Acta Cryst. (1976). B**32**, 1708

Accurate Dimensions of the Maleate Mono-Anion in a Symmetric Environment not Dictated by Crystallographic Symmetry: Imidazolium Maleate

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(*Received* 6 *November* 1975; *accepted* 11 *December* 1975)

The structure of imidazolium maleate, $C_3H_5N_2^+.C_4H_3O_4^-$, has been determined by X-ray diffraction. The space group is $P2_1/c$ with $Z=4$. Molecular symmetry is not required by the space group. The cell dimensions are $a=10{\cdot}869$ (1), $b=5{\cdot}523$ (1), $c=14{\cdot}614$ (3) Å, $\beta=102{\cdot}85$ (2)°. The structure was refined to $R=0{\cdot}039$ and $R_w=0{\cdot}029$ for 1621 reflexions with $I>3\sigma(I)$. The distance between the O atoms in the intramolecular hydrogen bond is 2·408 (1) Å. The geometry of the maleate moiety is symmetric and each half of the maleate mono-anion is in almost identical environments in the crystals. The short intramolecular hydrogen bond may possibly be symmetric in this symmetric environment.

Introduction

The short intramolecular hydrogen bond of the maleate mono-anion has been the subject of several crystallographic studies and molecular orbital calculations. The studies of KH maleate (Peterson & Levy, 1958; Darlow & Cochran, 1961), KH chloromaleate (Ellison & Levy, 1965) and the total energy calculations of Murthy, Bhat & Rao (1970) suggest strongly that the intramolecular hydrogen bond is symmetric. On the other hand three structures have been solved which show that the maleate mono-anion is not symmetric when the molecular anion is in a complex with other organic cations [*d*,*l*-brompheniramine maleate (James & Williams, 1971), (+)-chlorpheniramine maleate monohydrate (James & Williams, 1974*a*) and methoxypromazine (Marsau & Gauthier, 1973)]. The evidence from these three structures that the intramolecular hydrogen bond is asymmetric is not totally convincing, the main argument coming from the differences in the geometries of the two halves of the anion. One carboxyl group is definitely ionized whereas the other has distances akin to the protonated form. The dimensions of the carboxylate group of the mono-anion that is involved with the intermolecular hydrogen bond were closer to those of the maleate dianion (Town & Small, 1973; James & Williams, 1974*b*) than to those of the maleic acid parent (James & Williams, 1974*c*). However the electron density associated with the H atom of the intramolecular hydrogen bond was not well located, as might be expected in the presence of heavy atoms. The structure of imidazolium maleate was undertaken in order to describe this mono-anion as accurately as possible in a space group that did not have a required molecular symmetry element and with no heavy atoms present.

Experimental

Equal molar amounts of imidazole and maleic acid were dissolved in methanol. The principal salt compound was crystallized by evaporating the solution. Oscillation and Weissenberg photographs showed that the crystals belonged to the space group $P2_1/c$, with systematic absences $0k0$, $k=2n+1$; $h0l$, $l=2n+1$. A single crystal, 0·3 × 0·5 × 0·15 mm, was mounted with c^* coincident with the φ axis of a Picker FACS-1 diffractometer with graphite-monochromatized Mo $K\alpha$ radiation ($\lambda=0{\cdot}70926$ Å). The cell dimensions were deduced from the angular coordinates of 12 accurately centred reflexions by the least-squares method. The density was measured by flotation. The crystal data are summarized in Table 1.

