Deuteron Chemical Shift and EFG Tensors in α -Glycine

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By computer fitting of resonance lines in deuteron spectra of perdeuterated crystals, deuteron chemical shifts in crystals are measured with an accuracy of ± 0.3 ppm. Second-order quadrupole shifts must be taken into account. An important advantage of the method is that the measured chemical shifts and the shift tensors are automatically related to EFG tensors which can be assigned easily. The method is applied to α -glycine for which a shift anisotropy $\Delta \sigma = 21 \pm 9$ ppm has been reported for the methylene protons. Full EFG and chemical-shift tensors are reported at both methylene deuteron sites, and motionally averaged tensors are reported for the ND₃⁺ sites. The shift anisotropies $\Delta \sigma$ for the methylene deuterons are 4.7 and 9.4 ppm, respectively. Significant differences of the isotropic shifts and quadrupole coupling constants are also observed for these two deuterons. They are interpreted as evidence for the formation of a weak C-H···O hydrogen bond in α -glycine.

INTRODUCTION

The introduction of so-called multiple-pulse sequences into solid state NMR has provided the experimenter with a general technique for measuring the anisotropic properties of chemical shifts of protons and other nuclei (1). This development has stimulated interest in both chemical-shift tensors as such (2) and in alternative methods to measure them (3-5). Nevertheless the bulk of the experimental data on proton chemical-shift tensors accumulated to date has still been obtained by using the multiplepulse technique (6). This is so in spite of several severe limitations to the applicability of this technique. One of them is that it is more or less restricted to molecules which do not contain abundant quadrupolar nuclei with comparatively strong magnetic moments such as, e.g., ¹⁴N. Molecules containing such nuclei are not amenable to high-resolution solid state NMR because no one has succeeded so far in decoupling protons from nuclei which experience strong quadrupole interactions with electric field gradients. The problems are that the transition frequencies of these nuclei are scattered in a typical solid over a range of several, if not many, megahertz, that there are usually several transitions, and that the transition frequencies vary quickly as a function of the orientation of the sample crystal.

In spite of this unfavorable situation Voigtsberger *et al.* (7) applied the multiplepulse method to α -glycine. They did not attempt to decouple the protons from the ¹⁴N nuclei. They extracted from their spectra numbers for the chemical-shift anisotropies $\Delta \sigma$ pertaining to both the $-NH_3^+$ and $-CH_2$ protons. The value reported for $\Delta \sigma (CH_2)$, 21 ± 9 ppm, falls far outside the range of shift anisotropies found for other protons bound to carbons (6). We therefore judged it worthwhile to check this result and looked for a way to do it. Because of the difficulties sketched above we considered the multiple-pulse method inappropriate for the purpose.

It has been shown that chemical shifts of the order of 20 ppm can readily be observed in *deuteron* spectra of molecular solids (8, 9). The widths (FWHH) of lines in single-crystal deuteron spectra are about 1.5 kHz. At a spectrometer frequency of 55 MHz, which we use for our deuteron work, 1.5 kHz correspond to about 30 ppm. The shift anisotropy $\Delta\sigma(CH_2)$ in α -glycine reported by Voigtsberger *et al.* is, therefore, of comparable size as the linewidth and should be clearly detectable in deuteron spectra of deuterated crystals of α -glycine. In what follows we shall show that by fitting deuteron NMR lines to, say, gaussians, it is possible to locate the centers of gravity of lines, and, hence, chemical shifts of deuterons with an uncertainty not larger than ± 0.3 ppm. This is small enough to measure typical shift anisotropies of carbon-bonded deuterons (\sim 5 ppm) with an accuracy competitive to that obtainable with the multiple-pulse method under favorable circumstances. One advantage of the deuteron method is that the chemical shifts and, eventually, the chemical-shift tensors obtained in this way are immediately correlated to electric field gradient (EFG) tensors which can be assigned easily on the basis of the approximate parallelism of unique principal EFG axes and bond directions.

