Tetrahedron Vol 33, pp 1897 to 1903 Pergamon Press 1977 Printed in Great Britain

HYBRIDIZATION IN PROPELLANES

MONTY L. HERR†
Departments of Chemistry of The University of Malaya, Kuala Lumpur, Malaysia
and
The University of New Orleans, LA 70122, USA

(*Received in USA 11 December 1976; Received in UK for publication 26 January 1977*)

Abstract—Using the Maximum Overlap Approximation, the hybridization of a series of small ring propellanes is studied in order to arrive at a measure of the strain in these compounds

Propellanes are tricyclic hydrocarbons in which the three rings are fused together at a common carbon–carbon bond (called the conjoining bond) as shown schematically in Fig. 1. They could be considered as hexa-substituted ethanes and, when *l*, *m* and *n* are large, their chemistry is quite predictable on this basis.[1] When these numbers become smaller however, the molecules become increasingly strained and decreasingly stable. This is the situation that generated our interest in doing this study.

The compound [1.1.1] propellane, shown in Fig. 2a, will be used to point out one of the intriguing aspects of these molecules. If a plane is passed through one of the bridgehead carbons perpendicular to the conjoining bond, then all of the atoms bonded to that carbon will be seen to lie on one side of that plane. This is shown in Fig. 2, where it is contrasted with the case of methane where it is impossible to draw a plane through the carbon without having at least one hydrogen on either side.

This propellane is, of course, the most extreme case. However, the situation where all four bonded atoms are forced to lie within a single hemisphere has been experimentally shown to occur in the real world of known compounds. The crystal structure of 8,8-dichloro [3.2.1] propellane has been determined and this unique arrangement of atoms around the bridgehead carbon does, in fact, exist.[2]

Among the possible propellanes consisting of 5-, 4- and 3-membered rings, syntheses of [3.3.3]-,[3] [3.3.2]-,[4] [3.3.1]-,[5] [3.2.2]-[6] and [3.2.1]-[2,7] propellanes have been reported. Several attempts at the synthesis of [2.2.2] propellane[4a,8] have been published. A heterocyclic [2.2.1] propellane has been synthesized where the heteroatom is platinum.[9]

An intuitive understanding of angle strain would indicate, as we have already stated that as the sum $l + m + n$ from [*l.m.n*] prepellane became smaller, the propellane would become decreasingly stable.[10] Thus, for example, [3.3.2] propellane remained unchanged after being treated with trifluoroacetic acid at 100°C for 12 h or with bromine in carbon tetrachloride in the dark at room temperature.[4a] [3.3.1] Propellane was reported to be insensitive to oxygen and unchanged after heating at 180°C for 22 h or after 6 h of treatment with 40 p.s.i. of H_2 in ethanol with a palladium/carbon catalyst. However, it was reactive to bromine/dichloromethane and reacted with acetic acid at 100°C.[5a] [3.2.1] Propellane is thermally stable, having a half-life of 20 h at 195°C in diphenyl ether solution. It reacts readily with O_2 and acetic acid at room temperature, and reacts instantaneously with bromine/dichloromethane at 50°C.[7a] An amide derivative of [2.2.2] propellane manifested its thermal instability with a half-life of about 28 min at 25° and it reacted "very rapidly" with chlorine.[8b]

Hybridization, Overlap, and the Maximum Overlap Approximation

Our purpose in doing this study was to seek a measure of the strain in these compounds by determining the most favorable hybridization. Our method was the maximum overlap approximation. But, let us first try to get an intuitive picture of the orbital hybridization in these compounds.

When *l*, *m* and *n* are large, we would expect that the hybridization of the bridgehead carbons would be approximately sp^3. As *l*, *m* and *n* become smaller, the angle between the bonds from the bridgehead carbon to the other bridgehead carbon and to the neighbouring methylene groups must become smaller. However, the angles between these hybrid orbitals can become no smaller than 90° based on hybridization of s and p atomic orbitals.‡ Thus, at the extreme cases of the smallest rings, we would anticipate that the orbitals forming the conjoining bond would be pure p atomic orbitals (i.e. sp^∞ hybrid orbitals), and that sp^2 hybrids would go into bent bonds directed toward the neighbouring methylene groups.

The maximum overlap criterion[11] is based upon the supposition that the greater the overlap is between two atoms, the stronger the bond joining them; the stronger the bonds in a molecule are, the more stable it will be. The maximum overlap method, based on this criterion, has been developed and systematically applied to a broad range of hydrocarbon compounds by Randić and his collaborators. This work has recently been reviewed and evaluated in detail and references to their earlier work may be found therein.[12]

In this method,[12] a geometry is assumed for the molecule in question. For the individual bonds in the molecule, the component atomic orbital overlap integrals, $\langle s|s\rangle$, $\langle s|p\rangle$, $\langle p|p\rangle_\sigma$ and $\langle p|p\rangle_\pi$, are determined and given as data. Then hybrid orbitals are interatively generated by mixing these atomic orbitals in order to maximize the total overlap, S of the molecule. Those hybrids, $\Psi_{..}$, that yield a maximum S are optimal.

---

†Present address, Department of Chemistry, Xavier University, New Orleans, LA 70125, U.S.A.

‡This is assuming real coefficients.

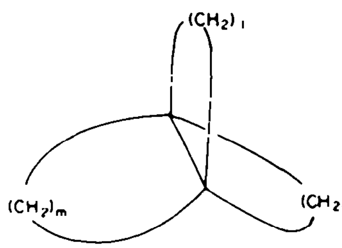


Fig. 1. The propellane structure.

