

Isomorphism in 1-(2-halidobenzyl)-4-[(*E*)-2-(3-hydroxyphenyl)ethenyl]pyridinium halide hemihydrates (halide = Cl, Br)

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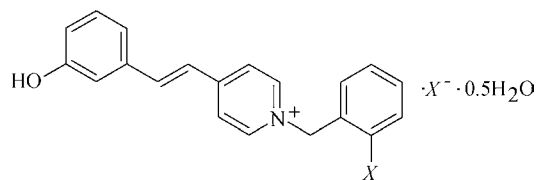
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The crystal structures of two (*E*)-stilbazolium salts, namely 1-(2-chlorobenzyl)-4-[(*E*)-2-(3-hydroxyphenyl)ethenyl]pyridinium chloride hemihydrate, $C_{20}H_{17}ClNO^+ \cdot Cl^- \cdot 0.5H_2O$, (I), and 1-(2-bromobenzyl)-4-[(*E*)-2-(3-hydroxyphenyl)ethenyl]pyridinium bromide hemihydrate, $C_{20}H_{17}BrNO^+ \cdot Br^- \cdot 0.5H_2O$, (II), are isomorphous; the isostructurality index is 99.3%. In both salts, the azastyryl fragments are almost planar, while the rings of the benzyl groups are almost perpendicular to the azastyryl planes. The building blocks of the structures are twofold symmetric hydrogen-bonded systems of two cations, two halide anions and one water molecule, which lies on a twofold axis. In the crystal structure, these blocks are connected by means of weaker interactions, *viz.* van der Waals, weak hydrogen bonding and stacking. This study illustrates the robustness of certain supramolecular motifs created by a spectrum of intermolecular interactions in generating these isomorphous crystal structures.

Comment

The salts of derivatives of (*E*)-stilbazolium have been found to be useful for nonlinear optics [for instance, *trans*-4'-(dimethylamino)-*N*-methyl-4-stilbazolium *p*-toluenesulfonate, DAST (Marder *et al.*, 1989, 1994)] or for the preparation of polymers (*e.g.* Bloch & Wright, 1989). Due to an almost planar conformation, similar to (*E*)-stilbene, and the conjugated double-bond system, some stilbazolium derivatives exhibit interesting photochemical properties (*e.g.* Usami *et al.*, 1990). The maximum in the UV absorption spectrum, shifted to long wavelength due to the conjugated double-bond system, can be used in the testing of chromatographic stationary phases (Prukała *et al.*, 2008). *N*-Alkyl- or *N*-benzyl-substituted (*E*)-stilbazole derivatives show a broad spectrum of antimicrobial activity (*e.g.* Wyrzykiewicz *et al.*, 1990; Prukała & Kędzia, 1999) and some have already been patented (*e.g.* MacDonald *et al.*, 2007; Klein *et al.*, 2007).

We decided to undertake a detailed structural study of the family of *N*-benzylstilbazole derivatives. We report here the crystal structures of two compounds, namely 1-(2-chlorobenzyl)-4-[(*E*)-2-(3-hydroxyphenyl)ethenyl]pyridinium chloride hemihydrate, (I), and 1-(2-bromobenzyl)-4-[(*E*)-2-(3-hydroxyphenyl)ethenyl]pyridinium bromide hemihydrate, (II).



(I) $X = Cl$

(II) $X = Br$

Compounds (I) and (II) are isomorphous; they crystallize in the same space group, and the unit-cell dimensions and packing modes are essentially identical (Fig. 1). In order to gain some insight into the degree of isomorphism, we have used the descriptors introduced by Kálmán *et al.* (1991). The unit-cell similarity index, Π , defined as the difference between unity and the ratio of the sums of the orthogonalized unit-cell parameters, is almost ideal, at 0.01. The isostructurality index, which shows how close the positions of the atoms in the unit cells are, is defined by the sum of the differences between the positions of analogous atoms. In the case of (I) and (II), the value of this index of 99.3% is also close to the ideal value. Kubicki & Szafranski (1998) proposed a modification of this latter parameter, which takes the point group symmetry into account and gives a more absolute measure of the degree of isostructurality; it should be 1 for ideally isomorphous compounds and 0 for randomly distributed atoms. The value of this modified index for (I) and (II) is 0.96. The structures of the two molecules are so similar (Figs. 2 and 3) that even normal probability plots (*International Tables for X-ray Crystallography*, 1974; Abrahams & Keve, 1971) for bond lengths (without C–X bonds) and all angles show no differences of a systematic nature. The correlation factors R^2 are

