Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* ($\mathring{A}^2$)

$$U_{eq} = \tfrac{1}{3}\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	*y*	*z*	U_{eq}
S1	−0.2537 (1)	0.1774 (1)	0.3850 (1)	0.036 (1)
S2	−0.2058 (1)	0.4876 (1)	0.3423 (1)	0.038 (1)
S3	−0.1372 (1)	0.5569 (1)	0.4666 (1)	0.033 (1)
O1	−0.2844 (1)	0.6423 (2)	0.3214 (1)	0.052 (1)
C1	−0.2695 (1)	0.5517 (3)	0.5981 (1)	0.036 (1)
C2	−0.3154 (2)	0.4154 (4)	0.6712 (1)	0.048 (1)
C3	−0.3874 (2)	0.2665 (5)	0.6180 (2)	0.060 (1)
C4	−0.3705 (2)	0.3267 (4)	0.5207 (1)	0.046 (1)
C5	−0.2729 (1)	0.2297 (3)	0.5015 (1)	0.031 (1)
C6	−0.2017 (1)	0.3966 (3)	0.5497 (1)	0.027 (1)
C7	−0.3514 (1)	0.5769 (4)	0.5279 (1)	0.047 (1)
C8	−0.1231 (1)	0.2923 (3)	0.6084 (1)	0.027 (1)
C9	−0.0822 (1)	0.4078 (3)	0.6814 (1)	0.035 (1)
C10	−0.0069 (1)	0.3165 (4)	0.7321 (1)	0.044 (1)
C11	0.0287 (1)	0.1117 (4)	0.7108 (1)	0.047 (1)
C12	−0.0099 (1)	−0.0028 (4)	0.6382 (2)	0.044 (1)
C13	−0.0852 (1)	0.0862 (3)	0.5870 (1)	0.035 (1)

Table 2. *Geometric parameters* ($\mathring{A}$, °)

S1—S2	2.088 (1)	C4—C5	1.549 (3)
S1—C5	1.810 (2)	C4—C7	1.522 (3)
S2—S3	2.090 (1)	C5—C6	1.566 (2)
S2—O1	1.470 (2)	C6—C8	1.513 (2)
S3—C6	1.857 (2)	C8—C9	1.390 (2)
C1—C2	1.542 (3)	C8—C13	1.389 (2)
C1—C6	1.550 (2)	C9—C10	1.388 (3)
C1—C7	1.528 (3)	C10—C11	1.369 (3)
C2—C3	1.542 (3)	C11—C12	1.372 (3)
C3—C4	1.534 (3)	C12—C13	1.385 (3)
S2—S1—C5	102.3 (1)	S3—C6—C1	110.7 (1)
S1—S2—S3	92.7 (1)	S3—C6—C5	110.6 (1)
S1—S2—O1	111.4 (1)	C1—C6—C5	101.1 (1)
S3—S2—O1	111.9 (1)	S3—C6—C8	102.9 (1)
S2—S3—C6	105.8 (1)	C1—C6—C8	115.7 (1)
C2—C1—C6	108.6 (2)	C5—C6—C8	116.1 (1)
C2—C1—C7	101.7 (2)	C1—C7—C4	94.5 (2)
C6—C1—C7	102.0 (1)	C6—C8—C9	120.7 (1)
C1—C2—C3	103.6 (2)	C6—C8—C13	121.0 (1)
C2—C3—C4	102.6 (2)	C9—C8—C13	118.1 (2)
C3—C4—C5	106.5 (2)	C8—C9—C10	120.5 (2)
C3—C4—C7	101.6 (2)	C9—C10—C11	120.5 (2)
C5—C4—C7	102.8 (2)	C10—C11—C12	119.6 (2)
S1—C5—C4	115.7 (1)	C11—C12—C13	120.5 (2)
S1—C5—C6	115.0 (1)	C8—C13—C12	120.7 (2)
C4—C5—C6	103.8 (1)		

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Diammonium Cyclopropane-1,1-dicarboxylate

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Abstract

Diammonium cyclopropane-1,1-dicarboxylate was prepared by neutralizing an aqueous solution of cyclopropane-1,1-dicarboxylic acid (Fluka) with 2 equivalents ammonium hydroxide. Each ammonium cation bridges two pairs of cyclopropane-1,1-dicarboxylate anions *via* hydrogen bonds; each anion is bridged to eight other anions in this way. The planes of the two carboxyl groups subtend an angle of 44.6° and the minimum COO⋯OOC distance is 2.839 (3) Å. The OOC—C—COO bond angle is 120.4 (2)° which may be accounted for by the sp^2 hybridization of the cyclopropyl C atoms.

