The X-ray crystal diffraction study of the title compound confirmed the *Z* configuration for this diastereoisomer, as suggested by NMR spectroscopy. Similarly, the analysis of the crystal structure of this vinyl sulfoxide shows that it is a true racemate and not a conglomerate. The two molecules in the unit cell correspond to the two enantiomers *ZR* and *ZS*. The absolute configurations of the chiral sulfur are *R* and *S*.

The lengths of the S(15)—C(14) and S(15)—C(17) bonds [1·765 (2) and 1·778 (4) Å respectively] are practically the same, and comparable to those given in the literature for other vinyl sulfoxides (Tranqui & Fillion, 1972; Madesclaire, Roche & Carpy, 1988). The S(15)—O(16) distance [1·499 (2) Å] suggests that this bond is closer to a double bond than to a single bond. In addition, the angle between the planes containing the vinyl [C(1), C(7), C(13), C(14), S(15)] and sulfoxide [C(14), S(15), O(16)] groups is 78 (2)°, which rules out any delocalization of the π electrons of the S(15)—O(16) and C(13)—C(14) bonds.

The S(15) atom is placed at the 'center' of an irregular tetrahedron the base of which is formed by C(14), O(16) and C(17) and the fourth apex of which is the lone pair of the S atom.

The angle between the phenyl and pyridyl rings is 87 (2)°. The plane containing the vinyl group, *i.e.* C(1), C(7), C(13), C(14), S(15), is at an angle of 30 (2)° to the plane of the phenyl ring and at an angle of 70 (2)° to the plane of the pyridyl ring, which prevents conjugation.

Crystal cohesion is ensured by a dense three-dimensional network of van der Waals interactions, listed in Table 2.

The authors are indebted to Professor R. Chevalier (CRMP, Université Blaise Pascal, Clermont-Ferrand, France) for the use of the X-ray diffractometer and crystallographic facilities. We would like to express our special gratitude to Professor D. Avignant for his suggestions during data measurement and refinement procedures.

References

Busing, W. R., Martin, K. O. & Levy, H. A. (1962). *ORFLS*. Report ORNL-TM-305. Oak Ridge National Laboratory, Tennessee, USA.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

Madesclaire, M. (1986). *Tetrahedron*, **42**, 5459–5495.

Madesclaire, M., Roche, D. & Carpy, A. (1988). *C. R. Acad. Sci. Sér. B*, **306**, 891–896.

Madesclaire, M., Roche, D., Carpy, A. & Boucherle, A. (1982). *Arch. Pharm.* (*Weinheim, Ger.*), **315**, 741–748.

Main, P., Fiske, S. J., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1982). *MULTAN*11/82. *A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.

Roche, D., Madesclaire, M., Veschambre, H. & Fauve, A. (1988). *Synthesis*. Accepted.

Tranqui, D. S. & Fillion, H. (1972). *Acta Cryst.* **B28**, 3306–3315.

Acta Cryst. (1990). **C46**, 281–286

Structures of Benzylammonium Hydrogen Malonate (I) and 4-Picolinium Hydrogen Malonate (II)

By Kristina Djinović, Ljubo Golič and Ivan Leban

Department of Chemistry and Chemical Technology, Edvard Kardelj University, Ljubljana, POB 537, Yugoslavia

(*Received* 11 *January* 1989; *accepted* 18 *May* 1989)

Abstract. (I): $C_7H_{10}N^+.C_3H_3O_4^-$, $M_r = 211·22$, triclinic, $P\bar{1}$, $a = 5·455$ (1), $b = 8·788$ (2), $c = 11·060$ (4) Å, $\alpha = 83·67$ (2), $\beta = 86·18$ (3), $\gamma = 78·07$ (2)°, $V = 515·0$ (5) Å^3, $Z = 2$, $D_x = 1·362$, $D_m = 1·36$ (4) g cm^{-3}, Mo $K\alpha$ radiation, $\lambda = 0·71069$ Å, $\mu = 0·948$ cm^{-1}, $F(000) = 224$, $T = 293$ (2) K, final $R = 0·039$ and $wR = 0·041$ for 1328 observed reflections. (II): $C_6H_8N^+.C_3H_3O_4^-$, $M_r = 197·19$, monoclinic, $P2_1/n$, $a = 3·955$ (1), $b = 21·663$ (5), $c = 11·259$ (3) Å, $\beta = 99·33$ (2)°, $V = 951·9$ (8) Å^3, $Z = 4$, $D_x = 1·376$, $D_m = 1·35$ (2) g cm^{-3}, Mo $K\alpha$ radiation, $\lambda = 0·71069$ Å, $\mu = 1·022$ cm^{-1}, $F(000) = 416$, $T = 293$ (2) K, final $R = 0·039$ and $wR = 0·040$ for 848 observed reflections. Short asymmetrical intramolecular hydrogen bonds [2·430 (2) and 2·493 (3) Å for (I) and (II) respectively] stabilize the planar hydrogen malonate ions. Benzylammonium groups are linked to hydrogen malonate ions by three intermolecular hydrogen bonds of 2·912 (2), 2·874 (2) and 2·969 (2) Å while 4-picolinium ions are hydrogen bonded to hydrogen malonate moieties by only one short hydrogen bond [2·639 (3) Å].

