

Table 2. Selected bond lengths (Å), bond angles (°) and torsion angles (°), with e.s.d.'s in parentheses

Sn1—Sn2	2.777 (1)	Range of Sn—C:	2.12 (1)–2.16 (1)
Sn2—Sn3	2.772 (1)		
C1—Sn1—C7	107.3 (4)	C37—Sn2—C42	106.0 (4)
C1—Sn1—C13	107.8 (4)	C37—Sn2—Sn3	110.0 (3)
C7—Sn1—C13	104.6 (4)	C42—Sn2—Sn3	109.4 (3)
C1—Sn1—Sn2	110.8 (3)	Sn2—Sn3—C19	111.7 (3)
C7—Sn1—Sn2	113.0 (3)	Sn2—Sn3—C25	113.2 (3)
C13—Sn1—Sn2	112.9 (3)	Sn2—Sn3—C31	110.8 (3)
Sn1—Sn2—Sn3	111.31 (3)	C19—Sn3—C25	106.5 (4)
Sn1—Sn2—C37	108.3 (3)	C19—Sn3—C31	106.4 (4)
Sn1—Sn2—C42	111.7 (3)	C25—Sn3—C31	107.9 (4)
C1—Sn1—Sn2—Sn3	179.3 (3)	Sn1—Sn2—Sn3—C25	−60.0 (3)
C7—Sn1—Sn2—Sn3	−60.3 (2)	Sn1—Sn2—Sn3—C31	178.6 (3)
C13—Sn1—Sn2—Sn3	58.2 (3)	C37—C38—C39—N1	180 (1)
Sn1—Sn2—Sn3—C19	60.2 (3)	C42—C43—C44—N2	76 (1)

[2.770 (1) Å; Preut, Haupt & Huber, 1973] and are only slightly shorter than those in *tert*-Bu<sub>2</sub>Sn(SnPh<sub>3</sub>)<sub>2</sub> [2.801, 2.795 Å; Adams & Dräger, 1987] and lie in the range generally observed for polytin species without special steric demands of the substituents (2.75–2.83 Å; Puff *et al.*, 1989). The Sn—C distances do not differ significantly [average 2.14 (3) Å] and are quite normal.

With respect to the Sn1—Sn2 and Sn2—Sn3 bonds, respectively, the six substituents at both tin atoms adopt in each case a nearly perfect staggered conformation. This is in agreement with the general existence of an all-*trans* conformation of the Sn<sub>n</sub> units observed for a series of linear organo-substituted polystannanes (Adams & Dräger, 1987). The three phenyl rings attached to one Sn atom are twisted in a propeller-like manner. Looking from Sn1 to Sn3, the six phenyl rings are perfectly eclipsed with regard to their Sn—C bonds. Surprisingly, the dimethylaminopropyl groups exhibit different conformations. As can be seen from Fig. 1 and Table 2,

the chain C37—N1 adopts an extended all-*trans* conformation whereas in the chain C42—N2 a *gauche* conformation is adopted.

Within the crystal lattice the molecules are separated by normal van der Waals distances.

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## Structure of Methylammonium Hydrogen Malonate (I) and Methylammonium Malonate (II)

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**Abstract.** (I), CH<sub>6</sub>N<sup>+</sup>.C<sub>3</sub>H<sub>3</sub>O<sub>4</sub><sup>−</sup>, *M<sub>r</sub>* = 135.12, monoclinic, *P*2<sub>1</sub>/*c*, *a* = 8.017 (1), *b* = 9.245 (1), *c* =

8.582 (1) Å, β = 92.78 (1)°, *V* = 635.3 (2) Å<sup>3</sup>, *T* = 293 (2) K, *D<sub>m</sub>* = 1.39 (2), *D<sub>x</sub>* = 1.413 g cm<sup>−3</sup>, *Z* = 4, *F*(000) = 288, Mo *K*α radiation, λ = 0.71069 Å, μ = 1.187 cm<sup>−1</sup>, final *R* = 0.033 and *wR* = 0.031 for 1191 observed reflections. (II), 2CH<sub>6</sub>N<sup>+</sup>.C<sub>3</sub>H<sub>2</sub>O<sub>4</sub><sup>2−</sup>, *M<sub>r</sub>* = 166.18, monoclinic, *P*2<sub>1</sub>/*c*, *a* = 9.185 (1), *b* =

