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Dibenzyl 3,3′,4,4′-tetramethyl-5,5′-(ethynediyl)bis(pyrrole-2-carboxylate)

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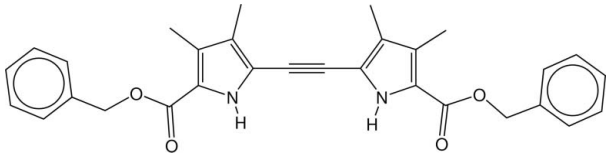
Key indicators: single-crystal X-ray study; T = 90 K; mean σ(C–C) = 0.001 Å; R factor = 0.044; wR factor = 0.124; data-to-parameter ratio = 28.3.

The title molecule, $C_{30}H_{28}N_2O_4$, has crystallographic twofold rotation symmetry, with the pyrrole planes forming a dihedral angle of 40.49 (4)°. The pyrrole N—H donor and adjacent ester carbonyl acceptor form $R_2^2(10)$ hydrogen-bonded rings about inversion centers, leading to chains of hydrogen-bonded molecules along [001].

Related literature

For background literature, see: Chinchilla & Najera (2007); Black *et al.* (1999); Etter (1990); Vogel (1996). For related structures, see: Xie *et al.* (1996); Weghorn *et al.* (1995).



Experimental

Crystal data

$C_{30}H_{28}N_2O_4$
M_r = 480.54
Monoclinic, $C2/c$
a = 19.340 (2) Å
b = 9.8955 (10) Å
c = 13.8495 (15) Å
β = 110.217 (6)°
V = 2487.2 (5) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.09 mm^{-1}
T = 90 K
0.30 × 0.22 × 0.15 mm

Data collection

Nonius KappaCCD diffractometer with Oxford Cryostream
Absorption correction: none
28071 measured reflections
4748 independent reflections
3948 reflections with $I > 2\sigma(I)$
R_{int} = 0.022

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.044
$wR(F^2)$ = 0.124
S = 1.03
4748 reflections
168 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.46 e Å^{-3}
$\Delta\rho_{min}$ = −0.39 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1N···O2^{i}	0.875 (14)	1.987 (14)	2.8565 (10)	172.1 (12)

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

Data collection: *COLLECT* (Nonius, 2000); cell refinement: *DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* and *SCALEPACK*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

The purchase of the diffractometer was made possible by grant No. LEQSF(1999–2000)-ENH-TR-13, administered by the Louisiana Board of Regents.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: DN2299).

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supplementary materials

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Dibenzyl 3,3',4,4'-tetramethyl-5,5'-(ethynediyl)bis(pyrrole-2-carboxylate)

H. K. Tanui, F. R. Fronczek and M. G. H. Vicente

Comment

Di(5-benzyloxycarbornyl-3,4-dimethyl-2-pyrrolyl)-ethyne (I) is an important intermediate in the synthesis of porphyrin analogues containing a two-carbon interpyrrolic bridge as in corrphycenes (Vogel, 1996). Compound (I) is also an interesting intermediate in the synthesis of dipyrroles with a two carbon bridge, which have shown selective binding properties to fluoride and other ions (Black *et al.* 1999). The title compound was prepared *via* an improved Sonogashira coupling reaction (Chinchilla & Najera, 2007), that took place between benzyl 5-iodo-3,4-dimethyl-1*H*-pyrrole-2-carboxylate and trimethylsilanyl-ethyne, in the presence of palladium(0) and copper(I) catalysts at room temperature. The exact experimental details are described below.

The structure of the title compound (I), which lies on a crystallographic twofold axis, is shown in Fig 1. The triple-bond distance is 1.2088 (17) Å, and the alkyne bridge is not quite linear, with C4—C5—C5^{i} angle 175.61 (10)° (i = 1 − *x*, *y*, 1/2 − *z*). The pyrrole ring is essentially planar, its five atoms having a mean deviation 0.003 Å from their best plane, with maximum 0.0051 (7) Å for C4. The two pyrrole rings are not coplanar, but form a dihedral angle of 40.49 (4)°. The ester COO group lies nearly in the pyrrole plane, with N1—C1—C6—O2 torsion angle 3.67 (13)°.

