C(10″)	0.5105 (2)	0.6231 (5)	0.3554 (2)	0.039 (1)
N(11″)	0.5332 (1)	0.4484 (5)	0.3909 (1)	0.027 (1)
O(12″)	0.5789 (1)	0.1243 (5)	0.4473 (1)	0.035 (1)

The program system employed was Siemens *SHELXTL-Plus* (Sheldrick, 1990).

We thank the Fonds der Chemischen Industrie for financial support.

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, bond distances, bond angles and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55943 (42 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HA1020]

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(−)-(*S*)-α-Phenylethylammonium (−)-(*R*)-[2.2]Paracyclophane-4-carboxylate

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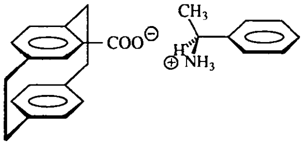
Abstract

The anion, tricyclo[8.2.2.2^{4,7}]hexadeca-4,6,10,12,13,15-hexaene-5-carboxylate, shows ring distortions typical of cyclophane systems. The cation forms three hydrogen bonds from the NH_3 group to carboxylate O atoms, with N···O distances 2.73–2.82 Å. The ions are thus linked to form hydrophilic ribbons parallel to the *y* axis.

Comment

As discussed in the previous paper (Jones, Döring, Laue & Hopf, 1993), substituted cyclophanes are chiral molecules, and we have therefore used (+)-(*S*)-[2.2]paracyclophane-4-carboxylic acid to resolve (±)-amines. However, it is first necessary to separate the enantiomers of the carboxylic acid, which can conveniently be achieved using (−)-(*S*)-α-phenylethylamine; full details of the separation are given by Laue (1991). Here we report the structure of the crystalline salt (−)-(*S*)-α-phenylethylammonium (−)-(*R*)-[2.2]paracyclophane-4-carboxylate (I), crystallized from ethanol.



(I)

Fig. 1 shows the asymmetric unit. Bond lengths and angles are normal. The cyclophane rings show the usual distortion (Vögtle, 1990), the bridgehead atoms lying 0.15–0.17 Å out of the plane of the remaining ring atoms. The carboxylate group is not coplanar with the ring [the dihedral angle between C(3), C(4), C(5) and C(17), O(1), O(2) is 45°].

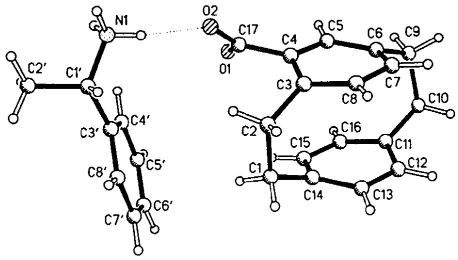


Fig. 1. The asymmetric unit of the title compound. Radii are arbitrary. The dotted line indicates a hydrogen bond.

H atoms were unambiguously located. Hydrogen bonds are formed from the cation —NH_3 to carboxylate O atoms [N(1)···O(2) 2.73, N(1)···O(2)($\frac{1}{2}-x$, $-\frac{1}{2}+y$, $1-z$) 2.82, N(1)···O(1)($\frac{1}{2}-x$, $\frac{1}{2}+y$, $1-z$) 2.74 Å]. The ions are thus linked to form a hydrophilic ribbon parallel to the short *y* axis (Fig. 2).

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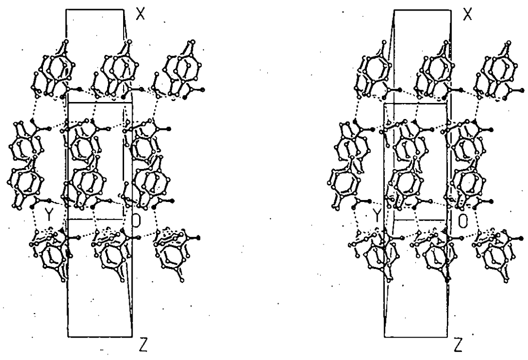

Fig. 2. Hydrogen bonding (broken lines) in the title compound. View direction perpendicular to the *xy* plane. (Radii arbitrary, H atoms omitted for clarity.)

