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N,*N*,*N*′,*N*′-Tetramethylethylenediammonium–succinate–succinic acid (1/1/1)

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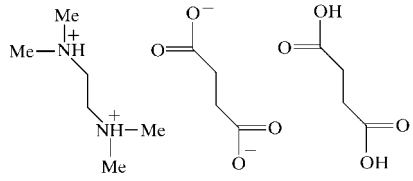
In the title compound, $C_6H_{18}N_2^{2+}\cdot C_4H_4O_4^{2-}\cdot C_4H_6O_4$, the components lie on centres of symmetry in space group $P\overline{1}$, such that the asymmetric unit contains three half-molecules. Despite the different mode (with respect to other dicarboxylic acids) adopted by the intermolecular self-interaction of succinic acid derivatives, the overall structure of the title compound consists of anionic layers that are typical of the packing structures exhibited by other dicarboxylic acid analogues.

Comment

In the course of a wide-ranging study concerning the solid-state aggregation of anions derived from dicarboxylic acids crystallized with solvents and/or positively charged counter-ions, we have crystallized and solved the structure of an interesting supramolecular solid, (I), formed from succinic acid and an alkyldiammonium succinate. Many studies of the behaviour of dicarboxylic acids in the solid state have been carried out (Thalladi *et al.*, 2000; MacDonald *et al.*, 2001) in order to investigate their trend towards self-aggregation, which stems from the hydrogen-bonding interactions (Aakeroy & Seddon, 1993) that these systems are able to develop among themselves. Therefore, dicarboxylic acids are suitable substrates for crystal engineering (Desiraju, 1995, 2003). Succinic acid can be considered the first in the series of dicarboxylic acids whose two functional groups do not interact sterically with one another unless they are constrained in the symmetric *cis* conformation (*e.g.* Sobota & Szafert, 1996). Recently, the structure of this acid (related to its physical behaviour) was analysed and compared with those of some longer chain dicarboxylic acids (Pedireddi *et al.*, 1998; Thalladi *et al.*, 2000). Moreover, its importance is evident when considering the many reported structures with nitrogenated compounds (Kalsbeek, 1991; Kalsbeek & Larsen, 1991; MacDonald *et al.*, 2001; Büyükgüngör & Mustafa, 2002) and amino acids thought to be present under prebiotic conditions (Prasad & Vijayan, 1991, 1993). Linear polyamines also form, in aqueous solution, fairly stable complexes with carboxylic ligands, such as dicarboxylates (malonates, succinates, *etc.*; De Robertis *et al.*, 2001, and references therein), and these interactions can be considered as useful models for the binding of polyanions by polyammonium cations in natural systems.



(I)

The asymmetric unit of (I) contains one-half of a succinic acid molecule, one-half of a succinate anion and one-half of an *N*,*N*,*N*′,*N*′-tetramethylethylenediammonium cation (Fig. 1 and Table 1). As expected, the succinate fragments are planar [the maximum deviations are 0.001 (1) Å for atom C2 and 0.004 (1) Å for atom C4], but they are also coplanar [the angle between their mean planes is 8.82 (5)°]. This disposition is driven by the stable planar conformation of the succinate derivatives, combined with the development of directional hydrogen-bonding interactions employing the lone pairs of carboxylate atoms O3 and O4 (*anti* towards the OH donors and *syn* towards NH). Succinic acid and succinate molecules, bound *via* an intermolecular hydrogen bond (H1*C*$\cdots$O3 = 1.70 Å), alternate along one-dimensional ribbons parallel to the crystallographic *ab* plane and along the [110] direction (Fig. 2).

In the carboxy moieties, O-atom lone pairs and/or H atoms can be positioned on the same side as the other O atom (*syn*) or on the opposite side (*anti*), so it is straightforward to infer that hydrogen-bonding interactions can be developed towards these two possible directions, either for O-atom donors or for O-atom acceptors. Usually the *syn* positions are less sterically hindered and thus are often exploited by strong molecular interactions and/or synthons (Fleishman *et al.*, 2003). A search of the Cambridge Structural Database (Allen, 2002) for ammonium succinates shows that these dicarboxylic acids often self-assemble along one-dimensional ribbons or strands (planar or not), obtained through different hydrogen-bonding pathways, *via anti–anti* (three examples), *syn–syn* (14 examples) and *syn–anti* (four examples) interactions. The structure of (I) confirms that succinate derivatives are able to self-aggregate *via anti–anti* (Fig. 2) interactions, unlike all of the previously reported dicarboxylic acids (MacDonald *et al.*, 2001), which adopt the more common *syn–syn* hydrogen bond for self-aggregation. We suggest that, in this way, succinate networks free their stronger O-atom donor *syn* sites, which are then able to bind tightly to specific guest counter-ions. To our knowledge, there is only one precedent, in which the acid has two highly symmetric ionization states that lead to this particular ribbon network (YOWDET; Prasad & Vijayan, 1990).

