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2-*tert*-Butyl-1-(4-nitroamino-1,2,5-oxadiazol-3-yl)diazene 1-oxide

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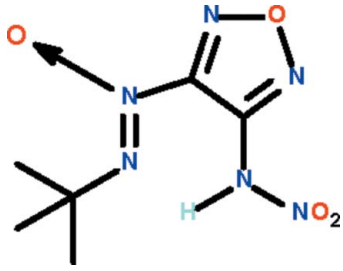
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.003 Å; R factor = 0.050; wR factor = 0.166; data-to-parameter ratio = 16.1.

In the title compound, $C_6H_{10}N_6O_4$, the nitroamine –$NHNO_2$ substituent and the C–N=N(→ O) unit of the other substituent of the oxadiazole ring are nearly coplanar with the five-membered ring [dihedral angles = 5.7 (1) and 3.0 (1)°]. The amino group of the –$NHNO_2$ substituent is a hydrogen-bond donor to the two-coordinate N atom of the C—N=N(→ O) unit.

Related literature

The synthesis required several steps; see: Churakov *et al.* (1995); Li *et al.* (2008); Mel'nikova *et al.* (2001).



Experimental

Crystal data

$C_6H_{10}N_6O_4$
M_r = 230.20
Monoclinic, $P2_1/n$
a = 6.2509 (5) Å
b = 9.1327 (8) Å
c = 18.6566 (16) Å
β = 92.134 (2)°
V = 1064.32 (16) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.12 mm^{-1}
T = 293 K
0.32 × 0.22 × 0.18 mm

Data collection

Bruker SMART APEX diffractometer
6176 measured reflections
2402 independent reflections
1711 reflections with $I > 2\sigma(I)$
R_{int} = 0.023

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.050
$wR(F^2)$ = 0.166
S = 1.05
2402 reflections
149 parameters
1 restraint
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.21 e Å^{-3}
$\Delta\rho_{min}$ = −0.21 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N5—H1···N1	0.87 (1)	2.18 (2)	2.758 (2)	124 (2)

Data collection: *APEX2* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *X-SEED* (Barbour, 2001); software used to prepare material for publication: *publCIF* (Westrip, 2010).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: XU5568).

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supporting information

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2-*tert*-Butyl-1-(4-nitroamino-1,2,5-oxadiazol-3-yl)diazene 1-oxide

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S1. Comment

The title compound (Scheme I) as well as the precusor compounds (Churakov *et al.*, 1995; Li *et al.*, 2008; Mel'nikova *et al.*, 2001) represent a class of high energy materials that has a low hydrogen content in the molecular formula. The nitroamine $–NHNO_2$ substituent and the C–N═N(→O) unit of the second substituent of the oxadiazole ring of $C_6H_{10}N_6O_4$ are nearly coplanar with the five-membered ring [dihedral angles 5.7 (1), 3.0 (1) °] (Fig. 1). The amino group of the $–NHNO_2$ substituent is hydrogen bond donor to the two-coordinate N atom of C–N═N(→O) (Table 1).

S2. Experimental

The steps given below were adapted from published procedures (Churakov *et al.*, 1995; Li *et al.*, 2008; Mel'nikova *et al.*, 2001)..

Synthesis of 3-amino-4-nitrosofurazan

To a mixture of benzene (200 ml), 30% hydrogen peroxide (145 ml, 1.29 mol) and sodium tungstate dihydrate (16.5 g, 0.05 mol), concentrated sulfuric acid (10 ml, 180 mmol) was added dropwise at 278–283 K followed by diaminofurazan (10.8 g, 0.10 mmol). The mixture was kept stirred at 288 K for 1.5 h. The organic layer was separated, washed with water and dried over magnesium sulfate. The solvent was removed to yield a yellow solid (5.19 g, 90% yield). CH&N elemental analysis. Calc. for $C_2H_2N_4O_2$: C 21.06, H 1.77, N 49.12%. Found: C 20.82, H 1.77, N 48.95%.

Synthesis of 3-amino-4-*(tert*-butyl-NNO-azoxy)furazan

A suspension solution of *N*,*N*-dibromo-*tert*-butylamine (11.5 g, 50 mmol), cuprous chloride (10 g, 0.1 mol), and the above compound (50 mmol) in dichloromethane (500 ml) was stirred at 288–298 K for 15 h. The reaction mixture was poured into ice-water (500 ml). Sodium thiosulfate was then added. The organic layer was separated, washed with water and dried over magnesium sulfate. The solvent was removed to give a yellow solid (6.8 g, 70%). CH&N elemental analysis. Calc. for $C_6H_{11}N_5O_2$: C 38.92, H 5.99, N37.82%. Found: C 39.36, H 5.96, N 35.60%.

