X–N Deformation Density Studies of the Hydrogen Maleate Ion and the Imidazolium Ion

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Abstract

Deformation densities for the hydrogen maleate ion in two salts (imidazolium and calcium) are presented along with the deformation density of the imidazolium ion (the Ca salt is the pentahydrate). The results are obtained from three-dimensional neutron and X-ray diffraction studies on both compounds. The final R values for the imidazolium salts are 0·062 and 0·080 for the X-ray and neutron data respectively, and the final R for the calcium salt is 0·058. The deformation maps are based on a difference between the observed X-ray intensities and those calculated using the neutron positional and thermal parameters. The general features of the deformation density of the hydrogen maleate ion are very similar for the two salts. The H atom in the short hydrogen bond is in an area of reduced density compared with the spherical atom. Precise geometrical parameters for the imidazolium and hydrogen maleate ions are presented. The effects of a major difference in crystallographic environment on the short hydrogen bond are clearly revealed. In the nearly symmetric environment of the imidazolium salt the O···O distance is 2·393 (3) Å and the O—H distances are identical [1·196 (4) and 1·197 (4) Å], while in the very asymmetric environment of the Ca salt the O···O distance is 2·424 (2) Å and the O—H distances are quite different [1·121 (3) and 1·305 (3) Å].

Introduction

As part of our studies of short, strong hydrogen bonds, an examination of the valence-electron distribution in these bonds by the *X–N* method (Coppens, 1974) seems appropriate. Relatively few studies of this type have been carried out. Especially noteworthy are the *X–X* study of $NaH(C_2H_3O_2)_2$ by Stevens, Lehmann & Coppens (1977) and the *X–N* studies of pyridine-2,3-dicarboxylic acid by Koetzle, Takusagawa & Kvick (1978) and of $N_2H_5^+.C_2HO_4^-$ by Thomas & Liminga (1978). The present study was undertaken for two reasons: (1) to compare the deformation density in the same ion in two different salts in order to check on the reproducibility of the qualitative features and (2) to

see if the subtle effects of changing from a nearly symmetric environment for the hydrogen bond to a much less symmetric environment would result in a significant change in the electron distribution.

X-ray diffraction studies of both calcium di(hydrogen maleate) (Hsu & Schlemper, 1978) and imidazolium hydrogen maleate (James & Matsushima, 1976) have been reported, but because the authors of the latter study reported the presence of a systematic error in their data, X-ray data on that compound as well as neutron data on both compounds were collected in order to generate the deformation density maps.

Experimental

Crystal preparation

Imidazolium hydrogen maleate was prepared as described by James & Matsushima (1976). Irregular prismatic crystals suitable for both X-ray and neutron diffraction were obtained by slow evaporation of aqueous solutions.

Calcium di(hydrogen maleate) was prepared as described by Hsu & Schlemper (1978). Plate-like crystals suitable for neutron diffraction were obtained by slow evaporation of aqueous solutions.

X-ray data collection for imidazolium hydrogen maleate

X-ray data were collected at room temperature (295 ± 2 K) using a crystal of approximate dimensions 0·4 × 0·5 × 0·5 mm. The orientation matrix and refined cell dimensions were obtained by a least-squares fit of the setting angles of 16 manually centered reflections. The monoclinic unit cell ($P2_1/c$, $Z = 4$) has the dimensions $a = 10·855$ (2), $b = 5·518$ (1), $c = 14·616$ (4) Å, and $\beta = 102·87$ (1)°. These are in fair agreement with the previously reported values (James & Matsushima, 1976). The data were collected on a Picker four-circle programmed diffractometer, equipped with a scintillation detector, by the θ–2θ scan technique (1° 2θ min^{-1}). Background was measured at each end of each scan for 20 s. Using Mo $K\alpha$ (Nb β filtered) radiation the intensities of 3281 hkl and $h\bar{k}l$ reflections were

measured out to $\sin \theta/\lambda = 0.70$ Å^{-1} ($2\theta = 60°$). Of these, 2486 were independent, and 1997 with $F_o^2 \geq 2\sigma(F_o^2)$ were used in the structure solution and refinement. The data were corrected for background and Lp factors in the normal manner. An analytical absorption correction ($\mu = 0.129$ mm^{-1}) was applied (range of transmission $= 0.95–0.97$).

