

C3—C7	1.55 (2)	C3A—C7A	1.50 (2)
C6—C7	1.53 (2)	C6A—C7A	1.57 (2)
C7—C8	1.49 (2)	C7A—C8A	1.54 (2)
C8—C9	1.31 (2)	C8A—C9A	1.31 (2)
C8—C18	1.48 (2)	C8A—C18A	1.49 (2)
C9—C10	1.50 (2)	C9A—C10A	1.52 (2)
C10—C11	1.54 (2)	C10A—C11A	1.50 (2)
C11—C12	1.37 (2)	C11A—C12A	1.39 (2)
C4—O5—C6	100 (1)	C4A—O5A—C6A	100 (1)
C2—C1—C6	93 (1)	C2A—C1A—C6A	94 (1)
C2—C1—C9	111 (1)	C2A—C1A—C9A	111 (1)
C2—C1—C12	120 (1)	C2A—C1A—C12A	118 (1)
C6—C1—C9	97 (1)	C6A—C1A—C9A	99 (1)
C6—C1—C12	129 (1)	C6A—C1A—C12A	129 (1)
C9—C1—C12	104 (1)	C9A—C1A—C12A	103 (1)
C1—C2—C3	103 (1)	C1A—C2A—C3A	104 (1)
C1—C2—C4	107 (1)	C1A—C2A—C4A	106 (1)
C1—C2—C17	122 (1)	C1A—C2A—C17A	124 (1)
C3—C2—C4	59.4 (9)	C3A—C2A—C4A	58.1 (9)
C3—C2—C17	124 (1)	C3A—C2A—C17A	123 (1)
C4—C2—C17	124 (1)	C4A—C2A—C17A	123 (1)
C2—C3—C4	59.9 (8)	C2A—C3A—C4A	59.9 (9)
C2—C3—C7	107 (1)	C2A—C3A—C7A	104 (1)
C4—C3—C7	109 (1)	C4A—C3A—C7A	105 (1)
O5—C4—C2	108 (1)	O5A—C4A—C2A	109 (1)
O5—C4—C3	107 (1)	O5A—C4A—C3A	110 (1)
C2—C4—C3	60.6 (9)	C2A—C4A—C3A	62.0 (9)
O5—C6—C1	105 (1)	O5A—C6A—C1A	105 (1)
O5—C6—C7	107 (1)	O5A—C6A—C7A	106 (1)
C1—C6—C7	96 (1)	C1A—C6A—C7A	92 (1)
C3—C7—C6	93 (1)	C3A—C7A—C6A	97 (1)
C3—C7—C8	110 (1)	C3A—C7A—C8A	112 (1)
C6—C7—C8	100 (1)	C6A—C7A—C8A	99 (1)
C7—C8—C9	111 (1)	C7A—C8A—C9A	107 (1)
C7—C8—C18	122 (1)	C7A—C8A—C18A	122 (1)
C9—C8—C18	127 (1)	C9A—C8A—C18A	130 (1)
C1—C9—C8	108 (1)	C1A—C9A—C8A	110 (1)
C1—C9—C10	110 (1)	C1A—C9A—C10A	111 (1)
C8—C9—C10	142 (1)	C8A—C9A—C10A	138 (1)
O19—C10—C9	110 (1)	O19A—C10A—C9A	109 (1)
O19—C10—C11	113 (1)	O19A—C10A—C11A	113 (1)
C9—C10—C11	102 (1)	C9A—C10A—C11A	102.4 (9)
C10—C11—C12	114 (1)	C10A—C11A—C12A	110 (1)
C10—C11—C16	124 (1)	C10A—C11A—C16A	126 (1)
C12—C11—C16	122 (1)	C12A—C11A—C16A	125 (1)
C1—C12—C11	109 (1)	C1A—C12A—C11A	114 (1)
C1—C12—C13	127 (1)	C1A—C12A—C13A	128 (1)
C11—C12—C13	124 (1)	C11A—C12A—C13A	119 (1)

The data for compounds (4) and (5) were corrected for Lorentz and polarization effects. Most H atoms were located in  $\Delta\rho$  maps, but were held fixed during refinements at calculated positions which were updated after each sequence of refinement cycles (no significant improvement in the agreement with experiment was achieved by refining hydrogen parameters). In compound (4), the F atoms at C10 are disordered. F4, F5 and F6 form the major component of the CF<sub>3</sub> group with a common fluorine site occupancy factor, *s*, which refined to 0.89(1); these atoms were otherwise refined individually and anisotropically. F7, F8 and F9 were refined as a triangular group with a group isotropic vibrational parameter; their common site occupancies were constrained to 1 - *s*.

