

from run to run. With the strict exclusion of light, however, no product was formed. $^1\text{H NMR}$ (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 \times $1/4$ 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. $^1\text{H NMR}$ (CDCl_3 , 500 MHz): δ 2.06 (s). $^{13}\text{C NMR}$ (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.

Calculations. The vibrational force field was calculated by using the program GAMES⁴¹ and the 6-31G* basis set.⁴² The calculation required 300 cpu hours on a VAX-11/750 computer. The normal coordinate calculations were carried out by using modified versions of the programs developed by Schachtschneider,⁴³ and the conversion of vibrational intensities to dipole moment derivatives and polar tensors was carried out by using programs written by Dempsey.⁴⁴ The calculations including electron correlation made use of GAUSSIAN-82.⁴⁵

Acknowledgment. The research at Yale was carried out with the aid of NSF Grants CHE81-21421 and CHE83-19955. The research at Brookhaven National Laboratory was carried out under contract DE-AC0276-CH00016 with the United States Department of Energy and supported by its Office of Basic Energy Sciences.

Registry No. 1, 35634-10-7; PhCH(CO $_2$ Et) $_2$, 83-13-6; HOCD $_2$ CH-(Ph)CD $_2$ OH, 98704-00-8; (*p*-MeC $_6$ H $_4$ SO $_2$ CD $_2$) $_2$ CHPh, 98704-01-9; CH $_2$ (CO $_2$ Et) $_2$, 105-53-3; Cl $_3$ CC(O)ONa, 650-51-1; diethyl 3-phenylcyclobutane-2,2,4,4- d_4 -1,1-dicarboxylate, 98704-02-0; 3-phenylcyclobutane-2,2,4,4- d_4 -1,1-dicarboxylic acid, 98704-03-1; 3-phenylcyclobutane-1,1-dicarboxylic acid, 1570-97-4; *cis*-methyl 3-phenylcyclobutane-1-carboxylate, 62485-19-2; *trans*-methyl 3-phenylcyclobutane-1-carboxylate, 62485-20-5; methyl 3-phenylcyclobutane-2,2,4,4- d_4 -1-carboxylate, 98704-04-2; *cis*-methyl 3-bromo-3-phenylcyclobutane-1-carboxylate, 98704-05-3; *trans*-methyl 3-bromo-3-phenylcyclobutane-1-carboxylate, 98704-06-4; methyl 3-bromo-3-phenylcyclobutane-2,2,4,4- d_4 -carboxylate, 98704-07-5; methyl 3-phenylbicyclo[1.1.0]butane-1-carboxylate, 30493-96-0; methyl 3-phenylbicyclo[1.1.0]butane-2,2,4,4- d_4 -1-carboxylate, 98704-08-6; methyl 3-phenyl-2,2-dichlorobicyclo[1.1.1]pentane-4,4,5,5- d_4 -1-carboxylate, 98704-09-7; 3-phenylbicyclo[1.1.1]pentane-2,2,4,4,5,5- d_6 -1-carboxylic acid, 98704-10-0; 3-phenylbicyclo[1.1.1]pentane-1-carboxylic acid, 83249-04-1; bicyclo[1.1.1]pentane-1,3-dicarboxylic acid, 56842-95-6; bicyclo[1.1.1]pentane-2,2,4,4,5,5- d_6 -1,3-dicarboxylic acid, 98704-11-1; 1,3-dibromobicyclo[1.1.1]pentane- d_6 , 98704-12-2; [1.1.1]propellane- d_6 , 98704-13-3; 3-methylenecyclobut-1-yl acetate, 18218-27-4.

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

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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_0), bond angles (\angle_α), and the more important root-mean-square amplitudes of vibration (l). $r(\text{C}_{\text{ax}}-\text{C}_{\text{eq}}) = 1.525$ (2) Å, $r(\text{C}_{\text{ax}}-\text{C}_{\text{ax}}) = 1.596$ (5) Å, $r(\text{C}-\text{H}) = 1.106$ (5) Å, $\angle\text{HCH} = 116.0$ (19) $^\circ$, $\angle\text{C}_{\text{ax}}\text{C}_{\text{eq}}\text{H} = 116.9$ (8) $^\circ$, $\angle\text{C}_{\text{eq}}\text{C}_{\text{ax}}\text{C}_{\text{eq}} = 95.1$ (1) $^\circ$, $\angle\text{C}_{\text{ax}}\text{C}_{\text{eq}}\text{C}_{\text{ax}} = 63.1$ (2) $^\circ$, $l(\text{C}_{\text{ax}}-\text{C}_{\text{eq}}) = 0.060$ (3) Å, $l(\text{C}_{\text{ax}}-\text{C}_{\text{ax}}) = 0.074$ (12) Å, $l(\text{C}-\text{H}) = 0.082$ (5) Å, and $l(\text{C}_{\text{eq}}-\text{C}_{\text{eq}}) = 0.064$ (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 studies¹ of this unusual molecule, it is clearly important that direct measurement of the internuclear distances be under-

