Crystal Structures of Mono-, Di-, and Tri(*p-tert*-butyl)-thiacalix[4]arenes: Dimeric Self-inclusion Behavior

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Abstract

X-Ray crystal structures of the mono-, di-, and tri(*p-tert*-butyl)-substituted thiacalix[4]arenes (TC4As; **1**, **2**, and **3**, respectively) have been determined. TC4As **1–3** adopt a cone conformation and form dimeric self-inclusion units in such a manner that phenol moieties are inserted into the cavity of each molecule. In all the crystal structures of **1–3**, lateral face-to-face interactions exist between the phenol rings that do not bear a *tert*-butyl substituent, and seemingly, this molecular assembly stabilizes the formation of self-inclusion. TC4As **1** and **2** adopt a cone conformation with C_2 symmetry, leading to the formation of rim-to-rim intermolecular hydrogen bonds so as to link the dimeric units up and down. On the other hand, **3** adopts a regular cone conformation with C_4 symmetry to form cyclic hydrogen bonds within the rim part of TC4A.

Introduction

Calix[*n*]arenes are very versatile host molecules for molecular recognition and supramolecular assembly [1, 2] because of the ready introduction of functional groups into the phenolic OH and/or the *para* position to realize a wide variety of functions [3]. On the contrary, we have recently revealed that replacement of the four methylene bridges of calix[4]arenes (C4As) by epithio linkages could endow the resulting thiacalix[4]arenes (TC4As) with several characteristic novel functions which could not be attained by the conventional C4As [4, 5]. The feasibility of chemical modifications of a sulfide bond such as oxidizability to the sulfoxide and sulfone could undoubtedly have expanded the utility of TC4As as a building block for functional materials [6–9]. In this context, the structures of TC4As are of much interest. For instance, Hosseini et al. reported that tetra(*p-tert*-butyl)-TC4A **4** includes CH_2Cl_2, $CHCl_3$, or MeOH into its cavity to form the 1 : 1 complexes of exact C_4 symmetry in the solid state. On the other hand, we revealed a guest-induced deformation of the TC4A host; in the 1 : 2 complex of **4** with CH_2ClCH_2Cl, the host adopts a distorted C_4 cone conformation so as to assemble the most stable crystal structure by including one guest molecule into the cavity as a *gauche* conformer, while clathrating another in the crystal lattice as the most stable *anti* conformer [4]. By contrast, bare TC4A **5** forms a 3 : 2 complex with water to give trimeric self-inclusion units without holding water in the

Scheme 1. Chemical structures of TC4As **1-3**.

1 : R^{1-3} =H, R^4 = Bu^t
2 : R^{1-2} =H, R^{3-4} = Bu^t
3 : R^1 =H, R^{2-4} = Bu^t
4 : R^{1-4} = Bu^t
5 : R^{1-4} =H

host-cavity [10]. These results indicate that *p*-alkyl substituents as well as guest molecules should greatly affect the crystal structures of the TC4A-class host molecules. Along this line, herein we report the X-ray structures of mono-, di- and tri(*p-tert*-butyl)thiacalix[4]arenes (**1–3**) to reveal their unique assemblies comprising dimeric self-inclusion units stabilized by $\pi-\pi$ interaction and hydrogen bonding.

X-ray experimental

Partially *p-tert*-butylated TC4As (**1–3**) were prepared by treatment of the parent tetra(*p-tert*-butyl)-TC4A **4** with $AlCl_3$ in toluene. The detailed procedure of preparation and properties of **1–3** are described previously [11]. The crystals suitable for X-ray study were formed by liquid–liquid slow

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Table 1. Crystal data and parameters of refinement

Compound	1	2	3
Molecular formula	$C_{28}H_{24}O_4S_4$	$C_{32}H_{32}O_4S_4$	$C_{36}H_{40}O_4S_4$
Molecular weight	552.74	608.84	664.95
Crystal color, sizes/mm	colorless, $0.3 \times 0.2 \times 0.2$	colorless, $0.15 \times 0.2 \times 0.4$	colorless, $0.15 \times 0.2 \times 0.2$
Temperature/K	200	200	220
Crystal system, Space Group	Triclinic, $P\bar{1}$ (No. 2)	Triclinic, $P\bar{1}$ (No. 2)	Triclinic, $P\bar{1}$ (No. 2)
Unit cell parameters/Å, °	$a = 12.5274(8), \alpha = 92.1570(7)$	$a = 10.394(1), \alpha = 94.778(4)$	$a = 9.8430(7), \alpha = 73.084(4)$
	$b = 12.7748(7), \beta = 104.003(1)$	$b = 12.385(2), \beta = 104.478(2)$	$b = 13.433(1), \beta = 78.522(4)$
	$c = 16.5053(9), \gamma = 91.148(2)$	$c = 12.961(2), \gamma = 112.129(1)$	$c = 14.439(1), \gamma = 69.406(2)$
$V/\text{Å}^3$	2560.0(3)	1466.9(3)	1699.8(3)
Z	4	2	2
$F(000)$	1152	640	704
$D_{calcd}/\text{gcm}^{-3}$	1.434	1.378	1.299
$\mu(\text{Mo-K}\alpha)/\text{cm}^{-1}$	4.05	3.61	3.17
$2\theta_{max}/°$	56.1	54.9	55.0
Measured data	16999	10418	14004
Unique data	10613 ($R_{int} = 0.02$)	6090 ($R_{int} = 0.03$)	7040 ($R_{int} = 0.02$)
Observed data	6372 [$I_0 > 4.5\sigma(I_0)$]	5173 [$I_0 > 5.0\sigma(I_0)$]	5271 [$I_0 > 3.0\sigma(I_0)$]
Number of variables	661	361	397
R, R_w	0.058, 0.067	0.044, 0.052	0.065, 0.071
GOF	1.39	2.11	2.19
Residual peaks in final Difference map/eÅ^{-3}	+0.46 to −0.78	+0.21 to −0.22	+0.44 to −0.2

diffusion of ethyl acetate into the CH_2Cl_2 solution of TC4As at room temperature.

All measurements of X-ray data were carried out on a Rigaku/MSC Mercury CCD diffractometer using monochromatized Mo-Kα radiation ($\lambda = 0.71073$ Å). In this type of crystals, we have often experienced the broadening of intensity peaks at very low temperature (150 K), probably due to the separation of *tert*-butyl carbons with large anisotropic temperature factors. Thus, temperatures of 200–220 K were set as suitable for measurements of **1**–**3**. The structures were solved by the direct method and refined by full-matrix least-squares method. All non-hydrogen atoms were refined with anisotropic temperature factors. Successive difference Fourier maps located all the hydrogen atoms except for some CH_3 hydrogen atoms. For **1** and **2**, OH hydrogen atoms were decided unequivocally in one direction, for which isotropic refinement was taken into account. By contrast, OH hydrogen atoms for **3** appeared on two sides of O atoms and thus disorder was assigned. The locations of the remaining CH_3 hydrogen atoms were assigned by geometrical calculations. Their hydrogen atoms were included in the refinement with appropriate isotropic temperature factors but not refined. Finally, for *tert*-butyl carbons, C(54), C(55), and C(56), of one molecule (Mol. A) in **1**, disorder was assigned in the ratio of 9 : 1 occupancy in consideration of the difference in the electron density, leading to a reasonable refinement. The corresponding carbon atoms with minor occupancy, C(54′), C(55′), and C(56′), were refined isotropically. All calculations were performed using the software package of Molecular Structure Corporation (Crystal Structure Analysis Package, Molecular Structure Corporation, 1985 and 1999).

