

## Two-dimensional networks in 2-methylanilinium picrate and 2,5-dichloroanilinium picrate

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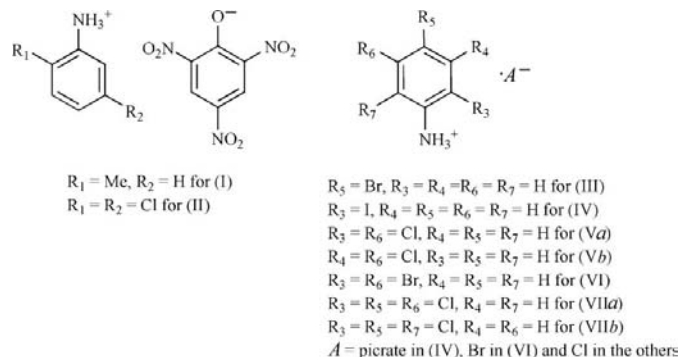
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Both the title molecular adducts of 2-methylaniline or 2,5-dichloroaniline with picric acid are 1:1 organic salts, namely 2-methylanilinium picrate,  $C_7H_{10}N^+ \cdot C_6H_2N_3O_7^-$ , (I), and 2,5-dichloroanilinium picrate,  $C_6H_6Cl_2N^+ \cdot C_6H_2N_3O_7^-$ , (II). In both structures, the phenoxide O atoms accept two N—H hydrogen bonds in a bifurcated acceptor fashion, which link the component ions by N—H $\cdots$ O hydrogen bonds into continuous two-dimensional zigzag layers, running parallel to the (100) plane in (I) and the (010) plane in (II). A  $\pi$ – $\pi$  interaction is observed between symmetry-related anilinium cations in (I), while in (II), Cl $\cdots$ O<sub>nitro</sub> and Cl $\cdots$ Cl interactions are observed. This study indicates that a substitution on aniline can exert a pivotal influence on the construction of its supramolecular structure.

### Comment

2,4,6-Trinitrophenol (picric acid) has often been used in fields such as the dye industry, civil explosives, nonlinear optical materials and separation of organic compounds. The presence of three electron-withdrawing nitro groups makes it not only an acceptor to form various  $\pi$ -stacking complexes with other aromatic molecules, but also an acidic ligand to form salts through specific electrostatic or hydrogen-bonding interactions (In *et al.*, 1997). In the past, many instances of organic-base–picrate complexes, including aliphatic amine (Ohba & Ito, 2002) or aniline derivatives (Ramesh *et al.*, 2010), azoles (Du & Zhao, 2003; Yan *et al.*, 2007; Jin *et al.*, 2006; Lyakhov *et al.*, 2005) and pyridines (Anitha *et al.*, 2006), have been crystallographically reported. With the aim of finding out the nature and directionality of the specific N—H $\cdots$ O hydrogen bonding between the protonated N atom and the phenolate O atom, and the packing mode in the crystal structure, we report here the structures of 2-methylanilinium picrate, (I), and 2,5-dichloroanilinium picrate, (II).

Compounds (I) and (II), crystallographically determined at 123 K, crystallize in the monoclinic space groups  $P2_1/c$  and  $Cc$ , respectively. In each structure, the phenolic H atom has been transferred to the aniline N1 atom to give 1:1 ionic structures (Figs. 1 and 2). The phenoxide O atom accepts two hydrogen bonds from different anilinium cations in a bifurcated fashion.



The traditional C7—O1 single bonds in the picrate anion [1.278 (3) Å in (I) and 1.286 (4) Å in (II)] are extremely short for such a bond (1.38 Å; Allen *et al.*, 1987) but are slightly longer than the mean literature value for C=O bonds in benzoquinones (1.222 Å; Allen *et al.*, 1987).

