fellowship. J.M.D. acknowledges financial support from Dalhousie University. We are grateful to Professor Cheves Walling for several useful suggestions regarding the manuscript.

Registry No. 4-Acetylbenzyl radical, 41876-38-4; 4-acetoxybenzyl radical, 84237-63-8; 4-benzoylbenzyl radical, 78906-08-8; 4-methoxycarbonylbenzyl radical, 84237-64-9; 4-cyanobenzyl radical, 4939-73-5; 4-*tert*-butylbenzyl radical, 5527-53-7; 4-methoxybenzyl radical, 3494-45-9; 4-chlorobenzyl radical, 3327-51-3; 4-methylbenzyl radical, 2348-52-9; 4-methylsulfinylbenzyl radical, 84237-65-0; 4-methoxysulfonylbenzyl radical, 84237-66-1; 4-(trifluoromethyl)benzyl radical, 84237-67-2; benzyl radical, 2154-56-5; 3-methylbenzyl radical, 2348-47-2; 3-chlorobenzyl radical, 3327-52-4; 3-methoxycarbonylbenzyl radical, 84278-82-0; 4-fluorobenzyl radical, 2194-09-4; 3-phenoxybenzyl radical, 84237-68-3; 3-(trifluoromethyl)benzyl radical, 84237-69-4; 3-fluorobenzyl radical, 2599-73-7; 3-cyanobenzyl radical, 61142-85-6.

Strain Energies of Small Ring Propellanes

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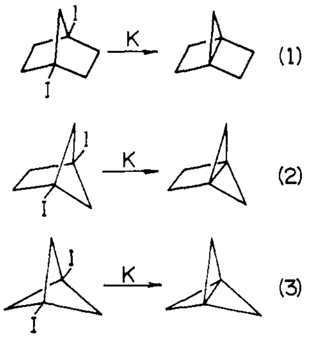
Abstract: Energies of hydrogenolysis of carbon–carbon bonds have been calculated by using extended basis sets and have been compared with experimental data. In most cases, a consistent difference between calculated and observed values of 5 ± 1 kcal/mol was obtained. It was found that the energies of hydrogenolysis of the propellanes became progressively more negative in the order [1.1.1], [2.1.1], [2.2.1]. Since the [2.2.1]propellane has been obtained from its bicyclic precursor, the calculations suggested that the other propellanes may be prepared in a similar fashion, and with greater ease. Subsequently, this was confirmed experimentally. The enthalpies of formation and strain energies were estimated. The effect of polarization functions on the energies and structures of the propellanes is discussed, and the electron density changes for the central bonds of the propellanes have been calculated.

We have recently observed that the gas-phase dehalogenation of 1,4-diiodobicyclo[2.2.1]heptane leads to the [2.2.1]propellane.[1] In this context, we should like to know the relative strain energy increases in the series of reactions: This might suggest whether or not the second and third reactions are practical.



In addition, we have examined the rates of thermolysis of a series of small ring propellanes containing cyclobutane rings and have suggested that strain energy relief,[2] rather than orbital symmetry considerations,[3] provides the main driving force leading to changes in activation energies. Better information on strain energies would be valuable in determining whether or not this is correct. Since it is unlikely that direct calorimetric measurements will be practical for many of these compounds and for other small ring propellanes of current interest,[4-7] we have attempted to estimate the energies via molecular orbital calculations. These calculations will also provide structural data for some of the propellanes for which such data are not available.[8,9]

Reasonably good energies and geometries are normally obtained for hydrocarbons with the 4-31G basis set.[10] Complete geometry optimizations have been carried out for four propellanes as well as a set of relevant small ring hydrocarbons, and the resulting energies are given in Table I. Some calculations dealing with the propellanes have been reported,[3,11] but in no case has complete geometry optimization been carried out.

It is known that polarization functions (d orbitals) are needed at carbon if one is to obtain reasonable estimates of energies of reaction of highly strained compounds.[12,13] Therefore, the energies of the 4-31G[14] optimized structures also were calculated with the 6-31G* basis set, and these energies are given in Table I, along with the zero-point energies and the change in enthalpy of formation on going from 0 to 298 K.[15]

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(1) Walker, F. H.; Wiberg, K. B.; Michl, J. *J. Am. Chem. Soc.* **1982**, *104*, 2056.

(2) Wiberg, K. B.; Matturro, M. G. *Tetrahedron Lett.* **1981**, 3481.

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

(4) [2.2.2]Propellane: Eaton, P. E.; Temme, G. H., Jr. *J. Am. Chem. Soc.* **1973**, *95*, 7508.

(5) [3.2.1]Propellane: Wiberg, K. B.; Hiatt, J. E.; Burgmaier, G. J. *Tetrahedron Lett.* **1968**, 5855. Wiberg, K. B.; Burgmaier, G. J. *Ibid.* **1969**, 317. Gassman, P. G.; Topp, A.; Keller, J. W. *Ibid.* **1969**, 1089. Wiberg, K. B.; Burgmaier, G. J. *J. Am. Chem. Soc.* **1972**, *94*, 7396. In this case, the enthalpy of formation has been obtained from an enthalpy of combustion (Wiberg, K. B.; Burgmaier, G. J.; Lupton, E. C., Jr. *Ibid.* **1969**, *91*, 3372) and an enthalpy of reaction (Wiberg, K. B.; Connon, H. A.; Pratt, W. E. *Ibid.* **1979**, *101*, 6970).

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(7) [4.1.1]Propellane: Hamon, D. P. G.; Trenberry, V. C. *J. Am. Chem. Soc.* **1981**, *103*, 4962. Szeimies, G. et al. in ref 6.

