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N-(2,4-Dinitrophenyl)-*N*′-[nitro(phenyl)-methylene]hydrazine

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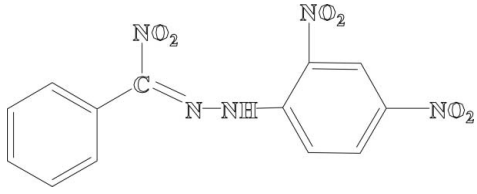
Key indicators: single-crystal X-ray study; T = 289 K; mean σ(C–C) = 0.003 Å; R factor = 0.039; wR factor = 0.059; data-to-parameter ratio = 13.6.

The title compound, $C_{13}H_9N_5O_6$, contains three nitro groups. It is prepared by the reaction of benzaldehyde 2,4-dinitrophenylhydrazone with nitric oxide at ambient temperature. The imine group is nearly coplanar with the (2,4-dinitrophenyl)hydrazine unit. The second benzene ring and the third nitro group are twisted away from this plane, with dihedral angles of 48.5 (3) and 15.2 (3)°, respectively. Weak intramolecular N—H···O interactions are observed.

Related literature

For related literature regarding NO, see: Garthwaite *et al.* (1989); Murad (1999). For arylhydrazones, see: Chan *et al.* (2001); Försterling & Barnes (2001); Paschalidis *et al.* (2000). For the structure of benzaldehyde 2,4-dinitrophenylhydrazone, see Shan *et al.* (2003).



Experimental

Crystal data

$C_{13}H_9N_5O_6$
M_r = 331.25
Orthorhombic, *Pbca*
a = 6.9790 (1) Å
b = 13.469 (2) Å
c = 29.448 (8) Å
V = 2768.1 (9) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 0.13 mm^{-1}
T = 289 (2) K
0.52 × 0.48 × 0.22 mm

Data collection

Siemens P4 diffractometer
Absorption correction: none
3591 measured reflections
3018 independent reflections
1537 reflections with $I > 2\sigma(I)$
R_{int} = 0.0000
3 standard reflections
every 97 reflections
intensity decay: 1.0%

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.039
$wR(F^2)$ = 0.059
S = 0.98
3018 reflections
222 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.20 e Å^{-3}
$\Delta\rho_{min}$ = −0.14 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2N···O2	0.894 (15)	1.966 (15)	2.591 (2)	125.7 (13)

Data collection: *XSCANS* (Siemens, 1996); cell refinement: *XSCANS*; data reduction: *SHELXTL* (Sheldrick, 2008); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL*; 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: EZ2141).

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supporting information

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N-(2,4-Dinitrophenyl)-*N*′-[nitro(phenyl)methylene]hydrazine

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S1. Comment

Nitric oxide (NO) has been found recently to play an important role in chemistry, biology and medicine (Garthwaite *et al.*, 1989; Murad, 1999). In recent years, arylhydrazones have been utilized for the analysis of carbonyl compounds (Chan *et al.*, 2001). Some arylhydrazones and their nitration products were found to have pharmacological properties (Försterling & Barnes, 2001; Paschalidis *et al.*, 2000). Here we report the reaction of NO with an arylhydrazone, where the title compound, (I), was obtained by the reaction of NO with benzaldehyde-2,4-dinitrophenylhydrazone.

The structure of (I) (Fig.1), shows that this reaction resulted in the addition of a third NO_2 group, which is attached to the carbon atom C7, with an O1—N3—C7—C6 torsion angle of -11.6 (3)°. The imine double bond in benzaldehyde 2,4-dinitrophenylhydrazone was preserved, as indicated by the N1═C7 distance [1.2779 (19) Å] being similar to that of 1.275 (2)Å in the original compound (Shan *et al.*, 2003). The other two nitro groups are co-planar with the benzene ring that they are attached to, with O4—N4—C12—C13 and O5—N5—C11—C12 torsion angles of 7.0 (3) and 0.0 (3)° respectively. There is a weak intramolecular N2—H(2 N)···O2 interaction.

S2. Experimental

A stock solution was prepared by dissolving 0.5 mol benzaldehyde -2,4-dinitrophenylhydrazine in 100 ml dry CH_2Cl_2. NO was produced by the reaction of 1 *M* H_2SO_4 solution trickled into an aqueous saturated $NaNO_2$ solution through a funnel at a pre-determined speed, while stirring under an argon atmosphere. NO was carried by argon and purified by passing it through a series of scrubbing bottles containing 4*M* NaOH, distilled water and $CaCl_2$ in turn. All the above bottles were under an argon atmosphere. The purified NO was bubbled through a previously degassed stirred stock solution at room temperature for an appropriate time. After the reaction was completed, as indicated by TLC, the reaction mixture was dried with anhydrous $MgSO_4$, concentrated under vacuum and purified by column chromatography on silica–gel (200–300 mesh, ethyl acetate–hexane) yielding the pure title compound.

