Journal of Organometallic Chemistry, 421 (1991) 265–273
Elsevier Sequoia S.A., Lausanne
JOM 22211

Bis-ferrocene derivatives of bridged calix[4]arenes: synthesis, X-ray crystal structure and electrochemical properties

Paul D. Beer *[,a,1], Anthony D. Keefe [a], Volker Böhmer *[,b], Helmut Goldmann [b], Walter Vogt [b], Sylvian Lecocq [c] and Monique Perrin [c]

[a] *Department of Chemistry, University of Birmingham, P O. Box 363, Birmingham B15 2TT (UK)*
[b] *Institut für Organische Chemie, Johannes Gutenberg Universitat, Johann-Joachim-Becher-Weg 34, SB1, W-6500 Mainz (Germany)*
[c] *Laboratoire de Minéralogie-Cristallographie, associé au CNRS (URA 0805), 43 Boulevard du 11 Novembre 1918, 69622 Villeurbanne Cedex (France)*

(Received May 17th, 1991)

Abstract

The reaction of chlorocarbonylferrocene (**2**) with bridged calix[4]arene macrocyclic compounds, in which two opposite *para*-positions are connected by an additional aliphatic chain where $n = 5$ (**1a**) or $n = 8$ (**1b**) respectively, gave the corresponding new redox-active bis-ferrocene derivatives of bridged calix[4]arenes, **3a** and **3b**. An X-ray diffraction study of **3a** shows that the calix[4]arene has a cone conformation in which the two ferrocene substituents are located on the phenolic units connected to each other by the aliphatic chain bridge. Cyclic voltammetric and coulometric studies in dichloromethane reveal that **3a** and **3b** undergo reversible two electron oxidations at +0.90 V (versus SCE), suggesting that the two respective ferrocene moieties are oxidised in one step. Proton NMR complexation studies (CD_3CN) showed neither **3a** or **3b** form solution host-guest complexes with t-butylamine and benzylamine.

There is considerable current interest being shown in the phenolformaldehyde cyclic host oligomers, the calixarenes [1,2]. In the so-called cone conformation the calix[4]arene family of macrocyclic receptors possess hydrophobic cavities capable of forming inclusion complexes with a variety of molecular species in the solid state [3]. However, in solution the parent calix[4]arenes are conformationally mobile [4], rapidly interconverting between two opposite cone conformations as revealed by variable temperature ^1H NMR investigations. In an effort to synthesise rigid calix[4]arenes a number of groups have introduced bulky substituents on the phenolic hydroxy groups, and this has met with some success, although the partial cone [5] or 1,3-alternate [6] conformations may occasionally be obtained instead.

---

[1] Present address: Inorganic Chemistry Laboratory, University of Oxford, South Parks Road, Oxford OX1 3QR (UK).

This intramolecular dynamic process is totally negated with the recently reported bridged calix[4]arenes (**1**) having two opposite phenolic units connected via their *para*-positions by an aliphatic chain of various lengths ($n = 5$–16) [7].

We have recently initiated a synthetic programme aimed at the incorporation of multiple redox-active centres into calixarene host structural frameworks [8] in an effort to produce a new class of molecular sensor and/or catalyst with a well defined rigid molecular cavity able electrochemically to recognise, respond, and catalyse redox reactions on an included organic guest substrate [9]. This paper reports the synthesis and electrochemical properties of the first bis-ferrocene bridged calix[4]arenes including the single crystal structure of one as determined by X-ray diffraction analysis.

Experimental

Reactions were carried out under dry nitrogen and solvents were distilled prior to use from an appropriate drying agent. ^{1}H NMR spectra were recorded at 400 and 270 MHz with tetramethylsilane (TMS) as internal standard. Microanalyses were performed by the Birmingham University Chemistry Department Microanalytical Service. Conductivity measurements were performed with a PAR 174A polarographic analyser. Cyclic voltammetric measurements were carried out in dry acetonitrile solution containing 0.2 M ^{n}Bu$_4$NBF$_4$ as supporting electrolyte using a platinum bead working electrode with ferrocene internal reference. Values are quoted relative to the saturated calomel reference electrode (SCE). Positive ion fast atom bombardment mass spectrometry was carried out using a primary atom beam of argon (6 keV) on a Kratos MS80 RF mass spectrometer coupled to a Kratos DS55 data system. The syntheses of the bridged calix[4]arenes (**1a**, **1b**) [7a] and chlorocarbonyl ferrocene (**2**) [10] have been described elsewhere.