The pyrrole N—H group and adjacent ester carbonyl form intermolecular hydrogen bonded rings about inversion centers, having graph-set notation (Etter, 1990) $R_2^2(10)$. Thus, each molecule engages in four hydrogen bonds with two other molecules, forming chains in the [0 0 1] direction, as shown in Fig. 2.

Experimental

To a 100 ml round bottom flask was added benzyl 5-iodo-3,4-dimethyl-1*H*-pyrrole-2-carboxylate (2.93 g, 10 mmol) followed by $Pd(PPh)_2Cl_2$ (0.7019 g, 0.1 mmol) and CuI (0.191 g 0.1 mmol). The flask was sealed and placed in a dry ice bath under N_2. Trimethylsilanyl-ethyne (0.6996 ml, 5 mmol), DBU (8.973 ml, 60 mmol) and water (0.072 ml, 40 molar equiv.) were dissolved in 30 ml of acetonitrile and added to the reaction flask. After the mixture froze in the dry ice bath, the flask was evacuated and N_2 gas added. The resulting reaction mixture was allowed to warm slowly to room temperature and was stirred until complete disappearance of the starting material by TLC. The reaction mixture was worked up by adding ethyl acetate (150 ml), and washing the organic layer three times with saline. The organic phase was dried over anhydrous sodium bicarbonate and concentrated under reduced pressure. The crude mixture was purified by flash column chromatography using hexane/ethyl acetate (5:1) for elution. The dipyrrole-ethyne (I) was obtained (0.755 g) in 54% yield and recrystallized from dichloromethane to afford colorless crystals. Spectroscopic analysis, ^{1}H NMR (250 MHz, $CDCl_3$, 293 K, δ): 11.99 (2*H*, s, NH), 7.47–7.32 (10*H*, m, Ar—H), 5.29 (4*H*, s, CH_2), 2.2 (6*H*, s, CH_3), 2.0 (6*H*, s, CH_3). MS (EI) m/*z*: 480.129 (M^+).

Refinement

H atoms were placed in idealized positions with C—H distances 0.95 − 0.99 Å and thereafter treated as riding. U_{iso} for H was assigned as 1.2 times U_{eq} of the attached C atoms (1.5 for methyl). A torsional parameter was refined for each methyl group.

Figures

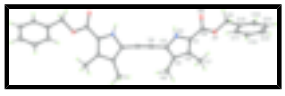

Fig. 1. Ellipsoids at the 50% level, with the asymmetric unit labeled. H atoms are represented with arbitrary radius.

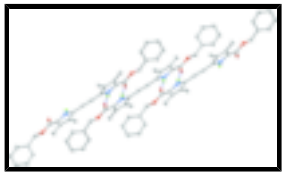

Fig. 2. View down the twofold axis, showing hydrogen bonding.

Dibenzyl 3,3',4,4'-tetramethyl-5,5'-(ethynediyl)bis(pyrrole-2-carboxylate)

Crystal data

$C_{30}H_{28}N_2O_4$	F_{000} = 1016
M_r = 480.54	D_x = 1.283 Mg m^{-3}
Monoclinic, *C*2/*c*	Mo *K*α radiation λ = 0.71073 Å
Hall symbol: -C 2yc	Cell parameters from 4869 reflections
a = 19.340 (2) Å	θ = 2.5–33.1º
b = 9.8955 (10) Å	μ = 0.09 mm^{-1}
c = 13.8495 (15) Å	*T* = 90 K
β = 110.217 (6)º	Prism, colorless
V = 2487.2 (5) Å^3	0.30 × 0.22 × 0.15 mm
Z = 4	

