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Planarization of the Cyclohexane Ring by Its Incorporation Into a Cyclophane Cage: Hexahydrosuperphane

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Calculations at the HF/6-311G(d,p), DFT B3LYP/6-311G(d,p), and MP2/6-311G(d,p) levels show that the hypothetical molecule hexahydrosuperphane should have a planar saturated ring imposed by its incorporation into a cyclophane. The calculated NMR chemical shifts are compared with the experimental literature data for a few compounds with similar structure fragments. The calculated vibrational frequencies and the analysis of possible decomposition routes of the title molecule indicate that the molecule should be stable. Thus, it represents a plausible synthetic target.

Introduction

Studying hydrocarbons with spatial structures that depart strongly from the standard ones is a fascinating domain that allows one to explore the limits of classical stereochemistry.[1–4] Being interested in such unusual molecules we have proposed, amongst others, the molecules bowlane **1** and **2**,[5,6] with pyramidal carbon atoms, which have inspired the Radom group to develop their modification **3** with a planar carbon.[7] We have also studied[8] the partial planarization of the cyclohexane ring by fusing several smaller rings to it, as in **4** and **5**, the former of which is less puckered than cyclohexane while the latter should be close to planarity.[9] The unusual planarity of the cyclohexane ring has been proved for a few molecules like **6** and **7** with epoxy rings fused to the cyclohexane ring,[1,10] while the structure of the analogous rings in **8**[11] and **9**[12] has not been discussed (Scheme 1). The planarization of the C6 ring could be produced by its incorporation into a macrocycle containing a benzene ring to form a cyclophane. In addition to **8** and **9**, in which the planarity could be enforced by the epoxy rings, two such compounds − hexahydrogenated [2,2]paracyclophanes **10** − have been synthesized[13,14] but, for obvious reasons, the saturated ring in these cannot be planar. In this work, the spatial structure of hypothetical hexahydrosuperphane **11** is studied together with its IR spectra and NMR chemical shifts using quantum chemistry calculations. The data calculated for **11** are compared with the corresponding experimental results for superphane **12**,[15–18] obtained by the Boekelheide group,[19] and perhydrogenated [2.2]paracyclophane **13** (Scheme 2).[20]

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Supporting information for this article is available on the WWW under http://www.eurjoc.org or from the author.