(8) Structural data on small ring propellanes: [3.2.1]—Wiberg, K. B.; Burgmaier, G. J.; Shen, K.; La Placa, J.; Hamilton, W. C.; Newton, M. D. *J. Am. Chem. Soc.* **1972**, *94*, 7402. [4.2.2]—Silverton, J. V.; Milne, G. W. A.; Eaton, P. E.; Nyi, K.; Temme, G. H., III. *Ibid.* **1974**, *96*, 7429. [3.1.1]—Szeimies-Seebach, U.; Szeimies, G.; van Meersche, M.; Germain, G.; Declercq, J.-P. *Nouv. J. Chim.* **1979**, *3*, 357 and ref 9. [4.1.1]—Declercq, J.-P.; Germain, G.; van Meersche, M. *Acta Crystallogr.* **1978**, *34*, 3472.

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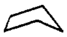
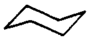
Table I. Energies of 431G and 631G* Optimized Structures

compound	energy (hartrees): 4-31G[b] / 4-31G	6-31G* / 4-31G	6-31G* / 6-31G*	6-31G** / 6-31G*	μ, D[c]	ZPE[d]	$\Delta\Delta H_f$[d] (298-0 K)
H_2	−1.126 827[a]	−1.126 828	−1.126 828	−1.131 329		6.0[a]	0.0
CH_4	−40.139 767[a]	−40.195 153	−40.195 172	−40.201 705		27.2[a]	−1.9
C_2H_6	−79.115 933[a]	−79.228 734	−79.228 755	−79.238 253		45.5[a]	−3.7
C_3H_8	−118.093 806	−118.263 636	−118.263 652	−118.276 158	0.066	62.5[e]	−5.3
n-C_4H_{10}	−157.071 592	−157.298 373	−157.298 402	−157.313 940		79.9[e]	−6.5
cyclopropane	−116.883 858[a]	−117.058 727	−117.058 865	−117.069 063		49.1[a]	−4.1
cyclobutane	−155.866 810	−156.096 851	−156.097 028	−156.109 526		67.1	−5.9
cyclopentane	−194.873 985	−195.161 236			0.113	85.3	−7.8
cyclohexane	−233.866 801	−234.207 957				103.5[f]	−9.4
bicyclo[1.1.0]butane	−154.624 716	−154.870 888	−154.871 690	−154.882 357	0.698	51.7[g]	−4.8
bicyclo[1.1.1]pentane	−193.610 156[a]	−193.904 653	−193.905 681	−193.918 816		70.5[a]	−6.2
bicyclo[2.1.0]pentane	−193.632 493[a]	−193.926 496	−193.926 966			71.7[a]	−6.0
cis-bicyclo[2.2.0]hexane	−232.620 206[a]	−232.965 203				89.1[a]	−7.8
bicyclo[2.1.1]hexane	−232.644 758[a]	−232.989 294				89.9[a]	−8.0
bicyclo[2.2.1]heptane	−271.664 674	−272.064 480			0.060	105.0[h]	
bicyclo[2.2.2]octane	−310.649 230	−311.103 531				124.1[i]	
[1.1.1]propellane	−192.361 856	−192.688 331	−192.691 062	−192.701 069		55.9	
[2.1.1]propellane	−231.349 221	−231.720 351	−231.721 877		0.693	75.3	
[2.2.1]propellane	−270.342 960	−270.759 561			0.507	90.4	
[2.2.2]propellane	−309.346 218	−309.808 540	−309.809 069			109.5	

[a] Data taken from ref 13. [b] The basis functions used in the calculation is given above the line, and that used in the geometry optimization[is given below the line. [c] Based on 631G*/431G wave functions. [d] These energies are given in kcal/mol. [e] George, P.; Trachtman, M.; Brett, A. M.; Bock, C. W. *J. Chem. Soc., Perkin Trans. 2* 1977, 1036. [f] Wiberg, K. B.; Shrake, A. *Spectrochim. Acta Part A* 1973, *29A*, 583. [g] Wiberg, K. B.; Peters K. *Ibid.* 1977, *33A*, 261. [h] Levin, I. W.; Harris, W. C. *Ibid.* 1973, *29A*, 1815. [i] Bruesch, P.; Gunthard, Hs. H. *Ibid.* 1966, *22*, 877. Yokozeki, A.; Kuchitsu, K.; Morino, Y. *Bull. Chem. Soc. Jpn.* 1970, *43*, 2017.

Table II. Energy Changes in C–C Bond Hydrogenolysis[a]

reaction	ΔE_{class}: 4-31G[b] / 4-31G	6-31G* / 4-31G	6-31G* / 6-31G*	6-31G** / 6-31G*	ΔZPE	$\Delta\Delta H_f$	ΔH_r: calcd[c]	obsd	dif
$CH_3\text{-}CH_3 + H_2 \rightarrow 2CH_4$	−23.1	−21.8	−21.8	−21.2	2.9	−0.1	−19.0	−15.5	3.5
$C_2H_5\text{-}C_2H_5 + H_2 \rightarrow 2C_2H_6$	−21.0	−20.2	−20.2	−19.6	5.1	−0.9	−16.0	−10.1	5.9
 + $H_2 \rightarrow CH_3CH_2CH_3$	−52.1	−49.0	−48.9	−47.5	7.4	−1.2	−42.7	−37.6	5.2
 + $H_2 \rightarrow CH_3CH_2CH_2CH_3$	−48.9	−46.9	−46.8	−45.9	6.8	−0.6	−40.6	−37.1	3.5
 + H_2 → 	−72.3	−62.2	−61.8	−60.1	9.4	−1.8	−54.2	−45.1	9.1
 + H_2 → 	−71.9	−67.7			7.6	−1.8	−61.9	−56.1	5.8
 + H_2 → 	−75.2	−72.7			8.4	−1.6	−65.9	−59.3	6.6
 + H_2 → 	−76.2	−56.2	−55.1	−54.2	8.5[d]	−1.7	−48.3	(−39)	
 + H_2 → 	−106.2	−89.1			8.5[d]	−1.7	−82.3	(−73)	
 + H_2 → 	−122.0	−111.8			8.5[d]	−1.7	−105.0	(−99)	
 + H_2 → 	−111.5	−105.5			8.5[d]	−1.7	−98.7	(−93)	

[a] All energies are given in kcal/mol. 1 H = 627.50 kcal/mol. [b] The basis set used in the calculation is given above the line and that used in the optimization is given below the line. [c] Based on 6-31G* energies. [d] Average of values for bicycloalkanes.