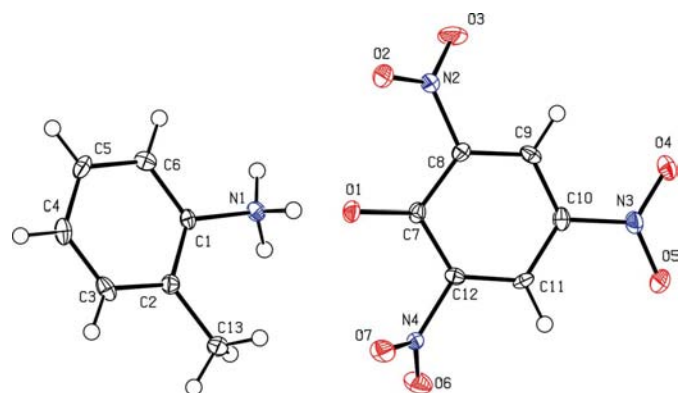


Figure 1

The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

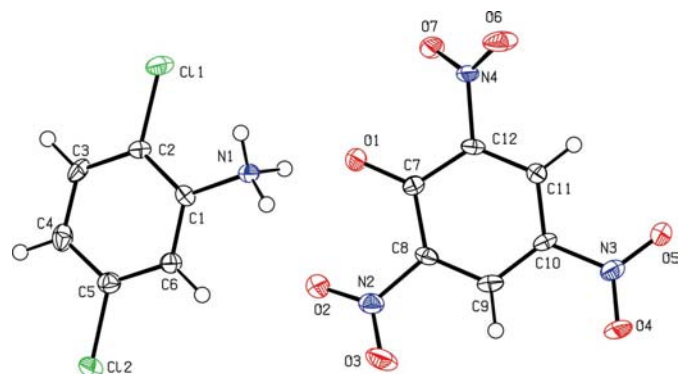
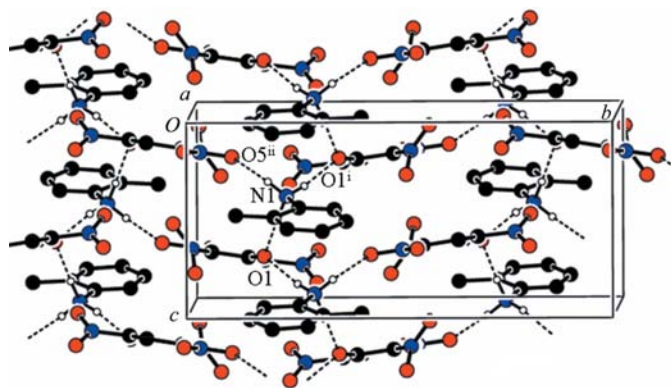


Figure 2

The molecular structure of (II), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

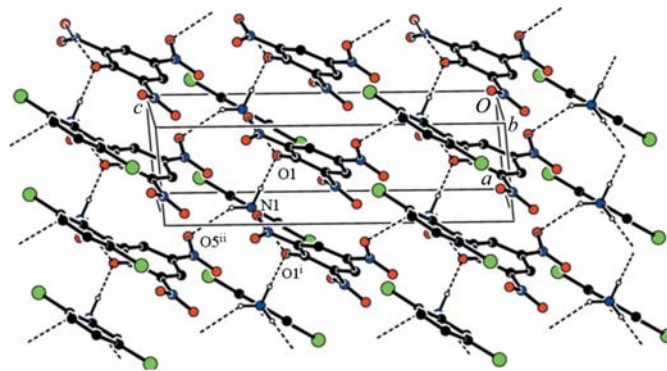
**Figure 3**

Part of the crystal structure of (I), showing the formation of the two-dimensional layer running parallel to the (100) plane. For the sake of clarity, H atoms not involved in the motifs shown have been omitted. [Symmetry codes: (i)  $x, \frac{1}{2} - y, -\frac{1}{2} + z$ ; (ii)  $2 - x, -y, 1 - z$ .]

The C—C bond distances within the picrate rings of (I) and (II) indicate very marked deviations from the geometry of a regular hexagon, with the C7—C8 and C7—C12 bonds [1.444 (4) and 1.440 (4) Å, respectively, in (I), and 1.446 (5) and 1.441 (5) Å in (II)] much longer than the others. The other four C—C bond lengths fall in range 1.366 (4)–1.398 (4) Å in (I) and 1.381 (5)–1.405 (5) Å in (II). The C—N<sub>nitro</sub> bond lengths are in the range 1.450 (3)–1.474 (4) Å in (I) and 1.465 (5)–1.477 (5) Å in (II). All these observations indicate a delocalized electronic structure rather than a quinoidal one in the picrate ring, which has been observed in some analogues (Kavitha *et al.*, 2006; Klapötke & Sabaté, 2008; Merz, 2003; Smith *et al.*, 2004).

