J Chem Crystallogr (2012) 42:1075–1079
DOI 10.1007/s10870-012-0355-0

COMMUNICATION

Face-to-Face Structures Formed by 3D Hydrogen-Bonded Networks of Tris(4-carboxyphenyl)cyclotriguaiacylene

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Received: 5 April 2012 / Accepted: 4 August 2012 / Published online: 23 August 2012

Abstract A novel tris(4-carboxyphenyl)cyclotriguaiacylene **2** was synthesized by hydrolysis of a novel tris[(4-(methoxycarbonyl)phenyl]cyclotriguaiacylene. The structure was determined by ^{1}H NMR, ^{13}C NMR and mass spectroscopic techniques. The crystal structure of **2** was shown by X-ray crystallography to have a face-to-face structure of a pair of molecules of **2**. The structure was constructed from 3D hydrogen-bonded network structure.

Keywords Cyclotriguaiacylene · Cyclotriveratrylene · Hydrogen-bonded networks · Face-to-face structure

Introduction

The design of an infinite network structure by using coordinate and/or hydrogen-bonding interactions has attracted considerable interest in the area of crystal engineering and host–guest chemistry [1–21]. In particular, the developments of network structures that include molecular cages is expected for multiple inclusion materials [22–27]. Cyclotriveratrylene (CTV) is a well-known macrocyclic host with a rigid pyramidally shaped crown conformation that gives it a shallow bowl-shaped cavity [28–34]. CTV can be incorporated into 1D, 2D, or 3D network structures either as a chelating ligand, or as a hydrogen bond acceptor. For example, Hardie and co-workers [35–44] have widely reported CTV-based ligands that can be coordinated to transition metals to form coordination polymers or discrete metallo-supramolecular assemblies. Zheng and co-workers [45] have recently reported a CTV-based metal–organic nanotube. However, CTV fragments themselves rarely act as hosts for small organic molecules in a manner analogous to the ubiquitous calixarenes. Therefore, the host–guest chemistry of CTV fragments is mainly focused on covalently linked cage-like molecules such as cryptophanes [22–27] and hemicryptophanes [46–55]. Cryptophanes, which are constructed from two CTV fragments covalently preorganized in a face-to-face fashion, exhibit good binding properties for small guest molecules. Although a number of crystalline hydrogen-bonded assemblies featuring CTV fragments arranged in a back-to-back fashion have been reported [56–59], documentation of hydrogen-bonded assemblies of CTV-related host molecules arranged in a face-to-face fashion is limited [60]. We report herein face-to-face structures formed by 3D hydrogen-bonding networks with the related ligand tris(4-carboxyphenyl)cyclotriguaiacylene **2** (Fig. 1).

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Experimental Section

Synthesis of tris[(4-(methoxycarbonyl)phenyl] cyclotriguaiacylene **1**

Cyclotriguaiacylene (409 mg, 1.00 mmol), Cs_2CO_3 (1.45 g, 4.45 mmol), and methyl 4-fluorobenzoate (915 mg, 5.94 mmol) were dissolved in DMF (2.0 mL) under nitrogen atmosphere. The resulting heterogeneous mixture was stirred at 120 °C for 24 h. The residue was taken up with a solution of 3 M HCl and chloroform. The separated organic layer was

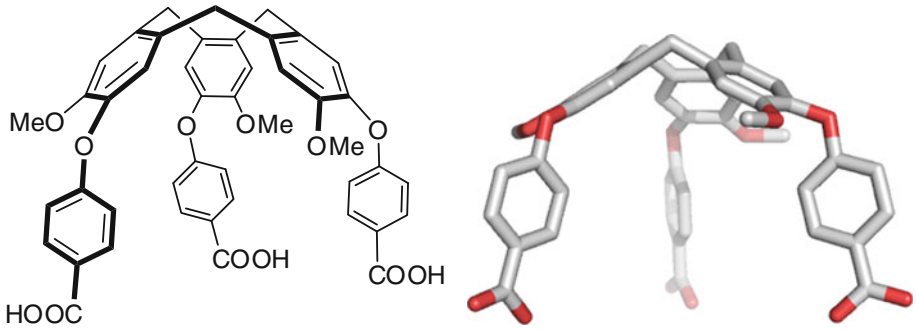

Fig. 1 Chemical structure and X-ray crystal structure of a tris(4-carboxyphenyl)cyclotriguaiacylene molecule **2**. Hydrogen atoms have been omitted for clarity