S3. Refinement

Atom H2N was located in a difference Fourier map and refined isotropically, with the N—H distance restrained to 0.89 Å. Other H atoms were placed in idealized positions and constrained to ride on their parent atoms, with C—H distances of 0.93Å and with U_{iso}(H)= 1.2U_{eq}(C,*N*).

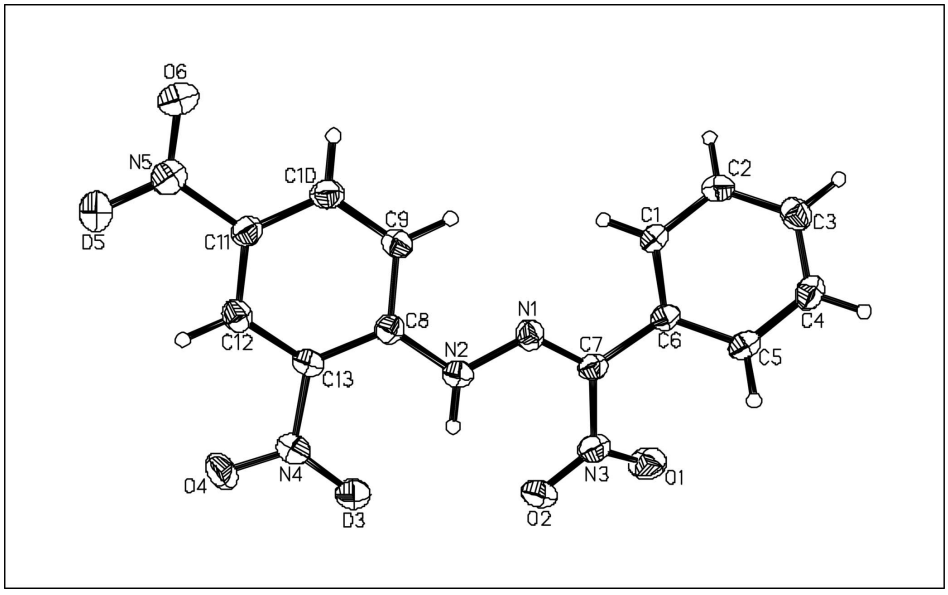

Figure 1

The structure of the dimer formation in (I),showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are not shown.

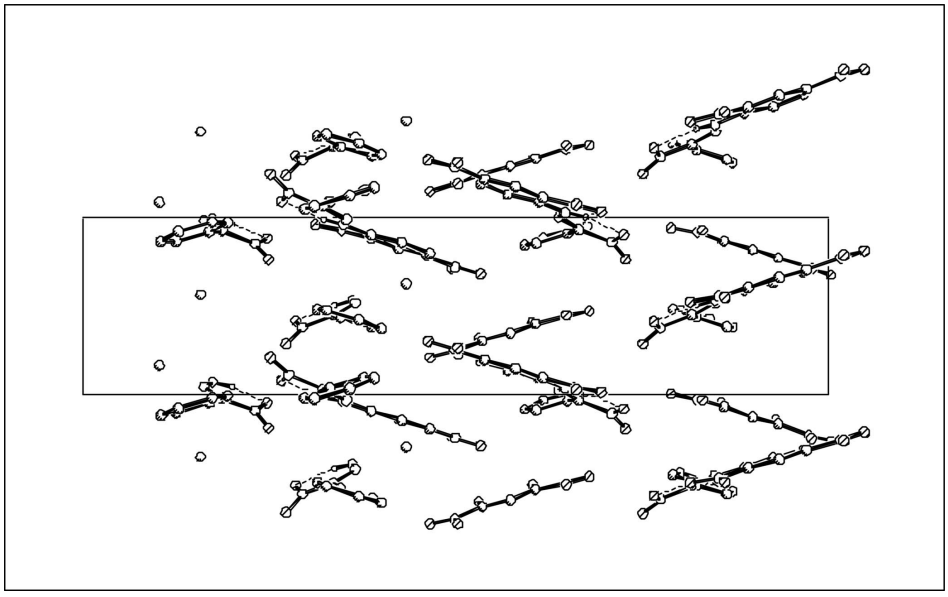

Figure 2

The crystal packing of (I), viewed along the *b* axis.

