

Neutron Diffraction Study of Deuterated Imidazolium Hydrogen Maleate: An Evaluation of Isotope Effect on the Hydrogen-Bond Length

BY M. SAKHAWAT HUSSAIN 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 24503, USA

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Abstract

Neutron diffraction results for deuterated imidazolium hydrogen maleate are presented. The normal and deuterated forms are isostructural (space group $P2_1/c$, $Z = 4$) with unit-cell dimensions of the latter: $a = 10.858$ (1), $b = 5.525$ (1), $c = 14.631$ (2) Å and $\beta = 102.85$ (1)°. The O...O distance [2.399 (4) Å] remains unchanged when H is replaced by D whereas the D atom is displaced significantly further from the midpoint of the bond ($\Delta O-D = 0.028$ Å) than is the H atom ($\Delta O-H = 0.001$ Å). A potential function of the slightly asymmetric, single-minimum type, is suggested for the short intramolecular hydrogen bond in imidazolium hydrogen maleate.

Introduction

The crystal structures of normal and deuterated analogs of several compounds containing O...O hydrogen bonds have been studied to investigate the effect of deuteration (isotope effect) on the crystal structures and on the short O...O hydrogen bonds. For example, structures of both forms of $H_2SO_4 \cdot 4H_2O$ (Kjallman & Olovsson, 1972), $YH(C_2O_4)_2 \cdot 3H_2O$ (Johnson & Brunton, 1972; Kollman & Bender, 1973), $HCrO_2$ (Hamilton & Ibers, 1963) and $NaHC_2O_4 \cdot H_2O$ (Tellgren & Olovsson, 1971) are all known. However, in all these compounds some symmetry operates on the O...O bond causing the effect of isotopic substitution within the bond to be obscured. Isotope-effect studies on compounds having crystallographically unrestricted O...O hydrogen bonds have so far been limited to the crystal structures of $KHCO_3$ (X-ray) (Thomas, Tellgren & Olovsson, 1974), bis(3-amino-3-methyl-2-butanone oximate)-nickel(II) chloride monohydrate, $[Ni(ao-H)_2]Cl \cdot H_2O$, (neutron) (Hsu, Schlemper & Fair, 1980), quinolinic acid (neutron) (Takusagawa & Koetzle, 1978, 1979)

and $(COOH)_2 \cdot 2H_2O$ (Sabine, Cox & Craven, 1969; Coppens & Sabine, 1969).

The X-ray and neutron diffraction work on normal imidazolium hydrogen maleate, $[ImH]^+[HMal]^-$, has already been reported (Hsu & Schlemper, 1979; James & Matsushima, 1976). These studies have revealed an apparently symmetric, symmetry-unrestricted O...O hydrogen bond among the shortest known (O...O = 2.393 Å). The neutron diffraction results on deuterated imidazolium hydrogen maleate, $[ImD]^+[DMal]^-$, are reported here in order to evaluate the effects of deuterium substitution on the O...O hydrogen bond and on the overall crystal structure.

Experimental

Crystal preparation

Imidazolium hydrogen maleate was prepared as described by James & Matsushima (1976). The deuterated analog was obtained by drying the normal form at room temperature under vacuum for 3–4 h and then recrystallizing three times from warm D_2O . Each recrystallization was followed by drying under vacuum. Crystals suitable for neutron diffraction were obtained by slow evaporation of a D_2O solution of the deuterated material over anhydrous calcium chloride in a desiccator. The completeness of deuteration was verified by comparing the 1H NMR spectra of the normal and deuterated forms.

Cell parameters

The cell dimensions were obtained by a least-squares fit of the setting angles of 20 manually centered reflections on a Picker four-circle programmed diffractometer with $Mo K\alpha$ radiation, using a small crystal of the deuterated material of approximate dimensions $0.3 \times 0.3 \times 0.7$ mm. The monoclinic unit cell ($P2_1/c$, $Z = 4$) has the dimensions $a = 10.858$ (1), $b = 5.525$ (1),

$c = 14.631$ (2) Å, $\beta = 102.85$ (1)° and $V = 855.8$ Å³, which are significantly different from the cell parameters of the normal form (see below).