Synthesis of 3-nitramino-4-(*tert*-butyl-NNO-azoxy)furazan

To a stirred and cooled (273 K) solution of the above compound (2 g, 10.8 mmol) in carbon tetrachloride, concentrated nitric acid (2.72 g, 21.6 mmol) was added. Thesolution was stirred for 2 h after after which the temperature was raised to room temperature. The solvent was removed. Dichloromethane (100 ml) was added and the organic phase was washed with cold water (20 ml). The aqueous layer was extracted with more dichloromethyane (2×50 ml). The combined organic layer was dried over magnesium sulfate, filtered and the solvent was removed to give the title compound as a yellow solid (2.47 g, 100% yield). CH&N elemental analysis. Calc. for $C_6H_1N_6O_3$: C31.30, H 4.35, N 36.52%. Found: C 31.73, H 4.41, N 36.12%. Crystals were obtained upon recrystallization from dichloromethane.

S3. Refinement

Carbon-bound H-atoms were placed in calculated positions (C–H 0.96 Å) and were included in the refinement in the riding model approximation, with U(H) set to 1.5U(C).

The amino H-atom was located in a difference Fourier map, and was refined with a distance restraint of N–H 0.84±0.01 Å; its temperature factor was refined.

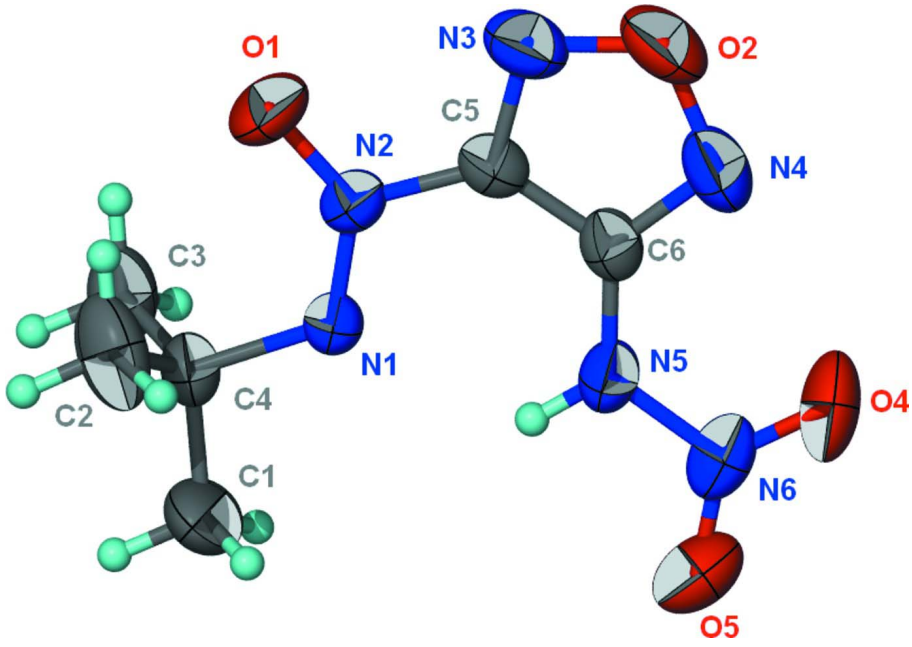

Figure 1

Thermal ellipsoid plot (Barbour, 2001) of $C_6H_{10}N_6O_4$ at the 50% probability level; hydrogen atoms are drawn as spheres of arbitrary radius.

2-*tert*-Butyl-1-(4-nitroamino-1,2,5-oxadiazol-3-yl)diazene 1-oxide

Crystal data

$C_6H_{10}N_6O_4$
M_r = 230.20
Monoclinic, $P2_1/n$
Hall symbol: -P 2yn
a = 6.2509 (5) Å
b = 9.1327 (8) Å
c = 18.6566 (16) Å
β = 92.134 (2)°
V = 1064.32 (16) Å^3
Z = 4
$F(000)$ = 480
D_x = 1.437 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 2279 reflections
θ = 2.2–26.2°
μ = 0.12 mm^{-1}
T = 293 K
Prism, yellow
0.32 × 0.22 × 0.18 mm

