exo–endo isomerism of a 1,3-diphenylbicyclobutane.[27] The rearrangement need not involve noninteracting phenyl-stabilized radicals, but rather the activation energy might be lowered by the phenyls coupling with each other through a long π bond.

At the level of calculation employed here, the *ab initio* method may be of use in elucidating the mechanisms of bicyclobutane rearrangements. In later papers in this series we shall apply the method to a number of strained systems, and, in particular, to the interesting propellane[28] series.

(27) R. B. Woodward and D. L. Dalrymple, *J. Amer. Chem. Soc.*, **91**, 4612 (1969).

(28) D. Ginsburg, *Accounts Chem. Res.*, **2**, 121 (1969).

Theoretical Studies of Tricyclo[1.1.1.0^{1,3}]pentane and Bicyclo[1.1.1]pentane[1a]

Marshall D. Newton*[1b] and Jerome M. Schulman[1c]

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Abstract: We have carried out *ab initio* molecular orbital studies on [1.1.1]propellane and the related system bicyclo[1.1.1]pentane. For the former in D_{3h} symmetry we calculate normal side bond lengths of 1.53 Å and a distance between bridgehead carbons of 1.60 Å. The analogous bridgehead–bridgehead distance in bicyclo[1.1.1]pentane is calculated to be 1.885 Å, in agreement with the X-ray value of its urethane derivative. The [1.1.1]propellane has a negative total overlap population between bridgehead carbons, and its charge density contours in that region resemble those of bicyclopentane. The localized orbital corresponding to the central bond has -0.002 overlap population between centers and is formed from sp^4 hybrids directed *away* from each other. Thus, no evidence for a central bond is found in terms of the charge distribution, although the bond length of 1.60 Å is significantly shorter than the corresponding nonbonded distance of 1.89 Å in bicyclo[1.1.1]pentane. Calculated triplet energies indicate that diradical states lie well above the closed-shell singlet ground state. The long-range spin–spin coupling constant between the two bridgehead protons in bicyclo[1.1.1]pentane, as calculated by the INDO finite perturbation method, is within a few hertz of the unusually large experimental value, 18 Hz (being somewhat dependent on the value chosen for interbridgehead distance), thus suggesting that the phenomenon can be accounted for adequately by the Fermi contact term. The *ab initio* equilibrium HCH angle for the methylene groups in bicyclopentane (111°) lies slightly outside the experimental uncertainty in the electron diffraction value (104 ± 5°), as is also the case for the interbridgehead distance.

The propellanes[2] of general structure I are a set of tricyclic hydrocarbons whose three rings are fused to a common carbon–carbon bond. These molecules,


I
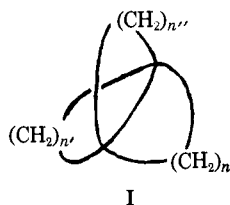
which may be regarded as hexasubstituted ethanes, are probably quite normal hydrocarbons for large $\{n\}$. However, as the three rings are reduced in size to the limiting case $n = n' = n'' = 1$ a number of intriguing, highly strained ring systems are evolved.[3]

Thus, tricyclo[1.1.1.0^{1,3}]pentane (II), known more simply as [1.1.1]propellane,[2] would, with the structural formula taken literally, contain four carbon–carbon bonds to the molecule side of a plane containing the bridgehead carbon. Similarly, [2.2.2]propellane (III)

II   III   IV
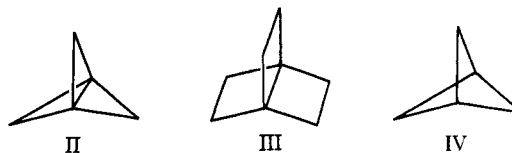
would be anticipated to contain three coplanar carbon–carbon bonds 120° apart (we eschew the term trigonal as it implies sp^2 hybridization) and a fourth axial bond.[4] Although neither of these molecules is known, several

(1) (a) An initial account of this work is given in the Abstracts of the XXIIIrd International Congress of Pure and Applied Chemistry, Boston, Mass., July 25–30, 1971; (b) Brookhaven National Laboratory; (c) Polytechnic Institute of Brooklyn; Alfred P. Sloan Fellow.
(2) D. Ginsburg, *Accounts Chem. Res.*, **2**, 121 (1969).

