# Vibrational Spectrum, Structure, and Energy of [1.1.1]Propellane

Kenneth B. Wiberg,[*†] **William P. Dailey,**[†] **Frederick H. Walker,**[†] **Sherman T. Waddell,**[†] **Louis S. Crocker,**[†] **and Marshall Newton***

Contribution from the Department of Chemistry, Yale University, New Haven, Connecticut 06511, and the Department of Chemistry, Brookhaven National Laboratory, Upton, New York. Received May 8, 1985

Abstract: The structure of [1.1.1]propellane (bond lengths and angles) was determined from an analysis of the rotational components of the infrared bands of the parent compound and of its d_6 derivative, and it was found to be in good agreement with the structure calculated including electron correlation. The central C–C bond length was 1.60 ± 0.02 Å which is ~0.09 Å longer than that in cyclopropane. The infrared and Raman spectra were obtained and are in good agreement with the calculated spectrum. A constrained adjustment of the calculated force field gave a set of "best" force constants. The stretching force constant for the central C–C bond was found to be about the same as that for the symmetric combination of the other C–C bonds. The intensities of the infrared bands were determined and were converted to dipole moment derivatives. The relationship of the derivatives to the charge distribution is discussed. The enthalpy of formation of the propellane was estimated from its enthalpy of reaction with acetic acid and was found to be in good agreement with that predicted via ab initio calculations.

The unique structure and remarkable stability of [1.1.1]propellane (**1**)[1] has prompted our interest in its geometrical parameters (bond lengths and angles), the strengths of its bonds, its charge distribution, and its energy. The study of **1** also provides a valuable test of theory since its structure, energy, and reactivity were predicted on the basis of ab initio molecular orbital theory before the compound was prepared. Information about the force constants and dipole moment derivatives may be related to the quantities mentioned above. We now present the results of a detailed investigation of its vibrational spectrum, as well as an experimental estimate of its enthalpy of formation.

1
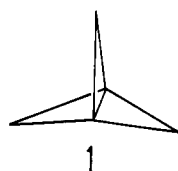
Assuming that the six hydrogens will be in a plane, the propellane will have D_{3h} symmetry. One would then expect $4A_1'$, $2A_2'$, $6E'$, $1A_1''$, $2A_2''$, and $3E''$ modes. Only the E' and A_2'' modes should be infrared active, whereas the A_1', E', and E'' modes should be Raman active. It is now possible to calculate the frequencies of the vibrational modes with reasonable accuracy,[2,3] and such a calculation can be of considerable help in assigning observed spectra. The calculation was carried out at the SCF level with use of the 6-31G* basis set. A flexible basis of this type is needed in order to accommodate the bonding in **1**.[4] The calculated equilibrium geometry was used as the starting point, and each of the symmetrically distinct atoms was moved in turn by 0.01 bohr in the x and then y and z directions. In each case, the gradient of the energy with respect to the coordinates was calculated analytically,[2] and the second derivatives (force constants) were obtained numerically. The vibrational problem was solved in cartesian coordinates,[5] giving the frequencies listed in Table I.

The calculated frequencies are somewhat larger than the observed frequencies for two reasons. First, they are harmonic whereas the latter are anharmonic. Second, correction for electron correlation tends to decrease force constants. We have found that the SCF C–H stretching frequencies calculated by using the 6-31G* basis set should be scaled with the factor 0.91 ± 0.01, whereas the other modes should be scaled with 0.88 ± 0.02.[6] The scaled frequencies are given in the second column of Table I. The ab initio calculation also gives the polar tensors[7] from which the infrared band intensities may be evaluated. The infrared spectrum

Scheme I
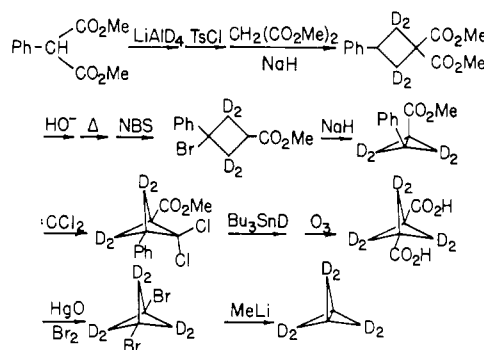
is predicted to have two strong A_2'' modes, two strong E' modes, and four weak E' modes.

The infrared spectrum of **1** is shown in Figure 1, and the band positions are given in Table II. The bands at 612 and 1096 cm⁻¹ are clearly parallel bands (Figure 2) and therefore must be A_2''. Their frequencies agree well with the predicted values. The two strong C–H stretching modes must be E', and their frequencies and intensities also agree well with the prediction. Perpendicular band types were found at 1186 and 1459 cm⁻¹ (Figure 3) and again must be E'. In addition, weak bands were found at 1083 cm⁻¹ in a matrix at 15 K and at 529 cm⁻¹ in the gas phase which agree with the predicted frequencies and intensities.

In order to have more information for a normal coordinate analysis, we have prepared **1**-d_6 as shown in Scheme I.[8] The infrared spectrum is shown in Figure 1. The A_2'' bands were readily located at 575 and 918 cm⁻¹. The E' CH stretching fundamentals were at 2328 and 2204 cm⁻¹, and the other E' bands were located at 1211, 1033, 913, and 430 cm⁻¹.

The Raman spectrum of **1** was determined both in the gas phase and in the liquid phase and is shown in Figure 4. The band positions are given in Table III. The A_1' bands are easily recognized because of their strong Q branches in the gas-phase spectra

(1) Wiberg, K. B.; Walker, F. H. *J. Am. Chem. Soc.* **1982**, *104*, 5239.
(2) Pulay, P. "The Force Concept in Chemistry"; Deb, B., Ed.; Van Nostrand: New York, 1981.
(3) Pople, J. A.; Schlegel, H. B.; Krishnan, R.; DeFrees, D. J.; Binkley, J. S.; Frisch, M. J.; Whiteside, R. A.; Hart, R. F.; Hehre, W. J. *Int. J. Quantum Chem. Quantum Chem. Symp.* **1981**, *15*, 269.
(4) Wiberg, K. B. *J. Am. Chem. Soc.* **1983**, *105*, 1227.
(5) Gwinn, W. D. *J. Chem. Phys.* **1971**, *55*, 477.
(6) Wiberg, K. B.; Wendoloski, J. J. *J. Phys. Chem.* **1984**, *88*, 586.
(7) Biarge, J. F.; Herranz, J.; Morcillo, J. *An. R. Soc. Esp. Fis. Quim. Ser. A* **1961**, *57*, 81. Person, W. B.; Newton, J. H. *J. Chem. Phys.* **1974**, *61*, 1040.
(8) The preparation of unlabeled bicyclo[1.1.1]pentane-1,3-dicarboxylic acid has been reported: Applequist, D. A.; Renken, D. L.; Wheeler, J. W. *J. Org. Chem.* **1982**, *47*, 4985.

[†]Yale University.

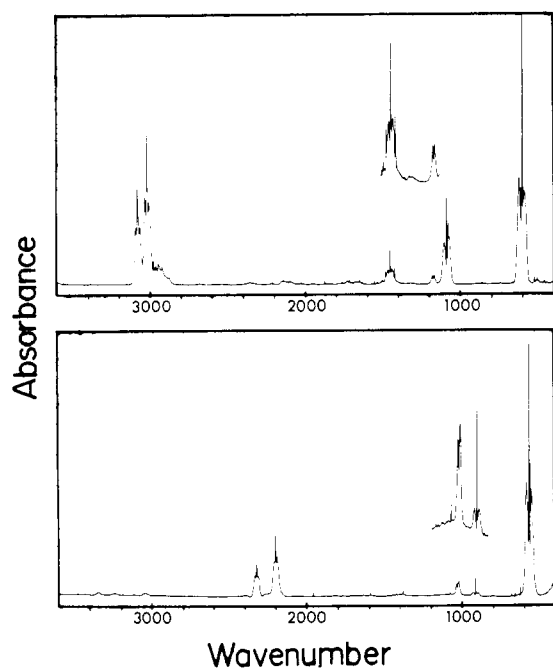**Table I.** Calculated Vibrational Spectrum of [1.1.1]Propellane (cm^{-1})

mode		d_0				d_6			
		calcd	scaled	obsd	int[a]	calcd	scaled	obsd	int[a]
A_1'	ν_1	3319.7	3020.9	3029.1		2418.7	2201.0	2209.8	
	ν_2	1696.5	1492.9	1501.7		1369.0	1228.5	1239.0	
	ν_3	1249.2	1099.3	1123.7		1146.2	1008.7	1022.1	
	ν_4	998.1	878.3	907.6		925.8	814.7	844.5	
A_2'	ν_5	3391.6	3086.4			2526.5	2299.1		
	ν_6	1059.0	931.9			812.1	714.6		
E'	ν_7	3396.8	3091.0	3079.9	34.0	2537.6	2309.2	2328.4	15.6
	ν_8	3311.8	3013.7	3019.6	64.2	2410.1	2193.2	2204.3	39.4
	ν_9	1652.2	1453.9	1458.9	0.6	1369.8	1205.4	1216	1.0
	ν_{10}	1356.0	1193.3	1186	2.8	1159.6	1020.4	1033	1.0
	ν_{11}	1202.5	1058.2	1083[b]	2.8	1008.0	887.0	913.4	3.2
	ν_{12}	584.0	513.9	529	1.0	472.9	416.2	430	0.6
A_1''	ν_{13}	1003.7	883.3			710.0	624.8		
A_2''	ν_{14}	1251.4	1101.2	1096.4	13.8	979.6	859.4	917.9	1.5
	ν_{15}	625.6	550.5	611.7	190.0	590.7	519.8	574.9	172.0
E''	ν_{16}	1275.2	1122.2	1145.8		1081.9	952.1	955.0	
	ν_{17}	1202.0	1057.8	1064.3		931.8	820.0		
	ν_{18}	784.2	690.1	713.9		661.1	581.8	607[c]	

