



IUCrData

ISSN 2414-3146

Bis(4-hydroxyphenyl) 1,4-phenylenebiscarbamate

Isabel Martínez-de la Luz,^a Delia López-Velázquez,^a Sylvain Bernès^{b*} and Jenaro L. Varela Caselis^c

^aFacultad de Ciencias Químicas, Benemérita Universidad Autónoma de Puebla, 72570 Puebla, Mexico, ^bInstituto de Física, Benemérita Universidad Autónoma de Puebla, 72570 Puebla, Mexico, and ^cCentro Universitario de Vinculación, Benemérita Universidad Autónoma de Puebla, 72570 Puebla, Pue., Mexico. *Correspondence e-mail: sylvain_bernes@hotmail.com

Received 14 September 2022

Accepted 15 September 2022

Edited by E. R. T. Tiekink, Sunway University, Malaysia

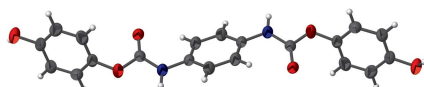
Keywords: crystal structure; urethane; hydrogen bond; centrosymmetric monomer.

CCDC reference: 2207709

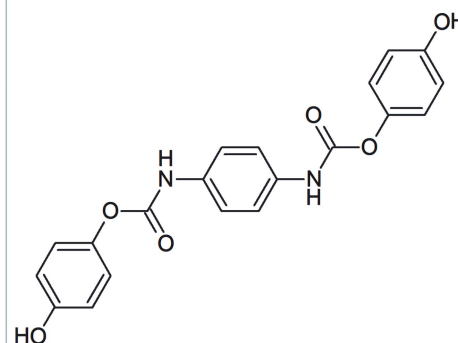
Structural data: full structural data are available from iucrdata.iucr.org

The title compound, C₂₀H₁₆N₂O₆ (systematic name: 4-hydroxyphenyl *N*-{4-[(4-hydroxyphenoxy)carbonyl]amino}phenyl}carbamate), contains two urethane groups substituting the central benzene ring in *para* positions. The molecule is centrosymmetric, and displays a twisted conformation for the three aromatic rings [the dihedral angle between central benzene ring and the urethane group is 33.4 (6)°, and that between the latter and the terminal ring is 65.1 (1)°]. In the crystal, a three-dimensional framework is formed through O—H···O and N—H···O hydrogen bonds involving the hydroxy and urethane functional groups, respectively.

3D view



Chemical scheme



Structure description

The title compound was obtained by reacting hydroquinone, 1,4-phenylene diisocyanate and triethylamine in dioxane. The resulting bis-urethane derivative crystallizes in the centrosymmetric space group $P2_1/c$, with the molecule having crystallographic inversion symmetry (Fig. 1). The urethane group displays the expected nearly planar geometry. This functional group is well represented in the CSD: 5700 hits are retrieved for organic compounds including an acyclic C—NH—(COO)—C fragment (CSD v. 5.43 with two updates, Groom *et al.*, 2016). However, most of these urethane derivatives originate from boc-protected amines, using the *tert*-butoxycarbonyl (boc) protecting group. In contrast, benzene rings substituted by two urethane groups are less studied by X-ray diffraction. For *para*-substituted benzene, only five structures have been deposited to date in the CSD. These occurrences include dimethyl 1,4-phenylenebiscarbamate (Stapf *et al.*, 2015), intended for anion complexation, and a dicholesterol derivative (Alegre-Requena *et al.*, 2020), intended for the preparation of supramolecular gels.



