References

Allen, M. S., Bishop, D. I., Harris, M., Hignett, G. J., Scopes, D. I. C., Wilson, N. D. V. & Joule, J. A. (1980). *Indole and Biogenetically Related Alkaloids*, edited by J. D. Phillipson & M. H. Zenk, pp. 229–247. New York: Academic Press.

Beddoes, R. L., Dalton, L., Joule, J. A., Mills, O. S., Street, J. D. & Watt, C. I. F. (1986). *J. Chem. Soc. Perkin Trans.* 2, pp. 787–797.

Dalton, L., Humphrey, G. L., Cooper, M. M. & Joule, J. A. (1983). *J. Chem. Soc. Perkin Trans.* 1, pp. 2417–2422.

Ibers, J. A. & Hamilton, W. C. (1964). *Acta Cryst.* **17**, 781–782.

Joule, J. A., Monteiro, H., Durham, L. J., Gilbert, B. & Djerassi, C. (1965). *J. Chem. Soc.* pp. 4773–4780.

Molecular Structure Corporation (1985). *TEXSAN. TEXRAY Structure Analysis Package.* MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Motherwell, W. D. S. & Clegg, W. (1978). *PLUTO. Program for Plotting Molecular and Crystal Structures.* Univ. of Cambridge, England.

Parthasarathi, V., Beurskens, P. T. & Slot, H. J. B. (1983). *Acta Cryst.* A**39**, 860–864.

Sheldrick, G. M. (1985). *SHELXS86. Crystallographic Computing 3*, edited by G. M. Sheldrick, C. Krüger & R. Goddard, pp. 175–189. Oxford Univ. Press.

Street, J. D., Harris, M., Bishop, D. I., Heatley, F., Beddoes, R. L., Mills, O. S. & Joule, J. A. (1987). *J. Chem. Soc. Perkin Trans.* 1, pp. 1599–1606.

Walker, N. & Stuart, D. (1983). *Acta Cryst.* A**39**, 158–166.

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5-Bromo-12-phenyltetracene

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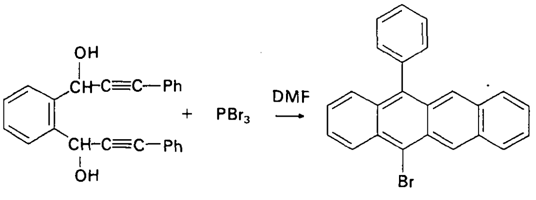
Abstract

X-ray structural analysis confirms that the title compound (5-bromo-12-phenylnapthacene, $C_{24}H_{15}Br$) consists of a tetracene ring system substituted in the 5 position by a Br atom and in the 12 position by a phenyl group. The tetracene portion of the compound is planar to within 0.05 Å, with the substituted phenyl group twisted out of the plane at angles of 108 and 102° for molecules *A* and *B*, respectively. The C—C bond lengths of the fused ring system are not identical, and are consistent with simple Pauling bond orders.

Comment

Although the crystal structures of tetracene, pentacene and hexacene (Robertson, Sinclair & Trotter, 1961; Campbell, Robertson & Trotter, 1961, 1962) were reported in the early sixties and an X-ray structural analysis was carried out on the monosubstituted compound 5-methyltetracene (Cox & Sim, 1979), no crystal structures of di-substituted tetracenes have been reported to date.

The title compound (I) was prepared by a modification of the literature method (Straub & Hambrecht, 1975) by treatment of a DMF solution of 1,2-bis(1-hydroxy-3-phenyl-2-propynyl)benzene with phosphorus tribromide at 273 K. The X-ray structural analysis described here confirmed that the product is 5-bromo-12-phenyltetracene. The molecular parameters of the two molecules in the asymmetric unit, *A* and *B*, are essentially the same and for the purpose of this work all bond lengths and angles are quoted as the mean of the respective values. The two molecules in the asymmetric unit are shown in Fig. 1.



