

Proton-bifurcated C—H···(O,O) hydrogen bonds in 2,3-dichloro-6-nitrobenzylaminium chloride

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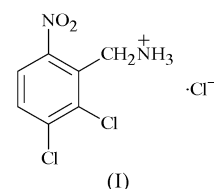
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In the crystal structure of the title salt, $C_7H_7Cl_2N_2O_2^+ \cdot Cl^-$, the chloride anions participate in extensive hydrogen bonding with the aminium cations and indirectly link the molecules through multiple $N^+—H \cdots Cl^-$ salt bridges. There are two independent molecules in the asymmetric unit, related by a pseudo-inversion center. The direct intermolecular coupling is established by $C—H \cdots O$, $C—H \cdots Cl$ and $C—Cl \cdots Cl^-$ interactions. A rare three-center (donor bifurcated) $C—H \cdots (O,O)$ hydrogen bond is observed between the methylene and nitro groups, with a side-on intramolecular component of closed-ring type and a head-on intermolecular component.

Comment

Identification and characterization of novel structural motifs, stabilized by intermolecular interactions, is one of the current topics of investigation in the geometric rule-based design of molecular solids possessing novel properties (Desiraju & Steiner, 1999). The three-center hydrogen-bond configuration (*i.e.* with a bifurcated donor or acceptor) is one such structural motif. Numerous examples of three-center bonds formed by conventional strong hydrogen bonds exist (Jeffrey & Saenger, 1991). In contrast, the bifurcation of weak interactions, such as between a weak donor and strong acceptors, are less well characterized. In this communication, we report the structure of a halide salt, namely 2,3-dichloro-6-nitrobenzylaminium chloride, (I), the crystal structure of which is predominantly stabilized by multiple $N^+—H \cdots Cl^-$ salt bridges and $C—H \cdots O$ and $C—H \cdots Cl$ bonds (Desiraju, 2005), including a rare bifurcated-donor $C—H \cdots (O,O)$ hydrogen bond. The asymmetric unit consists of two independent molecules, hereafter referred to as *A* and *B*, with protonated amine groups (N2A and N2B), and two discrete chloride anions, Cl3[−] and Cl4[−]

(Fig. 1). Apart from the N atom of the protruding methylaminium groups, the non-H atoms form a planar structure, with maximum atomic deviations of -0.13 (1) Å for O2A in molecule *A* and 0.12 (1) Å for C7B in molecule *B*. The aminium groups of the methylaminium substituents are twisted out of the planes of the aryl rings, with C1A—C2A—C7A—N2A and C1B—C2B—C7B—N2B torsion angles of -92.5 (4) and 84.4 (5)°, respectively. The interplanar angles between the benzene rings (C1A—C6A and C1B—C6B) and the attached nitro groups (N1A/O1/O2A/C1A and N1B/O1B/O2B/C1B) are 2.7 (2) and 5.0 (2)°, respectively, in molecules *A* and *B*. The two molecules are related by a pseudo-inversion center, and the r.m.s. deviation for all the corresponding superposed atoms of *A* and inverted *B* is 0.07 Å. (Fig. 3 of the supplementary material shows the superposition of molecules *A* and *B*.)



The crystal structure is held together by intermolecular $N^+—H \cdots Cl^-$, $C—H \cdots O$, $C—H \cdots Cl$ and $C—Cl \cdots Cl^-$ interactions (Fig. 2). Pertinent geometric details and symmetry codes are provided in Table 1. Intramolecular C7A—H72A···O1A and C7B—H71B···O1B hydrogen bonds form an *S*(6) closed pattern, while C6B—H6B···O2B, C7A—H71A···Cl1A and C7B—H72B···Cl1B bonds form an *S*(5) pattern (Bernstein *et al.*, 1995). Intermolecular C5A—H5A···Cl1B^v, C7A—H72A···O1B and C5B—H5B···O2A^{vi} bonds directly link molecules *A* and *B*. The intramolecular C7A—H72A···O1A and intermolecular C7A—H72A···O1B interactions collectively form a planar three-center hydrogen-bond configuration (Fig. 1), where the sum of the angles [350 (5)°] about atom H72A is slightly less than the ideal value (360°; Parthasarathy, 1969). The term three-center hydrogen

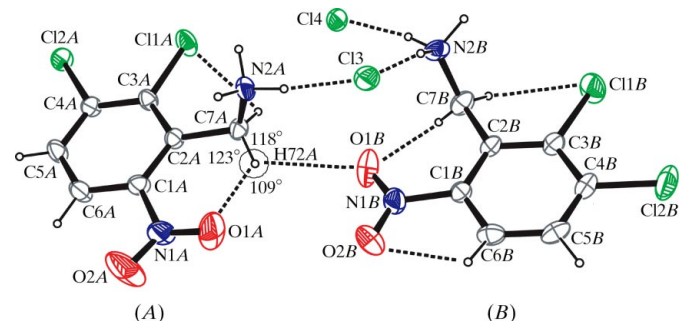


Figure 1

The asymmetric unit of (I), showing the three-center (donor bifurcated) $C—H \cdots (O,O)$ hydrogen-bond configuration. Hydrogen bonds (see *Comment*) are shown as dashed lines. The values given in the figure are the angles subtended at H72A, which participates in the bifurcated hydrogen bond. Displacement ellipsoids are drawn at the 30% probability level.