Neutron data collection for imidazolium hydrogen maleate

The single-crystal neutron diffraction data were measured on the PDP 11/40 computer-controlled Mitsubishi neutron diffractometer at the University of Missouri Research Reactor Facility. The crystal used for that study had approximate dimensions $1.5 \times 2 \times 3.5$ mm. From 14 carefully centered reflections, an orientation matrix was generated which was used to obtain the angle setting for measurement of the intensities of 3172 hkl and $hk\bar{l}$ reflections out to $2\theta = 95°$ [$\lambda = 1.109$ Å and $(\sin \theta/\lambda)_{max} = 0.665$ Å^{-1}]. The data were collected at 295 (2) K by the θ–2θ step-scan technique with $0.05°$ 2θ steps. The diffracted neutrons were detected with a BF$_3$ detector, and the steps were timed with a monitor counter in the direct beam. Averaging equivalent reflections yielded 2044 independent reflections of which the 1595 with $F_o^2 \geq 2\sigma(F_o^2)$ were used in the refinement of the structure. The data were analytically corrected for absorption (*International Tables for X-ray Crystallography*, 1974, Vol. IV, p. 197) ($\mu = 0.140$ mm^{-1})* with a transmission-factor range of 0.77 to 0.84.

Neutron data collection for calcium di(hydrogen maleate)

The data-collection and reduction procedures were generally the same as above. The orthorhombic crystal (*Pnam*) had approximate dimensions $2 \times 3.5 \times 3.5$ mm. 11 carefully centered reflections were used to derive the cell dimensions and orientation matrix used to measure the intensities of 3937 reflections to a maximum $\sin \theta/\lambda = 0.638$ Å^{-1} ($\lambda = 1.109$ Å). Averaging equivalent reflections gave 1632 independent reflections of which the 1342 with $F_o^2 \geq 2\sigma(F_o^2)$ were used for the structure solution and refinement. The data were analytically corrected for absorption ($\mu = 0.173$ mm^{-1} and transmission-factor range $= 0.58$ to 0.76). The somewhat less precise cell dimensions [$a = 11.719$ (6), $b = 6.475$ (3), $c = 19.565$ (11) Å] from this study agree reasonably well with the previously reported X-ray values [$a = 11.737$ (2), $b = 6.477$ (1), $c = 19.593$ (3) Å] (Hsu & Schlemper, 1978) which were used for all subsequent calculations.

* An incoherent scattering cross-section of 34×10^2 fm^2 for hydrogen was included in the calculation of μ.

Refinement of the structure of imidazolium hydrogen maleate

The previously reported parameters (James & Matsushima, 1976) were used as a starting model for the refinement with the X-ray data set. Full-matrix least-squares refinement, minimizing $\sum w(F_o^2 - kF_c^2)^2$, with all nonhydrogen atoms anisotropic and the H atoms isotropic converged with $R = \sum (F_o^2 - kF_c^2)/ \sum F_o^2 = 0.062$ and $R_w = [\sum w(F_o^2 - kF_c^2)^2/\sum wF_o^4]^{1/2} = 0.106$, where $w = 1/(\sigma^2_{counting} + 0.035F_o^2)$. The refinement included an isotropic extinction parameter (Zachariasen, 1967). The standard deviation of an observation of unit weight was 2.04. The largest residual on a final difference Fourier map was 0.3 e Å^{-3}. The final positional parameters from this refinement are given in Table 1 and the bond angles in Table 2. Fig. 1 presents the bond distances in the imidazolium ion and Fig. 2 those in the hydrogen maleate ion.*

* Lists of structure factors and anisotropic thermal parameters for all three data sets have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35364 (37 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
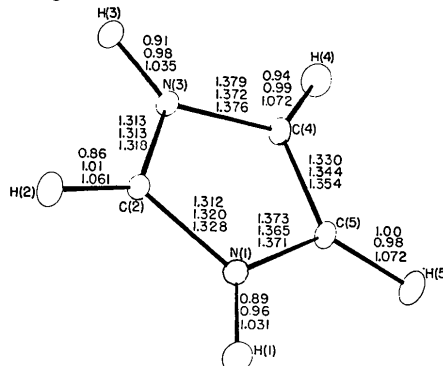
Fig. 1. Bond distances (Å) in the ImH$^+$ ion: the top line gives the previous X-ray results (James & Matsushima, 1976), the second line our X-ray results, and the bottom line our neutron results. The numbering system is as used by James & Matsushima (1976). Standard deviations from our X-ray (neutron) study are $\pm 0.001–0.002$ Å ($\pm 0.002–0.003$ Å) for nonhydrogen distances and $\pm 0.01–0.02$ Å ($\pm 0.003–0.005$ Å) for distances involving hydrogens.

Fig. 2. Bond distances (Å) for HMal$^-$ in [ImH]$^+$[HMal]$^-$. Details are as given for Fig. 1.