OPEN ACCESS

Published under a CC BY 4.0 licence

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$O14-H14\cdots O14^i$	0.85 (4)	1.91 (5)	2.754 (2)	172 (4)
$N4-H4\cdots O6^{ii}$	0.84 (3)	2.13 (4)	2.945 (3)	163 (3)

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

As for dimethyl 1,4-phenylenebiscarbamate, the title molecule is not planar. The dihedral angle between the central benzene ring and the urethane group is 33.4 (6)°, hindering the formation of an intramolecular hydrogen bond $C3-H3A\cdots O6$, although this could potentially stabilize the molecule through the formation of an $S(6)$ ring motif. The peripheral hydroxybenzene group is also rotated with respect to the urethane group, forming a dihedral angle of 65.1 (1)°.

This twisted molecular conformation helps in the formation of two kinds of hydrogen bonds, leading to a three-dimensional supramolecular architecture. First, hydroxy groups behave both as donor and acceptor, linking molecules through $O-H\cdots O$ hydrogen bonds. The resulting two-dimensional structure is nearly parallel to the (102) plane in the crystal (Table 1, entry 1; Fig. 2). These layers are further interconnected by urethane $N-H\cdots O$ hydrogen bonds oriented nearly perpendicular to the layers (Table 1, entry 2; Fig. 3). The three-dimensional framework is thermodynamically stable, although no intermolecular $\pi-\pi$ interactions are present in the crystal.

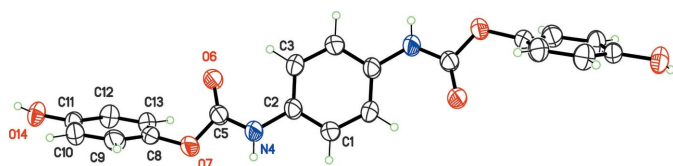


Figure 1
Molecular structure of the title compound, with displacement ellipsoids shown at the 50% probability level. Non-labelled atoms are generated by symmetry operation $1 - x, -y, 1 - z$.

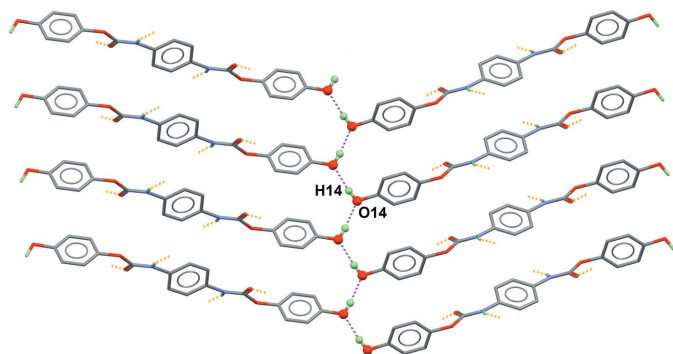


Figure 2
Supramolecular layers formed by $O-H\cdots O$ hydrogen bonds (see entry 1 in Table 1). Hydrogen bonds are shown as purple dashed lines, and the projection is nearly normal to [001]. Note the hanging contacts (orange dashed lines), corresponding to the hydrogen bonds described in Fig. 3. Benzene-H atoms are omitted for clarity.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{20}H_{16}N_2O_6$
M_r	380.35
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	295
a, b, c (Å)	19.0804 (17), 4.6758 (3), 10.1189 (8)
β (°)	101.169 (7)
V (Å ³)	885.67 (12)
Z	2
Radiation type	Ag $K\alpha$, $\lambda = 0.56083$ Å
μ (mm ⁻¹)	0.07
Crystal size (mm)	0.26 × 0.20 × 0.03
Data collection	
Diffractometer	Stoe Stadivari
Absorption correction	Multi-scan (<i>X-AREA</i> ; Stoe & Cie, 2019)
T_{min}, T_{max}	0.450, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	15028, 1678, 984
R_{int}	0.074
$(\sin \theta/\lambda)_{max}$ (Å ⁻¹)	0.609
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.051, 0.165, 1.06
No. of reflections	1678
No. of parameters	133
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å ⁻³)	0.16, -0.20

Computer programs: *X-AREA* (Stoe & Cie, 2019), *SHELXT2018/2* (Sheldrick, 2015a), *SHELXL2018/3* (Sheldrick, 2015b), *XP* in *SHELXTL-Plus* (Sheldrick, 2008), *Mercury* (Macrae *et al.*, 2020) and *pubCIF* (Westrip, 2010).

