

2,4-Dinitrophenylhydrazine, redetermined at 120 K: a three-dimensional framework built from N—H···O, N—H···(O)₂, N—H··· π (arene) and C—H···O hydrogen bonds

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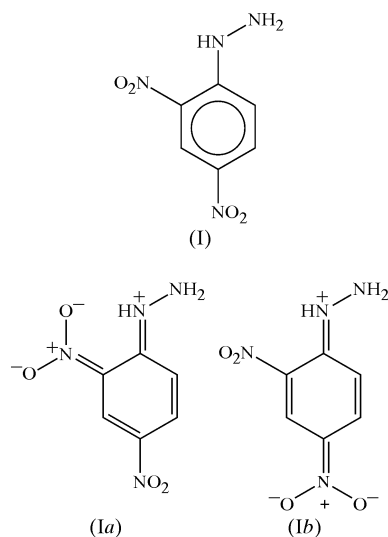
In the title compound, C₆H₆N₄O₄, the bond distances indicate significant bond fixation, consistent with charge-separated polar forms. The molecules are almost planar and there is an intramolecular N—H···O hydrogen bond. The molecules are linked into a complex three-dimensional framework by a combination of N—H···O, N—H···(O)₂, N—H··· π (arene) and C—H···O hydrogen bonds.

Comment

The structure of 2,4-dinitrophenylhydrazine, (I), was reported some years ago from diffraction data collected at ambient temperature (Okabe *et al.*, 1993). Although only a fairly small data set was available, the H-atom parameters were all refined, giving a data-to-parameter ratio of only 3.85. The bond distances and angles were reported without comment or discussion, and no description or discussion of the supramolecular aggregation was provided beyond a comment that the three-dimensional arrangement of the molecules is held together by hydrogen bonds. We have now taken the opportunity to redetermine this structure using diffraction data collected at 120 K, leading to a data-to-parameter ratio of 14.0, and we report here a full description of the molecular and supramolecular structures.

With the exception of the H atoms bonded to atom N11, the molecule of compound (I) is nearly planar, as shown by the key torsion angles (Table 1). The coordination of N1 is exactly planar, but that at N11 is markedly pyramidal, and the conformation is such that the lone-pair orbitals on atoms N1 and N11 are approximately orthogonal. The bond distances provide evidence for significant bond fixation. For example,

the C3—C4 and C5—C6 bonds are both very short compared with the remaining C—C bonds, the exocyclic bonds C4—N4 and, in particular, C2—N2 are shorter than the mean value for bonds of this type (1.468 Å; Allen *et al.*, 1987), and all of the N—O bonds are long for their type. Taken together, these observations point to a significant contribution of the charge-separated *o*-quinonoid form, (Ia), to the overall molecular electronic structure, with a lesser contribution for the *p*-quinonoid form, (Ib).



Each of the three independent N—H bonds acts as a hydrogen-bond donor, two in three-centre N—H···(O)₂ systems and the third in an N—H··· π (arene) interaction (Table 2). Together with a C—H···O hydrogen bond, these interactions link the molecules into a three-dimensional framework of some complexity whose formation is, however, readily analysed in terms of two independent two-dimensional substructures.

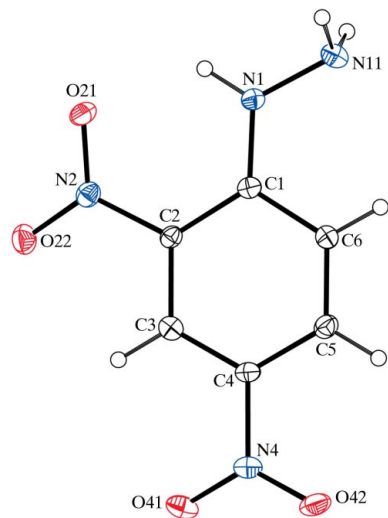


Figure 1
The molecule of compound (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

