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Bond Lengths and Quadratic Force Field for Cubane

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Abstract: The molecular structure of pentacyclo[4.2.0.0^{2,5}.0^{3,8}.0^{4,7}]octane (cubane) has been determined in the gas phase at a temperature of 77 °C. Parameter values were obtained from four types of refinements: those based on electron-diffraction (ED) data alone, ED data with inclusion of a microwave (MW) rotational constant for cubane-d_0 available from the literature, ED data with allowance for single-double multiple scattering (MS) effects, and the ED-MW data with allowance for MS effects. The results differ insignificantly. Bond lengths in terms of the distance types r_α^0 (geometrically consistent at 0 K) and r_g (vibrationally averaged at the experimental temperature) are respectively as follows: C–H, 1.098 (6) and 1.114 (6) Å; C–C, 1.571 (2) and 1.573 (2) Å. Estimated equilibrium values are r_e(C–H) = 1.0960 (130) and r_e(C–C) = 1.5618 (40) Å. Some amplitudes of vibration are l(C–H) = 0.075 (10), l(C–C) = 0.062 (3), $l(\mathrm{C\cdot C})$ = 0.065 (4), $l(\mathrm{C\cdot\cdot C})$ = 0.072 (9); values are in angstroms with estimated 2σ uncertainties in parentheses. O_h symmetry was assumed. A complete quadratic vibrational force field was also evaluated. The 32 independent force constants were fitted simultaneously to 156 observations consisting of 146 wavenumber fundamentals from eight isotopic species, 2 Coriolis constants, 1 centrifugal distortion constant, and 7 amplitudes of vibration. The values are in excellent agreement with recent ab initio results.

Pentacyclo[4.2.0.0^{2,5}.0^{3,8}.0^{4,7}]octane, $(CH)_8$, is a hydrocarbon consisting of eight CH units bound together to form a cube. For obvious reasons its common name is cubane. Cubane is an exceptionally strained system.[2] Rehybridization away from the usual sp^3 hybrid of tetravalent carbon is required to accommodate the geometry of the system; the carbon–carbon bonds are made up from p-richer orbitals and, complementarily, the C–H bonds are s-rich (31% calculated from $J_{^{13}\mathrm{C-H}}$ data). The cubane molecule was first synthesized in 1964,[3] and its crystal structure was determined that same year by X-ray diffraction.[4] The molecule was found to have cubic symmetry to within the uncertainties of that determination. The cubic symmetry of the free molecule has been demonstrated by a number of spectroscopic techniques: a particularly striking illustration is the observation of spherical-top fine structure with its attendant nuclear-spin statistical weight pattern in the high-resolution infrared spectrum.[5] In the crystal the average bond lengths (Å) were found to be r(C–C) = 1.551 ± 0.003 (from three each at 1.553 ± 0.003 and 1.549 ± 0.003) and r(C–H) = 1.03_5 ± 0.05 (from six at 1.01 ± 0.05 and two at 1.11 ± 0.05). More recently, an electron-diffraction (ED) investigation of cubane in the gas phase gave the values r_α(C–C) = 1.575 (1) Å and r_α(C–H) = 1.100 (6) Å.[6] Interpretation of the microwave spectrum of the monodeuterated species (the ratio r(C–H)/r(C–C) was assumed equal to the ED value) led to the result r_0(C–C) = 1.5708 Å and r_0(C–H) = 1.097 Å.[7]

The ever-increasing reliance on molecular mechanics and quantum mechanical calculations for structural information makes it imperative that precise data be available for benchmark compounds like cubane. Unfortunately, this condition does not prevail for cubane, as is apparent from the discrepancies in the structural data cited above. In particular, the difference seen between the X-ray and ED results is important because the r_α-type distances from ED contain allowance for thermal effects that should make these distances comparable to those from X-ray diffraction. The discrepancy could be due to the absence of corrections for the effects of libration in the crystal, but this conjecture is unproven.

