

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters ( $\text{\AA}^2$ )
$$U_{\text{eq}} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub>
P1	0.16207 (3)	0.43031 (10)	0.16173 (9)	0.041 (1)
O1	0.17235 (9)	0.5013 (3)	0.2921 (2)	0.057 (1)
O2	0.13699 (7)	0.2596 (2)	0.1722 (2)	0.048 (1)
O3	0.20979 (7)	0.3968 (3)	0.0715 (2)	0.054 (1)
O4	0.07147 (10)	0.7729 (3)	0.1417 (3)	0.082 (2)
O5	0.05538 (9)	0.52581 (9)	0.2121 (2)	0.058 (2)
C1	0.12217 (12)	0.5540 (4)	0.0553 (3)	0.038 (2)
C2	0.0979 (1)	0.4501 (4)	-0.0567 (3)	0.054 (2)
C3	0.0781 (1)	0.2851 (4)	-0.0141 (3)	0.060 (2)
C4	0.1181 (1)	0.1829 (4)	0.0515 (4)	0.060 (2)
C5	0.1552 (1)	0.6890 (4)	-0.0064 (3)	0.055 (2)
C6	0.2037 (1)	0.6279 (4)	-0.0740 (3)	0.065 (2)
C7	0.2371 (1)	0.5378 (4)	0.0206 (3)	0.066 (2)
C8	0.0809 (1)	0.6332 (4)	0.1394 (3)	0.045 (2)
C9	0.0180 (1)	0.5882 (4)	0.3036 (3)	0.062 (2)

Table 2. Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

P1—O2	1.567 (2)	O2—C4	1.454 (4)
C8—C1	1.523 (5)	C2—C3	1.527 (5)
P1—O1	1.455 (2)	O5—C8	1.334 (4)
C8—O4	1.186 (5)	C3—C4	1.504 (5)
P1—O3	1.573 (2)	O5—C9	1.441 (4)
C1—C2	1.551 (5)	C5—C6	1.535 (5)
P1—C1	1.814 (3)	O3—C7	1.465 (4)
C1—C5	1.548 (5)	C7—C6	1.492 (5)
O2—P1—O1	112.65 (14)	P1—O2—C4	119.1 (2)
P1—C1—C8	109.6 (2)	C1—C2—C3	116.0 (3)
O2—P1—O3	102.50 (13)	C8—O5—C9	116.9 (3)
P1—C1—C2	110.4 (2)	C2—C3—C4	112.7 (3)
O2—P1—C1	107.79 (14)	P1—O3—C7	116.8 (2)
P1—C1—C5	108.4 (2)	C1—C5—C6	114.0 (3)
O1—P1—O3	115.81 (14)	O5—C8—C1	111.9 (3)
C8—C1—C2	110.2 (3)	O2—C4—C3	110.9 (3)
O1—P1—C1	113.81 (15)	O5—C8—O4	122.4 (3)
C8—C1—C5	108.0 (3)	O3—C7—C6	109.3 (3)
O3—P1—C1	103.19 (14)	C1—C8—O4	125.7 (3)
C2—C1—C5	110.2 (3)	C5—C6—C7	112.2 (3)
O1—P1—O2—C4	171.6 (3)	O3—P1—O2—C4	-63.2 (2)
C1—P1—O2—C4	45.2 (2)	O1—P1—C1—C8	-38.9 (2)
O1—P1—O3—C7	-68.0 (2)	O1—P1—C1—C5	78.8 (3)
O2—P1—C1—C8	86.8 (2)	O1—P1—C1—C2	-160.4 (3)
O3—P1—C1—C5	-47.5 (2)		

All H-atoms were allowed to ride on the heavy atom with isotropic displacement factors 1.5 times the equivalent isotropic displacement factor of the heavy atom. The methyl group was refined as a rigid rotor. The data were globally sorted and collected using *PCXTL* data collection software (Weinrach & Bennett, 1991). Cell refinement and data reduction: *NRCVAX* (Gabe, Le Page, Charland, Lee & White, 1989). Program(s) used to solve structure: *NRCVAX SOLVER*. Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEPII* (Johnson, 1976) and *PLUTO84* (Motherwell, 1984).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, bond distances and angles involving non-H atoms and torsion angles have been deposited with the IUCr (Reference: BK1069). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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**(S)-1-Phenylethylammonium  
(S)-Mandelate–Mandelic Acid (1/2),  
C<sub>8</sub>H<sub>12</sub>N<sup>+</sup>.C<sub>8</sub>H<sub>7</sub>O<sub>3</sub><sup>-</sup>.2C<sub>8</sub>H<sub>8</sub>O<sub>3</sub>**

