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Ab Initio Studies of [1.1.1]- and [2.2.2]Propellane

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Abstract: The nature of the interaction between the bridgehead carbons in [1.1.1]propellane and [2.2.2]propellane has been investigated by two-configuration SCF and CI wave functions. On the basis of most criteria, it appears that [1.1.1]propellane is just a strained cage with little bridgehead to bridgehead through-space covalent bonding. The total energy compared to bicyclo[1.1.1]pentane, however, is indicative of a 60 kcal/mol stabilizing interaction which seems to be predominantly of the through-bond type. Even though two-configuration SCF calculations find that [2.2.2]propellane is stable to ring opening, and a substituted [2.2.2]propellane has been experimentally observed, our best CI calculations are unable to predict that it should exist.

Propellanes are a class of hydrocarbons characterized by three rings joined by a common pair of bridgehead carbon atoms which are usually considered to be singly bonded to each other. Simple examples include the highly strained [1.1.1]propellane (Figure 1), also known as tricyclo[1.1.1.0^{1,3}]pentane in IUPAC nomenclature, and [2.2.2]propellane (Figure 2), also known as tricyclo[2.2.2.0^{1,4}]octane. The present work concentrates on some unusual features of the interaction between the inverted-configuration bridgehead carbons (C_1 and C_3 in Figure 1) for these two molecules. This interaction is not the only point of interest in propellanes, but it is the one which has attracted the most theoretical interest. Ginsburg[1,2] has recently given an excellent general review of the wide range of work involving propellanes.

The earliest calculations on both [1.1.1]- and [2.2.2]propellane appear to be the extended Hückel calculations of Stohrer and Hoffmann.[3] A minimum energy, corresponding to double occupancy of the totally symmetric "bond" orbital, was predicted for [1.1.1]propellane in the vicinity of a bridgehead–bridgehead separation of 1.6 Å. Through-bond effects were found to reinforce the through-space effects in splitting the energies of the symmetric and asymmetric orbitals. Even so, their plot of the energy of the symmetric orbital vs. bond length showed a slight antibonding character (i.e., $d\epsilon/dR < 0$).

Two minima were predicted for [2.2.2]propellane as a result of the crossing in orbital energies of the symmetric and asymmetric orbital as a function of the bridgehead–bridgehead distance. This crossing was predicted to arise because of cancellation between through-space and through-bond effects in computing the orbital energy difference for [2.2.2]propellane. But it was also pointed out that ring opening to dimethylenecyclohexane (Figure 3) from the outer minimum was an allowed process which should occur with a small barrier. No corresponding low-energy ring-opening path is available to [1.1.1]propellane.

Early ab initio calculations on the lowest singlet and triplet states of [1.1.1]propellane by Newton and Schulman[4] inspired much of the successive theoretical interest by providing a number of seemingly conflicting results:

(1) Minimal and 4-31G basis set SCF calculations predicted the lowest state to be closed shell, with a surprisingly short bridgehead–bridgehead distance (R_{bb}) of 1.60 Å (compared to a normal, single C–C bond length of 1.54 Å). The same level of theory predicted a C_1–C_3 distance of 1.89 Å in bicyclo[1.1.1]pentane (Figure 4), a compound in which bonding between the bridgeheads is impossible because each bridgehead carbon has an additional hydrogen on it.

(2) While R_{bb} differs substantially between [1.1.1]propellane and bicyclo[1.1.1]pentane, the total electron density contour maps in the interbridgehead regions of the two compounds were described as strikingly similar. This would suggest little bonding in propellane. The electron density at the molecular centers actually differed by nearly a factor of 2, but a substantial bond length dependence of the density would be expected in both molecules, so a direct comparison of their densities at the respective equilibrium bond lengths is not very meanginful.

(3) The electron density of the localized bridgehead–bridgehead orbital is largely directed *away* from the center of the molecule. Deformation densities relative to spherical s^2p^2 carbon atoms, derived from high-resolution X-ray studies, were later to support this by showing no buildup of charge near the center of the molecule and significant buildup beyond the bridgehead atoms in a [3.1.1]propellane.[5]

(4) The SCF overlap population between the bridgehead carbons was −0.25, indicating an antibonding covalent interaction. This was much less antibonding, however, than the −0.91 overlap population in bicyclo[1.1.1]pentane. For localized molecular orbitals, the overlap population of the "bond" orbital was −0.002,

(1) Ginsburg, D. "Propellanes". In *Monographs in Modern Chemistry*; Ebel, H. F., Ed.; Verlag Chemie: Weinheim, Germany, 1975; Vol. 7.

(2) Ginsburg, D. *Propellanes, Sequel II*; Department of Chemistry: Technion, Haifa, Israel, 1985.

(3) Stohrer, W.; Hoffmann, R. *J. Am. Chem. Soc.* **1972**, *94*, 779.

(4) Newton, M. D.; Schulman, J. M. *J. Am. Chem. Soc.* **1972**, *94*, 773.

(5) Chakrabarti, P.; Seiler, P.; Dunitz, J. D.; Schulter, A. D.; Szeimies, G. *J. Am. Chem. Soc.* **1981**, *103*, 7378.

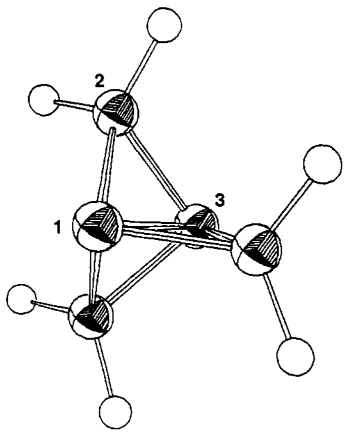

Figure 1. 6-31G* TCSCF D_{3h} geometry of [1.1.1]propellane: R_{13} = 1.57, R_{12} = 1.50, and R_{CH} = 1.08 Å; HCH = 114.5°; E = −192.7241.