(3) A general survey of the propellanes has been made by W.-D. Stohrer and R. Hoffmann, *J. Amer. Chem. Soc.*, **94**, 778 (1972).
(4) J. Schulman and G. Fisanick, *J. Amer. Chem. Soc.*, **92**, 6653 (1970).

related propellanes have been obtained.[5] For example, [1.2.3]propellane and its related epoxide have been prepared[5a] and shown to be thermally stable (though reactive to acids and radicals). The preparation of [4.2.2]- and [3.2.2]propellane has also been reported.[5b] In addition, [2.2.1]propellane has been suggested as a reaction intermediate in the dicarbonylation of 1,4-dichloronorbornane with lithium and CO_2.[6] The propellanes may be regarded as dehydro derivatives of appropriate parent bicyclic hydrocarbons, e.g., bicyclo[1.1.1]pentane (IV) and bicyclo[2.2.2]octane for II and III, respectively, both known systems.

In this paper we consider the possible stability and electronic structure of [1.1.1]propellane and relate our findings to corresponding results for the parent system, bicyclo[1.1.1]pentane. The methods used are based on ab initio molecular orbital theory, using both minimal (MBMO) and extended (EBMO) basis sets.[7] The electronic structure is analyzed in terms of population analysis and localized molecular orbitals, from which hybrid atomic orbitals are derived. Various features of the potential energy surface are also investigated, including the equilibrium geometries of the singlet and triplet states for D_{3h} symmetry. The approach adopted here has been previously used successfully in calculating the molecular properties of the related system, bicyclobutane,[7] and the reader is referred to this work for details concerning the basis set and the method of implementation. In the bicyclobutane study,[7] advantageous use was also made of the semi-empirical INDO perturbation method[8] for calculating spin–spin coupling constants, and in the present work, we apply this method to the interesting problem posed by the existence of an unusually large long-range coupling constant (18 Hz) between the two bridgehead protons in bicyclo[1.1.1]pentane.[8b,9]

Energetics of the Ring Systems

The first question we attempted to answer concerned the possible thermal stability of II. An ab initio determination of the enthalpy of II requires first a knowledge of the equilibrium geometry, and we therefore undertook a limited search of the potential energy surface using the EBMO basis, which has yielded accurate geometries in simpler systems.[10] Since the large number of nuclear degrees of freedom precludes a complete analysis of the potential energy surface of this molecule, several of the geometrical parameters were frozen.

(5) (a) K. B. Wiberg, J. E. Hiatt, and G. Burgmaier, Tetrahedron Lett., 5855 (1968); K. B. Wiberg and G. J. Burgmaier, ibid., 317 (1969); (b) P. E. Eaton and K. Nyi, J. Amer. Chem. Soc., 93, 2778 (1971).

(6) C. F. Wilcox, Jr., and C. Leung, J. Org. Chem., 33, 577 (1968).

(7) M. D. Newton and J. M. Schulman, J. Amer. Chem. Soc., 94, 767 (1972).

(8) (a) J. A. Pople, J. W. McIver, and N. S. Ostlund, J. Chem. Phys., 49, 2965 (1968). (b) Although this method has been most extensively applied to directly bonded coupling constants, it also appears to give reliable account of some long-range H–H interactions, including several cases of protons separated by 4 bonds.[8c,d] The calculated constants (M. D. Newton, unpublished work) for the exo–exo, endo–endo, and exo–endo proton pairs in bicyclobutane are within 2 Hz of the experimental values given by K. Wüthrich, S. Meiboom, and L. C. Snyder, ibid., 52, 230 (1970). (c) G. E. Maciel, J. W. McIver, Jr., N. S. Ostlund, and J. A. Pople, J. Amer. Chem. Soc., 92, 4151, 4497, 4406 (1970). (d) For a detailed discussion of calculated $^4J_{HH}$ values, see M. Barfield, J. Amer. Chem. Soc., 93, 1066 (1971).

(9) (a) K. B. Wiberg and D. S. Connor, ibid., 88, 4437 (1966); (b) A. Padwa, E. Shefter, and E. Alexander, ibid., 90, 3717 (1968).

(10) W. J. Hehre, R. Ditchfield, L. Radom, and J. A. Pople, ibid., 92, 4796 (1970); R. Ditchfield, W. J. Hehre, and J. A. Pople, J. Chem. Phys., 54, 724 (1971).