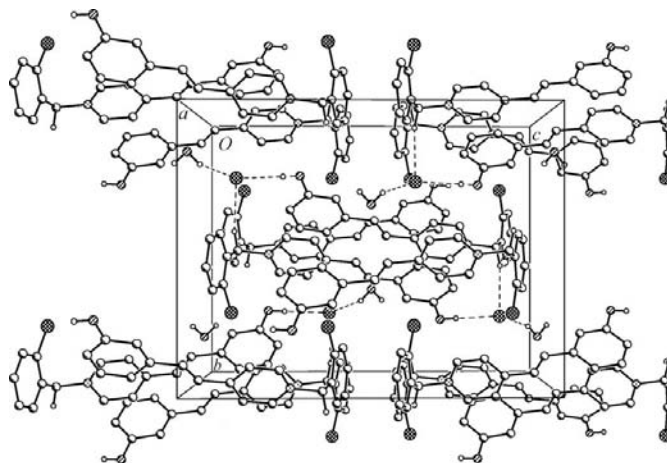
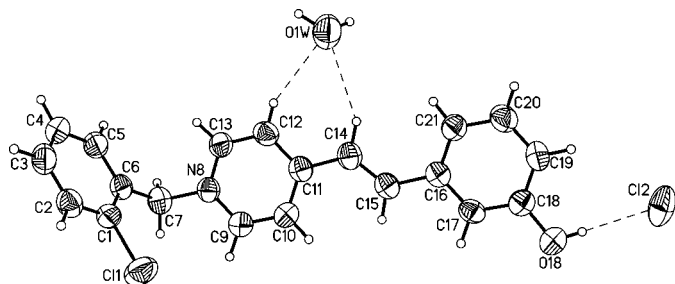
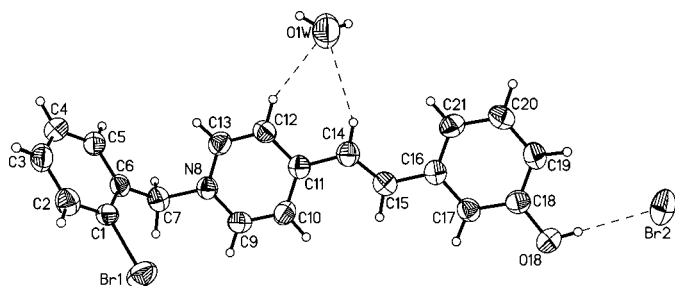


Figure 1

The crystal packing of (I), viewed along the *a* direction. Compound (II) is isomorphous and the packing is essentially identical to that of (I).


Figure 2

The molecule 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. Hydrogen bonds are drawn as dashed lines.


Figure 3

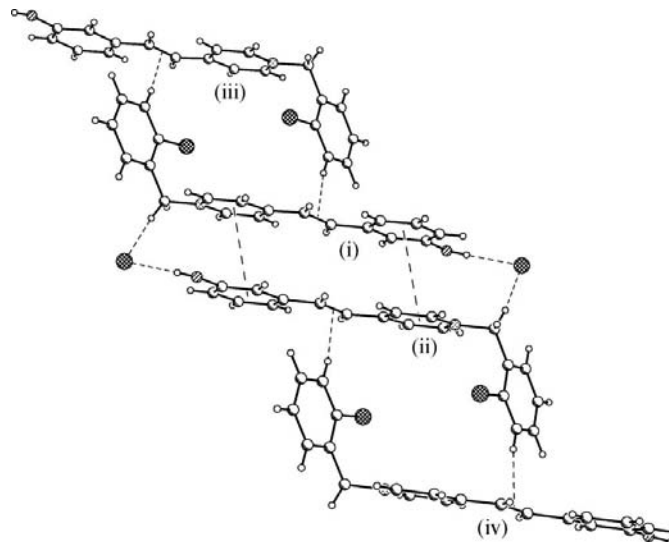
The molecule of (II), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. Hydrogen bonds are drawn as dashed lines.


