A Deuteron Magnetic Resonance Study of Urea-d_4

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Urea is perhaps one of the few compounds whose crystal structure has been extensively investigated. Recent structure analyses of urea include a neutron diffraction study by Worsham, Levy and Peterson¹⁾ and X-ray studies by Vaughan and Donohue,²⁾ and by Sklar, Senko and Post.³⁾ The last-named paper includes a study at −140°C. The temperature factors determined from these studies are anisotropic and quite large, especially for the nitrogen and hydrogen atoms. This is considered to be due to librational motion about one or more axes in urea. After the present work had been completed, another paper on the X-ay analysis of urea was published by Caron and Donohue.⁴⁾ These authors were able to derive mean amplitudes of the translational and librational motion from the temperature factors. On the other hand, from the proton magnetic resonance (PMR) linewidth transition centered at about 50°C, Kromhout and Moulton⁵⁾ deduced the setting-in of a free rotational motion of the NH_2 group about the C–N bond. In a more recent PMR investigation using a single crystal, Emsley and Smith⁶⁾ showed that the angular dependence of the second moment when the crystal is rotated about the c axis can be accounted for not by such a motion, but, instead, by a reorientation of the whole molecule about the C=O bond. They showed that the observed line shape is also consistent with the presence of a reorientation about the C=O axis, but that the line shape could not show whether or not a reorientation about the C–N bond is also present. Though their experimental evidence is quite convincing, the reorientational motion of a large molecule as a whole about the C=O axis seems rather unusual. Since deutron magnetic resonance (DMR) provides a powerful means for the study of the motion of a group with hydrogen atoms,⁷⁾ the present study was undertaken in the hope that new information could be obtained concerning both the molecular motion of urea and deuteron quadrupole coupling in amides which has not been observed so far.

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1) J. E. Worsham, H. A. Levy and S. W. Peterson, *Acta Cryst.*, **10**, 319 (1957).

2) P. Vaughan and J. Donohue, ibid., **5**, 530 (1952).

3) N. Sklar, M. E. Senko and B. Post, ibid., **14**, 716 (1961).

4) A. Caron and J. Donohue, ibid., **17**, 544 (1964).

5) R. A. Kromhout and W. G. Moulton, *J. Chem. Phys.*, **23**, 1673 (1955).

6) J. W. Emsley and J. A. S. Smith, *Trans. Faraday Soc.*, **57**, 1233 (1961).

7) a) T. Chiba, *J. Chem. Phys.*, **36**, 1122 (1962); b) **39**, 947 (1963).

