BAUR, W. H. (1978). *Acta Cryst.* B34, 1751–1756.

BONNER, O. D. & JORDAN, C. F. (1975). *Spectrochim. Acta Part A*, 32, 1243–1246.

*Gmelins Handbuch der Anorganischen Chemie* 53 (1974). Berlin: Verlag Chemie.

HAAS, D. J., HARRIS, D. R. & MILLS, H. H. (1965). *Acta Cryst.* 19, 676–679.

HEDMANN, B. (1978). *Acta Chem. Scand. Ser. A*, 32, 439–446.

*Inorganic Syntheses* (1939). Vol. I. New York, London: McGraw-Hill.

*International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press.

JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.

SAKURAI, T. (1967). *The Universal Crystallographic Computation Program System.* Crystallographic Society of Japan.

SCHRÖDER, F. A. (1975). *Acta Cryst.* B31, 2294–2309.

SMITH, P. M. (1971). PhD Thesis, Georgetown Univ., USA.

STRANDBERG, R. (1974). *Acta Chem. Scand. Ser. A*, 28, 217–225.

STRANDBERG, R. (1975). *Acta Chem. Scand. Ser. A*, 29, 359–364.

STRICKLAND, J. D. H. (1952). *J. Am. Chem. Soc.* 74, 862–867.

TRUESDALE, V. W. & SMITH, C. J. (1975). *Analyst (London)*, 100, 203–212.

# A Neutron Diffraction Study of the Effect of Deuteration in Bis(3-amino-3-methyl-2-butanone oximato)nickel(II) Chloride Monohydrate

By BENNETT HSU AND E. O. SCHLEMPER

*Department of Chemistry, University of Missouri, Columbia, Missouri 65211, USA*

AND C. K. FAIR

*Department of Chemistry, Randolph-Macon Woman's College, Lynchburg, Virginia, USA*

## Abstract

$[Ni(C_5H_9D_2N_2O)_2D]^+Cl^-.D_2O$, $C_{10}H_{18}D_5N_4NiO_2^+$. $Cl^-.D_2O$, monoclinic, $P2_1$, $a = 11\cdot033$ (4), $b = 12\cdot940$ (5), $c = 5\cdot862$ (2) Å, $\beta = 101\cdot97$ (1)°, $Z = 2$, $\rho_{obs} = 1\cdot42$ (1), $\rho_{calc} = 1\cdot424$ (2) Mg m$^{-3}$. The structure was solved directly from neutron data. The effects of deuteration on the short hydrogen bond $[O\cdots O = 2\cdot439$ (8) Å] are examined by comparison with the corresponding normal hydrogen compound which crystallizes in $P2_1/c$. The bond is much more asymmetric with O—D = $1\cdot058$ (9) and D$\cdots$O = $1\cdot391$ (10) Å compared to O—H = $1\cdot187$ (5) and H$\cdots$O = $1\cdot242$ (5) Å. All water and amine deuterons are involved in hydrogen bonds with the chloride ion, the water molecule, or one of the oxime O atoms. The Ni—N(oxime) $[1\cdot860$ (9) Å] and Ni—N(amine) $[1\cdot896$ (1) Å] distances are slightly shorter than those in the normal hydrogen form. Distances within the ligand are equivalent within experimental error to those in the normal hydrogen form.

## Introduction

The effect of deuteration on short symmetry-free hydrogen bonds has not been extensively studied, and the effect of deuteration is expected to yield significant information concerning the nature of the potential well describing the hydrogen position in various types of hydrogen bonds (*e.g.* Singh & Wood, 1969). An especially notable study of a short symmetry-free hydrogen bond has been carried out by Takusagawa & Koetzle (1979) on quinolinic acid at four temperatures. In that study the deuterium atom was found to shift slightly closer (~0·02 Å) to one O atom at all temperatures, and no significant change in the O$\cdots$O distance was observed on deuteration at any of the temperatures from 35 K to 298 K. Similar effects were observed at room temperature for imidazolium hydrogen maleate (Hussain, Schlemper & Fair, 1980).

Bis(3-amino-3-methyl-2-butanone oximato)nickel(II) chloride monohydrate {[Ni(ao)$_2$–H]$^+$Cl$^-$.H$_2$O} has a symmetry-free O$\cdots$O hydrogen bond [2·420 (3) Å]

with a slightly asymmetric hydrogen position [O–H = 1·187 (5) and 1·242 (5) Å] (Schlemper, Hamilton & LaPlaca, 1971). Deuteration by recrystallization from D$_2$O was found to give a change of crystal structure. The present study reports our neutron diffraction results on this deuterated form and a comparison with the normal hydrogen form.