[a] Calculated from ab initio force constants and polar tensors. Units: km/mol. The intensities for the E' modes is the sum of the calculated values for the two components. [b] Band observed in a matrix at 15 K. [c] Band observed in the liquid-phase Raman spectrum.
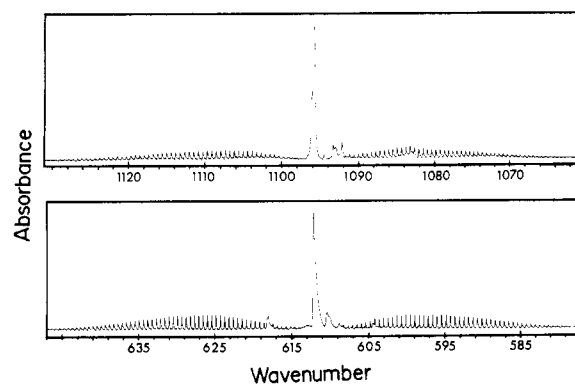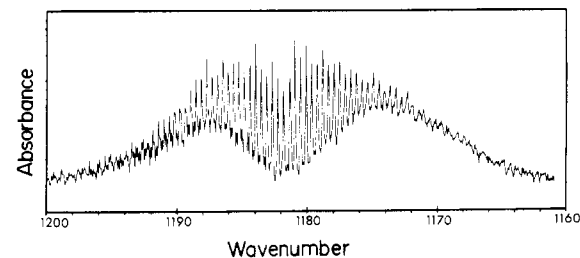
Table II. Infrared Bands

	1-d_0				1-d_6		
freq, cm^{-1}	rel int	band type	assign	freq, cm^{-1}	rel int	band type	assign
3079.9	s	⊥	ν_7	2328.4	m	⊥	ν_7
3019.6	s	⊥	ν_8	2204.3	m	⊥	ν_8
2980.7	w						
2949.0	w						
2924.0	w						
1458.9	m	⊥	ν_9	1216.	vw	⊥	ν_9
1186.	w	⊥	ν_{10}	1033	w	⊥	ν_{10}
1096.4	m	∥	ν_{14}	918	w	∥	ν_{14}
1083[a]	vw		ν_{11}				
611.7	vs	∥	ν_{15}	574.9	vs	∥	ν_{15}
529	w	⊥	ν_{12}	430	vw	⊥	ν_{12}

[a] Observed in the spectrum of a matrix at 15 K.

Figure 1. Infrared spectra of [1.1.1]propellane (upper) and [1.1.1]propellane-d_6.

Figure 2. High-resolution infrared spectra of ν_{14} and ν_{15} of [1.1.1]propellane.

Figure 3. High-resolution spectrum of ν_{10} of [1.1.1]propellane.

and their polarization which was determined for the liquid-phase spectra. Bands which met these criteria were found at 3029, 1502, 1124, and 908 cm^{-1} (gas phase) and are in good agreement with the predicted spectrum. In addition to bands which were coincident with the E' frequencies given above, depolarized bands were

found at 714, 1063, and 1146 cm^{-1} and must be assigned as E''.

The Raman spectrum of 1-d_6 also was determined and is shown in Figure 4. The A_1' bands were easily located at 2210, 1239, 1022, and 845 cm^{-1}. In addition to the bands which were coin-

Table III. Raman Bands[a]

gas phase	liquid phase	rel int	band type	polariz ratio	assign
			1-d_0		
3083.0	3075.2	m	E	0.61	ν_7
3029.1	3017.6	vs	A	0.04	ν_1
2988.6	2974.8	s	A	0.07	$2\nu_2$
2983.6	~2974		A		
2940.2	2919.9	m		0.02	$2\nu_4 + \nu_3$
2910.4	2898.0	w			
	2865.8	w			
1528.0	1528.0	vw	E	0.10	
1501.7	1496.6	w	A	0.08	ν_2
	1448.0	vw			
1435.0	1421.8	vw	E	0.60	$\nu_2 + \nu_{12}$
1222.5	1204.0	vw		0.02	$2\nu_{15}$
1182.4	1178	vw	E		ν_{10}
1145.8	1167	vw	E		ν_{16}
1129.8					
1123.7	1123.6	vs	A	0.05	ν_3
1116.7					
1084.7	1078	vw	E	0.51	ν_{11}
1064.3	1045	vw	E		ν_{17}
907.6	904.4	s	A	0.15	ν_4
713.9	710.6	w	E		ν_{18}
	529.4	w	E	0.55	ν_{12}
	464.8	vw			
			1-d_6		
2330.0	2324.5	m	E	0.61	ν_7
2262.0	2260.0	vw			$\nu_2 + \nu_3$
2209.8	2200.5	vs	A	0.11	ν_1
2180.8	2173.0	vw			
1284.0		vw	E		$\nu_{12} + \nu_{17}$
1239.0	1236.5	vs	A	0.05	ν_2
1211.1	1209.5	w	A	0.14	$2\nu_{18}$
1142.3	1124.0	vw	A	0.15	$2\nu_{15}$
1022.1	1021.5	vs	A	0.12	ν_3
955.0	949.5	w	E	0.62	ν_{16}
~918	913.5	w	E	0.59	ν_{11}
857.6	854.5	w	A	0.1	$2\nu_{12}$
844.5	841.5	vs	A	0.08	ν_4
	606.5	vw			ν_{18}
~432	426.5	w	E	0.60	ν_{12}

[a] An A-type band is characterized by a strong Q branch whereas the E-type bands have weak Q branches.

Table IV. Product Rule Ratios

species	calcd	obsd
A_1'	1.960	1.963
E'	3.822	3.626
A_2''	1.357	1.270

Figure 4. Raman spectra of [1.1.1]propellane (A, gas phase; B, liquid phase) and [1.1.1]propellane-d_6 (C, gas phase; D, liquid phase). In B and D the dashed line gives the spectrum observed with a crossed polarizer.

from the center of mass to a bridgehead carbon ($r_1/2$); the distance from the center of mass to a methylene carbon (r_2); the C–H bond length (r_H); and the HCH bond angle (β). It will not readily be possible to obtain four experimental parameters and so some assumptions must be made.
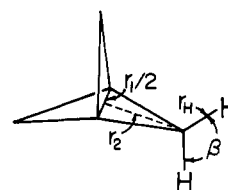
It is known that extended basis set SCF geometry optimizations reproduce bond angles quite well and that electron correlation does not significantly affect the calculated angles.[9] The HCH angle in **1** was predicted to be 114.52° and was taken as one of the assumed parameters. In the case of cyclopropane, the angle was calculated to be 114.0°,[10] which agrees with the observed values.[11] Thus, little error should be associated with the above angle.

The equilibrium CH bond lengths for cyclopropane and for **1** are calculated to be the same.[4,6] Assuming that equality also holds

cident with the E' infrared bands, depolarized bands were found at 955 and 607 cm⁻¹ which agreed with the predicted frequencies for the E'' modes. The final vibrational assignments are given in Table I where the values were derived from gas-phase spectra except where noted.

The product rule was well satisfied by the A_1' frequencies (Table IV). It was reasonably well satisfied by the E' frequencies, but there was a significant deviation for the A_2'' frequencies. However, the latter appear to be especially well established because of their unique band shapes. The deviation is not surprising since the calculated value is based on the observed (anharmonic) frequencies whereas the rule applies to the harmonic frequencies. The product rule ratio could not be calculated for the E'' frequencies because ν_{17} for **1-d_6** has not been located. The product rule suggests that it should be at ~825 cm⁻¹.

A further analysis of the vibrational spectrum requires that we have the structure parameters for **1** so that the appropriate **G** matrix may be constructed. These parameters are interesting in themselves so that one might compare them with the theoretically calculated structure.

The high symmetry of **1** makes it practical to obtain structural parameters from the vibrational spectrum. The structure of **1** may be completely defined by using only four parameters: the distance
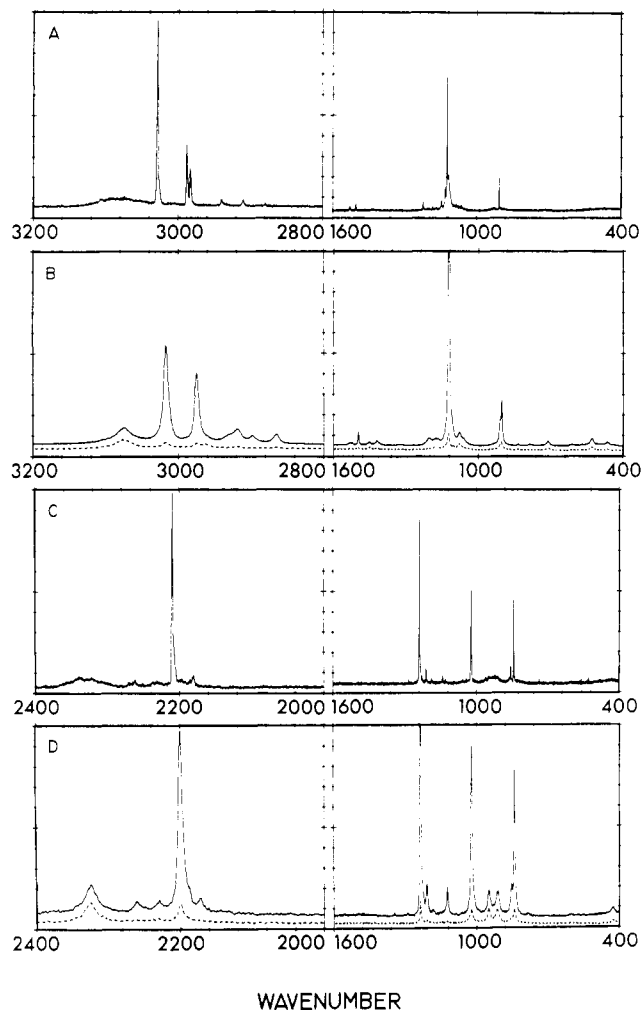
(9) DeFrees, D. J.; Levi, B. A.; Pollack, S. K.; Hehre, W. J.; Binkley, J. S.; Pople, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 4085. DeFrees, D. J.; Raghavachari, K.; Schlegel, H. B.; Pople, J. A. *Ibid.* **1982**, *104*, 5576.
(10) Wiberg, K. B.; Wendoloski, J. J. *J. Am. Chem. Soc.* **1982**, *104*, 5679.
(11) Butcher, R. J.; Jones, W. J. *J. Mol. Spectrosc.* **1964**, *47*, 64. Jones, W. J.; Stoicheff, B. P. *Can. J. Phys.* **1964**, *42*, 2259.

