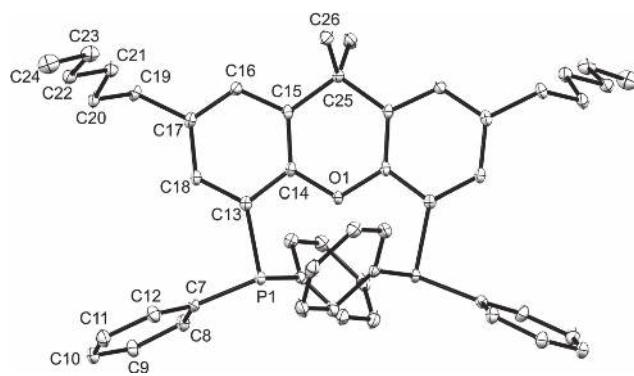


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Crystal structure of (2,7-dihexyl-9,9-dimethyl-9*H*-xanthene-4,5-diyl)bis(diphenylphosphane), C₅₁H₅₆OP₂



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Abstract

C₅₁H₅₆OP₂, monoclinic, C2/c (no. 15), $a = 20.1788(4)$ Å, $b = 13.0247(4)$ Å, $c = 18.0172(5)$ Å, $\beta = 119.874(2)^\circ$, $V = 4106.1(2)$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.0363$, $wR_{\text{ref}}(F^2) = 0.0981$, $T = 173(2)$ K.

CCDC no.: 1951463

The molecular 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.

Source of material

A solution of 2,7-di-*n*-hexyl-9,9-dimethylxanthene (1 g, 2.6 mmol), and tetramethylethylenediamine (1.0 mL, 6.7 mmol) in dry degassed Et₂O (30 mL) was cooled to 0 °C. To the chilled solution, *n*-BuLi (4.2 mL, 6.7 mmol) was added dropwise. The reaction mixture was allowed to warm to

Table 1: Data collection and handling.

Crystal:	Yellow block
Size:	0.39 × 0.25 × 0.17 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	0.14 mm ⁻¹
Diffractometer, scan mode:	Bruker SMART APEX-II, φ and ω
θ_{max} , completeness:	28.4°, >99%
$N(hk\ell)_{\text{measured}}, N(hk\ell)_{\text{unique}}, R_{\text{int}}$:	31002, 4945, 0.038
Criterion for I_{obs} , $N(hk\ell)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 4184
$N(\text{param})_{\text{refined}}$:	247
Programs:	Bruker [1], SHELX [2], WinGX/ORTEP [3]

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	$U_{\text{iso}}^* / U_{\text{eq}}$
P1	0.07415(2)	-0.02859(2)	0.20113(2)	0.01293(9)
O1	0.000000	0.11792(9)	0.250000	0.0144(2)
C1	0.14775(7)	-0.02316(9)	0.31482(8)	0.0143(2)
C2	0.20754(8)	0.04811(10)	0.34784(8)	0.0172(3)
H2	0.210134	0.098172	0.311025	0.021*
C3	0.26319(8)	0.04651(10)	0.43391(8)	0.0199(3)
H3	0.303750	0.094989	0.455597	0.024*
C4	0.25943(8)	-0.02611(11)	0.48821(8)	0.0210(3)
H4	0.297324	-0.027119	0.547102	0.025*
C5	0.20051(8)	-0.09693(11)	0.45653(9)	0.0228(3)
H5	0.198182	-0.146761	0.493662	0.027*
C6	0.14458(8)	-0.09535(10)	0.37027(8)	0.0189(3)
H6	0.103986	-0.143755	0.349029	0.023*
C7	0.12841(7)	-0.07824(9)	0.15180(8)	0.0137(2)
C8	0.20525(7)	-0.10703(10)	0.19706(8)	0.0169(3)
H8	0.234366	-0.094931	0.256938	0.020*
C9	0.23954(8)	-0.15352(10)	0.15477(9)	0.0197(3)
H9	0.291538	-0.174200	0.186273	0.024*
C10	0.19825(8)	-0.16965(10)	0.06731(9)	0.0210(3)
H10	0.222115	-0.200284	0.038755	0.025*
C11	0.12191(8)	-0.14102(11)	0.02132(9)	0.0227(3)
H11	0.093562	-0.151259	-0.038854	0.027*
C12	0.08712(8)	-0.09733(10)	0.06364(8)	0.0187(3)
H12	0.034402	-0.080115	0.032212	0.022*
C13	0.06851(7)	0.10943(9)	0.17670(7)	0.0125(2)
C14	0.03279(7)	0.17168(9)	0.21044(7)	0.0124(2)
C15	0.03150(7)	0.27749(9)	0.20529(7)	0.0125(2)

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Table 2 (continued)