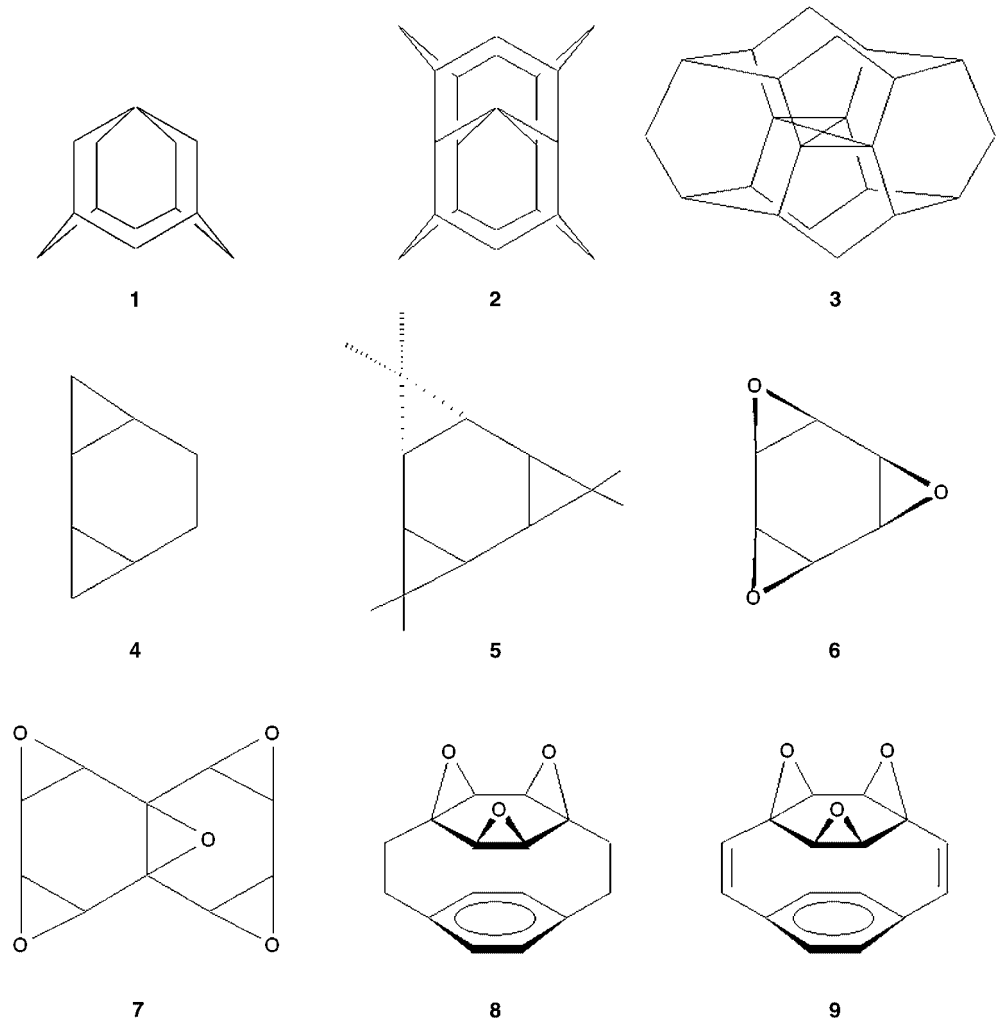
Results and Discussion

All calculated values of vibrational frequencies are positive, thus **11** represents a minimum on the energy hypersurface. The optimum bond lengths and bond angles for the title molecule calculated at the MP2/6-311G(d,p) level are presented in Figure 1 together with the literature data for superphane **12**, while the corresponding torsional angles and optimum energies for these molecules are collected in Table 1. The most important values of bond lengths and bond angles optimized at the HF/6-311G(d,p) and B3LYP/6-311G(d,p) levels, Cartesian coordinates of the optimized MP2/6-311G(d,p) structure, harmonic frequencies and IR intensities of **11**, and the Cartesian coordinates of the most plausible decomposition product **14** calculated at the DFT level are given as Supporting Information. The geometry obtained with the DFT B3LYP method using the 6-311G(d,p) basis set is only slightly different from that calculated at the MP2/6-311G(d,p) level, therefore only the MP2/6-311G(d,p) structure will be discussed below. All obtained geometries belong to the C_6 point group.

The calculated NMR chemical shifts are compared with the experimental ones for a few similar molecules in Table 2. The curve showing the dependence of DFT B3LYP/6-31G(d,p) energy on the elongation of the C1′–C2′ bond is presented in Figure 2, while the analogous dependence obtained for the simultaneous elongation of C1′–C2′, C3′–C4′, and C5′–C6′ is presented in Figure 3. The curves of similar dependencies for the elongation of the C1–C2, C1–Cb1, or C1′–Cb1′ bonds are given in the Supporting Information.

The Ring Planarity in 11

The most striking feature of the molecule under study is the planarity of the cyclohexane ring obtained at all calcu-



