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4,6-Dinitropyrogallol

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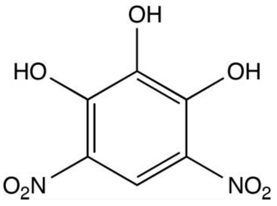
Key indicators: single-crystal X-ray study; T = 200 K; mean σ(C–C) = 0.002 Å; R factor = 0.031; wR factor = 0.089; data-to-parameter ratio = 10.2.

In the title molecule, $C_6H_4N_2O_7$, the two nitro groups are tilted with respect to the aromatic ring by 11.2 (1) and 10.9 (1)°. All three hydroxy groups are involved in the formation of bifurcated intra- and intermolecular O—H$\cdots$O hydrogen bonds. The crystal packing exhibits short O$\cdots$O distances of 2.823 (2) Å between two O atoms of the nitro groups.

Related literature

The synthesis of the title compound has recently been reported by Merten *et al.* (2012). The importance of hydrogen bonding, π stacking and donor–acceptor interactions in solid-state structures and in solution has been reviewed by Schneider (2009). The crystal structure of dinitrophloroglucinol, a constitutional isomer of the title compound, has been described by Schweitzer *et al.* (2008). H atoms were treated as recommended by Müller *et al.* (2006).



Experimental

Crystal data

$C_6H_4N_2O_7$
M_r = 216.11
Monoclinic, $P2_1/c$
a = 6.7612 (14) Å
b = 10.878 (2) Å
c = 10.297 (2) Å
β = 92.75 (3)°
V = 756.5 (3) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.18 mm^{-1}
T = 200 K
0.60 × 0.22 × 0.20 mm

Data collection

Stoe IPDS image plate diffractometer
5824 measured reflections
1488 independent reflections
1326 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.059

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.031
$wR(F^2)$ = 0.089
S = 1.06
1488 reflections
146 parameters
3 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\rm max}$ = 0.31 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.23 e Å^{-3}

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O2—H2O$\cdots$O3	0.85 (1)	2.14 (2)	2.6467 (14)	118 (2)
O2—H2O$\cdots$O4$^{\rm i}$	0.85 (1)	2.27 (2)	2.9531 (14)	138 (2)
O1—H1O$\cdots$O6	0.86 (2)	1.91 (2)	2.6359 (15)	141 (2)
O1—H1O$\cdots$O6$^{\rm ii}$	0.86 (2)	2.46 (2)	3.1361 (15)	137 (2)
O3—H3O$\cdots$O4	0.83 (2)	1.97 (2)	2.6357 (14)	137 (2)
O3—H3O$\cdots$O7$^{\rm iii}$	0.83 (2)	2.19 (2)	2.7658 (15)	127 (2)

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

Data collection: *IPDS Software* (Stoe & Cie, 1997); cell refinement: *IPDS Software*; data reduction: *IPDS Software*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 2011); software used to prepare material for publication: *SHELXL97*.

The authors thank Dr Volker Huch (Universität des Saarlandes) for the collection of the data set.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CV5241).

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supplementary materials

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Comment

As expected, the aromatic C_6-ring is planar (the positions of the six C atoms deviate from the mean plane by 0.0025 (8)–0.0196 (8) Å). The C_6-ring and the two nitro groups are also approximately coplanar, allowing significant π-delocalization. In the extended hydrogen bonding network all three phenolic hydroxy groups act as hydrogen donors and the nitro groups as hydrogen acceptors. The O atoms O1 and O6 of two neighbouring molecules form a planar, four-membered O1···O6···O1′···O6′ ring with two bifurcated hydrogen bonds. Remarkably, the O6···O6′ distance of 2.823 (2) Å (*i.e.* one of the diagonal of the corresponding parallelogram) is somewhat shorter than the sum of the van der Waals radii, although no direct hydrogen bond between these two atoms is operative. Some intermolecular C···C and C···O distances (C1···C1′: 3.279 Å, C5···O2": 3.046 Å) are slightly shorter than the sum of the van der Waals radii and may be interpreted in terms of π-stacking or weak donor–acceptor interactions.