A general method was used to prepare **3a** and **3b**. The appropriate bridged calix[4]arene (**1**) (0.6 mmol) and triethylamine (0.6 g, 6 mmol) were dissolved in dry toluene (100 cm^3) and the solution was warmed to 70 ° C. To this solution, the dropwise addition of a solution of chlorocarbonyl ferrocene (**2**) (0.6 g, 2.4 mmol) in toluene (50 cm^3) gave an orange-red reaction mixture which was then stirred for 1 h at 70 ° C. After cooling to room temperature the mixture was evaporated to dryness, and the residue dissolved in dichloromethane (100 cm^3). The solution was washed with water (3 × 100 cm^3), dried over magnesium sulphate, and subjected to column chromatography (alumina, dichloromethane) to give the respective bis-ferrocene derivatives of bridged calix[4]arenes.

3a: Orange solid (0.35 g, 56% yield); m.p. > 280 ° C decomp., m/z 1028 (M$^+$); IR: 1738 cm^{-1} (C=O str.). Anal. Found: C, 73.8; H, 6.5. $C_{63}H_{64}Fe_2O_6$ calc.: C, 73.5; H, 6.3%. ^{1}H NMR (CDCl$_3$): δ 1.05 (brs, 4H), 1.28 (brs, 2H), 1.34 (s, 18H), 2.25 (m, 4H), 3.41 (d, $J = 10$ Hz, 4H), 4.14 (d, $J = 10$ Hz, 4H); 4.42 (s, 10H), 4.16 (t, $J = 2$ Hz, 4H), 5.24 (t, $J = 2$ Hz, 4H), 5.31 (s, 2H), 6.42 (s, 4H), 7.12 (s, 4H).

3b: Orange solid (0.56 g, 87% yield); m.p. > 280 ° C decomp., m/z 1070 (M^+); IR: 1736 cm^{-1} (C=O str.). Anal. Found: C, 74.3, H, 6.9. $C_{66}H_{70}Fe_2O_6$ calc: C, 74.0, H, 6.6%. ^{1}H NMR (CDCl$_3$): δ 0.45 (brs, 4H), 0.92 (brs, 4H), 1.24 (s, 18H), 1.28 (br s, 4H), 2.42 (m, 4H), 3.51 (d, $J = 10$ Hz, 4H), 4.16 (d, $J = 10$ Hz, 4H), 4.38 (s, 10H), 4.59 (t, $J = 2$ Hz, 4H), 5.25 (t, $J = 2$ Hz, 4H), 5.88 (s, 2H), 6.78 (s, 4H), 7.07 (s, 4H).

X-Ray structure analysis

Crystals of **3a** obtained from a mixture of hexane and dichloromethane are red coloured. Lattice parameters were refined by least-squares fit of 25 (θ, χ, ϕ)*hkl* measurement taken on a Nonius CAD4 single crystal diffractometer (4.5° $< \theta <$ 15.0°).

A crystal of about $0.3 \times 0.3 \times 0.3$ mm^3 was used for data collection. Crystal data: $C_{63}H_{64}Fe_2O_6 \cdot 1/2CH_2Cl_2$; M = 1028 + 42.5; monoclinic, *C*2/*c* (no. 15); $a = 31.254(2)$, $b = 13.838(2)$, $c = 26.897(2)$ Å, $\beta = 104.33(3)°$, $V = 11271(3)$ Å^3, $Z = 8$, $D_c = 1.27$ g cm^{-3}, $F(000) = 3968$; Mo-K_α radiation; $\lambda = 0.71069$ Å, μ(Mo-K_α) = 5.60 cm^{-1}.

The ω-2θ scan technique was used to collect intensities of reflections up to $\theta = 25°$. One standard reflection $64\overline{10}$ measured every hour showed no significant fluctuation in intensity, and the same measured at 100 reflections intervals controlled the orientation of the crystal. Of 10149 unique data, 7254 having $I > 3\sigma(I)$ were used in structure determination. Lorentz and polarisation corrections were applied and absorption was corrected with the programs PSI and EAC of SDP [11].

