Isomorphous crystals of strychninium 4-chlorobenzoate and strychninium 4-nitrobenzoate

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In strychninium 4-chlorobenzoate, $C_{21}H_{23}N_2O_2^+ \cdot C_7H_4ClO_2^-$, (I), and strychninium 4-nitrobenzoate, $C_{21}H_{23}N_2O_2^+ \cdot C_7H_4NO_4^-$, (II), the strychninium cations form pillars stabilized by $C-H \cdots O$ and $C-H \cdots \pi$ hydrogen bonds. Channels between the pillars are occupied by anions linked to one another by $C-H \cdots \pi$ hydrogen bonds. The cations and anions are linked by ionic $N-H^+ \cdots O^-$ and $C-H \cdots X$ hydrogen bonds, where $X = O$, π and Cl in (I), and O and π in (II).

Comment

Strychnine is one of the resolving agents used for the separation of racemic acids by fractional crystallization of strychninium diastereomeric salts (Jacques *et al.*, 1991). During racemic resolution of *N*-4-nitrobenzoyl-DL-amino acids, strychninium diastereomeric salts have crystallized (Białonska & Ciunik, 2006*a*). In the crystals of the strychninium salts, strychninium cations are assembled in corrugated layers. Holes at the surfaces of these layers have been recognized by the 4-nitrobenzoyl group of the amino acid derivative. Since the 4-nitrobenzoyl group plays a significant role in the racemic resolution of *N*-4-nitrobenzoyl-DL-amino acids, we decided to investigate the importance of the 4-nitrobenzoyl group for strychninium self-assembly. Thus, we have crystallized the strychninium salts of 4-nitro- and 4-chlorobenzoic acid, *viz.* (I) and (II).

(I) *X*=Cl
(II) *X*=NO$_2$
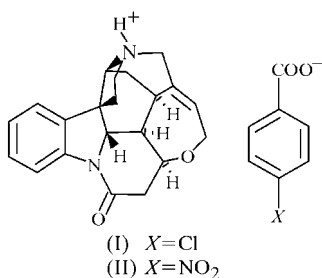
Strychninium cations have seven stereogenic centers. Taking into account the numbering scheme employed in this

paper these are N2(*S*), C7(*S*), C8(*S*), C11(*S*), C18(*R*), C19(*R*) and C21(*S*). The geometry of the strychninium cation in the crystal structures of (I) and (II) (Fig. 1) is comparable to that found in related compounds (Gould *et al.*, 1985, 1987; Mostad, 1985; Białońska & Ciunik, 2005, 2004, 2006*a*,*b*; Bottcher & Buchkremer-Hermanns, 1987; Ghosh *et al.*, 1989; Sato & Yano, 1989; Costante *et al.*, 1996; Robertson & Beevers, 1951; Bokhoven *et al.*, 1951; Yano *et al.*, 1994; Yuan *et al.*, 1994).

