

Picric acid–2,4,6-trichloroaniline (1/1)

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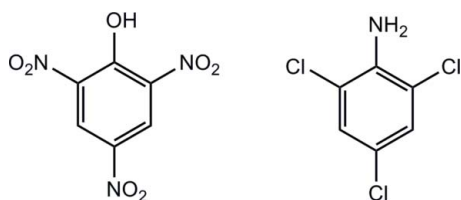
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 Key indicators: single-crystal X-ray study; $T = 298$ K; mean $\sigma(\text{C}-\text{C}) = 0.005$ Å; R factor = 0.058; wR factor = 0.120; data-to-parameter ratio = 13.1.

In the title adduct, $\text{C}_6\text{H}_4\text{Cl}_3\text{N}\cdot\text{C}_6\text{H}_3\text{N}_3\text{O}_7$, the two benzene rings are almost coplanar, with a dihedral angle of 1.19 (1)° and an inter-ring centroid–centroid separation of 4.816 (2) Å. The crystal structure is stabilized by intermolecular $\text{N}-\text{H}\cdots\text{O}_{\text{nitro}}$ hydrogen bonds, giving a chain structure. In addition, there are phenol–nitro $\text{O}-\text{H}\cdots\text{O}$ interactions.

Related literature

The crystal structures of picrate salts and picric acid complexes have been studied to investigate charge-transfer processes, see: Nagata *et al.* (1995); Smith *et al.* (2004). For the crystal structures of picric acid complexes, see: Li (2009); Sivaramkumar *et al.* (2010).



Experimental

Crystal data

 $\text{C}_6\text{H}_4\text{Cl}_3\text{N}\cdot\text{C}_6\text{H}_3\text{N}_3\text{O}_7$
 $M_r = 425.57$

 Orthorhombic, *Pbca*
 $a = 9.2162$ (14) Å

 $b = 10.0174$ (14) Å

 $c = 35.051$ (5) Å

 $V = 3236.0$ (8) Å³
 $Z = 8$

 Mo $K\alpha$ radiation
 $\mu = 0.61$ mm⁻¹
 $T = 298$ K
 $0.16 \times 0.12 \times 0.10$ mm

Data collection

Bruker SMART CCD area-detector diffractometer

Absorption correction: multi-scan

 (*SADABS*; Sheldrick, 1997)

 $T_{\text{min}} = 0.908$, $T_{\text{max}} = 0.941$

 19589 measured reflections
 3186 independent reflections
 2287 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.076$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.058$
 $wR(F^2) = 0.120$
 $S = 1.10$

3186 reflections

244 parameters

2 restraints

H atoms treated by a mixture of independent and constrained refinement

 $\Delta\rho_{\text{max}} = 0.21$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.27$ e Å⁻³
Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{O1}-\text{H1A}\cdots\text{O7}$	0.89 (4)	1.76 (4)	2.546 (4)	145 (4)
$\text{N4}-\text{H4A}\cdots\text{O5}^i$	0.85 (2)	2.39 (2)	3.159 (4)	150 (3)
$\text{N4}-\text{H4B}\cdots\text{O6}^{ii}$	0.84 (2)	2.40 (2)	3.194 (4)	156 (4)

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

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINTE* (Bruker, 1999); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: ZS2097).

References

- Bruker (1999). *SAINTE*. Bruker AXS Inc., Madison, Wisconsin, USA.
 Bruker (2001). *SMART*. Bruker AXS Inc., Madison, Wisconsin, USA.
 Li, Y. (2009). *Acta Cryst.* **E65**, o2566.
 Nagata, H., In, Y., Doi, M., Ishida, T. & Wakahara, A. (1995). *Acta Cryst.* **B51**, 1051–1058.
 Sheldrick, G. M. (1997). *SADABS*. University of Göttingen, Germany.
 Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
 Sivaramkumar, M. S., Velmurugan, R., Sekar, M., Ramesh, P. & Ponnuswamy, M. N. (2010). *Acta Cryst.* **E66**, o1820.
 Smith, G., Wermuth, U. D. & Healy, P. C. (2004). *Acta Cryst.* **E60**, o1800–o1803.

