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Methylene Rocking in Cyclobutanedicarboxylic Acid at 4.2 K. The Geometry of a Four-Membered Ring in Its Ground State†

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Abstract: The geometry of the four-membered ring in 2,2,4,4-deuterated 1,1-cyclobutanedicarboxylic acid in its lowest vibrational state was elucidated from a single-crystal ENDOR detected NMR (EDNMR) study at 4.2 K of the β-deuteron quadrupole coupling tensors. These data, combined with the location of the carbon atoms obtained from a 20 K X-ray study of the same material (Santarsiero, 1990), provide a direct measurement of the geometry of the ring in its ground state. The D–C–D bond angle was found to be 109.5 ± 0.5°, with the two methylene groups tilted (rocked) by 4.4 ± 0.5° toward each other. The ratio of the rocking angle to the pucker angle, 0.21 ± 0.01, is identical with the value obtained from a gas electron diffraction study of cyclobutane (Egawa, 1987). The remarkable agreement between these very different experiments supports the view that the ring atoms in this "highly strained" molecule retain their usual sp^3 symmetry, with all four orbitals simply pivoting as a unit to minimize the energy. A C–H bond length of 1.097 ± 0.005 Å (obtained from the γ H–H dipolar coupling tensor) is also consistent with this view of the ring atoms. The average value of e^2qQ/h is 176 ± 2 kHz with $\eta \approx 0.03$, in agreement with other measurements of carbon-bonded deuterons.

The nature of the bonds in 3- and 4-carbon saturated-ring systems has long been an intriguing question because of the large difference between the nominal ring angles (60° and 90°) and the typical 109.5° directed valence angles of tetrahedral carbon. The fact that these compounds are completely stable and for the most part behave like normal hydrocarbons is certainly somewhat surprising. Early attempts at a quantum-mechanical understanding of the bonding in such molecules in terms of a change in hybridization gave unacceptable results. Coulson and Moffit's introduction of the concept of "bent bonds",[1a] and the MO descriptions of Walsh,[1b] Wiberg,[1c] and others (see Hoffman and Davidson[1d] for an excellent review), have since provided significant insights that have been bolstered by numerous experimental and theoretical studies.

The first measurement of the geometry of a four-membered ring, the electron-diffraction study of cyclobutane by Dunitz and Schomaker,[2] suggested that the ring was puckered rather than planar (puckering is the out-of-plane displacement of opposite pairs of ring carbon atoms, see Figure 1). Since puckering further *decreases* the geometric bond angle, this phenomena was rationalized as a way for the molecule to reduce the nonbonded interactions (hydrogen eclipsing). The equilibrium pucker angle was thus seen as a measure of the balance between steric forces and strain energy.[3] Attempts to determine this angle as accurately as possible were frustrated by the high symmetry of the ring, which precluded direct IR or microwave measurements. The most significant vibrational mode of C_4H_8, for example, the ν_{14} puckering motion whose zero-point amplitude defines the pucker angle, is invisible except as a Raman or combination line. This fact led workers to study similar, less symmetric molecules, such as the 1,1-difluoro derivative,[4h] oxetane,[4i] and the silacyclobutanes.[4j]

After many years of careful spectroscopic work[4] the best value for the pucker angle in cyclobutane appeared to be about 35 ± 5°, although the data in a few cases[4e–g] suggested a possible systematic error. Lafferty[5a] and Kuchitsu[5b] also pointed out the problems inherent in obtaining geometric results for polyatomic molecules from spectroscopic data alone, since small uncertainties in the measured kinematic constants can lead to large errors in the calculated structure. In contrast, the potential energy surface is well determined by spectroscopic methods. The reader is referred to several excellent reviews of work on small cyclic molecules[5c–e] for further information.

In the midst of ongoing spectroscopic studies, Wright and Salem[6] made a surprising discovery: their ab initio calculations showed that the lowest-energy state of cyclobutane was, in fact, *always planar* at all levels of approximation, unless the methylene groups were allowed to "tilt" (rock) away from a symmetrical position with respect to the local C–C–C plane. Since the C_2CH_2 group had previously always been treated as a rigid unit, this observation confirmed suspicions of a systematic error in earlier work. A re-analysis of one set of data,[7] plus several additional theoretical calculations,[8] gave a revised pucker angle of about 27°, with an estimated rocking angle of 3–6°. Confirmation of these values required new measurements of not only the pucker angle but also the much smaller rocking angle—clearly a significant challenge.

Meiboom and Snyder[9a] were the first to report a value for the rocking angle based on simulations of the NMR spectrum of cyclobutane in a nematic solvent; an improved set of measure-

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(1) (a) Coulson, C. A.; Moffitt, W. E. *J. Chem. Phys.* **1947**, *15*, 151; *Philos. Magn.* **1949**, *40*, 1–35. (b) Walsh, A. D. *Trans. Faraday Soc.* **1949**, *45*, 179–190. (c) Wiberg, K. B.; Bader, R. F. W.; Lau, C. D. H. *J. Am. Chem. Soc.* **1987**, *109*, 985–1001, 1001–1012. (d) Hoffmann, R.; Davidson, R. B. *J. Am. Chem. Soc.* **1971**, *93*, 5699–5705.

(2) Dunitz, J. D.; Schomaker, V. *J. Chem. Phys.* **1952**, *20*, 1703–1707.

(3) Luntz, A. C. *J. Chem. Phys.* **1969**, *50*, 1109–1118.

(4) (a) Lord, R. C.; Stoicheff, B. P. *Can. J. Phys.* **1962**, *40*, 725–731. (b) Dows, D. A.; Rich, N. *J. Chem. Phys.* **1967**, *47*, 333–334. (c) Ueda, T.; Shimanouchi, T. *J. Chem. Phys.* **1968**, *49*, 470–471. (d) Miller, F. A.; Capwell, R. J. *Spectrochim. Acta* **1971**, *27A*, 947–956. (e) Laane, J.; Lord, R. C. *J. Chem. Phys.* **1968**, *48*, 1508–1513. (f) Stone, J. M. R.; Mills, I. M. *Mol. Phys.* **1970**, *18*, 631–652. (g) Malloy, T. B. *J. Mol. Spectrosc.* **1972**, *44*, 504–535. (h) Luntz, A. C. *J. Chem. Phys.* **1969**, *50*, 1109–1118. (i) Creswell, R. A.; Mills, I. M. *J. Mol. Spectrosc.* **1974**, *52*, 392–412. (j) Killough, P. M.; Irwin, R. M.; Laane, J. *J. Chem. Phys.* **1982**, *76*, 3890–3898.

(5) (a) Lafferty, W. J. In *Critical Evaluation of Chemical and Physical Structural Information*; Lide, D. R., Jr., Paul, M. A., Eds.; National Academy of Science: Washington, DC, 1974; p 386ff. (b) Kuchitsu, K.; Ovangi, K. *Faraday Discuss.* **1977**, *62*, 20–28. Kuchitsu, K. *Ibid.* **1977**, *62*, 49. (c) Carreira, L. A.; Lord, R. C.; Malloy, T. B. Jr. *Top. Current Chem.* **1979**, *82*, 1–95. (d) Legon, A. C. *Chem. Rev.* **1980**, *80*, 231–262. (e) Laane, J. *Pure Appl. Chem.* **1987**, *59*, 1307–1326.

