

Hydrogen bonds and  $\pi$ - $\pi$  interactions in two new crystalline phases of methylene blue

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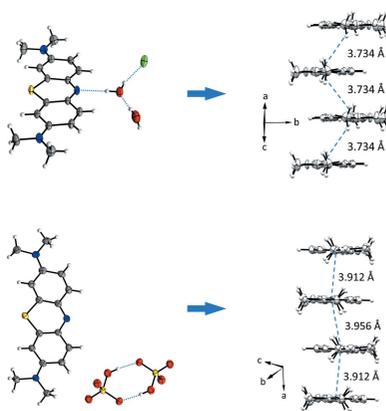
**Keywords:** crystal structure; methylene blue; chloride; bisulfite; hydrogen bonding;  $\pi$ - $\pi$  interactions; Hirshfeld surface analysis.**CCDC references:** 1811677; 1811678**Supporting information:** this article has supporting information at journals.iucr.org/e

Two unprecedented solid phases involving the 3,7-bis(dimethylamino)phenothiazin-5-ium cation, *i.e.* methylene blue ( $\text{MB}^+$ ), have been obtained and structurally characterized. In the crystals of 3,7-bis(dimethylamino)phenothiazin-5-ium chloride dihydrate,  $\text{C}_{16}\text{H}_{18}\text{N}_3\text{S}^+\cdot\text{Cl}^-\cdot 2\text{H}_2\text{O}$  (**I**) and 3,7-bis(dimethylamino)phenothiazinium bisulfite,  $\text{C}_{16}\text{H}_{18}\text{N}_3\text{S}^+\cdot\text{HSO}_4^-$  (**II**), the cationic dye molecules are planar and disposed in an antiparallel mode, showing  $\pi$ - $\pi$  stacking interactions, with mean interplanar distances of 3.326 (4) and 3.550 (3) Å in (**I**) and (**II**), respectively. In compound (**I**), whose phase was found affected by merohedral twinning [BASF = 0.185 (3)], the presence of water molecules allows a network of hydrogen bonds involving  $\text{MB}^+$  as both a donor and an acceptor, whereas in compound (**II**), the homo-interaction of the anions causes an effective absence of classical hydrogen-bond donors. This substantial difference has important consequences for the stacking geometry and supramolecular interactions of the  $\text{MB}^+$  cations, which are analysed by Hirshfeld fingerprint plots and subsequently discussed.

## 1. Chemical context

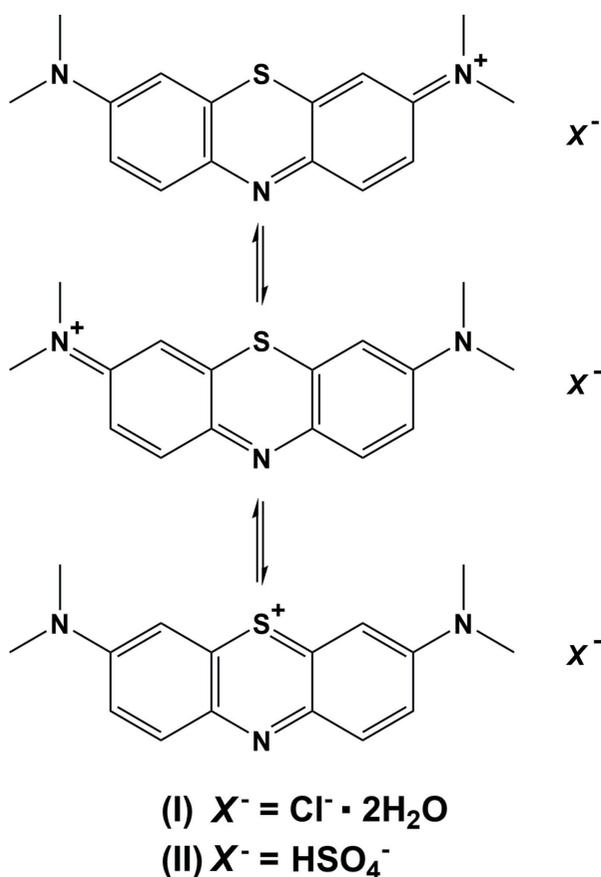
The 3,7-bis(dimethylamino)phenothiazin-5-ium ion, better known as **methylene blue cation** ( $\text{MB}^+$ ), is a renowned compound with important applications in medicine (Hanzlik, 1933; Wendel, 1935; Wischik *et al.*, 1996), biology (Jung & Metzger, 2013; Färber *et al.*, 1998) and chemistry (Bergamonti *et al.*, 2015; Kim *et al.*, 2014).  $\text{MB}^+$ , with formula  $\text{C}_{16}\text{H}_{18}\text{N}_3\text{S}^+$ , consists of three condensed six-membered rings with two heteroatoms in the central one, and two terminal dimethylamine groups. The delocalization of the +1 charge, which involves the whole molecule with the exception of the four peripheral methyl groups, causes an overall planarity and the typical intense blue colour exhibited by  $\text{MB}^+$  solutions in many solvents. The formal resonant structures are shown in the Scheme.

The  $\text{MB}^+$  chloride salt is the first fully synthetic drug to be used in medicine, originally as an antimalarial agent (Coulibaly *et al.*, 2009), an antidepressant (Eroğlu & Çağlayan, 1997), an antihemoglobinemic (Cawein *et al.*, 1964) and as a disinfectant (Lo *et al.*, 2014). In chemistry, it has various colourimetric and photocatalytic uses (Hang & Brindley, 1970; Kim *et al.*, 2014; Bergamonti *et al.*, 2015), which rely on its capability of undergoing a reduction process in the presence of weak reducing agents, turning into the colourless leukomethylene blue. The latter, in turn, can be oxidized to restore the original  $\text{MB}^+$  cation, and this feature makes it a valid redox agent in biochemistry where it plays relevant roles in the study of enzyme-catalysed redox reactions. Recently, despite the cationic nature of  $\text{MB}^+$ , we found that its peculiar electronic



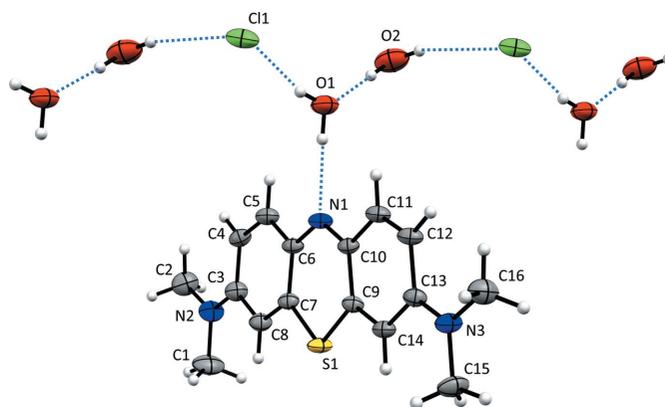
situation enables ligand behaviour towards  $MCl_2$  fragments ( $M = Cu$  and  $Ag$ ) through the central aromatic nitrogen atom (Canossa *et al.*, 2017), thus proving that some properties of this common and widespread molecule are still to be discovered.

Commercial **MB** is a pentahydrate chloride salt, whose structure was reported in 1973 (Marr *et al.*, 1973). Recently, Rager *et al.* (2012) reinvestigated its crystalline states at variable temperatures, which led to the observation of five different hydrates with clearly distinct structures, as shown by powder X-ray diffraction analyses. However, no structural data are available and, to date, only the structure of the commercial pentahydrate form is known. Herein, we report and discuss the molecular and crystal structures of the unreported dihydrate phase of **MB**<sup>+</sup> chloride (**I**), one of those predicted by Rager *et al.* (2012), and the crystal structure of a new anhydrous form of **MB**<sup>+</sup> bisulfite (**II**).



