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The 1:1 adduct of 1,3,5-trinitrobenzene with 1,2,3,4-tetrahydroquinoline

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.003 Å
Disorder in main residue
R factor = 0.055
wR factor = 0.174
Data-to-parameter ratio = 14.9

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

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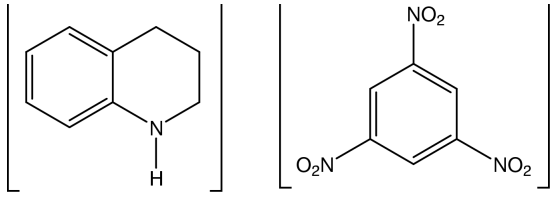
The crystal structure of the 1:1 adduct of 1,2,3,4-tetrahydroquinoline (THQ) with 1,3,5-trinitrobenzene (TNB), 1,2,3,4-tetrahydroquinoline 1,3,5-trinitrobenzene (1:1): $C_6H_3N_3O_6\cdot C_9H_{11}N$, formed as the sole product from the reaction of THQ with 2,4,6-trinitrobenzoic acid (with decarboxylation), shows stacks comprising π-bonded TNB and THQ molecules linked peripherally by weak hydrogen bonds [N···O 3.170 (3), C···O 3.432 (3) Å].

Comment

2,4,6-Trinitrobenzoic acid (TNBA) is a relatively strong organic acid (pK_a = 0.65) which has proved useful in the preparation of proton-transfer compounds with Lewis bases, a small number of which have been characterized crystallographically, *e.g.* with 2-aminopyrimidine (2-AP), [(2-AP)$^+$(TNBA)$^-$] (Byriel *et al.*, 1992), with 3-hydroxypyridine (3-HP) [(3-HP)$^+$(TNBA)$^-$] (Lynch *et al.*, 1992*a*), with 2,6-diaminopyridine (DAP), the modulated structure [(DAP)$^+$(TNBA)$^-$] (Smith *et al.*, 2000), and with 4-aminobenzoic acid (PABA), three forms, [(PABA)$^+$(TNBA)$^-$] (Lynch *et al.*, 1994), the hydrate [(PABA)$^+$(TNBA)$^-\cdot$(H$_2$O] (Lynch *et al.*, 1992*a*) and the unusual tri-heteromolecular crystal adduct [(PABA)$^+$(TNBA)$^-\cdot$2(PABA)·(TNB)] (where TNB = 1,3,5-trinitrobenzene) (Lynch *et al.*, 1992*b*). Non-transfer (1:1) compounds with triphenylphosphine oxide (Lynch *et al.*, 1993) and phenylurea (Bott *et al.*, 2000) are also known. As shown in the structure of the trimolecular compound (Lynch *et al.*, 1992*b*), which was prepared from the reaction of PABA with TNBA, the latter compound has a tendency to undergo facile decarboxylation (Coffey, 1977), often at a temperature lower than that of the usually employed refluxing conditions in 95% ethanol/water. The co-crystallized reaction products are stable 1:1 adducts involving 1,3,5-trinitrobenzene, which associates with the companion molecule through π–π stacking, together with weak N—H···O or C—H···O hydrogen bonds between the stacks. Examples of this type of compound are the (1:1) adducts with anthracene (Brown *et al.*, 1964), skatole (Hanson, 1964), indole (Hanson, 1964), azulene (Hanson, 1965; Mariezcurrena *et al.*, 1999), acepleiadylene (Hanson, 1966), 2,4,6-tri(dimethylamino)-1,3,5-triazine (Williams & Wallwork, 1966), 1,3,5-triaminobenzene (Iwasaki & Saito, 1970), 8-hydroxyquinoline (oxine) (Castellano & Prout, 1971), pyrene (Prout & Tickle, 1973), and azulene (Mariezcurrena *et al.*, 1999) and with indole-3-acetic acid (Lynch *et al.*, 1991). Adducts with (2:1) stoichiometry are also known [with *trans*-azobenzene and *N*-benzylideneaniline (Bar & Bernstein, 1981)].

Reported here is the crystal structure of the 1:1 adduct of 1,2,3,4-tetrahydroquinoline (THQ) with 1,3,5-trinitrobenzene

[(THQ)(TNB)], (I), formed as the sole product in the reaction of THQ with 2,4,6-trinitrobenzoic acid (with decarboxylation). The cell dimensions and space group for this compound were reported by Herbstein *et al.* (1976), who indicated that it was one of an isomorphous set (Herbstein, 1971; Herbstein & Kaftory, 1975), which included the azulene–TNB adduct (Hanson, 1965). The isomorphism is confirmed in the present study [comparative cell data for (I) from Herbstein *et al.* (1976) are a = 17.02, b = 6.80, c = 14.05 Å, β = 100°, space group $P2_1/a$, *cf.* azulene:TNB (Hanson, 1965): a = 16.39, b = 6.66, c = 13.77 Å, β = 100°, space group $P2_1/a$].



(I)

The molecular conformation and atom numbering scheme for the individual molecules of (I) are shown in Fig. 1. These alternating TNB and THQ molecules produce stacks down the cell b axis, involving π–π interactions between the aromatic ring systems of both molecules as well as the aromatic nitro substituents of TNB (Fig. 2). The aromatic rings are stacked alternately at centroid–centroid distances of 3.676 (1) and 3.728 (1) Å. The stacks are linked by N—H (THQ) to O (TNB) and weaker C—H (THQ) to O (TNB) hydrogen bonds [N11···O31 3.170 (3) Å, N11—H11···O31 163 (3)°; C61···O12^{i} 3.432 (3) Å, C61—H61···O12^{i} 156°; symmetry code: (i) = 1 + x, y, z].