supplementary materials

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Comment

2,4,6-Trinitrophenol (picric acid), was primarily used to manufacture explosives and is also used as an intermediate in dye manufacturing. The crystal structures of a large number of picrate salts and picric acid complexes have been studied to determine the conformational features and to understand charge transfer processes (Li *et al.*, 2009; Nagata *et al.*, 1995; Sivaramkumar *et al.*, 2010, Smith *et al.*, 2004). We herein report the 1:1 cocrystal structure of 2,4,6-trichloroaniline and picric acid $C_6H_4Cl_3N \cdot C_6H_3N_3O_7$ (I) (Fig. 1). In the title adduct, the two phenyl rings are almost coplanar with a dihedral angle of $1.19(1)^\circ$ and an inter-ring centroid separation of $4.816(2) \text{ \AA}$. The crystal structure is stabilized by intermolecular $N-H \cdots O_{\text{nitro}}$ hydrogen bonds giving a one-dimensional chain structure and in addition, intramolecular $N-H \cdots Cl$ and phenol $O-H \cdots O(\text{nitro})$ interactions are observed (Table 1).

Experimental

2,4,6-Trichloroaniline (0.19 g, 1.0 mmol) and picric acid (0.23 g, 1.0 mmol) were dissolved in MeOH- CH_2Cl_2 (3:1) and the mixture was kept at room temperature for one week. Red crystals suitable for single-crystal X-ray diffraction were obtained.

Refinement

The O- and N-bound H atoms were located in a difference map and refined isotropically. The remaining H atoms were positioned geometrically ($C-H = 0.93 \text{ \AA}$) and allowed to ride on their parent atoms, with $U_{\text{iso}}(H) = 1.2U_{\text{eq}}(C)$.

Figures

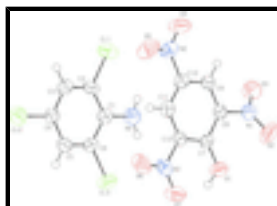


Fig. 1. The title compound with the atom-numbering scheme, with displacement ellipsoids drawn at the 30% probability level.

Picric acid-2,4,6-trichloroaniline (1/1)

Crystal data

$C_6H_4Cl_3N \cdot C_6H_3N_3O_7$

$M_r = 425.57$

Orthorhombic, *Pbca*

Hall symbol: -P 2ac 2ab

$F(000) = 1712$

$D_x = 1.747 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 1781 reflections

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$a = 9.2162 (14) \text{ \AA}$	$\theta = 2.5\text{--}19.2^\circ$
$b = 10.0174 (14) \text{ \AA}$	$\mu = 0.61 \text{ mm}^{-1}$
$c = 35.051 (5) \text{ \AA}$	$T = 298 \text{ K}$
$V = 3236.0 (8) \text{ \AA}^3$	Block, red
$Z = 8$	$0.16 \times 0.12 \times 0.10 \text{ mm}$

Data collection

Bruker SMART CCD area-detector diffractometer	3186 independent reflections
Radiation source: fine-focus sealed tube graphite	2287 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{\text{int}} = 0.076$
Absorption correction: multi-scan (SADABS; Sheldrick, 1997)	$\theta_{\text{max}} = 26.0^\circ$, $\theta_{\text{min}} = 2.3^\circ$
$T_{\text{min}} = 0.908$, $T_{\text{max}} = 0.941$	$h = -11 \rightarrow 11$
19589 measured reflections	$k = -12 \rightarrow 10$
	$l = -41 \rightarrow 43$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.058$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.120$	H atoms treated by a mixture of independent and constrained refinement
$S = 1.10$	$w = 1/[\sigma^2(F_o^2) + (0.0381P)^2 + 1.3007P]$
3186 reflections	where $P = (F_o^2 + 2F_c^2)/3$
244 parameters	$(\Delta/\sigma)_{\text{max}} = 0.001$
2 restraints	$\Delta\rho_{\text{max}} = 0.21 \text{ e \AA}^{-3}$
	$\Delta\rho_{\text{min}} = -0.27 \text{ e \AA}^{-3}$