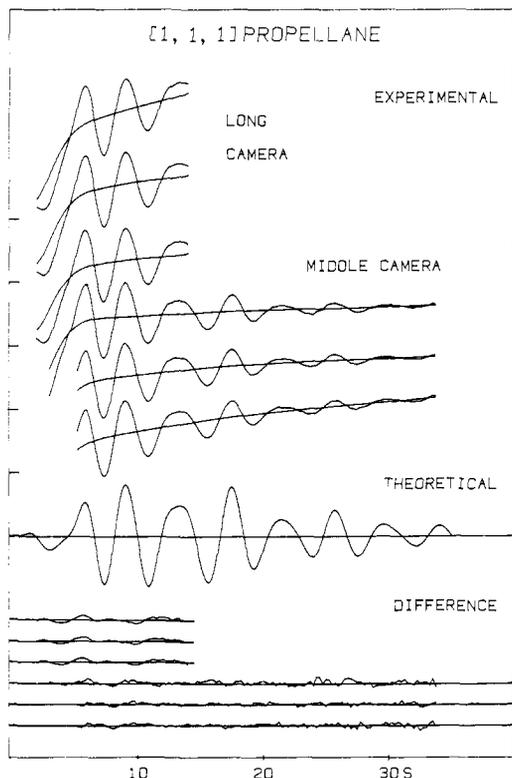


Figure 1. Intensity curves. The s^4I_t curves from each plate are shown superimposed on the final backgrounds and are magnified 2 times relative to the backgrounds. The theoretical curve is for model A of Table I. The difference curves are experimental minus theoretical; those from the long camera are from model B and those from the intermediate camera from model A.

taken. We report here the results of our electron diffraction study of the molecule in the gas phase.

Experimental Section

About 100 mg of freshly prepared sample contained in a small Pyrex tube equipped with a break-seal was packed in dry ice and sent to us by Professor K. Wiberg and Dr. William Dailey, to whom we are very grateful. The first set of diffraction experiments was done immediately after receipt of the sample and the second set the following day. The temperature of the nozzle tip was 20 °C. The bulk sample was held in a bath at -40 to -36 °C during the experiments (the temperature found necessary to provide sufficient sample vapor pressure) and kept in dry ice otherwise. Three diffraction photographs were first made at the intermediate camera distance with use of a beam stop of smaller diameter than usual because it was feared that the amount of sample might be insufficient for additional photographs at the long distance that is normally used to register small-angle scattering. Although this turned out not to be the case, the decision was fortunate in that it was found that the long-distance plates made the following day gave less reliable data than the intermediate-distance plates made earlier.

Conditions of the diffraction experiments were as follows: sector shape, r^3 ; plates, Kodak projector slide medium contrast 8×10 in.; development, 10 min in D-19 diluted 1:1, nominal camera distances, 750 and 300 mm; nominal electron wavelength, 0.058 Å (calibration standard: CO₂, with $r_a(\text{CO}) = 1.1646$ Å, $r_a(\text{O-O}) = 2.3244$ Å); exposure times, 100–240 s; beam currents, 0.30–0.43 Å; ambient apparatus pressure during exposures, 2.0×10^{-6} torr. Data over the range $2.00 \leq s \leq 14.00$ Å⁻¹ were obtained from each of the long camera distance plates, $3.00 \leq s \leq 33.75$ Å⁻¹ from one of the intermediate distance plates, and $5.25 \leq s \leq 33.75$ Å⁻¹ from the others; the data interval was $\Delta s = 0.25$ Å⁻¹. (Use of the small beam stop for preparation of the intermediate distance plates allows data to be obtained at s values as small as 2.5 Å⁻¹. However, the inner portion on two of the plates was too dark to be used for $s < 5.25$ Å⁻¹.) Procedures used for obtaining the total scattered intensities ($s^4I_t(s)$) and the molecular intensities ($sI_m(s)$) have been described.^{2,3} Figure 1 shows the total intensities superimposed on their