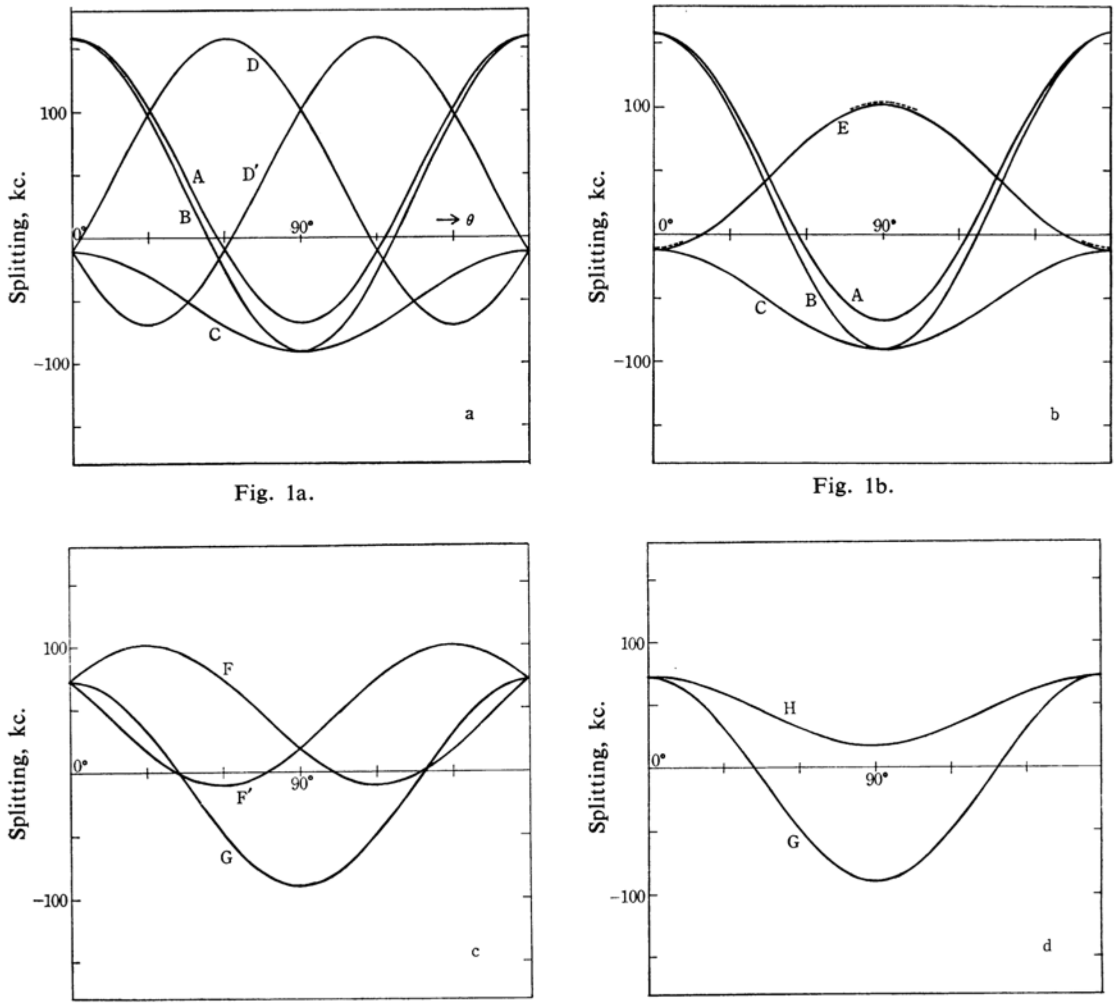

Fig. 1a.

Fig. 1b.

Fig. 1c.

Fig. 1d.

Fig. 1. Calculated rotation patterns of the deuteron quadrupole splitting of urea-d_4 crystal assuming, (a) a stationary molecule, (b) a molecule reorienting about the C=O axis, (c) a molecule reorienting about C-N axis, (d) a molecule reorienting about the C=O and C-N axes, with H_0 in the (110) plane. θ is the angle between H_0 and the c-axis direction. The other member of the satellite pair, which is a mirror image of the one in this figure with respect to the zero-splitting, is not shown.

Experimental

A single crystal of urea-d_4 was prepared by the gradual cooling of a saturated solution of urea-d_4 in methanol-d. Urea-d_4 was prepared by repeated evaporation of urea solution in heavy water. Methanol-d was prepared by refluxing dimethyl oxalate with potassium carbonate and heavy water,[8] followed by a fractionation. A small amount of deuterated ammonium bromide (a small percentage of the urea) was added to the solution to prevent the urea crystal from growing as long needles.[9]

The apparatus and the procedure of the measurement of DMR have been described elsewhere.[7] Measurements were made at the field strength of 16.6 kgauss.

Results

Observation at Room Temperatue. — Urea crystallizes in a tetragonal form belonging to the space group $D_{2d}^3-P\bar{4}\ 2_1m$.[1] All urea molecules in the lattice are in equivalent positions. The planar molecule lies on a plane parallel either to (110) or to $(1\bar{1}0)$. At room temperature, the spin-lattice relaxation time, T_1, is sufficiently short to give lines with good signal-to-noise ratio while at lower temperature

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[8] J. Beersmans and J. C. Jungers, *Bull. soc. chim. Belges.*, **56**, 81 (1947).

[9] E. A. Andrew and D. Hyndman, *Discussions Faraday Soc.*, **19**, 195 (1955).

only poor signal is obtained because of a strong saturation, indicating a long T_1. The spectra are observed as a function of the angle of the crystal about the axis perpendicular to the applied dc field. DMR was first observed with the crystal rotated about the c axis. Since the crystal structure is simple, the angular dependence of quadrupole splitting lines could be easily interpreted by assuming a quadrupole tensor in each N–D bond direction, with a small asymmetry parameter. Approximate eqQ and η values derived in this way are then used to set up a rotation pattern of quadrupole splitting when the crystal is rotated in the [110] direction. All subsequent observations are made at this crystal orientation. The expected rotation pattern of the quadrupole splitting for the molecule (a) at rest, (b) reorienting about the C=O bond, (c) reorienting about the C–N bond, and (d) reorienting about both the C=O and C–N bonds, are shown in Fig. 1. The observed rotation pattern at room temperature agreed completely with Fig. 1(a), the stationary molecule. eqQ, and η values and the principal axis directions of q-tensor are listed in Table I.

