds of bicyclo[1.1.0]butane subunit, with the central bond C1−C4, with the bond C2−C3 and their antibonding counterparts. The corresponding orbitals were used for the active space of transition structures **TS1**, **TS6** and **TS7**, of carbene **17**, and of **20** and **21**. The CAS(12,12) calculations on these structures were carried out with the program Molcas[10] using the Cartesian 6-31G(d) basis set. For all structure optimizations frequency calculations were completed for the stationary points to verify local energy minima and transition states. To assess the problem of dynamic electron correlation,[11] CAS(12,12)PT2N[12,13] calculations (in the following denoted as CAS(12,12)PT2) were performed on the stationary points with the CAS(12,12) wave functions as the reference space, using the program Molcas.

For most of the calculations of Scheme 1 DFT methods were used. On the basis of our recent experience that the B3LYP functionals computed [1.1.1]propellane **10** too unstable by nearly 9 kcal/mol and that the B3PW91 method gave more reasonable results,[8] the latter correlation functionals (PW91)[14] were used throughout with the 6-311G(d,p) basis set. In addition, the QCISD procedure was also applied to the reaction sequence of Scheme 1 with the 6-31G(d) basis set. The energies

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(12) Andersson, K.; Malmqvist, P.-A.; Roos, B. O.; Sadlej, A. J.; Wolinski, K. *J. Phys. Chem.* **1990**, *94*, 5483−5488.

(13) Andersson, K.; Malmqvist, P.-A.; Roos, B. O. *J. Chem. Phys.* **1992**, *96*, 1218−1226.

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TABLE 1. Relative Energies: CAS(12,12)PT2/6-31G(d)// CAS(12,12)/6-31G(d), ZPE Corrected

	CAS(12,12)PT2/6-31G(d) (kcal/mol)
1	= 0.0
TS1	33.24
carbene **17**	21.07
TS6	58.31
TS7	43.04
20	−28.59
21	−30.67

of these stationary points were improved by QCISD(T)/6-311G(d,p) single point calculations. All computations of this section were carried out with Gaussian 98.[15]

Results and Discussion

The unusual behavior of [2.2.2]propellane to give a biradical intermediate as a local energy minimum on stretching the central bond [16] is not detected with [2.1.1]-propellane **1**: diradical **3** collapsed back to **1** at the B3PW91/6-311G(d,p) or CAS(12,12)/6-31G(d) level of theory, indicating that on the energy hyper surface of the thermal isomerization of **1** a singlet structure resembling **3** is not an intermediate. This is in accord with older results of Hofmann and Stohrer.[17] In addition, we were unable to locate diradical **3** as a saddle point.

The CAS(12,12)PT2/6-31G(d) relative energies of the stationary points are given in Table 1. The computed geometries of all stationary points, their energies, and their zero-point energies are available as Supporting Information.

The reaction path using the barrier **TS1** (see Table 1) leading to carbene **17** (see Scheme 1) is energetically by far more favorable than the competing reactions via **TS6** or **TS7**, which should play no role in the thermal isomerization of **1**. It is interesting to note that our computed barrier for [2.1.1]propellane going to 1,2-bismethylenecyclobutane **21 (**58.3 kcal/mol) is rather close to the CAS(10,10)PT2 barrier obtained by Nguyen and Gordon for the "concerted disrotatory" isomerization of bicyclo[1.1.0]butane to 1,3-butadiene (56.3 kcal/mol).[9]

The reaction sequences shown in Scheme 1 were further investigated by the DFT-B3PW91/6-311G(d,p) and by ab initio QCISD/6-31G(d) procedures. The DFT calculations of the transition states were carried out with the spin-restricted and spin-unrestricted methodology. In the latter cases, $<s^2>$ was zero and the energies were identical to the results of the spin-restricted calculations. Therefore, the transition states of Scheme 1 should not contain a significant biradical character, justifying their computational treatment with single determinant based methods. The relative energies of the stationary points are given in Table 2.

The relative energies of **TS1** in Table 2 are only slightly lower than the CAS(12,12)PT2 barrier of Table 1, supporting our initial assumption that the retro-carbene reaction should be the favorable route for the thermal isomerization of [2.1.1]propellane **1**. On the basis of the last column of Table 2, the carbene **17** is higher in energy than **1** by 15.2 kcal/mol. The barrier for the cyclization back to **1** amounts to 13.1 kcal/mol. This barrier is strongly undercut by the barriers of migration of the vicinal hydrogens to the carbene carbon, which amount to 3.7 and 4.4 kcal/mol and are the only ones that should lead to products. Both ring contraction reactions to afford **20** and **21** via **TS4** and **TS5** have to cross barriers of 28.0 and 17.4 kcal/mol and will not compete favorably with hydrogen migration. At 10.6 kcal/mol, the energy difference of the barriers of ring contractions is unexpectedly high.

