the intrinsically linear FeXY fragment experiences structural distortion so as to accommodate substrates. This is clearly seen in the crystal structure of the carbon monoxide adduct of camphor-bound cytochrome P450cam, in which camphor is moved away from the CO molecule by about 0.8 Å and FeCO linkage is bent (168°).

E. Relevance to the Issue of Metabolic Regioselectivity. Cytochrome P450cam exhibits remarkable regiospecificity, metabolizing camphor exclusively to the 5-*exo*-hydroxycamphor, both in vivo and in the reconstituted system. On the other hand, Atkins and Sligar[8d] have recently shown that in the cytochrome P450cam catalyzed hydroxylation of norcamphor (a substrate analogue lacking the three methyl groups) at least three products were obtained and that the oxidase activity (gauged by the 4-electron reduction of atmospheric dioxygen to water) of the system is raised. The present RR study of the ferrous NO adducts with various substrates is thus of particular interest inasmuch as this derivative, like the physiologically relevant O_2 adduct, adopts an inherently bent configuration whereas those previously studied (ferrous–CO and ferric–NO) are intrinsically linear. Indeed, the present results, which document the lack of an effect of norcamphor upon the vibrational frequencies of the bound Fe^{II}–NO fragment, are thus consistent with the enzymatic studies by Atkins and Sligar, which imply that even partial relaxation of the steric constraints can result in a loss of metabolic specificity.

Acknowledgment. This work was supported by a grant from the National Institutes of Health (DK35153). The authors are sincerely grateful to Professor S. Sligar of the University of Illinois at Urbana—Champaign for the supply of *P. putida* cell paste.

Registry No. Adamantanone, 700-58-3; camphor, 76-22-2; norcamphor, 497-38-1.

Geometry of the Cyclopropane-1,1-dicarboxylic Acid Molecule at 5 K

J. Krzystek and Alvin L. Kwiram*

Contribution from the Department of Chemistry, University of Washington, Seattle, Washington 98195.

Received April 18, 1991

Abstract: In our continuing study of the conformation of small cyclic organic molecules at low temperatures we investigated single crystals of deuterated cyclopropane-1,1-dicarboxylic acid by ENDOR-detected nuclear magnetic resonance (EDNMR) at 5 K. The quadrupole tensors of the ring-bonded deuterons (e^2qQ/h = 185 kHz, η = 0.06) allow us to draw conclusions about the geometry of the ring itself. The D–C–D bond angle in both methylene groups (116°) and the angle between the methylene planes (132°) are discussed in terms of carbon hybridization and interactions between hydrogen atoms. The quadrupole splitting parameters of the carboxyl-bonded deuterons (e^2qQ/h = 160 kHz, η = 0.18) yield information on the length of hydrogen bonds. Since e^2qQ is essentially identical for both the intra- and intermolecular bonds, it appears that the bonds have approximately the same length of 1.63 Å. By contrast, the X-ray diffraction results at room temperature show a significant difference in hydrogen bond length defined as the O···H distance (1.63 versus 1.75 Å). This suggests that the intermolecular hydrogen bond has become considerably shorter at low temperature.

Introduction

The geometry of small cyclic molecules like cyclopropane or cyclobutane has been of considerable interest for years. Specifically, the objects of particular interest were the angles formed by the C–C bonds. The bond angles are of course much smaller than those typical of conventionally defined carbon hybridizations, and the molecules are apparently "strained". And yet both molecules mentioned, and many of their derivatives, are completely stable.

Many models have been invoked to account for this paradox (see reviews[1,2]). One of the most successful descriptions is the "bent bond" model devised by Coulson and Moffitt.[3] This model uses three sets of methane-like sp^3 carbon orbitals and constructs from then the alicyclic ring. The direction of maximum overlap in these orbitals in the cyclopropane model lies outside the line connecting the two carbon atoms, thereby justifying the name.

An alternative model of Walsh[4] introduced the concept of a rehybridization in cyclopropane. According to this model, the actual hybridization of the carbon orbitals pointing toward the hydrogen atoms is closer to sp^2 rather than the expected sp^3, which means that the s character is larger than the 0.25 value characteristic for sp^3 hybridization. To compensate for this shift, the s character of the orbitals participating in the C–C bonds must be smaller than 0.25.[1] These predictions were supported by ^{13}C NMR experiments, where the C–C and C–H coupling constants, *J*, yielded approximately 0.33 s character in the C–H bonds[5] and 0.17 s character in the C–C bonds.[6] In the case of cyclopropane one can thus speak of two sp^2 (0.33 s character) and two "sp^5" (0.17 s character) orbitals for each carbon atom.[1,7] The rehybridization has a direct effect on the spatial character of the orbitals. In fact, various experimental methods, directly or indirectly measuring the C–H bond lengths and H–C–H angles in cyclopropane and its derivatives, have confirmed the NMR data regarding the orbitals involved in C–H bonds. Information on these parameters is, however, far from being complete.

For this and other reasons we embarked on an investigation of cyclopropane-1,1-dicarboxylic acid (CPDA), using the method of ENDOR-detected nuclear magnetic resonance (EDNMR).

---

[1] Greenberg, A.; Liebman, J. F. *Strained Organic Molecules*; Academic Press: New York, 1978.

[2] Newton, M. D. In *Applications of Electronic Structure Theory*; Schaefer, H. F., Ed.; Plenum Press: New York, 1977.

[3] Coulson, C. A.; Moffitt, W. E. *Philos. Mag.* **1949**, *40*, 1-35.

