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Di-, tri-, and tetra-arylterephthalic acids as novel clathrate host compounds

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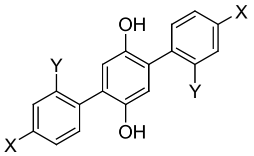
ABSTRACT

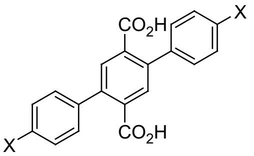
Novel terephthalic acid host compounds having aromatic substituent **1**–**4** have been prepared and their inclusion properties were investigated. These host compounds enclathrated several kinds of alcohols, ethers, ketones, amides, and sulfoxides. The X-ray structures of 1:1 **2a**/EtOH, 1:2 **2b**/DMF, 1:2 **3**/MeOH, and 1:1 **4**/EtOH complexes revealed complexation mode.

1. Introduction

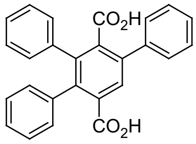
There has been increasing interest in host–guest inclusion compounds because of their potential applications such as separation of isomeric compounds,[1] optical resolution of racemates,[2] reaction medium of included molecules,[3] and sensor materials.[4] Previously, we have reported that 2,5-diaryl-hydroquinones (**1**) form crystalline inclusion complex with alcohols,[5] pyridone,[6] and 1,3-diphenyl-2-propen-1-one.[7] In each case of the inclusion complex, the guest molecules are linked to the host molecules by hydrogen bonds.[8] On the basis of the previous study, we have designed new carboxylic acid host molecules **2**–**4** by replacing the OH group of **1** by COOH group. Herein, we report the inclusion properties and X-ray structure of the inclusion crystals of the new host compounds (**2**–**4**).



1 a: X = Y = H
b: X = Y = Me
c: X = Cl; Y = H



2 a: X = H
b: X = F
c: X = Cl



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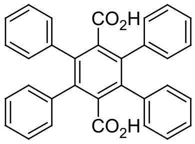

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2. Results and discussion

2.1. Preparation of hosts and their inclusion properties

The host compounds (**2**–**4**) were prepared by the previously reported method.[8] A variety of organic solvents including alcohols, cyclic ethers, cyclic and acyclic ketones, lactones, amides, and sulfoxides were used for the inclusion experiments (Table 1). The inclusion crystals were obtained by recrystallization of the host compounds from the respective guest solvents. The host–guest ratios were evaluated by ^{1}H NMR spectral integration. As shown in Table 1, diphenylterephthalic acids (**2a**–**2c**) showed poor inclusion ability for alcohols but included cyclic ethers, cyclic and acyclic ketones, lactones, amides, and sulfoxides in 1:1 or 1:2 ratio. However, triphenylterephthalic acid (**3**) showed poor inclusion ability and only complexed with MeOH (1:2), 3-methyl-2-cyclohexenone (1:2), dimethyl sulfoxide (1:2), and dimethyl acetamide (1:1). This is attributable to the low symmetry of the molecular structure of **3**. Tetraphenylterephthalic acid (**4**), in contrast, showed excellent inclusion ability and included all the guest solvents tested in Table 1. As for the inclusion of MeOH, host (**3** and **4**) showed somewhat higher guest release temperature than that of host (**2a** and **2c**). The data for thermogravimetric analysis (TGA) of these complexes are shown in Figure 1. The similar inclusion behavior was observed for the inclusion of EtOH. The 1:1 complex of **4** with EtOH showed higher guest release temperature than that of the 1:1 EtOH complex of **2a** in TGA spectra (Fig. 2).

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Table 1

Host–guest ratios[b] and guest release temperatures of the inclusion crystals of **2a**–**c**, **3**, and **4**

