Crystal Structure of Sodium Hydrogen Malonate

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Crystals of sodium hydrogen malonate are monoclinic, space group $P2_1/c$, $Z = 4$, with $a = 6{\cdot}664(1)$, $b = 7{\cdot}522(1)$, $c = 9{\cdot}337(1)$ Å, and $\beta = 100{\cdot}69(1)°$. The structure was solved from diffractometer data by the heavy-atom method, and refined to R 0·06 (1005 reflections) by the block-diagonal least-squares technique.

A short unsymmetrical hydrogen bond [2·556(3) Å] links the hydrogen malonate residues into infinite chains. The un-ionized and ionized carboxy-groups are twisted, with respect to the plane of the central carbon atoms, by 73·8 and 131·4°, and mutually are inclined at 61·4°.

THE acid salts, MHX_2, of monocarboxylic acids, HX, have been divided into classes A and B by Shrivastava and Speakman,[1] on the basis of the i.r. spectral study by Hadži and his co-workers.[2] In type A, the two acidic radicals are crystallographically (and chemically) equivalent and are related to one another by a symmetry element, across which they are linked by a hydrogen bond involving the acidic hydrogen atom. In type B, the acidic radicals are not only crystallographically but also chemically non-equivalent, and X and HX can be distinguished in the crystal structure. The i.r. spectra of type B are essentially a superposition of those of the free acid and the neutral salt. The i.r. spectra of type A are anomalous, the frequency of the absorption band attributable to the OH-stretching mode being shifted to a much lower value than the expected 3500 cm^{-1}. The i.r. spectrum of sodium hydrogen malonate (KBr pellet)† exhibits marked differences from that of potassium hydrogen malonate.[3]

We now report, as part of a programme of investigating the influence of ions on short hydrogen bonds in the structures of the acid salts of carboxylic acids, a three-dimensional single-crystal X-ray study of sodium hydrogen malonate (NaHM).

EXPERIMENTAL

Single crystals were obtained by slow evaporation of solutions of malonic acid and sodium hydroxide in water. Two different types of crystal forms were found: (i) large and hard, with well formed faces, and (ii) long and plate-like. The former were sodium hydrogen malonate, the latter disodium malonate trihydrate.

Crystal Data.—$C_3H_3NaO_4$, $M = 126{\cdot}1$. Monoclinic, $a = 6{\cdot}664(1)$, $b = 7{\cdot}522(1)$, $c = 9{\cdot}337(1)$ Å, $\beta = 100{\cdot}69(1)$, $D = 1{\cdot}80$, $Z = 4$, $D_c = 1{\cdot}78$. Space group, $P2_1/c$. Cu-$K_{\alpha 1}$ radiation, $\lambda = 1{\cdot}54051$ Å; $\mu(\text{Cu-}K_{\alpha 1}) = 23$ cm^{-1}. Crystal dimensions $0{\cdot}35 \times 0{\cdot}38 \times 0{\cdot}42$ mm.

By use of a GE XRD 5 diffractometer, equipped with goniostat, three-dimensional intensity data were collected, by the stationary-crystal–stationary-counter method,[4] to the limit 2θ 160°. Of 1011 non-equivalent reflections measured, only six had intensities below background. The crystal was mounted with c^* along the ϕ-axis of the goniostat. The difference in absorption as a function of the angle was measured for several $00l$ reflections and was used for correcting approximately for the anisotropy of absorption. Intensities were then corrected by the Lorentz and polarization factors, and were processed in the usual way.

Derivation and Refinement of the Structure.—The position of the sodium atom was established from the Harker section $(u,\frac{1}{2},w)$ and Harker line $(0,v,\frac{1}{2})$. The positions of all the eight non-hydrogen atoms were obtained from the heavy-atom phased electron density map and were used in the next cycle of structure-factor calculation, which gave R value 0·26. Least-squares refinement, with a block-diagonal approximation and individual isotropic temperature factors reduced R to 0·14. Six cycles of refinement, with individual anisotropic temperature factors, reduced R to 0·09. An electron-density difference map at this stage enabled location of all three hydrogen atoms. A further four cycles of refinement, in which the co-ordinates and isotropic thermal parameters of the hydrogen atoms were also allowed to vary, yielded R 0·06. In the earlier stages of refinement, the $1/f_C$ weighting scheme (f_C is the atomic scattering factor of carbon) and in the final stages the $1/\sigma$ weighting scheme[5] were used. Atomic scattering factors for sodium, oxygen, and carbon were taken from ref. 6, and for hydrogen from ref. 7. Final atomic positional and thermal parameters are given in Tables 1 and 2, with their estimated standard deviations obtained from the inverse of the block-diagonal matrix. The isotropic temperature factors for the hydrogen atoms are smaller than the corresponding values of the atoms to which they are covalently bonded, but this result, we feel, is not significant because of the large σ values for the B value of the hydrogen atoms. The refinements were carried out by minimizing the function