[4] Walsh, A. D. *Trans. Faraday Soc.* **1949**, *45*, 179-190.

[5] Muller, N.; Pritchard, D. E. *J. Chem. Phys.* **1959**, *31*, 768-771.

[6] Weigert, F. J.; Roberts, J. D. *J. Am. Chem. Soc.* **1967**, *89*, 5962-5963.

[7] Schleyer, P. v. R. *NATO ASI Series, Ser. C* (*Substituent Effects in Radical Chemistry*) **1986**, *189*, 69-81.

0002-7863/91/1513-9766$02.50/0

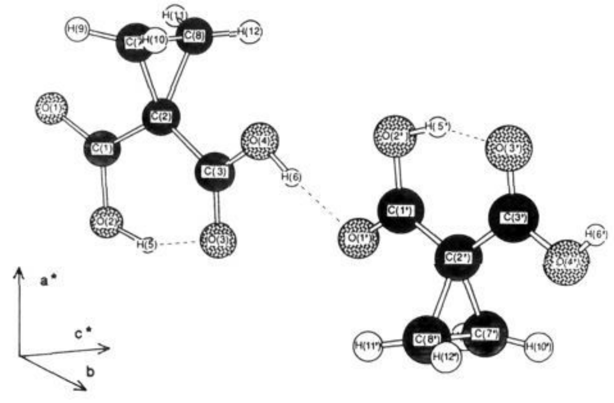

Figure 1. Perspective view of one of the two asymmetric units in the elementary cell of CPDA and atom numbering used in the text. The broken lines represent the hydrogen bonds.

The reason for choosing the dicarboxylic derivative of cyclopropane was that dicarboxylic acids are known to form stable crystals in which the individual molecules form hydrogen-bonded chains providing a nicely oriented and largely undisturbed ring. We assumed that substitution of two hydrogens by carboxyl groups would not dramatically change the geometry of the alicyclic ring and the distribution of electron density. This assumption is employed quite generally, and much of the experimental data on the geometry of cyclopropane comes from X-ray measurements of its derivatives in the crystalline phase.

Experimental details on the EDNMR technique can be found elsewhere.[8,9] Briefly, EDNMR depends on measuring the high field deuteron quadrupole spectrum of deuterated single crystals via an ENDOR (electron nuclear double resonance) experiment: one sweeps the rf in the region of the deuterium Larmor frequency and observes changes of the ESR signal associated with the X-ray-induced paramagnetic centers. In this way one can obtain, in principle, the full deuterium quadrupole coupling (DQC) tensors for all the magnetically nonequivalent deuterium atoms in the sample.

In one set of experiments we used crystals of the ring-deuterated compound. The orientation of the principal axes of the quadrupole tensors yields the directions of the C–D bonds, information not readily obtained by most other experimental methods. The second set of experiments was carried out on samples in which only the carboxyl groups were deuterated: the DQC constant, e^2qQ, depends on the length of the hydrogen bonds.[10] According to the X-ray diffraction study,[11] one of the two carboxyl groups forms an intramolecular hydrogen bond, and the other forms an intermolecular hydrogen bond. It is reported that at room temperature these two hydrogen bonds have significantly different lengths. This study of CPDA parallels our earlier studies of the DQC tensors in cyclobutane-1,1-dicarboxylic acid.[9c] A preliminary account of the CPDA work has been given elsewhere.[12]

Crystal Structure. The crystal structure of CPDA is known from the room-temperature X-ray study.[11] The crystal is triclinic, space group $P\bar{1}$, $Z = 4$, with the following parameters for the unit cell: $a = 12.045$ Å, $b = 13.822$ Å, $c = 5.286$ Å, $\alpha = 137.53°$, $\beta = 92.22°$, $\gamma = 89.82°$. Of the four molecules in the unit cell, one pair is related to the other by inversion. Since the crystal structure is almost monoclinic, the two molecules in the asymmetric pair are nearly magnetically equivalent. The molecules have their carbon rings almost exactly perpendicular to the *b* axis and are linked into a chain by an intermolecular hydrogen bond along the *b* axis. The intramolecular hydrogen bond is formed between the atoms H5 and O3 (Figure 1).

In order to interpret the EDNMR results it is convenient to establish a cartesian coordinate system. This was defined by the *b* axis, the axis perpendicular to it and lying in the *bc* plane (c^* axis) and the axis orthogonal to *b* and c^* (a^* axis).

Sample Preparation. The carboxyl-deuterated CPDA (CPDA-d_2) was prepared by four consecutive recrystallizations of the commercial compound (Fluka) from D_2O. The ring-deuterated compound (CPDA-d_4) was synthesized according to the method of Podder et al.[13] The deuterated starting material was perdeuterated 1,2-dibromoethane (Cambridge Isotopes).

The crystals were grown from solution. CPDA was dissolved in ethyl ether, and the insoluble residue which was always present was filtered out. Subsequently benzene was added to the solute to bring the solution to the verge of saturation, and the solvent was allowed to evaporate slowly. The ratio of ethyl ether to benzene was about 2:1. The crystals form as thick plates on the *bc* plane and are elongated along the *c* axis. Typical dimensions were $1.5 \times 3 \times 10$ mm^3. Most crystals obtained in this way were twinned.

To prepare samples of a size suitable for experiments, the crystals had to be cut by cleaving along the *ab* plane. The intersection between the cleavage plane and the *bc* plane provides unequivocal confirmation of the crystal morphology and establishes the axis system.

