

## Two isomorphous azastilbene derivatives: 1-(2-chlorobenzyl)-4-[(*E*)-2-(4-hydroxyphenyl)ethenyl]pyridinium chloride and 1-(2-bromobenzyl)-4-[(*E*)-2-(4-hydroxyphenyl)ethenyl]pyridinium bromide

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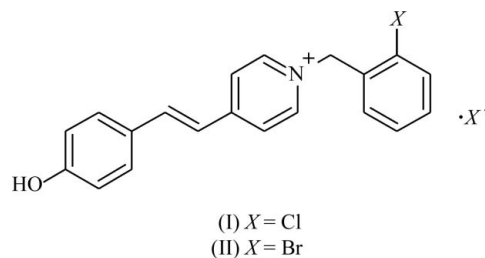
The crystal structures of the two title (*E*)-stilbazolium halogenates,  $C_{20}H_{17}ClNO^+ \cdot Cl^-$  and  $C_{20}H_{17}BrNO^+ \cdot Br^-$ , are isomorphous, with an isostructurality index of 0.985. The azastyryl fragments are almost planar, with dihedral angles between the benzene and pyridine rings of *ca* 4.5°. The rings of the benzyl groups are, in turn, almost perpendicular to the azastyryl planes, with dihedral angles larger than 80°. The cations and anions are connected by  $O-H \cdots X^-$  ( $X$  = halogen) hydrogen bonds. The halide anions are 'sandwiched' between the charged pyridinium rings of neighbouring molecules, and weak  $C-H \cdots O$  hydrogen bonds and  $C-H \cdots X$  and  $C-H \cdots \pi$  interactions also contribute to the crystal structures.

### Comment

Derivatives of (*E*)-stilbazolium and their salts have been used, for example, in the preparation of polymers (Bloch & Wright, 1989) and in nonlinear optics (*e.g.* Marder *et al.*, 1989). Some interesting photochemical properties have been utilized in the testing of chromatographic stationary phases (Prukała *et al.*, 2008). In particular, *N*-alkyl- and *N*-benzyl-substituted (*E*)-stilbazole derivatives show a broad spectrum of antimicrobial activity (*e.g.* Prukała & Kędzia, 1999; Klein *et al.*, 2007).

In the course of our structural studies of the family of *N*-benzylstilbazole derivatives, we reported the isomorphous pair of halides 1-(2-chlorobenzyl)-4-[(*E*)-2-(3-hydroxyphenyl)ethenyl]pyridinium chloride hemihydrate and its 2-bromo/bromide analogue (Prukała *et al.*, 2008). We report here the crystal structures of another isomorphous pair, this time without the solvent water, namely 1-(2-chlorobenzyl)-4-[(*E*)-2-(4-hydroxyphenyl)ethenyl]pyridinium chloride, (I), and

1-(2-bromobenzyl)-4-[(*E*)-2-(4-hydroxyphenyl)ethenyl]pyridinium bromide, (II).



Compounds (I) and (II) are highly isomorphous; they crystallize in the same space group,  $C2/c$ , and their unit-cell parameters and packing modes are similar. Kálmán *et al.* (1991) introduced the isostructurality index, which shows how close are the positions of the atoms in two unit cells. In its simplest form, this index is defined as unity minus the sum of the squares of differences between the positions of the appropriate atoms, divided by the number of pairs. Consequently, it would be 1 for an ideal isostructural pair [there have been some attempts to put these values on a more absolute scale, *e.g.* Kubicki & Szafranski (1998)]. In the case of (I) and (II), the value of this index is close to the ideal value, at 0.985. As in the previous related case (Prukała *et al.*, 2008), the two molecules are so similar that the normal probability plots (*International Tables for X-ray Crystallography*, 1974, Vol. IV, pp. 293–300; Abrahams & Keve, 1971) for bond lengths (without  $C-X$  bonds) and all bond angles show that the differences between the molecules are generally of a statistical nature; the correlation factors  $R^2$  are 0.94 and 0.96 for bond lengths and angles, respectively.

Because the two compounds are highly isomorphous, the following discussion will be on the chloro compound, (I), only; all data for the bromo compound, (II), are available in the archived CIF, and in the discussion below numerical data for (II) will be given in square brackets after the appropriate values for (I).

The conformation of the molecule is very similar to the 3-hydroxy analogues described earlier. The values of the descriptors of the molecular conformation, *i.e.* the dihedral angles between the planar fragments [Fig. 1; three rings (chlorophenyl = *A*, pyridine = *B* and hydroxyphenyl = *C*) and the  $C4-C7=C8-C9$  bridge (*D*)] are almost identical. The dihedral angles within the azastyryl fragments are small; for instance, that between rings *B* and *C* is 4.35 (9)° [4.43 (18)°].

