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Synthesis of an unusual, cage-functionalized molecular cleft

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The synthesis and X-ray crystal structure of a novel, cage-functionalized bis(α-diketone), **4**, is described. A molecular cleft is formed by two parallel planar aromatic diketone units bridged by a polycarbocyclic cage. Crystal data: $T = 100(1)$ K, monoclinic, $C2/c$, $a = 35.6383(2)$, $b = 11.8110(1)$, $c = 15.6319(2)$ Å, $\beta = 110.7745(2)^\circ$, $V = 6152.04(9)$ Å^3, $Z = 12$, $R = 0.0691$. Compound **4** is of potential interest as a new type of "host" molecule for the study of host–guest interactions in solution.

KEY WORDS: X-ray structure; polycarbocyclic cage; cage-functionalized molecular cleft.

Introduction

As part of an ongoing program devoted to the synthesis and chemistry of novel polycarbocyclic "cage" compounds,[1] we recently reported the preparation of several examples of cage-functionalized molecular clefts[2–4] and crown ethers.[5,6] Compounds of this type are of interest as members of a new class of "host" systems for the study of host–guest interactions (i.e., molecular recognition and inclusion phenomena). As an extension of these past studies, our attention has turned to the preparation and characterization of an unusual, cage-functionalized molecular cleft, **4** (Scheme 1).

Experimental section

Melting points are uncorrected. Elemental microanalytical data was obtained by personnel at M-H-W Laboratories, Phoenix, AZ.

exo-*8*,exo-*11-Bis(2′-phenylethynyl)pentacyclo [5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane*-endo-*8*,endo-*11-diol (2)*

A solution of phenylacetylene (1.86 g, 18.2 mmol) in dry THF (20 mL) under argon was cooled to 0°C via application of an external ice-water bath. To this cooled solution was added dropwise with stirring *n*-BuLi (7.3 mL of 2.5 M solution in hexane, 18.3 mmol). After all of the organometallic reagent had been added, the reaction mixture was stirred at 5°C for 0.5 h. Pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane-8,11-dione (**1**, 793 mg, 4.55 mmol) then was added to the reaction mixture in one portion, and the resulting mixture was refluxed at ca. 60°C for 24 h. The reaction mixture was cooled

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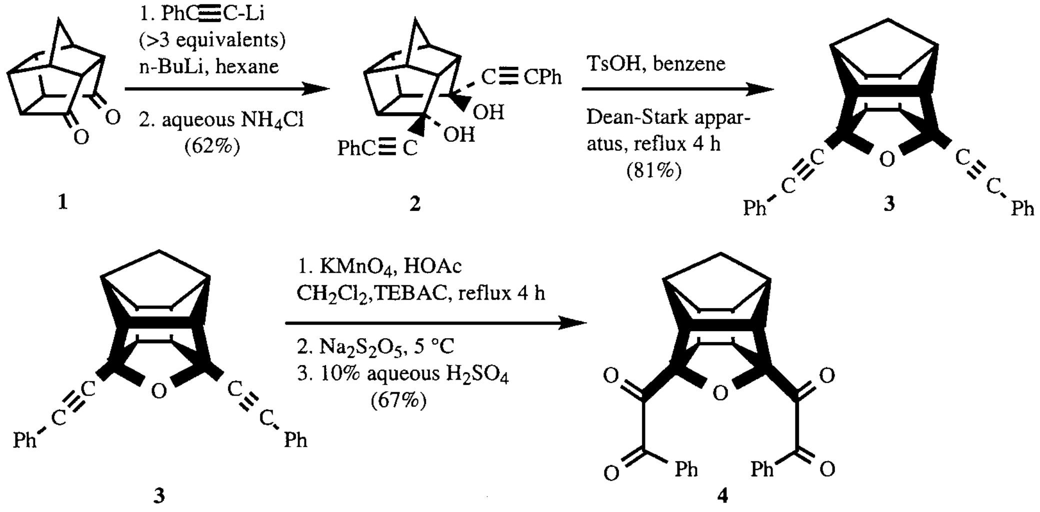