These matters have impelled us to reinvestigate the cubane structure. We expected to improve the precision of the electron-diffraction measurements, partly because the earlier ones[6] were based on data from a limited number of plates, but more importantly because the rotational constant from the microwave work on monodeuterated cubane[7] had become available. We note that new thermochemical studies to determine the standard heat of formation of cubane are underway, and a neutron-diffraction study aimed at an accurate measurement of the C–H bond is planned.

Experimental Section

The cubane sample was prepared at Chicago from cubane-1,4-dicarboxylic acid[8] by use of the Barton methodology,[9] viz., by radical decarboxylation via thermal decomposition of the bis-*N*-hydroxypyridine-2-thione ester in the presence of a hydrogen donor (*tert*-butylmercaptan). The hydrocarbon was carefully purified by crystallizations from benzene and methanol, dried by transfer under vacuum through 4A molecular sieves, and then finally sublimed at reduced pressure. The melting point of cubane is 130 °C; its vapor pressure at 25 °C is approximately 1.1 Torr.

The diffraction photographs were made in the Oregon State apparatus. Data concerning the experiments are as follows: sector, r^3; average sample temperature as measured by a thermocouple at the nozzle tip, 77 °C; nominal electron wavelength, 0.057 Å (calibration standard, CO_2 with r_a(C=O) = 1.1646 Å and $r_a(\mathrm{O\cdot O})$ = 2.3244 Å); electron-beam currents, 0.3–0.4 μA; photographic media, medium contrast Kodak projector slide plates; development, 10 min in D-19 diluted 1:1; nominal camera distances, 75 cm (long) and 30 cm (middle). Other data peculiar to the long (middle) camera distances were the following: exposure times, 60–120 s (150–240 s); number of plates used in the structure analysis, 4 (4); ranges of data, $2.00 \leq s/\text{Å}^{-1} \leq 13.75$ ($6.00 \leq s/\text{Å}^{-1} \leq 33.75$). Total scattered intensities ($s^4I_t(s)$) were obtained from the plates and the backgrounds removed by the usual procedures to generate molecular intensities in the form $sI_m(s)$.[10,11] Complex electron-scattering factors $|F(s)|$ and phases η used in various calculations were obtained from tables.[12] The final intensity curves are shown in Figure 1; the data are available as supplementary material.

The final experimental radial distribution curve (Figure 2) was calculated from the function $I'(s) = sI_m(s)Z_C^2A_C^{-2}\exp(-0.0025s^2)$, where

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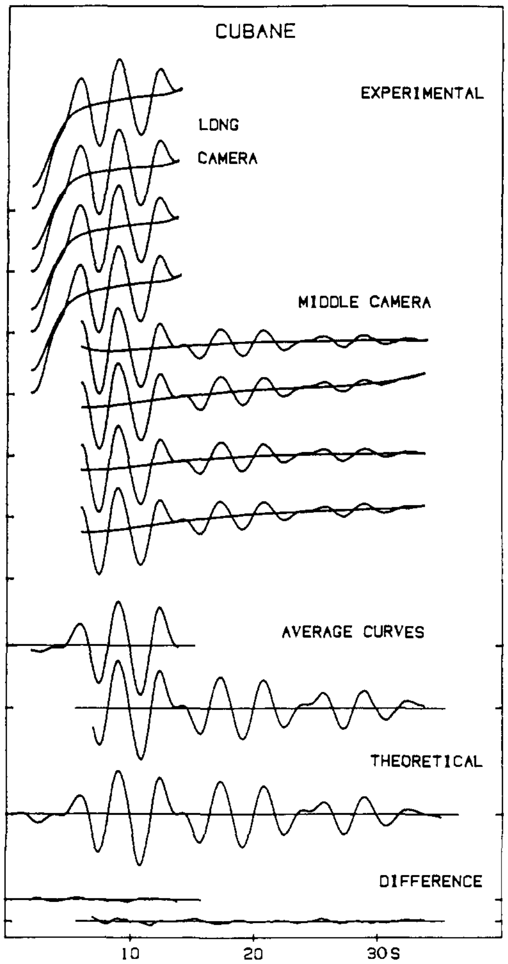

Figure 1. Scattered-intensity curves. The total intensities $(\langle s^4 I_t(s)\rangle)$ from each plate are magnified 5× with respect to the backgrounds on which they are superimposed. The average curves are $s[s^4 I_t - \text{background}]$. The theoretical curve is for model A. The difference curves are experimental minus theoretical.