Comment

We have recently reported that the kinetic labilities of platinum complexes of 1,1-cycloalkyldicarboxylato and dialkylmalonato ligands may be related to their molecular structure (Bréhin, Kozelka, Bois &

Chottard, unpublished results). 1,1-Cycloalkyldi-carboxylate residues are more rigid than malonate or dialkylmalonate moieties; this is indicated by the OOC—C—COO bond angle which varies from 109 to 125° in (dialkyl)malonato compounds but remains close to 109° in the 1,1-cyclobutyldicarboxylato derivatives (Jaulmes, Laruelle & Fabrègue, 1987; Pajunen & Pajunen, 1979; Bitha, Child, Hlavka, Lang & Lin, 1988; Neidle, Ismail & Sadler, 1980; Soltzberg & Margulis, 1971). The range of values for the OOC—C—COO angle is also quite narrow [123 (3)°] in 1,1-cyclopropyldicarboxylato compounds, although this case is less well documented (Meester, Schenk & MacGillavry, 1971; Bréhin, Kozelka, Bois & Chottard, unpublished results). In the present paper, we report the crystal structure of the diammonium salt of 1,1-cyclopropyldicarboxylic acid in which the OOC—C—COO angle is 120.4 (2)°.

Final positional parameters are given in Table 1, bond lengths and angles in Table 2. Fig. 1 displays an ORTEP drawing of the anion and Fig. 2 shows the crystal packing.
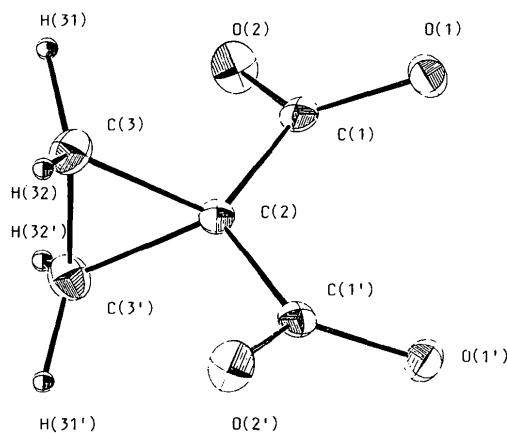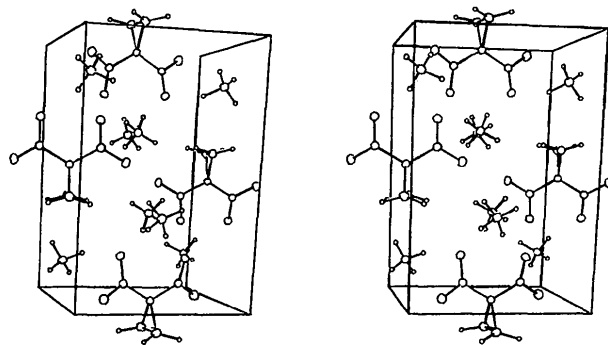
It is clear from Table 2 and Fig. 2 that each of the four dicarboxylate O atoms accepts two hydrogen bonds from two different ammonium ions. Thus, each ammonium ion bridges two pairs of dicarboxylate anions.

The cyclopropane-1,1-dicarboxylate anion possesses C_2 symmetry, the dyad axis passing through C(2). The planes of the two carboxyl groups subtend an angle of 44.6°. The shortest O···O distance is 2.839 (3) Å which is approximately equal to the sum of the van der Waals radii (Bondi, 1964). The value of the OOC—C—COO bond angle [120.4 (2)°] is between those observed in cyclopropane-1,1-dicarboxylic acid [118.3 (2)° (Meester, Schenk & MacGillavry, 1971)] and cis-[Pt(cyclopropane-1,1-dicarboxylato)(NH₃)₂] [124.0 (11)° (Bréhin, Kozelka, Bois & Chottard, unpublished results)]. The clustering of the OOC—C—COO angles around 120° in 1,1-cyclopropyldicarboxylato compounds is consistent with the sp^2 hybridization of the cyclopropyl C atoms (McQuillin, 1972) and confirms our hypothesis that the acids, salts and metal chelates of 1,1-cycloalkanedicarboxylate retain their characteristic OOC—C—COO bond angles.

Fig. 1. An ORTEP drawing of the anion (30% ellipsoids) showing the numbering scheme.

Fig. 2. Stereoview of the crystal packing.

Experimental

Crystal data

2NH₄⁺.C₅H₄O₄²⁻	Mo $K\alpha$ radiation
M_r = 164.2	λ = 0.7107 Å
Orthorhombic	Cell parameters from 25
Pcnb	reflections
a = 7.7819 (8) Å	θ = 7.5–8.5°
b = 8.069 (2) Å	μ = 0.12 mm⁻¹
c = 11.574 (2) Å	T = 291 K
V = 726.8 (4) Å³	Needle
Z = 4	0.4 × 0.25 × 0.25 mm
D_x = 1.50 Mg m⁻³	Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer	548 observed reflections [$I\geq3\sigma(I)$]
ω–2θ scans	h = 0 → 9
Absorption correction: none	k = 0 → 9
	l = 0 → 13
800 measured reflections	2 standard reflections
640 independent reflections	frequency: 120 min intensity variation: none

Refinement

Refinement on F	w = 1
Final R = 0.032	$(\Delta/\sigma)_{max}$ = 0.14
wR = 0.031	$\Delta\rho_{max}$ = 0.27 e Å⁻³
548 reflections	$\Delta\rho_{min}$ = −0.14 e Å⁻³
72 parameters	Atomic scattering factors
H atoms refined isotropically with an overall U	from CRYSTALS (Carruthers & Watkin, 1985)