TABLE I. OBSERVED DEUTERON QUADRUPOLE COUPLING, ASYMMETRY PARAMETER AND PRINCIPAL-AXIS DIRECTIONS OF THE FIELD GRADIENT[a] IN UREA-d_4

Room temperature

D_1 $eqQ/h=210.8\pm1.0$ kc./sec, $\eta=0.139\pm0.010$.
$q_{\rm I}$, 60.2° from [001] direction, in (110) plane (molecular plane), $q_{\rm II}$ in [1$\bar{1}$0] direction, and $q_{\rm III}$, 28.8° form [001] direction, in (110) plane.

D_2 $eqQ/h=210.7\pm1.0$ kc./sec., $\eta=0.146\pm0.010$.
$q_{\rm I}$, in [001] direction, $q_{\rm II}$ in [110] direction, and $q_{\rm III}$ in [1$\bar{1}$0] direction.

117°C

D_2 $eqQ/h=206.3\pm1.2$ kc./sec., $\eta=0.138\pm0.010$.

[a] $q_{\rm I}$, $q_{\rm II}$, $q_{\rm III}$ are the principal components of a field gradient tensor such that $|q_{\rm I}|>|q_{\rm II}|>|q_{\rm III}|$.

Observation at Elevated Temperatures. — As the temperature is raised, the lines D and D′ except at $\theta=0°$ and 90°, where θ is the angle of the rotation of the crystal measured from its c axis parallel to H_0, disappear at about 36°C. (The signal of line D already manifests slight broadening at room temperature). Above 100°C the signal corresponding to line E of Fig. 1 (b) begins to appear near $\theta=0°$ and 90°, as is shown by the broken line in the figure, where the frequency separation between line D and line D′ is small. This can be explained by the motion assumed in (b), namely, a reorientation about the C=O axis, but not by a free rotational motion. A further raising of the temperature (above 110°C), however, results in a collapse of the line E pattern, even at $\theta=0°$ or 90°, while the intensity and linewidth of line C at $\theta=90°$ remains almost unchanged. This can be reasonably explained by assuming the onset of an additional reorientation about the C–N bond, since this motion, which interchanges D_1 and D_2, alters all the line patterns except the one at $\theta=90°$ of line C. Because of this behavior, the observations of the line-width change due to the reorientation about the C=O bond could only be made over a small range of temperature. Likewise, for the motion about the C–N bond, the behavior of the line-width transition could only be observed on the low temperature side, limited by its melting point of 135°C. The exchange rates derived from these observations, by the procedure described in a previous report,[7b)] are shown in Fig. 2. These observations are not sufficient for the accurate determination of the potential barriers. However, assuming a frequency factor of 10^{13}, the order of magnitude often found in the case of hydration water, the barrier height is 12.5 kcal. and 16.1 kcal./mol. for the motion about C=O and for that about C–N respectively. Or, assuming frequency factor of $10^{11.1}$, which best fits the C=O reorientation data, 9.8 and 13.0 kcal./mol. are obtained for the two motions. Therefore, a reasonable estimate would be 11 ± 2 kcal./mol. for the motion about the C=O bond and 15 ± 3 kcal./mol. for that about the C–N bond.

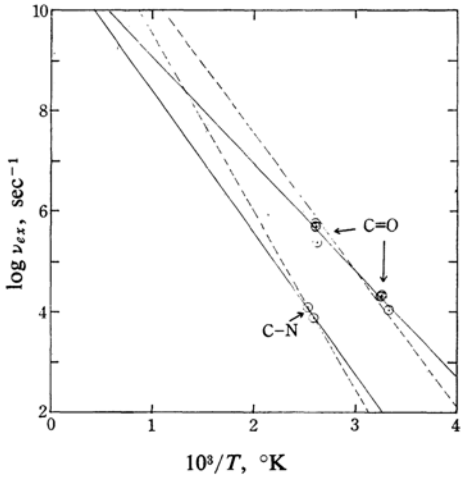

Fig. 2. Observed exchange rate with temperature, for reorientation about the C=O bond and that about the C–N bond. Solid lines are drawn assuming a frequency factor of $10^{11.1}$/sec. and broken line assuming that of 10^{13}/sec.