The synthesized molecule is a potential useful intermediate for obtaining other monomers, or cross-linking agents (Kothandaraman & Sultan Nasar, 1995; Lamba *et al.*, 1998): such diols are used for polycondensation reactions affording

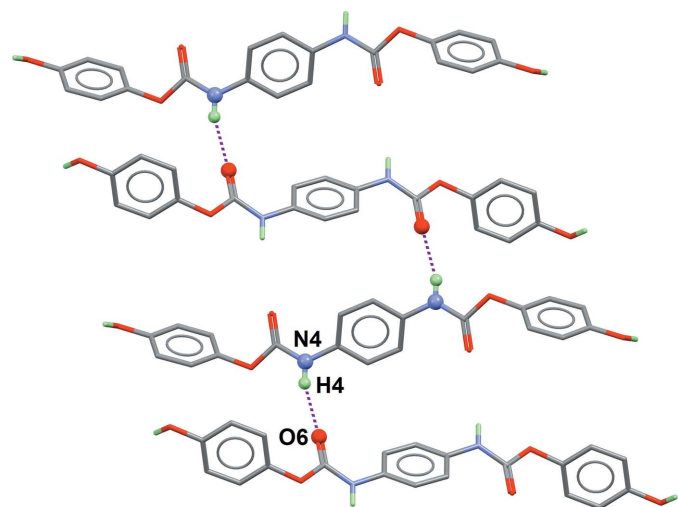


Figure 3
The two-dimensional supramolecular motif formed by $N-H\cdots O$ hydrogen bonds (see entry 2 in Table 1). Two neighbouring molecules are related by the glide plane of space group $P2_1/c$. The projection is nearly normal to [010]. Benzene-H atoms are omitted for clarity.

polymeric materials. On the other hand, some classes of urethane derivatives show diverse biological activity and have been used as fungicides, bactericides or analgesics, among other applications (Lamba *et al.*, 1998; Yagci *et al.*, 2011; Wang *et al.*, 2022).

Synthesis and crystallization

The synthesis was performed in a 100 ml three-mouth flask, sealed with silicone grease and evacuated with argon. In 5 ml of dry dioxane, hydroquinone (0.316 g), triethylamine (0.207 ml) and 1,4-phenylene diisocyanate (0.222 g) were added. The reaction was carried out at 353–363 K, under constant stirring. After a few minutes, it was observed that the reaction medium turned white. After 6 h, the reaction product was purified by column chromatography, using ethyl acetate:hexane (60:40) as the eluant. Once the purified monomer was obtained, it was dried in a furnace at 313 K for 24 h. Single crystals were obtained by evaporation of a saturated solution of the compound in an ethanol/dichloromethane mixture (4:1, *v:v*).

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

Funding information

Funding for this research was provided by: Consejo Nacional de Ciencia y Tecnología (scholarship No. 820488 to I. Martínez-de la Luz; grant No. 268178).