The energy hypersurface of the ring opening of **1** to **17** differs considerably from that of the thermal isomerization of [1.1.1]propellane **10**, where the lower homologue of **17**, 3-methylenecyclobutylidene, could be detected as a shallow minimum only with DFT methods.[8]

According to the results of Table 2, the triplet state of propellane **1** is much higher (48.4 kcal/mol) and of carbene **17** sufficiently higher in energy (4.9 kcal/mol) than the singlet states. The triplet states should play no significant role in the thermal isomerization of **1**.

The energies of **18**, **19**, **20**, and **21**, the final products of the corresponding reaction routes, are well below the energy of **1**. Their differences are in accord with different strain energies and 1,3-diene conjugation.

Structures of the Stationary Points. The structures of **1**, **17**, and the transition states **TS1**−**TS5** are depicted in Figure 1, which also shows selected bonding parameters.

Although the central C1C4 bond is the longest bond in all calculated structures of propellane **1**, the CAS-(12,12)/6-31G(d) result of 1.723 Å seems somewhat exaggerated. At 1.987 Å (QCISD), the C1C4 distance of triplet **1** is still considerably shorter than the corresponding distance in bicyclo[2.1.1]hexane, which was determined as (2.172 ± 0.016) Å by electron diffraction.[18]

The structures of **TS1** differ only slightly; one of the bicyclo[1.1.0)butane side bonds is nearly completely broken (QSISD, 2.429 Å) and the opposite side bond C1C6 is nearly a CC double bond (1.360 Å), whereas the central bond is lengthened to 1.955 Å. The five-membered ring of carbene **17** is not planar, the dihedral angles ω(C5C1C2C3), ω(C1C2C3C4), and ω(C2C3C4C5) were computed [B3PW91/6-311G(d,p)] as −9.1°, 23.0°, and −26.8°; ω(C6C4C5C1) and ω(C6C4C3C2) were −151.9° and 148.7° (for numbering see **17** in Scheme 1). The angle α(C5C1C2) at the carbenic center is 103.2°. In **17-triplet**, this angle is widened to 115.9°, and the five-membered ring is also nonplanar. In both transition states **TS2** and **TS3**, the breaking CH bond is shorter than the newly formed one, indicating an early transition state for a

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TABLE 2. Relative Energies (kcal/mol) of the Stationary Points of Scheme 1, Corrected for ZPE

	B3PW91/6-311G(d,p)// B3PW91/6-311G(d,p)	QCISD/6-31G(d)// QCISD/6-31G(d)	QCISD(T)/6-311G(d,p)// QCISD/6-31G(d)
1	= 0.0	= 0.0	= 0.0
1-triplet	46.11	45.61	48.22
TS1	29.34	29.27	28.36
17	14.33	12.66	15.23
17-triplet	19.23	16.17	
TS2	16.46	19.22	18.89
TS3	17.36	19.76	19.60
TS4	41.06	44.35	43.27
TS5	30.71	34.71	32.65
18	−56.03		
19	−51.36		
20	−31.11		
21	−33.86		