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s 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 $F^2 > \sigma(F^2)$ 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)

x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
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C1	0.4507 (4)	0.4557 (3)	0.57639 (9)	0.0373 (8)
C2	0.5792 (3)	0.4955 (3)	0.55888 (10)	0.0396 (8)
C3	0.5881 (4)	0.6056 (4)	0.53560 (10)	0.0422 (9)
H3	0.6760	0.6295	0.5245	0.051*
C4	0.4651 (4)	0.6801 (3)	0.52893 (9)	0.0390 (8)
C5	0.3352 (4)	0.6456 (3)	0.54541 (10)	0.0415 (9)
H5	0.2523	0.6960	0.5408	0.050*
C6	0.3293 (3)	0.5361 (3)	0.56874 (9)	0.0375 (8)
C7	0.4085 (3)	0.4501 (3)	0.70238 (9)	0.0325 (7)
C8	0.5325 (3)	0.3724 (3)	0.70914 (9)	0.0343 (8)
C9	0.6640 (3)	0.3992 (3)	0.69253 (9)	0.0360 (8)
H9	0.7437	0.3447	0.6972	0.043*
C10	0.6760 (4)	0.5082 (3)	0.66889 (9)	0.0379 (8)
C11	0.5597 (4)	0.5899 (3)	0.66136 (9)	0.0379 (8)
H11	0.5694	0.6642	0.6456	0.046*
C12	0.4278 (3)	0.5584 (3)	0.67784 (9)	0.0324 (8)
C11	0.73498 (10)	0.40282 (11)	0.56753 (3)	0.0607 (3)
C12	0.47396 (11)	0.81912 (11)	0.49911 (3)	0.0592 (3)
C13	0.16542 (10)	0.49502 (10)	0.59030 (3)	0.0560 (3)
N1	0.5268 (3)	0.2597 (3)	0.73550 (9)	0.0478 (8)
N2	0.8171 (3)	0.5390 (4)	0.65186 (9)	0.0507 (8)
N3	0.3064 (3)	0.6474 (3)	0.66942 (9)	0.0452 (8)
N4	0.4439 (4)	0.3486 (3)	0.60078 (10)	0.0520 (8)
H4A	0.512 (3)	0.290 (3)	0.6009 (11)	0.062*
H4B	0.359 (2)	0.332 (4)	0.6079 (11)	0.062*
O1	0.2826 (3)	0.4170 (2)	0.71812 (7)	0.0494 (7)
H1A	0.218 (5)	0.479 (4)	0.7114 (11)	0.074*
O2	0.4487 (4)	0.2669 (3)	0.76291 (9)	0.0979 (13)
O3	0.6055 (3)	0.1642 (3)	0.72928 (8)	0.0643 (8)
O4	0.9144 (3)	0.4573 (3)	0.65587 (9)	0.0711 (9)
O5	0.8294 (3)	0.6445 (3)	0.63491 (9)	0.0726 (9)
O6	0.3275 (3)	0.7422 (3)	0.64860 (8)	0.0672 (8)
O7	0.1878 (3)	0.6247 (3)	0.68450 (8)	0.0602 (8)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.041 (2)	0.035 (2)	0.0352 (19)	-0.0034 (16)	0.0003 (15)	-0.0064 (15)
C2	0.0318 (19)	0.042 (2)	0.045 (2)	0.0053 (16)	-0.0046 (15)	-0.0061 (17)
C3	0.0369 (19)	0.045 (2)	0.045 (2)	-0.0084 (17)	0.0048 (16)	-0.0036 (17)
C4	0.0398 (19)	0.037 (2)	0.040 (2)	-0.0048 (17)	-0.0010 (15)	0.0042 (16)
C5	0.0319 (18)	0.045 (2)	0.047 (2)	0.0040 (16)	-0.0042 (16)	0.0025 (17)
C6	0.0333 (18)	0.040 (2)	0.0395 (19)	-0.0019 (16)	0.0051 (15)	-0.0023 (16)
C7	0.0329 (18)	0.0345 (19)	0.0299 (17)	-0.0024 (15)	0.0016 (14)	-0.0052 (14)
C8	0.0383 (18)	0.0281 (19)	0.0365 (18)	0.0010 (15)	0.0009 (15)	0.0055 (14)
C9	0.0330 (17)	0.037 (2)	0.0377 (18)	0.0034 (15)	-0.0012 (15)	-0.0017 (15)
C10	0.0355 (19)	0.039 (2)	0.0392 (19)	-0.0075 (16)	0.0032 (15)	-0.0038 (16)
C11	0.044 (2)	0.032 (2)	0.0385 (19)	-0.0068 (16)	-0.0021 (15)	0.0007 (15)