Thus, the methylene CH bond lengths were fixed at their value in bicyclobutane,[11] geminal HCH angles were taken as 115°, the value in both bicyclobutane[11] and cyclopropane,[12] and D_{3h} symmetry was assumed. We then obtained the EBMO energies given in Table I

Table I. Total Molecular Energies (EBMO) for [1.1.1]Propellane and Bicyclo[1.1.1]pentane

Molecule	Inter-bridge-head distance, Å	Side-bond distance, Å	Total energy, au
[1.1.1]Propellane (II)	1.560	1.534	−192.3586
		1.554	−192.3547
	1.600	1.514	−192.3594
		1.534	−192.3601
		1.554	−192.3574
	1.640	1.534	−192.3595
	1.885[a]	1.534	−192.3197
Bicyclo[1.1.1]pentane (IV)[b]	1.845	1.545[c]	−193.6024
	1.885	1.545	−193.6061
	1.925	1.545	−193.6023
	2.005	1.545	−193.5887
	1.600[d]	1.545	−193.5344

[a] Equilibrium value for IV. [b] Experimental[13] side-bond lengths and CH bond lengths and angles were maintained. Subsequent optimization of the methylene HCH angles led to a value of α_{HCH} = 110.7° (cf. the experimental value of 103.9 ± 5°) and an energy of −193.6085 au. [c] Experimental value, ref 13. [d] Equilibrium value for II.

for several values of the central and side bond lengths, with the energy minimum found for a side bond of 1.53 Å and a central bond of 1.60 Å. The former value is 0.03 Å longer than the side bond in bicyclobutane[11] (1.497) and 0.01 Å larger than that in IV. The central bond at 1.60 Å is longer yet, but distinctly shorter than the 1.845-Å distance between nonbonded bridgehead carbons in IV obtained by electron diffraction[13] or the 1.89-Å X-ray diffraction value for the urethane derivative.[9b] We have, in fact, minimized the energy of IV with respect to interbridgehead distance, holding the side bonds at their experimental value, and obtained 1.885 Å.

The electron diffraction study of IV led to a value of 104 ± 5° for the methylene HCH angles. While most of our results are based on the 104° angle, subsequent calculations (EBMO) led to an equilibrium value of 110.5°, slightly outside the experimental uncertainty, but still appreciably smaller than the 115° HCH angles found in cyclopropane[12] and bicyclobutane.[11] Previous studies[10] with the extended basis set employed here have yielded HCH angles accurate to within 1°. The calculated HCH angle for IV suggests that the optimal HCH angle for the propellane might be somewhat smaller than the assumed value (115°); however, the propellane framework geometry would not be critically dependent on the choice of this angle.

Table I also indicates that II is distinctly averse to existing with the interbridgehead distance optimal for

(11) K. W. Cox, M. D. Harmony, G. Nelson, and K. B. Wiberg, ibid., 50, 1976 (1969).

(12) O. Bastiansen, F. N. Fritsch, and K. Hedberg, Acta Crystallogr., 17, 538 (1964).

(13) J. F. Chiang and S. H. Bauer, J. Amer. Chem. Soc., 92, 1614 (1970).

Table II. Total Overlap Populations and Atomic Charges (EBMO Basis) of [1.1.1]Propellane and Bicyclo[1.1.1]pentane at Equilibrium Geometries[a]

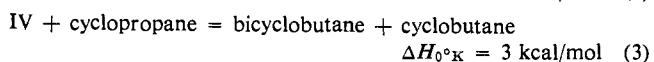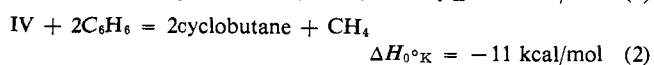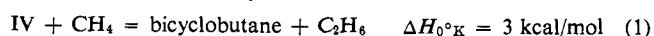|	[1.1.1]Propellane				Bicyclo[1.1.1]pentane		
Atoms[b]	Overlap population	Atom	Charge	Atoms[b]	Overlap population	Atom	Charge
C_1-C_2	+0.346	C_2, C_4, C_5	-0.332	C_1-C_2	0.494	C_2, C_4, C_5	-0.192
C_1-C_3	-0.252	C_1, C_3	-0.083	C_1-C_3	-0.908	C_1, C_3	-0.331
C_2-H	0.756	H	0.193	C_2-H	0.784	H (meth)	0.151
C_2-C_4	-0.285			C_1-H	0.781	H (brhd)	0.159
				C_2-C_4	-0.514		

[a] Note that the populations analysis given here is for the EBMO wave functions, while that given in ref 7 was for the minimal basis wave functions (MBMO). In spite of some differences in magnitude (*e.g.*, overlap populations for CC bonds), relative trends are generally similar for both basis sets. [b] Bridgehead carbon atoms are labeled 1 and 3; methylene carbon atoms, 2, 4, and 5.