The calculated energies cannot be used directly since they have not been corrected for electron correlation effects. However, the correlation energies roughly cancel when energies of reaction are calculated.[16] The energy changes resulting from hydrogenolysis of C–C bonds were calculated by using the data given in Table I, and the results are summarized in Table II. For the less geometrically distorted compounds ethane, butane, cyclopropane, cyclobutane, and bicyclo[2.2.0]hexane, the calculated energies of reaction decrease by approximately the same amount (1–3 kcal/mol) on going from the 4-31G to the 6-31G* basis set. However, with the more distorted compounds, the differences become much larger. It increases to 10 kcal/mol for bicyclo[1.1.0]butane, 17 kcal/mol for the [2.1.1]propellane, and 20 kcal/mol for the [1.1.1]propellane. This further indicates the need for polarization functions when energies of these compounds are to be considered.

The large change in calculated energies of reaction on inclusion of polarization functions (in this case, d orbitals at carbon) appears to be unique to the compounds which have severely distorted geometries or which incorporate a bicyclo[1.1.0]butane structural unit. This suggests that orbitals created with only s and p atomic

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(15) For the simpler compounds, $\Delta\Delta H$ (0–298 K) was available from the American Petroleum Institute Project 44 Tables of Thermodynamic Data for Hydrocarbons. The zero-point energies were taken from George et al. (George, P.; Trachtman, M.; Brett, A. M.; Bock, C. W. *J. Chem. Soc., Perkin Trans. 2* **1977**, 1036) or were calculated from the vibrational frequencies given by Sverdlov et al. (Sverdlov, L. M.; Kovner, M. H.; Krainov, E. P. "Vibrational Spectra of Polyatomic Molecules"; Halsted Press: New York, 1974).

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Table III. Enthalpies of Formation and Strain Energies[a]

compound	ΔH_f	SE
bicyclo[1.1.1]pentane[b]	49.6	66.6
bicyclo[2.1.1]hexane[b]	15.3	37.3
bicyclo[2.2.1]heptane[c]	−12.4	14.4
bicyclo[2.2.2]octane[d]	−24.3	7.4
[1.1.1]propellane	89	103
[2.1.1]propellane	88	106
[2.2.1]propellane	87	109
[2.2.2]propellane	69	97
[3.2.1]propellane[e]	39	67

[a] All energies are given in kcal/mol. [b] Reference 13. [c] Steele, W. V. *J. Chem. Thermodyn.* 1978, *10*, 919. [d] Cox, J. D.; Pilcher, G. "Thermodynamics of Organic and Organometallic Compounds"; Academic Press: London, 1970; p 160. [e] Wiberg, K. B.; Connon, H. A.; Pratt, W. E. *J. Am. Chem. Soc.* 1979, *101*, 6970.

orbitals do not have the directional characteristics required to give satisfactory bonding in these compounds, and d orbitals must be added to give greater flexibility to the basis set.

The large energy changes resulting from the inclusion of polarization functions led us to carry out 6-31G* geometry optimizations for some of the propellanes. This gave a significant decrease in energy (Table I) as well as an important change in geometry (see below). However, the change in calculated energies of reaction were relatively small. In a few cases, the effect of including polarization functions at hydrogen (i.e., p orbitals) was examined with the 6-31G** basis set.[14] No important changes in energy of reaction were observed.

In order to compare the calculated energy changes with experimental data, they must be corrected for the difference in zero-point energy between reactants and products, as well as for the difference in change of ΔH_f on going from 0 to 298 K. These data are available for many of the simpler compounds (Table I).[15] The average change in zero-point energy on hydrogenolysis of the bicyclic compounds was 8.5 kcal/mol, and the average value of $\Delta\Delta H_f$ was −1.7 kcal/mol. These values were assumed to be applicable to the hydrogenation of the propellanes. The resultant ΔH_r are given in Table II.

$$\Delta H_r(\text{calcd}) = \Delta E(\text{calcd}) + \Delta\text{ZPE} + \Delta\Delta H_f(0\text{–}298\ \text{K})$$

Excluding bicyclo[1.1.0]butane, the first seven reactions lead to enthalpies of reaction which are uniformly 5 ± 1 kcal/mol more negative than the observed values. Thus, the error associated with the assumption that correlation energies will cancel is small and essentially constant. In the case of bicyclobutane, it appears to be slightly larger which is not surprising in view of the large change in electron density distribution on going to cyclobutane.

In order to obtain better estimates of the enthalpies of hydrogenolysis of the propellanes, the two containing a bicyclobutane unit were assumed to give calculated ΔH_r which are 8.5 kcal/mol too negative, and the larger propellanes were assumed to give values which are 6 kcal/mol too negative. This allowed the estimation of the ΔH_r values given in parentheses. With these values and known enthalpies of formation for the bicyclic compounds, we were able to estimate enthalpies of formation and strain energies for the propellanes. They are summarized in Table III.

A surprising result of the calculations is that the [1.1.1]-, [2.1.1]-, and [2.2.1]propellanes appear to have essentially the same strain energies. It is known that the replacement of a cyclopropane ring by a cyclobutane ring (such as with bicyclo[2.1.0]pentane and bicyclo[2.2.0]hexane) usually leads to only a small change in strain energy.[13] Apparently, this also applies to these propellanes.