$A = s^2F$, with use of theoretical data over the unobserved or uncertain region $s \leq 2.75$ Å^{-1}. As expected, the peaks of the curve corresponded to the interatomic distances in a C_8H_8 molecule of symmetry O_h.

Structure Analysis

Vibrational Corrections. The importance of accurate values for the bond lengths in cubane requires especially careful assessment of the effects of molecular vibration on the distance measurements. The problem is that the set of vibrationally averaged distances obtained from electron diffraction is, in general, not consistent with the point group symmetry of the (rigid) molecule in question. What is needed for cubane are the quantities that convert a set of distances consistent with O_h symmetry (r_α or $r_\alpha{}^0$ types) to the r_a type measured from electron diffraction. Since we also wished to include the rotational constant measured for monodeuterated cubane as additional data to be fitted, the conversion $B_0 - B_z$ (B_z is consistent with $r_\alpha{}^0$-type distances) as well as corrections to the distances arising from the H → D isotope effect were also necessary. The following formulas are well-known.[13]

$$r_a{}^T = r_\alpha{}^0 + (3a/2)[(l^2)^T - (l^2)^0] + \delta r^T + K^0 - (l^2)^T/r \qquad (1)$$

$$= r_g{}^T - (l^2)^T/r \qquad (2)$$

$$r_\alpha{}^0 \simeq r_e + (3/2)(al^2)^0 - K^0 \qquad (3)$$

$$r_g{}^T \simeq r_e + (3al^2/2)^T \qquad (4)$$

$$B_z = B_0 + \sum_i \alpha_i{}^{\text{har}} d_i/2 \qquad (5)$$

In these formulas the superscripts are temperatures, a is a Morse anharmonicity constant, l is the rms amplitude of vibration, δr is the centrifugal distortion, K is the perpendicular amplitude correction, and d is the vibrational degeneracy; descriptive details may be found in the article cited.

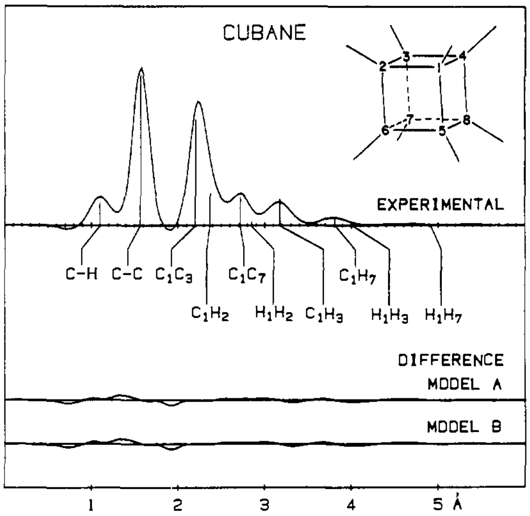

Figure 2. Radial distribution curves. The vertical bars have lengths proportional to the weights of the terms they represent.

