

N16	0.3585 (3)	0.1257 (2)	-0.3708 (2)	0.0365 (4)
O2	0.8072 (2)	0.3765 (2)	0.1485 (2)	0.0537 (6)
O6	0.5837 (2)	0.2708 (2)	-0.0758 (2)	0.0450 (4)
O11	0.2228 (3)	0.1060 (2)	0.1916 (2)	0.0484 (6)
O20	0.4168 (3)	0.0983 (2)	-0.6716 (2)	0.0535 (6)
C1	0.8413 (3)	0.2772 (3)	-0.0268 (3)	0.0485 (9)
C2	0.6911 (3)	0.3675 (3)	0.1301 (3)	0.0376 (7)
C3	0.5471 (4)	0.4558 (3)	0.2917 (3)	0.0447 (8)
C4	0.4259 (3)	0.3948 (2)	0.1730 (2)	0.0290 (4)
C5	0.4321 (3)	0.3499 (2)	0.0829 (2)	0.0283 (4)
C6	0.5668 (3)	0.3103 (2)	0.0084 (2)	0.0316 (4)
C7	0.2305 (3)	0.2978 (2)	0.0197 (2)	0.0298 (4)
C8	0.2005 (3)	0.4001 (2)	0.1773 (2)	0.0284 (4)
C11	0.2822 (3)	0.1544 (3)	0.0642 (2)	0.0356 (6)
C12	0.2298 (4)	0.0872 (3)	0.0035 (2)	0.0400 (7)
C14	0.4064 (3)	0.1405 (3)	-0.1896 (3)	0.0414 (8)
C15	0.4211 (4)	0.1980 (3)	-0.3274 (3)	0.0440 (7)
C17	0.2005 (4)	0.1297 (3)	-0.3105 (3)	0.0461 (8)
C18	0.1851 (4)	0.0749 (3)	-0.1743 (3)	0.0450 (8)
C19	0.3756 (4)	0.1776 (3)	-0.5039 (3)	0.0469 (7)
C20	0.3307 (4)	0.0948 (3)	-0.5537 (3)	0.0487 (8)
C21	-0.0354 (3)	0.4702 (3)	0.3028 (2)	0.0378 (7)
C22	-0.0849 (3)	0.3715 (3)	0.4225 (2)	0.0350 (6)
C23	-0.0726 (4)	0.2479 (3)	0.4319 (3)	0.0458 (8)
C24	-0.1219 (4)	0.1614 (3)	0.5444 (3)	0.0576 (8)
C25	-0.1824 (4)	0.1980 (4)	0.6469 (3)	0.0554 (8)
C26	-0.1949 (4)	0.3217 (4)	0.6375 (3)	0.0532 (8)
C27	-0.1470 (3)	0.4074 (3)	0.5256 (3)	0.0439 (8)

Table 2. Selected geometric parameters (Å, °)

N1—C1	1.469 (4)	N7—C8	1.360 (3)
N1—C2	1.382 (4)	N8—C8	1.343 (3)
N1—C6	1.415 (3)	N9—C4	1.351 (3)
N3—C2	1.373 (4)	N9—C8	1.347 (3)
N3—C3	1.461 (3)	O2—C2	1.227 (3)
N3—C4	1.378 (3)	O6—C6	1.228 (3)
N7—C5	1.404 (3)	C4—C5	1.363 (3)
N7—C7	1.459 (3)	C5—C6	1.409 (3)
C1—N1—C2	116.5 (2)	N3—C4—N9	125.2 (2)
C1—N1—C6	117.0 (2)	N3—C4—C5	121.4 (2)
C2—N1—C6	126.5 (2)	N9—C4—C5	113.4 (2)
C2—N3—C3	119.2 (2)	N7—C5—C4	104.9 (2)
C2—N3—C4	119.4 (2)	N7—C5—C6	131.6 (2)
C3—N3—C4	121.4 (2)	C4—C5—C6	123.5 (2)
C5—N7—C7	125.9 (2)	N1—C6—O6	120.1 (2)
C5—N7—C8	105.2 (2)	N1—C6—C5	111.6 (2)
C7—N7—C8	127.8 (2)	O6—C6—C5	128.3 (3)
C4—N9—C8	103.0 (2)	N7—C8—N8	122.5 (2)
N1—C2—N3	117.5 (2)	N7—C8—N9	113.4 (2)
N1—C2—O2	121.5 (3)	N8—C8—N9	123.9 (2)
N3—C2—O2	121.0 (3)		
C8—N7—C7—C11	-103.5 (3)	N7—C8—N8—C21	179.5 (3)
N7—C7—C11—C12	178.2 (2)	C8—N8—C21—C22	-96.4 (3)
C7—C11—C12—N13	46.0 (4)	N8—C21—C22—C27	170.2 (3)
C11—C12—N13—C14	63.1 (4)		