N-(2,4-Dinitrophenyl)-*N*′-[nitro(phenyl)methylene]hydrazine

Crystal data

$C_{13}H_9N_5O_6$
M_r = 331.25
Orthorhombic, *Pbca*
a = 6.9790 (1) Å
b = 13.469 (2) Å
c = 29.448 (8) Å
V = 2768.1 (9) Å^3
Z = 8
F(000) = 1360
D_x = 1.590 Mg m^{-3}

Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 26 reflections
θ = 3.4–12.5°
μ = 0.13 mm^{-1}

T = 289 K
Prism, yellow
0.52 × 0.48 × 0.22 mm

Data collection

Siemens P4 diffractometer
Radiation source: normal-focus sealed tube
Graphite monochromator
ω scans
3591 measured reflections
3018 independent reflections
1537 reflections with $I > 2\sigma(I)$

R_{int} = 0.000
θ_{max} = 27.0°, θ_{min} = 1.4°
h = 0→8
k = 0→17
l = 0→37
3 standard reflections every 97 reflections
intensity decay: 1.0%

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.039
$wR(F^2)$ = 0.059
S = 0.98
3018 reflections
222 parameters
0 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
$w = 1/[\sigma^2(F_o^2) + (0.0116P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.20 e Å^{-3}
$\Delta\rho_{min}$ = −0.14 e Å^{-3}
Extinction correction: *SHELXL*, $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.00375 (18)

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}
O1	0.2792 (2)	0.72703 (10)	0.26225 (4)	0.0655 (5)
O2	0.4128 (2)	0.58358 (10)	0.27056 (4)	0.0696 (5)
O3	0.5250 (2)	0.37214 (9)	0.30832 (4)	0.0587 (4)
O4	0.5513 (2)	0.23410 (9)	0.34501 (4)	0.0668 (5)
O5	0.7770 (3)	0.22039 (11)	0.49622 (4)	0.0826 (6)
O6	0.8082 (2)	0.35414 (10)	0.53534 (4)	0.0827 (6)
N1	0.5194 (2)	0.63895 (10)	0.35787 (5)	0.0411 (4)
N2	0.5362 (2)	0.54088 (11)	0.35121 (5)	0.0423 (4)
N3	0.3764 (3)	0.66797 (13)	0.28337 (5)	0.0489 (5)
N4	0.5574 (2)	0.32486 (12)	0.34320 (5)	0.0463 (4)
N5	0.7673 (3)	0.31066 (14)	0.50021 (5)	0.0599 (5)