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11·225 (1),  $c = 8·810(1) \text{ \AA}$ ,  $\beta = 97·05(1)^\circ$ ,  $V = 901·5(3) \text{ \AA}^3$ ,  $T = 293(2) \text{ K}$ ,  $D_m = 1·23(2)$ ,  $D_x = 1·224 \text{ g cm}^{-3}$ ,  $Z = 4$ ,  $F(000) = 360$ , Mo  $K\alpha$  radiation,  $\lambda = 0·71069 \text{ \AA}$ ,  $\mu = 0·979 \text{ cm}^{-1}$ , final  $R = 0·034$  and  $wR = 0·038$  for 1289 observed reflections. In methylammonium hydrogen malonate asymmetric intermolecular hydrogen bonds [ $2·544(1) \text{ \AA}$ ] link the non-planar hydrogen malonate groups in chains that are fixed in a three-dimensional network by O—N hydrogen bonds ranging from  $2·799(1)$  to  $2·990(1) \text{ \AA}$ . Methylammonium groups in methylammonium malonate take part in the hydrogen-bonding system to the malonate ion [ $2·735(2)$ – $2·810(2) \text{ \AA}$ ].

**Introduction.** The structures of methylammonium hydrogen malonate and of methylammonium malonate were determined as part of a systematic investigation into the influence of cations of various sizes and shapes on the conformation of the hydrogen malonate group and hydrogen-bonding scheme. The hydrogen malonate ion assumes, in its crystallized acid salts, various conformations and engages in different types of hydrogen bonds. In potassium hydrogen malonate (Sime, Speakman & Parthasarathy, 1970) it has  $C_{2v}$  symmetry and is nearly planar, and in the ammonium and sodium salts the carboxylate planes are perpendicular to each other (Chapuis, Zalkin & Templeton, 1975; Rao & Parthasarathy, 1974). In all these salts the hydrogen malonate moieties form infinite chains by means of intermolecular hydrogen-bond connections. In the 'superacid' salts of lithium and potassium (Soriano-Garcia & Parthasarathy, 1978; Currie, 1972), as well as in guanidinium hydrogen malonate (Djinović, Golič, Hadži & Orel, 1988), 4-picolinium hydrogen malonate and benzylammonium hydrogen malonate (Djinović, Golič & Leban, 1990), planar hydrogen malonate groups stabilized with short intramolecular hydrogen bonds are found.

The variety of conformations and hydrogen-bonding schemes observed in various solid hydrogen malonates makes an investigation of the factors affecting the structure of hydrogen malonates of interest.

**Experimental.** Crystals of the title compounds prepared from an aqueous solution containing portions of malonic acid and methylamine in 1:1 and 1:2 ratios, respectively. Densities determined by flotation. Unit-cell parameters and intensity data obtained on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated Mo  $K\alpha$  radiation.

(I). Crystal size  $0·30 \times 0·27 \times 0·44 \text{ mm}$ . Cell dimensions refined by least-squares fitting of 75 centred reflections in the range  $9 < \theta < 15^\circ$  using Mo  $K\alpha_1$  radiation ( $0·70920 \text{ \AA}$ ). Data-collection pa-

rameters:  $\omega$ - $2\theta$  scan, max. scan time 60 s, scan width =  $(0·8 + 0·3 \tan \theta)^\circ$ , aperture =  $(2·4 + 0·9 \tan \theta) \text{ mm}$ . 7563 reflections measured to  $(\sin \theta / \lambda)_{\max} = 0·7027 \text{ \AA}^{-1}$ ;  $-11 \leq h \leq 11$ ,  $-12 \leq k \leq 12$ ,  $-12 \leq l \leq 12$ . Orientation control monitored every 300 reflections, standard reflections measured every 7500 s of scanning time (423, 241, 162) did not show any significant change in intensity (1·7%). Among 1958 unique reflections 1191 considered as observed [ $I > 3·0\sigma(I)$ ],  $R_{\text{int}} = 0·017$  after merging for  $P2_1/c$  space group.