EDNMR Experiments. A sample was first X-irradiated in a standard X-ray machine (Rigaku Denki) with a Cu target (30 kV, 25 mA) at room temperature for up to 10 h to create the paramagnetic centers. It was then glued to a quartz rod and inserted into the cryostat.

The ENDOR spectrometer was based on a Varian E-line X-band ESR spectrometer equipped with a Bruker ER 200 cylindrical cavity. The low temperature was obtained by means of an Oxford Instruments E900 helium-flow cryostat. The rf was delivered by an Ailtech 360D11 synthesizer via an ENI 240L or 3200L amplifier to the rf helix which surrounded the quartz tail of the cryostat inside the microwave cavity. The experiment was controlled by an IBM PC/AT computer which drove the rf synthesizer by means of a custom interface.

Evaluation of Results. To obtain the elements of the quadrupole tensors, measurements were made in three mutually orthogonal planes. The elements were obtained by fitting the resulting angular dependences of the EDNMR splittings for each plane using the following expression:

$$\Delta\nu_{i,j} = A_{ii}\cos^2\phi + A_{ij}\sin 2\phi + A_{jj}\sin^2\phi \qquad (1)$$

where $\Delta\nu_{i,j}$ is the observed EDNMR splitting; $i, j = a^*, b, c^*$ for the three rotation planes; ϕ is the rotation angle in each plane. The 3×3 DQC tensor for each deuteron, consisting of the diagonal (A_{ii}) and nondiagonal (A_{ij}) elements, was diagonalized to obtain both the principal values of the tensor and the orientation of the principal axes relative to the crystal axes system. The refinement of the tensors was achieved by a simultaneous least-squares fit to the complete set of data points in three planes, which allowed for nonorthogonality of the rotation planes.

Results

CPDA-d_4. The crystal structure of CPDA indicates that the alicyclic rings of the molecules in each of the two asymmetric units almost transform into each other by inversion. Thus the direction of the C7–D9 bond in the first molecule is almost equivalent to that of the C7′–D10′ bond in the second molecule (in the following we will keep the notation of the original X-ray study[11]). This makes the quadrupole tensors of deuterons D9 and D10′ nearly identical. A similar situation exists for the D9′–D10, D11–D12′,

---

(8) (a) Terhune, R. W.; Lambe, J.; Makhov, G.; Cross, L. G. *Phys. Rev. Lett.* **1960**, *4*, 234–236. (b) Lambe, J.; Laurance, N.; McIrvine, E. C.; Terhune, R. W. *Phys. Rev.* **1961**, *122*, 1161–1170.

(9) (a) McCalley, R. C.; Kwiram, A. L. *Phys. Rev. Lett.* **1970**, *24*, 1279–1281. (b) Dalton, L. R.; Kwiram, A. L. *J. Am. Chem. Soc.* **1972**, *94*, 6930–6938. (c) van Zee, J. A.; Kwiram, A. L. *J. Am. Chem. Soc.* **1990**, *112*, 5012–5018.

(10) Soda, G.; Chiba, T. *J. Chem. Phys.* **1969**, *50*, 439–455.

(11) Meester, M. A. M.; Schenk, H.; MacGillavry, C. H. *Acta Crystallogr.* **1971**, *B27*, 630–634.

(12) Krzystek, J.; Kwiram, A. L. *Abstracts of the American Chemical Society Meeting*; Atlanta 1991.

(13) Podder, R. K.; Sarkar, R. K.; Ray, S. *Indian J. Chem. Sect. B* **1988**, *27B*, 530–536.

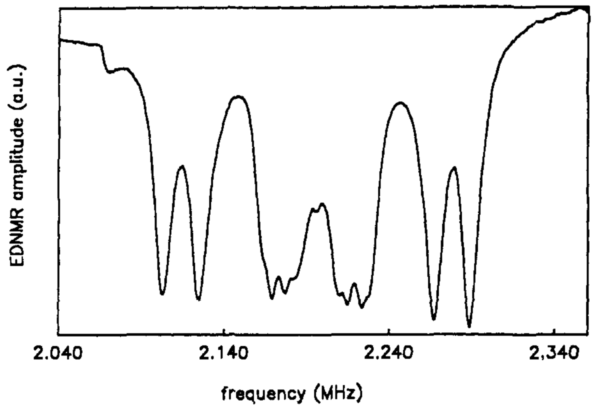

Figure 2. EDNMR spectrum of CPDA-d_4 at 5 K. The crystal was oriented so that the magnetic field was in the a^*b plane, 30° from the b axis.

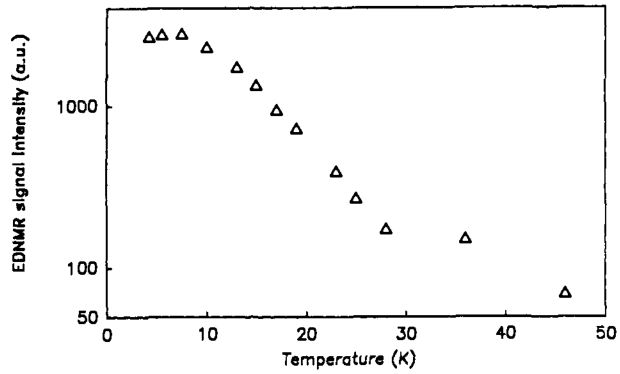

Figure 3. Temperature dependence of the intensity of the EDNMR signals in CPDA-d_4.