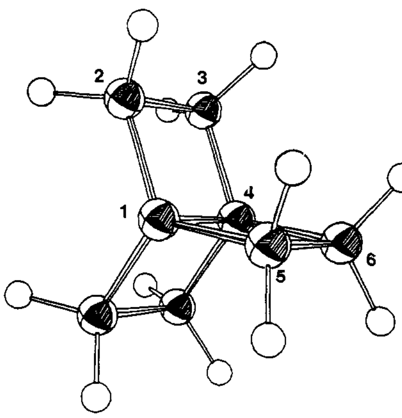

Figure 2. 3-21G TCSCF D_{3h} geometry of [2.2.2]propellane at the inner minimum: R_{14} = 1.57, R_{12} = 1.55, R_{23} = 1.59, and R_{CH} = 1.07 Å; HCH = 108.1° and C_1C_2H = 110.2°; E = −308.1084.

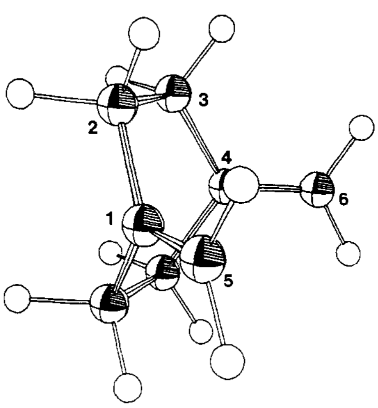

Figure 3. 3-21G TCSCF geometry of dimethylenecyclohexane: R_{12} = 1.52, R_{23} = 1.57, R_{14} = 2.60, R_{15} = 1.32, and R_{56} = 4.09 Å; R = −308.1771.

which also indicates no bonding from that electron pair.

(5) If the bridgehead–bridgehead "bond" pair of electrons is replaced by two triplet coupled open shells, the energy is increased by more than 70 kcal/mol at the optimal singlet geometry (R_{bb} = 1.60 Å) or 51 kcal/mol at the optimal triplet geometry (R_{bb} = 1.80 Å). The size of the energy gap between the closed-shell and diradical states is usually believed to be an indication of the magnitude of the bonding interaction in the former.

In the end, Newton and Schulman concluded that there was no evidence of direct bridgehead–bridgehead bonding. They speculated that the driving force for shortening R_{bb} compared to bicyclo[1.1.1]pentane was a reduction in the repulsion between the nonbridgehead CH_2 groups, as indicated by a *decrease* in the absolute value of the methylene–methylene overlap population from −1.66 (R_{bb} = 1.89 Å) to −0.86 (R_{bb} = 1.60 Å). By shortening

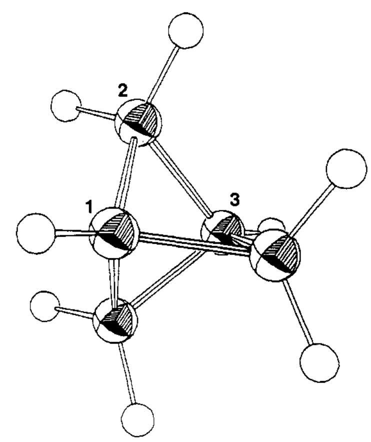

Figure 4. 6-31G* SCF D_{3h} geometry of bicyclo[1.1.1]pentane: R_{13} = 1.87, R_{12} = 1.55, R_{C_1H} = 1.08, and R_{C_2H} = 1.08 Å; HCH = 110.9°; E = −193.9072.

R_{bb}, the distance between the CH_2 groups is increased at the expense of increasing the repulsive interaction between the bridgehead carbons. The accompanying change in the bridgehead–bridgehead overlap population, −0.11, is comparatively small but unfavorable.

Newton and Schulman[6] also studied [2.2.2]propellane by means of a two-configuration procedure based on molecular orbitals defined by SCF calculations in which either only the symmetric or asymmetric bond orbital was doubly occupied. All geometry parameters, other than R_{bb}, were fixed at values taken from cyclobutane and bicyclooctane and held fixed. Using the STO-3G minimal basis[7] they found a double minimum, as predicted by Stohrer and Hoffmann. The two minima were nearly degenerate and separated by a barrier of approximately 29 kcal/mol. Breaking of the D_{3h} symmetry to form dimethylenecyclohexane was not considered.

This theoretical prediction seemingly was confirmed by the experimental work of Eaton and Temme.[8] They synthesized the dimethylcarboxamide derivative of [2.2.2]propellane and measured the temperature dependence of the rate of disappearance of its NMR signal. From this they obtained an Arrhenius activation energy of 22 kcal/mol for ring opening to the corresponding derivative of dimethylenecyclohexane.

Dannenberg and Prociv[9] carried out INDO calculations on both singlet and triplet [2.2.2]propellane. On the basis of these they proposed a novel synthetic route based on ring closure of triplet dimethylenecyclohexane.

Renewed interest in [1.1.1]propellane followed its recent synthesis by Wiberg and Walker[10] and the subsequent obtainment of IR/Raman spectra[11] and gas-phase electron diffraction data[12] which, for the first time, provided an experimental structure: R_{bb} = 1.60 ± 0.02 (IR/Raman) and 1.596 ± 0.005 Å (electron diffraction). In addition to confirming the accuracy of the previous ab initio geometry predictions, the work of Wiberg et al.[11] further established that theory could successfully predict the vibrational frequencies and enthalpy of formation of the compound. Based on their data, the enthalpy change for the conversion of bicyclo[1.1.1]pentane to [1.1.1]propellane plus two hydrogen atoms is only 143 kcal/mol, which is indicative of a 60 kcal/mol stabilizing effect in propellane. These authors also report a sizable 6-31G*[13] SCF stretching force constant of 6.2 mdyn/Å for R_{bb} as further evidence of bridgehead–bridgehead bonding.