0108-2701/90/020281-06$03.00

Introduction. The hydrogen malonate ion has been found to show various conformations in its acid salts. In sodium and ammonium hydrogen salts the carboxylate groups are nearly perpendicular to each other (Rao & Parthasarathy, 1974; Chapuis, Zalkin & Templeton, 1975) while hydrogen malonate groups are connected in chains by intermolecular hydrogen bonds. *Ab initio* calculations on the hydrogen malonate ion in vacuum show that a planar conformation assuming C_{2v} symmetry is the most probable, as it is stabilized by an intramolecular hydrogen bond (Merechan, Tomas & Nebot-Gil, 1984). A planar conformation with an asymmetric intramolecular hydrogen bond has been observed in guanidinium hydrogen malonate (Djinović, Golič, Hadži & Orel, 1988) and in 'superacid' salts of lithium and potassium (Soriano-García & Parthasarathy, 1978; Currie, 1972) while in the potassium acid salt, planar hydrogen malonate groups are connected by symmetric intermolecular hydrogen bonds (Sime, Speakman & Parthasarathy, 1970).

In the course of a systematic investigation of the influence of cations of various sizes and shapes on the conformation of the hydrogen malonate ion and hydrogen-bonding scheme we present the crystal and molecular structures of benzylammonium and 4-picolinium hydrogen malonate, where planar hydrogen malonate groups contain short asymmetric hydrogen bonds.

Experimental. Crystals of the title compounds were prepared by slow evaporation of acetonitrile solutions containing equimolar portions of malonic acid and benzylamine or 4-picoline. Densities of the substances determined by flotation (Wulf & Heigel, 1931). Space group and approximate cell constants from Weissenberg films. Data collected on an Enraf–Nonius CAD-4 diffractometer with graphite-monochromated Mo $K\alpha$ radiation.

(I): Crystal size $0{\cdot}97 \times 0{\cdot}04 \times 0{\cdot}58$ mm. Cell dimensions from least-squares treatment of 100 centered reflections in the range $10 < \theta < 15°$ using Mo $K\alpha_1$ radiation (0·70930 Å). Data-collection parameters: ω–2θ scan, max. scan time 60 s, scan width $= (0{\cdot}7 + 0{\cdot}3\tan\theta)°$, aperture $= (2{\cdot}4 + 0{\cdot}9\ \tan\theta)$mm. 4960 reflections measured to $[(\sin\theta)/\lambda]_{\max} = 0{\cdot}659\ \text{Å}^{-1}$, $-7 \le h \le 7$, $-11 \le k \le 11$, $-14 \le l \le 14$. Orientation control monitored after every 350 reflections, standard reflections measured every 10 000 s of scanning time ($1\bar{5}\bar{2}$, $1\bar{3}3$, $\bar{2}1\bar{6}$) did not show any significant change in intensity (−0·9%). After merging for $P\bar{1}$ 2480 unique reflections remained ($R_{\text{int}} = 0{\cdot}033$) of which 1328 were considered as observed $[I > 3{\cdot}0\sigma(I)]$.

Table 1. *Atom coordinates* ($\times 10^4$ *for non*-H *atoms*, $\times 10^3$ *for* H *atoms*) *and isotropic temperature factors* ($\times 10^4$ Å^2 *for non*-H *atoms*, $\times 10^3$ Å^2 *for* H *atoms*) *with their e.s.d.'s in parentheses for* (I)

U_{eq} defined according to Hamilton (1959).

	x	y	z	$U_{\text{eq}}/U_{\text{iso}}$
O(1)	4145 (3)	−1936 (1)	7424 (1)	568 (7)
O(2)	1382 (3)	−439 (1)	6234 (2)	692 (8)
O(3)	5043 (2)	3173 (1)	5877 (1)	549 (7)
O(4)	1808 (3)	2193 (1)	5452 (1)	627 (7)
C(1)	3385 (3)	−685 (1)	6848 (1)	407 (7)
C(2)	4784 (3)	639 (2)	6808 (2)	473 (8)
C(3)	3837 (3)	2121 (1)	5974 (1)	413 (7)
N	1699 (3)	6007 (1)	6251 (1)	444 (7)
C(11)	464 (3)	4319 (2)	8055 (1)	408 (7)
C(12)	−784 (4)	3104 (2)	8322 (2)	649 (11)
C(13)	−153 (5)	2024 (3)	9323 (3)	847 (14)
C(14)	1797 (5)	2114 (2)	10024 (2)	697 (12)
C(15)	3052 (4)	3307 (2)	9755 (2)	606 (10)
C(16)	2389 (4)	4416 (2)	8783 (2)	553 (9)
C(17)	−407 (3)	5535 (2)	7019 (2)	473 (8)
H(1)	118 (8)	43 (5)	590 (4)	91 (10)
H(2)	652 (6)	27 (4)	667 (3)	70 (7)
H(3)	482 (6)	89 (3)	765 (3)	69 (7)
H(12)	−221 (6)	307 (3)	784 (3)	70 (7)
H(13)	−116 (8)	126 (5)	956 (4)	97 (10)
H(14)	226 (6)	140 (4)	1073 (3)	78 (8)
H(15)	430 (5)	336 (3)	1025 (3)	61 (6)
H(16)	323 (6)	524 (4)	861 (3)	70 (7)
H(17)	−140 (6)	643 (4)	730 (3)	66 (7)
H(18)	−142 (5)	517 (3)	646 (2)	55 (6)
H(19)	243 (5)	650 (3)	665 (2)	50 (5)
H(20)	115 (4)	653 (3)	563 (2)	45 (5)
H(21)	282 (5)	517 (3)	601 (2)	48 (5)