Scheme 1

to 0° and then quenched via addition of saturated aqueous NH_4Cl (20 mL). The resulting aqueous suspension was extracted with EtOAc (2 × 40 mL). The combined extracts were washed with water (20 mL), dried ($MgSO_4$), and filtered, and the filtrate was concentrated in vacuo. The residue was purified via fractional recrystallization from acetone–hexane, thereby affording **2** (1.06 g, 62%) as a colorless microcrystalline solid: mp 186–187°C; IR (KBr): 3000–3300 (br, m), 2977 (m), 2867 (w), 1491 (s), 1132 (s), 1063 (m), 752 cm^{-1} (vs); ^1H NMR ($CDCl_3$): δ 1.19 (*A*B, $J_{AB} = 10.3$ Hz, 1H), 1.72 (A*B*, $J_{AB} = 10.3$ Hz, 1H), 2.63–3.04 (m, 8H), 4.70–6.01 (br, 2H, peak disappeared when sample was shaken with D_2O), 7.22–7.46 (m, 10H); ^{13}C NMR ($CDCl_3$): δ 34.1 (t), 39.9 (d), 45.1 (d), 45.8 (d), 52.0 (d), 74.2 (s), 84.0 (s), 92.5 (s), 122.8 (s), 128.2 (2 C, d, determined via integration of the gated-decoupled ^{13}C NMR spectrum), 131.6 (d). Anal. Calcd for $C_{27}H_{22}O_2$: C, 85.69; H, 5.86. Found: C, 85.43; H, 5.59.

3,5-Bis(2′-phenylethynyl)hexacyclo[5.4.1.0^{2,6}.0^{3,10}.0^{5,9}]dodecane (3)

To a solution of **2** (500 mg, 1.32 mmol) in dry benzene (50 mL) was added *p*-toluenesulfonic acid (TsOH, 50 mg, catalytic amount). The resulting mixture was refluxed in a Dean-Stark apparatus until the distillate was no longer cloudy (ca. 4 h). The reaction mixture was allowed to cool gradually to ambient temperature and was washed successively with 10% aqueous $NaHCO_3$ (10 mL) and water (10 mL). The organic layer was dried ($MgSO_4$) and filtered, and the filtrate was concentrated in vacuo. The residue was purified via column chromatography on neutral alumina by eluting with 1:1 CH_2Cl_2–hexane. Pure **3** (385 mg, 81%) was thereby obtained as a colorless microcrystalline solid: mp 114.0–114.5°C; IR (KBr): 2963 (m), 2860 (w), 1491 (m), 1374 (s), 1174 (s), 856 (s), 725 cm^{-1} (s); ^1H NMR ($CDCl_3$): δ 1.63 (*A*B, $J_{AB} = 10.1$ Hz, 1H), 1.99 (A*B*, $J_{AB} = 10.1$ Hz, 1H), 2.66–3.17 (m, 8H), 7.18–7.51 (m, 10H); ^{13}C NMR ($CDCl_3$): δ 42.0 (d), 43.4 (t), 44.5 (d), 52.1 (d), 61.7 (d), 85.8 (s), 87.3 (s), 87.4 (s), 122.6 (s), 128.2 (d), 128.4 (d), 131.7 (d). Anal. Calcd for $C_{27}H_{20}O$: C, 89.97; H, 5.59. Found: C, 89.72; H, 5.80.