Figure 4

The building block of the crystal structure of (I). Hydrogen bonds are drawn as dashed lines. [Symmetry codes: (i) $-\frac{1}{2} + x, \frac{1}{2} + y, \frac{1}{2} + z$; (ii) $\frac{1}{2} - x, y, 2 - z$.]

0.982 and 0.975 for the bond lengths and angles, respectively.

The conformation of each molecule can be described using the dihedral angles between the planar fragments, namely the three rings (chlorophenyl *A*, pyridine *B* and hydroxyphenyl *C*) and the C11–C14=C15–C16 bridge (*D*). The dihedral angles within the whole azastyryl fragments are small, while those between rings *B* and *C* are as low as 2.75 (12°) in (I) and 2.66 (17°) in (II). The plane of the ethenyl bridge is significantly more twisted with respect to the ring planes (the angles are around 6°). It might be noted that these twists have the same sense, so the rings are almost coplanar. The perfectly planar benzyl groups are almost perpendicular to the azastyryl groups; the dihedral angles between rings *A* and *B* are as high as 76.57 (6°) for (I) and 75.84 (9°) for (II). These are close to typical values; in the Cambridge Structural Database (Version 5.29 of November 2007; Allen, 2002) there are 778 similar fragments (both phenylpyridyl and benzylpyridyl) and the values of the dihedral angles between the rings are in the range 53–90°, with a mean value of 77.7 (3)°.


Figure 5

The molecules of (I), connected by weak interactions that involve π electrons (see *Comment* for details). The interactions and hydrogen bonds are drawn as dashed lines. [Symmetry codes: (i) x, y, z ; (ii) $1 - x, 1 - y, 1 - z$; (iii) $\frac{3}{2} - x, \frac{3}{2} - y, \frac{1}{2} - z$; (iv) $-\frac{1}{2} + x, -\frac{1}{2} + y, \frac{1}{2} + z$.]

The building blocks of the structures are symmetrical hydrogen-bonded fragments built of two cations, two halide anions and a water molecule which occupies a special position on a twofold axis (Table 1 and Fig. 4). All strong hydrogen-bond donors are involved in the creation of these structures, so the further construction of the crystal structures utilizes weaker interactions. The blocks are connected into a three-dimensional structure by means of relatively strong C–H...O and C–H...X hydrogen bonds (see Table 1 and Fig. 1). Additionally, an interesting network of weak interactions involving π -electron systems is created (Fig. 5). The distances between the centroids of rings *B* and *C* from molecules related by the centre of symmetry ($1 - x, 1 - y, 1 - z$) are 3.540 (2) Å in (I) and 3.676 (2) Å in (II). The planes of the rings are almost parallel (dihedral angles of *ca* 2.8°); taking the offset into account, the distances between the planes are *ca* 3.38 Å in both cases. These centrosymmetric dimers are connected to neighbouring dimers, related by another centre of symmetry, by means of weak but directional C–H... π interactions with the C14=C15 double bond (Table 1).

Experimental

The general procedure for the synthesis of (I) and (II) is as follows. (*E*)-Azastilben-2'-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 CH₃NO₂ and dried. The desired products were obtained by combining both fractions of solids and recrystallizing them from methanol. For (I), m.p. 470–473 K; for (II), m.p. 498–501 K. Spectroscopic data are available in the archived CIF.