The positions of the H atoms of the amino and hydroxy groups were located from difference electron-density maps and were refined; all other H atoms were placed in calculated positions and refined using a riding model. Isotropic displacement parameters of 1.5U<sub>eq</sub> of their respective parent C atoms were used for all H atoms.

The structure was solved by direct methods using *SHELXS86* (Sheldrick, 1990) and refined by full-matrix least squares using *SHELX76* (Sheldrick, 1976). Molecular graphics were prepared using *XP* (Sheldrick, 1989). *PARST* (Nardelli, 1983) and *CSU88* (Vicković, 1988) were used for geometrical calculations and to prepare material for publication.

The crystallographic studies were supported by grant No. 3 0302 91 01 from the Polish State Committee for Scientific Research.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BM1000). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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*Acta Cryst.* (1995). **C51**, 2612–2615

## Anti-Inflammatory Drugs. II. Salt of 2-(2,6-Dichlorophenylamino)phenylacetic Acid with Diethanolamine

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(Received 3 March 1995; accepted 5 June 1995)

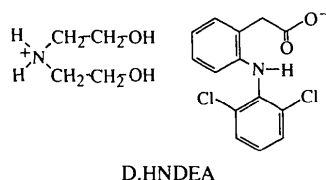
## Abstract

The structure of the title salt, bis(2-hydroxyethyl)-ammonium 2-(2,6-dichlorophenylamino)phenylacetate, C<sub>4</sub>H<sub>12</sub>NO<sub>2</sub><sup>+</sup>.C<sub>14</sub>H<sub>10</sub>Cl<sub>2</sub>NO<sub>2</sub><sup>-</sup>, has been determined by X-ray diffraction. The asymmetric unit consists of one cation and one anion. The structural unit is best

described as a double-ion pair built up around a centrosymmetric pair of cations, which are hydrogen bonded to each other and to the carboxylate O atoms. The crystal consists of stacked layers, each characterized by a network of hydrogen bonds.

### Comment

We report the molecular conformation and crystal packing of the 1:1 salt of 2-(2,6-dichlorophenylamino)phenylacetic acid (HD) with *N*-diethanolamine (NDEA), hereinafter abbreviated as D.HNDEA. Our study allows a comparison of the structural features of this salt with those previously reported for the adduct of D with the 1-(2-hydroxyethyl)pyrrolidinium cation (HEP) (Castellari & Sabatino, 1994). Our aim is to correlate structures, solubilities and pharmacological activities of adducts of the non-steroidal anti-inflammatory drug (NSAID) diclofenac (usually NaD) as a function of the counterion.



The molecular structure of D is strictly comparable to those reported for HD (Moser, Sallmann & Wiesenberg, 1990; Kovala-Demertzi, Mentzafos & Terzis, 1993), the complex  $[\text{Cd}_2(\text{H}_2\text{O})(\text{EtOH})_2(\text{D}_4)]$  (Kovala-Demertzi, Mentzafos & Terzis, 1993) and the 1:1 D.HEP salt (Castellari & Sabatino, 1994), with respect to the features affecting bond distances and angles in the two phenyl rings. Differences are found in the carboxyl groups. In both structures of the free acid and in the cadmium complex the two C—O bond lengths are different (1.22 and 1.30 Å), whereas in D.HNDEA the two C—O distances of the carboxylate group are equal within experimental error [C(14)—O(2) 1.247(3), C(14)—O(1) 1.250(3) Å]. This agrees with data observed for the D.HEP salt and is indicative of the lack of strong bonding interactions involving the carboxylate. The HNDEA cation exhibits a claw-shaped 'bidentate' conformation similar to that observed in other NDEA salts (Cody & Strong, 1980; Cody, 1981) with no significant differences in bond lengths. The asymmetric unit of the crystal comprises one molecule of D and one of HNDEA, stabilized by intra- and inter-ion hydrogen bonding (Fig. 1).