The planes of the *ortho*-nitro groups are twisted significantly away from the planes of the benzene rings, with dihedral angles of 34.7 (1) and 53.0 (1)° in (I), and 18.3 (1) and 41.7 (1)° in (II). However, the *para*-nitro groups suffer much less from rotation out of the benzene ring planes [3.4 (1)° in (I) and 14.8 (1)° in (II)] than the other two. This should be largely the result of (i) the bifurcated acceptor anilinium–phenoxide N—H...O hydrogen bonds (Tables 1 and 2) and (ii) the phenoxide–nitro O...O interactions [O1—O2 = 2.785 (1) Å and O1—O7 = 2.865 (1) Å in (I), and 2.660 (1) and 2.742 (1) Å, respectively, in (II)]. The bond distances and angles in the anilinium cations can be regarded as normal [Cambridge Structural Database (CSD), Version 5.28, November 2006 (Allen, 2002); *Mogul* Version 1.1 (Bruno *et al.*, 2004)].

In the supramolecular structure of (I), the picrate anions and 2-methylanilinium cations are linked by N1—H1A...O1, N1—H1B...O1<sup>i</sup> and N1—H1C...O5<sup>ii</sup> hydrogen bonds (details and symmetry codes are given in Table 1) into a two-dimensional undulating layer running parallel to the (100) plane (Fig. 3). Within this layer, a  $\pi$ – $\pi$  interaction between symmetry-related aniline rings is observed, consolidating the two-dimensional structure [ $Cg1 \cdots Cg1^i = 3.904$  (2) Å, interplanar spacing = 3.536 (2) Å and dihedral angle = 0.76°; Cg1 is the centroid of aniline ring C1–C6]. No other interactions are observed between adjacent layers. In the crystal packing,

**Figure 4**

Part of the crystal structure of (II), showing the formation of the two-dimensional layer running parallel to the (010) plane. For the sake of clarity, H atoms not involved in the motifs shown have been omitted. [Symmetry codes: (i)  $1 + x, y, z$ ; (ii)  $1 + x, 2 - y, \frac{1}{2} + z$ .]

although the picrate anions are homogeneously stacked in an offset manner (Fig. 3), no  $\pi$ – $\pi$  interactions are observed between them. This may be caused by the electron-withdrawing effect of the three nitro groups, thus reducing the electron density on the benzene ring.

Similar to (I), the component ions in (II) are also linked into a two-dimensional undulating structure running parallel to the (010) plane (Fig. 4) by three intermolecular N—H...O hydrogen bonds (Table 2). Between adjacent layers, Cl1...Cl2( $-\frac{1}{2} + x, \frac{3}{2} - y, z + \frac{1}{2}$ ) = 3.465 (1) Å and Cl2...O5( $\frac{3}{2} + x, -\frac{1}{2} + y, z$ ) = 3.108 (1) Å interactions are observed. If these two interactions are taken into account, then the whole structure in (II) can be regarded as a three-dimensional network. In the packing of (II), although homogeneous stacks are also formed for both cations and anions (Fig. 4), no  $\pi$ – $\pi$  interaction is found between them. This may be due to the two electron-withdrawing atoms, Cl1 and Cl2, which to some extent reduce the  $\pi$ -electron density localized on the benzene ring. A search of the CSD yielded some additional compounds to illustrate this, (III)–(VIIb) [refcodes TAWRAL (Portalone, 2005), ZEDPON (Tanaka *et al.*, 1994), EDUGOZ, EDUGUF and EDUHIU (Gray & Jones, 2002), JACREL01 (Jones & Lozano, 2003), and JACROV and JACSAI (López-Duplá *et al.*, 2003)], in which no  $\pi$ – $\pi$  interactions were observed involving the halogen-substituted benzene rings. We plan to carry out further research on this.

## Experimental

All reagents and solvents were used as obtained without further purification. For the preparation of (I), equivalent molar amounts of 2-methylaniline (0.2 mmol, 21.4 mg) and picric acid (0.2 mmol, 45.8 mg) were dissolved in methanol (10 ml). The mixture was stirred for 10 min at ambient temperature and then filtered. The resulting yellow solution was kept in air for three weeks. Yellow block-shaped crystals of (I) suitable for single-crystal X-ray diffraction analysis grew at the bottom of the vessel by slow evaporation of the solution. The crystals were filtered off carefully, washed with distilled water and dried in air (yield 30%, 20.2 mg, based on the 1:1 organic salt).

