



Crystal structure of 3-(2-hydroxyethyl)-2-methylsulfanyl-6-nitro-3*H*-benzimidazol-1-ium chloride monohydrate

Akoun Abou,^{a*} Siomenan Coulibali,^b Rita Kakou-Yao,^c T. Jérémie Zoueu^d and A. Jules Tenon^c

Received 18 August 2016

Accepted 25 August 2016

Edited by J. Simpson, University of Otago, New Zealand

Keywords: crystal structure; benzimidazole derivative; hydrogen bonding; π - π interactions.

CCDC reference: 1500918

Supporting information: this article has supporting information at journals.iucr.org/e

^aUnité Mixte de Recherche et d'Innovation en Electronique et d'Electricité Appliquées (UMRI EEA), Equipe de Recherche: Instrumentation Image et Spectroscopie (L2IS), DFR-GEE, Institut National Polytechnique Félix Houphouët-Boigny (INP-HB), BP 1093, Yamoussoukro, Côte d'Ivoire, Laboratoire de Cristallographie et Physique Moléculaire, UFR SSMT, Université de Cocody 22 BP 582 Abidjan 22, Côte d'Ivoire, ^bLaboratoire de Chimie Organique, UFR SSMT, Université de Cocody 22 BP 582 Abidjan 22, Côte d'Ivoire, ^cLaboratoire de Cristallographie et Physique Moléculaire, UFR SSMT, Université de Cocody 22 BP 582 Abidjan 22, Côte d'Ivoire, and ^dUnité Mixte de Recherche et d'Innovation en Electronique et d'Electricité Appliquées (UMRI EEA), Equipe de Recherche: Instrumentation Image et Spectroscopie (L2IS), DFR-GEE, Institut National Polytechnique Félix Houphouët-Boigny (INP-HB), BP 1093, Yamoussoukro, Côte d'Ivoire. *Correspondence e-mail: abouakoun@gmail.com

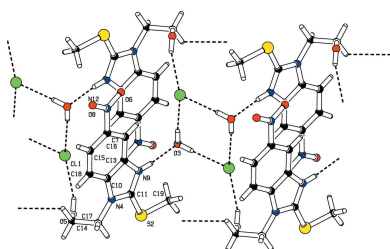
In the cation of the title hydrated molecular salt, $C_{10}H_{12}N_3O_3S^+ \cdot Cl^- \cdot H_2O$, the benzimidazolium ring system is almost planar (r.m.s. deviation = 0.006 Å) and the nitro group is inclined at an angle of 4.86 (9)° to this plane. In the crystal, C—H...O hydrogen bonds form centrosymmetric $R_2^2(20)$ dimers and these are further aggregated through N—H...O and O—H...Cl hydrogen bonds involving the water molecules and chloride anions. Aromatic π - π stacking interactions are also found between two parallel benzene rings or the benzene and imidazolium rings, with centroid-centroid distances of 3.5246 (9) and 3.7756 (9) Å, respectively. Analysis of the bond lengths and comparison with related compounds show that the nitro substituent is not involved in conjugation with the adjacent π -system and hence has no effect on the charge distribution of the heterocyclic ring.

1. Chemical context

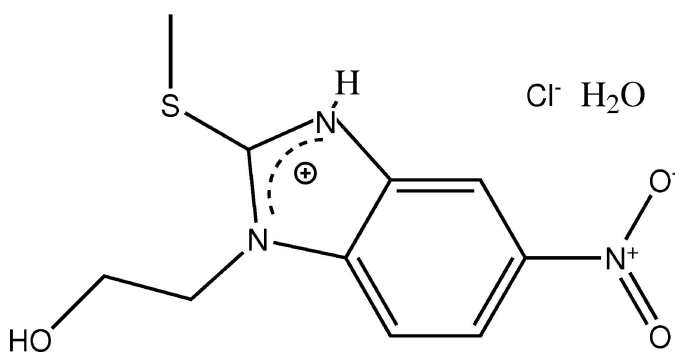
Numerous compounds with benzimidazole ring systems display versatile pharmacological activities such as anti-viral, anti-helminthic, spasmolytic, anti-hypertensive and vasodilator properties (Akkurt *et al.*, 2006). Many benzimidazole derivatives also have anti-microbial and anti-fungal activities (Küçükbay *et al.*, 2003, 2004; Puratchikody *et al.*, 2008; Alasmary *et al.*, 2015). The synthesis of new benzimidazole derivatives is therefore of considerable current interest. As part of our studies in this area, the title protonated benzimidazole compound (I) has been synthesized and its molecular structure is presented here.

