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Journal

Journal of Molecular Structure, 889

Authors

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Publication Date

2008

DOI

10.1016/j.molstruc.2008.02.023

Peer reviewed

Variable Temperature NMR Characterization of α -Glycine

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Abstract:

Proton NMR spin-lattice relaxation times in the laboratory frame (T_1) and in the rotating frame ($T_{1\rho}$) were measured as a function of temperature for a static sample of α -glycine. Both T_1 and $T_{1\rho}$ data can be fit quantitatively by a single thermally-activated motion (the modulation of the dipolar coupling by random hopping about the threefold axis of the $-\text{NH}_3$ group), with no addition of other mechanisms at any temperature between 173 K and 415 K. An activation energy of 21.7 ± 1 kJ/mol was extracted and is compared with previously reported values for both α - and γ -glycine. Such comparisons allow the correction of glycine polymorphs misidentified in the literature. The minimum in T_1 at 325 K corresponds to a correlation time of 0.53 ns. Chemical shifts as a function of temperature were measured by ^1H CRAMPS and by ^{13}C and ^{15}N CP/MAS experiments. These results are discussed relative to a previous report of anomalous electrical behavior in α -glycine within this temperature range.

Key Words:

NMR; ^1H NMR; ^1H CRAMPS; ^{13}C CP/MAS; ^{15}N CP/MAS; spin-lattice relaxation; T_1 ; $T_{1\rho}$; activation energy; glycine; anomalous electrical behavior.

Introduction

Glycine is the simplest amino acid. Its structure lacks chirality. In the solid state, the compound exists as a zwitterion in one of four polymorphic forms: α , β , γ , and the more recently characterized δ , formed under high pressure [1-4]. The basic molecular structure of the zwitterion is the same in each polymorph, with the resulting polymorphic crystal structures arising from differences in the hydrogen bonding between the zwitterions. As the subject of many theoretical [5-7] and spectroscopic [8-11] studies over the years, glycine is considered well characterized. It is frequently used as a model compound, as there is general agreement as to both its molecular structure and motions. Nevertheless, Boldyreva et al. [12] have highlighted a difficulty with quantitative information for glycine found in the chemical literature. Specifically, they have emphasized that the relative stability and the preferential growth of a particular polymorph of glycine are not directly correlated, and that this point explains "why much confusion and contradictory statements can be found in the literature even for seemingly simple and repeatedly studied systems." They also found that commercially available glycine usually contained a mixture of two polymorphs (α and γ) of varying content, depending upon the source.

Andrew et al. [13,14] have reported elegant and in-depth studies of proton magnetic relaxation and molecular motion in crystalline amino acids, including α -glycine. While the conclusions drawn from those studies, such as the relaxation minimum attributed to the reorientation of the $-\text{NH}_3$ group and their reported internuclear proton distances, remain valid, another report [15] has indicated that the glycine polymorph they used was mischaracterized, based on the reported activation energy for the reorientation of the $-\text{NH}_3$ group of 29 kJ/mol matching that of γ -glycine.

One purpose of this work is to measure the activation energy for a static sample of α -glycine. In this study, α -glycine has been prepared and characterized as to both polymorphic content and purity [16]. The proton nuclear magnetic resonance (NMR) relaxation times in the laboratory frame were measured as a function of temperature to characterize the activation energy for the reorientation of the amine group. In addition, the study was extended to include relaxation measurements in the rotating frame to investigate molecular motion on a time scale different from that for relaxation in the laboratory frame. Anomalous electrical behavior has been reported [17] in the conductance and capacitance measurements on a single crystal of α -glycine in the temperature range of 293 to 323 K. A second purpose of this work is to investigate possible explanations for this electrical behavior by searching for changes in mobility or motion on time scales appropriate to relaxation times and to the ^1H , ^{13}C , and ^{15}N chemical shifts.