(II). Crystal size  $0·65 \times 0·37 \times 0·73 \text{ mm}$ . Cell dimensions refined by least-squares fitting of 75 centred reflections monitored in the range  $9 < \theta < 15^\circ$  using Mo  $K\alpha_1$  radiation ( $0·70930 \text{ \AA}$ ). Data-collection parameters:  $\omega$ - $2\theta$  scan, max. scan time 60 s, scan width =  $(0·7 + 0·3 \tan \theta)^\circ$ , aperture =  $(2·4 + 0·9 \tan \theta) \text{ mm}$ . 9496 reflections measured to  $(\sin \theta / \lambda)_{\max} = 0·7027 \text{ \AA}^{-1}$ ;  $-12 \leq h \leq 12$ ,  $-15 \leq k \leq 15$ ,  $-12 \leq l \leq 12$ . Orientation control monitored every 600 reflections, standard reflections measured every 8000 s of scanning time (414, 341, 124) did not show any significant change in intensity (1·4%). After merging for  $P2_1/c$  space group 2605 unique reflections ( $R_{\text{int}} = 0·018$ ) of which 1289 considered as observed [ $I > 3·0\sigma(I)$ ].

The structures were solved by direct methods using *MULTAN80* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) system of computer programs. All non-H atoms were located from the initial  $E$  map; H atoms were revealed from a difference Fourier map. Least-squares refinement for non-H atoms, isotropic for H atoms, using the *XRAY76* (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976) system.

(I): empirical weighting function for  $w = 30 \times W_f \times W_s$ , where  $W_f(|F_o| < 3·1) = (|F_o|/3·1)^{1·0}$ ,  $W_f(|F_o| > 11·0) = (11·0/|F_o|)^{1·0}$ ,  $W_f(3·1 \leq |F_o| \leq 11·0) = 1·0$ ,  $W_s(\sin \theta < 0·39) = (\sin \theta / 0·39)^{4·0}$ ,  $W_s(\sin \theta > 0·50) = (0·50/\sin \theta)^{2·0}$ ,  $W_s(0·39 \leq \sin \theta \leq 0·50) = 1·0$  applied to keep  $\sum w(\Delta F)^2$  uniform over ranges of  $\sin \theta / \lambda$  and  $|F_o|$ . Refinement converged to  $R = 0·033$  and  $wR = 0·031$  for 118 parameters and 1355 contributing reflections including observed and less-thans for which  $|F_c| > |F_o|$ .  $(\text{Shift}/\text{e.s.d.})_{\max} = 0·005$ ,  $(\text{shift}/\text{e.s.d.})_{\text{av}} = 0·0007$ ,  $S = 0·62$ , excursions in final difference Fourier map within  $0·31$  and  $-0·22 \text{ e \AA}^{-3}$ .

(II): inspection of  $F_o$  and  $F_c$  values indicated a correction for secondary extinction [ $g = 11·2(4) \times 10^3$ ; Larson, 1967]. Empirical weighting function for  $w = 11 \times W_f \times W_s$ , where  $W_f(|F_o| < 4·3) = (|F_o|/4·3)^{0·3}$ ,  $W_f(|F_o| > 10·0) = (10·0/|F_o|)^{0·3}$ ,  $W_f(4·3 \leq |F_o| \leq 10·0) = 1·0$ ,  $W_s(\sin \theta < 0·39) = (\sin \theta / 0·39)^{3·3}$ ,  $W_s(\sin \theta > 0·50) = (0·50/\sin \theta)^{1·0}$ ,  $W_s(0·39 \leq \sin \theta \leq 0·50) = 1·0$  applied to keep  $\sum w(\Delta F)^2$  uniform over ranges of  $\sin \theta / \lambda$  and  $|F_o|$ . Refinement converged to

$R = 0.034$  and  $wR = 0.038$  for 157 parameters and 1645 contributing reflections including observed and less-thans for which  $|F_o| > |F_c|$ . (Shift/e.s.d.)<sub>max</sub> = 0.36, (shift/e.s.d.)<sub>av</sub> = 0.005,  $S = 1.12$ , excursions in final difference Fourier map within 0.35 and  $-0.19 \text{ e } \text{Å}^{-3}$ .

Atomic scattering factors for H atoms were taken from Stewart, Davidson & Simpson (1965), and for other neutral atoms from Cromer & Mann (1968), and dispersion corrections from Cromer & Liberman (1970). All calculations were performed on a DEC-10 computer at RCU-Ljubljana.