IV, the energy increasing by $\sim$1 eV for preference for a central bond 0.2 Å longer than that in [1.1.1]propellane.

The exploration of D_{3h} geometries just described refers to closed-shell singlet states. Because of the unusual nature of the bridgehead bonding in II, including our finding of a rather long central bond (1.60 Å), we must, however, consider the possibility of a diradical ground state. In searching for such a diradical state, we calculate the lowest *triplet* state energy (since single configuration triplet states are more readily calculated than their double configuration singlet counterparts), and assume that this is close to the energy of the corresponding *singlet* diradical state.[7] The triplet state at the optimal D_{3h} singlet geometry (A_2'' symmetry, antisymmetric with respect to the σ_h plane) lies 3.1 eV above the singlet. Optimization within the D_{3h} framework leads to a significant lengthening of the interbridgehead distance (1.80 Å), but the optimal triplet energy is still 2.2 eV above the best singlet energy, indicating that the D_{3h} ground state is not a diradical.

Some preliminary studies of departures from D_{3h} geometry have also been carried out. For example, the triplet diradical II corresponding to homolytic cleavage of a single side bond (effected by bending a CH_2-C bond outward so as to form an angle of 110° with the interbridgehead vector) is found to lie 1.3 eV above the closed shell singlet. We have not, however, pursued possible concerted pathways for rearrangement such as that leading to dimethylenecyclopropane, which, with a calculated ΔH_f of 68 kcal/mol,[14] we would estimate to be some 31 kcal/mol more stable than II, as discussed below.

From calculated total molecular energies, it is possible to estimate the heats of formation and hence strain energies of [1.1.1]propellane and bicyclo[1.1.1]pentane, by employing suitable reactions in which the enthalpies of all species are known, except those of the molecules in question.[7] The total energies for II and IV correspond to the calculated (EBMO) equilibrium geometries. Zero-point corrections are omitted due to lack of experimental data, but their contribution to the reaction enthalpies considered below is expected to be <5 kcal. For bicyclo[1.1.1]pentane, three different hypothetical reactions (1–3) all yield similar values for the heat

IV + CH_4 = bicyclobutane + C_2H_6 $\Delta H_{0°K}$ = 3 kcal/mol   (1)

IV + $2C_6H_6$ = 2cyclobutane + CH_4

$\Delta H_{0°K}$ = -11 kcal/mol   (2)

IV + cyclopropane = bicyclobutane + cyclobutane

$\Delta H_{0°K}$ = 3 kcal/mol   (3)

of formation (based on the EBMO reaction enthalpy, and the experimental enthalpies[15] of all molecules other than IV); *i.e.*, 53, 53, and 49 kcal/mol, respectively. (At 25°, these values would be $\sim$6 kcal/mol lower.) A significantly larger value for the heat of formation, 73 kcal/mol, has been calculated by Allinger and coworkers using force-field methods,[16] whereas a previous semiempirical MO calculation led to a value similar to ours, 50 kcal/mol.[17] To evaluate the strain energy we employed Franklin's tables,[18] finding for the heat of formation of an unstrained C_5H_8 analog, -11 kcal/mol. Thus the strain energy of IV is estimated to be 60–64 kcal/mol, according to our calculations.

For [1.1.1]propellane we may compute a heat of formation through the hypothetical reaction II + cyclopropane = 2bicyclobutane; $\Delta H_{0°K}$ = -7.2 kcal/mol. From the known heats of formation of cyclopropane and bicyclobutane[15b] we then obtain $\Delta H_{f,0°K}$ = 102.4 kcal/mol. The energy of an unstrained C_5H_6 analog is either -2.5 or -7.5 kcal/mol, depending on whether or not the correction for adjacent quaternary carbons is included.[17] Thus, the strain energy of [1.1.1]-propellane is 105–110 kcal/mol. A possible rationale for this value is the following. The 13-kcal/mol difference in strain energy between bicyclobutane (63 kcal/mol) and two cyclopropanes (50 kcal/mol)[15] represents the nonadditive strain energy of bicyclobutane, and since this effect occurs three times in [1.1.1]propellane, its total strain energy should then be 3 × (25 + 13) = 114 kcal/mol. (The existence of a nonadditive effect of three fused rings might lead to a slightly greater strain energy.)