For cubane, a reliable assessment of the vibrational r and B differences in eqs 1–5 requires an accurate quadratic force field; except for a, all the necessary quantities can be calculated from such a force field. Values of a for bonds may be obtained by approximating the atoms they link as diatomic molecules, but little is known about a values for nonbonds and they are usually set to zero. We used the force field determined in this work, as detailed below, to obtain the desired quantities. Assuming $a =$ 2.0 Å^{-1}, the $r_\alpha{}^0$ distances for the bonds of the parent molecule were generated with use of eq 1 from experimental r_a values obtained from preliminary refinements; the remaining $r_\alpha{}^0$ distances were defined by the O_h symmetry. We next calculated the differences between $r_\alpha{}^0$ distances for the monodeuterated molecule and parent with use of eq 3 ($\Delta r_\alpha{}^0 = (3a/2)[(l_{\text{iso}}{}^2)^0 - (l_{\text{par}}{}^2)^0] - K_{\text{iso}}{}^0 + K_{\text{par}}{}^0$). Of these differences, only $r_\alpha{}^0(\text{C–D}) - r_\alpha{}^0(\text{C–H}) = -0.00025$ Å was found to be significant in connection with fitting the rotational constant. Thus, the $r_\alpha{}^0$ structure used to fit the B_z value for the deuterium compound was defined by the $r_\alpha{}^0$ structure of cubane itself with one of the C–H distances replaced by a C–D distance that incorporated this correction. For the electron-diffraction fit, the differences $r_g - r_\alpha{}^0$ (seen in column 2 of Table I) were calculated with use of theoretical values. The r_a distances were generated from r_g with use of experimental amplitude values.

Structure Refinements. Our standard least-squares method[14] was used to refine the parameters $r_\alpha{}^0$(C–H) and $r_\alpha{}^0$(C–C) and the vibrational amplitudes l corresponding to all carbon–carbon and carbon–hydrogen distances. Although all H·H terms were included in the calculated intensities, the amplitudes for these terms were held at values close to the theoretical ones. We investigated the effect of possible three-atom (double–single) multiple scattering[15] on the derived parameter values as well as the effect of including the rotational constant B_z (=3219.67 MHz; $B_0{}^{\text{obsd}} = 3220.72$ MHz[7]) with different weights. The many refinements included ones that fitted the original diffraction data alone, these data and B_z simultaneously, the diffraction data corrected for multiple scattering alone, and finally the corrected data and B_z simultaneously. The corrected diffraction data were obtained by subtracting from the experimental intensity the multiple scattering intensity ($1TP_0$ approximation) calculated for a model similar to the final one.

Results are given in Table I for two models. The preferred model, A, was obtained from the corrected intensities with the rotational constant weighted to give $w_B(B_{\text{obsd}})^2/\sum_i w_i(s_i I_{\text{m,obsd}})^2 \simeq 280/1$. Model B resulted from a refinement based on the uncorrected diffraction data alone. The correlation matrix for the parameters of model A is given in Table II.

Quadratic Force Field. Force fields have been published previously for cubane, determined both by fitting experimental data[5,16] and from ab initio calculations.[17] However, a new determination from all the

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(13) See: Robiette, A. G. In *Molecular Structure by Diffraction Methods*; Specialist Periodical Reports, The Chemical Society: London, 1973; Vol. 1, also references cited therein.

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Table I. Distances (r/Å) and rms Amplitudes of Vibration (l/Å) in Cubane[a]

		model A[b]				model B[c]		
	$r_g - r_\alpha^{0}$ [d]	r_α^{0} [e]	r_g	r_a	l_{obsd}	r_α^{0}	l_{obsd} [d]	l_{calcd}
C–C	0.0024	1.571 (2)	1.573	1.571	0.062 (3)	1.571 (2)	0.062 (3)	0.054
C·C	0.0018	2.222 (3)	2.223	2.222	0.065 (4)	2.221 (3)	0.065 (4)	0.057
C··C	0.0015	2.721 (3)	2.722	2.721	0.072 (9)	2.721 (3)	0.072 (9)	0.061
C–H	0.0159	1.098 (6)	1.114	1.109	0.075 (10)	1.097 (9)	0.078 (10)	0.078
C·H	0.0075	2.380 (5)	2.388	2.383	0.104 (12)	2.379 (8)	0.104 (13)	0.108
C··H	0.0056	3.182 (5)	3.188	3.184	0.113 (15)	3.186 (8)	0.113 (15)	0.102
C···H	0.0047	3.819 (6)	3.824	3.821	0.113 (48)	3.817 (9)	0.111 (48)	0.095
H·H	0.0100	2.839 (7)	2.849	2.838	[0.176]	2.837 (10)	[0.176]	0.175
H··H	0.0072	4.015 (9)	4.022	4.017	[0.148]	4.012 (14)	[0.148]	0.146
H···H	0.0061	4.917 (11)	4.923	4.921	[0.117]	4.914 (18)	[0.117]	0.119
ΔB_z[f]/MHz		0.17				−1.62		
R[g]		0.0590				0.0599		