## Experimental

The crystal was obtained by isotopic exchange of the normal hydrogen form (Murmann, 1957) in D$_2$O. The amine, water, and hydrogen-bond H atoms undergo rapid exchange with the D$_2$O deuterium atoms. The material was dissolved and reprecipitated from three separate samples of D$_2$O to ensure complete exchange of those hydrogens. The completeness was checked by proton NMR spectroscopy. Slow evaporation from D$_2$O yielded the crystal used for data collection which had approximate dimensions 2·8 × 3·1 × 5·7 mm.

The neutron data were collected at the University of Missouri Research Reactor on a PDP 11/40 computer-controlled Mitsubishi Diffractometer equipped with a full circle. The data ($2\theta = 0$–92°) were collected by the $\theta$–$2\theta$ step-scan technique. The 1·109 (3) Å wavelength was calibrated using ethylenediamine D-tartrate and the reported cell dimensions (Pérez, 1976). 3851 reflection intensities were measured and corrected for background and Lorentz effects with a local program. An analytical absorption correction was applied ($\mu = 0·183$ mm$^{-1}$ and transmission-factor range = 0·55–0·72). Sorting and averaging reduced the data to 1905 reflections of which the 1740 with $F_o^2 \geq 2·0\sigma(F_o^2)$ were used in the solution and refinement of the structure [$\sigma^2(F_o^2) = \sigma^2$(counting) + $(0·035F_o^2)^2$].

The structure was solved using *MULTAN* and Fourier methods and refined by full-matrix least-squares methods minimizing $\sum w(F_o^2 - kF_c^2)$ where $w = 1/\sigma^2(F_o^2)$. For the final refinement, the 397 variables included positional and anisotropic thermal parameters for all 44 independent atoms as well as a scale factor and an isotropic secondary-extinction parameter [$g = 1·75 (9) \times 10^{-4}$] (Zachariasen, 1967). The final agreement factors were $R_w(F_o^2) = [\sum w(F_o^2 - kF_c^2)^2/ \sum F_o^4]^{1/2} = 0·105$ and $R(F_o^2) = \sum |F_o^2 - F_c^2|/\sum F_o^2 = 0·081$ and the final value of the standard deviation of an observation of unit weight was 1·98. Neutron atomic scattering factors were H −3·74, D 6·67, O 5·8, C 6·6, N 9·4, Ni 10·3, and Cl 9·6 fm. A separate refinement of the scattering factors for the deuterium atoms and the scale factor gave 6·61 (6) fm for the deuterium atoms attached to the amine nitrogens, 6·34 (8) fm for the water deuterium atoms, and 6·44 (8) fm for the short hydrogen-bond deuterium. The agreement factors were $R_w(F_o^2) = 0·103$ and

Table 1. *Positional parameters for* [Ni(ao)$_2$–D]Cl.D$_2$O

Standard deviations are given in parentheses in this table and other portions of the paper.