The corresponding bicyclic compounds do increase in energy as the number of carbons is decreased because of the increase in number of small rings. As a result, the largest energy change is found with the [2.2.1]propellane, and the smallest is found with the [1.1.1]propellane. Thus, the formation of the [2.2.1]propellane (eq 1) should be the most difficult of the group, and the formation of the [1.1.1]propellane (eq 3) should be the most facile! It has recently become possible to demonstrate that these predictions are correct.[17,18] Further, these data allow one to make an estimate of the energy changes in going from the propellanes to the possible intermediates in thermal rearrangements and free radical addition reactions.[17]

The strain energy of [2.2.2]propellane is calculated to be significantly smaller than that of the above compounds. Experimental data are available which indicates [3.2.1]propellane to have a strain energy of only 67 kcal/mol.[5] 30 kcal/mol less than that of [2.2.2]propellane. Since the diradical formed by cleaving the central bond of [2.2.2]propellane should have a significantly smaller strain energy than that from [3.2.1]propellane,[19] the combination of these factors can easily accommodate the large difference in activation energies for thermolysis (22[4] and 47[20] kcal/mol, respectively) without invoking a change in mechanism.[2]

We may now examine the calculated geometries (Table IV). Geometry optimization at the 6-31G* level normally leads to a small decrease in the C–C bond lengths and a small increase in C–H bond lengths are compared to a 4-31G optimization. A comparison with the experimental data shows that the bond angles obtained with the 6-31G* basis set are very good and that the calculated C–C and C–H bond lengths are generally too short by 0.005–0.01 Å. This is expected since anharmonicity will lead to elongated average bond lengths,[21] and since correction for electron correlation will lead to slightly more diffuse electron density distributions along the bonds with a resultant small increase in bond length.[22] Among the simpler compounds, only cyclobutane gives a significant error in the calculated bond angles.[23] Here, the ring-puckering potential is quite small and relatively large changes in geometry may occur with little change in energy.[24]

In the case of bicyclo[1.1.0]butane and the propellanes, the change in geometry on going from the 4-31G to the 6-31G* basis set is much larger. For example, with the [1.1.1]propellane, the central bond length decreases from 1.600 Å (4-31G) to 1.543 Å (6-31G*). These are the cases in which changes in energy were found when polarization functions were added and again indicates the need for an improved basis set in treating compounds having unusual bond angles.

The calculations suggest that the central bond lengths in the propellanes will generally be close to normal values of 1.54–1.56 Å. This is in agreement with the experimental data[8,9] for derivatives of the [3.2.1]propellane (1.57 Å), [3.1.1]propellane (1.55 Å, 1.57 Å), [4.1.1]propellane (1.55 Å), and [4.2.2]propellane (1.58 Å). The only case in which a relatively long central bond was calculated is the [2.1.1]propellane, but no experimental data are as yet available. Thus, despite the considerable differences in geometrical distortion and electron density distributions (see below), these propellanes have remarkable constant central bond lengths.

There is some variation in the other bond lengths. With [2.2.2]propellane for example, the C_2–C_3 bond is calculated to be 1.575 Å, whereas the C_1–C_2 bond is calculated to be 1.512 Å. The long C_2–C_3 bond decreases the strain at the bridgehead carbons, whereas the short C_1–C_2 bond corresponds to the expected

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(17) [1.1.1]Propellane: Wiberg, K. B.; Walker, F. H. *J. Am. Chem. Soc.* **1982**, *104*, 2056.

(18) [2.1.1]Propellane: Wiberg, K. B.; Walker, F. H.; Michl, J., to be published.

(19) Bicyclo[2.2.2]octane and bicyclo[3.2.1]octane are estimated to have essentially the same strain energies (Engler, E. M.; Andose, J. D.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1973**, *95*, 8005), but the greater flexibility of the bicyclo[2.2.2]octane ring system should better accommodate the distortions involved in forming a bridgehead–bridgehead diradical.

(20) Reynolds, R. N. Ph.D. Thesis, University of California, Santa Barbara, 1977.

(21) Bartell, L. S., Kuchitsu, K. *J. Chem. Phys.* **1961**, *68*, 1213. Pulay, P.; Meyer, W.; Boggs, J. E. *Ibid.* **1978**, 68, 5077. Gray, D. L.; Robiette, A. G. *Mol. Spectrosc.* **1979**, *37*, 1901. Hirota, E. *J. Mol. Spectrosc.* **1979**, *77*, 213.

(22) DeFrees, D. J.; Levi, B. A.; Pollack, S. K.; Hehre, W. J.; Binkley, J. S.; Pople, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 4085.

(23) This problem with the calculated geometry of cyclobutane has been noted previously: Wright, J. S.; Salem, L. *J. Am. Chem. Soc.* **1972**, *94*, 322.

(24) Rathjens, G. W., Jr.; Freeman, N. K.; Gwinn, W. D.; Pitzer, K. S. *J. Am. Chem. Soc.* **1953**, *75*, 5634.

