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CRYSTAL STRUCTURE OF AMMONIUM HYDROGEN MALONATE

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Crystal structure of ammonium hydrogen malonate*

198 1975

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Ammonium hydrogen malonate, $NH_4HC_3H_2O_4$, is monoclinic, space group $C2/c$, with cell dimensions at 22°: $a = 11.214(3)$, $b = 8.647(3)$, $c = 11.507(4)$ Å, $\beta = 107.29(2)°$; $Z = 8$, $D_x = 1.510(3)$ g cm^{-3}, $D_m = 1.51(1)$ g cm^{-3}. The structure was determined from x-ray diffraction data collected with an automatic diffractometer for 794 independent nonzero reflections, and the model was refined to $R = 0.040$. The two carboxyl groups lie in planes which are nearly perpendicular. They are linked by strong symmetrical hydrogen bonds [O–O = 2.488(3) and 2.476(3) Å], so that each can be regarded as half-ionized. Average bond lengths are C–O = 1.29, C=O = 1.23, C–C = 1.51, C–H = 1.05, N–H = 0.99 Å. The ammonium ion participates in four N–H···O hydrogen bonds with lengths from 2.80 to 2.99 Å.

I. INTRODUCTION

Recent developments in ^{13}C nuclear magnetic resonance spectroscopy make it possible to find the chemical shielding tensors of crystalline substances and to correlate the orientations of these tensors with respect to the molecular structure determined by x-ray diffraction. The results may give better understanding of the relation between electronic structure and magnetic shielding. If consistent results are found for the same groups in various crystals, then the NMR technique may be used with confidence as a probe of orientation in other phases. Pines and his co-workers have studied several carboxylic acids and salts for these purposes.[1]

In this paper we report the crystal structure of ammonium hydrogen malonate. We studied it by x-ray diffraction to complement the NMR study of Chang, Griffin, and Pines[1] in the article which follows. The combined study yields orientations for the tensors for carbon in the methylene group and in two independent carboxyl groups, and shows that the latter orientations are significantly affected by the nonequivalence of the oxygen atoms, one of which is involved in strong hydrogen bonding.

II. EXPERIMENTAL

Commerical "ammonium malonate" was recrystallized from water; this procedure invariably yields the acid salt, ammonium hydrogen malonate, rather than the neutral one.[2,3] A crystal with dimensions 0.20×0.12×0.08 mm was used for measurements with a Picker FACS-I automatic diffractometer using graphite-monochromatized Mo$K\alpha$ radiation ($\lambda = 0.70926$ Å for $K\alpha_1$). Unit cell dimensions $a = 11.214(3)$, $b = 8.647(3)$, $c = 11.507(4)$ Å, and $\beta = 107.29(2)°$ were determined by a least-squares refinement using the setting angles of 12 accurately centered reflections which were in the range $40° < 2\theta < 45°$. The $K\alpha_1$ and $K\alpha_2$ components were resolved. The temperature was 22 ± 1°. Intensities were measured by the θ–2θ scan technique for 2015 reflections in half the reciprocal sphere ($\pm h, +k, \pm l$) with $2\theta < 50°$. Averaging of equivalent reflections yielded 951 unique intensities of which 794 were greater than the standard deviation estimated from the counting statistics or the scatter of equivalent reflections, whichever gave the larger value. With an absorption coefficient $\mu = 0.96$ cm^{-1}, the absorption effect is almost negligible, and no correction was made. A series of azimuthal scans (rotation of the crystal about a scattering vector) showed a variation of the intensities less than 3%.

Preliminary photographic study, confirmed by the diffractometer measurements, showed monoclinic symmetry and the diffraction conditions $h + k = 2n$ for hkl and $l = 2n$ for $h0l$. The statistics of the normalized structure factors indicated centric symmetry. Accordingly, the space group was assumed to be $C2/c$, and this symmetry was confirmed by successful refinement of the structure.