The final *R* of 0.085 for compound (5) (*wR* = 0.059) occurs because of small electron density peaks in positions attributable to a fragmented and highly disordered H-bonded water network in the cavities and between the independent molecules; the water could not be removed totally by drying.

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0108-2701/93/030598-03\$06.00

Service at Daresbury used for crystallographic literature searches.

Lists of structure factors, anisotropic thermal parameters and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55655 (46 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AL1014]

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## Structure of Pentabenzylcyclopentadiene

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### Abstract

The crystal structure analysis of pentabenzylcyclopentadiene {1,1',1'',1''',1''''-[1,3-cyclopentadiene-1,2,3,4,5-pentayl]pentakis(methylene)]pentakis(benzene)} shows groups of two and three benzyl substituents on opposite sides of the planar cyclopentadiene ring. The compound is monomeric.

### Comment

Substituting the cyclopentadienyl ligand in organo-element and organometal compounds with the bulky pentabenzylcyclopentadienyl system [C<sub>5</sub>(CH<sub>2</sub>Ph)<sub>5</sub>]<sup>-</sup>

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increases their stability against air and moisture. This effect has been explained by the shielding of the reactive center by the benzyl groups.  $C_5(CH_2Ph)_5$  compounds of main-group elements with the central atom in a low oxidation state show an orientation of two or three benzyl substituents to the expected location of the 'free electron' pair. Compounds already investigated by X-ray structural analysis are  $C_5(CH_2Ph)_5In$ ,  $C_5(CH_2Ph)_5Tl$  (two modifications),  $C_5(CH_2Ph)_5M$  ( $M = Ge, Sn, Pb, Fe$ ),  $C_5(CH_2Ph)_5K$ ,  $C_5(CH_2Ph)_5Mn(CO)_3$ ,  $C_5(CH_2Ph)_5Co(CO)_2$ ,  $C_5(CH_2Ph)_5AuPPh_3$ ,  $(C_8H_8)Lu[C_5(CH_2Ph)_5]$  (Janiak & Schumann, 1991) and  $C_5(CH_2Ph)_5PCl_2$  (Schumann, Görlitz & Schäfers, 1993). In order to confirm the influence of packing effects in these compounds, the X-ray structural analysis of the ligand has been performed. Final fractional coordinates are given in Table 1 and important bond lengths and angles in Table 2. The molecular structure, along with the numbering scheme, is shown in Fig. 1.

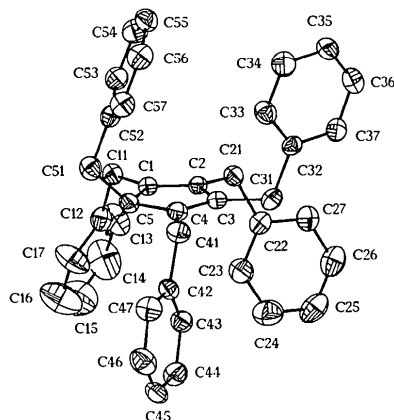


Fig. 1. Structure of the title compound showing the atom-numbering scheme. H atoms are omitted. Thermal ellipsoids (ORTEPII; Johnson, 1976) are drawn at the 50% probability level.

The title compound was synthesized by literature procedures (Hirsch & Bailey, 1978) and was recrystallized from methanol. X-ray analysis showed the title compound to be monomeric. The C=C double bonds in the cyclopentadienyl ring are located between C1 and C2 and C3 and C4. The cyclopentadiene ring is planar within standard deviations. The internal bonding parameters of  $C_5(CH_2Ph)_5H$  exhibit no unusual magnitudes and are consistent with the two other pure hydrocarbon-cyclopentadiene compounds which have been investigated so far,  $C_5H_6$  (Liebling & Marsh, 1965) and  $C_5H_2Ph_4$  (Evrard, Piret, Germain & Van Meerssche, 1971).

Groups of two and three benzyl groups are orientated on opposite sides of the cyclopentadiene

ring. It is interesting to note that the conformation of the title compound is retained in most of the known and structurally characterized metal complexes of the pentabenzylcyclopentadienyl anion. This indicates that the relative orientation of the benzyl groups is governed by steric rather than electronic effects. Indeed, the  $[C_5(CH_2Ph)_5]^-$  ligand exhibits a high degree of conformational flexibility. Thus, in crowded organometallic complexes such as  $(C_8H_8)Lu[C_5(CH_2Ph)_5]$  or  $[C_5(CH_2Ph)_5]_2Fe$ , four or even all five benzyl substituents can be accommodated on the same side of the cyclopentadienyl ring without apparent strain. This confirms the importance of packing effects in organometallic compounds with bulky ligands.