[a] Amplitudes in square brackets were assumed. Uncertainties in parentheses are estimated 2σ and include estimates of correlation among measured intensities. [b] Preferred model. Account taken of multiple scattering and rotational constant for C_8H_7D included as a constraint. Uncertainties for r_g and r_a are essentially similar to those for r_α^0. [c] Multiple scattering and rotational constant ignored. [d] See text. [e] Results leading to B_z^{calcd} are r_α^0(C–C) = 1.5709 Å and r_α^0(C–H) = 1.0980 Å. [f] $\Delta B_z = B_z(\text{obsd}) - B_z(\text{calcd})$. [g] $R = [\sum_i w_i \Delta_i^2 / \sum_i w_i (s_i I_i(\text{obsd}))^2]^{1/2}$ where $\Delta_i = s_i I_i(\text{obsd}) - s_i I_i(\text{calcd})$.

Table II. Correlation Matrix (×100) for Parameters of Cubane, Model A

	σ_{LS}[a]	r_1	r_2	l_3	l_4	l_5	l_6	l_7	l_8	l_9
1. r(C–C)	0.034	100	−80	13	−17	<1	−8	−37	6	−1
2. r(C—H)	0.205		100	−12	21	2	11	45	−4	<1
3. l(C—C)	0.064			100	31	10	<1	9	12	1
4. l(C·C	0.092				100	2	13	42	6	<1
5. l(C··C)	0.311					100	6	17	−10	−2
6. l(C—H)	0.349						100	13	6	−2
7. l(C·H)	0.409							100	15	−11
8. l(C··H)	0.493								100	−18
9. l(C···H)	1.70									100

[a] Standard deviations (×100) from least-squares refinements.

available experimental data was felt to be justified. The calculations were carried out with the program ASYM20.[18]

The data comprised the vibrational wavenumbers measured by Della et al.[19] (whose notation cubane-d_0, cubane-d_1, etc. we adopt in this section) for a range of isotopic species, the centrifugal distortion constant D_J for cubane-d_1 from the microwave study,[7] the Coriolis constants ζ_{11} and ζ_{12} for cubane-d_0 obtained from diode laser spectroscopy,[6] and the bonded and nonbonded CC and CH amplitudes for cubane-d_0 from the present work.

The wavenumber data were in all cases the condensed-phase measurements, since for many fundamentals these are the only data available. Most assignments were taken unchanged from Della et al.[19] For ν_{17} and ν_{18} of cubane-d_8, and the modes which correlate with these in cubane-d_6, the revised assignments of Pine et al.[5] were used. We also used the revised assignment of ν_4 suggested by Dunn et al.[17] and included experimental values for this mode in cubane-d_1 (1027 cm^{-1}), cubane-d_2 (1020 cm^{-1}), and cubane-d_7 (995 cm^{-1}). Besides the data for the five main species cubane-d_0, -d_1, -d_2, -d_6, and -d_8 where most of the fundamentals have been assigned, we included three fundamentals of cubane-^{13}C. We were able to make convincing assignments of 15 fundamentals of cubane-d_5 (C_s), out of a possible 42, and 13 of cubane-d_7 (C_{3v}), out of a possible 28; altogether 146 fundamentals were included from eight isotopic species.

The addition of two Coriolis constants, one distortion constant, and seven amplitudes brings the total number of experimental observations fitted to 156. Symmetry restricts the number of independent force constants to 32. It is unusual to find such a large ratio of data to force-constant parameters, particularly for a molecule containing so many atoms.