The temperature dependence of the splitting frequency is examined for line A at $\theta=0°$ and for line D (or E) at $\theta=90°$. The splitting frequency decreases about 3.5 kc. from 0°C to 100°C in the former case and about 2.5 kc. in the latter. *eqQ* has also been determined for D_2 at 117°C, as is listed in Table I. The line structure due to dipolar coupling with the directly-bonded nitrogen atom is observable in some orientations. The three-line structure at $\theta=0°$ of line A or at $\theta=90°$ of line D, which are actually more complicated with the D–D coupling and possibly also with H–D coupling from incomplete deuteration, are observed. The structure becomes obscured at about 70—80°C and coalesces to a broad single peak at about 100°C.

Discussion

The *eqQ*'s of D_1 and D_2 are almost identical, and they are close to that of ND_3 (200 kc.).[10] The q_{II} direction (see footnote to Table I) is perpendicular to the ND_2 plane in accord with the rule observed in the XOD bond.[11] $eQ(q_{III}-q_{II})$ is about 30 kc., a similar magnitude to those found in the OD bond.[11] The direction of the q_I of the D_1 deviates 1° from the N–D direction. The direction of the q_I of the D_2 is found to be along the c axis, whereas the N–D direction determined by neutron diffraction deviates 3.4° from the c axis (Fig. 3). If the q_I direction of the D_2 deviates only slightly from the c axis, the reorientational motion about the C=O bond of even a relatively slow exchange rate can average out the frequency splitting, resulting in an averaged q_I along the c axis. To see if this is the case, an observation of the pattern at −20°C is made of lines A and C, where, judging from Fig. 2, the exchange rate must be about 10^3/sec. or less. No additional splitting in these lines is found. Therefore, it may be concluded that the q_I of D_2 is indeed along the c axis within the limit of 1°.

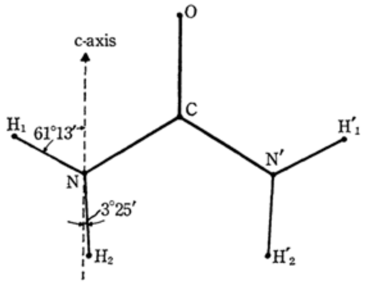

Fig. 3. Molecular structure of urea in the crystal (Ref. 1).

The reorientational motion about the C=O bond, as concluded from the temperature dependence of the line shape, is in agreement with the conclusion of the PMR study by Emsley and Smith. The estimated barrier height though not very accurate for the reason stated earlier, is in fair agreement with that estimated from the PMR, that is, 9 kcal.[6] If one urea molecule rotates 90° about the C=O bond, with all the neighboring molecules fixed, the closest-neighbor H–H distance will be 1.5 Å (H_1, H_2') or 1.8 Å (H_2, H_2') which is much less than the van der Waals' distance. Therefore, the motion is considered to be some sort of a correlated one which gears in neighboring molecucles as one molecule rotates. Since no phase transitions of the urea crystal in the temperature range of present interest has been reported, such correlated motion would involve a small number of molecules instead of the crystal as a whole. The potential barrier may be considered to be a sum of the hydrogen bond energy of N–D···O and the steric energy. The barrier arising from the hydrogen bond energy may not be greater than a few kcal., and the main origin of potential must be due to the steric effect. Therefore, we can expect a flatness of the potential at the bottom. We can also expect that the potential is somewhat dependent on the temperature, since the expansion of the lattice with the temperature is rather large.[3] The barrier of about 15 kcal./mol. to the motion about the C–N bond is mainly due to the partial double-bond character of the C–N bond. It should be noted that the present value is in fair agreement with the value of 12.24 kcal./mol. calculated by Das.[12]