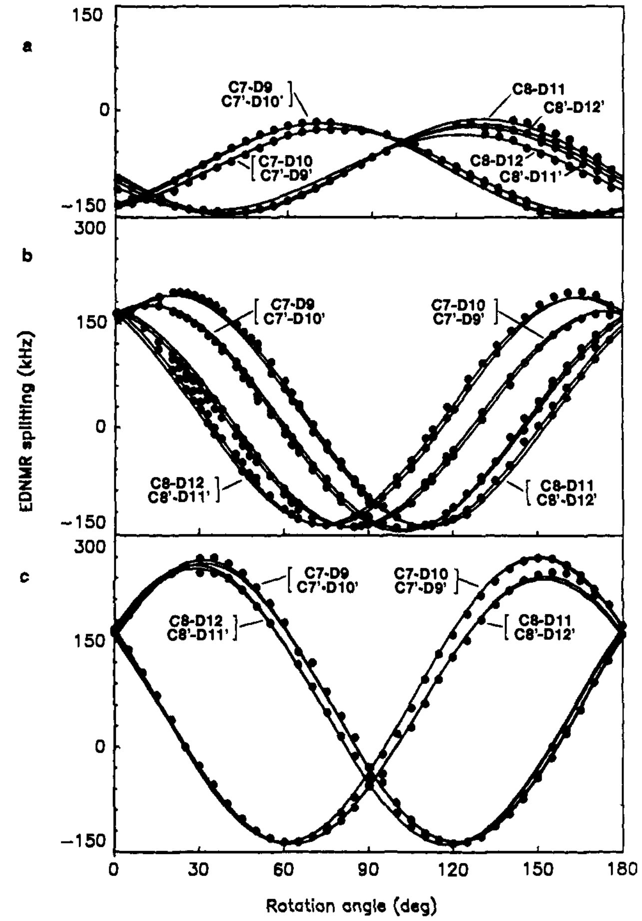

Figure 4. Angular dependences of the EDNMR signals in CPDA-d_4. The crystal was rotated in the a^*c^* (a), a^*b (b), an bc^* (c) plane. The field is along the first axis at 0° and the second axis at 90°.

Table I. Direction Cosines of the Z Components of the DQC Tensors and DQC Parameters in CPDA-d_4 at 5 K

bond	a^*	b	c^*	e^2qQ/h (kHz)	η
C7–D9	–0.1675	0.8521	0.4959	186.5	0.040
C7′–D9′	0.1607	0.8478	–0.5054	185.1	0.089
C7–D10	–0.1290	–0.8554	0.5016	184.1	0.047
C7′–D10′	0.1950	–0.8447	–0.4985	186.2	0.034
C8–D11	–0.3013	0.8362	–0.4583	186.1	0.064
C8′–D11′	0.2540	0.8525	0.4569	185.8	0.078
C8–D12	–0.2224	–0.8633	–0.4530	185.2	0.037
C8′–D12′	0.2790	–0.8459	0.4545	184.8	0.062

Table II. Interatom Angles in CPDA-d_4 Obtained from the DQC Tensors in Table I

angle[a]	value
δ	molecule 1: 117.3° (D9–C7–D10), 116.6° (D11–C8–D12)
	molecule 2: 115.6° (D9′–C7′–D10′), 116.3° (D11′–C8′–D12′)
ϵ	molecule 1: 90.2° (D9–C7–D10), 89.8° (D11–C8–D12)
	molecule 2: 91.5° (D9′–C7′–D10′), 89.6° (D11′–C8′–D12′)
α	molecule 1: 133.5°
	molecule 2: 130.2°
β	molecule 1: 46.5°
	molecule 2: 49.8°
γ	molecule 1: 1.4° (D9···D10), 2.9° (D11···D12)
	molecule 2: 0° (D9′···D10′), 1.3° (D11′···D12′)

[a] Explanations: δ, the angle between the directions of the **Z** elements of the DQC tensors of the two deuterons bonded to one carbon atom; ϵ, the angle between the bisector of the "D–C–D" angle (defined as for δ) and the b axis; α, the angle between the two bisectors of the "D–C–D" angles in a given molecule. β, the angle between the normals to the planes defined by the directions of the **Z** elements of the two pairs of deuterons in a given methylene group. γ, the angle between the D···D direction in a given methylene group and the b axis.

and D11′–D12 pairs. Consequently, instead of the eight pairs of EDNMR signals one expects from two magnetically inequivalent molecules in the unit cell, it was possible to observe only four except in a limited range of favorable orientations of the crystal (Figure 2). Due to the very high intensity of the EDNMR signals in CPDA-d_4 (typically 50% of the ESR signal) it was possible to operate at low (100 mW) RF power levels. The minimum line width observed was 10 kHz (fwhh). The EDNMR spectra could be followed to a temperature as high as 50 K (Figure 3), albeit with reduced intensity. No changes of line width or spectral position of the lines were observed upon increasing the temperature.

The angular dependences of the EDNMR lines are shown in Figure 4. Only in the a^*b rotation plane could we resolve all eight branches representing eight deuterons. In the bc^* plane only four branches could be seen, while in the a^*c^* plane the rotation patterns revealed as many as ten branches. Crystal twinning is the most probable explanation of this observation, particularly since the X-ray experiment revealed twinned areas in some of the crystals examined. However, one cannot exclude entirely a phase transition to a different crystal structure at low temperature. Of the ten branches it was possible to identify six branches originating from a given pair of molecules. Thus for one of the two magnetically inequivalent molecules it was possible to distinguish four branches, while for the other, only two (Figure 4a). Fortunately, this had practically no effect on the calculated magnitude and orientation of the largest element (**Z**) of the quadrupole splitting tensor, since it is determined largely from the other two planes of rotation. However, it made the error in the other elements of the tensor (**X** and **Y**) larger than for **Z** and consequently caused greater uncertainty in the value of η.

