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Butyl 2-[(azidocarbonyl)amino]benzoate

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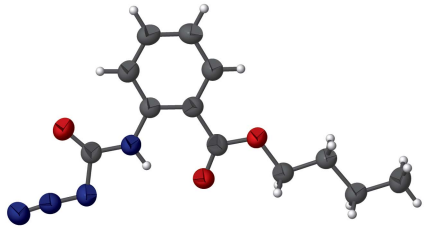
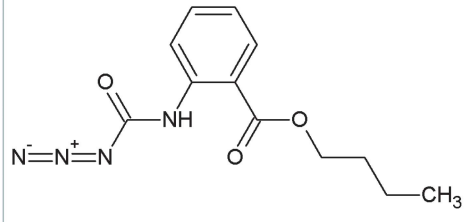
The title compound, $C_{12}H_{14}N_4O_3$, is planar with an r.m.s deviation of 0.025 Å from the plane through all 19 non-hydrogen atoms. An intramolecular N—H···O interaction closes an $S(6)$ ring. In the crystal, molecules are linked by C—H···π and weak offset π–π stacking interactions [inter-centroid distance = 3.614 (2) Å], forming undulating sheets parallel to (001).

3D view



Chemical scheme



Structure description

As part of our ongoing studies of azide derivatives, we now describe the title compound, $C_{12}H_{14}N_4O_3$, with the molecular structure shown in Fig. 1. All non-hydrogen atoms are almost co-planar, with an r.m.s deviation of 0.025 Å from the plane through all 19 non-hydrogen atoms. Bond lengths and angles in the azide group are normal, with the N2—N3 bond [1.246 (3) Å] longer than the terminal N1—N2 distance [1.114 (3) Å] which has more triple-bond character. The azide angle is slightly bent [N1—N2—N3 = 175.2 (2)°]. An intramolecular N—H···O interaction closes an $S(6)$ ring (Table 1; Fig. 1). A closely similar structure, ethyl 2-[(azidocarbonyl)amino]benzoate was reported recently (Yassine *et al.*, 2016).

In the crystal, molecules are linked by C—H···π and weak offset π–π stacking interactions [$Cg1\cdots Cg1^{i}$ = 3.614 (2) Å, where $Cg1$ is the centroid of the C2–C7 ring; symmetry code: (i) $-x, y, \frac{1}{2}-z$], forming sheets parallel to (001) (Table 1 and Fig. 2).

Synthesis and crystallization

A solution of 2-(butoxycarbonyl)benzoic acid (100 mg, 0.45 mmol), DPPA (0.194 ml, 0.90 mmol) and Et_3N (0.127 ml, 0.90 mmol) in toluene (5 ml) was refluxed for 4 h. After

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

*Cg*1 is the centroid of the C2–C7 ring

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N4—H4*N*···O2	0.86	1.93	2.644 (2)	139
C9—H9*A*···*Cg*1^{i}	0.97	2.89	3.681 (3)	139

Symmetry code: (i) $x+\frac{1}{2}, y+\frac{1}{2}, z+1$.

cooling to room temperature, the reaction mixture was concentrated. The residue was recrystallized from EtOAc–hexane (1:9 *v*/*v*) to give blue block-shaped crystals in a yield of 63%, m.p. = 317 K.

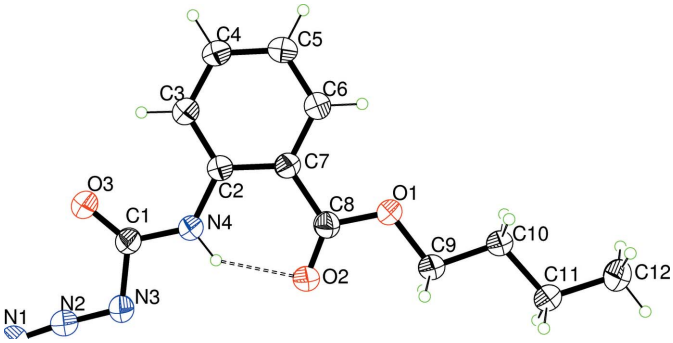


Figure 1
The molecular structure of the title compound, showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 30% probability level and the Intramolecular hydrogen bond is shown as a dashed line.