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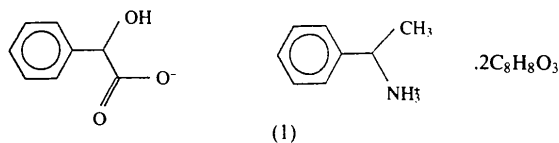
## Abstract

The asymmetric unit of the title compound contains one (*S*)-1-phenylethylammonium cation, one (*S*)-mandelate anion and two (*S*)-mandelic acid molecules. The entities are connected by an extensive hydrogen-bond system. The crystal structure is very similar to that of its diastereomeric less soluble compound (*R*)-1-phenylethylammonium (*S*)-mandelate–mandelic acid (1/2).

## Comment

The title compound, (1), has been isolated as part of an investigation of salts formed between 1-phenylethylamine and mandelic acid. When racemic 1-phenylethylamine and (*S*)-mandelic acid are mixed in equimolar amounts in water, (*S*)-1-phenylethylammonium (*S*)-mandelate precipitates as the less soluble salt (Larsen & Lopez de Diego, 1993*a*). When racemic 1-phenylethylamine and (*S*)-mandelic acid are mixed in the molar ratio 1:3 in water, the less soluble compound

isolated is (*R*)-1-phenylethylammonium (*S*)-mandelate, co-crystallized with two molecules of (*S*)-mandelic acid (Larsen & Lopez de Diego, 1993*b*). Crude calculations based on the estimated solubilities suggested that (*S*)-1-phenylethylammonium (*S*)-mandelate and (*S*)-mandelic acid would crystallize separately from the mother liquor.



Powder diffraction measurements were performed on the precipitate from a mixture of (*S*)-1-phenylethylamine and (*S*)-mandelic acid in the molar ratio 1:3. The resulting diagram is not consistent with a mechanical mixture of the salt and the acid. By very slow evaporation of the aqueous solution, crystals suitable for X-ray diffraction measurements were obtained. The crystal structure of the isolated compound, (*S*)-1-phenylethylammonium (*S*)-mandelate-mandelic acid (1/2) (1), has been determined. It is described and compared with the crystal structure of the less soluble compound, (*R*)-1-phenylethylammonium (*S*)-mandelate-mandelic acid (1/2) (2).

The asymmetric unit contains one (*S*)-1-phenylethylammonium ion, one (*S*)-mandelate ion (labelled *C*) and two molecules of (*S*)-mandelic acid (labelled *A* and *B*). The (*S*)-1-phenylethylammonium ion and one of the (*S*)-mandelic acid molecules are shown in Fig. 1. The conformation of the mandelic acid moieties is described by two torsion angles, O(1)—C(1)—C(2)—O(3) and O(3)—C(2)—C(3)—C(4), given in Table 2. The first torsion angle, describing the orientation of the acid group, is very similar in the three mandelic acid moieties, while the orientation of the phenyl ring in relation to the hydroxy group differs in *A*, *B* and *C*. In an investigation of structural features of mandelates, the torsion angle O(1)—C(1)—C(2)—O(3) was found to be within the range  $-40$  to  $10^\circ$  for all (*S*)-mandelate ions with most of the values in the interval  $-30$  to  $-10^\circ$  (Larsen & Lopez de Diego, 1993*a*). In the present structure, O(1)—C(1)—C(2)—O(3) is found within the range  $-30$  to  $-10^\circ$  in all three mandelic acid moieties. The bond lengths and angles in the —COO groups clearly reveal the difference in geometry of the carboxylic acid and carboxylate groups. In both acid molecules the protonated O atom is *anti* to the hydroxy group.

The conformation of the 1-phenylethylammonium ion, determined by the torsion angle N—C(10)—C(11)—C(12), is very close to the conformation that corresponds to minimum energy [N—C(10)—C(11)—C(12)  $\simeq 120^\circ$  (Larsen, Kozma & Acs, 1994)].