(6) Wright, J. S.; Salem, L. *J. Chem. Soc., Chem. Commun.* **1969**, 1370–1371.

(7) Malloy, T. B.; Lafferty, W. J. *J. Mol. Spectrosc.* **1975**, *54*, 20–38.

(8) (a) Nelson, J. L.; Frost, A. A. *J. Am. Chem. Soc.* **1972**, *94*, 3727–3731. (b) Wright, J. S.; Salem, L. *J. Am. Chem. Soc.* **1972**, *94*, 322–329. (c) Cremer, D. *J. Am. Chem. Soc.* **1977**, *99*, 1307–1309. (d) Skancke, P. N.; Gogarasi, G.; Boggs, J. E. *J. Mol. Struct.* **1980**, *62*, 259–273. (e) Wiberg, K. B.; Bader, R. F. W.; Lau, C. D. H. *J. Am. Chem. Soc.* **1987**, *109*, 985–1012. (f) Cremer, D.; Gauss, J. *J. Am. Chem. Soc.* **1986**, *108*, 7467–7477. (g) Runtz, G. R.; Bader, R. F. W.; Messer, R. R. *Can. J. Chem.* **1977**, *55*, 3040–3045.

(9) (a) Meiboom, S.; Snyder, L. C. *J. Am. Chem. Soc.* **1967**, *89*, 1038–1039. (b) Meiboom, S.; Snyder, L. C. *J. Chem. Phys.* **1970**, *52*, 3857–3863. (c) Cole, K. C.; Gilson, D. F. R. *J. Chem. Phys.* **1974**, *60*, 1191–1192.

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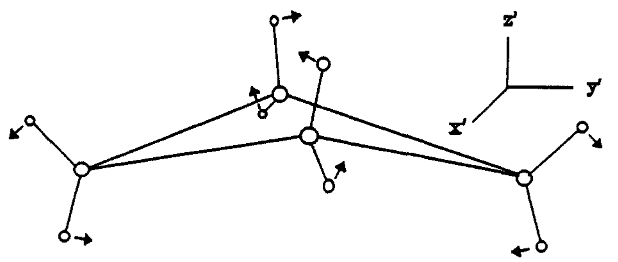

Figure 1. Rocking distortions in a four-membered ring.

ments[9b] and reinterpretation of the data,[9c] however, gave significantly different results. Dalton and Kwiram[10] then attempted to measure the orientation of the $>CH_2$ groups in a single crystal of 1,1-cyclobutanedicarboxylic acid (CBDA) at 4.2 K using the newly developed technique of ENDOR Detected NMR (EDNMR).[11] Unexpected difficulties in preparing the desired partially deuterated derivatives unfortunately limited the initial study to CBDA with only the acid protons exchanged. The resulting lack of resolution in the spectra of the ring protons, along with some ambiguity in the room temperature X-ray structure,[12] prevented a definitive conclusion. An intermittent search was then begun for a viable method of selectively deuterating the ring, the successful conclusion of which led to the work reported here.

During this same time period, Kuchitsu and co-workers continued refining the techniques of gas electron diffraction (GED), devising ways to combine the analysis of spectroscopic and diffraction data in order to get more reliable results for small cyclic molecules.[13] Their results for cyclobutane[13d] appeared shortly after this work was completed. In spite of the totally different experimental approaches used, the GED/FTIR measurements on gaseous C_4H_8 at 250 K and the EDNMR results on CBDA at 4.2 K give exactly the same picture of the ring.

Overview

The magnetic nuclei in CBDA interact with each other and with an external magnetic field according to the spin Hamiltonian

$$\mathcal{H} = g_n\beta_n\mathbf{I}\cdot\mathbf{H} + \mathbf{I}\cdot\mathbf{D}\cdot\mathbf{I}' + \mathbf{I}\cdot\mathbf{Q}\cdot\mathbf{I}$$

where $g_n\beta_n$ is the magnetic moment of a given nucleus, **I** is the nuclear spin vector ($\mathbf{I} = {}^1/_2$ for ^{1}H, $\mathbf{I} = 1$ for ^{2}H), H is the external (Zeeman) field, **D** is the magnetic dipole coupling between any two spins, and **Q** is the electric quadrupole interaction. The relative magnitudes of these terms (in MHz) are shown below; note that $\mathbf{Q} = 0$ for ^{1}H (or for any nucleus with $\mathbf{I} < 1$), while $\mathbf{D} \ll \mathbf{Q}$ for ^{2}H.

	$g_n\beta_n\mathbf{I}\cdot\mathbf{H}$	$\mathbf{I}\cdot\mathbf{D}\cdot\mathbf{I}'$	$\mathbf{I}\cdot\mathbf{Q}\cdot\mathbf{I}$
e^-	9000	30	0
^{1}H	13.7	0.060	0
^{2}H	2.0	0.006	0.270

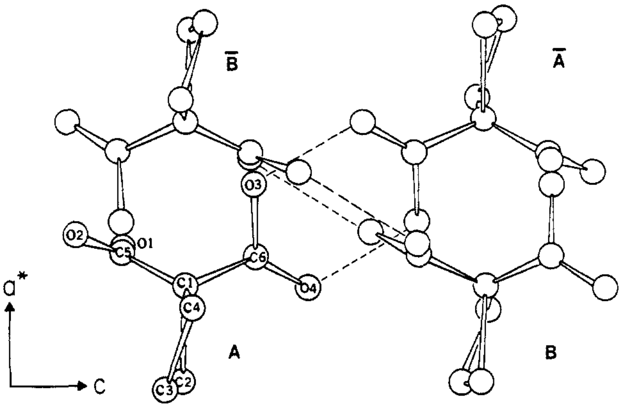

Figure 2. The unit cell of cyclobutanedicarboxylic acid (CBDA).

From a practical point of view then, protons have dipolar spectra, while deuterons have quadrupolar spectra. Since both **D** and **Q** are traceless second-rank tensors, both interactions have the same angular dependence, from which the geometric information of interest is derived. Because the Zeeman interaction is the largest term,[14] the proton and deuteron spin axes are essentially aligned along the magnetic field; turning the sample then "points" these nuclei in different molecular directions. The dipole and quadrupole splittings indicate when the field is along a H–H or C–D vector, since the respective splitting is largest along those directions. The macroscopic measurement of the orientation of the crystal with respect to the field thus gives a direct measurement of the molecular geometry.

In practice one systematically rotates the sample around three mutually perpendicular axes, recording the angular variation of all the splittings. The principal axes of the dipole and quadrupole tensors are then calculated from these data, rather than located directly as suggested above. The methylene (D–C–D) bond angle is obtained from the angular difference between the axes of the two quadrupole tensors in each $>CD_2$ group, while the relative orientation of those axes with respect to the carbon skeleton gives the rocking angle. Likewise the dipole tensor for the two protons in a $>CH_2$ group can be used to determine both the rocking angle and the C–H bond length, given knowledge of the bond angle (from the $>CD_2$ results, perhaps) and the fact that the dipole interaction varies like $1/r^3$.