Although initially motivated by the value of $\Delta\sigma(CH_2)$ reported in Ref. (7) the measurements reported here are by no means restricted to chemical-shift anisotropies but comprise full chemical-shift and quadrupole coupling tensors separately for both deuterons of the $-CD_2$ group of glycine and motionally averaged such tensors for the ND₃⁺ group. A remarkable difference in the bonding of the methylene protons becomes obvious in their QCCs, isotropic shifts, and, above all, shift anisotropies. It is interpreted as evidence of the formation of a weak $C-D \cdot \cdot O$ hydrogen bond in α -glycine.

It is common practice in deuteron NMR to assume that the unique axis of a deuteron EFG tensor and the deuteron bond direction are parallel. For α -glycine the C-D and N-D bond directions are available from precision neutron diffraction structure determinations (10, 11). Our results include the determination of the unique EFG axes of both -CD₂ deuterons. We are thus in a position to check the validity of the above mentioned assumption for the case of α -glycine. It holds to within better than 1°. This is an important side aspect of this work.

LIMITING ACCURACY OF LOCATING CENTERS OF SPECTRAL LINES

By least-squares fitting noisy NMR lines to, e.g., gaussians, it is possible to locate the center of gravity ν_0 of a line with an accuracy which exceeds by far the width $\Delta\nu$ (FWHH) of the line, and even the digital resolution of the spectrometer. For the error $\delta\nu$ in the determination of ν_0 the relation

$$\delta \nu = \pm \operatorname{const} \Delta \nu / (S/N)$$
^[1]

has been quoted by Klein *et al.* (12) and Segal *et al.* (13); S/N is the signal-to-noiseratio. To check Eq. [1] and to determine the constant of proportionality we made the following statistical tests. By firing the spectrometer without a sample we recorded pure, genuine spectrometer noise. Data sets of N = 4 k samples y_i were collected. The root-mean-square amplitude $\sigma = \{\sum_{i=1}^{N} (1/N - 1)(y_i - y_{A\nu})^2\}^{1/2}$ of the noise after Fourier transformation of the time domain data was computed. To see whether the noise from our spectrometer is really random we checked, and could confirm indeed, that, first, σ increases linearly with the gain of the preamplifier and, second, it increases linearly with the square root of the number of accumulated noise data sets. To the noise (in the frequency domain) we then added a computer generated gaussian "line" which simulates a resonance line. The amplitude S and the center frequency v_0 of this line are obviously precisely known. This noisy single-line spectrum was fitted to a gaussian. Our procedure is as follows: To fix the *baseline* of the gaussian the spectrum is displayed on a screen with a movable crosshair. The horizontal line of the crosshair is moved by the operator into what he (she) judges by eye is the center of gravity of the noise far away from the line. This position of the crosshair is taken as the baseline. To select the spectral range to be taken into account by the fit procedure the operator moves the vertical line of the crosshair once in the desired position on the left and once on the right hand side of the line. A Simplex (14) least-squares fit procedure then searches for the optimum values of the center frequency v_{opt} , amplitude S_{opt} , and width Δv_{out} of the gaussian. This procedure was repeated 10 times for each of five different values of S/N. For each value of S/N the distribution function $g(v_{opt} - v_0)$ was plotted vs $v_{opt} - v_0$ and its standard deviation $\delta v = \{\sum_{i=1}^{10} 1/9(v_{opt}^i)\}$ $(-\nu_0)^2$ ^{1/2} computed. The results may indeed be represented by Eq. [1] with const. = 0.34 \pm 0.06. A typical value of $\Delta \nu$ for a deuteron line from a perdeuterated molecular crystal is 1.5 kHz. The signal/noise ratio S/N in our spectra is typically about 30 or better, see below. With these numbers Eq. [1] with const = 0.34 implies $\delta \nu = \pm 17$ Hz which corresponds to about ± 0.3 ppm for $\nu_{\text{Larmor}} = 55$ MHz. This is much less than the digital resolution of our spectra, 244 Hz, which follows from the sampling rate of 1 MHz and the collection of 4k data sets. Nevertheless we shall see under Results and Discussion that the number quoted here for δv is definitely realistic.