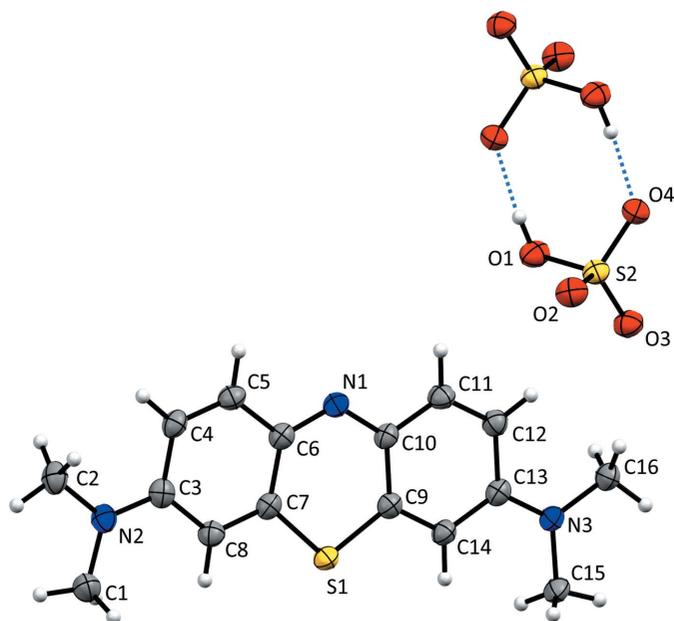
## 2. Structural commentary

The molecular structures of compounds (**I**) and (**II**) are illustrated in Figs. 1 and 2, respectively. Details of the hydrogen bonding in the crystals of compounds (**I**) and (**II**) are given in Tables 1 and 2, respectively. In compound (**I**), the asymmetric unit is composed of one **MB**<sup>+</sup> cation, a chloride anion, and two water molecules. The latter are linked head-to-tail by  $O-H \cdots O$  hydrogen bonds which, in turn, are linked by  $O-H \cdots Cl$  hydrogen bonds, forming chains propagating along [001], as shown in Fig. 1 (see also Table 1). The asymmetric unit of compound (**II**) consists of an **MB**<sup>+</sup> cation and a



**Figure 1**  
 The molecular structure of compound (**I**), with the atom labelling. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen bonds are shown as dashed lines (see Table 1).

bisulfite anion. In both compounds, the **MB**<sup>+</sup> cations display a typical resonance structure, as evidenced by the values of the C—C bond lengths in the rings, which range from 1.352 (3) to 1.447 (5) Å. This bond-length distribution range is the same as that observed in other reported structures containing **MB**<sup>+</sup> cations, for example, as for its chloride pentahydrate form (Marr *et al.*, 1973). The two C—S bond lengths, S1—C7 and S1—C9 [respectively, 1.731 (4) and 1.734 (4) Å in (**I**) and 1.732 (2) and 1.727 (2) Å in (**II**)], are very similar and in agreement with analogous data reported in the literature. The **MB**<sup>+</sup> cations are planar considering the three condensed six-membered rings [atoms S1/N1/C3—C14; r.m.s. deviations are 0.011 Å for (**I**) and 0.01 Å for (**II**)] and the external dimethylamine groups, with the only exception being the aliphatic hydrogen atoms. In compound (**II**), one of the four



**Figure 2**  
 The molecular structure of compound (**II**), with the atom labelling. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen bonds are shown as dashed lines (see Table 2).

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

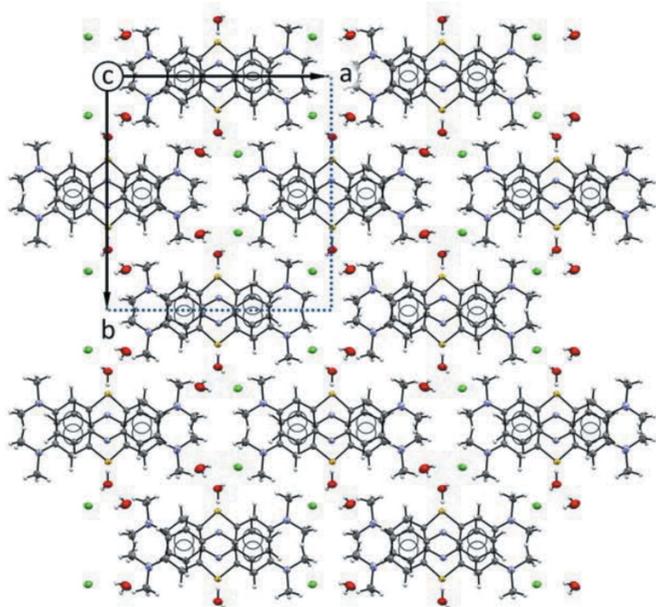
<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
O1—H1D···C11	0.87	2.30	3.153 (4)	168
O1—H1E···N1	0.87	2.07	2.936 (4)	177
O2—H2D···O1	0.87	1.97	2.837 (6)	174
O2—H2E···C11 <sup>i</sup>	0.87	2.71	3.559 (5)	165
C1—H1B···O1 <sup>iii</sup>	0.98	2.45	3.426 (6)	173
C2—H2B···C11 <sup>iii</sup>	0.98	2.72	3.611 (5)	152
C8—H8···C11 <sup>iv</sup>	0.95	2.71	3.573 (4)	152
C15—H15B···O1 <sup>v</sup>	0.98	2.44	3.387 (7)	162
C16—H16A···O2 <sup>vi</sup>	0.98	2.57	3.454 (7)	151

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

S—O bond lengths of the bisulfite anion [S2—O1 = 1.575 (3) Å] is longer than the other three, which vary from 1.439 (2) to 1.468 (2) Å, thus confirming the identity of the OH group in this anion. The anions are linked by a pair of O—H···O hydrogen bonds forming an inversion dimer (Fig. 2 and Table 2).

### 3. Supramolecular features

In the crystal packing of the two compounds, illustrated in Figs. 3 and 4, the planar **MB**<sup>+</sup> cations are stacked in an antiparallel mode, with the sulfur atom disposed alternatively on opposite sides. The aromatic systems exhibit offset  $\pi$ – $\pi$  interactions and form infinite layers as shown in Figs. 5 and 6. The average interplanar distances are 3.326 (4) Å in **(I)** and 3.550 (3) Å in **(II)**. This disposition differs from the one observed in the pentahydrate form where the **MB**<sup>+</sup> species are stacked together while adopting the same orientation, so that



**Figure 3**  
The crystal packing of compound **(I)** viewed along the *c* axis, with the unit cell highlighted in the upper left-hand corner. Displacement ellipsoids are drawn at the 50% probability level.

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

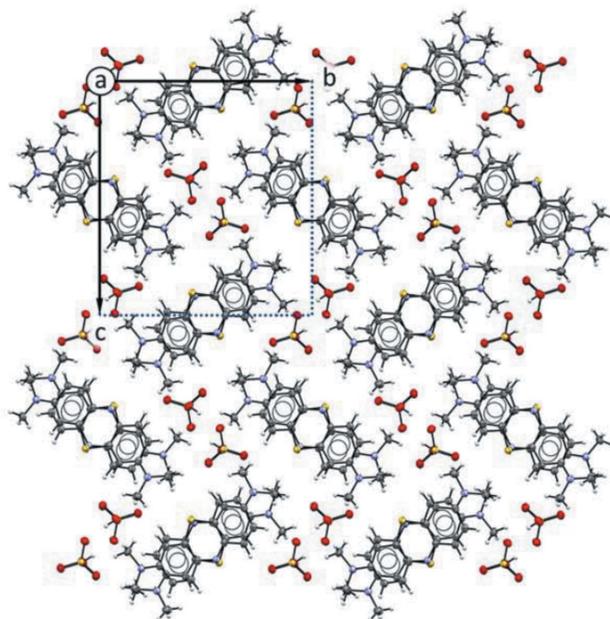
<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
O1—H1···O3 <sup>i</sup>	0.84	1.77	2.609 (4)	175
C1—H1C···O4 <sup>ii</sup>	0.98	2.39	3.349 (5)	167
C2—H2B···O2 <sup>iii</sup>	0.98	2.56	3.506 (5)	163
C4—H4···O3 <sup>iv</sup>	0.95	2.54	3.451 (5)	162
C12—H12···O4	0.95	2.46	3.372 (5)	162
C15—H15B···O2 <sup>v</sup>	0.98	2.47	3.382 (5)	155
C15—H15C···O3 <sup>vi</sup>	0.98	2.36	3.309 (5)	164
C16—H16B···O2 <sup>v</sup>	0.98	2.32	3.283 (5)	167
C16—H16C···O4	0.98	2.52	3.326 (5)	139

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

the sulfur atoms of all of the molecules lie on the same side along the stacking column. Moreover, as evidenced in Fig. 5ii–iii and Fig. 6ii–iii, the stacking geometry of **MB**<sup>+</sup> differs significantly in the two phases. In fact, in the case of **(I)**, the antiparallel mode is accompanied by a mutual shift of the cations, resulting in the formation of a zigzag chain with an inter-centroid distance between central thiazine rings of 3.734 (3) Å (Fig. 5iii). On the other hand, in **(II)** the stacked molecules are almost eclipsed and the equivalent inter-centroid distances are 3.912 (4) and 3.956 (5) Å (Fig. 6iii).