(6) Newton, M. D.; Schulman, J. M. *J. Am. Chem. Soc.* **1972**, *94*, 4391.
(7) Hehre, W. J.; Stewart, R. J.; Pople, J. A. *J. Chem. Phys.* **1969**, *51*, 2657.
(8) Eaton, P. E.; Temme, G. H. *J. Am. Chem. Soc.* **1973**, *95*, 7508.
(9) Dannenberg, J. J.; Prociv, T. M. *J. Chem. Soc., Chem. Commun.* **1973**, 291.
(10) Wiberg, K. B.; Walker, F. H. *J. Chem. Soc.* **1982**, *104*, 5239.
(11) Wiberg, K. B.; Dailey, W. P.; Walker, F. H.; Waddell, S. T.; Crocker, L. S.; Newton, M. *J. Am. Chem. Soc.* **1985**, *107*, 7247.
(12) Hedberg, L.; Hedberg, K. *J. Am. Chem. Soc.* **1985**, *107*, 257.
(13) Hehre, W.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257.

Basis sets which lack polarization functions often have problems describing small, highly strained ring systems. Thus, when Wiberg[14] demonstrated that the addition of d-type polarization functions to the carbon basis set decreased the optimal SCF value of R_{bb} by as much as 0.06 Å, the result was not entirely unexpected, although the size of the effect was larger than normal. A decrease in computed C–C bond lengths upon introducing d functions has been found for many small-ring systems, such as cyclopropane,[15] but the effect is usually smaller (~0.02 Å). In fact, a reduction of about that size was computed by Wiberg for the bridgehead–nonbridgehead bonds in propellane. Therefore, while the presumed central bond in [1.1.1]propellane behaves qualitatively like other small-ring C–C bonds when d functions are added to the basis, the size of the contraction is anomalously large.

The fact that the early ab initio SCF value of R_{bb} exactly matches the experimental value is fortuitous. Cancellation of errors from the small basis sets and neglect of electron correlation plays a large role in giving this agreement. Since the results are in perfect agreement with the small basis the introduction of d functions could only worsen the agreement. It is only with the inclusion of electron correlation effects via GVB or Møller–Plesset perturbation theory to second (MP2) or third order (MP3) that matters improve. The 6-31G* basis produced R_{bb} values of 1.543 (SCF), 1.596 (GVB), 1.594 (MP2), and 1.572 Å (MP3), respectively.

Jackson and Allen[16] have proposed a novel interpretation of the bonding in [1.1.1]propellane. From the six bridgehead to methylene bonds one can form two linear combinations that have the same symmetry as degenerate acetylenic π bonds between the bridgehead carbons. They have focused on these combinations and concluded that the apparent bonding stabilization of propellane arises from this three-center "σ-bridged π bond".

No irrefutable case can be made either proving or disproving the existence of a "bond" between the two bridgehead carbons in [1.1.1]propellane. While the concept of two-center (or more rarely three-center) bonds has been of widespread utility to chemists in many areas of research, it is not possible to translate the concept of a bond into something which can be universally extracted from theoretical calculations. Within a limited basis set of "atomic orbitals", bond order and overlap population give an indication of covalent bonding while net charge transfer can indicate ionic bonding. Both of these tests have trouble recognizing homonuclear ionic bonds, coordinate covalent bonds, ion–dipole interactions, and van der Waals interactions, etc. Generalization of these tests to basis sets of arbitrary functions centered at arbitrary points in the molecule is difficult. Even in the case of diatomic molecules, where the presence of a "substantial" (i.e., greater than 10 kcal/mol) potential well would satisfy most people's criterion for bonding, the analysis of bonding interactions from inspection of properties of the wave function has proven to be exceedingly difficult.[17] The analysis problem will be even more severe in a case as unusual as [1.1.1]propellane, where each bridgehead carbon sees all four neighboring atoms situated within a conical volume lying to one side. In a simple picture of this molecule, the "bond" would arise from backside overlap of sp^3 orbitals. But at the bond length of this molecule, this overlap is negative so that the in-phase combination would correspond simultaneously to a negative overlap population and a positive bond order.

Procedures and Results

With the exception of the most recent paper by Wiberg et al.,[11] all previous ab initio calculations on [1.1.1]propellane have been done at the single-configuration SCF level. As a consequence of this, the interbridgehead electron pair has usually been described by a single MO of a_1' symmetry. While SCF calculations have shown the diradical form of the molecule to be quite high in energy relative to the closed-shell ground state, the possibility of the wave function possessing a multiconfigurational nature has not been allowed. A single configuration wave function does not possess the flexibility to smoothly make the transition between a closed shell and a diradical.

The minimal wave function to accomplish this would include a second configuration corresponding to a $a_1' \rightarrow a_2''$ double excitation. The a_2'' orbital possesses a nodal plane perpendicular to the propellane's C_3 axis. Thus, for a qualitatively correct description of [1.1.1]propellane a two-configuration SCF (TCSCF) wave function of the form

$$\Psi_{TCSCF} = \Phi_{core}[c_1 5a_1'^2 + c_2 3a_2''^2]$$

where

$$\Phi_{core} = 1a_1'^2\, 1a_2''^2\, 1e'^4\, 2a_1'^2\, 3a_1'^2\, 2e'^4\, 4a_1'^2\, 2a_2''^2\, 3e'^4\, 1a_2'^2\, 4e'^4\, 1e''^4$$

should be used. In a simplified labeling convention the first configuration is sometimes referred to as the "s^2" configuration and the second as the "a^2" configuration.

Near the equilibrium geometry found by Wiberg (R_{bb} = 1.60 Å) the second configuration has a coefficient of −0.23 which increases to −0.34 at a distance near that found in bicyclo[1.1.1]pentane. The closer the second coefficient is to $-2^{-1/2}$ the more nearly the wave function corresponds to a singlet diradical. Orbital density contours of the $5a_1'$ and $3a_2''$ TCSCF orbitals near the [1.1.1]propellane optimal geometry are shown in Figure 5. The $5a_1'$ plot is qualitatively similar to previously published plots of this orbital. The $3a_2''$ plot shows a considerable amount of bridgehead–nonbridgehead density and is not simply the antibonding version of $5a_1'$.