The structure is stabilized by an extensive hydrogen-bond network. The geometry of the hydrogen bonds

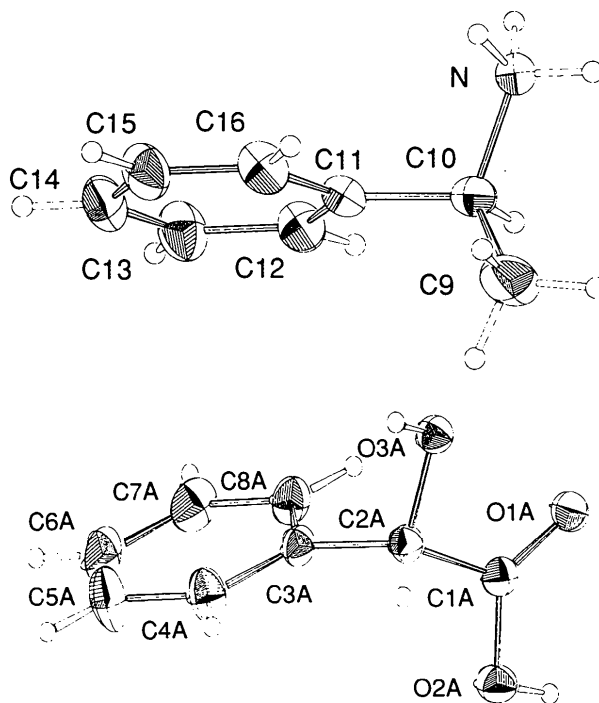


Fig. 1. ORTEP (Johnson, 1971) drawings of the (*S*)-1-phenylethylammonium ion and molecule *A* of (*S*)-mandelic acid, illustrating the atomic numbering scheme. The displacement ellipsoids enclose 50% probability and the H atoms are drawn as spheres of fixed radii.

is given in Table 3. All possible donor and acceptor atoms are involved in hydrogen bonding. The hydrogen bonds N—H(N3)···O(3A), N—H(N3)···O(1A) and O(3C)—H(O3C)···O(1C), O(3C)—H(O3C)···O(3B)(*x*, *y*−1, *z*) are bifurcated; this is reflected by significant deviations from linearity. The mandelic acid molecule *B* and the mandelate ion are connected by hydrogen bonds O(2B)—H(O2B)···O(2C) and O(3C)—H(O3C)···O(3B)(*x*, *y*−1, *z*), forming chains in the direction of the crystallographic *b* axis. These chains are linked by the mandelic acid molecules labelled *A* through hydrogen bonds from the acidic H(O2) in *A* to O(1) in *B* [O(2A)—H(O2A)···O(1B)], and from the hydroxy group in *A* to the carboxylate group in *C* [O(3A)—H(O3A)···O(2C)(*x*−1, *y*, *z*)] forming a two-dimensional network of hydrogen bonds parallel to the *ab* plane. The ammonium group is situated in the network, with bifurcated hydrogen bonds N—H(N3)···O(3A) and N—H(N3)···O(1A) to the acid molecule and a hydrogen bond to the hydroxy group of the mandelate ion [N—H(N2)···O(3C)]. Hydrogen bonds N—H(N1)···O(1C)(*x*− $\frac{1}{2}$ ,  $-\frac{1}{2}$ −*y*, −*z*) and O(3B)—H(O3B)···O(3A)( $\frac{1}{2}$ +*x*,  $\frac{1}{2}$ −*y*, −*z*), which occur between two-dimensional networks connected by  $P2_1$  symmetry along the *a* axis, link every entity in one layer to an entity in the other.

This structure is very similar to the crystal structure of the less soluble compound (2), which crystallizes in the orthorhombic space group  $P2_12_12_1$  with cell dimensions very close to those found in (1) (Larsen & Lopez de Diego, 1993b). The asymmetric unit of (2) contains two mandelic acid molecules, one mandelate ion and one 1-phenylethylammonium ion. The conformations of the mandelic acid moieties are similar in the two compounds. The torsion angles in the mandelic acid molecules differ by less than  $1^\circ$  from those found in the more soluble salt and the differences in the torsion angles in the mandelate ion are less than  $5^\circ$ . The geometry and protonation are also equivalent in the two compounds. The cations, however, differ in configuration as well as in conformation. In (2),  $N-C(10)-C(11)-C(12) = -98.2^\circ$  (Larsen & Lopez de Diego, 1993b). The hydrogen-bond pattern is the same in the two structures but the geometry of the hydrogen bonds is different.

