Bis(4-hydroxyphenyl) 1,4-phenylenebiscarbamate

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The title compound, C\textsubscript{20}H\textsubscript{16}N\textsubscript{2}O\textsubscript{6} (systematic name: 4-hydroxyphenyl N-[4-[4-hydroxyphenoxycarbonyl]amino]phenyl]carbamate), contains two urethane groups substituting the central benzene ring in \emph{para} positions. The molecule is centrosymmetric, and displays a twisted conformation for the three aromatic rings \[\text{the dihedral angle between central benzene ring and the urethane group is 33.4 (6)°, and that between the latter and the terminal ring is 65.1 (1)°.}\] 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.

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 \emph{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.
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°, hindering the formation of an intramolecular hydrogen bond C3–H3A···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°.

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⋯O hydrogen bonds. The resulting two-dimensional supramolecular motif formed by N–H⋯O hydrogen bonds (see entry 1 in Table 1). Two neighbouring molecules are further interconnected by urethane N–H⋯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 π–π interactions are present in the crystal.

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...
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.

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full crystallographic data

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

Crystal data

C₂₀H₁₆N₂O₆

F(000) = 396

Mr = 380.35

Monoclinic, P2₁/c

Ag Kα radiation, λ = 0.56083 Å

a = 19.0804 (17) Å

Cell parameters from 8468 reflections

b = 4.6758 (3) Å

θ = 2.6–25.0°

c = 10.1189 (8) Å

μ = 0.07 mm⁻¹

β = 101.169 (7)°

T = 295 K

V = 885.67 (12) Å³

Plate, colourless

Z = 2

0.26 × 0.20 × 0.03 mm

Data collection

Stoe Stadivari
diffractometer

Radiation source: Sealed X-ray tube, Axo Astix-
Gem Microfocus source

Graded multilayer mirror monochromator

Detector resolution: 5.81 pixels mm⁻¹

ω scans

Absorption correction: multi-scan

(X-AREA; Stoe & Cie, 2019)

Tmin = 0.450, Tmax = 1.000

15028 measured reflections

1678 independent reflections

984 reflections with I > 2σ(I)

Rint = 0.074

θmax = 20.0°, θmin = 2.6°

h = −23→23

k = −5→5

l = −12→11

Refinement

Refinement on F²

Least-squares matrix: full

R[F² > 2σ(F²)] = 0.051

wR(F²) = 0.165

S = 1.06

1678 reflections

133 parameters

0 restraints

0 constraints

Primary atom site location: dual

Secondary atom site location: difference Fourier map

Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement

w = 1/[σ²(Fo²) + (0.0826P)²]

where P = (Fc² + 2Fc²)/3

(Δ/σ)max < 0.001

Δρmax = 0.16 e Å⁻³

Δρmin = −0.19 e Å⁻³

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 (Å²)

|   | x     | y     | z     | U_{iso} / U_{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 (Å²)

|   | 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 (Å, °)

|   |   |   |   |   |   |   |
|---|---|---|---|---|---|---|
| C1—C2 | 1.381 (4) |   |   |   |   |
| C1—C3 | 1.384 (4) |   |   |   |   |

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*Data reports (2022).* 7, x220919

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**IUCrData (2022)**
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 121.0 (3) C13—C8—O7 121.3 (3)
C2—C1—H1A 119.5 C8—C9—C10 120.8 (3)
C3—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—C3—C2 119.5 (3) C9—C10—H10A 120.4
C1—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—C1—C2—C3 0.5 (6) C5—O7—C8—C13 69.9 (4)
C3—C1—C2—N4 −179.3 (3) C13—C8—C9—C10 0.9 (5)
C1—C2—C3—C1i −0.5 (6) O7—C8—C9—C10 −174.5 (3)
N4—C2—C3—C1i 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 (Å, °)

| D—H···A     | D—H | H···A | D···A  | D—H···A |
|------------|-----|-------|--------|---------|
| C3—H3A···O6 | 0.93| 2.47  | 2.939 (4)| 111     |
|          |  d   |  r   |  D   |  θ   |
|----------|------|------|------|------|
| C13—H13A···O6\textsuperscript{ii} | 0.93 | 2.63 | 3.451 (4) | 148  |
| O14—H14···O14\textsuperscript{iii} | 0.85 (4) | 1.91 (5) | 2.754 (2) | 172 (4) |
| N4—H4···O6\textsuperscript{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) \(-y+1/2, z-1/2\).