2. Structural commentary

The molecular structure of the title compound is shown in Fig. 1. The nine-membered benzimidazolium ring system (N4/C11/N9/C13/C16/C7/C15/C18/C10) is essentially planar, the maximum deviation from planarity being 0.013 (1) Å for atom N4. In addition, atoms N12, C17 and S2 of the nitro, hydroxyethyl and methylsulfanyl substituents lie close to the benzimidazolium ring plane with a maximum deviation of



−0.059 (1) Å for atom S2. The least-squares plane of the nitro group (C7/N12/O6/O8) lies close to the benzimidazolium ring system, making a dihedral angle of 4.86 (9)°. In the structure, the bond lengths and angles of the benzimidazolium ring are generally in good agreement with those observed in related structures (Morozov *et al.*, 2004; Verdan *et al.*, 2009; Chen *et al.*, 2010; Yuasa *et al.*, 2010; Gao *et al.*, 2013; Samsonov *et al.*, 2013; Liu *et al.*, 2014). In addition, the C7–N12 bond length, 1.4667 (19) Å shows that the nitro group is not involved in conjugation with the adjacent π -system and hence has no effect on the charge distribution of the heterocyclic ring.



3. Supramolecular features

In the crystal, C14–H14B···O8 hydrogen bonds (Table 1) link the organic fragments into centrosymmetric dimers with $R_2^2(20)$ ring motifs along the [100] direction (Fig. 2). These dimers are further connected along the [100] and [010] directions by N–H···O and O–H···Cl hydrogen bonds, respectively, generating $R_4^6(22)$ rings. In the latter ring motifs, both the water molecule and the oxygen atom of the hy-

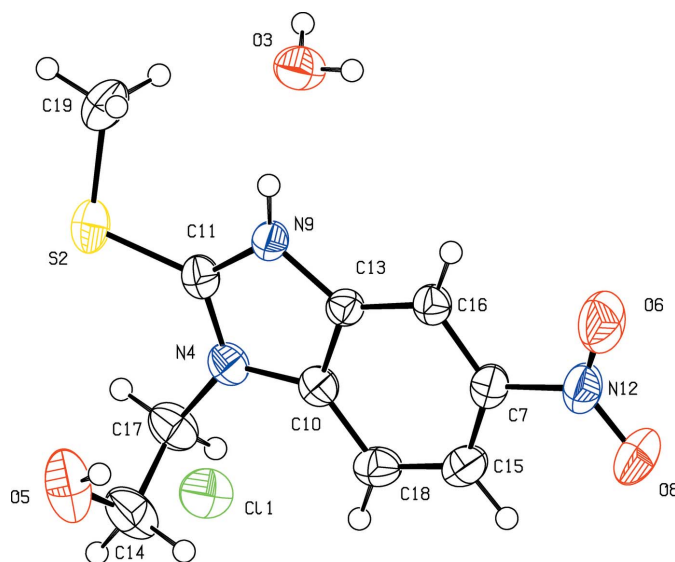


Figure 1
The molecular structure of (I), showing the atomic labelling scheme and displacement ellipsoids drawn at the 50% probability level. H atoms are shown as spheres of arbitrary radius.

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O5–H5···Cl1	0.82	2.40	3.1840 (15)	161
C17–H17B···S2	0.97	2.68	3.1514 (18)	110
O3–H3B···Cl1	0.83 (2)	2.28 (2)	3.1090 (14)	178 (2)
O3–H3A···CH ⁱ	0.79 (2)	2.37 (2)	3.1561 (14)	174 (2)
C14–H14B···O8 ⁱⁱ	0.97	2.60	3.189 (2)	119
N9–H9···O3 ⁱⁱⁱ	0.86	1.85	2.6949 (16)	165

Symmetry codes: (i) $-x, -y, -z + 1$; (ii) $-x, -y, -z$; (iii) $x + 1, y, z$.

droxyethyl substituent act as donors with the chloride anion as acceptor. The O3 atom of the water molecule serves as acceptor for the H9 atom of the imidazolium NH group (Fig. 3). The pattern formed by the water molecules connecting the chloride anions, and forming an $R_2^2(8)$ ring, is reminiscent of a parallelogram (Fig. 3). The supramolecular aggregation is completed by π – π stacking interactions between two parallel benzene rings and between the benzene and imidazolium rings: $Cg2\cdots Cg2(1-x, -y, -z) = 3.5246$ (9),