Structure analysis and refinement

The structure was solved by MULTAN [12] and refined by SHELX [13]. The first E.map computed with the most consistent set of signs revealed the positions of a large number of non-H atoms. Next a Fourier map revealed the last non-H atoms. At this time several cycles of full-matrix least-squares calculations with isotropic temperature factors adjusted the atomic parameters; then several difference Fourier gave all non-H atoms as well as a second position for the tert-butyl group; new cycles of refinement with anisotropic temperature factors for non-H atoms, isotropic ones for H-atoms lead to an *R* value of 0.07 and goodness of fit of 8.25; the difference Fourier map shows a residual peak of ca. 0.8 e Å^{-3} at a special position: 0.0, *y*, 0.25. So we attempted a different hypotheses with solvent molecules near this position; the best result was obtained with $1/2CH_2Cl_2$ disordered at 0.000, 0.067(3), 0.250, at which the *R* factor fell to 0.055 and goodness of fit to 5.0. The largest residual peak on difference Fourier has the value: 0.2 e Å^{-3}. As usual, hydrogen atoms on the two OH groups could not be located. Occupation factors for the tert-butyl group are refined and gave values near 0.65 and 0.35. Atomic fractional coordinates are listed in Table 1 with the numbering scheme given in Fig. 1. Selected bond distances and angles are given in Table 2. Tables of H atom coordinates, anisotropic thermal parameters and structure factors are available from the authors.

Results and discussion

Syntheses

The reaction of an excess of chlorocarbonyl ferrocene (**2**) [10] with the bridged calix[4]arenes **1a** and **1b** [7] in the presence of triethylamine gave, after column chromatography (alumina, CH_2Cl_2), the respective regioselective 1,3-disubstituted bis-ferrocene bridged calix[4]arenes **3a** (56% yield, orange-red crystals) and **3b** (87% yield, orange-red crystals) (Scheme 1). It is noteworthy that no evidence for the presence of tris- and tetra-substituted ferrocenoylcalix[4]arene isomers was found, suggesting that, as with the analogous condensation reactions of **2** with the