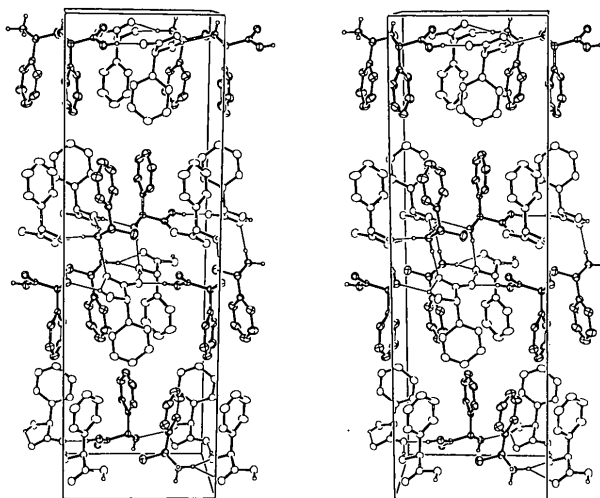


Fig. 2. Stereo drawing of the packing in (S)-1-phenylethylammonium (S)-mandelate-mandelic acid (1/2) viewed along the crystallographic  $a$  axis. Molecular identification: A, white atoms and open bonds; B, ball atoms and open bonds; C, white atoms and full bonds; cation, ball atoms and full bonds. The hydrogen bonds are drawn as thin lines.

## Experimental

### Crystal data

$C_8H_{12}N^+ \cdot C_8H_7O_3^- \cdot 2C_8H_8O_3$   
 $M_r = 577.61$   
 Orthorhombic  
 $P2_12_12_1$   
 $a = 9.7196$  (13) Å  
 $b = 9.848$  (2) Å  
 $c = 30.923$  (7) Å  
 $V = 2959.8$  (9) Å<sup>3</sup>  
 $Z = 4$   
 $D_x = 1.296$  Mg m<sup>-3</sup>

Cu  $K\alpha$  radiation  
 $\lambda = 1.5418$  Å  
 Cell parameters from 20 reflections  
 $\theta = 27.98-36.28^\circ$   
 $\mu = 0.785$  mm<sup>-1</sup>  
 $T = 122.0$  (5) K  
 Needle  
 $0.25 \times 0.07 \times 0.04$  mm  
 Colourless

### Data collection

Enraf-Nonius CAD-4 diffractometer  
 $\omega-2\theta$  scans  
 Absorption correction: none  
 11 650 measured reflections  
 6112 independent reflections  
 5791 observed reflections  
 $[|F_o| > 4\sigma(|F_o|)]$

$R_{int} = 0.0231$   
 $\theta_{max} = 74.98^\circ$   
 $h = 0 \rightarrow 12$   
 $k = 0 \rightarrow 12$   
 $l = -38 \rightarrow 38$   
 4 standard reflections  
 frequency: 167 min  
 intensity decay: 12%

### Refinement

Refinement on  $F^2$   
 $R(F) = 0.0440$   
 $wR(F^2) = 0.1298$   
 $S = 1.150$   
 6112 reflections  
 404 parameters  
 $w = 1/[\sigma^2(F_o^2) + (0.0763P)^2 + 0.64P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.001$   
 $\Delta\rho_{max} = 0.255$  e Å<sup>-3</sup>  
 $\Delta\rho_{min} = -0.273$  e Å<sup>-3</sup>  
 Atomic scattering factors from SHELXL93 (Sheldrick, 1993)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å<sup>2</sup>)