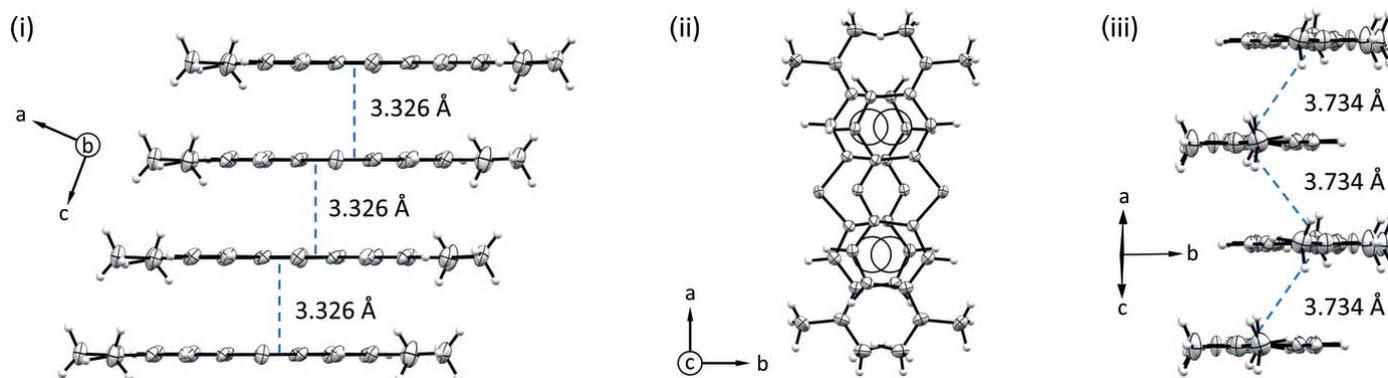
### 4. Hirshfeld surface analysis

An evaluation of the Hirshfeld fingerprint plots (Spackman & Jayatilaka, 2009) of compounds **(I)** and **(II)**, shown in Fig. 7, highlights some differences in the interactions of the **MB**<sup>+</sup> cations in the two phases. In phase **(I)**, the leading interactions can be grouped in two classes: hydrogen bonds and  $\pi$ – $\pi$



**Figure 4**  
The crystal packing of compound **(II)** viewed along the *a* axis, with the unit cell highlighted in the upper left-hand corner. Displacement ellipsoids are drawn at the 50% probability level.

## weak interactions in crystals



**Figure 5**  
Views of the stacking geometry of  $\text{MB}^+$  in compound (**I**): (i) displayed orthogonally to the stacking pillar axis by showing a tetramer of stacked molecules; (ii) the same group of  $\text{MB}^+$  cations is shown along the stacking direction; (iii) view along the  $\text{MB}^+$  longer dimension, highlighting the mutual shifts of the cations in the zigzag columns.

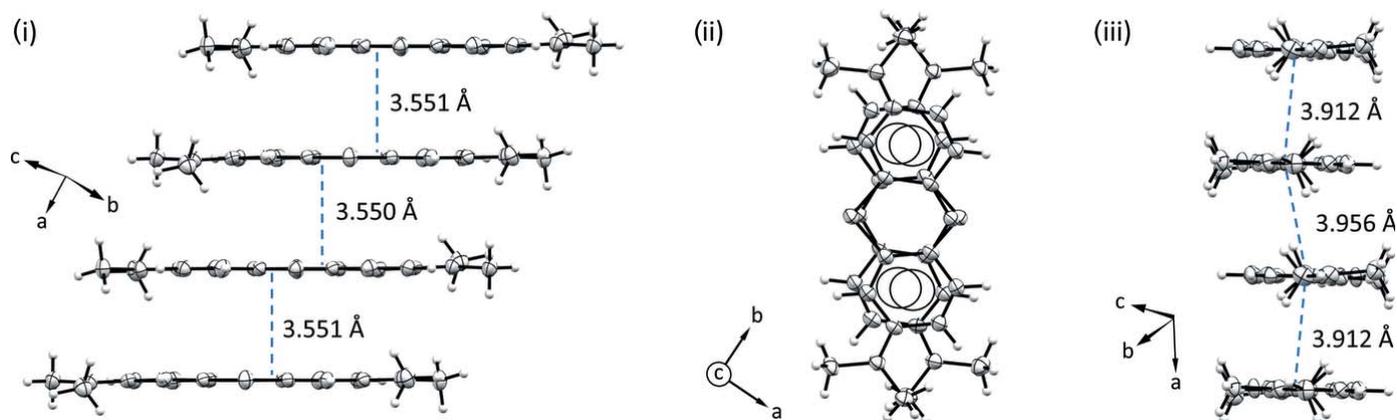
stacking. The first involves  $\text{MB}^+$  as a donor by means of aromatic and aliphatic C—H bonds (Table 1), and as an acceptor by means of the central N atom, whose  $\sigma$  lone pair pointing out of the molecule is readily exploited by a water molecule to form a strong hydrogen bond [N $\cdots$ O distance = 2.936 (4) Å; see Fig. 1 and Table 1). The presence of hydrogen-bond donors surrounding  $\text{MB}^+$ , *i.e.* water molecules, is therefore able to satisfy the region of the cation with the most prominent partial negative charge (the nitrogen atom).

On the other hand, considering the fingerprint plot of compound (**II**), it can be seen that the strongest interactions are  $\pi$ – $\pi$  stacking and C—H $\cdots$ O contacts (Table 2) between  $\text{MB}^+$  and the oxygen atoms of the bisulfite inversion dimer. Since no available hydrogen-bond donor is present near  $\text{MB}^+$ , no interaction is able to exploit the electron density concentrated on the central N atom. This has important consequences, since, on one side, it allows a better alignment of the  $\text{MB}^+$  cations in their stacking arrangement, as clearly shown in Fig. 6. However, although there is an improved geometrical match, the stacking distance increases as a consequence of the charge repulsion between the mono-cationic molecules.