TCSCF geometry optimizations were performed with the program GAMESS[18] at fixed values of R_{bb} by using the 6-31G* basis for [1.1.1]- and the 3-21G basis for [2.2.2]propellane. At each fixed ground-state TCSCF geometry, separate SCF calculations

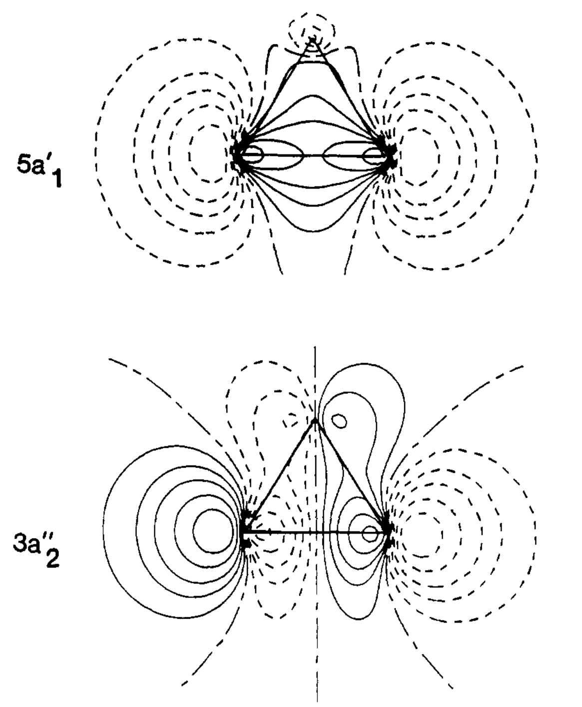

Figure 5. 6-31G* TCSCF $5a_1'$ and $3a_2''$ orbitals of [1.1.1]propellane at the geometry of Figure 1. The contours enclose 10%, 30%, 50%, 70%, and 90% of the probability.

(14) Wiberg, K. B. *J. Am. Chem. Soc.* **1983**, *105*, 1227.
(15) Whitehead, R. A.; Frisch, M. J.; Binkley, J. S.; DeFrees, D. J.; Schlegel, H. B.; Raghavachari, K.; Pople, J. A. In *The Carnegie-Mellon Quantum Chemistry Archive*, Department of Chemistry: Carnegie–Mellon University, Pittsburgh, 1981.
(16) Jackson, J. E.; Allen, L. E. *J. Am. Chem. Soc.* **1983**, *106*, 591.
(17) See, for example: Ruedenberg, K. *Rev. Mod. Phys.* **1962**, *326*, 2. Schwarz, W. H.; Valtazanos, P.; Ruedenberg, K. *Theor. Chim. Acta* **1985**, *68*, 471.
(18) Dupuis, M.; Spangler, D.; Wendoloski, J. National Resource for Computation in Chemistry, Program QG01, 1980.

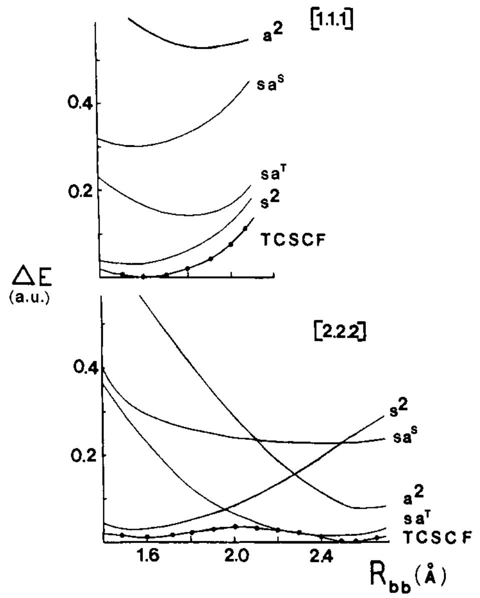

Figure 6. 6-31G* SCF energies of various electronic configurations of [1.1.1]propellane and [2.2.2]propellane as a function of R_{bb}. All other geometrical parameters are optimized for the respective 6-31G* or 3-21G $^1A_1'$ TCSCF wave functions.

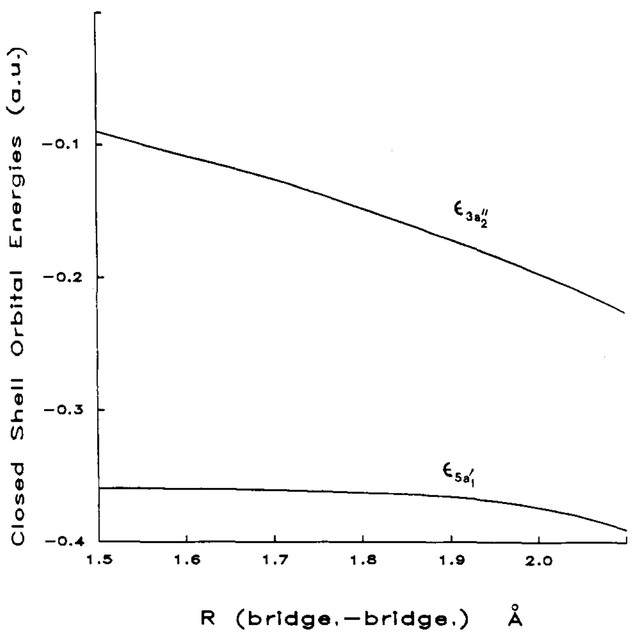

Figure 7. 6-31G* SCF orbital energies of [1.1.1]propellane as a function of R_{bb}. All other geometrical parameters are optimized for the 3-31G* $^1A_1'$ TCSCF wave function. Each orbital energy is taken from an SCF calculation in which that orbital is doubly occupied.

for the ($5a'^2$) and ($3a''^2$) wave functions, and for the ($5a'3a''$) $^3A_2''$ and $^1A_2''$ states, were performed. The resulting potential energy curves are shown in Figure 6. As predicted earlier, at this level of theory the [1.1.1] compound has a single minimum in the ground-state energy while the [2.2.2] compound has two.