The intensities were collected out to $2\theta=60°$ in a room where the temperature was controlled at 16 ± 1 °C. The θ–2θ mode was used at a scan rate of 2° per min over the basic width of 1·50°. The backgrounds were counted at both extremes of the 2θ driving for

Table 1. *Physical constants and other data for imidazolium maleate*

Molecular formula	$C_3H_5N_2^+ . C_4H_3O_4^-$
Molecular weight	184·15
Space group	$P2_1/c$
a	10·869 (1) Å
b	5·523 (1)
c	14·614 (3)
β	102·85 (2)°
V	855·29 Å^3
Z	4
D_o	1·426 g cm^{-3}
D_c	1·426
μ	1·29 cm^{-1}
2θ range explored	3 ~ 60° hkl and $\bar{h}kl$
Unique reflexions	2495
Reflexions for refinement	1621 (65·0 %)
Final R	0·038
Final R_w	0·029

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20 s each. Three standard reflexions were measured every 50 reflexions. No decay or moving of the crystal was observed. Since sixteen reflexions were considered to be suffering from the effects of counter coincidence loss, they were remeasured with an attenuator. The attenuator factor, 8·335, was determined from the intensities of 10 reflexions each measured twice.

Although μ is only 1·29 cm^{-1}, absorption correction curves were empirically obtained from the reflexions 002 ($2\theta=5{\cdot}75°$) and 008 ($2\theta=23{\cdot}02°$) (North, Phillips & Mathews, 1968). The ratio of the maximum to the minimum transmitted intensities was 1·05 for 002 and 1·02 for 008. The correction values from 002 were applied to the reflexions for which 2θ was less than 10·0°. The reflexions for which 2θ was more than 10·0° were multiplied by the values from 008. The standard deviations, $\sigma(I)$, of the intensities were estimated from

$$\sigma(I)=[P+(CP)^2+t^2(B_1+B_2+C^2B_1^2+C^2B_2^2)]^{1/2}$$

where P is the total count, C an instrumental instability coefficient, 0·01, t the ratio of the time spent on the peak to the total background counting time, and B_1 and B_2 are the background counts.

1621 reflexions with $I>3\sigma(I)$ were used in the structure solution and refinement. The intensities were corrected for Lorentz and polarization factors and reduced to structure amplitudes. The atomic numbering is shown in Fig. 1.

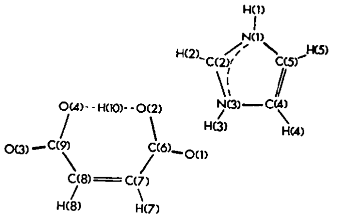

Fig. 1. Atomic numbering of imidazolium maleate.

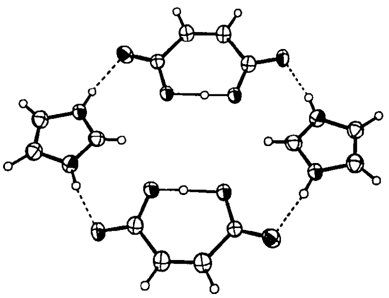

Fig. 2. Two units of imidazolium maleate related by a centre of symmetry.

Structure determination and refinement

The overall isotropic temperature factor $B=3{\cdot}81$ Å^2 and the scale factor 0·178 were calculated by least-squares fit to a Wilson (1942) plot. The structure amplitudes were reduced to E values (Karle & Karle, 1966), giving 871 with $E>1{\cdot}80$. The structure was determined by direct methods (Karle & Karle, 1966). One of the E maps clearly showed the non-hydrogen atoms with a reasonable packing in the cell. Two cycles of full-matrix least-squares refinement with isotropic individual temperature factors and one cycle with anisotropic temperature factors, with unit weights, reduced $R=(\sum||F_o|-|F_c||/\sum|F_o|)$ to 0·087. A difference map showed peaks for the H atoms, except for H(10).

H(10) appeared on a later difference map computed after two cycles of refinement with the weighting scheme $w^{1/2}=(2|F_o|)^{1/2}/\sigma(I)$. This peak was broad and elongated in the direction of O(2) and O(4). It was decided that the temperature parameters of H(10) were better refined anisotropically. When the refinement converged at $R=0{\cdot}036$ and $R_w=\sum w(|F_o|-k|F_c|)^2/\sum w|F_o|^2=0{\cdot}071$, it was found that several reflexions with strong intensities seemed to suffer from secondary extinction. A correction was applied as $F_c(\text{corr})=F_c/(1+C_\beta I_o)$ (Zachariasen, 1963). The final secondary extinction parameter C_β was 0·19 (7) × 10^{-6}. The ratios of the parameter shift to error were all less than 0·3. R, R_w and the goodness-of-fit were 0·038, 0·029 and