Table 1. *Positional parameters for imidazolium hydrogen maleate*

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

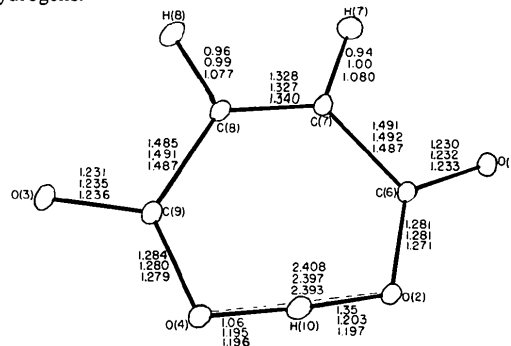|	X-ray			Neutron		
	x	y	z	x	y	z
N(1)	0·3972 (1)	0·1526 (2)	0·0708 (1)	0·3972 (1)	0·1532 (3)	0·0705 (1)
C(2)	0·3152 (1)	−0·0026 (2)	0·0919 (1)	0·3148 (2)	0·9968 (4)	0·0918 (1)
N(3)	0·3768 (1)	−0·1673 (2)	0·1492 (1)	0·3766 (1)	0·8319 (3)	0·1495 (1)
C(4)	0·5036 (1)	−0·1176 (3)	0·1652 (1)	0·5039 (2)	0·8814 (4)	0·1655 (1)
C(5)	0·5158 (1)	0·0837 (3)	0·1163 (1)	0·5163 (2)	0·0839 (4)	0·1161 (1)
C(6)	0·1210 (1)	0·5045 (2)	0·1587 (1)	0·1206 (2)	0·5050 (3)	0·1585 (1)
C(7)	0·0236 (1)	0·3150 (2)	0·1607 (1)	0·0243 (2)	0·3148 (4)	0·1609 (1)
C(8)	−0·1005 (1)	0·3183 (2)	0·1270 (1)	−0·1010 (2)	0·3181 (4)	0·1267 (1)
C(9)	−0·1834 (1)	0·5119 (2)	0·0750 (1)	−0·1833 (2)	0·5115 (4)	0·0747 (1)
O(1)	0·2312 (1)	0·4596 (2)	0·1980 (1)	0·2308 (2)	0·4592 (5)	0·1978 (2)
O(2)	0·0888 (1)	0·7063 (2)	0·1168 (1)	0·0890 (2)	0·7053 (4)	0·1168 (2)
O(3)	−0·2978 (1)	0·4707 (2)	0·0502 (1)	−0·2979 (2)	0·4711 (5)	0·0502 (2)
O(4)	−0·1353 (1)	0·7123 (2)	0·0560 (1)	−0·1348 (2)	0·7118 (4)	0·0563 (2)
H(10)	−0·0236 (15)	0·7048 (33)	0·0860 (11)	−0·0227 (4)	0·7139 (8)	0·0855 (4)
H(1)	0·3692 (15)	0·2848 (30)	0·0282 (12)	0·3700 (4)	0·2971 (9)	0·0256 (3)
H(2)	0·2205 (13)	0·0037 (26)	0·0669 (10)	0·2155 (4)	0·0033 (10)	0·0661 (4)
H(3)	0·3337 (14)	−0·3053 (28)	0·1706 (11)	0·3310 (4)	−0·3103 (8)	0·1742 (3)
H(4)	0·5670 (17)	−0·2258 (30)	0·2048 (13)	0·5737 (4)	−0·2297 (11)	0·2096 (4)
H(5)	0·5899 (15)	0·1732 (31)	0·1101 (11)	0·5985 (4)	0·1839 (10)	0·1092 (4)
H(7)	0·0632 (14)	0·1615 (29)	0·1902 (11)	0·0656 (5)	0·1513 (9)	0·1952 (5)
H(8)	−0·1488 (14)	0·1722 (28)	0·1370 (10)	−0·1537 (4)	0·1575 (9)	0·1354 (4)