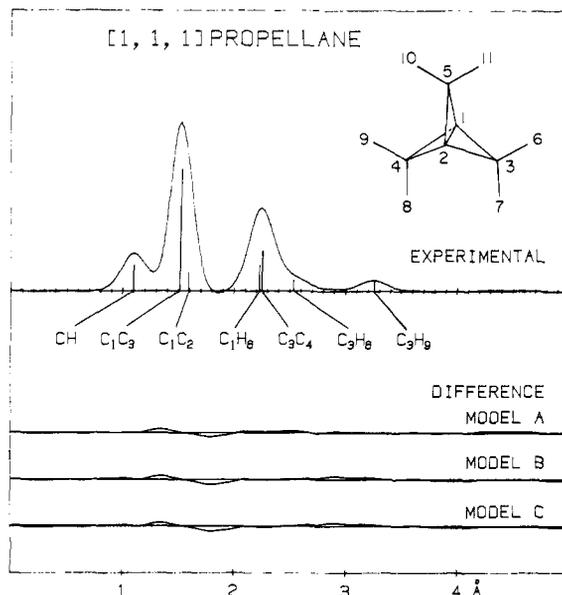


Figure 2. Radial distribution curves. The experimental curve was calculated from a composite of the intermediate camera curves of Figure 1 after addition of theoretical data from model A for $s < 3.00$ Å⁻¹. The difference curves are experimental minus theoretical. The experimental components of the difference curves for models B and C were calculated from composites of the long and intermediate camera experimental intensities to which was appended theoretical intensities for $s < 2.00$ Å⁻¹.

backgrounds; these data are available as supplementary material.

Radial distribution curves were calculated by Fourier transformation of the function $I_m'(s) = Z_C^2 A_C^{-2} s I_m(s) \exp(-0.0025s^2)$. The preliminary experimental curves were found to be completely consistent with a molecule of D_{3h} or D_3 symmetry with an axial carbon-carbon bond length of about 1.6 Å. The final curve is shown in Figure 2. Amplitudes and phases for all calculations were taken from tables.⁴

Structure Analysis. Convenient structural parameters for [1.1.1]propellane were the two types of carbon-carbon bond lengths, the C-H bond length, the H-C-H bond angle, and, to test the question of nonplanarity of the six hydrogen atoms, a torsion angle ϕ that reduced the overall molecular symmetry to D_3 . We elected to refine the structure in terms of the distance type r_a^0 that would permit use of the B_0 rotational constant recently determined from the fine structure of vibrational bands as a constraint. The B_0 value of $0.28714 \text{ cm}^{-1} = 8608.2 \text{ MHz}$ was corrected to $B_z = 8599.6 \text{ MHz}$ in order that the value be consistent with the r_a^0 distances. This correction of 8.6 MHz and the corrections for vibrational averaging necessary to convert the r_a^0 distances to the r_a ones used in the diffraction equations were calculated⁵ from the vibrational force field¹ with use of a geometry for the molecule very near that of our final model.

In addition to the structural parameters, there are seven vibrational amplitude parameters (root-mean-square amplitudes of vibration) arising from the seven important interatomic distances in the molecule, i.e., all distances except H...H which were shown by tests to contribute insignificantly to the scattered intensity.

The least-squares refinements were based on the simultaneous adjustment of a single theoretical intensity curve to the experimental curves derived from each of the plates. Each experimental curve was given a weight proportional to the average density of the plate from which it was obtained. A problem arose when it was found that the data from the experiments at the two different camera distances were slightly inconsistent in a way that could not be corrected by any model changes. Although it was unlikely that the inconsistencies could have arisen from any aspect of the data-reduction procedures, we re-analyzed both sets of plates under a variety of conditions, particularly those affecting the microphotometry, and obtained the same result. Since such inconsistencies do not arise, in our experience, with stable material, we have concluded that some deterioration of the sample probably occurred during the 24 h that elapsed between the two experiments. Fortunately,