The structure was solved by direct methods using *SHELXS*86 (Sheldrick, 1986). All non-H atoms obtained from the initial E map, the H atoms located from difference Fourier map. Least-squares refinement with anisotropic displacement parameters for non-H atoms and isotropic for H atoms. Empirical weighting function $w = 16{\cdot}0 W_f W_s$ where $W_f(|F_o| < 2{\cdot}4) = (|F_o|/2{\cdot}4)^{1{\cdot}2}$, $W_f(|F_o| > 4{\cdot}2) = (4{\cdot}2/|F_o|)^{3{\cdot}0}$, $W_f(2{\cdot}4 \le |F_o| \le 4{\cdot}2) = 1{\cdot}0$, $W_s(\sin\theta < 0{\cdot}37) = [(\sin\theta)/0{\cdot}37]^{4{\cdot}2}$, $W_s(\sin\theta > 0{\cdot}44) = [0{\cdot}44/(\sin\theta)]^{2{\cdot}5}$, $W_s(0{\cdot}37 \le \sin\theta \le 0{\cdot}44) = 1{\cdot}0$ applied to keep $\sum w(\Delta F)^2$ uniform over ranges of $(\sin\theta)/\lambda$ and $|F_o|$. Refinement converged to $R = 0{\cdot}039$ and $wR = 0{\cdot}041$ for 188 parameters and 1802 contributing reflections including observed and less-thans for which $|F_c| > |F_o|$. $(\text{Shift/e.s.d.})_{\max} = 0{\cdot}196$, $(\text{shift/e.s.d.})_{\text{av}} = 0{\cdot}009$, $S = 0{\cdot}559$, min. and max. heights in difference Fourier map −0·24 and 0·24 e Å^{-3}.

(II): Crystal size $0{\cdot}91 \times 0{\cdot}30 \times 0{\cdot}23$ mm. Cell dimensions from least-squares treatment of 75 centered reflections in the range $8 < \theta < 15°$ using Mo $K\alpha_1$ radiation (0·70930 Å). Data-collection parameters: ω–2θ scan, max. scan time 60 s, scan width $= (0{\cdot}8 + 0{\cdot}3\tan\theta)°$, aperture $= (2{\cdot}4 + 0{\cdot}9\tan\theta)$mm. 5307 reflections measured to $[(\sin\theta)/\lambda]_{\max} = 0{\cdot}659\ \text{Å}^{-1}$, $0 \le h \le 5$, $-28 \le k \le 28$, $-14 \le l \le 14$. Orientation control monitored after every 400 reflections, standard reflections measured every 7500 s of scanning time (123, $2\bar{2}1$, $1,10,\bar{1}$) showed change in intensity (−14·7%). After merging for $P2_1/n$ 2275

Table 2. *Atom coordinates* [$\times 10^4$, $\times 10^3$ *for* H(3) *and* H(11)] *and isotropic temperature factors* ($\times 10^3$ Å^2) *with e.s.d.'s in parentheses for* (II)

U_{eq} defined according to Hamilton (1959).

	x	y	z	U_{eq}/U_{iso}
O(11)	487 (6)	485 (1)	6632 (2)	60 (1)
O(12)	637 (6)	1404 (1)	7502 (2)	66 (1)
O(13)	7656 (6)	841 (1)	10326 (2)	73 (1)
O(14)	4487 (6)	1598 (1)	9447 (2)	66 (1)
C(11)	1501 (6)	847 (1)	7481 (2)	47 (1)
C(12)	3850 (7)	581 (1)	8556 (2)	48 (1)
C(13)	5521 (7)	1020 (1)	9521 (2)	52 (1)
N	6368 (6)	1030 (1)	4863 (2)	48 (1)
C(1)	5401 (7)	772 (1)	3796 (2)	54 (1)
C(2)	3491 (8)	1106 (1)	2889 (2)	54 (1)
C(3)	2603 (6)	1708 (1)	3079 (2)	45 (1)
C(4)	3629 (8)	1956 (1)	4216 (2)	59 (2)
C(5)	5494 (8)	1607 (1)	5094 (2)	60 (2)
C(6)	687 (8)	2092 (1)	2088 (3)	61 (2)
H(1)	6119	297	3637	54
H(2)	2671	892	2013	54
H(3)	747 (8)	83 (1)	537 (3)	43 (7)
H(4)	2945	2429	4407	59
H(5)	6278	1800	5990	60
H(6)	1787	2168	1442	61
H(7)	−1312	1896	1653	61
H(8)	−194	2457	2334	61
H(11)	315 (11)	163 (2)	880 (4)	77 (11)
H(12)	2346	253	8988	48
H(13)	5900	337	8213	48