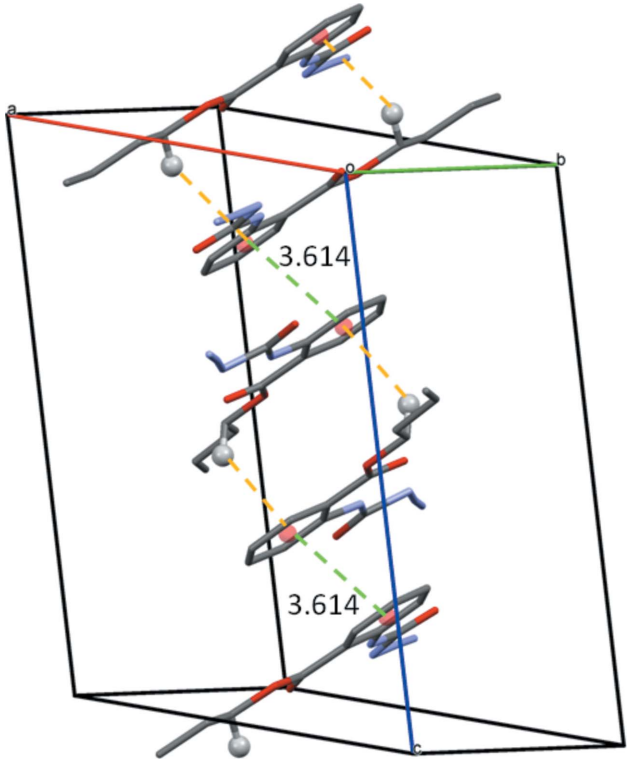


Figure 2
Partial crystal packing for the title compound showing π–π and C—H···π interactions between inversion-related molecules as dashed lines.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{12}H_{14}N_4O_3$
M_r	262.27
Crystal system, space group	Monoclinic, *C*2/*c*
Temperature (K)	299
a, *b*, *c* (Å)	9.780 (3), 17.698 (5), 15.819 (4)
β (°)	105.985 (16)
V (Å^3)	2632.2 (12)
Z	8
Radiation type	Mo *K*α
μ (mm^{-1})	0.10
Crystal size (mm)	0.30 × 0.22 × 0.15
Data collection	
Diffractometer	Bruker DUO APEXII CCD
Absorption correction	Multi-scan (*SADABS*; Bruker,2009)
T_{min}, T_{max}	0.662, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	28366, 2318, 1370
R_{int}	0.064
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.595
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.045, 0.117, 0.98
No. of reflections	2318
No. of parameters	173
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.18, −0.14

Computer programs: *APEX2* and *SAINT* (Bruker, 2009), *SHELXS2014* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015), *ORTEP-3 for Windows* (Farrugia, 2012), *Mercury* (Macrae *et al.*, 2008), *PLATON* (Spek, 2009) and *publCIF* (Westrip, 2010).

^{1}H NMR (300 MHz, $CDCl_3$, δ p.p.m.): 10.87 (1*H*, NH), 8.48 (1*H*, H6), 8.03 (1*H*, H3), 7.55 (1*H*, H4), 7.11 (1*H*, H5), 4.32 (2*H*, H9), 1.76 (2*H*, H10), 1.48 (2*H*, H11), 0.98 (3*H*, H12). ^{13}C NMR (75 MHz, $CDCl_3$, δ p.p.m.): 168.00(C8), 154.40(C1), 140.58(C2), 134.59(C4), 130.89(C6), 122.85(C5), 119.50(C3), 115.54(C7), 65.44(C9), 30.53(C10), 19.22(C11), 13.70(C12).

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The reflection (0 6 12) affected by the beam-stop was removed during refinement.

Acknowledgements

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full crystallographic data

IUCrData (2016). **1**, x161454 [doi:10.1107/S2414314616014541]

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Crystal data

$C_{12}H_{14}N_4O_3$
M_r = 262.27
Monoclinic, $C2/c$
a = 9.780 (3) Å
b = 17.698 (5) Å
c = 15.819 (4) Å
β = 105.985 (16)°
V = 2632.2 (12) Å^3
Z = 8
$F(000)$ = 1104
D_x = 1.324 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 2318 reflections
θ = 2.3–25.0°
μ = 0.10 mm^{-1}
T = 299 K
Block, purple
0.30 × 0.22 × 0.15 mm

Data collection

Bruker DUO APEXII CCD diffractometer
φ and ω scans
Absorption correction: multi-scan (SADABS; Bruker,2009)
T_{min} = 0.662, T_{max} = 0.746
28366 measured reflections
2318 independent reflections
1370 reflections with $I > 2\sigma(I)$
R_{int} = 0.064
θ_{max} = 25.0°, θ_{min} = 2.3°
h = −11→11
k = −20→20
l = −18→18