C1	0.3799 (3)	0.82777 (13)	0.38520 (6)	0.0409 (5)
H1	0.3459	0.7770	0.4050	0.049*
C2	0.3749 (3)	0.92498 (14)	0.39969 (6)	0.0459 (5)
H2	0.3372	0.9394	0.4293	0.055*
C3	0.4251 (3)	1.00085 (14)	0.37089 (6)	0.0490 (6)
H3	0.4223	1.0663	0.3810	0.059*
C4	0.4797 (3)	0.97942 (14)	0.32689 (6)	0.0509 (6)
H4	0.5137	1.0307	0.3073	0.061*
C5	0.4842 (3)	0.88204 (14)	0.31166 (6)	0.0449 (5)
H5	0.5195	0.8682	0.2819	0.054*
C6	0.4359 (3)	0.80519 (13)	0.34096 (6)	0.0368 (5)
C7	0.4514 (3)	0.69945 (13)	0.32858 (6)	0.0387 (5)
C8	0.5928 (3)	0.48344 (13)	0.38722 (6)	0.0376 (5)
C9	0.6383 (3)	0.52778 (13)	0.42912 (6)	0.0433 (5)
H9	0.6295	0.5964	0.4322	0.052*
C10	0.6953 (3)	0.47186 (14)	0.46549 (6)	0.0453 (5)
H10	0.7271	0.5023	0.4928	0.054*
C11	0.7052 (3)	0.37003 (14)	0.46136 (6)	0.0424 (5)
C12	0.6595 (3)	0.32304 (13)	0.42157 (6)	0.0422 (5)
H12	0.6654	0.2542	0.4194	0.051*
C13	0.6048 (3)	0.37961 (13)	0.38483 (6)	0.0376 (5)
H2N	0.508 (2)	0.5131 (11)	0.3244 (5)	0.045 (6)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0715 (11)	0.0759 (10)	0.0491 (9)	0.0080 (10)	−0.0181 (8)	−0.0017 (8)
O2	0.1089 (14)	0.0566 (9)	0.0433 (8)	0.0080 (10)	−0.0062 (9)	−0.0146 (7)
O3	0.0786 (12)	0.0550 (9)	0.0426 (8)	−0.0004 (9)	−0.0118 (8)	−0.0065 (7)
O4	0.0932 (13)	0.0360 (8)	0.0711 (10)	0.0018 (9)	−0.0160 (9)	−0.0131 (7)
O5	0.1295 (16)	0.0517 (10)	0.0666 (10)	0.0200 (12)	−0.0158 (11)	0.0040 (9)
O6	0.1324 (17)	0.0721 (11)	0.0437 (8)	0.0087 (11)	−0.0200 (10)	−0.0044 (8)
N1	0.0411 (11)	0.0381 (9)	0.0443 (9)	0.0011 (9)	0.0036 (8)	0.0007 (8)
N2	0.0489 (12)	0.0416 (10)	0.0365 (10)	−0.0013 (9)	−0.0036 (9)	−0.0058 (8)
N3	0.0519 (13)	0.0583 (12)	0.0366 (10)	−0.0064 (11)	0.0015 (9)	0.0009 (9)
N4	0.0429 (12)	0.0467 (11)	0.0492 (10)	0.0015 (9)	−0.0012 (10)	−0.0086 (9)
N5	0.0738 (15)	0.0586 (13)	0.0471 (11)	0.0100 (12)	−0.0023 (11)	0.0012 (10)
C1	0.0408 (13)	0.0460 (12)	0.0358 (11)	0.0008 (11)	−0.0005 (10)	0.0064 (9)
C2	0.0467 (13)	0.0548 (13)	0.0362 (11)	0.0046 (12)	0.0001 (10)	−0.0056 (10)
C3	0.0483 (14)	0.0410 (12)	0.0577 (13)	0.0047 (11)	−0.0079 (12)	−0.0038 (11)
C4	0.0557 (15)	0.0493 (13)	0.0478 (12)	−0.0006 (12)	−0.0034 (12)	0.0138 (10)
C5	0.0477 (14)	0.0556 (13)	0.0315 (10)	0.0000 (11)	−0.0016 (10)	0.0050 (10)
C6	0.0350 (12)	0.0441 (11)	0.0312 (10)	0.0009 (10)	−0.0025 (9)	0.0009 (9)
C7	0.0397 (13)	0.0449 (12)	0.0314 (10)	−0.0033 (11)	0.0025 (10)	−0.0002 (9)
C8	0.0357 (12)	0.0393 (11)	0.0377 (11)	−0.0021 (10)	0.0033 (10)	0.0007 (9)
C9	0.0518 (14)	0.0379 (11)	0.0404 (11)	0.0013 (11)	0.0042 (10)	−0.0063 (9)
C10	0.0509 (15)	0.0497 (12)	0.0352 (11)	0.0000 (12)	0.0022 (10)	−0.0045 (10)
C11	0.0462 (14)	0.0458 (12)	0.0352 (10)	0.0029 (12)	0.0016 (10)	0.0022 (10)

C12	0.0402 (12)	0.0377 (11)	0.0488 (12)	0.0020 (10)	0.0046 (10)	−0.0015 (10)
C13	0.0362 (12)	0.0398 (11)	0.0367 (10)	−0.0014 (10)	0.0006 (10)	−0.0080 (9)

Geometric parameters (Å, º)