TABLE 1

Atomic positional parameters ($\times 10^4$) with estimated standard deviations in parentheses

Atom	x	y	z
Na	2555(2)	470(2)	606(1)
O(1)	5635(3)	4051(4)	2175(3)
O(2)	5771(3)	1809(3)	656(3)
O(3)	10,092(3)	3992(4)	3537(2)
O(4)	11,921(3)	3053(4)	1903(3)
C(1)	6519(4)	3158(5)	1270(3)
C(2)	8508(4)	3928(5)	1019(3)
C(3)	10,309(4)	3622(4)	2264(3)
H(1)	8349(48)	5375(52)	832(38)
H(2)	8968(50)	3594(52)	300(40)
H(3)	4421(51)	3637(49)	2252(38)

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† This i.r. spectrum is given in Supplementary Publication No. SUP 21000 (3 pp.). For details of Supplementary Publications see Notice to Authors No. 7, in *J.C.S. Perkin II*, 1972, Index Issue.

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TABLE 2

Thermal parameters *

Atom	b_{11} (or B)	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
Na	56(2)	101(3)	66(2)	−20(4)	10(3)	−4(4)
O(1)	63(5)	171(6)	123(4)	−76(9)	80(7)	−165(8)
O(2)	70(5)	101(5)	90(3)	−60(8)	40(6)	−68(7)
O(3)	72(5)	192(6)	56(3)	32(9)	−6(6)	−34(7)
O(4)	41(5)	142(5)	100(3)	14(8)	25(6)	−73(7)
C(1)	40(6)	108(6)	54(4)	5(10)	−4(7)	−8(8)
C(2)	47(6)	117(7)	57(4)	−42(10)	5(7)	−6(8)
C(3)	42(6)	76(6)	67(4)	−37(10)	6(7)	−2(8)
H(1)	14(9)					
H(2)	19(9)					
H(3)	8(8)					

* $b_{ij} \times 10^4$ for non-hydrogen atoms; in the form: exp $(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{22}hk + b_{23}kl + b_{13}hl)$; for hydrogen atoms B values $\times 10^3$.

$\Sigma[\omega(|F_o| - 1/k|F_c|)^2]$. Observed and calculated structure factors are deposited in Supplementary Publication No. SUP 20914 (3 pp.).†

DISCUSSION

Geometry of the Molecule.—Bond distances and angles are listed in Table 3, with their estimated standard deviations obtained from the inverse of the block-diagonal matrix, which are smaller than the values obtained by comparing chemically equivalent bonds. The molecule is illustrated in Figure 1.

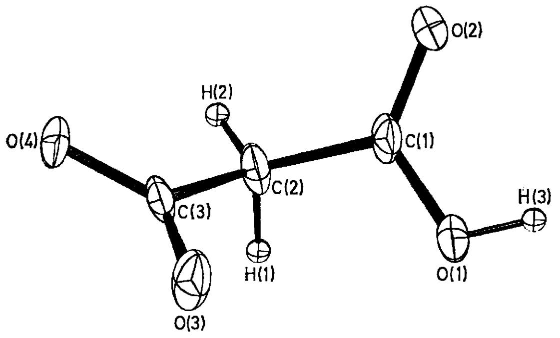

FIGURE 1 The molecule viewed along c^*, showing the atom numbering system used

The two C–C bond lengths to the un-ionized and ionized carboxy-groups are significantly different (1·505 and 1·526 Å). This inequality in the C–C bond lengths has been noticed previously.[8-10]

There are well-marked differences between the dimensions of the un-ionized and ionized carboxy-groups [11] and the structure of NaHM follows this pattern. It has been found that the sum of the carboxylic C–O distances, whether ionized or not, is reasonably constant (2·52 Å), their difference ranging from 0·03 to 0·10 Å.[12] In NaHM, the sums of the C–O distances are 2·516 and 2·533 Å, in agreement with the above observation.

