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A Computational Study of the Apparent Discrepancy between the Solid-State and Gas-Phase Value of the C−C Bond in Cubane

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The geometry of the cubane molecule, C_8H_8, has been studied by ab initio and empirical force field methods in both the gas phase and the crystalline state. The calculations support the hypothesis that the apparent shortening of the C−C bond distance by about 0.02 Å, as determined by X-ray diffraction compared to the gas-phase electron diffraction experiments, is the result of vibrational effects.

Introduction

The crystal structure of the aliphatic hydrocarbon cubane was determined by E. Fleisher in 1964.[1] The space group is $R\bar{3}$ (#148), with one molecule in the unit cell. Ignoring the hydrogen atoms, the geometry of the cubane skeleton is determined by the position of only two carbon atoms. One is on the general *f* position, and the other on the 3-fold axis and is denoted *c* in the Wyckoff notation. The remaining atoms are generated by the crystal symmetry, and this results in two distinct C−C distances. As stated in the original paper, the difference in bond lengths is small enough to warrant the conclusion that the cubane molecule essentially has cubic symmetry in the crystalline state. There are a few minor problems with the data reported by Fleisher, however.

According to the diagram in the original paper, the two C−C bond lengths are 1.553(3) and 1.549(3) Å, but the former is calculated to be 1.551 Å from the published coordinates. Although the difference is trivial and, in fact, strengthens the main conclusion about the high symmetry of the molecule, this discrepancy hints that either the diagram, the atomic coordinates, or the cell parameters reflect different stages in the refinement of the crystal structure.

Second, the temperature factors of the hydrogen atoms are 80−100 times larger than those for the carbon atoms. It would thus appear that the latter are not expressed as *B*'s, as indicated in the paper, but in terms of the now more commonly used *U*, the relation being $B = 8\pi^2 U$. This distinction has some bearing on the discussion later in this article.

Markedly different is the C−C bond length determined by electron diffraction in the gas phase,[2] however. Assuming O_h symmetry, as is shown to be the case from the vibrational spectrum,[3,4] the cubane molecule is ideally suited for this type of experiment, with all the peaks in the radial distribution function being well resolved. Despite the experimental difficulties encountered by the authors, the length of the C−C bond was established with high accuracy and found to be 1.575(1) Å. This distance is an r_α value (distance between average atomic positions) and is easily derived from the r_a value obtained directly from the diffraction results using a vibrational correction. The value for the latter is, in this case, also 1.575(1) Å.

The value also compares well with the r_g distance (thermally averaged distance) of 1.573(2) Å [1.571(2) Å for r_a] obtained by Hedberg et al.,[5] using a combined gas-phase electron diffraction/microwave approach. Differences between r_g, r_α, and r_a are small in the gas phase, typical values being in the range $2{-}5 \times 10^{-3}$ Å, and conversions between these various definitions and the equilibrium distance obtained by ab initio calculations, r_e, are well understood.[6]

However, in the solid state, the cubane molecule has an additional six vibrational modes, which, for hydrocarbons, typically are below 100−150 cm^{-1} and which will increase the difference between r_g and r_α by a factor of about 10. Therefore, in principle, molecular structures determined by X-ray diffraction studies require that a vibrational correction be applied to transform the distances obtained from the average atomic positions to an r_g geometry.

Unfortunately, such a correction is by no means standard practice because it requires that a model be defined to differentiate between intra- and intermolecular vibrations. Because of the rigidity of the cubane molecule, the "rigid-body" model would probably be the most suitable, but the correction was not applied by Fleisher,[1] and Hedberg et al.[5] have suggested that the observed discrepancy between the gas-phase and solid-state C−C distance is due to this lack of correction.

Cubane has a reputation of being a molecule that is difficult to handle,[7] and as a first step in an effort to investigate the nature of the observed discrepancy in the C−C bond length, a computational study was initiated to shed some light on this problem.