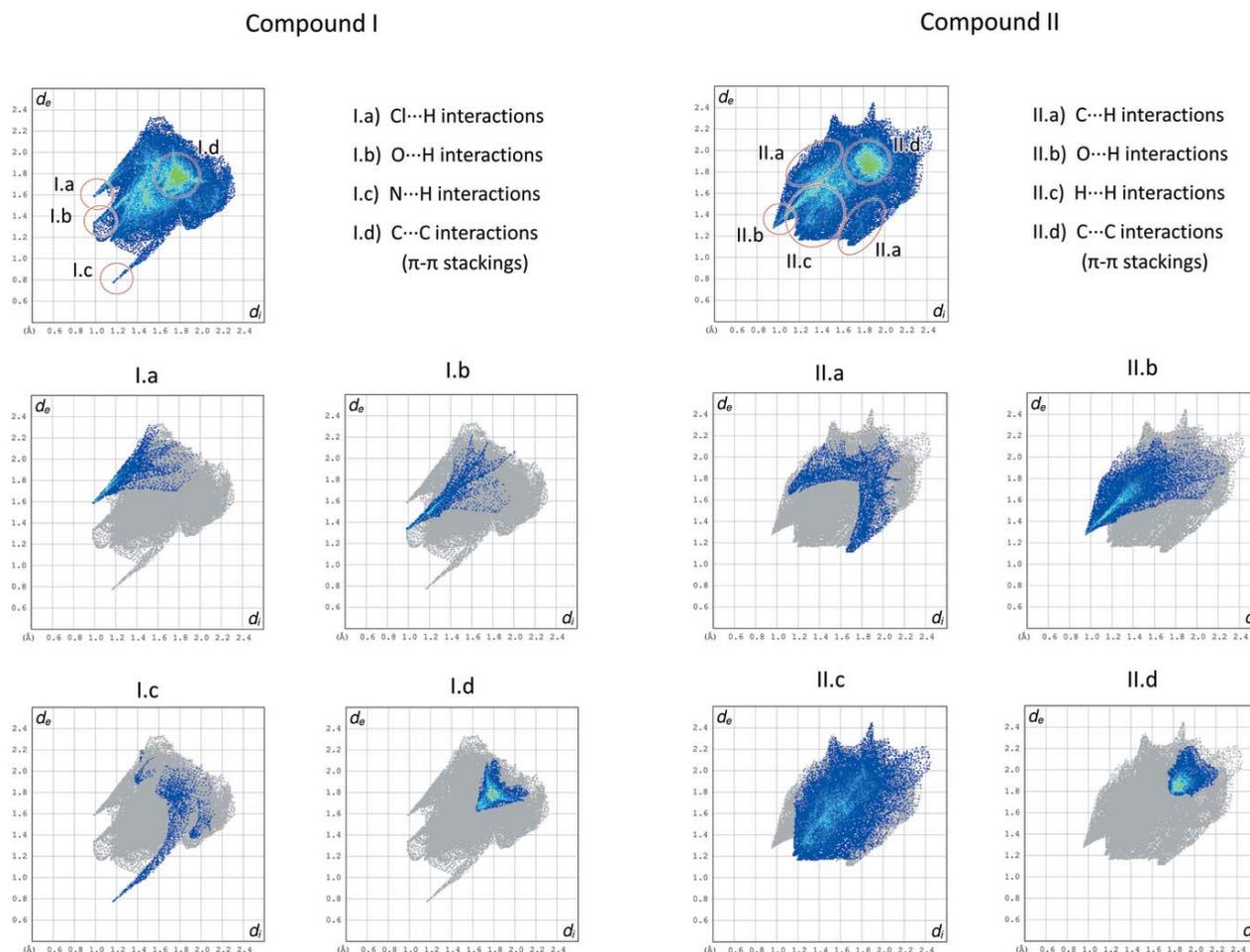
This evidence constitutes an exception to a general trend in the packing preferences of organic species. Indeed, in cases where both hydrogen bonds and  $\pi$  stacking can be found in the solid phase, the two interactions compete to maximize their efficiency. This competition is usually in favour of the more directional supramolecular interactions, *i.e.* hydrogen bonds (Gospodinova & Tomšík, 2015). In the present case, however, the cationic nature of the aromatic molecules does not favour the stacking disposition that is usually better (in energetic terms), and in the case where there are no strong hydrogen bonds involving  $\text{MB}^+$ , as in compound (**II**), the molecule is able to adopt a theoretically more stabilizing stacking geometry, which in this case is a less stabilizing one.

### 5. Database survey

In the Cambridge Structural Database (CSD, version 5.38, last updated May 2017; Groom *et al.*, 2016) the crystal structure of the 3,7-bis(dimethylamino)phenothiazin-5-ium hydrogen sulfate dihydrate can be found as a Private Communication (XUVROW; Lynch, 2009). Here, it was not possible to locate



**Figure 6**  
Views of the stacking geometry of  $\text{MB}^+$  in compound (**II**): (i) displayed orthogonally to the stacking pillar axis by showing a tetramer of stacked molecules; (ii) the same group of  $\text{MB}^+$  cations is shown along the stacking direction; (iii) view along the  $\text{MB}^+$  longer dimension, highlighting the nearly completely eclipsed superposition of the cations in the antiparallel columns.



**Figure 7** Hirshfeld fingerprint plots of compounds (**I**) and (**II**) (above) and some relevant components (I.a–d and II.a–d), highlighting the main interactions exhibited by  $\text{MB}^+$  in the respective solid phases.

the H atom of the inorganic moiety, nor those of the water molecules, because of the poor data quality due to problematic twinning affecting the solid phase. Considering the overall crystal packing of this phase, which features  $\text{MB}^+$  as both a hydrogen-bond donor and acceptor towards the water molecules and the anion, the interactions of the organic cation are much more similar to those observed for compound (**I**), than those observed for compound (**II**).

A search of the CSD found 30 compounds containing the aromatic unit 3,7-bis(dimethylamino)phenothiazin-5-ium cation. The anions present in the crystal structures include inorganic halogenide, nitrate, perchlorate, thiocyanate, triiodide, hydrogen sulfate and different metallates. The geometrical parameters of the cations (bond lengths, bond angles and torsion angles) are in the normal range for condensed ring systems.

## 6. Synthesis and crystallization

### Preparation of compound (**I**)

For the crystallization of compound (**I**), the commercial reagent 3,7-bis(dimethylamino)phenothiazin-5-ium chloride

was used without any preparative treatment. 50 mg of 3,7-bis(dimethylamino)phenothiazin-5-ium chloride pentahydrate (0.156 mmol) were transferred to a 10 ml glass vial containing 5 ml of dichloromethane. The container was then closed and placed in an ultrasound bath for 5 min. to reach the saturation limit of the compound. The mixture thus obtained was filtered into another 5 ml glass vial, and the resulting solution was left partially open for slow evaporation of the solvent. After 24 h, metallic dark-green needle-shaped crystals of compound (**I**), suitable for X-ray diffraction analysis, were obtained.

### Preparation of compound (**II**)

306 mg of 3,7-bis(dimethylamino)phenothiazin-5-ium chloride pentahydrate (0.957 mmol) were transferred to an agate mortar, together with 284 mg of  $\text{HgSO}_4$  (0.957 mmol). The two powders were subsequently mixed and ground for 30 min, resulting in a dark-green powder. X-ray powder diffraction analysis was performed on the as-obtained product. The resulting pattern showed peaks clearly belonging to the final compound (**II**) (see Fig. S1 in the supporting information). An excess of the powder was then placed in a glass vial, together with 3 ml of *N,N*-dimethylformamide. The container was closed and placed in an ultrasound bath for 5 min. to

**Table 3**  
Experimental details.

	(I)	(II)
Crystal data		
Chemical formula	$C_{16}H_{18}N_3S^+ \cdot Cl^- \cdot 2H_2O$	$C_{16}H_{18}N_3S^+ \cdot HSO_4^-$
$M_r$	355.87	381.46
Crystal system, space group	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/n$
Temperature (K)	200	100
$a, b, c$ (Å)	15.130 (2), 15.7219 (19), 7.1203 (12)	7.867 (10), 14.101 (10), 15.027 (10)
$\beta$ (°)	90.600 (8)	90.348 (10)
$V$ (Å <sup>3</sup> )	1693.6 (4)	1667 (3)
$Z$	4	4
Radiation type	Mo $K\alpha$	Synchrotron, $\lambda = 0.700$ Å
$\mu$ (mm <sup>-1</sup> )	0.36	0.35
Crystal size (mm)	$0.4 \times 0.2 \times 0.15$	$0.3 \times 0.15 \times 0.1$
Data collection		
Diffractometer	Bruker D8 Venture	ELETTRA XRD1
Absorption correction	Multi-scan (SADABS; Krause <i>et al.</i> , 2015)	Multi-scan (CrysAlis PRO; Agilent, 2014)
$T_{min}$ , $T_{max}$	0.491, 0.746	0.711, 1.000
No. of measured, independent and observed [ $I > 2\sigma(I)$ ] reflections	12731, 3359, 2650	20743, 3367, 2795
$R_{int}$	0.070	0.062
$(\sin \theta/\lambda)_{max}$ (Å <sup>-1</sup> )	0.625	0.625
Refinement		
$R[F^2 > 2\sigma(F^2)]$ , $wR(F^2)$ , $S$	0.088, 0.271, 1.08	0.041, 0.112, 1.06
No. of reflections	3359	3367
No. of parameters	220	232
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained
$\Delta\rho_{max}$ , $\Delta\rho_{min}$ (e Å <sup>-3</sup> )	0.69, -0.62	0.36, -0.46

Computer programs: APEX3 and SAINT (Bruker, 2015), CrysAlis PRO (Agilent, 2014), SHELXT (Sheldrick, 2015a), SHELXL2014 (Sheldrick, 2015b), OLEX2 (Dolomanov *et al.*, 2009) and publCIF (Westrip, 2010).

reach the saturation limit of the compound. The mixture obtained was filtered into another 5 ml glass vial, and the resulting solution was left partially open for slow evaporation of the solvent. After one week, metallic dark-green needle-like crystals of compound (II), suitable for X-ray diffraction analyses, were obtained.