Neutron data collection and reduction

An irregular crystal having the same general morphology as the normal hydrogen form was sealed in a thin-walled quartz capillary to insure preservation of the level of deuteration. The single-crystal neutron diffraction data were measured on the PDP 11/03 computer-controlled Mitsubishi neutron diffractometer at the University of Missouri Research Reactor Facility. The crystal used had approximate dimensions $1.7 \times 1.9 \times 2.9$ mm. From eighteen automatically centered reflections, an orientation matrix was generated which was used to obtain the angle settings for measurement of the intensities of hkl , $\bar{h}kl$ and $h\bar{k}l$ reflections out to $2\theta = 90^\circ$ [$\lambda = 1.106$ Å and $(\sin \theta/\lambda)_{\max} = 0.639$ Å⁻¹]. The neutron wavelength was obtained using a Si ($a = 5.4308$ Å) crystal. The data were collected at 295 (2) K by the θ - 2θ step-scan technique with 0.07° 2θ steps and scan ranges of 36 to 42 steps. The diffracted neutrons were detected with a BF₃ detector; the steps were timed with a monitor counter in the direct beam. Two standard reflections were measured every 75 reflections. The combined intensities of the standard reflections showed a random variation of about 5%, but no significant trend was observed. Therefore, no correction for the variation was made. A set of F_o^2 values was obtained by applying Lorentz and absorption corrections ($\mu = 0.093$ mm⁻¹) based on the crystal faces: (001), (00 $\bar{1}$), (010), (0 $\bar{1}$ 0), (100), (302) and ($\bar{1}$ 02). The linear-absorption coefficient (μ) was calculated using absorption-cross-section (σ_a) values given in *International Tables for X-ray Crystallography* (1962). The absorption cross-section for the H atom was taken as 34.19 (10^{-28} m²) which includes a value of 34 (10^{-28} m²) for incoherent scattering of neutrons by the H atom. The transmission-coefficient range was 0.87 to 0.89. 2468 reflections were sorted to yield 1370 unique data, out of which 1120 having $I > 2.0\sigma(I)$ were used in subsequent calculations. The agreement factor ($\sum |F^2 - F_{av}^2| / \sum |F^2|$) was 0.087.

Structure refinement

The atomic coordinates from the neutron diffraction study of normal imidazolium hydrogen maleate (Hsu & Schlemper, 1979) were used as initial values for a full-matrix least-squares refinement minimizing $\sum w(F_o^2 - kF_c^2)^2$. Three cycles of isotropic refinement on 21 atoms (85 variables) converged to $R(F_o^2) = \sum (F_o^2 - kF_c^2) / \sum F_o^2 = 0.265$ and $R_w(F_o^2) = [\sum w(F_o^2 - kF_c^2)^2 / \sum wF_o^4]^{1/2} = 0.323$, where $w = 1/(\sigma_{\text{counting}}^2 + 0.035F_o^2)$. The neutron scattering amplitudes were N (9.40), C

Table 1. *Positional parameters for [ImD]⁺[DMal]⁻*

Numbers in parentheses, in this table and elsewhere, represent estimated standard deviations.

	<i>x</i>	<i>y</i>	<i>z</i>
N(1)	0.3971 (2)	0.1524 (4)	0.0706 (2)
C(2)	0.3145 (2)	0.9977 (6)	0.0915 (2)
N(3)	0.3768 (2)	0.8334 (4)	0.1493 (1)
C(4)	0.5033 (2)	0.8813 (6)	0.1653 (2)
C(5)	0.5164 (3)	0.0851 (6)	0.1163 (2)
C(6)	0.1213 (2)	0.5034 (6)	0.1590 (2)
C(7)	0.0240 (2)	0.3138 (6)	0.1607 (2)
C(8)	-0.1004 (2)	0.3109 (6)	0.1271 (2)
C(9)	-0.1836 (2)	0.5113 (6)	0.0751 (2)
O(1)	0.2310 (3)	0.4607 (8)	0.1977 (3)
O(2)	0.0889 (3)	0.7053 (7)	0.1169 (3)
O(3)	-0.2972 (3)	0.4701 (8)	0.0511 (3)
O(4)	-0.1354 (3)	0.7122 (7)	0.0584 (3)
D(1)	0.3688 (4)	0.2972 (9)	0.0250 (3)
D(3)	0.3308 (3)	-0.3121 (8)	0.1741 (3)
D(10)	-0.0216 (4)	0.7114 (9)	0.0854 (4)
H(2)	0.2136 (5)	0.0049 (17)	0.0645 (6)
H(4)	0.5729 (6)	-0.2277 (17)	0.2069 (6)
H(5)	0.5977 (6)	0.1885 (18)	0.1094 (5)
H(7)	0.0652 (6)	0.1509 (15)	0.1952 (6)
H(8)	-0.1527 (6)	0.1570 (14)	0.1358 (6)

