Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

1,4-Phenylenebis(methylene) dicarbamate

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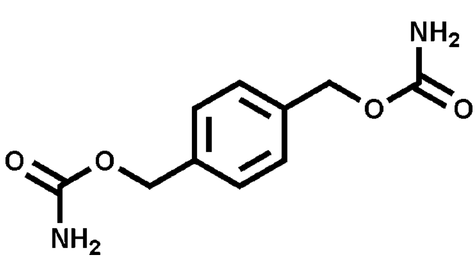
Received 16 February 2012; accepted 23 March 2012

Key indicators: single-crystal X-ray study; T = 294 K; mean σ(C–C) = 0.002 Å; R factor = 0.038; wR factor = 0.100; data-to-parameter ratio = 11.1.

The title compound, $C_{10}H_{12}N_2O_4$, is a phenyl dicarbamate with crystallographically imposed inversion symmetry. The dihedral angle between the carbamoyloxy plane [i.e. the plane of the N—C(O)—O fragment; r.m.s. deviation = 0.002 (3) Å] and the plane of the aryl ring is 29.2 (1)°. In the crystal, two different centrosymmetric N—H⋯O hydrogen-bond interactions are observed; these are described as $R_2^2(8)$ and $R_4^2(8)$ in graph-set notation. The rings form an alternating sequence, linking the molecules into a sheet structure parallel to (011).

Related literature

For self-assembled monolayers of alkyl carbamate and alkyl dicarbamate, see: Kim *et al.* (2003); Kim *et al.* (2005*a*,*b*). For the synthesis of the title compound, see: Takeuchi *et al.* (1971, 1974).



Experimental

Crystal data

$C_{10}H_{12}N_2O_4$
M_r = 224.22
Triclinic, $P\overline{1}$
a = 4.9542 (14) Å
b = 6.4194 (18) Å
c = 8.418 (2) Å
α = 79.290 (4)°
β = 79.351 (4)°
γ = 88.640 (4)°
V = 258.50 (13) Å^3
Z = 1
Mo $K\alpha$ radiation
μ = 0.11 mm^{-1}
T = 294 K
0.30 × 0.28 × 0.22 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.962, T_{max} = 0.975
1310 measured reflections
902 independent reflections
764 reflections with $I > 2\sigma(I)$
R_{int} = 0.022

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.038
$wR(F^2)$ = 0.100
S = 1.06
902 reflections
81 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.15 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
N1—H1A⋯O1^{i}	0.88 (2)	2.11 (2)	2.930 (2)	155.6 (17)
N1—H1B⋯O1^{ii}	0.93 (2)	2.07 (2)	2.9888 (19)	169.8 (16)

Symmetry codes: (i) $x+1, y, z$; (ii) $-x+1, -y+2, -z$.

Data collection: *SMART* (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: *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *Mercury* and *SHELXL97*.

The author thanks Beijing Jiaotong University for financial support. This research was supported by the Fundamental Research Funds for the Central Universities (2011JBM295).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: NK2147).

References

Bruker (2007). *SMART* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Kim, K., Plass, K. E. & Matzger, A. J. (2003). *Langmuir*, **19**, 7149–7152.
Kim, K., Plass, K. E. & Matzger, A. J. (2005*a*). *J. Am. Chem. Soc.* **127**, 4879–4887.
Kim, K., Plass, K. E. & Matzger, A. J. (2005*b*). *Langmuir*, **21**, 647–655.
Macrae, C. F., Bruno, I. J., Chisholm, J. A., Edgington, P. R., McCabe, P., Pidcock, E., Rodriguez-Monge, L., Taylor, R., van de Streek, J. & Wood, P. A. (2008). *J. Appl. Cryst.* **41**, 466–470.
Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Takeuchi, S. (1974). *Makromol. Chem.* **175**, 2241–2252.
Takeuchi, S. & Ninagawa, E. (1971). *Bull. Chem. Soc. Jpn*, **44**, 3184–3185.

supporting information

Acta Cryst. (2012). E**68**, o1227 [https://doi.org/10.1107/S1600536812012718]

1,4-Phenylenebis(methylene) dicarbamate

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S1. Comment

Recently, self-assembled monolayers of alkyl carbamate and alkyl dicarbamate have been investigated and characterizd (Kim *et al.*, 2003, 2005*a*,b). For further study of the self-assembled activities of dicarbamates, herein, we report the synthesis and structure of a phenyl dicarbamate, 1,4-phenylenebis(methylene) dicarbamate (I) (Fig. 1). In (I), The dihedral angle between the carbamoyloxy plane [O1, C1, N1, O2 plane, mean deviation: 0.002 (3) Å] and the benzene plane is 29.2 (1)°. As shown in Fig 2, the O atom (O1 atom) of the carbonyl group acts as a double H-receptor. The two H atoms of the same amino group interact with the O atom (O1 atom) of the carbonyl group in the adjacent molecule to form two different intermolecular N—H···O hydrogen bonds (N1—H1A···O1 and N1—H1B···O1; Table 1). These are described as $R_2^2(8)$ and $R^2_4(8)$ in graph set notation. The rings are located in an alternating sequence to link the molecules into a two dimensional sheet structure.