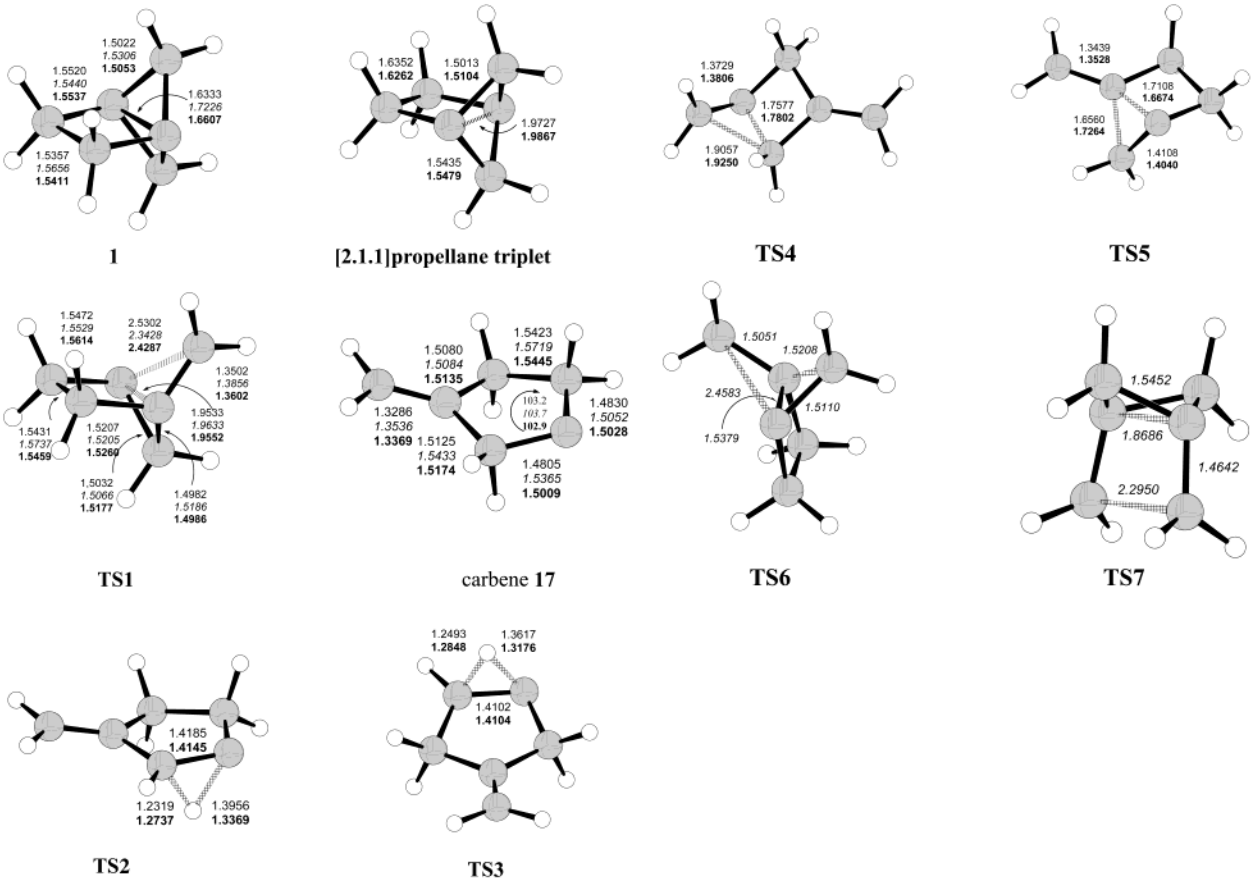

FIGURE 1. Structures of stationary points.

strongly exothermic reaction. The transition states of the ring-contraction reactions **TS4** and **TS5** differ considerably in their distances of the breaking and newly formed CC bonds: in **TS4**, the new bond is shorter by 0.14 Å than the breaking one, whereas in **TS5** breaking and forming CC bonds are shorter and at 1.66 and 1.71 Å rather similar [B3PW91/6-311G(d,p)], which results in a lower energy of about 10 kcal/mol with respect to **TS4**.

The CAS(12,12)/6-31G(d) structure of **TS6** shows a long C1C6 bond (for numbering see Scheme 2) of 2.46 Å, and a still unimpaired C4C5 bond of 1.52 Å. At 1.51 Å, the C4C6 bond is still a CC single bond. ω(C2C1C4C3) was computed as −4.5°. These values compare favorably with those of the CAS(10,10)/6-31G(d) transition state of the "concerted disrotatory process" of bicyclo[1.1.0]butane to 1,3-butadiene of Nguyen and Gordon,[9] who computed for the corresponding parameters 2.60, 1.56, and 1.51 Å, and 15.6°.

In **TS7** both breaking bonds are considerably lengthened, at 2.30 Å the C2C3 bond more so by 0.43 Å than the C1C4 bond (numbering as in Scheme 3). At 1.46 Å, the bonds C1C2 and C3C4 are short single bonds.

Conclusion

The computational investigation of the thermal rearrangement of [2.1.1]propellane by DFT and ab initio methods including multiconfigurational techniques and dynamic correlation has shown that the low energy isomerization path proceeds by a retro-carbene reaction

producing carbene **17** as an intermediate. The most favorable consecutive reactions are 1,2 hydrogen shifts to the carbenic carbon leading to dienes **18** and **19** as the final products. The computed barrier of isomerization was in the range of 28.4−32.9 kcal/mol and indicates that **1** is a persistent molecule at ambient temperature when kept under conditions, under which intermolecular reactions are excluded (low-pressure gas phase or matrix). Our computational results are in accord with the observations of Wiberg at al.[2]

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Supporting Information Available: Energies and Cartesian coordinates for all stationary points. This material is available free of charge via the Internet at http://pubs.acs.org.

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