The decrease in the splitting frequency from 0°C to 100°C for line D at $\theta=90°$ due to a simple torsional oscillation about the C=O bond, assuming that the potential curve $V=(V_0/2)\cdot(1-\cos 2\varphi)$, where φ is the angle of the rotation of the molecule, with $V_0=11$ kcal./mol., is calculated to be 1.7 kc., which is in fair agreement with the observed decrease of 2.5 kc. The r. m. s. amplitude of oscillation about the C=O bond obtained by Caron and Donohue is 13.13°,[4] which, by harmonic oscillation approximation gives 3.3 kc. for this frequency decrease, or corresponds to a V_0 value of 5.8 kcal. for the $\cos 2\varphi$ type potential. Such an apparent low V_0 value seems to indicate the flatness of the potential curve at the bottom, as has been mentioned earlier The torsional oscillation about the C=O bond would not give the temperature dependence of the frequency of line A at $\theta=0°$. On the other hand,

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[10] G. Herrmann, *J. Chem. Phys.*, **29**, 875 (1958).
[11] T. Chiba, ibid., **41**, 1352 (1964).
[12] T. P. Das, ibid., **35**, 1897 (1961).

that about the C–N bond can give rise to this frequency change, assuming that the V_0 of 15 kcal./mol. amounts to only 0.7 kc. from 0°C to 100°C. Caron and Donohue obtained a mean amplitude for the oscillation about the axis parallel to N–N′ of 6.08°, which can give rise to 0.9 kc. for the corresponding frequency decrease. Therefore, these effects can explain only half of the observed value of 3.5 kc. The reason for this is not clear.

The collapse of the line structure due to the dipolar coupling between N and D at 70—80°C is consistent with the PMR findings,$^{6)}$ that is, at temperatures above the line-width transition the proton second moment indicates no coupling between N and H. The temperature at which N–D coupling disappears is considerably higher than the temperature at which the ^{14}N pure quadrupole line disappears.$^{13)}$ A similar situation in PMR has been already pointed out and discussed by Emsley and Smith, who presented some mechanisms which possibly account for the situation. The vanishing of the ^{14}N line at about 22°C is likely to be associated with the reorientation about the C=O bond, as these authors point out. The effect on the ^{14}N PQR frequency of this motion can be estimated as follows. The direction of the field gradient tensor at N in urea are not known, but we can reasonably assume that the q_{I} is perpendicular to the molecular plane and that the q_{II} is along the C–N bond. The reorientation about the C=O bond does not change the q_{I} provided that the time during the flip is sufficiently short. However, this motion changes the q_{II} and q_{III} directions, and η decreases from the 0.32$^{14)}$ of the stationary molecule to 0.16 in the limit of rapid reorientation. The corresponding change in PQR frequency will be 0.14 Mc. This is of the same order with the corresponding frequency change in the D resonance line due to this motion. The difficulty lies in determining why the ^{14}N line should vanish at a temperature more than 10°C below that where the D resonance line vanishes. It is clear this is not due to a T_1 broadening of ^{14}N because N–D coupling is observable at higher temperatures. The reason is not well understood. However, it can be said that since the absolute magnitude of ^{14}N quadrupole coupling is much larger (3.5 Mc.)$^{14)}$ than that of D, the fluctuation of the field gradient due to the motion may be more effective in broadening the ^{14}N line.

Summary

A deuteron magnetic resonance study has been made on a single crystal of urea-d_4. At room temperature deuteron quadrupole coupling corresponding to a stationary molecule is obtained. The eqQ and η values determined are: $eqQ/h=210.8\pm1.0$ kc./sec. and $\eta=0.139\pm0.010$ for D_1, and $eqQ/h=210.7\pm1.0$ kc./sec. and $\eta=0.146\pm0.010$ for D_2 at room temperature, and $eqQ/h=206.3\pm1.2$ kc./sec., $\eta=0.138\pm0.010$ for D_2 at 117°C. In both cases the maximum field gradient component and the N–H direction are in good agreement.

The onset of reorientational motion about the C=O bond of a whole molecule has been concluded from the line-width change at high temperatures. Above 110°C the effect on the line-width of the reorientation about C–N bond has also been observed. The barrier heights for these motions are estimated to be 11 ± 2 kcal./mol. for the reorientation about the C=O bond and 15 ± 3 kcal./mol. for that about the C–N bond. The temperature dependence of the quadrupole splitting and that of the dipole coupling between ^{14}N and D have been observed and dicussed in relation to the motion of the urea molecule.

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13) T. Chiba, M. Toyama and Y. Morino, *J. Phys. Soc. Japan*, **14**, 379 (1959).

14) M. Minematsu, ibid, **14**, 1030 (1959).