washed with brine, dried over anhydrous $NaSO_4$, filtered, and evaporated to dryness. The residue was purified by silica gel column chromatography by using chloroform–ethyl acetate-hexane (5:1:4) as the eluent to give 243 mg (30 %) of racemic tris[(4-(methoxycarbonyl)phenyl]cyclotriguaiacylene as a white solid. Mp 135.1–136.4 °C; ^{1}H NMR ($CDCl_3$, 400 MHz, rt): δ 3.62 (d, 3H, $J = 13.6$ Hz), 3.68 (s, 9H), 3.88 (s, 9H), 4.79 (d, 3H, $J = 14.0$ Hz), 6.84 (s, 3H), 6.91 (d, 6H, $J = 8.8$ Hz), 7.05 (s, 3H), 7.95 (d, 6H, $J = 8.4$ Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, rt): δ 36.6, 52.1, 56.2, 114.6, 116.2, 123.3, 124.2, 131.7, 132.1, 137.1, 142.4, 150.4, 162.2, 166.8 ppm. HRMS (ESI-TOF) Calcd. for $C_{48}H_{42}Na_1O_{12}$: 833.2574 ($[M+Na]^+$); Found: 833.2573 $[M+Na]^+$.

Synthesis of tris(4-carboxyphenyl)cyclotriguaiacylene **2**

A mixture of tris[(4-(methoxycarbonyl)phenyl]cyclotriguaiacylene (120 mg, 0.15 mmol) and NaOH (25.1 mg, 0.63 mmol) in methanol (1.0 mL) was refluxed for 7 h and then allowed to cool to ambient temperature. 3 M HCl was added to the reaction mixture and the organic layer was extracted by ethyl acetate three times. The separated organic layer was washed with brine, dried over anhydrous $NaSO_4$, filtered, and evaporated to dryness. The residue was precipitated in hexane and filtered off to give 98.4 mg (86 %) of racemic **2** as a white solid. Mp 267.7–268.9 °C ^{1}H NMR (CD_3OD, 400 MHz, rt): δ 3.63 (s, 9H), 3.65–3.67 (brs, 3H), 4.78–4.82 (brs, 3H), 6.83 (d, 6H, $J = 8.4$ Hz), 7.07 (s, 3H), 7.23 (s, 3H), 7.90 (d, 6H, $J = 8.0$ Hz); ^{13}C NMR (CD_3OD, 100 MHz, rt): δ 36.7, 56.4, 115.8, 116.7, 124.8, 125.2, 132.7, 133.9, 139.1, 143.1, 151.6, 163.9, 169.5 ppm. HRMS (ESI-TOF) Calcd. for $C_{45}H_{36}Na_1O_{12}$: 791.2104 ($[M+Na]^+$); Found: 791.2106 $[M+Na]^+$.

Crystallization

Slow evaporation of a chloroform and methanol solution of **2** resulted in single crystals suitable for X-ray crystal structure analysis.

Measurements

X-ray diffraction data on single crystals were collected on a Rigaku R-AXIS RAPID diffractometer with graphite monochromated Mo Kα radiation ($\lambda = 0.71075$ Å) at 123 K. The structure was solved by a direct method with SHELXS-97. The disordered solvent molecules were removed by the SQUEEZE routine (PLATON) and the outputs from the SQUEEZE calculations were attached to a CIF file [61]. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were attached in a riding model. They were included at their calculated positions.