The crystal structure was solved by direct methods using the MULTAN program[4] and refined by our full-matrix least-squares program. A Fourier synthesis using the phased normalized structure factors showed clearly all the carbon, oxygen, and nitrogen atoms. All the hydrogen atoms showed up after two consecutive difference Fourier syntheses.

Isotropic temperature factors were used for the hydrogen atoms and anisotropic temperature factors for the other atoms in the least-squares calculations. In the last cycle, no parameter shifted more than 0.03 times its estimated standard deviation. An extinction correc-

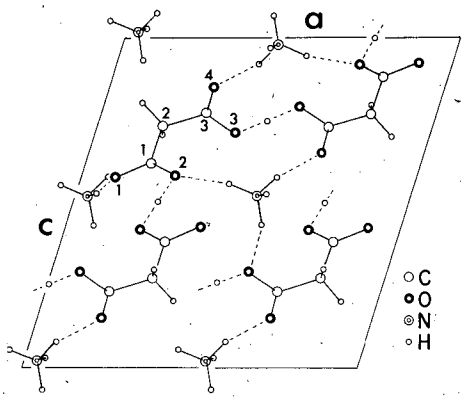

FIG. 1. Crystal structure of ammonium hydrogen malonate, viewed down the b axis. The numbers indicate how the carbon and oxygen atoms are designated in the tables. For clarity, only about half the contents of the unit cell are shown. Hydrogen bonds are indicated by broken lines.

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TABLE I. Observed structure factors, standard deviations, and values of $|F_0| - |F_c|$.

OBSERVED STRUCTURE FACTORS, STANDARD DEVIATIONS, AND DIFFERENCES (X10.0) FOR
AMMONIUM HYDROGEN MALONATE F(0,0,0) = 2562
SG = ESTIMATED STANDARD DEVIATION OF FOB. DEL = /FOB/-/FCA/. * INDICATES ZERO WEIGHTED DATA.