(6.626), O (5.75), H (-3.723) and D (6.67), all in fm. Several more cycles of anisotropic least-squares refinement with 194 variables, including an isotropic extinction parameter and a scale factor, converged to the final values of 0.072 for $R(F_o^2)$ and 0.110 for $R_w(F_o^2)$. The conventional R factor was 0.053. The standard deviation of an observation of unit weight was 1.43 and the value of the secondary-extinction parameter (Zachariasen, 1963) was 1.429×10^{-4} . Refinement of the deuterium scattering length indicated that about 5% H remains at these sites. A final difference Fourier synthesis of nuclear scattering density was virtually featureless. The shifts in all refined parameters on the last cycle were well below one-hundredth of their standard deviations.

Positional parameters along with their standard deviations are given in Table 1.*

Results and discussion

The normal and deuterated forms of imidazolium hydrogen maleate are isostructural and the general features of the latter are essentially as reported earlier (James & Matsushima, 1976; Hsu & Schlemper, 1979). The unit-cell dimensions of [ImD]⁺[DMal]⁻ are 0.003 (1), 0.007 (1) and 0.015 (3) Å longer for a , b

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34984 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

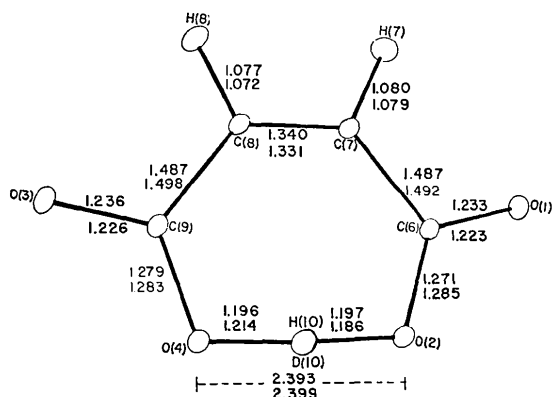


Fig. 1. Bond distances (Å) for the hydrogen maleate ion. Upper values give neutron results for the normal form and lower values are for the deuterated form. The numbering system is as used by previous workers (James & Matsushima, 1976; Hsu & Schlemper, 1979). Standard deviations for the normal form are ± 0.002 – 0.003 Å for nonhydrogen distances and ± 0.003 – 0.005 Å for distances involving H. For the deuterated form, standard deviations are ± 0.003 – 0.005 Å for nonhydrogen distances and ± 0.005 – 0.006 Å for distances involving H.

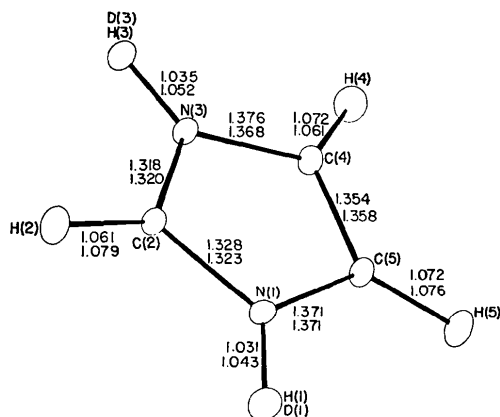


Fig. 2. Bond distances (Å) for the imidazolium ion. For details and e.s.d.'s see Fig. 1.