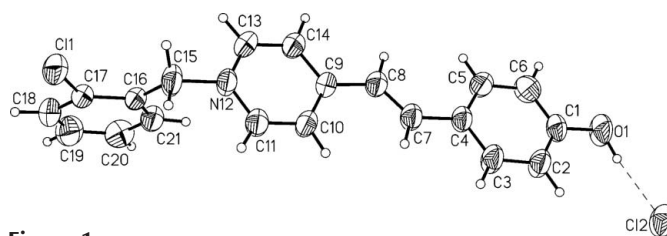
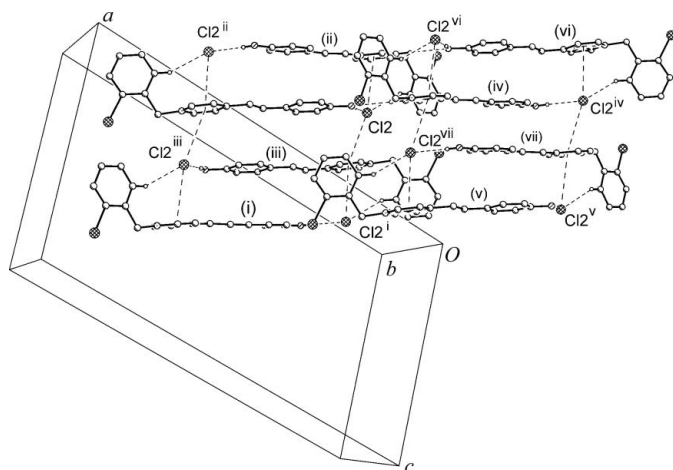


Figure 1

The ionic components of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. The dashed line indicates the hydrogen bond.


**Figure 2**

The stacks of molecules of (I), connected by weak interactions that 'trap' the  $\text{Cl}^-$  anions (see *Comment* for details). These interactions and relatively short  $\text{C}-\text{H}\cdots\text{O}$  hydrogen bonds are drawn as dashed lines. [Symmetry codes: (i)  $x, -y, \frac{1}{2} + z$ ; (ii)  $1 - x, y, -\frac{1}{2} - z$ ; (iii)  $1 - x, -y, -z$ ; (iv)  $-\frac{1}{2} - x, -\frac{1}{2} - y, -\frac{1}{2} + z$ ; (v)  $-\frac{1}{2} + x, -\frac{1}{2} + y, z$ ; (vi)  $\frac{1}{2} - x, -\frac{1}{2} - y, -1 + z$ ; (vii)  $\frac{1}{2} - x, -\frac{1}{2} + y, -\frac{1}{2} - z$ .]

The planar benzyl group is, as in the majority of cases found in the Cambridge Structural Database (CSD; Allen, 2002), almost perpendicular to the azasteryl fragments; the dihedral angle between rings *A* and *B* is  $84.66 (9)^\circ$  [ $84.07 (18)^\circ$ ]. This particular value is significantly larger in the present case, by *ca*  $10^\circ$ , than in the 3-hydroxy series. The two almost perpendicular rings *A* and *B* look quite different from the perspective of the  $\text{N12}-\text{C15}-\text{C16}$  bridge: ring *A* is almost coplanar with the bridge [dihedral angle =  $4.7 (2)^\circ$  [ $2.8 (3)^\circ$ ]], while ring *B* is almost perpendicular [ $82.2 (2)^\circ$  [ $83.2 (3)^\circ$ ]].