|        | $x$         | $y$         | $z$          |
|--------|-------------|-------------|--------------|
| Ni     | 0·6997 (2)  | 0·2365 (1)  | 0·2934 (3)   |
| Cl     | 0·8491 (3)  | 0·4023 (3)  | 0·8248 (4)   |
| N(1)   | 0·7808 (3)  | 0·1250 (2)  | 0·4620 (4)   |
| N(2)   | 0·5394 (2)  | 0·1878 (3)  | 0·2633 (4)   |
| N(3)   | 0·8637 (2)  | 0·2874 (2)  | 0·3262 (4)   |
| N(4)   | 0·6237 (2)  | 0·3498 (2)  | 0·1142 (4)   |
| C(1)   | 0·8985 (4)  | 0·1177 (3)  | 0·4853 (6)   |
| C(2)   | 0·4511 (3)  | 0·2369 (4)  | 0·1247 (6)   |
| C(3)   | 0·9563 (3)  | 0·2018 (3)  | 0·3654 (6)   |
| C(4)   | 0·4910 (4)  | 0·3309 (4)  | 0·0068 (6)   |
| C(5)   | 0·9729 (5)  | 0·0291 (4)  | 0·6017 (8)   |
| C(6)   | 0·3212 (5)  | 0·1994 (6)  | 0·0829 (11)  |
| C(7)   | 1·0786 (4)  | 0·2398 (4)  | 0·5115 (9)   |
| C(8)   | 0·9735 (5)  | 0·1620 (4)  | 0·1305 (7)   |
| C(9)   | 0·4138 (5)  | 0·4250 (5)  | 0·0441 (11)  |
| C(10)  | 0·4786 (6)  | 0·3105 (6)  | −0·2501 (7)  |
| O(1)   | 0·7231 (6)  | 0·0494·(4)  | 0·5555 (11)  |
| O(2)   | 0·5134 (5)  | 0·1034 (4)  | 0·3742 (9)   |
| W      | 0·3213 (6)  | 0·0276 (5)  | 0·5762 (10)  |
| D1(N3) | 0·8764 (4)  | 0·3324 (4)  | 0·1894 (7)   |
| D2(N3) | 0·8755 (4)  | 0·3332 (3)  | 0·4740 (7)   |
| D1(N4) | 0·6729 (4)  | 0·3689 (4)  | −0·0093 (8)  |
| D2(N4) | 0·6310 (4)  | 0·4136 (4)  | 0·2230 (7)   |
| D(OO)  | 0·6289 (8)  | 0·0680 (5)  | 0·4894 (14)  |
| D1($W$)| 0·3856 (7)  | 0·0618 (5)  | 0·5065 (12)  |
| D2($W$)| 0·2688 (7)  | −0·0045 (6) | 0·4418 (12)  |
| H1(C5) | 0·9259 (17) | −0·0146 (13)| 0·7054 (36)  |
| H2(C5) | 1·0471 (23) | 0·0518 (14) | 0·7216 (40)  |
| H3(C5) | 0·9977 (25) | −0·0163 (14)| 0·4809 (28)  |
| H1(C6) | 0·2634 (14) | 0·2428 (19) | −0·0386 (38) |
| H2(C6) | 0·3140 (18) | 0·1261 (18) | 0·0171 (53)  |
| H3(C6) | 0·2909 (12) | 0·1953 (22) | 0·2318 (34)  |
| H1(C7) | 1·1461 (10) | 0·1763 (10) | 0·5379 (25)  |
| H2(C7) | 1·0685 (11) | 0·2680 (10) | 0·6762 (19)  |
| H3(C7) | 1·1166 (10) | 0·3012 (9)  | 0·4177 (23)  |
| H1(C8) | 0·8853 (13) | 0·1402 (11) | 0·0200 (18)  |
| H2(C8) | 1·0319 (13) | 0·0952 (9)  | 0·1529 (19)  |
| H3(C8) | 1·0123 (14) | 0·2216 (10) | 0·0405 (20)  |
| H1(C9) | 0·4179 (14) | 0·4390 (11) | 0·2209 (26)  |
| H2(C9) | 0·3205 (13) | 0·4156 (13) | −0·0430 (31) |
| H3(C9) | 0·4499 (13) | 0·4922 (10) | −0·0260 (26) |
| H1(C10)| 0·5370 (19) | 0·2439 (13) | −0·2806 (23) |
| H2(C10)| 0·5120 (16) | 0·3769 (13) | 0·6638 (19)  |
| H3(C10)| 0·3896 (14) | 0·2883 (19) | −0·3367 (20) |

$R(F_o^2) = 0·080$, and the standard deviation of an observation of unit weight was reduced to 1·72.

The positional parameters from the last cycle of refinement are given in Table 1.*

---

\* Lists of calculated neutron structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35102 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

## Results and discussion

The crystal structure consists of discrete mononuclear square-planar $Ni^{II}$ complex cations, chloride ions, and water molecules of hydration. These are associated by hydrogen-bond interactions as shown in Fig. 1 and described in detail in Table 2. This interionic/intermolecular hydrogen-bonding network is quite different
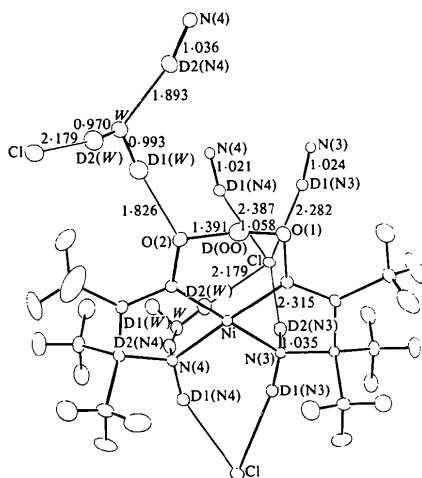