Data collection

Nonius KappaCCD (with Oxford Cryostream) diffractometer	3948 reflections with $I > 2\sigma(I)$
Radiation source: fine-focus sealed tube	R_{int} = 0.022
Monochromator: graphite	θ_{max} = 33.2º
T = 90 K	θ_{min} = 2.6º
ω scans with κ offsets	*h* = −29→29
Absorption correction: none	*k* = −15→15
28071 measured reflections	*l* = −21→21
4748 independent reflections	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.044$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.124$	$w = 1/[\sigma^2(F_o^2) + (0.067P)^2 + 1.378P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.03$	$(\Delta/\sigma)_{max} < 0.001$
4748 reflections	$\Delta\rho_{max} = 0.46$ e Å^{-3}
168 parameters	$\Delta\rho_{min} = -0.39$ 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 $F^2 > 2$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	0.38808 (4)	0.18151 (7)	0.63308 (5)	0.01536 (14)
O2	0.45716 (4)	0.03182 (7)	0.58415 (5)	0.01670 (14)
N1	0.46808 (4)	0.21012 (7)	0.43512 (5)	0.01204 (14)
H1N	0.4897 (7)	0.1328 (14)	0.4339 (10)	0.014*
C1	0.43250 (5)	0.24465 (9)	0.50220 (6)	0.01179 (15)
C2	0.40633 (5)	0.37712 (9)	0.48108 (6)	0.01253 (15)
C3	0.42701 (5)	0.42307 (8)	0.39832 (6)	0.01261 (15)
C4	0.46445 (5)	0.31725 (8)	0.37111 (6)	0.01224 (15)
C5	0.49073 (5)	0.31065 (9)	0.28744 (6)	0.01342 (15)
C6	0.42810 (5)	0.14317 (8)	0.57551 (6)	0.01202 (15)
C7	0.36367 (5)	0.45910 (9)	0.53229 (7)	0.01701 (17)
H7A	0.3974	0.5187	0.5838	0.026*
H7B	0.3389	0.3985	0.5660	0.026*
H7C	0.3268	0.5137	0.4806	0.026*
C8	0.40864 (6)	0.55667 (9)	0.34548 (7)	0.01793 (17)
H8A	0.4358	0.5673	0.2979	0.027*
H8B	0.4225	0.6292	0.3968	0.027*

H8C	0.3556	0.5612	0.3071	0.027*
C9	0.37901 (5)	0.07780 (9)	0.70202 (7)	0.01577 (16)
H9A	0.4274	0.0553	0.7543	0.019*
H9B	0.3584	−0.0052	0.6627	0.019*
C10	0.32768 (5)	0.13018 (9)	0.75362 (6)	0.01280 (15)
C11	0.26606 (5)	0.20803 (9)	0.70116 (7)	0.01592 (16)
H11	0.2572	0.2337	0.6318	0.019*
C12	0.21747 (5)	0.24831 (10)	0.74984 (8)	0.01892 (18)
H12	0.1761	0.3027	0.7141	0.023*
C13	0.22929 (6)	0.20909 (11)	0.85086 (8)	0.0228 (2)
H13	0.1954	0.2346	0.8835	0.027*
C14	0.29082 (6)	0.13248 (11)	0.90349 (8)	0.0235 (2)
H14	0.2992	0.1058	0.9725	0.028*
C15	0.34045 (5)	0.09438 (10)	0.85570 (7)	0.01773 (17)
H15	0.3831	0.0438	0.8928	0.021*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0226 (3)	0.0130 (3)	0.0161 (3)	0.0032 (2)	0.0138 (2)	0.0026 (2)
O2	0.0229 (3)	0.0139 (3)	0.0171 (3)	0.0063 (2)	0.0118 (2)	0.0028 (2)
N1	0.0154 (3)	0.0107 (3)	0.0129 (3)	0.0023 (2)	0.0085 (2)	0.0010 (2)
C1	0.0147 (3)	0.0117 (3)	0.0115 (3)	0.0011 (3)	0.0077 (3)	−0.0001 (3)
C2	0.0151 (3)	0.0117 (3)	0.0128 (3)	0.0017 (3)	0.0074 (3)	−0.0004 (3)
C3	0.0151 (4)	0.0111 (3)	0.0132 (3)	0.0015 (3)	0.0069 (3)	0.0005 (3)
C4	0.0145 (3)	0.0119 (3)	0.0124 (3)	0.0002 (3)	0.0073 (3)	0.0006 (3)
C5	0.0149 (4)	0.0125 (3)	0.0147 (3)	0.0001 (3)	0.0075 (3)	0.0000 (3)
C6	0.0142 (3)	0.0127 (3)	0.0107 (3)	0.0010 (3)	0.0063 (3)	0.0001 (3)
C7	0.0224 (4)	0.0148 (4)	0.0183 (4)	0.0043 (3)	0.0127 (3)	−0.0008 (3)
C8	0.0241 (4)	0.0128 (4)	0.0192 (4)	0.0035 (3)	0.0105 (3)	0.0038 (3)
C9	0.0220 (4)	0.0145 (4)	0.0152 (3)	0.0034 (3)	0.0119 (3)	0.0038 (3)
C10	0.0159 (4)	0.0120 (3)	0.0128 (3)	−0.0016 (3)	0.0080 (3)	−0.0005 (3)
C11	0.0158 (4)	0.0180 (4)	0.0145 (3)	−0.0009 (3)	0.0060 (3)	−0.0004 (3)
C12	0.0155 (4)	0.0186 (4)	0.0248 (4)	−0.0006 (3)	0.0095 (3)	−0.0019 (3)
C13	0.0274 (5)	0.0211 (4)	0.0285 (5)	−0.0009 (4)	0.0209 (4)	−0.0028 (4)
C14	0.0351 (5)	0.0238 (5)	0.0190 (4)	0.0027 (4)	0.0188 (4)	0.0021 (4)
C15	0.0240 (4)	0.0169 (4)	0.0150 (4)	0.0026 (3)	0.0101 (3)	0.0020 (3)