Intramolecular hydrogen bonds are present both in D and HNDEA. N(1) in the anion is linked *via* H(1) to both Cl(1) and O(1) [N(1)···O(1) 2.811(3) and N(1)···Cl(1) 2.982(2) Å], forming the characteristic bridge between the two phenyl rings; the dihedral angle between the two phenyl rings is 70.1(2)°. One hydroxy

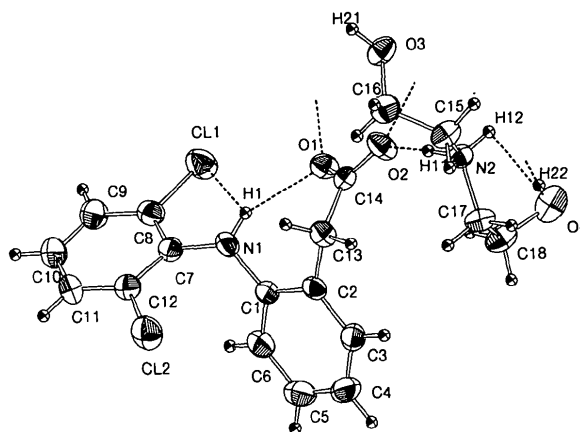


Fig. 1. Molecular conformation of the 1:1 adduct D.HNDEA, showing the atomic labelling and hydrogen bonds (50% probability displacement ellipsoids and H atoms of arbitrary size).

O atom in the cation is hydrogen bonded *via* H(12) to N(2) [O(4)···N(2) 2.877(3) Å].

Intermolecular interactions comprise strong hydrogen bonds which involve all H atoms of the donor groups (hydroxy and ammonium) of the cation and the negatively charged O atoms of the anion. They can be subdivided into (a) anion-cation and (b) cation-cation hydrogen bonds: (a) O(2) interacts twice, with H(11) [O(2)···N(2) 2.758(3) Å] inside the asymmetric unit and with H(12<sup>i</sup>) of a neighbouring cation [O(2)···N(2<sup>i</sup>) 2.790(3) Å; symmetry code: (i)  $-1-x, -y, 2-z$ ], whereas the other carboxylic O atom O(1) links *via* H(21<sup>ii</sup>) to a hydroxy group of a symmetry generated cation [O(1)···O(3<sup>ii</sup>) 2.666(3) Å; symmetry code: (ii)  $x-\frac{1}{2}, \frac{1}{2}-y, z$ ]; (b) one cation links *via* H(22) to another cation [O(4)···O(3<sup>i</sup>) 2.743(3) Å] giving a dimer very similar to that found in the neutral base (Mootz, Brodalla & Wiebcke, 1989). The crystal engineering is governed by the presence of these centrosymmetric dications held together by head-to-tail linking. This means, in fact, that the ammonium dimer acts as a kind of supramolecule, with all hydrogen bonds coming from it (Fig. 2) to form a two-dimensional network in the *ab* plane. In contrast, no bond arises between the ions along the *c* direction of the cell. In conclusion, the crystal structure of the present compound can be described as a stacking of layers each with a sandwich structure. The inner part of the sandwich contains all the polar interactions. The ring moieties of the anions crowd the surfaces of the layers and pack along the *c* axis with normal van der Waals contacts.

