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Dimethyl *N*,*N*′-(1,2-phenylene)dicarbamate

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The title compound, $C_{10}H_{12}N_2O_4$, crystallizes in the monoclinic non-centrosymmetric space group *Pn* with *Z* = 2. The two methyl carbamate groups, —N(H)—C(=O)—OCH$_3$, are twisted away from the aromatic ring mean plane, but form a semiflexible eight-membered cavity involving the atoms of the MeO—C(=O)—N(H)—CH$_2$—CH$_2$—N(H)—C(=O)—OMe group. The NH groups act as hydrogen-bond donors and the C=O groups as acceptors to form intermolecular N—H···O hydrogen bonding with an $R_2^1(7)$ motif, generating extended ribbons along the *b* direction.

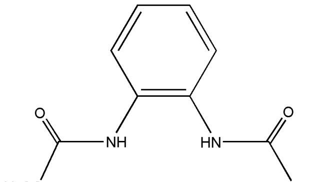
Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.003 Å
R factor = 0.031
wR factor = 0.081
Data-to-parameter ratio = 8.3

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

Continuing with our studies (Padilla-Martínez *et al.*, 2003) of molecular cavities, the analysis of the title structure, (I), is reported. Selected bond distances and torsion angles are listed in Table 1 and the molecular structure is shown in Fig. 1. Both methyl carbamate —N(H)—C(=O)—OCH$_3$ groups are almost planar, with C10—O9—C8—N7 and C14—O13—C12—N11 torsion angles of 175.17 (15) and −179.04 (16)°, respectively. The N7—C1 and N11—C2 bond lengths of 1.428 (2) and 1.410 (2) Å are very close to the value for the $C_{aromatic}$—Nsp^2 distance of 1.413 (3) Å reported for acetanilide (Brown, 1966). The N7—C8 and N11—C12 bond lengths of 1.339 (2) and 1.363 (2) Å are significantly different but this feature (the shorter bond length for N7—C8), in conjunction with the longer bond length for O8—C8 [1.224 (2) Å], in contrast with O12—C12 [1.201 Å], is probably the result of resonance effects caused by the carbonyl group containing atom O8 being involved in strong hydrogen-bonding interactions. The two methyl carbamate groups are twisted away from the aromatic ring mean plane, with C8—N7—C1—C6 and C12—N11—C2—C3 torsion angles of −57.2 (2) and 31.7 (3)°, respectively. The two amide H atoms are antiperiplanar to the carbonyl group, as has been observed for monosubstituted amides (Brown, 1966), but pointing towards the centre of the semiflexible eight-membered cavity formed by atoms O9/C8/N7/C1/C2/N11/C12/O13, giving an O9···O13 distance of 5.883 (2) Å.



(I)

The title structure is quite different from that obtained for diethyl *N*,*N*′-1,2-phenylenedioxamate (Martín *et al.*, 2002), for

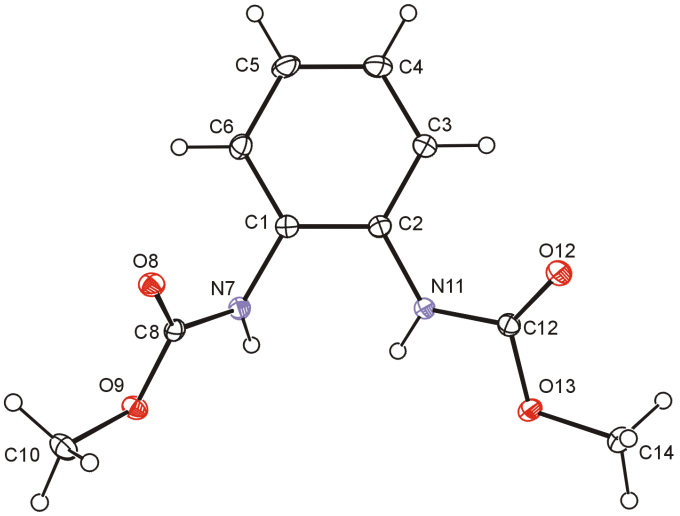


Figure 1
View of the molecular structure of the title compound, with displacement ellipsoids drawn at the 50% probability level.

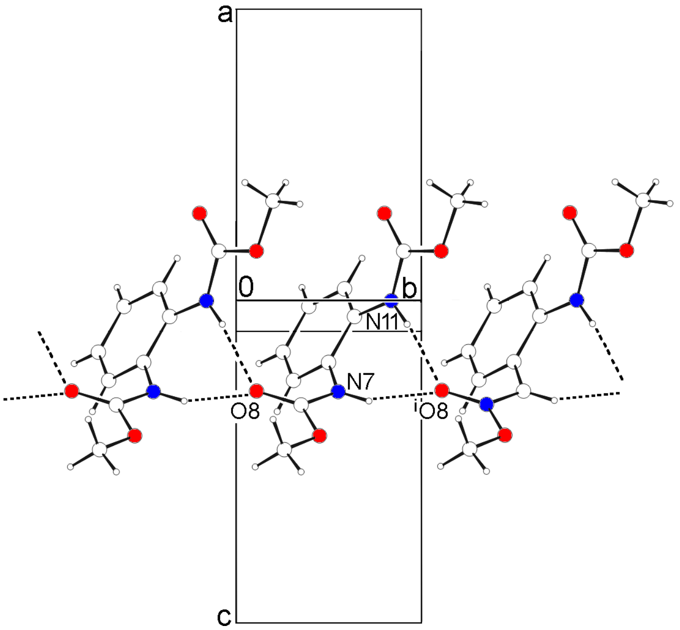


Figure 2
Partial packing diagram of the title compound, showing the hydrogen-bonded ribbons (dashed lines) formed by the $R_2^1(7)$ motif along the *b* direction. [Symmetry code: (i) *x*, 1 + *y*, *z*.]