(I)

The substituent phenyl ring bond distances in 5-bromo-12-phenyltetracene are consistent with π-electron delocalization and lie within the range 1.323 (11)–1.402 (13) Å. The phenyl group is twisted out of the plane of the tetracene backbone at angles of 108 and 102° for molecules *A* and *B*, respectively. This feature is probably a consequence of the

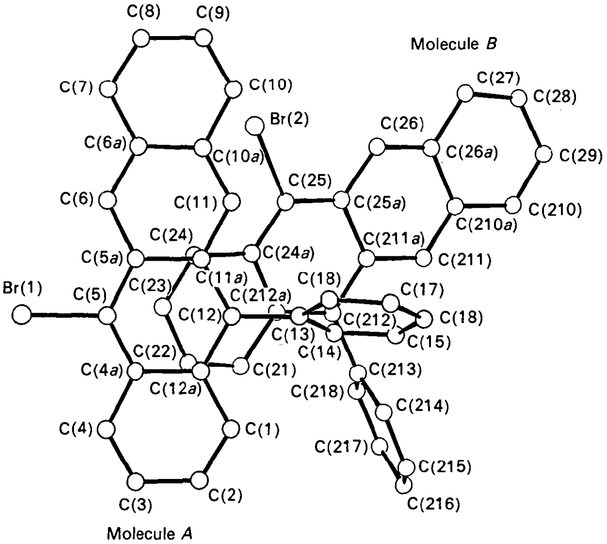


Fig. 1. The two independent molecules of 5-bromo-12-phenyltetracene in the asymmetric unit, drawn using *ORTEP*II (Johnson, 1976).

unfavourable *peri* interactions which would occur between the phenyl H atoms and the H atoms bonded to the C atoms C(1) and C(11) of the tetracene backbone if the phenyl substituent lay in the plane of the molecule. For both the phenyl ring and the four linked rings of the tetracene backbone, the C—C—C bond angles lie within the range 117.3 (7)–123.5 (5)°, which is normal for fused ring systems. The C(5)—Br bond distance [1.889 (8) Å] is shorter than that reported in the related bromoanthracene derivative 10-bromo-1,8-diphenylanthracene, in which the C—Br bond length is 1.931 (5) Å (House, Ghali, Haack & VanDerveer, 1980). For the tetracene backbone, the C—C bond lengths lie in the range 1.328 (10)–1.450 (12) Å, which is similar to the range reported for the related mono-substituted compound 5-methyltetracene [1.33 (8)–1.450 (6) Å; Cox & Sim, 1979]; these compare with the range of 1.38 (2)–1.46 (2) Å reported for the unsubstituted tetracene (Campbell, Robertson & Trotter, 1962). To date, the title compound and 5-methyltetracene are the only examples of tetracene derivatives for which X-ray crystal structure analyses have been carried out.

Five Kekule forms may be drawn for the tetracene nucleus of the title compound, giving rise to the Pauling bond orders illustrated in Fig. 2 (Herndon, 1974); the observed bond lengths for 5-bromo-12-phenyltetracene are in good agreement with this simple prediction. This is particularly notable in the high degree of bond alternation observed in the two terminal rings. For example, in the ring adjacent to the di-substituted ring, C(1)—C(2) and C(3)—C(4) are significantly shorter [mean 1.351 (13) Å] than the remaining three C—C bonds [mean 1.421 (14) Å]. A similar pattern occurs in the other terminal ring. The main bond-length distinction in the two central rings arises for the three cross-ring bonds [C(4a)—C(12a), C(5a)—C(11a) and C(6a)—C(10a)] which have a mean bond length of 1.426 (12) Å, compared to a mean of 1.394 (14) Å for the remaining C atoms of these rings.

Fig. 1 shows that molecule *B* in the asymmetric unit is twisted relative to molecule *A*, the closest interaction occuring between one of the terminal rings of the tetracene fragment on one molecule and the di-substituted ring of the second molecule [the closest C···C and C···H interactions are C(11a)···C(24) 3.50 and C(5a)···H(23) 3.16 Å]. These close intermolecular distances contrast with the structure of tetracene itself, in which the shortest intermolecular C···C distance is 3.70 Å. This is an example of edge-to-face interaction and it has been suggested that such packing of crystalline aromatic compounds (which brings a positively polarized H atom of one aromatic group into close contact with the electron-rich π-cloud of the other aromatic ring) is energetically favourable (Burley & Petsko, 1986). This type of arrangement arises in non-parallel ring systems, such as the two independent molecules in the asymmetric unit of the title compound. In addition, each of the two molecules in the asymmetric unit independently generates a second type of close interaction with an equivalent molecule related through an inversion centre. As shown in Fig. 3, these inversion-related molecules are aligned in a parallel slip π-stacking interaction. The centroid-to-centroid distances between the four rings of the tetracene backbone in the two molecules are *circa* 3.9 Å, with an interplanar distance of 3.55 Å, therefore the two molecules are offset relative to each other by a distance of 1.54 Å. This is evident in Fig. 3, which shows that the centroids of each of the four rings in one molecule lie directly over one of the C atoms in the rings of the other molecule, in a manner reminiscent of kekulene (Staab, Diederich, Krieger & Schweitzer, 1983). The ring π systems are parallel, stacked and offset, so that the π system of one molecule lies over the π cavity at the centre of its nearest neighbour. Fig. 4 illustrates an extended section of the crystal lattice showing the packing of the dimeric π-stacked inversion-related units, alternating through the crystal lattice. Dimeric units are an integral feature of the sandwich herringbone pattern observed for a number of hydrocarbons (Desiraju & Gavezzotti, 1989), while in contrast most of the unsubstituted polycenes, including tetracene, adopted a similar herringbone packing.