Table 3. *Interatomic distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

Benzylammonium hydrogen malonate

O(1)—C(1)	1·216 (2)	C(11)—C(12)	1·376 (3)
O(2)—C(1)	1·293 (2)	C(11)—C(16)	1·387 (3)
O(3)—C(3)	1·233 (2)	C(11)—C(17)	1·508 (2)
O(4)—C(3)	1·269 (2)	C(12)—C(13)	1·389 (4)
C(1)—C(2)	1·513 (2)	C(13)—C(14)	1·378 (4)
C(2)—C(3)	1·527 (2)	C(14)—C(15)	1·363 (3)
N—C(17)	1·484 (2)	C(15)—C(16)	1·382 (3)
H(1)—O(2)	0·80 (4)	H(15)—C(15)	0·92 (3)
H(2)—C(2)	0·94 (3)	H(16)—C(16)	0·93 (4)
H(3)—C(2)	0·99 (3)	H(17)—C(17)	0·93 (4)
H(12)—C(12)	0·98 (3)	H(18)—C(17)	0·98 (3)
H(13)—C(13)	0·96 (5)	H(19)—N	0·82 (3)
H(14)—C(14)	0·96 (3)	H(20)—N	0·82 (2)
		H(21)—H	0·90 (2)
O(2)—C(1)—O(1)	121·6 (2)	C(17)—C(11)—C(12)	118·5 (2)
C(2)—C(1)—O(1)	120·9 (2)	C(17)—C(11)—C(16)	122·7 (2)
C(2)—C(1)—O(2)	117·4 (1)	C(13)—C(12)—C(11)	120·1 (2)
C(3)—C(2)—C(1)	117·6 (2)	C(14)—C(13)—C(12)	120·5 (2)
O(4)—C(3)—O(3)	124·6 (1)	C(15)—C(14)—C(13)	119·4 (2)
C(2)—C(3)—O(3)	118·4 (2)	C(16)—C(15)—C(14)	120·5 (2)
C(2)—C(3)—O(4)	117·0 (1)	C(15)—C(16)—C(11)	120·6 (2)
C(16)—C(11)—C(12)	118·8 (2)	C(11)—C(17)—N	112·9 (1)
H(3)—C(2)—H(2)	97·7 (27)	H(21)—N—H(19)	108·0 (24)
H(18)—C(17)—H(17)	106·2 (25)	H(21)—N—H(20)	106·8 (22)
H(20)—N—H(19)	111·7 (25)		

4-Picolinium hydrogen malonate

O(11)—C(11)	1·251 (3)	N—C(1)	1·324 (3)
O(12)—C(11)	1·254 (3)	N—C(5)	1·334 (4)
O(13)—C(13)	1·199 (3)	C(1)—C(2)	1·373 (4)
O(14)—C(13)	1·315 (3)	C(2)—C(3)	1·377 (4)
C(11)—C(12)	1·515 (3)	C(3)—C(4)	1·387 (4)
C(12)—C(13)	1·513 (2)	C(4)—C(5)	1·362 (4)
		C(3)—C(6)	1·497 (4)
O(14)—H(11)	0·83 (4)	N—H(3)	0·78 (3)
O(12)—C(11)—O(11)	124·2 (2)	N—C(1)—C(2)	119·8 (2)
C(12)—C(11)—O(11)	116·8 (2)	C(1)—C(2)—C(3)	120·4 (2)
C(12)—C(11)—O(12)	119·0 (2)	C(2)—C(3)—C(4)	117·8 (2)
O(14)—C(13)—O(13)	122·0 (2)	C(3)—C(4)—C(5)	119·8 (2)
C(12)—C(13)—O(13)	120·8 (2)	C(4)—C(5)—N	120·4 (2)
C(12)—C(13)—O(14)	117·3 (2)	C(2)—C(3)—C(6)	121·5 (2)
C(13)—C(12)—C(11)	118·3 (2)	C(4)—C(3)—C(6)	120·7 (2)
C(1)—N—C(5)	121·7 (2)		

unique reflections remained ($R_{int} = 0{\cdot}026$) of which 848 were considered as observed [$I > 3{\cdot}0\sigma(I)$].