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Table I. Parameter Values for [1.1.1]Propellane^a

parameters	preferred model (A) ^b				model B		model C		<i>l</i> _{calcd} ^c
	<i>r</i> _α ⁰ , <i>∠</i> _α	<i>r</i> _g	<i>r</i> _a	<i>l</i>	<i>r</i> _α ⁰ , <i>∠</i> _α	<i>l</i>	<i>r</i> _α ⁰ , <i>∠</i> _α	<i>l</i>	
C-H	1.090 (5)	1.106	1.100	0.082 (5)	1.095 (4)	0.080 (5)	1.094 (4)	0.080 (5)	0.077
C ₁ -C ₃	1.522 (2)	1.525	1.522	0.060 (3)	1.523 (2)	0.060 (3)	1.523 (2)	0.060 (3)	0.055
C ₁ -C ₂	1.594 (5)	1.596	1.592	0.074 (12)	1.593 (5)	0.076 (11)	1.590 (6)	0.075 (10)	0.052
C ₃ -C ₄	2.247 (4)	2.248	2.246	0.064 (4)	2.248 (4)	0.065 (4)	2.250 (4)	0.065 (4)	0.057
C ₁ ·H ₆	2.238 (7)	2.245	2.239	0.114 (13)	2.237 (6)	0.109 (11)	2.231 (11)	0.107 (12)	0.106
C ₃ ·H ₈	2.532 (14)	2.537	2.529	0.144 (28)	2.528 (12)	0.122 (19)	2.517 (18)	0.119 (18)	0.132
C ₃ ·H ₉	3.250 (6)	3.255	3.252	0.103 (16)	3.253 (5)	0.111 (16)	3.250 (7)	0.110 (16)	0.094
∠HCH	116.0 (19)				116.8 (16)		118.2 (24)		
∠C ₁ C ₃ H ₆	116.9 (8)				116.5 (6)		116.0 (9)		
∠C ₃ C ₁ C ₄	95.1 (1)				95.2 (1)		95.2 (2)		
∠C ₁ C ₃ C ₂	63.1 (2)				63.1 (2)		62.9 (3)		
<i>W</i> (MW)/ <i>W</i> (ED) ^d	200				150		0		
Δ <i>B</i> ₂ /MHz ^e	-2.5				-1.0		-14.8		
<i>R</i> ^f	0.062				0.065		0.064		

^aDistances (*r*) and amplitudes (*l*) in angstroms, angles (*∠*) in degrees. ^b $r_a = r_g - l^2/r = r_\alpha^0 + \frac{3}{2}a_3[l^2 - (l^2)^0] + \delta r + K^0 - l^2/r$ where *a*₃ is a Morse function anharmonicity constant estimated to be $2.13 \times 10^{-6} \text{ \AA}^{-1}$ for C-C and $1.98 \times 10^{-6} \text{ \AA}^{-1}$ for C-H; and δr (centrifugal distortions) and *K*⁰ (perpendicular amplitude) corrections were calculated from the force field. ^cCalculated from the force field of ref 1. ^dSee text for description of weighting. ^e*B*₂(obsd) - *B*₂(calcd). ^f $R = [\sum_i w_i \Delta_i^2 / \sum_i w_i (s_i I_i(\text{obsd}) - s_i I_i(\text{calcd}))^2]^{1/2}$ where $\Delta_i = s_i I_i(\text{obsd}) - s_i I_i(\text{calcd})$.

Table II. Correlation Matrix (×100) for Parameters of [1.1.1]Propellane

	$\sigma_{LS} \times 100^a$	<i>r</i> ₁	<i>r</i> ₂	<i>r</i> ₃	<i>r</i> ₄	<i>r</i> ₅	<i>r</i> ₆	<i>r</i> ₇	<i>∠</i> ₈	<i>∠</i> ₉	<i>∠</i> ₁₀	<i>∠</i> ₁₁	<i>l</i> ₁₂	<i>l</i> ₁₃	<i>l</i> ₁₄	<i>l</i> ₁₅	<i>l</i> ₁₆	<i>l</i> ₁₇	<i>l</i> ₁₈
1. <i>r</i> (C-H)	0.16	100	3	8	-5	-3	-36	36	45	-45	-8	8	-2	6	5	-4	9	5	1
2. <i>r</i> (C ₁ -C ₃)	0.05		100	51	55	-91	-86	-70	85	-85	-24	24	18	31	89	-7	24	-2	5
3. <i>r</i> (C ₁ -C ₂)	0.18			100	-43	-48	-57	-72	44	-48	-96	96	16	5	50	-17	41	23	4
4. <i>r</i> (C ₃ -C ₄)	0.10				100	-48	-35	-3	46	-43	68	-68	4	29	45	10	-14	-24	2
5. <i>r</i> (C ₁ ·H ₆)	0.24					100	94	81	-91	91	24	-24	-17	-28	-80	9	-24	1	-4
6. <i>r</i> (C ₃ ·H ₈)	0.49						100	68	-99	99	35	-35	-16	-27	-77	11	-29	-4	-4
7. <i>r</i> (C ₃ ·H ₉)	0.16							100	-55	57	58	-58	-17	-14	-63	13	-30	-10	-4
8. ∠HCH	65.0								100	-100	-22	22	14	29	76	-9	24	<1	4
9. ∠C ₁ C ₃ H ₆	27.0									100	25	-25	-15	-29	-76	9	-26	-1	-4
10. ∠C ₃ C ₁ C ₄	4.6										100	-100	-12	6	-26	17	-38	-26	-2
11. ∠C ₁ C ₃ C ₂	6.8											100	12	-6	26	-17	38	26	2
12. <i>l</i> (C-H)	0.13												100	21	22	-3	17	4	3
13. <i>l</i> (C ₁ -C ₃)	0.03													100	42	5	27	1	6
14. <i>l</i> (C ₁ -C ₂)	0.39														100	-7	31	1	6
15. <i>l</i> (C ₃ -C ₄)	0.09															100	-63	-32	<1
16. <i>l</i> (C ₁ ·H ₆)	0.42																100	57	3
17. <i>l</i> (C ₃ ·H ₈)	0.97																	100	-1
18. <i>l</i> (C ₃ ·H ₉)	0.54																		100