bond (Jeffrey & Saenger, 1991) indicates that the H atom is at the center of the three participating donor and acceptor atoms, and indistinguishably refers to both bifurcated donor and acceptor bonds. While bifurcation of both donors and acceptors is observed in strong interactions, the bifurcation of weak interactions, such as C—H···O, between a weak donor and strong acceptors, is generally observed at the acceptor (C—H···O···H—C type; Desiraju & Steiner, 1999). H-atom- or donor-bifurcated C—H···(O,O) bonds have been observed in very few cases, and the present arrangement of a three-center bond, with one side-on intramolecular component of closed-ring type and a head-on intermolecular component, is the most favored arrangement (Steiner & Saenger, 1992). For interactions as weak as C—H···O, it is difficult to evaluate their contribution towards determining the overall crystal packing, especially in the presence of strong interactions such as the N⁺—H···Cl[−] interactions observed here. A qualitative assessment has been suggested by Desiraju (2005), who classifies such weak interactions into three different categories, namely, innocuous, supportive and intrusive. In terms of geometry and directionality, the present three-center configuration appears to belong to the supportive category, and hence is a structural determinant.

Molecules *A* and *B* are indirectly connected *via* chloride anions through multiple intermolecular N⁺—H···Cl[−] salt bridges. Each Cl[−] ion acts as an acceptor for three hydrogen bonds with aminium cations. The Cl3[−] anion forms intermolecular N2A—H22A···Cl3, N2A—H23A···Cl3ⁱⁱ and N2B—H23B···Cl3 hydrogen bonds. The Cl4[−] anion links

molecules *A* and *B* *via* N2A—H21A···Cl4ⁱ, N2B—H21B···Cl4ⁱⁱⁱ and N2B—H22B···Cl4 bonds. The H···Cl[−] and N⁺···Cl[−] distances are in the ranges 2.20 (5)–2.55 (5) and 3.062 (5)–3.255 (5) Å, while the database average values are 2.247 (5) and 3.207 (4) Å, respectively, for N⁺H₃···Cl[−] bonds (Steiner, 1998). Atom Cl4 is additionally involved in a linear C4A—Cl2A···Cl4^{iv} short contact interaction, with Cl2A···Cl4^{vi} = 3.302 (4) Å and C4A—Cl2A···Cl4^{vi} = 173.38 (13)^o [symmetry code: (vi) $-x + 1, -y, -z + 1$]. This type of short Cl···Cl[−] contact was also reported previously in the structure of 2-(chloromethyl)pyridinium chloride (Jones *et al.*, 2002). The type of X—halogen···halogen interaction observed here should be distinguished – in terms of both geometry and nature – from interhalogen interactions of the X—halogen···halogen—Y type, where X and Y are commonly C atoms (Desiraju & Parthasarathy, 1989; Price *et al.*, 1994). A short halogen–nitro contact [Cl3···O1B = 3.258 (5) Å] (Allen *et al.*, 1997) is also observed, which is presumably due to the presence of the other interactions described previously. Molecules *A* and *B* associate directly *via* intermolecular C—H···O, C—H···Cl and C—Cl···Cl[−] interactions and form a sheet structure approximately about the (224) plane (see Fig. 4 in the supplementary material). The intersheet link is established by N⁺—H···Cl[−] salt links and is devoid of any significant π – π overlaps among aryl rings. Two popular modes of packing, namely stacked (André *et al.*, 1997a), such as observed in (I), and herring-bone (André *et al.*, 1997b), have been widely observed among nitrobenzene derivatives.

The validity of the C—H···O hydrogen bond as a structural determinant is beyond doubt, and the important question that now emerges is ‘how it may be used and applied [in molecular recognition and crystal engineering]’ (Desiraju, 2005). Towards this end, the present example is a useful addition in the current body of knowledge on such weak interactions.

Experimental

The title compound was obtained from Cipla, Mumbai. Single crystals suitable for X-ray diffraction were grown by slow evaporation of a solution in methanol.

Crystal data

C₇H₇Cl₂N₂O₂⁺·Cl[−]
M_r = 257.50
 Triclinic, *P* $\bar{1}$
a = 6.889 (7) Å
b = 12.116 (12) Å
c = 13.286 (13) Å
 α = 102.128 (15)^o
 β = 100.939 (16)^o
 γ = 103.523 (16)^o
V = 1020.3 (17) Å³

Z = 4
D_x = 1.676 Mg m^{−3}
 Mo K α radiation
 Cell parameters from 363 reflections
 θ = 5–27^o
 μ = 0.87 mm^{−1}
T = 293 (2) K
 Plate, colorless
 0.55 × 0.52 × 0.21 mm

Data collection

Bruker SMART CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
T_{min} = 0.631, *T_{max}* = 0.842
 10895 measured reflections

4146 independent reflections
 3161 reflections with *I* > 2 σ (*I*)
R_{int} = 0.036
 θ_{max} = 26.4^o
h = −8 → 8
k = −15 → 15
l = −16 → 16