In the first substructure, atom N11 in the molecule at (x, y, z) acts a hydrogen-bond donor, *via* atom H11A, to atoms O21 and O22 in the molecules at $(2 - x, -\frac{1}{2} + y, \frac{1}{2} - z)$ and $(1 - x, -\frac{1}{2} + y, \frac{1}{2} - z)$, respectively, in a planar three-centre N—H \cdots (O)₂ system, so forming two independent *C*(7) (Bernstein *et al.*, 1995) chains running parallel to the [010] direction and generated by the 2₁ screw axes along $(1, y, \frac{1}{4})$ and $(\frac{1}{2}, y, \frac{1}{4})$, respectively. The combination of these two chains then generates an (001) sheet. This sheet is reinforced by an N—H \cdots π (arene) hydrogen bond, where atom N11 at (x, y, z) acts as donor, *via* atom H11B, to the aryl ring of the molecule at $(1 + x, y, z)$ (Fig. 2).

The planar atom N1 forms a short intramolecular N—H \cdots O contact with the nitro atom O21, and this interaction can be regarded as one component of a second three-centre N—H \cdots (O)₂ system. In the second component, atom N1 at (x, y, z) acts as hydrogen-bond donor to atom O42 in the molecule at $(1 + x, \frac{1}{2} - y, -\frac{1}{2} + z)$, so forming a *C*(8) chain along

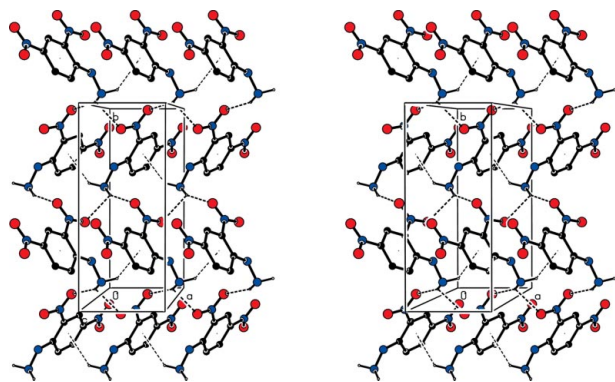


Figure 2

A stereoview of part of the crystal structure of (I), showing the formation of an (001) sheet built from a three-centre N—H \cdots (O)₂ hydrogen bond and an N—H \cdots π (arene) hydrogen bond. For the sake of clarity, H atoms not involved in the motifs shown have been omitted.

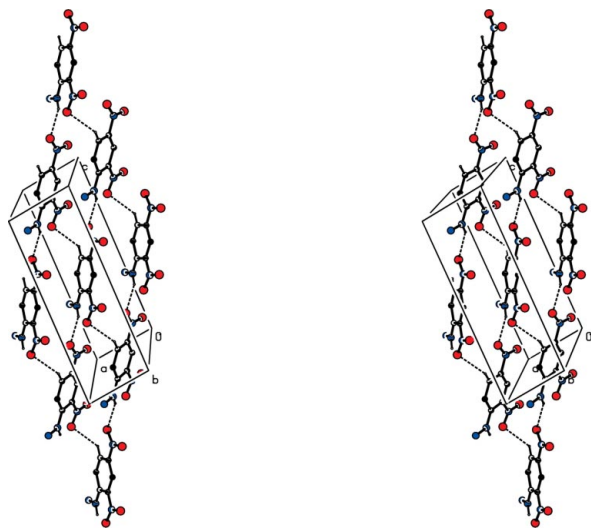


Figure 3

A stereoview of part of the crystal structure of (I), showing the formation of an (010) sheet built from N—H \cdots O and C—H \cdots O hydrogen bonds. For the sake of clarity, the intramolecular N—H \cdots O contact and H atoms not involved in the motifs shown have been omitted.

[20 $\bar{1}$] generated by the *c*-glide plane at $y = \frac{1}{4}$. At the same time, atom C5 in the molecule at (x, y, z) acts as hydrogen-bond donor to atom O21 in the molecule at $(x, \frac{1}{2} - y, \frac{1}{2} + z)$, so forming a *C*(7) chain along [001] generated by the same *c*-glide plane at $y = \frac{1}{4}$. The combination of these two chains then generates an (010) sheet of $R_4^2(24)$ rings (Fig. 3). The combination of the (010) and (001) sheets suffices to generate the three-dimensional framework structure.