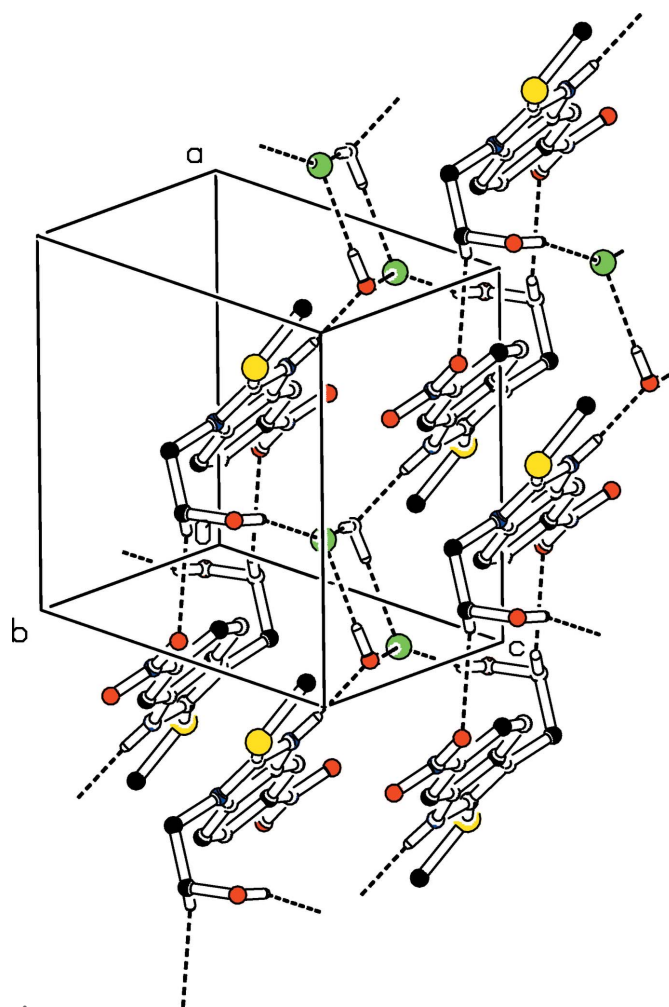


Figure 2
The crystal packing of (I), showing the supramolecular aggregation resulting from the three-dimensional hydrogen-bonded network. Dashed lines indicate hydrogen bonds. H atoms not involved in hydrogen bonding have been omitted for clarity.

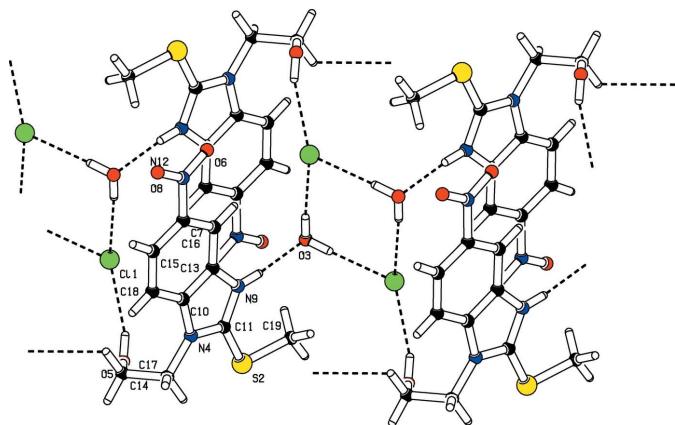


Figure 3
The molecular packing of (I), showing the pattern formed by the water molecules hydrogen bonded to the chloride anions.

$Cg1 \cdots Cg2(1 - x, -y, -z) = 3.7756(9) \text{ \AA}$, slippage = 1.190 \AA . $Cg1$ and $Cg2$ are the centroids of the imidazolium and benzene rings respectively. The centroid–centroid separations are less than 3.8 \AA , the maximum regarded as suitable for an effective π – π interaction (Janiak, 2000) (Fig. 4)).

4. Database survey

A CSD search (Web CSD version 5.37; August 19, 2016; Groom *et al.*, 2016) found eight benzimidazolium structures with substituents at the 1 and 2 positions of the imidazolium ring system (Morozov *et al.*, 2004; Verdan *et al.*, 2009; Chen *et al.*, 2010; Yuasa *et al.*, 2010; Gao *et al.*, 2013; Samsonov *et al.*,