Table 2. *Bond angles* (°) *in imidazolium hydrogen maleate*

	Neutron	X-ray		Neutron	X-ray		Neutron	X-ray
H(1)—N(1)—C(2)	122·5 (3)	121 (1)	H(4)—C(4)—C(5)	130·7 (3)	132 (1)	C(8)—C(7)—H(7)	117·8 (3)	118·3 (9)
H(1)—N(1)—C(5)	129·0 (3)	131 (1)	N(3)—C(4)—C(5)	106·8 (2)	106·8 (1)	C(7)—C(8)—C(9)	130·1 (2)	130·3 (1)
C(2)—N(1)—C(5)	108·4 (2)	108·5 (1)	H(5)—C(5)—C(4)	131·2 (4)	132·0 (9)	C(7)—C(8)—H(8)	117·8 (3)	117·4 (9)
H(2)—C(2)—N(1)	125·4 (3)	125·2 (8)	H(5)—C(5)—N(1)	121·7 (4)	121 (1)	C(9)—C(8)—H(8)	112·1 (3)	112·3 (9)
H(2)—C(2)—N(3)	125·6 (3)	125·9 (8)	C(4)—C(5)—N(1)	107·1 (2)	107·2 (1)	O(3)—C(9)—O(4)	122·0 (2)	121·9 (1)
N(1)—C(2)—N(3)	109·0 (2)	108·9 (1)	O(1)—C(6)—O(2)	122·1 (2)	122·1 (1)	O(3)—C(9)—C(8)	118·0 (2)	118·1 (1)
H(3)—N(3)—C(2)	122·2 (3)	122·0 (9)	O(1)—C(6)—C(7)	117·3 (2)	117·9 (1)	O(4)—C(9)—C(8)	120·0 (2)	120·0 (1)
H(3)—N(3)—C(4)	129·1 (3)	129·3 (9)	O(2)—C(6)—C(7)	120·6 (2)	120·0 (1)	C(6)—O(2)—H(10)	111·1 (3)	108·6 (8)
C(2)—N(3)—C(4)	108·7 (2)	108·6 (1)	C(6)—C(7)—C(8)	129·9 (2)	130·4 (1)	C(9)—O(4)—H(10)	111·5 (3)	108·7 (9)
H(4)—C(4)—N(3)	122·6 (3)	121 (1)	C(6)—C(7)—H(7)	112·3 (3)	111·3 (9)	O(2)—H(10)—O(4)	176·8 (4)	178 (2)

The parameters from the X-ray study were taken as starting values for the refinement with the neutron data. The neutron-scattering amplitudes (*International Tables for X-ray Crystallography*, 1974, Vol. IV, p. 270) were N 9·4, C 6·3, O 5·75, and H −3·72 fm. The structure was refined as above with all atoms anisotropic and with an isotropic extinction parameter. The weighting was also as above. The final agreement factors were $R = 0·080$ and $R_w = 0·115$. The standard deviation of an observation of unit weight was 1·86. The final positional parameters are in Table 1 and the bond angles in Table 2.* Fig. 1 presents a comparison of the bond distances with the X-ray values for the imidazolium ion and Fig. 2 those for the hydrogen maleate ion.

* See deposition footnote.

Refinement of the structure of calcium di(hydrogen maleate)

The previously reported parameters (Hsu & Schlemper, 1978) from the X-ray study were used as starting values for the nonhydrogen atoms. The H atoms were located as the largest negative peaks on a difference Fourier synthesis. The refinement with all atoms anisotropic and with an isotropic extinction parameter gave $R = 0·058$ and $R_w = 0·094$. The weighting was as above, and the standard deviation of an observation of unit weight was 1·86. The neutron-scattering amplitudes (Bacon, 1972) were Ca 4·7, O 5·8, C 6·65, and H −3·74 fm. The final positional parameters are in Table 3 and the bond angles in Table 4. The bond distances are compared with the X-ray values in Fig. 3.*

* See deposition footnote.

Deformation density calculations

Deformation densities for both structures were calculated using identical *X–N* methods. The final positional and thermal parameters from the neutron refinement were used in a refinement with the X-ray data sets (Ca X-ray data from Hsu & Schlemper, 1978) varying only the scale factor to give F_c values for

Table 3. *Positional parameters for calcium di(hydrogen maleate)*

	x	y	z
Ca	0·1068 (2)	0·1097 (4)	−0·2500
W(1)	−0·1024 (2)	0·0660 (4)	−0·2500
W(2)	0·2869 (2)	−0·0806 (4)	−0·2500
W(3)	0·0232 (4)	0·4425 (6)	−0·2365 (4)
W(4)	0·0711 (2)	−0·1377 (3)	−0·3361 (1)
O(1)	0·2846 (1)	0·2873 (3)	0·0548 (1)
O(2)	0·1395 (2)	0·2647 (3)	0·1256 (1)
O(3)	0·3182 (1)	0·2923 (3)	−0·0673 (1)
O(4)	0·2168 (2)	0·2740 (3)	−0·1613 (1)
C(1)	0·2219 (1)	0·2806 (2)	−0·0982 (1)
C(2)	0·1131 (1)	0·2753 (2)	−0·0588 (1)
C(3)	0·0951 (1)	0·2710 (2)	0·0090 (1)
C(4)	0·1783 (1)	0·2742 (2)	0·0669 (1)
OHO	0·3060 (2)	0·2927 (5)	−0·0105 (1)
H(C2)	0·0383 (3)	0·2745 (7)	−0·0913 (2)
H(C3)	0·0073 (3)	0·2659 (8)	0·0258 (2)
H(W1)	−0·1480 (3)	0·1053 (7)	−0·2880 (2)
H(W2)	0·3030 (3)	−0·1618 (6)	−0·2901 (2)
H2(W3)	0·0582 (7)	0·5689 (12)	−0·2233 (5)
H1(W3)	−0·0545 (7)	0·4695 (11)	−0·2419 (30)
H1(W4)	−0·0033 (3)	−0·1820 (5)	−0·3511 (2)
H2(W4)	0·1244 (3)	−0·1717 (5)	−0·3723 (2)