The Electronic Structures of [1.1.1]Propellane and Bicyclo[1.1.1]pentane

Assuming for the present the possible stability or metastability of [1.1.1]propellane in the geometry found in the previous section, we may proceed to investigate its electronic structure, making comparisons with the related cyclic molecules, bicyclobutane and IV. As discussed above, our calculations indicate that the ground state of II is a closed-shell singlet, and diradical states are expected to lie at significantly higher energies,

(14) N. C. Baird and M. J. S. Dewar, *J. Chem. Phys.*, **50**, 1262 (1968).

(15) (a) A cyclobutane total energy of -155.8554 au was obtained using geometries given by A. Almenningen, O. Bastiansen, and P. N. Skancke, *Acta Chem. Scand.*, **15**, 711 (1961), and J. Meiboom and L. C. Snyder, *J. Chem. Phys.*, **52**, 3857 (1970). For other total energies, see ref 7 and 10. (b) The experimental values (0°K) were determined as described in footnotes 18 and 19 of ref 7.

(16) N. L. Allinger, Jr., M. T. Tribble, M. A. Miller, and D.H. Wertz, *J. Amer. Chem. Soc.*, **93**, 1637 (1971).

(17) N. C. Baird, *Tetrahedron*, **26**, 2185 (1970).

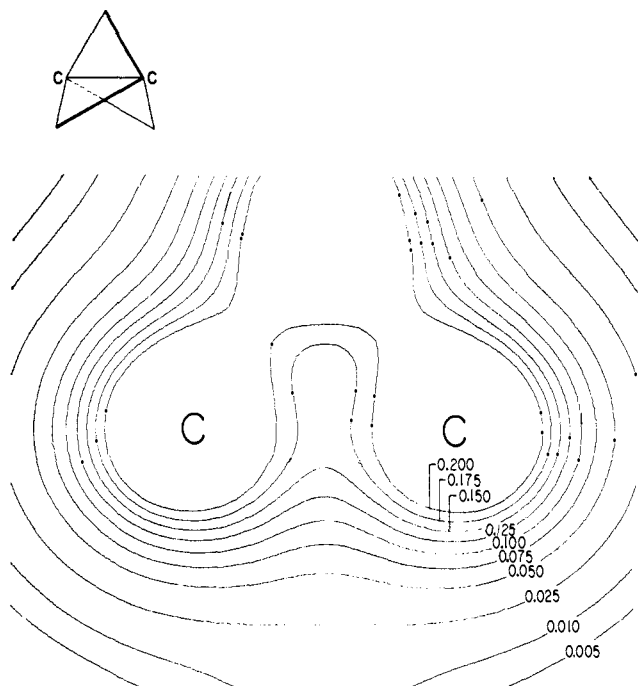(18) J. L. Franklin, *Ind. Eng. Chem.*, **41**, 1070 (1959).

Figure 1. Total electron density (atomic units) of [1.1.1]propellane. Contour values are the same for all three figures.
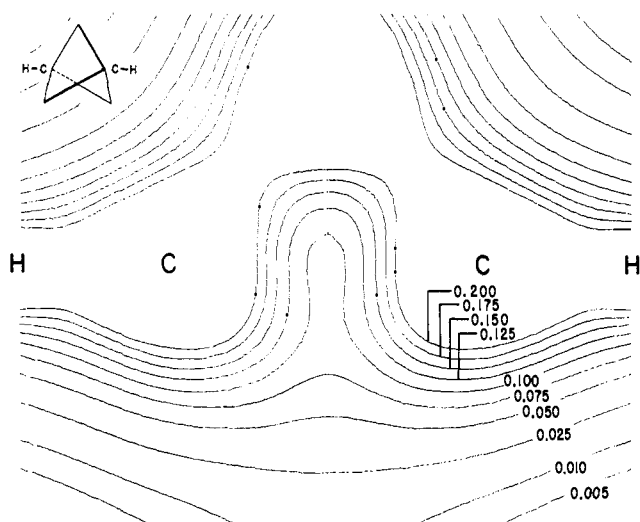

Figure 2. Total electron density (atomic units) of bicyclo[1.1.1]-pentane.

although the molecule might be extremely reactive toward other radicals, as is [1.2.3]propellane.[5a]