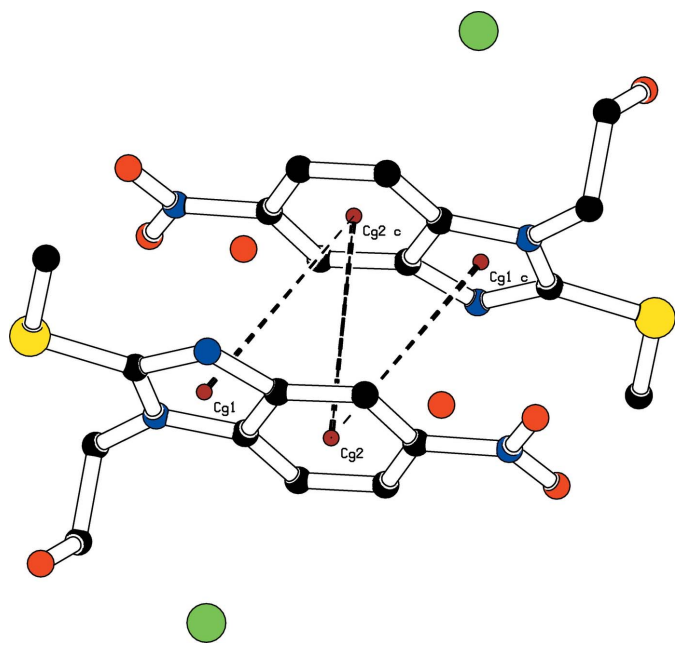


Figure 4
A view of the crystal packing, showing π – π stacking interactions (dashed lines). The brown dots are the centroids of the rings. H atoms have been omitted for clarity.

2013; Liu *et al.*, 2014; Kerimov *et al.*, 2012). In these structures, the imidazolium rings generally show two long (in the range 1.36–1.40 \AA) and two short (1.30–1.34 \AA) C–N distances. This pattern is clearly repeated here with $N4$ – $C11 = 1.3492(18)$ and $N9$ – $C11 = 1.3390(17) \text{ \AA}$ while $N4$ – $C10 = 1.3898(18) \text{ \AA}$ and $N9$ – $C13 = 1.3867(16) \text{ \AA}$. The sole exception to this pattern is the compound, 2-(4-chlorophenyl)-3-[(5-(3,5-dinitrophenyl)-1,3,4-oxadiazol-2-yl)methyl]-1*H*-benzimidazole (Kerimov *et al.*, 2012), with an imidazolium ring, which reveals three long (1.37–1.39 \AA) and one short (1.30 \AA) C–N bonds, a pattern that is also displayed in benzimidazole structures (Abou *et al.*, 2007; Yavo *et al.*, 2007; Kakou-Yao *et al.*, 2007; Akonan *et al.*, 2010; Lokaj *et al.*, 2009).

5. Synthesis and crystallization

2-Chloroethanol (1.3 ml, 19.2 mmol) and potassium carbonate (1.32 g, 9.6 mmol) were added to 2-methylthio-5-nitro-1*H*-benzimidazole (1.15 g, 4.8 mmol) in dimethyl sulfoxide (DMSO) (10 ml). The reaction mixture was agitated for 5 h at room temperature. 50 ml of water was then added to the reaction mixture, and the products were extracted with dichloromethane (3×50 ml). The combined organic extracts were washed with ammonium chloride solution (10 g of ammonium chloride in 100 ml of water), dried over Na_2SO_4 , filtered and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (elution: methanol/ethyl acetate, 20:80, *v/v*). The resulting powder was dissolved in dichloromethane and after three days, yellow crystals suitable for single-crystal X-ray diffraction analysis were obtained in 72% yield with a melting point of 425 K.

^1H NMR (DMSO, 300 MHz) δ (p.p.m.): 2.7 (s, 3H, CH_3); 3 (s, 2H, H_2O); 3.7 (m, 2H, CH_2O); 4.3 (m, 2H, CH_2N); 5 (t, 1H, OH); 7.5–8.5 (m, 3H, C_6H_3).

^{13}C (DMSO, 75 MHz) δ (p.p.m.): 114.28 (CH_3); 47 (CH_2O); 59 (CH_2N); 106.56; 110.03; 112.87; 117.13; 136.38; 147.37; 155.52 (C4, C5, C6, C7, C8, C9); 162.23 (C=N).

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The water H atoms were located in a difference Fourier map; their positional parameters and $U_{\text{iso}}(\text{H})$ were refined with O–H distances restrained to be 0.82 \AA with a standard deviation of 0.02 \AA . Other H atoms were placed in calculated positions [O–H = 0.82, N–H = 0.86, C–H = 0.93 (aromatic), 0.96 (methyl) or 0.97 \AA (methylene)] and refined using a riding-model approximation with $U_{\text{iso}}(\text{H})$ constrained to 1.2 (amine, aromatic and methylene group) or 1.5 (hydroxyl, methyl group) times U_{eq} of the respective parent atom.

Acknowledgements

The authors are grateful to the Spectropôle Service of the Faculty of Sciences and Techniques of Saint Jérôme (France) for the use of the diffractometer.