An  $\text{O}-\text{H}\cdots\text{X}^-$  hydrogen bond connects the ionic fragments into a relatively tightly bound pair. In the crystal structure, the anions are 'sandwiched' between the central pyridine (*B*) rings (Fig. 2). The  $\text{Cg}\cdots\text{X}^-$  distances (*Cg* is the centroid of the pyridine ring) are  $3.718 (1)$  [ $3.736 (2)$  Å] and  $3.739 (1)$  Å [ $3.739 (2)$  Å], and the  $\text{X}^{-\text{iii}}\cdots\text{Cg}\cdots\text{X}^{-\text{ii}}$  angle of  $160.7 (2)^\circ$  [ $167.4 (4)^\circ$ ] indicates an almost linear disposition [symmetry codes: (ii)  $1 - x, y, -\frac{1}{2} - z$ ; (iii)  $1 - x, -y, -z$ ]. Also, the  $\text{Cg}^{\text{iii}}\cdots\text{X}^{-\text{iii}}\cdots\text{Cg}^{\text{ii}}$  angle is close to linearity, at  $160.7 (2)^\circ$  [ $165.1 (4)^\circ$ ]. These interactions, in principle, can not be regarded as anion- $\pi$  interactions, which are currently receiving increasing attention for their possible importance in, for example, template-based synthesis or biological processes (see, for instance, Vilar, 2003; de Hoog *et al.*, 2004). In the light of the critical review by Hay & Custulcean (2009), the prerequisite for the existence of such an interaction is a neutral, not a charged, aromatic ring. In the CSD (Version 3.91 of November 2009, updated February 2010) there are 108 examples of such two-sided coordination of the halide anion by aromatic rings (organics only,  $R < 0.1$ , both  $\text{X}\cdots$ centroid distances less than 4.0 Å). Only in 32 cases is the  $\text{Cg}\cdots\text{X}^{-\text{iii}}\cdots\text{Cg}$  angle larger than  $140^\circ$ , which shows the high degree of linearity of the coordination, and another 26 structures have limited linearity, with angles between  $120$  and  $140^\circ$ . The vast majority of these structures contain charged aromatic rings; within the group of hits showing linear coordination,

we found only one example of an uncharged ring, namely 1,4-dibenzyl-1,4,8,11-tetraazoniacyclotetradecane tetrabromide dihydrate (Havlickova *et al.*, 2008).

These contacts, together with  $\text{O}-\text{H}\cdots\text{Cl}^-$  [ $\text{Br}^-$ ] and relatively short  $\text{C}-\text{H}\cdots\text{Cl}^-$  [ $\text{Br}^-$ ] hydrogen bonds, effectively 'trap' the anion in the structure (Table 1) and form infinite stacks of molecules along the [001] direction. A similar position of the  $\text{Cl}^-$  anion was observed in the structure of 1-methyl-3-hydroxypyridinium chloride (Szafran *et al.*, 2007). Neighbouring stacks are connected by relatively short and directional  $\text{C13}-\text{H}\cdots\text{O}$  hydrogen bonds. Table 1 also lists a number of relatively short  $\text{C}-\text{H}\cdots\text{Cl}$  [ $\text{Br}$ ] and  $\text{C}-\text{H}\cdots\text{Cl}^-$  [ $\text{Br}^-$ ] contacts. In the crystal structures, the hydroxyphenyl rings overlap significantly, with a  $\text{Cg}\cdots\text{Cg}^{\text{ii}}$  distance of  $3.815 (1)$  Å [ $3.788 (2)$  Å], which gives an interplanar distance of  $3.54 (1)$  Å [ $3.60 (2)$  Å].

## Experimental

(*E*)-Azastilben-4'-ol (5 mmol) was dissolved in boiling nitromethane (50 ml). Upon dissolution, the corresponding benzyl halide (25 mmol) was added. The reaction mixture was refluxed for 5 h and the precipitated solid was filtered off. Half the volume of nitromethane was then removed from the filtrate using a rotary evaporator. The residue was cooled for 24 h, and the precipitated solid was filtered off, washed with  $\text{CH}_3\text{NO}_2$  and dried. The desired products were obtained by combining both fractions of solids and recrystallizing them by slow evaporation from methanol.

## Compound (I)

### Crystal data

$\text{C}_{20}\text{H}_{17}\text{ClNO}^+\cdot\text{Cl}^-$	$V = 3441.8 (9)$ Å <sup>3</sup>
$M_r = 358.25$	$Z = 8$
Monoclinic, $C2/c$	Mo $K\alpha$ radiation
$a = 25.942 (4)$ Å	$\mu = 0.38$ mm <sup>-1</sup>
$b = 9.4027 (15)$ Å	$T = 295$ K
$c = 14.667 (2)$ Å	$0.2 \times 0.15 \times 0.15$ mm
$\beta = 105.842 (15)^\circ$	

**Table 1**

Geometry of hydrogen bonds and short contacts (Å, °).