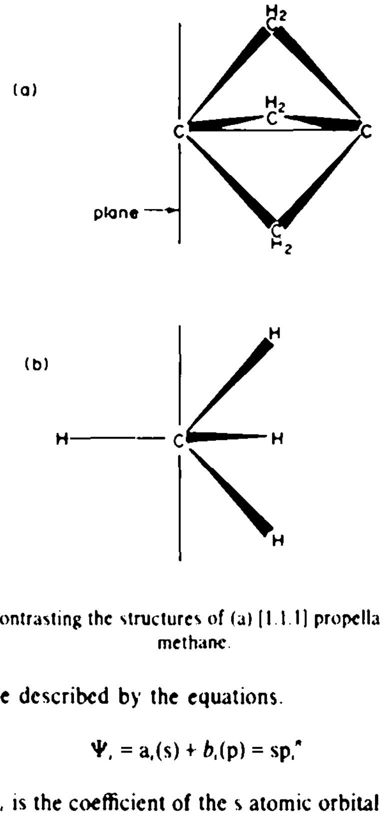


Fig. 2. Contrasting the structures of (a) [1.1.1] propellane and (b) methane.

They are described by the equations.

$$\Psi_i = a_i(s) + b_i(p) = sp_i^n$$

where a_i is the coefficient of the s atomic orbital and b_i is the coefficient of the p atomic orbitals. Ther term sp^n is the common designation for hybrid orbitals. The exponent, n is given by

$$n = \frac{b^2}{a^2}.$$

These coefficients are orthonormal, i.e.

$$a_i a_j + b_i b_j \cos \theta_{ij} = \delta_{ij}.$$

where θ_{ij} is the angle between the hybrids Ψ_i and Ψ_j and δ_{ij} is the Kronecker delta.

The bond lengths and bond angles adopted for all the compounds in this study are given in Table 1. The propellanes presented in this work are made up of all possible combinations of 3-, 4- and 5-membered rings. The structures of these rings are summarized in the structure of the [3.2.1] propellane shown in Table 1. The carbon-carbon bond distances and the bond angles given are taken from the X-ray structure of 8,8-dichloro [3,2,1] propellane published by Wiberg *et al.*[2] The given lengths for carbon-hydrogen bonds *e* and *h* are averages of the two C_5–H and the two C_6–H bond lengths, respectively, found by Wiberg. Specifically, Wiberg reported C_5–H bond lengths of 0.72 Å and 1.01 Å and C_6–H bond lengths of 0.96 Å and 0.93 Å.

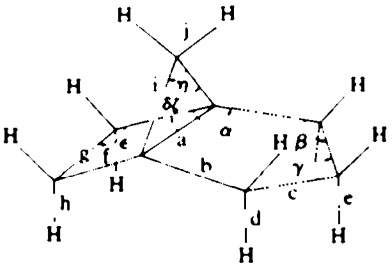
Since there were no C_3–H bonds in Wiberg's compound, it was necessary to estimate this bond length. The following stratagem was used. In cyclobutane, the experimental C–H bond length is 1.092 Å. In Wiberg's structure, however, the C–H bonds in the 4-membered ring have contracted by 0.147 Å to 0.945 Å. This same contraction was assumed to occur when free cyclopropane with C–H bond lengths 1.089 Å is incorporated into small-ring propellane. The resultant C–H bond lengths for our 3-membered rings is thus the difference, 0.94 Å.

All of the molecules in this study were assumed to have a plane of symmetry bisecting the conjoining bond between the bridgehead carbon atoms. The hybrids for the conjoining bond were assumed to be colinear with that bond. For methylene groups, the deviations from colinearity were assumed to be equal for both bonds to carbons, even if not required by symmetry. For C–H bonds, the hybrids and bonds were assumed to be colinear.

The atomic orbital overlaps were based on Slater-type atomic orbitals of the double-zeta type taken from Clementi's tables.[11] The carbon–carbon overlaps were interpolated from tables published by Randić *et al.*[14] The carbon–hydrogen overlaps were calculated using a program supplied by P. O'D. Offenhartz[15] adapted for use on an IBM 1130 by the author and modified by R. Fereday. The hydrogen 1s atomic orbital with exponent 1.0 was used.

Other theoretical work. Newton and Schulman[16] performed minimum basis set *ab initio* molecular orbital calculations on [1.1.1] propellane. Like us, they assumed a D_{3h} geometry. Their bond lengths were: C–H, 1.093 Å; C_1–C_2, 1.534 Å; C_1–C_3, 1.600 Å. The H–C–H bond angles were assumed to be 115°. The resulting molecular orbitals were then localized using the Edmiston–Ruedenberg procedure.[17] The following hybrid orbitals were obtained:

Table 1 Geometries



*Bond	Length A	Angle	Degrees
a	1.572	α	108.2
b	1.483	β	106.4
c	1.529	γ	109.7
d	0.89	δ	88.9
e	0.865	ε	91.1
f	1.526	ζ	57.4
g	1.512	η	65.3
h	0.945		
i	1.458		
j	0.94		

Hybrid orbital	Hybridization
Ψ_{12}	$sp^{1.33}$
Ψ_{21}	$sp^{4.11}$
Ψ_{11}	$sp^{4.13}$
Ψ_{2H}	$sp^{2.44}$

Several comments are appropriate. First, it is intereating to note that their Ψ_{11} hybrids point away from the bonded atoms, i.e. bonding takes place through the small lobes of these hybrids. The bond overlap is very small. Newton and Schulman calculated a CC overlap population of −0.002. Using their basis set[18] and the hybrid exponent 4.13, we calculated a hybrid orbital overlap of 0.190 between the two bridgehead carbons.

They also note that their localization procedure does not require the resulting hybrid orbitals to be orthogonal. Indeed, they reported that the hybrid orbital for the bond between the bridgehead carbons and the hybrid orbital directed toward a methylene group has an overlap of 0.31, rather than zero.

Finally, Newton and Schulman reported that the same localization procedure, when applied to the molecular orbitals obtained from an INDO method calculation, failed to produce equivalent hybridized orbitals for the bonds going from the bridgehead carbons to the methylene carbons.

Newton and Schulman also published a communication on the electronic structure of [2.2.2] propellane.[19] Their geometry had a C_1–C_4 interatomic distance of 1.52 Å, distances C_1–C_2 and C_2–C_3 of 1.57 Å, C–H distances of 1.10 Å, and an H–C–H angle of 114° and D_{3h} symmetry. Localization of their INDO molecular orbitals led to an sp^9 hybrid orbital for the C_1–C_4 bond.