## 7. Refinement details

Crystal data, data collection and structure refinement details are summarized in Table 3. For both compounds, the H atoms were positioned geometrically and refined using a riding model: C—H = 0.99 Å with  $U_{iso}(H) = 1.2U_{eq}(C)$ . The H atoms of the water molecules in (I) and the bisulfite anion in (II) were located in difference-Fourier maps and refined freely. Compound (I) was refined as a merohedral twin with twin matrix,  $\bar{1} 0 0, 0 \bar{1} 0, 0 0 1$ , with a refined BASF value of 0.185 (3).

Diffraction data for compound (I) were collected using a Bruker D8 Venture diffractometer, equipped with a CMOS PhotonII detector, a Mo High brilliance microsource (Incoatec) working at 50 KV and 1 mA. For compound (II), the data were collected at the ELETTRA Synchrotron facility (CNR Trieste) using monochromated 0.7 Å wavelength radiation and a Pilatus 2M Detector (Dectris).

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## supporting information

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### Computing details

Data collection: *APEX3* (Bruker, 2015) for (I); *CrysAlis PRO* (Agilent, 2014) for (II). Cell refinement: *S SAINT* (Bruker, 2015) for (I); *CrysAlis PRO* (Agilent, 2014) for (II). Data reduction: *S SAINT* (Bruker, 2015) for (I); *CrysAlis PRO* (Agilent, 2014) for (II). For both structures, program(s) used to solve structure: *SHELXT* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015b); molecular graphics: *OLEX2* (Dolomanov *et al.*, 2009); software used to prepare material for publication: *OLEX2* (Dolomanov *et al.*, 2009) and *publCIF* (Westrip, 2010).

### 3,7-Bis(dimethylamino)-phenothiazin-5-ium chloride dihydrate (I)

#### Crystal data

$C_{16}H_{18}N_3S^+ \cdot Cl^- \cdot 2H_2O$

$M_r = 355.87$

Monoclinic,  $P2_1/c$

$a = 15.130$  (2) Å

$b = 15.7219$  (19) Å

$c = 7.1203$  (12) Å

$\beta = 90.600$  (8)°

$V = 1693.6$  (4) Å<sup>3</sup>

$Z = 4$

$F(000) = 752$

$D_x = 1.396$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å

Cell parameters from 4183 reflections

$\theta = 2.9$ – $30.5$ °

$\mu = 0.36$  mm<sup>-1</sup>

$T = 200$  K

Needle, metallic dark green

$0.4 \times 0.2 \times 0.15$  mm

#### Data collection

Bruker D8 Venture  
diffractometer

$\varphi$  and  $\omega$  scans

Absorption correction: multi-scan  
(SADABS; Krause *et al.*, 2015)

$T_{\min} = 0.491$ ,  $T_{\max} = 0.746$

12731 measured reflections

3359 independent reflections

2650 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.070$

$\theta_{\max} = 26.4$ °,  $\theta_{\min} = 2.6$ °

$h = -18$ → $16$

$k = -19$ → $19$

$l = -6$ → $8$

#### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.088$

$wR(F^2) = 0.271$

$S = 1.08$

3359 reflections

220 parameters

0 restraints

Primary atom site location: dual

Secondary atom site location: difference Fourier  
map

Hydrogen site location: mixed

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.2P)^2]$

where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.69$  e Å<sup>-3</sup>

$\Delta\rho_{\min} = -0.62$  e Å<sup>-3</sup>

Extinction correction: SHELXL2014  
 (Sheldrick, 2015b),  
 $F_c^* = kFc[1 + 0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$   
 Extinction coefficient: 0.068 (12)

### Special details

**Geometry.** All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

**Refinement.** Refined as a 2-component twin.

### Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	0.25577 (6)	0.89471 (7)	0.49946 (15)	0.0277 (4)
C11	0.16600 (9)	0.41765 (7)	0.8231 (2)	0.0420 (5)
O1	0.2548 (2)	0.5092 (2)	0.4792 (5)	0.0415 (10)
H1D	0.2311	0.4912	0.5825	0.062*
H1E	0.2537	0.5644	0.4890	0.062*
N1	0.25085 (17)	0.6957 (2)	0.4980 (4)	0.0250 (9)
N2	-0.0525 (2)	0.8556 (2)	0.2382 (6)	0.0307 (9)
N3	0.5627 (2)	0.8421 (3)	0.7571 (7)	0.0357 (10)
C9	0.3375 (3)	0.8241 (3)	0.5706 (6)	0.0229 (9)
C7	0.1704 (3)	0.8285 (2)	0.4280 (6)	0.0220 (9)
O2	0.3352 (3)	0.4241 (3)	0.1739 (8)	0.0599 (12)
H2D	0.3141	0.4524	0.2684	0.090*
H2E	0.2925	0.4118	0.0957	0.090*
C10	0.3252 (3)	0.7342 (2)	0.5600 (6)	0.0229 (9)
C1	-0.0600 (3)	0.9479 (3)	0.2297 (9)	0.0384 (13)
H1A	-0.0629	0.9709	0.3574	0.058*
H1B	-0.1138	0.9635	0.1599	0.058*
H1C	-0.0084	0.9715	0.1660	0.058*
C4	0.0280 (3)	0.7263 (3)	0.3139 (7)	0.0262 (10)
H4	-0.0203	0.6916	0.2760	0.031*
C3	0.0207 (3)	0.8180 (3)	0.3033 (7)	0.0244 (9)
C12	0.4750 (3)	0.7173 (3)	0.6848 (7)	0.0277 (10)
H12	0.5215	0.6806	0.7242	0.033*
C6	0.1793 (3)	0.7374 (2)	0.4382 (6)	0.0220 (9)
C5	0.1037 (3)	0.6901 (3)	0.3777 (7)	0.0263 (10)
H5	0.1066	0.6298	0.3825	0.032*
C8	0.0943 (3)	0.8667 (2)	0.3643 (7)	0.0254 (9)
H8	0.0910	0.9270	0.3610	0.030*
C13	0.4866 (3)	0.8077 (3)	0.6945 (7)	0.0291 (10)
C11	0.3974 (3)	0.6836 (3)	0.6189 (7)	0.0274 (10)
H11	0.3917	0.6235	0.6126	0.033*
C14	0.4150 (3)	0.8592 (3)	0.6362 (7)	0.0288 (10)
H14	0.4205	0.9193	0.6425	0.035*
C15	0.5720 (4)	0.9346 (3)	0.7645 (10)	0.0494 (16)

H15A	0.5670	0.9580	0.6373	0.074*
H15B	0.6299	0.9492	0.8184	0.074*
H15C	0.5253	0.9586	0.8429	0.074*
C16	0.6382 (3)	0.7941 (3)	0.8289 (9)	0.0425 (13)
H16A	0.6225	0.7338	0.8378	0.064*
H16B	0.6548	0.8155	0.9537	0.064*
H16C	0.6881	0.8008	0.7436	0.064*
C2	-0.1328 (3)	0.8098 (3)	0.1796 (9)	0.0397 (13)
H2A	-0.1784	0.8170	0.2750	0.060*
H2B	-0.1193	0.7492	0.1653	0.060*
H2C	-0.1542	0.8326	0.0595	0.060*

