

Bis(dimethylammonium) 1,4-phenylenediacylate

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Key indicators

Single-crystal X-ray study
 $T = 148$ K
Mean $\sigma(\text{C}-\text{C}) = 0.003$ Å
 R factor = 0.053
 wR factor = 0.131
Data-to-parameter ratio = 14.1For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The title compound, $2 \text{C}_2\text{H}_8\text{N}^+ \cdot \text{C}_{12}\text{H}_8\text{O}_4^{2-}$, crystallizes as a salt in space group $P2_1/n$, the anion being located on an inversion center. The dimethylammonium cations link neighboring carboxylate anions *via* two $\text{N}^+ - \text{H} \cdots \text{O}$ hydrogen bonds [$\text{H} \cdots \text{O} = 1.72$ (3) and 1.84 (3) Å, $\text{N} \cdots \text{O} = 2.671$ (2) and 2.726 (2) Å, and $\text{N}-\text{H} \cdots \text{O} = 178$ (3) and 173 (2)°] resulting in molecular ribbons.

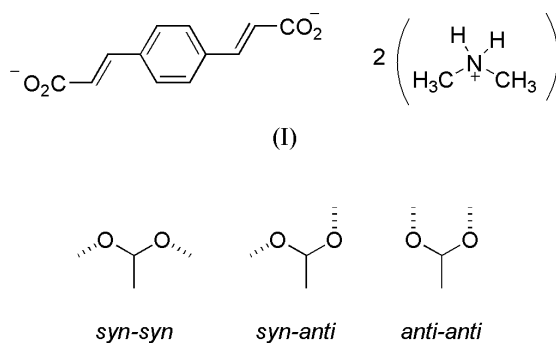
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Comment

Crystal engineering strategies that include multicomponent systems often seek to assess the degree of predictability of the corresponding supramolecular synthons. Although chemically unique, crystal organization of such systems is influenced by the complementary nature of the molecular components. Ideally, synthons of interest should be examined in the presence of a wide variety of crystal environments and chemical frameworks. This approach has proven successful and continues to develop the extant database of known structural tools for constructing predetermined molecular arrays (Aakeröy & Beatty, 2001; Desiraju, 2003; MacGillivray, 2004).



Since hydrogen bonds offer the advantage of strength and directionality, their use in constructing engineered materials is not surprising. A major current concern is that a set of homologous compounds may not lead to similar packing motifs; even so, inspecting sizeable families of related crystal

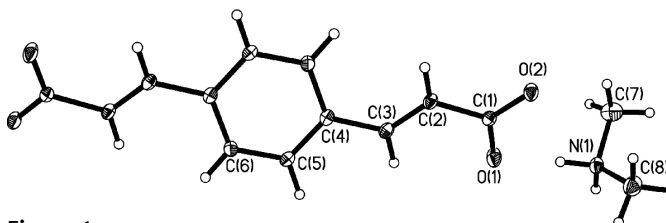


Figure 1

The structure of (I), showing the atom-labeling scheme and displacement ellipsoids at the 50% probability level.

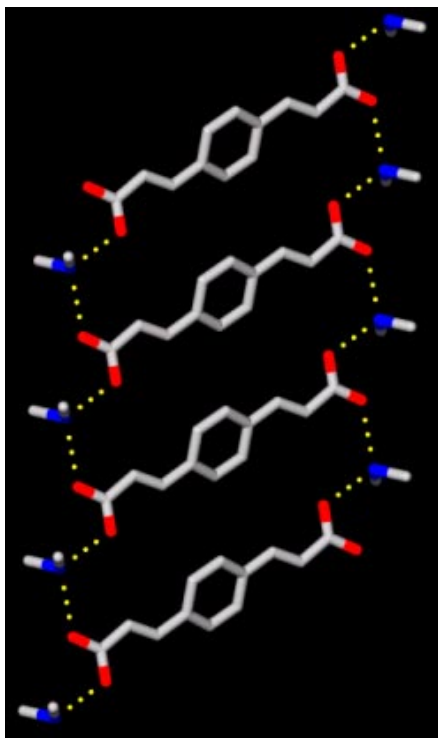


Figure 2
View of the packing of (I), showing the catemeric hydrogen-bond network propagated along the *a* axis. Hydrogen bonds are shown as dashed lines and H atoms have been omitted for clarity.

