A Short Intramolecular Hydrogen Bond in the Structure of the Superacid Salt Lithium Trihydrogen Dimalonate

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Crystals of the title compound are monoclinic, space group $P2_1/c$, $Z = 4$, with $a = 9.664(2)$, $b = 7.173(1)$, $c = 13.199(5)$ Å, $\beta = 108.74(3)°$. The structure was solved from diffractometer data by direct methods and refined by block-diagonal least-squares techniques to R 0.07 (1 939 observed reflections). The carboxy-groups of the planar hydrogen malonate ion are linked by an unsymmetrical and very short [2.481(3) Å] intramolecular hydrogen bond. The malonic acid molecule also is found to be nearly planar. The malonic acid and the hydrogen malonate ion are linked together by two short intermolecular O–H · · · O hydrogen bonds [2.655(3) and 2.575(3) Å] and form an infinite chain structure in which the two species alternate. The Li+ ions have tetrahedral co-ordination and link the infinite chains.

POTASSIUM HYDROGEN MALONATE [1] (KHM) forms crystals of type A_2 with short symmetrical hydrogen bond whereas sodium hydrogen malonate [2] (NaHM) forms crystals of type B_2 with a short unsymmetrical hydrogen bond. Frequently, the potassium salts exhibit shorter hydrogen bonds than the sodium salts, and the Cs+ or Rb+ salts form shorter hydrogen bonds than K+ salts, indicating a possible influence of the size and co-ordination of the ions on hydrogen bonding. Since Li+ has a smaller size and a different co-ordination from K+ and Na+, we decided to investigate the lithium salt. However, in our attempts to grow crystals of LiHM, we actually obtained crystals of the 'superacid' salt [3] lithium trihydrogen dimalonate LiH_3M_2. We report here the X-ray investigation of this superacid salt.

EXPERIMENTAL

We were attempting to grow lithium hydrogen malonate crystals by neutralizing aqueous solutions of malonic acid with equivalent amounts of lithium hydroxide, but ended up with two different types of crystals from two different batches: (i) slow evaporation of the solution gave rise to large, colourless and transparent crystals with well formed faces, (ii) warming the solution, followed by slow cooling yielded clear, well-shaped, prismatic crystals. The former were lithium trihydrogen dimalonate, the latter dilithium malonate.

Crystal Data.—$C_6H_7LiO_8$, $M = 214.0$. Monoclinic, $a = 9.664(2)$, $b = 7.173(1)$, $c = 13.199(5)$ Å, $\beta = 108.74(3)°$, $D_m = 1.68$, $Z = 4$, $D_c = 1.68$, $\lambda(Cu-K_{\alpha1}) = 1.540\ 51$ Å; $\mu(Cu-K_{\alpha1}) = 15$ cm^{-1}. Space group $P2_1/c$ (C_{2h}^5).

A single crystal of size $(0.30 \times 0.16 \times 0.14$ mm$)$ was chosen and mounted with a^* along the ϕ axis of the goniostat. Three-dimensional data (2 100 unique reflections to the limit 2θ 164° for Cu-$K_{\alpha1}$ radiation) were measured by the stationary-crystal–stationary-counter method,[4] using balanced Ni-Co filters on a General Electric XRD6 diffractometer. 1939 Reflections having $I > 2\sigma(I)$ were used in the refinement. Three reflections were periodically monitored during data collection. Data were corrected for Lorentz, polarization, and the $\alpha_1–\alpha_2$ splitting corrections. The

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[2] S. Narsinga Rao and R. Parthasarathy, *J.C.S. Perkin II*, 1974, 683.

[3] J. C. Speakman, *Structure and Bonding*, 1972, **12**, 141.

[4] T. C. Furnas, jun., and D. Harker, *Rev. Sci. Instr.*, 1955, **26**, 449.

difference in absorption as a function of the angle ϕ was measured for several $h00$ reflections and was used for correcting approximately the anisotropy of absorption.

TABLE 1

Final atomic fractional co-ordinates ($\times 10^4$)

Atom	x	y	z
O(1a)	996(3)	1 255(4)	2 299(2)
O(1b)	2 747(3)	3 381(4)	2 789(2)
O(3a)	4 060(2)	806(3)	5 804(2)
O(3b)	4 335(2)	3 354(3)	4 942(2)
2O(1a)	6 187(2)	897(4)	8 526(2)
2O(1b)	6 176(2)	2 603(3)	7 138(2)
2O(3a)	10 155(2)	2 766(4)	10 361(2)
2O(3b)	8 219(3)	1 105(5)	10 243(2)
C(1)	2 120(3)	2 059(4)	2 997(2)
C(2)	2 497(3)	1 079(4)	4 057(3)
C(3)	3 722(3)	1 875(4)	4 963(2)
2C(1)	6 757(3)	2 059(4)	8 080(2)
2C(2)	8 250(3)	2 832(5)	8 688(2)
2C(3)	8 948(3)	2 210(4)	9 830(2)
Li	5 664(5)	−8(8)	1 322(4)