Table V. Rovibrational Transitions for A$_2''$ Bands of [1.1.1]Propellane (cm^{-1})

J	d$_0$				d$_6$	
	R(J)	P(J)	R(J)	P(J)	R(J)	P(J)
6	615.747		1100.409			
7	616.319	607.699	1100.986			571.626
8	616.891	607.125	1101.563	1091.772	597.116	571.147
9	617.465	606.546	1102.150	1091.202	579.583	570.665
10		605.960	1102.728	1090.632	580.040	570.186
11	618.606	605.381	1103.306	1090.059	580.508	569.705
12	619.177	604.805	1103.891	1089.490	580.968	569.226
13	619.747	604.228	1104.472	1088.920	581.423	568.750
14	620.315	603.637	1105.051	1088.349	581.882	568.274
15	620.877	603.059	1105.638	1087.778	582.344	567.799
16	621.444	602.480	1106.222	1087.209	582.803	
17	622.012	601.887	1106.804	1086.639	583.260	566.837
18	622.581	601.307	1107.388	1086.073	583.713	566.354
19	623.144	600.726	1107.971	1085.507	584.167	565.870
20	623.703	600.141	1108.559	1084.944	584.620	565.388
21	624.271	599.559	1109.144	1084.376	585.072	564.904
22	624.841	598.967	1109.732	1083.813	585.523	564.419
23	625.407	598.387	1110.319	1083.249	585.975	563.928
24	625.963	597.802	1110.910	1082.691	586.427	563.439
25	626.530	597.213	1111.496	1082.124	586.878	562.953
26	627.094	596.631	1112.089	1081.566	587.329	562.468
27	627.651	596.040	1112.669	1081.001	587.778	561.977
28	628.217	595.461	1113.256	1080.442	588.219	561.482
29	628.777	594.871	1113.844	1079.881	588.663	560.992
30	629.336	594.288	1114.438	1079.319	589.109	560.504
31	629.900	593.703	1115.022	1078.763	589.556	560.005
32	630.461	593.114	1115.613	1078.201	589.990	559.515
33	631.020	592.533	1116.199	1077.645	590.435	559.015
34	631.584	591.941	1116.791	1077.084	590.870	558.520
35	632.137	591.360	1117.377	1076.528	591.310	558.015
36	632.701	590.766	1117.963	1075.968	591.750	557.523
37	633.255	590.184	1118.552	1075.410	592.185	557.021
38	633.818	589.591	1119.149	1074.851	592.625	556.531
39	634.371	589.008	1119.726	1074.289	593.058	556.028
40	634.934	588.414	1120.319	1073.731	593.492	555.537
41	635.484	587.830	1120.900	1073.170	593.929	555.034
42	636.048	587.237	1121.493	1072.617	594.355	554.527
43	636.597	586.647	1122.074	1072.058	594.786	554.023
44	637.159	586.060		1071.505	595.221	
45	637.709	585.466		1070.940	595.646	
46	638.262	584.881				
47	638.818	584.285				
48	639.366	583.697				
49	639.918	583.106				
50	640.474	582.508				
51		581.916				

Table VI. Inertial Constants for [1.1.1]Propellane

(a) 1

	ν_{15} 611.73	ν_{14} 1096.37
origin		
B$''$ (cm^{-1})	0.28708 ± 0.00004	0.28719 ± 0.00004
B$'$ (cm^{-1})	0.28687 ± 0.00004	0.28741 ± 0.00005

av B$'$ = 0.28714 ± 0.00006 cm^{-1}

(b) 1-d$_6$

origin	ν_{15} 574.93
B$'$ (cm^{-1})	0.23426 ± 0.0004
B$''$ (cm^{-1})	0.23466 ± 0.0004

for the zero-point CH bond lengths (r_H), we simply employed the observed cyclopropane value (r_H = 1.083 Å) for **1**.

The A$_2''$ bands (Figure 2) provide an opportunity to determine I_x or I_y (which are equal). The analysis may be carried out in the same fashion as for a diatomic molecule. The transitions were assigned, and a plot of $\nu_R(J) - \nu_P(J + 2)$ against $(2J + 3)$ gave a good linear relationship with a slope of $2B''$ (Figure 5).[12]

Figure 5. Plot of spacings of rotational components of ν_{14} against $2J + 3$ to give B''.

Similarly, a plot of $\nu_R(J) - \nu_P(J)$ against $(2J + 1)$ gave $2B'$. The values obtained from the two bands are summarized in Table VI. The two independent values of B'' are in good agreement, giving an average value of 0.28714 ± 0.00006 cm^{-1} or 58.739 amu Å^2.

(12) Herzberg, G. "Molecular Spectra and Molecular Structure. II. Infrared and Raman Spectra of Polyatomic Molecules"; Van Nostrand: Princeton, NJ, 1945.
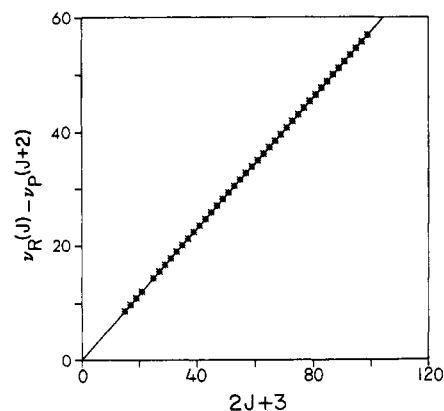
(13) Duncan, J. L.; McKean, D. C.; Bruce, A. J. *J. Mol. Spectrosc.* **1979**, *74*, 361.

The E_1 band at 1186 cm^{-1} is well enough resolved (Figure 3) so that its structure could be analyzed. The band consists of a series of Q branches arising from transitions between different K sublevels. After the K sublevels were assigned, a plot of $^RQ_{K-1}$ $- ^PQ_{K+1}$ against K gave a straight line with a slope of $4(C'' - \zeta C' - B'') = -0.84799 \pm 0.00092$. In order to obtain C'' it is necessary to have both C' and ζ. A reasonable assumption would be to set C' equal to C'', while ζ could be obtained from a normal coordinate analysis. However, the accuracy of this method of obtaining ζ is not sufficient for the present purpose.

Another way in which to obtain additional information is by examining an isotopically labeled derivative of **1**. The parallel band of **1**-d_6 at 575 cm^{-1} was examined and gave the rotational constants summarized in Table VI. The parallel band at 917 cm^{-1} could not be analyzed in the same fashion because the P branch was distorted by interaction with another transition. The R branch was, however, well reproduced by using the parameters in Table VI.

The $I_x = I_y$ moments of inertia are given by eq 1, and a similar expression may be written for **1**-d_6 replacing m_H by m_D and r_H by r_D. The difference between the moments for **1** and **1**-d_6 is then given by eq 2. Here, $\Theta = 60 - \beta/2$, $\o = 120 - \beta/2$, and $r_D = $

$$I_x = I_y = 2m_C(r_1/2)^2 + 2m_C(r_2 \sin 60)^2 +$$
$$2m_H(r_H \sin \beta/2)^2 + 2m_H(r_2 \sin 60 + r_H \sin (60 - \beta/2))^2 +$$
$$2m_H(r_2 \sin 60 + r_H \sin (\beta/2 - 30))^2 \quad (1)$$

$$I_x(H) - I_x(D) = 4(\sin 60)^2(m_D - m_H)(r_2)^2 +$$
$$4(\sin 60)(m_D r_D \sin \Theta + m_D r_D \sin \o - m_H r_H \sin \Theta -$$
$$m_H r_H \sin \o)r_2 + 2m_D r_D^2 \sin^2 \Theta + 2m_D r_D^2 \sin^2 \o -$$
$$2m_H r_H^2 \sin^2 \Theta - 2m_H r_H^2 \sin^2 \o + 2(m_D r_D^2 - m_H r_H^2) \sin^2 \beta/2 \quad (2)$$

$r_H - 0.002$.[13] After substituting the assumed H-C-H angle (β) and C-H bond length (r_H), the equation may be solved for r_2. It was found to be 1.290 Å. In order to see how the assumed methylene group parameters would affect r_2, the bond length was varied by 0.02 Å and the angle was varied by 2°. This led to a variation in r_2 of 0.01 Å. The bridgehead–bridgehead distance may now be calculated from eq 1 and is 1.60 ± 0.02 Å. The bridgehead–methylene C-C distance may be obtained from the above and was found to be 1.522 ± 0.002 Å. The structure has recently been examined by electron diffraction using our moment of inertia as a constraint,[14] and here the two C-C bond lengths were found to be 1.596 ± 0.005 and 1.525 ± 0.002 Å, respectively. It can be seen that the two structural determinations are in very good agreement.

Using the CC bond length of cyclopropane (1.514 Å)[11] as a reference value, we find that the side bonds in **1** are normal, whereas the bridgehead–bridgehead separation (r_1) reflects appreciable elongation. Previously reported SCF calculations[4] with the 6-31G* basis accounted for only about half of this elongation (defined relative to the cyclopropane value).

Accordingly, we have carried out a series of calculations for **1**, in which successively greater degrees of electron correlation are included in the wave function: namely, a 1-pair GVB[15] calculation in which the highest occupied SCF MO ($(a')^2$) is correlated with the corresponding antibonding molecular orbital ($(a_1)^2 \rightarrow (a_2'')^2$), and calculations based on second- and third-order Møller-Plesset theory (MP2 and MP3).[16] MP2 and MP3 calculations also were carried out for cyclopropane. In each case, the CC bond lengths were optimized, using the CH bond lengths and angles obtained at the SCF level.[4,6] To provide further comparisons with **1** we also carried out UHF, MP2, and MP3 calculations (with geometry optimization at the UHF level only)

(14) Hedberg, L.; Hedberg, K. *J. Am. Chem. Soc.*, following paper in this issue.