Table IV. Optimized Geometries

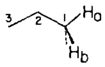
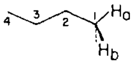
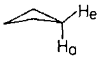
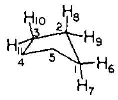
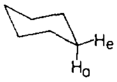
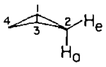
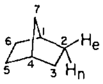
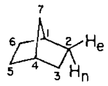
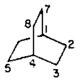
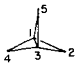
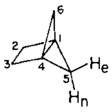
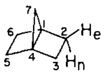
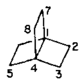
compound	bond/angle	calcd 4-31G	calcd 6-31G*	obsd	ref
propane	$r(CC)$	1.531	1.528	1.532 ± 0.003	*a*
	$r(C_2H)$	1.086	1.087	1.107 ± 0.005 (av)	
	$r(C_1H_a)$	1.084	1.086		
	$r(C_1H_b)$	1.085	1.087		
	$\angle(CCC)$	112.65	112.74	112.0 ± 1.0	
	$\angle(HC_2H)$	106.39	106.27	107.0 ± 3.0	
	$\angle(C_2C_1H_a)$	111.25	111.37		
	$\angle(C_2C_1H_b)$	111.02	111.08		
n-Butane (transoid)	$r(C_1C_2)$	1.530	1.528	1.531 ± 0.002	*b*
	$r(C_2C_3)$	1.532	1.530		
	$r(C_1H_a)$	1.083	1.085	1.117 ± 0.005 (av)	
	$r(C_1H_b)$	1.085	1.085		
	$r(C_2H)$	1.086	1.088		
	$\angle(CCC)$	112.83	112.97	113.8 ± 0.4	
	$\angle(CC_1H_a)$	111.34	111.46	110.0 ± 0.5	
	$\angle(CC_1H_b)$	110.98	111.04		
	$\angle(HC_2H)$	106.28	106.15		
cyclobutane	$r(CC)$	1.554	1.548	1.548 ± 0.003	*c*
	$r(CH_e)$	1.080	1.085	1.092 ± 0.010 (av)	
	$r(CH_a)$	1.082	1.085		
	$\angle(CCC)$	89.01	89.01	~87.2	
	$\angle(CCH_e)$	116.96	117.08		
	$\angle(CCH_a)$	112.17	112.30		
	$\angle(HCH)$	108.59	108.18		
	$\tau(CCCC)$	14.98	14.96	~25	
cyclopentane	$r(C_1C_2)$	1.538		1.546 ± 0.001	*d*
	$r(C_2C_3)$	1.545			
	$r(C_3C_4)$	1.552			
	$r(C_1H_6)$	1.084		1.114 ± 0.002 (av)	
	$r(C_1H_7)$	1.084			
	$r(C_2H_8)$	1.084			
	$r(C_2H_9)$	1.083			
	$r(C_3H_{10})$	1.083			
	$r(C_3H_{11})$	1.084			
	$\angle(C_5C_1C_2)$	104.55		102.13	
	$\angle(C_1C_2C_3)$	105.36		103.95	
	$\angle(C_2C_3C_4)$	106.57		106.13	
	$\angle(C_2C_1H_6)$	112.30			
	$\angle(C_2C_1H_7)$	110.22			
	$\angle(C_1C_2H_8)$	109.90			
	$\angle(C_1C_2H_9)$	112.19			
	$\angle(C_2C_3H_{10})$	111.14			
	$\angle(C_2C_3H_{11})$	110.51			
	$\angle(H_6C_1H_7)$	107.28			
	$\angle(H_8C_2H_9)$	107.10			
	$\angle(H_{10}C_3H_{12})$	106.78			
	$\tau(C_1C_2C_3C_4)$	20.37		25.01	
	$\tau(C_5C_1C_2C_3)$	40.27		33.04	
cyclohexane	$r(CC)$	1.534		1.536 ± 0.002	*e*
	$r(CH_e)$	1.086		1.121 ± 0.004 (av)	
	$r(CH_a)$	1.088			
	$\angle(CCC)$	111.37		111.4 ± 0.2	
	$\angle(CCH_e)$	110.08			
	$\angle(CCH_a)$	109.13			
	$\angle(HCH)$	106.94		107.5 ± 1.5	
	$\tau(CCCC)$	55.03		54.9 ± 0.4	
bicyclo[1.1.0]butane	$r(C_1C_3)$	1.478	1.466	1.497 ± 0.003	*f*
	$r(C_2C_3)$	1.502	1.489	1.498 ± 0.004	
	$r(C_1H)$	1.062	1.070	1.071 ± 0.004	
	$r(C_2H_e)$	1.074	1.078	1.093 ± 0.008	
	$r(C_3H_a)$	1.076	1.083	1.093 ± 0.008	
	$\angle(C_1C_2C_3)$	58.95	58.90	59.96	
	$\angle(C_1C_3C_2)$	60.52	60.50		
	$\angle(C_2C_1C_4)$	97.62	97.91	98.29	
	$\angle(C_3C_1H)$	133.43	132.51	128.36 ± 0.23	
	$\angle(C_1C_2H_e)$	117.31	117.10		
	$\angle(C_1C_2H_a)$	119.37	119.50		
	$\angle(HC_2H)$	113.90	113.98	115.57	
bicyclo[2.2.1]heptane	$r(C_1C_2)$	1.546		1.539 ± 0.012	*g*
	$r(C_2C_3)$	1.560		1.557 ± 0.025	
	$r(C_1C_7)$	1.544		1.560 ± 0.024	
	$r(C_1H)$	1.080			

Table IV (*Continued*)