References

- Alegre-Requena, J. V., Herrera, R. P. & Díaz Díaz, D. (2020). *ChemPlusChem*, **85**, 2372–2375.
- Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.* **B72**, 171–179.
- Kothandaraman, H. & Nasar, A. S. (1995). *J. Macromol. Sci. Part A*, **32**, 1009–1016.
- Lamba, N. M. K., Woodhouse, K. A. & Cooper, S. L. (1998). Editors. *Polyurethanes in Biomedical Applications*. Routledge: CRC Press.
- Macrae, C. F., Sovago, I., Cottrell, S. J., Galek, P. T. A., McCabe, P., Pidcock, E., Platings, M., Shields, G. P., Stevens, J. S., Towler, M. & Wood, P. A. (2020). *J. Appl. Cryst.* **53**, 226–235.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Sheldrick, G. M. (2015a). *Acta Cryst.* **A71**, 3–8.
- Sheldrick, G. M. (2015b). *Acta Cryst.* **C71**, 3–8.
- Stapf, M., Seichter, W. & Weber, E. (2015). *Z. Naturforsch. Teil B*, **70**, 409–419.
- Stoe & Cie (2019). *X-AREA and X-RED32*. Stoe & Cie, Darmstadt, Germany.
- Wang, Y., Du, J., Guo, H., Liu, R., Li, Z., Yang, T., Ai, J. & Liu, C. (2022). *J. Polym. Res.* **29**, 47.
- Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.
- Yagci, M. B., Bolca, S., Heuts, J. P. A., Ming, W. & de With, G. (2011). *Prog. Org. Coat.* **72**, 305–314.

full crystallographic data

IUCrData (2022). 7, x220919 [https://doi.org/10.1107/S2414314622009191]

Bis(4-hydroxyphenyl) 1,4-phenylenebiscarbamate

Isabel Martínez-de la Luz, Delia López-Velázquez, Sylvain Bernès and Jenaro L. Varela Caselis

4-Hydroxyphenyl *N*-{4-[(4-hydroxyphenoxycarbonyl)amino]phenyl}carbamate*Crystal data*

$C_{20}H_{16}N_2O_6$	$F(000) = 396$
$M_r = 380.35$	$D_x = 1.426 \text{ Mg m}^{-3}$
Monoclinic, $P2_1/c$	Ag $K\alpha$ radiation, $\lambda = 0.56083 \text{ \AA}$
$a = 19.0804 (17) \text{ \AA}$	Cell parameters from 8468 reflections
$b = 4.6758 (3) \text{ \AA}$	$\theta = 2.6\text{--}25.0^\circ$
$c = 10.1189 (8) \text{ \AA}$	$\mu = 0.07 \text{ mm}^{-1}$
$\beta = 101.169 (7)^\circ$	$T = 295 \text{ K}$
$V = 885.67 (12) \text{ \AA}^3$	Plate, colourless
$Z = 2$	$0.26 \times 0.20 \times 0.03 \text{ mm}$

Data collection

Stoe Stadivari diffractometer	$T_{\min} = 0.450, T_{\max} = 1.000$
Radiation source: Sealed X-ray tube, Axo Astix- f Microfocus source	15028 measured reflections
Graded multilayer mirror monochromator	1678 independent reflections
Detector resolution: $5.81 \text{ pixels mm}^{-1}$	984 reflections with $I > 2\sigma(I)$
ω scans	$R_{\text{int}} = 0.074$
Absorption correction: multi-scan (X-AREA; Stoe & Cie, 2019)	$\theta_{\max} = 20.0^\circ, \theta_{\min} = 2.6^\circ$
	$h = -23 \rightarrow 23$
	$k = -5 \rightarrow 5$
	$l = -12 \rightarrow 11$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: mixed
$R[F^2 > 2\sigma(F^2)] = 0.051$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.165$	$w = 1/[\sigma^2(F_o^2) + (0.0826P)^2]$
$S = 1.06$	where $P = (F_o^2 + 2F_c^2)/3$
1678 reflections	$(\Delta/\sigma)_{\max} < 0.001$
133 parameters	$\Delta\rho_{\max} = 0.16 \text{ e \AA}^{-3}$
0 restraints	$\Delta\rho_{\min} = -0.19 \text{ e \AA}^{-3}$
0 constraints	
Primary atom site location: dual	