(15) Hay, P. J.; Hunt, W. J.; Goddard, W. A., III *J. Am. Chem. Soc.* **1972**, *94*, 8293.

(16) (a) Moller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618. (b) Binkley, J. S.; Pople, J. A. *Int. J. Quantum Chem.* **1975**, *9*, 229. (c) Pople, J. A.; Binkley, J. S.; Seeger, R. *Ibid.* **1976**, *10S*, 1.

Table VII. Perpendicular Band of [1.1.1]Propellane

K	^RQ_K	^PQ_K
0	1181.424	
1	1181.046	1181.916
2	1180.626	1182.341
3	1180.209	1182.764
4	1179.773	1183.186
5	1179.352	1183.617
6	1178.916	1184.042
7	1178.487	1184.468
8	1178.064	1184.894
9	1177.637	1185.312
10	1177.198	1185.731
11	1176.778	1186.144
12	1176.341	1186.555
13	1175.898	1186.964
14	1175.479	1187.397
15	1175.041	1187.820
16	1174.598	1188.237

for the triplet state corresponding to the bridgehead–bridgehead diradical ($^3A_2''$). The bond length results are given in Table VIII (all calculations employed the 6-31G* basis[17] and maintained D_{3h} symmetry).

We see that the inclusion of electron correlation brings the calculated r_1 value into essentially quantitative agreement with the observed value when the experimental uncertainty is taken into account (the effect of correlation on the side bonds of **1** and the bonds of cyclopropane is quite small). As might be expected (e.g., see ref 9), the GVB and MP2 calculations yield a somewhat larger r_1 value than that obtained at the more elaborate MP3 level. Previous studies[9] have shown MP3 bond lengths to be accurate to better than 0.01 Å for many bonds involving carbon and generally preferable to the corresponding MP2 values, which are frequently on the large side of experiment. In the present case, the MP2 geometry is somewhat closer to the experimental values than MP3, but both are rather satisfactory. The similar central C-C bond length reported earlier by Newton and Schulman[18] using the 4-31G basis at the SCF level is evidently the fortuitous result of omitting both polarization basis functions and electron correlation.

The considerably longer bridgehead–bridgehead bond length exhibited by the $^3A_2''$ state (1.83 Å at the 6-31G* SCF level, similar to the previous value of 1.80 Å obtained with a 4-31G basis[18]) reinforces the conclusion that the bridgehead atoms are indeed "bonded" in the ground state ($^1A_1'$), even though some characteristics of the $^1A_1'$ wavefunctions (negative overlap population,[4,18] outward-directed hybrid atomic orbitals,[18] and *increase* in magnitude of the one-electron energy for the highest-filled MO (HFMO) as r_1 is extended beyond its equilibrium value[19]) might suggest otherwise.[20] In this connection, it might be noted that the energy of the HFMO is calculated to be greater in magnitude than that for bicyclo[1.1.0]butane (-0.36079 and -0.35605 hartree, respectively, and this is reflected in their observed first ionization potentials (9.7 eV for **1** and 9.3 eV for bicyclobutane).[21]

The earlier finding[18] that the $^3A_2''$ state lies at least ∼2 eV above the ground $^1A_1'$ state, even at the optimal $^3A_2''$ geometry, is confirmed by the more elaborate calculations in the present study: at the $^3A_2''$ geometry, the $^3A_2''$ state lies respectively 1.8, 3.9, and 3.2 eV above the $^1A_1'$ state, at the SCF, MP2, and MP3 levels.

Having experimental geometrical parameters, we may now proceed to a normal coordinate analysis of the observed frequencies, employing the calculated SCF values as the initial guess for the harmonic force constants. The symmetry coordinates for **1** are given in Table IX. From them, the **B** matrix was con-

(17) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213.

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

(19) Jackson, J. E.; Allen, L. C. *J. Am. Chem. Soc.* **1984**, *106*, 591.

(20) See also: Epiotis, N. D. *J. Am. Chem. Soc.* **1984**, *106*, 3170.

(21) Honegger, E.; Huber, H.; Heilbronner, E.; Dailey, W. P.; Wiberg, K. B. *J. Am. Chem. Soc.*, in press.

Table VIII. Calculated and Observed CC Bond Lengths

	bond length (Å)				
	calculated				
bond	SCF	GVB[a]	MP2	MP3	observed
(a) [1.1.1]propellane					
bridgehead–bridgehead	1.543[b] (1.823)[d]	1.596	1.594	1.572	1.60 ± 0.02,[c] 1.596 ± 0.005[h]
bridgehead–methylene	1.502[b] (1.547)[d]	1.509	1.515	1.514	1.522 ± 0.002[c,e], 1.525 ± 0.002[h]
(b) cyclopropane	1.498[f]		1.504	1.506	1.514 ± 0.002[g]

[a] The a'_1 and a''_2 MO's involved in the GVB pair are dominated by the bridgehead atoms. [b] Reference 4. [c] Present work. [d] $^3A''_2$ state (UHF). [e] In terms of r_1 and r_2, the bridgehead–methylene bond length is given by $((r_1/2)^2 + r_2^2)^{1/2}$. [f] Reference 6. [g] Reference 9. [h] Reference 14.

structed and was augmented by the rotational and translational terms needed to satisfy the Eckart conditions.[22] The use of the inverse of the augmented **B** matrix allowed the calculated force constants in Cartesian coordinate to be converted to those with respect to symmetry coordinates.

The A_1' force constants are of particular interest to us because this block includes the central C–C bond stretch and the symmetrical stretching mode for the other C–C bonds. The calculated force constants for this block include an unusually large interaction constant between the two C–C stretching modes: $f_{1,2} = -2.9$ mdyn/Å, compared to the diagonal values $f_{1,1} = 6.5$ mdyn/Å and $f_{2,2} = 6.2$ mdyn/Å.[23] Inclusion of electron correlation yields force constants with similar but somewhat smaller magnitudes: respectively –2.6, 6.3, and 5.4 (MP2) and –2.7, 6.4, and 5.6 (MP3).

In order to obtain the "best" force constants for **1**, the calculated force constants were first scaled in accordance with the scaling factors applied to the calculated frequencies listed in Table I. The scaled force constants were used with the **G** matrix derived from the experimental geometry to calculate the vibrational frequencies. The force constant matrix was then adjusted by allowing the diagonal elements to vary independently and allowing the off-diagonal elements to vary as a group (i.e., using a single scaling factor for all). The final calculated frequencies are given in Table X, and the corresponding force constants are given in Table XI. The root-mean-square error between the calculated and observed frequencies was 11 cm^{-1} which is quite satisfactory.

We have found with other molecules that the force constant scaling factors (sf) for a given type of symmetry coordinate usually lie in a small range.[24] The same is true in the present case. The average value of the sf for the CH stretching coordinates is 0.83 ± 0.01, that for the CC stretching coordinates is 0.84 ± 0.04, and that for the CCH bending coordinates is 0.80 ± 0.02. Thus, although a total of 16 scaling factors were used, a smaller number could have been employed without significantly increasing the rms error.

The relationship between the normal modes of **1** and **1**-d_6 is of interest with regard to understanding the effect of isotopic substitution and in understanding the changes in intensities between the two molecules. We have shown that it is useful to express the normal coordinates of the isotopically substituted compound in terms of those of the parent.[24] This is easily done by using the relationship
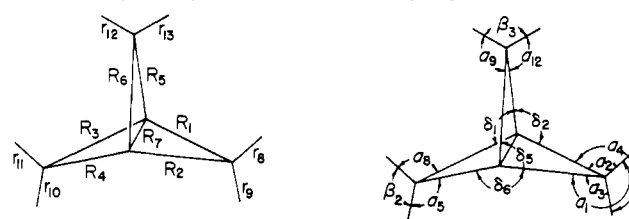
$$Q_D = L^{-1}{}_D L_H Q_H$$

(22) Eckart, C. *Phys. Rev.* **1935**, *47*, 552. Sayvetz, A. *J. Chem. Phys.* **1939**, *7*, 383.

(23) We were interested in having information on the anharmonicity of the stretching modes. Therefore the energies of a number of structures which had been distorted along one or more of the the A_1' symmetry coordinates were calculated. A 27 point fit for $S_1 - S_4$ which included anharmonic (cubic) terms for the stretching modes gave the following:

$V = -2.346\Delta S_1{}^3 + 3.259\Delta S_1{}^2 - 0.494\Delta S_2{}^3 + 3.110\Delta S_2{}^2 - 2.406\Delta S_3{}^3 +$
$\quad 3.149\Delta S_3{}^2 + 0.447\Delta S_4{}^2 - 2.936\Delta S_1\Delta S_2 + 0.202\Delta S_1\Delta S_3 -$
$\quad 0.406\Delta S_1\Delta S_4 - 0.266\Delta S_2\Delta S_3 + 0.388\Delta S_2\Delta S_4 + 0.099\Delta S_3\Delta S_4$

It may be noted that whereas the anharmonicity associated with S_2 is small (i.e., a small cubic term in the above expression), the calculated anharmonicity for S_1 is reasonably large.

(24) Wiberg, K. B.; Dempsey, R. C.; Wendoloski, J. J. *J. Phys. Chem.* **1984**, *88*, 5596. Wiberg, K. B.; Walters, V. A. *Ibid.* **1984**, *88*, 4723.