Table 1. *Fractional atomic coordinates and equivalent isotropic temperature factors* ($\mathring{A}^2$) *with e.s.d.'s in parentheses*

$$U_{eq} = \tfrac{1}{3}\sum_i\sum_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
O(1)	0.1762 (2)	0.2957 (2)	0.6906 (1)	0.0251
O(2)	0.2936 (2)	0.1747 (2)	0.5382 (1)	0.0282
N(1)	−0.0399 (2)	0.4862 (2)	0.8453 (1)	0.0257
C(1)	0.1673 (2)	0.2368 (2)	0.5901 (1)	0.0181
C(2)	0.0000	0.2500	0.5254 (2)	0.0162
C(3)	0.0159 (3)	0.3401 (2)	0.4109 (2)	0.0260
H(1a)	−0.098 (3)	0.424 (3)	0.899 (2)	0.051 (3)†
H(1b)	−0.136 (3)	0.558 (3)	0.811 (2)	0.051 (3)†
H(1c)	0.045 (3)	0.549 (3)	0.879 (2)	0.051 (3)†
H(1d)	0.010 (3)	0.421 (3)	0.782 (2)	0.051 (3)†
H(3a)	0.138 (3)	0.381 (3)	0.391 (2)	0.051 (3)†
H(3b)	−0.080 (3)	0.420 (3)	0.390 (2)	0.051 (3)†

† Isotropic *U*.

Table 2. *Interatomic distances* ($\mathring{A}$) *and angles* (°) *with e.s.d.'s in parentheses*

O(1)—C(1)	1.259 (2)	C(2)—C(3)	1.517 (3)
O(2)—C(1)	1.256 (2)	C(3)—C(3')	1.474 (4)
C(1)—C(2)	1.505 (2)		

O(2)—C(1)—O(1)	123.3 (2)	C(3)—C(2)—C(1')	118.1 (1)
C(2)—C(1)—O(1)	118.7 (2)	C(3)—C(2)—C(1)	113.4 (1)
C(2)—C(1)—O(2)	117.9 (1)	C(3)—C(2)—C(3')	58.1 (2)
C(1)—C(2)—C(1')	120.4 (2)	C(3)—C(3')—C(2)	60.93 (8)

Hydrogen bonds

O(1)···N(1)	2.897 (2)	O(2)···N(1^{iii})	2.890 (2)
O(1)···H(1d)	1.95 (3)	O(2)···H(1a^{iii})	1.99 (3)
O(1)···H(1d)—N(1)	161 (1)	O(2)···H(1a^{iii})—N(1^{iii})	168 (2)

O(1)···N(1^{ii})	2.855 (2)	O(2)···N(1^{iv})	2.794 (2)
O(1)···H(1b^{ii})	1.88 (3)	O(2)···H(1c^{iv})	1.87 (3)
O(1)···H(1b^{ii})—N(1^{ii})	158 (2)	O(2)···H(1c^{iv})—N(1^{iv})	175 (2)

Symmetry codes: (i) $-x, \tfrac{1}{2}-y, z$; (ii) $\tfrac{1}{2}+x, 1-y, \tfrac{3}{2}-z$; (iii) $\tfrac{1}{2}+x, \tfrac{1}{2}-y, z-\tfrac{1}{2}$; (iv) $\tfrac{1}{2}-y, y-\tfrac{1}{2}, \tfrac{3}{2}-z$.

Colourless needles of the compound were crystallized from water/ethanol at 277 K. The structure was solved by direct methods (*SHELXS*86; Sheldrick, 1986) and refined by full-matrix least squares.

We thank Professor J. C. Chottard for helpful discussions.

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Structure of the 1:1 Complex of 6,6'-Diquinolyl Ether with 5,5-Diethylbarbituric Acid

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Abstract

The crystal structure shows that barbital (5,5-diethylbarbituric acid) is bonded to 6,6'-diquinolyl ether by two short NH···N hydrogen bonds with N···N 2.88 Å. This arrangement is similar to those reported for hydrogen bonds in the molecular complexes of barbiturates.

Comment

Barbiturates are widely used medicinally and are among the most frequently encountered drugs for the treatment of epilepsy. This class of antiepileptic drug is of special interest since many of them and their active metabolites form metal complexes. Various metal complexes of barbiturates have been synthesized and studied (Caira, Fazakerley, Linder & Nassimbeni, 1973; Pezeshk, Greenaway & Sorenson, 1983). A series of crystal structure determinations of molecular complexes of barbiturates with other molecules, such as 9-ethyladenine (Voet & Rich, 1972; Voet, 1972), caffeine (Craven & Gartland, 1970), aminopyrine (Kiryu, 1971), urea (Gartland & Craven, 1974), acetamide (Hsu & Craven, 1974a), salicylamide (Hsu & Craven, 1974b) and imidazole (Hsu & Craven, 1974c), have been reported. In crystal complexes of barbiturates with these ligands there are stronger NH···O— —C and NH···N hydrogen bonds between the two components than are found in the crystal structures of the individual components.