Experimental

Crystal data

$C_8H_{12}N^+.C_{17}H_{15}O_2^-$
$M_r = 373.5$
Monoclinic
$C2$
$a = 23.343\ (9)$ Å
$b = 6.453\ (3)$ Å
$c = 17.683\ (6)$ Å
$\beta = 128.48\ (3)°$
$V = 2085\ (1)$ Å^3
$Z = 4$
$D_x = 1.190$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 48 reflections
$\theta = 10$–$12°$
$\mu = 0.07$ mm^{-1}
$T = 178$ K
Tablet
1.0 × 0.4 × 0.4 mm
Colourless

Data collection

Siemens *R*3 diffractometer
ω scans
Absorption correction: none
3380 measured reflections
3284 independent reflections
2835 observed reflections [$F > 4\sigma(F)$]

$\theta_{max} = 27.5°$
$h = 0 \rightarrow 24$
$k = -8 \rightarrow 2$
$l = -22 \rightarrow 22$
3 standard reflections monitored every 147 reflections intensity variation: 1.5%

Refinement

Refinement on F
Final $R = 0.038$
$wR = 0.044$
$S = 1.7$
255 parameters
H atoms: riding

$w = 1/[\sigma^2(F) + 0.00025F^2]$
$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 0.2$ e Å^{-3}
$\Delta\rho_{min} = -0.2$ e Å^{-3}
Atomic scattering factors from *SHELXTL-Plus*

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^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}
C(1)	0.4678 (2)	0.7722 (8)	0.8445 (2)	0.767 (18)
C(2)	0.4261 (1)	0.8614 (5)	0.7398 (1)	0.328 (10)
C(3)	0.4637 (1)	0.8113 (4)	0.6966 (1)	0.261 (8)
C(4)	0.4558 (1)	0.6191 (4)	0.6538 (1)	0.240 (8)
C(5)	0.5138 (1)	0.5431 (5)	0.6578 (1)	0.294 (9)
C(6)	0.5774 (1)	0.6599 (5)	0.6992 (1)	0.341 (9)
C(7)	0.5754 (1)	0.8671 (5)	0.7181 (1)	0.354 (9)
C(8)	0.5197 (1)	0.9404 (4)	0.7178 (1)	0.481 (11)
C(9)	0.6494 (1)	0.5533 (6)	0.7402 (2)	0.481 (11)
C(10)	0.7003 (1)	0.5255 (7)	0.8536 (2)	0.598 (13)
C(11)	0.6601 (1)	0.5620 (5)	0.8939 (1)	0.392 (9)
C(12)	0.6609 (1)	0.7536 (5)	0.9291 (1)	0.451 (11)
C(13)	0.6030 (1)	0.8155 (5)	0.9271 (1)	0.484 (13)
C(14)	0.5428 (1)	0.6864 (5)	0.8882 (1)	0.449 (12)
C(15)	0.5503 (1)	0.4820 (5)	0.8729 (1)	0.406 (10)
C(16)	0.6091 (1)	0.4188 (5)	0.8770 (1)	0.390 (10)
C(17)	0.3885 (1)	0.4875 (4)	0.6085 (1)	0.240 (8)
O(1)	0.3959 (1)	0.3000	0.6273 (1)	0.357 (7)
O(2)	0.3275 (1)	0.5806 (3)	0.5511 (1)	0.319 (6)
C(1′)	0.1876 (1)	0.5670 (5)	0.5803 (1)	0.300 (9)
C(2′)	0.1108 (1)	0.5155 (6)	0.5454 (1)	0.464 (11)
C(3′)	0.2464 (1)	0.4731 (5)	0.6785 (1)	0.294 (9)
C(4′)	0.2742 (1)	0.2770 (5)	0.6895 (1)	0.377 (11)
C(5′)	0.3250 (1)	0.1921 (5)	0.7817 (2)	0.452 (12)
C(6′)	0.3477 (1)	0.3054 (6)	0.8622 (1)	0.498 (12)
C(7′)	0.3201 (1)	0.4998 (6)	0.8518 (1)	0.552 (13)
C(8′)	0.2698 (1)	0.5848 (5)	0.7600 (1)	0.433 (11)
N(1)	0.1941 (1)	0.5004 (4)	0.5051 (1)	0.255 (7)