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C12	0.0355 (18)	0.0322 (19)	0.0296 (17)	-0.0002 (15)	-0.0040 (14)	-0.0033 (14)
C11	0.0420 (5)	0.0648 (7)	0.0754 (7)	0.0154 (5)	-0.0015 (5)	-0.0019 (5)
C12	0.0527 (6)	0.0609 (7)	0.0641 (6)	-0.0095 (5)	-0.0010 (5)	0.0236 (5)
C13	0.0402 (5)	0.0565 (6)	0.0712 (7)	-0.0038 (5)	0.0176 (5)	0.0094 (5)
N1	0.0449 (18)	0.050 (2)	0.0481 (19)	0.0053 (16)	0.0021 (15)	0.0120 (15)
N2	0.0446 (19)	0.052 (2)	0.056 (2)	-0.0106 (17)	0.0097 (16)	-0.0038 (17)
N3	0.0457 (19)	0.041 (2)	0.0492 (19)	0.0058 (15)	-0.0081 (15)	0.0014 (15)
N4	0.049 (2)	0.045 (2)	0.062 (2)	0.0031 (16)	0.0048 (18)	0.0101 (17)
O1	0.0370 (14)	0.0485 (17)	0.0626 (17)	0.0027 (12)	0.0115 (12)	0.0103 (13)
O2	0.105 (3)	0.114 (3)	0.075 (2)	0.052 (2)	0.051 (2)	0.0556 (19)
O3	0.0714 (19)	0.0479 (18)	0.073 (2)	0.0191 (15)	0.0092 (15)	0.0161 (14)
O4	0.0390 (16)	0.079 (2)	0.095 (2)	0.0047 (16)	0.0162 (15)	0.0066 (18)
O5	0.070 (2)	0.0587 (19)	0.089 (2)	-0.0161 (16)	0.0300 (16)	0.0133 (17)
O6	0.0654 (19)	0.0548 (18)	0.081 (2)	0.0084 (15)	-0.0129 (15)	0.0285 (16)
O7	0.0393 (15)	0.0554 (18)	0.086 (2)	0.0101 (13)	0.0032 (14)	0.0066 (15)

Geometric parameters (Å, °)

C1—N4	1.373 (4)	C9—C10	1.374 (4)
C1—C2	1.392 (5)	C9—H9	0.9300
C1—C6	1.404 (5)	C10—C11	1.375 (5)
C2—C3	1.374 (5)	C10—N2	1.464 (4)
C2—C11	1.736 (3)	C11—C12	1.382 (4)
C3—C4	1.377 (5)	C11—H11	0.9300
C3—H3	0.9300	C12—N3	1.461 (4)
C4—C5	1.373 (4)	N1—O2	1.202 (4)
C4—C12	1.743 (3)	N1—O3	1.221 (4)
C5—C6	1.370 (4)	N2—O5	1.218 (4)
C5—H5	0.9300	N2—O4	1.222 (4)
C6—C13	1.739 (3)	N3—O6	1.213 (4)
C7—O1	1.327 (4)	N3—O7	1.235 (4)
C7—C12	1.396 (4)	N4—H4A	0.854 (18)
C7—C8	1.404 (4)	N4—H4B	0.842 (18)
C8—C9	1.371 (4)	O1—H1A	0.89 (4)
C8—N1	1.460 (4)		
N4—C1—C2	122.5 (3)	C8—C9—H9	120.6
N4—C1—C6	122.0 (3)	C10—C9—H9	120.6
C2—C1—C6	115.4 (3)	C9—C10—C11	121.7 (3)
C3—C2—C1	122.8 (3)	C9—C10—N2	119.0 (3)
C3—C2—C11	118.9 (3)	C11—C10—N2	119.3 (3)
C1—C2—C11	118.3 (3)	C10—C11—C12	118.0 (3)
C2—C3—C4	119.1 (3)	C10—C11—H11	121.0
C2—C3—H3	120.4	C12—C11—H11	121.0
C4—C3—H3	120.4	C11—C12—C7	123.2 (3)
C5—C4—C3	120.7 (3)	C11—C12—N3	116.7 (3)
C5—C4—C12	119.6 (3)	C7—C12—N3	120.0 (3)
C3—C4—C12	119.8 (3)	O2—N1—O3	123.0 (3)
C6—C5—C4	119.1 (3)	O2—N1—C8	118.8 (3)
C6—C5—H5	120.4	O3—N1—C8	118.1 (3)