The structure was solved by direct methods using *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). All non-H atoms were located from the initial *E* map. The coordinates of methylene and aromatic H atoms computed with the assumption of idealized geometries. Methyl H atoms and H atoms taking part in hydrogen bonds located from difference Fourier map. Least-squares refinement with anisotropic displacement parameters for non-H atoms and isotropic for H atoms taking part in hydrogen bonds. H atoms with calculated positions and methyl H atoms included in the refinement with equivalent isotropic thermal parameters of the bonded atoms, but not refined. Inspection of F_o and F_c values indicated the correction for secondary extinction [$g = 2{\cdot}6\,(5) \times 10^{-3}$] (Larson, 1967). Empirical weighting function $w = 8{\cdot}0W_fW_s$, where $W_f(|F_o| < 5{\cdot}4) = (|F_o|/5{\cdot}4)^{0{\cdot}1}$, $W_f(|F_o| > 5{\cdot}9) = (5{\cdot}9/|F_o|)^{0{\cdot}05}$, $W_f(5{\cdot}4 \leq |F_o| \leq 5{\cdot}9) = 1{\cdot}0$, $W_s(\sin\theta < 0{\cdot}32) = [(\sin\theta/0{\cdot}32]^{3{\cdot}7}$, $W_s(\sin\theta > 0{\cdot}33) = [0{\cdot}33/(\sin\theta)]^{0{\cdot}1}$, $W_s(0{\cdot}32 \leq \sin\theta \leq 0{\cdot}33) = 1{\cdot}0$ applied to keep $\sum w(\Delta F)^2$ uniform over ranges of $(\sin\theta)/\lambda$ and $|F_o|$. Refinement converged to $R = 0{\cdot}039$ and $wR = 0{\cdot}040$ for 136 parameters and 1382 contributing reflections including observed and less-thans for which $|F_c| > |F_o|$. $(\text{Shift/e.s.d.})_{max} = 0{\cdot}451$, $(\text{shift/e.s.d.})_{av} = 0{\cdot}005$, $S = 0{\cdot}790$, min. and max. heights in difference Fourier map $-0{\cdot}25$ and $0{\cdot}24$ e Å^{-3}.

Least-squares refinement on *F* was performed using *XRAY*76 system of crystallographic programs (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976). 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 the DEC-10 computer at RCU–Ljubljana.

Discussion. Fractional coordinates and U_{eq} values (Hamilton, 1959) along with their e.s.d.'s are listed in Tables 1 and 2.* Interatomic distances and angles are presented in Table 3. The arbitrary numbering

---

* Lists of structure factors, anisotropic thermal parameters and least-squares-planes details have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52250 (22 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

schemes used in the crystal analyses are shown in Figs. 1 and 2, representing the perspective views of benzylammonium hydrogen malonate and 4-picolinium hydrogen malonate. The molecular packings of the title compounds are shown in Figs. 3 and 4.

The bond distances and angles of the hydrogen malonate groups in both compounds can be compared to the values observed in other salts of malonic acid (Chapuis *et al.*, 1975; Currie, 1972; Rao & Parthasarthy, 1974; Sime *et al.*, 1970; Soriano-García & Parthasarathy, 1978). The C(1)—C(2) and C(2)—C(3) distances in (I) differ [1·513 (2) and 1·527 (2) Å], but are within the range of accepted values for Csp^3—Csp^2 bond lengths in carboxylate anions (Allen, Kennard, Watson, Brammer, Orpen & Taylor, 1987). The longer C—C bond is adjacent to the non-ionized carboxyl group in the hydrogen malonate ion. A similar situation has been observed in other acid salts: potassium DL-methyl succinate (Schouwstra, 1972) and aminomalonic acid (Kanters, Kroon, Beurskens & Vliengenthart, 1966). In (II) the corresponding C—C bond distances are equal within the limits of the experimental error [1·515 (3) and 1·513 (2) Å]. It has been observed that the sum of the carboxylic C—O distances is reasonably constant (2·52 Å), whether the group is ionized or not (Manojlović & Speakman, 1967). In our compounds the sums of the C—O distances are in agreement with the above observation [(I): 2·509 (4) and 2·502 (4) Å; (II): 2·505 (6) and 2·514 (5) Å]. The hydrogen malonate ions in both structures are roughly planar, the carboxylate groups are twisted 4·9 (3) and 5·4 (3)° in (I) and 9·2 (3) and 8·2 (3)° in (II) with respect to the planes defined by the three C atoms. The C—C—C bond angles deviate from the ideal tetrahedral value [(I): 117·6 (2), (II): 118·3 (2)°] which can be explained by steric hindrance from O

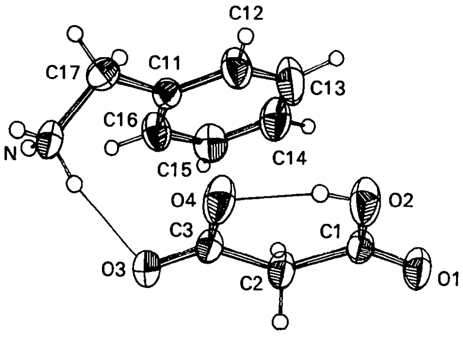

Fig. 1. *ORTEP* plot (Johnson, 1965) of the asymmetric unit of (I) with the atom-numbering scheme. Anisotropic ellipsoids enclose 40% probability.