Compound (I)

Crystal data

$C_{20}H_{17}ClNO^+ \cdot Cl^- \cdot 0.5H_2O$
 $M_r = 367.25$
 Monoclinic, $I2/a$
 $a = 15.6100$ (12) Å
 $b = 13.2847$ (10) Å
 $c = 17.2233$ (13) Å
 $\beta = 91.358$ (6)°

Data collection

Kuma KM-4 CCD area-detector diffractometer
 Absorption correction: multi-scan (*CrysAlis RED*; Oxford Diffraction, 2007)
 $T_{min} = 0.903$, $T_{max} = 0.928$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.036$
 $wR(F^2) = 0.104$
 $S = 1.21$
 3288 reflections
 294 parameters
 1 restraint

Compound (II)

Crystal data

$C_{20}H_{17}BrNO^+ \cdot Br^- \cdot 0.5H_2O$
 $M_r = 456.17$
 Monoclinic, $I2/a$
 $a = 15.6975$ (8) Å
 $b = 13.5505$ (7) Å
 $c = 17.2562$ (10) Å
 $\beta = 92.879$ (4)°

Data collection

Kuma KM-4 CCD area-detector diffractometer
 Absorption correction: multi-scan (*CrysAlis RED*; Oxford Diffraction, 2007)
 $T_{min} = 0.186$, $T_{max} = 0.412$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.028$
 $wR(F^2) = 0.074$
 $S = 1.07$
 3406 reflections
 225 parameters
 1 restraint

The choice of the nonstandard space group $I2/a$ (instead of $C2/c$) was a result of the large values of the β angle [131.44° for (I) and 130.70° for (II)] in the latter case. The positions of the hydroxyl H atom in (I) and the unique water H atom in (II) were refined with a restrained O—H distance of 0.84 (1) Å. The positions and $U_{iso}(H)$ values of all other H atoms in (I) were refined freely, while in (II) they were placed in idealized positions and refined using a riding model, with C—H = 0.93–0.97 Å. All H atoms in (II) were assigned $U_{iso}(H)$ values of $1.2U_{eq}(C)$.

Table 1

Geometry of hydrogen bonds for (I) and (II) (Å, °).

$Cg4$ denotes the mid-point of the $C14=C15$ double bond.

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
Compound (I)				
O18—H18 \cdots Cl2	0.83 (3)	2.27 (3)	3.092 (2)	179 (2)
O1W—H1WA \cdots Cl2 ⁱ	0.95 (3)	2.28 (3)	3.1844 (12)	158 (3)
C7—H7A \cdots Cl2 ⁱⁱ	0.97 (2)	2.60 (2)	3.557 (2)	167 (2)
C12—H12 \cdots O1W	0.89 (2)	2.49 (2)	3.327 (3)	157 (1)
C14—H14 \cdots O1W	0.99 (2)	2.66 (2)	3.520 (3)	145 (1)
C15—H15 \cdots Cl2 ⁱⁱⁱ	1.00 (2)	2.83 (2)	3.829 (2)	173 (1)
C2—H2 \cdots Cg4 ^{iv}	0.93 (2)	3.00 (2)	3.905 (2)	167 (1)
Compound (II)				
O18—H18 \cdots Br2	0.82	2.42	3.234 (2)	177
O1W—H1WA \cdots Br2 ⁱ	0.86 (3)	2.48 (3)	3.310 (2)	165 (3)
C7—H7A \cdots Br2 ⁱⁱ	0.97	2.77	3.672 (3)	155
C12—H12 \cdots O1W	0.93	2.46	3.328 (3)	156
C14—H14 \cdots O1W	0.93	2.68	3.487 (4)	146
C15—H15 \cdots Br2 ⁱⁱⁱ	0.93	3.00	3.915 (3)	168
C2—H2 \cdots Cg4 ^{iv}	0.93	3.14	4.032 (4)	162

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

For both compounds, data collection: *CrysAlis CCD* (Oxford Diffraction, 2007); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2007); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *XP* (Siemens, 1989); software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN3095). Services for accessing these data are described at the back of the journal.

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