In both (I) and (II), the cations form pillars (Fig. 2) extending in the [010] direction. The pillars are stabilized by $C-H \cdots O$(amide) and $C-H \cdots \pi$(arene) hydrogen bonds (see Tables 1 and 2). Similar pillars are present in the previously described crystals of (−)-strychninium (+)-neopentylphthalate chloroform solvate, (−)-strychninium (+)-neopentyl-1-deuterophthalate chloroform solvate (Yuan *et al.*, 1994) and strychninium *N*-phthaloyl-β-alaninate *N*-phthaloyl-β-alanine (Białońska & Ciunik, 2006*b*).
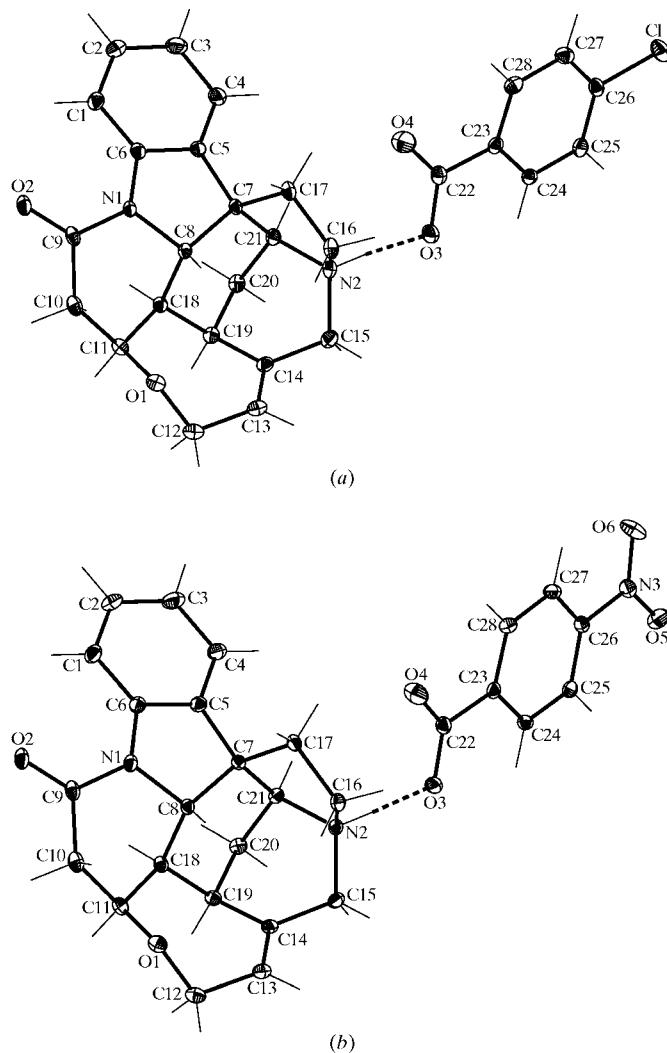

(*a*)

(*b*)

Figure 1
The molecular configuration and atom-numbering scheme in the crystal structures of (*a*) (I) and (*b*) (II). Non-H atoms are shown as 30% probability displacement ellipsoids. Dashed lines indicate $N-H^+ \cdots O^-$ hydrogen bonds.

organic compounds

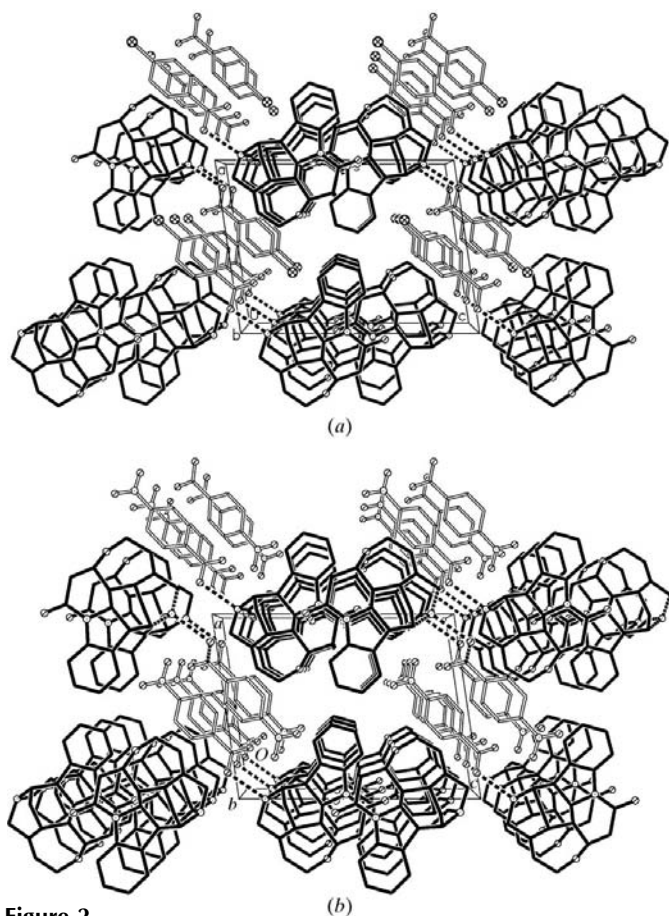Channels are formed between four neighboring strychninium pillars (see Fig. 3). The channels are occupied by 4-chloro- or 4-nitrobenzoate anions in the crystals of (I) and (II), respectively. The anions are linked to one another by C—H···π hydrogen bonds. The strychninium cations and the 4-chloro- or 4-nitrobenzoate anions are linked by ionic N—H$^+$···O$^-$ hydrogen bonds (Tables 1 and 2), in which the protonated amine atom N2 of the strychninium cation and atom O5 of the deprotonated carboxyl group of the 4-chloro- or 4-nitrobenzoate anion act as a donor and an acceptor, respectively. Moreover, the cations and the anions are linked by weak hydrogen bonds. In the crystal of (I), the 4-chlorobenzoate anions are acceptors of C—H···O, C—H···Cl and C—H···π hydrogen bonds (see Tables 1 and 2). In the crystal of (II), the 4-nitrobenzoate anions are acceptors of C—H···O and C—H···π hydrogen bonds (Tables 1 and 2).

