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A 2:1 complex of 2-nitroaniline and picric acid

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In the title molecular complex, $2C_6H_6N_2O_2 \cdot C_6H_3N_3O_7$, an undissociated picric acid molecule is sandwiched between two crystallographically independent nitroaniline molecules. The molecules stack in columns down the *a* axis, with the packing stabilized by N—H···O and C—H···O hydrogen bonds and π–π stacking interactions.

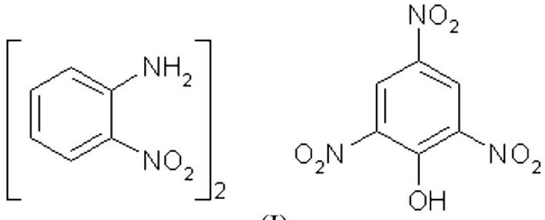
Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.009 Å
R factor = 0.056
wR factor = 0.179
Data-to-parameter ratio = 5.9

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

Picric acid (2,4,6-trinitrophenol) is a strong acid because of resonance stabilization of the phenoxide anion due to the presence of the nitro substituents. It is known to form salts with both aromatic and aliphatic amines (Takayanagi *et al.*, 1996; Thewalt & Bugg, 1972; Anitha *et al.*, 2005). As a part of our ongoing work aimed at understanding the specific N—H···O hydrogen bonds between the picrate anion and the corresponding cation (Saminathan *et al.*, 2005), we attempted to prepare and characterize the 2-nitroanilinium picrate salt. However, the crystal structure determination revealed the title 2:1 nitroaniline:picric acid complex, (I), with no salt formation. Interestingly, the title complex is isomorphous with a similar 2:1 molecular complex of 2-aminobenzoic acid (anthranilic acid) and picric acid (In *et al.*, 1997). In complex (I), the picric acid molecule (PA) is sandwiched between two crystallographically independent 2-nitroaniline (2NA) molecules, as was found in the structure of the anthranilic acid complex.



(I)

The N1 and N3 nitro groups *ortho* to the hydroxyl group deviate from the benzene ring plane by 1.5 (3) and 46.7 (4)°, respectively, with the *para* N2 nitro group subtending an angle of 8.6 (6)°. This tilting of the nitro groups facilitates C—H···O hydrogen bonding with neighbouring molecules. The N4*A* and N4*B* nitro groups of the 2NA molecules also lie close to their benzene ring planes, with dihedral angles of 4.8 (4) and 2.3 (6)°, respectively.

The dihedral angles between the 2NA and PA ring planes are 2.70 (2) and 1.60 (9)°, respectively, for molecules *A* and *B*. Hence the molecules in this complex lie parallel to one another such that columns made up of 2NA*A*–PA–2NA*B*–2NA*A*–PA–2NA*B* repeat units form down the *a* axis. The

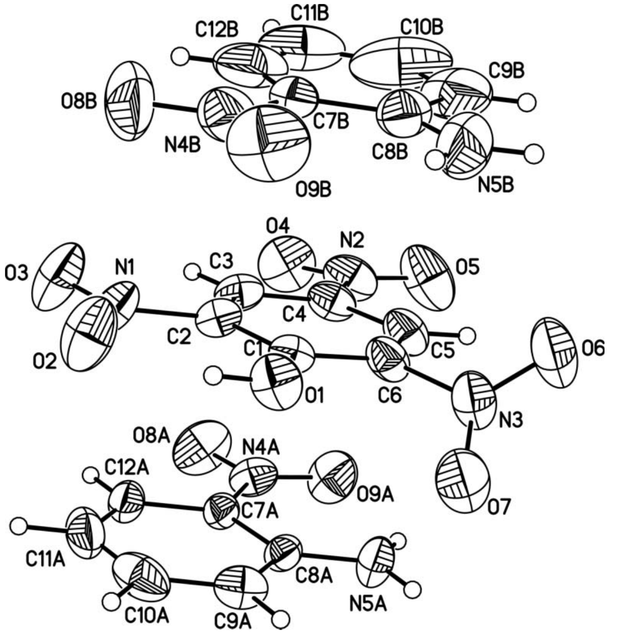


Figure 1
The asymmetric unit of (I), with 30% probability displacement ellipsoids and the atom-numbering scheme.

centroid-to-centroid separations between 2NA*A*–PA [3.603 (3) Å] and 2NA*B*–PA [3.588 (4) Å] indicate π–π interactions between them. The corresponding separation between 2NA*A* and 2NA*B* is 3.695 (4) Å, suggesting a weaker interaction.