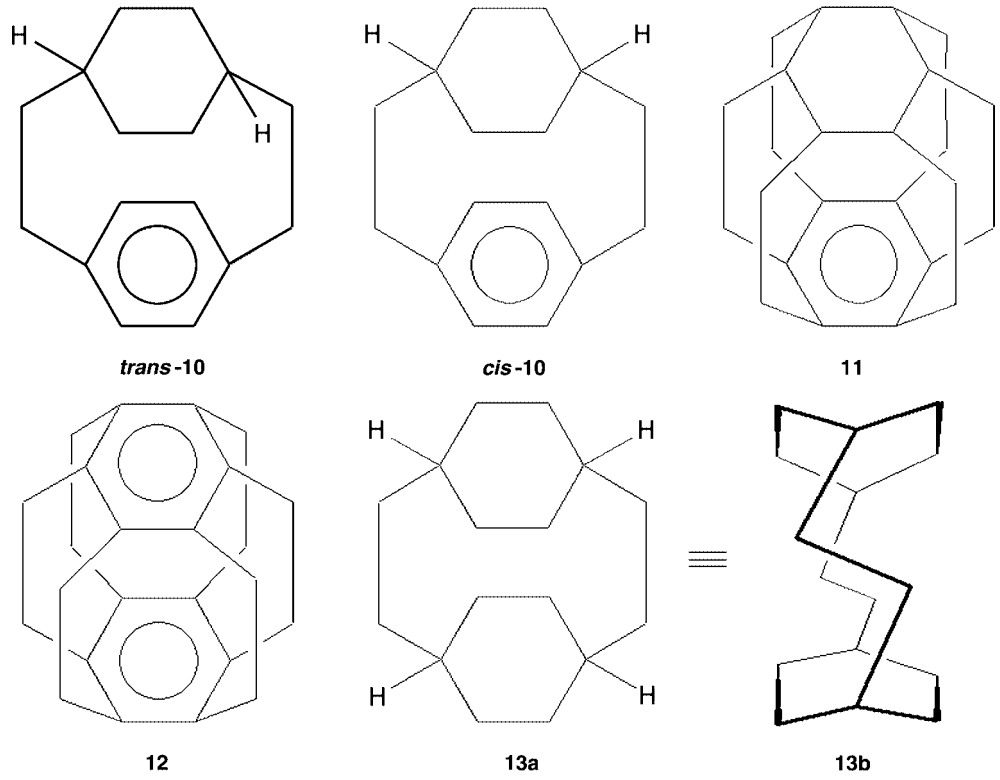
Scheme 1.

lational levels, i.e. the zero value of the C1′–C2′–C3′–C4′ torsional angle and the value of 120° for all C–C–C bond angles in the ring. Interestingly, the saturated and aromatic rings in **11** are twisted with respect to each other by an angle 6.4° for the optimized structure. A similar twisting of the rings has been postulated by Henseler[17] in superphane **12** on the basis of his MP2/6-31G calculations but was not observed in the X-ray study,[15] where a parallel arrangement of the rings was found. Henseler[17] explains this phenomenon by a low energy barrier between two twisted conformations that are rapidly interchanging at room temperature in the X-ray measurements. A similar effect could operate in the title molecule **11**. Thus, one can expect that the averaged structure of **11**, which could be that observed in the X-ray measurements, would have higher symmetry than the calculated one (C_{6v} instead of C_6).

The Bond Lengths and Distances

Most bond lengths in highly strained hexahydrosuperphane **11** (Figure 1a) are larger than the standard bond lengths for the corresponding unstrained hydrocarbons. For example, the C1′–C2′ bond length of 1.592 Å in the cyclohexane ring calculated at the MP2/6-311G(d,p) level is around 0.06 Å longer than the corresponding value in cyclohexane.[21] Interestingly, the bond lengths of the C1′–Cb1′ bond, which connects the cyclohexane ring with the ethano bridge, and that of the Cb1–Cb1′ bridge are very similar, although the former calculated value of 1.558 Å is significantly smaller than the corresponding experimental value of 1.580 Å found for **12**. Their bridge lengths of around 1.56 Å are somewhat larger than the standard C–C bond length for alkanes (1.53 Å), while the value of 1.406 Å calculated for the C1–C2 bond is only slightly larger than the C–C bond length in free benzene (1.399 Å).[21] Similarly, the bond length (1.502 Å) calculated for the C1–Cb1 bond is similar to the value of 1.507 Å for the Me–Ph bond in toluene.[22]

It should be stressed that the calculated values for the C1–C2 and C1–Cb1 bonds in **11** are reasonably close to the corresponding experimental values found for superphane **12**.[15] However, the length of the ethano bridge (Cb1–Cb1′ bond) measured in the latter molecule is slightly larger than the corresponding calculated value in **11**. We believe that



Scheme 2.