References

- Abou, A., Bany, G. E., Kakou-Yao, R., Seikou, T. & Ebby, N. D. (2007). *Acta Cryst.* **E63**, o4218.
- Akkurt, M., Türktekin, S., Şireci, N., Küçükbay, H. & Büyükgüngör, O. (2006). *Acta Cryst.* **E62**, o185–o187.
- Akonan, L., Molou, K. Y. G., Adohi-Krou, A., Abou, A. & Tenon, A. J. (2010). *Acta Cryst.* **E66**, o442.
- Alasmary, F. A. S., Snelling, A. M., Zain, M. E., Alafeefy, A. M., Awaad, A. S. & Karodia, N. K. (2015). *Molecules*, **20**, 15206–15223.
- Burla, M. C., Caliendo, R., Camalli, M., Carrozzini, B., Cascarano, G. L., De Caro, L., Giacovazzo, C., Polidori, G. & Spagna, R. (2005). *J. Appl. Cryst.* **38**, 381–388.
- Chen, S. H., Yang, F. R., Wang, M. T. & Wang, N. N. (2010). *C. R. Chim.* **13**, 1391–1396.
- Farrugia, L. J. (2012). *J. Appl. Cryst.* **45**, 849–854.
- Gao, X. J., Jin, S., Liang, S., Chen, W. & Wang, D. (2013). *J. Mol. Struct.* **1039**, 144–152.
- Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.* **B72**, 171–179.
- Hooft, R. (1998). *COLLECT*. Nonius BV, Delft, The Netherlands.
- Janiak, J. (2000). *J. Chem. Soc. Dalton Trans.* pp. 3885–3896.
- Kakou-Yao, R., Abou, A., Adjou, A., Bany, G. E. & Ebby, N. D. (2007). *Acta Cryst.* **E63**, o4463.
- Kerimov, I., İlgar, , Ayhan-Kılıçgil, G., Özdamar, E. D., Can-Eke, B., Çoban, T., Özbey, S. & Kazak, C. (2012). *Arch. Pharm. Pharm. Med. Chem.* **345**, 549–556.
- Küçükbay, H., Durmaz, R., Okuyucu, N., Günal, S. & Kazaz, C. (2004). *Arzneim.-Forsch. Drug. Res.* **54**, 64–68.
- Küçükbay, H., Durmaz, R., Orhan, E. & Günal, S. (2003). *Farmaco*, **58**, 431–437.
- Liu, J. & Pan, Q. (2014). *Z. Kristallogr. New Cryst. Struct.* **229**, 111–112.
- Lokaj, J., Kettmann, V., Milata, V. & Solčan, T. (2009). *Acta Cryst.* **E65**, o1788.
- Morozov, P. J., Kurbatov, S. V., Dolgushin, F. M., Antipin, M. Y. & Olekhovich, L. P. (2004). *Russ. Chem. Bull.* **9**, 1990–1994.
- Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
- Puratchikody, A., Nagalakshmi, G. & Doble, M. (2008). *Chem. Pharm. Bull.* **56**, 273–281.
- Samsonov, V. A., Gatilov, Y. V. & Savel'ev, V. A. (2013). *Russ. J. Org. Chem.* **49**, 1208–1214.

Table 2

Experimental details.

Crystal data	
Chemical formula	C ₁₀ H ₁₂ N ₃ O ₃ S ⁺ ·Cl ⁻ ·H ₂ O
<i>M_r</i>	307.75
Crystal system, space group	Monoclinic, <i>P</i> ₂ ₁ / <i>c</i>
Temperature (K)	298
<i>a</i> , <i>b</i> , <i>c</i> (Å)	8.8587 (5), 22.1427 (8), 7.1657 (2)
β (°)	108.497 (3)
<i>V</i> (Å ³)	1332.98 (10)
<i>Z</i>	4
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	0.46
Crystal size (mm)	0.30 × 0.15 × 0.10
Data collection	
Diffractometer	Nonius KappaCCD
No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections	15850, 3856, 3030
<i>R</i> _{int}	0.029
(sin θ/λ) _{max} (Å ⁻¹)	0.705
Refinement	
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.037, 0.110, 1.06
No. of reflections	3856
No. of parameters	183
No. of restraints	2
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e Å ⁻³)	0.29, -0.24

Computer programs: *COLLECT* (Hooft, 1998), *DENZO/SCALEPACK* (Otwinowski & Minor, 1997), *SIR94* (Burla *et al.*, 2005), *PLATON* (Spek, 2009), *SHELXL2014* (Sheldrick, 2015), *publCIF* (Westrip, 2010) and *WinGX* (Farrugia, 2012).