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.045
$wR(F^2)$ = 0.117
S = 0.98
2318 reflections
173 parameters
0 restraints
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0486P)^2 + 1.1042P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.18 e Å^{-3}
$\Delta\rho_{min}$ = −0.14 e Å^{-3}
Extinction correction: SHELXL-2014/7 (Sheldrick 2015), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.00046 (17)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.82291 (15)	−0.05566 (8)	0.54241 (9)	0.0619 (4)
O2	0.78779 (17)	0.06864 (9)	0.53246 (10)	0.0711 (5)
O3	1.13563 (18)	0.25170 (9)	0.69941 (11)	0.0749 (5)
N1	0.9649 (2)	0.40575 (13)	0.63239 (15)	0.0870 (7)
N2	0.9465 (2)	0.34416 (13)	0.61991 (13)	0.0656 (5)
N3	0.9168 (2)	0.27669 (11)	0.60087 (12)	0.0664 (6)
C1	1.0288 (2)	0.22860 (13)	0.64945 (14)	0.0555 (6)
C2	1.0654 (2)	0.09038 (12)	0.66053 (13)	0.0514 (5)
C7	1.0039 (2)	0.02017 (12)	0.62878 (13)	0.0522 (5)
C8	0.8622 (2)	0.01555 (13)	0.56352 (14)	0.0555 (6)
N4	0.99075 (19)	0.15649 (9)	0.62810 (11)	0.0581 (5)
H4N	0.9102	0.1502	0.5896	0.070*
C3	1.1961 (2)	0.09132 (13)	0.72320 (14)	0.0604 (6)
H3	1.2379	0.1372	0.7446	0.072*
C4	1.2644 (2)	0.02473 (14)	0.75398 (15)	0.0645 (6)
H4	1.3521	0.0263	0.7961	0.077*
C5	1.2056 (2)	−0.04399 (14)	0.72361 (15)	0.0668 (7)
H5	1.2529	−0.0886	0.7449	0.080*
C6	1.0765 (2)	−0.04600 (13)	0.66150 (15)	0.0621 (6)
H6	1.0365	−0.0924	0.6408	0.075*
C9	0.6860 (2)	−0.06591 (12)	0.47901 (15)	0.0600 (6)
H9A	0.6846	−0.0407	0.4243	0.072*
H9B	0.6115	−0.0444	0.5013	0.072*
C10	0.6622 (2)	−0.14899 (11)	0.46373 (14)	0.0567 (6)
H10A	0.6634	−0.1734	0.5188	0.068*
H10B	0.7390	−0.1700	0.4434	0.068*
C11	0.5212 (2)	−0.16541 (12)	0.39631 (15)	0.0673 (7)
H11A	0.4447	−0.1445	0.4170	0.081*
H11B	0.5199	−0.1403	0.3416	0.081*
C12	0.4946 (3)	−0.24873 (13)	0.37882 (17)	0.0868 (9)
H12A	0.4046	−0.2557	0.3360	0.130*
H12B	0.5688	−0.2697	0.3570	0.130*
H12C	0.4935	−0.2738	0.4324	0.130*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0566 (10)	0.0519 (9)	0.0651 (10)	0.0001 (7)	−0.0033 (8)	−0.0033 (7)
O2	0.0679 (11)	0.0531 (10)	0.0743 (11)	0.0064 (8)	−0.0106 (8)	−0.0025 (8)
O3	0.0629 (11)	0.0601 (10)	0.0861 (12)	−0.0046 (8)	−0.0058 (9)	−0.0045 (9)
N1	0.0811 (16)	0.0590 (15)	0.1032 (18)	0.0072 (12)	−0.0046 (13)	−0.0056 (13)
N2	0.0610 (13)	0.0582 (15)	0.0685 (13)	0.0045 (11)	0.0025 (10)	−0.0006 (11)
N3	0.0684 (13)	0.0497 (12)	0.0701 (13)	−0.0028 (10)	0.0006 (10)	−0.0021 (10)
C1	0.0562 (15)	0.0542 (14)	0.0525 (13)	−0.0018 (12)	0.0088 (12)	−0.0007 (11)
C2	0.0491 (13)	0.0511 (13)	0.0523 (13)	0.0007 (11)	0.0111 (11)	0.0007 (10)