**Discussion.** Fractional coordinates and  $U_{eq}$  (Hamilton, 1959) values along with their e.s.d.'s are listed in Table 1.\* Interatomic distances and angles are presented in Table 2. Figs. 1 and 2 represent molecular packings of the title compounds. Fig. 3 shows the O...N hydrogen-bonding scheme in methylammonium malonate.

Bond distances and angles in both compounds are within the limits of expected values. The C—C bond lengths in the hydrogen malonate group of methylammonium hydrogen malonate are different: 1.506 (1) and 1.530 (1) Å. The shorter bond is adjacent to the non-ionized carboxylate group and *vice versa*. A similar pattern has been observed in other acid salts: potassium DL-methyl succinate (Schouwstra, 1972), aminomalonic acid (Kanters, Kroon, Beurskens & Vliegthart, 1966). In methylammonium malonate the C—C bond lengths are similar: 1.525 (2) and 1.524 (2) Å which corresponds to the fact that both carboxylate groups are ionized. The sum of the angles around the C(1) and C(3) atoms in methylammonium hydrogen malonate [360.0 (1) and 360.0 (1)°] as well as in methylammonium malonate [360.0 (1) and 360.0 (1)°] indicate that the carboxylate C atoms are  $sp^2$  hybridized. The conformation of the hydrogen malonate group in methylammonium hydrogen malonate is similar to those found in other hydrogen malonate salts forming intermolecular hydrogen bonds: the two carboxyl groups are nearly perpendicular to each other, one group being roughly parallel to the plane defined by the three C atoms. This arrangement of the carboxyl groups is due to the steric hindrance between O atoms of one carboxyl group and the proximal O atoms of the other. The torsion angles C(1)—C(2)—C(3)—O(3) and O(1)—C(1)—C(2)—C(3) are 18.3 (1) and  $-82.3$  (1)°, respectively. The conformation of the malonate ion in methylammonium

Table 1. *Atom coordinates* ( $\times 10^5$ ) *for non-H atoms and* ( $\times 10^3$ ) *for H atoms and equivalent isotropic temperature factors* (Hamilton, 1959) ( $\text{Å}^2 \times 10^5$ ) *for non-H atoms and* ( $\text{Å}^2 \times 10^3$ ) *for H atoms with their e.s.d.'s in parentheses*

	x	y	z	$U_{eq}$
<b>Methylammonium hydrogen malonate</b>				
O(1)	47670 (9)	15600 (8)	41108 (9)	315 (3)
O(2)	74745 (11)	10563 (8)	39471 (11)	380 (4)
O(3)	58538 (11)	43424 (8)	25731 (9)	341 (4)
O(4)	72849 (12)	57304 (8)	42949 (10)	381 (4)
C(1)	63578 (12)	18604 (9)	43130 (10)	250 (4)
C(2)	67265 (13)	33174 (9)	50354 (10)	268 (4)
C(3)	66286 (11)	45642 (9)	38628 (10)	241 (4)
N	22699 (11)	33276 (9)	23778 (12)	324 (4)
C(4)	4542 (17)	34374 (22)	24215 (25)	598 (9)
H(1)	461 (3)	76 (3)	357 (3)	58 (6)
H(2)	782 (2)	329 (2)	550 (2)	42 (4)
H(3)	595 (2)	350 (2)	579 (2)	38 (4)
H(4)	257 (3)	257 (3)	186 (3)	51 (5)
H(5)	272 (3)	335 (3)	326 (3)	53 (5)
H(6)	263 (3)	407 (3)	189 (3)	49 (5)
H(7)	23 (5)	263 (5)	287 (5)	87 (9)
H(8)	8 (6)	350 (5)	135 (6)	103 (11)
H(9)	26 (5)	435 (5)	305 (5)	95 (10)
<b>Methylammonium malonate</b>				
O(1)	105587 (12)	16679 (14)	22358 (15)	640 (7)
O(2)	87557 (13)	12131 (19)	4786 (14)	772 (9)
O(3)	58275 (11)	14489 (10)	28154 (16)	563 (6)
O(4)	64778 (11)	-2425 (10)	18334 (16)	551 (6)
C(1)	92735 (13)	13152 (12)	18204 (16)	380 (6)
C(2)	83755 (14)	9718 (14)	30986 (16)	424 (6)
C(3)	67695 (13)	7139 (11)	25449 (15)	354 (6)
N(1)	36714 (13)	88457 (11)	16550 (15)	410 (6)
C(4)	29998 (24)	92640 (22)	29805 (26)	649 (11)
N(2)	81276 (14)	80933 (13)	4656 (16)	449 (6)
C(5)	68529 (21)	73878 (19)	-1741 (24)	593 (9)
H(1)	846 (2)	162 (2)	387 (3)	58 (5)
H(2)	882 (3)	28 (2)	352 (3)	67 (6)
H(11)	689 (2)	105 (2)	912 (3)	48 (5)
H(12)	616 (2)	190 (2)	826 (2)	46 (4)
H(13)	552 (3)	80 (2)	837 (2)	49 (5)
H(14)	280 (4)	2 (4)	285 (5)	107 (11)
H(15)	788 (4)	117 (3)	695 (4)	97 (9)
H(16)	638 (4)	85 (4)	611 (5)	106 (11)
H(21)	216 (2)	132 (2)	912 (3)	49 (5)
H(22)	134 (2)	231 (2)	887 (3)	51 (5)
H(23)	137 (3)	174 (2)	25 (3)	61 (6)
H(24)	280 (4)	177 (3)	567 (4)	89 (8)
H(25)	365 (3)	213 (3)	432 (3)	75 (7)
H(26)	373 (3)	214 (3)	86 (4)	81 (7)