Table 1

Fractional atomic coordinates with esd's in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
O(25)	0.3106(1)	0.1872(3)	0 1787(2)	C(100)	0.2204(3)	0.0440(5)	0 0701(3)
O(28)	0.2641(2)	0.0476(3)	0.0895(2)	O(100)	0.2026(2)	0.0619(4)	0.0271(2)
O(27)	0.3470(2)	−0.0370(5)	0.1555(2)	C(101)	0.1982(3)	0.0157(5)	0.1094(3)
O(26)	0.3783(1)	0.0847(3)	0 2553(2)	C(102)	0.1510(4)	0.0100(7)	0.1014(6)
C(1)	0.3502(2)	0.3366(5)	0.1998(2)	C(103)	0.1406(5)	−0 0271(9)	0.1453(7)
C(2)	0.3568(3)	0.4311(5)	0.1871(3)	C(104)	0.1811(7)	−0.0386(11)	0.1812(6)
C(3)	0.3330(3)	0.4726(5)	0.1409(3)	C(105)	0.2178(3)	−0.0163(6)	0.1596(3)
C(31)	0 3439(3)	0.5760(5)	0.1249(3)	Fe(1)	0 17955(4)	−0.12055(8)	0.11836(4)
C(311)	0 3463(9)	0 6433(8)	0.1687(5)	C(106)	0 1435(7)	−0.2441(14)	0.1037(11)
C(312)	0.3027(5)	0.6129(9)	0 0798(6)	C(107)	0.1835(13)	−0.2618(11)	0.1328(10)
C(313)	0.3831(7)	0.5632(9)	0.1048(9)	C(108)	0.2221(7)	−0.2327(11)	0 1169(7)
C(321)	0.2988(23)	0 6359(54)	0.1203(32)	C(109)	0.2020(6)	−0.2027(8)	0.0663(6)
C(322)	0.3798(20)	0.6006(35)	0.0912(19)	C(110)	0.1574(8)	−0.2059(9)	0.0553(5)
C(323)	0.3846(17)	0.6208(35)	0.1797(15)	C(200)	0.3896(2)	0 0488(5)	0.3048(2)
C(4)	0 3030(3)	0 4145(5)	0.1089(3)	O(200)	0.4270(2)	0.0461(4)	0.3285(2)
C(5)	0.2944(2)	0 3200(5)	0.1204(3)	C(201)	0.3513(2)	0.0192(4)	0.3201(2)
C(25)	0.3188(2)	0.2816(5)	0.1670(3)	C(202)	0.3056(2)	0 0248(5)	0.2926(3)
C(7)	0.2908(2)	0.1904(5)	0.0562(2)	C(203)	0 2795(3)	−0.0126(5)	0.3240(3)
C(8)	0 3198(3)	0.2271(6)	0.0309(3)	C(204)	0.3081(3)	−0 0405(6)	0 3707(3)
C(9)	0.3472(2)	0 1742(6)	0.0088(2)	C(205)	0.3518(3)	−0 0211(5)	0 3700(3)
C(10)	0.3446(3)	0 0751(6)	0.0135(3)	Fe(2)	0.32328(3)	−0 11365(7)	0 31162(4)
C(11)	0.3164(2)	0.0313(5)	0.0388(3)	C(206)	0.2884(6)	−0.2182(11)	0 2679(10)
C(28)	0.2897(2)	0.0898(5)	0.0591(2)	C(207)	0.3062(8)	−0.2544(8)	0.3160(8)
C(13)	0.3651(2)	−0.1013(5)	0.0800(3)	C(208)	0.3234(9)	−0.1864(7)	0.2466(5)
C(14)	0.3980(3)	−0 1381(6)	0.0603(4)	C(209)	0.3515(6)	−0 2457(8)	0.3242(5)
C(15)	0.4407(3)	−0.1491(5)	0.0862(4)	C(210)	0.3611(5)	−0.2060(8)	0.2821(7)
C(151)	0.4772(3)	−0.1825(8)	0.0604(4)				
C(152)	0.4689(0)	−0.2482(0)	0.0276(0)				
C(153)	0.5196(0)	−0.2220(0)	0.1004(0)				
C(154)	0.5033(18)	−0 0902(30)	0.0511(35)				
C(252) [a]	0.4662(7)	−0 2906(17)	0.0427(12)				
C(253) [a]	0.5234(7)	−0.1703(26)	0 0933(11)				
C(254) [a]	0 4686(12)	−0.1188(21)	0.0078(11)				
C(16)	0.4505(3)	−0.1225(6)	0.1374(4)				
C(17)	0.4195(2)	−0.0856(5)	0.1605(3)				
C(27)	0.3776(2)	−0.0754(5)	0.1324(3)				
C(19)	0.4376(2)	0.0642(5)	0.2135(2)				
C(20)	0.4660(2)	0.1056(6)	0 1881(3)				
C(21)	0 4691(2)	0 2043(5)	0.1826(2)				
C(22)	0 4418(2)	0 2616(5)	0.2042(3)				
C(23)	0.4123(2)	0 2242(5)	0.2292(2)				
C(26)	0.4113(2)	0 1245(5)	0.2339(2)				
C(6)	0 2641(2)	0.2561(6)	0.0819(3)				
C(18)	0 4333(3)	−0.0454(5)	0.2147(3)				
C(24)	0 3797(3)	0.2902(6)	0.2459(3)				
C(12)	0.3205(3)	−0.0774(6)	0 0488(4)				
C(211)	0.4980(3)	0.2471(7)	0.1513(3)				
C(212)	0.4711(3)	0.2989(7)	0.1026(3)				
C(213)	0.4396(3)	0.2339(6)	0.0674(3)				
C(214)	0.4126(3)	0.2869(6)	0.0201(3)				
C(215)	0.3798(3)	0.2205(7)	−0.0159(3)				

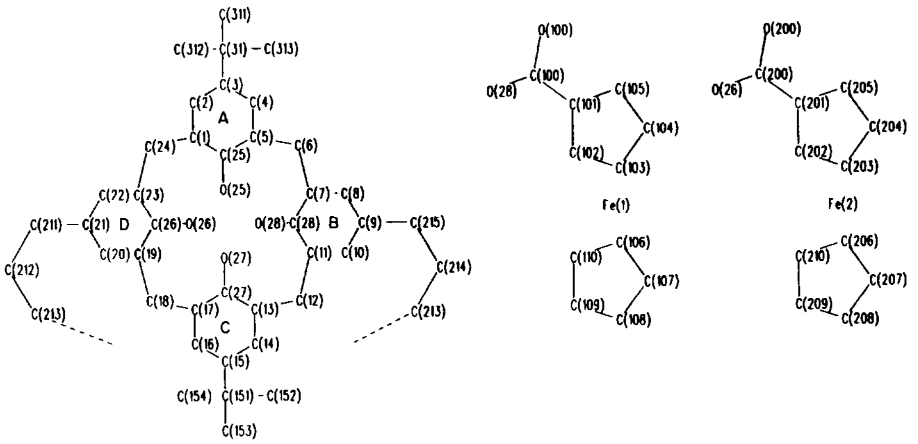


Fig. 1. Numbering scheme.

parent *p*-t-butylcalix[4]arene and calix[4]arenes [14], adjacent 1,2-*cis* substitution is sterically unfavourable. In addition, of the two possible respective 1,3-diester derivatives only one is formed in which, as shown by the crystal structure of **3a** (discussed below), the two ferrocene substituents are located on the phenolic units connected to each other by the aliphatic carbon chain bridge. This may be a result of these hydroxyl groups being relatively more sterically accessible as a consequence of the 'pinching' effect of the bridge. A similar observation was made for the methylation of bridged calix[4]arenes, where only the analogous 1,3-dimethylether was obtained [15], while a tetra ester derivative was easily obtained by reaction with ethyl bromoacetate [15,16].