Oxidation of 3

To a solution of **3** (1.10 g, 3.05 mmol) in dry CH_2Cl_2 (100 mL) under argon was added sequentially $KMnO_4$ (8.70 g, 55 mmol), benzyl tri(*n*-butyl)ammonium bromide (TEBAC, 200 mg, catalytic amount), and HOAc (3.30 g, 55 mmol), and the resulting mixture was refluxed for 4 h. The reaction mixture then was cooled to 5°C via application of an external ice-water bath. To this cooled solution was added portionwise solid $Na_2S_2O_5$ (10 g, 53 mmol) with stirring. After all of the $Na_2S_2O_5$ had been added, the reaction mixture was stirred at 5°C for 20 min, at which time water (25 mL) and 10% aqueous H_2SO_4 (10 mL) were added sequentially to the reaction mixture. The organic layer was separated, washed with water (10 mL), dried ($MgSO_4$), and filtered, and the filtrate was concentrated in vacuo. The residue was purified via column chromatography on silica gel by eluting with 1:1 CH_2Cl_2–hexane). Pure **4** (866 mg, 67%) was thereby obtained as a pale yellow microcrystalline solid: mp 112–113°C; IR (KBr): 2998 (w), 2984 (w), 2867 (w), 1720 (s), 1678 (vs), 1594 (m), 1443 (m), 1264 (m), 787 (m), 718 cm^{-1} (m); ^1H NMR (CDCl3): δ 1.64 (*A*B, $J_{AB} = 10.1$ Hz, 1H), 2.02 (A*B*, $J_{AB} = 10.1$ Hz, 1H), 2.71–3.42 (m, 8H), 7.34–7.81 (m, 10H); ^{13}C NMR ($CDCl_3$): δ 42.6 (d), 43.5 (t), 45.5 (d), 50.4 (d), 59.1 (d), 99.5 (s), 128.7 (d), 129.6 (d), 132.0 (s), 134.6 (d), 193.2 (s), 201.6 (s). Anal. Calcd for $C_{27}H_{20}O_5$: C, 76.40; H, 4.75. Found: C, 76.62; H, 4.87.

Crystallography

A colorless fragment of **4** was mounted on a fine glass fiber with epoxy resin. Preliminary examination and data collection were carried out at 100(1) K on a Siemens SMART 1k CCD Platform diffractometer. 0.1° ω scans with 60 sec. exposure time were carried out at three different ϕ settings corresponding to a nominal hemisphere of data. The intensities were corrected for absorption and decay (SADABS[7]). The structure was solved by direct methods (SHELXS-86[8]) in the space group $C2/c$. All non-hydrogen atoms were refined using full-matrix least-squares (SHELXL-93[9]) with anisotropic displacement parameters. Positional parameters and isotropic displacement parameters were refined for all hydrogen atoms. Structure solution and refinement are summarized in Table 1, final refined coordinates are reported in Table 2, and selected distances and angles in Table 3.

Table 1. Crystal Data and Summary of Intensity Data Collection and Structure Refinement

Compound	**4**
Formula	$C_{27}H_{20}O_5$
CCDC deposit no.	CCDC-1003/6014
Color/shape	Colorless/plate
Formula weight	424.46
Temperature, K	100(1)
Crystal system	Monoclinic
Space group	$C2/c$
Unit cell dimensions (8192 reflections in full θ range)	$a = 35.6383(2)$ Å $b = 11.8110(1)$ Å $c = 15.6319(2)$ Å $\beta = 110.7745(2)°$
Volume, $Å^3$	6152.04(9)
Z	12
Density (calculated), Mg/m^3	1.375
Absorption coefficient, mm^{-1}	0.095
Diffractometer/scan	Siemens SMART/1k CCD area detector/ω scan
Radiation, graphite monochromator	Mo Kα, 0.71073 Å
θ range for data collection, deg	2.16–28.29
Reflections measured	19839
Independent/observed reflections	7597 ($R_{int} = 0.0465$)/5203 [$I > 2\sigma(I)$]
Data/restraints/parameters	7597/0/562
Goodness of fit on F^2	1.030
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0691$, $wR2 = 0.1849$
R indices (all data)	$R1 = 0.1000$, $wR2 = 0.2043$

Results and discussion

The procedure that we employed to prepare **4** is analogous to a portion of the reaction sequence used recently to synthesize “albatrossenes,” a class of molecular clefts that contain large benzenoid aromatic groups attached to α-diketone “arms.”[10] Thus, reaction of a readily available pentacyclic cage diketone, i.e. pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane-8,11-dione (**1**)[11] with excess 1-lithio-2-phenylethyne