malonate can be compared to the arrangements of other neutral salts of malonic acid: lithium malonate dihydrate (Soriano-Garcia & Rao, 1983), sodium malonate dihydrate (Oskarsson, 1978), sodium malonate trihydrate (Soriano-Garcia & Parthasarathy, 1978), where the two carboxylate groups are again perpendicular to each other. The torsion angles describing this conformation are: O(2)—C(1)—C(2)—C(3) [ $-9.7$  (2)°] and C(1)—C(2)—C(3)—O(4) [73.1 (2)°].

The conformations of methylammonium ions in both compounds are close to staggered, which corresponds to the energy minimum. The same conformation can also be observed in methylamine (Atoji & Lipscomb, 1953) and in methylammonium hydrogen oxalate (Thomas, 1975). The methylammonium ions in methylammonium hydrogen malonate are hydrogen bonded to O atoms of the hydrogen malonate groups, O...N distances are 2.799 (1), 2.829 (1) and

\* Lists of structure factors, anisotropic thermal parameters and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53956 (20 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Interatomic distances (Å) and angles (°) with e.s.d.'s in parentheses*

## Methylammonium hydrogen malonate

O(1)—C(1)	1.309 (1)	C(1)—C(2)	1.506 (1)
O(2)—C(1)	1.217 (1)	C(2)—C(3)	1.530 (1)
O(3)—C(3)	1.259 (1)	N—C(4)	1.461 (2)
O(4)—C(3)	1.248 (1)		
H(1)—O(1)	0.88 (3)	H(5)—N	0.82 (3)
H(2)—C(2)	0.95 (2)	H(6)—N	0.86 (2)
H(3)—C(2)	0.93 (2)	H(7)—C(4)	0.86 (4)
H(4)—N	0.87 (3)	H(8)—C(4)	0.96 (5)
		H(9)—C(4)	1.02 (4)
O(2)—C(1)—O(1)	124.1 (1)	C(2)—C(3)—O(3)	117.6 (1)
C(2)—C(1)—O(1)	114.5 (1)	C(2)—C(3)—O(4)	116.6 (1)
C(2)—C(1)—O(2)	121.4 (1)	C(3)—C(2)—C(1)	113.6 (1)
O(4)—C(3)—O(3)	125.8 (1)		
H(3)—C(2)—H(2)	110 (2)	H(8)—C(4)—H(7)	115 (4)
H(5)—N—H(4)	112 (2)	H(9)—C(4)—H(7)	116 (4)
H(6)—N—H(4)	107 (2)	H(9)—C(4)—H(8)	114 (4)
H(6)—N—H(5)	107 (2)		