*Atomic displacement parameters (Å<sup>2</sup>)*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
S1	0.0228 (6)	0.0139 (6)	0.0464 (8)	-0.0017 (3)	-0.0042 (6)	-0.0009 (4)
C11	0.0391 (7)	0.0225 (6)	0.0646 (10)	-0.0042 (5)	0.0082 (7)	-0.0071 (5)
O1	0.044 (2)	0.0234 (18)	0.057 (2)	0.0012 (12)	-0.005 (2)	0.0011 (13)
N1	0.0219 (18)	0.0151 (18)	0.038 (2)	-0.0011 (10)	0.005 (2)	-0.0001 (12)
N2	0.0236 (18)	0.0213 (18)	0.047 (2)	-0.0005 (14)	-0.0015 (17)	0.0009 (16)
N3	0.0221 (18)	0.034 (2)	0.051 (3)	-0.0055 (15)	-0.0016 (18)	0.0002 (18)
C9	0.0204 (18)	0.0196 (18)	0.029 (2)	-0.0017 (15)	0.0044 (17)	0.0013 (16)
C7	0.0183 (18)	0.0185 (18)	0.029 (2)	-0.0010 (14)	0.0030 (17)	-0.0015 (16)
O2	0.058 (2)	0.039 (2)	0.082 (3)	0.0142 (19)	0.014 (3)	0.006 (2)
C10	0.0212 (19)	0.0171 (18)	0.030 (2)	-0.0007 (15)	0.0068 (18)	0.0005 (16)
C1	0.026 (2)	0.025 (2)	0.064 (4)	0.0051 (17)	-0.006 (2)	0.006 (2)
C4	0.0240 (19)	0.0167 (19)	0.038 (3)	-0.0024 (15)	0.005 (2)	-0.0019 (18)
C3	0.0210 (19)	0.0211 (19)	0.031 (2)	0.0005 (15)	0.0037 (18)	-0.0020 (18)
C12	0.022 (2)	0.025 (2)	0.035 (3)	0.0034 (16)	0.004 (2)	0.0041 (19)
C6	0.0207 (18)	0.0175 (18)	0.028 (2)	-0.0010 (15)	0.0041 (17)	0.0015 (16)
C5	0.025 (2)	0.0163 (17)	0.037 (3)	-0.0016 (15)	0.004 (2)	-0.0019 (17)
C8	0.028 (2)	0.0164 (18)	0.032 (2)	-0.0002 (16)	0.0033 (19)	-0.0002 (17)
C13	0.021 (2)	0.028 (2)	0.038 (3)	-0.0015 (16)	0.002 (2)	0.001 (2)
C11	0.025 (2)	0.0196 (17)	0.038 (3)	0.0005 (16)	0.004 (2)	-0.0001 (18)
C14	0.025 (2)	0.024 (2)	0.037 (3)	-0.0034 (16)	0.002 (2)	0.0004 (19)
C15	0.033 (2)	0.031 (2)	0.085 (5)	-0.010 (2)	-0.007 (3)	-0.005 (3)
C16	0.024 (2)	0.044 (3)	0.059 (4)	-0.0019 (19)	-0.001 (2)	0.005 (3)
C2	0.024 (2)	0.033 (2)	0.062 (4)	0.0003 (18)	-0.006 (2)	-0.002 (2)

*Geometric parameters (Å, °)*

S1—C9	1.734 (4)	C9—C14	1.373 (6)
S1—C7	1.731 (4)	C7—C6	1.441 (5)
N1—C10	1.347 (5)	C7—C8	1.371 (6)
N1—C6	1.331 (5)	C10—C11	1.411 (6)
N2—C1	1.458 (6)	C4—C3	1.447 (5)
N2—C3	1.334 (6)	C4—C5	1.353 (6)
N2—C2	1.468 (6)	C3—C8	1.417 (6)

N3—C13	1.344 (6)	C12—C13	1.433 (6)
N3—C15	1.462 (6)	C12—C11	1.367 (6)
N3—C16	1.458 (6)	C6—C5	1.427 (6)
C9—C10	1.427 (5)	C13—C14	1.411 (6)
C7—S1—C9	103.2 (2)	C11—C10—C9	116.2 (4)
C6—N1—C10	123.9 (4)	C5—C4—C3	120.1 (4)
C1—N2—C2	114.4 (4)	N2—C3—C4	121.5 (4)
C3—N2—C1	121.3 (4)	N2—C3—C8	121.0 (4)
C3—N2—C2	124.2 (4)	C8—C3—C4	117.5 (4)
C13—N3—C15	119.6 (4)	C11—C12—C13	120.3 (4)
C13—N3—C16	125.0 (4)	N1—C6—C7	125.5 (4)
C16—N3—C15	115.3 (4)	N1—C6—C5	119.1 (4)
C10—C9—S1	121.8 (3)	C5—C6—C7	115.4 (4)
C14—C9—S1	116.5 (3)	C4—C5—C6	123.7 (4)
C14—C9—C10	121.8 (4)	C7—C8—C3	121.3 (3)
C6—C7—S1	120.9 (3)	N3—C13—C12	121.3 (4)
C8—C7—S1	117.1 (3)	N3—C13—C14	121.3 (4)
C8—C7—C6	122.0 (4)	C14—C13—C12	117.5 (4)
N1—C10—C9	124.7 (4)	C12—C11—C10	122.9 (4)
N1—C10—C11	119.1 (4)	C9—C14—C13	121.3 (4)

#### Hydrogen-bond geometry (Å, °)

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
O1—H1 <i>D</i> ···C11	0.87	2.30	3.153 (4)	168
O1—H1 <i>E</i> ···N1	0.87	2.07	2.936 (4)	177
O2—H2 <i>D</i> ···O1	0.87	1.97	2.837 (6)	174
O2—H2 <i>E</i> ···C11 <sup>i</sup>	0.87	2.71	3.559 (5)	165
C1—H1 <i>B</i> ···O1 <sup>ii</sup>	0.98	2.45	3.426 (6)	173
C2—H2 <i>B</i> ···C11 <sup>iii</sup>	0.98	2.72	3.611 (5)	152
C8—H8···C11 <sup>iv</sup>	0.95	2.71	3.573 (4)	152
C15—H15 <i>B</i> ···O1 <sup>v</sup>	0.98	2.44	3.387 (7)	162
C16—H16 <i>A</i> ···O2 <sup>vi</sup>	0.98	2.57	3.454 (7)	151

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

### 3,7-Bis(dimethylamino)phenothiazinium bisulfite (II)

#### Crystal data

$C_{16}H_{18}N_3S^+ \cdot HSO_4^-$

$M_r = 381.46$

Monoclinic,  $P2_1/n$

$a = 7.867$  (10) Å

$b = 14.101$  (10) Å

$c = 15.027$  (10) Å

$\beta = 90.348$  (10)°

$V = 1667$  (3) Å<sup>3</sup>

$Z = 4$

$F(000) = 800$

$D_x = 1.520$  Mg m<sup>-3</sup>

Synchrotron radiation,  $\lambda = 0.700$  Å

Cell parameters from 1235 reflections

$\theta = 3.1$ – $30.2$ °

$\mu = 0.35$  mm<sup>-1</sup>

$T = 100$  K

Needle, metallic green

$0.3 \times 0.15 \times 0.1$  mm

*Data collection*

ELETTRA XRD1 diffractometer	20743 measured reflections 3367 independent reflections
Radiation source: Elettra Synchrotron - XRD1 BL	2795 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.062$
Rotation around the Phi axis scans	$\theta_{\text{max}} = 25.9^\circ$ , $\theta_{\text{min}} = 2.0^\circ$
Absorption correction: multi-scan (CrysAlis PRO; Agilent, 2014)	$h = -9 \rightarrow 9$ $k = -17 \rightarrow 17$ $l = -18 \rightarrow 18$
$T_{\text{min}} = 0.711$ , $T_{\text{max}} = 1.000$	