## Experimental

### Crystal data

$C_5(CH_2Ph)_5H$   
 $M_r = 516.73$   
 Orthorhombic  
 $Pca2_1$   
 $a = 35.499$  (9) Å  
 $b = 10.289$  (2) Å  
 $c = 8.275$  (3) Å  
 $V = 3022.4$  (15) Å<sup>3</sup>  
 $Z = 4$   
 $D_x = 1.14$  Mg m<sup>-3</sup>  
 Mo K $\alpha$  radiation

$\lambda = 0.71073$  Å  
 Cell parameters from 25 reflections  
 $\theta = 6.8-12.45^\circ$   
 $\mu = 0.059$  mm<sup>-1</sup>  
 $T = 293$  (5) K  
 Parallelepiped  
 $0.68 \times 0.54 \times 0.32$  mm  
 Colorless  
 Crystal source: recrystallization from methanol

### Data collection

Enraf-Nonius CAD-4 diffractometer  
 $\theta-2\theta$  scans  
 Absorption correction: none  
 3504 measured reflections  
 2953 independent reflections  
 2229 observed reflections  
 $[F_o > 4\sigma F_o]$

$R_{int} = 0.011$   
 $\theta_{max} = 26.5^\circ$   
 $h = 0 \rightarrow 44$   
 $k = 0 \rightarrow 12$   
 $l = 0 \rightarrow 10$   
 3 standard reflections  
 frequency: 120 min  
 intensity variation:  $-1.2\%$

### Refinement

Refinement on  $F$   
 Final  $R = 0.058$   
 $wR = 0.052$   
 2229 reflections  
 360 parameters  
 H-atom parameters not refined

$w = 1.069/(\sigma^2 + 0.00003F_o^2)$   
 $(\Delta/\sigma)_{max} = \leq 0.002$   
 $\Delta\rho_{max} = 0.19$  e Å<sup>-3</sup>  
 $\Delta\rho_{min} = -0.23$  e Å<sup>-3</sup>  
 Atomic scattering factors from SHELX76 (Sheldrick, 1976)

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters (Å<sup>2</sup>)

$$B_{eq} = (8\pi^2/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	$B_{eq}$
C1	0.1341 (1)	0.5018 (4)	0.3300	3.67
C11	0.1462 (1)	0.4315 (4)	0.4822 (7)	4.46
C12	0.1759 (1)	0.3271 (4)	0.4565 (8)	4.79

C13	0.1678 (1)	0.2003 (5)	0.4856 (11)	7.84
C14	0.1954 (2)	0.1066 (6)	0.4682 (13)	10.87
C15	0.2297 (2)	0.1368 (7)	0.4230 (14)	12.04
C16	0.2383 (2)	0.2614 (7)	0.3945 (15)	12.85
C17	0.2117 (1)	0.3588 (5)	0.4121 (11)	8.67
C2	0.1072 (1)	0.4666 (4)	0.2274 (7)	3.52
C21	0.0833 (1)	0.3446 (4)	0.2279 (8)	4.22
C22	0.0939 (1)	0.2490 (4)	0.0981 (8)	4.26
C23	0.1290 (1)	0.2403 (5)	0.0333 (9)	6.07
C24	0.1369 (2)	0.1525 (5)	-0.0888 (10)	8.14
C25	0.1103 (2)	0.0703 (5)	-0.1473 (9)	7.33
C26	0.0754 (2)	0.0765 (5)	-0.0819 (10)	6.93
C27	0.0667 (1)	0.1655 (5)	0.0371 (9)	5.42
C3	0.1050 (1)	0.5602 (4)	0.0934 (8)	3.94
C31	0.0758 (1)	0.5554 (4)	-0.0360 (8)	4.73
C32	0.0370 (1)	0.6005 (4)	0.0220 (8)	3.99
C33	0.0337 (1)	0.7153 (4)	0.1059 (9)	5.06
C34	-0.0014 (1)	0.7573 (5)	0.1567 (9)	5.95
C35	-0.0327 (1)	0.6840 (5)	0.1272 (8)	5.48
C36	-0.0295 (1)	0.5688 (5)	0.0484 (8)	5.56
C37	0.0053 (1)	0.5257 (5)	-0.0076 (8)	4.97
C4	0.1321 (1)	0.6500 (4)	0.1148 (8)	3.92
C41	0.1423 (1)	0.7595 (4)	0.0034 (8)	4.90
C42	0.1773 (1)	0.7335 (4)	-0.0993 (8)	4.17
C43	0.1873 (1)	0.6093 (5)	-0.1442 (8)	4.79
C44	0.2180 (1)	0.5879 (6)	-0.2454 (8)	6.05
C45	0.2379 (1)	0.6914 (7)	-0.3019 (9)	6.50
C46	0.2286 (1)	0.8135 (6)	-0.2594 (10)	6.99
C47	0.1982 (1)	0.8365 (5)	-0.1570 (9)	5.82
C5	0.1530 (1)	0.6233 (4)	0.2690 (7)	4.16
C51	0.1550 (1)	0.7387 (4)	0.3871 (9)	4.95
C52	0.1174 (1)	0.7976 (4)	0.4334 (8)	4.29
C53	0.0943 (1)	0.7350 (4)	0.5433 (8)	4.94
C54	0.0598 (1)	0.7875 (5)	0.5880 (9)	5.80
C55	0.0483 (1)	0.9034 (5)	0.5239 (9)	5.49
C56	0.0709 (2)	0.9658 (4)	0.4155 (9)	5.90
C57	0.1051 (1)	0.9146 (4)	0.3701 (8)	5.28