Fig. 1. The interionic/intermolecular hydrogen-bonding network in $[Ni(ao)_2-D]Cl.D_2O$. Distances are in Å.

from that in the normal hydrogen form. In that case, the oxime O atoms are not involved in any hydrogen bonds with water molcules while in this complex there is a very significant hydrogen bond between the water molecule and the oxime O(2) atom involving deuterium atom $D1(W)$. In the normal hydrogen form the water H atoms only form hydrogen bonds with the chloride ions, and a one-dimensional chain of hydrogen bonds involving the waters and chlorides traverses the crystal with the amine H atoms interacting with both the chloride ion and the water O atom. In contrast to the five hydrogen bonds to the chloride atoms (3 amine hydrogens from one cation and 2 water hydrogens) in that structure, the present structure has only four hydrogen bonds to the chloride (range of D—Cl—D angles $= 60.5-146.5°$) with the second water H atom bonded instead to an oxime O atom. This latter hydrogen bond is associated with the shift of the deuterium atom in the intramolecular hydrogen bond toward the other oxime O and the resulting much more asymmetric short hydrogen bond in this structure. The cause and effect relationship is, of course, not established. It is tempting, however, to attribute the change in crystal structure on deuteration to the more asymmetric short hydrogen bond which makes O(2) a better acceptor for the intermolecular hydrogen bond with water, resulting in an entirely different hydrogen-bonding scheme. The loss of symmetry on going from $P2_1/c$ to $P2_1$ upon deuteration is accompanied by a 1% increase in molar volume.

Bond distances are given in Table 3 and compared with those in the normal hydrogen form; bond angles are presented in Table 4. Other than the intramolecular O···O hydrogen-bond parameters, the most significant differences in bond distances are for the Ni—N(amine) distances which are about 0.01 Å shorter in the deuterated compound. This effect is undoubtedly related to the deuteration of those nitrogens. The uncorrected C—H distances show a range consistent

Table 2. *Intermolecular hydrogen-bond parameters*

| $X-D\cdots Y$ | $X-D$ (Å) | $D\cdots Y$ (Å) | $X-D\cdots Y$ (°) | $X\cdots Y$ (Å) |
|---|---|---|---|---|
| $W-D1(W)\cdots O(2)$ | 0.993 (8) | 1.826 (8) | 170.7 (7) | 2.810 (8) |
| $W-D2(W)\cdots Cl$ | 0.970 (8) | 2.179 (8) | 171.0 (6) | 3.200 (7) |
| $N(3)-D1(N3)\cdots Cl$ | 1.024 (4) | 2.282 (4) | 161.1 (4) | 3.268 (4) |
| $N(3)-D2(N3)\cdots Cl$ | 1.035 (4) | 2.315 (5) | 161.3 (4) | 3.312 (4) |
| $N(4)-D1(N4)\cdots Cl$ | 1.021 (5) | 2.387 (5) | 158.4 (4) | 3.358 (4) |
| $N(4)-D2(N4)\cdots W$ | 1.036 (5) | 1.893 (7) | 168.6 (4) | 2.916 (6) |

Table 3. *Bond distances in normal and deuterated* $[Ni(ao)_2-H]^+Cl^-$ (Å)