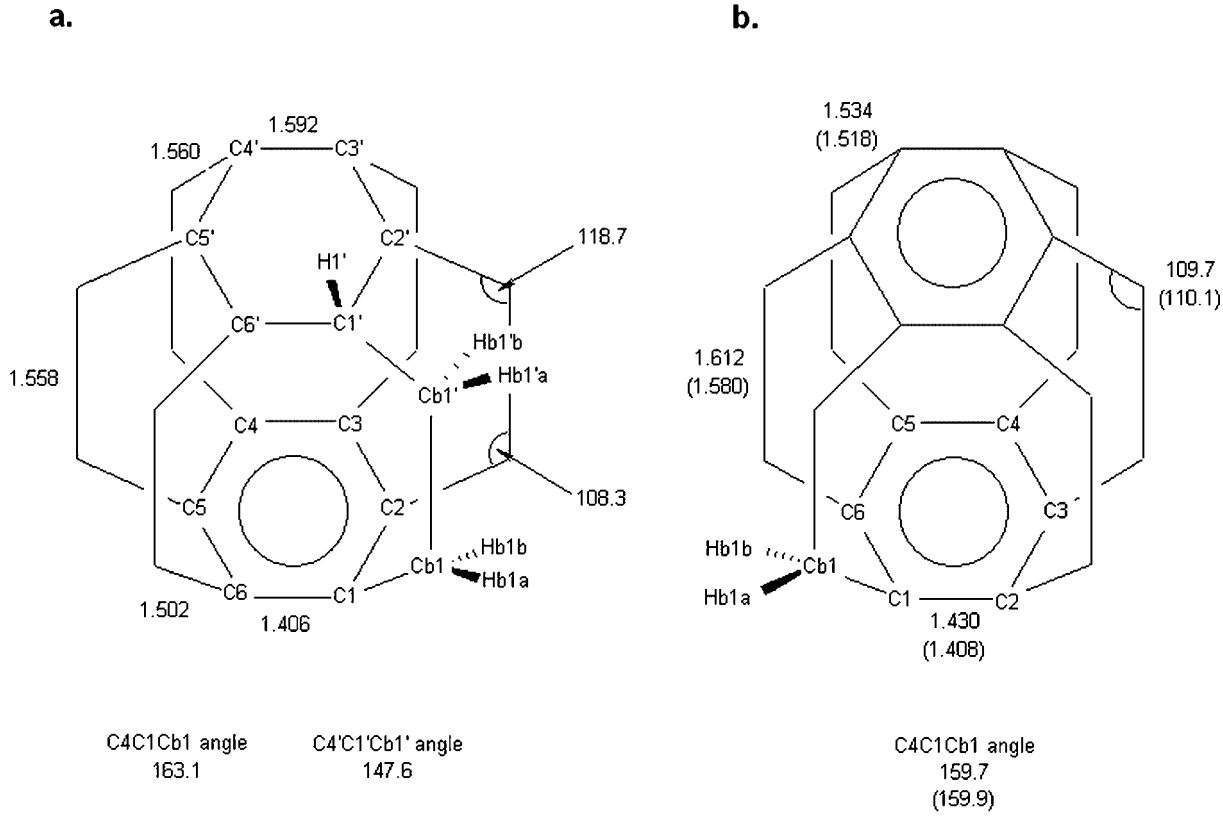


Figure 1. The most important values of bond lengths and bond angles of (a) hexahydrosuperphane **11** obtained in this work calculated at the MP2/6-311G(d,p) level and (b) the corresponding literature values for superphane **12** calculated at the MP2/6-31G level (no brackets)[17] and measured ones (in brackets).[15] Only the symmetry-independent CH bonds are shown.

