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..Cl⁻ salt bridges and C-H..O and C-H..Cl bonds (Desiraju, 2005), including a rare bifurcated-donor C-H..(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.
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\textsuperscript{+}-H, Cl\textsuperscript{-}, C-H, O, C-H, Cl and C-Cl, Cl\textsuperscript{-} 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, C11A and C7B-H72B, C11B bonds form an S(5) pattern (Bernstein et al., 1995). Intermolecular C5A-H5A, C11B\textsuperscript{v}, C7A-H72A, O1B and C5B-H5B, O2A\textsuperscript{v} 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 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, 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\textsuperscript{+}-H...Cl\textsuperscript{-} 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\textsuperscript{+}-H...Cl\textsuperscript{-} salt bridges. Each Cl\textsuperscript{-} ion acts as an acceptor for three hydrogen bonds with aminium cations. The Cl\textsuperscript{3-} anion forms intermolecular N2A-H22A, C13, N2A-H23A, C13\textsuperscript{ii} and N2B-H23B, C13 hydrogen bonds. The Cl\textsuperscript{4-} anion links molecules A and B via N2A-H21A, C14\textsuperscript{i}, N2B-H21B, C14\textsuperscript{iii} and N2B-H22B, C14 bonds. The H...Cl and N\textsuperscript{+}...Cl\textsuperscript{-} 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\textsuperscript{+}H...Cl\textsuperscript{-} bonds (Steiner, 1998). Atom Cl4 is additionally involved in a linear C4A-C12A, C14\textsuperscript{iv} short contact interaction, with Cl2A., C14\textsuperscript{vi} = 3.302 (4) Å and C4A-C12A., C14\textsuperscript{vi} = 173.38 (13)° [symmetry code: (vi) -x+1, -y, -z+1]. This type of short Cl...Cl\textsuperscript{-} 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**

- C$_{9}$H$_{7}$Cl$_{2}$N$_{2}$O$_{2}$H$^{+}$Cl$^{-}$
- $M_r = 257.50$
- Triclinic, $P\overline{1}$
- $a = 6.889 (7)$ Å
- $b = 12.116 (12)$ Å
- $c = 13.286 (13)$ Å
Data collection

- \( \alpha = 102.128 \) (15)°
- \( \beta = 100.939 \) (16)°
- \( \gamma = 103.523 \) (16)°
- \( V = 1020.3 \) (17) Å\(^3\)
- \( Z = 4 \)
- \( D_x = 1.676 \text{ Mg m}^{-3} \)
- Mo \( K\alpha \) radiation
- Cell parameters from 363 reflections
- \( \theta = 5-27° \)
- \( \mu = 0.87 \text{ mm}^{-1} \)
- \( T = 293 \) (2) K
- Plate, colorless
- \( 0.55 \times 0.52 \times 0.21 \text{ mm} \)

Data collection

- Bruker SMART CCD area-detector diffractometer
- \( \varphi \) and \( \omega \) scans
- Absorption correction: multi-scan (SADABS; Sheldrick, 1996) \( T_{\text{min}} = 0.631, T_{\text{max}} = 0.842 \)
- 10895 measured reflections
- 4146 independent reflections
- 3161 reflections with \( I > 2\sigma(I) \)
- \( R_{\text{int}} = 0.036 \)
- \( \theta_{\text{max}} = 26.4° \)
- \( h = -8 \rightarrow 8 \)
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 $P = (F_o^2 + 2F_c^2)/3$
- $(\Delta/\sigma)_{\text{max}} = 0.003$
- $\Delta\rho_{\text{max}} = 0.72 \text{ e Å}^{-3}$
- $\Delta\rho_{\text{min}} = -0.71 \text{ e Å}^{-3}$

<table>
<thead>
<tr>
<th>Table 1</th>
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<tbody>
<tr>
<td>Hydrogen-bond and short-contact geometry (Å, °)</td>
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<tr>
<td>---------------------------------</td>
</tr>
<tr>
<td>N2A-H21A , . Cl4</td>
</tr>
<tr>
<td>N2A-H22A , . Cl3</td>
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<tr>
<td>N2A-H23A , . Cl3</td>
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<tr>
<td>N2B-H21B , . Cl4</td>
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<tr>
<td>N2B-H22B , . Cl3</td>
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<tr>
<td>C5A-H5A , . Cl1B</td>
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<tr>
<td>C7A-H71A , . Cl1A</td>
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<td>C7A-H72A , . O1A</td>
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<td>C5B-H5B , . O2A</td>
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<td>C6B-H6B , . O2B</td>
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<td>C7B-H71B , . O1B</td>
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<tr>
<td>C7B-H72B , . Cl1B</td>
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</table>
H atoms were located in difference electron-density maps and were refined isotropically without any restraints, except for the N2-B23 bond, which was restrained to 0.87 (1) Å. The H-atom distances are in the following ranges: aryl C-H = 0.88 (4)-0.94 (4) Å and methylene C-H = 0.87 (4)-0.94 (4) Å, with $U_{iso}(H) = 1.2U_{eq}(C)$, and N-H = 0.87 (1)-0.94 (5) Å, with $U_{iso}(H) = 1.5U_{eq}(N)$. 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.

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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References


(IUCr) Proton-bifurcated C-H...(O,O) hydrogen bonds in 2,3-dichloro-6-nitrobenzylamine...