Attempts were also made at condensing 1,1'-bis(chlorocarbonyl)ferrocene (**4**) with **1a** and **1b**. Surprisingly no reaction took place which is in contrast to the trimer and dimer ferrocene-calix[4]arene products obtained from **4** and calix[4]arene and *p*-t-butylcalix[4]arene respectively [17]. This may be a consequence of the differing distances of separation of the respective transannular 1,3-hydroxyl groups in the calix[4]arene starting materials or more likely the inherent extreme rigidity of the bridged calix[4]arene system.

X-Ray structural investigation of compound 3a

Orange crystals of compound **3a** suitable for X-ray structural investigations were obtained from a dichloromethane–hexane mixture.

The calix[4]arene is in a cone conformation as shown in Fig. 2. The intramolecular contacts between oxygen atoms are 2.928(6), 3.114(7), 2.993(7) and 3.146(6) Å [in the order O(25)–O(26)–O(27)–O(28)–O(25)]. Furthermore we note the distance of 5.000(6) Å between O(26) and O(28) compared to 4.85 Å in a similar compound not bridged at opposite *para* positions [14]. The dihedral angles between the mean plane through the four methylene carbons C(6), C(12), C(18) and C(24) and the phenyl rings A–D are: 137.4(2), 90.7(2), 136(2) and 90.5(2)°. Furthermore the two phenyl rings A and C are almost perpendicular (86.4(2)°) and the two others, B and D, are almost parallel (0.5(2)°). This geometry for calix[4]arenes is already found for calixarene with hydrogen of the hydroxyl group substituted by CH_2COCH_3 [18] or $CH_2COOC(CH_3)_3$ [19].

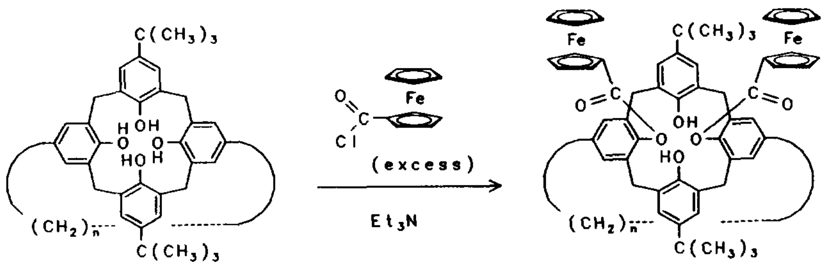
Table 2

Selected bond distances (Å) bond angles (deg) and torsion angles (deg)

C(1)–C(24)	1 495(9)	C(5)–C(6)	1.506(9)	C(101)–Fe(1)	2.005(7)	Fe(2)–C(206)	2.007(18)
C(25)–O(25)	1.384(8)	C(7)–C(6)	1.514(11)	C(102)–Fe(1)	2.017(10)	Fe(2)–C(207)	2.031(13)
C(9)–C(215)	1.491(13)	C(11)–C(12)	1 527(11)	C(103)–Fe(1)	2.029(16)	Fe(2)–C(208)	2.019(13)
C(28)–O(28)	1.404(9)	O(28)–C(100)	1.339(9)	C(104)–Fe(1)	2.025(16)	Fe(2)–C(209)	2.021(13)
C(100)–O(100)	1.180(9)	C(100)–C(101)	1.454(12)	C(105)–Fe(1)	2.021(9)	Fe(2)–C(210)	2.032(17)
C(13)–C(12)	1.476(11)	C(15)–C(151)	1 545(15)	Fe(1)–C(106)	2.031(20)		
C(17)–C(18)	1.521(10)	C(27)–O(27)	1 368(11)	Fe(1)–C(107)	1.990(16)		
C(19)–C(18)	1.524(10)	C(21)–C(211)	1.500(12)	Fe(1)–C(108)	2.050(18)		
C(23)–C(24)	1.515(11)	C(26)–O(26)	1.410(8)	Fe(1)–C(109)	2.057(18)		
O(26)–C(200)	1.383(7)	C(200)–C(201)	1.421(11)	Fe(1)–C(110)	2.041(13)		
C(200)–O(200)	1.186(8)	C(211)–C(212)	1 546(11)	C(201)–Fe(2)	2.024(6)		
C(212)–C(213)	1.488(11)	O(25)–O(26)	2.928(6)	C(202)–Fe(2)	2 025(7)		
C(213)–C(214)	1.530(11)	O(26)–O(27)	3 114(7)	C(203)–Fe(2)	2.041(8)		
C(214)–C(215)	1 530(12)	O(27)–O(28)	2.993(7)	C(204)–Fe(2)	2.037(9)		
		O(28)–O(25)	3.143(6)	C(205)–Fe(2)	2.052(7)		