The structure of the D.HEP salt displayed discrete double-bonded ion pairs packed together by weak C—H···A (A = Cl and O) interactions. In contrast, the present structure shows a sequence of 2:2 ion pairs, (D.HNDEA)<sub>2</sub>, hydrogen bonded to each other. It is the hydrogen bond between the ion pairs that might be preferentially broken in the dissolution process, since

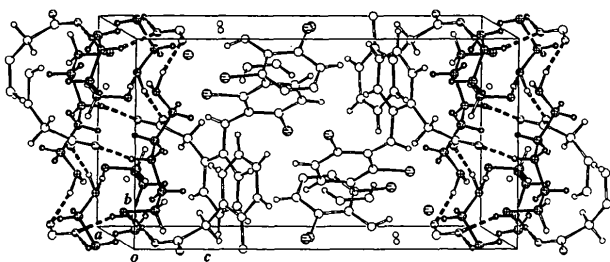


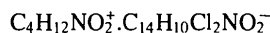
Fig. 2. Crystal packing of D.HNDEA.

the (D.HNDEA)<sub>2</sub> units are stabilized by the presence of four ionic interactions between negative O(2) atoms and the ammonium groups within the pairs. The existence of solvent-separated 2:2 ion pairs could explain the fact that the solubility in water of D.HNDEA (Fini, Fazio & Rapaport, 1993) is lower than expected on the basis of the number of hydrophilic groups present in the cation.

### Experimental

Acidic diclofenac (IBSA, Lugano, Switzerland) was dissolved in acetone. To the solution an equivalent amount of *N*-diethanolamine (Fluka, Buchs, Switzerland) was added and single crystals of D.HNDEA were obtained at room temperature. Full preparation details are reported by Fini, Fazio & Rapaport (1993). The density  $D_m$  was measured by flotation in 2-bromo-2-chloro-1,1,1-trifluoroethane and *p*-xylene.

### Crystal data

 $M_r = 401.28$ 

Monoclinic

 $P2_1/a$  $a = 11.772(5) \text{ \AA}$  $b = 9.346(3) \text{ \AA}$  $c = 17.186(8) \text{ \AA}$  $\beta = 91.70(4)^\circ$  $V = 1890.0(13) \text{ \AA}^3$  $Z = 4$  $D_x = 1.410 \text{ Mg m}^{-3}$  $D_m = 1.42 \text{ Mg m}^{-3}$ Mo  $K\alpha$  radiation $\lambda = 0.71069 \text{ \AA}$ 

Cell parameters from 25 reflections

 $\theta = 8-12^\circ$  $\mu = 0.370 \text{ mm}^{-1}$  $T = 293(2) \text{ K}$ 

Prisms

 $0.25 \times 0.25 \times 0.10 \text{ mm}$ 

Colourless

### Data collection

Enraf-Nonius CAD-4 diffractometer

Profile data from  $\omega$  scans

Absorption correction: none

3416 measured reflections

3301 independent reflections

1712 observed reflections

 $[I > 2\sigma(I)]$  $R_{\text{int}} = 0.022$  $\theta_{\text{max}} = 24.98^\circ$  $h = -13 \rightarrow 13$  $k = 0 \rightarrow 11$  $l = 0 \rightarrow 20$ 

3 standard reflections

frequency: 120 min

intensity decay: none

### Refinement

Refinement on  $F^2$  $R[F^2 > 2\sigma(F^2)] = 0.0344$  $wR(F^2) = 0.0773$  $(\Delta/\sigma)_{\text{max}} = 0.113$  $\Delta\rho_{\text{max}} = 0.239 \text{ e \AA}^{-3}$  $\Delta\rho_{\text{min}} = -0.232 \text{ e \AA}^{-3}$  $S = 1.125$ 

3301 reflections

257 parameters

 $w = 1/[\sigma^2(F_o^2) + (0.0381P)^2 + 0.5124P]$ where  $P = (F_o^2 + 2F_c^2)/3$ 

