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3,4-Dimethoxybenzohydrazide

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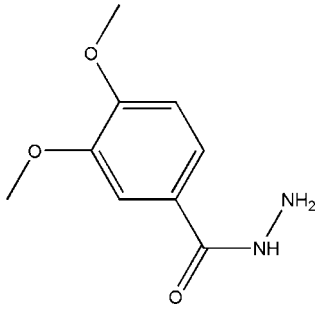
Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.003 Å; R factor = 0.046; wR factor = 0.094; data-to-parameter ratio = 15.7.

The title compound, $C_9H_{12}N_2O_3$, is an important intermediate for the synthesis of biologically active heterocyclic compounds. The planar hydrazide group is oriented with respect to the benzene ring at a dihedral angle of 63.27 (3)°. In the crystal structure, intermolecular N—H···O hydrogen bonds link the molecules to form a supramolecular structure.

Related literature

For general background, see: Zheng *et al.* (2003); Al-Talib *et al.* (1990); Yousif *et al.* (1986); Ahmad *et al.* (2001); Al-Soud *et al.* (2004); El-Emam *et al.* (2004); Allen *et al.* (1987); Furniss *et al.* (1978).



Experimental

Crystal data

$C_9H_{12}N_2O_3$
M_r = 196.21
Monoclinic, $P2_1/c$
a = 13.610 (3) Å
b = 8.9130 (19) Å
c = 7.9780 (17) Å
β = 105.266 (4)°
V = 933.6 (3) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.11 mm^{-1}
T = 100 (2) K
0.25 × 0.20 × 0.20 mm

Data collection

Bruker APEX diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.974, T_{max} = 0.979
5477 measured reflections
2148 independent reflections
1279 reflections with $I > 2\sigma(I)$
R_{int} = 0.064

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.046
$wR(F^2)$ = 0.094
S = 0.83
2148 reflections
137 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.29 e Å^{-3}
$\Delta\rho_{min}$ = −0.23 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O1^{i}	0.88	2.10	2.894 (2)	150
N2—H2A···O1^{ii}	0.90 (2)	2.17 (2)	2.944 (2)	144.0 (18)

Symmetry codes: (i) $-x, y+\frac{1}{2}, -z-\frac{1}{2}$; (ii) $x, -y+\frac{3}{2}, z-\frac{1}{2}$.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1999); 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: HK2256).

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supplementary materials

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3,4-Dimethoxybenzohydrazide

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Comment

Aromatic hydrazides are important intermediates in heterocyclic chemistry and have been used for the synthesis of various biologically active five-membered heterocycles such as 2,5-disubstituted-1,3,4-oxadiazoles (Zheng *et al.*, 2003; Al-Talib *et al.*, 1990) and 5-substituted-2-mercapto-1,3,4-oxadiazoles (Yousif *et al.*, 1986; Ahmad *et al.*, 2001; Al-Soud *et al.*, 2004; El-Emam *et al.*, 2004). In view of the versatility of these compounds, we have synthesized the title compound, (I), and reported its crystal structure.

In the molecule of the title compound, (I), (Fig. 1), the bond lengths and angles are within normal ranges (Allen *et al.*, 1987). The dihedral angle between the planar hydrazidic group (C7/O1/N1/N2) and benzene ring (C1—C6) is 63.27 (3)°.

In the crystal structure, the intermolecular N—H···O hydrogen bonds (Table 1) link the molecules to form a supramolecular structure (Fig. 2).

Experimental

The title compound, (I), is synthesized by the reaction of methyl ester of 3,4-dimethoxybenzoic acid with hdyrazine hydrate using the reported procedure (Furniss *et al.*, 1978). For the preparation of (I), a mixture of methyl-3,4-dimethoxybenzoate (2.10 g, 10 mmol) and hydrazine hydrate (80%, 15 ml) in absolute ethanol (50 ml) was refluxed for 5 h at 413–423 K. The excess solvent was removed by distillation. The solid residue was filtered off, washed with water and recrystallized from ethanol (30%) to give the title compound (yield: 1.89 g, 90%, m.p. 391–392 K). Colorless single crystals of (I) were obtained by slow evaporation of an ethanol solution at room temperature.