An indication of bonding is sometimes claimed to be the splitting between the "s" and "a" orbital energies and the states formed from them. For [1.1.1]propellane the a_1' orbital energy, shown in Figure 7, is nonbonding even though the corresponding a_2'' orbital is strongly antibonding. The energy splitting between the orbitals is large, however, over the entire range of geometry accessible to this cage compound. Consequently, the triplet state and excited diradical singlet state lie considerably above the ground state. Also, at the largest R values possible, the a^2 configuration is still well above the s^2, so the molecule is not a diradical even at the optimal bicyclo[1.1.1]pentane SCF geometry. On the other hand, [2.2.2]propellane's cage allows a large R value without

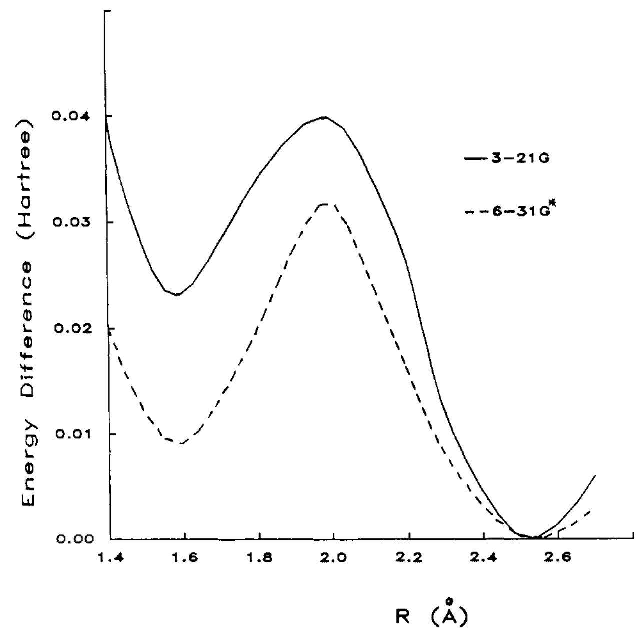

Figure 8. 6-31G* and 3-21G TCSCF energies of [2.2.2]propellane as a function of R_{bb}. All other geometrical parameters are optimized for the 3-21G $^1A_1'$ TCSCF wave function.

excessive strain. As anticipated by Hoffmann, the s and a orbital energies cross near an R of 2.3 Å; near there, the wave function is typical of a diradical with a triplet SCF ground state. Strangely, near the outer TCSCF minimum, the a^2 configuration has become dominant, and the molecule is no longer a diradical. From these results one can conclude only that the size of the splitting of orbital energies or single–triplet energies is unrelated to the question of the existence of a chemical bond in the ground state.

The behavior of [1.1.1]propellane upon removal of an electron from the highest occupied molecular orbital was studied since it is also widely believed that this provides a test of the bonding or antibonding nature of the orbital. A 6-31G* UHF geometry optimization was performed on the $^2A_1'$ state. It gave a value of R_{bb} = 1.55 Å compared to 1.60 Å for the neutral. This contraction of the bond agrees with the slightly antibonding slope of the a_1' orbital energy in Figure 7. On the other hand, the population analysis of the canonical HOMO shows a small net positive overlap popultion of 0.10. As Newton and Schulman showed, if localized orbitals are formed, the bond orbital then shows a small negative overlap population.

As noted previously, the addition of d functions to the basis produces a large effect on the optimal R_{bb} value of the [1.1.1] compound at the SCF level. This *geometric* effect can be viewed as basically a statement about the effects of polarization functions on a local region of the potential surface. From a global perspective the *energetic* effect of polarization functions on the relative stabilities of molecular shapes which are some distance apart on the potential surface can also be large. An indication of this in regard to [2.2.2]propellane can be seen in Figure 8, where a comparison is made between the TCSCF energy curves computed with the 3-21G and 6-31G* basis sets for the same geometries used in Figure 6. As might be expected from the earlier discussion of the effect of d functions on small ring systems, the 6-31G* curve shows increased stability in the small R_{bb} region compared to the 3-21G results. Thus, the minimum at small R_{bb} comes out almost 9 kcal/mol lower with the 6-31G* basis than with 3-21G relative to the large R_{bb} minimum.

An attempt was made to determine the effects of electron correlation on the [2.2.2] curve by means of a configuration interaction calculation which included single and double excitations from the TCSCF wave function. The virtual orbital space was transformed to K-orbitals[19] in order to improve the CI convergence.

(19) Feller, D.; Davidson, E. *J. Chem. Phys.* **1981**, *84*, 3997.

The large number of such configurations necessitated an energy selection based on second-order Raleigh–Schroedinger perturbation theory. Somewhat over 80% of the estimated multireference singles and doubles correlation energy was variationally recovered with expansion lengths of 40 000–60 000 spin-adapted configurations. Estimates of the effects of the unselected configurations, as well as the effects of higher order excitations, were added to the variational energies to yield E(est full CI).

With the 3-21G basis the double minimum present at the TCSCF level disappears entirely when CI is included. Instead, a single minimum near an R_{bb} of 2.5 Å is found while D_{3h} symmetry constraints are imposed. At the TCSCF level the minimum at R_{bb} = 1.58 Å was 10 kcal/mol below the transition state (near R_{bb} = 2.0 Å). At the estimated full CI level these relative energies are reversed so that the computed energy at R_{bb} = 2.00 Å is 8 kcal/mol below the energy at 1.58 Å. When the D_{3h} symmetry constraint is removed, the potential surface becomes monotonic downhill from the outer minimum, at R_{bb} = 2.53 Å, to dimethylenecyclohexane.

Since the inner minimum was stabilized by the addition of d functions to the basis set (the barrier height increased to 14 kcal/mol), it is conceivable that at the 6-31G* CI level the inner minimum might still exist. However, the polarized basis set presents certain computational problems since the total number of basis functions now equals 142. In order to reduce the computational problem the s component of the Cartesian d's, which is present in the 6-31G* basis, was eliminated. Likewise, the six innershell orbitals were treated as frozen cores from which no excitations were allowed. additionally, the top 10 K-orbitals were removed from the calculation to get the total number of orbitals down to 120. Even with these steps it proved very difficult to recover a large enough percent of the correlation energy to make the extrapolation to E(full CI) sufficiently reliable. keeping 62 000 configurations out of the nearly 1 million possible single and double excitations recovered barely 70% of the perturbation estimate of E_{SD}. After two cycles of iterative natural orbitals[20] the estimated full CI energies at R_{bb} = 1.58 and 2.00 Å were within a few kilocalories per mole of each other. The number of configurations was roughly 67 000, and the percentage kept and increased to 76%. These results should not be viewed as definitive, because of the relatively large amount of energy which is being treated with an extrapolation procedure, as well as the small size of the reference space. The sum of the squares of the CI coefficients corresponding to the two reference configurations, which is a loose indicator of the reference space quality, is only 0.85. However, there are no coefficients larger than 0.03 which are outside the reference space.

