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Indole–picric acid (1/1)

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Key indicators

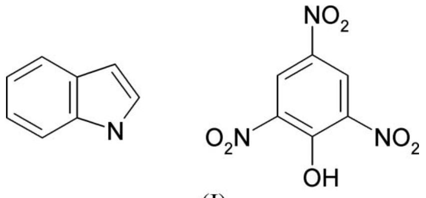
Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.009 Å
Disorder in main residue
R factor = 0.069
wR factor = 0.271
Data-to-parameter ratio = 11.0

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

In the title molecular complex, $C_8H_7N\cdot C_6H_3N_3O_7$, the picric acid molecule is disordered, corresponding to a rotation about one H—C···C—N axis and resulting in two sites for the hydroxyl group. In the crystal structure, the indole and picric acid molecules are stacked in columns parallel to the *b* axis with significant π–π interactions. In addition, intermolecular hydrogen bonds link molecules in a zigzag fashion along the *a* axis, giving ring patterns with graph-set motifs $R_2^2(8)$ and $R_2^2(7)$.

Comment

Picric acid acts not only as an acceptor forming various π-stacking arrangements but also as an acid forming salts through electrostatic or hydrogen-bonding interactions (In *et al.*, 1997; Shriner *et al.*, 1980). Indole derivatives form donor–acceptor (charge-transfer) complexes with a variety of aromatic electron acceptors (Gartland *et al.*, 1974). The indole molecule, with a lone pair of electrons on the N atom, does not act like a base as do amines or anilines, because the lone pair is delocalized and contributes to the aromatic system. Hence, very strong acids are needed to protonate a substantial amount of indole. Our attempts to co-crystallize picric acid and indole resulted in the formation of the 1:1 complex (I) and not the salt form, as expected.



(I)

The asymmetric unit of (I) is shown in Fig. 1. The positional disorder of the hydroxyl group observed in the picric acid molecule is similar to that in the structure of the indole-3-acetic acid–picric acid complex (Nagata *et al.*, 1995). The essentially planar indole group and the aromatic ring of the picric acid are almost parallel to each other with a dihedral angle of 2.47 (1)° and are packed alternately in columns along the *b* axis. This arrangement gives significant π–π stacking interactions with a $Cg1\cdots Cg2(1-x, \frac{1}{2}+y, \frac{1}{2}-x)$ distance of 3.507 (3) Å (where *Cg*1 and *Cg*2 are the centroids defined by the rings N4/C7–C9/C14 and C1–C6, respectively) and a perpendicular distance of 3.35 Å.

The three nitro groups of the picric acid molecule are oriented at angles of 8.2 (4) (O2/N1/O3), 8.1 (6) (O4/N2/O5) and 1.6 (8)° (O6/N3/O7) to the benzene ring. These values,

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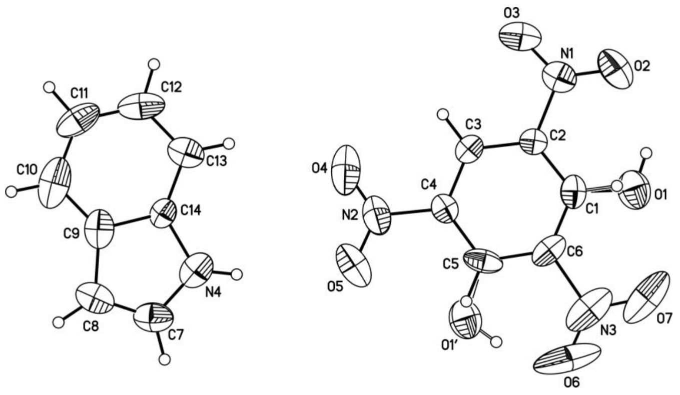

Figure 1
The asymmetric unit of (I), showing 30% probability displacement ellipsoids with the atom-numbering scheme. Both disorder components are shown.

two essentially equal to each other and one showing the nitro group to be almost in the plane of the benzene ring, may explain why the rotational disorder is about the C6···C3 axis so that both disorder components of the hydroxyl group of at positions C1 and C-5 have similar environments. The C—N distances show varying lengths, with C6—N3 having more single bond character (see Table 1). The C7—N4 and C14—N4 bond lengths in the indole molecule show clear bond fixation, indicating the absence of electron delocalization within the pyrole ring.

