# organic compounds

# Biphenyl-4,4'-diyl bis(2,2,5,5-tetramethyl-1-oxyl-3-pyrroline-3-carboxylate)

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In the title compound, $C_{30}H_{34}N_2O_6$, the complete molecule is generated by a crystallographic $2/m$ symmetry operation. The 1-oxyl-3-pyrroline-3-carboxylate group lies on a mirror plane. The dihedral angle between the ring planes of the biphenyl fragment is constrained by symmetry to be zero, resulting in rather short intramolecular H···H contact distances of 2.02 Å. In the crystal, molecules are connected along the $a$-axis direction by very weak intermolecular methyl–phenyl C—H···$\pi$ interactions. The C—H bond is not directed to the center of the benzene ring, but mainly to one C atom [C—H···C($x - 1$, $y$, $z$): H···C = 2.91 Å and C—H···C = 143°].

## Related literature

For the preparation of the title compound see: Weber *et al.* (2002). For the crystal structures of related compounds see: Boeyens & Kruger (1970); Bolte (2006); Duskova *et al.* (2001); Godt *et al.*, 2000; Papoutsakis *et al.* (1999); Wiley *et al.*, 1989 and Wiley *et al.*, 1991.
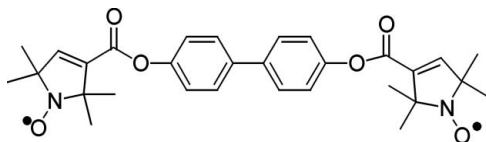


## Experimental

### Crystal data

| | |
|---|---|
| $C_{30}H_{34}N_2O_6$ | $V$ = 1356.6 (6) Å$^3$ |
| $M_r$ = 518.59 | $Z$ = 2 |
| Monoclinic, $C2/m$ | Mo $K\alpha$ radiation |
| $a$ = 6.931 (2) Å | $\mu$ = 0.09 mm$^{-1}$ |
| $b$ = 9.461 (3) Å | $T$ = 169 K |
| $c$ = 20.805 (4) Å | 0.44 × 0.30 × 0.10 mm |
| $\beta$ = 96.059 (14)° | |

### Data collection

| | |
|---|---|
| Siemens SMART 1K CCD diffractometer | 2074 independent reflections |
| | 1552 reflections with $I > 2\sigma(I)$ |
| Absorption correction: none | $R_{int}$ = 0.056 |
| 11267 measured reflections | |

### Refinement

| | |
|---|---|
| $R[F^2 > 2\sigma(F^2)]$ = 0.049 | 105 parameters |
| $wR(F^2)$ = 0.126 | H-atom parameters constrained |
| $S$ = 1.03 | $\Delta\rho_{max}$ = 0.39 e Å$^{-3}$ |
| 2074 reflections | $\Delta\rho_{min}$ = −0.21 e Å$^{-3}$ |

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| C11—H11$C$···C3$^i$ | 0.98 | 2.91 | 3.745 (2) | 143 |

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

Data collection: *SMART* (Siemens, 1995); cell refinement: *SMART*; data reduction: *SAINT* (Siemens, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LH2852).

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# supporting information

## Biphenyl-4,4′-diyl bis(2,2,5,5-tetramethyl-1-oxyl-3-pyrroline-3-carboxylate)

**Dominik Margraf, Denise Schuetz, Thomas F. Prisner and Jan W. Bats**

### S1. Comment

The title compound was prepared as a reference compound for pulsed electron-electron double resonance measurements (Weber *et al.*, 2002).

The molecular structure is shown in Fig. 1. The molecule has 2/m symmetry: atoms C1, C4, O1, C5, O2, C6, C7, C8, C9, N1 and O3 lie on a mirror plane. There is a twofold axis perpendicular to this mirror plane and passing through the center of the central C—C single bond. There also is an inversion center at the midpoint of the central C—C single bond. The two six-membered rings of the biphenyl group are coplanar by symmetry, resulting in rather short intramolecular H···H contact distances of 2.02 A. The 1-oxyl-3-pyrroline-3-carboxylate group is planar. Approximate planarity of this group also has been observed in a number of related crystal structures (Papoutsakis *et al.*, 1999; Boeyens & Kruger, 1970; Bolte, 2006; Duskova *et al.*, 2001; Godt *et al.*, 2000; Wiley *et al.*, 1989 and Wiley *et al.*, 1991)

The crystal packing is shown in Fig 2. The molecules are connected along the a-direction by four symmetry-equivalent very weak intermolecular $C_{methyl}$—H···$\pi$(phenyl) interactions (Table 1). The $C_{methyl}$—H bond is not directed to the center of the phenyl ring, but mainly to one C atom. There are no other short intermolecular contacts.