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Therefore, we are currently studying the possible influence of different counter-ions on the succinate self-assembly mode. In (I), counter-ions bear positively charged monohydrogenated N atoms, which lie close to the mean plane of the succinate molecule [the deviation from the plane is 0.272 (1) Å], so we might infer that this interaction between the two oppositely charged ions is directional. This strong hydrogen bond (H1···O4 = 1.82 Å), together with some weaker bonds (Table 2), holds the succinate ribbons side-by-side, such that they appear as supermolecular layers. These layers are, in turn, connected along the third dimension by ethylenediammonium chains (see Fig. 3).

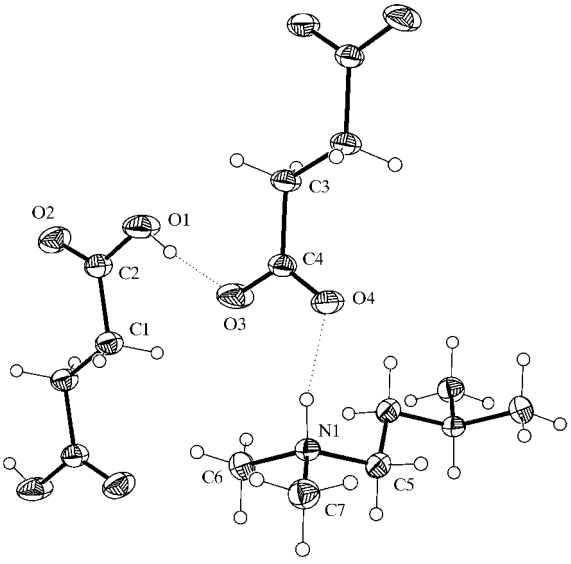

Figure 1
A view of the components of (I) (30% probability displacement ellipsoids).

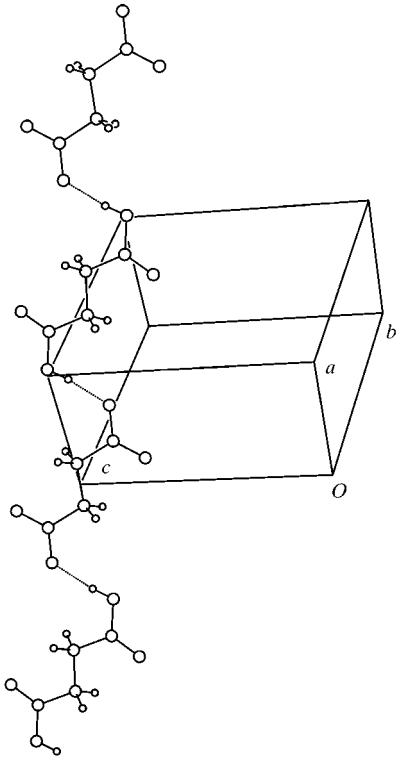

Figure 2
A view of the centrosymmetric molecular ribbons in (I), composed of succinate anions and succinic acid molecules.

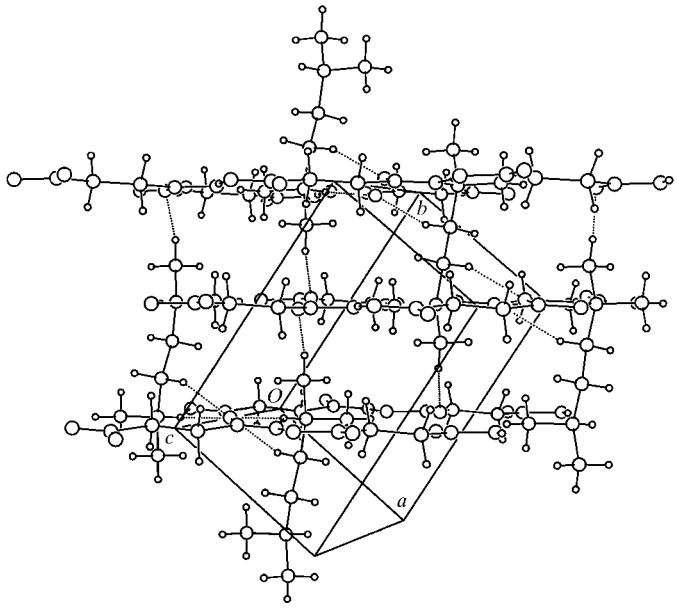

Figure 3
The three-dimensional packing in the crystal structure of (I).