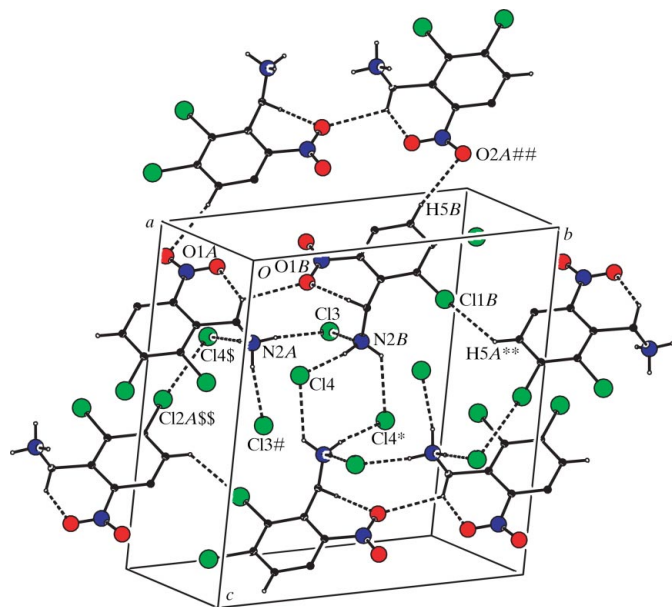


Figure 2

The intermolecular interactions in (I), including the three-center hydrogen-bond configuration. For clarity, only relevant H atoms and intramolecular interactions are shown. Atoms marked with symbols are at the following positions: (\$) $x + 1, y, z$; (#) $-x + 2, -y + 1, -z + 1$; (*) $-x + 1, -y + 1, -z + 1$; (§§) $-x + 2, -y, -z + 1$; (##) $-x + 2, -y + 1, -z$; (***) $x - 1, y + 1, z$.

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.056$
 $wR(F^2) = 0.152$
 $S = 1.05$
 4146 reflections
 295 parameters
 Only H-atom coordinates refined

$$w = 1/[\sigma^2(F_o^2) + (0.076P)^2 + 0.7937P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.003$
 $\Delta\rho_{\max} = 0.72 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.71 \text{ e } \text{\AA}^{-3}$

Table 1

Hydrogen-bond and short-contact geometry (\AA , $^\circ$).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$N2A-H21A \cdots Cl4^i$	0.89 (6)	2.28 (6)	3.168 (5)	180 (6)
$N2A-H22A \cdots Cl3$	0.92 (5)	2.39 (5)	3.255 (5)	158 (4)
$N2A-H23A \cdots Cl3^{ii}$	0.92 (5)	2.36 (5)	3.200 (5)	151 (4)
$N2B-H21B \cdots Cl4^{iii}$	0.94 (5)	2.55 (5)	3.223 (4)	129 (4)
$N2B-H22B \cdots Cl4$	0.88 (5)	2.20 (5)	3.062 (5)	170 (5)
$N2B-H23B \cdots Cl3$	0.87 (3)	2.33 (2)	3.191 (5)	170 (5)
$C5A-H5A \cdots Cl1B^{iv}$	0.94 (5)	2.82 (4)	3.476 (6)	128 (3)
$C7A-H71A \cdots Cl1A$	0.91 (5)	2.59 (4)	2.982 (5)	107 (3)
$C7A-H72A \cdots O1A$	0.89 (4)	2.14 (4)	2.729 (7)	123 (3)
$C7A-H72A \cdots O1B$	0.89 (4)	2.56 (4)	3.082 (6)	118 (3)
$C5B-H5B \cdots O2A^v$	0.93 (5)	2.60 (5)	3.497 (8)	163 (4)
$C6B-H6B \cdots O2B$	0.88 (5)	2.28 (5)	2.640 (7)	105 (4)
$C7B-H71B \cdots O1B$	0.87 (5)	2.31 (5)	2.704 (7)	108 (4)
$C7B-H72B \cdots Cl1B$	0.94 (5)	2.57 (5)	2.972 (6)	106 (3)

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

H atoms were located in difference electron-density maps and were refined isotropically without any restraints, except for the $N2B-H23B$ bond, which was restrained to 0.87 (1) \AA . The H-atom distances are in the following ranges: aryl C-H = 0.88 (4)–0.94 (4) \AA and methylene C-H = 0.87 (4)–0.94 (4) \AA , with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$, and N-H = 0.87 (1)–0.94 (5) \AA , with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{N})$. The inclusion and restrained refinement of multiple sites of the nitro group (O1A/O2A) of molecule A, carried out in view of the relatively large displacement parameter, did not yield satisfactory results.

Data collection: SMART (Bruker, 2001); cell refinement: SAINT-Plus (Bruker, 2001); data reduction: SAINT-Plus; program(s) used to

solve structure: SHELXTL (Bruker, 2001); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEP-3 (Farrugia, 1997) and PLATON (Spek, 2003); software used to prepare material for publication: SHELXL97 and PLATON.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV1275). Services for accessing these data are described at the back of the journal.

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