Table 2. *Final atomic parameters*

(*a*) The final parameters (× 10^4) of the anisotropically refined atoms. The thermal parameters are in the form: $\exp[-2\pi^2(U_{11}h^2a^{*2}+\ldots+2U_{12}hka^*b^*\ldots)]$.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
N(1)	3970 (1)	11518 (3)	709 (1)	435 (7)	455 (8)	511 (9)	−45 (6)	119 (6)	43 (7)
C(2)	3158 (1)	9975 (3)	920 (1)	353 (8)	468 (9)	552 (10)	−39 (7)	58 (7)	28 (8)
N(3)	3768 (1)	8324 (2)	1492 (1)	374 (7)	456 (8)	526 (8)	−72 (6)	47 (6)	44 (7)
C(4)	5039 (1)	8838 (3)	1652 (1)	353 (8)	601 (11)	540 (10)	−23 (8)	36 (7)	3 (9)
C(5)	5162 (1)	10826 (3)	1166 (1)	368 (8)	612 (11)	532 (10)	−102 (8)	118 (7)	−44 (9)
C(6)	1212 (1)	5036 (3)	1590 (1)	405 (8)	407 (9)	457 (9)	−31 (7)	80 (7)	17 (8)
C(7)	234 (1)	3154 (3)	1605 (1)	473 (9)	370 (9)	541 (10)	−25 (7)	89 (7)	104 (8)
C(8)	−1005 (1)	3185 (3)	1264 (1)	446 (9)	401 (9)	568 (10)	−99 (7)	98 (7)	93 (8)
C(9)	−1838 (1)	5106 (3)	751 (1)	411 (8)	404 (9)	523 (9)	−80 (7)	91 (7)	24 (8)
O(1)	2312 (1)	4586 (2)	1980 (1)	370 (5)	579 (7)	728 (8)	−9 (5)	−7 (5)	134 (6)
O(2)	891 (1)	7053 (2)	1171 (1)	359 (5)	441 (7)	832 (9)	−79 (5)	36 (6)	162 (6)
O(3)	−2977 (1)	4700 (2)	505 (1)	352 (5)	592 (7)	811 (8)	−113 (5)	58 (5)	138 (6)
O(4)	−1357 (1)	7121 (3)	563 (1)	382 (6)	454 (7)	928 (10)	−66 (6)	−13 (7)	203 (7)
H(10)	−37* (3)	713* (4)	83* (2)	37** (4)	3** (1)	17** (3)	4** (3)	20** (3)	5** (2)

Table 2 (*cont.*)

(*b*) The final parameters ($\times 10^3$) of the isotropically refined atoms

	x	y	z	U_{iso}
H(1)	374 (1)	1278 (3)	33 (1)	52 (5)
H(2)	235 (1)	1004 (3)	73 (1)	46 (4)
H(3)	337 (1)	705 (3)	169 (1)	71 (6)
H(4)	565 (1)	789 (3)	205 (1)	66 (5)
H(5)	594 (1)	1172 (3)	112 (1)	66 (5)
H(7)	58 (1)	173 (3)	191 (1)	55 (4)
H(8)	−150 (1)	180 (3)	134 (1)	56 (5)

3·021 respectively.* R_w was greatly improved by inclusion of the extinction parameter but the goodness-of-fit was extraordinarily high, indicating that there is possibly still some systematic error in either the data or model. The final positional and thermal parameters are listed in Table 2. An *ORTEP* drawing (Johnson, 1965) of two units of imidazolium maleate is shown in Fig. 2. Scattering factors for C, N and O were taken from Cromer & Mann (1968) and for H from Stewart, Davidson & Simpson (1965).

The calculations were mainly done with the X-RAY 70 programs (Stewart, Kundell & Baldwin, 1970).

Results and discussion

All the atomic parameters have been independently determined, because the space group symmetry does not require mirror or twofold symmetry for either the maleate or imidazole ions.