Experimental

Crystals of (I) were obtained by stirring, at room temperature, a 50 m*M* solution (6 ml) of *N*,*N*,*N*′,*N*′-tetramethylethylenediamine with the same volume of an equimolar (1:1 ratio) aqueous succinic acid solution. The final stoichiometry of the crystal was 1:2, probably as a result of the acid and base strengths; diammonium salts usually crystallize with semi-carboxylate ions of dicarboxylic acids (Barnes & Weakley, 2000), resulting in an overall ratio of 1:2. The mother solution, containing the remaining amine, was filtered and samples suitable for X-ray analysis were selected from the dried crystals.

Crystal data

$C_6H_{18}N_2^{2+}\cdot C_4H_6O_4^{2-}\cdot C_4H_4O_4$
M_r = 352.38
Triclinic, $P\overline{1}$
a = 5.6370 (4) Å
b = 8.7100 (8) Å
c = 8.8431 (6) Å
α = 96.219 (7)°
β = 93.414 (6)°
γ = 97.604 (7)°
V = 426.63 (6) Å^3
Z = 1
D_x = 1.372 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 46 reflections
θ = 7.1–17.4°
μ = 0.11 mm^{-1}
T = 298 (2) K
Irregular, colourless
0.40 × 0.32 × 0.18 mm

Data collection

Siemens *P*4 diffractometer
$2\theta/\omega$ scans
Absorption correction: empirical (North *et al.*, 1968)
T_{min} = 0.273, T_{max} = 0.299
3194 measured reflections
2495 independent reflections
1926 reflections with $I > 2\sigma(I)$
R_{int} = 0.015
θ_{max} = 30°
$h = -7 \rightarrow 1$
$k = -12 \rightarrow 12$
$l = -12 \rightarrow 12$
3 standard reflections
every 197 reflections
intensity decay: 1%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0553P)^2 + 0.073P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.042$	$(\Delta/\sigma)_{max} < 0.001$
$wR(F^2) = 0.117$	$\Delta\rho_{max} = 0.32$ e Å^{-3}
$S = 1.06$	$\Delta\rho_{min} = -0.21$ e Å^{-3}
2495 reflections	
109 parameters	
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

O1—C2	1.319 (1)	C3—C3^{ii}	1.511 (2)
O2—C2	1.206 (1)	C3—C4	1.520 (1)
C1—C1^{i}	1.514 (2)	N1—C6	1.487 (1)
C1—C2	1.514 (2)	N1—C5	1.491 (1)
O3—C4	1.260 (1)	N1—C7	1.493 (2)
O4—C4	1.244 (1)		
O2—C2—O1	120.2 (1)	O4—C4—O3	122.3 (1)
O2—C2—C1	123.4 (1)	O4—C4—C3	120.1 (1)
O1—C2—C1	116.3 (1)	O3—C4—C3	117.5 (1)
C1^{i}—C1—C2—O2	6.0 (2)	C3^{ii}—C3—C4—O4	−2.3 (2)
C1^{i}—C1—C2—O1	−174.2 (1)	C3^{ii}—C3—C4—O3	178.5 (1)

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

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O4	0.91	1.82	2.710 (1)	166
N1—H1···O3	0.91	2.45	3.159 (1)	134
O1—H1*C*···O3	0.82	1.70	2.514 (1)	173
C5—H5*B*···O4^{ii}	0.97	2.49	3.424 (1)	161
C7—H7*C*···O2^{iii}	0.96	2.48	3.392 (2)	158

Symmetry codes: (ii) $-x, -y, 1-z$; (iii) $1-x, 1-y, 2-z$.

All H atoms were located in difference Fourier maps, and then placed in idealized positions (O—H = 0.82 Å, N—H = 0.91 Å and C—H = 0.96 Å) and allowed to ride on their parent atoms, with fixed isotropic displacement parameters (0.05 Å^2).

Data collection: *XSCANS* (Siemens, 1989); cell refinement: *XSCANS*; data reduction: *XPREPW* (Bruker, 1997); program(s) used to solve structure: *SIR*97 (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *XPW* (Bruker, 1997); software used to prepare material for publication: *PARST*97 (Nardelli, 1995) and *WinGX* (Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1646). Services for accessing these data are described at the back of the journal.

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