Guest	2a	2b	2c	3	4
MeOH	1:1 (74)	—[a]	2:3 (72)	1:2 (117)	1:1 (135)[c]
EtOH	1:1 (100)	—	—	—	1:1 (150)
n-PrOH	—	—	—	—	1:1 (147)
n-BuOH	—	—	—	—	1:1(141)
Ethylene glycol	—	—	—	—	1:2 (84, 120)
Cyclohexanol	2:1 (162)	1:1 (110)	1:2 (103)	—	1:4 (114)
Acetone	—	—	—	—	1:2 (55)
Cyclopentanone	—	1:2 (72)	—	—	1:2 (133)
2-Cyclopentenone	1:1 (120)	—	1:2 (98)	—	1:2 (132)
2-Cyclohexenone	1:1 (129)	1:1 (98)	—	—	1:2 (120)
3-Methyl-2-cyclohexenone	3:2 (109)	2:3 (81, 119)	1:2 (85, 119)	1:2 (90, 127)	1:2 (137)
γ-Butyrolactone	1:1 (121)	—	—	—	1:2 (99)
Tetrahydrofuran	1:1 (93)	1:1 (72)	—	—	1:2 (96)
Tetrahydropyran	1:1 (60)	1:1 (88)	1:1 (64)	—	1:1 (104)
Dimethyl sulfoxide	1:1 (213)	1:2 (172)	1:2 (162)	1:2 (113, 173)	1:3 (143, 195)
Dimethyl formamide	1:2 (120)	1:2 (119)	1:2 (123)	—	1:2 (99)
Dimethyl acetamide	1:2 (146)	1:2 (152)	1:2 (150)	1:1 (139)	1:2 (99)

[a] No inclusion complexation.

[b] Host–guest ratios were determined by TG and ^{1}H NMR.

[c] Guest release temperature (°C).

Another remarkable point is the host/guest stoichiometric ratios of 1:3 (dimethyl sulfoxide) and 1:4 (cyclohexanol), which are exceptionally high with reference to the guest component. Host **4** may include additional guests to fill the voids between the hydrogen-bonded entities.

2.2. X-ray structural analyses

2.2.1. 1:1 Complex of 2a with EtOH

The 1:1 complex between **2a** and ethanol consists of two centrosymmetric carboxylic acid hosts (two halves of each in asymmetric unit) and one EtOH molecule. Figure 3 presents *ac* view of the hydrogen-bonded chains involving EtOH and one of the two dicarboxylic acid molecules. The second host molecule forms arrays roughly perpendicular to the former chains of the hosts assembled via intermolecular dimeric motif characteristic for carboxyl group.

2.2.2. 1:2 Complex of 2b with DMF

The 1:2 complex between **2b** and DMF molecule consists of a half of centrosymmetric dicarboxylic host and one solvent molecule with one methyl group disordered over two equally populated positions rotated by ca. 30°. Figure 4 shows hydrogen bond geometry of the host/guest complex. In this case apart of the relatively strong C–H···O hydrogen bond no other particular intermolecular interactions strengthening crystal construction are observed. Crystal lattice is formed by alternative layers of the host and guest molecules.

2.2.3. 1:2 Complex of 3 with MeOH

The 1:2 complex between **3** and MeOH molecule consists of a dicarboxylic host and two solvent molecules. Figure 5 shows hydrogen bond geometry of the host/guest complex. One of the guest MeOH molecules and the dicarboxylic host make a cyclic structure. This cyclic structure is bonded by the intermediary of the other guest MeOH molecule along the *c* axis.

2.2.4. 1:1 Complex of 4 with EtOH

The 1:1 complex between **4** and ethanol consists of two centrosymmetric carboxylic acid hosts (two halves of each in asymmetric unit) and one EtOH molecule with ethyl group disordered over two equally populated positions. Figure 6 shows cyclic H-bond system consisting two host molecules and one ethanol molecule.

3. Conclusions

The new arylterephthalic acid compounds carrying two carboxyl functions constitute a new class of versatile host molecules with the ability for inclusion complex formation with guest molecules of various character (protic, aprotic, polar, and apolar) and size (from MeOH to 3-methyl-2-cyclohexenone). Especially, tetraphenylterephthalic acid (**4**) showed excellent inclusion ability with higher guest release temperature. Steric hindrance introduced by an aryl moiety located in the vicinity of carboxy groups breaks down the usual cyclic dimeric recognition pattern characteristic for carboxylic acids. Solid state structures of the four complexes show that guest molecule contributes to the cyclic H-bonded system (1:1 **2a** with EtOH; Fig. 3, 1:2 **3** with MeOH; Fig. 5, and 1:1 **4** with MeOH; Fig. 6) or forms its own H-bond with carboxyl host (in the case of 1:2 inclusion complex of **2b** and DMF; Fig. 4).