Crystal data and parameters of refinement for **1**–**3** are summarized in Table 1. All crystallographic data of **1**–**3** have been deposited at the Cambridge Crystallographic Data Center in CIF format (CCDC No. 173854, 173855, 173856). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (e-mail: deposit@ccdc.cam.ac.uk).

Results and discussion

Molecular geometry

Final atomic coordinates for the non-hydrogen atoms of TC4As **1**–**3** are listed in Table 2. Bond lengths and bond angles in the macro ring parts are shown in Table 3. Two independent molecules (Mol. A and Mol. B) exist in the crystal of **1**, which have almost the same molecular conformation as well as molecular assembly.

The conformations of the present TC4As are of great interest in comparison with those of the parent calix[4]arenes. Structural parameters relevant to the conformational features are summarized in Table 4. All TC4A molecules **1**–**3** adopt a cone conformation (Figure 1); however, they can be divided into two categories: approximately C_2 symmetry in **1** and **2**, and approximately C_4 symmetry in **3** as seen in **4** [4, 10]. The difference between the two conformations can be best defined in terms of the interplanar angles between the opposite rings ($p1/p3$ and $p2/p4$). The former C_2 conformation, called "pinched" cone, is characterized by an obtuse angle (102.9–107° for $p1/p3$) and an acute angle (32.2–39.6° for $p2/p4$). On the other hand, the corresponding angles for **3**

Table 2a. Selected atomic coordinates for TC4As

(a) Mol. A of **1**

Atom	x	y	z	B_{eq}
S(1)	0.0890(1)	0.07169(10)	0.35222(8)	2.63(3)
S(2)	−0.1838(1)	0.2449(1)	0.5306(1)	3.80(4)
S(3)	−0.2677(1)	0.5577(1)	0.31134(10)	3.53(3)
S(4)	0.0152(1)	0.3908(1)	0.13840(8)	2.87(3)
O(1)	−0.1004(3)	0.1872(3)	0.3759(2)	3.30(9)
O(2)	−0.2596(3)	0.3378(3)	0.3680(3)	3.45(10)
O(3)	−0.1555(3)	0.3895(3)	0.2411(3)	3.11(9)
O(4)	−0.0428(3)	0.2085(3)	0.2208(2)	2.80(8)
C(1)	−0.0341(4)	0.1630(4)	0.4500(3)	2.6(1)
C(2)	0.0603(4)	0.1100(4)	0.4484(3)	2.5(1)
C(3)	0.1300(5)	0.0815(4)	0.5224(3)	3.1(1)
C(4)	0.1050(5)	0.1026(5)	0.5973(3)	3.5(1)
C(5)	0.0121(5)	0.1552(4)	0.5993(3)	3.5(1)
C(6)	−0.0588(5)	0.1859(4)	0.5264(3)	3.0(1)
C(7)	−0.2074(4)	0.4096(4)	0.4274(3)	2.7(1)
C(8)	−0.1636(4)	0.3761(4)	0.5076(4)	3.0(1)
C(9)	−0.1087(4)	0.4481(5)	0.5696(3)	3.1(1)
C(10)	−0.0967(4)	0.5500(5)	0.5530(4)	3.2(1)
C(11)	−0.1424(4)	0.5830(4)	0.4734(4)	3.0(1)
C(12)	−0.1987(4)	0.5138(4)	0.4108(3)	2.7(1)
C(13)	−0.1170(4)	0.4852(4)	0.2279(3)	0.5(1)
C(14)	−0.1607(4)	0.5710(4)	0.2591(3)	2.9(1)
C(15)	−0.1274(5)	0.6693(4)	0.2454(4)	3.4(1)
C(16)	−0.0485(5)	0.6833(4)	0.2019(4)	3.5(1)
C(17)	−0.0021(5)	0.5985(5)	0.1727(3)	3.3(1)
C(18)	−0.0373(4)	0.4988(4)	0.1850(3)	2.5(1)
C(19)	0.0617(4)	0.2430(4)	0.2560(3)	2.17(10)
C(20)	0.0997(4)	0.3321(4)	0.2262(3)	2.3(1)
C(21)	0.2061(4)	0.3695(4)	0.2624(3)	2.5(1)
C(22)	0.2751(4)	0.3230(4)	0.3278(3)	2.2(1)
C(23)	0.2350(4)	0.2324(4)	0.3543(3)	2.2(1)
C(24)	0.1319(4)	0.1919(4)	0.3200(3)	2.2(1)
C(25)	0.3905(4)	0.3646(4)	0.3720(3)	2.8(1)
C(26)	0.3919(5)	0.3953(5)	0.4615(3)	3.6(1)
C(27)	0.4249(5)	0.4557(5)	0.3295(4)	4.2(2)
C(28)	0.4729(5)	0.2771(6)	0.3731(4)	4.4(2)
H(O1)	−0.149(4)	0.220(4)	0.378(3)	1.6(10)
H(O2)	−0.270(4)	0.365(4)	0.326(3)	1.4(10)
H(O3)	−0.131(4)	0.348(4)	0.221(3)	1(1)
H(O4)	−0.056(5)	0.164(5)	0.249(4)	3(1)