Table 2. *Geometric parameters* (Å, °)

C(1)—C(2)	157.0 (4)	C(1)—C(14)	151.1 (5)
C(2)—C(3)	151.4 (4)	C(3)—C(4)	140.4 (4)
C(3)—C(8)	139.0 (3)	C(4)—C(5)	139.9 (3)
C(4)—C(17)	150.5 (3)	C(5)—C(6)	139.9 (3)
C(6)—C(7)	138.5 (4)	C(6)—C(9)	151.9 (4)
C(7)—C(8)	138.2 (4)	C(9)—C(10)	158.1 (3)
C(10)—C(11)	150.8 (4)	C(11)—C(12)	138.0 (5)
C(11)—C(16)	138.5 (4)	C(12)—C(13)	138.9 (5)
C(13)—C(14)	139.3 (4)	C(14)—C(15)	137.8 (5)
C(15)—C(16)	139.2 (4)	C(17)—O(1)	123.8 (3)
C(17)—O(2)	127.2 (2)	C(1′)—C(2′)	152.8 (3)
C(1′)—C(3′)	151.7 (2)	C(1′)—N(1)	149.0 (3)
C(3′)—C(4′)	137.9 (4)	C(3′)—C(8′)	138.4 (4)
C(4′)—C(5′)	139.9 (3)	C(5′)—C(6′)	138.0 (4)
C(6′)—C(7′)	136.9 (5)	C(7′)—C(8′)	139.4 (3)
C(2)—C(1)—C(14)	114.1 (3)	C(1)—C(2)—C(3)	112.8 (2)
C(2)—C(3)—C(4)	122.5 (2)	C(2)—C(3)—C(8)	118.6 (2)
C(4)—C(3)—C(8)	117.4 (2)	C(3)—C(4)—C(5)	118.9 (2)
C(3)—C(4)—C(17)	121.9 (2)	C(5)—C(4)—C(17)	119.1 (2)
C(4)—C(5)—C(6)	121.1 (3)	C(5)—C(6)—C(7)	117.5 (2)
C(5)—C(6)—C(9)	120.3 (3)	C(7)—C(6)—C(9)	121.0 (2)
C(6)—C(7)—C(8)	120.1 (2)	C(3)—C(8)—C(7)	121.4 (3)
C(6)—C(9)—C(10)	113.1 (2)	C(9)—C(10)—C(11)	112.5 (2)
C(10)—C(11)—C(12)	121.1 (3)	C(10)—C(11)—C(16)	119.9 (3)
C(12)—C(11)—C(16)	117.6 (3)	C(11)—C(12)—C(13)	120.5 (3)
C(12)—C(13)—C(14)	120.5 (3)	C(1)—C(14)—C(13)	121.7 (3)
C(1)—C(14)—C(15)	119.9 (3)	C(13)—C(14)—C(15)	117.2 (3)
C(14)—C(15)—C(16)	120.8 (3)	C(11)—C(16)—C(15)	120.3 (3)
C(4)—C(17)—O(1)	118.9 (2)	C(4)—C(17)—O(2)	115.9 (2)
O(1)—C(17)—O(2)	125.1 (2)	C(2′)—C(1′)—C(3′)	111.9 (2)
C(2′)—C(1′)—N(1)	108.8 (2)	C(3′)—C(1′)—N(1)	112.6 (2)
C(1′)—C(3′)—C(4′)	122.7 (2)	C(1′)—C(3′)—C(8′)	118.3 (2)
C(4′)—C(3′)—C(8′)	119.0 (2)	C(3′)—C(4′)—C(5′)	120.5 (2)
C(4′)—C(5′)—C(6′)	119.8 (3)	C(5′)—C(6′)—C(7′)	120.0 (2)
C(6′)—C(7′)—C(8′)	120.1 (3)	C(3′)—C(8′)—C(7′)	120.5 (3)

The program system employed was Siemens *SHELXTL-Plus* (Sheldrick, 1990).

We thank the Fonds der Chemischen Industrie for financial support.