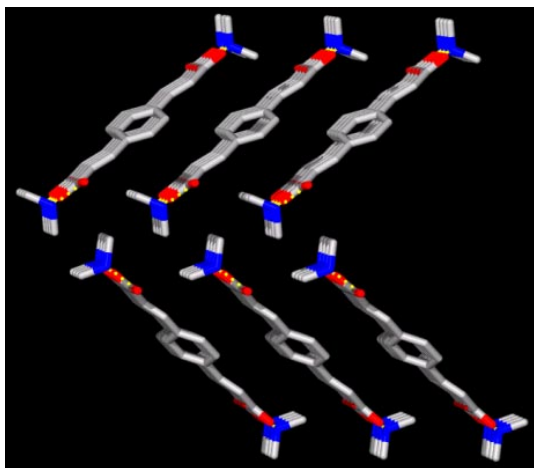


Figure 3
View of the crystal structure of (I), projected on the *bc* plane, showing ions arranged in a herring-bone motif.

structures can lead to greater understanding of the transferability of specific interactions. To this extent, the title binary compound, (I), was synthesized and compared with similar crystal structures in the Cambridge Structural Database (CSD, Version 5.25 of April 2004; Allen, 2002).

Fig. 1 shows that the asymmetric unit of (I) contains a 1,4-phenylenediacyrylate anion positioned on an inversion center and a dimethylammonium cation. From inspection of the C1—O1 and C1—O2 distances [1.266 (2) and 1.267 (2) Å], the electron density of the carboxylate anion is delocalized over the entire group. Other selected geometric parameters are

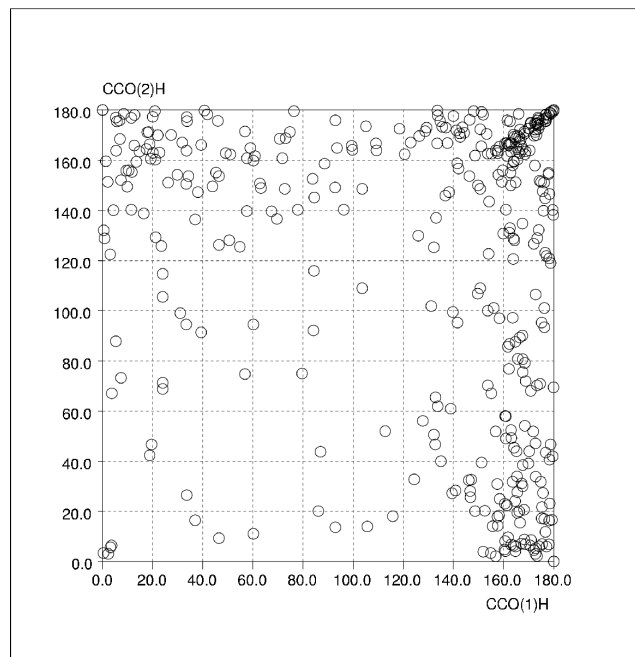


Figure 4
Correlation plot of C—C=O...H torsion angles retrieved from the CSD for 1:2 carboxylate/secondary ammonium fragments.

given in Table 1. Each carboxylate moiety is linked to two adjacent ammonium N⁺—H donors *via* C—O^{δ-}...H—⁺N interactions (Table 2). These close contacts form *syn-anti* patterns that extend along the *a* axis. By virtue of symmetry, this pattern is replicated on the other end of the dicarboxylate to give molecular ribbons (Fig. 2). Inspection of Fig. 3 shows a different perspective of these catemeric motifs arranged in herring-bone patterns that lack further stabilization from additional non-bonded contacts.

The *syn-anti* hydrogen-bond conformation of (I) prompted the question as to the degree of persistence of the observed pattern. A search of the CSD resulted in 404 organic structures comprised of 1:2 carboxylate and secondary ammonium fragments with intermolecular contacts ≤ 3.2 Å. Closer inspection revealed nearly 60% of these entries (228) exist with each carboxylate O atom participating in C—O^{δ-}...H—⁺N interactions similar to (I). A correlation plot (Fig. 4) of the contact torsion angles about the carboxylate groups shows a concentration of data that correspond to the *syn* ($0^\circ \leq \text{C—C} \cdots \text{O} \cdots \text{H} \leq 40^\circ$) and *anti* ($140^\circ \leq \text{C—C} \cdots \text{O} \cdots \text{H} \leq 180^\circ$) conformations. This investigation also revealed that a nearly equal number of fragments exist in the *syn-anti* (111) and *anti-anti* (107) forms, with a much smaller subset participating in *syn-syn* (6) motifs.