4. Experimental

4.1. General

^{1}H NMR spectra were recorded in $CDCl_3$ on a JEOL JNM-EX270 FT-NMR spectrometer. IR spectra were recorded with a JASCO FT-IR

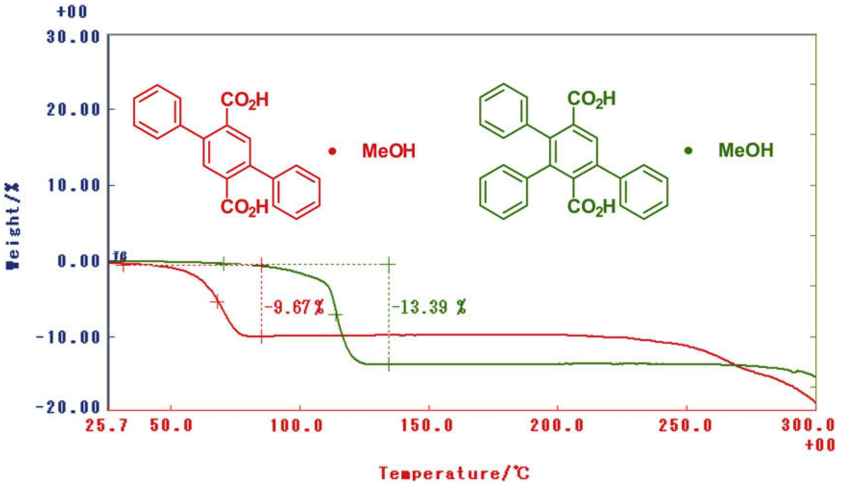

Figure 1. TGA traces for MeOH complex of **2a** and **3**.

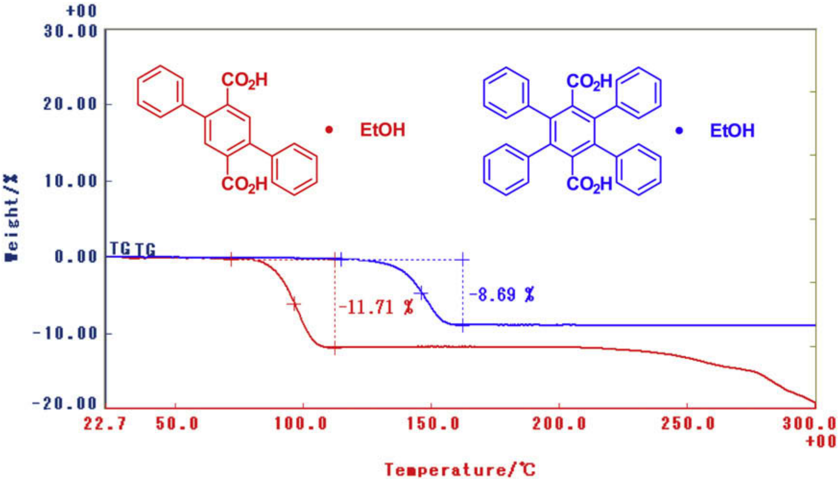

Figure 2. TGA traces for EtOH complex of **2a** and **4**.

4100 spectrometer. Thermogravimetric analyses (TG) were performed on a Rigaku TG-8120 instrument. X-ray diffraction data were collected on a Nonius BV MACH3 diffractometer for (1:1) **2a**/EtOH complex using Cu Kα radiation, on the Bruker–Nonius Kappa CCD diffractometer using Mo Kα radiation for (1:2) **2b**/DMF complex, and on a Rigaku RAXIS RAPID imaging plate area detector using Mo Kα radiation for (1:2) **3**/MeOH and (1:1) **4**/EtOH complex.

4.2. Synthesis of host compounds

The host compounds **2**–**4** were synthesized according to the methods reported in the literatures.[8] Crystals of the inclusion complex were obtained by recrystallization of the host compounds from neat guest solvents listed in Table 1. The host–guest ratios were determined by TG and ^{1}H NMR spectra.