Computational Details

Ab initio calculations were performed with the Gaussian-98 program.[8] Geometry optimization was done with the "tight" convergence criteria. Because of problems with the recognition and handling of the existing cubane symmetry by the Gaussian program, all calculations were performed with molecular

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symmetry ignored. The solid state was simulated by surrounding the central molecule by a layer of point charges at positions generated with the experimental cell parameters. All complete unit cells within 20 Å were included, and charge values were taken to be equal to those calculated for the isolated molecule at the same level of theory as used for the solid-state simulation.

Molecular mechanics calculations were performed with the program PEFF. [9] Parameters for all empirical force fields were taken from the literature. These were the author's EFF90[10] and EFF93;[11] Allinger's MM2,[12] MM3,[13] and MM4;[14] and a force field by Engler, Andose, and Schleyer (EAS).[15] For the MM3 force field, the bend/bend interaction between angles sharing only a common atom was not included in the calculations, as this interaction is not implemented in the PEFF program. Comparisons with results generated by the MM3(92) program show that the effect of this omission is negligible. For all force fields, the crystal structure of cubane was calculated by including all interactions between complete unit cells within a 30 Å radius of the central unit cell. A direct summation was performed. The crystal system was enforced during the minimization, but no other symmetry was assumed to be present. A Newton−Raphson scheme was applied. Acoustic and libration modes were simulated using a method described elsewhere,[16] in which the contents of the central unit cell are considered to vibrate in the average field of a rigid block surrounding it. Despite its simplicity, this model gives good qualitative and quantitative results for alkanes.

Results and Discussion

For the purpose of the discussion below, two possible reasons are identified for the observed difference in bond length between the gas and solid phases: (i) the difference is due to vibrational effects, as suggested by Hedberg et al., and (ii) the C−C bond length in the crystal is shortened as a result of changes in electron density compared to the isolated molecule.

To test the latter, a number of ab initio calculations were performed on cubane. As mentioned earlier, these give r_e distances, but the results are easily converted to other definitions. The "experimental" r_e value reported by Hedberg et al. is 1.561 8(40) Å, and as stated by the authors, this compares favorably with a number of HF/6-31G(d) values available at that time.

In this study, a variety of different combinations of basis sets and levels of theory are employed to calculate the cubane geometry. In a recent paper by Allinger et al.,[17] the effect of the size of the basis set and the level of theory was evaluated for a number of small molecules. The results of this study show that a computational effort at the CCSD/TZ2P+f level is required to obtain equilibrium distances that will transform the r_e values correctly to observed r_g distances. Even given today's available hardware, such a calculation is not very practical, and Allinger et al. propose a more modest B3LYP/6-31G(d) level for bonds involving first-row atoms, or MP2/6-31G(d) if second-row atoms are present.

The error of 0.004 Å on r_e reported by Hedberg et al. is quoted to be 2σ; thus, any calculated value outside 1.555 8−1.567 8 Å, or a 3σ (99%) confidence interval, can be considered to be significantly different from the experimental value.

Calculations are summarized in Table 1. Results show that, in contrast to the results from Allinger et al., the density functional B3LYP level of theory gives bond lengths that are outside, or just bordering the acceptable range defined above. It also appears that standard HF calculations fall comfortably within this range, but it should be mentioned that no exhaustive comparison between the two methods was made and, hence, that this observation does not necessarily indicate a trend.

TABLE 1: Ab Initio Results (r_e) for the C−C Bond Length of Cubane in the Gas Phase and the Solid State[a]

method	C−C (gas)	C(3)−C(1)	C(1)−C(1)
HF/6-31G(d)	1.5590	1.5578	1.5596
MP2/6-31G(d)	1.5653	1.5642	1.5668
B3LYP/6-31G(d)	1.5705	1.5697	1.5708
HF/6-31++G(d,p)	1.5602	1.5587	1.5610
B3LYP/6-31++G(d,p)	1.5713	1.5698	1.5721
B3LYP/6-311++G(3df,2pd)	1.5682		
exp,[b] X-ray, r_α		1.551(3)	1.549(3)
exp,[c] GED, r_α	1.575(1)		
exp,[d] GED, r_g	1.573(2)		

[a] For the solid state, the point symmetry of the C atom is give in parentheses. [b] Ref 1. [c] Ref 2. [d] Ref 5.