Table 2b. Continued

(a) Mol. B of **1**

Atom	x	y	z	B_{eq}
S(5)	−0.1987(1)	−0.0431(1)	0.16210(8)	2.97(3)
S(6)	−0.4883(1)	0.2692(1)	0.15100(10)	4.06(4)
S(7)	−0.3647(3)	0.4236(1)	−0.1170(1)	8.00(6)
S(8)	−0.0985(1)	0.0953(2)	−0.1204(1)	7.35(6)
O(5)	−0.1555(4)	0.1152(5)	0.0419(3)	4.4(1)
O(6)	−0.2700(3)	0.1715(3)	0.1716(2)	3.27(9)
O(7)	−0.3378(5)	0.3139(4)	0.0444(3)	4.8(1)
O(8)	−0.1764(5)	0.2937(5)	−0.0534(3)	6.9(2)
C(29)	−0.1573(4)	0.0162(6)	0.0151(3)	3.8(1)
C(30)	−0.1783(4)	−0.0667(5)	0.0611(3)	3.4(1)
C(31)	−0.1774(5)	−0.1671(6)	0.0305(4)	4.5(2)
C(32)	−0.1549(6)	−0.1880(8)	−0.0461(5)	6.4(2)
C(33)	−0.1339(6)	−0.1059(10)	−0.0903(5)	6.9(3)
C(34)	−0.1355(5)	−0.0043(7)	−0.0621(4)	4.9(2)
C(35)	−0.3570(4)	0.1033(4)	0.1465(3)	2.3(1)
C(36)	−0.3371(4)	−0.0023(4)	0.1377(3)	2.09(10)
C(37)	−0.4231(4)	−0.0718(4)	0.1121(3)	2.6(1)
C(38)	−0.5308(4)	−0.0393(4)	0.0946(3)	2.9(1)
C(39)	−0.5496(4)	0.0646(4)	0.1042(3)	2.7(1)
C(40)	−0.4643(4)	0.1364(4)	0.1307(3)	2.5(1)
C(41)	−0.4410(7)	0.3414(4)	0.0091(4)	4.8(2)
C(42)	−0.5214(7)	0.3214(4)	0.0507(4)	4.6(2)
C(43)	−0.6284(7)	0.3532(5)	0.0185(5)	5.7(2)
C(44)	−0.6537(9)	0.4017(6)	−0.0562(7)	7.9(3)
C(45)	−0.577(1)	0.4213(6)	−0.0973(5)	8.0(3)
C(46)	−0.4687(8)	0.3896(4)	−0.0672(4)	6.0(2)
C(47)	−0.2457(6)	0.2502(6)	−0.1241(4)	5.1(2)
C(48)	−0.3406(7)	0.3013(5)	−0.1603(4)	4.9(2)
C(49)	−0.4131(6)	0.2578(5)	−0.2299(4)	4.0(1)
C(50)	−0.3955(5)	0.1650(5)	−0.2662(3)	3.3(1)
C(51)	−0.2987(5)	0.1157(5)	−0.2309(4)	3.9(1)
C(52)	−0.2241(5)	0.1577(7)	−0.1605(4)	4.6(2)
C(53)	−0.4764(5)	0.1159(5)	−0.3443(3)	3.5(1)
C(54)[a]	−0.5075(7)	0.0067(7)	−0.3296(5)	5.5(2)
C(54′)[a]	−0.426(7)	0.008(7)	−0.374(6)	6(1)
C(55)[a]	−0.5817(8)	0.1794(8)	−0.3670(6)	7.4(3)
C(55′)[a]	−0.507(6)	0.186(5)	−0.404(4)	4(1)
C(56)[a]	−0.4233(8)	0.119(1)	−0.4162(5)	8.6(3)
C(56′)[a]	−0.580(6)	0.084(6)	−0.320(5)	5(1)
H(O5)	−0.169(6)	0.122(6)	0.080(4)	4(1)
H(O6)	−0.296(7)	0.227(7)	0.156(5)	8(1)
H(O7)	−0.299(4)	0.315(4)	0.020(3)	0.5(10)
H(O8)	−0.142(8)	0.241(7)	−0.043(6)	7(2)

[a]There is assigned disorder of a tert-butyl group in the 9 : 1 ratio of occupancy.

having C_4 symmetry are 70.7° and 70.6°, indicating almost regular C_4 cone conformation. More importantly, in the C_2 conformation of **1** and **2**, OH oxygen atoms are not arranged on an identical plane but deviate up and down by ~0.2 Å. Such deviations would obstruct the formation of cyclic OH···O bonds within the rim part of TC4A, being rather advantageous for the formation of intermolecular rim-to-rim hydrogen bonds. Especially in **2**, such tendency appears clearly; O···O distances within TC4A are alternately long (3.057, 3.162 Å, no hydrogen bond) and short (2.718, 2.851 Å, possible hydrogen bond), suggesting no formation of cyclic OH···O linkage. On the other hand, the oxygen atoms of **3** are arranged on a plane, suggesting the formation of

circular OH···O hydrogen bonds, being consistent with the finding of disordered OH hydrogen atoms.

Additionally, various types of deviations from the $C2$ and $C4$ symmetries of **1**–**3** due to the unsymmetrical situations of the *p*-substituted groups are observed. For instance, apparent distortions are shown in the inclination angles (α) of the phenol rings from the mean planes defined by the bridging S atoms (Table 4). Also, some distortions of the exocyclic bond angles, such as the O(1)–C(1)–C(2) and O(1)–C(1)–C(6) angles, are observed as a deviation from 120° (Table

Table 2c. Continued

(c) **2**				
Atom	x	y	z	B_{eq}
S(1)	−0.08127(7)	0.07096(6)	0.28564(5)	1.84(1)
S(2)	0.26831(8)	0.34753(6)	0.69331(5)	2.01(1)
S(3)	0.35427(8)	0.76168(6)	0.53801(5)	1.84(1)
S(4)	−0.06332(7)	0.48445(6)	0.15455(5)	1.59(1)
O(1)	0.0362(2)	0.2791(2)	0.4803(2)	2.26(4)
O(2)	0.1911(2)	0.5377(2)	0.6019(2)	1.84(4)
O(3)	0.0871(2)	0.5426(2)	0.3888(2)	2.10(4)
O(4)	−0.1452(2)	0.2813(2)	0.2759(2)	1.98(4)
C(1)	0.1027(3)	0.2041(2)	0.4889(2)	1.72(5)
C(2)	0.2157(3)	0.2257(2)	0.5845(2)	1.75(5)
C(3)	0.2838(3)	0.1484(2)	0.5991(2)	2.10(6)
C(4)	0.2443(3)	0.0507(3)	0.5186(3)	2.23(6)
C(5)	0.1372(3)	0.0306(2)	0.4222(2)	1.90(5)
C(6)	0.0655(3)	0.1067(2)	0.4066(2)	1.65(5)
C(7)	0.3303(3)	0.5517(2)	0.6098(2)	1.59(5)
C(8)	0.4186(3)	0.6511(2)	0.5778(2)	1.50(5)
C(9)	0.5622(3)	0.6688(2)	0.5878(2)	1.93(5)
C(10)	0.6155(3)	0.5882(3)	0.6265(2)	1.99(5)
C(11)	0.5264(3)	0.4893(2)	0.6566(2)	1.94(5)
C(12)	0.3829(3)	0.4693(2)	0.6480(2)	1.59(5)
C(13)	0.1590(3)	0.6262(2)	0.3385(2)	1.46(5)
C(14)	0.2862(3)	0.7275(2)	0.3928(2)	1.52(5)
C(15)	0.3510(3)	0.8110(2)	0.3346(2)	1.53(5)
C(16)	0.2947(3)	0.7959(2)	0.2226(2)	1.55(5)
C(17)	0.1696(3)	0.6920(2)	0.1693(2)	1.60(5)
C(18)	0.1017(3)	0.6096(2)	0.2259(2)	1.47(5)
C(19)	−0.0527(3)	0.2811(2)	0.2182(2)	1.45(5)
C(20)	0.0004(3)	0.3698(2)	0.1607(2)	1.39(5)
C(21)	0.1004(3)	0.3668(2)	0.1076(2)	1.42(5)
C(22)	0.1490(3)	0.2762(2)	0.1071(2)	1.55(5)
C(23)	0.0902(3)	0.1862(2)	0.1621(2)	1.55(5)
C(24)	−0.0073(3)	0.1879(2)	0.2176(2)	1.43(5)
C(25)	0.3648(3)	0.8830(2)	0.1545(2)	1.90(5)
C(26)	0.4857(3)	0.9991(3)	0.2252(3)	2.79(6)
C(27)	0.2486(3)	0.9129(3)	0.0794(3)	2.82(6)
C(28)	0.4290(4)	0.8239(3)	0.0851(3)	3.48(8)
C(29)	0.2555(3)	0.2711(3)	0.0463(2)	1.96(6)
C(30)	0.3249(4)	0.3870(3)	0.0084(3)	3.24(8)
C(31)	0.3803(3)	0.2496(3)	0.1202(2)	2.39(6)
C(32)	0.1721(4)	0.1687(3)	−0.0535(3)	3.27(7)
H(O1)	−0.031(5)	0.257(4)	0.426(4)	4.5(10)
H(O2)	0.147(4)	0.469(3)	0.607(3)	2.9(8)
H(O3)	0.124(4)	0.557(3)	0.455(3)	3.3(8)
H(O4)	−0.150(4)	0.344(3)	0.281(3)	3.5(9)