The highest occupied molecular orbital in II is symmetric with respect to reflection in the σ_h plane and the lowest unoccupied orbital is antisymmetric. Their orbital energies are -0.349 and $+0.159$ au, respectively, and are not especially different from their bicyclobutane counterparts,[7] -0.347 and $+0.264$. However, the fact that the highest occupied orbital is symmetric does not prove the presence of a bond between the bridgehead carbons, as one might ordinarily assume, and in fact, the nature of the interaction between the two bridgehead carbon atoms is the most interesting issue in the present study. In Table II are given the total overlap populations and atomic charges of II and IV in the EBMO basis. (Qualitatively simi-
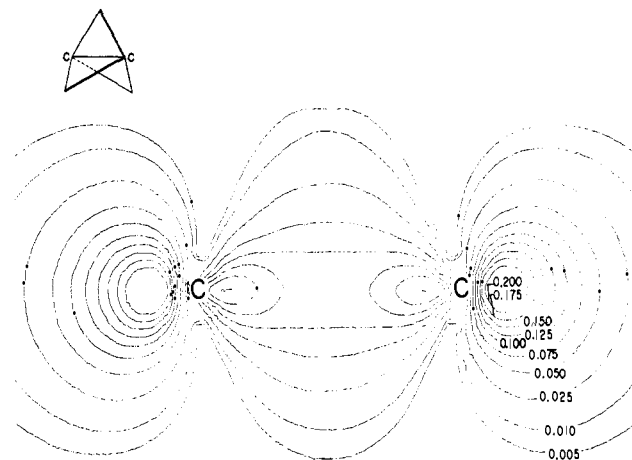

Figure 3. Electron density (atomic units) from double occupancy of localized MO associated with the bridgehead carbon atoms of [1.1.1]propellane.

lar results would be obtained from the population analysis of the MBMO wave function.[19]) Most striking is the *negative* overlap population in II between the bridgeheads, -0.25. This value contrasts with the corresponding *positive* quantity in bicyclobutane, $+0.13$ (EBMO basis), and is, in fact, quite similar to the population (-0.28) associated with the "nonbonded" interactions between each pair of methylene carbon atoms in II. The negative bridgehead–bridgehead population for II is, however, considerably smaller in magnitude than the corresponding quantity in IV, -0.91.

From the preceding discussion we may conclude that the interaction between the bridgehead carbon atoms in II corresponds to weak bonding at best, though we bear in mind that overlap populations are only a qualitative guide to bond strength.[19] Insight into the bonding in II is given by direct examination of the electron density. Figures 1 and 2 give the total charge densities of [1.1.1]propellane and bicyclo[1.1.1]pentane in a plane containing the bridgeheads and a methylene carbon. The similarity between the two sets of contours is striking. Further information on the nature of the central bond in II can be obtained by localizing the MBMO orbitals according to the Edmiston–Ruedenberg procedure.[20,21] The hybridizations obtained (Table III) show that the central "bond" is formed from $sp^{4.1}$ hybrids of the form $\phi = 0.44(2s)_C + 089(2p_z)_C$, with z the threefold molecular axis, and relative signs causing the two bridgehead hybrids to point away from each other. The total CC overlap population for the localized molecular orbital formed from these hybrids is -0.002. A charge density plot for this molecular orbital is given in Figure 3, and the deficiency of density between

(19) The magnitude of overlap populations may be rather dependent on the particular basis set chosen, and probably should not be used to estimate bond strengths in any absolute sense. In this discussion we are mainly interested in comparisons between different CC interactions in a given molecule, and in particular, to see how these change with variations in interbridgehead distance. For this limited purpose, we feel that overlap populations in any reasonable basis set provide useful measures of bonding.

(20) C. Edmiston and K. Ruedenberg, *J. Chem. Phys.*, 43, S97 (1965).

(21) Similar localization results would be expected from the extended (EBMO) basis wave functions. However, we have limited ourselves to MBMO localizations because of the considerably longer time needed to transform from atomic to molecular integrals, in the case of the EBMO basis.

Table III. Localized Molecular Orbitals (LMO's) for
[1.1.1]Propellane and Bicyclo[1.1.1]pentane
(Generated from the MBMO Orbitals)

Molecule	Bond	Hybridization
[1.1.1]Propellane[a]	C_1–C_2 (side)	$sp^{1.33}$, $sp^{4.31}$
	C_1–C_3 (central)[b]	$sp^{4.13}$
	C_2H_1	$sp^{2.66}$
Bicyclo[1.1.1]pentane	C_1–C_2	$sp^{3.46}$, $sp^{3.64}$
	C_1H	$sp^{2.22}$
	C_2H	$sp^{2.62}$

[a] INDO molecular orbitals for this molecule localize to two different sets of three equivalent CC LMO's (rather than one set of six) for the side bonds. [b] The overlap population in this LMO is −0.002, and the two hybrids are directed *away* from each other.

bridgehead carbons relative to that in the external lobe region is again clearly apparent.