Table 2. Atomic Coordinates and Equivalent Isotropic Displacement Parameters (Å^2) for **4**

	x	y	z	$U_{\mathrm{eq}}{}^{a}$
O1	0.16927(4)	0.20348(11)	0.25468(9)	0.0199(3)
O2	0.15894(5)	0.14502(13)	0.02803(11)	0.0362(4)
O3	0.22483(4)	0.31059(13)	0.14519(12)	0.0364(4)
O4	0.17970(5)	0.15128(12)	0.48265(10)	0.0298(4)
O5	0.11144(4)	0.30644(12)	0.36845(11)	0.0294(4)
O6	0.0000	0.31017(14)	0.2500	0.0167(4)
O7	0.01149(4)	0.36402(12)	0.47805(9)	0.0263(3)
O8	−0.05612(4)	0.20547(12)	0.36355(11)	0.0302(4)
C1	0.12554(7)	−0.1477(2)	0.2219(2)	0.0309(5)
C2	0.14452(6)	−0.0794(2)	0.16487(15)	0.0272(4)
C3	0.13277(6)	0.0441(2)	0.17508(14)	0.0209(4)
C4	0.16893(5)	0.1216(2)	0.18613(13)	0.0191(4)
C5	0.20498(6)	0.0423(2)	0.23626(14)	0.0252(4)
C6	0.18971(6)	−0.0805(2)	0.2242(2)	0.0288(5)
C7	0.14372(7)	−0.0765(2)	0.3085(2)	0.0280(5)
C8	0.13196(6)	0.0461(2)	0.27503(13)	0.0213(4)
C9	0.16855(6)	0.1238(2)	0.32372(13)	0.0199(4)
C10	0.20430(6)	0.0444(2)	0.33540(14)	0.0245(4)
C11	0.18892(6)	−0.0787(2)	0.32501(14)	0.0283(5)
C12	0.16998(6)	0.1854(2)	0.10419(14)	0.0232(4)
C13	0.18837(6)	0.3044(2)	0.12251(14)	0.0242(4)
C14	0.16162(5)	0.4032(2)	0.10975(13)	0.0198(4)
C15	0.17825(6)	0.5121(2)	0.11938(15)	0.0259(4)
C16	0.15354(7)	0.6061(2)	0.1055(2)	0.0291(5)
C17	0.11233(7)	0.5924(2)	0.08287(15)	0.0280(5)
C18	0.09561(6)	0.4849(2)	0.07398(14)	0.0249(4)
C19	0.12025(6)	0.3896(2)	0.08761(14)	0.0222(4)
C20	0.16786(5)	0.1893(2)	0.40553(13)	0.0202(4)
C21	0.14757(6)	0.3057(2)	0.38621(13)	0.0205(4)
C22	0.17257(6)	0.4076(2)	0.39371(13)	0.0202(4)
C23	0.21373(6)	0.3995(2)	0.41072(14)	0.0236(4)
C24	0.23673(6)	0.4970(2)	0.4198(2)	0.0291(5)
C25	0.21843(7)	0.6026(2)	0.4117(2)	0.0305(5)
C26	0.17763(7)	0.6114(2)	0.3949(2)	0.0292(5)
C27	0.15459(6)	0.5142(2)	0.38552(14)	0.0239(4)
C28	0.04195(11)	0.6641(3)	0.2833(3)	0.0194(7)
C29	0.02226(6)	0.5934(2)	0.3298(2)	0.0283(5)
C30	0.03586(5)	0.46981(15)	0.32996(12)	0.0159(4)
C31	−0.00012(5)	0.39117(14)	0.31897(12)	0.0159(4)
C32	−0.03649(5)	0.46971(15)	0.26956(13)	0.0161(4)
C33	−0.02296(6)	0.5930(2)	0.2926(2)	0.0333(5)
C34	−0.00051(5)	0.32637(15)	0.40087(13)	0.0182(4)
C35	−0.01993(5)	0.2084(2)	0.38246(13)	0.0196(4)
C36	0.00580(5)	0.10730(15)	0.39278(13)	0.0190(4)
C37	−0.01139(6)	−0.0004(2)	0.38452(15)	0.0234(4)
C38	0.01236(7)	−0.0960(2)	0.3973(2)	0.0285(5)
C39	0.05351(7)	−0.0848(2)	0.41887(15)	0.0284(5)
C40	0.07095(6)	0.0220(2)	0.42653(14)	0.0254(4)
C41	0.04705(6)	0.1184(2)	0.41324(13)	0.0209(4)

[a] $U_{\mathrm{eq}} = (1/3)\sum_i \sum_j U^{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$.