C(2)–C(3)–C(4)	116.6(7)	C(1)–C(25)–C(5)	120.6(6)
C(5)–C(25)–O(25)	118.2(6)	C(1)–C(25)–O(25)	121.3(6)
C(8)–C(9)–C(10)	115.7(7)	C(7)–C(28)–C(11)	122 8(7)
C(11)–C(28)–O(28)	118.5(6)	C(7)–C(28)–O(28)	118 3(6)
C(28)–O(28)–C(100)	117.6(5)	O(28)–C(100)–C(101)	110.6(6)
O(28)–C(100)–O(100)	124.1(7)	O(100)–C(100)–C(101)	125 3(7)
C(102)–C(101)–C(105)	108.3(8)	C(100)–C(101)–C(105)	127.5(8)
C(100)–C(101)–C(102)	124.1(8)	C(14)–C(15)–C(16)	115.5(9)
C(13)–C(27)–C(17)	121.5(7)	C(17)–C(27)–O(27)	118.6(7)
C(13)–C(27)–O(27)	119.9(7)	C(20)–C(21)–C(22)	116.9(6)
C(19)–C(26)–C(23)	122.5(6)	C(23)–C(26)–O(26)	117 4(6)
C(19)–C(26)–O(26)	119.6(6)	C(26)–O(26)–C(200)	119.6(5)
O(26)–C(200)–C(201)	110.5(5)	O(26)–C(200)–O(200)	120.9(6)
O(200)–C(200)–C(201)	128.6(6)	C(202)–C(201)–C(205)	106.1(6)
C(200)–C(201)–C(205)	124.3(6)	C(200)–C(201)–C(202)	129.5(6)
C(5)–C(6)–C(7)	110.0(6)	C(17)–C(18)–C(19)	110.4(6)
C(1)–C(24)–C(23)	109.7(6)	C(11)–C(12)–C(13)	110 3(6)
C(21)–C(211)–C(212)	112.5(7)	C(211)–C(212)–C(213)	113 1(7)
C(212)–C(213)–C(214)	112.4(7)	C(213)–C(214)–C(215)	112.6(7)
C(9)–C(215)–C(214)	113.5(7)		

C(25)–C(1)–C(24)–C(23)	71.2(8)	O(28)–C(100)–C(101)–C(102)	176.7(8)
C(28)–C(7)–C(6)–C(5)	118.9(7)	O(28)–C(100)–C(101)–C(105)	−7 6(11)
C(27)–C(13)–C(12)–C(11)	71.6(9)	O(100)–C(100)–C(101)–C(102)	−3.0(13)
C(26)–C(19)–C(18)–C(17)	117.2(7)	O(100)–C(100)–C(101)–C(105)	172.7(8)
C(4)–C(5)–C(6)–C(7)	99 1(8)	C(28)–O(28)–C(100)–O(100)	10 5(10)
C(10)–C(11)–C(12)–C(13)	59.5(9)	O(26)–C(200)–C(201)–C(202)	−2.0(10)
C(16)–C(17)–C(18)–C(19)	97.8(8)	O(26)–C(200)–C(201)–C(205)	−179.5(6)
C(22)–C(23)–C(24)–C(1)	61.8(9)	O(200)–C(200)–C(201)–C(202)	177.7(7)
C(25)–C(5)–C(6)–C(7)	−73.6(8)	O(200)–C(200)–C(201)–C(205)	0.3(12)
C(28)–C(11)–C(12)–C(13)	−112.5(8)	C(26)–O(26)–C(200)–O(200)	−4 3(9)
C(27)–C(17)–C(18)–C(19)	−74 6(9)	C(21)–C(211)–C(212)–C(213)	−59.8(9)
C(26)–C(23)–C(24)–C(1)	−112.1(7)	C(211)–C(212)–C(213)–C(214)	178.6(7)
C(6)–C(5)–C(25)–O(25)	−7.0(10)	C(212)–C(213)–C(214)–C(215)	−179 4(7)
C(8)–C(9)–C(215)–C(214)	57.6(11)	C(213)–C(214)–C(215)–C(9)	59.3(10)
C(10)–C(9)–C(215)–C(214)	−118.7(9)	C(11)–C(28)–O(28)–C(100)	−110.1(7)
C(7)–C(28)–O(28)–C(100)	77 7(8)	C(16)–C(17)–C(27)–C(13)	−0.3(11)
C(18)–C(17)–C(27)–C(13)	172.2(7)	C(18)–C(17)–C(27)–O(27)	−6.4(10)
C(20)–C(21)–C(211)–C(212)	113.4(8)	C(22)–C(21)–C(211)–C(212)	−61.6(10)
C(23)–C(26)–O(26)–C(200)	−105 9(7)	C(19)–C(26)–O(26)–C(200)	81.4(7)