Results and Discussion

Tris[(4-(methoxycarbonyl)phenyl]cyclotriguaiacylene **1** was prepared by a nucleophilic aromatic substitution (SNAr) reaction onto cyclotriguaiacylene in 30 % yield as a racemic compound. The hydrolysis reaction of **1**

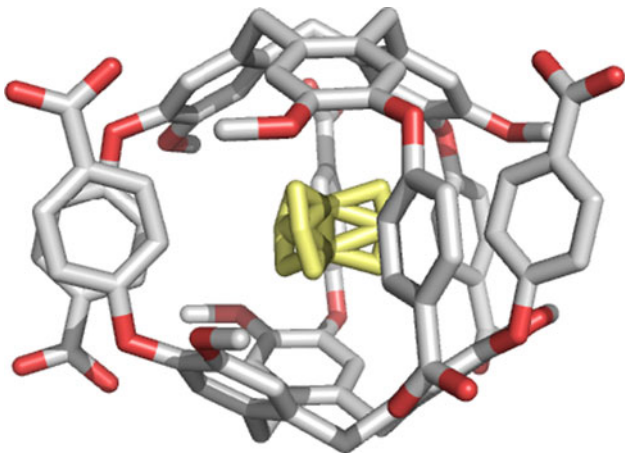

Fig. 2 Stick representation of the face-to-face structure of a pair of molecules of (*M*,*M*)-**2** and a disordered solvent molecule. Hydrogen atoms have been omitted for clarity

Table 1 Crystal data of tris(4-carboxyphenyl)cyclotriguaiacylene **2**

Empirical formula	C_{45} $H_{36}O_{12}$
Formula weight	768.77
Crystal system	Trigonal
Space group	R-3c
Z	12
a (Å)	14.7891(3)
b (Å)	14.7891(3)
c (Å)	57.3970(11)
α (deg)	90.0000
β (deg)	90.0000
γ (deg)	120.0000
V(Å^3)	10871.9(4)
μ(Mo Kα) (mm^{-1})	0.71075
*R*1	0.0722
wR_2	0.2087
Goodness of fit (GOF) for F^2	1.075

furnished tris[(4-(methoxycarbonyl)phenyl]cyclotriguaiacylene **2** in 86 % yield. The resulting racemic **2** was characterized by ^{1}H and ^{13}C NMR spectroscopy and electrospray ionization (ESI) mass spectroscopy. The analysis data were in full agreement with the structures presented. Colorless crystals of **2**·solvent were obtained from slow evaporation of a chloroform/methanol solution of **2**. The crystal structure of **2**·solvent was determined by single-crystal X-ray diffraction techniques. The fundamental face-to-face structure of a pair of molecules of **2** and a disordered solvent molecule are shown in Fig. 2. The composition of **2**·solvent was estimated **2**·(0.5$CHCl_3$) by ^{1}H NMR spectrum. The diameter of the cavity of the face-to-face structure was about 10.2 Å. The disordered solvent molecule was observed in the cavity of the face-to-face structure and removed by the SQUEEZE routine (PLATON). The crystal data of **2** are shown in Table 1. The crystalline structure of **2** belongs to the trigonal system and space group R-3c. The two CTV fragments were interdigitated with each other. All of these structures were stabilized through CH–*π* interactions [d(C···C=C) = 3.8 Å] between a phenyl ring of the carboxy phenyl group and a methoxy carbon. The CH–O interaction [d(C···O) = 3.8 Å] was observed in a carboxy group and the phenyl group of CTV. Crystal lattice structure of **2** was shown in Fig. 3. The racemic face-to-face structures of (*P*,*P*)- or (*M*,*M*)-structures were alternately-stacked along the *c* axle. The face-to-face structures were stabilized through *π*–*π* interactions [d(C=C···C=C) = 3.4 Å] between phenyl rings of CTV fragments and hydrogen-bonded networks of carboxy groups.

To clarify the 3D hydrogen-bonded networks of carboxy groups, the crystal structures which have been omitted a pair of face-to-face structures of **2** was shown in Fig. 4. The intermolecular hydrogen bonds were stabilized by six carboxyl groups (the O···O distances are 2.69 and 2.99 Å, respectively). The 3D hydrogen-bonded networks were probably concerned in densely-stacked face-to-face structures of **2**.