Experimental

A commercial sample of (I) (Aldrich) was crystallized from ethanol.

Crystal data

$C_6H_6N_4O_4$	$Z = 4$
$M_r = 198.15$	$D_x = 1.705 \text{ Mg m}^{-3}$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 4.7917(2) \text{ \AA}$	$\mu = 0.15 \text{ mm}^{-1}$
$b = 11.5905(6) \text{ \AA}$	$T = 120(2) \text{ K}$
$c = 14.0496(5) \text{ \AA}$	Plate, orange
$\beta = 98.372(3)^\circ$	$0.46 \times 0.30 \times 0.05 \text{ mm}$
$V = 771.97(6) \text{ \AA}^3$	

Data collection

Bruker–Nonius KappaCCD area-detector diffractometer	12045 measured reflections
φ and ω scans	1775 independent reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 2003)	1165 reflections with $I > 2\sigma(I)$
$T_{\min} = 0.961, T_{\max} = 0.993$	$R_{\text{int}} = 0.031$
	$\theta_{\max} = 27.6^\circ$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.084P)^2 + 0.0429P]$
$R[F^2 > 2\sigma(F^2)] = 0.052$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.143$	$(\Delta/\sigma)_{\max} < 0.001$
$S = 1.04$	$\Delta\rho_{\max} = 0.30 \text{ e \AA}^{-3}$
1775 reflections	$\Delta\rho_{\min} = -0.32 \text{ e \AA}^{-3}$
127 parameters	
H-atom parameters constrained	

Table 1

Selected geometric parameters ($\text{\AA}, ^\circ$).

C1—C2	1.426 (3)	C2—N2	1.436 (2)
C2—C3	1.390 (3)	N2—O21	1.241 (2)
C3—C4	1.374 (3)	N2—O22	1.237 (2)
C4—C5	1.402 (3)	C4—N4	1.450 (2)
C5—C6	1.361 (3)	N4—O41	1.228 (2)
C6—C1	1.425 (3)	N4—O42	1.238 (2)
C1—N1	1.346 (2)	N1—N11	1.415 (2)
C2—C1—N1—N11	−176.64 (18)	C3—C4—N4—O41	8.9 (3)
C1—C2—N2—O21	−8.3 (3)		

Table 2

Hydrogen-bond geometry ($\text{\AA}, ^\circ$).

Cg1 is the centroid of the C1—C6 ring.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1 \cdots O21	0.88	1.98	2.612 (2)	127
N1—H1 \cdots O42 ⁱ	0.88	2.23	2.961 (2)	140
N11—H11A \cdots O21 ⁱⁱ	0.96	2.45	2.948 (2)	112
N11—H11A \cdots O22 ⁱⁱⁱ	0.96	2.15	3.038 (2)	154
N11—H11B \cdots Cg1 ^{iv}	0.98	2.80	3.509 (2)	129
C5—H5 \cdots O21 ^v	0.95	2.48	3.193 (2)	132

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

The space group $P2_1/c$ was uniquely assigned from the systematic absences. All H atoms were located in difference maps and then treated as riding atoms; the H atoms bonded to C atoms were assigned C—H distances of 0.95 Å, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$, while the H atoms bonded to N atoms were allowed to ride at the N—H distances determined from the difference maps (0.88 Å for N1, and 0.96 and 0.98 Å for N11), with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N})$.

Data collection: *COLLECT* (Nonius, 1999); cell refinement: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT*; data reduction: *DENZO* and *COLLECT*; program(s) used to solve structure: *OSCAIL* (McArdle, 2003) and *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *OSCAIL* and *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97* and *PRPKAPPA* (Ferguson, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK3017). Services for accessing these data are described at the back of the journal.

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