The numerical results of the curve fitting procedure are collected in Table I. The consistency of parameters e^2qQ for all the eight magnetically inequivalent deuterons in the unit cell is very good (185 ± 1 kHz). The parameters η are somewhat more divergent (0.06 ± 0.03), which was to be expected considering the problems with the spectral data in the a^*c^* crystal plane, which lies close to the **XY** principal plane of all the quadrupole tensors. As our

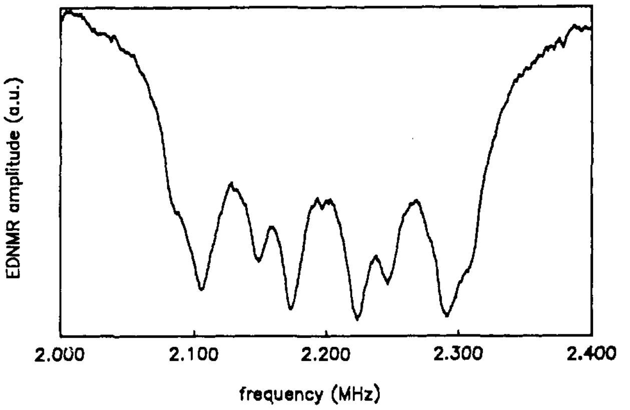

Figure 5. EDNMR spectrum of CPDA-d_2 at 5 K. The crystal was oriented so that the magnetic field was in the a^*b plane, 50° from the b axis.

main point of interest is the orientation of the largest principal value of the DQC tensor, **Z**, the discrepancies of the η parameters do not influence the subsequent discussion.

Several angles of interest in the following discussion can be calculated from the values shown in Table I. They are presented in Table II.

The fact that the angle between the D–C–D bisectors and the angle between the D–C–D normals sum to 180° suggests that the methylene groups are not twisted (i.e., the normal lies in the ring plane). This is further confirmed by the calculation of the direction joining the two deuterons in a given methylene group. For example, the angles between the interdeuteron direction and the b axis in a given molecule agree on average to within 1.5°.

CPDA-d_2. A typical EDNMR spectrum of CPDA-d_2 consists of four pairs of lines (Figure 5) for an arbitrary orientation of the crystal relative to the magnetic field. This is to be expected on the basis of the crystal structure (two magnetically inequivalent molecules in the unit cell, each of them containing two deuterons). At orientations where the magnetic field is perpendicular to the b axis, the number of lines is doubled in most crystals, similar to the d_4 samples, indicating crystal twinning. The intensities of the signals for the d_2 case are relatively low, on the order of 2% of the ESR signal. The line width is about 20 kHz (FWHH), although the recorded spectra are probably power-broadened, as the rf power necessary to obtain a favorable signal/noise ratio was somewhat higher (>2 W). The most troublesome plane was a^*c^* where for most of the orientations the four pairs of signals either overlapped and could not be resolved, or where the splittings were very close to zero, which caused the two signals in a given pair to merge into a broad single line (Figure 6a). Additional problems in this plane were probably caused by crystal twinning, although the lower number of lines in the d_2 system meant that this was not as serious a problem as in the d_4 case. In the other two rotation planes one could resolve four pairs of lines for most of the orientations (Figure 6b,c).

Table III shows the DQC parameters of the four deuterons in the unit cell together with the orientation matrices linking the principal axes of the quadrupole tensors to the crystal axes. The quality of the fits for CPDA-d_2 was somewhat lower than for the d_4 system, particularly for the molecule labeled no. 2 (smaller number of unequivocally determined experimental points). Correspondingly, the error for the parameter e^2qQ/h can be estimated as ±2 kHz for deuterons D5 and D6, while that of deuterons D5′ and D6′ is at least ±3 kHz. It follows from Table III that the e^2qQ values for all the deuterons in both molecules are equal within experimental error.