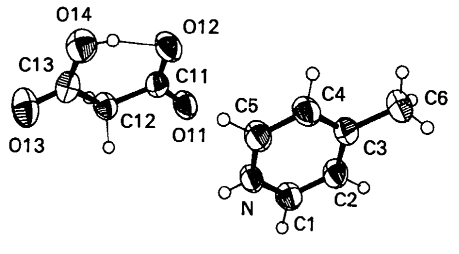

Fig. 2. *ORTEP* plot (Johnson, 1965) of the asymmetric unit of (II) with the atom-numbering scheme. Anisotropic ellipsoids enclose 50% probability.

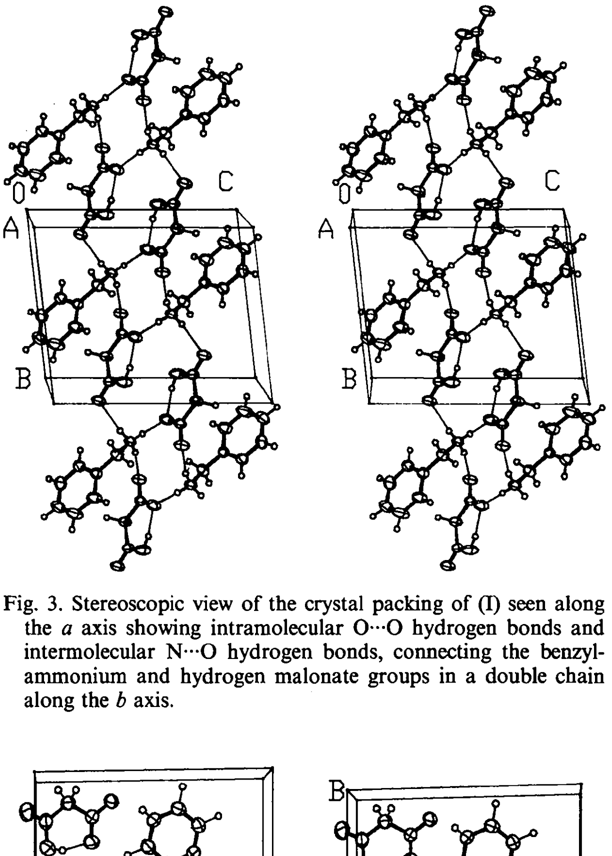

Fig. 3. Stereoscopic view of the crystal packing of (I) seen along the *a* axis showing intramolecular O···O hydrogen bonds and intermolecular N···O hydrogen bonds, connecting the benzylammonium and hydrogen malonate groups in a double chain along the *b* axis.

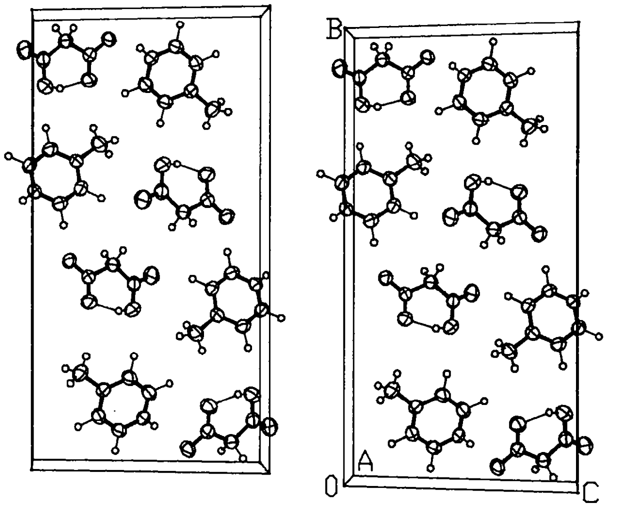

Fig. 4. Stereoscopic view of the crystal packing of (II) seen along the *a* axis showing intramolecular O···O hydrogen bonds.

atoms contributing to the intramolecular hydrogen bond. This has also been observed in other acid salts of malonic acid in which the hydrogen malonate moiety is planar: lithium and potassium trihydrogen dimalonate (117·8, 117·0°) (Soriano-García & Parthasarathy, 1978; Currie, 1972), potassium hydrogen malonate [119·4 (6·4)°] (Sime *et al.*, 1970), guanidinium hydrogen malonate [117·3 (2)°] (Djinović *et al.*, 1988) and magnesium bis(hydrogen malonate) dihydrate [119·8 (1)°] (Briggman & Oskarsson, 1978). The carboxylate groups are essentially planar, as shown by the sums of the angles around the C atoms, which are 360·0 (5) and 360·0 (4)° in (I) and 360·0 (6) and 360 (8)° in (II). The longer C—O bond distances 1·293 (2) and 1·269 (2) Å in benzylammonium hydrogen malonate correspond to O atoms taking part in intramolecular hydrogen bonding while the O atoms hydrogen bonded to benzylammonium ions have C—O bond distances of length 1·216 (2) and 1·233 (2) Å. Similarly, in 4-picolinium hydrogen malonate O atoms bonded to the C atoms at distances of 1·315 (3) and 1·254 (3) Å contribute to the intramolecular hydrogen bond.