Randić, himself, has published MOA results on [2.2.2] propellane.[12b] Based on C–C bond lengths of 1.54 Å and C–H bond lengths of 1.102 Å, he arrived at the following results.

Hybrid	Exponent	Overlap
Ψ_{12}	2.57	$S_{12} = 0.6443$
Ψ_{21}	3.52	
Ψ_{23}	3.06	$S_{23} = 0.6494$
Ψ_{14}	5.30	S_{14} 0.5915
Ψ_{2H}	2.76	$S_{2H} = 0.7228$
$\delta_{12} - 0.2746$		δ_{21} 0.1440

In their report of the crystal structure of 8,8-dichloro [3.2.1] propellane, Wiberg *et al.*[2] included calculations of hybrids. In this instance, molecular orbitals, obtained from a CNDO/2 calculation using the experimental geometry, were localized, again using the Edmiston–Reudenberg technique. The resulting hybrid orbitals, presumable nonorthogonal, follow:

Orbital	Hybrid value
Ψ_{12}	$sp^{1.73}$
Ψ_{15}	$sp^{3.64}$
Ψ_{17}	$sp^{2.28}$
Ψ_{18}	$sp^{3.36}$
Ψ_{21}	$sp^{2.81}$
Ψ_{81}	$sp^{2.71}$

For sake of completeness, it should be noted that Stohrer and Hoffmann[20] have published other calculations on [3.2.1], [2.2.2], [2.2.1], [2.1.1] and [1.1.1] propellanes and that Dannenberg and Prociv[21] have published INDO studies on [2.2.2] propellane.

Schleyer and coworkers[21b] have published force field calculations on [3.3.3]-propellane that indicate that it is quite stable.

RESULTS

Our maximum overlap calculations were performed on an IBM 1130 computer at the University of Malaya for each of the propellanes discussed in this paper. Some of these calculations were rerun on a DEC-10 System computer at the University of New Orleans. The DEC-10 results of [3.2.2]- and [3.3.2] propellane are used in this paper. Overlap calculations done while reviewing Newton and Schulman's results were also performed on the DEC-10.

Programs were individually written for each of the molecules studied. These programs were based on sample programs (kindly supplied by Prof. Randić) for other types of molecules.

Our results are given in Tables 2–11. In these tables, each molecule is designated by the first part of the [*l.m.n*]

Table 2. [1.1.1]

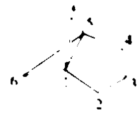
Hybrids		Overlaps
$\Psi_{12} - 0.5709\,(s) + 0.8210\,(p)$	$sp^{2.07}$	$S_{12} = 0.625$
$\Psi_{11} = 0.1493\,(s) + 0.9888\,(p)$	$sp^{43.86}$	$S_{11} \cdot 0.400$
$\Psi_{21} - 0.4477\,(s) + 0.8942\,(p)$	$sp^{3.99}$	
$\Psi_{2H} - 0.5473\,(s) + 0.8369\,(p)$	$sp^{2.34}$	$S_{2H} \cdot 0.790$
Interhybrid angles (degrees)		Deviation angles (degrees)
θ_1^{23} 96.0		δ_{12} 38.6
$\theta_2^{13} = 104.5$		$\delta_{21} = 19.6$
$\theta_2^{HH} - 115.3$		

Table 3. [2.1.1]

Hybrids		Overlaps
$\Psi_{12} - 0.5653\,(s) + 0.8249\,(p)$	$sp^{2.13}$	$S_{12} = 0.657$
$\Psi_{14} - 0.2352\,(s) + 0.9719\,(p)$	$sp^{17.08}$	S_{14} 0.468
$\Psi_{15} = 0.5591\,(s) + 0.8291\,(p)$	$sp^{2.20}$	$S_{15} = 0.611$
$\Psi_{21} \cdot 0.4537\,(s) + 0.8911\,(p)$	$sp^{3.86}$	
Ψ_{23} 0.4625 (s) + 0.8866 (p)	$sp^{3.68}$	$S_{23} - 0.637$
$\Psi_{2H} = 0.5386\,(s) + 0.8425\,(p)$	$sp^{2.45}$	$S_{2H} = 0.785$
$\Psi_{51} = 0.4469\,(s) + 0.8946\,(p)$	$sp^{4.01}$	
$\Psi_{5H} = 0.5480\,(s) + 0.8365\,(p)$	$sp^{2.33}$	$S_{5H} - 0.790$

Interhybrid angles (degrees)		Deviation angles (degrees)	
$\theta_1^{24} = 99.5$	θ_2^{13} 105.4	$\delta_{12} = 10.6$	δ_{15} 42.0
$\theta_1^{45} - 99.4$	$\theta_4^{14} - 104.5$	$\delta_{21} -$ 7.2	$\delta_{51} - 19.6$
$\theta_2^{HH} - 114.1$	$\theta_5^{HH} = 115.4$		

Table 4. [3.1.1]



Hybrids		Overlaps
$\Psi_{12} = 0.5770\,(s) + 0.8168\,(p)$	$sp^{2.00}$	$S_{12} = 0.677$
$\Psi_{15} = 0.2913\,(s) + 0.9566\,(p)$	$sp^{10.78}$	$S_{15} = 0.510$
$\Psi_{16} = 0.5395\,(s) + 0.8420\,(p)$	$sp^{2.44}$	$S_{16} = 0.599$
$\Psi_{21} = 0.4601\,(s) + 0.8879\,(p)$	$sp^{3.72}$	
$\Psi_{23} = 0.4467\,(s) + 0.8947\,(p)$	$sp^{4.01}$	$S_{23} = 0.627$
$\Psi_{2H} = 0.5426\,(s) + 0.8400\,(p)$	$sp^{2.40}$	$S_{2H} = 0.803$
$\Psi_{32} = 0.4521\,(s) + 0.8919\,(p)$	$sp^{3.89}$	
$\Psi_{3H} = 0.5437\,(s) + 0.8393\,(p)$	$sp^{2.38}$	$S_{3H} = 0.810$
$\Psi_{61} = 0.4467\,(s) + 0.8947\,(p)$	$sp^{4.01}$	
$\Psi_{6H} = 0.5481\,(s) + 0.8364\,(p)$	$sp^{2.33}$	$S_{6H} = 0.790$