Table 2d. Continued

(d) **3**				
Atom	x	y	z	B_{eq}
S(1)	0.6451(1)	0.11711(9)	0.42178(8)	3.92(2)
S(2)	0.0924(1)	0.33733(8)	0.55913(7)	2.73(2)
S(3)	0.2390(1)	0.17817(9)	0.93591(7)	3.07(2)
S(4)	0.7923(1)	−0.05127(9)	0.79991(9)	3.74(2)
O(1)	0.6102(3)	0.0053(3)	0.6344(2)	3.81(7)
O(2)	0.3547(3)	0.1450(2)	0.5449(2)	3.72(7)
O(3)	0.2219(3)	0.1677(2)	0.7323(2)	3.40(6)
O(4)	0.4666(3)	0.0340(2)	0.8140(2)	3.37(6)
C(1)	0.7259(4)	0.0431(3)	0.6095(3)	3.20(9)
C(2)	0.7549(5)	0.0995(3)	0.5131(3)	3.40(9)
C(3)	0.8756(5)	0.1352(4)	0.4876(4)	4.4(1)
C(4)	0.9677(6)	0.1184(4)	0.5556(5)	4.9(1)
C(5)	0.9394(5)	0.0653(4)	0.6506(4)	4.4(1)
C(6)	0.8190(5)	0.0266(3)	0.6792(3)	3.49(9)
C(7)	0.3764(5)	0.2403(3)	0.4903(3)	2.88(8)
C(8)	0.5046(5)	0.2432(3)	0.4314(3)	3.14(9)
C(9)	0.5214(5)	0.3428(3)	0.3758(3)	3.23(9)
C(10)	0.4126(4)	0.4424(3)	0.3780(3)	2.98(8)
C(11)	0.2850(4)	0.4378(3)	0.4370(3)	2.62(8)
C(12)	0.2636(4)	0.3395(3)	0.4930(3)	2.54(8)
C(13)	0.1676(4)	0.2709(3)	0.7470(3)	2.47(7)
C(14)	0.1054(4)	0.3594(3)	0.6725(3)	2.44(7)
C(15)	0.0437(4)	0.4634(3)	0.6882(3)	2.95(8)
C(16)	0.0403(4)	0.4838(3)	0.7770(3)	3.03(8)
C(17)	0.1093(5)	0.3955(3)	0.8493(3)	3.15(9)
C(18)	0.1737(4)	0.2895(3)	0.8350(3)	2.63(8)
C(19)	0.5225(4)	0.0779(3)	0.8651(3)	2.56(8)
C(20)	0.4334(4)	0.1498(3)	0.9206(3)	2.69(8)
C(21)	0.4948(4)	0.1905(3)	0.9750(3)	2.88(8)
C(22)	0.6456(4)	0.1619(3)	0.9742(3)	3.05(9)
C(23)	0.7323(4)	0.0915(3)	0.9174(3)	3.14(9)
C(24)	0.6741(4)	0.0491(3)	0.8633(3)	2.98(8)
C(25)	0.4351(5)	0.5514(4)	0.3160(3)	3.73(10)
C(26)	0.550(1)	0.5744(7)	0.3556(6)	9.3(3)
C(27)	0.4937(9)	0.5394(5)	0.2109(4)	7.3(2)
C(28)	0.2952(7)	0.6449(4)	0.3092(6)	8.7(2)
C(29)	−0.0387(5)	0.5990(4)	0.7963(3)	4.0(1)
C(30)	−0.1095(9)	0.6865(6)	0.7070(5)	8.1(2)
C(31)	−0.1728(9)	0.5925(6)	0.8760(6)	8.7(2)
C(32)	0.0676(9)	0.6387(6)	0.8279(8)	9.7(3)
C(33)	0.7159(5)	0.2043(4)	1.0346(3)	3.9(1)
C(34)	0.6083(8)	0.2858(9)	1.0840(9)	13.5(4)
C(35)	0.8262(9)	0.2569(7)	0.9684(5)	8.6(2)
C(36)	0.801(1)	0.1082(6)	1.1078(6)	9.7(3)

3). Clearly, these distortions bring about the unsymmetrical OH···O interactions in the rim part of TC4As **1–3**.

Molecular assembly

Crystal structures of TC4As **1–3** are shown in Figure 2. Three modes of molecular assembly appear. First, all TC4As of **1–3** form self-inclusion dimeric units in such manner that phenol moieties are inserted into the inside of the cavity of each molecule (Figure 3). In **1** and **2**, the phenol rings not bearing a *tert*-butyl substituent are inserted into each other, where face-to-face interaction between the inserted aromatic rings may stabilize the dimeric unit to some extent (Scheme 2a, $p2···p2'$, 3.396–3.467 Å). In contrast, in **3**, a *tert*-butyl group enters into the cavity, apparently accompanied by some CH···π interactions.