Table IX. Symmetry Coordinates for [1.1.1]Propellane[a]

A_1' $S_1 = R_1 + R_2 + R_3 + R_4 + R_5 + R_6$
$\quad\quad S_2 = R_7$
$\quad\quad S_3 = r_8 + r_9 + r_{10} + r_{11} + r_{12} + r_{13}$
$\quad\quad S_4 = \beta_1 + \beta_2 + \beta_3$

A_2' $S_5 = r_8 - r_9 + r_{10} - r_{11} + r_{12} - r_{13}$
$\quad\quad S_6 = \alpha_1 + \alpha_2 - \alpha_3 - \alpha_4 + \alpha_5 + \alpha_6 - \alpha_7 - \alpha_8 + \alpha_9 + \alpha_{10} - \alpha_{11} - \alpha_{12}$

E_α' $S_7 = 2R_1 + 2R_2 - R_3 - R_4 - R_5 - R_6$
$\quad\quad S_8 = 2r_8 + 2r_9 - r_{10} - r_{11} - r_{12} - r_{13}$
$\quad\quad S_9 = r_{10} - r_{11} - r_{12} + r_{13}$
$\quad\quad S_{10} = 2\alpha_1 + 2\alpha_2 + 2\alpha_3 + 2\alpha_4 - \alpha_5 - \alpha_6 - \alpha_7 - \alpha_8 - \alpha_9 - \alpha_{10} - \alpha_{11} - \alpha_{12}$
$\quad\quad S_{11} = \alpha_5 + \alpha_6 - \alpha_7 - \alpha_8 - \alpha_9 - \alpha_{10} + \alpha_{11} + \alpha_{12}$
$\quad\quad S_{12} = 2\delta_1 - \delta_2 - \delta_3 + 2\delta_4 - \delta_5 - \delta_6$

A_1'' $S_{13} = \alpha_1 - \alpha_2 - \alpha_3 + \alpha_4 + \alpha_5 - \alpha_6 - \alpha_7 + \alpha_8 + \alpha_9 - \alpha_{10} - \alpha_{11} + \alpha_{12}$

A_2'' $S_{14} = R_1 - R_2 + R_3 - R_4 + R_5 - R_6$
$\quad\quad S_{15} = \alpha_1 - \alpha_2 + \alpha_3 - \alpha_4 + \alpha_5 - \alpha_6 + \alpha_7 - \alpha_8 + \alpha_9 - \alpha_{10} + \alpha_{11} - \alpha_{12}$

E_a'' $S_{16} = R_3 - R_4 - R_5 + R_6$
$\quad\quad S_{17} = 2\alpha_1 - 2\alpha_2 - 2\alpha_3 + 2\alpha_4 - \alpha_5 + \alpha_6 + \alpha_7 - \alpha_8 - \alpha_9 + \alpha_{10} + \alpha_{11} - \alpha_{12}$
$\quad\quad S_{18} = \alpha_5 - \alpha_6 + \alpha_7 - \alpha_8 - \alpha_9 + \alpha_{10} - \alpha_{11} + \alpha_{12}$

E_b' $S_{19} = R_3 + R_4 - R_5 - R_6$
$\quad\quad S_{20} = r_{10} + r_{11} - r_{12} - r_{13}$
$\quad\quad S_{21} = -2r_8 + 2r_9 + r_{10} - r_{11} + r_{12} - r_{13}$
$\quad\quad S_{22} = \alpha_5 + \alpha_6 + \alpha_7 + \alpha_8 - \alpha_9 - \alpha_{10} - \alpha_{11} - \alpha_{12}$
$\quad\quad S_{23} = -2\alpha_1 - 2\alpha_2 + 2\alpha_3 + 2\alpha_4 + \alpha_5 + \alpha_6 - \alpha_7 - \alpha_8 + \alpha_9 + \alpha_{10} - \alpha_{11} - \alpha_{12}$
$\quad\quad S_{24} = \delta_2 - \delta_3 + \delta_5 - \delta_6$

E_b'' $S_{25} = 2R_1 - 2R_2 - R_3 + R_4 - R_5 + R_6$
$\quad\quad S_{26} = -\alpha_5 + \alpha_6 + \alpha_7 - \alpha_8 + \alpha_9 - \alpha_{10} - \alpha_{11} + \alpha_{12}$
$\quad\quad S_{27} = 2\alpha_1 - 2\alpha_2 + 2\alpha_3 - 2\alpha_4 - \alpha_5 + \alpha_6 - \alpha_7 + \alpha_8 - \alpha_9 + \alpha_{10} - \alpha_{11} + \alpha_{12}$

[a] The normalization factors are not given.

The product $L^{-1}{}_D L_H$ is shown in Table XII. It can be seen that mode mixing is rather large in some of the vibrational modes. In the case of the 1216- and 1033-cm^{-1} bands of **1**-d_6, the mode mixing is so large that they cannot be directly related to single vibrational modes of the parent molecule. We shall return to the question of the effect of mode mixing when the intensities are examined.

Force constants are best discussed by the use of comparisons among related molecules. We are in the process of reanalyzing the vibrational spectrum of bicyclo[1.1.0]butane with the aid of calculated vibrational frequencies and intensities using the 6-31G*

Table X. Results of Normal Coordinate Analysis

mode		d_0			d_6		
		calcd	obsd	type	calcd	obsd	type
A_1'	1	3031	3029	$93S_3$	2207	2209	$87S_3$, $12S_1$
	2	1504	1502	$54S_4$, $22S_2$, $18S_1$	1231	1239	$46S_1$, $22S_2$, $19S_4$
	3	1131	1124	$56S_1$, $31S_2$	1021	1022	$60S_2$, $26S_4$
	4	902	908	$50S_2$, $44S_1$	839	845	$45S_1$, $41S_2$
A_2'	5	3110		$100S_5$	2316		$99S_5$
	6	940		$84S_6$, $16S_5$	721		$74S_6$, $26S_5$
E'	7	3093	3080	$94S_9$	2310	2328	$92S_9$
	8	3024	3020	$91S_8$	2199	2204	$88S_8$, $10S_7$
	9	1461	1459	$63S_{10}$, $25S_7$	1210	1216	$57S_7$, $15S_{10}$
	10	1204	1186	$53S_7$, $17S_{11}$	1032	1033	$36S_{10}$, $24S_7$, $19S_{12}$
	11	1074	1083	$51S_7$, $17S_{10}$	904	913	$33S_7$, $22S_{11}$, $15S_{10}$
	12	531	529	$69S_{12}$, $16S_{11}$	428	430	$64S_{11}$, $22S_{10}$
A_1''	13	913		$100S_{13}$	646		$100S_{13}$
A_2''	14	1124	1096	$81S_{15}$, $19S_{14}$	883	918	$88S_{15}$, $12S_{14}$
	15	615	612	$88S_{14}$, $12S_{15}$	579	575	$78S_{14}$, $22S_{15}$
E''	16	1141	1146	$51S_{17}$, $41S_{16}$	968	955	$75S_{16}$, $36S_{17}$
	17	1064	1064	$63S_{18}$, $24S_{16}$	821		$83S_{18}$, $12S_{16}$
	18	710	714	$78S_{16}$, $20S_{17}$	600	607	$60S_{16}$, $32S_{17}$
			rms error = 10.1			rms error = 12.5	

Table XI. Force Constants for [1.1.1]Propellane

(a) Diagonal Constants

f	calcd	sf	adj
1,1	6.519	0.841	5.483
2,2	6.220	0.821	5.109
3,3	6.299	0.826	5.204
4,4	0.895	0.800	0.716
5,5	6.112	[0.841][a]	5.140
6,6	0.451	[0.819][b]	0.370
7,7	5.002	0.801	4.007
8,8	6.211	0.834	5.179
9,9	6.145	0.829	5.097
10,10	1.291	0.817	1.055
11,11	0.519	0.819	0.425
12,12	1.962	0.879	1.726
13,13	1.029	[0.800][c]	0.823
14,14	2.574	0.912	2.347
15,15	1.327	0.787	1.044
16,16	3.574	0.822	2.939
17,17	1.272	0.783	0.996
18,18	1.200	0.762	0.915

(b) Off-Diagonal Constants
sf = 0.855

A_1'	2	3	4
1	-2.510	0.173	-0.347
2		-0.227	0.332
3			0.085

A_2'	6
5	0.060

E'	8	9	10	11	12
7	0.122	0.018	0.135	-0.098	-0.113
8		0.008	-0.134	-0.014	-0.011
9			0.010	0.084	0.129
10				-0.017	-0.088
11					0.055

A_2''	15
14	-0.516

E''	17	18
16	0.019	-0.494
17		0.062

[a] Set equal to sf for $f_{1,1}$. [b] Set equal to sf for $f_{11,11}$. [c] Set equal to sf for $f_{4,4}$.

Table XII. Mode Mixing in the Vibrations of [1.1.1]Propellane-d_6

d_6, cm^{-1}	vibrational modes for [1.1.1]propellane			
	1	2	3	4
2209	1.366	-0.044	-0.029	0.023
1239	0.220	0.981	0.536	-0.057
1022	-0.040	-0.751	0.839	0.359
839	0.177	-0.540	0.385	-0.977

d_6, cm^{-1}	vibrational modes for [1.1.1]propellane					
	7	8	9	10	11	12
2328	1.334	-0.042	0.003	-0.028	0.025	-0.007
2199	0.045	1.368	0.037	-0.027	-0.028	0.003
1211	-0.062	-0.221	0.783	-0.677	-0.296	-0.006
1032	0.128	-0.033	0.979	0.823	-0.102	0.054
903	-0.217	0.104	0.505	-0.204	1.098	-0.079
428	0.119	-0.062	-0.077	-0.303	0.340	-0.079

d_6, cm^{-1}	vibrational modes for [1.1.1]propellane	
	14	15
883	1.238	0.162
579	-0.451	1.035

d_6, cm^{-1}	vibrational modes for [1.1.1]propellane		
	16	17	18
955	1.118	0.011	0.236
(821)	-0.097	1.272	0.152
607	-0.597	-0.333	1.099

basis set. At a later time we will present the results of this investigation which will permit us to make a detailed comparison of the force constants for cyclopropane, bicyclobutane, and [1.1.1]propellane. There are, however, some observations which may be made at the present time. The totally symmetric (S_1) and non-totally-symmetric (S_7, S_{14}, S_{16}, S_{19}, and S_{25}) stretching modes associated with the outer C–C bonds exhibit large force constant variations (e.g., 5.47 mdyn/Å for S_1 vs. 2.34 mdyn/Å for S_{14}). This is in marked contrast to the situation in cyclopropane, where the two framework coordinates (A_1' and E') have similar force constants (4.04 and 4.25 mdyn/Å),[25] and indicates that there are large interactions among the outer C–C bonds of **1**. In fact, transformation to a basis of individual CC stretching coordinates yields a diagonal constant of 3.62 mdyn/Å for each outer CC bond, with an interaction constant of 0.84 mdyn/Å between CC bonds common to a given methylene group (as well as a value of –1.02 mdyn/Å coupling central and outer CC bonds). Somewhat smaller coupling is found between outer CC bonds sharing a common bridgehead atom (0.15 mdyn/Å) and between those with no common C atoms (0.35 mdyn/Å). Finally, we note that the force constant for stretching individual CH bonds was found to be 5.15 mdyn/Å, close to the value found for cyclopropane (5.25 mdyn/Å).[25]

(25) Shrake, A. S., Ph.D. Thesis, Yale University, 1969.

