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

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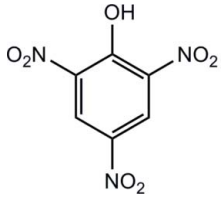
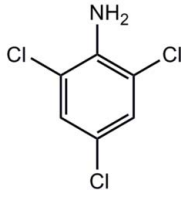
Key indicators: single-crystal X-ray study; T = 298 K; mean σ(C–C) = 0.005 Å; R factor = 0.058; wR factor = 0.120; data-to-parameter ratio = 13.1.

In the title adduct, $C_6H_4Cl_3N\cdot C_6H_3N_3O_7$, 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 N—H···O_{nitro} hydrogen bonds, giving a chain structure. In addition, there are phenol–nitro O—H···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

$C_6H_4Cl_3N\cdot C_6H_3N_3O_7$
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) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 0.61 mm^{-1}
T = 298 K
0.16 × 0.12 × 0.10 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1997)
T_{min} = 0.908, T_{max} = 0.941
19589 measured reflections
3186 independent reflections
2287 reflections with $I > 2\sigma(I)$
R_{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
$\Delta\rho_{max}$ = 0.21 e Å^{-3}
$\Delta\rho_{min}$ = −0.27 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1A···O7	0.89 (4)	1.76 (4)	2.546 (4)	145 (4)
N4—H4A···O5^{i}	0.85 (2)	2.39 (2)	3.159 (4)	150 (3)
N4—H4B···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: *SAINT* (Bruker, 1999); data reduction: *SAINT*; 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).

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supporting information

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Wan-Qiang Wang

S1. 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 $C_6H_4Cl_3N$. $C_6H_3N_3O_7$ (I) (Fig. 1). In the title adduct, the two phenyl rings are almost coplanar with a dihedral angle of 1.19 (1)° and an inter-ring centroid separation of 4.816 (2) Å. The crystal structure is stabilized by intermolecular N—H···O_{nitro} hydrogen bonds giving a one-dimensional chain structure and in addition, intramolecular N—H···Cl and phenol O—H···O(nitro) interactions are observed (Table 1).

S2. 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.

S3. 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 Å) and allowed to ride on their parent atoms, with U_{iso}(H) = 1.2U_{eq}(C).

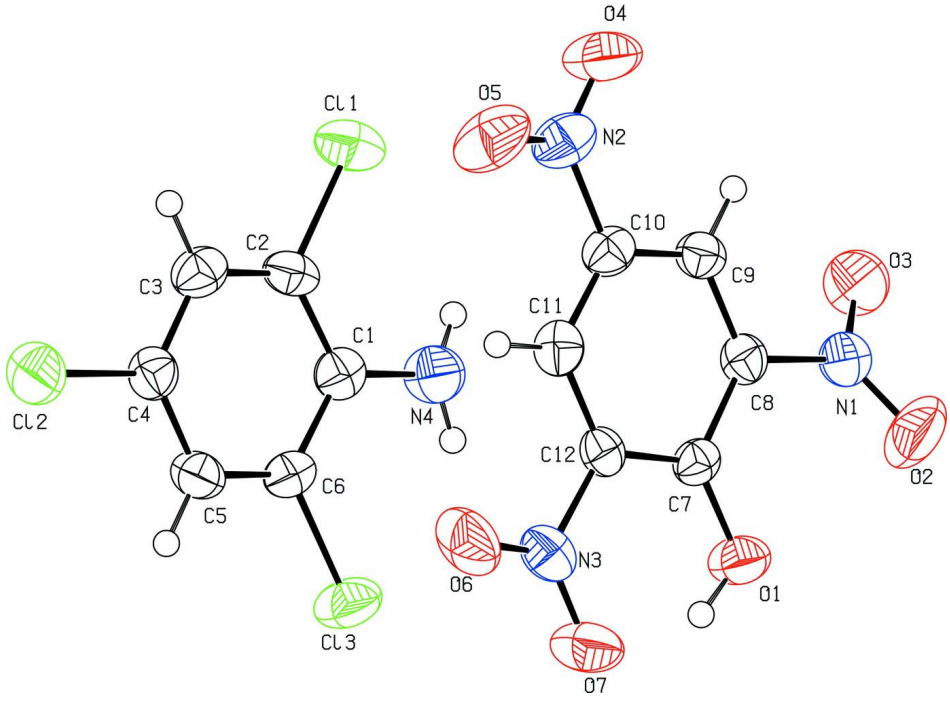

Figure 1

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

$C_6H_4Cl_3N·C_6H_3N_3O_7$
$M_r = 425.57$
Orthorhombic, *Pbca*
Hall symbol: -P 2ac 2ab
$a = 9.2162$ (14) Å
$b = 10.0174$ (14) Å
$c = 35.051$ (5) Å
$V = 3236.0$ (8) Å^3
$Z = 8$
$F(000) = 1712$
$D_x = 1.747$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 1781 reflections
$\theta = 2.5$–19.2°
$\mu = 0.61$ mm^{-1}
$T = 298$ K
Block, red
0.16 × 0.12 × 0.10 mm

Data collection

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

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.058$
$wR(F^2) = 0.120$
$S = 1.10$
3186 reflections
244 parameters
2 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0381P)^2 + 1.3007P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.21$ e Å^{-3}
$\Delta\rho_{min} = -0.27$ e Å^{-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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
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)
Cl1	0.73498 (10)	0.40282 (11)	0.56753 (3)	0.0607 (3)
Cl2	0.47396 (11)	0.81912 (11)	0.49911 (3)	0.0592 (3)
Cl3	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 (Å²)

	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)
C12	0.0355 (18)	0.0322 (19)	0.0296 (17)	−0.0002 (15)	−0.0040 (14)	−0.0033 (14)
Cl1	0.0420 (5)	0.0648 (7)	0.0754 (7)	0.0154 (5)	−0.0015 (5)	−0.0019 (5)
Cl2	0.0527 (6)	0.0609 (7)	0.0641 (6)	−0.0095 (5)	−0.0010 (5)	0.0236 (5)
Cl3	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, º)

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—Cl1	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—Cl2	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—Cl3	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—Cl1	118.9 (3)	C11—C10—N2	119.3 (3)
C1—C2—Cl1	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—Cl2	119.6 (3)	C7—C12—N3	120.0 (3)
C3—C4—Cl2	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—Cl3	118.9 (3)	O4—N2—C10	117.6 (3)
C1—C6—Cl3	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—Cl1	1.6 (5)	C9—C10—C11—C12	−1.0 (5)
C6—C1—C2—Cl1	179.0 (2)	N2—C10—C11—C12	−180.0 (3)
C1—C2—C3—C4	−0.4 (5)	C10—C11—C12—C7	1.7 (5)
Cl1—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—Cl2	−179.4 (3)	C8—C7—C12—C11	−0.8 (5)
C3—C4—C5—C6	0.2 (5)	O1—C7—C12—N3	2.9 (5)
Cl2—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—Cl3	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—Cl3	−1.4 (5)	C9—C10—N2—O5	−171.2 (3)
C2—C1—C6—Cl3	−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, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1*A*···O7	0.89 (4)	1.76 (4)	2.546 (4)	145 (4)
N4—H4*A*···Cl1	0.85 (2)	2.62 (4)	2.975 (3)	106 (3)
N4—H4*A*···O5^{i}	0.85 (2)	2.39 (2)	3.159 (4)	150 (3)
N4—H4*B*···Cl3	0.84 (2)	2.49 (3)	2.979 (3)	118 (3)
N4—H4*B*···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*.