| | Deuterated | Normal* | | Deuterated | Normal* | | Deuterated | Normal* |
|---|---|---|---|---|---|---|---|---|
| Ni—N(1) | 1.869 (3) | 1.869 (1) | C(4)—C(10) | 1.507 (5) | 1.522 (2) | C(7)—H2(C7) | 1.060 (14) | 1.068 (5) |
| Ni—N(2) | 1.852 (3) | 1.862 (1) | O(1)—O(2) | 2.439 (8) | 2.420 (3) | C(7)—H3(C7) | 1.098 (13) | 1.086 (4) |
| Ni—N(3) | 1.896 (3) | 1.907 (1) | N(3)—H1(N3) | 1.024 (4) | 1.014 (5) | C(8)—H1(C8) | 1.088 (15) | 1.080 (5) |
| Ni—N(4) | 1.895 (3) | 1.909 (1) | N(3)—H2(N3) | 1.035 (4) | 1.023 (5) | C(8)—H2(C8) | 1.069 (11) | 1.085 (5) |
| N(1)—O(1) | 1.345 (5) | 1.346 (2) | N(4)—H1(N4) | 1.021 (5) | 1.025 (5) | C(8)—H3(C8) | 1.073 (12) | 1.091 (4) |
| N(2)—O(2) | 1.332 (5) | 1.335 (2) | N(4)—H2(N4) | 1.036 (5) | 1.032 (5) | C(9)—H1(C9) | 1.044 (16) | 1.070 (5) |
| N(1)—C(1) | 1.280 (5) | 1.287 (2) | N(3)—C(3) | 1.492 (4) | 1.491 (2) | C(9)—H2(C9) | 1.058 (17) | 1.084 (5) |
| N(2)—C(2) | 1.298 (5) | 1.290 (5) | N(4)—C(4) | 1.489 (5) | 1.494 (2) | C(9)—H3(C9) | 1.073 (16) | 1.089 (4) |
| C(1)—C(3) | 1.507 (5) | 1.509 (2) | C(5)—H1(C5) | 1.044 (13) | 0.930 (9) | C(10)—H1(C10) | 1.112 (19) | 1.080 (5) |
| C(2)—C(4) | 1.509 (5) | 1.516 (2) | C(5)—H2(C5) | 1.006 (23) | 0.962 (8) | C(10)—H2(C10) | 1.098 (14) | 1.074 (5) |
| C(1)—C(5) | 1.492 (5) | 1.495 (2) | C(5)—H3(C5) | 1.001 (14) | 0.996 (7) | C(10)—H3(C10) | 1.048 (15) | 1.075 (5) |
| C(2)—C(6) | 1.485 (6) | 1.486 (2) | C(6)—H1(C6) | 1.020 (17) | 1.038 (6) | $W$—H1($W$) | 0.993 (8) | 0.964 (7) |
| C(3)—C(7) | 1.522 (6) | 1.535 (2) | C(6)—H2(C6) | 1.021 (21) | 1.045 (6) | $W$—H2($W$) | 0.970 (8) | 0.935 (8) |
| C(3)—C(8) | 1.519 (5) | 1.517 (2) | C(6)—H3(C6) | 0.999 (21) | 1.064 (5) | O(1)—H(OO) | 1.058 (9) | 1.187 (5) |
| C(4)—C(9) | 1.527 (7) | 1.528 (2) | C(7)—H1(C7) | 1.098 (11) | 1.085 (5) | O(2)—H(OO) | 1.391 (10) | 1.242 (5) |

\* Schlemper, Hamilton & LaPlaca (1971). The atom-labeling system has been changed to agree with that of the present study.

Fig. 2. The atom-labeling scheme for [Ni(ao)₂–D]Cl.D₂O.

with the normal hydrogen form. The methyl groups attached to the $sp^2$ ring carbon again show the greatest thermal motion and have the shorter average C—H distance [1·015 (13) compared with 1·076 (19) Å for the other four methyl groups]. (Average deviations from the mean are given for these and other average distances.) After thermal-motion correction using the same rigid-body approach (Schomaker & Trueblood, 1968) as for the normal hydrogen form, the average values are 1·122 (10) and 1·103 (5) Å, respectively, which are in excellent agreement with the corresponding values of 1·120 (12) and 1·108 (5) Å in the previous study. Details of this correction, along with