Table XIII. Infrared Intensities[a]

band, cm⁻¹	mode	d_0				d_6 calcd[f]
		calcd[b]	obsd (gas)[c]	% error[d]	obsd (soln)[e]	
3050–3117	ν_7	34.0	17.5	1.4	16.6	7.9
2986–3050	ν_8	64.2	28.0	1.2	27.1	16.2
1359–1519	ν_9	0.6	6.65	g		0.04
1146–1206	ν_{10}	2.8	1.55	g	2.0	2.8
	ν_{11}	2.8	1.8	h		2.7
490–541	ν_{12}	1.0	0.76	g		0.5
1053–1136	$\nu_{14} + \nu_{11}$	16.6	22.0[h]	1.8	43.9	0.3
564–660	ν_{15}	190.0	78.9	2.1	120.0	75.1

[a] Units: km/mol. [b] Derived from ab initio calculation (Table I). The intensities for the E′ modes include the statistical factor of 2. [c] Observed by using 300 psi of nitrogen pressure, see Experimental Section. [d] Percent error in A (i.e., in the slopes of Figure 6). [e] Observed in carbon disulfide solution. [f] Calculated from the observed dipole moment derivatives for **1** (Table XIV) and the L^{-1} matrix for **1**-d_6. The intensities for the E′ modes include the statistical factor of 2. [g] These intensities were obtained from the 33-torr spectrum. [h] The ν_{10} band is a shoulder on ν_{14}. The separation of the two bands was approximated manually, giving 20.2 for ν_{14} and 1.8 for ν_{10}.
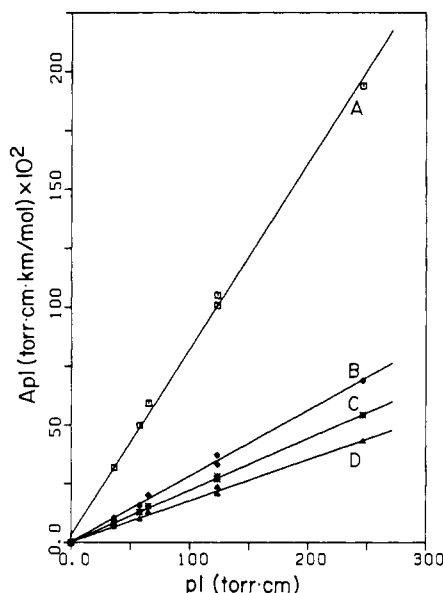
Figure 6. Beer's law plot for infrared intensities of [1.1.1]propellane. The lines are (A) ν_{15}, (B) ν_8, (C) $\nu_{11} + \nu_{14}$, (D) ν_7.

We have shown that there is a relationship between the charge distribution for a molecule and the dipole moment derivatives.[6] The latter may be obtained from the infrared band intensities.[26] The intensities were obtained in the gas phase in the presence of ~300 psi of nitrogen in order to broaden the rotational components so that the intensity will not be affected by instrumental resolution.[27] It was not possible to use the more precise bourdon gauges to measure the sample pressures because **1** reacted rapidly with some metal surfaces and polymerized inside the gauge. The pressures could be measured with somewhat lower accuracy by using a mercury manometer. Beer's law plots derived from the data were linear (Figure 6) and the intensities thus obtained are given in Table XIII. In addition, the spectrum was obtained in carbon disulfide solution, and the intensities were again determined. The two sets of intensity measurements are compared in Table XIII. Although there is generally good agreement, it is interesting to note the remarkable enhancement of the intensity of ν_{11} on going to the solution phase.

The observed intensities are generally somewhat smaller than the calculated values, as frequently is found.[6] The main exception is found with ν_9 where the observed intensity is an order of magnitude greater than the calculated value. This is a complex mode and the intensity is strongly dependent on the form of the normal coordinate. This can be seen from the low intensity of ν_9 for **1**-d_6 and will be further considered below.

(26) For a review of infrared intensities, see: Person, W. B.; Steele, D. *Mol. Spectrosc.* **1974,** *2,* 357. Steele, D. *Ibid.* **1978,** *5,* 106.

(27) Wilson, E. B., Jr.; Wells, A. *J. Chem. Phys.* **1946,** *14,* 578. Penner, S. S.; Weber, D. *Ibid.* **1951,** *19,* 807.
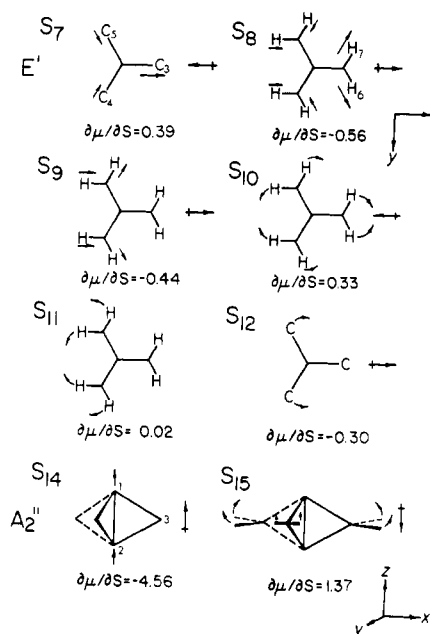

Figure 7. Infrared active symmetry coordinates and induced dipoles for [1.1.1]propellane.

Table XIV. Dipole Moment Derivatives[a]

coordinate		calcd	obsd
E′	S_7	0.66	0.39
	S_8	−0.82	−0.56
	S_9	−0.61	−0.44
	S_{10}	0.18	0.33
	S_{11}	0.01	0.02
	S_{12}	−0.24	−0.30
A_2''	S_{14}	−6.96	−4.56
	S_{15}	1.56	1.37

[a] Units: $D/(\text{Å amu}^{1/2})$. The values for the E′ modes correspond to each of the two components.

The L^{-1} matrix derived from the normal coordinate analysis was used to convert the intensities observed in the gas phase to dipole moment derivatives with respect to the symmetry coordinates. The sign problem was resolved by using those obtained from the ab initio calculation. They are compared with the calculated values in Table XIV. The agreement is generally quite good. The calculated derivative for S_{10} is somewhat too low, and that for S_{14} is somewhat too large in magnitude, but the agreement for the others is remarkably good.

The intensities expected for **1**-d_6 were calculated from the experimental dipole moment derivatives and the L^{-1} matrix obtained for the labeled species. They are shown in Table XIII. The large decrease in intensity for ν_9 on deuteration as well as the decrease in observed intensity for ν_{14} (Figure 1) are well reproduced, indicating that the dipole moment derivatives are satis-

Table XV. Atomic Polar Tensors[a]

	calcd			obsd		
	x	y	z	x	y	z
C_1	-0.346	0.000	0.000	-0.195	0.000	0.000
	0.000	-0.346	0.000	0.000	-0.195	0.000
	0.000	0.000	-4.007	0.000	0.000	-2.520
C_3	1.094	0.000	0.000	0.534	0.000	0.000
	0.000	0.295	0.000	0.000	0.188	0.000
	0.000	0.000	1.686	0.000	0.000	0.812
H_6	-0.162	-0.185	0.000	-0.007	-0.124	0.000
	-0.460	-0.302	0.000	-0.377	-0.224	0.000
	0.000	0.000	0.493	0.000	0.000	0.434

[a]Units: D/Å. The coordinate system is shown in Figure 7.

factory. These changes in intensity result from the mode mixing seen in Table XII.

In order to discuss the derivatives conveniently, they are shown in diagrammatic form in Figure 7. The large dipole moment derivative for S_{14} is of particular interest. It suggests that the electron population at the bridgehead carbons is unusually large. An examination of the polar tensors (Table XV) shows that movement of C_1 in the positive sense along any of the coordinate directions leads to a negative value, but it is considerably larger for movement along z than along x or y. Bader has examined the electron populations at C_1 derived from ab initio wave functions and found a large electron population which increased as a result of a distortion along S_{14}.[28] On the other hand, the polar tensors for C_3 are all positive, suggesting that the methylene carbons are relatively electron deficient. This also is seen in the induced dipole resulting from a distortion along S_7.

The C–H bending and stretching modes are generally fairly easy to interpret. The stretching coordinates, S_8 and S_9, lead to signs for the induced dipoles which correspond to C^+–H^-, as is found for most hydrocarbons.[6] This also is the sign of the C–H bond dipole derived from integration of electron populations for hydrocarbons. The only exception is acetylene, for which the sign of both the induced dipole and the C–H bond moment is reversed.[6]

The bending coordinates, S_{10} and S_{15}, lead to signs for the induced dipoles which suggest a bond moment in the sense C^-–H^+, or reversed from that found for the stretching coordinates. The C–C–H bending motion leads to the formation of a bent bond in which the proton moves ahead of the electron density in the bonding region. This is the result of limited orbital following and leads to an apparent motion of a positively charged species.[6] The bending modes are not useful in determining signs of bond dipoles.