Secondly, commonly in **1–3**, lateral face-to-face interaction exists in the crystal structures (Figure 2), which is possible only between the phenol rings not bearing a *tert*-
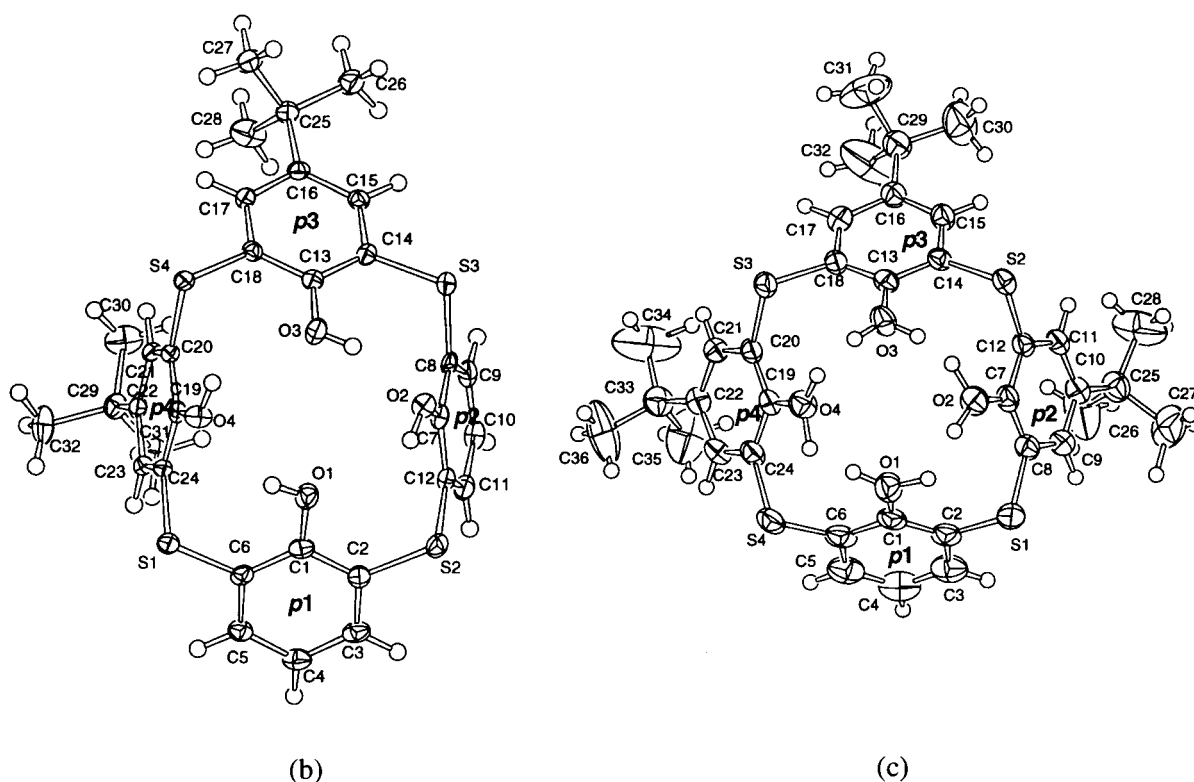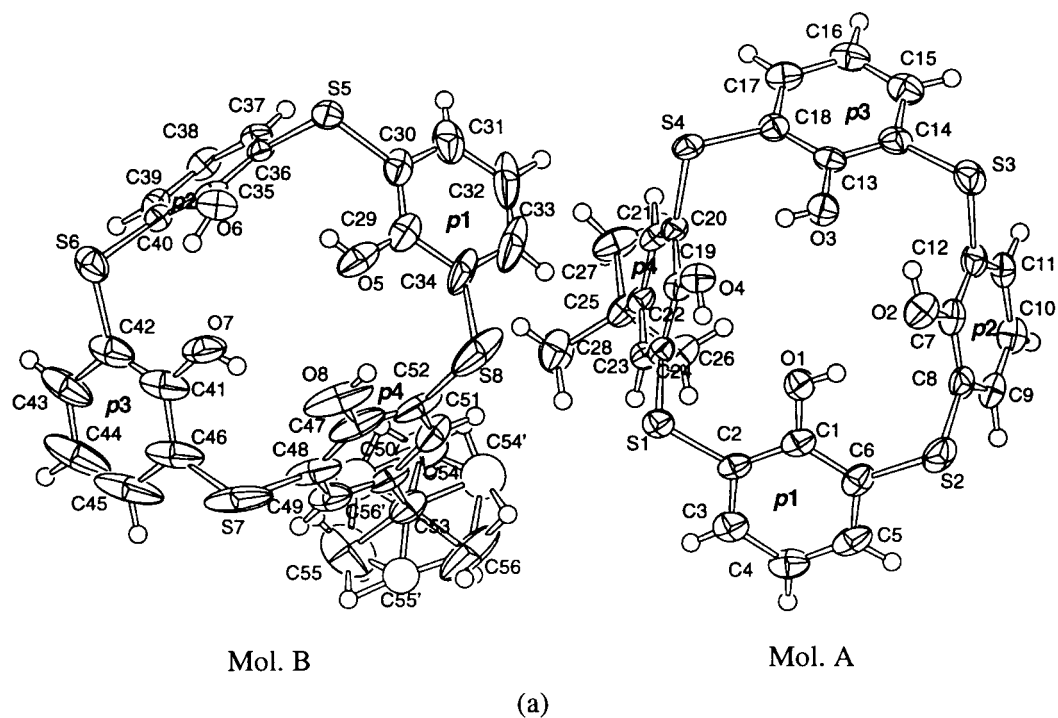
Mol. B   Mol. A

(a)

(b)   (c)

Figure 1. ORTEP drawings of TC4As **1–3** together with the numbering scheme for (a) **1**, (b) **2**, and (c) **3**. *tert*-Butyl carbons of C(54), C(55) and C(56) in Mol. B of **1** are disordered with the ratio 9 : 1 of occupancy. Hydrogen atoms for OH groups in **3** are disordered in two parts. Thermal Ellipsoids are drawn at the 50% probability level.

Table 3a. Selected bond lengths (Å) and bond angles (°) for **1**

Molecule A

S(1)–C(2)	1.764(6)	O(3)–C(13)	1.350(6)
S(1)–C(24)	1.760(5)	O(4)–C(19)	1.355(6)
S(2)–C(6)	1.765(6)	C(1)–C(2)	1.379(8)
S(2)–C(8)	1.759(6)	C(1)–C(6)	1.393(8)
S(3)–C(12)	1.778(5)	C(7)–C(8)	1.391(8)
S(3)–C(14)	1.770(6)	C(7)–C(12)	1.377(8)
S(4)–C(18)	1.769(6)	C(13)–C(14)	1.373(8)
S(4)–C(20)	1.775(5)	C(13)–C(18)	1.369(8)
O(1)–C(1)	1.353(6)	C(19)–C(20)	1.377(7)
O(2)–C(7)	1.353(6)	C(19)–C(24)	1.394(6)
C(2)–S(1)–C(24)	101.4(2)	S(2)–C(8)–C(7)	119.8(4)
C(6)–S(2)–C(8)	103.9(3)	S(3)–C(12)–C(7)	119.3(4)
C(12)–S(3)–C(14)	103.2(2)	O(3)–C(13)–C(14)	117.9(5)
C(18)–S(4)–C(20)	102.4(2)	O(3)–C(13)–C(18)	122.3(5)
O(1)–C(1)–C(2)	117.7(5)	C(14)–C(13)–C(18)	119.7(5)
O(1)–C(1)–C(6)	123.0(5)	S(3)–C(14)–C(13)	121.4(4)
C(2)–C(1)–C(6)	119.3(5)	S(4)–C(18)–C(13)	121.2(4)
S(1)–C(2)–C(1)	120.3(4)	O(4)–C(19)–C(20)	117.9(4)
S(2)–C(6)–C(1)	120.7(4)	O(4)–C(19)–C(24)	123.0(4)
O(2)–C(7)–C(8)	118.4(5)	C(20)–C(19)–C(24)	119.1(4)
O(2)–C(7)–C(12)	121.7(5)	S(4)–C(20)–C(19)	119.3(3)
C(8)–C(7)–C(12)	119.9(5)	S(1)–C(24)–C(19)	119.5(4)