The π interaction between aromatic groups is a substantial area of research spanning very different areas from proteins through to large macrocyclic systems (Burley & Petsko, 1985, 1986; Desiraju & Gavezzotti, 1989; Hunter & Sanders, 1990). Two important interaction patterns which have been found to be of significance in these systems (offset π-stacking and edge-to-face ring interactions) have been established in the title compound.

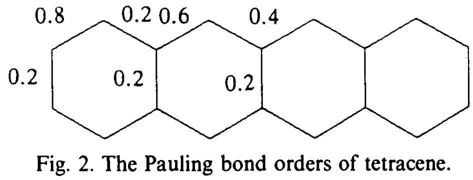


Fig. 2. The Pauling bond orders of tetracene.

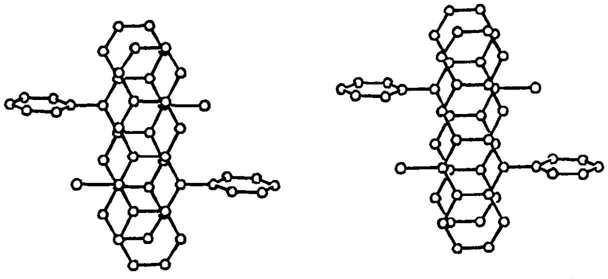


Fig. 3. A stereoview of two molecules related through an inversion centre, showing offset π-stacking interactions.

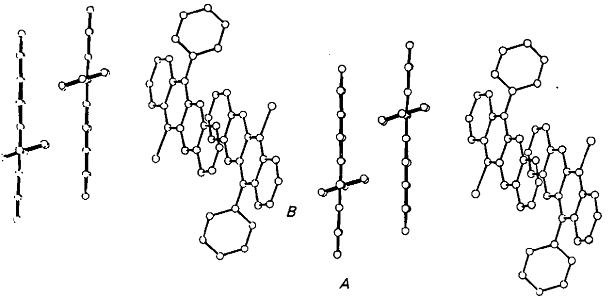


Fig. 4. Extended view of the crystal lattice of 5-bromo-12-phenyltetracene with the two molecules *A* and *B* in the asymmetric unit labelled.

Experimental

Crystal data

$C_{24}H_{15}Br$
$M_r = 383.29$
Triclinic
$P\overline{1}$
$a = 12.118$ (3) Å
$b = 13.723$ (3) Å
$c = 11.807$ (2) Å
$\alpha = 101.64$ (2)°
$\beta = 119.22$ (4)°
$\gamma = 87.42$ (1)°
$V = 1675.1$ (9) Å^3
$Z = 4$
$D_x = 1.52$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 9$–11°
$\mu = 2.38$ mm^{-1}
$T = 298$ K
Rectangular block
0.49 × 0.48 × 0.34 mm
Orange
Crystal source: recrystallized from ethanol

Data collection

Philips PW1100 diffractometer
ω–2θ scans
Absorption correction: empirical
$T_{\min} = 0.849$, $T_{\max} = 1.000$
6199 measured reflections
5892 independent reflections
3343 observed reflections [$I > 3\sigma(I)$]

$R_{\rm int} = 0.0278$
$\theta_{\max} = 25°$
$h = -14 \rightarrow 12$
$k = -16 \rightarrow 15$
$l = 0 \rightarrow 14$
3 standard reflections
frequency: 300 min
intensity variation: $<\pm 1\%$

Refinement

Refinement on F
$R = 0.0564$
$wR = 0.0552$
3343 reflections
391 parameters
H-atom parameters not refined
$w = 1/\sigma^2(F_o)$