Geometric parameters (Å, °)

O1—C6	1.3436 (10)	C8—H8A	0.9800
O1—C9	1.4530 (10)	C8—H8B	0.9800
O2—C6	1.2240 (10)	C8—H8C	0.9800
N1—C4	1.3680 (11)	C9—C10	1.5018 (12)
N1—C1	1.3767 (10)	C9—H9A	0.9900
N1—H1N	0.875 (14)	C9—H9B	0.9900
C1—C2	1.3992 (12)	C10—C11	1.3940 (12)
C1—C6	1.4514 (11)	C10—C15	1.3941 (12)
C2—C3	1.4133 (11)	C11—C12	1.3910 (13)

C2—C7	1.4987 (12)	C11—H11	0.9500
C3—C4	1.3969 (12)	C12—C13	1.3925 (15)
C3—C8	1.4932 (12)	C12—H12	0.9500
C4—C5	1.4185 (12)	C13—C14	1.3866 (16)
C5—C5^{i}	1.2088 (17)	C13—H13	0.9500
C7—H7A	0.9800	C14—C15	1.3931 (13)
C7—H7B	0.9800	C14—H14	0.9500
C7—H7C	0.9800	C15—H15	0.9500
C6—O1—C9	114.55 (7)	H8A—C8—H8B	109.5
C4—N1—C1	108.62 (7)	C3—C8—H8C	109.5
C4—N1—H1N	125.7 (8)	H8A—C8—H8C	109.5
C1—N1—H1N	125.7 (8)	H8B—C8—H8C	109.5
N1—C1—C2	108.70 (7)	O1—C9—C10	108.58 (7)
N1—C1—C6	117.66 (7)	O1—C9—H9A	110.0
C2—C1—C6	133.63 (7)	C10—C9—H9A	110.0
C1—C2—C3	106.71 (7)	O1—C9—H9B	110.0
C1—C2—C7	128.81 (8)	C10—C9—H9B	110.0
C3—C2—C7	124.47 (8)	H9A—C9—H9B	108.4
C4—C3—C2	107.22 (7)	C11—C10—C15	119.27 (8)
C4—C3—C8	126.09 (8)	C11—C10—C9	121.96 (7)
C2—C3—C8	126.60 (8)	C15—C10—C9	118.70 (8)
N1—C4—C3	108.75 (7)	C12—C11—C10	120.32 (8)
N1—C4—C5	122.75 (8)	C12—C11—H11	119.8
C3—C4—C5	128.34 (8)	C10—C11—H11	119.8
C5^{i}—C5—C4	175.61 (10)	C11—C12—C13	120.22 (9)
O2—C6—O1	122.38 (8)	C11—C12—H12	119.9
O2—C6—C1	123.73 (8)	C13—C12—H12	119.9