S2. Experimental

The title compound was synthesized by transesterification of ethyl carbamate with 1,4-phenylenedimethanol (Takeuchi *et al.* 1971, 1974) as followed: A solution of 8.9 g (100 mmol) ethyl carbamate and 1.38 g (10 mmol) 1,4-phenylenedimethanol in 25 ml of toluene was heated to reflux in the presence of catalytic amount of zinc chloride for 10 h. After cooling to room temperature, the solvent was evaporated under vacuum. The residue was subjected to flash chromatography and the title compound was obtained as colorless crystal. (1.34 g, Yield: 60%; m.p. 484–486 K). Crystals suitable for single-crystal X-ray analysis were grown by slow evaporation of a DMF solution.

S3. Refinement

H atoms were placed in calculated positions [C—H = 0.93–0.97 Å] and allowed to ride on the parent atoms, with U_{iso} values constrained to be $1.2U_{eq}$ of the parent atom. The bond length of N1—H1A is 0.88 (2) Å and the bond length of N1—H1B is 0.93 (2) Å.

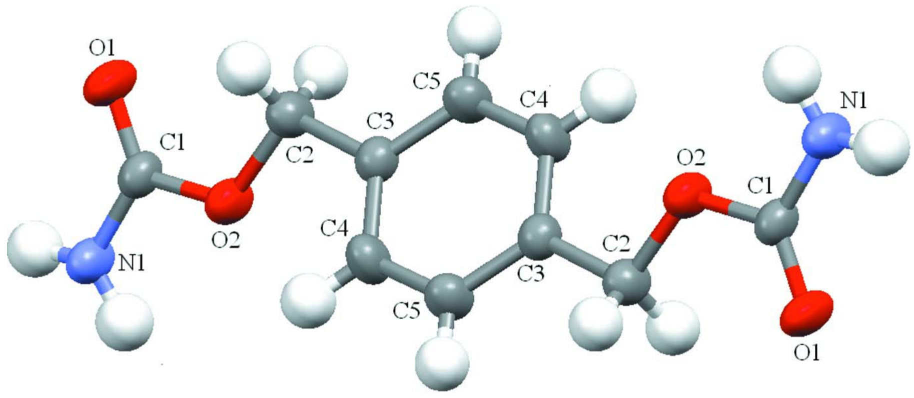

Figure 1

The structure of the title compound. Displacement ellipsoids are drawn at the 30% probability level.

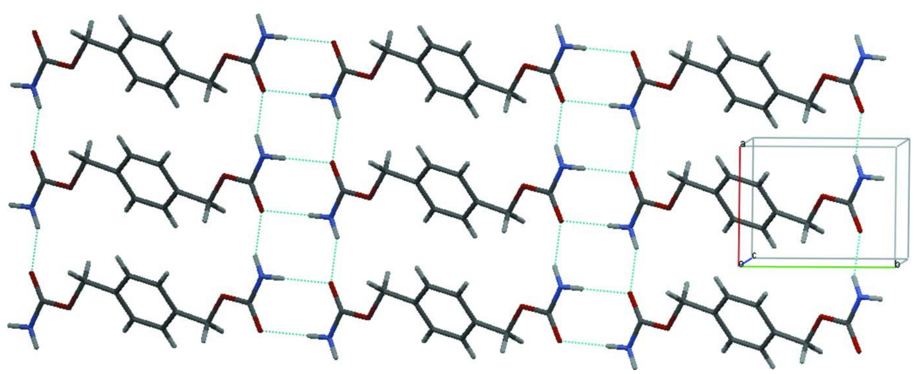

Figure 2

Packing diagram for (I). The dashed lines show N—H···O hydrogen bonds between neighboring molecules.

1,4-Phenylenebis(methylene) dicarbamate

Crystal data

$C_{10}H_{12}N_2O_4$
M_r = 224.22
Triclinic, $P\overline{1}$
Hall symbol: -P 1
a = 4.9542 (14) Å
b = 6.4194 (18) Å
c = 8.418 (2) Å
α = 79.290 (4)°
β = 79.351 (4)°
γ = 88.640 (4)°
V = 258.50 (13) Å^3
Z = 1
F(000) = 118
D_x = 1.440 Mg m^{-3}
Melting point: 485 K
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 819 reflections
θ = 2.5–26.1°
μ = 0.11 mm^{-1}
T = 294 K
Needle, colourless
0.30 × 0.28 × 0.22 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
phi and ω scans

Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.962$, $T_{max} = 0.975$
1310 measured reflections
902 independent reflections
764 reflections with $I > 2\sigma(I)$
$R_{int} = 0.022$
$\theta_{max} = 25.0°$, $\theta_{min} = 2.5°$
$h = -4 \rightarrow 5$
$k = -7 \rightarrow 5$
$l = -9 \rightarrow 9$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.100$
$S = 1.06$
902 reflections
81 parameters
0 restraints
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
$w = 1/[\sigma^2(F_o^2) + (0.0539P)^2 + 0.0526P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.15$ e Å^{-3}
$\Delta\rho_{min} = -0.21$ e Å^{-3}