O1—N3	1.2163 (17)	C2—H2	0.9300
O2—N3	1.2244 (17)	C3—C4	1.381 (2)
O3—N4	1.2296 (17)	C3—H3	0.9300
O4—N4	1.2244 (17)	C4—C5	1.386 (2)
O5—N5	1.2233 (17)	C4—H4	0.9300
O6—N5	1.2227 (18)	C5—C6	1.389 (2)
N1—C7	1.2779 (19)	C5—H5	0.9300
N1—N2	1.3405 (18)	C6—C7	1.474 (2)
N2—C8	1.371 (2)	C8—C13	1.403 (2)
N2—H2N	0.894 (15)	C8—C9	1.407 (2)
N3—C7	1.492 (2)	C9—C10	1.368 (2)
N4—C13	1.468 (2)	C9—H9	0.9300
N5—C11	1.462 (2)	C10—C11	1.379 (2)
C1—C2	1.378 (2)	C10—H10	0.9300
C1—C6	1.394 (2)	C11—C12	1.369 (2)
C1—H1	0.9300	C12—C13	1.377 (2)
C2—C3	1.373 (2)	C12—H12	0.9300
C7—N1—N2	124.20 (15)	C4—C5—H5	120.0
N1—N2—C8	117.91 (15)	C6—C5—H5	120.0
N1—N2—H2N	121.5 (10)	C5—C6—C1	119.08 (16)
C8—N2—H2N	120.6 (10)	C5—C6—C7	123.26 (16)
O1—N3—O2	124.43 (17)	C1—C6—C7	117.56 (16)
O1—N3—C7	117.78 (16)	N1—C7—C6	118.45 (16)
O2—N3—C7	117.76 (17)	N1—C7—N3	123.46 (16)
O4—N4—O3	123.17 (16)	C6—C7—N3	117.99 (16)
O4—N4—C13	118.22 (16)	N2—C8—C13	122.75 (17)
O3—N4—C13	118.61 (15)	N2—C8—C9	120.25 (16)
O6—N5—O5	122.99 (18)	C13—C8—C9	116.98 (17)
O6—N5—C11	118.00 (17)	C10—C9—C8	121.21 (17)
O5—N5—C11	119.01 (17)	C10—C9—H9	119.4
C2—C1—C6	120.27 (17)	C8—C9—H9	119.4
C2—C1—H1	119.9	C9—C10—C11	119.55 (17)
C6—C1—H1	119.9	C9—C10—H10	120.2
C3—C2—C1	120.63 (17)	C11—C10—H10	120.2
C3—C2—H2	119.7	C12—C11—C10	121.58 (18)
C1—C2—H2	119.7	C12—C11—N5	119.07 (17)
C2—C3—C4	119.61 (17)	C10—C11—N5	119.35 (17)
C2—C3—H3	120.2	C11—C12—C13	118.75 (17)
C4—C3—H3	120.2	C11—C12—H12	120.6
C3—C4—C5	120.49 (18)	C13—C12—H12	120.6
C3—C4—H4	119.8	C12—C13—C8	121.91 (17)
C5—C4—H4	119.8	C12—C13—N4	116.14 (16)

C4—C5—C6	119.90 (17)	C8—C13—N4	121.95 (17)
C7—N1—N2—C8	−173.30 (18)	N2—C8—C9—C10	−179.95 (17)
C6—C1—C2—C3	−0.1 (3)	C13—C8—C9—C10	1.3 (3)
C1—C2—C3—C4	0.5 (3)	C8—C9—C10—C11	−1.2 (3)
C2—C3—C4—C5	0.0 (3)	C9—C10—C11—C12	0.1 (3)
C3—C4—C5—C6	−0.8 (3)	C9—C10—C11—N5	179.60 (17)
C4—C5—C6—C1	1.2 (3)	O6—N5—C11—C12	179.67 (19)
C4—C5—C6—C7	−175.08 (19)	O5—N5—C11—C12	0.0 (3)
C2—C1—C6—C5	−0.7 (3)	O6—N5—C11—C10	0.2 (3)
C2—C1—C6—C7	175.76 (18)	O5—N5—C11—C10	−179.5 (2)
N2—N1—C7—C6	178.19 (17)	C10—C11—C12—C13	0.8 (3)
N2—N1—C7—N3	1.8 (3)	N5—C11—C12—C13	−178.71 (17)
C5—C6—C7—N1	137.61 (19)	C11—C12—C13—C8	−0.6 (3)
C1—C6—C7—N1	−38.7 (3)	C11—C12—C13—N4	−179.89 (16)
C5—C6—C7—N3	−45.8 (3)	N2—C8—C13—C12	−179.11 (17)
C1—C6—C7—N3	137.86 (16)	C9—C8—C13—C12	−0.4 (3)
O1—N3—C7—N1	164.76 (18)	N2—C8—C13—N4	0.1 (3)
O2—N3—C7—N1	−13.5 (3)	C9—C8—C13—N4	178.85 (16)
O1—N3—C7—C6	−11.6 (3)	O4—N4—C13—C12	7.0 (3)
O2—N3—C7—C6	170.13 (18)	O3—N4—C13—C12	−173.35 (17)
N1—N2—C8—C13	176.35 (17)	O4—N4—C13—C8	−172.31 (18)
N1—N2—C8—C9	−2.3 (3)	O3—N4—C13—C8	7.4 (3)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2*N*···O2	0.894 (15)	1.966 (15)	2.591 (2)	125.7 (13)