(i) *Imidazolium moiety*

The bond lengths and angles of the imidazolium moiety are given in Fig. 3. Protonation on one of the N atoms of the imidazole ring can create either mirror or twofold symmetry in the molecular ion along the bond joining C(2) and H(2). The observed values of the bond lengths and angles agree well with this postulate.

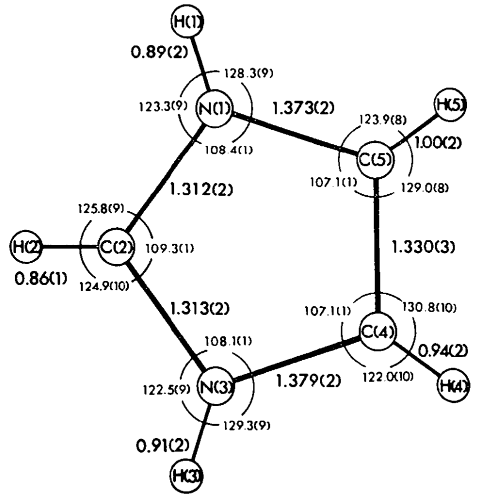

Fig. 3. The bond lengths (Å) and angles (°) of the imidazolium moiety.

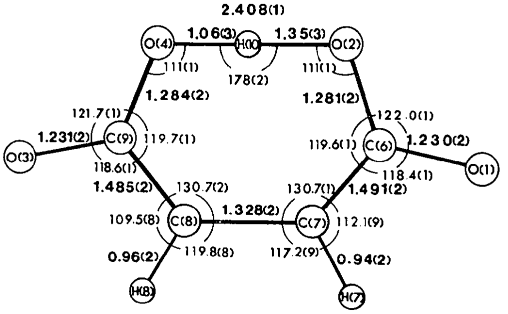

Fig. 4. The bond lengths (Å) and angles (°) of the maleate moiety.

Table 3. *Displacements* (Å) *of atoms from the least-squares planes of imidazolium maleate*

Atom	Plane I	Atom	Plane II	Plane III	Plane IV	Plane V
N(1)	0·001*	C(6)	0·000*	0·002*	0·0001*	
C(2)	−0·001*	C(7)	0·015*	−0·001*	−0·0001*	
N(3)	0·001*	C(8)	−0·012*	0·032	0·0002*	−0·002*
C(4)	−0·001*	C(9)	0·008*		−0·0001*	0·005*
C(5)	0·001*	O(1)	0·026*	−0·001*	0·0329	
H(1)	0·001	O(2)	0·021*	−0·001*	−0·0410	
H(2)	0·015	O(3)	0·010*		0·0029	−0·002*
H(3)	−0·041	O(4)	0·003*		−0·0235	−0·002*
H(4)	0·000	H(7)	−0·038		−0·0084	
H(5)	0·010	H(8)	−0·026		−0·0021	
O(1)	−0·154					
O(3^{v})†	−0·001					
Standard deviation	0·001		0·015	0·001	0·0001	0·004
χ^2	1·51		800	2·61	0·02	16·76
Degrees of freedom	4		7	3	3	3

* Atoms included in the least-squares plane calculations. † Atom which was operated on by the symmetry ($-x, 2{\cdot}0-y, -z$).

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31557 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 3 (*cont.*)

The equations of the least-squares planes, $Pi+Qj+Rk=S$ in orthogonal Å space.