K	FOB	SG	DEL
H,L=	0,	0	
2	551	11	30
4	180	4	-5
6	63	2	0
8	35	2	2
10	9	15	4*
H,L=	0,	1	
2	269	6	5
4	33	2	1
6	25	2	-5
8	42	3	-1
10	49	2	2
H,L=	0,	3	
2	627	15	32
4	185	4	-8
6	154	3	4
8	19	4	-0
10	33	6	1
H,L=	0,	4	
0	25	2	-3
2	13	4	1
4	311	7	2
6	94	2	-1
8	111	3	0
H,L=	0,	5	
2	141	3	-3
4	157	3	4
6	52	2	2
8	57	2	-1
H,L=	0,	6	
0	234	5	1
2	187	4	4
4	79	2	-1
6	138	3	-0
8	43	3	0
H,L=	0,	7	
2	80	2	-5
4	38	2	-2
6	44	2	-4
8	13	9	12
H,L=	0,	8	
0	83	2	1
2	35	2	7
4	37	2	-2
6	47	2	-2
8	27	4	1
H,L=	0,	9	
2	20	5	-3
4	66	2	-1
6	30	2	1
H,L=	0,	10	
0	26	3	-7
2	30	2	-2
4	28	3	1
6	13	29	0*
H,L=	0,	11	
2	35	2	-7
4	10	16	-6*
H,L=	0,	12	
0	10	15	-2*
2	29	3	-4
4	18	3	3
H,L=	1,	-13	
1	11	20	-13*
H,L=	1,	-12	
1	14	17	3*
3	43	3	5
H,L=	1,	-11	
1	55	2	2
3	85	3	1*
5	13	20	4*
H,L=	1,	-10	
1	7	20	-0*
3	30	4	-3
5	31	4	3
H,L=	1,	-9	
1	44	4	-4
3	45	2	-2
5	100	3	-4
7	47	5	-4
H,L=	1,	-8	
1	168	4	-1
3	73	2	0
5	37	2	0
7	38	3	1
H,L=	1,	-7	
1	174	4	-0
3	20	5	-2
5	53	2	-3
7	58	3	-2
H,L=	1,	-6	
1	179	4	-1
3	34	6	3
5	57	2	-2
7	20	4	3
9	12	14	6*
H,L=	1,	-5	
1	303	6	4
3	21	2	-1
5	94	3	-5
7	96	2	-2
9	22	13	0
H,L=	1,	-4	
1	352	8	6
3	46	2	1
5	41	3	-8
7	43	2	0
9	23	9	4
H,L=	1,	-3	
1	6	20	-5*
3	304	8	4
5	64	2	-5
7	41	2	-2
9	46	2	1
H,L=	1,	-2	
1	29	3	8
3	177	4	-6
5	190	4	-1
7	48	2	1
9	38	46	-15*
H,L=	1,	-1	
1	156	4	2
3	221	5	-2
5	128	3	4
7	142	3	1
9	56	9	6
H,L=	1,	0	
1	41	12	-11
3	150	3	-6
5	16	4	4
7	11	19	-2*
9	49	3	5
H,L=	1,	1	
1	78	2	-7
3	150	3	-4
5	130	3	-1
7	74	3	2
9	8	15	5*
H,L=	1,	2	
1	496	15	6
3	131	3	-4
5	38	4	1
7	74	4	1
9	118	5	2
H,L=	1,	3	
1	132	3	-8
3	108	2	8
5	69	3	-1
7	62	3	2
9	0	16	-8*
H,L=	1,	4	
1	14	14	3*
3	173	4	2
5	14	5	-6
7	81	2	1
9	10	14	4*
H,L=	1,	5	
1	91	2	4
3	59	2	-2
5	44	3	3
7	47	2	-3
H,L=	1,	7	
1	35	3	4
3	20	6	-3
5	104	3	-2
7	8	11	2*
H,L=	1,	8	
1	114	3	-5
3	58	2	-4
5	5	12	-2*
7	27	12	1
H,L=	1,	9	
1	59	2	1
3	24	4	-6
5	35	5	5
7	27	5	-2
H,L=	1,	10	
3	26	14	9
5	57	3	2
7	34	6	3
H,L=	1,	11	
1	48	3	6
3	15	13	3
5	10	14	1*
H,L=	1,	12	
1	48	4	3
3	17	20	-0*
H,L=	2,	-13	
2	35	5	3
H,L=	2,	-12	
0	41	7	-3
2	74	8	-4
4	27	3	-1
H,L=	2,	-11	
0	31	6	-5
2	66	2	6
4	62	2	-1
6	69	2	-3
8	20	20	2*
H,L=	2,	-7	
2	52	3	2
4	135	4	-0
6	47	3	-1
8	72	2	4
H,L=	2,	-6	
0	374	9	25
H,L=	2,	-5	
2	8	9	-2*
4	26	2	4
6	0	11	-4*
H,L=	2,	-4	
0	56	4	5
2	31	4	1