TABLE 2

Final atomic fractional co-ordinates ($\times 10^3$) for hydrogen atoms

Atom	x	y	z
H(1)	75(6)	180(8)	166(4)
H(2)	477(5)	145(6)	637(3)
H(5)	743(5)	86(7)	980(4)
H(3)	275(4)	−16(6)	398(3)
H(4)	156(4)	112(6)	428(3)
H(6)	893(5)	254(6)	835(3)
H(7)	816(4)	406(6)	866(3)

Solution and Refinement of the Structure.—The structure determination was carried out by the application of the multisolution tangent-refinement technique, employing the program MULTAN.[5] The structure was refined by least-squares methods (block-diagonal) to R 0.07. Difference electron-density maps were used to locate the hydrogen and Li+ atoms. The function minimized was $\Sigma w(|F_o| - 1/k|F_c|)$ [2] with $w = 1/f_C$, where f_C is the scattering factor for carbon. Atomic scattering factors for oxygen and carbon were taken from ref. 6, for Li+ atoms from ref. 7, and for the hydrogen atoms from ref. 8.

[5] G. Germain, P. Main, and M. M. Woolfson, *Acta Cryst.*, 1971, **A27**, 368.

[6] D. T. Cromer and D. Liberman, *J. Chem. Phys.*, 1970, **53**, 1891.

[7] 'International Tables for X-Ray Crystallography,' vol. III, 1968, Kynoch Press, Birmingham, p. 202.

[8] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

Atomic positional parameters for non-hydrogen atoms, obtained from the least-squares refinement, are given in Table 1 and those for the hydrogen atoms in Table 2, with their estimated standard deviations obtained from the inverse of the block-diagonal matrix. Observed and calculated structure factors and thermal parameters are deposited in Supplementary Publication No. SUP 22196 (16 pp., 1 microfiche).*

DISCUSSION

Geometry of the Molecule.—The covalent bond lengths and interbond angles for LiH_3M_2, which consist of an ionized (HM^-) and un-ionized (H_2M) residue are listed in Table 3, with their estimated standard deviations

TABLE 3

Intramolecular distances (Å) and bond angles (°), with estimated standard deviations in parentheses

(a) Distances

(i) in H_2M

C(1)–O(1a)	1.311(4)	O(1a)–H(1)	0.89(6)
C(1)–O(1b)	1.204(4)	O(3a)–H(2)	0.95(4)
C(3)–O(3a)	1.303(3)	C(2)–H(3)	0.94(4)
C(3)–O(3b)	1.220(4)	C(2)–H(4)	1.03(4)
C(1)–C(2)	1.503(4)		
C(2)–C(3)	1.501(4)		

(ii) In HM^-

2C(1)–2O(1a)	1.247(4)	2O(3b)–H(5)	0.81(5)
2C(1)–2O(1b)	1.251(3)	2C(2)–H(6)	0.92(4)
2C(3)–2O(3a)	1.220(4)	2C(2)–H(7)	0.88(4)
2C(3)–2O(3b)	1.291(4)		
2C(1)–2C(2)	1.513(4)		
2C(2)–2C(3)	1.508(4)		

(b) Angles

(i) in H_2M

C(2)–C(1)–O(1a)	110.2	C(1)–O(1a)–H(1)	112
C(2)–C(1)–O(1b)	126.3	C(3)–O(3a)–H(2)	107
C(2)–C(3)–O(3a)	111.9	C(1)–C(2)–H(3)	110
C(2)–C(3)–O(3b)	125.3	C(1)–C(2)–H(4)	106
O(1a)–C(1)–O(1b)	123.4	C(3)–C(2)–H(3)	106
O(3a)–C(3)–O(3b)	122.8	C(3)–C(2)–H(4)	107
C(1)–C(2)–C(3)	117.2	H(3)–C(2)–H(4)	110

(ii) In HM^-

2C(2)–2C(1)–2O(1a)	119.0	2C(3)–2O(3b)–H(5)	110
2C(2)–2C(1)–2O(1b)	117.4	2C(1)–2C(2)–H(6)	112
2C(2)–2C(3)–2O(3a)	121.0	2C(1)–2C(2)–H(7)	106
2C(2)–2C(3)–2O(3b)	118.3	2C(3)–2C(2)–H(6)	104
2O(1a)–2C(1)–2O(1b)	123.6	2C(3)–2C(2)–H(7)	110
2O(3a)–2C(3)–2O(3b)	120.7	H(6)–2C(2)–H(7)	106
2C(1)–2C(2)–2C(3)	117.8		

obtained from the inverse of the block-diagonal matrix. The HM^- and H_2M portions are illustrated in Figure 1. Their dimensions are quite similar to that of the corresponding H_2M and HM^- moieties in the analogous superacid salt, KH_3M_2 (ref. 9). The two C–C bond lengths adjacent to the un-ionized and ionized carboxy-groups have been noted [10] to be significantly different in several cases. However, in LiH_3M_2, this difference is not significant. It has been pointed out that the sum of the carboxylic C–O distances, whether un-ionized or ionized, was found to be reasonably constant (2.52 Å).[11] The

* See Notices to Authors No. 7 in *J.C.S. Perkin II*, 1977, Index issue.