		calcd			
compound	bond/angle	4-31G	6-31G*	obsd	ref
bicyclo[2.2.1]heptane	$r(C_2H_e)$	1.084			
	$r(C_2H_n)$	1.083			
	$r(C_7H)$	1.084			
	$\angle(C_1C_2C_3)$	103.19		103.3	
	$\angle(C_2C_1C_6)$	108.32			
	$\angle(C_1C_7C_4)$	94.39		93.1 ± 1.7	
	$\angle(C_1C_2H_e)$	110.89			
	$\angle(C_1C_2H_n)$	112.09			
	$\angle(HC_2H)$	107.49			
	$\angle(HC_7H)$	112.09			
bicyclo[2.2.2]octane	$r(C_1C_2)$	1.536		1.538 ± 0.015	*h*
	$r(C_2C_3)$	1.551		1.552 ± 0.029	
	$r(C_1H)$	1.084		1.107 ± 0.009	
	$r(C_2H)$	1.084			
	$\angle(C_1C_2C_3)$	109.64		109.7 ± 0.7	
	$\angle(C_6C_1C_2)$	109.31			
	$\angle(C_1C_2H)$	109.56			
	$\angle(C_3C_2H)$	110.75			
	$\angle(HC_2H)$	106.53		110.1 ± 5.6	
[1.1.1]propellane	$r(C_1C_2)$	1.528	1.502		
	$r(C_1C_3)$	1.600	1.543		
	$r(C_2H)$	1.070	1.075		
	$\angle(C_1C_2C_3)$	63.13	59.11		
	$\angle(HC_2H)$	114.72	114.52		
[2.1.1]propellane	$r(C_1C_2)$	1.556	1.547		
	$r(C_1C_4)$	1.647	1.594		
	$r(C_1C_5)$	1.510	1.493		
	$r(C_2C_3)$	1.550	1.539		
	$r(C_2H)$	1.079	1.082		
	$r(C_5H_e)$	1.073	1.078		
	$r(C_5H_n)$	1.072	1.077		
	$\angle(C_1C_2C_3)$	91.71	91.03		
	$\angle(C_1C_5C_4)$	66.06	64.57		
	$\angle(C_2C_1C_4)$	88.21	88.97		
	$\angle(C_4C_1C_5)$	56.96	57.72		
	$\angle(C_5C_1C_6)$	96.50	97.27		
	$\angle(C_1C_2H)$	112.96	113.13		
	$\angle(C_1C_5H_e)$	116.27	116.82		
	$\angle(C_1C_5H_n)$	118.47	118.42		
	$\angle(HC_2H)$	108.33	108.12		
	$\angle(HC_5H)$	113.47	113.48		
[2.2.1]propellane	$r(C_1C_2)$	1.545			
	$r(C_1C_4)$	1.534			
	$r(C_2C_3)$	1.581			
	$r(C_1C_7)$	1.497			
	$r(C_2H_e)$	1.082			
	$r(C_2H_n)$	1.080			
	$r(C_7H)$	1.071			
	$\angle(C_1C_2C_3)$	89.14			
	$\angle(C_2C_1C_4)$	90.86			
	$\angle(C_2C_1C_6)$	128.49			
	$\angle(C_1C_7C_4)$	61.64			
	$\angle(HC_7H)$	113.57			
	$\angle(HC_2H)$	108.38			
	$\angle(C_1C_2H_e)$	115.66			
	$\angle(C_1C_2H_n)$	113.68			
[2.2.2]propellane	$r(C_1C_2)$	1.553	1.551		
	$r(C_1C_4)$	1.526	1.512		
	$r(C_2C_3)$	1.585	1.575		
	$r(C_2H)$	1.082	1.082		
	$\angle(C_1C_2C_3)$	88.91	88.85		
	$\angle(HC_2H)$	107.50	107.19		

[a] Iijima, T. *Bull. Chem. Soc. Jpn.* **1972**, *45* 1291. [b] Bradford, W. F.; Fitzwater, S.; Bartell, L. S. *J. Mol. Struct.* **1977**, *38*, 185. [c] Almennigen, A.; Bastiansen, O.; Skanke, P. N. *Acta Chem. Scand.* **1961**, *15*, 711. [d] Adams, W. J.; Geise, H. J.; Bartell, L. S. *J. Am. Chem. Soc.* 1970, *92*, 5013. [e] Bastiansen, O.; Fernholt, L.; Seip, H. M. *J. Mol. Struct.* 1973, *18*, 163. [f] Cox, K. W.; Harmony, M. D.; Nelson, G.; Wiberg, K. B. *J. Am. Chem. Soc.* **1968**, *90*, 3395. [g] Yokozeki, A.; Kuchitsu, K. *Bull. Chem. Soc. Jpn.* 1971, *44*, 2356. [h] Yokozeki, A.; Kuchitsu, K.; Morino, Y. *Ibid.* 1970, *43*, 2017.

greater s character in these bonds.

Previous calculations[11] and experimental data from an X-ray crystallographic study of a [3.1.1]propellane derivative[9] suggested that the electron density in the region of the central propellane bond of the small ring propellanes would be much smaller than for a normal C–C bond. With good wave functions in hand, we

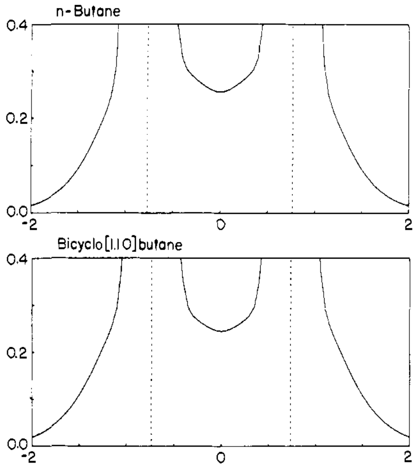


Figure 1. Electron density (e. Bohr^{-3}) along the C_2–C_3 bond of butane (upper curve) and along the central bond of bicyclo[1.1.0]butane (lower curve). The locations of the carbons are shown by the vertical dashed lines, and the distances are given in Å.

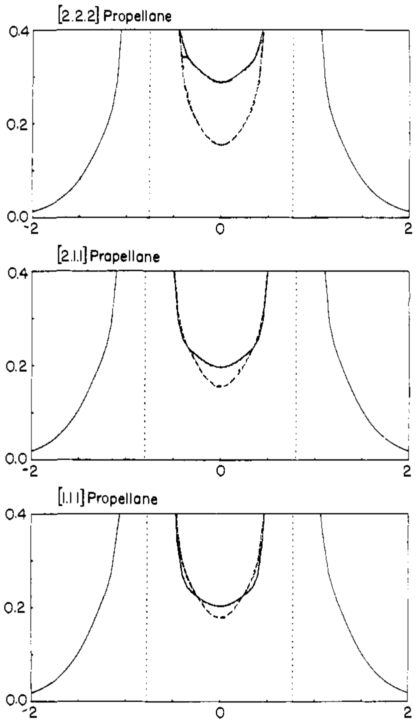


Figure 2. Electron density along the central bonds of the [2.2.2]-, [2.1.1]-, and [1.1.1]propellanes. The solid lines give the calculated values, and the dashed lines give the densities expected for isolated carbon atoms at the calculated bond length using the model described in the text. The shaded area represents the deformation density.

have examined the calculated electron density distributions in these compounds.