EXPERIMENTAL

Samples. Perdeuterated glycine (glycine- d_5) was prepared as follows. Glycine- d_3 (ND₂CH₂COOD), obtained by repeated exchange (three times) with 99.8% D₂O, was furthermore exchanged by catalytic treatment with prereduced (D₂ gas) Adam's catalyst at 150°C in a pressure vessel for 3 days. Two equilibrations were sufficient to prepare glycine- d_5 at high isotopic and chemical purity; ²H > 98%, checked by NMR.

Glycine is known to crystallize in three different forms, called α -, β -, and γ -glycine (15). Single crystals of α -glycine were grown by slowly (0.2°/hr) lowering the temperature of a D₂O solution of glycine-d₅ which was saturated at 45°C.

Three crystals were prepared as NMR samples. They were first oriented optically and then by means of X rays. The X-ray diffraction patterns confirmed the α modification. The oriented crystals were glued on PVC rods with, respectively, their a^* , b, and c^* axis parallel to the rod axis. Subsequently they were machined on a lathe to fit in standard 5 mm NMR tubes.

NMR. The spectrometer used has been described previously (16). It operates at 55 MHz.

Our intention is to measure the chemical-shift tensors of the deuterons in glycine. The main result of the considerations of the previous section is that this is possible provided S/N > 30 can be realized. To optimize S/N it is important to select the proper pulse rate during data taking. To do this a knowledge of the relaxation times T_1 is required. Prior to the main measurements we therefore measured T_1 of the $-CD_2$ and $-ND_3$ deuterons of α -glycine at room temperature. As the $-ND_3$ groups in α -glycine are reorienting rapidly at room temperature (17) they give rise to only one pair of deuteron NMR lines per molecule in the unit cell. Its intensity is, as a consequence, three times as large as the intensities of the $-CD_2$ lines. On this basis it is easy to distinguish the $-ND_3$ from the $-CD_2$ lines. We measured at room temperature the dependence on the rotation angle α of $T_1(ND_3)$ and $T_1(CD_2)$ for rotating a crystal of glycine about its monoclinic axis, which is the *b* axis (10). $T_1(ND_3)$ varied between 2.5 and 3.5 msec whereas, depending on α , $T_1(CD_2)$ may be as long as 210 sec. The relevance of this finding with regard to the efficiency of spin diffusion in spin-1 systems will be discussed on a later occasion. For the present purpose it is sufficient to note that in view of the rather long T_1 of the CD₂ deuterons we eventually chose to pulse the spectrometer every 10 min.

Four FIDs were finally accumulated for each spectrum. A typical one is shown in Fig. 1a. The S/N ratios of the $-ND_3^+$ and $-CD_2$ resonances in this spectrum are about 90 and 30, respectively. Figure 1b shows a spectrum in which chemical shifts are obvious. Spectra of the quality as demonstrated in Fig. 1 were recorded in steps of 5° for rotating the sample crystals mentioned above about their a^* , $b^* = b$, and



FIG. 1. Deuteron spectra of a single-crystal of glycine. Spectrum a demonstrates $S/N \sim 30$ for the $-CD_2$, and $S/N \sim 90$ for the $-ND_3^+$ resonances. In the spectrum b chemical shifts are obvious in the innermost and outermost resonances.

