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The C_1–C_3 Bond in [1.1.1]Propellane

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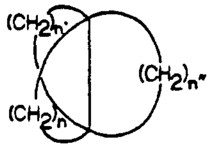
Abstract: Wiberg and Walker have recently synthesized [1.1.1]propellane, the most strained organic molecule known to be stable at room temperature. Although each of the two bridgehead carbons, C_1 and C_3, possesses inverted configurations, Wiberg has found them to be separated by a normal carbon–carbon single bond distance (1.54 Å) and to be stable against formation of the diradical by 65 kcal/mol. We have applied ab initio electronic structure methods to investigate the C_1–C_3 bond and find a novel, nonaxial orbital arrangement which we term σ-bridged π. This bonding pattern appears characteristic of inverted configurations held together by short bridges, and we show that 1,3-diborabicyclo[1.1.1]pentane contains a BB bond almost identical with that in [1.1.1]propellane. An unusually short BB separation of 1.61 Å is predicted. Although bicyclo[1.1.1]pentane and 1,3-diazabicyclo[1.1.1]pentane do not formally possess 1–3 bonds, their 1,3 separations are considerably shorter than expected for nonbonded interactions (computed to be 1.87 and 1.96 Å, respectively). Both molecules retain some σ-bridged π character.

I. Introduction

Small-ring organic molecules have fascinated organic chemists since 1883, when Perkin synthesized the first known cyclobutane and cyclopropane derivatives. In 1959, Wiberg and Ciula[1] reported the first bicyclo[1.1.0]butane derivative, and during the intervening 25 years experimental[2] and theoretical[3] study on strained polycyclic hydrocarbons has burgeoned. The $[n.n'.n'']$-propellanes,[4] which consist of three rings fused at a common C–C bond as shown, are especially intriguing.

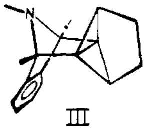


Wiberg and Walker's recent synthesis of [1.1.1]propellane[5] (I), the most highly strained and interesting of this class, provides the motivation for the electronic structure analysis reported here.

A decade ago, sophisticated, state-of-the-art calculations for this molecule were carried out by several investigators. Using


I


II


III

the 4-31G basis set,[6a] Newton and Schulman[7] obtained an energy optimized geometry for I by ab initio methods, thereby suggesting that it might be at least metastable. They found the ground state to be a singlet with a C_1–C_3 separation of 1.60 Å and a HOMO symmetric in σ_h (the plane containing the three methylene carbons). Transformation to localized orbitals by the Edmiston–Ruedenberg procedure led to a C_1–C_3 associated orbital hybridized *outward* and possessing a small negative C–C overlap population. Newton and Schulman also determined that the total overlap population between the bridgeheads was sizable and negative[8] and that the electron density in the interbridgehead region is little different from that in bicyclo[1.1.1]pentane (II), a compound in which no formal bridgehead–bridgehead bond exists. These authors therefore concluded that the calculated 1.60-Å C_1–C_3 distance in I was due to methylene–methylene repulsive interactions rather than to C_1–C_3 bonding.

In the same year, Stohrer and Hoffman,[9] using extended Hückel wave functions, investigated a variety of small-ring propellanes. They were interested in bond-stretch isomerism, and their work clearly indicated that [1.1.1]propellane should be more stable than its stretched diradical. They found an equilibrium C_1–C_3 separation only slightly larger than a normal C–C single bond. Their results also suggested that the HOMO of I was slightly antibonding (despite being symmetric in σ_h). In addition, these authors investigated the reactivity of I and correctly[5] predicted it to be stable against base attack but to react rapidly with acids and radicals.

More recently, Wiberg[10,11] has reported ab initio molecular orbital calculations with the extended, polarized 6-31G* basis set[6b] for a wide range of strained cyclic and polycyclic organic molecules, including cyclopropane, cyclobutane, the bicyclo$[i.j.k]$alkanes ($i,j = 2$; $k = 0$–2) and the $[i.j.k]$propellanes ($i,j,k = 1$–2). He has determined geometries, enthalpies of hydrogenolysis, and strain energies for these species, and found that inclusion of d functions significantly affects geometries and energies. Extensive comparison of his calculations with experimental results has validated the computational level of accuracy employed, permitting Wiberg to draw some important conclusions. Thus, he has estimated I to be approximately 65 kcal/mol more stable than its diradical, indicating a strong interaction holding C_1 to C_3. He has also found that the C_1–C_3 distance in I shortens from 1.600 Å at 4-31G to 1.543 Å at 6-31G*. This separation is now that of a normal carbon–carbon single bond and therefore demands an explanation. In search of such understanding, Wiberg constructed plots of total molecular electron density minus simulated free atoms in planes containing the C_1–C_3 bond. His results have confirmed those of Newton and Schulman[7] in finding very little bonding charge density along the C_1–C_3 axis.

A recent X-ray study by Chakrabarti et al.[12] strongly supports the concept of a charge-loss region between formally bonded

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[1] Wiberg, W. B.; Ciula, R. P. *J. Am. Chem. Soc.* **1959**, *81*, 526.

[2] See, for example: Lemal, D. M.; Menger, F.; Clark, G W. *J. Am. Chem. Soc.* **1963**, *85*, 2529. Wiberg, K. B.; Lampman, G. M.; *Tetrahedron Lett.* **1963**, 2173. For a review, see also ref 4b.

[3] For a review see: Newton, M. D. "Modern Theoretical Chemistry"; Schaefer, H. F., Ed.; Plenum Press: New York, 1977; Vol. 4, p 223.

[4] (a) Ginsburg, D. "Propellanes; Verlag Chemie: Weinheim, Germany, 1975. (b) Greenberg, A.; Liebman, J. F. "Strained Organic Molecules"; Academic Press: New York, 1978.

[5] Wiberg, K. B.; Walker, F. H. *J. Am. Chem. Soc.* **1982**, *104*, 5239. Note that the IUPAC name for [1.1.1]propellane is tricyclo[1.1.1.0]pentane.

[6] (a) Ditchfield, R.; Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* **1971**, *54*, 724. Hehre, W. J.; Pople, J. A. *Ibid.* **1972**, *56*, 4233. (b) Harihan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213.

[7] Newton, M. D.; Schulman, J. M. *J. Am. Chem. Soc.*, **1972**, *94*, 773.

[8] Bader et al. [Bader, R. F. W.; Henneker, W. H.; Cade, P. E. *J. Chem. Phys.* **1967**, *46*, 3341. Bader, R. F. W.; Keaveny, I.; Cade, P. E. *Ibid.* **1967**, *47*, 3381] and Deakyne and Allen [Deakyne, C. A.; Allen, L. C. *J. Am. Chem. Soc.* **1977**, *99*, 3895,] have shown that total overlap population between pairs of atoms depends not only on the amount of charge between the atoms, but also on its disposition in space. This does not change the analysis or conclusions that have been put forth concerning the nature of the [1.1.1]propellane HOMO itself. But for highly strained systems the total population summed over all molecular orbitals is not necessarily indicative of the true forces holding some pairs of atoms together, e.g., C_1 to C_3.

[9] Stohrer, W.-D.; Hoffmann, R. *J. Am. Chem. Soc.* **1972**, *94*, 779.

[10] Wiberg, K. B. *J. Am. Chem. Soc.* **1983**, *105*, 1227.

[11] Wiberg, K. B.; Wendoloski, J. J. *J. Am. Chem. Soc.* **1982**, *104*, 5679.

[12] Chakrabarti, P.; Seiler, P.; Dunitz, J. D.; Schluter, A.-D.; Szeimies, G. *J. Am. Chem. Soc.* **1981**, *103*, 7378.