- Sheldrick, G. M. (2015). *Acta Cryst.* **C71**, 3–8.
- Spek, A. L. (2009). *Acta Cryst.* **D65**, 148–155.
- Verdan, S., Melich, X., Bernardinelli, G. & Williams, A. F. (2009). *CrystEngComm*, **11**, 1416–1426.
- Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.
- Yavo, E. A., Kakou-Yao, R., Coulibaly, S., Abou, A. & Tenon, A. J. (2007). *Acta Cryst.* **E63**, o4551.
- Yuasa, J., Ogawa, T. & Kawai, T. (2010). *Chem. Commun.* **46**, 3693–3695.

supporting information

Acta Cryst. (2016). E72, 1356-1359 [doi:10.1107/S2056989016013657]

Crystal structure of 3-(2-hydroxyethyl)-2-methylsulfanyl-6-nitro-3*H*-benzimidazol-1-ium chloride monohydrate

Akoun Abou, Siomenan Coulibali, Rita Kakou-Yao, T. Jérémie Zoueu and A. Jules Tenon

Computing details

Data collection: *COLLECT* (Hooft, 1998); cell refinement: *DENZO/SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO/SCALEPACK* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SIR94* (Burla *et al.*, 2005); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *SHELXL2014* (Sheldrick, 2015), *pubCIF* (Westrip, 2010) and *WinGX* (Farrugia, 2012).

3-(2-Hydroxyethyl)-2-methylsulfanyl-6-nitro-3*H*-benzimidazol-1-ium chloride monohydrate

Crystal data

$C_{10}H_{12}N_3O_3S^+ \cdot Cl^- \cdot H_2O$

$M_r = 307.75$

Monoclinic, $P2_1/c$

Hall symbol: -P 2ybc

$a = 8.8587$ (5) Å

$b = 22.1427$ (8) Å

$c = 7.1657$ (2) Å

$\beta = 108.497$ (3)°

$V = 1332.98$ (10) Å³

$Z = 4$

$F(000) = 640$

$D_x = 1.534$ Mg m⁻³

Melting point: 425 K

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

Cell parameters from 15850 reflections

$\theta = 4.1\text{--}30.1^\circ$

$\mu = 0.46$ mm⁻¹

$T = 298$ K

Block, yellow

0.30 × 0.15 × 0.10 mm

Data collection

Nonius KappaCCD

diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

θ and ω scans

15850 measured reflections

3856 independent reflections

3030 reflections with $I > 2\sigma(I)$

$R_{int} = 0.029$

$\theta_{max} = 30.1^\circ$, $\theta_{min} = 4.1^\circ$

$h = -12 \rightarrow 12$

$k = -31 \rightarrow 31$

$l = -9 \rightarrow 9$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.037$

$wR(F^2) = 0.110$

$S = 1.06$

3856 reflections

183 parameters

2 restraints

48 constraints

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0512P)^2 + 0.4116P]$

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

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

$$\Delta\rho_{\max} = 0.29 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.24 \text{ e } \text{\AA}^{-3}$$

Extinction correction: SHELXL2014 (Sheldrick
2015, $F_c^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.010 (3)

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. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2 , conventional R-factors R are based on F, with F set to zero for negative F^2 . The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C11	0.13738 (5)	0.08560 (2)	0.42268 (6)	0.05068 (14)
S2	0.57871 (5)	0.21143 (2)	0.26622 (7)	0.04747 (14)
O3	-0.15176 (14)	0.05681 (6)	0.56505 (18)	0.0472 (3)
N4	0.36705 (14)	0.12789 (5)	0.06943 (17)	0.0345 (3)
O5	0.1477 (2)	0.20574 (6)	0.1828 (3)	0.0718 (4)
H5	0.1668	0.1773	0.2603	0.108*
O6	0.45778 (19)	-0.14042 (6)	0.3012 (2)	0.0634 (4)
C7	0.34801 (17)	-0.05387 (6)	0.1321 (2)	0.0342 (3)
O8	0.24519 (18)	-0.14988 (6)	0.0528 (2)	0.0679 (4)
N9	0.56755 (14)	0.08753 (5)	0.29958 (17)	0.0314 (2)
H9	0.6563	0.0838	0.3931	0.038*
C10	0.33709 (16)	0.06625 (6)	0.06760 (19)	0.0313 (3)
C11	0.50505 (17)	0.13941 (6)	0.2131 (2)	0.0333 (3)
N12	0.35085 (17)	-0.11931 (6)	0.1646 (2)	0.0430 (3)
C13	0.46514 (15)	0.04077 (6)	0.21301 (19)	0.0288 (3)
C14	0.1141 (2)	0.18374 (9)	-0.0101 (3)	0.0561 (5)
H14A	0.0477	0.2127	-0.1014	0.067*
H14B	0.0548	0.1463	-0.0229	0.067*
C15	0.21856 (18)	-0.02957 (7)	-0.0142 (2)	0.0395 (3)
H15	0.1372	-0.0546	-0.0881	0.047*
C16	0.47534 (16)	-0.02074 (6)	0.2500 (2)	0.0310 (3)
H16	0.5606	-0.0383	0.3459	0.037*
C17	0.26321 (19)	0.17270 (8)	-0.0631 (2)	0.0443 (4)
H17A	0.2347	0.1583	-0.1977	0.053*
H17B	0.3207	0.2104	-0.0550	0.053*
C18	0.21161 (17)	0.03179 (7)	-0.0491 (2)	0.0390 (3)
H18	0.1269	0.0493	-0.1461	0.047*
C19	0.7761 (2)	0.19682 (8)	0.4278 (3)	0.0560 (5)
H19A	0.7703	0.1756	0.5421	0.084*
H19B	0.8311	0.2344	0.4673	0.084*
H19C	0.8327	0.1727	0.3606	0.084*
H3B	-0.076 (2)	0.0647 (10)	0.524 (3)	0.060 (6)*