Experimental

The title compound has been prepared by nitration of pyrogallol-triacetate. ^{1}H NMR ([D$_6$]acetone): δ (p.p.m.) = 8.51. ^{13}C NMR ([D$_6$]acetone): δ (p.p.m.) = 114.4, 128.7, 136.6, 148.8. Elemental analysis calculated for $C_6H_4N_2O_7$ (%): C 33.35, H 1.87, N 12.96; found (%): C 33.19, H 2.24, N 12.83. Single crystals were obtained directly from the reaction mixture at 278 K.

Refinement

All non-hydrogen atoms were refined using anisotropic displacement parameters. H atoms were treated as recommended by Müller *et al.* (2006). A riding model was used for the C-bonded H5. The positional parameters of the O-bonded H1O, H2O and H3O were refined using isotropic displacement parameters which were set to $1.5U_{eq}$ of the pivot atom. In addition, a restraint of 0.84 Å was used for the O—H distances.

Computing details

Data collection: *IPDS Software* (Stoe & Cie, 1997); cell refinement: *IPDS Software* (Stoe & Cie, 1997); data reduction: *IPDS Software* (Stoe & Cie, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 2011); software used to prepare material for publication: *SHELXL97* (Sheldrick, 2008).

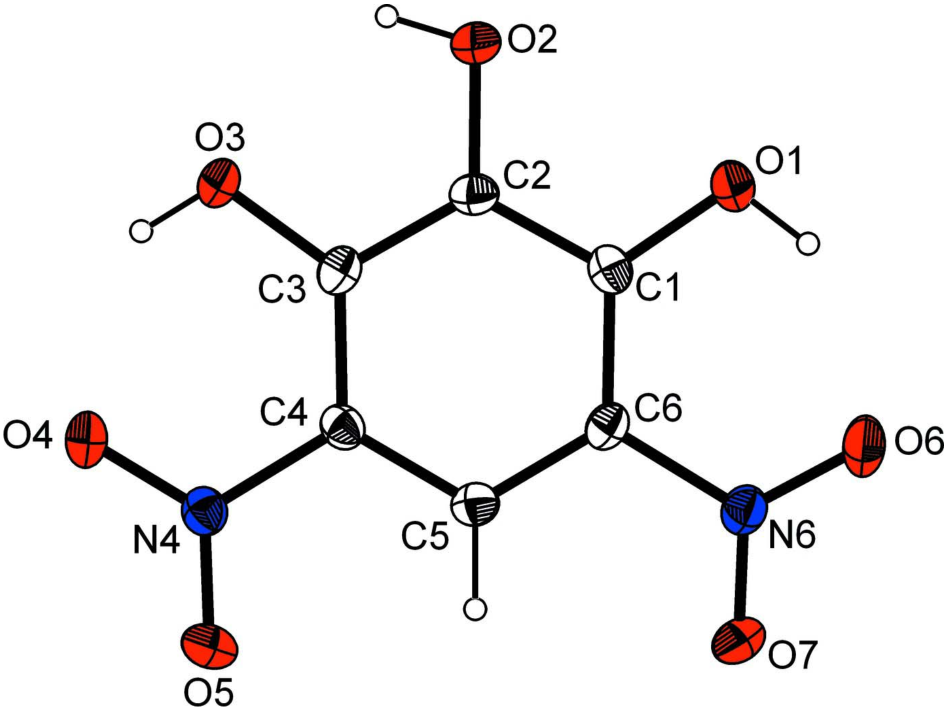

Figure 1

Molecular structure of the title compound. Displacement ellipsoids are drawn at the 50% probability level.

