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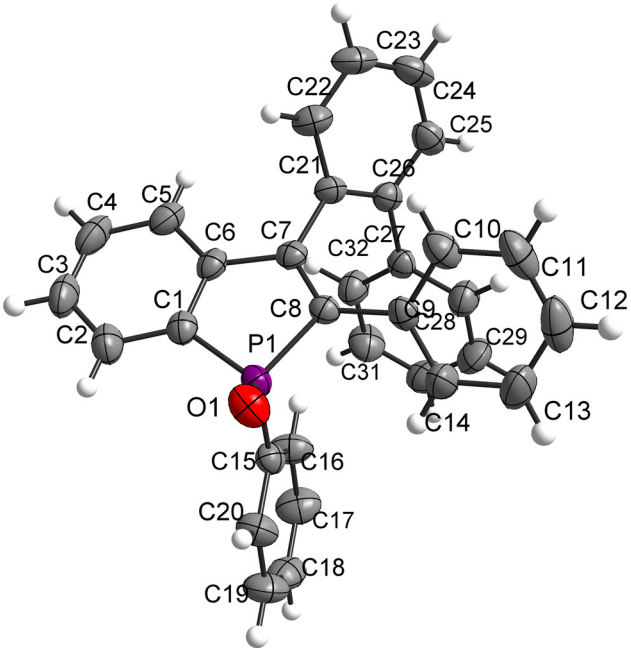
The crystal structure of 3-([1,1′-biphenyl]-2-yl)-1,2-diphenylbenzo[*b*]phosphole-1-oxide, $C_{32}H_{23}OP$



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Abstract

$C_{32}H_{23}OP$, monoclinic, $P2_1/n$ (no. 14), a = 9.1869(11) Å, b = 27.940(3) Å, c = 9.6992(11) Å, β = 107.422(2)°, V = 2375.4(5) Å^3, Z = 4, $R_{gt}(F)$ = 0.0486, w$R_{ref}(F^2)$ = 0.1255, T = 296 K.

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The crystal structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

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Table 1: Data collection and handling.

Crystal:	Block, clear light colourless
Size:	0.03 × 0.02 × 0.02 mm
Wavelength:	MoKα radiation (0.71073 Å)
μ:	0.14 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω-scans
θ_{max}, completeness:	27.7°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	14340, 5474, 0.023
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 4283
$N(param)_{refined}$:	307
Programs:	Bruker programs [1], OLEX2 [2], SHELX [3], DIAMOND [4]

Source of materials

A modified synthesis similar to a previously reported one was performed [5]: 1-(*o*-biphenylyl)-2-phenylethyne (5 mmol), diphenylphosphine oxide (10 mmol), and $K_2S_2O_8$ (15 mmol) were added to a sealed tube under argon, and then CH_3CN (20 mL) was added to the reaction tube by syringe. The reaction mixture was kept stirring at 100 °C for 20 h and then was cooled down to ambient temperature. After the reaction was quenched by adding the concentrated aqueous NaCl solution, the aqueous phase was extracted with 3 × 20 mL of CH_2Cl_2. The organic phase was dried using $MgSO_4$, filtered, and the solvent was removed *in vacuo*. The residue was column chromatography (petroleum ether/ethyl acetate) to afford the title compound (1.6 g, 71%). Crystals of the title compound were obtained by slow evaporation (n-hexane/CH_2C_{l2}) within seven days.

Experimental details

Coordinates of hydrogen atoms were added using riding models. Their U_{iso} values were set to 1.2U_{eq} of the parent atoms.

Comment

Many efforts have been devoted to the development of aggregation-induced emission (AIE) [6]. To date, the