Plane	P	Q	R	S (Å)
I	−0·25720	0·56427	0·78450	3·33118
II	−0·33654	0·37907	0·86200	2·73735
III	−0·35576	0·38595	0·85116	2·71484
IV	−0·33652	0·36431	0·86835	2·71090
V	−0·32929	0·37478	0·86666	2·71709

Most of the bond lengths of this positively charged imidazole ring are similar to those in imidazolium phosphate (Blessing & McGandy, 1972), with the exception of C(4)–C(5), 1·330 (3) Å, which is much shorter than the weighted average, [1·357 (1) Å] observed in imidazolium phosphate (Blessing & McGandy, 1972), histidine derivatives (Kistenmacher, Hunt & Marsh, 1972; Oda & Koyama, 1972; Kistenmacher & Sorrell, 1974; Edington & Harding, 1974), histamine diphosphate (Veidis, Palenik, Schaffrin & Trotter, 1969) and pilocarpine (Codding & James, 1973). The inclusion of an extinction parameter in the refinement had a large effect on C(4)–C(5), *i.e.* a decrease from 1·343 (3) to 1·330 (3) Å. It is unlikely that thermal vibration of the ring atoms would result in this much apparent shortening (Busing & Levy, 1964), and so we accept 1·330 Å as a valid estimate for C(4)–C(5) in the present compound. N(1)–C(5) and N(3)–C(4) agree well with the weighted averages in the above imidazolium derivatives, 1·380 (1) and 1·378 (1) Å, respectively. These distances are longer than the aromatic C–N length, 1·340 (1) Å, in pyridine (Bak, Hansen-Nygaard & Rastrup-Anderson, 1958). In addition N(1)–C(2), 1·312 (2), and N(3)–C(2), 1·313 (2) Å, are almost equal and are shorter than the aromatic C–N length, 1·340 (1) Å. The geometry of this ring as a whole indicates that in the present environment the π-delocalization is over N(1), C(2), N(3) with little, if any, involvement of C(4) and C(5) as this is clearly a C–C double bond. The positive charge is equally distributed on both N atoms rather than over the whole ring.

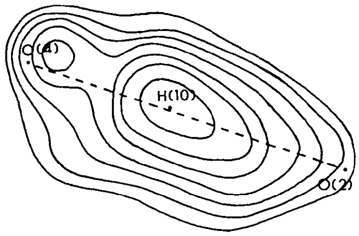

Fig. 5. The contribution of H(10) to the final difference map. The first contour is drawn at 0·132 e Å^{-3} and the increment is 0·044 e Å^{-3}.

The bond angles agree closely with the protonated imidazole derivatives referred to previously. The weighted average of the C–N–C angles in these derivatives is 109·0 (1) and that of N–C–N is 108·6 (1)°.

The C and N atoms of the imidazole moiety lie in a plane, within experimental error (Table 3). The largest displacement of an atom covalently bonded to the ring is of H(3), 0·04 Å, whereas the displacement of O(1), which is hydrogen-bonded to N(3), is 0·154 Å on the same side of this plane as H(3). H(1) and the hydrogen-bonded O(3) are essentially in the imidazole ring plane.

(ii) H-*maleate anion*

The best planes through three atomic groupings of the maleate mono-anion are given in Table 3. The same calculation through all eight non-hydrogen atoms of the anion (plane II, Table 3) shows that this moiety deviates significantly from planarity ($\chi^2=800$). However, the two carboxyl groups (plane III, $\chi^2=2{\cdot}61$; plane V, $\chi^2=16{\cdot}8$) and the four backbone C atoms (plane IV, $\chi^2=0{\cdot}02$) are all planar. This is a common feature of maleate anion crystal structures. In addition the two O atoms involved in the intramolecular hydrogen bond, O(2) and O(4), are on the same side of plane IV through the four C atoms. Deviations of O(2) and O(4) have been observed in other maleate mono-anion structures (James & Williams, 1974*c*) and are brought about by torsional rotations of 1·9° about C(6)–C(7) and 0·7° about C(8)–C(9) for O(2) and O(4) respectively. Relative to the other maleic acid, maleate mono-anion structures these deviations are very small. The angle between the best planes of the maleate (plane II) and imidazolium (plane I) moieties is 12·4°.