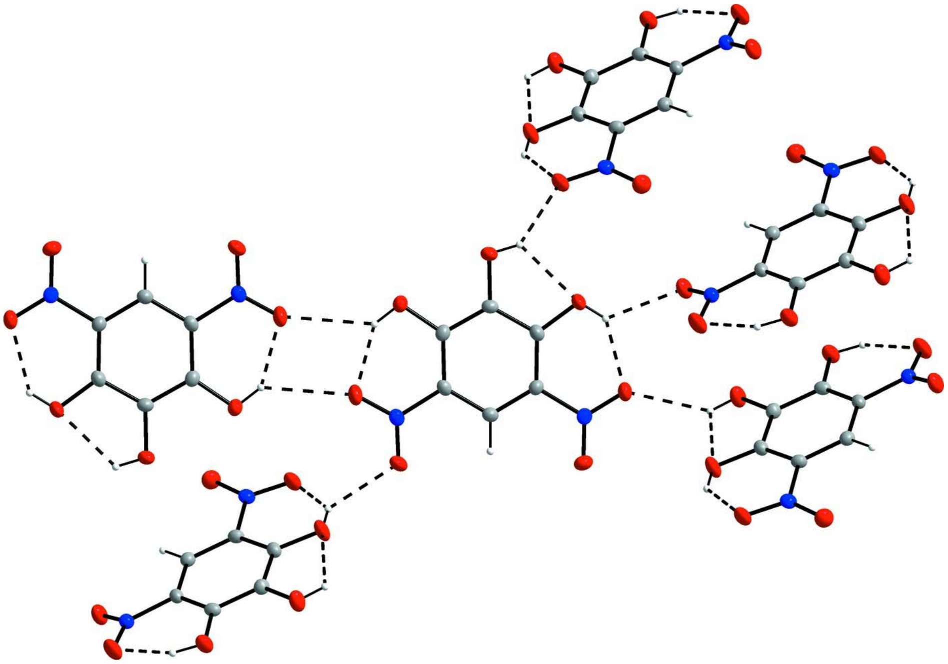

Figure 2

Section of the hydrogen bonding network, showing bifurcated hydrogen bonds for all three hydroxy groups (displacement ellipsoids are drawn at the 50% probability level).

4,6-Dinitrobenzene-1,2,3-triol

Crystal data

$C_6H_4N_2O_7$	$Z = 4$
$M_r = 216.11$	$F(000) = 440$
Monoclinic, $P2_1/c$	$D_x = 1.898$ Mg m^{-3}
$a = 6.7612$ (14) Å	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$b = 10.878$ (2) Å	$\mu = 0.18$ mm^{-1}
$c = 10.297$ (2) Å	$T = 200$ K
$\beta = 92.75$ (3)°	Prism, light brown
$V = 756.5$ (3) Å^3	0.60 × 0.22 × 0.20 mm

Data collection

Stoe IPDS image plate diffractometer	1326 reflections with $I > 2\sigma(I)$
Radiation source: fine-focus sealed tube	$R_{\text{int}} = 0.059$
Graphite monochromator	$\theta_{\text{max}} = 26.0°$, $\theta_{\text{min}} = 2.7°$
φ scans	$h = -8\rightarrow8$
5824 measured reflections	$k = -13\rightarrow13$
1488 independent reflections	$l = -12\rightarrow12$

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.031$	$w = 1/[\sigma^2(F_o^2) + (0.0484P)^2 + 0.1574P]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.089$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.06$	$\Delta\rho_{\text{max}} = 0.31$ e Å^{-3}
1488 reflections	$\Delta\rho_{\text{min}} = -0.23$ e Å^{-3}
146 parameters	Extinction correction: *SHELXL97* (Sheldrick, 2008), $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
3 restraints	Extinction coefficient: 0.093 (9)
Primary atom site location: structure-invariant direct methods	
Secondary atom site location: difference Fourier map	

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 (Å^2)

	x	y	z	U_{iso}*/U_{eq}
C5	0.03683 (18)	0.22251 (11)	0.46470 (11)	0.0173 (3)
H5	0.0181	0.1542	0.5203	0.021*
C2	0.09313 (18)	0.42549 (12)	0.30137 (11)	0.0176 (3)
C6	−0.10033 (17)	0.31771 (12)	0.45731 (11)	0.0166 (3)
C1	−0.07860 (17)	0.42018 (11)	0.37270 (11)	0.0168 (3)