Figure 2
The packing of (a) (I) and (b) (II). Strychninium cations [solid lines in (a)] form pillars. Channels between neighboring strychninium pillars are occupied by (a) 4-chlorobenzoate (open lines) and (b) 4-nitrobenzoate anions. For clarity, H atoms have been omitted. Dashed lines indicate hydrogen bonds.
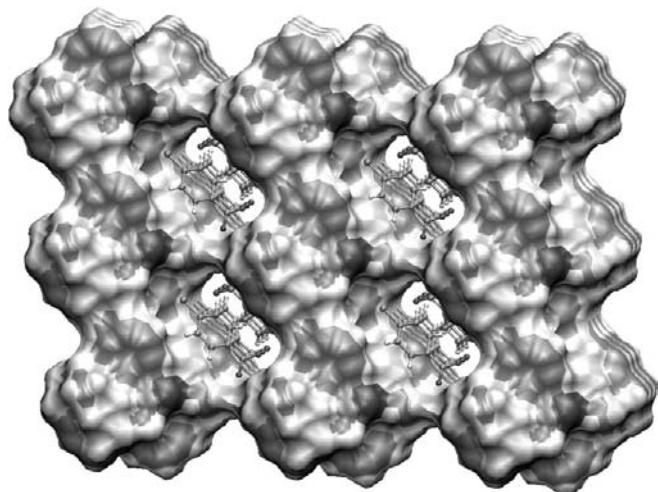

Figure 3
The surface of strychninium self-assembly together with the channels occupied by 4-chlorobenzoate anions. In (II), similar channels are occupied by 4-nitrobenzoate anions (Humphrey et al., 1996).

Experimental

Crystals of (I) and (II) were grown from methanol solutions containing equimolar amounts of strychnine and 4-chloro- or 4-nitrobenzoic acid, respectively. The crystallizations were performed at room temperature by slow evaporation of the solvent.

Salt (I)

Crystal data

$C_{21}H_{23}N_2O_2{}^+ \cdot C_7H_4ClO_2{}^-$	$Z = 2$
$M_r = 490.97$	$D_x = 1.414$ Mg m^{-3}
Monoclinic, $P2_1$	Mo $K\alpha$ radiation
$a = 10.557\,(4)$ Å	$\mu = 0.21$ mm^{-1}
$b = 7.682\,(2)$ Å	$T = 100\,(2)$ K
$c = 14.376\,(8)$ Å	Needle, colorless
$\beta = 98.47\,(4)°$	$0.35 \times 0.20 \times 0.20$ mm
$V = 1153.2\,(8)$ Å^3	

Data collection

Kuma KM-4 CCD diffractometer	5047 reflections with $I > 2\sigma(I)$
ω scan	$R_{int} = 0.053$
15981 measured reflections	$\theta_{max} = 31.0°$
6470 independent reflections	