The bond lengths and angles of the maleate moiety are illustrated in Fig. 4. The values agree with the weighted means of six maleate mono-anion derivatives, KH maleate (Darlow, 1961), KH chloromaleate (Ellison & Levy, 1965), CaH maleate (Prout, Carruthers & Rossotti, 1971), K_2 *cis*-aconitate (Glusker, Orehowsky, Casciato & Carrell, 1972), DL-brompheniramine maleate (James & Williams, 1971), (+)-chlorpheniramine maleate (James & Williams, 1974*a*) and methoxypromazine (Marsau & Gauthier, 1973). C(6)–O(2), 1·281 (2), and C(9)–O(4), 1·284 (2) Å, are intermediate between C–O single and double bonds of the antiplanar α,β-unsaturated carboxyl groups in KH fumarate (Gupta & Prasad, 1972), dimethyl dichloromuconate (Einspahr & Donohue, 1973), itaconic acid

Table 4. *Geometries of the intermolecular hydrogen bonds of imidazolium maleate*

	Distances		Angles	
	O···N	O···H	O···H–N	C=O···H
C(6)=O(1)···H(3)–N(3)	2·789 (2) Å	1·89 (2) Å	171 (1)°	109 (3)°
C(9)=O(3)···H(1^{v})–N(1^{v})	2·797 (2)	1·92 (2)	170 (1)	108·8 (3)

H(1^{v}) and N(1^{v}) are operated on by the symmetry ($-x,2{\cdot}0-y,-z$).

(Harlow & Pfluger, 1973) and maleic acid (James & Williams, 1974*c*), and are comparable with those in the maleate dianion in Na_2 maleate (James & Williams, 1974*b*) and Li_2 maleate (Town & Small, 1973).

C(6)–C(7), 1·491 (2), C(7)–C(8), 1·328 (2), and C(8)–C(9), 1·485 (2) Å, are shorter than the corresponding weighted means in the six maleate mono-anion derivatives, 1·501 (1), 1·343 (1) and 1·506 (1) Å respectively, but are close to those of the α,β-unsaturated carboxyl groups referred to previously. The weighted means are 1·321 (2) for C=C double bonds and 1·486 (2) Å for a C–C single bond.

The bond angles in this structure agree with those in the maleate mono-anion derivatives. The greatest difference between the maleate mono-anion derivatives and the antiplanar α,β-unsaturated carboxyl groups is found at C=C–C. The angles, 130·7 (1) and 130·7 (2)°, in this structure are expanded by 8·1° from that of the antiplanar α,β-unsaturated carboxyl groups, and have been discussed previously (Darlow, 1961).

The distance, 2·408 (1) Å, between the intramolecular hydrogen-bonded O atoms is one of the shortest hydrogen bonds in the maleate mono-anions. The distances from H(10) are 1·35 (3) to O(2) and 1·06 (3) Å to O(4). O(2)–H(10)–O(4) is 178 (2)°. These distances were not corrected for thermal motion. It would seem from these distances and angles that this strong intramolecular hydrogen bond is asymmetric. We would prefer not to accept this conclusion for the following reasons. Firstly, it is well known that positional parameters of H atoms derived from X-ray data are subject to systematic error due to bond polarization. Secondly, it is worth noting the electron density distribution in this region on a difference map computed without the contribution of H(10) (Fig. 5). This section was computed at $y=0{\cdot}71$ and is 0·03 Å above O(2) and 0·01 Å below O(4). It is clear that the electron density is smeared over the volume between the two O atoms and it is fortuitous that the maximum corresponds to an asymmetric hydrogen bond. The smaller secondary peak close to O(4) is not interpretable in terms of thermal anisotropy of O(4).

As a result, the most plausible model is one in which H(10) lies in a single, broad and probably symmetric energy well, in spite of the fairly large difference in the calculated O–H distances. This result is supported by the symmetric geometry of the maleate ion (Fig. 4) in which the two halves are almost identical.

(iii) *Molecular packing*

Fig. 6 shows a view of part of the contents of the cell. The maleate anions are stacked in a herring-bone fashion in a sheet parallel to the *bc* plane and centred at $x/a=0$. The imidazolium cations are similarly arranged in a stacked sheet parallel to the *bc* plane but at $x=0{\cdot}5$.