Extinction correction: none

Atomic scattering factors

from *International Tables*for *Crystallography* (1992,

Vol. C, Tables 4.2.6.8 and

6.1.1.4)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}$
C11	-0.00974 (7)	0.18502 (10)	0.76532 (5)	0.0572 (3)
C12	-0.27265 (7)	-0.02104 (10)	0.52724 (5)	0.0585 (3)
N1	-0.2054 (2)	0.0213 (3)	0.69619 (15)	0.0404 (6)
C1	-0.2271 (2)	-0.1275 (3)	0.69871 (15)	0.0345 (7)
C2	-0.3237 (2)	-0.1742 (3)	0.73691 (15)	0.0347 (7)
C3	-0.3461 (3)	-0.3198 (3)	0.7377 (2)	0.0437 (8)
C4	-0.2759 (3)	-0.4172 (4)	0.7027 (2)	0.0547 (9)
C5	-0.1802 (3)	-0.3713 (4)	0.6666 (2)	0.0528 (9)
C6	-0.1561 (3)	-0.2259 (4)	0.6652 (2)	0.0440 (8)
C7	-0.1349 (2)	0.0848 (3)	0.6426 (2)	0.0370 (7)
C8	-0.0425 (3)	0.1699 (3)	0.6659 (2)	0.0418 (7)
C9	0.0240 (3)	0.2404 (4)	0.6139 (2)	0.0541 (9)
C10	-0.0001 (3)	0.2283 (4)	0.5354 (2)	0.0594 (10)
C11	-0.0899 (3)	0.1459 (3)	0.5095 (2)	0.0527 (9)
C12	-0.1560 (3)	0.0768 (3)	0.5620 (2)	0.0419 (8)
C13	-0.4026 (2)	-0.0703 (3)	0.7745 (2)	0.0380 (7)
C14	-0.3587 (2)	-0.0016 (3)	0.8502 (2)	0.0320 (7)
O1	-0.2570 (2)	0.0368 (2)	0.85460 (11)	0.0411 (5)
O2	-0.4272 (2)	0.0153 (2)	0.90340 (11)	0.0482 (6)
N2	-0.6362 (2)	-0.0896 (3)	0.94419 (15)	0.0325 (6)
C15	-0.7436 (2)	-0.0102 (3)	0.9250 (2)	0.0425 (8)
C16	-0.7261 (3)	0.1253 (3)	0.8813 (2)	0.0469 (8)
C17	-0.6394 (2)	-0.2397 (3)	0.9158 (2)	0.0429 (8)
C18	-0.5365 (3)	-0.3205 (3)	0.9436 (2)	0.0507 (9)
O3	-0.6784 (2)	0.2327 (2)	0.93006 (12)	0.0453 (6)
O4	-0.5342 (2)	-0.3281 (3)	1.02574 (15)	0.0614 (7)

Table 2. Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

C14—O2	1.247 (3)	N2—C17	1.486 (4)
C14—O1	1.250 (3)	N2—C15	1.494 (3)
C7—N1—C1	123.5 (3)	C17—N2—C15	112.5 (2)
C2—C13—C14	116.1 (2)	O3—C16—C15	111.3 (2)
O2—C14—C13	117.9 (2)	O4—C18—C17	109.6 (3)
C1—N1—C7—C12	60.4 (4)	N2—C17—C18—O4	62.8 (3)
N2—C15—C16—O3	-73.4 (3)		

Table 3. Hydrogen-bonding geometry ( $\text{\AA}$ ,  $^\circ$ )

$D-H \cdots A$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
N1—H1 $\cdots$ C11	2.59 (3)	2.982 (3)	110 (2)
N1—H1 $\cdots$ O1	2.07 (3)	2.811 (3)	146 (3)
N2—H12 $\cdots$ O4	2.51 (3)	2.877 (3)	104 (2)
N2—H11 $\cdots$ O2	1.87 (2)	2.758 (3)	160 (3)
N2—H12 $\cdots$ O2'	1.89 (2)	2.790 (3)	161 (3)
O3—H21 $\cdots$ O1''	1.77 (3)	2.666 (3)	165 (2)
O4—H22 $\cdots$ O3'	1.82 (3)	2.743 (3)	170 (4)

Symmetry codes: (i)  $-1 - x, -y, 2 - z$ ; (ii)  $x - \frac{1}{2}, \frac{1}{2} - y, z$ .