C4—C5—H5	120.4	O5—N2—O4	124.7 (3)
C5—C6—C1	122.8 (3)	O5—N2—C10	117.7 (3)
C5—C6—C13	118.9 (3)	O4—N2—C10	117.6 (3)
C1—C6—C13	118.3 (3)	O6—N3—O7	122.9 (3)
O1—C7—C12	124.2 (3)	O6—N3—C12	118.4 (3)
O1—C7—C8	120.2 (3)	O7—N3—C12	118.6 (3)
C12—C7—C8	115.5 (3)	C1—N4—H4A	120 (3)
C9—C8—C7	122.6 (3)	C1—N4—H4B	112 (3)
C9—C8—N1	116.9 (3)	H4A—N4—H4B	123 (4)
C7—C8—N1	120.4 (3)	C7—O1—H1A	108 (3)
C8—C9—C10	118.9 (3)		
N4—C1—C2—C3	-177.4 (3)	C8—C9—C10—C11	-0.4 (5)
C6—C1—C2—C3	-0.1 (5)	C8—C9—C10—N2	178.5 (3)
N4—C1—C2—C11	1.6 (5)	C9—C10—C11—C12	-1.0 (5)
C6—C1—C2—C11	179.0 (2)	N2—C10—C11—C12	-180.0 (3)
C1—C2—C3—C4	-0.4 (5)	C10—C11—C12—C7	1.7 (5)
C11—C2—C3—C4	-179.4 (3)	C10—C11—C12—N3	179.8 (3)
C2—C3—C4—C5	0.4 (5)	O1—C7—C12—C11	-179.0 (3)
C2—C3—C4—C12	-179.4 (3)	C8—C7—C12—C11	-0.8 (5)
C3—C4—C5—C6	0.2 (5)	O1—C7—C12—N3	2.9 (5)
C12—C4—C5—C6	179.9 (3)	C8—C7—C12—N3	-178.8 (3)
C4—C5—C6—C1	-0.7 (5)	C9—C8—N1—O2	144.8 (4)
C4—C5—C6—C13	178.7 (3)	C7—C8—N1—O2	-33.6 (5)
N4—C1—C6—C5	178.0 (3)	C9—C8—N1—O3	-32.8 (5)
C2—C1—C6—C5	0.6 (5)	C7—C8—N1—O3	148.8 (3)
N4—C1—C6—C13	-1.4 (5)	C9—C10—N2—O5	-171.2 (3)
C2—C1—C6—C13	-178.8 (2)	C11—C10—N2—O5	7.8 (5)
O1—C7—C8—C9	177.6 (3)	C9—C10—N2—O4	8.4 (5)
C12—C7—C8—C9	-0.7 (5)	C11—C10—N2—O4	-172.6 (3)
O1—C7—C8—N1	-4.1 (5)	C11—C12—N3—O6	0.4 (4)
C12—C7—C8—N1	177.6 (3)	C7—C12—N3—O6	178.5 (3)
C7—C8—C9—C10	1.4 (5)	C11—C12—N3—O7	-178.0 (3)
N1—C8—C9—C10	-177.0 (3)	C7—C12—N3—O7	0.2 (5)

Hydrogen-bond geometry (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O1—H1A...O7	0.89 (4)	1.76 (4)	2.546 (4)	145 (4)
N4—H4A...C11	0.85 (2)	2.62 (4)	2.975 (3)	106 (3)
N4—H4A...O5 ⁱ	0.85 (2)	2.39 (2)	3.159 (4)	150 (3)
N4—H4B...C13	0.84 (2)	2.49 (3)	2.979 (3)	118 (3)
N4—H4B...O6 ⁱⁱ	0.84 (2)	2.40 (2)	3.194 (4)	156 (4)

Symmetry codes: (i) $-x+3/2, y-1/2, z$; (ii) $-x+1/2, y-1/2, z$.

Fig. 1