Table 3. Bond Lengths (Å) and Angles (deg) for **4**[a]

Molecule 1		Molecule 2	
Bond length			
O1—C4	1.441(2)	C28—C29	1.442(4)
O1—C9	1.439(2)	C28—C33$^{\mathrm{I}}$	1.415(4)
O2—C12	1.211(2)	C29—C30	1.538(3)
O3—C13	1.222(2)	C29—C33	1.507(3)
O4—C20	1.214(2)	C30—C31	1.543(2)
O5—C21	1.217(2)	C30—C32$^{\mathrm{I}}$	1.564(3)
O6—C31	1.442(2)	C31—C32	1.558(2)
O7—C34	1.212(2)	C31—C34	1.496(2)
O8—C35	1.217(2)	C32—C30$^{\mathrm{I}}$	1.564(3)
C1—C2	1.526(3)	C32—C33	1.536(3)
C2—C3	1.542(3)	C33—C28$^{\mathrm{I}}$	1.414(4)
C3—C4	1.539(3)	C33—C29$^{\mathrm{I}}$	1.922(4)
C5—C4	1.558(3)	C34—C35	1.536(3)
C5—C6	1.537(3)	C35—C36	1.480(2)
C5—C10	1.559(3)	C36—C37	1.398(3)
C6—C2	1.547(3)	C36—C41	1.395(3)
C6—C11	1.586(3)	C37—C38	1.383(3)
C7—C1	1.529(3)	C38—C39	1.390(3)
C7—C8	1.546(3)	C39—C40	1.393(3)
C7—C11	1.539(3)	C40—C41	1.393(3)
C8—C3	1.573(3)		
C8—C9	1.555(3)		
C9—C10	1.540(2)		
C9—C20	1.502(3)		
C10—C11	1.543(3)		
C12—C4	1.498(3)		
C12—C13	1.534(3)		
C13—C14	1.475(3)		
C14—C15	1.403(3)		
C14—C19	1.399(3)		
C15—C16	1.385(3)		
C16—C17	1.393(3)		
C17—C18	1.389(3)		
C18—C19	1.397(3)		
C20—C21	1.532(2)		
C21—C22	1.477(3)		
C22—C23	1.398(3)		
C22—C27	1.398(3)		
C23—C24	1.391(3)		
C24—C25	1.392(3)		
C25—C26	1.387(3)		
C26—C27	1.389(3)		
Bond angle			
C9—O1—C4	96.95(13)	C29—C28—C33$^{\mathrm{I}}$	84.6(2)
C7—C1—C2	95.2(2)	C28—C29—C30	109.9(2)
C1—C2—C3	104.3(2)	C28—C29—C33	116.9(2)
C6—C2—C1	103.2(2)	C30—C29—C33$^{\mathrm{I}}$	83.31(14)
C6—C2—C3	102.1(2)	C30—C29—C33	106.9(2)
C2—C3—C4	109.1(2)	C33—C29—C33$^{\mathrm{I}}$	90.3(2)
C8—C3—C2	102.6(2)	C29—C30—C31	108.81(14)