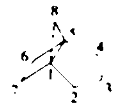
Interhybrid angles (degrees)		Deviation angles (degrees)	
$\theta_1^{23} = 102.4$	$\theta_1^{56} = 101.3$	$\delta_{12} = -5.8$	$\delta_{16} = 43.9$
$\theta_2^{13} = 105.0$	$\theta_2^{HH} = 114.7$	$\delta_{21} = -0.7$	
$\theta_3^{24} = 104.9$	$\theta_3^{HH} = 114.8$	$\delta_{32} = -2.4$	
$\theta_6^{15} = 104.4$	$\theta_6^{HH} = 115.4$	$\delta_{61} = 19.6$	

Table 5. [2.2.1]

Hybrids		Overlaps
$\Psi_{12} = 0.5540\,(s) + 0.8325\,(p)$	$sp^{2.26}$	$S_{12} = 0.652$
$\Psi_{14} = 0.3115\,(s) + 0.9503\,(p)$	$sp^{9.31}$	$S_{14} = 0.525$
$\Psi_{17} = 0.5377\,(s) + 0.8432\,(p)$	$sp^{2.46}$	$S_{17} = 0.596$
$\Psi_{21} = 0.4537\,(s) + 0.8912\,(p)$	$sp^{3.86}$	
$\Psi_{23} = 0.4645\,(s) + 0.8856\,(p)$	$sp^{3.63}$	$S_{23} = 0.638$
$\Psi_{2H} = 0.5378\,(s) + 0.8431\,(p)$	$sp^{2.46}$	$S_{2H} = 0.785$
$\Psi_{71} = 0.4464\,(s) + 0.8948\,(p)$	$sp^{4.02}$	
$\Psi_{7H} = 0.5484\,(s) + 0.8362\,(p)$	$sp^{2.33}$	$S_{7H} = 0.790$

Interhybrid angles (degrees)		Deviation angles (degrees)	
$\theta_1^{24} = 102.6$	θ_1^{47} 102.1	$\delta_{12} = 13.7$	$\delta_{17} = 44.7$
$\theta_2^{13} = 105.5$	$\theta_2^{HH} = 114.0$	$\delta_{21} = 7.2$	$\delta_{71} = 19.6$
$\theta_7^{14} = 104.4$	$\theta_7^{HH} = 115.5$		

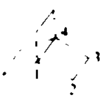
Table 6. [3.2.1]



Hybrids		Overlaps
$\Psi_{12} = 0.5770\,(s) + 0.8168\,(p)$	$sp^{2.00}$	$S_{12} = 0.679$
$\Psi_{15} = 0.3594\,(s) + 0.9332\,(p)$	$sp^{6.74}$	$S_{15} = 0.582$
$\Psi_{17} = 0.5314\,(s) + 0.8471\,(p)$	$sp^{2.54}$	$S_{17} = 0.644$
$\Psi_{18} = 0.5055\,(s) + 0.8628\,(p)$	$sp^{2.91}$	$S_{18} = 0.582$
$\Psi_{21} = 0.4622\,(s) + 0.8868\,(p)$	$sp^{3.68}$	
$\Psi_{23} = 0.4482\,(s) + 0.8939\,(p)$	$sp^{3.98}$	$S_{23} = 0.623$
$\Psi_{2H} = 0.5410\,(s) + 0.8410\,(p)$	$sp^{2.42}$	$S_{2H} = 0.802$
$\Psi_{32} = 0.4522\,(s) + 0.8919\,(p)$	$sp^{3.89}$	
$\Psi_{3H} = 0.5436\,(s) + 0.8393\,(p)$	$sp^{2.38}$	$S_{3H} = 0.810$
$\Psi_{67} = 0.4657\,(s) + 0.8849\,(p)$	$sp^{3.61}$	$S_{67} = 0.639$
$\Psi_{6H} = 0.5372\,(s) + 0.8435\,(p)$	$sp^{2.47}$	$S_{6H} = 0.785$
$\Psi_{71} = 0.4538\,(s) + 0.8911\,(p)$	$sp^{3.86}$	
$\Psi_{81} = 0.4469\,(s) + 0.8946\,(p)$	$sp^{4.01}$	
$\Psi_{8H} = 0.5480\,(s) + 0.8365\,(p)$	$sp^{2.33}$	$S_{8H} = 0.790$

Interhybrid angles (degrees)			Deviation angles (degrees)	
$\theta_1^{27} = 105.8$	$\theta_1^{57} = 104.0$	$\theta_1^{58} = 103.0$	$\delta_{12} = -2.4$	$\delta_{17} = 15.1$
$\theta_2^{13} = 105.2$	$\theta_2^{HH} = 114.4$	$\theta_3^{24} = 104.9$	$\delta_{18} = 45.6$	$\delta_{21} = -0.6$
$\theta_3^{HH} = 114.8$	$\theta_6^{57} = 105.5$	$\theta_6^{HH} = 113.9$	$\delta_{32} = -2.4$	$\delta_{71} = 7.2$
$\theta_8^{15} = 104.4$		$\theta_8^{HH} = 115.4$		$\delta_{81} = 19.6$

Table 7. [2.2.2]



Hybrids		Overlaps
$\Psi_{12} = 0.5348\,(s) + 0.8450\,(p)$	$sp^{2.50}$	$S_{12} = 0.644$
$\Psi_{14} = 0.3766\,(s) + 0.9264\,(p)$	$sp^{6.05}$	$S_{14} = 0.571$
$\Psi_{21} = 0.4535\,(s) + 0.8912\,(p)$	$sp^{3.86}$	
$\Psi_{2H} = 0.5370\,(s) + 0.8436\,(p)$	$sp^{2.47}$	$S_{2H} = 0.785$
$\Psi_{23} = 0.4664\,(s) + 0.8846\,(p)$	$sp^{3.60}$	$S_{23} = 0.639$