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

	x	*y*	*z*	U_{iso}*/U_{eq}
P1	−0.31526 (5)	−0.62460 (2)	−1.10926 (5)	0.03187 (13)
O1	−0.23310 (16)	−0.64811 (5)	−1.20055 (14)	0.0456 (3)
C15	−0.2687 (2)	−0.56190 (6)	−1.08523 (19)	0.0339 (4)
C7	−0.43804 (19)	−0.65970 (6)	−0.92058 (18)	0.0314 (4)
C1	−0.5195 (2)	−0.62843 (6)	−1.16406 (19)	0.0357 (4)
C8	−0.29812 (19)	−0.65141 (6)	−0.93524 (18)	0.0308 (4)
C6	−0.5666 (2)	−0.64660 (6)	−1.0494 (2)	0.0348 (4)
C9	−0.1482 (2)	−0.66506 (7)	−0.83577 (18)	0.0346 (4)
C27	−0.3507 (2)	−0.61312 (6)	−0.62986 (18)	0.0337 (4)
C21	−0.4634 (2)	−0.68314 (6)	−0.79218 (19)	0.0340 (4)
C26	−0.40587 (19)	−0.66356 (6)	−0.65347 (19)	0.0340 (4)
C20	−0.1948 (2)	−0.54123 (7)	−1.1750 (2)	0.0478 (5)
H20	−0.1692	−0.5597	−1.2440	0.057*
C5	−0.7214 (2)	−0.65133 (7)	−1.0659 (2)	0.0466 (5)
H5	−0.7546	−0.6630	−0.9907	0.056*
C22	−0.5319 (2)	−0.72819 (7)	−0.8084 (2)	0.0447 (5)
H22	−0.5752	−0.7406	−0.9007	0.054*
C16	−0.3067 (3)	−0.53379 (7)	−0.9842 (2)	0.0497 (5)
H16	−0.3574	−0.5473	−0.9239	0.060*
C25	−0.4070 (2)	−0.69139 (7)	−0.5345 (2)	0.0454 (5)
H25	−0.3655	−0.6793	−0.4417	0.054*
C10	−0.1248 (2)	−0.70930 (7)	−0.7662 (2)	0.0471 (5)
H10	−0.2054	−0.7308	−0.7810	0.056*
C23	−0.5362 (2)	−0.75470 (7)	−0.6894 (3)	0.0519 (5)
H23	−0.5840	−0.7844	−0.7014	0.062*
C28	−0.2023 (2)	−0.60206 (8)	−0.5523 (2)	0.0486 (5)
H28	−0.1327	−0.6265	−0.5161	0.058*
C32	−0.4515 (2)	−0.57576 (7)	−0.6797 (2)	0.0477 (5)
H32	−0.5518	−0.5825	−0.7324	0.057*
C2	−0.6242 (2)	−0.61585 (7)	−1.2938 (2)	0.0483 (5)
H2	−0.5919	−0.6040	−1.3694	0.058*
C18	−0.1961 (2)	−0.46567 (7)	−1.0615 (3)	0.0531 (5)
H18	−0.1714	−0.4333	−1.0533	0.064*
C4	−0.8264 (2)	−0.63825 (8)	−1.1974 (3)	0.0577 (6)
H4	−0.9303	−0.6411	−1.2093	0.069*
C31	−0.4060 (3)	−0.52869 (8)	−0.6527 (3)	0.0573 (6)
H31	−0.4760	−0.5041	−0.6856	0.069*
C24	−0.4694 (3)	−0.73672 (8)	−0.5535 (3)	0.0527 (5)
H24	−0.4661	−0.7553	−0.4731	0.063*
C30	−0.2578 (3)	−0.51829 (8)	−0.5774 (2)	0.0576 (6)
H30	−0.2265	−0.4866	−0.5598	0.069*
C3	−0.7782 (3)	−0.62122 (8)	−1.3093 (3)	0.0582 (6)
H3	−0.8498	−0.6132	−1.3965	0.070*
C17	−0.2698 (3)	−0.48576 (8)	−0.9721 (3)	0.0578 (6)
H17	−0.2950	−0.4670	−0.9033	0.069*
C19	−0.1588 (3)	−0.49295 (8)	−1.1624 (3)	0.0588 (6)
H19	−0.1090	−0.4791	−1.2230	0.071*
C14	−0.0246 (2)	−0.63459 (9)	−0.8135 (2)	0.0531 (5)
H14	−0.0367	−0.6053	−0.8612	0.064*
C29	−0.1563 (3)	−0.55475 (8)	−0.5281 (3)	0.0586 (6)
H29	−0.0554	−0.5477	−0.4779	0.070*
C11	0.0173 (3)	−0.72151 (9)	−0.6754 (2)	0.0618 (7)
H11	0.0317	−0.7512	−0.6297	0.074*
C12	0.1374 (3)	−0.69019 (11)	−0.6522 (3)	0.0683 (7)
H12	0.2324	−0.6984	−0.5896	0.082*
C13	0.1171 (3)	−0.64713 (11)	−0.7209 (3)	0.0691 (7)
H13	0.1987	−0.6260	−0.7058	0.083*

primarily accepted AIE mechanism of AIE is derived from the restriction of intramolecular motion including intramolecular rotations and intramolecular vibrations [7]. Therefore, the study on intramolecular motion-mechanical property relationship has received an unprecedented amount of attention [8, 9]. Recently, the benzophospholecores, phosphindole oxides, were developed to construct AIEgens [10], because of their unique high stabilities and electronic structures. Their impacts of steric, conjugation and electronic effects on the AIE properties were also showed based on the results of crystallography analysis [11]. The structure-property relationship is of crucial importance for the fundamental understanding and application exploration on AIE luminogens. Therefore, the crystal structure of benzo[*b*]phosphole with rotatable π-conjugated planes is crucial for understanding their intramolecular motion-mechanical property relationships.

The title compound (see the Figure) consists of a benzo[*b*]phosphole-core and two rotatable π-conjugated subunits (phenyl and biphenyl). The benzo[*b*]phosphole-core keeps a perfect co-plane and the quinquevalent phosphorus with four ligands shows a tetrahedral geometry, where the dihedral angle between the phosphole plane and the plane of the phenyl group of the *P*-substituent is 86.41° due to intramolecular hydrogen-bond of O–H–C20 (2.6023(14) Å). In addition, the motion-restricted *o*-biphenyl and motion-free phenyl are linked to adjacent C7 (bond length of C7–C21 is 1.486(2) Å) and C8 (bond length of C8–C9 is 1.475(2) Å), respectively.

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Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

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