### S2. Experimental

The title compound was prepared similar to the procedure described by Weber *et al.* (2002). Single crystals were obtained by recrystallization of the compound from a mixture of toluene and n-hexane (3:1).

### S3. Refinement

The H atoms were positioned geometrically and treated as riding: $C_{methyl}$—H=0.98 Å, $C_{planar}$—H=0.95 Å, $U_{iso}(H)=1.2U_{eq}(C_{non-methyl})$ and $U_{iso}(H)=1.5U_{eq}(C_{methyl})$. The torsion angles about the $C$—$C_{methyl}$ bonds were refined for the methyl groups.
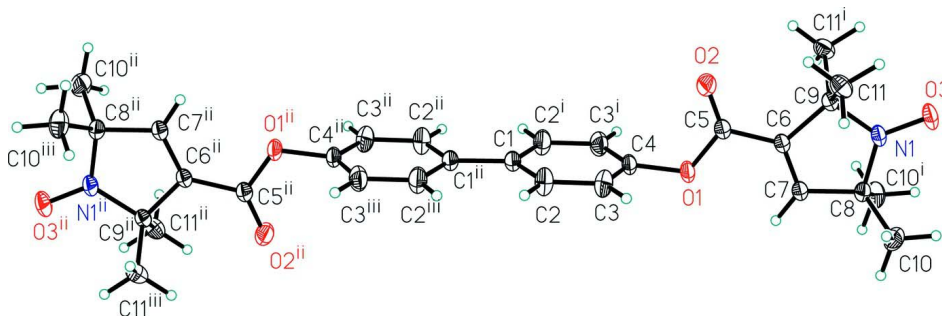


**Figure 1**

The structure of the title compound shown with 50% probability displacement ellipsoids. The H atoms are drawn as small spheres of arbitrary radius. Symmetry equivalent atoms are related by i: *x, -y, z*, ii: 2 - *x*, -*y*, 1 - *z* and iii: 2 - *x, y*, 1 - *z*.
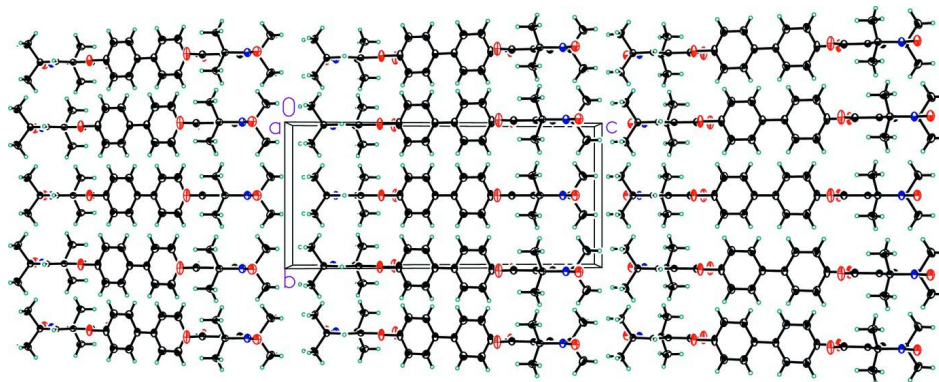
**Figure 2**
The crystal packing of the title compound, viewed down the *a* axis.