## Table 4. *Bond angles in normal and deuterated* [Ni(ao)₂–H]⁺Cl⁻ (°)

| | Deuterated | Normal | | Deuterated | Normal | | Deuterated | Normal |
|---|---|---|---|---|---|---|---|---|
| N(1)–Ni–N(2) | 97·4 (1) | 97·34 (6) | C(9)–C(4)–C(10) | 110·2 (4) | 110·6 (1) | C(3)–C(7)–H2(C7) | 112·0 (7) | 111·3 (3) |
| N(1)–Ni–N(3) | 82·7 (1) | 82·93 (6) | Ni–N(3)–C(3) | 111·5 (2) | 111·0 (1) | C(3)–C(7)–H3(C7) | 109·8 (7) | 111·1 (3) |
| N(2)–Ni–N(4) | 84·6 (1) | 83·20 (6) | Ni–N(3)–D1(N3) | 113·6 (3) | 114·8 (2) | H1(C7)–C(7)–H2(C7) | 109 (1) | 108·0 (4) |
| N(3)–Ni–N(4) | 95·2 (1) | 96·53 (6) | Ni–N(3)–D2(N3) | 103·6 (3) | 103·5 (2) | H1(C7)–C(7)–H3(C7) | 107 (1) | 107·4 (4) |
| Ni–N(1)–O(1) | 124·2 (1) | 122·6 (1) | C(3)–N(3)–D1(N3) | 110·0 (3) | 110·5 (3) | H2(C7)–C(7)–H3(C7) | 109 (1) | 108·9 (4) |
| Ni–N(1)–C(1) | 118·5 (2) | 118·2 (1) | C(3)–N(3)–D2(N3) | 109·4 (3) | 109·5 (3) | C(3)–C(8)–H1(C8) | 111·3 (7) | 110·8 (3) |
| C(1)–N(1)–O(1) | 117·3 (4) | 119·2 (1) | D1(N3)–N(3)–D2(N3) | 108·4 (4) | 107·2 (4) | C(3)–C(8)–H2(C8) | 110·4 (6) | 110·8 (3) |
| Ni–N(2)–O(2) | 122·0 (3) | 122·3 (1) | Ni–N(4)–D1(N4) | 110·0 (3) | 113·8 (2) | C(3)–C(8)–H3(C8) | 109·8 (7) | 109·9 (3) |
| Ni–N(2)–C(2) | 118·1 (2) | 118·3 (1) | Ni–N(4)–D2(N4) | 107·8 (3) | 105·4 (2) | H1(C8)–C(8)–H2(C8) | 108 (1) | 108·4 (4) |
| C(2)–N(2)–O(2) | 119·8 (3) | 119·4 (1) | Ni–N(4)–C(4) | 113·0 (2) | 111·0 (1) | H1(C8)–C(8)–H3(C8) | 107 (1) | 108·2 (4) |
| N(1)–C(1)–C(3) | 114·5 (3) | 114·5 (1) | C(4)–N(4)–D1(N4) | 111·1 (3) | 110·6 (3) | H2(C8)–C(8)–H3(C8) | 110 (1) | 108·7 (4) |
| N(1)–C(1)–C(5) | 123·7 (3) | 122·8 (1) | C(4)–N(4)–D2(N4) | 109·6 (3) | 109·7 (3) | C(4)–C(9)–H1(C9) | 111·7 (9) | 111·7 (3) |
| C(3)–C(1)–C(5) | 121·5 (4) | 122·6 (1) | D1(N4)–N(4)–D2(N4) | 105·0 (4) | 106·0 (4) | C(4)–C(9)–H2(C9) | 111 (1) | 111·7 (3) |
| N(2)–C(2)–C(4) | 115·4 (3) | 114·6 (1) | C(1)–C(5)–H1(C5) | 113·0 (9) | 113·2 (4) | C(4)–C(9)–H3(C9) | 109·2 (9) | 109·6 (3) |
| N(2)–C(2)–C(6) | 121·1 (4) | 123·0 (1) | C(1)–C(5)–H2(C5) | 112·7 (9) | 112·7 (4) | H1(C9)–C(9)–H2(C9) | 110 (1) | 108·7 (4) |
| C(4)–C(2)–C(6) | 123·4 (4) | 122·3 (1) | C(1)–C(5)–H3(C5) | 109·5 (9) | 112·5 (4) | H1(C9)–C(9)–H3(C9) | 107 (1) | 107·8 (4) |
| C(1)–C(3)–N(3) | 105·4 (3) | 105·9 (1) | H1(C5)–C(5)–H2(C5) | 100 (2) | 101·3 (5) | H2(C9)–C(9)–H3(C9) | 108 (1) | 107·2 (4) |
| C(1)–C(3)–C(7) | 112·5 (3) | 112·8 (1) | H1(C5)–C(5)–H3(C5) | 110 (2) | 102·8 (5) | C(4)–C(10)–H1(C10) | 111·2 (8) | 111·3 (3) |
| C(1)–C(3)–C(8) | 108·8 (3) | 109·1 (1) | H2(C5)–C(5)–H3(C5) | 111 (2) | 113·3 (5) | C(4)–C(10)–H2(C10) | 110·7 (9) | 110·7 (3) |
| C(7)–C(3)–N(3) | 110·3 (3) | 109·9 (1) | C(2)–C(6)–H1(C6) | 112 (1) | 111·7 (4) | C(4)–C(10)–H3(C10) | 114·4 (9) | 111·4 (3) |
| C(7)–C(3)–C(8) | 110·9 (3) | 110·2 (1) | C(2)–C(6)–H2(C6) | 111 (1) | 111·4 (4) | H1(C10)–C(10)–H2(C10) | 106 (1) | 107·5 (4) |
| C(8)–C(3)–N(3) | 108·8 (3) | 109·0 (1) | C(2)–C(6)–H3(C6) | 111 (1) | 111·4 (4) | H1(C10)–C(10)–H3(C10) | 103 (2) | 106·0 (4) |
| C(2)–C(4)–N(4) | 107·0 (3) | 105·7 (1) | H1(C6)–C(6)–H2(C6) | 105 (2) | 105·6 (5) | H2(C10)–C(10)–H3(C10) | 111 (1) | 109·8 (4) |
| C(2)–C(4)–C(9) | 110·7 (3) | 111·9 (1) | H1(C6)–C(6)–H3(C6) | 111 (2) | 109·4 (5) | O(1)–D(OO)–O(2) | 169·7 (7) | 169·9 (3) |
| C(2)–C(4)–C(10) | 110·0 (4) | 109·7 (1) | H2(C6)–C(6)–H3(C6) | 105 (2) | 107·1 (5) | D(OO)–O(1)–N(1) | 101·4 (5) | 102·7 (3) |
| N(4)–C(4)–C(9) | 109·7 (4) | 110·1 (1) | C(3)–C(7)–H1(C7) | 109·5 (8) | 110·1 (3) | D(OO)–O(2)–N(2) | 103·8 (4) | 103·4 (3) |
| N(4)–C(4)–C(10) | 109·2 (3) | 108·7 (1) | | | | | | |