Employing a plane-wave density approximation, Richardson and Martins[18] were able to confirm the existence of two different C−C bonds in the solid state. The values obtained for the bond lengths are 1.59 and 1.62 Å. These are equilibrium distances and differ markedly from the 1.549 and 1.551 Å found experimentally in the crystal, but they are comparable with the calculations summarized in Table 1. Unfortunately, this author has no access to quantum codes using plane waves, and thus, the method of surrounding charges was used to simulated the solid state, as explained earlier. The results, give in Table 1, show that, irrespective of basis set or level of theory, the C−C bond splits into two different values, one lengthening and the other shortening by 1−2 × 10^{-3} Å. This is about the same order of magnitude as found experimentally but quite different from the results reported by Richardson and Martins.[17] In addition, the current calculations do not predict the correct order of this change, the effect being the opposite of the experimental findings. Placing the charges on positions based on the gas-phase geometry rather than on those of the crystal results in a similar conclusion. Because care was taken to surround the central molecule by a layer of complete and thus electrically neutral molecules, it is not clear what causes this discrepancy.

Table 1 makes clear, however, that there appears to be no reason to suspect that electronic effects will shorten the C−C bond in the solid state to the values found by X-ray diffraction on the crystal. Hence, to test the first hypothesis, namely, that the observed shortening of the bond is the result of vibrational effects, a number of molecular mechanics calculations were performed.

Taking a 3σ confidence interval below the lowest, and the same amount above the highest, crystallographically determined C−C distance, a calculated vibrational correction on r_g should result in an r_α value between 1.540 and 1.560 Å for the molecule in the solid state. Results with a variety of force fields and a number of different models are summarized in Table 2.

The MM3 force field is the only force field used that employs a special set of parameters for four-membered rings. However, these are specifically tailored to deal with the energetic implications of the small C−C−C angles and have no direct effect on the resulting C−C bond lengths. For the isolated molecule, this bond, which, as in most force fields, is considered to represent an r_g value, is calculated to be 1.561 Å, or 0.012 Å too short. Considering that the MM3 value is parametrized to fit a relatively large number of molecules containing four-membered rings, this discrepancy is a bit puzzling. Using the PEFF program, the r_α value of a fully optimized cubane molecule in the crystal is calculated to be 1.520 Å. Adjustment of the reference distance r_o parameter to give a gas-phase

TABLE 2: Molecular Mechanics Calculations of the r_α Value[a] (Å) for the C−C Distance of Cubane in the Crystal and Average Thermal Parameter (Å^2) for the C Atoms

force field	C−C	$<U_{ii}>$
MM3, full opt[b]	1.520	0.0788
MM3, full opt, adj r_o[c]	1.533	0.0798
MM3	1.547	0.0689
MM3 + charges[d]	1.549	0.0678
MM4	1.552	0.0616
MM2	1.562	0.0314
EFF93	1.560	0.0345
EFF90	1.560	0.0349
EAS	1.562	0.0342
exp[e]	1.550	0.0438

[a] Unless noted otherwise, all calculations were performed using a rigid molecule with C−C equal to 1.573 Å. [b] Full optimization with original force-field parameters [c] Full optimization with r_o adjusted to give a C−C bond length for the isolated molecule equal to 1.5730 Å. [d] Atomic charges taken from the HF/6-31G(d) calculations on the isolated molecule. [e] Ref 1.

geometry equal to the GED result of 1.573 Å produces an r_α value in the solid state of 1.535 Å, still outside the acceptable range. The figures above are for a fully optimized molecule and thus contain intramolecular and lattice vibrations. A rigid-body treatment removes the intramolecular contribution from the calculated thermal motion of the atoms and, hence, decreases the difference between r_g and r_α, but the difference for MM3 is quite large, resulting in a value of $r_\alpha = 1.547$ Å. This figure is somewhat unexpected but may be due to the fact that MM3 underestimates the torsional frequencies of cubane severely. For example, the E_u deformation frequency is calculated to be 303 cm^{-1}, whereas the experimental figure[4] is 617 cm^{-1}. Similarly, the F_{2g} band is 441 cm^{-1}, compared to 665 cm^{-1} experimentally. The lower frequencies will artificially increase the thermal motions of the atoms and thus also the vibrational correction.