## Methylammonium malonate

O(1)—C(1)	1.256 (2)	C(1)—C(2)	1.525 (2)
O(2)—C(1)	1.224 (2)	C(2)—C(3)	1.524 (2)
O(3)—C(3)	1.240 (2)	N(1)—C(4)	1.463 (3)
O(4)—C(3)	1.255 (2)	N(2)—C(5)	1.468 (2)
C(2)—H(1)	1.00 (2)	N(1)—H(11)	0.81 (2)
C(2)—H(2)	0.94 (3)	N(1)—H(12)	0.85 (2)
N(1)—H(13)	0.85 (2)	N(2)—H(21)	0.82 (2)
N(2)—H(22)	0.84 (2)	N(2)—H(23)	0.85 (3)
C(4)—H(14)	0.87 (5)	C(5)—H(24)	0.90 (4)
C(4)—H(15)	0.95 (4)	C(5)—H(25)	0.97 (3)
C(4)—H(16)	0.94 (4)	C(5)—H(26)	0.92 (3)
O(2)—C(1)—O(1)	123.4 (1)	C(2)—C(3)—O(3)	118.9 (1)
C(2)—C(1)—O(1)	116.0 (1)	C(2)—C(3)—O(4)	117.5 (1)
C(2)—C(1)—O(2)	120.5 (1)	C(3)—C(2)—C(1)	113.7 (1)
O(4)—C(3)—O(3)	123.6 (1)		
H(1)—C(2)—H(2)	110 (2)	H(14)—C(4)—H(15)	110 (4)
H(11)—N(1)—H(12)	108 (2)	H(14)—C(4)—H(16)	110 (4)
H(11)—N(1)—H(13)	113 (2)	H(15)—C(4)—H(16)	108 (3)
H(12)—N(1)—H(13)	109 (2)	H(24)—C(5)—H(26)	110 (3)
H(21)—N(2)—H(22)	108 (2)	H(24)—C(5)—H(25)	113 (3)
H(21)—N(2)—H(23)	113 (2)	H(25)—C(5)—H(26)	113 (3)
H(22)—N(2)—H(23)	108 (2)		

2.990 (1) Å. There are two additional O atoms at distances shorter than the sum of the van der Waals radii [2.933 (1) and 3.019 (1) Å] but not hydrogen bonded to the N atom. Similar coordination is typical of the ammonium ion in ammonium hydrogen malonate (Chapuis, Zalkin & Templeton, 1975), where four O atoms are hydrogen bonded to the central N atom while the fifth O atom is at a distance of 2.897 (3) Å from it. Malonate ions in methylammonium malonate form a three-dimensional network by means of O···N hydrogen bonds. Each N atom is coordinated by three O atoms, the O···N distances being 2.735 (2), 2.760 (2), 2.760 (2) Å for N(1) and 2.742 (2), 2.772 (2) and 2.810 (2) Å for N(2). The fact that the O···N hydrogen bonds of the title compounds are shorter than the corresponding ones in the ammonium hydrogen malonate [2.939 (3), 2.992 (3), 2.901 (3), 2.803 (3) Å] could be explained by the positive inductive effect of the methyl substituent in the methylammonium ion. Shortening of the O···N hydrogen bonds with the increasing number of the methyl substituents has also been observed in the series of the hydrogen oxalate salts with ammonium

cations having the empirical formula (CH<sub>3</sub>)<sub>n</sub>NH<sub>4-n</sub><sup>+</sup>, n = 1, 2, 3 (Kuppers, 1973).

In methylammonium hydrogen malonate the hydrogen malonate groups are connected in chains parallel to the [010] direction by asymmetric intermolecular hydrogen bonds [2.544 (1) Å]. These hydrogen bonds are longer than the hydrogen bonds found in potassium hydrogen malonate [2.459 (5) Å] (Sime, Speakman & Parthasarathy, 1970), but can be compared to the asymmetric intermolecular hydrogen bond in sodium hydrogen malonate (Rao & Parthasarathy, 1974).