**Biphenyl-4,4′-diyl bis(2,2,5,5-tetramethyl-1-oxyl-3-pyrroline-3-carboxylate)**

*Crystal data*

| | |
|---|---|
| $C_{30}H_{34}N_2O_6$ | $F(000) = 552$ |
| $M_r = 518.59$ | $D_x = 1.270$ Mg m$^{-3}$ |
| Monoclinic, $C2/m$ | Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å |
| Hall symbol: -C 2yc | Cell parameters from 77 reflections |
| $a = 6.931$ (2) Å | $\theta = 3–23°$ |
| $b = 9.461$ (3) Å | $\mu = 0.09$ mm$^{-1}$ |
| $c = 20.805$ (4) Å | $T = 169$ K |
| $\beta = 96.059$ (14)° | Plate, yellow |
| $V = 1356.6$ (6) Å$^3$ | $0.44 \times 0.30 \times 0.10$ mm |
| $Z = 2$ | |

*Data collection*

| | |
|---|---|
| Siemens SMART 1K CCD diffractometer | 1552 reflections with $I > 2\sigma(I)$ |
| Radiation source: normal-focus sealed tube | $R_{int} = 0.056$ |
| Graphite monochromator | $\theta_{max} = 30.5°$, $\theta_{min} = 2.0°$ |
| $\omega$ scans | $h = -9 \rightarrow 9$ |
| 11267 measured reflections | $k = -13 \rightarrow 12$ |
| 2074 independent reflections | $l = -29 \rightarrow 29$ |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | Secondary atom site location: difference Fourier map |
| Least-squares matrix: full | Hydrogen site location: inferred from neighbouring sites |
| $R[F^2 > 2\sigma(F^2)] = 0.049$ | H-atom parameters constrained |
| $wR(F^2) = 0.126$ | $w = 1/[\sigma^2(F_o^2) + (0.06P)^2 + 0.9P]$ |
| $S = 1.03$ | where $P = (F_o^2 + 2F_c^2)/3$ |
| 2074 reflections | $(\Delta/\sigma)_{max} = 0.001$ |
| 105 parameters | $\Delta\rho_{max} = 0.39$ e Å$^{-3}$ |
| 0 restraints | $\Delta\rho_{min} = -0.21$ e Å$^{-3}$ |
| Primary atom site location: structure-invariant direct methods | |

## 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   | 0.58234 (19)  | 0.0000        | 0.29187 (6)  | 0.0310 (3) |
| O2   | 0.2989 (2)    | 0.0000        | 0.33551 (6)  | 0.0396 (4) |
| O3   | −0.0951 (2)   | 0.0000        | 0.09831 (7)  | 0.0323 (3) |
| N1   | 0.0672 (2)    | 0.0000        | 0.13356 (7)  | 0.0231 (3) |
| C1   | 0.9329 (3)    | 0.0000        | 0.46943 (8)  | 0.0231 (4) |
| C2   | 0.8678 (2)    | 0.12604 (16)  | 0.43958 (6)  | 0.0317 (3) |
| H2A  | 0.9076        | 0.2135        | 0.4592       | 0.038* |
| C3   | 0.7462 (2)    | 0.12691 (16)  | 0.38187 (7)  | 0.0321 (3) |
| H3A  | 0.7036        | 0.2137        | 0.3622       | 0.039* |
| C4   | 0.6887 (3)    | 0.0000        | 0.35376 (8)  | 0.0261 (4) |
| C5   | 0.3862 (3)    | 0.0000        | 0.28870 (8)  | 0.0211 (4) |
| C6   | 0.2971 (2)    | 0.0000        | 0.22093 (8)  | 0.0179 (3) |
| C7   | 0.3911 (3)    | 0.0000        | 0.16826 (8)  | 0.0190 (3) |
| H7A  | 0.5285        | 0.0000        | 0.1696       | 0.023* |
| C8   | 0.2570 (3)    | 0.0000        | 0.10658 (8)  | 0.0205 (3) |
| C9   | 0.0794 (2)    | 0.0000        | 0.20539 (8)  | 0.0185 (3) |
| C10  | 0.2784 (2)    | 0.13302 (16)  | 0.06612 (7)  | 0.0324 (3) |
| H10A | 0.1799        | 0.1325        | 0.0287       | 0.049* |
| H10B | 0.4079        | 0.1348        | 0.0512       | 0.049* |
| H10C | 0.2611        | 0.2169        | 0.0925       | 0.049* |
| C11  | −0.01778 (19) | 0.13337 (14)  | 0.22809 (7)  | 0.0261 (3) |
| H11A | −0.1535       | 0.1360        | 0.2093       | 0.039* |
| H11B | 0.0503        | 0.2170        | 0.2142       | 0.039* |
| H11C | −0.0125       | 0.1327        | 0.2753       | 0.039* |