O1—C6—C1	113.89 (7)	C14—C13—C12	119.58 (9)
C2—C7—H7A	109.5	C14—C13—H13	120.2
C2—C7—H7B	109.5	C12—C13—H13	120.2
H7A—C7—H7B	109.5	C13—C14—C15	120.35 (9)
C2—C7—H7C	109.5	C13—C14—H14	119.8
H7A—C7—H7C	109.5	C15—C14—H14	119.8
H7B—C7—H7C	109.5	C14—C15—C10	120.22 (9)
C3—C8—H8A	109.5	C14—C15—H15	119.9
C3—C8—H8B	109.5	C10—C15—H15	119.9
C4—N1—C1—C2	−0.61 (10)	C9—O1—C6—C1	176.08 (7)
C4—N1—C1—C6	178.33 (7)	N1—C1—C6—O2	3.67 (13)
N1—C1—C2—C3	0.08 (10)	C2—C1—C6—O2	−177.72 (9)
C6—C1—C2—C3	−178.63 (9)	N1—C1—C6—O1	−175.51 (7)
N1—C1—C2—C7	179.36 (9)	C2—C1—C6—O1	3.10 (14)
C6—C1—C2—C7	0.65 (16)	C6—O1—C9—C10	−174.76 (7)
C1—C2—C3—C4	0.47 (10)	O1—C9—C10—C11	38.88 (11)
C7—C2—C3—C4	−178.85 (8)	O1—C9—C10—C15	−144.09 (8)
C1—C2—C3—C8	177.24 (9)	C15—C10—C11—C12	−0.68 (14)
C7—C2—C3—C8	−2.09 (14)	C9—C10—C11—C12	176.33 (9)
C1—N1—C4—C3	0.92 (10)	C10—C11—C12—C13	−1.15 (14)
C1—N1—C4—C5	−174.76 (8)	C11—C12—C13—C14	1.62 (16)

C2—C3—C4—N1	−0.86 (10)	C12—C13—C14—C15	−0.25 (16)
C8—C3—C4—N1	−177.64 (8)	C13—C14—C15—C10	−1.59 (16)
C2—C3—C4—C5	174.51 (8)	C11—C10—C15—C14	2.04 (14)
C8—C3—C4—C5	−2.28 (15)	C9—C10—C15—C14	−175.07 (9)
C9—O1—C6—O2	−3.12 (12)		

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

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1N···O2^{ii}	0.875 (14)	1.987 (14)	2.8565 (10)	172.1 (12)

Symmetry codes: (ii) −*x*+1, −*y*, −*z*+1.

Fig. 1

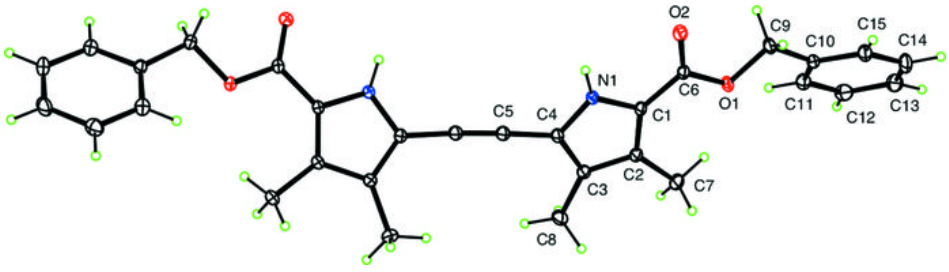

Fig. 2