Table 3. Continued

Molecule 1		Molecule 2	
C8—C3—C4	100.89(15)	C29—C30—C32$^{\mathrm{I}}$	96.60(15)
O1—C4—C3	105.56(14)	C31—C30—C32$^{\mathrm{I}}$	101.15(14)
O1—C4—C5	103.99(15)	O6—C31—C30	105.07(13)
O1—C4—C12	107.56(15)	O6—C31—C32	104.29(13)
C5—C4—C3	101.97(15)	O6—C31—C34	107.68(14)
C5—C4—C12	117.8(2)	C30—C31—C32	102.08(14)
C12—C4—C3	118.5(2)	C30—C31—C34	118.2(2)
C6—C5—C4	108.2(2)	C32—C31—C34	118.05(14)
C6—C5—C10	90.4(2)	C31—C32—C30$^{\mathrm{I}}$	100.99(13)
C10—C5—C4	100.92(14)	C31—C32—C33	108.16(14)
C5—C6—C2	108.3(2)	C33—C32—C30$^{\mathrm{I}}$	96.8(2)
C5—C6—C11	89.8(2)	C28—C33—C29$^{\mathrm{I}}$	116.7(2)
C11—C6—C2	102.4(2)	C28—C33—C32	110.5(2)
C8—C7—C1	103.7(2)	C29—C33—C29$^{\mathrm{I}}$	89.7(2)
C8—C7—C11	102.4(2)	C29—C33—C32	107.3(2)
C11—C7—C1	103.2(2)	C32—C33—C29$^{\mathrm{I}}$	83.31(15)
C7—C8—C3	102.90(15)	O7—C34—C31	123.8(2)
C7—C8—C9	107.9(2)	O7—C34—C35	119.7(2)
C9—C8—C3	100.82(15)	C31—C34—C35	116.4(2)
O1—C9—C8	104.70(14)	O8—C35—C34	116.1(2)
O1—C9—C10	104.66(15)	O8—C35—C36	124.4(2)
O1—C9—C20	108.15(15)	C34—C35—C36	119.4(2)
C8—C9—C10	102.4(2)	C35—C36—C37	119.4(2)
C8—C9—C20	117.2(2)	C35—C36—C41	120.7(2)
C10—C9—C20	118.4(2)	C37—C36—C41	119.9(2)
C5—C10—C9	101.30(15)	C36—C37—C38	120.3(2)
C5—C10—C11	90.6(2)	C37—C38—C39	119.8(2)
C9—C10—C11	108.3(2)	C38—C39—C40	120.5(2)
C6—C11—C7	102.7(2)	C39—C40—C41	119.8(2)
C6—C11—C10	89.2(2)	C36—C41—C40	119.7(2)
C7—C11—C10	108.2(2)		
O2—C12—C4	123.0(2)		
O2—C12—C13	120.8(2)		
C13—C12—C4	116.1(2)		
O3—C13—C12	116.7(2)		
O3—C13—C14	124.2(2)		
C12—C13—C14	119.1(2)		
C13—C14—C15	118.9(2)		
C13—C14—C19	121.1(2)		
C15—C14—C19	120.0(2)		
C14—C15—C16	119.8(2)		
C15—C16—C17	120.1(2)		
C16—C17—C18	120.5(2)		
C17—C18—C19	119.8(2)		
C14—C19—C18	119.7(2)		
O4—C20—C9	123.4(2)		
O4—C20—C21	120.1(2)		
C9—C20—C21	116.3(2)		
O5—C21—C20	116.0(2)		
O5—C21—C22	124.9(2)		
C20—C21—C22	119.1(2)		
C21—C22—C23	121.5(2)		
C21—C22—C27	118.9(2)		
C23—C22—C27	119.7(2)		

Table 3. Continued

Molecule 1		Molecule 2	
C22—C23—C24	120.2(2)		
C23—C24—C25	119.5(2)		
C24—C25—C26	120.7(2)		
C25—C26—C27	119.9(2)		
C22—C27—C26	120.0(2)		

[a] Symmetry operation to generate equivalent atoms: I $-x$, y, $-z+1/2$.

afforded the corresponding cage diol **2** (62% yield). Subsequent acid promoted cycloelimination of water from **2** afforded 3,5-bis(2′-phenylethynyl)hexacyclo[5.4.1.0.0^{2,6}.0^{3,10}.0^{5,9}]dodecane (**3**, 81% yield). Finally, application of the oxidation procedure described by Pascal *et al.*[7] converted **3** into the target tetraketone **4** (67% yield). The structure of **4** was established unambiguously via application of X-ray crystallographic techniques.