(1a) n = 5

(1b) n = 8

(3a) n = 5

(3b) n = 8

Scheme 1.

The four cycles of the ferrocene parts are almost parallel; angles between them vary from 1.2(5) to 4.1(4)°. Distances between Fe and the carbon atoms of the four cycles vary from 1.99(2) to 2.06(2) Å.

Electrochemical studies

The electrochemical properties of **3a** and **3b** were investigated in dichloromethane solution by cyclic voltammetry and coulometry. Both compounds exhibit reversible two electron oxidations at +0.90 V (versus standard calomel electrode SCE) which suggests that the respective two ferrocene moieties present in both compounds become oxidised in one step. These ferrocene oxidation values are of similar magnitude to those obtained from the bis-ferrocene calix[4]arene compounds [14] suggesting the presence of the rigid aliphatic carbon bridge in **3a** and **3b** has little effect on the redox properties of the appended ferrocene moieties.

Proton NMR solution complexation studies

High field ^1H NMR spectroscopy has been used by Bauer and Gutsche [20] to demonstrate the solution complexation of t-butylamine by allylcalix[4]arene, the

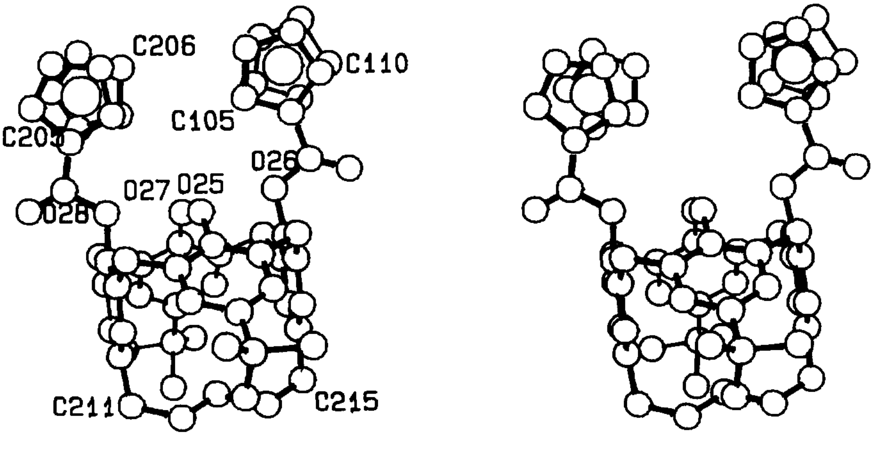


Fig. 2. Stereoscopic view of the molecule of **3a** with one ^{t}Bu group omitted because of disorder.

changes in the chemical shift values of both the calixarene host and amine guest being monitored.

Addition of stoichiometric amounts of t-butylamine or benzylamine to room temperature acetonitrile solutions of compounds **3a** and **3b** had little effect ($\Delta\delta \leq 0.05$ ppm) on the respective ^1H chemical shifts for either the respective host or amine guest, implying that there is no host–guest complexation under these conditions. These disappointing observations may reflect unfavourable steric interactions between the bridge methylenes of the respective host and t-butyl or benzyl methylene groups of the amine guests.

Conclusion

The synthesis of the first redox-active bis-ferrocene-bridged calix[4]arene molecules has been achieved. These compounds have been shown to undergo independent reversible two electron oxidations in dichloromethane. The failure of either **3a** or **3b** to form solution inclusion complexes with t-butylamine or benzylamine may be attributed to unfavourable steric interactions between the aliphatic bridge methylenes of the host and alkyl, benzyl groups of the respective amine guest.