Refinement

H atoms of NH_2 group were located in difference syntheses and refined isotropically [N—H = 0.90 (2) and 0.95 (2) Å and U_{iso}(H) = 0.040 (7) and 0.053 (8) Å^2]. The remaining H atoms were positioned geometrically, with N—H = 0.88 Å (for NH) and C—H = 0.95 and 0.98 Å for aromatic and methyl H atoms, respectively, and constrained to ride on their parent atoms, with U_{iso}(H) = xU_{eq}(C,*N*), where x = 1.5 for methyl H, and x = 1.2 for all other H atoms.

Figures

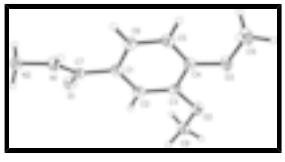


Fig. 1. The molecular structure of the title molecule, with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

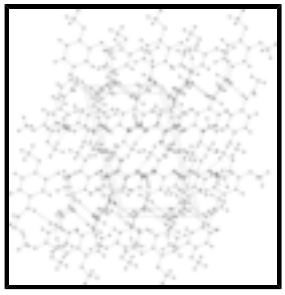


Fig. 2. A packing diagram for (I). Hydrogen bonds are shown as dashed lines.

Fig. 3. The synthesis route for the formation of the title compound.

3,4-Dimethoxybenzohydrazide

Crystal data

$C_9H_{12}N_2O_3$	F_{000} = 416
	D_x = 1.396 Mg m^{-3}
M_r = 196.21	D_m = 1.375 Mg m^{-3}
	D_m measured by not measured
Monoclinic, $P2_1/c$	Melting point: 391(1) K
Hall symbol: -P 2ybc	Mo $K\alpha$ radiation λ = 0.71073 Å
a = 13.610 (3) Å	Cell parameters from 927 reflections
b = 8.9130 (19) Å	θ = 2.8–25.1º
c = 7.9780 (17) Å	μ = 0.11 mm^{-1}
β = 105.266 (4)º	T = 100 (2) K
V = 933.6 (3) Å^3	Block, colourless
Z = 4	0.25 × 0.20 × 0.20 mm

Data collection

Bruker APEXII diffractometer	2148 independent reflections
Radiation source: fine-focus sealed tube	1279 reflections with $I > 2\sigma(I)$
Monochromator: graphite	R_{int} = 0.064
T = 100(2) K	θ_{max} = 28.3º
φ and ω scans	θ_{min} = 2.8º
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	h = −15→17
T_{min} = 0.974, T_{max} = 0.979	k = −7→11
5477 measured reflections	l = −10→10

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)]$ = 0.046	H atoms treated by a mixture of

	independent and constrained refinement
$wR(F^2) = 0.094$	$w = 1/[\sigma^2(F_o^2) + (0.035P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.83$	$(\Delta/\sigma)_{max} < 0.001$
2148 reflections	$\Delta\rho_{max} = 0.29$ e Å^{-3}
137 parameters	$\Delta\rho_{min} = -0.23$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

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 $F^2 > 2\text{sigma}(F^2)$ 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}
C1	0.15181 (14)	0.9587 (2)	−0.0649 (2)	0.0184 (4)
C2	0.19359 (15)	0.9328 (2)	0.1130 (2)	0.0193 (4)
H2	0.1589	0.8700	0.1749	0.023*
C3	0.28501 (15)	0.9982 (2)	0.1984 (2)	0.0184 (4)
C4	0.33684 (14)	1.0898 (2)	0.1051 (3)	0.0193 (5)
C5	0.29693 (15)	1.1115 (2)	−0.0706 (3)	0.0210 (5)
H5	0.3329	1.1707	−0.1339	0.025*
C6	0.20398 (14)	1.0468 (2)	−0.1558 (3)	0.0205 (5)
H6	0.1763	1.0633	−0.2767	0.025*
C7	0.05527 (15)	0.8802 (2)	−0.1522 (2)	0.0188 (4)
C8	0.29096 (15)	0.8730 (2)	0.4659 (3)	0.0238 (5)
H8A	0.2210	0.9002	0.4646	0.036*
H8B	0.3330	0.8693	0.5862	0.036*
H8C	0.2912	0.7744	0.4117	0.036*
C9	0.48231 (15)	1.2419 (3)	0.1152 (3)	0.0315 (5)
H9A	0.5055	1.1820	0.0299	0.047*
H9B	0.5414	1.2842	0.2000	0.047*
H9C	0.4385	1.3235	0.0556	0.047*
N1	−0.00531 (12)	0.94684 (18)	−0.2911 (2)	0.0200 (4)
H1	0.0109	1.0367	−0.3209	0.024*
N2	−0.09501 (13)	0.8771 (2)	−0.3922 (2)	0.0229 (4)
O1	0.03265 (10)	0.75694 (15)	−0.09871 (17)	0.0232 (3)
O2	0.33148 (10)	0.98293 (14)	0.37109 (16)	0.0222 (3)
O3	0.42607 (10)	1.14850 (14)	0.20274 (17)	0.0235 (4)