C4	0.20152 (17)	0.22875 (11)	0.38968 (11)	0.0167 (3)
C3	0.23403 (17)	0.33087 (12)	0.30757 (11)	0.0176 (3)
O2	0.11938 (14)	0.52556 (9)	0.22378 (9)	0.0253 (3)
H2O	0.235 (2)	0.5179 (17)	0.1964 (17)	0.038*
O1	−0.20607 (13)	0.51466 (9)	0.35774 (9)	0.0228 (3)
H1O	−0.310 (2)	0.4983 (17)	0.3996 (17)	0.034*
O3	0.38713 (14)	0.34789 (10)	0.23055 (10)	0.0265 (3)
H3O	0.467 (3)	0.2905 (15)	0.2362 (18)	0.040*
N4	0.34037 (15)	0.12578 (10)	0.39485 (10)	0.0184 (3)
N6	−0.26572 (15)	0.31109 (10)	0.54231 (10)	0.0195 (3)
O4	0.50228 (13)	0.14010 (9)	0.34200 (9)	0.0250 (3)
O5	0.29368 (14)	0.03088 (9)	0.44938 (9)	0.0259 (3)
O6	−0.40392 (14)	0.38686 (10)	0.52605 (9)	0.0288 (3)
O7	−0.26491 (15)	0.23213 (9)	0.62784 (10)	0.0289 (3)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C5	0.0202 (6)	0.0161 (6)	0.0156 (5)	−0.0017 (5)	0.0016 (4)	−0.0004 (5)
C2	0.0208 (6)	0.0168 (6)	0.0152 (6)	−0.0010 (5)	0.0011 (4)	0.0022 (4)
C6	0.0159 (6)	0.0189 (6)	0.0154 (6)	−0.0021 (5)	0.0029 (4)	−0.0024 (4)
C1	0.0179 (6)	0.0171 (6)	0.0151 (6)	0.0020 (5)	−0.0010 (4)	−0.0027 (4)
C4	0.0189 (6)	0.0150 (6)	0.0162 (6)	0.0017 (4)	0.0007 (5)	−0.0014 (4)
C3	0.0165 (6)	0.0208 (6)	0.0158 (6)	−0.0009 (5)	0.0025 (4)	−0.0013 (5)
O2	0.0246 (5)	0.0238 (5)	0.0283 (5)	0.0039 (4)	0.0084 (4)	0.0113 (4)
O1	0.0209 (5)	0.0231 (5)	0.0247 (5)	0.0065 (4)	0.0048 (4)	0.0036 (4)
O3	0.0227 (5)	0.0280 (6)	0.0300 (5)	0.0065 (4)	0.0135 (4)	0.0090 (4)
N4	0.0199 (5)	0.0191 (6)	0.0163 (5)	0.0019 (4)	0.0011 (4)	−0.0012 (4)
N6	0.0189 (5)	0.0196 (6)	0.0204 (5)	−0.0016 (4)	0.0041 (4)	−0.0027 (4)
O4	0.0208 (5)	0.0265 (5)	0.0284 (5)	0.0056 (4)	0.0084 (4)	0.0003 (4)
O5	0.0306 (5)	0.0186 (5)	0.0288 (5)	0.0030 (4)	0.0040 (4)	0.0062 (4)
O6	0.0214 (5)	0.0345 (6)	0.0314 (5)	0.0085 (4)	0.0091 (4)	0.0023 (4)
O7	0.0319 (5)	0.0252 (5)	0.0310 (5)	0.0009 (4)	0.0155 (4)	0.0071 (4)

Geometric parameters (Å, º)