H3A	-0.152 (3)	0.0212 (7)	0.573 (4)	0.070 (8)*
-----	------------	------------	-----------	------------

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C11	0.0492 (2)	0.0521 (3)	0.0514 (2)	-0.00027 (17)	0.01683 (18)	0.00853 (17)
S2	0.0580 (3)	0.02568 (18)	0.0586 (3)	-0.00229 (15)	0.0185 (2)	-0.00067 (15)
O3	0.0382 (6)	0.0495 (7)	0.0520 (7)	0.0023 (5)	0.0116 (5)	0.0069 (5)
N4	0.0362 (6)	0.0320 (6)	0.0354 (6)	0.0051 (4)	0.0116 (5)	0.0048 (4)
O5	0.1054 (13)	0.0430 (7)	0.0891 (11)	0.0073 (7)	0.0620 (10)	0.0007 (7)
O6	0.0788 (10)	0.0336 (6)	0.0715 (9)	-0.0019 (6)	0.0152 (7)	0.0062 (6)
C7	0.0393 (7)	0.0307 (6)	0.0376 (7)	-0.0053 (5)	0.0193 (6)	-0.0049 (5)
O8	0.0661 (9)	0.0436 (7)	0.0917 (11)	-0.0218 (6)	0.0217 (8)	-0.0198 (7)
N9	0.0322 (6)	0.0264 (5)	0.0335 (6)	-0.0009 (4)	0.0075 (4)	-0.0016 (4)
C10	0.0325 (6)	0.0329 (6)	0.0299 (6)	0.0013 (5)	0.0119 (5)	0.0003 (5)
C11	0.0380 (7)	0.0283 (6)	0.0360 (7)	0.0018 (5)	0.0150 (5)	0.0011 (5)
N12	0.0507 (8)	0.0323 (6)	0.0540 (8)	-0.0091 (5)	0.0278 (6)	-0.0085 (6)
C13	0.0276 (6)	0.0301 (6)	0.0296 (6)	-0.0013 (5)	0.0103 (5)	-0.0019 (5)
C14	0.0517 (10)	0.0490 (10)	0.0725 (12)	0.0175 (8)	0.0269 (9)	0.0167 (9)
C15	0.0352 (7)	0.0463 (8)	0.0379 (7)	-0.0097 (6)	0.0129 (6)	-0.0094 (6)
C16	0.0330 (6)	0.0297 (6)	0.0322 (6)	-0.0002 (5)	0.0128 (5)	-0.0003 (5)
C17	0.0451 (8)	0.0437 (8)	0.0447 (8)	0.0122 (7)	0.0151 (7)	0.0151 (7)
C18	0.0317 (7)	0.0491 (8)	0.0335 (7)	0.0004 (6)	0.0066 (5)	-0.0011 (6)
C19	0.0531 (10)	0.0394 (8)	0.0723 (12)	-0.0149 (7)	0.0153 (9)	-0.0057 (8)

Geometric parameters (Å, °)

S2—C11	1.7194 (14)	N9—H9	0.8600
S2—C19	1.794 (2)	C10—C18	1.388 (2)
O3—H3B	0.833 (16)	C10—C13	1.3932 (18)
O3—H3A	0.792 (16)	C13—C16	1.3849 (18)
N4—C11	1.3492 (18)	C14—C17	1.506 (2)
N4—C10	1.3898 (18)	C14—H14A	0.9700
N4—C17	1.4758 (18)	C14—H14B	0.9700
O5—C14	1.405 (3)	C15—C18	1.379 (2)
O5—H5	0.8200	C15—H15	0.9300
O6—N12	1.219 (2)	C16—H16	0.9300
C7—C16	1.3853 (19)	C17—H17A	0.9700
C7—C15	1.393 (2)	C17—H17B	0.9700
C7—N12	1.4667 (19)	C18—H18	0.9300
O8—N12	1.2251 (18)	C19—H19A	0.9600
N9—C11	1.3390 (17)	C19—H19B	0.9600
N9—C13	1.3867 (16)	C19—H19C	0.9600
C11—S2—C19	101.51 (8)	C17—C14—H14A	109.2
H3B—O3—H3A	105 (2)	O5—C14—H14B	109.2
C11—N4—C10	108.48 (11)	C17—C14—H14B	109.2
C11—N4—C17	126.35 (13)	H14A—C14—H14B	107.9