Experimental

The NMR data were acquired with a Bruker Avance 300 spectrometer. Proton data from static samples were measured with a standard Bruker ^1H wideline probe with a 5-mm solenoid coil. The ^1H $\pi/2$ pulse width was 1 μs . The ^1H spin-lattice relaxation (T_1) data were acquired with an inversion recovery sequence ($\pi - \tau - \pi/2 - \text{acquire}$) [18] and

the ^1H spin-lattice relaxation in the rotation frame ($T_{1\rho}$) data were acquired with a spin-locking sequence ($\pi/2_x - (\text{spin lock})_y$) [18].

The ^{13}C and ^{15}N cross-polarization/magic-angle-spinning (CP/MAS) [19] spectra were acquired with a MAS probe with a 4-mm (outside diameter) zirconia rotor. The experiments used a ^1H $\pi/2$ pulse width of 4 μs , a contact time of 1.5 ms, a data acquisition time of 65 ms, and a recycle delay of 5 times the ^1H spin-lattice relaxation time. The sample spin rate was 5 kHz. The ^1H CRAMPS [20] spectra were acquired on the same 4-mm MAS probe with a ^1H $\pi/2$ pulse width of 2 μs and $\tau = 4 \mu\text{s}$ for the quadrature-detected BR-24 pulse sequence [21]. The sample spin rate for the CRAMPS experiments was 3 kHz.

The melting point (decomposition) temperature of α -glycine is 535 K [22]. However, Boldyreva et al. [12] have observed sublimation at temperatures as low 420 K. For this reason, no NMR measurements were made above 415 K.

Results and Discussion

The polymorph α -glycine (existing in a $P2_1/n$ space group with four molecules per unit cell) is generally prepared by slow evaporation from aqueous solution [16,23]. This procedure results in a double-layer structure. In one layer the zwitterionic glycine molecules align in a head-to-tail fashion, linked by two shorter $-\text{N}-\text{H}\cdots\text{O}-$ hydrogen bonds (to different molecules). Alternate layers are antiparallel. These two antiparallel layers are held together by a longer $-\text{N}-\text{H}\cdots\text{O}$ hydrogen bond that is bifurcated between two oxygen atoms belonging to different glycine molecules. As a result, each glycine molecule in one plane is hydrogen-bonded to four molecules in the adjacent plane. Each oxygen atom in a single molecule participates in two hydrogen bonds with different molecules, one shorter in-plane $-\text{N}-\text{H}\cdots\text{O}-$ bond and a longer, shared bifurcated bond with a molecule in the adjacent layer. Only weak $-\text{C}-\text{H}\cdots\text{O}$ interactions are present between the different double (anti-parallel) layers [23]. *Ab initio* modeling by Peeters et al [7] suggests that these interactions are so weak as not to alter the C-H bond distance. Indeed, they describe the double layers as "held together by much weaker van der Waals forces," as compared with the hydrogen bonds holding the extended sheets together.

For illustration, the ^{13}C CP/MAS spectrum of a physical admixture of 92% of α -glycine with 8% γ -glycine is shown in Figure 1A. The individual polymorphs are easily identified on the basis of the isotropic ^{13}C chemical shift of the carboxyl group, with the α -glycine resonance at 176.45 ppm and the γ -glycine resonance at 174.48 ppm as measured at 296 K. Due to the separation of the carboxyl chemical shifts, the presence of small amounts of the other polymorphs can be easily identified and quantified in a ^{13}C CP/MAS spectrum [16]. The ^{13}C CP/MAS spectrum of the sample of α -glycine used for the measurements reported here is shown in Figure 1B.

The temperature-dependent ^1H spin-lattice relaxation times in the laboratory frame (T_1) and in the rotating frame ($T_{1\rho}$) are shown in Figure 2. The laboratory-frame relaxation data were fit, assuming that relaxation was dominated by random modulation of the proton-proton dipolar coupling, to the equation [14,24]

$$\frac{1}{T_1} = C \left[\frac{\tau_c}{1 + \omega^2 \tau_c^2} + \frac{4\tau_c}{1 + 4\omega^2 \tau_c^2} \right], \quad (1)$$

where C , a constant with units of s^{-2} , represents the magnitude of the dipolar interaction; τ_c is the correlation time; and ω is the Larmor frequency of the proton. The temperature dependence of the relaxation time reflects the variation of the correlation time, which is assumed to be thermally activated:

$$\tau_c(T) = \tau_0 \exp \left[\frac{E_a}{RT} \right], \quad (2)$$

where τ_0 specifies the magnitude of the correlation time, and E_a is an activation energy for the process that modulates the proton dipole-dipole interaction, in this case the random fluctuation of the $-\text{NH}_3$ group. The fit of Figure 2 yields an activation energy for this process of 21.7 ± 1 kJ/mol. The minimum T_1 is at 325 K. At this minimum, the correlation time, τ , is equal to inverse of the Larmor frequency, $\omega^{-1} = (2\pi\nu)^{-1}$, and has a value of 0.53 ns.

Spin-lattice relaxation in the rotating frame is also induced by fluctuating dipolar couplings. Look and Lowe use the formula of equation (3) to describe the effects on $T_{1\rho}$ [25].

$$\frac{1}{T_{1\rho}} = C \left\{ \frac{3}{2} \frac{\tau_c}{1 + \omega_1^2 \tau_c^2} + \frac{5}{2} \frac{\tau_c}{1 + \omega^2 \tau_c^2} + \frac{\tau_c}{1 + 4\omega^2 \tau_c^2} \right\} \quad (3)$$

Here, ω_1 is the amplitude of the spin-lock field, expressed as an angular frequency. The line in Figure 2 shows the fit of equation (3) to the $T_{1\rho}$ data using the same parameters as for T_1 .

As mentioned, Andrew et al. [13, 14] have reported an activation energy of 29 ± 1 kJ/mol for a static sample of α -glycine. This value is closer to the activation energy for γ -glycine of 30 ± 3 kJ/mol [26] determined from indirect ^1H T_1 measurements from ^{13}C CP/MAS experiments and of 33 ± 2 kJ/mol [15] obtained from both ^1H T_1 and wide-line ^2H measurements on static samples. These latter results suggest a mischaracterization of the glycine polymorph used by Andrew et al [13,14]. The activation energy of 21.7 ± 1 kJ/mol for α -glycine measured here on a static sample differs only slightly from the 23 ± 2 kJ/mol for α -glycine obtained from indirect ^1H T_1 measurements from ^{13}C CP/MAS measurements [26]. However, Gil and Alberti [27] have shown that the spin-lattice relaxation time measured in chemical systems in which rapid molecular motions occur (including an unspecified polymorph of glycine) is strongly dependent upon the sample spinning rate used for MAS. As proton spin diffusion between the protons of the amine group and those of the methylene has been shown to be responsible for the single-exponential proton spin-lattice relaxation decay in γ -glycine [15], it was deemed necessary to make these measurements on a static sample to see if the spin rate used by Gu et al [26] affected the relaxation measurements.

Values of the ^1H spin-lattice relaxation times in the rotating frame ($T_{1\rho}$) have been reported for α -glycine at only a few temperatures [16,28]. The $T_{1\rho}$ data of Figure 2 show the relaxation profile over a wide range of temperature from 173 K to 415 K. The relaxation observed in the rotating frame is fully explained by the same motional mechanism, in this case the random fluctuation of the $-\text{NH}_3$ group, invoked to fit the T_1 relaxation data.

The ^1H CRAMPS spectrum of α -glycine at ambient temperature has been reported in the literature [11,29]. Three ^1H CRAMPS spectra obtained at 223, 296.5, and 415 K are shown in Figure 3. The three resonances are well-characterized: the $-\text{NH}_3$ resonance at 8.5 ppm and the two inequivalent methylene proton resonances at 4.3 and 3.3 ppm. The spectra of Figure 3 demonstrate that there is no appreciable change in the observed proton chemical shifts (of either the $-\text{NH}_3$ or the two inequivalent methylene protons) as a function of temperature over this range. While not shown, ^1H CRAMPS spectra were also acquired at all the same intermediate temperatures as for the ^{13}C and ^{15}N CP/MAS spectra (*vide infra*). The ^1H shifts, within the resolution of the CRAMPS experiment, over this temperature range remained constant. In the neutron-diffraction study [23], a change in the bifurcated hydrogen-bond length that links the antiparallel layers was noted. Between 288 K and 323 K, the donor-acceptor distance increased by 1.5 pm with an increase of 1.4 pm in the proton-acceptor distance. Due to the short correlation time for protons hopping between the three hydrogen-bond sites on the nitrogen, any observable change in the ^1H chemical shift as a result of expansion is averaged out by this rapid motion.