The average C—C bond length in the benzene ring of the benzylammonium ion is 1·379 (4) Å which is in agreement with C_{ar}—C_{ar} values (1·380 Å) (Allen *et al.*, 1987) as well as with the average C_{ar}—C_{ar} distance in bis(benzylammonium) bis(oxalato)-cuprate(II) (1·382 Å) (Bloomquist, Hansen, Landee, Willett & Buder, 1981). The benzene rings are almost planar, deviations of the aromatic C atoms ranging from 0·001 (2) to 0·015 (3) Å. The largest deviation from the mean plane is shown by the *meta* carbon atom C(13), which has the largest equivalent isotropic thermal parameter of the atoms of the benzene ring. The methylene atom C(17) and N atom are displaced from the benzene plane with deviations of 0·076 (2) and 0·820 (2) Å respectively. The C(17)—C(11) bond distance [1·508 (2) Å] is similar to the corresponding value in tribenzylamine (Iwasaki & Iwasaki, 1972) and in *p*-toluic acid (1·514 Å) (Takwale & Pant, 1971). The C—N bond distance [1·484 (2) Å] is longer than that observed in gaseous trimethylamine (1·472 Å) (Lide & Mann, 1958), but in good agreement with the average Csp^3—NH_3^+ values (1·488 Å) (Allen *et al.*, 1987).

The bond distances and angles in the 4-picolinium groups are in agreement with chemically expected values. The N—C bond distances [1·324 (3), 1·334 (4) Å] are shorter than the C—C values. In aromatic rings where the C atom is substituted by a more electronegative N atom, the C—N—C angle is often smaller than the expected 120° value. This can be observed in aquabis(4-picoline)bis(succinimidato)copper(II) (Latavalya & Taylor, 1975) [116·7 (2), 116·7 (2)°] and in morpholinium tetrachlorobis(4-picoline)tungstate(III) (Brenčič, Čeh, Kobe & Leban, 1989) [118·0 (12), 115·5 (4)°], while in our compound the corresponding angle is close to the ideal value [121·7 (2)°].

Benzylammonium and hydrogen malonate ions are connected by three asymmetrical O···N hydrogen bonds of 2·912 (2), 2·874 (2) and 2·969 (2) Å. The O···N distances are similar to those found in guanidinium hydrogen malonate [2·875 (4), 2·963 (4), 2·881 (5) Å] (Djinović *et al.*, 1988) and in bis(benzylammonium) bis(oxalato)cuprate(II) (Bloomquist *et al.*, 1981) [2·881 (10), 2·811 (10), 2·963 (10) Å]. Two hydrogen malonate and two benzylammonium groups form an eight-membered ring (excluding H atoms), which has the chair conformation, by means of O···N hydrogen bonds. One hydrogen malonate and one benzylammonium ion of this ring are hydrogen bonded to two more groups of this kind to form another, roughly planar, eight-membered ring. The hydrogen-bonding scheme in (I) can therefore be interpreted as a double chain parallel to the [010] direction in the structure, the chains consisting of alternating eight-membered rings, which causes the zigzag shape of the chain. The polar parts of the anions and cations form the core of the chain, the non-polar parts are on the surface of the chain. Hydrogen malonate and benzylammonium groups in the asymmetric unit are roughly parallel; the dihedral angle between the mean plane through the aromatic ring and the plane through the three C atoms of the hydrogen malonate ion is 13·4 (4)°.

The O···N hydrogen bonds connecting 4-picolinium and hydrogen malonate ions are short [2·639 (3) Å] in comparison with the average O···N hydrogen-bond length (2·89 Å) (Kuleshova & Zorkii, 1981) derived from 4000 homomolecular organic crystals. The O···N hydrogen bond is nearly linear [170 (3)°], which is in agreement with the theoretical calculations for the pyridine–HF dimer; these calculations indicate that the favored geometry for the F—H—N angle is 180° (Del Bene, 1975). The hydrogen malonate and 4-picolinium groups are connected by one hydrogen bond, forming isolated dimers in the structure. The cation and anion in the asymmetric unit are nearly parallel, the dihedral angle between the mean plane through the heterocyclic ring of the cation and the plane defined by the three C atoms of the anion being 17·3 (4)°.

The intramolecular hydrogen bonds stabilizing the hydrogen malonate ions in (I) and (II) are bent, as found in other hydrogen malonate salts containing intramolecular hydrogen bonds. Table 4 presents a comparison of the intramolecular hydrogen bonds in various hydrogen malonate ions. The intramolecular hydrogen bonds in (I) and (II) are short and are of Speakman's (1972) B_2 type. The O···O hydrogen-bond length in (II) is similar to the hydrogen bonds

Table 4. *Comparison of the* O···O *intramolecular hydrogen bonds in hydrogen malonate ions*

Compound	O—H—O (°)	O···O (Å)
Lithium trihydrogen dimalonate	153 (5)	2·481 (3)
Potassium trihydrogen dimalonate	155	2·513 (9)
Guanidinium hydrogen malonate	153 (6)	2·407 (3)
Benzylammonium hydrogen malonate	158 (5)	2·430 (2)
4-Picolinium hydrogen malonate	159 (4)	2·493 (3)

in lithium and potassium trihydrogen dimalonate (Soriano-García & Parthasarathy, 1978; Currie, 1972), while the corresponding O···O hydrogen bond in (I) can be compared to the intramolecular hydrogen bond in guanidinium hydrogen malonate.