Interhybrid angles (degrees)	Deviation angles (degrees)
$\theta_1^{24} = 104.9$	$\delta_{12} = 16.0$
$\theta_2^{13} = 105.6$	$\delta_{21} = 7.2$
$\theta_2^{HH} = 113.9$	

propellane formalism and a partially numbered structural diagram. The optimal hybrid orbitals are then given, both in terms of the atomic orbital coefficients and by the sp^n formalism. The bond overlaps, S_{ij}, are given for each kind of bond in the molecule. The interhybrid orbital angle, θ_i^{jk}, indicates the angle between the directional vectors of hybrid orbitals centered on atom *i* and directed towards atoms *j* and *k*. The deviation angle, δ_{ij}, is the deviation of the direction of the hybrid orbital directed from atom *i* toward atom *j* from the straight line connecting these two atoms.

In line with our above description, the hydridization of the bridgehead carbon atoms of [3.3.3] propellane approximates that of methane, and, as the ring sizes are decreased, this hybridization varies until, in the case of [1.1.1] propellane, the conjoining bond hybrid orbitals have very large p character, while the hybrid orbitals to the methylene groups are nearly sp^2.

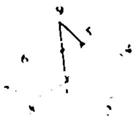
Our results for [1.1.1] propellane differ dramatically from those of Newton and Schulman.[16] One cause would be that our conjoining bond hybrids were mathematically constrained toward conventional overlap between the larger lobes of the hybrid orbitals. Also, it is possible that their results would be considerably different if their hybrids were required to be orthogonal.[22]

Agreement between our results and those of other methods are better for other compounds though it is interesting that Wiberg *et al.*[3] show more p character in the conjoining bond of [3.2.1] propellane than we do.

The differences between our results and those of Randić[12b] reflect the effect that varying geometries have on these calculations.

As we hinted before, our interest in doing these calculations was to see if we could get a measure of the strain in these molecules. We, in fact, obtained several measures. These are summarized in Table 12. Here we

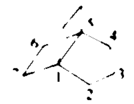
Table 8. [3.3.1]



Hybrids		Overlaps
$\Psi_{12} = 0.5589\,(s) + 0.8292\,(p)$	$sp^{2.20}$	$S_{12} = 0.675$
$\Psi_{15} = 0.3979\,(s) + 0.9174\,(p)$	$sp^{5.32}$	$S_{15} = 0.585$
$\Psi_{19} = 0.4658\,(s) + 0.8849\,(p)$	$sp^{3.61}$	$S_{19} = 0.568$
$\Psi_{21} = 0.4634\,(s) + 0.8862\,(p)$	$sp^{3.66}$	
$\Psi_{23} = 0.4487\,(s) + 0.8937\,(p)$	$sp^{3.97}$	$S_{23} = 0.628$
$\Psi_{2H} = 0.5404\,(s) + 0.8414\,(p)$	$sp^{2.42}$	$S_{2H} = 0.802$
$\Psi_{32} = 0.4523\,(s) + 0.8918\,(p)$	$sp^{3.89}$	
$\Psi_{3H} = 0.5435\,(s) + 0.8394\,(p)$	$sp^{2.39}$	$S_{3H} = 0.810$
$\Psi_{91} = 0.4477\,(s) + 0.8942\,(p)$	$sp^{3.99}$	
$\Psi_{9H} = 0.5473\,(s) + 0.8369\,(p)$	$sp^{2.34}$	$S_{9H} = 0.790$

Interhybrid angles (degrees)		Deviation angles (degrees)	
$\theta_1^{25} = 107.0$	$\theta_1^{29} = 103.2$	$\delta_{12} = 1.2$	$\delta_{19} = 45.8$
$\theta_2^{13} = 105.2$	$\theta_2^{HH} = 114.4$	$\delta_{21} = 0.6$	$\delta_{32} = -2.4$
$\theta_3^{24} = 104.9$	$\theta_3^{HH} = 114.8$	$\delta_{91} = 19.6$	
$\theta_9^{15} = 104.5$	$\theta_9^{HH} = 115.3$		

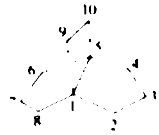
Table 9. [3.2.2]



Hybrids		Overlaps
$\Psi_{12} = 0.5662\,(s) + 0.8243\,(p)$	$sp^{2.12}$	$S_{12} = 0.677$
$\Psi_{15} = 0.4141\,(s) + 0.9102\,(p)$	$sp^{4.83}$	$S_{15} = 0.595$
$\Psi_{17} = 0.5040\,(s) + 0.8637\,(p)$	$sp^{2.94}$	$S_{17} = 0.635$
$\Psi_{21} = 0.4642\,(s) + 0.8857\,(p)$	$sp^{3.64}$	
$\Psi_{23} = 0.4499\,(s) + 0.8931\,(p)$	$sp^{3.94}$	$S_{23} = 0.628$
$\Psi_{2H} = 0.5395\,(s) + 0.8420\,(p)$	$sp^{2.44}$	$S_{2H} = 0.802$
$\Psi_{32} = 0.4529\,(s) + 0.8916\,(p)$	$sp^{3.88}$	
$\Psi_{3H} = 0.5430\,(s) + 0.8397\,(p)$	$sp^{2.39}$	$S_{3H} = 0.809$
$\Psi_{67} = 0.4670\,(s) + 0.8843\,(p)$	$sp^{3.59}$	$S_{67} = 0.640$
$\Psi_{6H} = 0.5365\,(s) + 0.8439\,(p)$	$sp^{2.47}$	$S_{6H} = 0.785$
$\Psi_{71} = 0.4542\,(s) + 0.8909\,(p)$	$sp^{3.85}$	