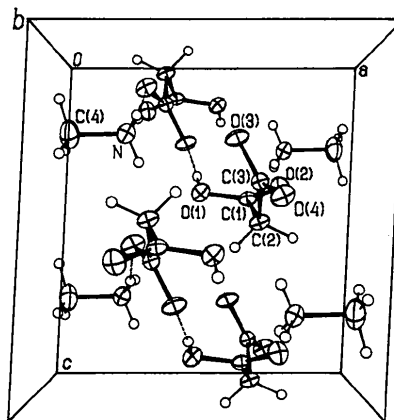


Fig. 1. ORTEP (Johnson, 1965) plot of the crystal packing of methylammonium hydrogen malonate as seen along the *b* axis showing O1···O3 and N···O4 hydrogen bonds.

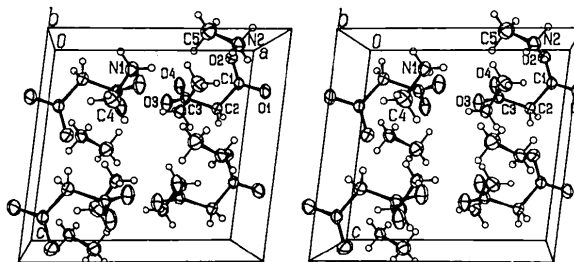


Fig. 2. Stereoscopic ORTEP (Johnson, 1965) plot of the crystal packing of methylammonium malonate as seen along the *b* axis.

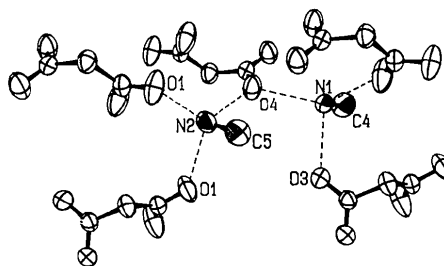


Fig. 3. Presentation of the O···N hydrogen-bonding scheme in methylammonium malonate.

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## Structure of 6-(4-Chlorobenzylidene)-2,3-dihydroimidazo[2,1-*b*]thiazol-5(6*H*)-one. Conformational Analysis of *Z* Isomers of 5-Benzylidenethiohydantoin Derivatives

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**Abstract.** C<sub>12</sub>H<sub>9</sub>ClN<sub>2</sub>OS, *M<sub>r</sub>* = 264.73, monoclinic, *P*2<sub>1</sub>/*n*, *a* = 6.837 (2), *b* = 12.053 (1), *c* = 14.251 (10) Å, β = 96.98 (3)°, *V* = 1165.6 (2) Å<sup>3</sup>, *Z* = 4, *D<sub>x</sub>* = 1.508 Mg m<sup>-3</sup>, λ(Cu *K*α) = 1.54178 Å, μ = 4.27 mm<sup>-1</sup>, *F*(000) = 544, room temperature. All available samples were twinned with *c*' = 28.502 (1) Å in the twin. The intensity data were collected on a twinned sample. 5044 reflections measured [*F* > 4σ(*F*)]; 1458 reflections used for structure solution. Final *R* = 0.043 for 1126 reflections with *F* > 4σ(*F*). The nearly planar molecule has a *Z* configuration. Molecular mechanics calculations for *Z* isomers of 5-(chloro-substituted)benzylidene-2-thiohydantoin derivatives with 1,2- or 2,3-dialkylation indicated some differences in the preferred orientations of the aromatic ring. These orientations depend on the Cl-substituent position and on the type of alkylation.

**Introduction.** To search for new compounds influencing the central nervous system we have examined annelated 2-thiohydantoin derivatives. Comparisons of physicochemical properties, stability and X-ray structure analysis results for 5,5-diphenyl-2-thiohydantoin (DPTH) derivatives have been performed (Kieć-Kononowicz, Zejc, Mikołajczyk, Zatorski, Karolak-Wojciechowska & Wieczorek, 1980, 1981; Kieć-Kononowicz, Zatorski & Karolak-Wojciechowska, 1989; Karolak-Wojciechowska, Mikołajczyk, Zatorski, Kieć-Kononowicz & Zejc, 1985). In the continuation of our studies we have investigated 5-(substituted)benzylidene-2-thiohydantoin derivatives of types (1) and (2) (Karakolak-Wojciechowska, Kwiatkowski & Kieć-Kononowicz, 1989; Kwiatkowski, Karolak-Wojciechowska & Kieć-Kononowicz, 1991). The derivatives of DPTH have shown sedative properties while the derivatives