*Refinement*

Refinement on $F^2$	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.041$	$w = 1/[\sigma^2(F_o^2) + (0.0656P)^2 + 0.4958P]$
$wR(F^2) = 0.112$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.06$	$(\Delta/\sigma)_{\text{max}} = 0.001$
3367 reflections	$\Delta\rho_{\text{max}} = 0.36 \text{ e } \text{\AA}^{-3}$
232 parameters	$\Delta\rho_{\text{min}} = -0.46 \text{ e } \text{\AA}^{-3}$
0 restraints	Extinction correction: SHELXL2014 (Sheldrick, 2015b), $F_c^* = kF_c[1 + 0.001x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$
Primary atom site location: dual	Extinction coefficient: 0.0109 (15)
Secondary atom site location: difference Fourier map	

*Special details*

**Geometry.** All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
S2	0.11198 (6)	0.58607 (3)	0.40576 (3)	0.02746 (16)
S1	-0.23619 (7)	0.56658 (4)	-0.09373 (3)	0.02953 (16)
O1	-0.08785 (19)	0.57885 (11)	0.40548 (11)	0.0357 (4)
H1	-0.1178	0.5308	0.4345	0.054*
O3	0.16539 (19)	0.56866 (11)	0.49810 (10)	0.0336 (4)
O2	0.1747 (2)	0.51512 (10)	0.34552 (10)	0.0359 (4)
O4	0.1447 (2)	0.68213 (10)	0.37808 (10)	0.0349 (4)
N3	0.0335 (2)	0.80042 (12)	0.12112 (12)	0.0283 (4)
N1	-0.2590 (2)	0.44637 (12)	0.08106 (11)	0.0274 (4)
N2	-0.5250 (2)	0.27281 (12)	-0.21818 (12)	0.0307 (4)
C1	-0.5450 (3)	0.32180 (18)	-0.30356 (15)	0.0377 (5)
H1A	-0.5970	0.3841	-0.2937	0.056*
H1B	-0.6182	0.2841	-0.3430	0.056*
H1C	-0.4334	0.3300	-0.3311	0.056*
C3	-0.4545 (2)	0.31656 (14)	-0.14777 (14)	0.0283 (4)
C12	-0.0597 (3)	0.65139 (15)	0.18233 (14)	0.0292 (4)
H12	-0.0224	0.6698	0.2400	0.035*
C13	-0.0398 (2)	0.71517 (14)	0.10920 (14)	0.0264 (4)

C14	-0.0987 (3)	0.68593 (14)	0.02425 (14)	0.0277 (4)
H14	-0.0889	0.7278	-0.0250	0.033*
C9	-0.1702 (2)	0.59759 (14)	0.01219 (14)	0.0258 (4)
C6	-0.3185 (2)	0.40896 (13)	0.00539 (14)	0.0257 (4)
C10	-0.1897 (2)	0.53309 (14)	0.08529 (13)	0.0252 (4)
C7	-0.3180 (2)	0.45347 (14)	-0.08064 (14)	0.0258 (4)
C4	-0.4539 (3)	0.27152 (15)	-0.06247 (14)	0.0297 (4)
H4	-0.4992	0.2094	-0.0565	0.036*
C8	-0.3812 (3)	0.40837 (14)	-0.15486 (14)	0.0292 (4)
H8	-0.3760	0.4387	-0.2112	0.035*
C16	0.0901 (3)	0.83218 (16)	0.20952 (15)	0.0334 (5)
H16A	-0.0092	0.8481	0.2457	0.050*
H16B	0.1625	0.8883	0.2033	0.050*
H16C	0.1546	0.7813	0.2386	0.050*
C11	-0.1314 (3)	0.56496 (15)	0.17006 (14)	0.0302 (4)
H11	-0.1433	0.5241	0.2199	0.036*
C15	0.0592 (3)	0.86560 (15)	0.04613 (15)	0.0338 (5)
H15A	0.1302	0.8348	0.0012	0.051*
H15B	0.1157	0.9233	0.0674	0.051*
H15C	-0.0511	0.8821	0.0197	0.051*
C5	-0.3894 (3)	0.31642 (15)	0.00972 (15)	0.0305 (5)
H5	-0.3916	0.2848	0.0655	0.037*
C2	-0.5894 (3)	0.17565 (15)	-0.21258 (16)	0.0358 (5)
H2A	-0.6818	0.1729	-0.1692	0.054*
H2B	-0.4974	0.1332	-0.1937	0.054*
H2C	-0.6320	0.1557	-0.2711	0.054*

*Atomic displacement parameters (Å<sup>2</sup>)*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
S2	0.0290 (3)	0.0236 (3)	0.0298 (3)	0.00176 (19)	0.00111 (19)	0.00149 (19)
S1	0.0359 (3)	0.0239 (3)	0.0287 (3)	-0.0047 (2)	-0.0019 (2)	0.00329 (19)
O1	0.0306 (8)	0.0360 (9)	0.0406 (9)	0.0030 (6)	-0.0003 (6)	0.0104 (7)
O3	0.0353 (8)	0.0347 (8)	0.0308 (8)	-0.0022 (6)	-0.0045 (6)	0.0052 (6)
O2	0.0410 (8)	0.0280 (8)	0.0386 (9)	0.0057 (6)	0.0051 (7)	-0.0011 (6)
O4	0.0428 (9)	0.0264 (8)	0.0355 (8)	-0.0013 (6)	0.0023 (7)	0.0018 (6)
N3	0.0303 (9)	0.0246 (8)	0.0301 (9)	-0.0035 (7)	-0.0012 (7)	0.0011 (7)
N1	0.0296 (9)	0.0224 (8)	0.0301 (9)	0.0007 (7)	0.0009 (7)	0.0010 (7)
N2	0.0331 (9)	0.0261 (9)	0.0328 (9)	0.0002 (7)	-0.0021 (7)	-0.0030 (7)
C1	0.0370 (12)	0.0421 (13)	0.0339 (12)	-0.0052 (10)	-0.0004 (9)	-0.0014 (10)
C3	0.0243 (9)	0.0258 (10)	0.0347 (11)	0.0049 (8)	0.0002 (8)	-0.0036 (8)
C12	0.0308 (10)	0.0264 (10)	0.0306 (10)	-0.0002 (8)	-0.0006 (8)	-0.0008 (8)
C13	0.0233 (9)	0.0219 (9)	0.0340 (11)	0.0015 (7)	0.0019 (8)	-0.0003 (8)
C14	0.0279 (10)	0.0242 (10)	0.0308 (11)	-0.0012 (8)	0.0006 (8)	0.0020 (8)
C9	0.0228 (9)	0.0251 (10)	0.0296 (10)	0.0027 (7)	0.0016 (8)	0.0006 (8)
C6	0.0242 (9)	0.0217 (10)	0.0311 (10)	0.0028 (7)	0.0018 (8)	-0.0005 (8)
C10	0.0236 (9)	0.0205 (9)	0.0313 (10)	0.0012 (7)	-0.0001 (8)	0.0002 (8)
C7	0.0227 (9)	0.0221 (9)	0.0328 (10)	0.0014 (7)	0.0024 (8)	-0.0003 (8)

C4	0.0282 (10)	0.0228 (10)	0.0380 (11)	-0.0008 (8)	0.0006 (8)	-0.0001 (8)
C8	0.0304 (10)	0.0249 (10)	0.0321 (11)	0.0016 (8)	-0.0009 (8)	0.0015 (8)
C16	0.0389 (12)	0.0275 (10)	0.0339 (11)	-0.0070 (9)	-0.0026 (9)	-0.0009 (9)
C11	0.0357 (11)	0.0250 (10)	0.0299 (11)	-0.0002 (8)	-0.0008 (8)	0.0035 (8)
C15	0.0373 (11)	0.0268 (11)	0.0372 (12)	-0.0083 (9)	-0.0037 (9)	0.0061 (9)
C5	0.0333 (11)	0.0249 (10)	0.0331 (11)	0.0003 (8)	0.0020 (9)	0.0038 (8)
C2	0.0385 (12)	0.0258 (10)	0.0431 (13)	-0.0009 (9)	-0.0048 (10)	-0.0066 (9)