Data collection

Bruker SMART APEX diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω scans
6176 measured reflections
2402 independent reflections
1711 reflections with $I > 2\sigma(I)$
R_{int} = 0.023
θ_{max} = 27.5°, θ_{min} = 2.2°
h = −8→7
k = −11→11
l = −14→24

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.050$
$wR(F^2) = 0.166$
$S = 1.05$
2402 reflections
149 parameters
1 restraint
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
$w = 1/[\sigma^2(F_o^2) + (0.0903P)^2 + 0.1496P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.21$ e Å^{-3}
$\Delta\rho_{min} = -0.21$ e Å^{-3}

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.0322 (3)	0.3824 (2)	0.18681 (9)	0.0936 (6)
O2	0.2815 (3)	0.3201 (2)	0.38149 (7)	0.0895 (5)
O4	0.8233 (3)	0.0997 (2)	0.34861 (9)	0.0993 (6)
O5	0.9040 (3)	0.04877 (19)	0.24053 (10)	0.0906 (5)
N1	0.3219 (2)	0.25696 (16)	0.15264 (7)	0.0506 (4)
N2	0.2040 (2)	0.31596 (16)	0.19716 (7)	0.0541 (4)
N3	0.1665 (3)	0.3517 (2)	0.32062 (9)	0.0761 (5)
N4	0.4710 (3)	0.2504 (2)	0.36761 (8)	0.0782 (5)
N5	0.6222 (2)	0.17780 (19)	0.25756 (8)	0.0630 (4)
N6	0.7946 (3)	0.10260 (19)	0.28501 (10)	0.0678 (5)
C1	0.4246 (5)	0.1849 (4)	0.03862 (11)	0.1183 (12)
H1A	0.4277	0.0852	0.0549	0.177*
H1B	0.5609	0.2299	0.0493	0.177*
H1C	0.3948	0.1871	−0.0122	0.177*
C2	0.0397 (4)	0.1911 (4)	0.06269 (13)	0.1051 (9)
H2A	−0.0692	0.2447	0.0864	0.158*
H2B	0.0471	0.0932	0.0813	0.158*
H2C	0.0056	0.1880	0.0121	0.158*
C3	0.2466 (4)	0.4235 (3)	0.05127 (11)	0.0851 (7)
H3A	0.1365	0.4744	0.0758	0.128*
H3B	0.2158	0.4270	0.0005	0.128*
H3C	0.3822	0.4694	0.0619	0.128*
C4	0.2546 (3)	0.2664 (2)	0.07571 (9)	0.0600 (5)
C5	0.2791 (3)	0.30095 (19)	0.27008 (9)	0.0525 (4)
C6	0.4692 (3)	0.23759 (19)	0.29834 (9)	0.0536 (4)
H1	0.602 (3)	0.170 (2)	0.2114 (5)	0.056 (5)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0717 (9)	0.1239 (14)	0.0855 (11)	0.0512 (9)	0.0053 (8)	0.0056 (9)
O2	0.1138 (13)	0.1042 (12)	0.0515 (8)	0.0024 (10)	0.0179 (8)	−0.0145 (8)
O4	0.0878 (11)	0.1234 (14)	0.0836 (11)	0.0008 (10)	−0.0391 (9)	0.0258 (10)

O5	0.0688 (10)	0.0861 (11)	0.1168 (13)	0.0227 (8)	0.0031 (10)	0.0077 (10)
N1	0.0488 (7)	0.0592 (8)	0.0438 (7)	0.0092 (6)	−0.0008 (6)	−0.0007 (6)
N2	0.0491 (8)	0.0583 (8)	0.0549 (8)	0.0101 (6)	0.0022 (6)	0.0009 (6)
N3	0.0848 (12)	0.0828 (12)	0.0617 (10)	0.0064 (10)	0.0172 (9)	−0.0119 (9)
N4	0.1005 (14)	0.0881 (13)	0.0456 (8)	−0.0036 (11)	−0.0042 (9)	−0.0002 (8)
N5	0.0591 (9)	0.0774 (11)	0.0520 (8)	0.0157 (8)	−0.0053 (7)	0.0085 (8)
N6	0.0552 (9)	0.0646 (10)	0.0825 (12)	−0.0009 (8)	−0.0130 (8)	0.0146 (9)
C1	0.136 (2)	0.167 (3)	0.0522 (12)	0.068 (2)	0.0072 (14)	−0.0082 (15)
C2	0.110 (2)	0.131 (2)	0.0727 (14)	−0.0425 (18)	−0.0282 (14)	0.0022 (15)
C3	0.1064 (18)	0.0854 (15)	0.0623 (12)	−0.0030 (13)	−0.0119 (12)	0.0188 (11)
C4	0.0629 (11)	0.0721 (12)	0.0443 (9)	0.0054 (9)	−0.0068 (7)	0.0025 (8)
C5	0.0587 (10)	0.0507 (9)	0.0485 (9)	−0.0033 (7)	0.0088 (7)	−0.0030 (7)
C6	0.0646 (10)	0.0516 (9)	0.0442 (8)	−0.0055 (8)	−0.0017 (7)	0.0036 (7)