The changes in electron density along the central carbon–carbon bonds are shown in Figures 1 and 2. It can be seen that the electron density along the C–C bond is rather similar for the 2,3-bond in butane and the central bond of bicyclo[1.1.0]butane (Figure 1). With the propellanes, however, large differences are found (Figure 2), with a relatively high electron density at the center of the central C–C bond of the [2.2.2]propellane, and a rather low value at the center of the corresponding bonds of the [1.1.1] and [2.1.1]propellanes.

A quantity of interest is the deformation density, or the difference between the observed density and that expected for the isolated atoms.[25] This requires a suitable model for the isolated

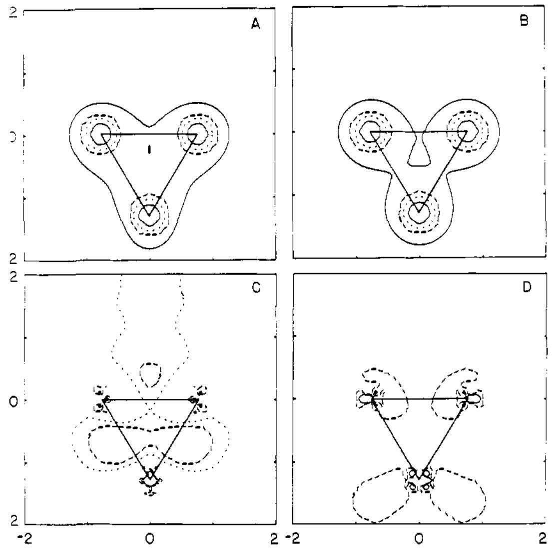


Figure 3. Electron density contours for the [1.1.1]propellane. Plot A is the calculated density for a plane containing the central bond and one of the methylene carbons. Plot B gives the density expected for three isolated carbon atoms placed at the bonding distances. Plot C gives the contours for increased electron density in A over that in B, and plot D gives the contours for decreased electron density.

atom. In the case of the small ring propellanes, these are no atoms in the direction away from the central bonds. Thus, a conservative estimate[26] of the isolated atom electron density may be derived by taking a line drawn through the bridgehead carbons and using the density along this line in the direction away from the central bond. Summing the densities contributed by the two carbons, one obtains the dashed line shown in Figure 2. The deformation density is then given by the shaded area in the figure.

In the case of the [1.1.1]propellane, the deformation density is rather low, in accord with the earlier results,[9,11] and the [2.1.1]propellane is rather similar. Thus, these compounds have very little traditional bonding character (i.e., bond order,[4] or deformation density). Despite this, the [1.1.1]propellane has a relatively strong "bond" in the sense that dissociation to the singlet diradical involves a large increase in energy.[19] In contrast, the [2.2.2]propellane, which is thermally quite labile, shows a considerably larger deformation density, and its central bond is quite similar to that of the C_2–C_3 bond of butane. The consequence of these differences with respect to bond strengths, vibrational frequencies, and other properties remain to be determined.

We should like to have a better understanding of the electron density distribution in compounds such as the [1.1.1]propellane. The electron density contours were calculated for a plane containing the central bond and one of the methylene carbons (Figure 3). The contours expected for three carbon atoms, using the model described above, also were calculated and are given in plot B. The regions of increased electron density in the propellane are shown in plot C, whereas the regions of decreased density are shown in plot D. It can be seen that there is little variation along the propellane bond, with both increases and decreases in electron density with respect to the model atoms. In the case of the methylene group, there is a large electron density shift into the bonding region, as is found with most normal bonds. The deformation density plots (Figure 3C,D) are remarkably similar to the experimental plots for the [3.1.1]propellane studied by Dunitz et. al.[9]

Despite the lack of traditional bonding character for the central bond, our estimates of the difference in energy between the [1.1.1]propellane and a singlet diradical with the geometry of bicyclo[1.1.1]pentane suggests a large "bond dissociation energy".[17]

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(25) Dunitz, J. D. "X-ray Analysis and the Structure of Organic Molecules"; Cornell University Press: Ithaca, NY 1979; p 391 ff.

(26) This is conservative in the sense that if the bonding character is low in the bonding region, one might expect a larger than normal electron density away from the bonding region. Thus, the latter might be larger than the "best" estimate for the atom in question.

How can one have a relatively strong "bond" without much bonding character? This question is being explored by calculating the energy changes on stretching the central bond in the propellane by using the GVB formalism,[27] which allows correct dissociation, as well as by both a theoretical and experimental study of the molecular vibrations of the [1.1.1]propellane. The results of these investigations will be reported at a later time.

Calculations

The calculations were carried out with the program GAMESS[28] along with standard basis sets.[14] The geometry optimization criterion for the smaller compounds was 0.0005 H/Bohr, whereas for the larger compounds it was 0.001 H/Bohr. In the tables, the basis set for the calculation is given above the line, and that used for the optimization is given below the line.

Acknowledgment. This investigation was supported by NSF Grant CHE-81-21421. The computer was obtained with the aid of grants from the NSF (CHE-80-23366) and the Dreyfus and Heyl Foundations.

