

the C—S bonds are not equivalent (see above), is similar to that in DEAP, in which, however, the C—S bond lengths are nearly equal, and not to that in DEAE. As a result, the contribution of the N—H...S hydrogen bonds to the observed alteration in the relative C—S bond distances in going from DEAP to DEAE or DMAP is not easily discerned.

The molecular packing is shown in Fig. 2. The N—H...S hydrogen bonds result in interconnected infinite zigzag chains of molecules extending along the *b* axis.

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## Structure of Diethylmalonic Acid

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**Abstract.**  $C_7H_{12}O_4$ ,  $M_r = 160.17$ , monoclinic,  $P2_1$ ,  $a = 7.338$  (1),  $b = 10.626$  (1),  $c = 11.237$  (2) Å,  $\beta = 93.47$  (1)°,  $V = 874.6$  (2) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.22$  g cm<sup>-3</sup>,  $\lambda(\text{Cu } K\alpha) = 1.54180$  Å,  $\mu = 9.7$  cm<sup>-1</sup>,  $F(000) = 344$ ,  $T = 291$  K,  $R = 0.038$  for 1431 observed reflections. The asymmetric unit contains two independent molecules linked by two intermolecular hydrogen bonds. The two carboxylic groups are rotated by 79° and give extensive zigzag chains along the *c* axis.

**Introduction.** In a previous spectroscopic paper, Delarbre, Maury & Bardet (1985) have concluded that, in aqueous solution, the diethylmalonic acid molecule belongs to the point group  $C_2$  corresponding to a twisted conformation and that, in addition, the acid salt is intramolecularly hydrogen bonded while the acid is not. The dissociation constant ratio  $K_1/K_2$  (Ebersson, 1969) is very high in disubstituted malonic acids. Diethylmalonic acid was therefore presumed to exhibit an intramolecular hydrogen bond in the crystalline state

Table 1. Fractional atomic coordinates ( $\times 10^4$ ) and equivalent isotropic temperature factors ( $\text{\AA}^2$ ) for non-H atoms with e.s.d.'s in parentheses

	x	y	z	$U_{eq}$
C1	5966 (4)	8651 (4)	-1097 (3)	3.85
C2	4764 (4)	8524 (4)	-2250 (3)	3.82
C3	4778 (4)	8543 (4)	-39 (3)	3.77
C4	7392 (5)	7586 (5)	-1036 (3)	5.17
C5	8590 (6)	7540 (6)	-2093 (4)	7.22
C6	6794 (5)	9986 (5)	-1062 (3)	4.69
C7	7926 (6)	10318 (6)	75 (3)	6.77
O1	4740 (3)	9288 (0)	-3039 (2)	4.85
O2	3807 (4)	7487 (4)	-2304 (2)	5.96
O3	5236 (3)	7956 (4)	848 (2)	5.16
O4	3254 (3)	9185 (4)	-167 (2)	5.42
C1'	594 (4)	8083 (5)	3684 (3)	3.81
C2'	1729 (5)	8225 (5)	4851 (3)	3.84
C3'	1848 (4)	8322 (4)	2673 (3)	3.83
C4'	-944 (5)	9070 (5)	3628 (3)	4.79
C5'	-2313 (6)	8898 (6)	4581 (4)	6.27
C6'	-80 (5)	6764 (5)	3561 (3)	4.73
C7'	-1196 (6)	6423 (6)	2412 (3)	6.01
O1'	1784 (4)	7420 (3)	5630 (2)	5.67
O2'	2622 (4)	9282 (3)	4954 (2)	4.76
O3'	1430 (3)	8965 (4)	1817 (2)	5.65
O4'	3397 (3)	7711 (4)	2805 (2)	4.95

Table 2. Bond distances ( $\text{\AA}$ ), bond angles ( $^\circ$ ), hydrogen-bond distances ( $\text{\AA}$ ) and torsion angles ( $^\circ$ )

E.s.d.'s for bond distances and bond angles are given in parentheses; e.s.d.'s are ca 0.004  $\text{\AA}$  for hydrogen-bond distances and ca 0.6 $^\circ$  for torsion angles.