Conformation of the Molecule.—The atoms C(1), C(2), O(1), and O(2), and C(2), C(3), O(3), and O(4) of the two carboxy-groups lie in the planes of equation $0{\cdot}3539X - 0{\cdot}5490Y + 0{\cdot}7572Z = 1{\cdot}0318$Å and $0{\cdot}3325X + 0{\cdot}9369Y - 0{\cdot}1083Z = 4{\cdot}4909$ Å, where the coefficients of X, Y, and Z are the direction cosines of the normal to the plane relative to the a, b, and c^* axes. These two planes are mutually inclined at 61·4°. In KHM, they are twisted by 9·5°, and in free malonic acid,[13] by 92·0°.

TABLE 3

Molecular geometry, with estimated standard deviations in parentheses

(*a*) Bond distances (Å)			
C(1)–O(1)	1·308(4)	C(2)–H(1)	1·11(4)
C(1)–O(2)	1·225(4)	C(2)–H(2)	0·83(4)
C(2)–O(3)	1·256(4)	O(1)–H(3)	0·89(3)
C(3)–O(4)	1·260(3)		
C(1)–C(2)	1·505(4)		
C(2)–C(3)	1·526(4)		
(*b*) Bond angles (deg.)			
C(2)–C(1)–O(1)	114·6(3)	C(1)–C(2)–H(1)	110
C(2)–C(1)–O(2)	122·7(3)	C(3)–C(2)–H(1)	108
C(2)–C(3)–O(3)	118·4(2)	C(1)–C(2)–H(2)	119
C(2)–C(3)–O(4)	115·9(3)	C(3)–C(2)–H(2)	102
O(1)–C(1)–O(2)	122·7(3)	H(1)–C(2)–H(3)	102
O(3)–C(2)–O(4)	125·7(3)	C(1)–O(1)–H	113
C(1)–C(2)–C(3)	114·5(3)		

Owing to steric hindrance from the oxygens of one carboxy-group to the proximal oxygen of the other, the two groups cannot be in the same plane through the central carbon atoms C(1)—(3), but must twist with respect to this plane. In free malonic acid,[13] one carboxy-group, but not the other, is twisted nearly at right-angles relative to the plane through the central carbon atoms. In KHM, the two groups are twisted by *ca.* 5° in opposite direction; in NaHM, the un-ionized group is twisted by 75·8° and the ionized one by 131·4°. H(2) Lies in the intersection of the planes through the two carboxy-groups.[14]

Hydrogen Bonding.—Only one hydrogen, H(3) [on O(1)], is able to take part in hydrogen bonding, and its position was clearly revealed in the electron-density difference map. This hydrogen bonds with O(4′) of the ionized carboxyl group of another molecule with an O(1)–H(3) · · · O(4′) 2·556(3) Å and O(1)–H(3) · · · O(4′) 164°. Such short hydrogen bonds have been found in salts of a number of carboxylic acids.[15-17] Hydrogen bonds of lengths 2·4—2·6 Å have three possible potential functions.[16] The first has an asymmetric double minimum, with one minimum lower than the other, and corresponds to an asymmetric hydrogen bond; the second has a symmetric potential function, with a single minimum, and corresponds to a truly symmetric hydrogen bond; the third has a symmetric double minimum, and the proton will be found to lie in either one of the

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† See Notice to Authors No. 7 in *J.C.S. Perkin II*, 1972, Index issue.

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energy wells with equal probability. The critical barrier height occurs at an O $\cdots$ O separation in the range 2·47—2·54 Å.[17]

Pimentel and McClellan [17] distinguish these three O–H $\cdots$ O types in terms of O $\cdots$ O distance. For O $\cdots$ O >2·54 Å, the proton can be expected to be closer to one oxygen atom than the other, and for <2·47 Å, the proton will display a centrosymmetric distribution. The range 2·47—2·54 Å is a transition region in which either type of behaviour might be found. This structure belongs to the first category. No elongated peak for the hydrogen atom was found in the difference electron-density map for NaHM, unlike the case of potassium hydrogen malonate.