 c^* axes. For all spectra the centers of gravity of all lines which did not overlap seriously with neighbor lines were determined by the fit procedure described above. Because of the large redundancy of our data we could easily afford to discard data from overlapping lines. Figure 2 shows one out of three rotation patterns of line splittings together with curves which were obtained by standard least squares fitting of the data to symmetrical, traceless second rank (EFG) tensors. The root-mean-square deviation of the experimental points from the fitted curves, 1.5 kHz on the average, is much larger than the number quoted above as the possible precision of determining line centers. The comparison is, however, not fair since the experimental number includes errors which result from imperfectly orienting the sample crystals and from imperfections of the one-circle goniometer which is part of the NMR probe. We estimate the error limits of the deviations of the true rotation axes of the sample crystals from the intended ones (the a^* , b, and c^* axes) to be about $\pm 0.3^\circ$. A misalignment of about the same size of the axis of the goniometer from the plane perpendicular to **B**₀ is obvious from the fact that spectra obtained for rotation angles α and $\alpha + 180^{\circ}$ are noticeably different.

The conclusion is that the accuracy of measuring EFG tensors with our present equipment is limited by the precision of the goniometer and by our limited ability to orient precisely crystals and to mount them thereafter on glass or plastic rods for insertion into the NMR probe, and not by the precision of measuring NMR transition frequencies. The opposite, however, is true with respect to measuring chemical-shift tensors, because the orientational dependence of the chemical shifts of deuterons is so small.



FIG. 2. Angular dependence of the deuteron quadrupole splittings for rotating a single crystal of glycine about its a^* axis. (*)D4, (\Box)D5, (O)ND₃⁺.

RESULTS AND DISCUSSION

Electric Field Gradients at Deuteron Sites in Glycine

From the data shown in Fig. 2 and two other such patterns we extracted by standard procedures the electric field gradient tensors at the deuteron sites in glycine. Table 1 gives the tensor parameters. The labeling of the deuterons is indicated in Fig. 3. The assignment of the EFGs to the deuteron sites was made on the basis of the well-known near parallelism of the deuteron bond directions and unique principal EFG axes, i.e., axes of approximate cylindrical symmetry. Because of the rapid reorientations of the $-ND_3^+$ groups at room temperature an averaged EFG tensor is obtained for deuterons $D_1 \cdot \cdot \cdot D_3$. Since glycine contains two molecules per unit cell our data give six EFG tensors which are, however, pairwise related by a plane. The parameters presented in Table 1 have been obtained by transforming one set of EFG tensors into the sites of the other set (those for which the atomic coordinates are listed in Ref. (10)) and then taking averages. This procedure, together with combining data from three independently oriented crystals, may be expected to lead to some cancellations of the errors originating in imperfect sample preparation.

Two aspects of the EFGs at the sites of the D_4 and D_5 deuterons are of particular interest. The first concerns the abovementioned parallelism of the bond direction and unique principal axis of the EFG. This parallelism is an often quoted *assumption*, a

	Eigenvalues (kHz)	Polar angles of eigenvector in SO system ^a		
Site			ઈ (°)	φ(°)
D(4)	$ V_{xx} = 125.1$	e _x	8.5	105.7
	$ V_{yy} = 114.9$	ev	86.9	354.3
	$ V_{zz} = 240.0$	ez	97.9	83.8
	$e^2 q Q/h = 159.99$	kHz, $\eta =$	0.043	
D(5)	$ V_{xx} = 137.8$	e _x	131.1	66.4
	$ V_{yy} = 116.3$	e _y	69.3	137.2
	$ V_{zz} = 254.1$	e _z	48.3	27.5
	$e^2 q Q/h = 169.41$	kHz, $\eta =$	0.085	
D(1, 2, 3)	$ V_{xx} = 49.0$	e _x	93.1	67.6
	$ V_{yy} = 27.2$	\mathbf{e}_{y}	13.1	351.1
	$ V_{zz} = 76.2$	ez	102.7	336.9

TABLE 1

The Quadrupole Coupling Tensors at the Deuteron Sites in α-Glycine

^a Polar angles defined in the standard orthogonal frame (SO) with a || x, b in the xy plane and $c^* || z$.