Crystals of (II) were obtained by mixing 1:1 molar amounts of 2,5-dichloroaniline (0.2 mmol, 32.4 mg) and picric acid (0.2 mmol,

45.8 mg) in water (10 ml). The mixture was stirred for 30 min at ambient temperature and then filtered. The resulting yellow solution was kept in air for one week. Yellow plate-shaped crystals of (II) suitable for single-crystal X-ray diffraction analysis grew at the bottom of the vessel by slow evaporation of the solution. The crystals were filtered off carefully, washed with distilled water and dried in air (yield 45%, 35.2 mg, based on the 1:1 organic salt).

## Compound (I)

### Crystal data

$C_7H_{10}N^+ \cdot C_6H_2N_3O_7^-$	$V = 1450.51 (6) \text{ \AA}^3$
$M_r = 336.27$	$Z = 4$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 11.6501 (3) \text{ \AA}$	$\mu = 0.13 \text{ mm}^{-1}$
$b = 16.4813 (4) \text{ \AA}$	$T = 123 \text{ K}$
$c = 7.5754 (2) \text{ \AA}$	$0.16 \times 0.12 \times 0.10 \text{ mm}$
$\beta = 94.269 (2)^\circ$	

### Data collection

Bruker SMART APEX CCD area-detector diffractometer	9575 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 2008)	2852 independent reflections
$T_{\min} = 0.970$ , $T_{\max} = 0.987$	2267 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.049$

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.067$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.172$	
$S = 1.10$	$\Delta\rho_{\text{max}} = 0.51 \text{ e \AA}^{-3}$
2852 reflections	$\Delta\rho_{\text{min}} = -0.31 \text{ e \AA}^{-3}$
227 parameters	

## Compound (II)

### Crystal data

$C_6H_6Cl_2N^+ \cdot C_6H_2N_3O_7^-$	$V = 1542.2 (11) \text{ \AA}^3$
$M_r = 391.12$	$Z = 4$
Monoclinic, $Cc$	Mo $K\alpha$ radiation
$a = 4.3288 (18) \text{ \AA}$	$\mu = 0.47 \text{ mm}^{-1}$
$b = 23.372 (10) \text{ \AA}$	$T = 123 \text{ K}$
$c = 15.292 (6) \text{ \AA}$	$0.36 \times 0.20 \times 0.05 \text{ mm}$
$\beta = 94.606 (7)^\circ$	

### Data collection

Bruker SMART APEX CCD area-detector diffractometer	3948 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 2008)	2666 independent reflections
$T_{\min} = 0.840$ , $T_{\max} = 0.977$	2362 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.066$

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.041$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.094$	
$S = 0.98$	$\Delta\rho_{\text{max}} = 0.37 \text{ e \AA}^{-3}$
2666 reflections	$\Delta\rho_{\text{min}} = -0.26 \text{ e \AA}^{-3}$
235 parameters	Absolute structure: Flack (1983), with 1131 Bijvoet pairs
2 restraints	Flack parameter: 0.00 (6)

For both compounds, H atoms bonded to C atoms were positioned geometrically, with C—H = 0.93 (aromatic) or 0.98 Å (methyl), and refined in riding mode, with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{aromatic C})$  or  $1.5U_{\text{eq}}(\text{methyl C})$ . H atoms bonded to N atoms were found in

**Table 1**

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

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$N1-H1A \cdots O1$	1.00 (3)	1.79 (4)	2.786 (3)	172 (3)
$N1-H1B \cdots O1^i$	0.91 (4)	1.86 (4)	2.767 (3)	170 (3)
$N1-H1C \cdots O5^{ii}$	0.92 (4)	2.10 (3)	2.840 (3)	137 (3)

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

**Table 2**

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

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$N1-H1A \cdots O1$	0.99 (4)	1.83 (4)	2.823 (4)	174 (3)
$N1-H1B \cdots O1^i$	0.93 (4)	1.78 (4)	2.709 (4)	174 (4)
$N1-H1C \cdots O5^{ii}$	0.90 (4)	2.43 (4)	3.230 (4)	148 (3)

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

difference maps and the N—H distances were refined freely (see Tables 1 and 2), with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N})$ . For (II), the correct orientation of the structure with respect to the polar-axis directions was established by means of the Flack parameter (Flack, 1983).

For both compounds, data collection: *SMART* (Bruker, 2001); cell refinement: *SMART*; data reduction: *SAINT-Plus* (Bruker, 2001); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *PLATON*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD3342). Services for accessing these data are described at the back of the journal.

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