the deformation density calculations. This gave $R = 0·086$ and $R_w = 0·158$ for imidazolium hydrogen maleate and $R = 0·081$ and $R_w = 0·126$ for calcium hydrogen maleate. Least-squares planes were then calculated for the hydrogen maleate ion in each structure and for the imidazolium ion (Table 5). These were used as special planes for difference Fourier (deformation density) syntheses using the slant-plane Fourier-transform method of B. W. van de Waal as adapted to *JIMPLAN* by N. K. Hansen. These deformation density maps are presented in Figs. 4, 5 and 6. Details of the maps are presented in the figure captions. In addition, deformation density maps in water planes and planes perpendicular to the water molecules bisecting the H—O—H angle were calculated.
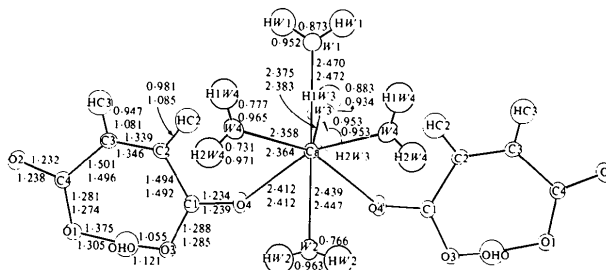

Fig. 3. Bond distances (Å) for Ca(HMal)$_2$. The top line gives X-ray results and the bottom line neutron results. Neutron standard deviations are for Ca—O, C—C, and C—O 0·002–0·003 Å and for O—H and C—H 0·003–0·004 Å, except for the half-occupied W(3) where they are roughly doubled.

Table 4. *Bond angles* (°) *in calcium di(hydrogen maleate)*

	Neutron	X-ray		Neutron	X-ray		Neutron	X-ray
W(1)–Ca–W(3)	72·2 (1)	72·45 (8)	O(4)–Ca–W(4)*	83·12 (7)	83·09 (4)	C(4)–O(1)–OHO	111·9 (2)	114 (1)
W(1)–Ca–W(2)	143·2 (1)	143·10 (6)	Ca–O(4)–C(1)	139·5 (1)	139·44 (9)	C(1)–O(3)–OHO	110·8 (2)	113 (1)
W(1)–Ca–W(4)	75·28 (9)	75·20 (4)	O(4)–C(1)–O(3)	121·0 (1)	120·8 (1)	O(1)–OHO–O(3)	175·9 (3)	171 (3)
W(1)–Ca–O(4)	125·59 (8)	125·66 (3)	O(3)–C(1)–C(2)	120·7 (1)	120·5 (1)	H(W1)–W(1)–H(W1)*	103·0 (5)	–
W(2)–Ca–W(4)	79·15 (9)	79·16 (4)	O(4)–C(1)–C(2)	118·3 (1)	118·7 (1)	H(W1)–W(1)–Ca	121·9 (3)	–
W(2)–Ca–W(3)	144·3 (2)	144·06 (8)	C(1)–C(2)–C(3)	130·2 (1)	130·7 (1)	H(W2)–W(2)–H(W2)*	109·1 (5)	–
W(2)–Ca–O(4)	76·12 (9)	72·02 (4)	H(C2)–C(2)–C(1)	112·9 (2)	–	H(W2)–W(2)–Ca	116·4 (2)	–
W(3)–Ca–W(4)	128·2 (2)	128·37 (17)	H(C2)–C(2)–C(3)	116·9 (2)	–	H1(W3)–W(3)–H2(W3)	106·9 (12)	–
W(3)–Ca–W(4)*	117·5 (2)	117·59 (17)	C(2)–C(3)–C(4)	130·2 (1)	130·3 (1)	H1(W3)–W(3)–Ca	124·0 (9)	–
W(3)–Ca–O(4)*	75·0 (2)	75·02 (15)	H(C3)–C(3)–C(2)	116·7 (2)	–	H2(W3)–W(3)–Ca	129·0 (6)	–
W(3)–Ca–O(4)	84·3 (2)	84·33 (15)	H(C3)–C(3)–C(4)	113·1 (2)	–	H1(W4)–W(4)–H2(W4)	106·9 (3)	–
W(4)–Ca–W(4)*	91·0 (1)	90·86 (6)	O(1)–C(4)–O(2)	122·4 (1)	122·7 (1)	H1(W4)–W(4)–Ca	125·5 (2)	–
O(4)–Ca–O(4)*	92·2 (1)	92·29 (5)	O(1)–C(4)–C(3)	120·0 (1)	119·4 (1)	H2(W4)–W(4)–Ca	124·1 (2)	–
O(4)–Ca–W(4)	155·2 (1)	155·14 (4)	O(2)–C(4)–C(3)	117·6 (1)	117·9 (1)			

* In a position related to that in Table 3 by mirror symmetry.