$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	$x$	$y$	$z$	$U_{eq}$
O(1A)	-0.1466 (2)	0.0563 (2)	0.0237 (1)	0.027 (1)
O(2A)	-0.1486 (2)	0.2728 (2)	0.0467 (1)	0.028 (1)
C(1A)	-0.2034 (2)	0.1502 (2)	0.0418 (1)	0.024 (1)
C(2A)	-0.3450 (2)	0.1402 (2)	0.0620 (1)	0.023 (1)
O(3A)	-0.4008 (2)	0.0150 (1)	0.0463 (1)	0.024 (1)
C(3A)	-0.3322 (2)	0.1447 (2)	0.1108 (1)	0.025 (1)
C(4A)	-0.4189 (3)	0.2262 (3)	0.1349 (1)	0.037 (1)
C(5A)	-0.4054 (3)	0.2320 (3)	0.1796 (1)	0.049 (1)
C(6A)	-0.3050 (3)	0.1584 (3)	0.2003 (1)	0.044 (1)
C(7A)	-0.2168 (3)	0.0764 (3)	0.1763 (1)	0.040 (1)
C(8A)	-0.2306 (2)	0.0696 (2)	0.1320 (1)	0.033 (1)
O(1B)	0.1187 (2)	0.2502 (1)	0.0324 (1)	0.025 (1)
O(2B)	0.3215 (2)	0.2555 (2)	0.0659 (1)	0.028 (1)
C(1B)	0.2074 (2)	0.3111 (2)	0.0525 (1)	0.022 (1)
C(2B)	0.1949 (2)	0.4606 (2)	0.0658 (1)	0.023 (1)
O(3B)	0.0816 (2)	0.5226 (2)	0.0451 (1)	0.028 (1)
C(3B)	0.1729 (2)	0.4607 (2)	0.1143 (1)	0.025 (1)
C(4B)	0.2804 (2)	0.4927 (2)	0.1422 (1)	0.032 (1)
C(5B)	0.2622 (3)	0.4840 (3)	0.1866 (1)	0.041 (1)
C(6B)	0.1379 (3)	0.4444 (3)	0.2034 (1)	0.041 (1)
C(7B)	0.0305 (3)	0.4124 (3)	0.1761 (1)	0.038 (1)
C(8B)	0.0467 (2)	0.4205 (2)	0.1316 (1)	0.030 (1)
O(1C)	0.2878 (2)	-0.2166 (1)	0.0458 (1)	0.026 (1)
O(2C)	0.3355 (2)	-0.0009 (1)	0.0624 (1)	0.026 (1)
C(1C)	0.2571 (2)	-0.1038 (2)	0.0615 (1)	0.022 (1)
C(2C)	0.1149 (2)	-0.0887 (2)	0.0824 (1)	0.024 (1)
O(3C)	0.0312 (2)	-0.2023 (2)	0.0719 (1)	0.029 (1)
C(3C)	0.1316 (2)	-0.0735 (2)	0.1311 (1)	0.024 (1)
C(4C)	0.1730 (3)	0.0507 (2)	0.1490 (1)	0.037 (1)
C(5C)	0.1944 (3)	0.0651 (3)	0.1928 (1)	0.043 (1)
C(6C)	0.1737 (3)	-0.0442 (3)	0.2203 (1)	0.037 (1)
C(7C)	0.1298 (3)	-0.1672 (2)	0.2034 (1)	0.034 (1)
C(8C)	0.1097 (2)	-0.1821 (2)	0.1590 (1)	0.029 (1)
N	-0.2442 (2)	-0.2255 (2)	0.0427 (1)	0.026 (1)
C(9)	-0.3353 (4)	-0.4578 (3)	0.0519 (1)	0.053 (1)
C(10)	-0.3548 (2)	-0.3091 (2)	0.0641 (1)	0.028 (1)
C(11)	-0.3548 (2)	-0.2851 (2)	0.1123 (1)	0.026 (1)
C(12)	-0.4685 (2)	-0.2274 (2)	0.1321 (1)	0.033 (1)
C(13)	-0.4729 (3)	-0.2088 (3)	0.1767 (1)	0.041 (1)
C(14)	-0.3614 (3)	-0.2468 (3)	0.2016 (1)	0.044 (1)
C(15)	-0.2470 (3)	-0.3023 (3)	0.1822 (1)	0.042 (1)
C(16)	-0.2428 (2)	-0.3218 (3)	0.1381 (1)	0.035 (1)

Table 2. Selected geometric parameters (Å, °)