4.3. X-ray structure determinations

Suitable crystals were mounted on a glass fiber. Data collection was performed at 295 on a Nonius BV MACH3 diffractometer with graphite monochromated Cu Kα (λ=1.54178 Å). Structures were solved with direct methods using the SHELXS97[9] and refined with SHELXL97[10] software. Refinement was performed anisotropically for all non-hydrogen atoms using the full-matrix least-squares method. In general, hydrogen atoms were assigned to idealized positions and were allowed to ride with thermal parameters fixed at 1.2U_{eq} of the parent atom. Carboxyl group H-atoms were localized from $\Delta\rho$ maps and refined. The residual electron densities were of no chemical significance. Suitable crystals were mounted on glass capillaries with a small amount of mother liquor. Data collection was performed on a Rigaku RAXIS RAPID imaging plate diffractometer with graphite monochromated Mo Kα (λ=0.71075 Å) at 173(1) K for (1:2) **3**/MeOH and (1:1) **4**/EtOH with Rigaku low temperature equipment. The crystal structures were solved by direct methods (SIR97[11] for (1:2) **3**/MeOH and (1:1) **4**/EtOH) and refined by full-matrix least-squares methods (SHELXL97[10]). All non-hydrogen atoms were refined anisotropically,

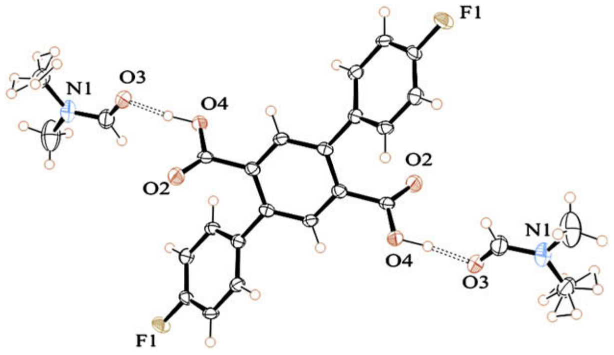

Figure 4. X-ray structure of the 1:2 complex of **2b** and DMF; two DMF molecules are bound with the host by H-bond: O4··· O3[x, $-y$+3/2, z−1/2]=2.540 Å, O4–H4=1.01(5) Å, H4···O3=1.538(5) Å, angle=168.7(5)°.

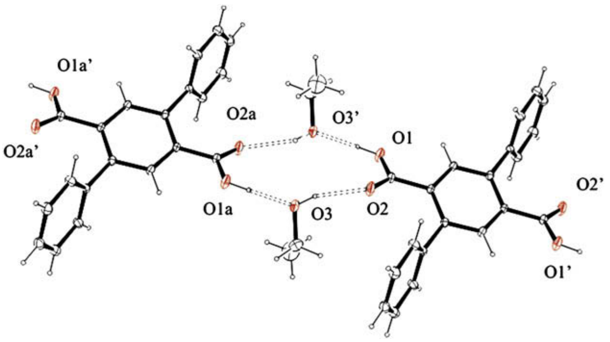

Figure 3. X-ray structure of the (1:1) complex of **2a** and EtOH showing host/guest hydrogen bonding pattern involving one host molecule: O1···O3′ 2.593(3), H1···O3′ 1.72(3) Å, angle 174.0(8)°; O3···O2 2.776(4), H3···O2 1.99(4) Å, angle 153.5(9)°; second host molecule omitted for clarity.

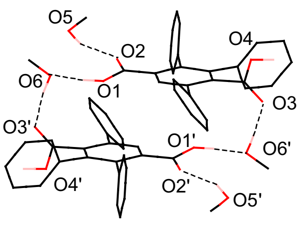

Figure 5. X-ray structure of the (1:2) complex of **4** and MeOH showing host/guest cyclic hydrogen bonding structure: O1···O6 2.559(2) Å, O1–H17 0.97(2) Å, H17···O6 1.59(2) Å, angle 172(2)°; O4··· O5 [x, y, z−1] 2.562(2) Å, O4–H18 0.96(2) Å, H18···O5 1.63(2) Å, angle 165(2)°; O5···O2 2.744(2) Å, O5–H25 0.90(3) Å, H25···O2 1.90(3) Å, angle 155(2)°; O5···O6 2.946(2) Å, O5–H25 0.90(3) Å, H25···O6 2.49(2) Å, angle 111.5(16)°; O6···O3 [1−x, 1−y, 1−z] 2.692(2), O6–H26 0.93(2), H26···O3 1.77(2) Å, angle 169.6(18); hydrogen atoms of benzene rings and MeOH molecules are omitted for clarity.