Experimental

Suitable crystals of (I) were prepared by dissolution of 1,4-phenylenediacyrylic acid (50 mg, 0.229 mmol) in 1 ml of a 40% aqueous solution of dimethylamine (8.88 mmol) followed by slow evaporation at room temperature. Sample quality was assessed by polarized microscopy and a single crystal was adhered with epoxy adhesive to a glass fiber for subsequent crystallographic analysis.

Crystal data

$2\text{C}_2\text{H}_8\text{N}^+\cdot\text{C}_{12}\text{H}_8\text{O}_4^{2-}$
 $M_r = 308.38$
 Monoclinic, $P2_1/n$
 $a = 5.8270$ (7) Å
 $b = 23.980$ (3) Å
 $c = 6.1406$ (8) Å
 $\beta = 92.306$ (2)°
 $V = 857.35$ (19) Å³
 $Z = 2$

$D_x = 1.195$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 4922 reflections
 $\theta = 2.5\text{--}28.3^\circ$
 $\mu = 0.09$ mm⁻¹
 $T = 148$ (2) K
 Block, transparent colorless
 $0.36 \times 0.22 \times 0.18$ mm

Data collection

Bruker SMART 1000 CCD diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Bruker, 2000)
 $T_{\min} = 0.967$, $T_{\max} = 0.985$
 5113 measured reflections

1556 independent reflections
 1290 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.048$
 $\theta_{\text{max}} = 25.3^\circ$
 $h = -6 \rightarrow 7$
 $k = -28 \rightarrow 28$
 $l = -7 \rightarrow 7$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.053$
 $wR(F^2) = 0.131$
 $S = 1.12$
 1556 reflections
 110 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0609P)^2 + 0.2787P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.20$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.23$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

N1—C8	1.472 (3)	C3—C4	1.474 (3)
N1—C7	1.481 (3)	C4—C5	1.402 (3)
C1—C2	1.502 (3)	C4—C6 ⁱ	1.407 (3)
C2—C3	1.328 (3)	C5—C6	1.390 (3)
C8—N1—C7	113.31 (18)	C2—C3—C4	127.37 (16)
H1A—N1—H1B	108 (2)	C5—C4—C6 ⁱ	117.83 (17)
O1—C1—O2	123.94 (17)	C5—C4—C3	119.61 (16)
O1—C1—C2	117.68 (17)	C6 ⁱ —C4—C3	122.56 (18)
O2—C1—C2	118.37 (15)	C6—C5—C4	121.63 (17)
C3—C2—C1	122.82 (16)	C5—C6—C4 ⁱ	120.53 (18)

Symmetry code: (i) $1 - x, -y, -z$.

Table 2

Hydrogen-bonding geometry (Å, °).

$D\text{—}H\cdots A$	$D\text{—}H$	$H\cdots A$	$D\cdots A$	$D\text{—}H\cdots A$
N1—H1B ⁱⁱ ···O1	0.95 (3)	1.72 (3)	2.671 (2)	178 (3)
N1—H1A···O2 ⁱⁱ	0.89 (3)	1.84 (3)	2.726 (2)	173 (2)

Symmetry code: (ii) $x - 1, y, z$.

The ammonium H atoms (H1A and H1B) were located in a difference density map and refined independently with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N})$. The remaining H atoms were treated as riding, with C—H distances of 0.95 (Csp²) and 0.98 Å (CH₃), and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. Riding methyl H atoms were allowed to rotate freely during refinement.

Data collection: SMART (Bruker, 2001); cell refinement: SMART; data reduction: SAINT (Bruker, 2002) and XPREP (Bruker, 2001); program(s) used to solve structure: SHELXTL (Bruker, 2000); program(s) used to refine structure: SHELXTL; molecular graphics: XSEED (Barbour, 2001); software used to prepare material for publication: XSEED.

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