Conclusions

We have directly synthesized novel densely-stacked face-to-face structures formed by 3D hydrogen-bonded

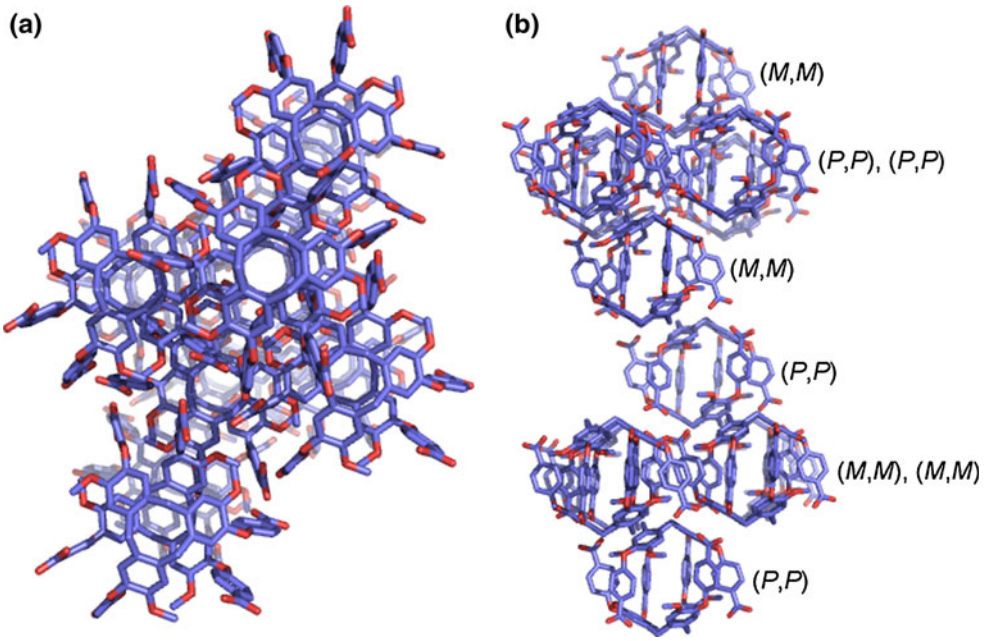

Fig. 3 Crystal lattice of **2**. **a** Packing in layers in the *ab* plane. **b** Packing in layers in the *ac* plane

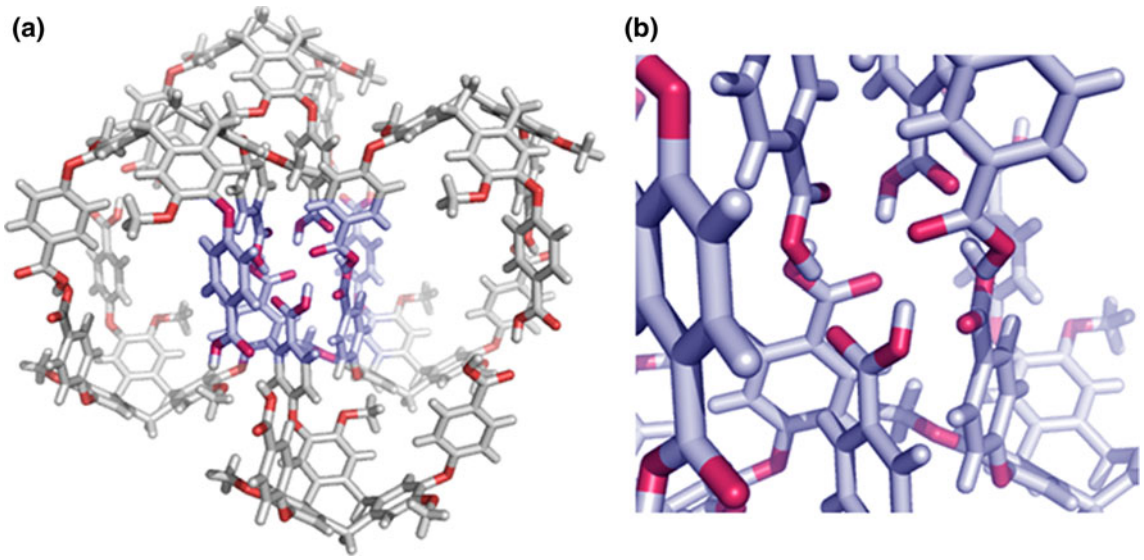

Fig. 4 Stick representation of crystal structure of **2**. **a** A pair molecules of face-to-face structures. **b** Details of the hydrogen-bonding interactions between six carboxylic acids

networks involving **2**. The results reported herein provide an unusual example of a face-to-face arrangement of CTV fragments. The inner cavity of face-to-face structures can trap small molecules. Further research on chiral crystalline molecular flasks chemistry is currently under way by using the stacked face-to-face structure as a platform.