^aStandard deviations from least squares. Distances (*r*) and amplitudes (*l*) in angstroms, angles (*∠*) in degrees.

as will be seen, the effect of this uncertainty on our structural conclusions is negligible.

We refined models of *D*_{3h} symmetry first. After good fits were obtained we tested models that had a nonplanar, propellor-like arrangement of the hydrogen atoms (*D*₃ molecular symmetry) with methylene torsion angles of 5 and 10°. In these refinements the quality of agreement worsened as the torsion angle increased; at 0° the torsion angle parameter obtained a very large uncertainty. Since we found no suggestion of a nonplanar hydrogen arrangement, our results are given in terms of *D*_{3h} symmetry for the molecule.

Table I shows refinement results obtained under several sets of conditions. In view of the evidence suggesting that the long camera distance data reflect an impure sample, our preferred model A was derived with use of diffraction data from the intermediate camera distance plates only, with the rotational constant¹ included as an observable. The weight assigned to the rotational constant was such that the weighted square of its value was about 200 times greater than the sum of the weighted squares of the diffraction intensities. Model B presents the results obtained when the data from the long camera distance are included with weights proportional to the densities of the plates; the weight assigned to the rotational constant was slightly smaller than that for model A. Model C is based on the same diffraction data as B, but the rotational constant was given zero weight. The theoretical intensity curve for model A is shown in Figure 1. The difference curves (experimental minus theoretical) for the long and intermediate camera distances were calculated respectively from models B and A. Table II is a correlation matrix for the parameters of model A.

Discussion of Results

It is pleasing that the results for the three models of Table I are very similar. Those for models A and B show that the inconsistencies between the data sets from the intermediate and long camera distances (these can be seen in the difference curves of

Figure 1) that we have attributed to sample deterioration introduce no uncertainties about the most important aspect of the molecular structure: the shape and size of the carbon skeleton. The differences between these two models are found mainly in the distances involving hydrogen atoms and are probably a consequence of the fact that the intensity data involving hydrogens are damped more rapidly than those from the carbon skeleton and thus tend to be relatively more concentrated in the low-angle region. The results for model C compared with B illustrate the effect of excluding the rotational constant as data—the main consequence is a slightly large value for the HCH angle. The agreement of the observed value for the (converted) rotational constant and that calculated from model C is very good and is evidence for the consistency of the diffraction and spectroscopic data. We note that although these results are based on an assumed *D*_{3h} symmetry for the molecule, our tests of a nonplanar arrangement of the hydrogen atoms showed that the values of the other principal parameters are virtually independent of the assumption.

The carbon-carbon bond distances (*r*_α⁰) we find for [1.1.1]-propellane are in excellent agreement with the zero-point values found by Wiberg et al.¹ from analysis of the vibrational spectrum [*C*₁-*C*₂ = 1.60 (2) Å, *C*₁-*C*₃ = 1.522 (2) Å]. These authors assumed a value for the HCH bond angle that is well within the range of uncertainty determined by us and a value for the C-H bond length that, although about 0.007 Å smaller than ours, is quite consistent with it when it is remembered that no account was taken of vibrational anharmonicity in our analysis.