Notwithstanding the constancy of the ^1H CRAMPS spectra, the ^{13}C CP/MAS spectra do reveal changes, as shown in Figure 4. The changes are small, amounting to only a few tenths of a ppm over the temperature range 200 K to 400 K. It is interesting to note that the carboxyl resonance becomes less shielded as temperature increases below about 300 K, but then becomes more shielded with increased temperature above 300 K. Theoretical calculations of the principal values of the ^{13}C chemical shift tensors in carboxylic acids have shown the effect of the atomic hybridization of the carbon atom upon the shielding [30, 31]. In general, the σ_{11} component of the carboxyl shielding tensor is the bisector of the O-C-O angle with the σ_{33} component perpendicular to the O-C-O plane. The σ_{22} component of the carboxyl shielding tensor, orthogonal to σ_{11} and σ_{33} , was shown to be a strong function of the difference between the two C-O bond distances. It is these changes in the σ_{22} component which result in the variation of the isotropic chemical shift [16]. The change in the observed isotropic chemical shift with thermal expansion of the lattice appears to indicate that these bond distances are altered slightly. The methylene-carbon resonance becomes consistently less shielded as temperature is increased over the whole range.

The ^{15}N chemical shift of α -glycine at 296 K is 32.4 ppm. Most biochemical applications of ^{15}N NMR have used liquid NH_3 as a secondary reference for ^{15}N in aqueous solutions [32]. This referencing has been used here rather than that based on nitromethane. Nitromethane has a ^{15}N chemical shift of 381.9 ppm on this scale.

The nitrogen resonance, shown in Figure 5, also changes with temperature. The ^{15}N resonance becomes less shielded as the temperature increases. The chemical shift monotonically increases as a function of temperature. However, there appear to be regions, beginning around 250 K and again around 300 K, over which the chemical shift

remains constant. The very small variation of the nitrogen chemical shift change around 300 K occurs concurrently with a similar small change of the methylene chemical shift. This change is coincident with the maximum of the chemical shift of the carboxyl carbon.

The variations in the chemical shifts are not indicative of a major change in mobility, since (as is shown in Figure 2) both spin-lattice relaxation in the laboratory frame and the rotating frame can be fit quantitatively by a single thermally-activated motion (presumably the modulation dipolar coupling by random hopping about the threefold axis of the $-\text{NH}_3$ group), with no addition of other mechanisms at any temperature between 173 K and 415 K.

As mentioned in the introduction, anomalous behavior has been observed in the results of electrical measurements [17] of the conductance and capacitance of a single crystal of α -glycine in the temperature range of 293 to 304 K. The conductance exhibited an extraordinary change of four orders of magnitude over this small temperature range. The proposed explanation for such behavior is pyroelectricity arising from a phase transition to a noncentrosymmetric structure, the onset of which was put at 304 K. However, no indication of such a phase transition in α -glycine has been observed in thermodynamic studies spanning the temperature range from 5 to 500 K [33]. Furthermore, no change in the centrosymmetric space group $P2_1/n$ to a noncentrosymmetric space group, necessary for the onset of pyroelectricity, was observed in a neutron diffraction study [23] over the range of 288 to 427 K. In the neutron study, an anisotropic expansion of the unit cell was observed.

A zwitterionic glycine molecule has a large dipole moment (a few 10^{-29} Cm) lying approximately along the molecular axis [23]. The explanation of the observed electrical change may lie in some molecular motion or rearrangement. However, as noted in the neutron study [23], the small change in the hydrogen-bond length will not greatly affect the dipole moment. Thus, some change in mobility of the glycine molecule could be the underlying cause of the observed electrical change.