Acknowledgments We thank Mr. S. Katao for his support in carrying out the X-ray crystal structure analysis at the Nara Institute of Science and Technology under the Kyoto Advanced Nanotechnology Network program. This work was supported by a Grant-in-Aid for Young Scientists (B) (23792302).

References

1. Eddaoudi M, Moler DB, Li H, Chen B, Reineke TM, O'Keeffe M, Yaghi OM (2001) Acc Chem Res 34:319–330
2. Evans OR, Lin W (2002) Acc Chem Res 35:511–522
3. Rao C, Natarajan S, Vaidhyanathan R (2004) Angew Chem Int Ed 43:1466–1496
4. Férey G (2007) Chem Soc Rev 37:191–214
5. Desiraju GR (1995) Angew Chem Int Ed 34:2311–2327
6. Endo K, Sawaki T, Koyanagi M, Kobayashi K, Masuda H, Aoyama Y (1995) J Am Chem Soc 117:8341–8352
7. Bhyrappa P, Wilson SR, Suslick KS (1997) J Am Chem Soc 119:8492–8502
8. Diskin-Posner Y, Goldberg I (1999) Chem Commun 1961:1962
9. Kobayashi K, Shirasaka T, Sato A, Horn E, Furukawa N (1999) Angew Chem Int Ed 38:3483–3486
10. Kobayashi K, Shirasaka T, Horn E, Furukawa N (2000) Tetrahedron Lett 41:89–93
11. Bong DT, Clark TD, Granja JR, Ghadiri MR (2001) Angew Chem Int Ed 40:988–1011
12. Prins LJ, Reinhoudt DN, Timmerman P (2001) Angew Chem Int Ed 40:2382–2426
13. Steiner T (2002) Angew Chem Int Ed 41:48–76
14. Kobayashi K, Sato A, Sakamoto S, Yamaguchi K (2003) J Am Chem Soc 125:3035–3045
15. Saied O, Maris T, Wuest JD (2003) J Am Chem Soc 125:14956–14957
16. Kobayashi K, Kobayashi N, Ikuta M, Therrien B, Sakamoto S, Yamaguchi K (2005) J Org Chem 70:749–752
17. Malek N, Maris T, Perron MÈ, Wuest JD (2005) Angew Chem Int Ed 44:4021–4025
18. Malek N, Maris T, Simard M, Wuest JD (2005) J Am Chem Soc 127:5910–5916
19. Saied O, Maris T, Wang X, Simard M, Wuest JD (2005) J Am Chem Soc 127:10008–10009
20. Wuest JD (2005) Chem Commun 5830:5837
21. Tominaga M, Masu H, Azumaya I (2011) Cryst Growth Des 11:542–546
22. Smaldone RA, Forgan RS, Furukawa H, Gassensmith JJ, Slawin AMZ, Yaghi OM, Stoddart JF (2010) Angew Chem Int Ed 49:8630–8634
23. Gassensmith JJ, Furukawa H, Smaldone RA, Forgan RS, Botros YY, Yaghi OM, Stoddart JF (2011) J Am Chem Soc 133:15312–15315
24. Ikemoto K, Inokuma Y, Fujita M (2011) J Am Chem Soc 133:16806–16808
25. Inokuma Y, Kawano M, Fujita M (2011) Nat Chem 3:349–358
26. Inokuma Y, Kojima N, Arai T, Fujita M (2011) J Am Chem Soc 133:19691–19693
27. Forgan RS, Smaldone RA, Gassensmith JJ, Furukawa H, Cordes DB, Li Q, Wilmer CE, Botros YY, Snurr RQ, Slawin AMZ (2012) J Am Chem Soc 134:406–417
28. Collet A (1987) Tetrahedron 43:5725–5759
29. Brotin T, Dutasta JP (2009) Chem Rev 109:88–130
30. Hardie MJ (2010) Chem Soc Rev 39:516–527
31. Holman KT, Orr GW, Atwood JL, Steed JW (1998) Chem Commun 2109:2110
32. Arduini A, Calzavacca F, Demuru D, Pochini A, Secchi A (2004) J Org Chem 69:1386–1388
33. Galán H, Fragoso A, de Mendoza J, Prados P (2008) J Org Chem 73:7124–7131
34. Holman KT, Drake SD, Steed JW, Orr GW, Atwood JL (2010) Supramol Chem 22:870–890