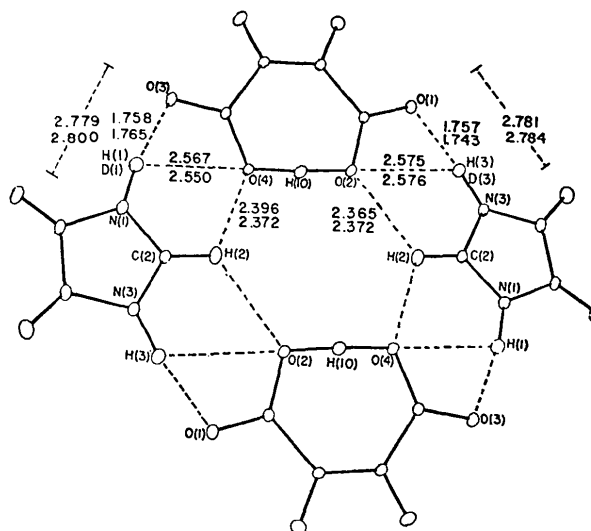


Fig. 3. Hydrogen-bond environment for $[\text{ImH}]^+[\text{HMal}]^-$ (upper values) and $[\text{ImD}]^+[\text{DMal}]^-$ (lower values). Standard deviations for the deuterated form are ± 0.004 – 0.005 Å for O–N distances and ± 0.005 – 0.008 Å for O–H distances. For the normal form standard deviations are ± 0.003 Å for O–N and ± 0.005 Å for distances involving hydrogen.

and c , respectively, compared with $[\text{ImH}]^+[\text{HMal}]^-$. The change in β is 0.02° and the volume increase is 2.3 \AA^3 . These discrepancies are significant particularly in the direction of the c axis. The neutron diffraction results for both forms are compared in Figs. 1 and 2 and in Table 2. As expected, significant differences are found in the N(1)–D(1) and N(3)–D(3) bonds. An average elongation of 0.015 (3) Å of the N–H bonds was observed as a result of replacement of H by D. Similar lengthenings were observed for the N–H bonds in quinolinic acid (Takusagawa & Koetzle, 1979) and $[\text{Ni}(\text{ao-D})_2]\text{Cl}\cdot\text{D}_2\text{O}$ (Hsu, Schlemper & Fair, 1980). The changes in the interionic distances O(1)···N(3) and O(3)···N(1) (Fig. 3) are insignificant, though changes in the O(1)···D(3) and O(3)···D(1) distances are probably significant when H is replaced by D.

Table 2. Bond angles ($^\circ$) in normal and deuterated imidazolium hydrogen maleate

	$[\text{ImH}]^+$ $[\text{HMal}]^-$	$[\text{ImD}]^+$ $[\text{DMal}]^-$	$[\text{ImH}]^+$ $[\text{HMal}]^-$	$[\text{ImD}]^+$ $[\text{DMal}]^-$	$[\text{ImH}]^+$ $[\text{HMal}]^-$	$[\text{ImD}]^+$ $[\text{DMal}]^-$		
D(1)–N(1)–C(2)	122.5 (3)	121.6 (3)	N(3)–C(4)–C(5)	106.8 (2)	106.8 (3)	C(7)–C(8)–H(8)	117.8 (3)	117.8 (5)
D(1)–N(1)–C(5)	129.0 (3)	129.2 (3)	H(5)–C(5)–C(4)	131.2 (4)	132.4 (6)	C(9)–C(8)–H(8)	112.1 (3)	112.1 (5)
C(2)–N(1)–C(5)	108.4 (2)	109.1 (3)	H(5)–C(5)–N(1)	121.7 (4)	121.1 (6)	O(3)–C(9)–O(4)	122.0 (2)	122.2 (3)
H(2)–C(2)–N(1)	125.4 (3)	125.2 (5)	C(4)–C(5)–N(1)	107.1 (2)	106.5 (2)	O(3)–C(9)–C(8)	118.0 (2)	117.8 (3)
H(2)–C(2)–N(3)	125.6 (3)	126.4 (5)	O(1)–C(6)–O(2)	122.1 (2)	121.6 (3)	O(4)–C(9)–C(8)	120.0 (2)	120.0 (2)
N(1)–C(2)–N(3)	109.0 (2)	108.4 (2)	O(1)–C(6)–C(7)	117.3 (2)	118.5 (3)	C(6)–O(2)–D(10)	111.1 (5)	110.9 (4)
D(3)–N(3)–C(2)	122.2 (3)	122.1 (3)	O(2)–C(6)–C(7)	120.6 (2)	119.9 (2)	C(9)–O(4)–D(10)	111.5 (3)	110.8 (4)
D(3)–N(3)–C(4)	129.1 (3)	128.7 (3)	C(6)–C(7)–C(8)	129.9 (2)	130.5 (3)	O(2)–D(10)–O(4)	176.8 (4)	177.3 (5)
C(2)–N(3)–C(4)	108.7 (2)	109.2 (2)	C(6)–C(7)–H(7)	112.3 (3)	111.8 (4)	N(1)–D(1)–O(3)	170.5 (4)	171.3 (4)
H(4)–C(4)–N(3)	122.6 (3)	123.1 (5)	C(8)–C(7)–H(7)	117.8 (3)	117.7 (4)	N(3)–D(3)–O(1)	169.3 (4)	169.2 (4)
H(4)–C(4)–C(5)	130.7 (3)	130.0 (5)	C(7)–C(8)–C(9)	130.1 (2)	130.1 (3)			