The preceding discussion has shown that most of the properties of **1** which were first predicted by calculation have been verified experimentally. One particularly important quantity is the enthalpy of formation. It has been estimated to be 89 kcal/mol on the basis of 6-31G* energy calculations.[4,29] In order to obtain an experimental estimate of its enthalpy of formation, we have examined the reaction of **1** with acetic acid calorimetrically:
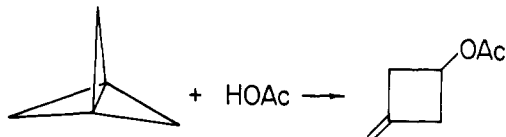
The reaction proceeded without side reactions and gave ΔH_r = -35.2 ± 0.4 kcal/mol (Table XVI). In order to convert this to ΔH_f for **1**, the enthalpy of formation of 3-methylenecyclobutyl acetate is needed. It was estimated as follows. The ΔH_f of methylenecyclobutane in the liquid phase is 22.4 ± 0.2 kcal/mol.[30] The difference in ΔH_f between propane and isopropyl acetate is -95.5 kcal/mol in the liquid phase.[31] Thus, for **11**, ΔH_f = -73.1 kcal/mol with an estimated uncertainty of about 0.5 kcal/mol.

With use of the known ΔH_f of acetic acid (-115.8 ± 0.2 kcal/mol),[31] the enthalpy of formation of liquid **1** becomes 77.9 ± 1 kcal/mol. With use of an estimated enthalpy of vaporization of 6.4 ± 0.5 kcal/mol,[32] ΔH_f of **1** in the gas phase becomes 84 ± 1 kcal/mol. This may be compared with the values estimated on the basis of our ab initio calculations, 89 kcal/mol. Considering the unusual nature of **1**, the agreement may be considered to be quite good.

[1.1.1]Propellane is unique in that the calculated energy of hydrogenolysis of the central C–C bond giving bicyclo[1.1.1]-pentane is markedly affected by the inclusion of polarization functions at carbon (cf. Table XVII).[4] It seemed likely that electron correlation might also be more important in this case than with more ordinary hydrocarbons. This was examined by using the Møller–Plesset perturbation method, giving the results summarized in Table XVII. The MP2 calculation frequently overcorrects the relative correlation energy change, but MP3 is usually quite good. Whereas the calculated energy of hydrogenolysis of *n*-butane to ethane drops by 7 kcal/mol on going from 6-31G* RHF to MP3, it drops by 9 kcal/mol in the case of **1**. We cannot readily use these results to give an improved calculated enthalpy of formation of **1** since the ΔH_f of bicyclo[1.1.1]pentane has not been determined experimentally. However, the results suggest that the difference between the calculated and observed ΔH_f for **1** may be due to a larger than usual effect of electron correlation.

Experimental Section

3-Phenylcyclobutane-*2,2,4,4-d₄*-1,1-dicarboxylic Acid. The synthesis of 3-phenylcyclobutane-*2,2,4,4-d₄*-1,1-dicarboxylic acid followed the procedure of Beard and Berger for the unlabeled acid.[33] Thus, treatment of 29.0 g (0.123 mmol) of diethyl phenylmalonate with 6.0 g (0.143 mmol) of lithium aluminum deuteride (99% d_4, KOR Isotopes) in ether produced a 55% yield of 2-phenylpropane-1,3-diol-*1,1,3,3-d₄*. Conversion of 10.2 g (65.4 mmol) of diol-d_4 to the ditosylate using 28.0 g (147 mmol) of *p*-toluenesulfonyl chloride in 55 mL of dry pyridine occurred in 85% yield. When treated with 10.2 g (63.7 mmol) of diethyl malonate and 4.8 g (126 mmol) of 60% sodium hydride dispersion in oil in boiling dioxane, the ditosylate furnished a 74% yield of diethyl 3-phenylcyclobutane-*2,2,4,4-d₄*-1,1-dicarboxylate. The diester, 11.3 g (40.4 mmol), was saponified with potassium hydroxide (7.5 g, 130 mmol) in 50% aqueous ethanol to give an 81% yield of 3-phenylcyclobutane-*2,2,4,4-d₄*-1,1-dicarboxylic acid.

Methyl 3-Phenylcyclobutane-*2,2,4,4-d₄*-1-carboxylate. A 500-mL flask containing 124.5 g (0.566 mol) of 3-phenylcyclobutane-1,1-dicarboxylic acid was heated under nitrogen for 30 min at 210 °C, during which time the solid melted and carbon dioxide evolved. The flask was cooled and 54.3 g (1.70 mol) of methanol, 1.8 mL of concentrated sulfuric acid, and 175 mL of ethylene dichloride along with a few boiling chips were added. After the solution had been heated to reflux overnight, the organic layer was separated, diluted with ether, washed with water, saturated sodium bicarbonate, water, and brine, and dried. Evaporation of the solvent followed by distillation of the residue under vacuum gave 102.3 g (95%)of clear colorless liquid, bp 85–89 °C at 0.2 mm. An NMR spectrum showed this to be a 53:47 mixture of cis and trans isomers. Although no attempt was made to separate the isomers, their separate absorbances could easily be identified in the proton NMR at 500 MHz. The major isomer had the following ^{1}H NMR (CDCl$_3$, 500 MHz): δ 2.39–2.47 (m, 4 H), 2.58–2.64 (m, 2 H), 3.70 (s, 3 H), 7.18–7.33 (m, 5 H). The minor isomer had the following ^{1}H NMR: δ 2.67–2.72 (m, 2 H), 3.04–3.17 (m, 2 H), 3.41–3.48 (m, 1 H), 3.75 (s, 3 H), 3.77 (m, 1 H), 7.18–7.33 (m, 5 H).

In a similar manner, the 2,2,4,4-tetradeuterio compound was prepared in 93% yield from 7.35 g (32.8 mmol) of diacid-d_4, 13 mL of ethylene dichloride, 3.2 g of methanol, and 0.1 g of concentrated sulfuric acid.

Methyl 3-Bromo-3-phenylcyclobutane-*2,2,4,4-d₄*-1-carboxylate. In a dry 2-L flask fitted with a reflux condenser and nitrogen inlet was placed 89.3 g (0.470 mol) of methyl 3-phenylcyclobutane-1-carboxylate, 83.8 g (0.471 mol) of *N*-bromosuccinimide (pumped in vacuo for 3 h), 0.99 g of benzoyl peroxide, and 550 mL of carbon tetrachloride. The

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(32) The enthalpy of vaporization of bicyclo[1.1.1]pentane is 6.36 ± 0.05 kcal/mol (Wiberg, K. B.; Connor, D. S. *J. Am. Chem. Soc.* **1966**, *88*, 4437) and the loss of two hydrogens from an alkane usually leads to a relatively small change in enthalpy of vaporization (±0.3 kcal/mol).

Table XVI. Enthalpy of Reaction with Acetic Acid

sample, mg	mmol	ϵ, cal/K	ΔT, K	Q_{obsd}, cal	Q_{corr},[a] cal	$-\Delta H_r$, kcal/mol
7.569	114.5	69.47	0.05578	3.875	3.973	34.70
8.073	122.1	69.98	0.05890	4.122	4.220	34.56
13.037	197.2	72.73	0.09446	6.870	6.968	35.33
5.755	87.1	70.93	0.04215	2.990	3.088	35.45
						av 35.01 ± 0.44[b,c]

[a] Corrected for the amount of propellane in the gas phase, assuming vp = 500 torr and ΔH_v = 6.4 kcal/mol. The sample size was 0.57 mL. [b] The uncertainty interval is taken as two times the standard deviation from the mean (2s). [c] The enthalpy of solution of 3-methylenecyclobutyl acetate was found to be 0.17 ± 0.01 kcal/mol. The enthalpy of reaction of the propellane with all compounds in the pure liquid form is then −35.18 ± 0.44 kcal/mol.

Table XVII

Calculated Energies

		6-31G*			
compound	4-31G RHF	RHF	MP2	MP3	MP4
hydrogen	−1.12683	−1.12863	−1.14410	−1.14925	−1.15082
ethane	−79.11593	−79.22875	−79.49451	−79.52061	−79.52606
butane	−157.07159	−157.29840	−157.82549	−157.87068	−157.87975
bicyclopentane	−193.61016	−193.90568	−194.55688	−194.59265	
[1.1.1]propellane	−192.36186	−192.69106	−193.34957	−193.37008	

Calculated Energy Changes

	4-31G	6-31G*				
reaction	RHF	RHF	MP2	MP3	MP4	obsd
$C_4H_{10} + H_2 \rightarrow 2C_2H_6$	−21.0	−20.2	−12.2	−13.4	−13.5	−14.1
1 + $H_2 \rightarrow$ bicyclopentane	−76.5	−55.1	−39.7	−46.0		

mixture was slowly heated to reflux with an oil bath. The reaction initiated with a strong exotherm and the oil bath had to be quickly removed. When the reaction slowed to a gentle reflux, the oil bath was replaced under the flask and the mixture was allowed to reflux the 1 h. After the mixture was cooled, the succinimide was removed by filtration. Evaporation of the solvent at room temperature left 129.3 g of an off-white solid (102%), mp 95–103 °C, which was suitable for use in the next reaction. Integration of the methyl ester peaks in the ^{1}H NMR spectrum showed a 7:1 mixture of isomers. The major isomer had the following ^{1}H NMR spectrum (CDCl$_3$, 500 MHz): δ 3.05 (m, 2 H), 3.11 (m, 2 H), 3.67 (s, 3 H), 3.79 (quintet, 1 H), 7.26 (m, 1 H), 7.33 (m, 4 H). The methyl ester of the minor isomer had a singlet at δ 3.74.

A sample for elemental analysis was prepared by recrystallization from hexane followed by sublimation (90 °C at 0.05 mm) to give a white solid, mp 102–105 °C. Anal. C, H, Br.

A similar reaction using 5.80 g (29.9 mmol) of the 2,2,4,4-tetradeterio compound, 5.35 g (30.0 mmol) of N-bromosuccinimide, 0.1 g of benzoyl peroxide, and 45 mL of carbon tetrachloride gave a quantitative yield of the bromide-d_4.

