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Ethyl 2-[(azidocarbonyl)amino]benzoate

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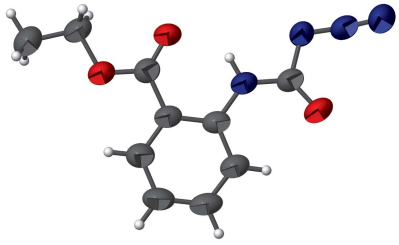
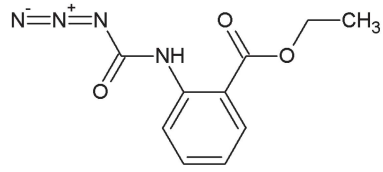
Structural data: full structural data are available from iucrdata.iucr.org

In the almost planar (r.m.s. deviation = 0.038 Å) title compound, $C_{10}H_{10}N_4O_3$, an intramolecular N—H···O interaction closes an $S(6)$ ring. In the crystal, aromatic π–π stacking interactions occur [inter-centroid distance = 3.65 (2) Å].

3D view



Chemical scheme



Structure description

Direct conversion of carboxylic acids to acyl azides can be achieved by using diphenylphosphoryl azide (DPPA) in the presence of a base (Katritzky *et al.*, 2007). In an attempt to synthesize ethyl 2-isocyanatobenzoate, the title compound was formed and its structure is reported here.

The molecular structure is shown in Fig. 1. The molecule is approximately planar, with an r.m.s. deviation of 0.038 Å for the non-H atoms. The geometry of the azide group is normal for covalent azide groups, with longer Nα—Nβ distances [N2—N3 = 1.264 (2) Å] and shorter terminal Nβ—Nγ distances [N3—N4 = 1.131 (2) Å], with more triple-bond character. The azide angle is slightly bent [N2—N3—N4 = 174.7 (2)°]. An intramolecular N—H···O interaction closes an $S(6)$ ring (Table 1 and Fig. 1). Aromatic π–π stacking interactions occur in the crystal [inter-centroid distance = 3.653 (2) Å].

Synthesis and crystallization

A solution of 2-(ethoxycarbonyl) benzoic acid (100 mg, 0.53 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 cooling to room temperature, the reaction mixture was concentrated. The residue was purified by column chromatography using EtOAc–hexane (1:9 *v*/*v*) as eluent to give purple parallelepiped-shaped crystals (yield 71%, m.p. = 337 K).

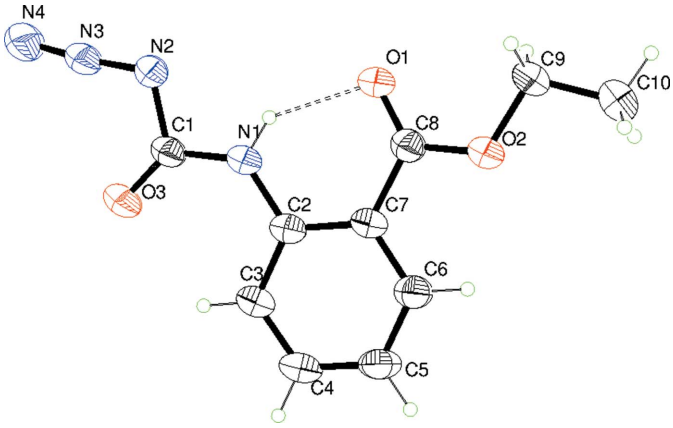


Figure 1
The molecular structure of the title compound, showing displacement ellipsoids drawn at the 30% probability level. The intramolecular hydrogen bond is drawn as a dashed line.

^{1}H NMR (300 MHz, $CDCl_3$): δ 1.37 (3*H*, H10), 4.40 (2*H*, H9), 7.13 (1*H*, H5), 7.58 (1*H*, H4), 8.06 (1*H*, H3), 8.51 (1*H*, H6), 10.90 (1*H*, NH).

^{13}C NMR (75 MHz, $CDCl_3$): δ 14.17 (C10), 61.62 (C9), 115.50 (C7), 119.52 (C3), 122.83 (C5), 130.94 (C6), 134.62 (C4), 140.64 (C2), 154.43 (C1), 167.98 (C8)

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The reflection $\bar{3}39$ was removed during refinement due to poor agreement.