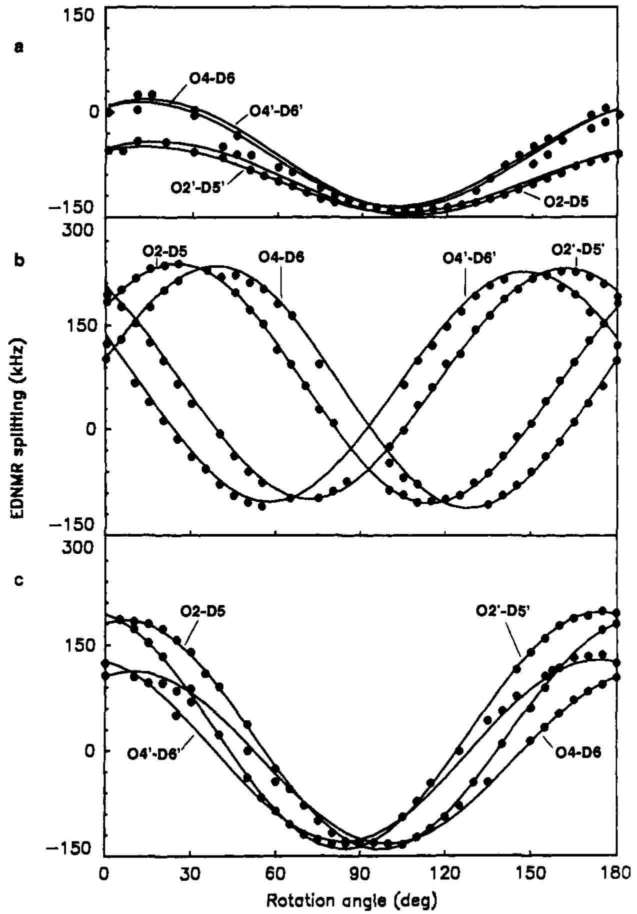

Figure 6. Angular dependences of EDNMR signals in CPDA-d_2. The crystal was rotated in the a^*c^* (a), a^*b (b), and bc^* (c) plane. The field is along the first axis at 0° and the second axis at 90°.

Table III. DQC Tensors in CPDA-d_2 at 5 K

	direction cosines				
bond	a^*	b	c^*	e^2qQ/h (kHz)	η
O2–D5	0.8690	0.4120	−0.2741	162.6	0.186
	0.3002	0.0016	0.9539		
	−0.3933	0.9112	0.1223		
O2′–D5′	0.9157	−0.3769	−0.1397	158.8	0.192
	0.1718	0.0527	0.9837		
	0.3634	0.9248	−0.1131		
O4–D6	0.7163	0.5853	−0.3800	160.6	0.130
	0.3762	0.1348	0.9167		
	−0.5877	0.7996	0.1237		
O4′–D6′	0.8117	−0.5830	−0.0357	156.3	0.135
	0.1070	0.0884	0.9903		
	0.5742	0.8077	−0.1341		

Discussion

D–C–D Angles. The importance of the angular values presented in the Results section for CPDA-d_4 lies in the fact that the direction of the largest component (**Z**) of the DQC tensor of a deuteron essentially coincides with the direction of the C–D bond. This has been established both experimentally[10] and theoretically.[14] The values quoted above can therefore be considered as the directions of the C–D bonds to a first approximation. To our knowledge, no dependable values exist in the literature for the C–D directions in CPDA, and even the D–C–D angles reported for the parent compound (cyclopropane) vary by several degrees depending on the experimental method used.

The angle between the two deuterons linked to one carbon atom in CPDA can be estimated by our study as 116.5 ± 1° (the average of both molecules). This is at variance with the X-ray study,[11] which gives values of 116.9° and 120.4° for one molecule and 121.1 and 121.5°, respectively, for the other. However, the EDNMR results and the X-ray study are nicely consistent with regard to the orientation of the cyclopropane ring. The X-ray study shows that the normal to the carbon ring is parallel to the

---

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

b axis, while the directions joining the two deuterons in a given methylene group, obtained from the EDNMR data, lie within 1.5° of the *b* axis.

Given the lack of data for the H–C–H angle from other studies on CPDA, we can compare our value (116.5°) with that of cyclopropane itself. Our results agree very well with an H–C–H angle of 115.1 ± 1° obtained for gaseous cyclopropane in an electron diffraction study.[15] This agreement reinforces our argument that substituting two hydrogen atoms by two carboxyl groups does not change this angle at the other carbon atoms significantly.

According to Wardeiner et al.[16] the s character of the carbon orbitals in cyclopropane involved in the C–C bonds is 0.1792 and those involved in the C–H bonds is 0.3208, based on the ^{13}C NMR studies of cyclopropane. These values represent small corrections to those obtained using the theory of Walsh and the other NMR data.[6,17] They imply a hybridization of the C–C bond of $sp^{4.58}$ and $sp^{2.12}$ for the C–H bond. The $sp^{2.12}$ hybridization corresponds to an angle for the H–C–H bond of 118.2° rather than 120° typical for an sp^2 hybridization. Our value (in single crystals) of 116.5° lies between 118.2° obtained from NMR (in solution) and 115.1° from electron diffraction (in the gas phase). Our results suggest the s character in this bond of about 0.31.

Another indirect method of measuring the geometry of small molecules is rotational spectroscopy in the gas phase. Raman studies on cyclopropane and cyclopropane-d_6[18] yield an H–C–H angle of 116.5°, while microwave studies on cyclopropyl chloride find an angle of 116.2 ± 0.3°.[19] These values are virtually identical to ours.

It should be noted that EDNMR does not provide the C–C–C angle and thus yields only indirect information about the relative s and p character of the C–C bonds.

Angle between the Bisectors of the D–C–D Angles (or between the D–C–D Planes). The assumption made in choosing CPDA for our study, as stated in the Introduction, was that the substitution of two protons by two carboxylic groups would not *dramatically* change the geometry of the cyclopropane ring. We have already shown that this is the case for the H–C–H angles for carbons 2 and 3 (atoms 7 and 8 in Figure 1). However, as expected, the X-ray data show that the C–C bond lengths do change:[11] the substitution results in a slight lengthening of the proximate (1–2, 1–3) C–C bonds while shortening the distal (2–3) bond, just as expected for a π-acceptor substituent on the basis of Hoffmann's theory.[20] The effect of substituents on the C–C bond lengths has been discussed extensively[21] for a wide range of cyclopropane derivatives. The change of geometry of the cyclopropane ring upon substitution is reflected also by the change of the ^{13}C *J–J* coupling constants: while in cyclopropane this value is 12.4 Hz;[16] in CPDA it becomes 9.95 Hz for the long bonds.[17]

Our EDNMR data point toward another change of the cyclopropane geometry upon substitution: the angle formed by the planes of the two unsubstituted methylene groups. This parameter has not been investigated and interpreted very extensively for cyclopropane derivatives, largely because of the unavailability of precise experimental data on the positions of the hydrogen atoms. EDNMR thus yields new information on this subject.