Special details

Refinement. H atoms bonded to heteroatoms were refined freely, while H atoms of aromatic CH groups were placed in calculated positions and refined as riding to their carrier C atom.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.47748 (17)	0.1997 (8)	0.4010 (3)	0.0515 (9)
H1A	0.462350	0.335166	0.334332	0.062*
C2	0.42963 (15)	0.0948 (7)	0.4754 (3)	0.0429 (8)
C3	0.45239 (16)	−0.1062 (8)	0.5758 (3)	0.0476 (8)
H3A	0.420723	−0.177251	0.626969	0.057*
N4	0.35804 (14)	0.1974 (7)	0.4457 (3)	0.0519 (8)
H4	0.3413 (19)	0.235 (8)	0.365 (4)	0.062*
C5	0.31708 (16)	0.2435 (7)	0.5367 (3)	0.0431 (8)
O6	0.33018 (11)	0.1848 (5)	0.65433 (18)	0.0521 (7)
O7	0.25538 (11)	0.3727 (6)	0.47506 (19)	0.0613 (8)
C8	0.20244 (17)	0.4238 (8)	0.5511 (3)	0.0462 (8)
C9	0.13914 (17)	0.2829 (8)	0.5162 (3)	0.0487 (8)
H9A	0.133664	0.144948	0.448748	0.058*
C10	0.08313 (17)	0.3420 (7)	0.5796 (3)	0.0461 (8)
H10A	0.039714	0.247497	0.554220	0.055*
C11	0.09221 (16)	0.5420 (7)	0.6806 (3)	0.0398 (7)
C12	0.15670 (17)	0.6839 (7)	0.7167 (3)	0.0479 (8)
H12A	0.162645	0.819364	0.785254	0.058*
C13	0.21180 (17)	0.6259 (8)	0.6520 (3)	0.0507 (9)
H13A	0.255094	0.721890	0.675983	0.061*
O14	0.03802 (12)	0.6086 (5)	0.7487 (2)	0.0505 (6)
H14	0.011 (2)	0.464 (10)	0.749 (4)	0.076*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0432 (19)	0.073 (3)	0.0396 (15)	0.0162 (17)	0.0118 (14)	0.0108 (15)
C2	0.0348 (17)	0.060 (2)	0.0349 (14)	0.0080 (15)	0.0093 (13)	−0.0035 (14)
C3	0.0380 (18)	0.066 (2)	0.0420 (16)	0.0044 (16)	0.0162 (14)	0.0038 (15)
N4	0.0366 (16)	0.086 (2)	0.0351 (12)	0.0135 (14)	0.0118 (12)	0.0053 (14)
C5	0.0351 (17)	0.058 (2)	0.0359 (15)	0.0054 (15)	0.0059 (13)	−0.0010 (15)
O6	0.0419 (13)	0.0833 (19)	0.0320 (11)	0.0149 (12)	0.0097 (9)	0.0029 (10)
O7	0.0401 (13)	0.105 (2)	0.0415 (11)	0.0267 (13)	0.0142 (10)	0.0150 (12)
C8	0.0367 (18)	0.067 (2)	0.0364 (15)	0.0132 (16)	0.0117 (13)	0.0128 (15)
C9	0.0443 (19)	0.062 (2)	0.0386 (15)	0.0063 (16)	0.0056 (14)	−0.0052 (15)
C10	0.0347 (17)	0.054 (2)	0.0502 (17)	−0.0009 (15)	0.0100 (14)	−0.0042 (15)
C11	0.0373 (17)	0.0401 (19)	0.0446 (15)	0.0056 (14)	0.0145 (13)	0.0050 (14)
C12	0.047 (2)	0.047 (2)	0.0518 (18)	−0.0047 (16)	0.0141 (15)	−0.0109 (15)
C13	0.0343 (17)	0.064 (2)	0.0541 (18)	−0.0046 (16)	0.0092 (15)	0.0063 (17)
O14	0.0458 (13)	0.0474 (15)	0.0659 (14)	0.0011 (11)	0.0294 (11)	−0.0022 (11)

Geometric parameters (\AA , $^\circ$)

C1—C2	1.381 (4)	C8—C13	1.377 (5)
C1—C3 ⁱ	1.384 (4)	C9—C10	1.377 (4)