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55694 (17 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: MU1020]

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Structure of α-Tetrachlorothiophene 1,1-Dioxide at 150 K

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Abstract

Tetrachlorothiophene 1,1-dioxide is polymorphic, crystallizing either in space group $C2/c$ (α-form) or in $P2_1/c$ (β-form). Crystals of the α-form at 150 K are built from molecules with approximate C_s (m) symmetry; the thiophene ring is non-planar, the C—S—C plane being folded by 4.1° out of the plane of the butadiene unit. The C—Cl distances are 1.682 (3)-1.696 (3) Å.

Comment

The title compound was first synthesized in 1980; it has been used as a Diels-Alder reagent because it readily loses sulfur dioxide when attacked by dienophiles (Raasch, 1980). In the course of charge-density studies of cyclic sulfones we have found that two crystalline forms of the title compound exist; both are monoclinic but the α-form has space group $C2/c$ whereas the β-form has space group $P2_1/c$. The structure of the α-form, based on data collected to conventional resolution limits, is presented here. The structure was determined to supplement a study of the β-form, based on high-resolution data measured at 123 K, which will be described elsewhere (Frampton, Laidig & Muir, 1992).

The tetrachlorothiophene 1,1-dioxide molecule (Fig. 1) has approximate C_s (m) symmetry; the non-crystallographic mirror plane is defined by S, O(1), O(2) and the midpoint of the C(2)—C(3) bond. The conformation of the thiophene ring is that of a shallow envelope: the atoms of the *cis*-diene unit, defined by C(1)-C(4), are coplanar to within 0.007 (2) Å, but the S atom is displaced by 0.087 (1) Å from the mean plane defined by C(1)-C(4). The rather irregular displacements of the four Cl atoms from the diene plane [−0.127 (1), −0.088 (1), 0.074 (1) and 0.042 (1) Å] represent the most significant departure from C_s symmetry. Corresponding bond lengths agree to within 0.009 (4) Å and corresponding valence angles to within 1.9 (2) ° (see Table 2). The bond lengths also agree well with the mean values proposed by Allen, Kennard, Watson, Brammer, Orpen & Taylor (1987), though the C(sp^2)—Cl distance of 1.713 (11) Å given by these authors is slightly longer than the values of 1.682 (3)-1.696 (3) Å found here.

All intermolecular contacts shorter than the sum of the van der Waals radii [S 1.85, Cl 1.80, O 1.40, C 1.70 Å (Pauling, 1960)] are listed in Table 2. Each molecule is

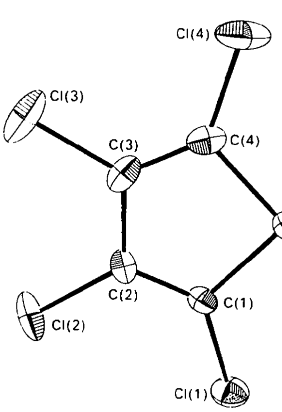

Fig. 1. A view of the molecule showing the atom labels and 50% probability ellipsoids.

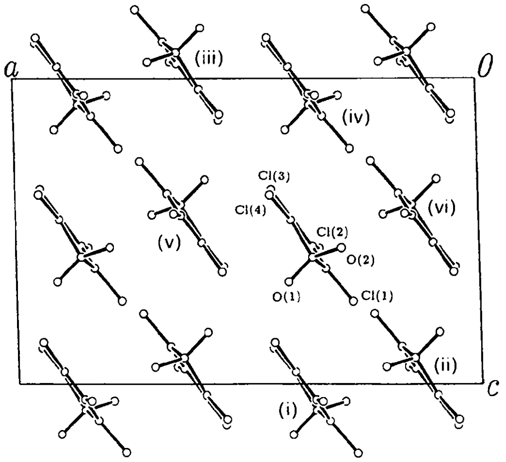

Fig. 2. The molecular packing viewed in projection down the b axis. Atom labels are attached to the reference molecule defined by the coordinates in Table 1. Roman numerals (see also Table 2) refer to the following symmetry operations: (i) $x, 1 - y, \frac{1}{2} + z$; (ii) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{3}{2} - z$; (iii) $1 - x, y, \frac{1}{2} - z$; (iv) $x, 1 - y, z - \frac{1}{2}$; (v) $1 - x, 1 - y, 1 - z$; (vi) $\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$.

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