Results of the refinement are given in Table III (for verification purposes the force-constant values are given with more figures than significance justifies); G-matrix elements for cubane-d_0 and cubane-d_8 are found in the supplementary material as Table VIII. The symmetry coordinates used were those of Cyvin et al.,[16] except that (a) all angle-bending coordinates were unscaled with dimensions of radians and (b) coordinates involving deformations of the C_8 cube in species A_{2u}, E_u, and F_{2g} were expressed in terms of CCC angle-bending internal coordinates alone instead of a CCC + CCH combination. The structural parameters were the r_α^0 bond lengths of Table I.

Table III. Quadratic Force Constants for Cubane[a]

A_{1g}	CH str	4.9618 (90)			
	CC str	0.1221 (273)	3.8727 (80)		
E_g	CC str	3.5820 (105)			
	CCH bend	0.1482 (23)	0.4695 (16)		
F_{1g}	CCH bend	0.4827 (6)			
F_{2g}	CH str	4.8829 (80)			
	CC str	0.0291 (90)[b]	3.8214 (458)		
	CCC bend	−0.0510 (158)[b]	0.0340 (323)	1.1800 (283)	
	CCH bend	0.0221 (68)[b]	−0.8497 (77)	0.2508 (282)	1.3684 (62)
A_{2u}	CH str	4.9256 (97)			
	CCC bend	−0.1399 (164)	1.2634 (31)		
E_u	CCC bend	2.1867 (105)			
	CCH bend	0.1471 (47)	0.4944 (24)		
F_{1u}	CH str	4.9157 (71)			
	CC str	0.1287 (261)	3.7183 (88)		
	CCH bend	0.0392 (126)	−0.4504 (25)	1.5718 (25)	
F_{2u}	CC str	3.1543 (123)			
	CCH bend	−0.0737 (16)	0.4006 (14)		

[a] Units: aJ/Å^2 for stretches, aJ/rad^2 for bends. Quantities in parentheses are estimated standard deviations. [b] Constants refined as a group with fixed ratios. See text.

Full details of the fit, weighting scheme, etc., are not given here, but may be obtained on request.[20] The quality of the fit is very pleasing. Setting aside for the moment CH and CD stretching modes, and considering only fundamentals below 1250 cm^{-1}, 119 wavenumber data are fitted with an rms deviation of 1.7 cm^{-1} and a worst case error of 5.0 cm^{-1}.

As is well-known, the CH and CD stretching modes are strongly anharmonic, so that a greater degree of misfit must be expected for these than for the skeletal and bending modes. We adjusted the refinement conditions to give an almost constant offset (observed minus calculated) of −20 cm^{-1} for CH modes and +20 cm^{-1} for CD modes: in fact, the former deviations are all within −20 ± 3.6 cm^{-1} and the latter within +20 ± 2.8 cm^{-1}. These results show that the calculation is successful in

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(18) Hedberg, L. Abstracts, Seventh Austin Symposium on Gas Phase Molecular Structure, Austin, TX, Feb 1978, p 49.

(19) Della, E. W.; McCoy, E. F.; Patney, H. K.; Jones, G. L.; Miller, F. A. *J. Am. Chem. Soc.* **1979**, *101*, 7441.

(20) From A. G. Robiette.

Table IV. Theoretical Results for Bond Lengths (r/Å) of Cubane

	6-31G*[b]	STO-3G[c]	4-31G[c]	6-31G*[c]	STO-3G[d]	DZ + d[a,e]	4-21G[f]	4-31G[g]	MINDO/3[h]
r_e(C–C)	1.5632	1.562	1.573	1.557	1.562	1.570	1.580	1.572	1.566
r_e(C–H)	1.0852	1.087	1.075	1.079	1.082	1.081	1.075	1.076	1.106

[a] Basis was C7,3/H4 contracted to C4,2/H2 with a set of d functions added to C. [b] Reference 24a. [c] Reference 24b. [d] Reference 24c. [e] Reference 24d. [f] Reference 24e. [g] Reference 24f. [h] Reference 23.

reproducing both the spread of fundamentals within each isotopic species and the pattern of change between different isotopic species. All other data are fitted to within their respective experimental uncertainties.