H2A	−0.0736 (16)	0.802 (3)	−0.449 (3)	0.040 (7)*
H2B	−0.1309 (18)	0.845 (3)	−0.311 (3)	0.053 (8)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0218 (11)	0.0121 (10)	0.0222 (10)	0.0025 (8)	0.0076 (9)	−0.0011 (8)
C2	0.0239 (11)	0.0127 (10)	0.0231 (11)	0.0013 (8)	0.0091 (9)	0.0016 (8)
C3	0.0240 (11)	0.0141 (10)	0.0174 (10)	0.0032 (9)	0.0060 (9)	−0.0015 (8)
C4	0.0199 (11)	0.0129 (10)	0.0256 (11)	0.0001 (8)	0.0067 (9)	−0.0018 (8)
C5	0.0244 (11)	0.0158 (11)	0.0243 (11)	−0.0008 (9)	0.0088 (9)	0.0027 (9)
C6	0.0225 (11)	0.0179 (11)	0.0208 (10)	0.0030 (9)	0.0051 (9)	0.0008 (8)
C7	0.0224 (11)	0.0151 (11)	0.0208 (11)	0.0018 (9)	0.0093 (9)	−0.0024 (9)
C8	0.0267 (12)	0.0216 (12)	0.0232 (11)	−0.0002 (9)	0.0070 (9)	0.0061 (9)
C9	0.0248 (12)	0.0327 (13)	0.0353 (13)	−0.0076 (10)	0.0048 (10)	0.0095 (11)
N1	0.0202 (9)	0.0135 (9)	0.0250 (9)	−0.0036 (7)	0.0036 (8)	0.0005 (7)
N2	0.0212 (10)	0.0203 (10)	0.0263 (10)	−0.0020 (8)	0.0046 (8)	−0.0035 (8)
O1	0.0282 (8)	0.0133 (7)	0.0277 (8)	−0.0023 (6)	0.0064 (6)	0.0015 (6)
O2	0.0266 (8)	0.0201 (8)	0.0185 (8)	−0.0034 (6)	0.0036 (6)	0.0023 (6)
O3	0.0216 (8)	0.0220 (8)	0.0252 (8)	−0.0051 (6)	0.0031 (6)	0.0041 (6)

Geometric parameters (Å, °)

C1—C6	1.385 (3)	C7—N1	1.334 (2)
C1—C2	1.402 (2)	C8—O2	1.434 (2)
C1—C7	1.490 (3)	C8—H8A	0.9800
C2—C3	1.381 (3)	C8—H8B	0.9800
C2—H2	0.9500	C8—H8C	0.9800
C3—O2	1.363 (2)	C9—O3	1.431 (2)
C3—C4	1.413 (3)	C9—H9A	0.9800
C4—O3	1.363 (2)	C9—H9B	0.9800
C4—C5	1.377 (2)	C9—H9C	0.9800
C5—C6	1.393 (3)	N1—N2	1.417 (2)
C5—H5	0.9500	N1—H1	0.8800
C6—H6	0.9500	N2—H2A	0.90 (2)
C7—O1	1.247 (2)	N2—H2B	0.95 (2)
C6—C1—C2	119.75 (18)	O2—C8—H8A	109.5
C6—C1—C7	122.13 (18)	O2—C8—H8B	109.5
C2—C1—C7	117.97 (17)	H8A—C8—H8B	109.5
C3—C2—C1	120.18 (18)	O2—C8—H8C	109.5
C3—C2—H2	119.9	H8A—C8—H8C	109.5
C1—C2—H2	119.9	H8B—C8—H8C	109.5
O2—C3—C2	125.08 (17)	O3—C9—H9A	109.5
O2—C3—C4	115.31 (17)	O3—C9—H9B	109.5
C2—C3—C4	119.61 (18)	H9A—C9—H9B	109.5
O3—C4—C5	125.55 (17)	O3—C9—H9C	109.5
O3—C4—C3	114.45 (17)	H9A—C9—H9C	109.5
C5—C4—C3	119.99 (18)	H9B—C9—H9C	109.5