Interhybrid angles (degrees)		Deviation angles (degrees)	
$\theta_1^{25} = 108.2$	$\theta_1^{27} = 105.4$	$\delta_{12} = 0.0$	$\delta_{17} = 16.5$
$\theta_2^{13} = 105.3$	$\theta_2^{HH} = 114.2$	$\delta_{21} = -0.5$	$\delta_{71} = 7.3$
$\theta_3^{24} = 105.0$	$\theta_3^{HH} = 114.7$	$\delta_{32} = -2.4$	
$\theta_6^{57} = 105.6$	$\theta_6^{HH} = 113.8$		

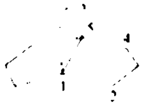
Table 10. [3.3.2]



Hybrids		Overlaps
$\Psi_{12} = 0.5369\,(s) + 0.8436\,(p)$	$sp^{2.47}$	$S_{12} = 0.669$
$\Psi_{15} = 0.4454\,(s) + 0.8953\,(p)$	$sp^{4.04}$	$S_{15} = 0.615$
$\Psi_{19} = 0.4744\,(s) + 0.8803\,(p)$	$sp^{3.44}$	$S_{19} = 0.626$
$\Psi_{21} = 0.4647\,(s) + 0.8855\,(p)$	$sp^{3.63}$	
$\Psi_{23} = 0.4495\,(s) + 0.8933\,(p)$	$sp^{3.95}$	$S_{23} = 0.628$
$\Psi_{2H} = 0.5394\,(s) + 0.8420\,(p)$	$sp^{2.44}$	$S_{2H} = 0.802$
$\Psi_{32} = 0.4527\,(s) + 0.8917\,(p)$	$sp^{3.88}$	
$\Psi_{3H} = 0.5432\,(s) + 0.8396\,(p)$	$sp^{2.39}$	$S_{3H} = 0.809$
$\Psi_{91} = 0.4545\,(s) + 0.8908\,(p)$	$sp^{3.84}$	
$\Psi_{910} = 0.4678\,(s) + 0.8839\,(p)$	$sp^{3.57}$	$S_{910} = 0.640$
$\Psi_{9H} = 0.5360\,(s) + 0.8442\,(p)$	$sp^{2.48}$	$S_{9H} = 0.785$

Interhybrid angles (degrees)		Deviation angles (degrees)	
$\theta_1^{25} = 108.5$	$\theta_1^{29} = 105.5$	$\delta_{12} = 0.3$	$\delta_{19} = 16.6$
$\theta_2^{13} = 105.3$	$\theta_2^{HH} = 114.2$	$\delta_{21} = -0.5$	$\delta_{32} = -2.4$
$\theta_3^{24} = 104.9$	$\theta_3^{HH} = 114.7$	$\delta_{91} = 7.3$	
$\theta_9^{110} = 105.7$	$\theta_9^{HH} = 113.8$		

Table 11. [3.3.3]



Hybrids		Overlaps
$\Psi_{12} = 0.5090\,(s) + 0.8608\,(p)$	$sp^{2.86}$	$S_{12} = 0.661$
$\Psi_{15} = 0.4721\,(s) + 0.8815\,(p)$	$sp^{3.49}$	$S_{15} = 0.631$
$\Psi_{21} = 0.4649\,(s) + 0.8854\,(p)$	$sp^{3.63}$	
$\Psi_{23} = 0.4491\,(s) + 0.8935\,(p)$	$sp^{3.96}$	$S_{23} = 0.628$
$\Psi_{2H} = 0.5395\,(s) + 0.8420\,(p)$	$sp^{2.44}$	$S_{2H} = 0.802$
$\Psi_{32} = 0.4524\,(s) + 0.8918\,(p)$	$sp^{3.89}$	
$\Psi_{3H} = 0.5434\,(s) + 0.8394\,(p)$	$sp^{2.39}$	$S_{3H} = 0.809$

Interhybrid angles (degrees)		Deviation angles (degrees)
$\theta_1^{25} = 108.5$	$\theta_2^{13} = 105.3$	$\delta_{12} = 0.3$
$\theta_2^{HH} = 114.2$	$\theta_3^{24} = 104.9$	$\delta_{21} = -0.5$
$\theta_3^{HH} = 114.8$		$\delta_{32} = -2.4$

have assembled the data for the conjoining bond from all of the calculations. The final column is the sum of the deviation angles for one of the bridgehead carbons. We initially had thought that this would be our sought-after measure. As it turned out, we feel that the bond overlap is a better indicator of the strain. This is interesting because it assumed that the relative instability of the entire molecule is somehow registered in this one bond. Other results support this assumption as will be pointed out later. We have ordered this table with respect to increasing bond overlap and we claim that this represents the relative stabilities of these compounds. This certainly appears to be true with respect to [3.3.2]-, [3.3.1]- and [3.2.1] propellanes. All of the compounds above [3.2.1] propellane remain synthetic challenges.

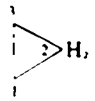
Indeed the bond overlaps of successive pairs of compounds below [3.2.1] propellane differ by about 1–3%. The bond overlaps of [2.2.1] and [3.2.1] propellane, however, differ by more than 6%, suggesting that this might be an insurmountable synthetic barrier. We predict that [3.1.1] propellane would prove to be less stable than [2.2.1], although, at least intuitively, we would not have guessed that fusion of a 5-membered ring onto the relatively stable bicyclobutane would have made it less stable than the norbornane derivative formed by joining the bridgehead carbon atoms.

Certainly, [1.1.1] propellane would be the least stable of these molecules. Indeed, as Newton and Schulman[16] have pointed out, the strain in this compound would be greater than the strongest of carbon–carbon single bonds.