Experimental Section

The details of the EDNMR experiment have been described previously.[10,11,15] In brief, one monitors the strength of a nearly saturated ESR signal arising from a low concentration of free radicals created by X-ray damage,[16] while simultaneously sweeping the RF power over the range of frequencies corresponding to the expected nuclear Zeeman (NMR) transitions. Inducing nuclear spin flips in molecules distant from the radicals causes (by means of rather complex spin dynamics[17]) a large change in the population of the electron spin levels, hence a large change in the ESR signal. In essence, power absorbed by the nuclei is transferred to the unpaired electrons rather than to the lattice, thereby creating a very sensitive NMR detector.

The enhanced sensitivity (which can be 10^3 greater than a conventional low-temperature NMR experiment) is due to (1) the large magnetic moment of the electron compared to the nuclei, (2) the high Q and low noise figure of a resonant cavity compared to a typical NMR coil, (3)

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(10) Dalton, L. R.; Kwiram, A. L. *J. Am. Chem. Soc.* **1972**, *94*, 6930–6938.

(11) McCalley, R. C.; Kwiram, A. L. *Phys. Rev. Lett.* **1970**, *24*, 1279–1281. The descriptive label ENDOR Detected NMR (EDNMR) was introduced to indicate clearly that normal NMR transitions of nuclei on the bulk diamagnetic molecules are observed. These NMR transitions occur at $\nu_n = g_n\beta_nH_0$, *unshifted* in frequency by the presence of the dilute (~1:10000) paramagnetic centers in the sample. The term distant ENDOR, used in earlier papers to describe this effect, has also been used more recently to refer to matrix ENDOR or to what should properly be called local ENDOR of weakly coupled nuclei. Such weakly coupled nuclei can be located either on the free radical itself or on a neighboring diamagnetic molecule. However, in contrast to EDNMR transitions, the transitions of weakly coupled nuclei are generally *shifted* in frequency and appear near but not at ν_n.

(12) Solızberg, L.; Margulis, T. N. *J. Chem. Phys.* **1971**, *55*, 4907–4913.

(13) (a) Kamabara, H.; Kuchitsu, K.; Morino, Y. Unpublished data cited in *Bull. Chem. Soc. Jap.* **1970**, *43*, 2017. (b) Takabayashi, F.; Kambara, H.; Kuchitsu, K. *7th Austin Symposium of Gas Phase Molecular Structure 1978*, Austin, Texas, Paper WA6 63–64. (c) Kuchitsu, K. Gas Electron Diffraction In *Molecular Structure and Properties*; MTP Review of Phys. Chem., Series One, 1972; Vol. 2, Chapter 6; Allen, G., Ed.; Butterworths: London. (d) Egawa, T.; Fukuyama, T.; Yamamoto, S.; Takakbayashi, F.; Kambara, H.; Ueda, T.; Kuchitsu, K. *J. Chem. Phys.* **1987**, *86* 6018–6026.

(14) With the field used in this experiment (≈3200 G) the ^{1}H resonance was at 13 MHz and the ^{2}H resonance at 2.0 MHz. This choice of field was dictated by the frequency of the ESR transition (9.0 GHz), which was determined by the dimensions and design of the microwave cavity.

(15) Boroske, E.; Möbius, K. *J. Magn. Reson.* **1977**, *28*, 325–338.

(16) The radicals were introduced by irradiating the sample on a standard Mo-target X-ray machine (tube power = 2500 W) for an hour. The concentration was not determined, but is believed (from experience with other samples) to be less than 0.1%.

(17) (a) Redfield, A. G. *Phys. Rev.* **1955**, *98*, 1787; Redfield, A. G. *Science* **1969**, *164*, 1015. (b) Provotorov, B. N. *Zh. Eksper. Teor. Fiz.* **1961**, *41*, 1582. (c) Abragam, A.; Borghini, M. *Prog. Low Temp. Phys.* **1964**, *4*, 384. (d) Wenckeback, W. Th.; v. d. Heuvel, G. M.; Hoogstraate, H.; Swaneburg T. J. B.; Poulis, N. J. *Phys. Rev. Lett.* **1969**, *22*, 581–583. (e) de Boer, W. *Dynamic Orientation of Nuclei at Low Temperatures*; CERN 74-11 1974.

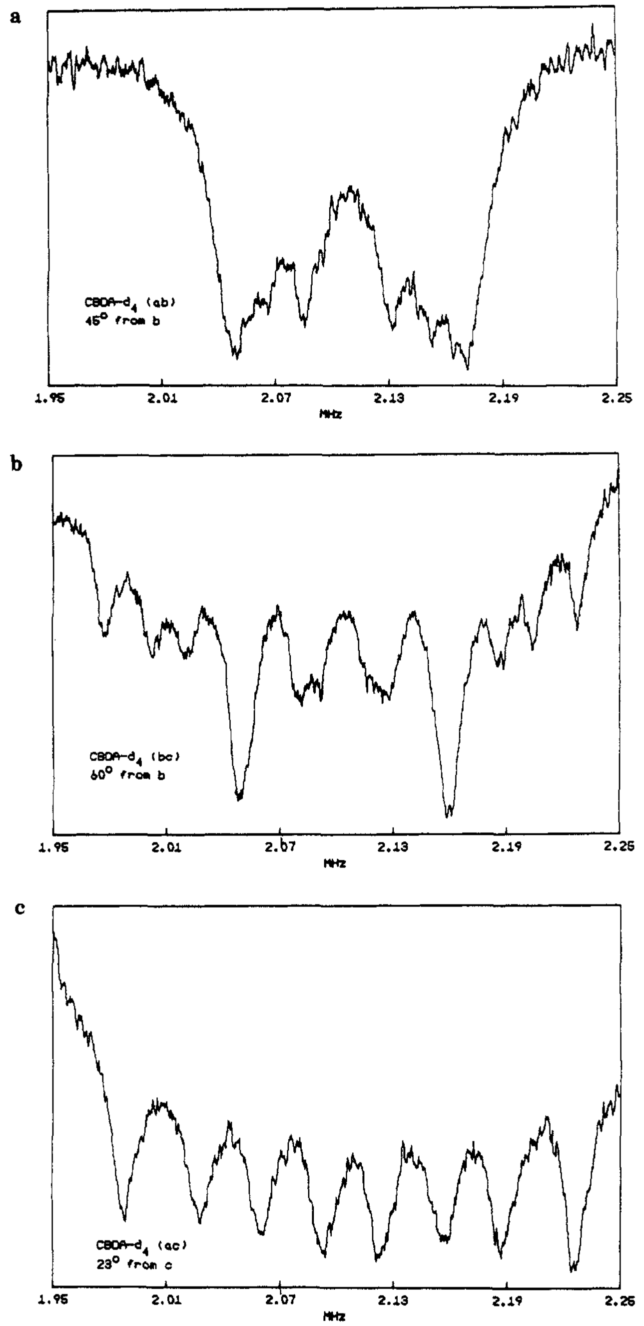


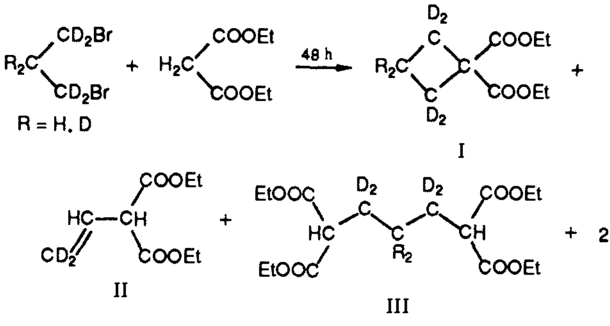
Figure 3. Deuterium quadrupole spectra of cyclobutanedicarboxylic-*2,2,4,4-d$_4$* acid at 4.2 K observed by electron-detected NMR.

the short relaxation time of the nuclear spins in the presence of paramagnetic centers (seconds vs hours), and (4) the enhanced nuclear polarization caused by pumping the ESR transition.[17e] The high sensitivity permits the use of small samples—a valuable advantage for work involving single crystals of isotopically labeled compounds. The most important feature of this technique, however, is that it provides a way to make geometric measurements at very low temperatures (1-4 K) where only the lowest vibrational state is populated. The "raw data" are thus the r_0 values, free of corrections for vibrational or torsional averaging.