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 $F^2 > \sigma(F^2)$ 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}
O1	0.2931 (2)	0.76540 (17)	0.12334 (15)	0.0498 (4)
O2	0.5723 (2)	0.51407 (16)	0.22471 (13)	0.0427 (4)
N1	0.7519 (3)	0.7787 (2)	0.02862 (18)	0.0451 (4)
C1	0.5223 (3)	0.6939 (2)	0.12480 (18)	0.0361 (4)
C2	0.3389 (3)	0.4099 (2)	0.3354 (2)	0.0419 (4)
H2A	0.1959	0.3894	0.2749	0.050*
H2B	0.2661	0.4963	0.4162	0.050*
C3	0.4273 (3)	0.1990 (2)	0.41993 (17)	0.0348 (4)
C4	0.6516 (3)	0.0921 (2)	0.35056 (19)	0.0432 (4)
H4	0.7555	0.1532	0.2496	0.052*
C5	0.2772 (3)	0.1045 (2)	0.57031 (19)	0.0417 (4)
H5	0.1262	0.1741	0.6189	0.050*
H1A	0.912 (4)	0.735 (3)	0.053 (2)	0.057 (5)*
H1B	0.740 (4)	0.914 (3)	−0.031 (2)	0.054 (5)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0332 (7)	0.0417 (7)	0.0668 (8)	0.0023 (5)	−0.0147 (5)	0.0152 (5)

O2	0.0355 (6)	0.0318 (6)	0.0531 (7)	0.0018 (4)	−0.0082 (5)	0.0120 (5)
N1	0.0345 (8)	0.0387 (8)	0.0538 (8)	0.0008 (6)	−0.0088 (6)	0.0135 (6)
C1	0.0359 (8)	0.0287 (8)	0.0421 (8)	0.0007 (6)	−0.0127 (6)	0.0029 (6)
C2	0.0373 (9)	0.0350 (9)	0.0468 (9)	0.0009 (6)	−0.0043 (7)	0.0060 (7)
C3	0.0364 (8)	0.0291 (8)	0.0373 (8)	−0.0008 (6)	−0.0086 (6)	−0.0001 (6)
C4	0.0470 (10)	0.0375 (9)	0.0368 (8)	0.0027 (7)	0.0021 (7)	0.0042 (6)
C5	0.0417 (9)	0.0348 (8)	0.0432 (9)	0.0071 (7)	−0.0005 (7)	−0.0013 (7)

Geometric parameters (Å, º)

O1—C1	1.2163 (19)	C2—H2B	0.9700
O2—C1	1.3430 (17)	C3—C5	1.383 (2)
O2—C2	1.4348 (18)	C3—C4	1.386 (2)
N1—C1	1.331 (2)	C4—C5^{i}	1.384 (2)
N1—H1A	0.88 (2)	C4—H4	0.9300
N1—H1B	0.93 (2)	C5—C4^{i}	1.384 (2)
C2—C3	1.503 (2)	C5—H5	0.9300
C2—H2A	0.9700		
C1—O2—C2	116.37 (12)	C3—C2—H2B	109.9
C1—N1—H1A	119.3 (12)	H2A—C2—H2B	108.3
C1—N1—H1B	116.7 (11)	C5—C3—C4	118.33 (14)
H1A—N1—H1B	118.9 (16)	C5—C3—C2	119.38 (14)
O1—C1—N1	125.38 (14)	C4—C3—C2	122.27 (14)
O1—C1—O2	123.02 (14)	C5^{i}—C4—C3	120.78 (15)
N1—C1—O2	111.59 (13)	C5^{i}—C4—H4	119.6
O2—C2—C3	108.74 (12)	C3—C4—H4	119.6
O2—C2—H2A	109.9	C3—C5—C4^{i}	120.89 (15)
C3—C2—H2A	109.9	C3—C5—H5	119.6
O2—C2—H2B	109.9	C4^{i}—C5—H5	119.6
C2—O2—C1—O1	−1.5 (2)	C5—C3—C4—C5^{i}	0.2 (3)
C2—O2—C1—N1	179.38 (13)	C2—C3—C4—C5^{i}	−178.21 (15)
C1—O2—C2—C3	172.41 (12)	C4—C3—C5—C4^{i}	−0.2 (3)
O2—C2—C3—C5	156.37 (14)	C2—C3—C5—C4^{i}	178.25 (15)
O2—C2—C3—C4	−25.2 (2)		

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

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*A*···O1^{ii}	0.88 (2)	2.11 (2)	2.930 (2)	155.6 (17)
N1—H1*B*···O1^{iii}	0.93 (2)	2.07 (2)	2.9888 (19)	169.8 (16)

Symmetry codes: (ii) $x+1, y, z$; (iii) $-x+1, -y+2, -z$.