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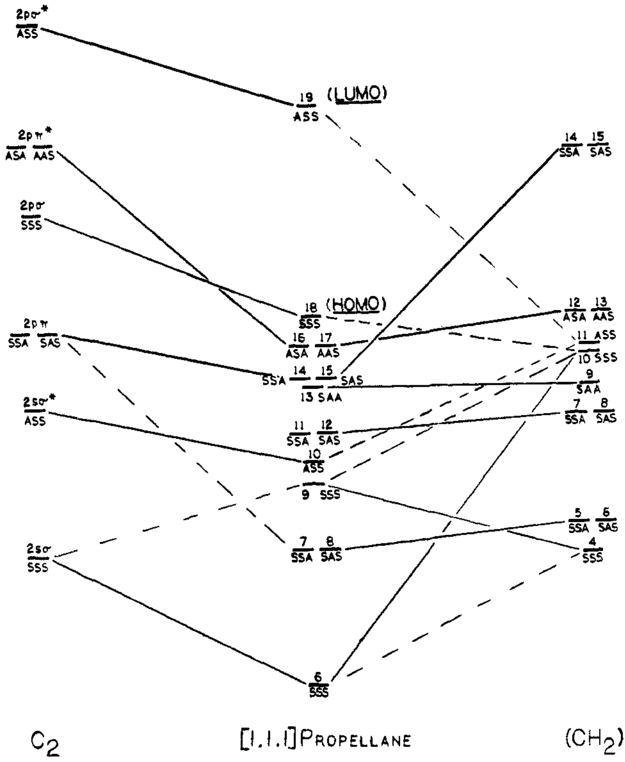


Figure 1. Interaction diagram between $(CH_2)_3$ and C_2 fragments to form [1.1.1]propellane. The three-letter code designates each orbital as (pseudo-) symmetric (S) or antisymmetric (A) with respect to the σ_h plane, one of the vertical planes, and its perpendicular plane, in that order. Orbital energies were calculated at 6-31G* using singlet wave functions for C_2 and I and a triplet for $(CH_2)_3$ (to maximize its symmetry). Solid lines connect propellane orbitals with their major components among the fragment orbitals; dotted lines indicate less significant fragment contributions.

inverted carbons. Deformation densities derived from high resolution spectroscopic measurements of a [3.1.1]propellane derivative (III) show no charge buildup in the interbridgehead "bonding" region of this compound, but rather a region of enhanced charge beyond the bridgeheads.

In sum, traditional criteria such as internuclear distance and heat of hydrogenation clearly imply a robust C_1–C_3 bond for I. Yet the overlap populations and deformation density analysis discussed above reveal no evidence for a conventional C_1–C_3 bond. It is the purpose of this paper to address these questions. We find that it is necessary to consider the molecular orbitals lying at lower energies than the highest and that these give rise to a bonding pattern not previously observed.

II. Methods

Ab Initio MO calculations in the RHF approximation were carried out using the Gaussian 80[13a] program. 1,3-Diborabicyclo[1.1.1]pentane and 1,3-diazabicyclo[1.1.1]pentane were optimized at both 4-31G[6a] and 6-31G*[6b] assuming D_{3h} symmetry, and the bicyclo[1.1.1]pentyl-1-carbenium ion was globally optimized at 4-31G. The force relaxation method of Pulay[13b] was employed for all optimizations. Considerable differences in the geometries of 1,3-diborabicyclo[1.1.1]pentane and 1,3-diazabicyclo[1.1.1]pentane were observed between 4-31G and 6-31G*, confirming[10,11] that polarization functions are necessary to adequately describe highly strained systems.

A modified form of the orbital plotting program of Jorgensen[14] was used to generate three-dimensional perspective representations for the molecular orbitals. Deformation density plots were obtained by subtraction of the sum of spherically averaged one-electron densities for each atom from the total molecular densities. The 6-31G* basis was used for both the Jorgensen plots and deformation densities.

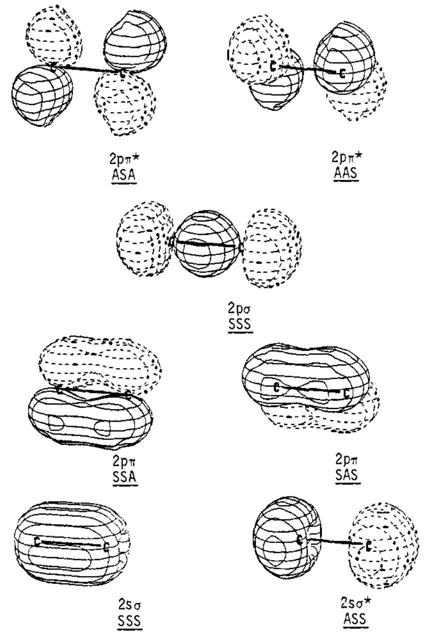
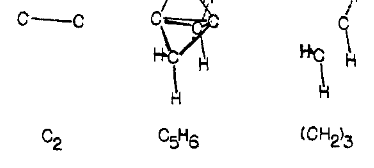


Figure 2. Valence molecular orbitals for the C_2 fragment in [1.1.1]-propellane. Three-dimensional orbital representations were generated from 6-31G* wave functions using the plotting routines of Jorgensen.

Preliminary configuration interaction calculations on I and II, using double substitutions of the virtual orbitals and Møller–Plesset perturbation theory to third order[13a] with the 4-31G basis, indicate no significant modification of our conclusions. Several other lines of evidence should be noted here in support of the assumptions and level of ab initio calculation employed. Thus, Newton and Schulman carried out an extensive search at 4-31G for spectroscopic states of I other than the closed-shell singlet in D_{3h} assumed here. Triplet diradicals were found at an excitation energy of 51 kcal/mol in D_{3h} and at 30 kcal/mol for a lower symmetry appropriate to homolytic cleavage of a side bond. Wiberg's quantitative success in explaining geometries and enthalpies for a great many strained, small-ring molecules, including II and others closely related to I, at the MO SCF level with the 6-31G* basis provides very strong support.[5,10,11] More recently, Wiberg[15] has carried out an extensive potential energy surface exploration of I at 6-31G* and determined a vibrational frequency spectrum which quantitatively agrees with experiment (including the unusually intense asymmetrical IR band between 500 and 600 cm^{-1}).

III. Results

A molecular orbital diagram which aids in understanding the bonding in I may be constructed from C_2 and three CH_2 fragments as indicated. Using Wiberg's [1.1.1]propellane geometry,[10] we



calculated 6-31G* wave functions for the C_2 fragment and the $(CH_2)_3$ fragment, fixed at the propellane geometries, as well as the parent molecule I. The resulting one-electron orbital energy interaction diagram is given in Figure 1. Jorgensen plots of the relevant valence orbitals for the two fragments and for I itself are

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(13) (a) Binkley, J. S.; Whiteside, R. A.; Krishnana, R.; Seeger, R.; DeFrees, D. J.; Schlegel, H. B.; Topiol, S.; Kahn, L. R.; Pople, J. A. QCPE **1981**, 406 (Gaussian-80). Topiol, S., private communication; Krough-Jespersen, K., private communication: (b) Pulay, P. *Mol. Phys.* **1969**, *17*, 197.

(14) Jorgensen, W. L., QCPE Program No. 340, 1977.

(15) Wiberg, K. B., private communication.