C5—C4	1.3870 (17)	C4—N4	1.4609 (16)
C5—C6	1.3898 (17)	C3—O3	1.3467 (15)
C5—H5	0.9500	O2—H2O	0.846 (14)
C2—O2	1.3669 (15)	O1—H1O	0.859 (15)
C2—C3	1.4019 (18)	O3—H3O	0.827 (15)
C2—C1	1.4046 (17)	N4—O5	1.2237 (15)
C6—C1	1.4267 (17)	N4—O4	1.2554 (14)
C6—N6	1.4545 (15)	N6—O7	1.2301 (15)
C1—O1	1.3454 (15)	N6—O6	1.2512 (15)
C4—C3	1.4195 (18)		
C4—C5—C6	118.97 (11)	C5—C4—N4	118.28 (11)
C4—C5—H5	120.5	O3—C3—C2	114.34 (11)
C6—C5—H5	120.5	O3—C3—C4	127.14 (12)

O2—C2—C3	120.29 (11)	C2—C3—C4	118.51 (11)
O2—C2—C1	118.18 (11)	C2—O2—H2O	105.3 (13)
C3—C2—C1	121.53 (11)	C1—O1—H1O	108.5 (13)
C5—C6—C1	121.85 (11)	C3—O3—H3O	111.9 (13)
C5—C6—N6	117.42 (11)	O5—N4—O4	123.58 (11)
C1—C6—N6	120.71 (11)	O5—N4—C4	118.95 (11)
O1—C1—C2	116.73 (11)	O4—N4—C4	117.47 (10)
O1—C1—C6	125.64 (11)	O7—N6—O6	122.24 (11)
C2—C1—C6	117.61 (11)	O7—N6—C6	119.22 (11)
C5—C4—C3	121.43 (11)	O6—N6—C6	118.54 (10)

C4—C5—C6—C1	1.40 (18)	O2—C2—C3—C4	179.79 (11)
C4—C5—C6—N6	−176.90 (10)	C1—C2—C3—C4	−0.88 (18)
O2—C2—C1—O1	0.65 (16)	C5—C4—C3—O3	179.92 (11)
C3—C2—C1—O1	−178.70 (11)	N4—C4—C3—O3	−1.37 (19)
O2—C2—C1—C6	−177.52 (10)	C5—C4—C3—C2	−1.28 (18)
C3—C2—C1—C6	3.13 (17)	N4—C4—C3—C2	177.43 (10)
C5—C6—C1—O1	178.59 (11)	C5—C4—N4—O5	10.41 (16)
N6—C6—C1—O1	−3.17 (18)	C3—C4—N4—O5	−168.34 (11)
C5—C6—C1—C2	−3.43 (17)	C5—C4—N4—O4	−169.81 (10)
N6—C6—C1—C2	174.81 (10)	C3—C4—N4—O4	11.44 (16)
C6—C5—C4—C3	1.01 (18)	C5—C6—N6—O7	9.35 (16)
C6—C5—C4—N4	−177.72 (10)	C1—C6—N6—O7	−168.96 (11)
O2—C2—C3—O3	−1.27 (17)	C5—C6—N6—O6	−171.03 (10)
C1—C2—C3—O3	178.07 (10)	C1—C6—N6—O6	10.65 (16)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2*O*···O3	0.85 (1)	2.14 (2)	2.6467 (14)	118 (2)
O2—H2*O*···O4^{i}	0.85 (1)	2.27 (2)	2.9531 (14)	138 (2)
O1—H1*O*···O6	0.86 (2)	1.91 (2)	2.6359 (15)	141 (2)
O1—H1*O*···O6^{ii}	0.86 (2)	2.46 (2)	3.1361 (15)	137 (2)
O3—H3*O*···O4	0.83 (2)	1.97 (2)	2.6357 (14)	137 (2)
O3—H3*O*···O7^{iii}	0.83 (2)	2.19 (2)	2.7658 (15)	127 (2)

Symmetry codes: (i) −*x*+1, *y*+1/2, −*z*+1/2; (ii) −*x*−1, −*y*+1, −*z*+1; (iii) *x*+1, −*y*+1/2, *z*−1/2.