$(\Delta/\sigma)_{\max} < 0.1$
$\Delta\rho_{\max} = 0.9$ e Å^{-3}
$\Delta\rho_{\min} = -0.7$ e Å^{-3}
Atomic scattering factors from *SHELX*76 (Sheldrick, 1976)

Table 1. *Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters* (Å^2)

$U_{\rm iso}$ for C(13) to C(218), $U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$ for Br(1) to C(212a).

	x	y	z	$U_{\rm eq}/U_{\rm iso}$
Br(1)	−0.07823 (7)	0.20481 (6)	0.22919 (8)	0.0661 (6)
C(1)	0.3952 (7)	0.1008 (5)	0.4300 (7)	0.051 (4)
C(2)	0.4033 (7)	0.1255 (6)	0.5516 (7)	0.059 (5)
C(3)	0.2979 (8)	0.1622 (6)	0.5613 (7)	0.067 (6)
C(4)	0.1889 (7)	0.1738 (5)	0.4566 (7)	0.057 (5)
C(4a)	0.1751 (6)	0.1481 (5)	0.3262 (6)	0.045 (4)
C(5)	0.0634 (6)	0.1584 (4)	0.2125 (6)	0.043 (4)
C(5a)	0.0523 (6)	0.1356 (5)	0.0857 (6)	0.043 (4)
C(6)	−0.0562 (6)	0.1523 (5)	−0.0282 (7)	0.047 (4)
C(6a)	−0.0661 (6)	0.1276 (5)	−0.1530 (7)	0.044 (4)
C(7)	−0.1777 (7)	0.1423 (5)	−0.2688 (8)	0.056 (5)
C(8)	−0.1838 (8)	0.1159 (6)	−0.3896 (8)	0.062 (6)
C(9)	−0.0783 (8)	0.0802 (6)	−0.4003 (7)	0.067 (6)
C(10)	0.0284 (7)	0.0673 (5)	−0.2929 (8)	0.059 (5)
C(10a)	0.0393 (6)	0.0896 (5)	−0.1655 (6)	0.043 (4)
C(11)	0.1472 (6)	0.0756 (5)	−0.0536 (7)	0.048 (4)
C(11a)	0.1591 (6)	0.0980 (4)	0.0743 (7)	0.042 (4)
C(12)	0.2734 (6)	0.0850 (4)	0.1885 (6)	0.039 (4)
C(12a)	0.2823 (6)	0.1117 (5)	0.3137 (7)	0.046 (4)
Br(2)	0.21672 (7)	0.31967 (6)	−0.16543 (7)	0.0531 (5)
C(21)	0.4754 (6)	0.3922 (5)	0.3587 (6)	0.047 (4)
C(22)	0.3639 (7)	0.3770 (5)	0.3549 (7)	0.062 (5)
C(23)	0.2495 (7)	0.3561 (5)	0.2350 (8)	0.059 (5)
C(24)	0.2508 (6)	0.3470 (5)	0.1190 (7)	0.051 (5)
C(24a)	0.3645 (6)	0.3606 (4)	0.1152 (6)	0.037 (4)
C(25)	0.3691 (6)	0.3523 (4)	−0.0029 (6)	0.038 (4)
C(25a)	0.4811 (6)	0.3680 (4)	−0.0040 (6)	0.035 (4)
C(26)	0.4871 (6)	0.3626 (4)	−0.1218 (6)	0.043 (4)
C(26a)	0.6002 (7)	0.3760 (5)	−0.1195 (6)	0.046 (4)
C(27)	0.6062 (8)	0.3698 (5)	−0.2400 (7)	0.060 (5)
C(28)	0.7184 (9)	0.3840 (6)	−0.2323 (8)	0.075 (6)
C(29)	0.8308 (8)	0.4015 (6)	−0.1144 (9)	0.071 (6)
C(210)	0.8303 (7)	0.4065 (5)	0.0014 (7)	0.057 (5)
C(210a)	0.7154 (6)	0.3943 (4)	0.0026 (7)	0.047 (4)
C(211)	0.7105 (6)	0.3997 (5)	0.1180 (6)	0.043 (4)
C(211a)	0.5972 (6)	0.3879 (4)	0.1192 (6)	0.035 (4)
C(212)	0.5943 (6)	0.3957 (4)	0.2409 (6)	0.035 (4)
C(212a)	0.4811 (6)	0.3829 (4)	0.2372 (6)	0.038 (4)
C(13)	0.3824 (6)	0.0452 (5)	0.1752 (6)	0.040 (2)
C(14)	0.3796 (6)	−0.0545 (5)	0.1186 (7)	0.051 (2)
C(15)	0.4813 (7)	−0.0944 (5)	0.1095 (7)	0.058 (2)
C(16)	0.5878 (7)	−0.0355 (6)	0.1575 (8)	0.065 (2)
C(17)	0.5933 (7)	0.0604 (6)	0.2086 (8)	0.065 (2)
C(18)	0.4913 (6)	0.1042 (5)	0.2196 (7)	0.054 (2)
C(213)	0.7152 (6)	0.4167 (4)	0.3680 (6)	0.038 (1)
C(214)	0.7722 (6)	0.5114 (5)	0.4272 (7)	0.048 (2)
C(215)	0.8831 (7)	0.5292 (5)	0.5467 (7)	0.057 (2)
C(216)	0.9386 (6)	0.4544 (5)	0.6104 (7)	0.055 (2)
C(217)	0.8841 (7)	0.3600 (5)	0.5557 (7)	0.061 (2)
C(218)	0.7732 (6)	0.3402 (5)	0.4354 (7)	0.049 (2)