H,L=	2,	-3	
0	15	18	5*
2	56	2	4
H,L=	2,	-2	
1	84	4	0
3	53	3	0
H,L=	2,	-1	
5	14	13	-10
7	21	23	2*
H,L=	2,	0	
1	56	3	-0
3	142	3	3
5	18	21	-8*
7	6	17	-8*
H,L=	2,	1	
1	12	15	-7*
3	30	5	8
5	13	22	-9*
H,L=	2,	2	
1	17	20	8*
3	34	4	-12
H,L=	2,	3	
1	16	19	13*
H,L=	2,	4	
1	161	5	2
H,L=	2,	5	
1	77	6	2*
1	110	2	-3
1	105	3	0
2	142	3	-3
1	46	2	-1
1	30	9	-4
H,L=	2,	6	
1	46	2	-2
1	219	6	2
3	154	3	-1
5	50	3	2
7	42	4	-2
9	14	16	13*
H,L=	2,	7	
1	322	7	20
3	46	2	1
5	55	2	-1
7	33	9	-0
9	52	2	0
H,L=	2,	8	
1	248	7	0
3	198	6	2
5	211	5	0
7	18	3	5
9	73	2	1
H,L=	2,	9	
1	86	2	-3
3	91	2	3
5	26	2	-0
7	46	5	0
9	20	6	-2
H,L=	2,	10	
1	38	2	4
3	52	2	-2
5	47	5	3
7	28	5	2
9	13	16	-14*
H,L=	2,	11	
1	110	2	-3
3	105	3	0
5	33	2	-1
7	46	2	-1
9	30	9	-4
H,L=	2,	12	
1	31	2	-1
3	37	2	-1
5	24	2	-2
7	20	3	0
H,L=	2,	13	
1	91	4	-2
3	81	2	4
5	41	2	-1
7	11	16	8*
H,L=	2,	14	
1	58	2	-2
3	88	2	-3
5	61	3	-2
7	58	2	-3
H,L=	2,	15	
1	75	2	3
3	43	4	-4
5	22	4	-2
7	12	16	12*
H,L=	2,	16	
1	47	3	-1
3	23	4	-2
5	11	20	-1*
7	8	2	5
H,L=	3,	0	
1	30	4	-4
3	39	3	0
H,L=	3,	1	
1	12	15	10*
H,L=	3,	2	
2	77	3	2
H,L=	3,	3	
1	28	5	2
3	47	2	-1
5	21	8	1
7	33	5	2
H,L=	3,	4	
1	7	11	2*
3	49	2	-1
5	20	6	-9
7	89	2	0
H,L=	3,	5	
1	95	2	-1
3	16	6	-4
5	58	3	-9
7	28	5	2
H,L=	3,	6	
1	104	2	3
3	66	4	1
5	13	16	10*
7	49	5	9
H,L=	3,	7	
1	242	5	7
3	37	4	-1
5	131	3	1
7	116	3	1
H,L=	3,	8	
1	242	5	7
3	123	3	2
5	128	3	-2
7	131	3	1
H,L=	3,	9	
1	248	7	0
3	198	6	2
5	211	5	0
7	18	3	5
9	73	2	1
H,L=	3,	10	
1	86	2	-3
3	91	2	3
5	26	2	-0
7	46	5	0
9	20	6	-2
H,L=	3,	11	
1	38	2	4
3	52	2	-2
5	47	5	3
7	28	5	2
9	13	16	-14*
H,L=	3,	12	
1	110	2	-3
3	105	3	0
5	33	2	-1
7	46	2	-1
9	30	9	-4
H,L=	3,	13	
1	31	2	-1
3	37	2	-1
5	24	2	-2
7	20	3	0
H,L=	3,	14	
1	91	4	-2
3	81	2	4
5	41	2	-1
7	11	16	8*
H,L=	3,	15	
1	58	2	-2
3	88	2	-3
5	61	3	-2
7	58	2	-3
H,L=	3,	16	
1	75	2	3
3	43	4	-4
5	22	4	-2
7	12	16	12*
H,L=	3,	17	
1	47	3	-1
3	23	4	-2
5	11	20	-1*
7	8	2	5
H,L=	4,	0	
1	30	4	-4
3	39	3	0
H,L=	4,	1	
1	12	15	10*
H,L=	4,	2	
2	77	3	2
H,L=	4,	3	
1	28	5	2
3	47	2	-1
5	21	8	1
7	33	5	2
H,L=	4,	4	
1	7	11	2*
3	49	2	-1
5	20	6	-9
7	89	2	0
H,L=	4,	5	
1	95	2	-1
3	16	6	-4
5	58	3	-9
7	28	5	2
H,L=	4,	6	
1	104	2	3
3	66	4	1
5	13	16	10*
7	49	5	9
H,L=	4,	7	
1	242	5	7
3	37	4	-1
5	131	3	1
7	116	3	1
H,L=	4,	8	
1	242	5	7
3	123	3	2
5	128	3	-2