The results reported here were obtained from a 2 × 2 × 4 mm sample immersed in liquid helium. The ESR signal, modulated at 100 KHz, was monitored with a Varian E9 X-band spectrometer connected to a home-built LN$_2$-cooled TE$_{011}$ cylindrical cavity.[18] RF power from an ENI 310L 3-W amplifier driven by an Ailtech Model 360 synthesizer passed through a two-turn loop surrounding the sample inside the cavity. The experimental parameters (sample orientation and RF frequency) were controlled by a PDP8/e minicomputer using LDF, a high-level, real-time control language developed by one of the authors.[19] This allowed unattended data acquisition, with each scan taking approximately 15 min (10-12 h per plane). The S/N was sufficiently high (Figure 3) that signal averaging was necessary in only a few cases.

CBDA was initially selected for this study because dicarboxylic acids generally form[20] strong, hydrogen-bonded crystals that cycle well between room temperature and 4.2 K; such compounds also readily produce stable free radicals when X-irradiated for a few hours. Since the two carboxyl groups are about the same size as the ring and are both attached to the same carbon, one might worry that the ring itself will be significantly distorted. In fact, however, the doubly-linked chains formed by the COOH groups create a very open structure in which the cyclobutane rings appear to be almost suspended in free space (Figure 2), with no measurable distortion[21] other than the obvious loss of symmetry. Evidence for this is that both dihedral angles (the "folds" along C$_1$-C$_3$ and C$_2$-C$_4$) are equal, though not strictly required to be so. The initial EDNMR[10] and X-ray studies[12] also showed that the ring was free to pucker at temperatures as low as 77 K, freezing into a single conformation only with further cooling.[22] This observation suggests an asymmetry of ≈20 cm^{-1} in a puckering potential[4c-8] with a barrier of about 500 cm^{-1} and a $v = 1$ state at about 200 cm^{-1}. The crystal forces are thus only a minor perturbation, making a single crystal of CBDA at 4.2 K essentially an ordered array (actually two magnetically inequivalent arrays) of virtually undistorted cyclobutane rings in their lowest vibrational state.

Deuterated CBDA. As is well-known in solid-state NMR, the strength and long-range (r^{-3}) nature of the H-H dipolar interaction leads to unresolved spectra if there are more than a few inequivalent protons in the sample. The deuterium quadrupole interaction, while subject to similar broadening mechanisms, is roughly three times larger; this allows as many as 8-10 inequivalent deuterons to be resolved. Following the inconclusive results of the initial CBDA experiments (in which only the acid protons were replaced by deuterons),[10] a successful method for deuterating the ring was sought and eventually realized. The basic reaction is just the condensation of deuterated dibromopropane with diethyl malonate:



The key to success is the extremely slow addition of the reagents by means of a syringe pump, combined with the use of a two-phase mixture (H$_2$O/CH$_2$Cl$_2$) to keep the starting materials and product separated while the cyclization takes place. The workup consists of treating the reaction mixture with 50% NaOH for 48 h, after which I and II are removed by continuous extraction with ether for 24 h and then separated by flash chromatography[23] using a 1:1 mixture of ethyl acetate and

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(18) The cavity was designed by A. L. Kwiram; it is constructed from fired lava and silver plated on the inside.

(19) Lab Data FOCAL (LDF, also called U/W-FOCAL or UWF) was developed by J. van Zee to provide a general-purpose interactive laboratory control environment for PDP-8/12 users, maintaining full compatibility with the original FOCAL '69 language supplied by Digital Equipment Corporation. LDF offers many significant improvements for users with the OS/8 operating system and 12-32K of memory. A few of the features used in this work were direct access to machine-level programming, foreground/background operation, enhanced execution speed and numerical precision, matrix routines, graphics commands, file and communications support, and more than fifty laboratory-related functions. *See*: *Proc. Digital Equipment Computer Users Soc.* **Fall USA 1975**, *2*, 405; **Canada, 1977**, *3*, 989.

(20) CBDA is monoclinic, with a $P2_1/c$ unit cell, the most common space group for organic compounds. Nowacki, W.; Matsumoto, T.; Edenharter A. report [*Acta Crystallogr.* **1967**, *22*, 935] that the zigzag chain found in CBDA "is the most important 'building unit' (Baustein) of crystalline organic compounds".

(21) Santarsiero, B. *J. Chem. Phys.* **1990**, *92*, 3794-3797.

(22) Soltzberg and Margulis[12] found that at room temperature C$_3$ appeared to occupy two positions with about equal probability, in agreement with a dynamic puckering model. Santarsiero's 20 K study[21] found no disorder, indicating that the rings adopted the lowest energy conformation as the sample cooled.

(23) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923-2925.

Table I. Deuteron Quadrupole Coupling Tensors for 2,2,4,4-d_4 Cyclobutanedicarboxylic-*2,2,4,4-d_4* Acid[a]

bond	direction cosines a'	b	c	splitting, kHz (±2)	η	e^2qQ/h
C_2-D_{21}	0.852	±0.156	−0.499	−130.3	0.029	
	0.461	∓0.675	0.576	−138.1		
	−0.247	∓0.721	−0.647	268.5		179.0
C_2-D_{22}	−0.547	∓0.728	−0.413	−127.1	0.024	
	0.738	∓0.653	0.174	−133.2		
	−0.396	∓0.210	0.894	260.3		173.5
C_4-D_{41}	−0.511	±0.812	0.281	−131.0	0.016	
	0.629	±0.131	0.766	−135.1		
	0.585	±0.569	−0.578	266.0		177.3
C_4-D_{42}	−0.680	∓0.687	0.258	−127.8	0.032	
	0.733	∓0.624	0.270	−136.2		
	−0.024	±0.372	0.928	264.0		176.0
O_1-D_1[b]	0.312	±0.932	−0.185	−113.8	0.112	
	0.850	∓0.186	0.493	−141.8		
	0.425	∓0.311	−0.840	250.1		166.7
O_3-D_3[b]	0.795	∓0.144	−0.589	−115.6	0.110	
	0.349	±0.906	0.240	−144.5		
	0.499	∓0.397	0.770	261.8		174.5

[a] The upper sign refers to molecule A and the lower sign to molecule B. [b] Data taken from ref 10 (Dalton, L. R.; Kwiram, A. L. *J. Am. Chem. Soc.* **1972**, *94*, 6930–6938).

hexane. The overall yield was 25–30%.