FIG. 3. The molecular structure of glycine; geometry after Ref. (10).

check of which is clearly desirable. It requires a reliable independent measurement of the bond direction. The accuracy attainable with X rays in determining C-D bond directions, about 5°, is not sufficient for the purpose since the parallelism in question seems to hold much better than that. The only method to measure reliably C-D bond directions is the neutron-scattering method. Fortunately it has been applied recently to glycine. We may thus compare directly the C-D₄ and C-D₅ bond directions \mathbf{b}_4 and \mathbf{b}_5 with the respective unique axes of the deuteron EFGs, $\mathbf{e}_z^Q(4)$ and $\mathbf{e}_z^Q(5)$, see Table 1. The assumed parallelism between \mathbf{b}_k and $\mathbf{e}_z^Q(k)$ holds indeed quite well: $\triangleleft(\mathbf{b}_4, \mathbf{e}_z^Q(4)) = 0.37^\circ$; $\triangleleft(\mathbf{b}_5, \mathbf{e}_z^Q(5)) = 0.68^\circ$. It is an open question whether these angles indicate errors of the deuteron NMR and neutron-scattering experiments or genuine deviations of \mathbf{b} and \mathbf{e}_z^Q . In any event their smallness supports the view that C-D bond directions can be measured by deuteron NMR via unique principal EFG axes with an accuracy which is substantially superior to that attainable with X-ray scattering.

The second point of interest of the EFGs at the D_4 and D_5 sites concerns the size of the quadrupole coupling constants, $QCC(D_4) = 160.0$ kHz and $QCC(D_5) = 169.4$ kHz. We may compare these values with the QCCs of the $-CD_2$ deuterons in malonic acid, 165.0 ± 0.2 and 165.2 ± 0.2 kHz. Malonic acid seems to be the only other molecular system in which the quadrupole coupling tensors of the two deuterons of a $-CD_2$ group have been measured separately (9, 18). In malonic acid the QCC of the two $-CD_2$ deuterons are equal within the accuracy of the measurement, in glycine, by contrast, they are remarkably different. Further below, we shall take up this point again and shall see that a drastic difference exists also in the chemical shifts, and, in particular, in the chemical shift *anisotropy* of these deuterons.

We turn now to the $-ND_3^+$ group. Derbyshire *et al.* have measured as early as 1967 the motionally averaged quadrupole coupling tensor of the $-ND_3^+$ deuterons in a crystal of $ND_3^+CH_2COO^-$ (17). Our respective results agree with theirs. Hunt and Mackay (19) have studied the pure quadrupole resonance of α -glycine at 77 K

where the motion of the $-ND_3^+$ group is essentially frozen in and obtained separate values for the QCCs and asymmetry factors η for each of $D(1) \cdot \cdot \cdot D(3)$. They tentatively assigned the measured QCCs on the basis that the smallest QCC should belong to the deuteron with the shortest $N-H \cdots O$ hydrogen bond, etc. We are now in a position to check this assumption in the following way: The tensor average $\langle QC \rangle_{av}$ of the correctly assigned low-temperature QC tensors of $D(1) \cdot \cdot \cdot D(3)$ should agree in all its features, e.g., its principal directions with the measured high-temperature QC tensor. To calculate $\langle QC \rangle_{av}$ we shall approximate the individual QC tensors at the $D(1) \cdots D(3)$ sites as axially symmetric and shall assume that the N-D bond directions are the symmetry axes. Both these simplifications are justified by the very small values of η reported by Hunt and Mackay. Now, there are six possible ways k of assigning the measured QCC values to the $D(1) \cdot \cdot \cdot D(3)$ sites. For each one we computed the direction \mathbf{e}_{z}^{k} of the principal axis which corresponds to the largest component of $\langle QC \rangle_{av}^k$. Now consider the angles $\delta^k = 4[e_z^k, e_z(ND_3^+, exptl.)]$. The assignment proposed by Hunt and Mackay (k = 1) gives $\delta^1 = 0.75^\circ$, all others give $\delta^k > 5.2^\circ$. Although the smallness of δ^1 in comparison to δ^k , k > 1, is not a proof of the correctness of Hunt's assignment it is a very strong support for it.