Thus within the uncertainties of this calculation, the barrier between the s^2 and a^2 D_{3h} electronic isomers of [2.2.2]propellane is essentially zero. With the 6-31G* basis, the TCSCF energies, relative to the energy at R_{bb} = 1.58 Å, were +14 kcal/mol at 2.00 Å and −6 kcal/mol at 2.53 Å. The best CI energies we could obtain were −8 kcal/mol at 2.00 Å and −38 kcal/mol at 2.53 Å. These CI energies were little changed from the more precise 3-21G basis results.

While the CI calculations are not conclusive, they suggest that there may be substantial correlation effects beyond the TCSCF model. They also raise the possibility that [2.2.2]propellane, as an isolated unsubstituted gas-phase molecule, may not exist. These results are certainly disturbing, as they run counter to current wisdom on this subject[6,14] and are drawn from calculations whose precision is inadequate. They are not quite in contradiction with experiments since the synthesis of unsubstituted [2.2.2]propellane has not yet been reported. The exact results are likely to be even more difficult to establish than they have been for the analogous ring opening of cyclobutane to two ethylenes via tetramethylene.[21]

As mentioned earlier, Wiberg and co-workers reported a stretching force constant for the central C–C "bond" in [1.1.1]-propellane which was similar to C–C stretches in other singly bonded hydrocarbons. The force constants were derived by transforming the mass-weighted, Cartesian Hessian matrix into a matrix over internal symmetry coordinates, with one of the coordinates being R_{bb}. However, the particular choice of 27 ($3N$–6, where N = 11) independent internal coordinates selected by Wiberg et al. represents only one of a large number of possible choices. For example, rather than choose the bridgehead–bridgehead distance as one of the four totally symmetric (A_1') coordinates, a symmetric combination of CCC bends about the nonbridgehead carbons might have been used. This reinterpretation of the force field would lead one to conclude only that the cage-bending force constants were significant.

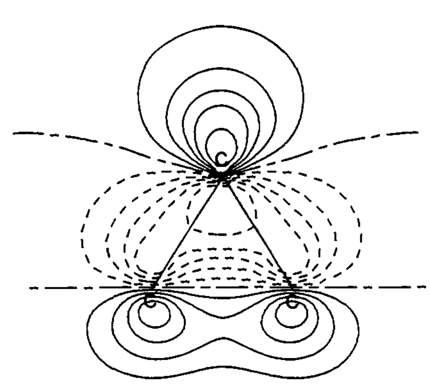

Figure 9. 6-31G* TCSCF 4e′ orbital at the geometry of Figure 1.

To illustrate the problem with interpreting the R_{bb} force constant, we have computed the stretching force constant for bicyclo[1.1.1]pentane by using the same procedure as was used for [1.1.1]propellane. At the 6-31G* SCF level we obtained $f_{2,2}$ = 7.8 mdyn/Å, using the Wiberg notation. The propellane value of $f_{2,2}$ was only 6.2 mdyn/Å with the same basis. Thus, if we consider only $f_{2,2}$, we could mistakenly conclude that a considerable bond exists in bicyclo[1.1.1]pentane when, in fact, it does not. Conclusions about the existence of a bond based on the stretching force constants do not seem warranted.

In an SCF study of [1.1.1]propellane, Jackson and Allen proposed an explanation of the short bridgehead–bridgehead distance based on a degenerate pair of three-center, two-electron bonds which they call σ-bridged π bonds. One orbital of the pair is shown in Figure 9. These bonds are composed of lobes on the nonbridged carbons which are directed toward the center of the molecule combining with in-phase combinations of the p functions on the bridgeheads. On the basis of a study of the molecular charge density deformation plots, the authors argue that "three filaments of charge gain bind C_1 to C_2 and simultaneously contribute to C–C framework bonding". It is suggested that the effects of σ-bridged π bonding are evident even in bicyclo-[1.1.1]pentane where the 1,3 separation is considerably shorter than expected for nonbonded interactions.

The difficulties with this analysis are twofold. The first is an inherent problem with deformation densities in general. The way in which one defines the atomic densities for nonspherical atoms can have a large effect on the deformation density.[22] The second problem is that it is almost impossible to label some fraction of the bridgehead–nonbridgehead bonds as "extra bonding" resulting from the interaction of the two bridgehead atoms. There are in fact six symmetry orbitals resulting from the six bridgehead–nonbridgehead bonds. One of these, 1e″, is bridgehead–bridgehead π antibonding as shown in Figure 10. Because of this orbital, the net π–π bridgehead to bridgehead overlap population is in fact −0.22. Not only is this antibonding, it in fact accounts for most of the total of −0.25 negative overlap population. The total σ–σ overlap population, by contrast, is only −0.03, which is essentially nonbonding.

One of the strongest pieces of evidence suggesting some type of bridgehead–bridgehead bonding is the sequence of molecules and energies shown in Figure 11. All calculations were carried out at the MP2 level by using the 6-31G* basis and the GAUSSIAN

(20) Bender, C. F.; Davidson, E. R. *J. Chem. Phys.* **1966**, *70*, 2675.
(21) Doubleday, C.; McIver, J. *J. Am. Chem. soc.* **1985**, *107*, 7904.
(22) Schwarz, W. H.; Valtazanos, P.; Ruedenberg, K. *Theor. Chim. Acta* **1985** *68*, 471.