Table 5. *Least-squares planes*

Plane	Equation*	Maximum deviation
10 atoms of imidazolium	$0·258x − 0·564y − 0·784z = −0·205$	0·012 (1) Å
11 atoms of HMal⁻ in ImH⁺ salt	$0·338x − 0·373y − 0·864z = −2·716$	0·036 (2)
11 atoms of HMal⁻ in Ca²⁺ salt	$0·042x − 0·999y − 0·0065z = −1·708$	0·061 (2)

* x, y, and z are in ångströms in an orthonormal axis system related to the crystallographic axes such that the y axis is coincident with the crystallographic b axis, the z axis with the crystallographic c^* axis, and the x axis with the crystallographic a axis.
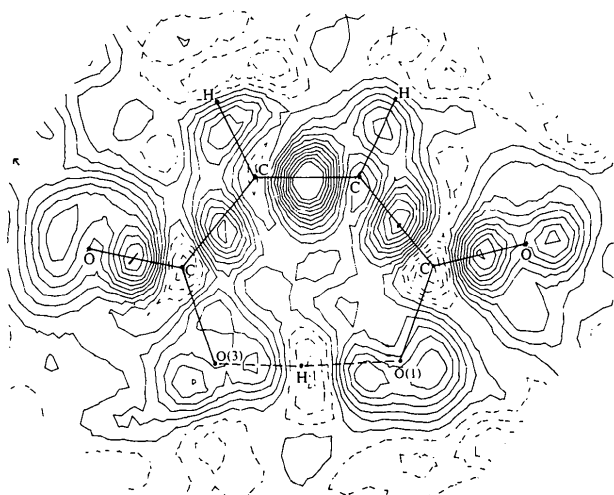
Fig. 4. Deformation density map for HMal⁻ in Ca(HMal)₂. Contours are drawn at 0·05 e Å⁻³ intervals. Dashed lines represent negative contours (deficiency of electron density). The arrow points in the direction of the Ca atom. The orientation and atom numbers are as in Fig. 3.
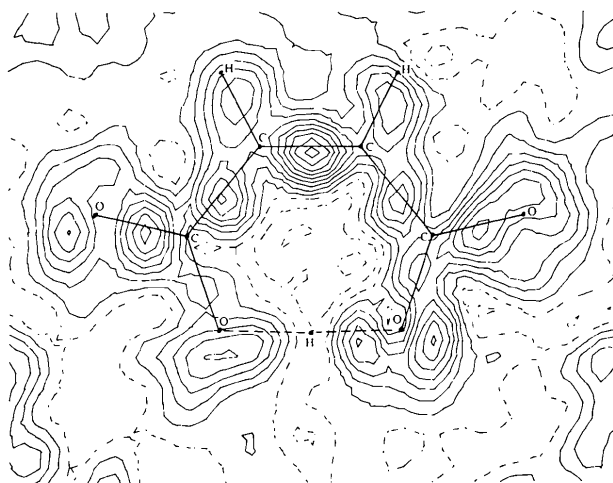

Fig. 6. Deformation density map for ImH⁺ in [ImH]⁺[HMal]⁻. Details are as in Fig. 4. Atom numbers are given in Fig. 1.

Fig. 5. Deformation density map for HMal⁻ in [ImH]⁺[HMal]⁻. Details are as in Fig. 4. The orientation and atom numbers are as in Fig. 2.

Results and discussion

The structural features of imidazolium hydrogen maleate are essentially as previously reported (James & Matsushima, 1976) (see Figs. 1 and 2 and Table 2). The largest discrepancy in the nonhydrogen atom bond distances for the two X-ray studies is that of the C—C distance in the imidazolium ion [1·344 (2) Å in the present study and 1·330 (3) Å in the previous study]. In most cases the C—H and N—H distances are longer in the present study but as is normally the case they are significantly shorter than the expected covalent distances. The neutron refinement, in general, gives bond

distances for the nonhydrogen atoms in agreement with the present X-ray values. The largest discrepancy is in the middle C—C bond of the hydrogen maleate ion [1·327 (2) X-ray and 1·340 (3) Å neutron]. The neutron value is in good agreement with that found for the Ca salt [1·346 (2) Å] which is also longer than the corresponding X-ray value [1·339 (2) Å]. Although these differences are of marginal significance and the X-ray value for the Ca salt is in agreement with the neutron value for the imidazolium salt, the effect may be an apparent shortening of the distance in the X-ray case because of the nonspherical electron distribution as a result of the multiple bond. The C—H [av. 1·072 (4) Å] distances from the neutron results are obviously the most reliable.