Table 1. Dihedral angles and optimum energies obtained for hexahydrosuperphane **11**, superphane **12**, and perhydrogenated [2.2]paracyclophane **13b**.

Molecule	**11** (this work)			**12**		**13b**
Method	HF	DFT B3LYP	MP2	MP2[17]	X-ray[15]	X-ray[28]
Basis set	6-311G(d,p)	6-311G(d,p)	6-311G(d,p)	6-31G		
Dihedral angles [°]:						
C1–C2–C3–C4	0.0	0.0	0.0	0.0	0.0	
C1′–C2′–C3′–C4′	0.0	0.0	0.0	–	–	46.4
C1–Cb1–Cb1′–C1′	12.4	10.6	16.6	11.6	0.0	146.9
C4–C1–C1′–C4′	4.5	3.8	6.4	2.4	0.0	–
Energy [10^{-3} kcal mol^{-1}]	–581.3	–585.3	–583.5	–580.2	–	–

Table 2. Comparison of calculated chemical shifts[a] [ppm] of **11** with the corresponding values for *cis*-**10**, **12**, and **13b**.

Atom (i = 1, 2 ... 6)	**11**	*cis*-**10**[b][13]	**12**[16]	**13b**[20]
C*i*	148.6	130.9 141.4[c]	144.6	–
C*i*′	38.0	32.2 35.6[c]	–	24.3 27.4[c]
Cb*i*	29.5	24.4	32.3	–
Cb*i*′	34.7	30.2	–	30.8
H*i*[d]	–	7.29	–	–
H*i*′	2.2	0.89–1.06	–	1.56–1.48 1.80–1.67[e]
Hb*i*a	3.2	2.75	2.98	–
Hb*i*b	3.1			
Hb*i*′a	2.1	1.60–1.71	–	1.63–1.57
Hb*i*′b	2.2			

[a] Relative to δ_{abs}TMS(C) = 184.5 ppm and δ_{abs}TMS(H) = 31.7 ppm calculated with GIAO DFT B3LYP/cc-pVTZ for the TMS structure optimized on the same level. [b] No signal assignment given in ref.[13]. [c] Bridgehead carbon. [d] Aromatic ring hydrogen atoms. [e] No assignment given in ref.[20].

this effect is due to a smaller strain in the latter molecule, as reflected by the smaller distortion of some angles in **11** from the standard values as compared to **12**.

The distance of 2.798 Å between the rings, measured as the distance between the geometric centers of the aromatic and saturated rings in **11**, calculated at the MP2/6-311G(d,p) level is larger, although similar to, Henseler's value of 2.663 Å[17] calculated at the MP2/6-31G level and the X-ray result of 2.624 Å[15] for the analogous distance in **12**.

The Angles

In addition to the cyclohexane ring planarity and the averaging of the torsional angles discussed earlier, another characteristic feature, which is expected for a cyclophane with short bridges, is the fact that the Cbi atoms connected to the aromatic ring do not lie in the plane of this ring. The C4–C1–Cb1 angle characterizes this distortion from the standard structure. This angle, which is equal to 163.1°, is higher than, but reasonably close to, the analogous experi-