Table 3. Bond distances (Å) in normal and deuterated imidazolium hydrogen maleate after correction for thermal motion

	[ImH] ⁺ - [HMal] ⁻	[ImD] ⁺ - [DMal] ⁻		[ImH] ⁺ - [HMal] ⁻	[ImD] ⁺ - [DMal] ⁻		[ImH] ⁺ - [HMal] ⁻	[ImD] ⁺ - [DMal] ⁻
N(1)—C(2)	1.340	1.334	C(4)—C(5)	1.366	1.369	C(7)—H(7)	1.098	1.096
N(1)—C(5)	1.387	1.389	C(4)—H(4)	1.084	1.073	C(8)—C(9)	1.509	1.517
N(1)—H/D(1)	1.041	1.053	C(5)—H(5)	1.083	1.086	C(8)—H(8)	1.094	1.088
C(2)—N(3)	1.332	1.334	C(6)—C(7)	1.506	1.510	C(9)—O(3)	1.243	1.233
C(2)—H(2)	1.073	1.093	C(6)—O(1)	1.241	1.230	C(9)—O(4)	1.300	1.304
N(3)—H/D(3)	1.044	1.060	C(6)—O(2)	1.294	1.306	O(2)—H/D(10)	1.204	1.192
N(3)—C(4)	1.391	1.384	C(7)—C(8)	1.348	1.338	O(4)—H/D(10)	1.203	1.220

Table 4. Comparison of the symmetry-unrestricted O...O hydrogen-bond geometries at room temperature (Å and deg)

	O...O	Δ(O...O)	O—H(D)	Δ(O—H)	O...H(D)	∠O—H(D)...O	References
KHCO ₃	2.585 (2)	—	1.09 (3)	—	1.50 (3)	169.8 (5.7)	Thomas, Tellgren & Olovsson (1974)
KDCO ₃	2.607 (2)	0.022 (2)	0.95	0.14 (3)	1.66 (4)	170.6 (4.4)	Thomas, Tellgren & Olovsson (1974)
[Ni(ao-H) ₂]Cl·H ₂ O	2.420 (3)	—	1.187 (5)	—	1.242 (5)	169.9	Schlemper, Hamilton & LaPlaca (1971)
[Ni(ao-D) ₂]Cl·D ₂ O	2.439 (8)	0.019 (6)	1.058 (9)	0.129 (7)	1.391 (10)	169.7 (7)	Hsu, Schlemper & Fair (1980)
QNA-H	2.398 (3)	—	1.163 (5)	—	1.238 (5)	174.4 (4)	Takusugawa & Koetzle (1978)
QNA-D	2.393 (2)	-0.005 (3)	1.138 (2)	0.025 (4)	1.257 (2)	175.2 (2)	Takusugawa & Koetzle (1979)
(COOH) ₂ ·2H ₂ O	2.506 (4)	—	1.026 (7)	—	1.480 (7)	179.3 (6)	Sabine, Cox & Craven (1969)
(COOD) ₂ ·2D ₂ O	2.524 (2)	0.018 (3)	1.031 (2)	-0.005 (5)	1.493 (2)	177.4 (1)	Coppens & Sabine (1969)
[ImH] ⁺ [HMal] ⁻	2.393 (3)	—	1.196 (5)	—	1.197 (5)	176.8 (4)	Hsu & Schlemper (1979)
[ImD] ⁺ [DMal] ⁻	2.399 (4)	0.006 (4)	1.186 (5)	0.010 (5)	1.214 (6)	177.3 (5)	This work