*Atomic displacement parameters (Å$^2$)*

|      | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|------|----------|----------|----------|----------|----------|----------|
| O1   | 0.0170 (6) | 0.0590 (9)  | 0.0159 (6) | 0.000      | −0.0032 (5) | 0.000 |
| O2   | 0.0240 (7) | 0.0753 (12) | 0.0194 (6) | 0.000      | 0.0022 (5)  | 0.000 |
| O3   | 0.0215 (7) | 0.0429 (8)  | 0.0295 (7) | 0.000      | −0.0116 (5) | 0.000 |
| N1   | 0.0176 (7) | 0.0302 (8)  | 0.0200 (7) | 0.000      | −0.0050 (5) | 0.000 |
| C1   | 0.0194 (8) | 0.0309 (9)  | 0.0182 (8) | 0.000      | −0.0018 (6) | 0.000 |
| C2   | 0.0363 (8) | 0.0306 (7)  | 0.0256 (7) | 0.0027 (6) | −0.0087 (6) | −0.0022 (5) |
| C3   | 0.0340 (8) | 0.0360 (8)  | 0.0244 (6) | 0.0067 (6) | −0.0066 (5) | 0.0026 (6) |
| C4   | 0.0166 (8) | 0.0452 (11) | 0.0157 (8) | 0.000      | −0.0023 (6) | 0.000 |

| | | | | | |
|---|---|---|---|---|---|
| C5 | 0.0183 (8) | 0.0246 (8) | 0.0195 (8) | 0.000 | −0.0017 (6) | 0.000 |
| C6 | 0.0164 (7) | 0.0172 (7) | 0.0192 (8) | 0.000 | −0.0020 (6) | 0.000 |
| C7 | 0.0179 (8) | 0.0188 (8) | 0.0193 (8) | 0.000 | −0.0021 (6) | 0.000 |
| C8 | 0.0211 (8) | 0.0226 (8) | 0.0169 (7) | 0.000 | −0.0015 (6) | 0.000 |
| C9 | 0.0159 (7) | 0.0193 (8) | 0.0199 (8) | 0.000 | −0.0006 (6) | 0.000 |
| C10 | 0.0376 (8) | 0.0321 (7) | 0.0262 (7) | −0.0044 (6) | −0.0032 (6) | 0.0093 (6) |
| C11 | 0.0200 (6) | 0.0234 (6) | 0.0346 (7) | 0.0024 (5) | 0.0012 (5) | −0.0035 (5) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| O1—C5 | 1.354 (2) | C6—C7 | 1.332 (2) |
| O1—C4 | 1.414 (2) | C6—C9 | 1.509 (2) |
| O2—C5 | 1.199 (2) | C7—C8 | 1.503 (2) |
| O3—N1 | 1.2766 (19) | C7—H7A | 0.9500 |
| N1—C8 | 1.484 (2) | C8—C10$^i$ | 1.5299 (17) |
| N1—C9 | 1.488 (2) | C8—C10 | 1.5299 (17) |
| C1—C2$^i$ | 1.3970 (17) | C9—C11 | 1.5285 (16) |
| C1—C2 | 1.3971 (17) | C9—C11$^i$ | 1.5285 (16) |
| C1—C1$^{ii}$ | 1.495 (3) | C10—H10A | 0.9800 |
| C2—C3 | 1.3922 (19) | C10—H10B | 0.9800 |
| C2—H2A | 0.9500 | C10—H10C | 0.9800 |
| C3—C4 | 1.3760 (17) | C11—H11A | 0.9800 |
| C3—H3A | 0.9500 | C11—H11B | 0.9800 |
| C4—C3$^i$ | 1.3761 (17) | C11—H11C | 0.9800 |
| C5—C6 | 1.478 (2) | | |
| | | | |
| C5—O1—C4 | 117.92 (14) | N1—C8—C7 | 99.78 (13) |
| O3—N1—C8 | 123.07 (14) | N1—C8—C10$^i$ | 110.45 (10) |
| O3—N1—C9 | 122.02 (15) | C7—C8—C10$^i$ | 112.51 (9) |
| C8—N1—C9 | 114.91 (13) | N1—C8—C10 | 110.45 (10) |
| C2$^i$—C1—C2 | 117.19 (16) | C7—C8—C10 | 112.51 (9) |
| C2$^i$—C1—C1$^{ii}$ | 121.40 (8) | C10$^i$—C8—C10 | 110.69 (15) |
| C2—C1—C1$^{ii}$ | 121.40 (8) | N1—C9—C6 | 99.50 (13) |
| C3—C2—C1 | 121.74 (13) | N1—C9—C11 | 109.27 (9) |
| C3—C2—H2A | 119.1 | C6—C9—C11 | 113.40 (9) |
| C1—C2—H2A | 119.1 | N1—C9—C11$^i$ | 109.28 (9) |
| C4—C3—C2 | 118.90 (13) | C6—C9—C11$^i$ | 113.40 (9) |
| C4—C3—H3A | 120.6 | C11—C9—C11$^i$ | 111.28 (15) |
| C2—C3—H3A | 120.6 | C8—C10—H10A | 109.5 |
| C3—C4—C3$^i$ | 121.52 (17) | C8—C10—H10B | 109.5 |
| C3—C4—O1 | 119.12 (8) | H10A—C10—H10B | 109.5 |
| C3$^i$—C4—O1 | 119.12 (8) | C8—C10—H10C | 109.5 |
| O2—C5—O1 | 123.36 (16) | H10A—C10—H10C | 109.5 |
| O2—C5—C6 | 125.39 (17) | H10B—C10—H10C | 109.5 |
| O1—C5—C6 | 111.25 (14) | C9—C11—H11A | 109.5 |
| C7—C6—C5 | 126.39 (16) | C9—C11—H11B | 109.5 |
| C7—C6—C9 | 112.83 (14) | H11A—C11—H11B | 109.5 |
| C5—C6—C9 | 120.78 (14) | C9—C11—H11C | 109.5 |