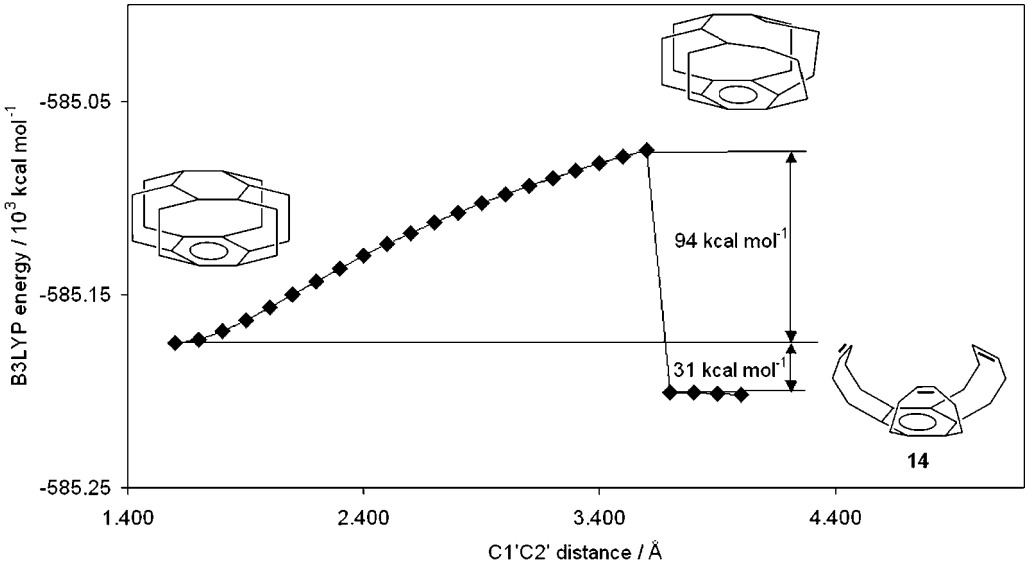


Figure 2. Dependence of the B3LYP energy on the change of the C1′–C2′ interatomic distance by 0.01 Å.

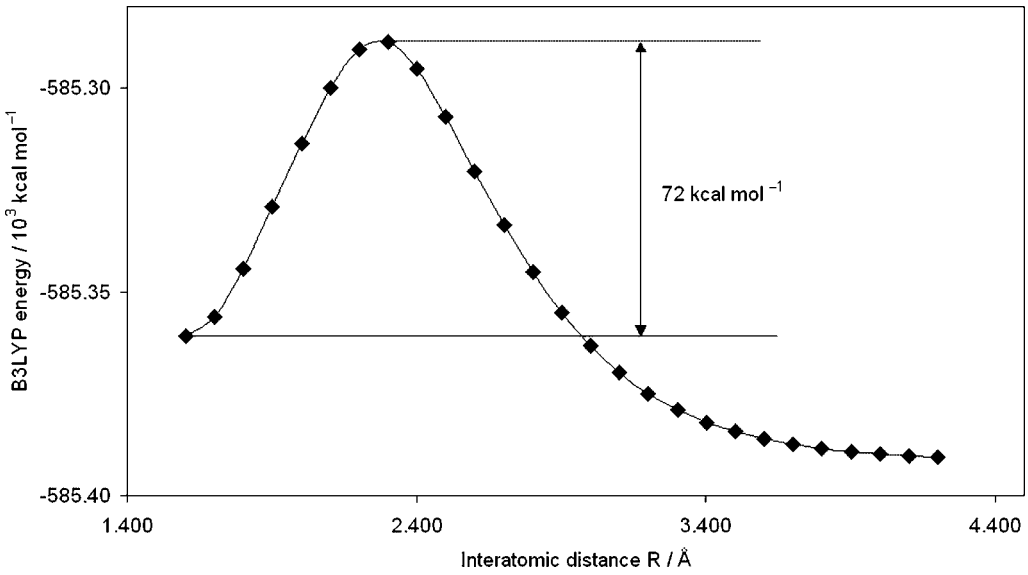


Figure 3. Dependence of the B3LYP energy on the simultaneous change of the C1′–C2′, C3′–C4′, and C5′–C6′ distances by 0.01 Å.

mental value of 159.9° found for **12**,[15] thus mirroring the higher strain in the latter molecule. Understandably, a considerably smaller value of 147.6° has been calculated for the C4′–C1′–Cb1′ angles due to the larger departure of the substituents from the plane of the saturated ring.

The calculated value of 108.3° for the C1–Cb1–Cb1′ bond angle in **11** is reasonably close to the corresponding experimental value of 110.1° in superphane **12**. As expected, a much larger value of 118.7° is found at the same level of calculations for the corresponding angle in the vicinity of the saturated ring C1′–Cb1′–Cb1.