Table 12. Conjoining bond

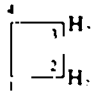
Compound	Hybrid orbitals		Bond overlap	Deviation angle sum
[1.1.1]	0.1493 (s) + 0.9888 (p)	$sp^{43.89}$	0.400	115.8
[2.1.1]	0.2352 (s) + 0.9719 (p)	$sp^{17.08}$	0.468	94.6
[3.1.1]	0.2913 (s) + 0.9566 (p)	$sp^{10.78}$	0.510	93.6
[2.2.1]	0.3115 (s) + 0.9503 (p)	$sp^{9.31}$	0.525	72.1
[3.2.1]	0.3594 (s) + 0.9332 (p)	$sp^{6.74}$	0.559	63.1
[2.2.2]	0.3766 (s) + 0.9264 (p)	$sp^{6.05}$	0.571	48.0
[3.3.1]	0.3979 (s) + 0.9174 (p)	$sp^{5.32}$	0.585	48.2
[3.2.2]	0.4143 (s) + 0.9101 (p)	$sp^{4.83}$	0.596	33.0
[3.3.2]	0.4458 (s) + 0.8951 (p)	$sp^{4.03}$	0.615	17.2
[3.3.3]	0.4721 (s) + 0.8815 (p)	$sp^{3.49}$	0.631	0.9

Table 13. The cyclopropane ring



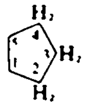
Compound	Hybrid orbitals n_{12}	n_{21}	n_{2H}	n_{13}	Bond S_{12}	Overlaps S_{2H}	S_{13}	Deviation angle δ_{12}	δ_{21}
[1.1.1]	2.07	3.99	2.34	43.89	0.625	0.790	0.400	38.6	19.6
[2.1.1]	2.20	4.01	2.33	17.08	0.611	0.790	0.468	42.0	19.6
[3.1.1]	2.44	4.01	2.33	10.78	0.599	0.790	0.510	43.9	19.6
[2.2.1]	2.46	4.02	2.33	9.31	0.596	0.790	0.525	44.7	19.6
[3.2.1]	2.91	4.01	2.33	6.74	0.582	0.790	0.559	45.6	19.6
[3.3.1]	3.61	3.99	2.34	5.32	0.568	0.790	0.585	45.8	19.6

Table 14. The cyclobutane ring



Compound	Hybrid orbitals n_{12}	n_{21}	n_{23}	n_{2H}	n_{14}	Bond overlaps S_{12}	S_{23}	S_{2H}	S_{14}	Deviation angles δ_{12}	δ_{21}
[2.1.1]	2.13	3.86	3.68	2.45	17.08	0.657	0.637	0.785	0.468	10.6	7.2
[2.2.1]	2.26	3.86	3.63	2.46	9.31	0.652	0.638	0.785	0.525	13.7	7.2
[3.2.1]	2.54	3.86	3.61	2.47	6.74	0.644	0.639	0.785	0.559	15.1	7.2
[2.2.2]	2.50	3.86	3.60	2.47	6.05	0.644	0.639	0.785	0.571	16.0	7.2
[3.2.2]	2.94	3.85	3.59	2.47	4.83	0.635	0.640	0.785	0.595	16.5	7.3
[3.3.2]	3.44	3.84	3.57	2.48	4.04	0.626	0.640	0.785	0.615	16.6	7.3

Table 15. The cyclopentane ring



Compound	Hybrid orbitals n_{12}	n_{21}	n_{23}	n_{2H}	n_{32}	n_{3H}	n_{15}	Bond overlap S_{12}	S_{23}	S_{2H}	S_{3H}	S_{15}	Deviation angles δ_{12}	δ_{21}	δ_{32}
[3.1.1]	2.00	3.72	4.01	2.40	3.89	2.38	10.78	0.677	0.627	0.803	0.810	0.510	-5.8	-0.7	2.4
[3.2.1]	2.00	3.68	3.98	2.42	3.89	2.38	6.74	0.679	0.628	0.802	0.810	0.559	-2.4	0.6	-2.4
[3.2.1]	2.20	3.66	3.97	2.42	3.89	2.39	5.32	0.675	0.628	0.802	0.810	0.585	1.2	-0.6	-2.4
[3.2.2.]	2.12	3.64	3.94	2.44	3.88	2.39	4.83	0.677	0.628	0.802	0.809	0.595	0.0	-0.5	2.4
[3.3.2]	2.47	3.63	3.95	2.44	3.88	2.39	4.04	0.669	0.628	0.802	0.809	0.615	0.3	-0.5	-2.4
[3.3.3]	2.86	3.63	3.96	2.44	3.89	2.39	3.49	0.661	0.628	0.802	0.809	0.631	0.3	-0.5	-2.4

Furthermore, being a derivative of bicyclobutane, it could undergo a thermally alllowed pericyclic rearrangement to form a much more stable dimethylene cyclopropane.

Finally, in Tables 13–15, we have summarized the results for the 3-, 4- and 5-membered rings from all of our calculations. It is interesting to note that all the results for atoms other than the bridgehead atoms are remarkably consistent as we go from compound to compound, the more so the further the atom is removed from the conjoining bond. This supports our contention that the strain peculiar to the propellane structure localized itself to a large extent in this one bone.

One other comment might be made with regard to the negative deviation angles found for the 5-membered rings. These indicate that the hybrid is directed to the inside of the ring. Unlike in the case of positive deviation angles, a real-life molecule would be able to remove these negative deviations by ring flexing. The various forms of the cyclohexane ring can be viewed as resulting from efforts of the ring to alter the negative deviation angles it would have if it were planar.

CONCLUSION

Maximum overlap calculations have been found to give fairly good agreement with the results of other methods of calculation.[23] We were, therefore, surprised to find our results in these calculations differed widely from those of others. This is doubtlessly a result of the extreme geometries involved in the present class of compounds and the nonorthogonality of the hybrid orbitals computed by the competition. Further study of these differences is planned. Our results are internally self-consistent in any case, and the method is extremely simple in comparison. As an extension of this work, it is possible to use these data to empirically correlate ^{13}C–H coupling constants, C–H stretching frequencies, C–H acidities, etc.[12a]

Acknowledgements—Most of this work was carried out while the author was at the University of Malaya in 1972–75. It was completed at the University of New Orleans. Appreciation must be expressed to Prof. R. L. Flurry, Jr. For his support and encouragement.