Table I. Optimized Geometries of [1.1.1]Propellane and Related Systems at 4-31G and 6-31G*

compound	parameter[a]	4-31G	6-31G*	observed	ref
ethane (staggered)	r(CC)	1.529	1.527	1.531 ± 0.002	11
	r(CH)	1.083	1.086	1.095 ± 0.002	
	∡(HCH)	107.7	107.7	107.8 ± 0.2	
cyclopropane	r(CC)	1.503	1.497	1.514 ± 0.002	11
	r(CH)	1.072	1.076	1.082 ± 0.003	
	∡(HCH)	113.7	114.0	116.5	
bicyclobutane	$r(C_1C_2)$	1.502	1.489	1.498 ± 0.004	10
	$r(C_1C_3)$	1.478	1.466	1.497 ± 0.003	
	$r(C_1H)$	1.062	1.070	1.071 ± 0.004	
	$r(C_2H_e)$	1.074	1.078	1.093 ± 0.008	
	$r(C_2H_a)$	1.076	1.083	1.093 ± 0.008	
	∡$(C_1C_2C_3)$	58.95	58.90	59.96	
	∡$(C_2C_1C_4)$	97.62	97.91	98.29	
	∡(C_3C_1H)	133.43	132.10	128.36 ± 0.23	
	∡$(C_1C_2H_e)$	117.31	117.51		
	∡$(C_1C_2H_a)$	119.37	119.50		
	∡(HC_2H)	113.90	113.98	115.57	
[1.1.1]propellane (I)	$r(C_1C_2)$	1.528	1.502		10
	$r(C_1C_3)$	1.600	1.543		
	$r(C_2H)$	1.070	1.075		
	∡(HC_2H)	114.72	114.52		
bicyclo[1.1.1]pentane (II)	$r(C_1C_2)$	1.563	1.546	1.545 ± 0.006	11
	$r(C_1H)$	1.075	1.082	1.100 ± 0.010	
	$r(C_2H)$	1.080	1.085	1.100 ± 0.010	
	∡$(C_1C_2C_3)$	74.7	74.4	73.3 ± 1.0	
	∡(HC_2H)	111.4	111.0	103.9 ± 5.0	
1,3-diborabicyclo[1.1.1]pentane (IV)	$r(B_1C_2)$	1.613	1.607		this work
	$r(B_1B_3)$	1.630	1.606		
	$r(C_2H)$	1.078	1.081		
	∡(HC_2H)	113.20	113.28		
bicyclo[1.1.1]pentyl-1-carbenium ion[b] (V)	$r(C_1C_2)$	1.476			this work
	$r(C_2C_3)$	1.612			
	$r(C_1C_3)$	1.591			
	$r(C_2H)$	1.071			
	$r(C_3H)$	1.068			
	∡(C_1C_2H)	153.77			
	∡(HC_2H)	115.92			
1,3-diazabicyclo[1.1.1]pentane (VII)	$r(N_1C_2)$	1.542	1.498		this work
	$r(N_1N_3)$	1.991	1.963		
	$r(C_2H)$	1.075	1.082		
	∡(HC_2H)	112.30	110.78		

[a] Distances in A, angles in degrees. [b] Total energy, $E_T = -192.726\,873$ (4-31G).

given in Figures 2, 3, and 4 respectively. Figure 5 shows plots of the (6-31G*) σ HOMOs in I and three reference molecules: ethane, cyclopropane, and bicyclo[1.1.0]butane. Figure 8 compares orbitals 14 and 15 in 1,3-diborabicyclo[1.1.1]pentane with I. Figures 6 and 7 display deformation density plots computed in two perpendicular planes for I and our three reference molecules. The deformation density distribution in II, for the same pair of planes (Figure 9), permits comparison between I and the closely related structure without a formal C_1–C_3 bond. Calculated equilibrium geometries and total energies for all species studied are listed in Table I. The 6-31G* orbital energies for I, II, 1,3-diborabicyclo[1.1.1]pentane, and 1,3-diazabicyclo[1.1.1]-pentane are tabulated in Table II.

IV. Bonding in [1.1.1]Propellane

A. Molecular Orbitals in [1.1.1]Propellane. There are two principal features which characterize the unusual bonding in [1.1.1]propellane. The first concerns the nonbonding or slightly antibonding character of its HOMO. This aspect was discovered and quantified by Newton and Schulman,[7] and we further elucidate it below. The second concerns the origin of the C_1–C_3 binding. We find this to result from novel three-center, two-electron orbitals arising from $2p\pi$ AOs on C_1 and C_3 and the inward-pointing sp^2 hybrid orbital of the methylene bridge. We describe the nature of this new bonding pattern in the second part of this section.

A useful way to understand the HOMO in I is by comparing the σ HOMOs of three other related hydrocarbons: eclipsed ethane, cyclopropane, and bicyclo[1.1.0]butane (Figure 5). In each of these molecules, the HOMO is quite similar to the localized MO obtained by Newton and Schulman[7,16] using the

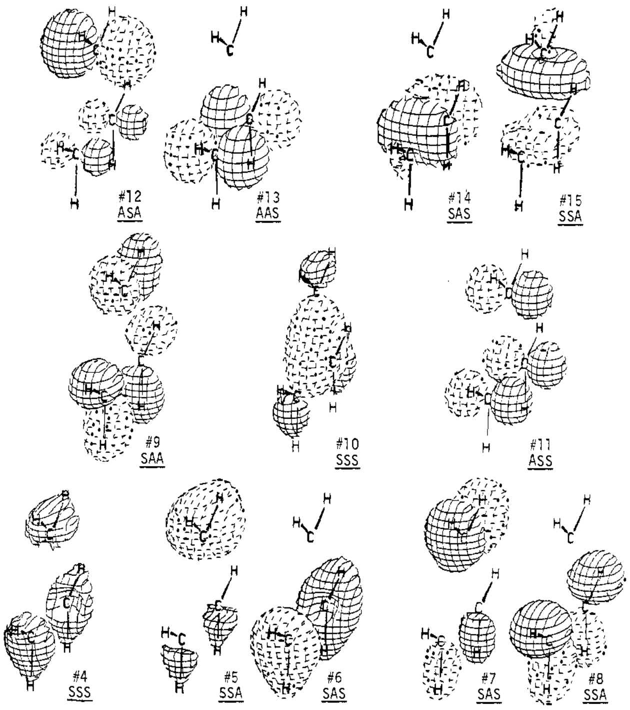

Figure 3. Valence molecular orbitals for the $(CH_2)_3$ fragment in [1.1.1]propellane. Note that all nine atoms are coplanar (geometry from the 6-31G* optimized structure of [1.1.1]propellane). Plots obtained as described in Figure 2.

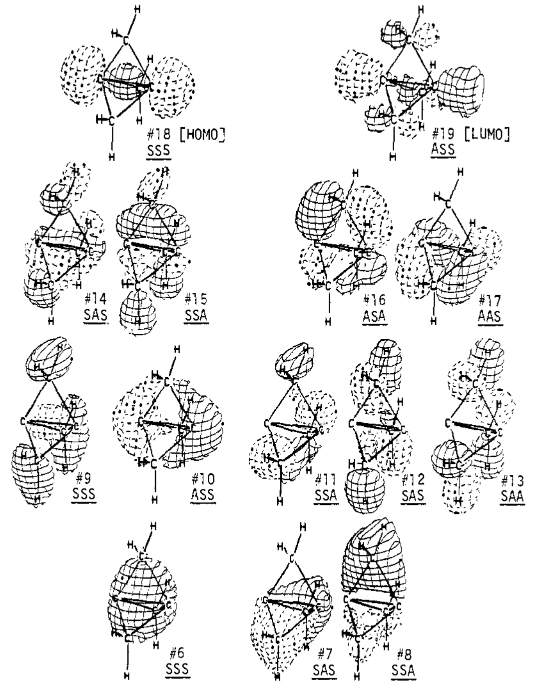

Figure 4. The filled valence molecular orbitals of [1.1.1]propellane, plus MO 19, the LUMO. Note that this orbital numbering begins at 6, as 1–5 are combinations of carbon 1s orbitals. Plots obtained as described in Figure 2.