Table 2. *Selected geometric parameters* (Å, °)

Br(1)—C(5)	1.889 (8)	Br(2)—C(25)	1.887 (5)
C(1)—C(2)	1.362 (13)	C(21)—C(22)	1.354 (13)
C(1)—C(12a)	1.419 (8)	C(21)—C(212a)	1.450 (12)
C(2)—C(3)	1.400 (14)	C(22)—C(23)	1.401 (9)
C(3)—C(4)	1.328 (10)	C(23)—C(24)	1.358 (14)
C(4)—C(4a)	1.435 (12)	C(24)—C(24a)	1.422 (12)
C(4a)—C(5)	1.393 (8)	C(24a)—C(25)	1.405 (12)
C(4a)—C(12a)	1.432 (12)	C(24a)—C(212a)	1.428 (7)
C(5)—C(5a)	1.406 (11)	C(25)—C(25a)	1.391 (11)
C(5a)—C(6)	1.400 (8)	C(25a)—C(26)	1.415 (12)
C(5a)—C(11a)	1.429 (11)	C(25a)—C(211a)	1.430 (7)
C(6)—C(6a)	1.389 (12)	C(26)—C(26a)	1.377 (12)
C(6a)—C(7)	1.422 (9)	C(26a)—C(27)	1.444 (13)
C(6a)—C(10a)	1.420 (11)	C(26a)—C(210a)	1.419 (8)
C(7)—C(8)	1.364 (14)	C(27)—C(28)	1.339 (16)
C(8)—C(9)	1.403 (15)	C(28)—C(29)	1.376 (10)
C(9)—C(10)	1.335 (10)	C(29)—C(210)	1.357 (15)
C(10)—C(10a)	1.414 (12)	C(210)—C(210a)	1.417 (13)
C(10a)—C(11)	1.373 (8)	C(210a)—C(211)	1.380 (12)
C(11)—C(11a)	1.414 (12)	C(211)—C(211a)	1.396 (11)
C(11a)—C(12)	1.421 (8)	C(211a)—C(212)	1.437 (11)
C(12)—C(12a)	1.401 (11)	C(212)—C(212a)	1.369 (11)
C(12)—C(13)	1.474 (11)	C(212)—C(213)	1.482 (7)
C(13)—C(14)	1.391 (9)	C(213)—C(214)	1.378 (9)
C(13)—C(18)	1.386 (10)	C(213)—C(218)	1.398 (10)
C(14)—C(15)	1.369 (12)	C(214)—C(215)	1.377 (8)

C(15)—C(16)	1.355 (11)	C(215)—C(216)	1.352 (11)
C(16)—C(17)	1.323 (11)	C(216)—C(217)	1.362 (10)
C(17)—C(18)	1.402 (13)	C(217)—C(218)	1.383 (8)
C(4a)—C(5)—Br(1)	118.9 (6)	C(24a)—C(25)—Br(2)	118.3 (5)
C(5a)—C(5)—Br(1)	118.8 (4)	C(25a)—C(25)—Br(2)	119.2 (6)