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} = 0.001$
$R[F^2 > 2\sigma(F^2)] = 0.040$	$\Delta\rho_{max} = 0.28$ e Å^{-3}
$wR(F^2) = 0.084$	$\Delta\rho_{min} = -0.27$ e Å^{-3}
$S = 1.01$	Absolute structure: Robertson & Beevers (1951) and Flack (1983), 2539 Friedel pairs
6470 reflections	
316 parameters	Flack parameter: $-0.01\,(5)$
H-atom parameters constrained	
$w = 1/[\sigma^2(F_o^2) + (0.038P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$	

Table 1
Hydrogen-bond geometry (Å, °) for (I).

$Cg1$ and $Cg2$ represent the centroids of the C1–C6 and C23–C28 rings.

D—H···A	D—H	H···A	D···A	D—H···A	Offset
N2—H22···O3	0.93	1.66	2.589 (2)	174	–
C17—H17B···O2^{i}	0.99	2.35	3.311 (2)	164	–
C18—H18···O2^{ii}	1.00	2.46	3.374 (2)	152	–
C17—H17A···O4	0.99	2.52	3.235 (3)	129	–
C17—H17A···Cl^{iii}	0.99	2.84	3.512 (2)	126	–
C10—H10B···$Cg1^{i}$	0.99	3.00	3.939 (2)	159	1.20
C12—H12A···$Cg2^{iv}$	0.99	2.93	3.705 (2)	136	0.86
C28—H28···$Cg2^{iii}$	0.95	2.85	3.724 (2)	154	0.74

Symmetry codes: (i) $-x + 2, y - \frac{1}{2}, -z + 1$; (ii) $-x + 2, y + \frac{1}{2}, -z + 1$; (iii) $-x + 3, y - \frac{1}{2}, -z$; (iv) $-x + 2, y + \frac{1}{2}, -z$.

Salt (II)

Crystal data

$C_{21}H_{23}N_2O_2{}^+ \cdot C_7H_4NO_4{}^-$
$M_r = 501.53$
Monoclinic, $P2_1$
$a = 10.976$ (2) Å
$b = 7.545$ (1) Å
$c = 14.187$ (2) Å
$\beta = 98.29$ (3)°
$V = 1162.6$ (3) Å^3

$Z = 2$
$D_x = 1.433$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 0.10$ mm^{-1}
$T = 100$ (2) K
Needle, colorless
$0.35 \times 0.15 \times 0.15$ mm

Data collection

Kuma KM-4 CCD diffractometer
ω scan
7610 measured reflections
2666 independent reflections

2541 reflections with $I > 2\sigma(I)$
$R_{int} = 0.028$
$\theta_{max} = 27.0°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.031$
$wR(F^2) = 0.079$
$S = 1.06$
2666 reflections
334 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0517P)^2 + 0.1263P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.19$ e Å^{-3}
$\Delta\rho_{min} = -0.22$ e Å^{-3}
Absolute structure: Robertson & Beevers (1951)

Table 2
Hydrogen-bond geometry (Å, °) for (II).

$Cg1$ and $Cg2$ represent the centroids of the C1–C6 and C23–C28 rings, respectively.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$	Offset
N2—H22$\cdots$O3	0.93	1.72	2.637 (2)	171	–
C17—H17$B\cdots$O2^i	0.99	2.35	3.270 (2)	154	–
C18—H18$\cdots$O2^{ii}	1.00	2.41	3.312 (2)	150	–
C17—H17$A\cdots$O4	0.99	2.47	3.212 (2)	131	–
C17—H17$A\cdots$O5^{iii}	0.99	2.52	3.279 (2)	133	–
C2—H2$\cdots$O5^{iv}	0.95	2.50	3.408 (3)	159	–
C21—H21$\cdots$O6^v	1.00	2.53	3.220 (2)	126	–
C10—H10$B\cdots Cg1^i$	0.99	3.03	3.963 (2)	158	1.41
C12—H12$A\cdots Cg2^{vi}$	0.99	2.92	3.685 (2)	135	0.48
C28—H28$\cdots Cg2^{iii}$	0.94	2.74	3.600 (2)	152	0.33

Symmetry codes: (i) $-x+2, y-\frac{1}{2}, -z+1$; (ii) $-x+2, y+\frac{1}{2}, -z+1$; (iii) $-x+3, y-\frac{1}{2}, -z$; (iv) $x, y, z+1$; (v) $-x+3, y+\frac{1}{2}, -z$; (vi) $-x+2, y+\frac{1}{2}, -z$.