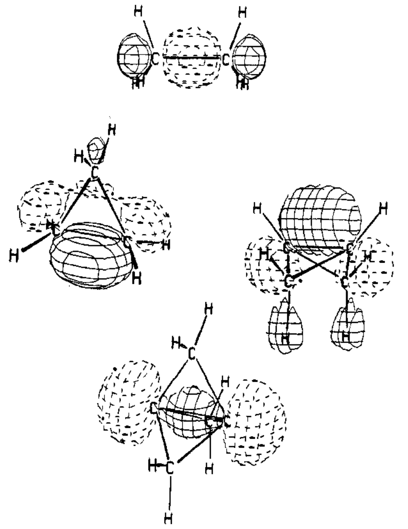

Figure 5. Highest occupied σ C–C orbitals in eclipsed ethane (not HOMO), cyclopropane (one of a degenerate pair), bicyclo[1.1.0]butane, and [1.1.1]propellane. Plots obtained as described in Figure 2.

Table II. 6-31G* Valence Orbital Energies

compd	MO	ϵ_i (hartrees)	total energy[a] (hartrees)	no. of corre-sponding MO in I
I[b]	6	−1.292 97		
	7, 8	−0.952 01		
	9	−0.777 90		
	10	−0.727 78	$\frac{\text{4-31G}^{d}}{\text{4-31G}}$: −192.361 860	
	11, 12	−0.655 65		
	13	−0.540 97	$\frac{\text{6-31G*}}{\text{6-31G*}}$: −192.691 061	
	14, 15	−0.520 37		
	16, 17	−0.442 03		
	18 (HOMO)	−0.361 22		
	19 (LUMO)	+0.176 02		
II[c]	6	−1.213 01		6
	7, 8	−0.903 50		7, 8
	9	−0.850 40		10
	10	−0.729 51	$\frac{\text{4-31G}}{\text{4-31G}}$: −193.610 156	9
	11	−0.672 14		18
	12, 13	−0.613 27		11, 12
	14	−0.496 53	$\frac{\text{6-31G*}}{\text{6-31G*}}$: −193.905 676	13
	15, 16	−0.452 91		16, 17
	17, 18	−0.445 61		14, 15
	19 (HOMO)	−0.432 77		19
IV	6	−1.063 99		6
	7, 8	−0.885 99		7, 8
	9	−0.689 18		9
	10, 11	−0.591 01	$\frac{\text{4-31G}}{\text{4-31G}}$: −166.060 646	11, 12
	12	−0.513 78		10
	13	−0.506 98	$\frac{\text{6-31G*}}{\text{6-31G*}}$: −166.310 301	13
	14, 15	−0.456 65		14, 15
	16, 17 (HOMO)	−0.364 99		16, 17
	18 (LUMO)	−0.000 13		18
	19	+0.189 03		19
VII	6	−1.396 85		6
	7	−1.044 04		10
	8, 9	−0.953 53	$\frac{\text{4-31G}}{\text{4-31G}}$: −225.452 677	7, 8
	10	−0.791 08		9
	11, 12	−0.666 00		11, 12
	13	−0.585 41	$\frac{\text{6-31G*}}{\text{6-31G*}}$: −225.836 977	18
	14, 15	−0.540 80		16, 17
	16	−0.521 83		13
	17, 18	−0.481 79		14, 15
	19 (HOMO)	−0.352 79		19

[a] 1 hartree = 627.5 kcal/mol. [b] Geometries from ref 10. [c] Geometries from ref 11. [d] The upper basis set is that used to calculate the energy; the lower one is used for geometry optimization.

Table III. Orbital Energy Variations in [1.1.1]Propellane upon C_1–C_3 Stretching

orbital	E(stretching)[a]	orbital	E(stretching)[a]
6	+0.053 37	16, 17	−0.018 61
10	−0.050 59	18 (HOMO)	−0.012 39
14, 15	+0.048 87	19 (LUMO)	−0.087 09

[a] Energies in atomic units. Below orbital 14 only those changes were tabulated which exceeded 0.03 au. C_1–C_3 was stretched 0.33 Å (to the C_1–C_3 separation in bicyclo[1.1.1]pentane).

Edmiston–Ruedenberg orbital localization procedure. This similarity indicates that the canonical σ HOMO, shown in Figure 5, is the primary C–C σ bonding orbital for each species. Each of these σ HOMOs has both bond-pair and lone-pair components. The unique feature in I is that its HOMO contains more density outside the binding region than in it.[17] Another characterization of these orbitals is achieved by stretching their CC bonds and observing the changes in their energies. For eclipsed ethane, cyclopropane, and bicyclobutane, the σ HOMO energies all rise (become less stable)—appropriate behavior for bonding MOs. However, when the central bond in I is stretched by distorting I to the geometry of II, the HOMO energy decreases. (Values for the energy change on stretching HOMO (orbital 18) of I, along with some of the other important orbitals in I, are collected in

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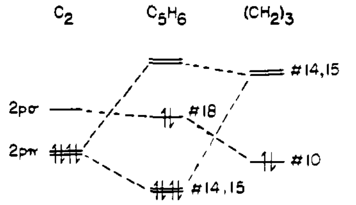
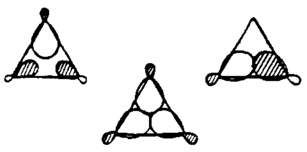
(16) Newton, M. D.; Schulman, J. M. *J. Am. Chem. Soc.* **1972**, *94*, 767. See also: Schulman, J. M.; Fisanick, G. J. *Ibid.* **1970**, *92*, 6653.

(17) As pointed out by Dr. Marvin Waldman (private conversation), a quantitative evaluation of whether the propellane HOMO is binding or antibinding can be determined by application of the Hellman–Feynman theorem. This result can be obtained by measuring the amount of HOMO charge density which falls into Berlin's binding and antibinding regions [Berlin, T. *J. Chem. Phys.* **1951**, *19*, 208. See: Levine I. N. "quantum Chemistry", 2nd ed.; Allyn and Bacon: Boston, Mass., 1974; pp 378–379, for relevant discussion and figures.] It is clear from the boundary lines for homonuclear distances shown in the latter reference that the binding or antibinding of the HOMOs in Figure 5 will follow intuitive estimates of the percent bond-pair and lone-pair components in these orbitals.

Table III.) Thus, despite being symmetric, this unusual MO is actually non- or slightly antibonding with respect to the central C_1–C_3 bond of I. It puts very little charge density between C_1 and C_3 and therefore contributes nil to holding C_1 to C_3. This finding is in accord with Stohrer and Hoffmann's results[9] for the variation of E(HOMO) with $r(C_1C_3)$, and affirms the conclusion by Newton and Schulman that I lacks any "normal" C_1–C_3 σ bonding.

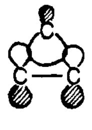
To find out what holds C_1 to C_3 and to simultaneously understand why the HOMO of I is nonbonding, we examine the composition of the highest two energy levels which are symmetric in σ_h and therefore may contribute to interbridgehead bonding. These are the HOMO (orbital 18) and the degenerate pair 14 and 15. In the simplified interaction diagram shown below, the three orbitals of the diatomic C_2 fragment are the simple 2pπ and 2pσ orbitals (Figure 2). The three orbitals of the $(CH_2)_3$ fragment are the a′ and e′ set of methylene sp^2 hybrids pointing into the triangle in the σ_h plane (10; 14, 15, respectively, in Figure 3). The orbital amplitudes and phases for these three orbitals follow the familiar triangle node pattern:



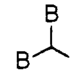


Formation of orbitals 14, 15, and 18 occurs through a pair of interactions in which the C_2 2pπ orbital donates electrons into MOs 14 and 15 of the $(CH_2)_3$ cage, and back-donation by MO 10 of the cage gives rise to occupancy of the C_2 2pσ. It is apparent from Figure 2 that the C_2 2pσ itself is principally a lone-pair orbital and its outward hybridization is accentuated by interaction with MO 10.[18]

C_1–C_3 bonding in I comes from the quadruply occupied e′ pair of orbitals 14 and 15, which sharply rise in energy when I is stretched (Table III). They contribute no density along the C_1–C_3 line of centers and we designate them a "σ-bridged π" bond:



These orbitals come into play because the inverted configuration at the bridgehead carbons forces the σ lobes of MO 18 to point outward rather than inward. This leaves the C_2 fragment's 2pπ orbitals as the lowest energy ones available for participation in C_1–C_3 bonding. To understand the detailed nature of this bond's contribution to the totality of bonding in C_5H_6, we identify the dominant role of each propellane MO in Figure 4: MOs 7, 8, 9, 11, 12, and 13 are predominantly C–H bonds. The six framework C–C bonds that connect the methylenes to C_1–C_3 are identified with MOs, 6, 10, 14, 15, 16, and 17. Thus we have used MOs 14 and 15 twice: they supply the bonding for two legs of the framework and simultaneously hold C_1 and C_3 together. This attribute is the hallmark of electron-deficient binding, and these are indeed three-center, two-electron orbitals. [1.1.1]Propellane is de facto electron deficient because its HOMO is nonbonding. This immediately suggests analogy to the bonding in boron hydrides and carboranes which has been studied extensively by Lipscomb and collaborators.[19] The closest analogue is the central three-center BBB type:



Four other filled C–C framework orbitals show sensitivity to C_1–C_3 stretching. Two, MO 6 and MO 10 (Figure 4), are low in energy and correspond respectively to the 2sσ and 2sσ^* MOs of the central C_2 fragment. They rise (2sσ) and fall (2sσ^*) by nearly equal amounts upon C_1–C_3 stretching (see Table III). Thus, as in C_2, this pair of orbitals may be considered to contribute zero to C_1–C_3 bonding.[20] The other two, degenerate orbitals 16 and 17, arise from the interaction of degenerate orbitals 12 and 13 of $(CH_2)_3$ with 2pπ^* of C_2. Since orbitals 16 and 17 are antisymmetric in the σ_h plane, they contribute exclusively to the framework C–C bonding. Likewise, they are antibonding with respect to C_1–C_3 and their energy is lowered when this separation is increased.

B. Deformation Densities in [1.1.1]Propellane and Reference Molecules. Deformation densities are an especially useful method for analysis of bonding charge distributions.[21] Plots in the C–C bond bisector plane (Figure 6) and in the plane containing the C–C bond and the side bonds (Figure 7) are presented for I and the three reference molecules discussed above. The deformation density distribution in ethane is representative of a normal C–C σ bond, showing maximum charge buildup localized in the C–C axis at its midpoint. In cyclopropane the three C–C bonds are similar to that in ethane, except that the maximum charge buildup regions are displaced from the C–C axes by ~0.2 Å. In bicyclobutane the distortion is even greater, displacing the central bond's deformation density maximum by ~0.35 Å from the C_1–C_3 axis. It is interesting to note a region of charge buildup beyond the ends of the C_1–C_3 bond in bicyclobutane which parallels that shown in its HOMO plot (Figure 5) and supports the idea that the C_1–C_3 bond is composed of nearly pure p orbitals.[16] The side bonds (C_1–C_2) in bicyclobutane are essentially similar to those in cyclopropane.

In I the situation is radically different. First, instead of a gain in electron density, there is a deep hole (electron density loss region) in the center of the molecule. Second, as shown in Figure 7, the deformation density increases associated with the side bonds have fused, resulting in three narrow charge gain regions between the C_1–C_3 axis and the methylene bridges. In the σ_h plane (Figure 6), we see the cross section of this bonding density, displaced approximately 0.8 Å from the interbridgehead axis. Instead of an ethane-like σ bond, three filaments of charge gain bind C_1 to C_3 and simultaneously contribute to C–C framework bonding. These are the σ-bridged π bond. Finally, the large charge density gain immediately outward from C_1 and C_3 is, of course, primarily the nonbonding HOMO, orbital 18 (see Figure 5).

V. 1,3-Diborabicyclo[1.1.1]pentane (IV)

If it is true that the HOMO of I contributes nothing to bonding, then an analogue of I with two fewer electrons should have essentially the same orbital structure. Thus we have obtained 4-31G

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[18] MOs 10 and 4 of $(CH_2)_3$ mix with 2pσ and 2sσ of C_2 to form three occupied C_5H_6 MOs 6, 9, and 18 (HOMO). MO 10 of $(CH_2)_3$ has high density between C_1 and C_3 along the C_1–C_3 axis and its shape is reflected in C_5H_6 MO 9. But MO 9 cannot form a significant σ C_1–C_3 bond because C–H bond orbitals have lower energy than C–C bond orbitals, thus making it primarily a C–H bond. Orthogonality of C_5H_6 MO 9 to MO 18 therefore accentuates the lone-pair character of the latter.

[19] Lipscomb, W. N. "Boron Hydride Chemistry"; Muetterties, E. L., Ed.; Academic Press: New York, 1975, Chapter 2.

[20] Another way to view MO 6, the cage orbital which is the lowest valence MO, is as an in-phase combination of core atomic orbitals that primarily lower the energies of the individual carbon atoms rather than contributing to molecular bonding. Thus in MO 6 the 2s dominates and makes a larger contribution than in any other MO (except for a similar situation in C_1–C_3 antibonding MO 10). More particularly, the coefficient of the inner part of this split-valence 2s AO is greater than the coefficient of the outer part—a reverse of the case in the other MOs. In sum, MO 6 is not contributing significantly to holding C_1 to C_3 even though it is a fully symmetric orbital which appreciably lowers the total molecular energy.

[21] See, for example: "Proceedings of the ACS Symposium on Electron Distribution and the Chemical Bond" (Atlanta, 1981); Coppens, P., Hall, M., Eds.; Plenum Press: New York, 1982.

