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Dibenzophospholanic acid anhydride

Andreas Decken,* Erin D. Gill and Frank Bottomley

Department of Chemistry, University of New Brunswick, Fredericton, NB, PO Box 45222, Canada E3B 6E2

Correspondence e-mail: adecken@unb.ca

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Key indicators

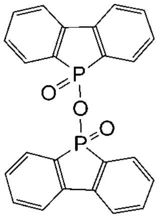
Single-crystal X-ray study
T = 173 K
Mean *σ*(C–C) = 0.005 Å
R factor = 0.051
wR factor = 0.142
Data-to-parameter ratio = 10.8

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The title compound [alternatively called 9,9′-oxydi(9-phosphafluoren-9-one) or bis(5-hydroxy-5-oxodibenzo-5*H*-phosphole) anhydride], $C_{24}H_{16}O_3P_2$, is the only example of a crystallographically characterized phospholanic acid anhydride. The molecule is highly twisted as evident by its O═P···P═O angle [72.9 (1)°].

Comment

To date, there are no reports of crystallographically authenticated phospholanic acid anhydrides. The title compound, (I), is highly twisted, forcing atoms O1 and O2 out of the P1—O3—P2 plane. The resulting O1—P1···P2—O2 twist angle measures 72.9 (1)°. However, this angle is low in comparison to those in related phosphinic acid anhydrides, *viz.* 77.9° (no s.u. available) in $[(Me_2PhC)(Ph)P(O)]_2O$ (Ware *et al.*, 2002) and 84.9° (no s.u. available) in $[Me_2P(O)]_2O$ (Weisbarth & Jansen, 2002). The dibenzophosphole units are further tilted and are almost orthogonal to one another [89.03 (5)°].



(I)

The molecule adopts an unusual orientation, analogous to that observed in bis(9*H*-fluorenyl)methane (Nakano & Yade, 2003), where a skewed orientation of the fluorenyl groups is preferred due to the small end groups (hydrogen). Bulkier end groups result in *π*–*π* stacking, facilitated by a cofacial alignment of the fluorene rings, as reported for substituted derivatives (Rathore *et al.*, 2003; Nakano & Yade, 2003), as well as oligomeric compounds with 3–6 fluorenyl groups. Mixed cofacial/skewed orientations have also been reported (Nakano & Yade, 2003). We denote the cofacial configuration as compound (II) (see *Experimental*), based on NMR assignments of the fluorenyl analogues (Rathore *et al.*, 2003).

Experimental

H_2O_2 (30%, 0.4 ml, 3.5 mmol) was added to a slurry of bis(1,1′-dibenzophospholyl) (0.200 g, 0.55 mmol) in ethanol (12 ml). The mixture was heated to reflux for 3.5 h and the solvent removed under reduced pressure to yield 0.226 g (0.55 mmol) of a mixture of (I) and (II) (ratio 1:2). Single crystals of (I) were obtained by recrystallization from ethanol.

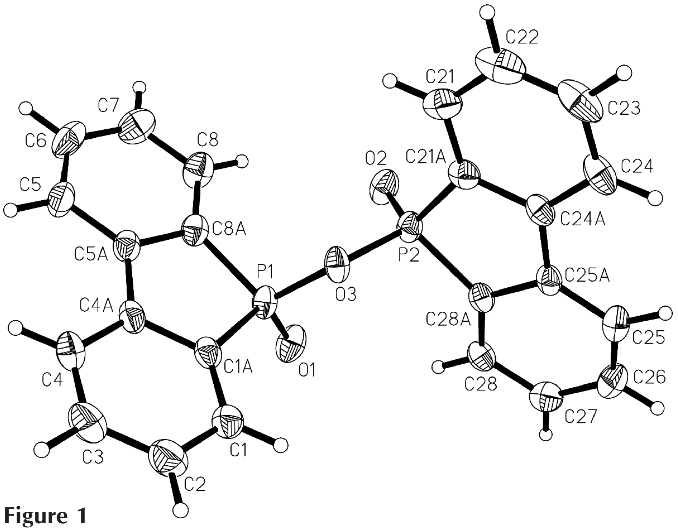


Figure 1
A view of the title compound, with displacement ellipsoids drawn at the 30% probability level.

Characterization of (I): ^{1}H NMR (CD_3OD, 399.945 MHz): δ 7.96 (*dd*, J = 4.0, 8.0 Hz, 2H), 7.77 (*tdd*, J = 0.8, 7.2, 10.8 Hz, 2H), 7.69 (*tdd,* J = 1.2, 7.2, 7.2 Hz, 2H), 7.51 (*dddd*, J = 0.8, 4.0, 8.0, 8.0 Hz, 2H). ^{31}P{^{1}H} NMR (CD_3OD, 121.356 MHz): δ 44.9. MS (*m*/*e*, %, assignment): 414 (5) $[M]^+$, 215 (100) $[C_{12}H_8PO_2]^+$, 199 (75) $[C_{12}H_8PO]^+$, 183 (4) $[C_{12}H_8P]^+$, 168 (38) $[C_{12}H_8O]^+$, 152 (32) $[C_{12}H_8]^+$, 140 (18) $[C_6H_5PO_2]^+$.

Characterization of (II): ^{1}H NMR (CD_3OD, 399.945 MHz): δ 7.92 (*dd*, J = 4.0, 8.0 Hz, 2H), 7.72 (*tdd*, J = 0.8, 7.2, 10.8 Hz, 2H), 7.62 (*tdd*, J = 1.2, 7.2, 7.2 Hz, 2H), 7.46 (*dddd*, J = 0.8, 4.0, 8.0, 8.0 Hz, 2H). ^{31}P{^{1}H} NMR (CD_3OD, 121.356 MHz): δ 40.4. MS: as for compound (I).

Crystal data

$C_{24}H_{16}O_3P_2$
M_r = 414.31
Orthorhombic, *Pbca*
a = 11.0105 (7) Å
b = 13.6596 (10) Å
c = 26.8832 (18) Å
V = 4043.2 (5) Å^3
Z = 8
D_x = 1.361 Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 6595 reflections
θ = 2.4–25.1°
μ = 0.24 mm^{-1}
T = 173 (2) K
Plate, colourless
0.45 × 0.25 × 0.05 mm

Data collection

Bruker AXS SMART1000/*P*4 diffractometer
ω and φ scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.832, T_{max} = 0.990
19599 measured reflections

3530 independent reflections
2286 reflections with $I > 2\sigma(I)$
R_{int} = 0.041
θ_{max} = 25.0°
$h = -13 \rightarrow 13$
$k = -16 \rightarrow 15$
$l = -28 \rightarrow 30$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.051
$wR(F^2)$ = 0.142
S = 1.08
3530 reflections
326 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0738P)^2 + 1.2419P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.33 e Å^{-3}
$\Delta\rho_{min}$ = −0.27 e Å^{-3}

H atoms were placed in calculated positions and refined as riding atoms, with C—H distances fixed at 0.95 Å and with $U_{iso}(H) = 1.2U_{eq}(C)$.

Data collection: *SMART* (Bruker, 1997–1999); cell refinement: *SAINT* (Bruker, 1997–1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997*a*); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997*a*); molecular graphics: *SHELXTL* (Sheldrick, 1997*b*); software used to prepare material for publication: *SHELXTL*.

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