Table 2. Bond lengths (Å) and angles (°)

C1—C2	1.328 (5)	C2—C21	1.515 (5)
C1—C5	1.507 (6)	C3—C31	1.490 (6)
C2—C3	1.470 (6)	C4—C41	150.0 (6)
C3—C4	1.346 (5)	C5—C51	1.539 (6)
C4—C5	1.502 (6)		
C1—C11	1.515 (6)		
C(CH <sub>2</sub> )—C(Ph)	1.505 (6)—1.532 (5)	C(Ph)—C(Ph)*	1.3504 (7)—1.393 (7)
C2—C1—C5	109.5 (4)	C4—C3—C31	127.8 (4)
C1—C2—C3	109.9 (3)	C3—C31—C32	113.0 (4)
C2—C3—C4	108.3 (4)	C31—C32—C33	119.8 (4)
C3—C4—C5	109.8 (4)	C31—C32—C37	120.5 (4)
C4—C5—C1	102.5 (3)	C3—C4—C41	127.4 (4)
C2—C1—C11	127.3 (4)	C5—C4—C41	122.7 (4)
C11—C1—C5	123.2 (4)	C4—C41—C42	114.0 (3)
C1—C11—C12	114.7 (4)	C41—C42—C43	121.4 (4)
C11—C12—C13	120.3 (5)	C41—C42—C47	119.7 (4)
C11—C12—C17	121.0 (4)	C1—C5—C51	116.6 (4)
C1—C2—C21	128.8 (4)	C4—C5—C51	114.9 (4)
C3—C2—C21	121.0 (4)	C5—C1—C11	123.2 (4)
C2—C21—C22	113.5 (4)	C5—C51—C52	115.4 (4)
C21—C22—C23	123.7 (4)	C51—C52—C53	120.2 (4)
C21—C22—C27	119.2 (4)	C51—C52—C57	122.1 (4)
C2—C3—C31	123.8 (4)		
C(Ph)—C(Ph)—C(Ph)	117.0 (5)—121.3 (5)		

\*Inaccurate bond lengths concerning the atoms C14, C15 and C16 are not considered.

Data reduction: *SDP* (Frenz, 1988). Program used to solve structure: *SHELXS86* (Sheldrick, 1986). Program used to refine structure: *SHELX76*.

The  $\omega$ -scan width was  $(0.80+0.35\tan\theta)^\circ$  and the maximum scan time 60 s. Refinement was by full-matrix least-squares methods. H-atom positions were calculated [ $d(\text{C—H}) = 0.95 \text{ \AA}$ ] with a fixed  $U_{\text{iso}}$  of 0.06 ( $-\text{CH}_2-$ ) or  $0.08 \text{ \AA}^2$  ( $\text{C}_6\text{H}_5-$ ).

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55672 (21 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HU1006]

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## (+)-2,2'-(1,1'-Binaphthyl)phosphate Salt of Methyl (11*R*)-11-{[2-(4-Benzylpiperidino)ethyl]thio}-6,11-dihydrodibenz[*b,e*]oxepin-2-carboxylate

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## Abstract

The absolute configuration of methyl 11-{[2-(4-benzylpiperidino)ethyl]thio}-6,11-dihydrodibenz[*b,e*]-