The O···O distance [2·393 (3) Å] for the hydrogen maleate ion is among the shortest reported, and its environment is nearly symmetric (Fig. 7) although not restricted by crystallographic symmetry. In this nearly symmetric environment the H atom is found to be perfectly centered [O—H = 1·197 (5) Å from the neutron study]. In such a situation O—H values derived from careful X-ray results [1·195 (16) and 1·203 (16) Å] can be reliable since the electron distribution is essentially identical on either side of the H atom. This hydrogen bond can be contrasted with that in the Ca salt which has a very unsymmetrical crystallographic environment (Fig. 8). In that case the O···O distance [2·424 (2) Å] is significantly longer, and the hydrogen bond is much less symmetric [O(1)—H = 1·305 (3) and O(3)—H = 1·121 (3) Å]. Ellison & Levy (1965) found a nearly symmetric hydrogen bond in the K salt of the hydrogen chloromaleate ion. In that symmetry-unrestricted case the O···O distance is 2·403 (3) Å and the O—H distances are 1·199 (5) and 1·206 (5) Å, whereas the K

salt of hydrogen maleate (Ibers, 1964) has a symmetry-restricted, centered hydrogen bond [O···O = 2·468 (6) Å].

In the Ca salt two mirror-related hydrogen maleate ions are coordinated to each Ca^{2+} ion through a carboxylic O atom. The monocapped trigonal-prismatic seven-coordination of the Ca (Fig. 9) is completed by five water molecules. The Ca–O distances range from 2·36 to 2·47 Å. All five waters of hydration are coordinated to the Ca. The mode of interaction of the water lone pairs with the Ca atom is apparently variable (Table 6). While the $W(3)$ and $W(4)$ planes are nearly coplanar with their Ca–O vectors, the $W(1)$ and $W(2)$ planes are tilted by 32 and 40° respectively. This suggests that $W(1)$ and $W(2)$ are interacting essentially through a single sp^3 lone pair while $W(3)$ and $W(4)$ are interacting through both lone pairs. A difference in Ca–O distances is also observed in that the average Ca–$W(1)$ and Ca–$W(2)$ distance is 2·46 (1) Å while that for Ca–$W(3)$ and Ca–$W(4)$ is 2·37 (1) Å. Deformation density maps in the planes perpendicular to water molecular planes and bisecting the H–O–H angles were examined for lone-pair density. Although density maxima of ~0·5 e Å^{-3} were revealed, the details were not clearly resolved, probably

Fig. 9. Surroundings of the Ca^{2+} ion, showing the O–O distances in the monocapped distorted trigonal prism [X-ray distances (Å) are given].

Table 6. *Hydrogen-bond parameters and water parameters*

Bond angles (°)

H(W1)–W(1)–H(W1)	103·0 (5)	Ca–W(3)–H1(W3)	124·0 (9)
Ca–W(1)–H(W1)	121·9 (3)	Ca–W(3)–H2(W3)	129·0 (6)
H(W2)–W(2)–H(W2)	109·1 (5)	H1(W4)–W(4)–H2(W4)	106·9 (3)
Ca–W(2)–H(W2)	116·4 (2)	Ca–W(4)–H1(W4)	125·5 (2)
H1(W3)–W(3)–H2(W3)	106·9 (1·2)	Ca–W(4)–H2(W4)	124·1 (2)

Hydrogen-bond parameters

	O···O (Å)	O–H (Å)	H···O (Å)	O–H···O (°)
W(2)–W(3)	2·925 (5)	0·934 (13)	2·001 (10)	169·6 (1·1)
W(4)–W(3)	3·120 (6)	0·953 (10)	2·233 (9)	154·5 (9)
W(1)–O(4)	2·932 (3)	0·952 (4)	2·028 (4)	157·8 (4)
W(2)–O(2)	2·774 (2)	0·963 (4)	1·848 (4)	160·2 (4)
W(4)–O(2)	2·711 (3)	0·965 (4)	1·747 (4)	177·3 (3)
W(4)–O(1)	2·771 (2)	0·971 (4)	1·803 (3)	173·6 (4)

Angles between water planes and the Ca–W bonds

	Angle (°)	Ca–W (Å)		Angle (°)	Ca–W (Å)
W(1)	32 (1)	2·472 (2)	W(3)	3 (1)	2·383 (3)
W(2)	40 (1)	2·447 (2)	W(4)	17 (1)	2·364 (2)

Fig. 7. Hydrogen-bond environment (distances in Å) for [ImH]$^+$[HMal]$^-$. The O(2)–H(10) distance is 1·197 (4) Å, and the O(4)–H(10) distance is 1·196 (4) Å. The standard deviations in the O···H distances are 0·003–0·004 Å.