Table I. Comparison of Bicyclo[1.1.1]pentane and [1.1.1]Propellane[a,b] Orbital Energies

molecule geometry	propellane, pentane	propellane, propellane		pentane, pentane	pentane, propellane	
	(+0.090)	(+0.176)	$3a_2''$	−0.433	−0.331	CH
	−0.373	−0.361	$5a_1'$	−0.674	−0.663	CH
	−0.460	−0.442	$1e''$	−0.453	−0.452	C–C
	−0.472	−0.520	$4e'$	−0.446	−0.502	CH_2
	−0.521	−0.521	$1a_2'$	−0.498	−0.518	CH_2
	−0.639	−0.655	$3e'$	−0.614	−0.635	C–C
	−0.754	−0.727	$4a_1'$	−0.731	−0.755	CH_2
	−0.778	−0.778	$2a_2''$	−0.852	−0.837	C–C
	−0.929	−0.952	$2e'$	−0.904	−0.936	CH_2
	−1.239	−1.292	$3a_1$	−1.213	−1.285	C–C
total energy	−192.6393	−192.6911		−193.9056	−193.8358	
electron density at center of molecule	0.114	0.203		0.098	0.167	

[a] RHF 6-31G* calculations using all six components of the Cartesian d set. All quantities in atomic units. [b] The corresponding UHF (α, β) orbital energies after removal of only one hydrogen at the bicyclo[1.1.1]pentane geometry are (−1.228, −1.210), (−0.913, −0.909), (−0.847, −0.813), (−0.738, −0.731), (−0.622), −0.620), (−0.504, −0.504), (−0.465, −0.453), (−0.456, −0.443), (−0.628, −0.540), (−0.354, +0.136).

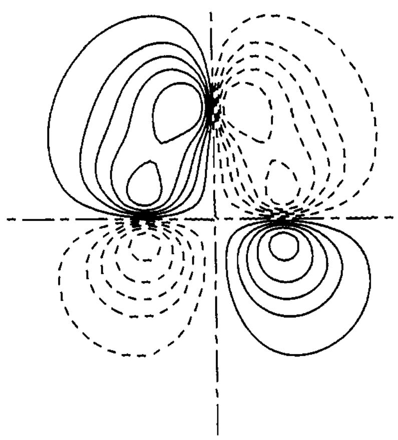

Figure 10. 6-31G* TCSCF 1e″ orbital at the geometry of Figure 1.

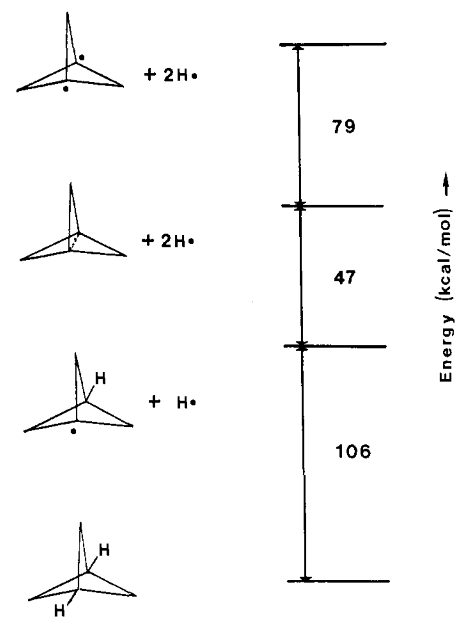

Figure 11. Computed 6-31G* UHF/MP2 relative energies at the geometry of Figure 4.

82 program.[23] The geometries were frozen at the optimal bicyclo[1.1.1]pentane SCF geometry. Removal of the first hydrogen costs 106 kca/mol in accord with most textbook estimates of a normal C–H bond strength. However, removal of the second hydrogen costs only 47 kcal/mol, indicating that propellane was able to recover part of the cost of the broken C–H bond (perhaps by forming some sort of interbridgehead bond). Geometry relaxation, of course, would allow propellane to gain even more energy. By contrast, the energy cost to remove the second hydrogen and leave the molecule in a triplet state, where presumably no interbridgehead bonding is possible, is around 126 kcal/mol. These calculations were done at a fixed geometry in order to eliminate from consideration any change in strain energy during the process. Strictly speaking the strain energy does change, even at fixed geometry, because the reference "unstrained" molecules relative to which strain is defined are chosen differently. Some rehybridization of the orbitals does take place, for example, upon removal of the bridgehead hydrogens, which changes the bond strengths of the bridgehead to methylene bonds.

Table I gives some further comparison between [1.1.1]propellane and bicyclo[1.1.1]pentane at the two equilibrium geometries. It will be noted in the table that the charge density in the center of the molecule is about 20% larger for propellane than for bicyclopentane when compared at the same geometry. The electron pair which has been removed along with the two terminal hydrogen atoms had a_2'' symmetry and made no contribution to the density at the molecular center. Renormalization of $5a_1'$ after removal of the hydrogen contribution accounts for most of the increase.

Upon removal of the hydrogens, the $5a_1'$ orbital initially rehybridizes to give increased s character. As R_{bb} is decreased this reverses, and at the propellane geometry $5a_1'$ of propellane has more p character than in bicyclopentane. This loss of s character as R_{bb} decreases is probably also responsible for the net increase in $5a_1'$ orbital energy. This should also lead to stronger bridgehead to methylene bonds as the s character in these bonds is increased.

The splitting in the $5a_1'$ and $3a_2''$ orbital energies in these two molecules is remarkably similar. For making this comparison, the definition of the $3a_2''$ orbital energy used in Figure 7 is probably preferable to the RHF virtual orbital energy used for propellane in Table I. This seems to be a through-bond effect due to the proximity of a nearby a_2'' orbital of the same energy. When the hydrogens are removed the $2a_2''$ orbital energy increases in energy, which indicates that it has some C–H bonding character. From the MO coefficients it is clear that $2a_2''$ has considerably more C–H character than $3a_1'$ or $4a_1'$ combined. This is not surprising since $3a_1'$, which is the a_1' bridgehead to methylene bond MO, is far away in energy and $4a_1'$, which is the a_1' C–H bond MO of the methylenes, is far away in space.