The side bonds in II are also somewhat unusual, as they involve $sp^{1.4}$ bridgehead hybrids (42% s character), in contrast to the $sp^{2.97}$ bridgehead side-bond hybrids of bicyclobutane (25% s character).[7] In addition, the bridgehead side-bond hybrids in II are directed at an angle of 33° with respect to the side-bond vector, and 88° with respect to the external z axis. Thus, in contrast with the nominal structure implied by II, which places four bridgehead bonds in one hemisphere, the hybridization analysis suggests three roughly coplanar $sp^{1.4}$ hybrids and a fourth perpendicular sp^4 orbital directed outward from the molecule. In short, the population analysis, the electron density, and the hybrid orbitals all suggest a lack of significant bonding between the bridgehead carbons in II.

The reader is reminded that the localization procedure employed leads to hybrid orbitals which are *not* constrained to be orthonormal. While interhybrid overlap integrals on a given atom are generally found to be small ($\lesssim 0.1$), we note that the $sp^{4.1}$ and $sp^{1.4}$ bridgehead hybrids of II discussed above have a larger overlap, 0.31.

Localization of the MBMO wave function of IV (based on the equilibrium geometry obtained from the more accurate EBMO calculation) leads to bridgehead CH bonds formed from $sp^{2.2}$ hybrids, and carbon–carbon side bonds containing $sp^{3.46}$ and $sp^{3.64}$ hybrids for the bridgehead and methylene carbons, respectively. Both of the hybrids are bent outward from the bond vector by $\sim 15°$. The hybrids for the methylene CH bonds, $sp^{2.7}$, are of interest, since they contain appreciably more p character than methylene CH hybrids for other ring systems.[7] This result is not surprising in view of the unusually small HCH angles (104°) obtained in the electron diffraction study,[13] and used in obtaining the localized orbitals. In actual fact, the methylene CH hybrids are bent outward from their respective bond vectors by 5.5°, so that geminal hybrid pairs form angles of 115°, intermediate between idealized sp^3 and sp^2 hybrid angles. This deviation of hybrids from interatomic directions is larger than is usually observed[7] for CH bonds ($\lesssim 1°$), and is probably related in part to the fact that the HCH angle employed in the localization calculations (*i.e.*, the electron diffraction value,[13] 104°) was subsequently found to be 7° smaller than the *calculated* equilibrium value (110.7°), as noted above.

As a final aspect of electronic structure, we turn to the spin–spin coupling constants of bicyclo[1.1.1]pen-

tane. The unusually large long-range coupling constant between the two bridgehead protons, 18 Hz, has been discussed previously.[9] Since the INDO finite perturbation method was successful in correlating directly bonded CH and CC coupling constants in cyclopropane and bicyclobutane,[7,8] we thought it worthwhile to apply the same method to IV. The results obtained were found to be rather sensitive to the nonbonded distance assumed between the bridgehead carbon atoms, keeping the side bonds fixed at the experimental value, 1.545 Å. Thus, at the electron diffraction distance of 1.845 Å, the calculated long-range $^4J_{HH}$ value is 26.9 Hz, and it decreases monotonically with distance as the bridgehead–bridgehead distance is increased. At our calculated (EBMO) equilibrium distance, 1.89 Å, a value of 23.5 Hz is obtained. These values demonstrate that the Fermi contact term can account for the large magnitude of the long-range constant, and the sensitivity to the interbridgehead distance suggests that direct interaction between the bridgehead atoms is an important factor in the observed coupling.

The experimentally known values for the directly bonded ^{13}CH coupling constants provide a test of the linear relationship between J_{CH} value and s character presented in our bicyclobutane study:[7] $J_{^{13}C-H}/f = 522 \pm 23$ Hz, where f is the fraction of s character for hybrids obtained from *ab initio* (MBMO) localized CH orbitals. Using the hybridization presented above, we estimate $J_{^{13}C-H}$ values of 140 ± 6 (CH$_2$) and 162 ± 7 (CH) Hz, in good agreement with the experimental[9] values 144 and 164 Hz, respectively. INDO finite perturbation theory, using the EBMO calculated bridgehead–bridgehead distance (1.89 Å) and the experimental HCH angle (104°), reproduces the correct relative order, but underestimates the magnitudes, with values of 128 (CH$_2$) and 139 (CH) Hz. It should be noted, however, that the calculated bridgehead CH coupling is rather sensitive to interbridgehead distance (increasing with distance), while the methylene CH coupling is somewhat sensitive to HCH angle (*e.g.*, with the calculated angle of 111°, a coupling constant of 134 Hz is found).