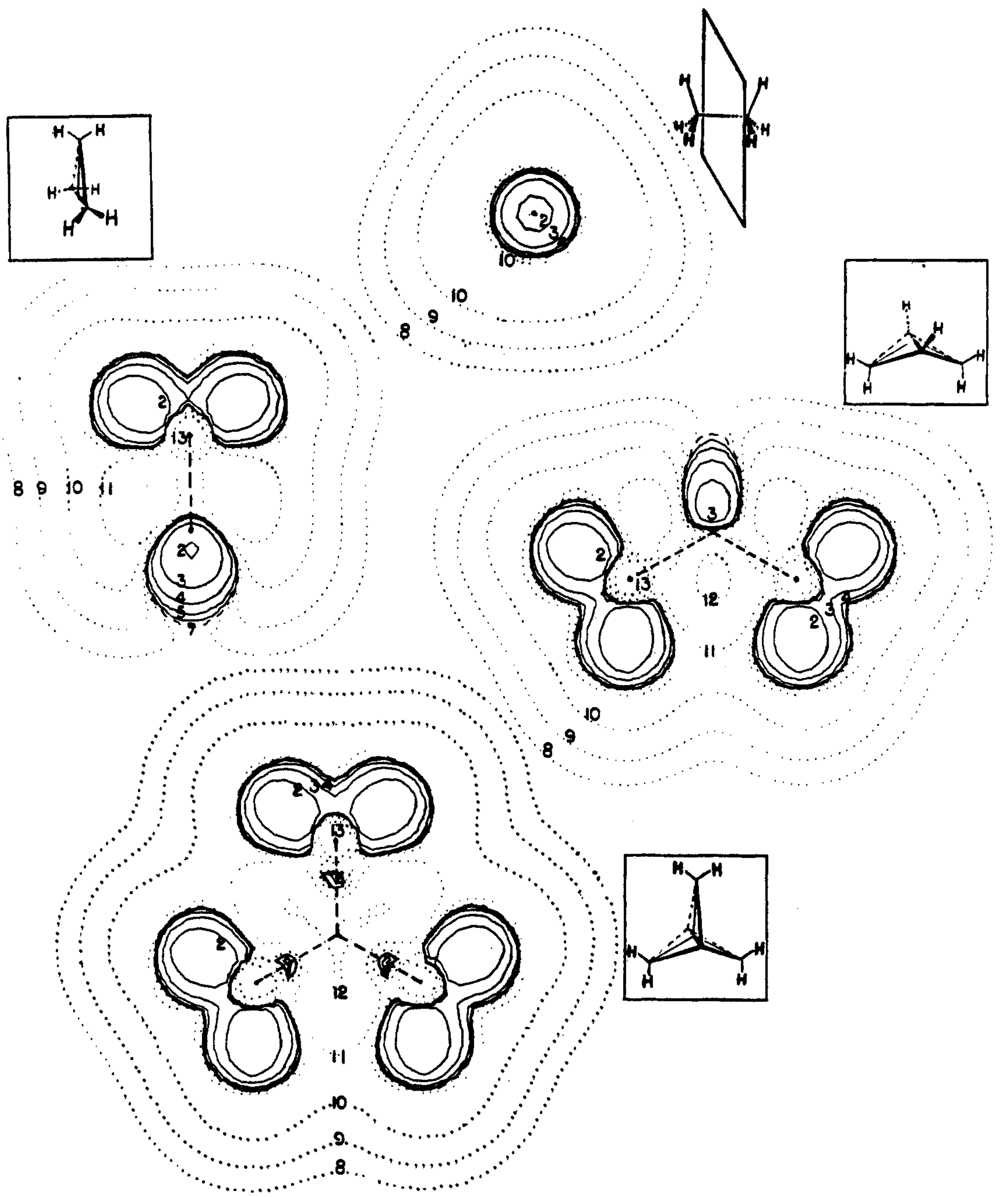


Figure 6. Deformation densities of eclipsed ethane, cyclopropane, bicyclo[1.1.0]butane, and [1.1.1]propellane. In each case, the plane depicted is the mirror plane bisecting the C–C bond in question, as shown by the insets.

and 6-31G* optimized structures for 1,3-diborabicyclo[1.1.1]pentane (IV) (see Table I), a molecule in which the formal electron count does not provide for a bridgehead–bridgehead bond. IV is formally, as well as de facto, electron deficient, suggesting comparison with known carboranes and boron hydrides. The 6-31G* optimized B_1-C_2 and B_1-B_3 distances in IV are almost identical at 1.61 Å. This is a typical length for B–C bonds but quite short for B–B. B–B distances in carboranes and boron hydrides are typically in the range 1.65–1.90 Å[22] (although one boron hydride has a reported B–B separation of 1.60 Å[23]).

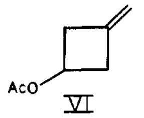
IV

The MOs of principal interest in IV, 14 and 15, are essentially identical with those in I, as can be seen from their Jorgensen plots in Figure 8. The B_1–B_3 separation is indicative of a strong B_1–B_3 bond and supports the notion that in this highly condensed ring system 24 electrons can do the bonding of 26. Except for the omission of MO 18, the molecular orbital diagram for IV parallels that for I. The one-electron energy levels of IV are shifted upward because of boron's smaller nuclear charge.

VI. Bicyclo[1.1.1]pentyl-1-carbenium Ion (V)

The protonation reaction of I to give the cation V is obviously of interest, and the geometrical changes which take place give further evidence of the nonbonding nature of the HOMO in I.

V



VI

The 4-31G optimized structure (Table I) of this species, a presumptive intermediate in the known acetolysis[5] of I to VI, shows

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(22) Onak, T. In footnote 19, Chapter 10.

(23) Hirschfeld, F. L.; Erlks, K.; Dickerson, R. E.; Lippert, E. L.; Lipscomb, W. N. *J. Chem. Phys.* **1958**, *28*, 56.

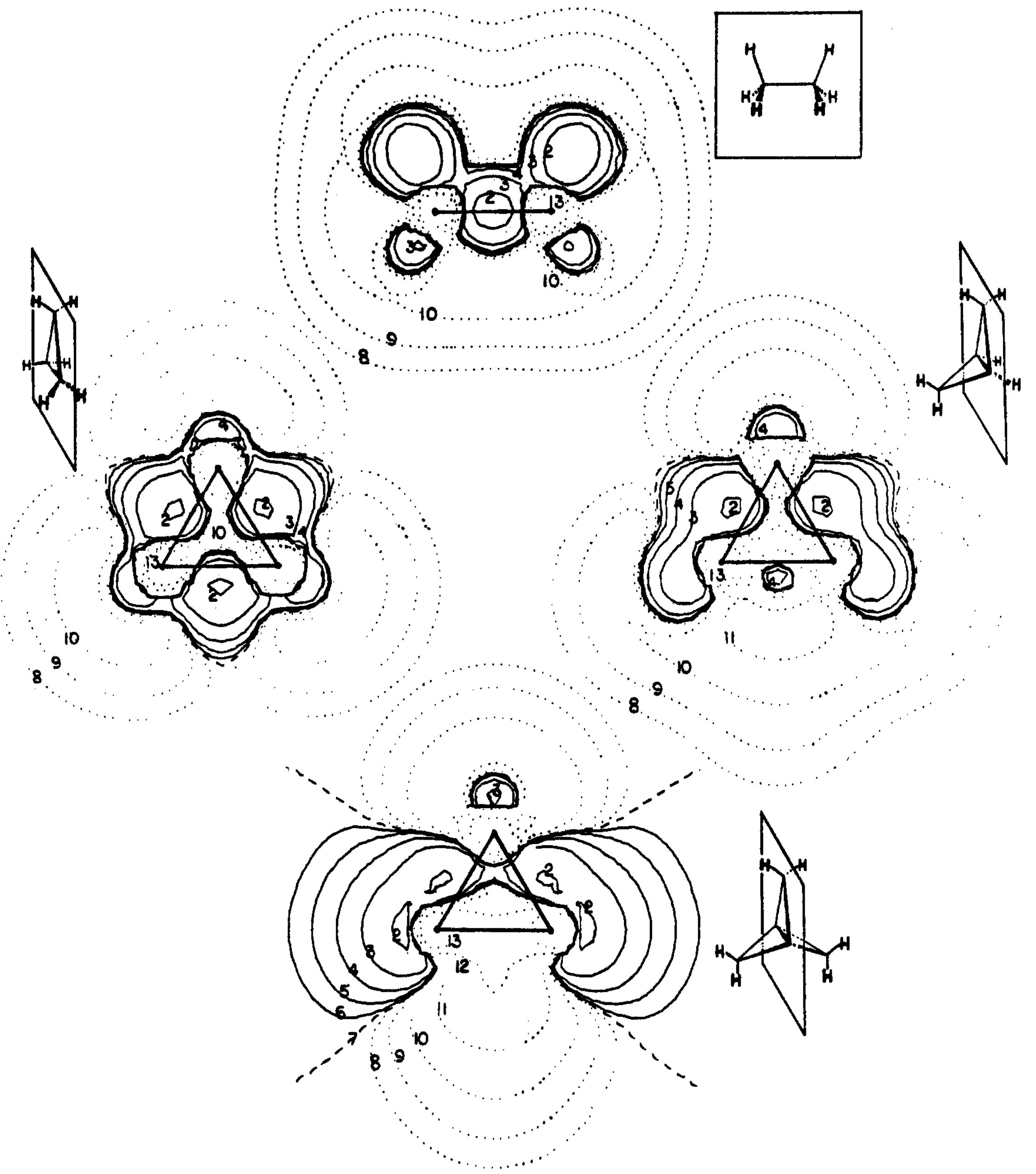


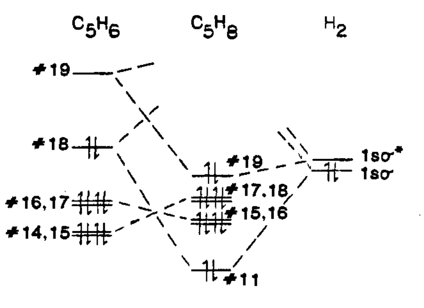
Figure 7. Deformation densities of eclipsed ethane HCCH plane, cyclopropane $C_1C_2C_3$ plane, bicyclbutane $C_1C_2C_3$ plane, and [1.1.1]propellane $C_1C_2C_3$ plane. In each case, the plane shown contains the C–C axis of the bond in question and an eclipsed pair of side bonds, except for ethane.