C2—C1	1.529 (4)	C2'—C1'	1.518 (4)
C3—C1	1.521 (4)	C3'—C1'	1.525 (4)
C4—C1	1.540 (5)	C4'—C1'	1.539 (5)
C6—C1	1.544 (5)	C6'—C1'	1.551 (5)
O1—C2	1.202 (4)	O1'—C2'	1.222 (4)
O2—C2	1.306 (4)	O2'—C2'	1.303 (4)
O3—C3	1.206 (4)	O3'—C3'	1.204 (4)
O4—C3	1.310 (4)	O4'—C3'	1.310 (4)
C5—C4	1.521 (5)	C5'—C4'	1.523 (5)
C7—C6	1.522 (5)	C7'—C6'	1.516 (5)
C3—C1—C2	109.1 (3)	C3'—C1'—C2'	107.6 (3)
C4—C1—C2	109.2 (3)	C4'—C1'—C2'	109.3 (3)
C4—C1—C3	109.3 (3)	C4'—C1'—C3'	109.3 (3)
C6—C1—C2	108.0 (3)	C6'—C1'—C2'	109.0 (3)
C6—C1—C3	107.0 (3)	C6'—C1'—C3'	107.2 (3)
C6—C1—C4	114.2 (3)	C6'—C1'—C4'	114.3 (3)
O1—C2—C1	123.2 (3)	O1'—C2'—C1'	122.8 (3)
O2—C2—C1	113.2 (3)	O2'—C2'—C1'	114.1 (3)
O2—C2—O1	123.5 (3)	O2'—C2'—O1'	123.0 (3)
O3—C3—C1	122.7 (3)	O3'—C3'—C1'	123.6 (3)
O4—C3—C1	113.7 (3)	O4'—C3'—C1'	113.0 (3)
O4—C3—O3	123.6 (3)	O4'—C3'—O3'	123.3 (3)
C5—C4—C1	114.4 (3)	C5'—C4'—C1'	113.8 (3)
C7—C6—C1	115.4 (3)	C7'—C6'—C1'	114.5 (3)
O4'...O3	2.662	O2'...O1'	2.660
O4'...O3'	2.679	O1'...O2'	2.680

Symmetry code: (i) x, y, z + 1

C3—C1—C2—O1	127.5	C3'—C1'—C2'—O1'	-127.5
C3—C1—C2—O2	-56.	C3'—C1'—C2'—O2'	53.
C4—C1—C2—O2	60.	C4'—C1'—C2'—O2'	-64.5
C2—C1—C3—O3	138.5	C2'—C1'—C3'—O3'	136.7
C2—C1—C3—O4	-44.5	C2'—C1'—C3'—O4'	48.5
C6—C1—C3—O4	72.5	C6'—C1'—C3'—O4'	-68.

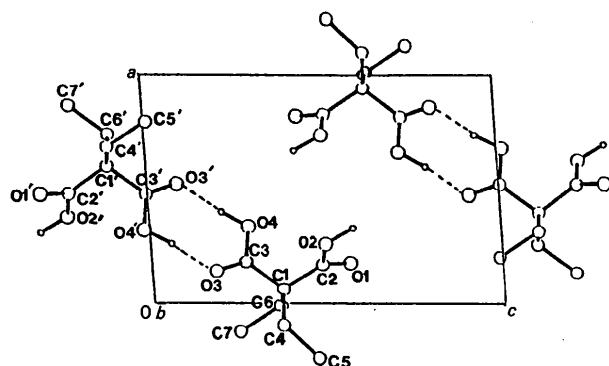


Fig. 1. Projection of the structure on the  $ac$  plane. Hydrogen bonds are represented by dashed lines.

but to exist in an open nonbonded form in aqueous solution (de Klein, 1970). Raman and infrared spectra showed that if the intramolecular hydrogen bonding did not take place in the acid, the acid salt would have been cyclic. Thus, it seemed of interest to investigate the molecular and crystal structure of both the acid and the acid salt as a part of a systematic study of these malonic acid derivatives. Here, we report the structure of the acid.

**Experimental.** Colourless transparent crystal,  $0.15 \times 0.2 \times 0.3$  mm, obtained by recrystallization from water. Lattice parameters refined using 14 reflections in the range  $10 \leq 2\theta \leq 25^\circ$ . Absorption correction: transmission factors 0.89–1.04. Huber 424 + 511 diffractometer, graphite-monochromatized  $\text{Cu K}\alpha$  radiation. 1673 independent reflections with  $\sin\theta/\lambda \leq 0.599 \text{\AA}^{-1}$ , 1431 with  $I \geq 2.5\sigma(I)$ . Index range  $h-8/8$ ,  $k0/12$ ,  $l0/13$ . Standard reflection (011) checked every 50

reflections; no significant deviation. Structure solved by direct methods using *MULTAN80* (Main *et al.*, 1980). H atoms of carboxylic groups from difference Fourier synthesis. H atoms of the carbon chain included in the calculation in theoretical positions. Anisotropic least-squares refinement on  $F$  with *SHELX76* (Sheldrick, 1976). H atoms of carboxylic groups refined; all H with common refined isotropic temperature factor ( $B = 9.5 \text{\AA}^2$ ).  $R = 0.038$ ,  $wR = 0.039$ ,  $S = 2.25$  for 1431 observed reflections. Final max.  $\Delta/\sigma = 0.5$ ; max. and min. heights in final difference Fourier synthesis 0.13 and  $-0.16 \text{ e \AA}^{-3}$ .