Discussion

The most intriguing aspect of the molecule [1.1.1]propellane is the anomalous nature of the interaction between its bridgehead carbon atoms. On the one hand, the existence of an equilibrium interbridgehead bond length only 0.06 Å longer than normal C–C bonds, the clear preference for a closed-shell singlet ground state, as opposed to possible diradical states, and the existence of a totally symmetric highest filled molecular orbital, all suggest the existence of a central bond. On the other hand, the similarities of the total charge density around the bridgehead carbon atoms in II and IV, the fact that the hybrids in the localized orbital associated with the bridgehead carbon atoms are directed away from each other, and the existence of a *negative* total overlap population between the two bridgeheads, all tend to indicate a nonbonding, or possibly, antibonding interaction.

If, indeed, there is no appreciable bonding between the bridgehead carbon atoms in II, the question arises as to why these atoms prefer to be separated by only 1.60 Å, fully 0.2 Å less than the corresponding distance in IV, supposedly the shortest nonbonded CC distance

on record.[18] The principal reason is that IV contains one more occupied antisymmetric MO (a_2'' symmetry). The extra a_2'' MO in IV, qualitatively identifiable as the antisymmetric combination of two bridgehead CH-bond orbitals, introduces a strong degree of repulsion between the bridgehead carbon atoms; i.e., the contribution to the overlap population between the bridgehead carbon atoms from this a_2'' MO is −0.94, essentially the same as the *total* population between these two atoms, −0.91. The absence of such a strongly antibonding MO in [1.1.1]propellane (the highest filled-MO of II correlates with the *symmetric* combination of CH bonds in IV) makes it energetically favorable for the interbridgehead distance to contract (relative to that in IV), with consequent relief of methylene–methylene repulsions. Thus, in proceeding from an interbridgehead distance of 1.89 Å to the equilibrium value for II, the small *increase* in bridgehead repulsion (the overlap population goes from −0.14 to −0.25) is more than offset by the *reduction* in total methylene–methylene repulsions (the total intermethylene overlap population changes from −1.66 to −0.86). The slight *increase* in bridgehead repulsion attending contraction underscores the fact that contraction *per se* is not evidence of direct bridgehead–bridgehead bonding.

The importance of nonbonded interactions in strained systems brings into question the reliability of maximum-overlap methods for such molecules,[22] since the maximum overlap approach generally includes only the overlaps between bonded atoms. Overlap populations do, in fact, provide a means for treating bonded and nonbonded interactions on a formally equivalent basis, and their significance as bonding criteria is undoubtedly worthy of further investigation. The previously noted[7] difference in hybrid atomic orbitals derived from the maximum overlap method and from localized SCF molecular orbitals may be partially due to omission of nonbonded repulsions in the former method.

(22) *E.g.*, Z. Maksić, L. Klasinc, and M. Randić, *Theoret. Chim. Acta*, **4**, 273 (1966).

The large calculated strain energy (110 kcal/mol) of [1.1.1]propellane deserves comment, since it is somewhat larger than the bond energy of a typical carbon–carbon bond (∼80 kcal/mol). A useful comparison of molecular strain energies is provided by the per-bond strain energy, which we obtain by dividing the total strain energy by the number of CC bonds. These values for several strained molecules are given in Table IV. On this basis, II lies between bicyclobutane

Table IV. Strain Energies of Some Hydrocarbons

Molecule	Strain energy, kcal/mol	No. of framework bonds	Strain energy/bond
Cyclopropane	25[a]	3	8
Bicyclo[1.1.1]pentane	60–64	6	10–11
Bicyclobutane	63[a]	5	13
Cubane	125[b]	12	10
[1.1.1]Propellane	105 (110)[c]	7 (6)[c]	15 (18)[c]
Tetrahedrane	137[b]	6	23

[a] Reference 7. [b] Cited by W. J. S. Dewar in "The Molecular Orbital Theory of Organic Chemistry," McGraw-Hill, New York, N. Y., 1969. [c] Entries in parentheses are based on assumption of six formal CC bonds.

and the unknown molecule tetrahedrane in strain energy, thus reemphasizing that its stability is problematical.

In future papers of this series, similar techniques, both in the *ab initio* and semiempirical framework, will be applied to other members of the propellane series.