Unfortunately, MM2 and MM3 are the only force fields in Table 2 that have been parametrized explicitly for four-membered rings, and therefore, calculations with the other force fields were performed by treating cubane as a rigid body fixed at the GED geometry. In view of the effect of intramolecular modes on the calculation of the vibrational corrections with MM3, the rigid-body results should probably be considered to be a minimum bond shortening for the particular force field. Inclusion of atomic charges, taken from the HF/6-31G(d) calculations, is found to have only a minimal effect on the results, and because all force fields in the table have been designed to be used without charges for saturated hydrocarbons, they were left out.

It is noted from Table 2 that, employing a rigid-body treatment, both MM3 and MM4 give a C−C distance for cubane in the solid state that is within the acceptable range discussed above, with the other force fields situated near the top border of this range. It is also worth noting that the largest and smallest vibrational corrections of 0.024 and 0.011 Å are found for the MM3, and MM2 and EAS force fields, respectively, thus demonstrating the profound effect of differences in nonbonded parameters on the calculations.

It is also instructive to compare the calculated thermal parameters of the atoms. Because of the limitations of the vibrational model used, only average values are reported here, being the mean values of the diagonal vibrational amplitudes, $<U_{ii}>$, averaged over all C-atoms. As is evident from Table 2, the numerical values of the amplitudes follow the same pattern as the vibrational corrections calculated with the various force fields. Thus, the various models calculated with MM3 overestimate, and with all other force fields underestimate, the vibrational effects.

TABLE 3: Calculated Accoustic and Librational Lattice Modes (cm^{-1}) with a Number of Empirical Force Fields Using the Rigid-Body Approximation

	A_u	E_u	A_g	E_g
MM2	53	55	82	80
MM3	37	38	53	52
MM4	38	39	60	56
EFF90	52	52	77	74
EFF93	51	53	77	74
EAS	51	51	86	80
exp (300 K)[a]	−	−	63	85
exp (100 K)[b]	(78)	(78)	94	114

[a] Ref 19. [b] Ref 20.

Finally, accoustic and librational lattice modes are summarized in Table 3. The Raman-active librational modes have been indentified[19] at room temperature to be 63 and 85 cm^{-1}. At 100 K, a neutron scattering study[20] positions the same peaks at 94 and 114 cm^{-1}, respectively, and identifies one accoustic peak at 78 cm^{-1}. The molecular mechanics calculations clearly distinguish between the accoustic and librational modes in terms of wavenumbers, but the spread on the individual modes is not as large as found experimentally. The numbers are much in line with the conclusion that both MM3 and MM4 predict a lower frequency for these modes than the other force fields and thus larger thermal motions of the atoms. All force fields predict the E_g mode to have a lower wavenumber than the A_g mode, in contrast with the observations.

Conclusions

The molecular structure of the cubane molecule has been studied in the gas phase and the solid state by ab initio and molecular mechanics calculations. The quantum calculations indicate that there is no reason to assume that the distribution of electron density is responsible for the differences in the experimental C−C distance determined by electron diffraction in the gas phase and X-ray diffraction on the crystal.

Molecular mechanics studies with a variety of empirical force fields support the hypothesis formulated by Hedberg et al.[5] that the apparent discrepancy between these values is a result of vibrational effects. Using a rigid-body approximation, the vibrational correction needed to transform the r_g distance calculated with the force field to an r_α value as observed in the crystal is, for most force fields used in this study, within, or on the border of, what is identified as an acceptable range. However, considering the sizable influence of intramolecular vibrations on this correction found with the MM3 force field, a proper parametrization of the force fields to four-membered rings to allow inclusion of these modes in the calculations is likely to improve the results toward strengthening this hypothesis.

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