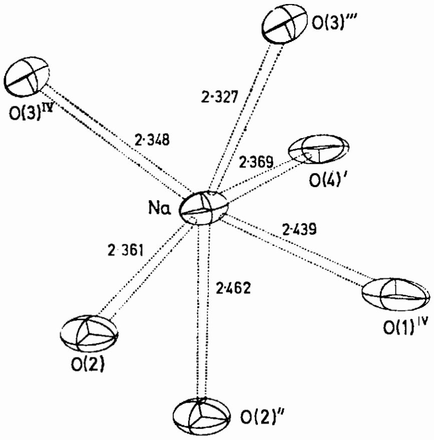

FIGURE 2 Co-ordination of Na$^+$; mean σ for distances is 0·003 Å. Atoms are identified as follows:

Superscript	Cell	Data Set
None	000	1
Prime	$\bar{1}00$	1
2 Primes	100	2
3 Primes	$\bar{1}0\bar{1}$	3
IV	$1\bar{1}0$	4

1 x, y, z
2 x, y, z
3 $x, \frac{1}{2}-y, \frac{1}{2}+z$
4 $x, \frac{1}{2}+y, \frac{1}{2}-z$

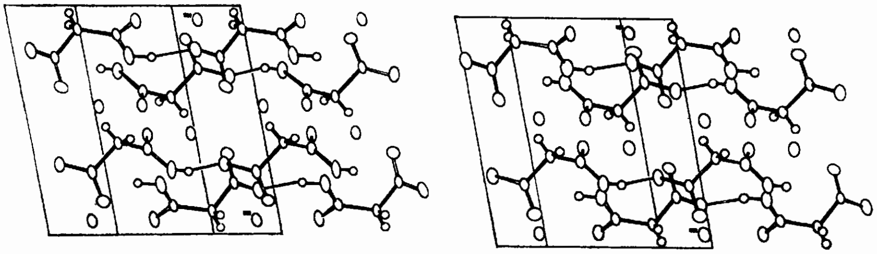

FIGURE 3 A stereo-view of the packing of the molecules in the crystal

The structures of NaHM and KHM are chemically very similar, each consisting of infinite chains of hydrogen anions linked by hydrogen bonds. In KHM, the hydrogen malonate residues have two-fold crystallographic symmetry and are linked into infinite chains by 'very short' hydrogen bonds lying across centres of inversion. The hydrogen malonate residues in NaHM are linked by a short hydrogen bond, but less short than in KHM. The hydrogen-bonded molecules in NaHM are related to each other by a translation along the *a* axis. The presence of the 'very short' and symmetrical hydrogen bond in KHM blurs the distinction between the ionized and un-ionized carboxy-groups, and a molecular two-fold rotation axis is introduced. Since the short hydrogen bond in NaHM is neither symmetrical nor very short, the distinction between the ionized and un-ionized carboxy-groups is manifested in terms of molecular geometry.

Sodium Co-ordination and Packing.—The co-ordination of Na$^+$ is illustrated in Figure 2. The sodium ion is surrounded by six oxygen atoms in an approximately octahedral arrangement, in contrast to the eight-co-ordinated K$^+$ atom in KHM. The mean Na $\cdots$ O distance [2·384(3) Å] agrees well with the sum of the ionic radii of 2·37 Å.[18] Six-fold co-ordination of Na$^+$ has also been found in sodium salts of other carboxylic acids, such as sodium hydrogen diacetate,[19] sodium hydrogen fumarate,[20] and sodium D-tartrate dihydrate.[21] There are also two other Na $\cdots$ O distances of 3·541 and 3·582 Å, respectively, to atoms O(1) and O(4''').

A stereoscopic pair illustrating the packing of molecules is shown in Figure 3. In addition to the ionic forces between the sodium and oxygen atoms, the structure is stabilized by hydrogen bonds. The molecules are hydrogen bonded end-to-end and form extended chains nearly parallel to the *a* axis, which is the shortest.

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[3/236 *Received, 2nd February,* 1973]

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