The near geometrical identity of the two carboxyl groups of the maleate anion has already been discussed. A group of two imidazolium ions and two maleate ions encircle a centre of symmetry (Fig. 2). The two intermolecular hydrogen bonds O(1)···H(3)–N(3) and O(3)···H(1)–N(1) have almost identical dimensions (Table 4). Other close contacts around the two carboxyl groups are listed in Table 5. All these contacts show that the two carboxyl groups have similar environments. The packing scheme observed here is similar to those found in NaH maleate.$3H_2O$ (Gupta, Prasad & Yadav, 1972) and LiH maleate.H_2O (Gupta, Prasad & Gupta, 1975).

Table 5. *The dimensions of intermolecular contacts around the carboxyl groups*

A	B	C	Distance B···C	Angle A–B–C
C(6) ——	O(2)···	C(9^{i})	3·414 Å	89·4°
C(9) ——	O(4)···	C(6^{i})	3·401	90·0
C(6) ——	O(1)···	C(4^{ii})	3·146	168·2
C(9) ——	O(3)···	C(5^{iii})	3·247	133·5
C(6) ——	O(1)···	N(1^{iv})	3·326	115·8
C(9) ——	O(3)···	N(3^{i})	3·305	113·4
C(6) ——	O(1)···	C(2^{iv})	3·220	106·8
C(9) ——	O(3)···	C(2^{i})	3·294	104·1
H(3)····	O(1)···	N(1^{iv})		79·9
H(1^{v})···	O(3)···	N(3^{i})		80·2
H(3)····	O(1)···	C(2^{iv})		102·9
H(1^{v})···	O(1)···	C(2^{i})		103·0
N(1^{iv})···	O(1)···	C(2^{iv})		23·1
N(3^{i})····	O(3)···	C(2^{i})		23·0

Symmetry operations

(i) $-x,\ 1{\cdot}0-y,\ -z$; (ii) $1{\cdot}0-x,\ y-0{\cdot}5,\ 0{\cdot}5-z$
(iii) $-x,\ 1{\cdot}0-y,\ z$; (iv) $x,\ y-1{\cdot}0,\ z$
(v) $-x,\ 2{\cdot}0-y,\ -z$;

Since the same number and kinds of atoms surround both carboxyl groups at similar distances and directions, it may be concluded that these two groups have almost identical electronic environments. This fact and the similar molecular geometries of the two carboxyl groups allow one to conclude that the very

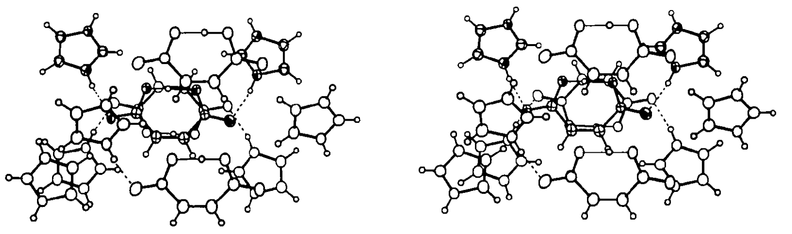

Fig. 6. A stereoscopic diagram (Johnson, 1965) of the packing of imidazolium maleate: *a* is horizontal, *b* is vertical and the view is approximately down *c**.

short intramolecular hydrogen bond is symmetric. It is likely that in structures which have only one carboxyl group of the maleate anion involved in an intermolecular hydrogen bond the intramolecular hydrogen bond is asymmetric. Support for this comes from theoretical calculations which took environmental factors into account, for *p*-toluidinium difluoride (Williams & Schneemeyer, 1973) resulting in an asymmetric difluoride hydrogen bond (Ostlund & Ballenger, 1975).

The authors thank the Medical Research Council of Canada for financial support. One of us (M.M.) is indebted to the MRC and the University of Alberta for financial assistance.

References

Bak, B., Hansen-Nygaard, L. & Rastrup-Anderson, J. (1958). *J. Mol. Spectrosc.* **2**, 361–368.

Blessing, R. H. & McGandy, E. L. (1972). *J. Amer. Chem. Soc.* **94**, 4034–4035.