In cyclopropane itself the dihedral angle between the planes of the two methylene groups is of course 120° as required by the 3-fold symmetry of the molecule. The substituents in CPDA increase this angle to 132 ± 2° (see Table II, where this angle is designated as α). No twisting of the methylene planes relative to each other was detected. Again, the EDNMR result is at variance with the X-ray analysis which yields an angle of 138° (average of both molecules). However, the "opening" of the dihedral angle is plainly visible in both the EDNMR and X-ray data. A similar effect has also been reported in ethylene oxide, a molecule similar in certain ways to CPDA. In ethylene oxide this angle was found to be as much as 139°.[22] The opening of α is correlated with a shortening of the C–C bond from 1.51 Å in cyclopropane to 1.472 Å in ethylene oxide. In CPDA the corresponding C7–C8 bond length is 1.46 Å.

The changes in the C–C bond lengths upon substitution of COOH groups for hydrogen atoms in cyclopropane can be easily understood by considering the molecular orbitals in cyclopropane. The overlapping orbitals are bonding in the proximate (long) bonds and antibonding in the distal (short) bond for the highest filled MO. Hence, substitution of electron-withdrawing groups at C2 will tend to strengthen the latter and weaken the former, leading to the observed changes in those bond lengths.

The increase of α from 120 to 139° in ethylene oxide might be intuitively interpreted as the result of removing two hydrogens from the molecule, thereby removing the balance in steric repulsion and allowing the repulsion of the two remaining methylene groups to open α. In the case of CPDA this explanation fails, as a simple geometric analysis shows that replacing two hydrogen atoms by carboxyl groups causes *greater* steric repulsion of the remaining methylene groups due to the presence of the bulkier carboxyl groups. This should decrease α instead of increasing it.

Alternatively, the divergence of α from 120° in CPDA and ethylene oxide can be understood as an electrostatic effect caused by substitution of an electron-accepting group on the ring. However, classically defined electrostatic interaction would not account for the magnitude of the observed effect, as the hydrogens generally do not have much positive charge.[23] Also, this does not explain why α in ethylene oxide is larger (139°) than in CPDA (132°).

Curiously, we have noticed that opening the angle α in CPDA by 12° makes the overlap integrals of the hybrid orbitals forming the C–C bonds equal for all the three C–C bonds in the molecule (assuming that the sp^n hybrid orbitals for a given methylene group rotate as a rigid unit). If α were 120° as in cyclopropane, the overlap integral between the distal methylenes would be significantly larger than for the proximate bonds in CPDA (for the bond lengths determined in X-ray analysis). This could suggest that the increase of α may serve in part to compensate for the difference in bond lengths (between the carbon atoms) and ensure that the relative overlap is roughly the same for all three bonds reflecting a dynamic balance between the carbon atom centers. This increase in α would result in a slight *decrease* in the overlap between the distal methylenes and a corresponding increase in the overlap for the longer C–C bonds.

Preliminary RHF/6-31G* calculations show that when cyclopropane itself is distorted so that the carbon–carbon bond lengths have the same values as in CPDA, a lower energy geometry can be achieved if the methylene hydrogens are not forced to bisect the C–C–C angle at the distal carbons but are allowed to move so as to increase the angle α as observed experimentally in CPDA. However, a population analysis shows that this relaxation of the methylene geometry is accompanied by an *increase* in the overlap populations between the distal methylenes. This result is consistent with a model in which one views the distal fragment as increasingly approximating the character of an ethylene molecule as the proximate methylene moiety moves toward infinity. The angle α in a few cyclopropane derivatives has also been discussed by Fujimoto et al.[23]

e^2qQ Parameters in CPDA-d_4. The e^2qQ/h parameter of the deuterons linked to carbon atoms (185 kHz) is quite high. For comparison, the corresponding value in cyclobutanedicarboxylic acid (CBDA) is 176 ± 2 kHz.[9c] Unfortunately, no unequivocal dependence of this value with the character of the C–D bond has

---

(15) Bastiansen, O.; Fritsch, F. N.; Hedberg, K. *Acta Crystallogr.* **1964**, *17*, 538–543.

(16) Wardeiner, J.; Luettke, W.; Bergholz, R.; Machinek, R. *Angew. Chem.* **1982**, *94*, 873–874.

(17) Stöcker, M. *Org. Magn. Reson.* **1982**, *20*, 175–179.

(18) Jones, W. J.; Stoicheff, B. P. *Can. J. Phys.* **1964**, *42*, 2259–2263.

(19) Schwendeman, R. H.; Jacobs, G. D.; Krigas, T. M. *J. Chem. Phys.* **1964**, *40*, 1022–1028.

(20) Hoffmann, R. *J. Chem. Phys.* **1963**, *39*, 1397–1412.

(21) (a) Allen, F. H. *Acta Crystallogr.* **1980**, *B36*, 81–96. (b) Allen, F. H. *Acta Crystallogr.* **1981**, *B37*, 890–900.

(22) Igarashi, M. *Bull. Chem. Soc. Jpn.* **1953**, *26*, 330–331.