Geometric parameters (Å, º)

O1—N2	1.2417 (19)	C1—C4	1.489 (3)
O2—N3	1.352 (2)	C1—H1A	0.9600
O2—N4	1.378 (3)	C1—H1B	0.9600
O4—N6	1.194 (2)	C1—H1C	0.9600
O5—N6	1.200 (2)	C2—C4	1.520 (3)
N1—N2	1.2527 (18)	C2—H2A	0.9600
N1—C4	1.483 (2)	C2—H2B	0.9600
N2—C5	1.429 (2)	C2—H2C	0.9600
N3—C5	1.284 (2)	C3—C4	1.506 (3)
N4—C6	1.297 (2)	C3—H3A	0.9600
N5—C6	1.358 (2)	C3—H3B	0.9600
N5—N6	1.362 (2)	C3—H3C	0.9600
N5—H1	0.869 (9)	C5—C6	1.407 (2)
N3—O2—N4	112.00 (13)	C4—C2—H2C	109.5
N2—N1—C4	117.65 (13)	H2A—C2—H2C	109.5
O1—N2—N1	129.32 (15)	H2B—C2—H2C	109.5
O1—N2—C5	116.51 (15)	C4—C3—H3A	109.5
N1—N2—C5	114.15 (13)	C4—C3—H3B	109.5
C5—N3—O2	104.54 (17)	H3A—C3—H3B	109.5
C6—N4—O2	104.67 (17)	C4—C3—H3C	109.5
C6—N5—N6	123.77 (16)	H3A—C3—H3C	109.5
C6—N5—H1	120.6 (12)	H3B—C3—H3C	109.5
N6—N5—H1	114.5 (13)	C1—C4—N1	103.85 (15)
O4—N6—O5	127.57 (19)	C1—C4—C3	110.6 (2)
O4—N6—N5	118.2 (2)	N1—C4—C3	110.69 (16)
O5—N6—N5	114.21 (17)	C1—C4—C2	110.0 (2)
C4—C1—H1A	109.5	N1—C4—C2	110.20 (16)
C4—C1—H1B	109.5	C3—C4—C2	111.28 (19)
H1A—C1—H1B	109.5	N3—C5—C6	110.60 (16)
C4—C1—H1C	109.5	N3—C5—N2	119.65 (17)
H1A—C1—H1C	109.5	C6—C5—N2	129.75 (15)

H1B—C1—H1C	109.5	N4—C6—N5	127.89 (18)
C4—C2—H2A	109.5	N4—C6—C5	108.18 (17)
C4—C2—H2B	109.5	N5—C6—C5	123.90 (15)
H2A—C2—H2B	109.5		
C4—N1—N2—O1	0.8 (3)	N1—N2—C5—N3	−177.04 (17)
C4—N1—N2—C5	179.52 (14)	O1—N2—C5—C6	−177.20 (18)
N4—O2—N3—C5	1.0 (2)	N1—N2—C5—C6	3.9 (3)
N3—O2—N4—C6	−1.0 (2)	O2—N4—C6—N5	179.06 (18)
C6—N5—N6—O4	−6.7 (3)	O2—N4—C6—C5	0.6 (2)
C6—N5—N6—O5	174.83 (19)	N6—N5—C6—N4	9.1 (3)
N2—N1—C4—C1	−179.1 (2)	N6—N5—C6—C5	−172.60 (17)
N2—N1—C4—C3	62.2 (2)	N3—C5—C6—N4	0.0 (2)
N2—N1—C4—C2	−61.4 (2)	N2—C5—C6—N4	179.17 (17)
O2—N3—C5—C6	−0.7 (2)	N3—C5—C6—N5	−178.51 (18)
O2—N3—C5—N2	−179.88 (15)	N2—C5—C6—N5	0.6 (3)
O1—N2—C5—N3	1.8 (3)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N5—H1···N1	0.87 (1)	2.18 (2)	2.758 (2)	124 (2)