Chemical Shifts

The chemical shifts calculated for **11** are compared with the experimental literature values for *cis*-**10**, **12**, and **13**, which contain similar structural fragments although, in the case of the latter molecule, we assume a conformation **13b** different from that of **11**, in Table 2. There is a good agreement between the corresponding calculated values for hexahydrosuperphane **11** and its parent molecule **12**[16] (δ_C = 148.6 and 144.6 ppm, respectively). As expected, the aromatic carbon signals in the latter molecules are shifted with respect to the signal in benzene (δ_C = 130.9 ppm[23]) due to the ring distortions. A similar difference has been found for the aliphatic carbons of the planar saturated ring in **11** in comparison to the corresponding value in the chair cyclohexane conformation (δ = 38.0 vs. 27.0 ppm,[24] respectively). Interestingly, the corresponding chemical shifts in *cis*-**10** and **13**, which have a boat conformation, and therefore a different arrangement of the bridge bonds, assume intermediate values between those in **11** and cyclohexane. It should be stressed that a comparison between the calculated values for **11** and the experimental ones in *cis*-**10**[13] and **13**[20] is very difficult since (a) no accurate signal assignment was carried out for these compounds and (b) the differences in their spatial structure. In general (except for δ_{Cbi} for **11** and **12**), all chemical shifts calculated for **11** are larger than the corresponding experimental values for the other two compounds. Concerning proton chemical shifts, the lack of experimental assignments does not allow us to compare the trends determined for the calculated values with the experimental ones. In any case, the values of δ = 3.2 and 3.1 ppm obtained for the protons on the saturated bridge atoms next to the aromatic ring are in good agreement with the corresponding value of δ = 3.0 ppm in **12**. The chemical shifts calculated for the bridge protons close to the saturated ring (δ = 2.1 and 2.2 ppm) are difficult to compare with the experimental value of δ = 1.61–1.71 ppm for *cis*-**10**[13] since, in the latter molecule, the corresponding ring is in the boat conformation while that in **11** is planar. Similarly, the calculated values for the Hbi′ protons of the bridges and that for the Hi′ protons on the saturated rings are higher than those in *cis*-**10** and **12**. This difference could also be due to the differences in the conformation of the saturated rings.

Possible Routes of Decomposition of 11

To get an insight into the stability of **11**, its possible decomposition routes were analyzed by elongating, in separate runs, each of the C1–C2, C1′–C2′, C1–Cb1, C1′–Cb1′, and Cb1–Cb1′ bonds by 0.1 Å, starting from their equilibrium values, to 4.0 Å, with subsequent reoptimization of all remaining parameters at the DFT B3LYP/6-31G(d,p) level. Only one of these routes, shown in Figure 2, leads to a stable decomposition product (**14**), which has an energy that is about 31 kcal mol^{-1} lower than that of **11**. The barrier to the bond breaking (94 kcal mol^{-1}) is higher than the corresponding value for a standard saturated C–C bond (80 kcal mol^{-1}). Other studied routes corresponding to the elongation of other C–C bonds are given in the Supporting Information. Based on this result, it seems probable that the real mechanism of decomposition of **11** includes simul-

taneous cleavage of three alternate C–C bonds in the cyclohexane ring. This route was also checked, and the dependence of B3LYP energy on the simultaneous elongation of the C1′–C2′, C3′–C4′, and C5′–C6, interatomic distances is presented in Figure 3. As can be seen, the energetic barrier of decomposition of **11** obtained in this way (72 kcal mol^{-1}) is slightly lower than the standard value of bond breaking for a saturated C–C bond. The structure corresponding to the maximum on the curve at Figure 3 was used as the starting point in the transition state (TS) search. The obtained structure of the transition state is close to the previous maximum. Its energy is 73 kcal mol^{-1} higher than the energy of the original equilibrium structure of **11**. The transition state is characterized by one negative frequency of –727.7 cm^{-1}. Cartesian coordinates and the full vibrational spectrum of TS are given in the Supporting Information, where the structure of triene **14** obtained in the previous constrained optimization and reoptimized without any constraints is also given.