35. Sumby CJ, Fisher J, Prior TJ, Hardie MJ (2006) Chem Eur J 12:2945–2959
36. Ronson TK, Fisher J, Harding LP, Hardie MJ (2007) Angew Chem Int Ed 119:9244–9246
37. Carruthers C, Ronson TK, Sumby CJ, Westcott A, Harding LP, Prior TJ, Rizkallah P, Hardie MJ (2008) Chem Eur J 14:10286–10296
38. Ronson TK, Hardie MJ (2008) CrystEngComm 10:1731–1734
39. Westcott A, Fisher J, Harding LP, Rizkallah P, Hardie MJ (2008) J Am Chem Soc 130:2950–2951
40. Ronson TK, Fisher J, Harding LP, Rizkallah PJ, Warren JE, Hardie MJ (2009) Nat Chem 1:212–216
41. Carruthers C, Fisher J, Harding LP, Hardie MJ (2010) Dalton Trans 39:355–357
42. Little MA, Halcrow MA, Harding LP, Hardie MJ (2010) Inorg Chem 49:9486–9496
43. Ronson TK, Carruthers C, Fisher J, Brotin T, Harding LP, Rizkallah PJ, Hardie MJ (2010) Inorg Chem 49:675–685
44. Ronson TK, Nowell H, Westcott A, Hardie MJ (2010) Chem Commun 47:176–178
45. Yu JT, Sun J, Huang ZT, Zheng QY (2011) CrystEngComm 14:112–115
46. Gosse I, Dutasta J-P, Perrin M, Thozet A (1999) New J Chem 23:545–548
47. Perraud O, Raytchev PD, Martinez A, Dutasta JP (2010) Chirality 22:885–888
48. Raytchev PD, Perraud O, Aronica C, Martinez A, Dutasta JP (2010) J Org Chem 75:2099–2102
49. Perraud O, Martinez A, Dutasta JP (2011) Chem Commun 47:5861–5863
50. Perraud O, Robert V, Martinez A, Dutasta JP (2011) Chem Eur J 17:4177–4182
51. Perraud O, Robert V, Martinez A, Dutasta JP (2011) Chem Eur J 17:13405–13408
52. Perraud O, Lefevre S, Robert V, Martinez A, Dutasta JP (2012) Org Biomol Chem 10:1056–1059
53. Perraud O, Robert V, Gornitzka H, Martinez A, Dutasta JP (2012) Angew Chem Int Ed 51:504–508
54. Makita Y, Sugimoto K, Furuyoshi K, Ikeda K, Fujiwara S, Shinike T, Ogawa A (2010) Inorg Chem 49:7220–7222
55. Makita Y, Sugimoto K, Furuyoshi K, Ikeda K, Fujita T, Fujiwara S, Ogawa A (2011) Supramol Chem 23:269–272
56. Hardie MJ, Raston C, Salinas A (2001) Chem Commun 1850:1851
57. Ahmad R, Hardie MJ (2002) CrystEngComm 4:227–231
58. Ahmad R, Dix I, Hardie MJ (2003) Inorg Chem 42:2182–2184
59. Sumby CJ, Hardie MJ (2005) Cryst Growth Des 5:1321–1324
60. Abrahams BF, FitzGerald NJ, Hudson TA, Robson R, Waters T (2009) Angew Chem Int Ed 48:3129–3132
61. Spek AL (2009) Acta Cryst D65:148–155