C4—C5—C6	120.17 (18)	C7—N1—N2	121.93 (17)
C4—C5—H5	119.9	C7—N1—H1	119.0
C6—C5—H5	119.9	N2—N1—H1	119.0
C1—C6—C5	120.27 (19)	N1—N2—H2A	105.5 (14)
C1—C6—H6	119.9	N1—N2—H2B	105.3 (14)
C5—C6—H6	119.9	H2A—N2—H2B	114.3 (19)
O1—C7—N1	121.50 (18)	C3—O2—C8	117.45 (14)
O1—C7—C1	121.37 (18)	C4—O3—C9	117.05 (15)
N1—C7—C1	117.13 (17)		
C6—C1—C2—C3	1.8 (3)	C4—C5—C6—C1	−0.9 (3)
C7—C1—C2—C3	177.49 (17)	C6—C1—C7—O1	147.43 (18)
C1—C2—C3—O2	178.76 (16)	C2—C1—C7—O1	−28.1 (3)
C1—C2—C3—C4	−0.9 (3)	C6—C1—C7—N1	−31.9 (3)
O2—C3—C4—O3	0.3 (2)	C2—C1—C7—N1	152.58 (17)
C2—C3—C4—O3	179.92 (17)	O1—C7—N1—N2	−4.3 (3)
O2—C3—C4—C5	179.36 (16)	C1—C7—N1—N2	175.03 (17)
C2—C3—C4—C5	−1.0 (3)	C2—C3—O2—C8	10.0 (3)
O3—C4—C5—C6	−179.15 (18)	C4—C3—O2—C8	−170.31 (15)
C3—C4—C5—C6	1.9 (3)	C5—C4—O3—C9	0.7 (3)
C2—C1—C6—C5	−1.0 (3)	C3—C4—O3—C9	179.77 (16)
C7—C1—C6—C5	−176.43 (18)		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O1^{i}	0.88	2.10	2.894 (2)	150
N2—H2A···O1^{ii}	0.90 (2)	2.17 (2)	2.944 (2)	144.0 (18)

Symmetry codes: (i) −*x*, *y*+1/2, −*z*−1/2; (ii) *x*, −*y*+3/2, *z*−1/2.