## Table 5. *Thermal-motion analysis for methyl groups*

| Methyl carbon[a] | $U'_{11}$ | $U'_{22}$[b] | $U'_{33}$ | $r_{C–H}$ (Å) | $\langle\theta\rangle$ (°) | $r_{C–H}/\cos\langle\theta\rangle$ | $\omega^d$ (mm⁻¹) | $V_o$ (kcal mol⁻¹; 1 kcal ≃ 4·2 kJ) |
|---|---|---|---|---|---|---|---|---|
| C(5)[c] | 9 (5) | 225 (45) | 22 (23) | 1·017 (18) | 25·0 | 1·122 | 9·6 | 0·58 |
| C(6)[c] | 10 (5) | 232 (30) | 30 (13) | 1·013 (10) | 25·4 | 1·122 | 9·5 | 0·57 |
| C(7) | 19 (1) | 12 (22) | −5 (10) | 1·085 (17) | 5·8 | 1·091 | 42·5 | 10·9 |
| C(8) | 7 (9) | 57 (11) | 12 (19) | 1·077 (8) | 12·5 | 1·103 | 19·3 | 2·30 |
| C(9) | 24 (5) | 49 (22) | 19 (3) | 1·058 (10) | 11·8 | 1·081 | 21·3 | 2·68 |
| C(10) | 15 (11) | 111 (25) | 34 (32) | 1·086 (25) | 17·1 | 1·136 | 13·4 | 1·18 |

(a) The $U'$ values are mean-square amplitudes $U_{\rm exp} - U_{\rm rigid\,body}$ (×10³ Å²). $r_{C–H}$ is the uncorrected bond length, $\theta$ is the r.m.s. amplitude of rotation calculated by tan $\langle\theta\rangle = (U_{22})^{1/2}/r_{C–H}$, $V_o$ is the barrier height obtained from $V_o = 0·0040T/U'_{22}n^2$ where $T = 295$ K (*i.e.* approximate room temperature).

(b) The natural axes are defined so that $U'_{22}$ is the hindered rotation, *i.e.* axis 1 is along the C—C bond, axis 3 is in the C—C—H plane, and axis 2 completes the orthogonal system.

(c) Methyl C atoms attached to $sp^2$ C atoms.