Molecule B

S(5)–C(30)	1.763(6)	O(7)–C(41)	1.346(9)
S(5)–C(36)	1.776(5)	O(8)–C(47)	1.361(8)
S(6)–C(40)	1.762(5)	C(29)–C(30)	1.38(1)
S(6)–C(42)	1.767(7)	C(29)–C(34)	1.384(9)
S(7)–C(46)	1.75(1)	C(35)–C(36)	1.386(7)
S(7)–C(48)	1.756(7)	C(35)–C(40)	1.385(7)
S(8)–C(34)	1.745(9)	C(41)–C(42)	1.37(1)
S(8)–C(52)	1.771(7)	C(41)–C(46)	1.395(9)
O(5)–C(29)	1.323(9)	C(47)–C(48)	1.38(1)
O(6)–C(35)	1.354(6)	C(47)–C(52)	1.37(1)
C(30)–S(5)–C(36)	100.8(2)	S(5)–C(36)–C(35)	118.7(3)
C(40)–S(6)–C(42)	103.5(3)	S(6)–C(40)–C(35)	119.0(4)
C(46)–S(7)–C(48)	101.1(3)	O(7)–C(41)–C(42)	118.5(6)
C(34)–S(8)–C(52)	103.5(3)	O(7)–C(41)–C(46)	122.3(8)
O(5)–C(29)–C(30)	123.0(5)	C(42)–C(41)–C(46)	119.2(8)
O(5)–C(29)–C(34)	117.8(7)	S(6)–C(42)–C(41)	120.9(6)
C(30)–C(29)–C(34)	119.1(7)	S(7)–C(46)–C(41)	119.4(7)
S(5)–C(30)–C(29)	120.1(5)	O(8)–C(47)–C(48)	119.3(7)
S(8)–C(34)–C(29)	121.8(7)	O(8)–C(47)–C(52)	121.9(6)
O(6)–C(35)–C(36)	118.7(4)	C(48)–C(47)–C(52)	118.8(5)
O(6)–C(35)–C(40)	121.7(4)	S(7)–C(48)–C(47)	118.9(5)
C(36)–C(35)–C(40)	119.6(4)	S(8)–C(52)–C(47)	120.0(5)

Table 3b. Selected bond lengths (Å) and bond angles (°) for **2**

S(1)–C(6)	1.778(3)	O(3)–C(13)	1.352(3)
S(1)–C(24)	1.783(3)	O(4)–C(19)	1.359(4)
S(2)–C(2)	1.790(3)	C(1)–C(2)	1.403(4)
S(2)–C(12)	1.784(3)	C(1)–C(6)	1.404(4)
S(3)–C(8)	1.796(3)	C(7)–C(8)	1.398(4)
S(3)–C(14)	1.788(3)	C(7)–C(12)	1.398(5)
S(4)–C(18)	1.779(2)	C(13)–C(14)	1.398(3)
S(4)–C(20)	1.778(3)	C(13)–C(18)	1.397(4)
O(1)–C(1)	1.347(4)	C(19)–C(20)	1.397(4)
O(2)–C(7)	1.367(4)	C(19)–C(24)	1.402(4)
C(6)–S(1)–C(24)	101.8(1)	S(3)–C(8)–C(7)	120.5(2)
C(2)–S(2)–C(12)	102.1(1)	S(2)–C(12)–C(7)	119.0(2)
C(8)–S(3)–C(14)	106.5(1)	O(3)–C(13)–C(14)	123.7(2)
C(18)–S(4)–C(20)	100.0(1)	O(3)–C(13)–C(18)	117.6(2)
O(1)–C(1)–C(2)	118.1(2)	C(14)–C(13)–C(18)	118.7(2)
O(1)–C(1)–C(6)	123.2(2)	S(3)–C(14)–C(13)	120.8(2)
C(2)–C(1)–C(6)	118.7(3)	S(4)–C(18)–C(13)	120.0(2)
S(2)–C(2)–C(1)	121.2(3)	O(4)–C(19)–C(20)	123.1(3)
S(1)–C(6)–C(1)	121.0(2)	O(4)–C(19)–C(24)	118.2(2)
O(2)–C(7)–C(8)	117.7(3)	C(20)–C(19)–C(24)	118.7(3)
O(2)–C(7)–C(12)	121.4(2)	S(4)–C(20)–C(19)	119.3(2)
C(8)–C(7)–C(12)	120.9(3)	S(1)–C(24)–C(19)	118.8(2)

Table 3c. Selected bond lengths (Å) and bond angles (°) for **3**

S(1)–C(2)	1.780(5)	O(3)–C(13)	1.363(5)
S(1)–C(8)	1.793(4)	O(4)–C(19)	1.356(6)
S(2)–C(12)	1.769(4)	C(1)–C(2)	1.405(6)
S(2)–C(14)	1.783(5)	C(1)–C(6)	1.413(7)
S(3)–C(18)	1.789(3)	C(7)–C(8)	1.380(6)
S(3)–C(20)	1.795(4)	C(7)–C(12)	1.408(5)
S(4)–C(6)	1.775(4)	C(13)–C(14)	1.397(5)
S(4)–C(24)	1.789(4)	C(13)–C(18)	1.381(6)
O(1)–C(1)	1.349(6)	C(19)–C(20)	1.386(5)
O(2)–C(7)	1.357(5)	C(19)–C(24)	1.401(6)
C(2)–S(1)–C(8)	101.7(2)	S(1)–C(8)–C(7)	119.4(3)
C(12)–S(2)–C(14)	102.9(2)	S(2)–C(12)–C(7)	119.7(3)
C(18)–S(3)–C(20)	105.3(2)	O(3)–C(13)–C(14)	120.1(4)
C(6)–S(4)–C(24)	103.6(2)	O(3)–C(13)–C(18)	120.8(3)
O(1)–C(1)–C(2)	119.9(4)	C(14)–C(13)–C(18)	119.2(4)
O(1)–C(1)–C(6)	120.9(4)	S(2)–C(14)–C(13)	120.1(3)
C(2)–C(1)–C(6)	119.3(4)	S(3)–C(18)–C(13)	121.1(3)
S(1)–C(2)–C(1)	120.8(4)	O(4)–C(19)–C(20)	121.7(4)
S(4)–C(6)–C(1)	120.5(4)	O(4)–C(19)–C(24)	119.6(3)
O(2)–C(7)–C(8)	122.3(3)	C(20)–C(19)–C(24)	118.7(4)
O(2)–C(7)–C(12)	118.9(3)	S(3)–C(20)–C(19)	120.5(4)
C(8)–C(7)–C(12)	118.8(4)	S(4)–C(24)–C(19)	119.9(4)

butyl substituent (Scheme 2b, $p1\cdots p1'$). The overlapping modes are shown in Figure 4, indicating the presence of effective π-π interactions. The distances between the benzene rings, $p1$–$p1'$, are 3.274–3.345 Å, which are significantly shorter than the $p2$–$p2'$ distance (Table 4). This suggests that the inter-dimer face-to-face interaction is stronger than the intra-dimer interaction. Therefore, it may be said that these molecular assemblies could stabilize the dimeric self-inclusion unit.