Each of the three intramolecular hydrogen bonds found in this complex (Table 1) forms a graph-set motif of $S_1^1(6)$ (Bernstein *et al.*, 1995). Intermolecular N—H···O and C—H···O hydrogen bonds link the molecules of adjacent columns (Fig. 2).

Experimental

The title compound was prepared by mixing equimolar volumes of 2-nitroaniline and picric acid and dissolving them in ethanol. Slow evaporation of the solution resulted in the formation of transparent red prism-shaped single crystals.

Crystal data

$2C_6H_6N_2O_2\cdot C_6H_3N_3O_7$
$M_r = 505.37$
Monoclinic, *Cc*
$a = 10.3644\ (17)$ Å
$b = 15.1394\ (19)$ Å
$c = 14.1042\ (15)$ Å
$\beta = 106.943\ (11)^\circ$
$V = 2117.0\ (5)$ Å^3
$Z = 4$
$D_x = 1.586$ Mg m^{-3}
Cu $K\alpha$ radiation
$\mu = 1.17$ mm^{-1}
$T = 293\ (2)$ K
Prism, red
0.40 × 0.26 × 0.15 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min} = 0.755$, $T_{\max} = 0.871$
2035 measured reflections
1923 independent reflections
1654 reflections with $I > 2\sigma(I)$
$\theta_{\max} = 68.0^\circ$
2 standard reflections every 100 reflections intensity decay: none

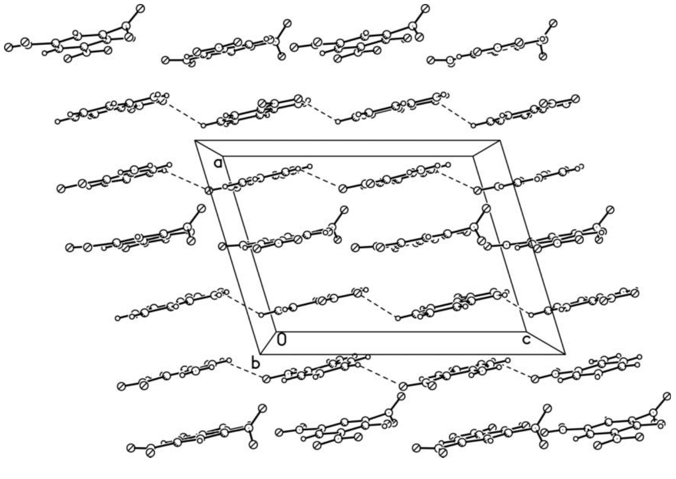


Figure 2
The crystal packing of (I), viewed down the *b* axis. Dashed lines indicate hydrogen bonds.

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.056$
$wR(F^2) = 0.179$
$S = 1.09$
1923 reflections
326 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.1298P)^2 + 0.4588P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.41$ e Å^{-3}
$\Delta\rho_{\min} = -0.26$ e Å^{-3}

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···O2	0.82	1.85	2.547 (6)	142
N5*A*—H5*A*···O9*A*	0.86	2.00	2.610 (7)	128
N5*B*—H5*C*···O9*B*	0.86	2.03	2.635 (12)	127
N5*A*—H5*B*···O4^{i}	0.86	2.32	3.090 (7)	150
N5*B*—H5*D*···O9*A*^{ii}	0.86	2.38	3.100 (8)	142
C5—H5···O8*B*^{iii}	0.93	2.48	3.228 (10)	138
C10*A*—H10*A*···O8*A*^{iv}	0.93	2.57	3.308 (9)	137
C11*B*—H11*B*···O9*B*^{v}	0.93	2.51	3.224 (13)	134
C3—H3···O9*B*^{v}	0.93	2.62	3.272 (9)	128

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

In the absence of significant anomalous dispersion effects, Friedel pairs were averaged. All H atoms were located in difference Fourier maps and refined as riding on their parent atoms, with C—H = 0.93–0.98 Å, N—H = 0.86 Å and O—H = 0.82 Å, and with $U_{\rm iso}$(H) = $1.2U_{\rm eq}$(C,N) or $1.5U_{\rm eq}$(O).

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); 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*.

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