Atom	x	y	z	<i>U</i> _{iso} */* <i>U</i> _{eq}
C16	0.06258(7)	0.32205(10)	0.15837(7)	0.0141(2)
H16	0.061264	0.394628	0.152597	0.017*
C17	0.09513(7)	0.26415(10)	0.12011(7)	0.0137(2)
C18	0.09870(7)	0.15756(10)	0.13103(7)	0.0136(2)
H18	0.122254	0.117080	0.106742	0.016*
C19	0.12675(7)	0.31459(10)	0.06852(8)	0.0156(2)
H19A	0.177979	0.285839	0.086530	0.019*
H19B	0.132862	0.389053	0.081221	0.019*
C20	0.07554(7)	0.29937(10)	-0.02841(8)	0.0167(3)
H20A	0.102408	0.326397	-0.057655	0.020*
H20B	0.067409	0.224904	-0.040643	0.020*
C21	-0.00208(7)	0.35201(10)	-0.06542(8)	0.0175(3)
H21A	-0.029124	0.325222	-0.036295	0.021*
H21B	0.005799	0.426607	-0.053768	0.021*
C22	-0.05184(7)	0.33523(10)	-0.16158(8)	0.0176(3)
H22A	-0.028241	0.370977	-0.191150	0.021*
H22B	-0.053047	0.260956	-0.173866	0.021*
C23	-0.13352(8)	0.37351(11)	-0.19782(9)	0.0213(3)
H23A	-0.156566	0.340123	-0.166682	0.026*
H23B	-0.132651	0.448454	-0.188195	0.026*
C24	-0.18303(8)	0.35160(12)	-0.29307(9)	0.0270(3)
H24A	-0.158288	0.379460	-0.323718	0.040*
H24B	-0.233149	0.383967	-0.314555	0.040*
H24C	-0.189530	0.277266	-0.302273	0.040*
C25	0.000000	0.34456(13)	0.250000	0.0136(3)
C26	0.06485(8)	0.41270(10)	0.31693(8)	0.0194(3)
H26A	0.105010	0.369119	0.360421	0.029*
H26B	0.044455	0.457919	0.344252	0.029*
H26C	0.086252	0.454322	0.288607	0.029*

room temperature and left to stir for 16 hours. The resulting dark red mixture was cooled to 0 °C and PPh₂Cl (1.3 mL, 6.8 mmol) in dry hexane (4 mL) added dropwise. The reaction mixture slowly decolourised and a fine precipitate formed. The reaction was allowed to stir for further 16 hours. The reaction was slowly hydrolysed with a 25 mL 10% HCl/brine mixture (1/1). The organic layer was removed, and the aqueous layer extracted with DCM. Combined fractions were dried over anhydrous MgSO₄, filtered, and evaporated to give a yellow oil. The crude product was washed with hexane (3 × 10 mL), dissolved in DCM, and an equal volume of EtOH added slowly. The solution was left to recrystallise at room temperature to give yellow crystals: yield 1.1 g (56%); ¹H NMR (CDCl₃, 400 MHz) δ/ppm: 7.59–6.96 (m, 20 H P(C₆H₅)₂ and 2H xanthene ring), 6.32 (bs, 2H), 2.38 (t, *J* = 7.5 Hz, 4H), 1.62 (s, 6H), 1.48–0.98 (m, 16H), 0.84 (t, *J* = 6.9 Hz, 6H); ¹³C NMR (CDCl₃, 101 MHz) δ/ppm: 150.9 (t, *J* (P,C) = 19.6 Hz, CO), 137.7 (dd, *J* (P,C) = 7.2, 5.9 Hz, phenyl C-ipso, PC), 137.1 (C), 133.9 (t, *J* (P,C) = 10.4 Hz, CH phenyl), 131.9 (CH), 129.5 (C), 128.0–128.5 (m, CH phenyl), 126.2 (CH), 125.1 (dd, *J* = 10.6, 2.4 Hz, CHC-P), 35.3 (CH₂), 31.9 (CH₃), 31.6 (CH₂), 31.2 (CH₂), 28.6 (CH₂), 22.6 (CH₂), 14.1 (CH₃); ³¹P NMR (CDCl₃, 162 MHz) δ/ppm: -17.8 (s); IR (neat) ν/cm⁻¹ 3069, 3054, 2955, 2921, 2831, 1585, 1569, 1419,

1252, 1240, 737, 692; HR-MS (ESI): [M + H]⁺ m/z 747.3878, calcd. for C₅₁H₅₇OP₂: 747.3879.

Experimental details

Non-hydrogen atoms were initially refined isotropically and then by anisotropic refinement with the full-matrix least-squares method against *F*² using the SHELXL program [2] and molecular graphics were done using ORTEP-3 [3]. All hydrogen atoms were positioned geometrically, allowed to ride on their parent atoms and refined isotropically. The C—H_{aromatic}, C—H_{methylene} and C—H_{methyl} distances were constrained to 0.950 Å, 0.99 Å and 0.98 Å.

Comment

Phosphorus is a very good heteroatom for ligand design as it can form particularly strong chelate complexes with late transition metals, as explained by hard soft acid base theory. Furthermore, the possibility of analysis by ³¹P NMR makes it an excellent choice for developing new ligands [4]. We have been particularly interested in bidentate phosphorus ligands with wide bite angles, with a focus upon the steric and electronic properties of the chiral phosphorus moieties [5, 6]. In this paper we report the synthesis and crystal structure of (2,7-dihexyl-9,9-dimethyl-9*H*-xanthene-4,5-diyl) bis(diphenylphosphane).

The asymmetric unit contains half a molecule of the title compound with an inversion centre at the pyran ring. In this structure, the *n*-hexyl chains project away from the xanthene rings in an extended zigzag, anti-conformation. The addition of alkyl group substituents to phenyl rings can result in the loss of aromaticity and subsequent solubility increase in a wider variety of polar and apolar solvents [7, 8]. The xanthene backbone is comparably planar with a smaller dihedral angle of 8.27(2)^o when compared to values obtained for two different crystals of xantphos, 23.43(2)^o [9] and 23.75(2)^o [10]. A relatively longer intramolecular P—P distance of 4.181(2) Å compared to xantphos, 4.046(2) Å [9] and 4.059(2) Å [7] is also found for this compound. Other geometric parameters are within the expected ranges [11].

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