All H atoms were included in idealizing positions and were treated as riding atoms, with C—H and N—H distances of 0.95–1.00 and 0.93 Å, respectively. Friedel pairs were merged before the final refinement of (II). The absolute configurations of (I) and (II) were chosen on the basis of the known absolute configurations of strychnine (Robertson & Beevers, 1951) and for (I) was confirmed by the value of the Flack (1983) parameter.

For both salts, data collection: *CrysAlis CCD* (Oxford Diffraction, 2001); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2001); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL-NT* (Bruker, 1999); software used to prepare material for publication: *SHELXL97*.

References

Białońska, A. & Ciunik, Z. (2004). *CrystEngComm*, **6**, 276–279.
Białońska, A. & Ciunik, Z. (2005). *Acta Cryst.* C**61**, o161–o164.
Białońska, A. & Ciunik, Z. (2006*a*). *Acta Cryst.* B**62**. In the press.
Białońska, A. & Ciunik, Z. (2006*b*). *Acta Cryst.* **62**, o182–o185.
Bokhoven, C., Schoone, J. C. & Bijvoet, J. M. (1951). *Acta Cryst.* **4**, 275–280.
Bottcher, P. & Buchkremer-Hermanns, H. (1987). *Z. Naturforsch. Teil B*, **42**, 431–434.
Bruker (1999). *SHELXTL-NT*. Version 5.1. Bruker AXS Inc., Madison, Wisconsin, USA.
Costante, J., Ehlinger, N., Perrin, M. & Collet, A. (1996). *Enantiomer*, **1**, 377–386.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Ghosh, R., Roychowdhury, P., Chattopadhyay, D. & Iitaka, Y. (1989). *Acta Cryst.* **45**, 1794–1797.
Gould, R. O., Kelly, R. & Walkinshaw, M. D. (1985). *J. Chem. Soc. Perkin Trans. 2*, pp. 847–852.
Gould, R. O., Taylor, P., Walkinshaw, M. D. & Bruins Slot, H. J. (1987). *Acta Cryst.* C**43**, 2405–2410.
Humphrey, W., Dalke, A. & Schelten, K. (1996). *J. Mol. Graph.* **14**, 33–38.
Jacques, J., Collet, A. & Wilen, S. H. (1991). *Enantiomers, Racemates and Resolutions.* Malabar, Florida: Krieger Publishing Company.
Mostad, A. (1985). *Acta Chem. Scand. Ser. B*, **39**, 705–716.
Oxford Diffraction (2001). *CrysAlis CCD* and *CrysAlis RED*. Oxford Diffraction Poland, Wrocław, Poland.
Robertson, J. H. & Beevers, C. A. (1951). *Acta Cryst.* **4**, 270–275.
Sato, M. & Yano, S. (1989). *Bull. Chem. Soc. Jpn*, **62**, 3932–3938.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
Yano, S., Kato, M., Tsukahara, K., Sato, M., Shibahara, T., Lee, K., Sugiara, Y., Iida, M., Goto, K., Aoki, S., Shibahara, Y., Nakahra, H., Yanagisawa, S. & Miyagawa, H. (1994). *Inorg. Chem.* **33**, 5030–5035.
Yuan, H. S. H., Stevens, R. C., Bau, R., Mosher, H. S. & Koetzle, T. F. (1994). *Proc. Natl Acad. Sci. USA*, **91**, 12872–12876.