*CgC* denotes the centroid of phenyl ring *C* (atoms C1–C6).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
(I)				
$\text{O1}-\text{H1}\cdots\text{Cl2}$	0.82	2.20	3.0172 (16)	172
$\text{C6}-\text{H6}\cdots\text{Cl1}^{\text{viii}}$	0.93	2.79	3.701 (2)	168
$\text{C21}-\text{H21}\cdots\text{Cl2}^{\text{ii}}$	0.93	2.68	3.5078 (19)	149
$\text{C13}-\text{H13}\cdots\text{O1}^{\text{ix}}$	0.93	2.40	3.311 (2)	165
$\text{C2}-\text{H2}\cdots\text{Cl1}^{\text{x}}$	0.93	2.88	3.516 (2)	127
$\text{C3}-\text{H3}\cdots\text{Cl1}^{\text{x}}$	0.93	2.88	3.524 (2)	128
$\text{C10}-\text{H10}\cdots\text{CgC}^{\text{xi}}$	0.93	2.90	3.688 (2)	144
(II)				
$\text{O1}-\text{H1}\cdots\text{Br2}$	0.82	2.43	3.226 (3)	163
$\text{C6}-\text{H6}\cdots\text{Br1}^{\text{viii}}$	0.93	2.89	3.801 (4)	166
$\text{C21}-\text{H21}\cdots\text{Br2}^{\text{ii}}$	0.93	2.88	3.717 (4)	151
$\text{C13}-\text{H13}\cdots\text{O1}^{\text{ix}}$	0.93	2.52	3.417 (4)	160
$\text{C2}-\text{H2}\cdots\text{Br1}^{\text{x}}$	0.93	2.99	3.635 (5)	128
$\text{C3}-\text{H3}\cdots\text{Br1}^{\text{x}}$	0.93	3.00	3.643 (4)	128
$\text{C10}-\text{H10}\cdots\text{CgC}^{\text{xi}}$	0.93	2.99	3.778 (6)	143

Symmetry codes: (ii)  $-x + 1, y, -z - \frac{1}{2}$ ; (viii)  $x - \frac{1}{2}, -y - \frac{1}{2}, z - \frac{1}{2}$ ; (ix)  $x + \frac{1}{2}, -y - \frac{1}{2}, z + \frac{1}{2}$ ; (x)  $x - \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$ ; (xi)  $-x + \frac{3}{2}, -y + \frac{3}{2}, -z$ .

## Data collection

Oxford Xcalibur Sapphire2  
diffractometer (large Be window)  
Absorption correction: multi-scan  
(*CrysAlis Pro*; Oxford  
Diffraction, 2009)  
 $T_{\min} = 0.938$ ,  $T_{\max} = 1.000$

13504 measured reflections  
3867 independent reflections  
2368 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.026$

## Refinement

$R[F^2 > 2\sigma(F^2)] = 0.036$   
 $wR(F^2) = 0.094$   
 $S = 0.94$   
3866 reflections

218 parameters  
H-atom parameters constrained  
 $\Delta\rho_{\text{max}} = 0.21 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.23 \text{ e } \text{\AA}^{-3}$

## Compound (II)

## Crystal data

$\text{C}_{20}\text{H}_{17}\text{BrNO}^+\cdot\text{Br}^-$   
 $M_r = 447.17$   
Monoclinic,  $C2/c$   
 $a = 26.462 (3) \text{ \AA}$   
 $b = 9.4974 (15) \text{ \AA}$   
 $c = 14.813 (2) \text{ \AA}$   
 $\beta = 105.793 (15)^\circ$

$V = 3582.3 (8) \text{ \AA}^3$   
 $Z = 8$   
Mo  $K\alpha$  radiation  
 $\mu = 4.53 \text{ mm}^{-1}$   
 $T = 295 \text{ K}$   
 $0.15 \times 0.1 \times 0.1 \text{ mm}$

## Data collection

Oxford Xcalibur Sapphire2  
diffractometer (large Be window)  
Absorption correction: multi-scan  
(*CrysAlis Pro*; Oxford  
Diffraction, 2009)  
 $T_{\min} = 0.494$ ,  $T_{\max} = 1.000$

8330 measured reflections  
3299 independent reflections  
2046 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.021$

## Refinement

$R[F^2 > 2\sigma(F^2)] = 0.032$   
 $wR(F^2) = 0.083$   
 $S = 1.05$   
3299 reflections

218 parameters  
H-atom parameters constrained  
 $\Delta\rho_{\text{max}} = 0.41 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.38 \text{ e } \text{\AA}^{-3}$

H atoms were placed geometrically in idealized positions, with  
 $\text{C}-\text{H} = 0.93$  (aromatic and alkene) or  $0.97 \text{ \AA}$  (methylene) and

$\text{O}-\text{H} = 0.82 \text{ \AA}$ , and refined as rigid groups, with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C},\text{O})$ .

For both compounds, data collection: *CrysAlis Pro* (Oxford Diffraction, 2009); cell refinement: *CrysAlis Pro*; data reduction: *CrysAlis Pro*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *Stereochemical Workstation Operation Manual* (Siemens, 1989); software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG3177). Services for accessing these data are described at the back of the journal.

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