which no cavity is formed, in spite of the close similarity to the title compound. In the crystal structure of (I), there are two intermolecular hydrogen-bonding interactions between the two amide H atoms and carbonyl atom O8, namely N7—H7···O8^{i} [N7···O8^{i} = 2.819 (2) Å and N7—H7···O8^{i} = 155°; symmetry code: (i) *x*, 1 + *y*, *z*] and N11—H11···O8^{i} [N11···O8^{i} = 2.976 (2) Å and N11—H11···O8^{i} = 170°], forming the seven-membered ring described by the graph-set descriptor $R_2^1(7)$ (Bernstein *et al.*, 1995). Extended tapes are generated by the continuous repetition of this motif along the *b* direction (Fig. 2). Hydrogen-bonding geometries are listed in Table 2.

Experimental

The title compound was prepared from 1,2-phenylenediamine (5.0 g, 46.3 mmol) and methyl chloroformate (7.2 ml, 92.6 mmol) in tetrahydrofuran (THF), in the presence of triethylamine (12.9 ml, 92.6 mmol). After filtering, evaporation of THF, several washings with distilled water and drying, 9.0 g (87% yield) of (I) were obtained as a colourless solid (m.p. 420–421 K). IR (neat solid, cm^{-1}): 3310 (NH), 1679 (CO); ^{1}H NMR (300.08 MHz, DMSO-d_6, p.p.m.): 8.79 (*s*, 2H, NH), 7.47–7.07 (*AA′*–*BB′*, 4H, H$_{ar}$), 3.65 (*s*, 6H, CH$_3$); ^{13}C NMR (75.46 MHz, DMSO-d_6, p.p.m.): 154.6 (CO), 130.2 (C$_i$), 125.0 (C$_o$), 124.5 (C$_m$), 51.9 (CH$_3$). Crystals suitable for X-ray analysis were obtained after slow crystallization from ethanol.

Crystal data

$C_{10}H_{12}N_2O_4$
$M_r = 224.22$
Monoclinic, *Pn*
$a = 9.306$ (2) Å
$b = 4.840$ (1) Å
$c = 11.843$ (2) Å
$\beta = 100.181$ (3)°
$V = 525.00$ (19) Å^3
$Z = 2$
$D_x = 1.418$ Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 600 reflections
$\theta = 20$–25°
$\mu = 0.11$ mm^{-1}
$T = 293$ (2) K
Block, colourless
0.52 × 0.42 × 0.36 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
4221 measured reflections
1203 independent reflections
1168 reflections with $I > 2\sigma(I)$
$R_{int} = 0.024$
$\theta_{max} = 27.5°$
$h = -11 \rightarrow 12$
$k = -6 \rightarrow 6$
$l = -15 \rightarrow 14$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.031$
$wR(F^2) = 0.081$
$S = 1.10$
1203 reflections
145 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0548P)^2 + 0.0358P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.25$ e Å^{-3}
$\Delta\rho_{min} = -0.24$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O8—C8	1.224 (2)	O13—C14	1.439 (2)
O9—C8	1.335 (2)	N7—C1	1.428 (2)
O9—C10	1.444 (2)	N7—C8	1.339 (2)
O12—C12	1.201 (2)	N11—C2	1.410 (2)
O13—C12	1.347 (2)	N11—C12	1.362 (2)
O8—C8—O9	123.68 (17)	O12—C12—N11	127.11 (18)
O8—C8—N7	125.65 (17)	O13—C12—N11	108.27 (16)
O9—C8—N7	110.67 (16)	O12—C12—O13	124.59 (17)
C10—O9—C8—N7	175.17 (15)	C8—N7—C1—C6	−57.2 (2)
C14—O13—C12—N11	−179.04 (16)	C12—N11—C2—C3	31.7 (3)

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N7—H7···O8^{i}	0.86	2.02	2.819 (2)	155
N11—H11···O8^{i}	0.86	2.13	2.976 (2)	170

Symmetry code: (i) *x*, 1 + *y*, *z*.

Acta Cryst. (2004). E**60**, o1488–o1490 Efrén V. García-Báez *et al.* • $C_{10}H_{12}N_2O_4$ **o1489**

All H atoms were included in calculated positions, with C—$H_{aromatic}$ = 0.93 Å, C—H_{methyl} = 0.96 Å and N—H = 0.86 Å. They were included in the riding-model approximation, with U_{iso} = 1.2U_{eq} (1.5U_{eq} for methyl) of the carrier atom. In the absence of anomalous dispersion effects, 1088 Friedel pairs were merged.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2000); software used to prepare material for publication: *SHELXL*97 and *WinGX*-2003 (Farrugia, 1999).

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