7	131	3	1
H,L=	4,	9	
1	248	7	0
3	198	6	2
5	211	5	0
7	18	3	5
9	73	2	1
H,L=	4,	10	
1	86	2	-3
3	91	2	3
5	26	2	-0
7	46	5	0
9	20	6	-2
H,L=	4,	11	
1	38	2	4
3	52	2	-2
5	47	5	3
7	28	5	2
9	13	16	-14*
H,L=	4,	12	
1	110	2	-3
3	105	3	0
5	33	2	-1
7	46	2	-1
9	30	9	-4
H,L=	4,	13	
1	31	2	-1
3	37	2	-1
5	24	2	-2
7	20	3	0
H,L=	4,	14	
1	91	4	-2
3	81	2	4
5	41	2	-1
7	11	16	8*
H,L=	4,	15	
1	58	2	-2
3	88	2	-3
5	61	3	-2
7	58	2	-3
H,L=	4,	16	
1	75	2	3
3	43	4	-4
5	22	4	-2
7	12	16	12*
H,L=	4,	17	
1	47	3	-1
3	23	4	-2
5	11	20	-1*
7	8	2	5
H,L=	5,	0	
1	30	4	-4
3	39	3	0
H,L=	5,	1	
1	12	15	10*
H,L=	5,	2	
2	77	3	2
H,L=	5,	3	
1	28	5	2
3	47	2	-1
5	21	8	1
7	33	5	2
H,L=	5,	4	
1	7	11	2*
3	49	2	-1
5	20	6	-9
7	89	2	0
H,L=	5,	5	
1	95	2	-1
3	16	6	-4
5	58	3	-9
7	28	5	2
H,L=	5,	6	
1	104	2	3
3	66	4	1
5	13	16	10*
7	49	5	9
H,L=	5,	7	
1	242	5	7
3	37	4	-1
5	131	3	1
7	116	3	1
H,L=	5,	8	
1	242	5	7
3	123	3	2
5	128	3	-2
7	131	3	1
H,L=	5,	9	
1	248	7	0
3	198	6	2
5	211	5	0
7	18	3	5
9	73	2	1
H,L=	5,	10	
1	86	2	-3
3	91	2	3
5	26	2	-0
7	46	5	0
9	20	6	-2
H,L=	5,	11	
1	38	2	4
3	52	2	-2
5	47	5	3
7	28	5	2
9	13	16	-14*
H,L=	5,	12	
1	110	2	-3
3	105	3	0
5	33	2	-1
7	46	2	-1
9	30	9	-4
H,L=	5,	13	
1	31	2	-1
3	37	2	-1
5	24	2	-2
7	20	3	0
H,L=	5,	14	
1	91	4	-2
3	81	2	4
5	41	2	-1
7	11	16	8*
H,L=	5,	15	
1	58	2	-2
3	88	2	-3
5	61	3	-2
7	58	2	-3
H,L=	5,	16	
1	75	2	3
3	43	4	-4
5	22	4	-2
7	12	16	12*
H,L=	5,	17	
1	47	3	-1
3	23	4	-2
5	11	20	-1*
7	8	2	5
H,L=	6,	0	
1	152	3	2
3	42	2	-2
5	20	2	1
7	73	3	0
H,L=	6,	1	
1	33	4	7
3	16	6	-4
5	48	3	-6
7	15	18	3*
H,L=	6,	2	
1	23	3	8
3	9	16	-3*
5	10	19	3*
H,L=	6,	3	
1	13	20	-10*
3	11	17	5*
5	27	9	11
H,L=	6,	4	
1	38	2	3
3	42	3	2
5	13	16	10*
7	11	13	5*
H,L=	6,	5	
1	28	3	-0
3	40	4	1
5	61	3	-2
7	45	7	-2
H,L=	6,	6	
1	21	4	-3
3	22	7	1
5	154	4	-1
7	11	13	5*
H,L=	6,	7	
1	21	5	-11
3	9	16	-3*
5	27	9	11
H,L=	6,	8	
1	9	12	-3*
3	11	14	0*
H,L=	6,	9	
1	54	3	2
3	32	4	1
H,L=	6,	-8	
1	76	2	2
3	48	3	-1
5	22	5	4
H,L=	6,	-7	
1	36	3	2
3	14	18	6*
5	58	4	6
H,L=	6,	-6	
1	16	13	16
3	138	3	-0
5	49	4	-4
H,L=	6,	-5	
1	38	2	4
3	48	3	-1
5	66	3	2
7	9	15	1*
H,L=	6,	-4	
1	28	3	-6
3	43	2	5
5	31	3	0
7	62	2	3
H,L=	6,	-3	
1	135	3	-1
3	140	4	1
5	38	9	2
7	65	4	4
H,L=	6,	-2	
1	17	10	6
3	45	2	-1
5	61	4	-2
7	45	7	-2
H,L=	6,	-1	
1	21	4	-3
3	22	7	1
5	154	4	-1
7	11	13	5*