significant changes in the C_1–C_2 and C_2–C_3 bond lengths, but little change in the C_1–C_3 distance. In fact, V shows a C_1–C_3 distance of 1.591 Å at 4-31G, slightly shorter than the corresponding 1.600-Å C_1–C_3 distance in I.[10] In addition, the C_1–H distance has relaxed to 1.068 Å, a slightly short C–H bond distance (compare 1.075 Å for the C_1–H bond in II at 4-31G[11]).[24]

Stohrer and Hoffmann[9] have partially explored the relationship between the C_1–C_3 distance and C_1–B distance on interaction of I with a different Lewis acid—a molecule of BH_3 approaching along the C_1C_3 line of centers. Although their discussion was limited to the effects of this interaction on the C_1–C_3 distance, they too found almost no change in C_1–C_3 bond length as the C_1–B distance decreased. Chandrasekhar, Schleyer, and Schlegel[25] have discussed the STO-3G optimized structure of V in another context, relating it to II and to isolobal $(OC)_3Fe[(CH_2)_3C]$ complexes. Their results corroborate our findings in this area, suggesting that V is a true intermediate, with a relatively low barrier to ring opening.

VII. Bicyclo[1.1.1]pentane (II) and 1,3-Diazabicyclo[1.1.1]pentane (VII)

It is instructive to construct an MO picture of bicyclo[1.1.1]pentane (II) by interacting [1.1.1]propellane with a fragment consisting of a pair of hydrogen atoms placed at the bridgeheads and distorting I to the geometry of II. The simplified MO diagram is shown below. The addition of the symmetric



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[24] It is interesting to note that the proton affinity of I is 229 kcal/mol, very close to that of ammonia, calculated at 4-31G: Desmeules, P. J.; Allen, L. C. *J. Chem. Phys.* **1980**, *72*, 4721.

[25] Chandrasekhar, J.; Schleyer, P. v. R.; Schlegel, H. B. *Tetrahedron Lett.* **1978**, *36*, 3393.

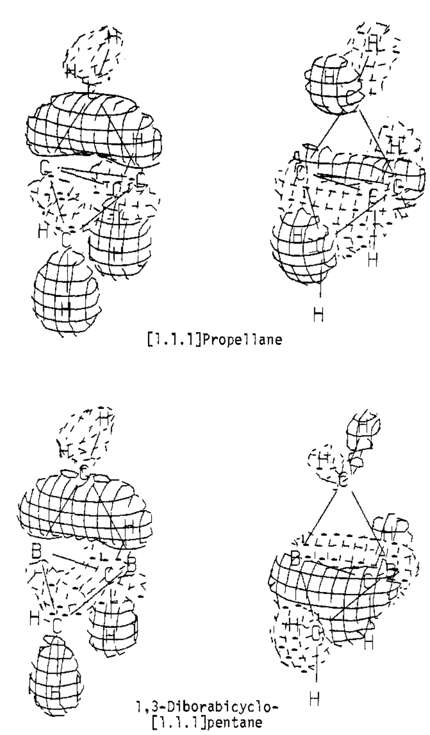


Figure 8. Orbitals 14 and 15 for comparison between [1.1.1]propellane and 1,3-diborabicyclo[1.1.1]pentane.

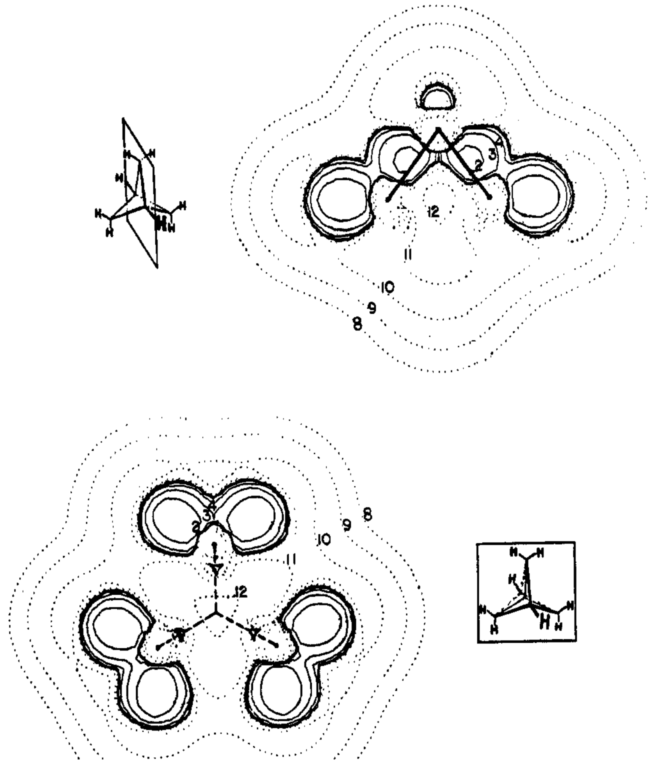
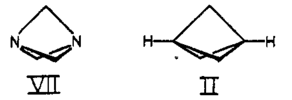


Figure 9. Deformation density plots of bicyclo[1.1.1]pentane in the planes corresponding to those used in Figures 6 and 7 for the propellane. Note the essential similarity in deformation density distribution between the two compounds. The primary differences lie in the bridgehead C–H bonding region.

and antisymmetric combination of hydrogen 1s orbitals plus two electrons converts the propellane nonbonding HOMO (18) into a low-lying C–H bonding orbital. The other new C–H bond arises from the interaction between the LUMO of I, orbital 19, and the asymmetric combination of hydrogen orbitals. This orbital is strongly antibonding vis-à-vis the C_1–C_3 bond, and its introduction counteracts the σ-bridged π bonding, thereby elongating the C_1–C_3 bond in II by 0.35 Å (to 1.87 Å at 6-31G*). The one-electron energy of MOs 14 and 15 rises approximately 47 kcal/mol from C_5H_6 to C_5H_8, corresponding to a major, but not complete, loss of C_1–C_3 bonding. The C_1–C_3 distance of 1.87 Å (1.84 Å experimental)[11] is still the shortest nonbonded C–C separation known. Thus the deformation density plots for II (Figure 9) show that the σ-bridged π filaments of electron density remain in place, albeit attenuated. 1,3-Diazabicyclo[1.1.1]pentane (VIII) has an MO diagram similar to that of II (Table II) but with most of the MOs slightly more stable than their counterparts in II because of nitrogen's greater nuclear charge. The HOMO of VII is less tightly bound than the HOMO of II because it is a lone pair rather than a C–H bond pair. The N_1–N_3 separation of 1.96 Å (Table I) implies an even greater bridgehead–bridgehead repulsion than in II. In II and VII the nonbonded interaction consists of π-type bonding opposed by σ-type antibonding in contrast to the usual competition in a molecule like F_2 where a σ-type bond is opposed by a π-type antibond.



VII II

VIII. Summary

1. For typical hydrocarbons, e.g., ethane, cyclopropane, and bicyclo[1.1.0]butane, the σ HOMO is a central C–C bonding orbital. In sharp contrast, the [1.1.1]propellane HOMO is nonbonding. There is very little charge density along the C_1–C_3 line of centers, in spite of the fact that the C_1–C_3 separation is that of a normal C–C σ bond (1.54 Å) and that the molecule is 65 kcal/mol more stable than its diradical. This result confirms and extends previous experimental and theoretical work.