The refined values of the amplitudes of vibration are uniformly greater than the calculated ones. In particular, the calculated amplitudes for the skeletal distances lie outside the experimental

uncertainties. We have no explanation, but it is widely recognized that the differences between experimental and calculated amplitudes are subject to greater fluctuations than, say, are structural differences obtained by different structural methods. In any case, these amplitude differences do not affect our conclusions about the structure.

Acknowledgment. This work was supported by the National Science Foundation under Grant CH84-11165. We thank Pro-

fessor K. Wiberg and Dr. W. Dailey for the sample of [1.1.1]-propellane.

Registry No. [1.1.1]Propellane, 35634-10-7.

Supplementary Material Available: From each plate: tables of total intensities, final backgrounds, and molecular intensities (9 pages). Ordering information is given on any current masthead page.

Theoretical Study of the Stability of Molecular P_2 , P_4 (T_d), and P_8 (O_h)

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Received February 21, 1985

Abstract: Results of ab initio calculations are reported for P_2 , P_4 , and P_8 on the SCF level and with inclusion of valence correlation effects, except for P_8 . Extended polarization basis sets are employed, up to (3d2f1g) for P_2 , (2d1f) for P_4 , and (1d) for P_8 . R_e values obtained on the highest level of theory are in excellent agreement with experiment (in parentheses): $R_e(P_2) = 189.6$ pm (189.4), $R_e(P_4) = 221$ pm (221 ± 2). Computed reaction energies still suffer from basis saturation problems, $D_e(P_2) = 437$ kJ/mol (490), $\Delta E(P_4 \rightarrow 2P_2) = 201$ kJ/mol (232). P_8 is computed to be less stable than $2P_4$ by 158 kJ/mol. The remarkable stability of P_4 is attributed to (i) a relatively small strain energy arising from 60° bond angles and (ii) stabilizing multicenter bonding closely connected to enhanced 3d contributions (as compared to P_8), which are typical for three-membered rings. P_8 is destabilized by the repulsion between parallel PP bonds.

I. Introduction

The remarkable stability of the tetrahedral P_4 molecule constitutes one of the so far not well understood peculiarities of the chemistry of phosphorus and other group V elements such as arsenic.¹ Despite the strain expected for 60° bond angles, one finds a P-P bond energy of ≈ 200 kJ/mol in P_4 , which may be considered as typical for P-P bonds.¹ Virtually no strain should be present in cubic P_8 , but this molecule has never been observed.

Theoretical investigations have so far not been too successful to elucidate the just mentioned problems. Results of electronic structure calculations usually underestimate the stability of P_4 with respect to $2P_2$ to a considerable extent.^{2,3} Trinquier et al.² find P_4 to be 125 kJ/mol more stable than $2P_2$ (on the DZP SCF level), as compared to the experimental value of 228 kJ/mol.⁴ The same authors obtained P_8 to be 42 kJ/mol more stable than $2P_4$, but it was argued quite convincingly that this result reflects merely basis set problems. The comparison of P_4 and P_8 could be done on the DZ SCF level only, and d functions should stabilize $2P_4$ more than P_8 .²

The availability of improved computer hardware, especially supercomputers, and of efficient program packages⁵ now opens the way for more accurate treatments of the relative stability of P_2 , P_4 , and P_8 which will be reported in this work.

II. Details of Computation

The computations were performed with the Karlsruhe version⁵ of the Columbus system of programs,⁶⁻⁸ which has been especially

adapted for the CYBER 205. Effects of valence electron correlation were included for the smaller systems P , P_2 , and P_4 (P_8 could only be treated on the SCF level) by means of the recently developed coupled pair functional method (CPF).⁹ The CPF procedure is based on the variation of an energy functional derived from the CI(SD) energy expression by the introduction of partial normalization denominators in order to achieve size extensivity for the energy. The CPF method is related to CEPA-1^{10,11} and has already proved useful in various applications.^{9,12,13}

The following CGTO basis sets were employed:

$$(s,p): (11,7)/[6.4]^{14}$$

polarization sets:

(1d)

$$\eta(d) = 0.4$$

(2d1f)

$$(d) = 0.23, 0.7; \eta(f) = 0.5$$

(3d2f1g)

$$(d) = 0.167, 0.468, 1.307$$

$$\eta(f) = 0.252, 0.919$$

$$\eta(g) = 0.585$$

The (1d) orbital exponent η is optimal for P_2 on the CPF level

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