[9] M. Currie, *J.C.S. Chem. Comm.*, 1972, 972.
[10] Y. Schouwstra, *Acta Cryst.*, 1972, **B28**, 2217; J. L. Derissen, H. J. Endeman, and A. F. Peerdeman, *Acta Cryst.*, 1968, **B24**, 1349; J. A. Kanters, J. Kroon, P. T. Beurskens, and J. A. Vliegenthart, *Acta Cryst.*, 1966, **21**, 990.

sum of the two C–O bond distances is 2.515 and 2.523 Å for the H_2M residue and 2.498 and 2.511 Å for the HM^- residue, in agreement with the foregoing observation.
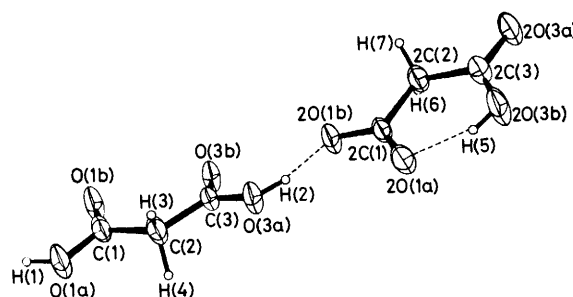

FIGURE 1 Lithium trihydrogen dimalonate showing the atom numbering system. Note the internal hydrogen bond from 2O(3b) to 2O(1a) in the malonic acid ion

The C–OH bond distance in HM^- is slightly shorter than that in H_2M.

Conformation of the Molecules.—Both the HM^- and H_2M residues are nearly planar. In HM^-, the two carboxy-groups which are intramolecularly hydrogen bonded are inclined to each other by 3.3°, but in H_2M, this angle is 9.4°. The equations to the planes through the atoms O(1a), O(1b), C(1), and C(2), and O(3a), O(3b), C(2), and C(3) are $0.041\ 7X - 0.612\ 5Y - 0.273\ 5Z = 1.349$, and $0.814\ 9X - 0.476\ 5Y - 0.329\ 8Z = -1.476$ (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, and X, Y, and Z are the Cartesian coordinates in Å). The corresponding equations to the two carboxy-groups in HM^- are $0.573\ 7X - 0.747\ 1Y - 0.335\ 7Z = -2.706$, and $0.538\ 2X - 0.784\ 0Y - 0.309\ 2Z = -2.640$. The near-coplanarity of the carboxy-groups in H_2M is rather surprising in view of the expected steric hindrance between them.[12] In malonic acid,[12] one carboxy-group, but not the other, is twisted almost at right angles to the plane of the three central carbon atoms. In the malonate ions (KHM,[1] $NaHM$,[2] and Li_2M [13]) with no intramolecular hydrogen bonding, the two carboxy-groups are mutually twisted by 9.5, 61.4, and 48.5°. The nearest approach of the two oxygen atoms [O(1b) · · · O(3b) 2.763(3) Å] in the H_2M

TABLE 4

Hydrogen bonds in LiH_3M_2; distances (Å), angles (°)

D–H · · · A	H · · · A	D · · · A	D–H · · · A
2O(3b)–H(5) · · · 2O(1a)	1.73(5)	2.481(3)	153(5)
O(1a)–H(1) · · · 2O(3a^IV)	1.77(5)	2.655(4)	175(5)
O(3a)–H(2) · · · 2O(1b)	1.63(4)	2.575(3)	167(4)

D is the donor, and A the acceptor atom. For symmetry code, see Table 5.

residues is nearly equal to the sum of the van der Waals' radii for carbonyl oxygens in directions parallel to the bond [14] (1.35 and 1.63 Å are the values for radii parallel end perpendicular to the bonds).

[11] L. J. Monojlović and J. C. Speakman, *J. Chem. Soc. (A)*, 1967, 971.
[12] J. A. Goedkoop and C. H. Macgillavry, *Acta Cryst.*, 1957, **10**, 125.
[13] M. Soriano-Garcia and R. Parthasarathy, to be published.
[14] A. Bondi, *J. Phys. Chem.*, 1964, **68**, 441.