Busing, W. R. & Levy, H. A. (1964). *Acta Cryst.* **17**, 142–146.

Codding, P. W. & James, M. N. G. (1973). Amer. Cryst. Assoc. Summer Meeting, Storrs, Conn. P185 Abstract 02 and personal communication.

Cromer, D. T. & Mann, J. B. (1968). *Acta Cryst.* A**24**, 321–324.

Darlow, S. F. (1961). *Acta Cryst.* **14**, 1257–1259.

Darlow, S. F. & Cochran, W. (1961). *Acta Cryst.* **14**, 1250–1257.

Edington, P. & Harding, M. M. (1974). *Acta Cryst.* B**30**, 204–206.

Einspahr, H. & Donohue, J. (1973). *Acta Cryst.* B**29**, 1875–1880.

Ellison, R. D. & Levy, H. A. (1965). *Acta Cryst.* **19**, 260–268.

Glusker, J. P., Orehowsky, W. Jr, Casciato, C. A. & Carrell, H. L. (1972). *Acta Cryst.* B**28**, 419–425.

Gupta, M. P. & Prasad, N. (1972). *Acta Cryst.* B**28**, 2628–2630.

Gupta, M. P., Prasad, S. M. & Gupta, T. N. P. (1975). *Acta Cryst.* B**31**, 37–40.

Gupta, M. P., Prasad, S. M. & Yadav, B. (1972). *Cryst. Struct. Commun.* **1**, 211–213.

Harlow, R. L. & Pfluger, C. E. (1973). *Acta Cryst.* B**29**, 2965–2966.

James, M. N. G. & Williams, G. J. B. (1971). *J. Med. Chem.* **14**, 670–675.

James, M. N. G. & Williams, G. J. B. (1974*a*). *Canad. J. Chem.* **52**, 1872–1879.

James, M. N. G. & Williams, G. J. B. (1974*b*). *Acta Cryst.* B**30**, 1257–1262.

James, M. N. G. & Williams, G. J. B. (1974*c*). *Acta Cryst.* B**30**, 1249–1257.

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

Karle, J. & Karle, I. L. (1966). *Acta Cryst.* **21**, 849–859.

Kistenmacher, T. J., Hunt, D. J. & Marsh, R. E. (1972). *Acta Cryst.* B**28**, 3352–3361.

Kistenmacher, T. J. & Sorrell, T. (1974). *J. Cryst. Mol. Struct.* **4**, 419–432.

Marsau, P. & Gauthier, J. (1973). *Acta Cryst.* B**29**, 992–998.

Murthy, A. S. N., Bhat, S. N. & Rao, C. N. R. (1970). *J. Chem. Soc.* (*A*), pp. 1251–1256.

North, A. C., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.

Oda, K. & Koyama, H. (1972). *Acta Cryst.* B**28**, 639–642.

Ostlund, N. S. & Ballenger, L. W. (1975). *J. Amer. Chem. Soc.* **97**, 1237–1238.

Peterson, S. W. & Levy, H. A. (1958). *J. Chem. Phys.* **29**, 948–949.

Prout, C. K., Carruthers, J. R. & Rossotti, F. J. C. (1971). *J. Chem. Soc.* (*A*), pp. 3342–3349.

Stewart, J. M., Kundell, F. A. & Baldwin, J. C. (1970). The X-RAY 70 system. Computer Science Center, Univ. of Maryland, College Park, Maryland.

Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

Town, W. G. & Small, R. W. H. (1973). *Acta Cryst.* B**29**, 1950–1955.

Veidis, M. V., Palenik, G. J., Schaffrin, R. & Trotter, J. (1969). *J. Chem. Soc.* (*A*), pp. 2659–2669.

Williams, J. M. & Schneemeyer, L. F. (1973). *J. Amer. Chem. Soc.* **95**, 5780–5781.

Wilson, A. J. C. (1942). *Nature, Lond.* **150**, 151–152.

Zachariasen, W. H. (1963). *Acta Cryst.* **16**, 1139–1144.