2. C_1–C_3 is held together by three-center, two-electron orbitals that are made from 2pπ orbitals on C_1 and C_3 and the sp^2 lone pairs of the methylene bridges. We term this a σ-bridged π bond. If one visualizes [1.1.1]propellane as constructed from a C_2 fragment interacting with a $(CH_2)_3$ methylene cage, the σ-bridged π-bonding orbitals and the nonbonding HOMO are seen to arise from a π-type orbital interaction between C_2 and $(CH_2)_3$ fragments, followed by a σ-type backbonding interaction.

3. Because the HOMO of [1.1.1]propellane is nonbonding, 1,3-diborabicyclo[1.1.1]pentane, with no formal B_1–B_3 bond, should also show B_1 and B_2 strongly held together. This is found to be the case: its σ-bridged π-bonding orbitals are essentially identical with those in I, and the B_1–B_3 separation is 1.61 Å—shorter than BB distances in known carboranes. [1.1.1]Propellane is de facto electron deficient, while 1,3-diborabicyclo[1.1.1]pentane is truly so. σ-Bridged π bonds are somewhat analogous to central BBB bonds in carboranes and boron hydrides.

4. Bicyclo[1.1.1]pentane and 1,3-diazabicyclo[1.1.1]pentane, both of which lack a formal 1–3 bond, nevertheless show significant, albeit weaker, σ-bridged π bonding. This bonding is responsible for the well-known fact that bicyclo[1.1.1]pentane has the shortest observed C–C nonbonded separation (1.84 Å). The extra pair of electrons in these two molecules resides in an antibonding σ HOMO which counteracts part of the σ-bridged π bonding. This σ antibond cancellation of π bonds may be constrasted with the usually observed π antibond cancellation of σ bonds that occurs, e.g., in F_2.

5. The structure of an intermediate in the acetolysis of [1.1.1]propellane was calculated in a study of the propellane protonation reaction. Thus the C_1–C_2 and C_2–C_3 side bond lengths in the bicyclo[1.1.1]pentyl-1-carbenium cation are significantly shorter and longer, respectively, than those in [1.1.1]propellane, but there is little change in the C_1–C_3 bond. This result gives further evidence of the nonbonding nature of the propellane HOMO and is in accord with previous work.

Acknowledgment. The authors thank Dr. Charles M. Cook, Celeste M. Rohlfing, Kim Ferris, Professor Joel F. Liebman, and Professor Maitland Jones, Jr., for helpful and stimulating conversations. They also wish to thank Professor Kenneth B. Wiberg for copies of manuscripts prior to publication. Financial support from the National Institutes of Health, No. GM26462, is gratefully acknowledged. One of us (J.E.J.) thanks the National Science Foundation for support through Grant CHE 8101212 to Maitland Jones, Jr.

Note Added in Proof. (a) Bader[26] has applied his topological theory of molecular structure to the interpretation of the charge distribution along the C_1–C_3 axis in [1.1.1]propellane (computed with the 4-31G basis). He finds a long and weak C_1–C_3 bond in the equilibrium structure which upon elongation passes through an unstable coalescence of critical points to a cage structure of three inwardly curved four-membered rings. In agreement with Newton and Schulman,[7] we interpret our 6-31G* charge density along C_1–C_3 as antibonding at equilibrium separation.

(b) Epiotis has employed his bond-diagrammatic molecular orbital valence bond theory[27,28] to qualitatively discuss bond-deficient molecules and [1.1.1]propellane in particular.[28,29] In the latter reference,[29] he has set up an in principle computable ratio, λ_U/λ_D, that predicts whether or not a molecule has one less bond than expected from Lewis dot structures, and he has given several examples in addition to propellane.

(c) Deformation densities from a recent X-ray study[30] of 1,5-dimethyltricyclo[2.1.0.0^{2,5}]pentan-3-one show nothing extraordinary about the central bond in this species. Thus, the unusual deformation density reported for III specifically characterized bonding between inverted bridgehead atoms and is not simply peculiar to molecules containing the bicyclobutane skeleton.

Registry No. [1.1.1]Propellane, 35634-10-7; 1,3-diborabicyclo[1.1.1]pentane, 87902-15-6; bicyclo[1.1.1]pentane, 311-75-1; 1,3-diazabicyclo[1.1.1]pentane, 71634-25-8; bicyclo[1.1.1]pentyl-1-carbenium ion, 22907-79-5.

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(26) Bader, R. F. W.; Tang, T.-H.; Tal, Y.; Biegler-König, F. W. *J. Am. Chem. Soc.* **1982**, *104*, 940.

(27) Epiotis, N. D.; Larson, J. R.; Eaton, H. "Unified Valence Bond Theory of Electronic Structure" (Lecture Notes in Chemistry); Springer-Verlag: New York and Berlin, 1982; Vol. 29.

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(30) Irngartinger, H.; Goldman, A. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 775.

A Theoretical Study of the Formation of Carbonic Acid from the Hydration of Carbon Dioxide: A Case of Active Solvent Catalysis

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Contribution from the Department of Chemistry, University of Leuven, B-3030 Heverlee, Belgium, and the Laboratory of Physical Chemistry, Swiss Federal Institute of Technology, CH-8092 Zürich, Switzerland. *Received May 27, 1983*

Abstract: The activation energy of CO_2 toward hydration has been calculated as 15.5 kcal/mol by ab initio SCF calculations using the split-valence 3-21G basis set, which is in good agreement with the experimental value. A quite stable six-membered cyclic complex of CO_2 and the water dimer has been obtained by the calculation. The preferred hydration reaction is found to be that with the water dimer, the reaction with the water monomer being far less favored. The catalytic effect of the second water molecule in the hydration process has been discussed.

I. Introduction

The hydration of carbon dioxide, CO_2, is one of the more fundamental reactions in several biological and ecological process.[1] When CO_2 is dissolved at neutral pH, the dominant reactions are[2]

$$(CO_2)_{aq} + H_2O \overset{I}{\rightleftharpoons} (H_2CO_3)_{aq} \overset{II}{\rightleftharpoons} (HCO_3^-)_{aq} + (H^+)_{aq}$$

where the formation of carbonic acid (reaction I) is the rate-determining step, whereas the equilibrium (reaction II) with the bicarbonate ion is very fast. Even though carbonic acid has not yet been isolated or directly observed by any spectroscopic means, its existence has been inferred from kinetic evidence: the activation energy for the hydration of CO_2 in neutral solution is reported at 17.7 kcal/mol.[3]

From a theoretical point of view, several studies are available on the gas-phase reaction of the isolated entities:

$$CO_2 + H_2O \rightarrow H_2CO_3$$

From their SCF calculations, Jönsson et al.[4,5] found an activation barrier for this reaction of 55.9 kcal/mol; the introduction of the electron correlation effect lowered the barrier only slightly to yield 52.3 kcal/mol. The very large discrepancy between theoretical and experimental values suggests that the reaction mechanism in solution might be fundamentally different from the mechanism in the gas phase.

In studying solvent effect, the solvent has perhaps too often been regarded as a continuous medium rather than as an active participant in the reaction. In what follows, we intend to show that the participation of a second water molecule in the reaction amounts to a significant catalytic effect. As a matter of fact, the idea of a second water molecule involvement was already advanced in Jönsson's original paper,[5] but it was not pursued any further at that time. Quite recently, however, the role of the water dimer

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[†] University of Leuven.

[‡] Swiss Federal Institute of Technology.

(1) Zelitch, I. *Ann. Rev. Biochem.* **1975**, *44*, 923 and references therein.

(2) Pocker, Y.; and Bjorkquist, D. W. *J. Am. Chem. Soc.* **1977**, *99*, 6537 and references therein.

(3) Magid, E.; Turbeck, B. O. *Biochim. Biophys. Acta* **1968**, *165*, 515.

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