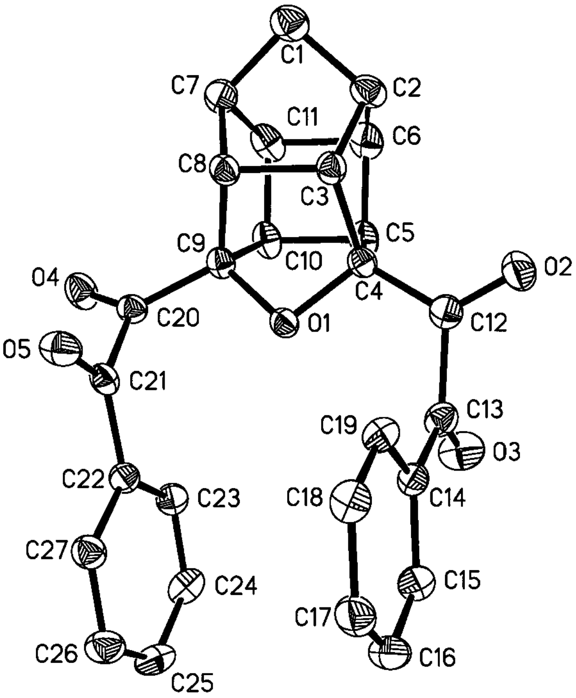

Fig. 1. Molecule 1 showing the cage and molecular cleft and atom numbering (50% probability ellipsoids). Hydrogen atoms have been omitted for clarity.

The structure consists of two crystallographically distinct molecules. The atoms of one molecule (O1–O5, C1–C27) lie on general positions. The second molecule has a symmetry imposed disorder with the molecule lying across the twofold axis with O6 lying on the twofold axis. The CH_2 group of the cage is disordered with atoms C28, H28A, and H28B having 50% site occupancies. The probability ellipsoids of C29 and C33 are slightly elongated along the C29–$C33^I$ and C33–$C29^I$ bonds as would be anticipated for this type of disorder. A structurally similar disorder was also apparent for the solution obtained in the noncentrosymmetric space group *Cc*, hence, the description in the centrosymmetric space group is preferred. ORTEP plots of the two molecules showing the atom numbering scheme and the disorder model are shown in Figs. 1 and 2.

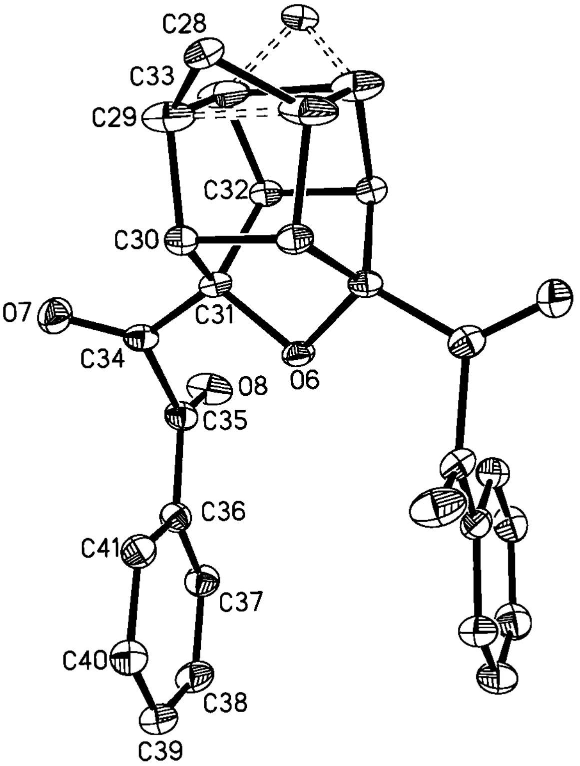

Fig. 2. Molecule 2 showing the disorder model for the cage and atom numbering (50% probability ellipsoids). Hydrogen atoms have been omitted for clarity.

It is clearly shown in Fig. 1 that a molecular cleft with potential for behaving as a host for a variety of guest molecules is formed by two planar aromatic diketone moieties linked by a polycarbocyclic cage. An indication of the size of the cleft may be obtained from the distances between pairs of atoms in the ordered molecule. The opposite pairs of carbonyl carbons are separated by 4.738(3) and 4.833(3) Å. Opposite pairs of phenyl carbons are separated by 4.403(3) to 4.738(3) Å.

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Supplementary material

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC-1003/6014. Copies of available material can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (e-mail: deposit@ccdc.cam.ac.uk).

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