The thermal-motion parameters of the 11 atoms of the hydrogen maleate ion and the 10 atoms of the imidazolium ion of both the normal and the deuterated material were each fitted separately to a rigid-body model of 21 parameters as described by Schomaker & Trueblood (1968). Except for some of the H atoms, the thermal motion was found to be in excellent agreement with the rigid-body model. The distances after correction for thermal motion are compared in Table 3. In general, the corrected distances are slightly longer than the uncorrected ones and the agreement between the corresponding corrected distances for the normal and deuterated forms is similar to that observed for the uncorrected bond distances. A significant displacement of D(10) towards O(2) is observed in the deuterated form compared to the normal form, even after correction for thermal motion, which indicates that the shift is an effect of deuterium substitution and not a manifestation of thermal-motion effects.

Table 4 contains a comparison of the effects of deuterium substitution on the geometry of the intramolecular hydrogen bond of [ImD]⁺[DMal]⁻ with those in some known structures having crystallographically unrestricted O...O bonds. In the O(2)...D(10)...O(4) system, the H atom moves approximately 0.01 Å towards O(2) as a result of isotopic substitution, but the O(2)...O(4) distance exhibits no significant change, being 2.393 (3) Å in the normal form compared with 2.399 (4) Å in the deuterated compound. A similar shift of 0.025 Å towards one O atom without any significant change in the O...O distance was observed in the case of quinolinic acid. On the other hand, the isotope effect results in a 0.022 Å lengthening of the O...O bond in KDCO₃. Similarly, a 0.019 Å lengthening in the O...O distance and a shift of ~0.129 Å towards one O atom was observed in [Ni(ao-D)₂]Cl·D₂O. Thus, a significant expansion of the O...O distance (positive isotope effect) was

observed in KHCO_3 and $[\text{Ni}(\text{ao-H})_2]\text{Cl}\cdot\text{H}_2\text{O}$, in contrast to an insignificant change in the cases of $[\text{ImH}]^+[\text{HMal}]^-$ and quinolinic acid. These observations are perhaps indicative of a potential function of single-minimum type, symmetric or slightly asymmetric, for the latter two compounds, whereas a double-minimum-type potential function with a potential barrier close to ground level for H and D, but at least above the ground level for D, are suggested for KHCO_3 and $[\text{Ni}(\text{ao-H})_2]\text{Cl}\cdot\text{H}_2\text{O}$. Similar conclusions have been reached by Rundle (1964) and Singh & Wood (1969) for the isotope effect on an independent hydrogen-bond length, on the basis of theoretical calculations. In the crystals exhibiting a network of hydrogen bonds, conclusions about the potential functions based upon the room-temperature isotope effect should be regarded as qualitative since intramolecular constraints in these structures would complicate the situation, as noted by Delaplane & Ibers (1969). In the present case, the constraints are rather severe due to the preference of the conjugated system to remain planar. The least-squares plane calculation through all eleven atoms of the hydrogen maleate ion shows an essentially planar anion with a maximum deviation of 0.04 Å for O(1). The large values (130°) for the angles C(6)–C(7)–C(8) and C(7)–C(8)–C(9), dictated by the planarity, give rise to repulsive O(2)···O(4) contacts, introducing further strains into the remainder of the molecule which make interpretation of the null isotope effect still more complicated. An ideal situation which would conform to the theoretical predictions would be a single, structurally independent hydrogen bond (Olovsson & Jonsson, 1975), in which the observed changes would represent a genuine isotope effect.

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