Chemical Shift Tensors

The centers of gravity of corresponding pairs of lines in spectra such as those shown in Figs. 1a and b represent chemical shifts plus a common offset from the spectrometer frequency, plus, in addition, so-called second-order quadrupole shifts. Assuming axial symmetry of the EFG tensor the second-order shift is given by

$$S^{(2)}(\Omega) = \frac{\nu_{\rm Q}^2}{24\nu_{\rm L}} \left[1 - \frac{\Delta^2(\Omega)}{\nu_{\rm Q}^2} \right]$$
[2]

where v_L , v_Q and $\Delta(\Omega)$ are, respectively, the Larmor frequency, the maximum doublet splitting (equal to 3/2 · QCC), and the doublet splitting at the actual orientation Ω of the crystal. The assumption of axial symmetry is an excellent one for the EFGs at the -CD₂, and still a fair one for the *average* EFG at the -ND₃⁺ sites, see Table 1. Note that the second-order shifts are always toward higher frequencies. All quantities on the rhs of Eq. [2] are known in our case: $v_L = 55$ MHz, v_Q is given in Table 1 as V_{ZZ} , and $\Delta(\Omega)$ can be taken directly from the spectrum under study. Therefore we may compute the second-order shift $S^{(2)}(\Omega)$ for each pair of lines in our spectra and subtract it from the measured shift of the center of gravity of the doublet. What remains as the difference is the chemical shift proper. The largest second-order shifts occurring in α -glycine at $v_L = 55$ MHz are, expressed in ppm,

$$\frac{S^{(2)}(\Delta=0)}{\nu_{\rm L}} = \frac{1}{24} \frac{\nu_{\rm Q}^2}{\nu_{\rm L}^2} = 0.9 \text{ ppm}.$$

The variation of the measured shifts as a function of the crystal orientation ranges from about 5 ppm for the $-ND_3^+$ deuterons up to more than 9 ppm for D_4 . The dominant part of the measured shifts thus represents *chemical* shifts, the second-order quadrupole shifts are, on the other hand, by no means negligible.

Figure 4 shows the orientational dependence of the chemical shifts in α -glycine.





Data are shown for only one molecule in the unit cell. Since we analysed the quadrupole splittings and assigned the EFG tensors before we can tell already at this stage of the processing of the chemical shift data which of the curves in Fig. 4 belongs to which deuteron. Note the scatter of the measured data points in Fig. 4. It is indicative of the basic correctness of our error analysis described above. Most of the larger deviations of data points from the solid curves in Fig. 4 can be traced back to problems originating in partial overlap of lines. The solid curves were obtained by least-squares fitting the data to chemical-shift tensors. The tensor parameters are listed in Table 2.

The first point to note is that the shift anisotropies of the $-CD_2$ deuterons D_4 and D_5 measured in this experiment are much smaller than reported by Voigtsberger *et al.* (7). Even our raw data exclude a shift anisotropy of (21 ± 9) ppm of these deuterons. $\Delta\sigma(D5)$ is, as a matter of fact, of similar size as is $\Delta\sigma$ of both $-CH_2$ protons in malonic acid (20).

Most interesting, however, is the finding that $\Delta\sigma(D4)$ is larger than $\Delta\sigma(D5)$ by more than a factor of two. This difference of the shift anisotropies is accompanied by a difference of the isotropic chemical shifts, σ . This shift difference may be compared with results obtained by MAS: Lippmaa *et al.* have reported a MAS high-resolution