Fig. 8. Hydrogen-bond environment (distances in Å) for Ca(HMal)$_2$.

because of the relatively high thermal motion of the water atoms and, in the case of $W(3)$, the problem of disorder of the H atoms. [$W(3)$ has 50% occupancy in positions related by the molecular mirror (see Hsu & Schlemper, 1978).] Geometrical parameters for the water molecules and their hydrogen bonds are described in Table 6 and in part in Fig. 3. Each water H atom is involved in one and only one hydrogen bond with either another water O atom or a carboxylate O atom.

The primary purpose of this study was to compare the deformation density maps of hydrogen maleate in the two compounds, one having a nearly symmetric hydrogen-bond environment and the other a quite asymmetric environment. The study also provides a deformation density map of the imidazolium ion. Since the studies are at room temperature, only the

qualitative features of the maps should be considered. Based on the background features, the estimated error is approximately ± 0.10 e Å^{-3} except at positions very near nuclear centers where the errors are much larger. In the imidazolium ion (Fig. 4), the density distribution is quite reasonable with about a 0·35 e Å^{-3} maximum in the C—C bond and 0·20 to 0·25 e Å^{-3} maxima in each of the C—H and N—H bonds. The N—H and N—C bonds are clearly polarized with a shift of valence electrons toward the more electronegative N atom, the effect being much more pronounced in the N—C bonds.

The deformation density distributions for the hydrogen maleate ion (Figs. 4 and 5) are remarkably similar for the two salts. The similarity between the two independent studies and between the two halves of each hydrogen maleate ion adds credence to the results and supports the estimated error of about ± 0.10 e Å^{-3}. The results are not able to distinguish between the symmetrical environment of the hydrogen bond in $[\text{ImH}]^+[\text{HMal}]^-$ and the much more asymmetric case in $\text{Ca(HMal)}_2.5\text{H}_2\text{O}$. The maximum density in both cases is found in the C—C double bond. High density is also found in the C—O bonds not involved in the short intraionic hydrogen bond, but the C—O bonds involved in the short hydrogen bond appear in all cases to be extremely deficient in bonding density. The explanation for this deficiency is not obvious. A similar effect was observed by Thomas & Liminga (1978) for one of C—O bonds in the $X-N$ map of C_2HO_4^-. Lone pairs are clearly visible on all the carboxyl O atoms. In particular, one can see evidence of lone pairs on appropriate O atoms directed toward the hydrogen-bonded H atom and toward the Ca^{2+} ion. Reduction in electron density at the hydrogen-bonded H atom position compared with that observed at the covalently bonded H atom positions is evident in both salts. This is consistent with the large downfield shift of these protons in the PMR spectra. The results for the deformation density at the H atom position in the hydrogen bonds obtained from this study are intermediate between that for $\text{NaH(C}_2\text{H}_3\text{O}_2)_2$ (Stevens, Lehmann & Coppens, 1977) obtained by $X-X$ methods (no significant charge depletion) and that for pyridine-2,3-dicarboxylic acid (Koetzle, Takusagawa & Kvick, 1978) by $X-N$ methods at 35 K or that for $[\text{N}_2\text{H}_5]^+[\text{HC}_2\text{O}_4]^-$ (Thomas & Liminga, 1978) (both highly charge depleted). The low-temperature studies

clearly give a more quantitative description of the deformation density than that obtained from the present room-temperature work. Kvick (1980) reveals that the deformation density maps obtained at low temperature for sodium hydrogen maleate are remarkably similar.

All calculations were performed on the University of Missouri IBM 370/168 computer system with the following programs: *ANGSET*, angle-settings program; W. C. Hamilton's *SORTH*, sorting program; W. C. Hamilton's *HORSE*, general absorption correction program; A. Zalkin's *FORDAP*, Fourier synthesis program; P. Doedens and J. A. Ibers's *NUCLS*, least-squares program; *ORFFE* (Busing, Martin & Levy, 1964); *ORTEP* (Johnson, 1965); *JIMPLAN*, N. K. Hansen's adaption of the slant-plane Fourier transform of B. W. van de Waal.

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