Conclusions

Calculations at the HF/6-311G(d,p), DFT B3LYP/6-311G(d,p), and MP2/6-311G(d,p) levels indicate that hypothetical hexahydrosuperphane **11** should have a planar saturated ring. Contrary to **6** and **7**, the planarity of this ring in **11** is not enforced by its fusion with three-membered rings but is imposed by its incorporation into a cyclophane. The calculated ^{13}C NMR chemical shifts and the ^{1}H shifts for the bridge protons Hbi connected to the aromatic ring are in reasonable agreement with experimental literature data for the few known compounds with a similar structure. The calculated chemical shifts for other protons on the tetravalent carbon atoms seem too high, although their comparison with experimental data is difficult in view of the differences in conformation and/or lack of assignment in the pertaining works for the *cis* isomer of hexahydro[2.2]paracyclophane and perhydrogenated [2.2]paracyclophane. Analysis of the possible decomposition routes of the title molecule reveals that the molecule should be stable. These results and the literature reports on the known molecules *cis*-**10** and **12** indicate that the title hexahydrosuperphane **11** is a plausible synthetic target.

Experimental Section

Computational Methods: The geometry optimizations for the molecule under investigation were performed at the HF/6-311G(d,p), DFT B3LYP/6-311G(d,p), and MP2/6-311G(d,p) levels. Initial calculations were carried out with the 6-31G(d,p) basis set and these optimized geometries were used as initial parameters for the geometry optimizations with the larger 6-311G(d,p) basis set at the HF, DFT B3LYP, and MP2 levels.

The vibrational spectrum was calculated at the DFT B3LYP/6-31G(d,p) level for the structure optimized at this level. Only real values of the harmonic vibrational frequencies confirmed that **11** corresponds to a minimum-energy structure.

NMR isotropic chemical shifts were calculated by the DFT GIAO method[25,26] at the B3LYP/cc-pVTZ level for the geometry optimized at this level. The chemical shifts of TMS were calculated for the structure optimized at the same level to enable the comparison of chemical shifts of **11** with the experimental values for hexahydroparacyclophane (*cis*-**10**),[13] superphane (**12**), and perhydrogenated [2.2]paracyclophane (**13**),[20] which in the solid state assumes a conformation different from that of **11** and **12**.

A constrained geometry optimization was carried out to analyze possible decomposition modes of the highly strained molecule **11**. In this procedure, each of the C1–C2, C1′–C2′, C1–Cb1, C1′–Cb1′, and Cb1–Cb1′ bond lengths was increased, in separate runs, by 0.1 Å increments from their equilibrium values to 4.0 Å. After each incremental change all remaining parameters were reoptimized at the DFT B3LYP/6-31G(d,p) level. In a separate experiment, a similar procedure, but with simultaneous increase of three bonds (C1′–C2′, C3′–C4′, and C5′–C6′) was performed at the same level of theory. The structure corresponding to the energetic maximum obtained in this experiment was the starting point in the transition state search at the same level of theory.

All calculations were performed with the Gaussian 03 package.[27]

Supporting Information (see footnote on the first page of this article): The most important values of bond lengths and bond angles of **11** calculated at the HF/6-311G(d,p), DFT B3LYP/6-311G(d,p), and MP2/6-311G(d,p) levels, Cartesian coordinates of atoms in the title structure **11** optimized at MP2/6-311G(d,p), IR frequencies and intensities for **11** calculated at the DFT B3LYP/6-31G(d,p) level, Cartesian coordinates of atoms in the only stable decomposition product **14**, figures showing dependence of the B3LYP energy on the C1–C2, C1–Cb1, C1′–Cb′, and Cb1–Cb1′ interatomic distances, Cartesian coordinates of atoms in the transition state, and IR frequencies and intensities for the transition state.

Acknowledgments

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