Acknowledgements

P.D.B. thanks the SERC for an 'earmarked' studentship (to A.D.K.) and for use of the high field NMR service at the University of Warwick, and The Research Corporation Trust, L. and D. Blond for additional financial support. V.B., H.G., W.V. are indebted to the Deutsche Forschungsgemeinschaft for providing financial support for this research.

References

1 For reviews on calixarenes see C D. Gutsche, Top. Curr. Chem., 123 (1984) 1; Prog. Marcrocycl. Chem., 3 (1987) 93; Calixarenes, in J.F. Stoddart (Ed.), Monographs in Supramolecular Chemistry, Vol 1, The Royal Society of Chemistry, 1989

2 See also J. Vicens and V. Bohmer (Eds), Calixarenes: a Versatile Class of Macrocyclic Compounds, Kluwer Academic, Dordrecht, 1990

3 G D Andretti, R Ungaro and A. Pochini, J. Chem. Soc., Chem. Commun., (1979) 1005; (b) G.D. Andretti, A. Pochini and R Ungaro, J. Chem Soc , Perkin Trans., 2 (1983) 1773, (c) R. Ungaro, A. Pochini, G.D. Andretti and V Sangermano, J. Chem Soc., Perkin Trans., 2 (1984) 1979

4 G Happel, B. Mathiasch and H Kämmerer, Makromol Chem., 176 (1975) 3317, see also C.D. Gutsche and L.J. Bauer, Tetrahedron Lett , 22 (1981) 4763

5 C Rizzoli, G.D Andretti, R. Ungaro and A. Pochini, J. Mol. Struct , 88 (1982) 133.

6 C D Gutsche, B Dhawam, J.A. Levine, K H. No and L.J Bauer, Tetrahedron, 39 (1983) 409.

7 (a) H Goldmann, W. Vogt, E Paulus and V. Bohmer, J Am Chem. Soc., 110 (1988) 6811; (b) V. Bohmer, H Goldmann, W Vogt, E.F. Paulus, F L. Tobiason and M.J Thielman, J. Chem. Soc., Perkin Trans , 2 (1990) 1769.

8 (a) P D. Beer and E.L. Tite, Tetrahedron Lett., (1988) 2349, (b) P.D. Beer, E.L Tite, M.G.B. Drew and A. Ibbotson, J Chem. Soc., Dalton Trans., (1990) 2543; (c) P.D. Beer, E.L. Tite and A. Ibbotson, J Chem. Soc , Chem. Commun , (1989) 1874, (d) P.D. Beer and A.D. Keefe, J. Inclusion Phenom., 5 (1987) 499.

9 P.D. Beer, Chem Soc. Rev , 18 (1989) 401.

10 H.H. Lan and H Hart, J. Org Chem , 24 (1959) 280

11 B.A Frenz, Enraf-Nonius Structure Determination Package, College Station, Texas, USA, 1985

12 P. Main, S.J. Fiske, S.E. Hull, L. Lessinger, G. Germain, J.P. Declereq and M.M. Woolfson, A System of Computer Programmes for the Automatic Solution of Crystal Structures from X-ray Diffraction Data, Universities of York, UK and Louvain, Belgium, 1982.

13 G.M. Sheldrick, SHELX. Programme for Crystal Determination, University of Cambridge, UK, 1976.

14 P D. Beer, A.D. Keefe and M.G.B. Drew, J. Organomet. Chem., 378 (1989) 437.

15 V. Bohmer and A. Rodriguez, W. Vogt, unpublished results.

16 V. Bohmer, W. Vogt, H. Goldmann, M.A. McKervey, M. Owens, S. Cremin and E.M Collins, J. Org. Chem , 55 (1990) 2569.

17 P.D. Beer, A.D. Keefe, A.M.Z. Slawin and D.J Williams, J. Chem. Soc., Dalton Trans., (1990) 3675.

18 G. Ferguson, B. Kaitner, A. McKervey and E.M. Seward, J. Chem Soc., Chem. Commun., (1987) 584.

19 A. Arduini, A. Pochini, S. Reverberi, R Ungaro, G D. Andretti and F. Ugozzoli, Tetrahedron, 42 (1986) 2089.

20 L.J. Bauer and C.D. Gutsche, J. Am. Chem Soc., 107 (1985) 6063