Of the 32 force-constant parameters, 29 were refined independently. The five 2 × 2 blocks (A_{1g}, E_g, A_{2u}, E_u, and F_{2u}) and the sole 1 × 1 block (F_{1g}) are well-determined essentially from wavenumber data alone. The 3 × 3 F_{1u} block is also well-determined by virtue of the inclusion of the infrared Coriolis constants. The 4 × 4 F_{2g} block, however, remains underdetermined even though the distortion constant and amplitudes contribute to the definition of the force constants in this block.

After various sets of constraints were tried, the final results were obtained by constraining $F_{6,7}$, $F_{6,8}$, and $F_{6,9}$ to refine together with their values fixed in the ratios calculated ab initio by Dunn et al.[17] These three force constants are the interaction constants between the F_{2g} CH stretching coordinate and the other three F_{2g} coordinates, and it is not altogether surprising that they are not well-defined by the existing data.

Overall the agreement between our force field and the ab initio values[17] is striking, especially as regards the signs and magnitudes of the off-diagonal force constants. This agreement confirms the good quality of the ab initio calculation and also lends confidence to our experimental determination.

Discussion

It is gratifying that the structural results for cubane are independent of whether or not the rotational constant is included as a constraint in the refinement. This circumstance inspires a high degree of confidence in the accuracy of the distance values, and in the distance corrections that relate the electron-diffraction structure to the microwave data; the accuracy of the distance corrections in turn implies high quality for the vibrational force field. Our value for r_a(C–C), 1.571 (2) Å, is slightly shorter than the 1.575 (2) Å found by Almenningen et al.,[6,21] but the two measurements of r_a(C–H) (1.109 (6) Å, this work; 1.112 (12) Å[6]) are equal to within the uncertainties of the measurements. In view of the experimental difficulties encountered by the earlier investigators the agreement for both parameters must be regarded as very good.

Molecular mechanics results for cubane are r_g(C–C) = 1.561 (MM3) and 1.557 Å (MM2), and r_g(C–H) = 1.104 (MM3) and 1.114 Å (MM2).[22] The MM3 result for r_g(C–C) is nearer our value, but still too small by about 0.01 Å. The MM2 value for r_g(C–H) agrees exactly with ours; MM3 predicts it to be smaller.

There have been several quantum mechanical investigations of the cubane structure by both semiempirical[23] and HF/SCF ab initio[24] methods. A summary of some of the distance results is given in Table IV. As is evident from eqs 2 and 3, these equilibrium distances are expected to differ slightly from the experimental ones which display the effects of molecular vibration. If the uncertainties associated with the experimental r and l values are taken into account, the r_e lengths of the C–C and C–H bonds in cubane are calculated to be 1.5618 (40) and 1.0960 (130) Å. Here the uncertainties in parentheses are estimated 2σ that include allowance for possible systematic error in, and correlation among, the experimental data. For the C–C bond the r_e values from the MINDO/3 calculation, and from the ab initio calculations with the 6-31G* and the STO-3G basis sets, are in good agreement with our experimentally derived one; the other basis sets yield values too large by 0.004–0.014 Å. For the C–H bond our experimental r_e range of 1.0830–1.1090 Å is consistent only with the MINDO/3 and one of the ab initio 6-31G* results; the other values are too small by 0.001–0.008 Å.

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Supplementary Material Available: Tables of total intensities and backgrounds from each plate, average molecular intensities from each camera distance, calculated multiple scattering, and G-matrix elements (12 pages). Ordering information is given on any current masthead page.

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(21) The uncertainties quoted in ref 6 did not include estimates of systematic error and data correlation. Accordingly, to bring them more closely into correspondence with our uncertainties which do reflect these estimates, we have multiplied them by three.

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