| | | | |
|---|---|---|---|
| C6—C7—C8 | 112.99 (16) | H11A—C11—H11C | 109.5 |
| C6—C7—H7A | 123.5 | H11B—C11—H11C | 109.5 |
| C8—C7—H7A | 123.5 | | |
| | | | |
| C2ⁱ—C1—C2—C3 | −1.2 (3) | C9—N1—C8—C10ⁱ | 118.61 (10) |
| C1ⁱⁱ—C1—C2—C3 | 178.55 (19) | O3—N1—C8—C10 | 61.39 (10) |
| C1—C2—C3—C4 | 0.1 (2) | C9—N1—C8—C10 | −118.61 (10) |
| C2—C3—C4—C3ⁱ | 1.0 (3) | C6—C7—C8—N1 | 0.0 |
| C2—C3—C4—O1 | −173.34 (14) | C6—C7—C8—C10ⁱ | −117.08 (11) |
| C5—O1—C4—C3 | −92.77 (15) | C6—C7—C8—C10 | 117.08 (11) |
| C5—O1—C4—C3ⁱ | 92.77 (15) | O3—N1—C9—C6 | 180.0 |
| C4—O1—C5—O2 | 0.0 | C8—N1—C9—C6 | 0.0 |
| C4—O1—C5—C6 | 180.0 | O3—N1—C9—C11 | −60.99 (10) |
| O2—C5—C6—C7 | 180.0 | C8—N1—C9—C11 | 119.01 (10) |
| O1—C5—C6—C7 | 0.0 | O3—N1—C9—C11ⁱ | 60.99 (10) |
| O2—C5—C6—C9 | 0.0 | C8—N1—C9—C11ⁱ | −119.01 (10) |
| O1—C5—C6—C9 | 180.0 | C7—C6—C9—N1 | 0.0 |
| C5—C6—C7—C8 | 180.0 | C5—C6—C9—N1 | 180.0 |
| C9—C6—C7—C8 | 0.0 | C7—C6—C9—C11 | −115.91 (11) |
| O3—N1—C8—C7 | 180.0 | C5—C6—C9—C11 | 64.09 (11) |
| C9—N1—C8—C7 | 0.0 | C7—C6—C9—C11ⁱ | 115.92 (11) |
| O3—N1—C8—C10ⁱ | −61.39 (10) | C5—C6—C9—C11ⁱ | −64.08 (11) |

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

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| C11—H11*C*···C3ⁱⁱⁱ | 0.98 | 2.91 | 3.745 (2) | 143 |

Symmetry code: (iii) *x*−1, *y*, *z*.