Hydrogen Bonding.—The hydrogen bonding observed in LiH_3M_2 (Figure 2, Table 4) is quite similar to that in

The HM^- ion in LiH_3M_2 is linked on either side to one MH_2 residue by the two intermolecular hydrogen bonds.
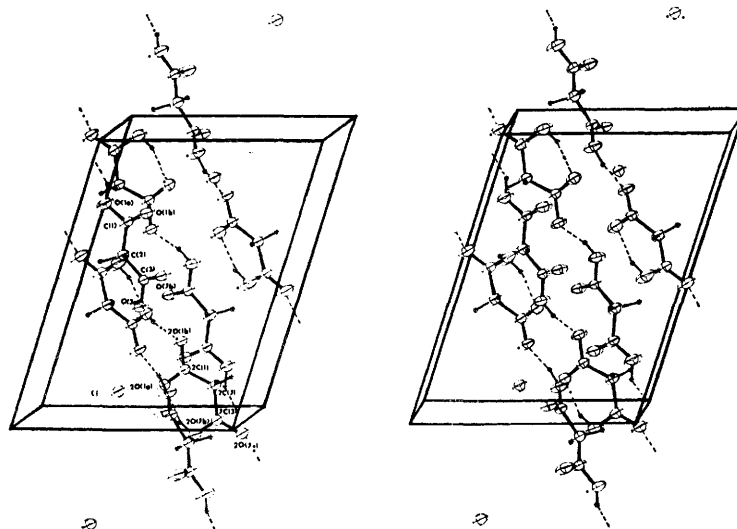

FIGURE 2 A stereoview of the hydrogen bonding and packing

KH_3M_2 (ref. 9). There are three short and unsymmetrical hydrogen bonds in these structures, of which

TABLE 5

Lithium environment

(a) Distances (Å)

$Li-O(1b^{III})$	1.978
$Li-O(3b^{III})$	2.042
$Li-2O(1a^I)$	1.977
$Li-2O(1b^{II})$	2.010

(b) Angles (°)

$O(1b^{III})-Li-O(3b^{III})$	86.8
$O(1b^{III})-Li-2O(1a^I)$	108.0
$O(1b^{III})-Li-2O(1b^{II})$	100.0
$O(3b^{III})-Li-2O(1a^I)$	97.8
$O(3b^{III})-Li-2O(1b^{II})$	150.2
$2O(1a^I)-Li-2O(1b^{II})$	107.4

Roman numeral superscripts denote the following equivalent positions relative to the reference molecule at x, y, z:

I $1 - x, -y, 1 - z$ III $1 - x, -\frac{1}{2} + y, -\frac{1}{2} + z$

II $x, -\frac{1}{2} + y, -\frac{1}{2} + z$ IV $-1 + x, y, -1 + z$

the intramolecular hydrogen bond in the HM^- residue is very short. This intramolecular hydrogen bond in LiH_3M_2 is shorter (by 0.03 Å) than the corresponding bond in KH_3M_2, but not as short as such intramolecular hydrogen bonds in maleate ions.[15] Both the intermolecular hydrogen bonds in LiH_3M_2 are longer than the corresponding bonds in KH_3M_2.

Similarly, the MH_2 residue is linked on either side to HM^- giving rise to an infinite-chain structure approximately along the [101] direction. This packing of the neutral and charged species is quite different from that of potassium trihydrogen disuccinate where 'the acid anions form an infinite chain to which the neutral molecules are attached as festoons'.[16] The infinite chains in LiH_3M_2 are linked by Li^+ ions which are co-ordinated to four oxygens: $O(1b^{III})$, $O(3b^{III})$, $2O(1a^I)$, and $2O(1b^{II})$. The angles and distances involved are given in Table 5. The lithium ion has two oxygen neighbours from the same HM^- residue which form an approximate tetrahedron around the lithium ion. The mean $Li \cdots O$ distance is 2.00 Å and agrees well with the sum of the ionic radii of lithium and oxygen (2.00 Å) obtained from the values given by Pauling.[17] The four-fold co-ordination of lithium has also been found in its salts of other carboxylic and dicarboxylic acids.[13,18,19] There is a second $Li-O$ distance of 2.208 Å to atom $O(3b^{II})$.

[15] M. N. G. James and G. J. B. Williams, *Acta Cryst.*, 1974, **B30**, 1249.

[16] R. S. Dunlop and J. C. Speakman, *Z. Krist.*, 1973, **138**, 100.

[17] L. Pauling, 'The Nature of the Chemical Bond,' Cornell University Press, Ithaca, New York, 1960.

[18] W. G. Town and R. W. H. Small, *Acta Cryst.*, 1973. **B29**, 1950.

[19] W. Gonschorek and H. Küppers, *Acta Cryst.*, 1975, **B31**, 1068.