Site	Eigenvalues" (ppm)	Polar angles of eigenvector in SO system ^b		
			ઝ (°)	φ(°)
D(4)	$\sigma_{xx} = -4.55$	e _x	19.2	44.1
	$\sigma_{yy} = -1.71$	e _v	105.8	6.6
	$\sigma_{zz} = 6.26$	ez	100.7	99.7
	$\sigma^{isoc} = -4.34$ ppm,	$\Delta \sigma^d = 9.4 \text{ ppm},$	$\eta^e = 0.454$	
D(5)	$\sigma_{xx} = -2.25$	e _x	117.9	77.6
	$\sigma_{xx} = -0.87$	\mathbf{e}_{y}	42.0	131.6
	$\sigma_{zz} = 3.12$	ez	61.5	4.4
	$\sigma^{\rm iso} = -3.5$ ppm,	$\Delta \sigma = 4.7$ ppm,	$\eta = 0.438$	
D(1, 2, 3)	$\sigma_{xx} = -2.66$	e _x	83.1	130.8
	$\sigma_{yy} = -0.09$	e _v	86.0	40.3
	$\sigma_{zz} = 2.75$	ez	8.0	281.4
	$\sigma^{\rm iso} = -7.8$ ppm,	$\Delta \sigma = 4.1$ ppm,	$\eta = 0.933$	

TABLE	2
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THE DEUTERON CHEMICAL-SHIFT TENSORS IN α -GLYCINE

^a Principal components of traceless, symmetric part of σ .

^b See footnote *a* to Table 1.

^c Isotropic shift relative to TMS.

 $^{d}\Delta\sigma = \sigma_{zz} - 1/2(\sigma_{xx} + \sigma_{yy}).$

$${}^{e}\eta=\frac{\sigma_{yy}-\sigma_{xx}}{\sigma_{yy}}.$$

spectrum of a powder sample of perdeuterated α -glycine (21). It shows a doublet for the -CD₂ group. The splitting, about 0.8 ppm, compares very favorably with our number (0.9 ppm) for this quantity. The MAS result is obtained from a single spectrum. It is not subject to problems related to the combination of information from three different crystals. The good agreement of the MAS and our experiment with regard to the isotropic shift difference of the -CD₂ deuterons supports the reliability of the chemical-shift *tensor* results reported here.

Note that our data, in contradistinction to the MAS result, allow us immediately and unequivocally to tell which of the chemically shifted lines in the MAS spectrum belongs to D_4 and which to D_5 , cf. Table 2.

The C-D bond directions **b** are, as in malonic acid, roughly the directions of maximum shielding: $\triangleleft [\mathbf{e}_Z^{CS}(4), \mathbf{b}_4] = 16^\circ, \ \triangleleft [\mathbf{e}_Z^{CS}(5), \mathbf{b}_5] = 22.5^\circ$. We are now in the possession of three NMR quantities (QCC values, chemical shifts, and shift anisotropies) which all point toward a pronounced difference in the bonding of D_4 and D_5 . According to the neutron diffraction data of Jonsson and Kvick the C_2-H_4 and C_2-H_5 bond distances are, respectively, 1.090 ± 0.002 and 1.089 ± 0.002 Å and thus do not suggest any bonding difference. However, H₄ has two unusually short contacts, 2.390 and 2.453 Å, with two oxygens in an adjacent layer of hydrogen-bonded glycine molecules, whereas the C_2-H_5 bond should represent an undisturbed C-H bond (10). Characteristic features of protons and deuterons in hydrogen bonds are *large* shift anisotropies (22) and a decrease of the QCC with increasing strength of the H bond (23). The large shift anisotropy $\Delta \sigma = 9.4$ ppm and the small QCC = 160.0 kHz of D_4 in comparison with $\Delta\sigma(D_5) = 4.7$ ppm and QCC(D_5) = 169.4 kHz may, therefore, be interpreted as evidence for the formation of a weak C_2 - D_4 ···O hydrogen bond in α -glycine. As a matter of fact, the two short H₄-O contacts suggest a bifurcated hydrogen bond. In this connection it may be interesting to note that spectroscopic evidence for C-H \cdot ··O hydrogen bonding in polyglycine II has been provided by Krimm et al. (24).

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