The H atoms bonded to N and O atoms were experimentally located and their coordinates and displacement coefficients were refined with distance restraints for the N—H and O—H bond lengths. The remaining H atoms not involved in hydrogen bonding were placed in calculated positions and refined riding on parent atoms (aromatic C—H = 0.93  $\text{\AA}$ , C<sub>sp<sup>3</sup></sub>—H = 0.97  $\text{\AA}$ ).

Data collection: *CAD-4 Software* (Enraf-Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure:

*SHELXL93* (Sheldrick, 1993). Molecular graphics: *SCHAKAL92* (Keller, 1992). Software used to prepare material for publication: *SHELXL93*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: NA1170). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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*Acta Cryst.* (1995). **C51**, 2615–2617

## (±)-3-Oxo-*trans*-2-phenylcyclohexaneacetic Acid: Structure and Hydrogen-Bonding Pattern of a Partially Hydrated $\delta$ -Keto Acid

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(Received 2 November 1994; accepted 20 June 1995)

### Abstract

In the title compound,  $C_{14}H_{16}O_3 \cdot 0.25H_2O$ , enantiomeric pairs of molecules form centrosymmetric dimers by mutual hydrogen bonding of carboxyl groups; the dimers are centered on the *b* and *c* edges of the chosen unit cell. The ketone has a close contact of 2.738 (7) Å to the O atom of a water molecule (which has an occupancy of approximately 25%).

### Comment

Of the four hydrogen-bonding motifs known to occur in simple crystalline keto carboxylic acids, the commonest, in which the ketone does not participate, is the dimer pattern typical of almost all functionally unsubstituted acids. Less commonly, intermolecular carboxyl-to-ketone hydrogen bonds repeat infinitely along one cell axis to yield a chain, or catemer. A third, rare arrangement has an internal hydrogen bond and one instance is known of acid-to-ketone dimerization. We have previously referenced and discussed numerous examples (Thompson, Lalancette & Vanderhoff, 1992; Coté, Thompson & Lalancette, 1995).

The title compound, (I), is a  $\delta$ -keto acid which crystallizes as a partial hydrate (25%) from 60:40 water-ethanol. The  $\delta$ -keto acids include catemers of both the helical and translational type, as well as dimers. However, hydrates are remarkably rare among the simple keto acids for which X-ray structures have been determined. Those known include a carboxyl-to-water-to-ketone catemer (Winkler, Hong, Hey & Williard, 1991) and a dimer containing two inserted hydrogen-bonded water molecules (Lalancette, Vanderhoff & Thompson, 1990). The latter is apparently the only one with crystal structures known for both hydrated and anhydrous forms.

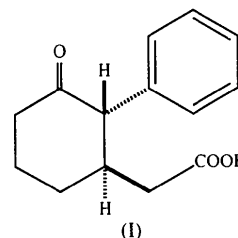


Fig. 1 presents a view of the title compound, with its numbering scheme. As expected, the cyclohexanone has a chair conformation with both substituents equatorial. The aromatic ring adopts a conformation that is nearly orthogonal [ $86.32(8)^\circ$ ] to the plane through C(1), C(3), C(4) and C(6) of the cyclohexanone. The aromatic ring is thus nearly coplanar [ $3.3(2)^\circ$ ] with the plane defined by C(9)—C(2)—H(2). The substituent methylene C atom adopts a staggered conformation relative to the adjacent ring C atom [torsion angles H(1)—C(1)—C(7)—H(7B)  $64.9(3)^\circ$  and H(1)—C(1)—C(7)—H(7A)  $-176.3(3)^\circ$ ] with the carboxyl directed away from the aromatic ring. The dihedral angle between the planes described by C(7)—C(8)—O(2) and H(1)—C(1)—C(2) is  $17.1(3)^\circ$ .

Although disorder of carboxyl C=O bond lengths and C—C=O angles is common in dimeric acids (Dieterich, Paul & Curtin, 1974), it is not substantial here. The lengths are 1.224(4) and 1.287(4) Å, with angles of  $115.7(3)^\circ$  and  $123.0(3)^\circ$ ; typical values for