Methyl 3-Phenylbicyclo[1.1.0]butane-2,2,4,4-d_4-1-carboxylate. With use of a positive pressure of nitrogen, the oil was removed from 13.4 g (0.343 mol) of a 61% oil dispersion of sodium hydride by washing with dry ether on a sintered glass frit. The sodium hydride was quickly transferred to a dry 3-L three-necked flask containing 700 mL of dry tetrahydrofuran (THF). The flask was fitted with a mechanical stirrer, a condenser, a nitrogen inlet, and an addition funnel which was charged with 70.9 g (0.264 mol) of methyl 3-bromo-3-phenylcyclobutane-1-carboxylate, 2 mL of methanol, and 290 mL of THF. After adding about 10 mL of this latter solution to the flask, the reaction mixture was warmed to reflux and the rest of the bromide solution was added over the course of 30 min. After being refluxed for five hours, the solution was cooled in an ice bath and was carefully quenched with 25 mL of water. Most of the THF was removed under reduced pressure. The residue was diluted with ether and washed with water (3 × 200 mL) and brine. After the mixture was dried over magnesium sulfate, the solvent was evaporated to leave 45.2 g (91%) of tan crystals, mp 61–69 °C (lit.[34] mp 68–69 °C). The material thus obtained was used without further purification in the next reaction. ^{1}H NMR (CDCl$_3$, 90 MHz): δ 1.57 (br s, 2 H), 2.90 (br s, 2 H), 3.45 (s, 3 H), 7.26 (br s, 5 H).

The 2,2,4,4-tetradeuterio compound was prepared in 85% yield in a similar way by using 8.2 g (30 mmol) of bromide-d_4, 1.55 g (38.7 mmol) of a 60% dispersion of sodium hydride in oil, and 0.5 mL of methanol in 135 mL of THF.

3-Phenylbicyclo[1.1.1]pentane-2,2,4,4,5,5-d_3-1-carboxylic Acid. The preparation of this compound was performed as described by Applequist, Renken, and Wheeler.[35] The 2,2,4,4,5,5-hexadeuterio compound was prepared in a similar fashion. Addition of sodium trichloroacetate, 19 g (102 mmol), to a solution of methyl 3-phenylbicyclo[1.1.0]butane-2,2,4,4-d_4-1-carboxylate (4.9 g, 25.5 mmol) produced a 22% yield of methyl 3-phenyl-2,2-dichlorobicyclo[1.1.1]pentane-4,4,5,5-d_4-1-carboxylate. Dechlorination of 1.7 g (6.2 mmol) of this dichloride with tri-n-butyltin deuteride, prepared in 86% yield from the action of 1.0 g (23.8 mmol) of lithium aluminum deuteride (99% D, Stohler Isotope) on 20.0 g (61.5 mmol) of tri-n-butyl chloride,[36] followed by saponification with sodium hydroxide, gave a 77% yield of 3-phenylbicyclo[1.1.1]pentane-d_6-carboxylic acid. An ^{1}H NMR spectrum revealed less than 1% residual methylene protons as compared to the phenyl group.

Bicyclo[1.1.1]pentane-1,3-dicarboxylic Acid. A solution of 3.8 g (20 mmol) of 3-phenylbicyclo[1.1.1]pentane-1-carboxylic acid in 70 mL of glacial acetic acid, 20 mL of water, and 20 mL of ethyl acetate was cooled to 0 °C. Ozone was bubbled into the solution through a glass dispersion tube at a rate of 9 g/h for 4 h.[37] The clear colorless solution was warmed to room temperature and 25 mL of 30% hydrogen peroxide was added. After the mixture was left to stand at room temperature for 48 h, the solvent was evaporated and the white solid residue was sublimed twice (150 °C at 0.05 mm) to give 1.95 g (62%) of product as a white powder which did not melt below 250 °C. ^{1}H NMR (CD$_3$COCD$_3$, 90 MHz): δ 2.29 (s). The solid protons were not observed.

A similar procedure using 0.845 g (4.40 mmol) of 3-phenylbicyclo-[1.1.1]pentane-d_6-1-carboxylic acid gave 0.525 g (75%) of 1,3-bicyclo-[1.1.1]pentane-d_6-dicarboxylic acid.

1,3-Dibromobicyclo[1.1.1]pentane-d_6. To a 100-mL round-bottomed flask equipped with a condenser and nitrogen inlet was added 0.50 g (2.3 mmol) of red mercuric oxide, 0.40 g (3.3 mmol) of anhydrous magnesium sulfate, 0.200 g (1.28 mmol) of 1,3-bicyclo[1.1.1]pentanedicarboxylic acid, and 15 mL of methylene chloride. The mixture was stirred under nitrogen for 5 min and 0.686 g (4.30 mmol) of bromine was added in one portion. The vigorously stirred mixture was heated to a gentle reflux while it was irradiated with a 67 W incandescent light bulb[38] placed close to the flask. After 45 min, the light and heat were removed and the pale orange mixture was filtered through Celite. The salts were washed with methylene chloride (3 × 10 mL) and pentane (1 × 10 mL) and the combined filtrates were evaporated. The off-white solid residue was sublimed twice (70 °C at 20 mm) to give 0.197 g (68%) of beautiful white crystals, mp 119.5–120.5 °C. Yields varied between 50 and 70%

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from run to run. With the strict exclusion of light, however, no product was formed. ^{1}H NMR (CDCl$_3$, 90 MHz): δ 2.57 (s). Anal. C, H, Br.

A similar procedure using 1,3-bicyclo[1.1.1]pentane-d_6-dicarboxylic acid produced a 50% yield of 1,3-dibromobicyclo[1.1.1]pentane-d_6.

[1.1.1]Propellane. To a dry 10-mL round-bottom flask with a Teflon-coated stir bar was added 151 mg (0.67 mmol) of 1,3-dibromobicyclo[1.1.1]pentane, 0.3 mL of dry pentane (from LiAlH$_4$), and 0.2 mL of dry ether. The flask was capped with a rubber septum, purged with dry nitrogen, and cooled to −78 °C. A 700-μL portion of 1.36 M halide free methyl lithium in ether (Alfa) was added to the vigorously stirred solution via syringe over the course of 3 min. The mixture was stirred at −78 °C for 15 min and was then placed in an ice/salt (−10 °C) bath and stirred for an additional 30 min. The solution was recooled to −78 °C and quenched with 0.2 mL of water. After the solution was warmed to 0 °C, the organic layer was separated. [1.1.1]Propellane was isolated by preparative GC (18 ft × ^{1}/$_4$ in. 15% Apiezon L on Chromosorb W HP 80/100, column 55 °C, 100 mL/min) using 150-μL injections. Methyl bromide eluted first followed by solvent and finally [1.1.1]propellane (rt = 5.0 min). The propellane was collected in a dry ice/acetone cooled U-tube. Rechromatography of the trap contents gave almost pure [1.1.1]propellane as a clear, colorless liquid (20 mg, 46%). Propellane should be stored in degassed glass storage bulbs which have been washed with concentrated ammonium hydroxide and water and dried under vacuum. ^{1}H NMR (CDCl$_3$, 500 MHz): δ 2.06 (s). ^{13}C NMR (CDCl$_3$, 500 MHz): δ 74.1 (t, J = 165 Hz), 1.0.

In a similar manner, 1,3-dibromobicyclo[1.1.1]pentane-d_6 gave a 35% yield of [1.1.1]propellane-d_6.

Vibrational Spectra. The infrared spectra were obtained on a Nicolet Model 7199 FT–IR spectrometer. Most of the spectra were obtained at a resolution of 0.06 cm^{-1}. The intensities were measured with use of a 72.5-cm pressure cell of the type described by Dickson et al.[39] The spectra were taken with use of 300 psi of nitrogen for pressure broadening and a spectrometer resolution of 0.24 cm^{-1}. The gas-phase Raman spectra were obtained by using a Spex Ramalog spectrometer with a 2-cm^{-1} band-pass, a 4 cm^3 multi-pass gas cell fitted with elliptical Brewster windows, and the 488-nm line of an Argon-ion laser operating at 700 mW. Signal averaging was carried out with use of 100 scans.

Calorimetry. The enthalpy of reaction of **1** with acetic acid was determined by using the automated reaction calorimeter previously described.[40] Ampules containing known amounts of **1** were broken into 100 mL of glacial acetic acid. The heat capacity was determined electrically for each run, giving the data shown in Table XVI. The enthalpy of solution of 3-methylenecyclobutyl acetate was determined in the same

fashion, allowing the enthalpy of reaction in the pure liquid phase to be obtained.

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The Molecular Structure of Gaseous [1.1.1]Propellane: An Electron-Diffraction Investigation

Lise Hedberg and Kenneth Hedberg*

Contribution from the Department of Chemistry, Oregon State University, Corvallis, Oregon 97331. Received May 6, 1985

Abstract: The molecular structure of [1.1.1]propellane has been investigated by gas-phase electron diffraction. The radial distribution of distances was found to be completely consistent with the D_{3h} symmetry proposed from other work. The assumption of this symmetry with the hydrogen atoms lying in the equatorial plane gave the following results for the bond distances (r_g), bond angles ($\angle_\alpha$), and the more important root-mean-square amplitudes of vibration (l). $r(C_{ax}-C_{eq})$ = 1.525 (2) Å, $r(C_{ax}-C_{ax})$ = 1.596 (5) Å, r(C–H) = 1.106 (5) Å, $\angle$HCH = 116.0 (19)°, $\angle C_{ax}C_{eq}H$ = 116.9 (8)°, $\angle C_{eq}C_{ax}C_{eq}$ = 95.1 (1)°, $\angle C_{ax}C_{eq}C_{ax}$ = 63.1 (2)°, $l(C_{ax}-C_{eq})$ = 0.060 (3) Å, $l(C_{ax}-C_{ax})$ = 0.074 (12) Å, l(C–H) = 0.082 (5) Å, and $l(C_{eq}-C_{eq})$ = 0.064 (4) Å. The structural results are in good agreement with parameters deduced from IR and Raman data.

Although the structure of [1.1.1]propellane (see diagram in Figure 2) seems to be well established from spectroscopic and

theoretical studies[1] of this unusual molecule, it is clearly important that direct measurement of the internuclear distances be under-