One perspective on [1.1.1]propellane strain energy can be obtained by considering it to be composed of two nonbonded distorted methyl radical sites coupled together by three methylene groups, which are also distorted. At the 6-31G* SCF geometry the CCC bond angle at the methylenes has closed down to 62° from the tetrahedral value of 109.5°. Relieving this strain would require *lengthening* the bridgehead–bridgehead distance. On the other hand, the methyl radical sites would prefer to be planar, with CCC angles of 120°, while in propellane they are closer to 95°. In order to relieve this strain the molecule would *shorten* the bridge-

(23) Binkley, J. S.; Frisch, M. J.; DeFrees, D. J.; Raghavachari, K.; Whiteside, R. A.; Schlegel, H. B.; Frisch, M. J.; Fluder, G.; Pople, J. A., Department of Chemistry, Carnegie-Mellon University, 1983.

Figure 12. Atom–atom overlap populations in the ground state of [1.1.1]propellane computed with the 4-31G TCSCF wave function as a function of R_{bb}. All other geometrical parameters are optimized for the 6-31G* $^1A_1'$ TCSCF wave function. Bridgehead carbons are labeled as C_B, methylene carbons are labeled as C_M.

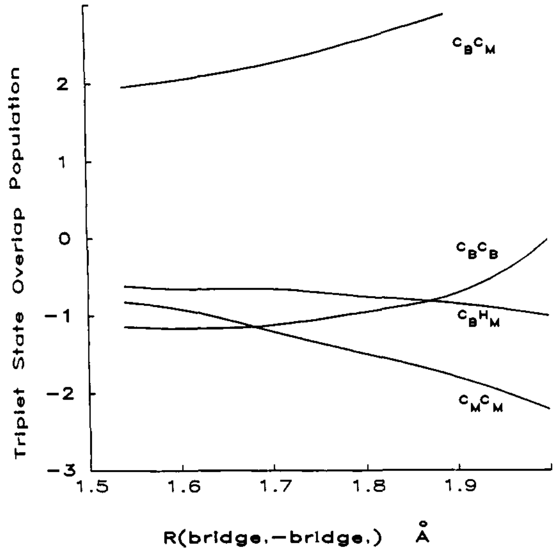

Figure 13. Atom–atom overlap populations in the $^3A_2''$ state of [1.1.1]propellane computed with the 4-31G RHF wave function as a function of R_{bb}. All other geometrical parameters are optimized for the 6-31G* $^1A_1'$ TCSCF wave function.

head–bridgehead distance. The actual propellane geometry can be viewed as a compromise between these opposing forces.

Translating this qualitative argument into a semiquantitative rationalization of the short bridgehead–bridgehead distance is difficult because of the ambiguities involved in modeling the strain energies of the component pieces. If the bridgehead centers are modeled by methyl radicals and the nonbridgehead centers are modeled by methanes, the strain energies arising from the two sources do not appear to balance. At the optimal SCF geometry 6-31G* MP4 calculations predict that it costs 38 kcal/mol to distort three methanes from their optimal, tetrahedral geometry to the geometry found for the nonbridgehead carbons in [1.1.1]propellane and only 13 kcal/mol for the two methyls.

Obviously, this analysis is too simplistic. A more elaborate model, which still retains a simple mechanical approach to predicting molecular geometries, is that of molecular mechanics. This model optimizes geometries by minimizing the total energy of a molecule. It could conceivably answer the question of whether strain energies alone can explain the short R_{bb} value. In practice, however, molecular mechanics requires that the carbons at the bridgehead positions be specified as either radical centers or as carbons which are bonded to four other atoms. The program cannot dynamically choose between these options. When the bridgeheads are labeled as being bonded to each other, molecular mechanics (MM2) finds a C–C bond length of 1.4336 Å and a heat of formation of 100 kcal/mol (experimental 89 kcal/mol). This is a large error compared with most predictions of the MM2 program.

Another indication of strain appears in the overlap population between various atoms. Figure 12 shows the variation of the overlap population with bond length for [1.1.1]propellane in the TCSCF approximation. As noted by Newton and Schulman, the driving force for shortening the R_{bb} distance is the methylene–methylene overlap population. This is, of course, equivalent to angle strain at the methyl center in a molecular mechanics approach and suggests that our calculation of angle strain in $\cdot CH_3$ is not a good model for the strain in propellane where the bulkier groups produce larger strain energies. By contrast, the triplet-state overlap population in Figure 13 shows a strongly repulsive C_bC_b overlap population which opposes the C_MC_M interaction. In a molecular mechanics approach, this would appear as a different methylene angle force constant for these two electronic states if the bridgehead carbons were treated as nonbonded or as a different valence interaction if they were treated as bonding or antibonding.

The effect of homonuclear ionic resonance escapes any one-electron analysis. A crude estimate of the contribution of ionic structure to the two-electron bridgehead bond in [1.1.1]propellane can be made from the magnitude of the coefficients in the TCSCF wave function and the overlap between the hybrid orbitals. The square of the overlap with an ideal ionic structure is 0.32 while the square of the overlap with an ideal covalent structure is 0.72. These do not add to unity because the ionic and covalent structures are nonorthogonal. Nevertheless, because of the low overlap between the hybrid orbitals, the ionic character can be stated as 30 ± 2%. This is larger than normal for a two-electron bond.

Conclusion

It has been shown that all of the arguments put forward for the existence of a central bond in [1.1.1]propellane can be matched with a counterargument except for the heat of formation. Naively, a driving force for the low energy of the vertical detachment of two hydrogens from bicyclo[1.1.1]pentane to form [1.1.1]propellane is the removal of the repulsive four-electron H–C···C–H bond–bond interaction. Whether the two-electron •C···C• interaction is actually bonding is unclear. The difficulty with a nonbonding view of the energetics is that the three-electron interaction •C···C–H is not midway between the four-electron and two-electron interactions. A more sophisticated view emerges from considering through-bond interactions. The a_2'' C–H bond MO (or a_2'' C–C MO) is destabilized by through-bond interaction with the bridgehead–methylene bond MO of the same symmetry. The a_1' C–H bond MO (or a_1' C–C MO) is less affected because the extraordinary stability of the a_1' bridgehead–methylene bond MO places it far away in energy.

For [2.2.2]propellane it is unclear whether there are two minima in the D_{3h} constrained potential surface or only one broad flat region. In the latter case, it is likely that there is no barrier to ring opening to dimethylenecyclohexane.

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