Langan et al. [23] suggest that the observed electrical behavior may result from "libration-driven changes in the interaction and separation of molecular layers" that allow the molecular dipoles to reorient. Neither the ^1H relaxation data in the laboratory frame nor in the rotating frame, sensitive either to motions on the order of the Larmor frequency or to motions on the order of tens of kHz (respectively), indicate significant librations in these frequency ranges. Those data can be explained by the modulation of the dipolar coupling by random hopping about the threefold axis of the $-\text{NH}_3$ group. The observed proton linewidths of the wide-line spectra of the static sample are sensitive to motions in the very low frequency region. The ^1H resonance narrows only slightly as the temperature is increased throughout the range. For example, the linewidths vary from 49.4 kHz at 200 K to 44.6 kHz at 296 K and to 43.1 kHz at 415 K.

Very small changes in the chemical shifts correspond approximately to the point at which the onset of conductivity has been reported. Chemical shielding, resulting from the electron density around the nucleus, is affected by very low frequency motions to which relaxation would be insensitive, as well as high-frequency motions that strongly affect relaxation times. Thus, one is tempted to ascribe the slight changes in the chemical shifts in this region to low-frequency modes like the expansion of the lattice (essentially a zero-frequency mode) or very long wavelength lattice modes.

The reported electrical behavior was essentially d.c. (using a modulation of $f = 0.84063$ Hz), so the likelihood is very small that the modes producing conduction are affecting relaxation in this range, consistent with the observations of no observed transitions detected through relaxation. Clearly, the minor changes in chemical shielding are not indicative of a major rearrangement of the structure such as one would expect by a transition to a pyroelectric state, so the chemical shift changes and relaxation time measurements rule out such a transition. However, the small changes in chemical shift that do occur within the range of the conductivity changes suggest that low-frequency modes that would affect the chemical shift (but not relaxation) do exist. Given the reported electrical behavior, these may be the origin of the changes in conductivity.

Conclusions

The ^1H NMR spin-lattice relaxation times in the laboratory frame (T_1) and in the rotating frame ($T_{1\rho}$) were measured for a static sample of α -glycine as a function of temperature. Both T_1 and $T_{1\rho}$ can be fit quantitatively by a single-thermally activated motion (the modulation of the dipolar coupling by random hopping about the threefold axis of the $-\text{NH}_3$ group), with no addition of other mechanisms at any temperature between 173 K and 415 K. An activation energy of 21.7 ± 1 kJ/mol was extracted from the analysis. The minimum in the T_1 relaxation at 325 K gives a correlation time of 0.53 ns.

The ^1H chemical shifts were independent of temperature over the range of 200 to 415 K. The ^{13}C and ^{15}N chemical shifts showed only very small changes of a few tenths of a ppm over this same temperature range. The size of these changes or their absence altogether are consistent with both neutron and calorimetry data indicating that α -glycine undergoes no phase transition in this temperature range, as would be required by the onset of pyroelectric behavior. These shift data also suggest that the separation of the α -glycine bilayers from thermal expansion do not alter the ability of the zwitterionic dipoles to reorient in the presence of an applied electric field.

Acknowledgment

This material is based upon work supported by the National Science Foundation under Equipment Grant # DMR-9975975. CRD acknowledges support of NMR studies by the National Science Foundation under Grant CHE-0411790.

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Figure 1: ^{13}C CP/MAS spectra of (A) a physical admixture of 92% of α -glycine with 8% γ -glycine and (B) the α -glycine sample used in this study.

Figure 2: ^1H spin-lattice relaxation times in the laboratory frame (T_1) [●] and the rotating frame ($T_{1\rho}$) [■] of α -glycine as a function of temperature. The solid lines represent the fit of equations (1) and (3) in the text to the data.

Figure 3: ^1H CRAMPS spectra of α -glycine at 415 K (A), 296.5 K (B) and 223 K (C).

Figure 4: The temperature dependence of the ^{13}C chemical shifts of the carboxyl (top) and methylene (bottom) resonances of α -glycine as a function of temperature.

Figure 5: The ^{15}N chemical shift of α -glycine as a function of temperature