Acknowledgements

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References

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*N*···O1	0.86	1.95	2.6593 (19)	139

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{10}H_{10}N_4O_3$
M_r	234.22
Crystal system, space group	Monoclinic, *C*2/*c*
Temperature (K)	300
a, *b*, *c* (Å)	9.330 (6), 18.724 (4), 13.484 (3)
β (°)	102.898 (8)
V (Å^3)	2296.3 (17)
Z	8
Radiation type	Mo *K*α
μ (mm^{-1})	0.10
Crystal size (mm)	0.32 × 0.24 × 0.17
Data collection	
Diffractometer	Bruker DUO APEXII CCD
Absorption correction	Multi-scan (*SADABS*; Bruker, 2009)
T_{min}, T_{max}	0.695, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	16533, 2352, 1302
R_{int}	0.038
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.625
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.043, 0.096, 1.61
No. of reflections	2352
No. of parameters	154
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.14, −0.15

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

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full crystallographic data

IUCrData (2016). **1**, x161155 [https://doi.org/10.1107/S241431461601155X]

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Ethyl 2-[(azidocarbonyl)amino]benzoate

Crystal data

$C_{10}H_{10}N_4O_3$
M_r = 234.22
Monoclinic, $C2/c$
a = 9.330 (6) Å
b = 18.724 (4) Å
c = 13.484 (3) Å
β = 102.898 (8)°
V = 2296.3 (17) Å^3
Z = 8
$F(000)$ = 976
D_x = 1.355 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 2352 reflections
θ = 2.2–26.4°
μ = 0.10 mm^{-1}
T = 300 K
Parallelepiped, purple
0.32 × 0.24 × 0.17 mm

Data collection

Bruker DUO APEXII CCD diffractometer
φ and ω scans
Absorption correction: multi-scan (SADABS; Bruker, 2009)
T_{min} = 0.695, T_{max} = 0.746
16533 measured reflections
2352 independent reflections
1302 reflections with $I > 2\sigma(I)$
R_{int} = 0.038
θ_{max} = 26.4°, θ_{min} = 2.2°
h = −11→11
k = −22→23
l = −16→16

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.043
$wR(F^2)$ = 0.096
S = 1.61
2352 reflections
154 parameters
0 restraints
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.022P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.14 e Å^{-3}
$\Delta\rho_{min}$ = −0.15 e Å^{-3}

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	1.03497 (14)	0.23713 (7)	−0.00286 (9)	0.0749 (4)

O2	1.00146 (14)	0.35584 (6)	−0.00214 (9)	0.0742 (4)
O3	0.80897 (14)	0.07009 (6)	0.20144 (9)	0.0828 (4)
N1	0.89748 (15)	0.15816 (8)	0.11107 (10)	0.0644 (4)
H1N	0.9479	0.1624	0.0652	0.077*
N2	0.94011 (18)	0.04318 (9)	0.07886 (11)	0.0757 (5)
N3	0.92839 (18)	−0.02151 (11)	0.10254 (11)	0.0760 (5)
N4	0.9226 (2)	−0.08071 (11)	0.11767 (14)	0.1044 (7)
C1	0.87368 (19)	0.09018 (11)	0.13835 (12)	0.0608 (5)
C2	0.85122 (18)	0.22285 (9)	0.14731 (12)	0.0570 (5)
C3	0.7684 (2)	0.22489 (10)	0.22159 (13)	0.0672 (5)
H3	0.7418	0.1825	0.2487	0.081*
C4	0.7258 (2)	0.28947 (11)	0.25512 (14)	0.0763 (6)
H4	0.6706	0.2900	0.3047	0.092*
C5	0.7638 (2)	0.35352 (11)	0.21619 (14)	0.0787 (6)
H5	0.7347	0.3968	0.2394	0.094*
C6	0.8451 (2)	0.35222 (10)	0.14275 (13)	0.0708 (5)
H6	0.8705	0.3951	0.1165	0.085*
C7	0.89052 (19)	0.28814 (9)	0.10673 (11)	0.0581 (5)
C8	0.9820 (2)	0.28912 (10)	0.02929 (12)	0.0604 (5)
C9	1.0927 (2)	0.36288 (10)	−0.07630 (14)	0.0796 (6)
H9A	1.0502	0.3363	−0.1376	0.096*
H9B	1.1907	0.3446	−0.0485	0.096*
C10	1.0989 (2)	0.44148 (11)	−0.09986 (16)	0.0963 (7)
H10A	1.1583	0.4485	−0.1487	0.144*
H10B	1.0013	0.4588	−0.1272	0.144*
H10C	1.1411	0.4671	−0.0386	0.144*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0898 (10)	0.0688 (9)	0.0801 (9)	0.0021 (7)	0.0486 (8)	−0.0069 (7)
O2	0.0891 (10)	0.0708 (9)	0.0754 (8)	0.0005 (7)	0.0455 (7)	−0.0005 (7)
O3	0.0948 (10)	0.0884 (10)	0.0811 (9)	−0.0028 (8)	0.0532 (8)	0.0071 (7)
N1	0.0729 (11)	0.0685 (11)	0.0612 (9)	−0.0005 (9)	0.0347 (8)	−0.0029 (8)
N2	0.1067 (14)	0.0605 (11)	0.0740 (10)	−0.0056 (10)	0.0501 (10)	−0.0004 (8)
N3	0.0918 (13)	0.0790 (13)	0.0691 (10)	0.0015 (11)	0.0436 (9)	0.0044 (10)
N4	0.1434 (19)	0.0794 (14)	0.1117 (15)	0.0070 (13)	0.0739 (13)	0.0190 (12)
C1	0.0625 (12)	0.0719 (14)	0.0529 (10)	−0.0017 (10)	0.0229 (10)	−0.0007 (9)
C2	0.0504 (11)	0.0710 (13)	0.0514 (10)	0.0027 (10)	0.0152 (9)	−0.0057 (9)
C3	0.0635 (13)	0.0816 (14)	0.0625 (11)	0.0027 (10)	0.0270 (10)	−0.0004 (10)
C4	0.0696 (14)	0.0977 (17)	0.0702 (12)	0.0097 (12)	0.0342 (11)	−0.0065 (12)
C5	0.0806 (15)	0.0854 (16)	0.0789 (13)	0.0172 (12)	0.0363 (11)	−0.0081 (11)
C6	0.0752 (14)	0.0730 (14)	0.0698 (12)	0.0075 (11)	0.0283 (11)	−0.0012 (10)
C7	0.0561 (12)	0.0701 (13)	0.0513 (10)	0.0046 (10)	0.0188 (9)	−0.0027 (9)
C8	0.0617 (13)	0.0654 (14)	0.0561 (11)	−0.0015 (10)	0.0173 (10)	−0.0002 (10)
C9	0.0885 (15)	0.0813 (15)	0.0833 (13)	−0.0096 (12)	0.0495 (12)	−0.0035 (11)
C10	0.1081 (18)	0.0911 (17)	0.1038 (16)	−0.0088 (14)	0.0540 (14)	0.0110 (12)