C7	0.0501 (13)	0.0535 (13)	0.0506 (12)	0.0011 (11)	0.0096 (10)	−0.0008 (10)
C8	0.0591 (15)	0.0519 (14)	0.0536 (13)	0.0016 (12)	0.0122 (11)	−0.0030 (11)
N4	0.0552 (11)	0.0491 (12)	0.0602 (11)	−0.0004 (9)	−0.0005 (9)	−0.0003 (9)
C3	0.0557 (14)	0.0585 (15)	0.0614 (14)	−0.0027 (12)	0.0069 (11)	−0.0013 (11)
C4	0.0523 (14)	0.0653 (16)	0.0675 (15)	0.0023 (12)	0.0021 (11)	0.0035 (13)
C5	0.0604 (16)	0.0602 (15)	0.0726 (16)	0.0092 (12)	0.0064 (13)	0.0057 (13)
C6	0.0599 (15)	0.0534 (14)	0.0674 (15)	0.0004 (11)	0.0080 (12)	−0.0012 (12)
C9	0.0562 (14)	0.0536 (14)	0.0617 (14)	0.0035 (11)	0.0022 (11)	−0.0019 (11)
C10	0.0543 (13)	0.0528 (13)	0.0567 (14)	0.0018 (10)	0.0047 (11)	0.0003 (10)
C11	0.0585 (15)	0.0610 (16)	0.0707 (15)	−0.0001 (12)	−0.0021 (12)	−0.0023 (12)
C12	0.083 (2)	0.0685 (18)	0.090 (2)	−0.0093 (15)	−0.0069 (15)	−0.0108 (14)

Geometric parameters (Å, º)

O1—C8	1.333 (2)	C4—H4	0.9300
O1—C9	1.446 (2)	C5—C6	1.371 (3)
O2—C8	1.207 (2)	C5—H5	0.9300
O3—C1	1.195 (2)	C6—H6	0.9300
N1—N2	1.114 (2)	C9—C10	1.498 (3)
N2—N3	1.246 (3)	C9—H9A	0.9700
N3—C1	1.433 (3)	C9—H9B	0.9700
C1—N4	1.346 (3)	C10—C11	1.521 (3)
C2—C3	1.385 (3)	C10—H10A	0.9700
C2—N4	1.400 (2)	C10—H10B	0.9700
C2—C7	1.411 (3)	C11—C12	1.510 (3)
C7—C6	1.393 (3)	C11—H11A	0.9700
C7—C8	1.485 (3)	C11—H11B	0.9700
N4—H4N	0.8600	C12—H12A	0.9600
C3—C4	1.376 (3)	C12—H12B	0.9600
C3—H3	0.9300	C12—H12C	0.9600
C4—C5	1.374 (3)		
C8—O1—C9	116.14 (16)	C5—C6—C7	121.3 (2)
N1—N2—N3	175.2 (2)	C5—C6—H6	119.4
N2—N3—C1	110.28 (19)	C7—C6—H6	119.4
O3—C1—N4	128.4 (2)	O1—C9—C10	107.97 (17)
O3—C1—N3	123.5 (2)	O1—C9—H9A	110.1
N4—C1—N3	108.10 (19)	C10—C9—H9A	110.1
C3—C2—N4	122.53 (19)	O1—C9—H9B	110.1
C3—C2—C7	119.0 (2)	C10—C9—H9B	110.1
N4—C2—C7	118.50 (19)	H9A—C9—H9B	108.4
C6—C7—C2	119.0 (2)	C9—C10—C11	111.82 (17)
C6—C7—C8	119.6 (2)	C9—C10—H10A	109.3
C2—C7—C8	121.38 (19)	C11—C10—H10A	109.3
O2—C8—O1	122.3 (2)	C9—C10—H10B	109.3
O2—C8—C7	125.7 (2)	C11—C10—H10B	109.3
O1—C8—C7	112.08 (19)	H10A—C10—H10B	107.9
C1—N4—C2	128.32 (19)	C12—C11—C10	113.11 (19)

C1—N4—H4N	115.8	C12—C11—H11A	109.0
C2—N4—H4N	115.8	C10—C11—H11A	109.0
C4—C3—C2	120.4 (2)	C12—C11—H11B	109.0
C4—C3—H3	119.8	C10—C11—H11B	109.0
C2—C3—H3	119.8	H11A—C11—H11B	107.8
C5—C4—C3	121.2 (2)	C11—C12—H12A	109.5
C5—C4—H4	119.4	C11—C12—H12B	109.5
C3—C4—H4	119.4	H12A—C12—H12B	109.5
C6—C5—C4	119.2 (2)	C11—C12—H12C	109.5
C6—C5—H5	120.4	H12A—C12—H12C	109.5
C4—C5—H5	120.4	H12B—C12—H12C	109.5

Hydrogen-bond geometry (Å, º)

Cg1 is the centroid of the C2–C7 ring

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N4—H4*N*···O2	0.86	1.93	2.644 (2)	139
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Symmetry code: (i) *x*+1/2, *y*+1/2, *z*+1.