Only minor deviations from planarity in TNB, due to rotation of the nitro group, is observed [torsion angles C6—C1—N1—O12, C2—C3—N3—O32, C4—C5—N5—O52 being 163.8 (2), 177.9 (2) and −178.8 (2)°, respectively], the largest being with the only unassociated nitro group. The THQ molecule is similar to that found in its 1:1 proton-transfer compound with 3,5-dinitrosalicylic acid (Smith *et al.*, 2002). However, there is significant vibrational disorder in the C atoms of the saturated ring of THQ (particularly C21, C31 and C41), largely in the direction of the molecular stacks. The worst of these, C31, was therefore modelled over two disorder sites [C31 (SOF = 0.733) and C31*A* (SOF = 0.267)]. This phenomenon is probably due to the presence of two possible conformational orientations of this ring, although similar disorder is also present in the isomorphous azulene–TNB adduct (Hanson, 1965) and in other adducts which involve π–π stacking (Herbstein & Kaftory, 1975).

Experimental

The synthesis of the title compound, (I), was carried out by heating 1 mmol quantities of 2,4,6-trinitrobenzoic acid and 1,2,3,4-tetrahydroquinoline in 50 ml of 80% ethanol/water under reflux for *ca.* 10 min. After concentration to *ca.* 30 ml, partial room temperature evaporation of the hot-filtered solution gave black crystals suitable for X-ray diffraction.

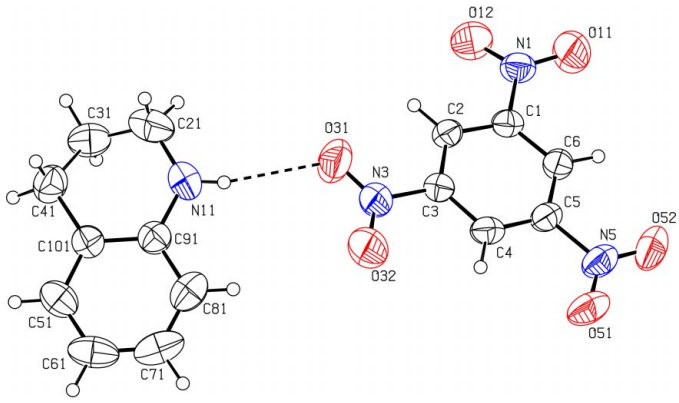


Figure 1
Molecular structure and atom numbering scheme for the individual species in (I), with non-H atoms shown as 40% probability ellipsoids. Only the major conformer of the THQ molecule is shown.

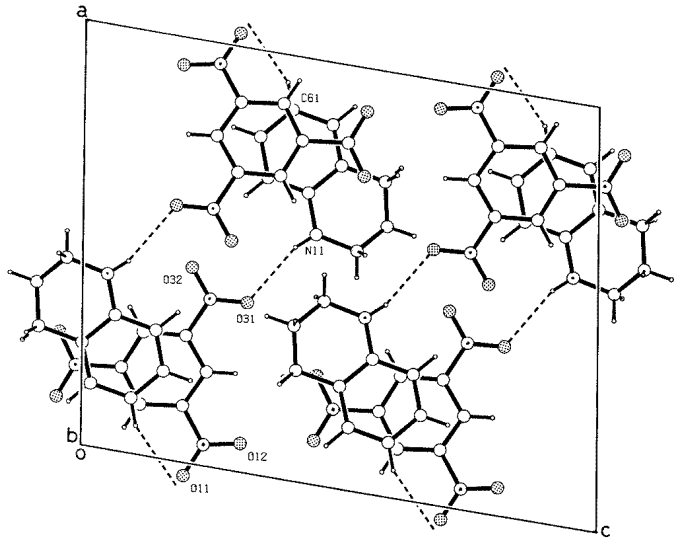


Figure 2
Packing in the unit cell, viewed down b, showing hydrogen-bonding interactions as broken lines.

Crystal data

$C_9H_{11}N{\cdot}C_6H_3N_3O_6$
M_r = 346.30
Monoclinic, $P2_1/c$
a = 13.8474 (12) Å
b = 6.8830 (6) Å
c = 16.8328 (15) Å
β = 99.273 (3)°
V = 1583.4 (2) Å^3
Z = 4
D_x = 1.453 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3297 reflections
θ = 2.5–27.1°
μ = 0.12 mm^{-1}
T = 293 (2) K
Block, black
0.45 × 0.40 × 0.24 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: none
9501 measured reflections
3583 independent reflections
2519 reflections with $I > 2\sigma(I)$
R_{int} = 0.055
θ_{max} = 27.5°
$h = -17 \rightarrow 16$
$k = -8 \rightarrow 6$
$l = -21 \rightarrow 21$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.1118P)^2 + 0.1838P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.055$	$(\Delta/\sigma)_{max}$
$wR(F^2) = 0.174$	$\Delta\rho_{max} = 0.21$ e Å^{-3}
$S = 1.07$	$\Delta\rho_{min} = -0.24$ e Å^{-3}
3583 reflections	
240 parameters	
H atoms treated by a mixture of independent and constrained refinement	

Data collection: *SMART* (Bruker, 2000); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1999); program(s) used to solve structure: *SHELXTL* (Bruker, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *PLATON* (Spek, 1999); software used to prepare material for publication: *SHELXTL*.

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