Geometric parameters (Å, º)

O1—C8	1.2147 (19)	C4—C5	1.387 (2)
O2—C8	1.3445 (19)	C4—H4	0.9300
O2—C9	1.4566 (19)	C5—C6	1.376 (2)
O3—C1	1.2079 (18)	C5—H5	0.9300
N1—C1	1.357 (2)	C6—C7	1.395 (2)
N1—C2	1.409 (2)	C6—H6	0.9300
N1—H1N	0.8600	C7—C8	1.489 (2)
N2—N3	1.264 (2)	C9—C10	1.510 (2)
N2—C1	1.423 (2)	C9—H9A	0.9700
N3—N4	1.131 (2)	C9—H9B	0.9700
C2—C3	1.395 (2)	C10—H10A	0.9600
C2—C7	1.421 (2)	C10—H10B	0.9600
C3—C4	1.380 (2)	C10—H10C	0.9600
C3—H3	0.9300		
C8—O2—C9	116.17 (13)	C5—C6—C7	121.66 (18)
C1—N1—C2	129.11 (14)	C5—C6—H6	119.2
C1—N1—H1N	115.4	C7—C6—H6	119.2
C2—N1—H1N	115.4	C6—C7—C2	118.78 (15)
N3—N2—C1	112.16 (14)	C6—C7—C8	119.97 (16)
N4—N3—N2	174.74 (18)	C2—C7—C8	121.23 (15)
O3—C1—N1	128.37 (16)	O1—C8—O2	122.55 (16)
O3—C1—N2	123.62 (17)	O1—C8—C7	125.65 (17)
N1—C1—N2	108.01 (15)	O2—C8—C7	111.80 (16)
C3—C2—N1	122.27 (16)	O2—C9—C10	106.76 (15)
C3—C2—C7	119.00 (16)	O2—C9—H9A	110.4
N1—C2—C7	118.72 (14)	C10—C9—H9A	110.4
C4—C3—C2	120.35 (17)	O2—C9—H9B	110.4
C4—C3—H3	119.8	C10—C9—H9B	110.4
C2—C3—H3	119.8	H9A—C9—H9B	108.6
C3—C4—C5	121.13 (17)	C9—C10—H10A	109.5
C3—C4—H4	119.4	C9—C10—H10B	109.5
C5—C4—H4	119.4	H10A—C10—H10B	109.5
C6—C5—C4	119.07 (17)	C9—C10—H10C	109.5
C6—C5—H5	120.5	H10A—C10—H10C	109.5
C4—C5—H5	120.5	H10B—C10—H10C	109.5

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*N*···O1	0.86	1.95	2.6593 (19)	139