Fig. 1

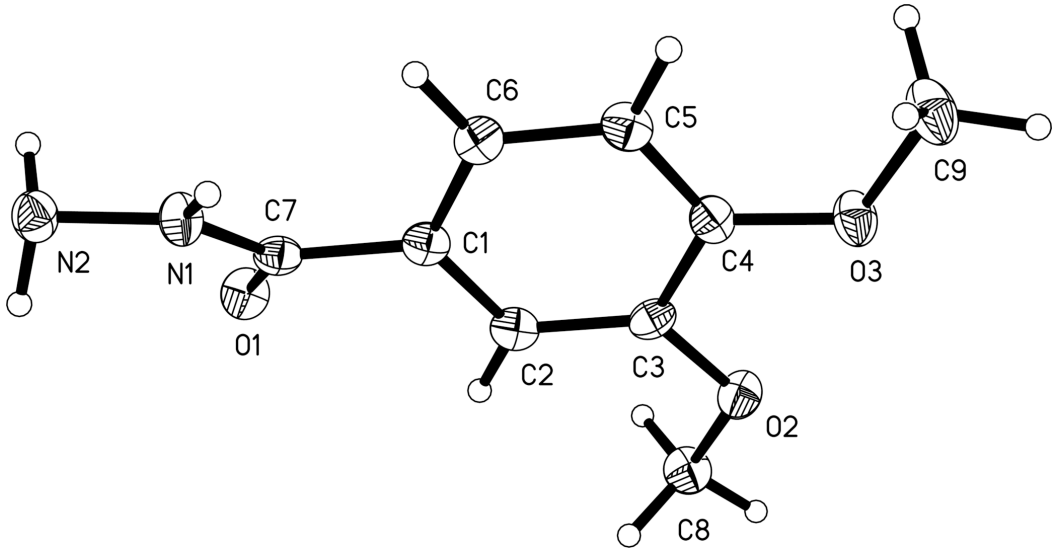


Fig. 2

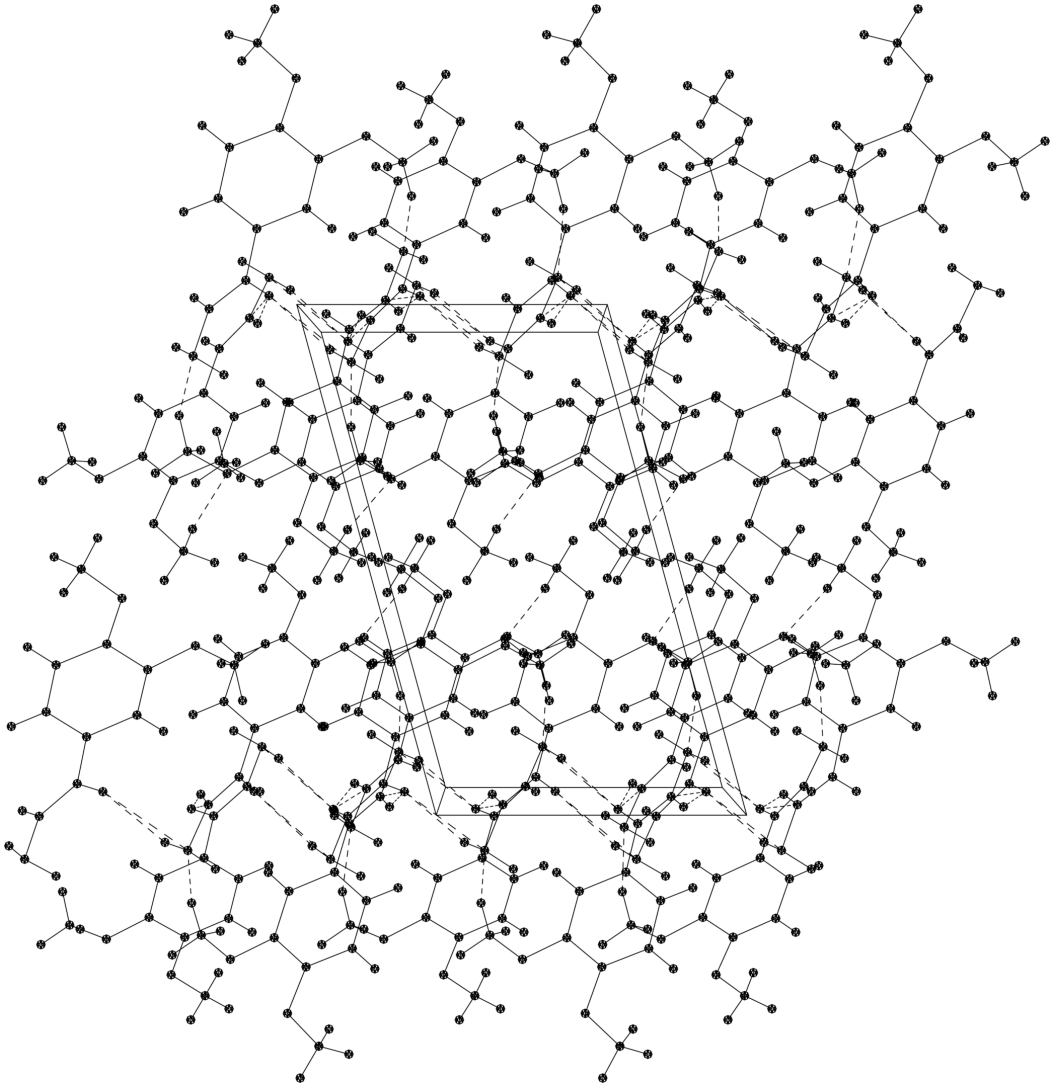
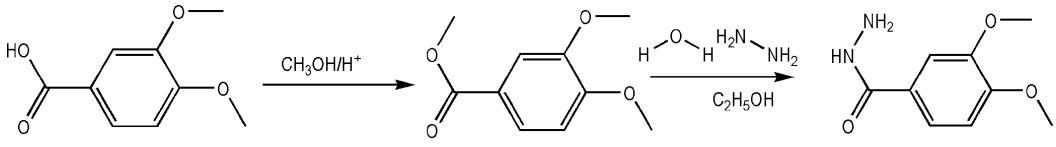


Fig. 3



3,4-dimethoxybenzoic acid

methyl 3,4-dimethoxybenzoate

3,4-dimethoxybenzohydrazide