(23) Fujimoto, H.; Minato, T.; Inagaki, S.; Fukui, K. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 1508–1511.

yet been established. However, in anthracene, the sp^2 deuterons show an e^2qQ/h value of 184 kHz,[24] confirming indirectly the near sp^2 character of the C–D bond in CPDA, consistent with the D–C–D angle discussed above.

DQC Parameters in CPDA-d_2. The e^2qQ/h values for all the oxygen-bonded deuterons in CPDA are equal (160 kHz) within experimental error. We know from the crystal structure that these deuterons are involved in hydrogen bonds. It is generally known that the e^2qQ parameter of a deuteron involved in such a bond depends on the O···D distance.[10] This dependence may be expressed by the following empirical equation:[9b]

$$e^2qQ/h = 290 - 562/r^3 \qquad (2)$$

(r is the distance O···D in Å, e^2qQ/h is in kHz). Using our value of 160 kHz in this equation yields the O···D distance of 1.628 Å. This value agrees very well with the distance of 1.63 Å obtained from the room-temperature crystal structure results for the O3···H5 bond.

The same value of 1.63 Å disagrees with the length of the intermolecular O1···H6′ bond, as reported in the room-temperature study of the crystal structure (1.75 Å). This is a significant difference, as the value of 1.75 Å when inserted into the eq 2 yields the parameter e^2qQ/h = 185 kHz, much larger than the one observed by us for any of the carboxyl deuterons.

This prompted us to repeat the experiment with the crystal carefully oriented in such a way that the magnetic field was almost parallel to the O4–D6 bond, where the largest splitting of the quadrupole signals, equal to $(^3/_2)e^2qQ/h$, is to be expected. This experiment confirmed that the largest possible value of the e^2qQ/h is 160 kHz.

Such a large difference of the calculated O···D bond length in the case of the intermolecular hydrogen bond compared with a perfect agreement in the case of the intramolecular bond can be tentatively explained by invoking a shortening of the intermolecular distance along the *b* axis at reduced temperature. This would mean that the dimension of the unit cell along the *b* axis should decrease as the temperature is reduced. An X-ray diffraction experiment at 163 K showed no decrease at this temperature. Unfortunately, we were unable to make X-ray diffraction experiments at lower temperatures. A similar difference between the room- and liquid helium-temperature DQC parameters is observed for deuterated malonic acid crystal: the e^2qQ/h parameter decreases from 182 kHz at room temperature[25] to 174 kHz at 4.2 K.[9a] This corresponds to a decrease of the O···D distance by about 0.08 Å. Malonic acid is known to undergo a phase transition at 38 K (protonated crystal) or 55 K (perdeuterated crystal).[26]

The η parameter is quite large for all the carboxyl deuterons. In our study $\eta \approx 0.16$. This is typical for many carboxyl–hydrogen bonds.[27] In two other systems examined in this laboratory, malonic acid-d_4 and CBDA-d_2, $\eta \approx 0.11$.[9a,b]

Orientation of the Oxygen-Bonded Deuteron DQC Tensors. Differences between the X-ray results for the O–D bond directions and the EDNMR measurements (in deg) for the **Z** components of the DQC tensors are

O2–D5, 5.1; O2′–D5′, 6.9; average, 6.0

O4–D6, 0.6; O4′–D6′, 3.3; average, 2.0

As expected, the largest positive (by definition) element **Z** of the DQC tensor lies near the bond axis for all the deuterons. Some deviation is expected since the hydrogen bonds are nonlinear. This is particularly the case for the O2–D5···O3 bond, in which the O–D···O bond angle is 150°.[11] In addition to the nonlinear contributions, the values shown above also contain contributions due to experimental errors and temperature effects.

The largest negative element **Y** of the DQC tensor was found to lie approximately perpendicular to the plane formed by the carboxyl group. This was also found previously in malonic acid and CBDA.[9a,b] The actual values are not very reliable because the EDNMR spectra were not well-resolved in the a^*c^* plane (close to the **XY** plane), and the angular dependence in this rotation plane is small.

Acknowledgment. We are very grateful to Dr. James A. van Zee, who designed and built the rf synthesizer interface. We also thank Dr. Sue Critchlow who carried out the determination of the low-temperature unit cell of CPDA. We appreciate the advice of Dr. Tina Weeding, who carried out some early EDNMR experiments on CPDA. Dr. Roderick C. McCalley wrote the QDFIT computer program used by us in the fitting procedures and critically read the manuscript, contributing several valuable suggestions. Finally, discussions with Prof. Weston Borden are also gratefully acknowledged. Professor Borden, together with Dr. David Hrovat and Andrew B. Kwiram, carried out the preliminary calculations on the geometry of the "distorted" cyclopropane.

Registry No. CPDA, 598-10-7; CPDA-d_2, 136503-98-5; CPDA-d_4, 136503-99-6.

---

(24) Ellis, D. M.; Bjorkstam, J. L. *J. Chem. Phys.* **1967**, *46*, 4460–4463.

(25) Derbyshire, W.; Gorvin, T. C.; Warner, D. *Mol. Phys.* **1969**, *17*, 401–407.

(26) Pigenet, C.; Lucazeau, G.; Novak, A. *Molecular Spectroscopy of Dense Phases*; Grosmann, M., Elkmoss, S. G., Ringeissen, J., Eds.; Elsevier: Amsterdam, 1975; p 311.

(27) Brown, T. L.; Butler, L. G.; Curtin, D. Y.; Hiyama, Y.; Paul, I. C.; Wilson, R. B. *J. Am. Chem. Soc.* **1982**, *104*, 1172–1177.