REFERENCES

[1] D. Ginsburg has published a number of different reviews of these compounds.[a] *Accounts Chem. Res.* **2**, 121 (1969); *Ibid* **5**, 249 (1972); *Ibid* **7**, 286 (1974); *Tetrahedron* **30**, 1487 (1974); [b]J. Altman, E. Babad, J. Itzchaki and D. Ginsburg *Tetrahedron Suppl.* **8** (1), 279 (1966)

[2] K. B. Wiberg, G. J. Burgmaier, K.-W. Shen, S. J. La Placa, W. C. Hamilton and M. D. Newton, *J. Am. Chem. Soc.* **94** 7402 (1972).

[3] Only derivatives of [3.3.3] propellanes are known. see [a]J. Altman, E. Cohen, T. Maymon, J. B. Petersen, N. Reshef and D. Ginsburg, *Tetrahedron* **25**, 5115 (1969); [b]J. Drouin, F. Leyendecker and J. M. Conia, *Tetrahedron Letters* 4053 (1975).

[4a] W. T. Borden, J. L. Reich, L. A. Sharpe and H. J. Reich *J. Am. Chem. Soc.* **92**, 3808 (1970); W. T. Borden, I. L. Reich, L. A. Sharpe, R. B. Weinberg and H. J. Reich, *J. Org. Chem.* **40**, 2438 (1975); [b]R. L. Cargill, J. R. Damewood and M. M. Cooper, *J. Am. Chem. Soc.* **88**, 1330 (1966); [c]R. L. Cargill, A. C. Miller, D. M. Pond, P. de Mayo, M. F. Tchir, K. R. Newberger and J. Saltiel, *Mol. Photochem.* **1**, 301 (1969).

[5a] P. Warner, R. LaRose and T. Schleis, *Tetrahedron Letters* 1409 (1974); [b]P. G. Gassman, R. N. Steppel and E. A. Armour, *Ibid* 3287 (1973); [c]an interesting tetracyclic derivative of [3.3.1] propellane is described in R. E. Pincock and E. J. Torupka, *J. Am. Chem. Soc.* **91**, 4593 (1969).

[6] P. E. Eaton and K. Nyi, *Ibid* **93**, 2786 (1971).

[7a] K. B. Wiberg and G. J. Burgmaier, *Tetrahedron Letters* **317** (1069); *J. Am. Chem. Soc.* **94**, 7396 (1972); [b]P. G. Gassman, A. Topp and J. W. Keller, *Tetrahedron Letters* 1093 (1969); [c]For a [3.2.1] propellane with an oxygen heteroatom, see Ref. 2, K. B. Wiberg, J. E. Hiatt and G. Burgmaier, *Tetrahedron Letters* 5855 (1968); K. W. Wiberg, E. C. Jupton, Jr. and G. J. Burgmaier, *J. Am. Chem. Soc.* **91**, 3372 (1969).

[8a] K. B. Wiberg, G. A. Epling and M. Jason, *Ibid* **96**, 912 (1974); [b]J. J. Dannenberg, T. M. Prociv and C. Hutt, *Ibid* **96**, 913 (1974); [c]A simple derivative of [2.2.2] propellane has been synthesized. P. E. Eaton and G. H. Temme, III *Abstracts ACS Nat'l Meeting April* 1974 ORGN 58, *J. Am. Chem. Soc.* **95**, 7508 (1973); [d]See also J. J. Gejewski, L. K. Hoffman and N. C. Chung, *Ibid.* **96**, 3705 (1974); H. Bohm, J. Kalo, Ch. Yarnitzky and D. Ginsburg, *Tetrahedron* **30**, 217 (1974); G. Märkland and A. Mayr. *Tetrahedron Letters* 1817 (1974).

[9] M. E. Jason, J. A. McGinnety and K. B. Wiberg, *J. Am chem. Soc.* **96**, 6531 (1974).

[10] For a discussion of stability and other matters very relevant to this paper, see the recent review on strained organic molecules by J. F. Liebmann and A. Greenberg, *Chem. Revs.* **76**, 311 (1976). In particular, they discuss the relationships between strain and reactivity used in this paper.

[11] L. Pauling, *J. Am. Chem. Soc.* **53**, 3225 (1931); J. C. Slater, *Phys. Rev.* **37**, 481 (1931); R. S. Mulliken, *Phys. Rev.* **41**, 67 (1932).

[12a] M. Randić and Z. B. Maksić, *Chem. Rev.* **72**, 43 (1972); [b]M. Randić, *Intern. J. Quant. Chem* **8**, 643 (1974).

[13] E. Clementi, *Tables of Atomic Functions*, a supplement to *IBM J. Res. Devel.* **9**, 2 (1965).

[14] L. Klasinc, D. Schulte-Frohlinde and M. Randić, *Croat Chem. Acta.* **39**, 125 (1967).

[15] QCPE 118

[16] M. D. Newton and J. M. Schulman, *J. Am. Chem. Soc.* **94**, 773 (1972).

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

[18a] M. D. Newton and J. M. Schulman, *J. Am. Chem. Soc.* **94**, 767 (1972); [b]Note: there appears to be an error in Table 1 of this paper For our overlap calculation we used a value for the second 2p exponent of 2.9743110.

[19] M. D. Newton and J. M. Schulman, *J. Am. Chem. Soc.* **94**, 4391 (1972).

[20] W. D. Stohrer and R. Hoffmann, *Ibid* **94**, 779 (1972).

[21a] J. J. Dannenberg and T. M. Prociv, *Chem. Commun* 291 (1973); [b]M. Farcasiu, K. R. Blanchard, E. M. Engler and P. V. R. Schleyer, *Chem. Letters* (Japan) 1189 (1973).

[22] Personal communication from Dr. N. K. Ray.

[23] Z. B. Maksić and M. Randić, *J. Am. Chem. Soc.* **95**, 6522 (1973).