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: LI1080). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Burley, S. K. & Petsko, G. A. (1985). *Science*, **229**, 23–28.
Burley, S. K. & Petsko, G. A. (1986). *J. Am. Chem. Soc.* **108**, 7995–8001.
Campbell, R. B., Robertson, J. M. & Trotter, J. (1961). *Acta Cryst.* **14**, 705–711.
Campbell, R. B., Robertson, J. M. & Trotter, J. (1962). *Acta Cryst.* **15**, 289–290.
Cox, P. J. & Sim, G. A. (1979). *Acta Cryst.* **B35**, 404–410.
Desiraju, G. R. & Gavezzotti, A. (1989). *J. Chem. Soc. Chem. Commun.* pp. 621–623.
Herndon, W. C. (1974). *J. Am. Chem. Soc.* **96**, 7605–7614.
House, H. O., Ghali, N. I., Haack, J. L. & VanDerveer, D. (1980). *J. Org. Chem.* **45**, 1807–1817.
Hunter, C. A. & Sanders, J. K. M. (1990). *J. Am. Chem. Soc.* **112**, 5525–5534.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Robertson, J. M., Sinclair, V. C. & Trotter, J. (1961). *Acta Cryst.* **14**, 697–704.
Sheldrick, G. M. (1976). *SHELX76. Program for Crystal Structure Determination*. Univ. of Cambridge, England.
Staab, H. A., Diederich, F., Krieger, C. & Schweitzer, D. (1983). *Chem. Ber.* **116**, 3504–3512.
Straub, H. & Hambrecht, J. (1975). *Synthesis*, pp. 425–426.

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(*R*,*S*)-1-Phenylethylammonium (*S*)-Mandelate

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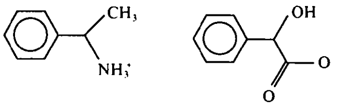
Abstract

The asymmetric unit of the title compound, $C_8H_{12}N^+.C_8H_7O_3^-$, contains two 1-phenylethylammonium cations with opposite configurations and two (*S*)-mandelate anions (α-hydroxybenzeneacetate). The ions are shown to be nearly related by a pseudo inversion centre. This gives rise to an unusual conformation of one of the (*S*)-mandelate ions. An extensive hydrogen-bond system connects the ions in a similar way to the hydrogen-bond patterns found in (*S*)-1-phenylethylammonium (*S*)-mandelate and (*R*)-mandelate.

Comment

The title compound has been isolated as part of an investigation into salts formed between 1-phenylethylamine and mandelic acid. When racemic 1-phenylethylamine and (*S*)-mandelic acid are mixed in equimolar amounts, (*S*)-1-phenylethylammonium (*S*)-mandelate precipitates as the less soluble salt (Larsen & Lopez de Diego, 1993; Brianso, Leclercq & Jacques, 1979). After filtration of the solution, (*R*,*S*)-1-phenylethylammonium (*S*)-mandelate, (I), precipitates from the mother liquor. The crystal structure of this salt is described below and its pseudo-inversion symmetry is discussed.



(I)

The four ions in the asymmetric unit are shown in Fig. 1. In the numbering of the atoms, O1 is selected as the carboxylate O atom with the smaller torsion angle O1—C1—C2—O3 to the hydroxy atom O3, and the phenyl ring is numbered with C4 in the *anti* position with respect to the OH group. In the 1-phenylethylammonium ion, C12 is *anti* to the amine group.

The conformation of the 1-phenylethylammonium ion is determined by the torsion angle N—C10—C11—C12, given in Table 2. If the torsion angles of two enantiomers have the same numerical values but opposite signs, they adopt the same conformation. As seen from Table 2, the conformation of the two cations differs only by 10°. A similar conformation is found in the less soluble salt (*S*)-1-phenylethylammonium (*S*)-mandelate, where N—C10—C11—C12 = 144.2 (2)°. In an investigation of the structural features of mandelate compounds, the torsion angle O1—C1—C2—O3 for all (*S*)-mandelate ions was found to be within the range −40 to +10°, with most values between −20 and +10° (Larsen & Lopez de Diego, 1993). In the present structure, the (*S*)-mandelate ion labelled *A* has this torsion angle within the most common range while the ion labelled *B* adopts an unusual conformation with O1—C1—C2—O3 = −56.8 (2)°. The atom numbering is related to the position of O3. Inspection of the torsion angles in the mandelate ions, given in Table 2, shows that opposite numbering of the carboxylic O atoms and the C atoms in the phenyl ring of the *B* anion would give torsion angles similar to those in the *A* anion, but with opposite signs. This would have been the numbering if O3*B* and H2*B* (attached to C2*B*) were interchanged, thus giving a common conformation of the resulting (*R*)-