C10—N4—C17	125.16 (12)	C18—C15—C7	119.69 (13)
C14—O5—H5	109.5	C18—C15—H15	120.2
C16—C7—C15	124.82 (13)	C7—C15—H15	120.2
C16—C7—N12	117.17 (13)	C13—C16—C7	114.40 (12)
C15—C7—N12	118.01 (13)	C13—C16—H16	122.8
C11—N9—C13	108.53 (11)	C7—C16—H16	122.8
C11—N9—H9	125.7	N4—C17—C14	111.36 (13)
C13—N9—H9	125.7	N4—C17—H17A	109.4
C18—C10—N4	131.27 (13)	C14—C17—H17A	109.4
C18—C10—C13	122.29 (13)	N4—C17—H17B	109.4
N4—C10—C13	106.44 (11)	C14—C17—H17B	109.4
N9—C11—N4	109.42 (12)	H17A—C17—H17B	108.0
N9—C11—S2	128.39 (11)	C15—C18—C10	116.82 (13)
N4—C11—S2	122.18 (11)	C15—C18—H18	121.6
O6—N12—O8	123.47 (15)	C10—C18—H18	121.6
O6—N12—C7	118.44 (13)	S2—C19—H19A	109.5
O8—N12—C7	118.09 (15)	S2—C19—H19B	109.5
C16—C13—N9	130.92 (12)	H19A—C19—H19B	109.5
C16—C13—C10	121.98 (12)	S2—C19—H19C	109.5
N9—C13—C10	107.10 (11)	H19A—C19—H19C	109.5
O5—C14—C17	112.04 (17)	H19B—C19—H19C	109.5
O5—C14—H14A	109.2		
C11—N4—C10—C18	179.32 (14)	C11—N9—C13—C10	0.53 (15)
C17—N4—C10—C18	-0.1 (2)	C18—C10—C13—C16	0.1 (2)
C11—N4—C10—C13	-1.53 (14)	N4—C10—C13—C16	-179.10 (12)
C17—N4—C10—C13	179.07 (13)	C18—C10—C13—N9	179.86 (12)
C13—N9—C11—N4	-1.51 (15)	N4—C10—C13—N9	0.61 (14)
C13—N9—C11—S2	178.15 (11)	C16—C7—C15—C18	-0.1 (2)
C10—N4—C11—N9	1.90 (15)	N12—C7—C15—C18	179.95 (13)
C17—N4—C11—N9	-178.70 (13)	N9—C13—C16—C7	179.86 (13)
C10—N4—C11—S2	-177.78 (10)	C10—C13—C16—C7	-0.51 (19)
C17—N4—C11—S2	1.6 (2)	C15—C7—C16—C13	0.5 (2)
C19—S2—C11—N9	11.50 (16)	N12—C7—C16—C13	-179.58 (12)
C19—S2—C11—N4	-168.88 (13)	C11—N4—C17—C14	-106.73 (18)
C16—C7—N12—O6	5.1 (2)	C10—N4—C17—C14	72.56 (19)
C15—C7—N12—O6	-174.94 (15)	O5—C14—C17—N4	60.0 (2)
C16—C7—N12—O8	-174.90 (14)	C7—C15—C18—C10	-0.2 (2)
C15—C7—N12—O8	5.0 (2)	N4—C10—C18—C15	179.29 (14)
C11—N9—C13—C16	-179.79 (14)	C13—C10—C18—C15	0.3 (2)

Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O5—H5 \cdots C11	0.82	2.40	3.1840 (15)	161
C17—H17B \cdots S2	0.97	2.68	3.1514 (18)	110
O3—H3B \cdots C11	0.83 (2)	2.28 (2)	3.1090 (14)	178 (2)
O3—H3A \cdots C11 ⁱ	0.79 (2)	2.37 (2)	3.1561 (14)	174 (2)

C14—H14B···O8 ⁱⁱ	0.97	2.60	3.189 (2)	119
N9—H9···O3 ⁱⁱⁱ	0.86	1.85	2.6949 (16)	165

Symmetry codes: (i) $-x, -y, -z+1$; (ii) $-x, -y, -z$; (iii) $x+1, y, z$.