(d) $\omega(\text{mm}^{-1}) = 7·68n[V_o(\text{kcal mol}^{-1})/I(\text{a.m.u. Å}^2)]^{1/2}$ where $n = 3$, moment of inertia $I = \sum m_i r_i^2$; $m_{\rm H} = 1·008$ a.m.u., $r = r_{C–H}$ (corrected) × cos 19·5. For more details, see Schlemper, Hamilton & LaPlaca (1971).

calculated barrier heights and librational frequencies, are given in Table 5. These latter parameters are also in general agreement with the previous study. The average thermally uncorrected N—D distance [1·029 (7) Å] is very close to that of 1·024 (4) Å in the normal hydrogen form. A more pronounced lengthening upon deuteration (0·015 Å) was observed in imidazolium hydrogen maleate (Hussain, Schlemper & Fair, 1980). The average water O—D distance [0·981 (11) Å] is slightly longer than that of 0·950 (15) Å in the undeuterated form. This difference is more significant if one considers the individual distances (Table 3) which are not really chemically equivalent. (For the atom numbering, see Fig. 2.)

The most dramatic change in the molecular structure on deuteration involves the short $O\cdots O$ hydrogen bond. Deuteration increases the $O\cdots O$ distance slightly from 2·420 (3) to 2·439 (8) Å, with a concurrent major increase in asymmetry of the deuterium atom position. Whereas the two O—H distances in the normal hydrogen form [1·187 (5) and 1·242 (5) Å] are significantly different, this difference is much larger in the deuterated form with O(1)—D(OO) = 1·058 (9) and O(2)—D(OO) = 1·391 (10) Å. As mentioned earlier this major shift is accompanied by the formation of a hydrogen bond between O(2) and the water of hydration [O(2)$\cdots$D1($W$) = 1·826 (8) Å]. As a result, the bond summations (Brown & Shannon, 1973) remain essentially unchanged with the bond orders of O(1) = 2·041, O(2) = 2·133 and D(OO) = 0·991 compared with 2·089, 2·031 and 0·947, respectively, in the normal hydrogen form. The shift in the deuterium atom position of 0·13 Å toward O(1) is considerably larger than those in imidazolium hydrogen maleate (0·01 Å) (Hussain, Schlemper & Fair, 1980) and quinolinic acid (0·025 Å) (Takusagawa & Koetzle, 1979). In the latter compounds there is no significant change in the $O\cdots O$ distance or in the external environment of the short hydrogen bond on deuteration, probably indicative of a single-minimum potential function (Singh & Wood, 1969). The lengthening of the $O\cdots O$ distance in the present compound is accompanied by the formation of the external hydrogen bond with the water molecule and for that reason may

or may not be indicative of a double-minimum potential. Subtraction of rigid-body thermal-motion parameters from the individual atom ellipsoids results in difference ellipsoids for the hydrogen-bond atoms which support a broad single-minimum or a low-barrier double-minimum potential well. Whereas the O atoms have essentially no non-rigid-body motion, the deuterium atom shows a much larger, and highly significant, residual r.m.s. amplitude in the direction parallel to the bond than in the direction perpendicular to the bond, as was observed for the normal hydrogen form.

Although the isotope effect in the present study is somewhat clouded by the change in crystal structure on deuteration, the results are consistent with those in the limited number of previous neutron diffraction studies of deuteration effects on short symmetry-unrestricted hydrogen bonds (e.g. Takusagawa & Koetzle, 1979; Hussain, Schlemper & Fair, 1980). These studies have all shown an increased asymmetry in the deuterium position as compared to the hydrogen position and either no change in the $O\cdots O$ distance or a relatively small change as observed here.

### References

BROWN, I. D. & SHANNON, R. D. (1973). Acta Cryst. A29, 266–282.

HUSSAIN, M. S., SCHLEMPER, E. O. & FAIR, C. K. (1980). Acta Cryst. B36, 1104–1108.

MURMANN, R. K. (1957). J. Am. Chem. Soc. 79, 521–526.

PÉREZ, S. (1976). Acta Cryst. B32, 2064–2070.

SCHLEMPER, E. O., HAMILTON, W. C. & LAPLACA, S. J. (1971). J. Chem. Phys. 54, 3990–4000.

SCHOMAKER, V. & TRUEBLOOD, K. N. (1968). Acta Cryst. B24, 63–76.

SINGH, T. R. & WOOD, J. L. (1969). J. Chem. Phys. 50, 3572–3576.

TAKUSAGAWA, F. & KOETZLE, T. F. (1979). Acta Cryst. B35, 2126–2135.

ZACHARIASEN, W. H. (1967). Acta Cryst. 23, 558–564.