Thirdly, OH$\cdots$O bonds between the rims of two calix-arenes as shown in **1** and **2** having C_2 cone conformation (Scheme 2b, Figure 5) lead to the up and down mode of the OH oxygen atoms in the rim part (*vide supra*). In the case of **1**, Mol. A and Mol. B are linked by hydrogen bonding with a short O$\cdots$O distance of 2.790 Å. In the case of **2**, two inversion-centered molecules were linked with an even shorter intermolecular O(2)$\cdots$O(3)$'$ distance of 2.718 Å.
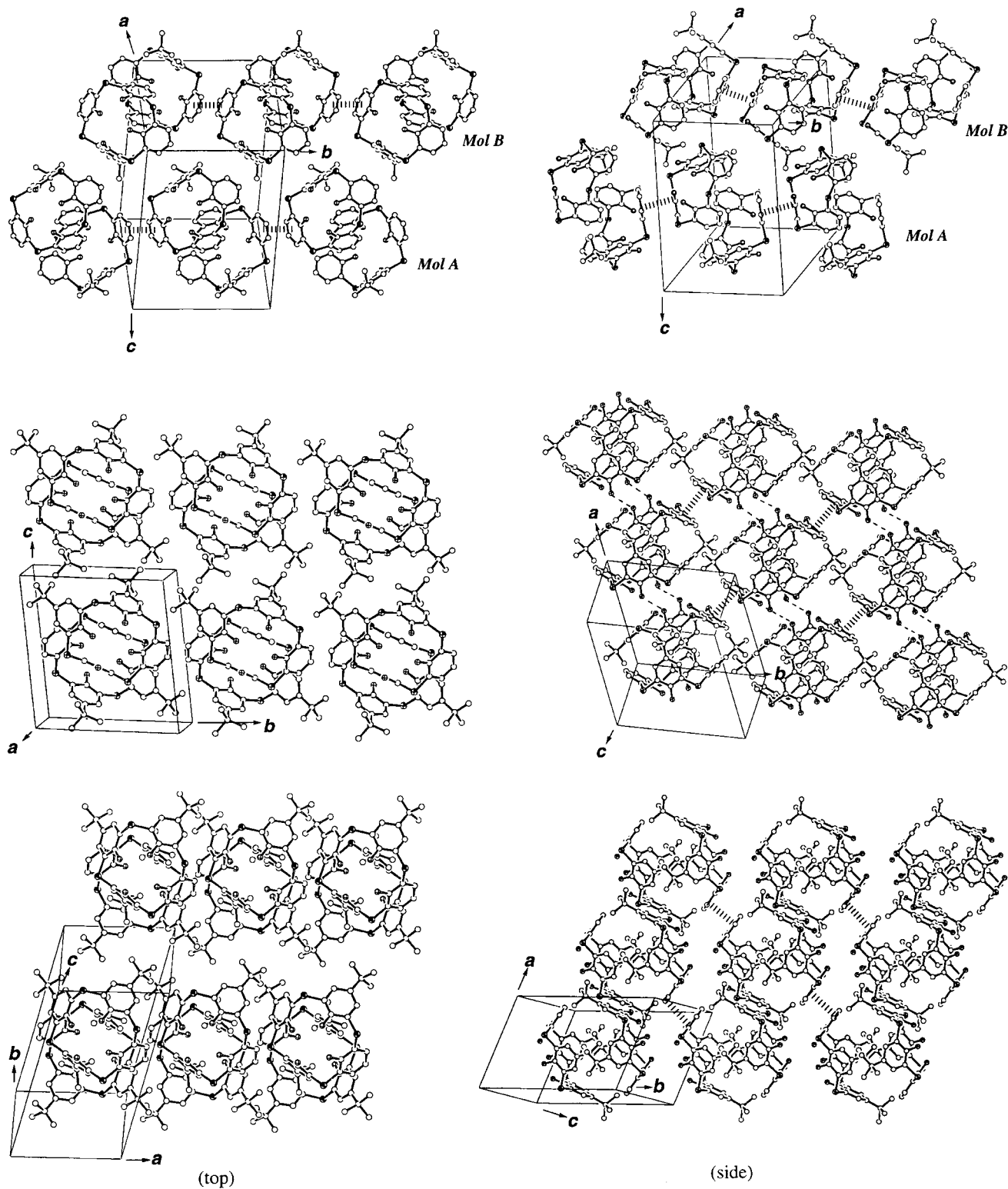
Figure 2. a–c. Crystal structures of TC4As for **1** (top), **2** (middle), **3** (bottom), respectively, showing the arrangement of self-inclusion dimeric units. There are drawn the lateral face-to-face interactions and possible rim-to-rim hydrogen bonds.

Table 4. Relevant structural features of TC4As

	1		**2**	**3**	**4**
	(Mol. A)	(Mol. B)[a]			[Ref. 4]
Molecular Conformations					
Inter-planar angles between opposite phenyl rings (°)					
p1/p3	106.1	102.9	107.8	70.7	82.5
p2/p4	39.6	36.7	32.2	70.6	62.7
Deviations of oxygen atoms from planarity (Å)					
O(1)	−0.195	−0.203	−0.223	−0.003	−0.080
O(2)	0.207	0.108	0.191	0.002	0.082
O(3)	−0.182	−0.224	−0.202	−0.002	−0.086
O(4)	0.162	0.263	0.200	0.002	0.077
Intra-molecular O$\cdots$O distances (Å)					
O(1)$\cdots$O(2)	2.783	2.926	3.057	2.842	2.79
O(2)$\cdots$O(3)	2.814	2.816	2.718	2.813	2.72
O(3)$\cdots$O(4)	2.781	2.877	3.162	2.697	2.78
O(4)$\cdots$O(1)	2.845	2.794	2.851	2.759	2.86
Inclination angles of phenol rings from S atoms plane (°)					
α1	37.1	40.1	38.7	53.0	54.1
α2	68.6	71.8	67.7	56.0	61.3
α3	36.7	35.5	33.5	47.0	43.5
α4	71.8	71.5	80.2	49.9	55.9
Deviations of sulfur atoms from the planarity (Å)					
S(1)	−0.0319	−0.0325	−0.2035	−0.0335	−0.0511
S(2)	0.0459	0.0474	0.2313	0.0211	0.0511
S(3)	−0.0421	−0.1586	−0.2210	−0.0265	−0.0513
S(4)	0.0360	0.1416	0.1829	0.0291	0.0504
Molecular Assembly					
Face-to-face distances of phenol rings (Å)					
p2$\cdots$p2′	3.396	3.467	3.432	No	No
p1$\cdots$p1′	3.298	3.274	3.285	3.345	No
Rim-to-rim inter-molecular O–O distances (Å)					
Shortest O$\cdots$O	2.790[b]		2.718[b]	No	No