The financial support of Slovene Research Council is gratefully acknowledged.

References

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans.* 2, pp. S1–S19.

Bloomquist, D. R., Hansen, J. J., Landee, C. P., Willett, R. D. & Buder, R. (1981). *Inorg. Chem.* **20**, 3308–3314.

Brenčič, J. V., Čeh, B., Kobe, B. & Leban, I. (1989). *God. Jugosl. Cent. Kristalogr.* **24**, S19.

Briggman, B. & Oskarsson, Å. (1978). *Acta Cryst.* **B34**, 3357–3359.

Chapuis, G., Zalkin, A. & Templeton, D. H. (1975). *J. Chem. Phys.* **62**(12), 4919–4922.

Cromer, D. T. & Liberman, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.

Cromer, D. T. & Mann, J. B. (1968). *Acta Cryst.* **A24**, 321–324.

Currie, M. (1972). *J. Chem. Soc. Chem. Commun.* **17**, 972–973.

Del Bene, J. E. (1975). *J. Am. Chem. Soc.* **17**, 5330–5335.

Djinović, K., Golič, L., Hadži, D. & Orel, B. (1988). *Croat. Chem. Acta*, **61**(2), 405–412.

Hamilton, W. C. (1959). *Acta Cryst.* **12**, 609–610.

Iwasaki, F. & Iwasaki, H. (1972). *Acta Cryst.* **B28**, 3370–3376.

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

Kanters, J. A., Kroon, J., Beurskens, P. T. & Vliegenthart, J. A. (1966). *Acta Cryst.* **21**, 990–995.

Kuleshova, L. N. & Zorkii, P. M. (1981). *Acta Cryst.* **B37**, 1363–1366.

Larson, A. C. (1967). *Acta Cryst.* **23**, 664–665.

Latavalya, N. & Taylor, M. R. (1975). *Cryst. Struct. Commun.* **4**, 163–166.

Lide, D. R. & Mann, D. E. (1958). *J. Chem. Phys.* **28**, 572–579.

Main, P., Fiske, S. J., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1980). *MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.

Manojlović, L. & Speakman, J. C. (1967). *J. Chem. Soc. A*, pp. 971–979.

Merechan, M., Tomas, F. & Nebot-Gil, J. (1984). *J. Mol. Struct.* (*Theochem.*), **109**, 51–60.

Rao, S. N. & Parthasarathy, R. (1974). *J. Chem. Soc. Perkin Trans* 2, **6**, 683–685.

Schouwstra, Y. (1972). *Acta Cryst.* **B28**, 2217–2221.

Sheldrick, G. M. (1986). *SHELX86*. Program for the solution of crystal structures. Univ. of Göttingen, Federal Republic of Germany.

Sime, J. S., Speakman, J. C. & Parthasarathy, R. (1970). *J. Chem. Soc. A*, pp. 1919–1923.

Soriano-García, M. & Parthasarathy, R. (1978). *J. Chem. Soc. Perkin Trans* 2, **7**, 668–670.

Speakman, J. S. (1972). *Struct. Bonding* (*Berlin*), **12**, 141–199.

Stewart, J. M., Machin, P. A., Dickinson, C. W., Ammon, H. L., Heck, H. & Flack, H. (1976). The *XRAY76* system. Tech. Rep. TR-446. 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.

Takwale, H. G. & Pant, L. M. (1971). *Acta Cryst.* **B27**, 1152–1158.

Wulf, P. & Heigel, A. (1931). *Z. Phys. Chem. Abt. A*, **153**, 187.

Acta Cryst. (1990). C**46**, 286–290

Absolute Configuration of 1,1′-(1,2-Ethanediyl)bis(L-pyroglutamic acid), (*S*,*S*)-eddpg

By Thomas J. Emge, Larry C. Strickland and Christopher M. Perkins

The Procter and Gamble Company, Miami Valley Laboratories, PO Box 398707, *Cincinnati, Ohio* 45239-8707, *USA*

(*Received* 28 *October* 1988; *accepted* 9 *May* 1989)

Abstract. $\mathrm{C_{12}H_{16}N_2O_6}$, $M_r = 284\cdot3$, tetragonal, $P4_1$, $a = 7\cdot511$ (1), $c = 24\cdot278$ (3) Å, $V = 1369\cdot6$ (2) Å^3, $Z = 4$, $D_x = 1\cdot378$ g cm^{-3}, λ(Cu $K\alpha$) = 1·5418 Å, $\mu = 9\cdot6$ cm^{-1}, $F(000) = 600$, $T = 293$ K, final $R = 0\cdot022$ for 1371 observed reflections with $I > 2\sigma(I)$. The structure was solved by direct methods; the absolute configuration and space group were determined by synthesis and confirmed by use of the method of Rogers [*Acta Cryst.* (1981), A37, 734–741]. Both glutamate groups have the *S* configuration and are lactams. The dihedral angle and center-of-mass distance between the five-membered lactam rings are

0108-2701/90/020286-05$03.00