Registry No. [1.1.1]Propellane, 35634-10-7; [2.1.1]propellane, 36120-91-9; [2.2.1]propellane, 36120-90-8; [2.2.2]propellane, 36120-88-4; ethane, 74-84-0; butane, 106-97-8; cyclopropane, 75-19-4; cyclobutane, 287-23-0; bicyclo[1.1.0]butane, 157-33-5; bicyclo[2.1.0]pentane, 185-94-4; bicyclo[2.2.0]hexane, 186-04-9; hydrogen, 1333-74-0; methane, 74-82-8; propane, 74-98-6; cyclopentane, 287-92-3; cyclohexane, 110-82-7; bicyclo[1.1.1]pentane, 311-75-1; bicyclo[2.1.1]hexane, 285-86-9; bicyclo[2.2.1]heptane, 279-23-2; bicyclo[2.2.2]octane, 280-33-1.

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(27) Bobrowicz, F. W.; Goddard, W. A. *Mod. Theor. Chem.* **1978**, *3*.

(28) Dupuis, M.; Spangler, D.; Wendoloski, J. J. National Resource for Computation in Chemistry Program QG01, 1980. The program is based on HONDO: Dupuis, M.; Rys, J.; King, H. *QCPE* **1977**, *11*, 338.

Carbon–Carbon Bond Formation by Condensation of Metal-Activated Olefins. Regio- and Stereoselectivity of Cycloaddition Reactions

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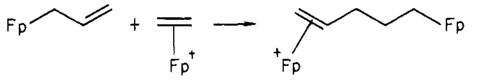
Contribution from the Department of Chemistry, Brandeis University, Waltham, Massachusetts 02254. *Received April 27, 1982*

Abstract: Monodeprotonation of $Fp_2(\eta^2,\eta^2\text{-}1,7\text{-octadiene})(BF_4)_2$ [**4**, Fp = $C_5H_5Fe(CO)_2$] at 0 °C with $n\text{-}Bu_3N$ leads to the formation of the trans-1,2-disubstituted cyclopentane complex **6**-t as the major product. Evidence is provided that this is the kinetic product. The structure of **6**-t is established by degradation to *trans*-1-methyl-2-vinylcyclopentane and by comparison of this with synthetic material. By contrast, the homologous 1,8-nonadiene complex **11** is converted to a 1:1 mixture of cis- and trans-1,2-disubstituted cyclohexane complexes **13**-c and **13**-t on treatment with $n\text{-}Bu_3N$. The structures of these complexes were also established by degradation and synthesis. The relationship between geometrical isomerism in the intermediate dinuclear complexes **5** and **12**, generated by deprotonation of **4** and **11**, and the stereochemistry of the product complexes **6** and **13** have been examined. The synthesis of cis and trans isomers of **5** and **12** has been accomplished through monoprotonation of the related *cis,cis*- and *trans,trans*-octadiene and -nonadiene complexes **17** and **18**. Protonation of **17**-t gave almost entirely **6**-t, while similar treatment of **17**-c led to the formation of a mixture of **6**-c and **6**-t in low yield. The behavior of the homologous diene complexes **18**-c and **18**-t was substantially different. Monoprotonation of **18**-c gave a 3:1 mixture of **13**-c and **13**-t, while protonation of **18**-t gave a 2:1 mixture of **13**-t and **13**-c. These are minimum measures of the stereoselectivities for these reactions since recovered starting material is partially isomerized. The results may be accommodated if the cyclization reaction is initiated by preferential interaction of the proton with *both* activated olefin centers in an extended form of complexes **17** and **18**. This results in the generation of transition state III from **18**-c and of II′ from **18**-t, which in turn leads to the formation of cyclization products **13**-c and **13**-t, respectively.

Polyene cyclization is now well established as an important step in the biogenesis of terpenes, and an extensive literature concerned with the mechanism and synthetic applications of polyene cyclization and of the closely related ene reaction exists.[1] Within this class of reaction may be included the large number of transition-metal-catalyzed polyene cyclizations,[2] although a detailed mechanism for some of these reactions is as yet undefined. For those cyclization reactions which proceed through well-defined ionic intermediates the methodologies by which initiating electrophile centers are generated and by which ultimate cationic centers are quenched have been classical ones. However, we have shown that olefins may be activated as nucleophilic centers or transformed to electrophilic centers through allylic substitution by the $C_5H_5Fe(CO)_2$ group or by π complexation with the $C_5H_5Fe(CO)_2$ cation.[3] The olefin components so activated undergo a rapid condensation at room temperature, in a reaction which may be regarded as an analogue of a classical ionic condensation (eq 1, Fp = $C_5H_5Fe(CO)_2$).



(1)

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(1) For a recent review, with leading references, see: Sutherland, J. K. *Chem. Soc. Rev.* **1980**, *13*, 426.

(2) Jolly, P. W.; Wilke, G. "The Organic Chemistry of Nickel"; Academic Press: New York, 1975; Vol. II, Chapter III. Tsuji, J. "Organic Synthesis by Means of Transition Metal Complexes"; Springer-Verlag: Berlin, 1975; Chapter VII. Baker, R.; Cookson, R. C.; Vinson, J. R. *J. Chem. Soc., Chem. Commun.* **1974**, 575. Davis, R. E.; Dodds, T. A.; Hseu, T.-H.; Wagnon, J. C.; Devon, T.; Tancrede, J.; McKennis, J. S.; Pettit, R. *J. Am. Chem. Soc.* **1974**, *96*, 7562. Davis, R.; Green, M.; Hughes, R. P. *J. Chem. Soc., Chem. Commun.* **1975**, 405. Paquette, L. A.; Ley, S. V.; Maiorana, S.; Schneider, D. F.; Broadhurst, M. J.; Boggs, R. A. *J. Am. Chem. Soc.* **1975**, *97*, 4658.

(3) Lennon, P. J.; Rosan, A.; Rosenblum, M.; Tancrede, J.; Waterman, P. *J. Am. Chem. Soc.* **1980**, *102*, 7033.

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