In the crystal structure, picric acid and indole molecules are linked by N—H···O and C—H···O hydrogen bonds to form chains of alternating $R^2_2(8)$ and $R^2_2(7)$ rings (Bernstein *et al.*, 1995) propagating in the *a*-axis direction (Table 2 and Fig. 2). In addition, intramolecular O1—H1···O2 and O1′—H1′···O6 hydrogen bonds form six-membered rings, both with a graph-set motif of *S*(6).

Experimental

The title compound was prepared by dissolving equimolar amounts (1:1) of picric acid and indole in ethanol. Slow evaporation of the solution resulted in the formation of transparent red needle-shaped single crystals.

Crystal data

$C_8H_7N{\cdot}C_6H_3N_3O_7$
M_r = 346.26
Monoclinic, $P2_1/c$
a = 13.4586 (19) Å
b = 6.723 (3) Å
c = 16.158 (4) Å
β = 94.912 (19)°
V = 1456.7 (8) Å^3

Z = 4
D_x = 1.579 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 0.13 mm^{-1}
T = 293 (2) K
Needle, red
0.4 × 0.2 × 0.2 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min}$ = 0.989, $T_{\max}$ = 1.000
2659 measured reflections

2546 independent reflections
816 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.015
$\theta_{\max}$ = 25.0°
2 standard reflections every 100 reflections intensity decay: 1%

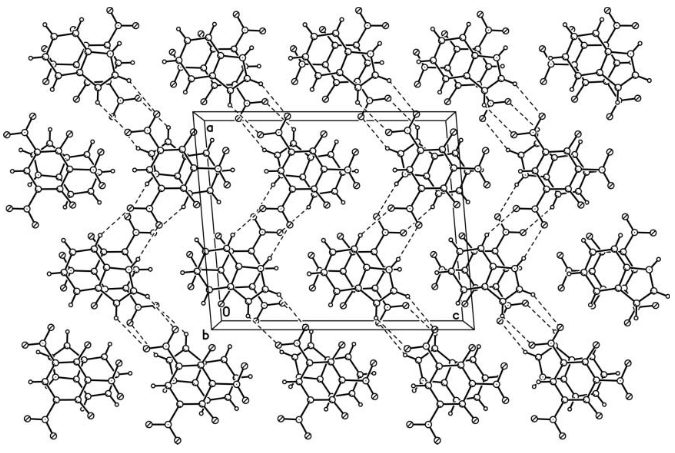

Figure 2
Part of the crystal structure of (I), with hydrogen bonds shown as dashed lines.

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.069
$wR(F^2)$ = 0.271
S = 0.91
2546 reflections
231 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.1531P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max}$ = 0.40 e Å^{-3}
$\Delta\rho_{\min}$ = −0.24 e Å^{-3}

Table 1
Selected bond lengths (Å).

N1—C2	1.480 (6)	C5—O1′	1.298 (7)
N2—C4	1.450 (6)	N4—C7	1.353 (7)
N3—C6	1.514 (7)	N4—C14	1.400 (6)
C1—O1	1.286 (7)		

Table 2
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N4—H4···O5	0.86	2.50	3.346 (7)	168
C13—H13···O4	0.93	2.56	3.423 (8)	155
C7—H7···O2$^{\rm i}$	0.93	2.69	3.524 (8)	150
C8—H8···O3$^{\rm i}$	0.93	2.70	3.391 (7)	132
O1—H1···O2	0.82	1.90	2.590 (6)	142
O1′—H1′···O6	0.82	1.53	2.302 (6)	156

Symmetry code: (i) $x - 1, y, z$.

The hydroxyl group of the picric acid molecule is disordered over two sites at positions C1 and C5, as are the H atoms bonded to atoms C1 and C5. The relative occupancies of all disordered atoms were initially refined but were fixed at 0.5 in the final cycles of refinement. All H atoms were located in difference Fourier maps, and then refined as riding on their parent atoms, with C—H = 0.93 Å, O—H = 0.82 Å and N—H = 0.86 Å, and with $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C,N) and 1.5$U_{\rm eq}$(O). The crystal used was very small and diffracted very poorly, resulting in a structure with lower than normal precision, as reflected in the higher than normal weighted *R* factor of 0.271 and the very low proportion of significant observed data.

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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