C1—H1A	0.9300	C9—H9A	0.9300
C2—C3	1.390 (5)	C10—C11	1.371 (4)
C2—N4	1.424 (4)	C10—H10A	0.9300
C3—H3A	0.9300	C11—C12	1.383 (4)
N4—C5	1.336 (4)	C11—O14	1.385 (3)
N4—H4	0.84 (3)	C12—C13	1.369 (4)
C5—O6	1.199 (3)	C12—H12A	0.9300
C5—O7	1.362 (4)	C13—H13A	0.9300
O7—C8	1.404 (3)	O14—H14	0.85 (4)
C8—C9	1.361 (5)		
C2—C1—C3 ⁱ	121.0 (3)	C13—C8—O7	121.3 (3)
C2—C1—H1A	119.5	C8—C9—C10	120.8 (3)
C3 ⁱ —C1—H1A	119.5	C8—C9—H9A	119.6
C1—C2—C3	119.5 (3)	C10—C9—H9A	119.6
C1—C2—N4	118.3 (3)	C11—C10—C9	119.1 (3)
C3—C2—N4	122.2 (3)	C11—C10—H10A	120.4
C1 ⁱ —C3—C2	119.5 (3)	C9—C10—H10A	120.4
C1 ⁱ —C3—H3A	120.3	C10—C11—C12	120.1 (3)
C2—C3—H3A	120.3	C10—C11—O14	121.7 (3)
C5—N4—C2	125.1 (3)	C12—C11—O14	118.2 (3)
C5—N4—H4	118 (2)	C13—C12—C11	120.3 (3)
C2—N4—H4	117 (2)	C13—C12—H12A	119.8
O6—C5—N4	127.6 (3)	C11—C12—H12A	119.8
O6—C5—O7	123.5 (3)	C12—C13—C8	119.3 (3)
N4—C5—O7	109.0 (2)	C12—C13—H13A	120.4
C5—O7—C8	118.3 (2)	C8—C13—H13A	120.4
C9—C8—C13	120.4 (3)	C11—O14—H14	110 (3)
C9—C8—O7	118.2 (3)		
C3 ⁱ —C1—C2—C3	0.5 (6)	C5—O7—C8—C13	69.9 (4)
C3 ⁱ —C1—C2—N4	-179.3 (3)	C13—C8—C9—C10	0.9 (5)
C1—C2—C3—C1 ⁱ	-0.5 (6)	O7—C8—C9—C10	-174.5 (3)
N4—C2—C3—C1 ⁱ	179.3 (3)	C8—C9—C10—C11	-1.2 (5)
C1—C2—N4—C5	-144.0 (3)	C9—C10—C11—C12	0.7 (5)
C3—C2—N4—C5	36.2 (5)	C9—C10—C11—O14	-179.4 (3)
C2—N4—C5—O6	-7.1 (6)	C10—C11—C12—C13	0.0 (5)
C2—N4—C5—O7	172.8 (3)	O14—C11—C12—C13	-179.8 (3)
O6—C5—O7—C8	-4.1 (5)	C11—C12—C13—C8	-0.3 (5)
N4—C5—O7—C8	175.9 (3)	C9—C8—C13—C12	-0.2 (5)
C5—O7—C8—C9	-114.7 (4)	O7—C8—C13—C12	175.1 (3)

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

Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C3—H3A \cdots O6	0.93	2.47	2.939 (4)	111

C13—H13A···O6 ⁱⁱ	0.93	2.63	3.451 (4)	148
O14—H14···O14 ⁱⁱⁱ	0.85 (4)	1.91 (5)	2.754 (2)	172 (4)
N4—H4···O6 ^{iv}	0.84 (3)	2.13 (4)	2.945 (3)	163 (3)

Symmetry codes: (ii) $x, y+1, z$; (iii) $-x, y-1/2, -z+3/2$; (iv) $x, -y+1/2, z-1/2$.