[a]The numbering for O(1) $\sim$ O(4) and S(1) $\sim$ S(4) in Mol. A corresponds to O(5) $\sim$ O(8) and S(5) $\sim$ S(8) in Mol. B, respectively.
[b]The shortest intermolecular O–O distances were observed between O(4) and O(6) in **1**, whereas between O(2) and O(3′) (or O(3) and O(2′)) in **2**.
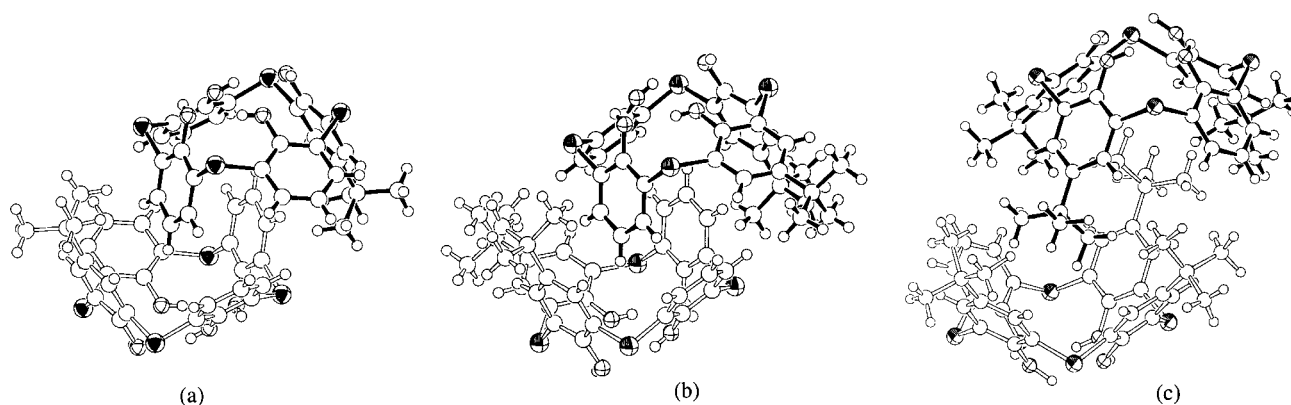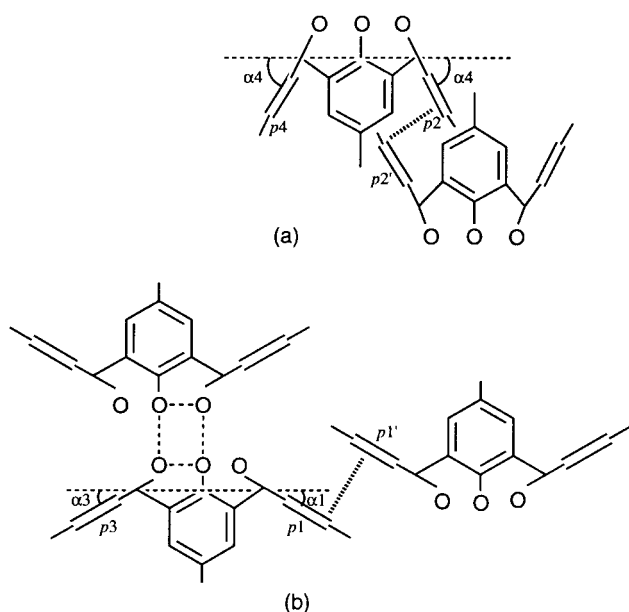

(a)   (b)   (c)

Figure 3. Perspective drawings of dimeric self-inclusion structures; (a), (b) and (c) show for Mol A of **1**, **2** and **3**, respectively.

Scheme 2. Schematic drawings of self-assemblies for **2** (a) within the dimeric unit, and (b) between the dimeric units.
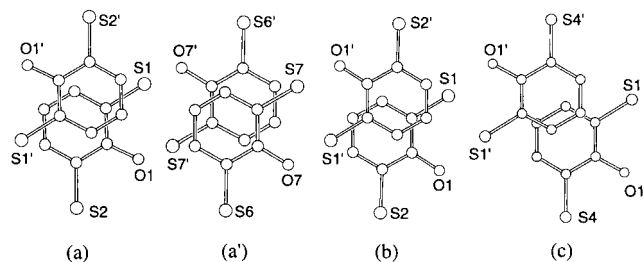

Figure 4. Modes of overlapping between two phenol rings with face-to-face interaction in the adjacent dimeric units; (a) and (a′) show for two independent molecules in **1**, and (b) and (c) show for **2** and **3**, respectively.
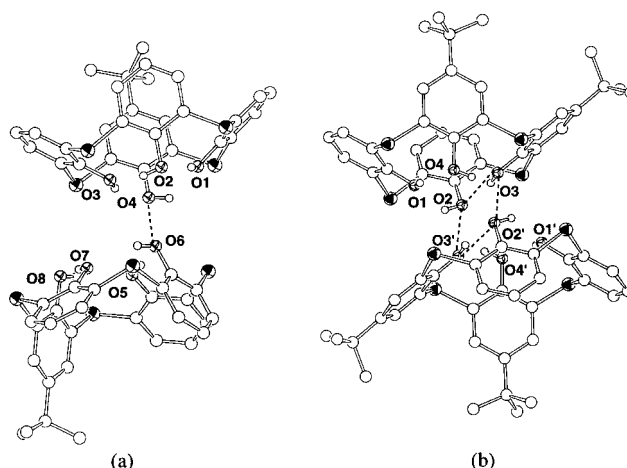

Figure 5. Modes of intermolecular rim-to-rim hydrogen bonding scheme; (a) between Mol. A and Mol. B of **1** and (b) between inversion-centered molecules of **2**. Bond lengths (Å) and angles (°) around hydroxyls are as follows: in Mol. A of **1**; O(1)–H(O1)=0.76(5), O(2)–H(O2)=0.77(5), O(3)–H(O3)=0.73(5), O(4)–H(O4)=0.80(6), C(1)–O(1)–H(O1)=115(3), C(7)–O(2)–H(O2)=106(3), C(13)–O(3)–H(O3) =111(4), C(19)O(4)H(O4)=106(4), in Mol. B of **1**; O(5)-H(O5)=0.69(7), O(6)–H(O6)=0.81(8), O(7)–H(O7)=0.70(4), O(8)–H(O8)=0.81(9), C(29)–O(5)–H(O5)=114(6), C(35)–O(6)–H(O6)=102(6), C(41)–O(7)– H(47)=118(4), C(47)–O(8)–H(48)=93(7), in **2**; O(1)–H(O1)=0.80(4), O(2)–H(O2)=0.82(4), O(3)–H(O3)=0.82(4), O(4)–H(O4)=0.79(4), C(1)–O(1)–H(O1)=111(3), C(7)–O(2)–H(O2)=109(2), C(13)–O(3)–H(O3) =113(2), C(19)–O(4)–H(O4)=109(2).

Thus cyclic hydrogen bonds are formed between the rim-to-rim OH groups, associated with a short O(2)$\cdots$O(3) distance of 2.718 Å within the rim part of TC4A (Figure 5b). In **3** having C_4 cone conformation, the shortest intermolecular O$\cdots$O distance is 3.618 Å, suggesting no OH$\cdots$O bond formation between molecules.

weakened intramolecular OH$\cdots$O bonds of TC4As may not always be strong enough to stabilize C_4 conformation.

Conclusion

We have shown here that partially *p-tert*-butylated TC4As **1-3** prefer a dimeric self-inclusion structure. It is quite interesting to note that only two precedents have been reported for the conventional methylene-bridged C4As to crystallize in such a self-inclusion structure as observed in the present TC4As **1–3**. One example is the *p*-tetra(isopropyl)calix[4]arene crystals formed barely after the complete removal of solvated *p*-xylene on heating up to 150 °C [12]. The other is incidentally formed crystals of *p*-nitrocalix[4]arene derivatives [13, 14]. From these results, it seems that the present TC4As **1–3** are unique in preferring the dimeric self-inclusion structure so as to form single crystals. Although the crystal structures of the corresponding partially *p-tert*-butylated C4As have not been available, the greater flexibility and distortability of TC4As than that of C4As with enlarged macrocyclic ring size may, at least partly, play an important role in the formation of the self-included dimer.

In conclusion, the present X-ray studies revealed that dimeric self-inclusion units of TC4As **1-3** strongly interact with each other by the face-to-face overlapping between the aromatic rings not bearing a *tert*-butyl substituent. Furthermore, TC4As **1** and **2** are prone to adopt C_2 rather than C_4 conformation to lead to the intermolecular OH$\cdots$O bonds, which is unique among calix[4]arenes. In other words, the

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