About 400 mg (each) of the d_4 (C_2,C_4) and d_6 (C_2,C_3,C_4) compounds were prepared. Since this much CBDA easily dissolves in a large drop of water, the crystals were grown from a diethyl ether solution in a small serum-capped vial, allowing the ether to slowly evaporate through the seal over a period of 1–2 days. Crystals grown this way exhibited large *bc* faces (*c* is parallel to the hydrogen-bonded chains), rather than the *ac* faces obtained from aqueous solutions.[10]

Data Collection and Analysis. The sample was glued to a cylindrical carrier (boat) that allowed the crystal to be accurately oriented in three perpendicular planes without remounting. A careful attempt was made to align the edge of the boat with one of the crystallographic axes in order to simplify the data analysis, but this was only possible to an accuracy of ≈1°. The exact orientation of the crystal was deduced later from the splitting patterns of the two magnetically inequivalent molecules.

Spectra were recorded every 4.5° over a span of 180°. The resonance frequencies were then determined with the aid of a computer program that automatically located the midpoint of peaks (and shoulders) in a consistent way. At no orientation were all 16 possible lines resolved: the maximum number observed was 12 (Figure 3b), while the average was about six. Splittings were calculated from the difference of the ν_+ and ν_- lines. Since the resolution was such that a typical peak came from the superposition of three deuterons, some with "positive" splittings and some with "negative" splittings (the sign refers to the orientation of the spin axis with respect to the field gradient), the individual deuterons were identified by overlaying a plot of all the observed splittings with a computer-generated curve based on data from the X-ray study.[21] This generally led to identification of at least 10 splittings belonging to a given deuteron; those points were then used to calculate a more accurate curve, which identified still more points, and so on. Ultimately only a few splittings out of several hundred per plane could not be assigned.[24] Figure 4 illustrates the final result of this procedure. Note that symmetry-related molecules were treated independently during this analysis.

The angle corresponding to the direction of the crystallographic axes (the 'zero point' on the goniometer) was then determined by minimizing the differences between measurements corresponding to the same direction in different planes (taking advantage of the two magnetically inequivalent molecules in the unit cell[25]), and the resulting coefficients for each set of rotation curves were then diagonalized to get the principal axes of the tensor relative to the laboratory axis system (which, within experimental error, was the *a'bc* system). Table I summarizes the results for all eight deuterons (four for each inequivalent molecule in the unit cell). The labels follow the convention of ref 21. For completeness this table also shows the data collected by Dalton and Kwiram[10] on the acid deuterons, transformed to the *a'bc* axis system.

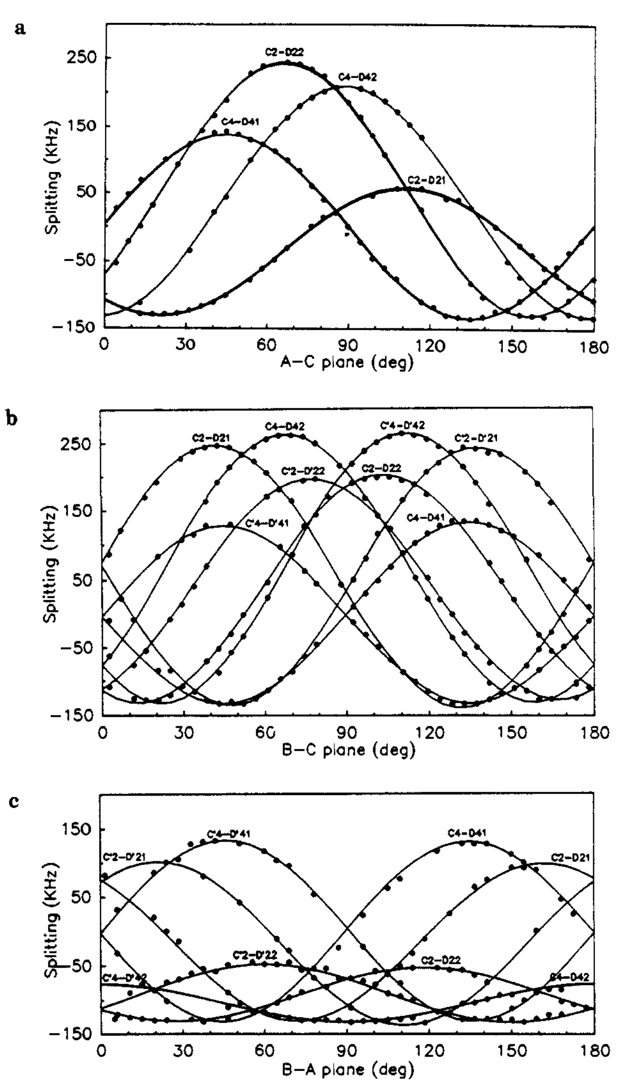

Figure 4. Deuteron quadrupole splitting as a function of the angle of the magnetic field in the indicated planes. The field is along the first axis at 0° and the second axis at 90°.

Discussion

The basic assumption required to correlate the quadrupole data with the molecular geometry is that the direction of Q_{zz} (the largest interaction) is along the C–D internuclear axis. This assumption has been thoroughly investigated[26]—a careful theoretical analysis[27] showing that even in the case of an extremely polar molecule like glycine, Q_{zz} is typically within 0.2° of the bond direction. We can check this empirical relationship by comparing the D–C–D angles obtained from the EDNMR data with those from the 20 K X-ray study.[21] As is well-known, X-ray measurements give only nominal results for hydrogen atoms due to their low scattering power—typically, in fact, only the angle is refined, the C–H distance being arbitrarily fixed during the analysis. The data from Table I and ref 21 give the following results (all values ±1°):

angle	X-ray	EDNMR
$D-C_2-D$	109.3°	109.2°
$D-C_4-D$	111.1°	109.8°

The EDNMR results are in excellent agreement with the tetrahedral angles expected for sp^3 hybridization. The uncertainty in

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(24) By way of contrast, the attempted analysis of the d_6-CBDA data was unsuccessful in spite of the fact that spectra were recorded every 2.25°. The combination of 24 lines with a typical line width of 10–15 KHz, spread over a frequency interval of about 140 KHz, simply gave too many overlapping peaks.

(25) Alternatively all three planes of data were simultaneously fit to the general tensor expression with a program developed by Dr. R. C. McCalley.

(26) (a) Bersohn, R. *J. Chem. Phys.* **1960**, *32*, 85–88. (b) Soda, G.; Chiba, T. *J. Chem. Phys.* **1969**, *50*, 439–455.

(27) Weeding, T.; Kwiram, A. L.; Rawlings, D. C.; Davidson, E. R. *J. Chem. Phys.* **1985**, *82*, 3516–3526.

the EDNMR values is based on differences between the two magnetically inequivalent molecules in the unit cell, as well as on changes noted during the course of the analysis in which adding or deleting a point to one of the rotation curves typically changed the results by a few tenths of a degree.