Mandelic acid moieties	Acid A	Acid B	Anion C
O(1)—C(1)	1.213 (3)	1.219 (2)	1.248 (2)
O(2)—C(1)	1.328 (2)	1.305 (2)	1.268 (3)
C(1)—C(2)	1.514 (3)	1.533 (3)	1.534 (3)
C(2)—O(3)	1.432 (2)	1.412 (2)	1.421 (2)
O(1)—C(1)—O(2)	124.2 (2)	123.8 (2)	125.2 (2)
O(1)—C(1)—C(2)	123.6 (2)	123.6 (2)	117.8 (2)
O(2)—C(1)—C(2)	112.1 (2)	112.6 (2)	117.0 (2)
O(3)—C(2)—C(1)	105.1 (2)	110.8 (2)	110.0 (2)
O(3)—C(2)—C(3)	113.2 (2)	109.8 (2)	111.4 (2)
C(1)—C(2)—C(3)	109.5 (2)	106.2 (2)	109.4 (2)
O(1)—C(1)—C(2)—O(3)	-12.6 (3)	-10.9 (3)	-12.2 (2)
O(3)—C(2)—C(3)—C(4)	-108.6 (2)	-137.4 (2)	-160.6 (2)

## 1-Phenylethylammonium ion

N—C(10)	1.507 (3)
C(9)—C(10)	1.523 (3)
C(10)—C(11)	1.510 (3)
N—C(10)—C(11)	110.3 (2)
N—C(10)—C(9)	109.2 (2)
C(11)—C(10)—C(9)	113.2 (2)
N—C(10)—C(11)—C(12)	116.7 (2)
C(9)—C(10)—C(11)—C(12)	-120.6 (3)

Table 3. Hydrogen-bonding geometry (Å, °)

D—H...A	H...A	D...A	D—H...A
N—H(N1)...O(1C <sup>i</sup> )	1.90 (3)	2.812 (2)	180 (3)
N—H(N2)...O(3C)	1.92 (3)	2.834 (2)	165 (3)
N—H(N3)...O(3A)	1.91 (3)	2.818 (2)	149 (2)
N—H(N3)...O(1A)	2.22 (3)	2.991 (2)	133 (2)
O(2A)—H(O2A)...O(1B)	1.71 (3)	2.645 (2)	169 (3)
O(3A)—H(O3A)...O(2C <sup>ii</sup> )	1.85 (3)	2.616 (2)	173 (3)
O(2B)—H(O2B)...O(2C)	1.68 (4)	2.531 (2)	171 (3)
O(3B)—H(O3B)...O(3A <sup>iii</sup> )	2.06 (3)	2.857 (2)	174 (3)
O(3C)—H(O3C)...O(1C)	2.03 (3)	2.626 (2)	123 (3)
O(3C)—H(O3C)...O(3B <sup>iv</sup> )	2.17 (3)	2.875 (2)	135 (3)

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

The data reduction was performed using the *DREADD* programs (Blessing, 1987). The structure was solved by direct methods using *SHELXS86* (Sheldrick, 1990) and refined by least-squares methods using *SHELXL93* (Sheldrick, 1993). All H atoms were shown in a difference electron density map. H atoms bonded to tertiary and aromatic C atoms were fixed in ideal positions, the H atoms in the methyl group were refined with the restraint of a fixed angle and distance to the C atom and the remaining H atoms were located from a difference Fourier map. The absolute configuration was chosen to be in agreement with the known absolute configuration for (*S*)-mandelic acid and the choice was supported by a Flack (1983)  $\chi$  parameter of  $-0.06$  (16).

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Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: AS1116). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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### Three Polychloromononitrobenzenes: C<sub>6</sub>H<sub>3</sub>Cl<sub>2</sub>NO<sub>2</sub>, C<sub>6</sub>H<sub>2</sub>Cl<sub>3</sub>NO<sub>2</sub> and C<sub>6</sub>HCl<sub>4</sub>NO<sub>2</sub>

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## Abstract

3,5-Dichloronitrobenzene (I), 3,4,5-trichloronitrobenzene (II) and 2,3,5,6-tetrachloronitrobenzene (III) are frequently used as intermediates in the manufacture of dyes as well as phyto-sanitary and drug products. In both compounds (I) and (II), the NO<sub>2</sub> plane and the benzene ring plane are coplanar, but in (III) these planes have a mean dihedral angle of 88°.

## Comment

In the field of substituted chloro derivatives of nitrobenzene, important synthetic problems often occur because some of these compounds can only be obtained using an indirect route. One method, of great potential interest, is the selective hydrodechlorination of 'overchlorinated' compounds (Tassara, Metzger & Aune, 1975). We are interested in this hydrodechlorination reaction in connection with polychloronitrobenzenes and we have undertaken the X-ray analysis of a