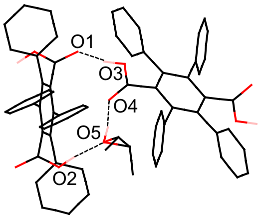

Figure 6. X-ray structure of the (1:1) complex of **4** and EtOH showing host/guest hydrogen bonding pattern involving one host molecule: O3⋯O1 2.619(3), O3–H22 1.09(4), H22⋯O1 1.56(5) Å angle 161(6)°; O2⋯O5[1−*x*, 1−*y*, 1−*z*] 2.554(5) Å, O2–H21 1.05(6) Å, H21⋯O5 1.55(5), angle 176(6); O5⋯O4 2.691(6) Å, O5–H29 0.99(6) Å, H29⋯O4 1.71(7) Å angle 170(4)°; hydrogen atoms of benzene rings and ethanol molecule are omitted for clarity.

and hydrogen atoms were refined using the riding model. H-Atoms of carboxyl group, hydroxy group of EtOH, and all H-atoms of (1:2) **3**/MeOH complex were localized from $\Delta\rho$ maps and refined. All calculations were performed using a crystallographic software package CrystalStructure.[12]

4.3.1. *Crystal data: 1:1 inclusion complex of* ***2a*** *with EtOH*

$C_{22}H_{20}O_5$, F_W=364.390, triclinic space group $P(-)1$: a=9.552(1), b=9.9281(9), c=12.0551(10) Å, α=109.116(9), β=95.689(9), γ=113.553(8)°, V=954.67(15) Å^3, Z=2, d_{calcd}=1.268 Mg m^{-3}, $F(000)$=384, μ(Cu Kα)=0.74 mm^{-1}, 2921 reflections collected in θ-range 4.03–59.9; 2731 used for structure refinement. Final R index R_1=0.0601 [1105 reflections with $I>2\sigma(I)$], and for all data wR=0.1771, S=1.053.

4.3.2. *Crystal data: 1:2 inclusion complex of* ***2b*** *and DMF*

$C_{23}H_{19}O_4F_2\cdot C_{28}H_{26}O_6$, F_w=458.51; monoclinic space group $P2_1/c$, a=8.7500(8), b=5.5820(5), c=25.387(2) Å, β=95.335(3)°, V=1234.59(19) Å^3, Z=2, d_{calcd}=1.346 Mg m^{-3}, $F(000)$=524.0; 27,229 reflections collected in the θ-range .998–23.36°, 3136 unique [R(int)=0.035]; μ(Mo Kα)=0.106 mm^{-1}. Final R index R_1=0.0540 [1495 reflections with $I>2\sigma(I)$], and for all data wR=0.1474, S=0.891.

4.3.3. *Crystal data: 1:2 inclusion complex of* ***3*** *with MeOH*

$C_{28}H_{26}O_6$, F_W=458.51, triclinic space group $P(-)1$: a=9.4011(7), b=11.5140(8), c=12.0027(7) Å, α=108.130(2), β=103.825(2), γ=94.217(3)°, V=1183.46(14) Å^3, Z=2, d_{calcd}=1.287 Mg m^{-3}, $F(000)$=484.00, μ(Mo Kα)=0.090 mm^{-1}, 11,572 reflections collected in θ-range 3.1–27.5; 3864 used for structure refinement. Final R index R_1=0.0411[3864 reflections with $I>2\sigma(I)$], and for all data wR=0.1271, S=1.080.

4.3.4. *Crystal data: 1:1 inclusion complex of* ***4*** *with EtOH*

$C_{34}H_{28}O_5$, F_W=516.59, triclinic space group $P(-)1$: a=11.1504(14), b=11.4433(13), c=12.7057(14) Å, α=68.011(3), β=89.129(4) , γ=68.477(3)°, V=1384.4(3) Å^3, Z=2, d_{calcd}=1.239 Mg m^{-3}, $F(000)$=544.00, μ(Mo Kα)=0.082 mm^{-1}; 13,756 reflections collected in θ-range 3.2–27.5; 6305 used for structure refinement. Final R index R_1=0.0701[2276 reflections with $I>2\sigma(I)$], and for all data wR=0.1999, S=1.056.

5. Supplementary data

CCDC-703938, CCDC-703939, CCDC-706440, and CCDC-706441 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at 'http://www.ccdc.cam.ac.uk/conts/retrieving.html' [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; e-mail: deposit@ccdc.cam.sc.uk].

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