The simplest way to calculate the rocking angle from the quadrupole data is to first determine the direction of the bisector of each $>CD_2$ group, and then compare the angle between the bisectors with the pucker angle obtained from the low-temperature X-ray study.[21] This method has the advantage that any deviations between the direction of Q_{zz} and the C–D bond (which are expected to be very small) will tend to cancel to first order when calculating the direction of the bisector due the local symmetry of the $>CD_2$ group. Furthermore, in making such calculations it is not even necessary that the EDNMR and X-ray measurements refer to the same set of axes since only angular differences are involved. The data in Table I give the following direction cosines for the $>CD_2$ bisectors (referred to the *a′bc* axis system):

	a′	*b*	*c*
C_2	−0.556	−0.804	+0.213
C_4	+0.488	+0.818	+0.304

The angle between the bisectors is thus 149.8°; comparing this value with the pucker angle from the X-ray study[21] (158.9) gives a rocking angle of 4.6 ± 0.5°.

Wagging and Twisting. If the ring in CBDA had the symmetry of cyclobutane no other distortions would be possible, so the analysis above would suffice. However, the crystalline environment and the two carboxyl groups at C_1 reduce the symmetry, allowing wagging and twisting distortions as well. To determine the magnitude of these we define a *local* coordinate system at each $>CD_2$ group, with x' perpendicular to the CD_2 plane and y' the bisector of the CD_2 angle (see Figure 1). Rocking in this local coordinate system is a rotation about x', twisting a rotation about y', and wagging a rotation about z'. The results of this analysis are summarized below with X-ray data[21] shown in parentheses for comparison. Note that the absolute orientation of the crystal axes now directly affects the results since the local coordinates are derived from X-ray measurements while the $>CD_2$ bisectors come from the quadrupole data. Note also that in this reduced-symmetry environment, deviations of Q_{zz} from the C–D axis will only cancel within the $>CD_2$ plane: the wag and twist data could thus (in principle) be subject to small systematic errors.

atom	rock	wag	twist
C_2	4.0 (5.9)	2.4 (3.7)	0.2 (0.9)
C_4	4.9 (4.2)	2.0 (1.6)	0.2 (1.0)

Combining the results for the two symmetry-related molecules gives a rocking angle of 4.0° at C_2 and 4.9° at C_4. The overall average (4.4°) is only slightly different from the value (4.6°) obtained using the assumption of higher symmetry.

Since the estimated uncertainty in the absolute direction of Q_{zz} is at least 0.5°, the difference between the rocking angles at C_2 and C_4 is only marginally significant. Such a difference, however, is not unreasonable as a result of steric forces. A careful examination of the unit cell indicates that the acid groups are oriented so that the interactions are expected to be different for the $>CD_2$ group at C_2 and at C_4 in a manner consistent with the results above. The wag data, on the other hand, indicate that the $>CD_2$ groups are bent *toward* C_1, i.e. toward the carboxyl groups, which is obviously difficult to explain in terms of steric forces. (One could argue, however, that the inductive effect of the electron-withdrawing carboxyl groups reduces the electron density in the C_1–C_2 and C_1–C_4 bonds, which alters the electrostatic equilibrium and allows the C_2–C_3–C_4 angle to open up in agreement with the observed wag.) The $>CD_2$ groups do not appear to be twisted—at least to within the accuracy of the measurements.

The other interesting observation (see Tables I and II) is that the direction of the most negative tensor element (Q_{yy}) is not well correlated with the local geometry. Typically Q_{yy} is the "out-of-plane" element;[10] while this is true for the two "axial" deuterons (the ones tipped toward each other), it is not true (at least to within the uncertainty of the analysis) for the "radial" deuterons. We suggest that this is due to the distorted nature of the ring, which places each deuteron in a unique electrostatic environment.

Coupling between the Rock and Pucker Angles. The results above indicate that the methylene groups are tilted toward each other so as to bring the axial protons closer together—a result found from ab initio calculations as well.[6,8] This seems somewhat counter-intuitive: one might reasonably expect the opposing methylene groups to tilt *away* from each other as the ring folds in order to reduce the nonbonded interactions. This view, however, overlooks the fact that the orientation of the $>CH_2$ group is not independent of the bonds that hold it in the ring, or, put another way, that the four sp^3 orbitals are all coupled together. Ring pucker and methylene rock are thus interrelated motions, the extent to which they are independent being determined by the relative energies of electronic and vibrational parts of the Hamiltonian. This coupling affects both static values (such as the equilibrium angles discussed above) as well as the dynamic values involved in a kinematic model of the molecule.

Ab initio calculations[6,8] reveal only the static relationship between the rock and pucker angles, i.e. the values that give the lowest energy configuration. Spectroscopic analyses, on the other hand, need a dynamic model—a functional relationship between these angles from which to calculate kinematic constants. Malloy and Lafferty,[7] for example, empirically introduced a linear coupling between the rock and pucker angles based on the idea that these two "independent" motions had the same symmetry. In their model this coupling was allowed to have either phase, consistent with the view that the two motions really were independent. They found that an in-phase coupling constant of 0.22–0.25 resolved the discrepancy between the C_4H_8 and C_4D_8 spectroscopic results, although they rejected this value as being too large.

The ratio we find for these two angles in CBDA at 4.2 K is 0.21 ± 0.01, which, within experimental uncertainty, is exactly the same as the ratio (0.22 ± 0.05) found by Egawa et al.[13d] from vibrationally corrected measurements on gaseous cyclobutane; it is also similar to results of ab initio calculations[6,8] and falls within the range of coupling constants determined by Malloy and Lafferty.[7] Note that the first three comparisons are static values, while the last comes from a dynamic model. The fact that the static and dynamic ratios are similar suggests a linear relationship between these two angles over at least the range of values encompassed by the data.

If the equilibrium rock and pucker angles were, in fact, simply averages of independent motions, then one might well expect the "coupling constant" between them to be quite different under different circumstances. The pucker angle of cyclobutane in the gas phase near room temperature, for example, is 27.9°,[13d] while in CBDA at 4.2 K it is only 21.1°—yet the ratio of the rock/pucker angles is identical. Similarly, MO calculations based on different levels of approximation[8] predict a variety of angles with rather similar rock/pucker ratios (the theoretical values are about 0.17, rather than 0.21). Is this just an accident or is there a model that predicts this result?

Actually there are two such models: the "minimum bond tortuosity" model of Bartell and Anderson,[28a] and the "maximum overlap" model of Pasternak and Meyer.[28b] These authors independently argued that the proper description of "methylene rocking" is really geometrical in nature rather than some unusual or unexpected "distortion" of the molecule. In the geometrical view the "bent bonds" formed by the overlapping sp^3 orbitals are not only out-of-line with respect to the C–C internuclear axis (which is easy to visualize), but also out-of-plane with respect to the local C–C–C coordinate system (which is harder to see). The extent of this rocking, estimated from either a hypothesis of minimum bond tortuosity (Bartell and Anderson) or maximum overlap (Pasternak and Meyer), gives a value of ≈3° for an assumed dihedral angle of ≈20°.

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(28) (a) Bartell, L. S.; Anderson, B. *J. Chem. Soc., Chem. Commun.* **1973**, 786–787. (b) Pasternak, R.; Meyer, A. Y. *J. Mol. Struct.* **1974**, *20*, 351–355.