*Geometric parameters (Å, °)*

S2—O1	1.575 (3)	C13—C14	1.417 (3)
S2—O3	1.4680 (18)	C14—H14	0.9500
S2—O2	1.4385 (17)	C14—C9	1.378 (3)
S2—O4	1.4407 (18)	C9—C10	1.435 (3)
S1—C9	1.727 (2)	C6—C7	1.437 (3)
S1—C7	1.732 (2)	C6—C5	1.421 (3)
O1—H1	0.8400	C10—C11	1.424 (3)
N3—C13	1.345 (3)	C7—C8	1.374 (3)
N3—C16	1.468 (3)	C4—H4	0.9500
N3—C15	1.469 (3)	C4—C5	1.352 (3)
N1—C6	1.336 (3)	C8—H8	0.9500
N1—C10	1.340 (3)	C16—H16A	0.9800
N2—C1	1.465 (3)	C16—H16B	0.9800
N2—C3	1.342 (3)	C16—H16C	0.9800
N2—C2	1.463 (3)	C11—H11	0.9500
C1—H1A	0.9800	C15—H15A	0.9800
C1—H1B	0.9800	C15—H15B	0.9800
C1—H1C	0.9800	C15—H15C	0.9800
C3—C4	1.430 (3)	C5—H5	0.9500
C3—C8	1.421 (3)	C2—H2A	0.9800
C12—H12	0.9500	C2—H2B	0.9800
C12—C13	1.429 (3)	C2—H2C	0.9800
C12—C11	1.355 (3)		
O3—S2—O1	105.77 (9)	C5—C6—C7	116.46 (18)
O2—S2—O1	107.42 (10)	N1—C10—C9	125.96 (19)
O2—S2—O3	112.41 (10)	N1—C10—C11	117.33 (18)
O2—S2—O4	114.18 (10)	C11—C10—C9	116.71 (18)
O4—S2—O1	103.89 (9)	C6—C7—S1	120.50 (15)
O4—S2—O3	112.31 (9)	C8—C7—S1	117.84 (16)
C9—S1—C7	103.79 (10)	C8—C7—C6	121.66 (19)
S2—O1—H1	109.5	C3—C4—H4	119.7
C13—N3—C16	121.37 (17)	C5—C4—C3	120.7 (2)
C13—N3—C15	121.20 (17)	C5—C4—H4	119.7
C16—N3—C15	117.43 (17)	C3—C8—H8	119.8
C6—N1—C10	122.76 (18)	C7—C8—C3	120.37 (19)
C3—N2—C1	121.04 (19)	C7—C8—H8	119.8
C3—N2—C2	121.77 (19)	N3—C16—H16A	109.5

C2—N2—C1	117.17 (18)	N3—C16—H16B	109.5
N2—C1—H1A	109.5	N3—C16—H16C	109.5
N2—C1—H1B	109.5	H16A—C16—H16B	109.5
N2—C1—H1C	109.5	H16A—C16—H16C	109.5
H1A—C1—H1B	109.5	H16B—C16—H16C	109.5
H1A—C1—H1C	109.5	C12—C11—C10	122.5 (2)
H1B—C1—H1C	109.5	C12—C11—H11	118.8
N2—C3—C4	120.1 (2)	C10—C11—H11	118.8
N2—C3—C8	121.7 (2)	N3—C15—H15A	109.5
C8—C3—C4	118.19 (19)	N3—C15—H15B	109.5
C13—C12—H12	119.7	N3—C15—H15C	109.5
C11—C12—H12	119.7	H15A—C15—H15B	109.5
C11—C12—C13	120.6 (2)	H15A—C15—H15C	109.5
N3—C13—C12	120.60 (19)	H15B—C15—H15C	109.5
N3—C13—C14	121.19 (18)	C6—C5—H5	118.7
C14—C13—C12	118.21 (19)	C4—C5—C6	122.6 (2)
C13—C14—H14	119.6	C4—C5—H5	118.7
C9—C14—C13	120.83 (19)	N2—C2—H2A	109.5
C9—C14—H14	119.6	N2—C2—H2B	109.5
C14—C9—S1	118.04 (16)	N2—C2—H2C	109.5
C14—C9—C10	121.17 (19)	H2A—C2—H2B	109.5
C10—C9—S1	120.79 (16)	H2A—C2—H2C	109.5
N1—C6—C7	126.19 (18)	H2B—C2—H2C	109.5
N1—C6—C5	117.35 (19)		
S1—C9—C10—N1	-0.8 (3)	C9—C10—C11—C12	-0.5 (3)
S1—C9—C10—C11	179.98 (15)	C6—N1—C10—C9	0.6 (3)
S1—C7—C8—C3	-178.17 (15)	C6—N1—C10—C11	179.83 (18)
N3—C13—C14—C9	178.51 (19)	C6—C7—C8—C3	2.0 (3)
N1—C6—C7—S1	-0.4 (3)	C10—N1—C6—C7	0.1 (3)
N1—C6—C7—C8	179.4 (2)	C10—N1—C6—C5	-179.86 (18)
N1—C6—C5—C4	179.82 (19)	C7—S1—C9—C14	-179.56 (16)
N1—C10—C11—C12	-179.78 (19)	C7—S1—C9—C10	0.33 (18)
N2—C3—C4—C5	-177.30 (19)	C7—C6—C5—C4	-0.1 (3)
N2—C3—C8—C7	176.55 (19)	C4—C3—C8—C7	-2.5 (3)
C1—N2—C3—C4	172.77 (18)	C8—C3—C4—C5	1.8 (3)
C1—N2—C3—C8	-6.3 (3)	C16—N3—C13—C12	-2.1 (3)
C3—C4—C5—C6	-0.5 (3)	C16—N3—C13—C14	178.11 (18)
C12—C13—C14—C9	-1.3 (3)	C11—C12—C13—N3	-179.08 (19)
C13—C12—C11—C10	0.1 (3)	C11—C12—C13—C14	0.7 (3)
C13—C14—C9—S1	-179.09 (15)	C15—N3—C13—C12	178.25 (18)
C13—C14—C9—C10	1.0 (3)	C15—N3—C13—C14	-1.6 (3)
C14—C9—C10—N1	179.14 (19)	C5—C6—C7—S1	179.52 (15)
C14—C9—C10—C11	-0.1 (3)	C5—C6—C7—C8	-0.6 (3)
C9—S1—C7—C6	0.18 (18)	C2—N2—C3—C4	-5.5 (3)
C9—S1—C7—C8	-179.67 (16)	C2—N2—C3—C8	175.48 (19)

*Hydrogen-bond geometry (Å, °)*

<i>D</i> —H $\cdots$ <i>A</i>	<i>D</i> —H	H $\cdots$ <i>A</i>	<i>D</i> $\cdots$ <i>A</i>	<i>D</i> —H $\cdots$ <i>A</i>
O1—H1 $\cdots$ O3 <sup>i</sup>	0.84	1.77	2.609 (4)	175
C1—H1C $\cdots$ O4 <sup>ii</sup>	0.98	2.39	3.349 (5)	167
C2—H2B $\cdots$ O2 <sup>iii</sup>	0.98	2.56	3.506 (5)	163
C4—H4 $\cdots$ O3 <sup>iv</sup>	0.95	2.54	3.451 (5)	162
C12—H12 $\cdots$ O4	0.95	2.46	3.372 (5)	162
C15—H15B $\cdots$ O2 <sup>v</sup>	0.98	2.47	3.382 (5)	155
C15—H15C $\cdots$ O3 <sup>vi</sup>	0.98	2.36	3.309 (5)	164
C16—H16B $\cdots$ O2 <sup>v</sup>	0.98	2.32	3.283 (5)	167
C16—H16C $\cdots$ O4	0.98	2.52	3.326 (5)	139

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