TABLE III. Coordinates and isotropic thermal parameters for hydrogen atoms.

	x	y	z	$B(Å^2)$
H(1)	0.112(2)	0.005(2)	0.194(2)	3.1(5)
H(2)	0.195(2)	−0.134(3)	0.291(2)	2.7(4)
H(3)	0.250	0.250	0.500	9.1(13)
H(4)	0.500	−0.053(6)	0.250	9.3(12)
H(5)	0.045(5)	0.259(5)	0.548(4)	12.2(15)
H(6)	−0.073(3)	0.309(3)	0.428(3)	5.8(7)
H(7)	−0.083(3)	0.328(3)	0.574(2)	5.5(6)
H(8)	−0.064(4)	0.165(6)	0.525(3)	9.6(12)

For all data, $R = 0.052$. The standard deviation of an observation of unit weight was 1.22. For the nonhydrogen atoms we used the scattering factors given by Doyle and Turner.[5] For hydrogen we used the scattering factors calculated by Stewart, Davidson, and Simpson.[6] The spherical values were used for the two hydrogen atoms in the special positions, and the polar values were used for the others as described elsewhere.[7] The anomalous dispersion coefficients given by Cromer and Liberman[8] were included in our calculations. Table I gives a listing of F_0, its standard deviation, and $\Delta = |F_0| - |F_c|$.

III. RESULTS AND DISCUSSION

The final atomic parameters are listed in Tables II and III. Interatomic distances are given in Table IV and bond angles in Table V. The crystal structure is shown in Fig. 1.

The configuration of the malonate is similar to that found in malonic acid by Goedkoop and MacGillavry.[9] The planes of the two carboxyl groups are nearly perpendicular to each other. This configuration differs totally from that in most of the dicarboxylic acids and in potassium hydrogen malonate,[10] where the nonhydrogen atoms lie nearly in a plane. In the present compound, the malonate residue lies on a general position with two carboxyl groups geometrically almost identical although not related by symmetry. As in the potassium salt,[10] the malonate ions are connected in infinite chains by strong symmetric hydrogen bonds. In this case, half these bonds are on centers of inversion (O–O = 2.488(3) Å) and half are on twofold axes (O–O = 2.476(3) Å). The result is that the two crystallographically independent carboxyl groups are chemically equivalent, and each can be regarded as half-ionized. The bond distances clearly differentiate the carbonyl oxygen atoms (C–O = 1.232 or 1.222 Å) from those bonded to hydrogen (C–O = 1.283 or 1.287 Å).

TABLE IV. Interatomic distances (in Å).