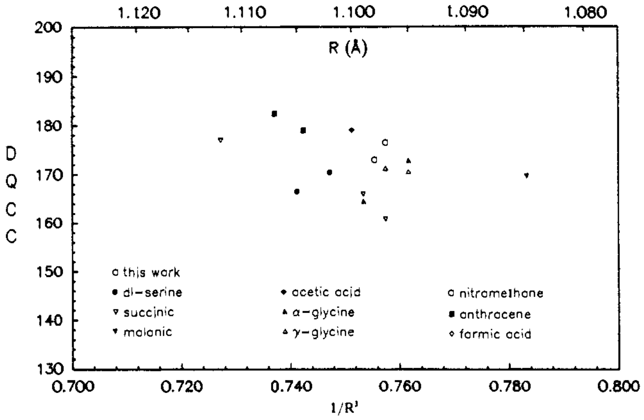

Figure 5. Quadrupole coupling constants vs bond length for C-D bonds. References: serine (31); succinic acid (29, 32); formic acid (30, 33); acetic acid (33); α-glycine (27, 34); γ-glycine (35); nitromethane (36); anthracene (37); malonic acid (38).

Neither the Maximum Overlap nor Minimum Bond Tortuosity model is in full accord with the experimental data since the molecule actually minimizes all of its energy terms rather than just the orbital overlap or "twist strain". Nor does either model predict a linear relationship between the rock and pucker angles except as a reasonable approximation over a limited range of pucker angles. But the viewpoint is quite valuable: we have come to accept the idea of "bent bonds" to account for the existence of molecules like cyclobutane and cyclopropane, but we need to appreciate the fact that in nonplanar systems such bonding may require the $>CH_2$ groups to be tipped toward each other, i.e. rocked with respect to the local C–C–C plane.

Table II. Local Geometry for C–C–C, D–C–D, and O–C–O Planes

	direction cosines			
	a′	*b*	*c*	direction
C_1–C_2–C_3[a]	0.803	∓0.540	0.252	in plane
	0.129	∓0.256	−0.958	out of plane
	−0.582	∓0.802	0.136	bisector
D_{21}–C_2–D_{22}	0.826	∓0.506	0.248	out of plane
	0.091	∓0.313	−0.945	in plane
	−0.556	∓0.804	0.213	bisector
C_1–C_4–C_3[a]	0.807	∓0.534	0.253	in plane
	0.329	±0.051	−0.943	out of plane
	0.491	±0.844	0.216	bisector
D_{41}–C_4–D_{42}	0.789	∓0.562	0.246	out of plane
	0.372	±0.120	−0.920	in plane
	0.488	±0.818	0.304	bisector
O_1–C_5–O_2[a]	−0.036	∓0.880	0.474	in plane
	0.900	±0.178	0.398	out of plane
	0.435	∓0.441	−0.785	bisector
O_3–C_6–O_4[a]	0.830	±0.342	−0.441	in plane
	−0.153	±0.899	0.411	out of plane
	0.537	∓0.273	0.798	bisector

[a] Data taken from ref 21 (Santarsiero, B. D. *J. Phys. Chem.* **1990**, *92*, 3794–3797.

Both models assume that the hybridization (nominally sp^3, though it may depart from that exact mixture) remains the same as the molecule undergoes a low-energy distortion-like puckering. This seems quite reasonable given the relative energies involved—in fact, the idea that it is the entire set of sp^3 orbitals which rocks (rather than just the two hydrogen atoms) seems much more plausible upon reflection than perhaps it does initially. Such a view then suggests that the ratio of the rocking and pucker angles should be a constant of the ring, determined by the length of the bonds and the effective hybridization of the orbitals. The theoretical observation[6] that methylene rocking is required for the existence of a puckered ring can alternatively be seen as simply a statement that the supposed effects of ring strain and hydrogen eclipsing have very little effect on the hybridization.

Methylene rocking is thus best thought of as an artifact of our analysis: a value we assign to the structure because we can "see" the atoms but not the orbitals. As shown above, a variety of measurements and calculations are consistent with one ramification of this perspective: namely that the rock/pucker ratio should be roughly the same for similar systems—a measure of just how the sp^3 orbitals are *oriented*, rather than how they are *distorted*. The ratio of these two angles is thus a very valuable parameter since it provides direct information about the electron distribution within the molecule as well as simply allowing the orientation of the methylene group to be estimated once the pucker angle is known.

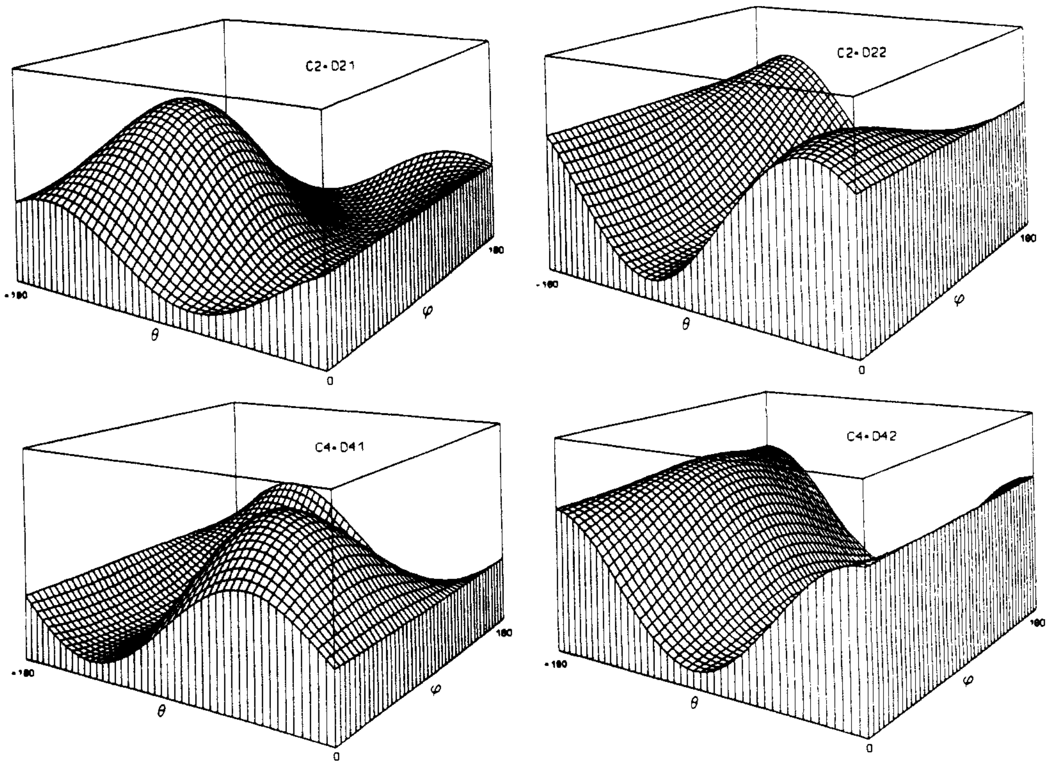

Figure 6. Deuteron quadrupole splitting (vertical axis) vs magnetic field direction for one of two magnetically inequivalent pairs of molecules in a crystal of cyclobutanedicarboxylic-*2,2,4,4-d*$_4$ acid. *a′* is at θ = 90°, φ = 0°; *b* is at θ = 90°, φ = 90°; *c* is along θ = 0°.