Atomic scattering factors from *International Tables for X-ray Crystallography* (1974).

**Discussion.** Atomic fractional positional parameters are given in Table 1.\* Bond lengths and angles are given in Table 2. The atomic numbering is shown in Fig. 1.

\* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51044 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

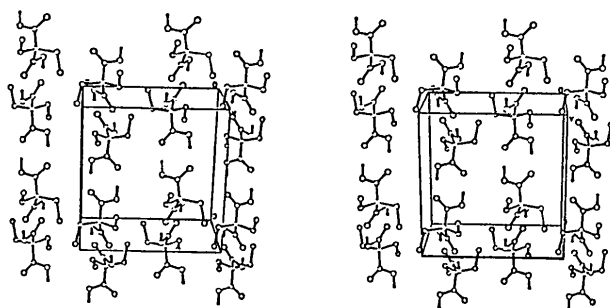


Fig. 2. Stereoscopic view of diethylmalonic acid drawn with PLUTO78 (Motherwell & Clegg, 1978).

The C—O and C—OH bond lengths and O—C—O angles are in good agreement with values found in a previous study on carboxylic acids (Leiserowitz, 1976). The two independent molecules in the asymmetric unit are linked by two hydrogen bonds (Table 2) and form a dimer *via* a ring of six atoms (Fig. 1). Each dimer is bonded with two others by the second carboxylic group and the hydrogen bonds form dihedral angles of 147 and 152 (1)°. So, as in malonic acid (Goedkoop & MacGillavry, 1957), methylmalonic acid (Derissen, 1970) and dimethylmalonic acid (Haas & Brenner, 1966; Sheng-Zhi & Mak, 1986), the diethylmalonic acid molecules are arranged in infinite chains along the *c* axis (Fig. 2). The two carboxylic groups of one molecule are not coplanar as in even-number dicarboxylic acids but are rotated in opposite directions, the angle between the C(2)—O(1)—O(2) and C(3)—

O(3)—O(4) planes being 79 (1)° (XANADU; Roberts & Sheldrick, 1975). The chains are zigzag. The values of the O—C—C—C torsion angles (Table 2) give a twist conformation about the  $\alpha$ -C atom. As in the odd-member malonic derivatives there is nearly a twofold symmetry axis through the  $\alpha$ -C atom. All the results agree well with the spectroscopic study.

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## Evidence for Rotational Isomerism of the Fluorophenyl Ring in the Crystal Structure of 5-(2-Fluorophenyl)-1,3-dihydro-1,6,8-trimethyl-2H-1,4-benzodiazepin-2-one\*

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**Abstract.** C<sub>18</sub>H<sub>17</sub>FN<sub>2</sub>O, *M<sub>r</sub>* = 296.3, monoclinic, *P2<sub>1</sub>/c*, *a* = 14.215 (3), *b* = 8.135 (1), *c* = 13.449 (3) Å,  $\beta$  = 98.12 (2)°, *V* = 1539.6 Å<sup>3</sup>, *Z* = 4, *D<sub>x</sub>* = 1.278 Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha)$  = 0.71069 Å,  $\mu$  = 0.05 mm<sup>-1</sup>, *F*(000) = 624, *T* = 293 K, *R* = 0.046 for 1939 observed reflections. The seven-membered ring adopts a moderately distorted cycloheptatriene-like boat conformation with bow and stern angles of

59.6 (5) and 41.3 (5)° respectively. The N—C amide bond length is 1.367 (3) Å. The angle between the 5-phenyl ring and the fused benzo moiety is 76.6 (5)°.

**Introduction.** The title compound, described by Finner, Zeugner & Milkowski (1984), differs from the clinically used psychoactive benzodiazepines, such as diazepam,† in the nature of the substitution of the fused benzene

\* Contribution from the Crystallography Unit, Universities of Aston and Birmingham, England.

† 7-Chloro-1,3-dihydro-1-methyl-5-phenyl-2H-1,4-benzodiazepin-2-one, marketed as Valium (Roche).