C(1)–C(2)	1.508(3)	O(3)–H(4)	1.240(3)
C(2)–C(3)	1.510(2)	O(2)–O(2)	2.488(3)
C(1)–O(1)	1.232(2)	O(3)–O(3)	2.476(3)
C(1)–O(2)	1.283(2)	N–O(1)[a]	2.897(3)
C(3)–O(3)	1.287(2)	N–O(1)	2.939(3)
C(3)–O(4)	1.222(2)	N–O(2)	2.992(3)
C(2)–H(1)	1.07(2)	N–O(3)	2.901(3)
C(2)–H(2)	1.02(2)	N–O(4)	2.803(3)
N–H(5)	0.97(5)	O(1)–H(8)	2.05(5)
N–H(6)	1.03(3)	O(2)–H(5)	2.06(5)
N–H(7)	1.06(3)	O(3)–H(6)	1.90(3)
N–H(8)	0.90(5)	O(4)–H(7)	1.78(3)
O(2)–H(3)	1.244(1)		

[a]This neighbor is not hydrogen bonded.

TABLE V. Bond angles (in degrees).

O(1)–C(1)–O(2)	123.7(2)
O(1)–C(1)–C(2)	119.8(2)
O(2)–C(1)–C(2)	116.5(2)
C(1)–C(2)–C(3)	114.2(2)
O(3)–C(3)–O(4)	124.4(2)
O(3)–C(3)–C(2)	114.9(2)
O(4)–C(3)–C(2)	120.7(2)
H(1)–C(2)–C(1)	106(1)
H(1)–C(2)–C(3)	111(1)
H(2)–C(2)–C(1)	107(1)
H(2)–C(2)–C(3)	109(1)
H(1)–C(2)–H(2)	110(2)
H(5)–N–H(6)	112(5)
H(5)–N–H(7)	110(4)
H(5)–N–H(8)	100(5)
H(6)–N–H(7)	112(3)
H(6)–N–H(8)	118(4)
H(7)–N–H(8)	105(4)
O(2)–H(3)–O(2)	180
O(3)–H(4)–O(3)	174(5)
N–H(5)–O(2)	159(4)
N–H(6)–O(3)	162(2)
N–H(7)–O(4)	160(2)
N–H(8)–O(1)	169(4)

The hydrogen atoms of the ammonium ion are regular tetrahedral within two standard deviations. Nitrogen has five oxygen neighbors, from five different molecules, at distances between 2.80 and 3.00 Å. Four of these are located so as to participate in N–H . . . O hydrogen bonds, as depicted in Fig. 1.

The relatively low thermal parameters for H(1) and H(2) reflect the fact that they are rigidly attached to the backbone of the malonate ion. The hydrogen atoms in the hydrogen bonds are evidently less restricted in their motion. A reviewer raised the question of single or double potential minima for the protons in the short hydrogen bonds. The resolution of the diffraction data (terminated at $d = 0.84$ Å) does not permit one to distinguish motion in a single minimum (rms amplitude estimated as 0.3 Å) from disorder among two positions close together, each with a smaller amplitude of motion.

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[1]J. J. Chang, R. G. Griffin, and A. Pines, following paper, J. Chem. Phys. 62, 4923 (1975), and references cited therein.
[2]B. Finkelstein, Ann. Chem. 133, 338 (1865).
[3]L. McMaster, Am. Chem. J. 49, 294 (1913).
[4]G. Germain, P. Main, and M. M. Woolfson, Acta Crystallogr. A 27, 368 (1971).

[5]P. A. Doyle and P. S. Turner, Acta Crystallogr. A 24, 390 (1968).
[6]R. F. Stewart, E. R. Davidson, and W. T. Simpson, J. Chem. Phys. 42, 3175 (1965).
[7]D. H. Templeton, A. J. Olson, A. Zalkin, and L. K. Templeton, Acta Crystallogr. A 28, S252 (1972).
[8]D. R. Cromer and D. Liberman, J. Chem. Phys. 53, 1891 (1970).
[9]J. A. Goedkoop and C. H. MacGillavry, Acta Crystallogr. 10, 125 (1957).
[10]J. G. Sime, J. C. Speakmann, and R. Parthasarathy, J. Chem. Soc. A 1919 (1970).

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