Conclusion

Deuteron quadrupole resonance measurements of a single crystal of 1,1-cyclobutanedicarboxylic-*2,2,4,4-d_4* acid at 4.2 K show that the β-methylene groups are at an angle of 4.4 ± 0.5° with respect to the local C–C–C plane, causing the two axial deuterons to be closer together. The D–C–D bond angles are 109.5 ± 0.5°. These results are a direct measurement of the geometry of a four-membered saturated ring in its zero-point vibrational state—no corrections have been applied. Previous measurements of such systems have all been made on molecules in excited vibrational states, which thus requires some form of correction. The ratio of rock/pucker angles in CBDA is 0.21 ± 0.01, the same as in other systems with different pucker angles; our results thus suggest that this ratio is a constant of the ring system—a static as well as a dynamic effect that can be explained by postulating that the methylene groups simply pivot as a unit.

Acknowledgment. We acknowledge the dedicated efforts of Linda Mihalik who first synthesized microgram quantities of the d_6 derivative as an undergraduate research project using a procedure suggested by Prof. Stanley Raucher. Dr. David McCrae then refined the synthesis, eventually providing us with milligram quantities of the fully deuterated compound and much additional help in our preparation of the d_4 derivative. The contributions of these individuals to the success of this work are gratefully acknowledged. The thoughtful reading of the manuscript and the insightful comments of Dr. R. C. McCalley are greatly appreciated; discussions with Dr. L. C. Andrews regarding the reliability of C–H bond lengths determined by diffraction methods were also helpful. Finally, our special thanks go to Prof. B. D. Santarsiero for determining the low-temperature crystal structure and to Prof. Kuchitsu for providing us with a summary of his final results on cyclobutane in advance of publication.

Appendix I. Determination of the C–H Bond Length

The results above are all based on the deuterium quadrupole spectra of the two β >CD_2 groups in d_4-CBDA. In principle, the proton dipolar spectra from the undeuterated >CH_2 group at C_3 could also be used to obtain an independent measurement of the rocking angle. Unfortunately, the protons from the two COOH groups not only broadened all the lines significantly but doubled their number as well, making it impossible to resolve the individual interactions in spite of an extensive effort to do so.

However, using the X-ray data to get the *directions* of the >CH_2 bonds (which, as shown above, were within ≈1° of the EDNMR values at C_2 and C_4) made it possible to obtain a very good estimate of the *length* of those bonds (which the X-ray analysis arbitrarily set to 0.98 Å). This estimate was made by comparing simulated data for the $a'c$ plane (where the lines had the largest splitting) with the experimental results. The r^{-3} dependence made the H–H distance a very sensitive parameter, giving a best fit value of r_{H-H} = 1.7924 (2) Å. With an assumed >CH_2 angle of 109.5° (the average of the values found for C_2 and C_4) and equal bond lengths, this gives a C–H distance of 1.097 (5) Å—a result consistent with typical values for C–H bonds as well as with the EDNMR measurements of >CH_2 groups in glycine by Weeding[27] and succinic acid by Boroske.[29] This value also agrees with the results of Egawa et al. for cyclobutane.[13d]

We can show that this bond length is typical in another way as well by comparing it and the measured quadrupole coupling constant (QCC) with values for other molecules. As shown in Figure 5, the value for CBDA falls within the cluster of points for all other C–D systems in which the bond length[30] has been measured by neutron diffraction. This observation adds to the evidence that both the quadrupole coupling constant and the C–D bond length are roughly the same for all C–D bonds (independent even of hybridization)—a result that is in contrast to O–D···O bonds where the O–D bond length and the magnitude of the QCC vary significantly from one compound to another. It is for this reason the value of the QCC for deuterons in such bonds can be directly and accurately related to the internuclear separation.[10,26b]

Registry No. I-d_4 acid, 125927-52-8; I-d_6 acid, 125927-53-9; $BrD_2CCH_2CD_2Br$, 64528-94-5; $BrD_2CCD_2CD_2Br$, 120404-22-0; $EtO_2CCH_2CO_2Et$, 105-53-3.

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(29) Boroske, E.; Mayas, L.; Möbius, K. *J. Magn. Reson.* **1979**, *35*, 231–246.

(30) "Corrected" bond lengths are shown in the figure; the "corrections" (generally for libration, and sometimes other effects) are typically on the order of 0.01–0.02 Å. Not all workers make the same corrections, which makes the *X*-axis somewhat uncertain. C–H and C–D bonds (after correction) have been assumed to have the same length. The neutron diffraction bond length for formic acid (ref 33b) appears to be anomalous; the value shown is from a microwave study: Kwei, G. H.; Curl, R. F., Jr. *J. Chem. Phys.* **1960**, *32*, 1592–1594. The authors of ref 33a also compare their DQCC measurements in the solid state to gas-phase results.

(31) (a) Hartzell, C. J.; Kwiram, A. L. *J. Magn. Reson.* **1987**, *73*, 315–322. (b) Frey, M. N.; Lehman, M. S.; Koetzle, T. F.; Hamilton, W. C. *Acta Crystallogr.* **1973**, *B29*, 876–884.

(32) Leviel, J.; Auvert, G. *Acta Crystallogr.* **1981**, *B37*, 2185–2189.

(33) (a) Adriaenssens, G. J.; Bjorkstam, J. L. *J. Chem. Phys.* **1972**, *56*, 1223–1225. The value of 180 kHz for acetic acid was calculated from the average value found for the deuterons in the rotating methyl group; the authors' estimate was 170 kHz. (b) Albinati, A.; Rouse, K. D.; Thomas, M. W. *Acta Crystallogr.* **1978**, *B34*, 2184–2190. (c) Jönsson, P.-G. Ibid. **1971**, *B27*, 893–898 (acetic acid, reference only, data not used).

(34) Jönsson, P. G.; Kvick, Å. *Acta Crystallogr.* **1972**, *B28*, 1827–1833.

(35) (a) Edmonds, D. T.; Summers, C. P. *Chem. Phys. Lett.* **1976**, *41*, 482–485. (b) Kvick, Å.; Canning, W. M.; Koetzle, T. F.; Williams, G. J. B. *Acta Crystallogr.* **1980**, *B36*, 115–120.

(36) (a) Rinne, M.; Depireau, J. *Adv. Nucl. Quadrupole Reson.* **1979**, *1*, 357–374. (b) Trevino, S.; Prince, E.; Hubbard, C. R. *J. Chem. Phys.* **1980**, *73*, 2996–3000.

(37) (a) Ellis, D. M.; Bjorkstam, J. L. *J. Chem. Phys.* **1967**, *46*, 4460–4463. (b) Chaplot, S. L.; Lehner, N.; Pawley, G. S. *Acta. Crystallogr.* **1982**, *B38*, 483–487.

(38) Room temperature neutron diffraction measurements by Robert G. Delaplane, private communication; r_{C-H} = 1.085 Å. The DQCC data are from McCalley, R. C. Thesis, Harvard University, 1971.