Trifluoromethanesulfonic Acid-Catalyzed Synthesis of Resorcinarenes: Cyclocondensation of 2-Bromoresorcinol with Aldehydes

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Abstract: The resorcin[4]arenes bearing bromine substituents on their extraannular positions were directly prepared from 2-bromoresorcinol with aldehydes by trifluoromethanesulfonic

acid-catalyzed cyclocondensation. In each case, a single stereoisomer was isolated. The main factors for the determination of the products are the reversibility of the C–C bond formation and the difference in the solubility of the isomers.

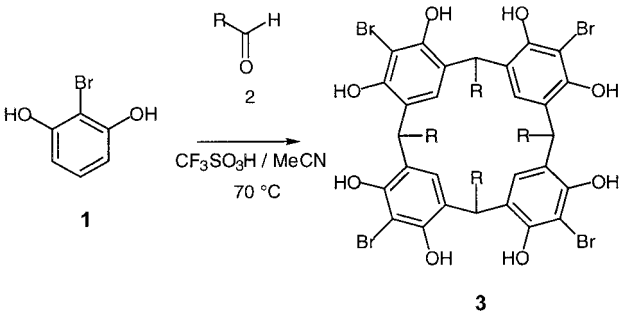
Key words: condensation, cyclophanes, resorcin[4]arene, supramolecular chemistry, trifluoromethanesulfonic acid

Resorcinarenes are macrocyclic compounds in which resorcinol units are linked via methylene bridges at their 4,6-positions. A variety of cyclic tetramers can be easily prepared by the HCl-catalyzed cyclocondensation of resorcinols with aldehydes.[1–4] However, the reaction of the resorcinols bearing electron-withdrawing group such as bromo or nitro group at the 2-position dose not give cyclic compounds but gives only lower linear oligomers.[5] Since the cyclocondensation is an aromatic electrophilic substitution, namely Friedel–Crafts alkylation, the failure of the synthesis may be attributable to the deactivation of the resorcinol nucleus by the electron-withdrawing groups. The highly selective synthesis of resorcin[4]arenes is due to the reversible C–C bond formation, that is, fast propagation and degradation of linear oligomers and reconstruction of cyclic oligomers.[6,7] Therefore, we anticipated that if a superacid is used as a catalyst, the C–C bond formation of deactivated oligomers might be reversible and the functionalized resorcinarenes are then obtained by a one-step reaction.

The resorcin[4]arenes having bromine substituents at their extraannular positions have been prepared by bromination of resorcinarenes, and widely used for construction of container molecules such as cavitands[8] and carcerands.[9,10] Here we report the direct synthesis of brominated resorcinarenes catalyzed by trifluoromethanesulfonic acid (CF_3SO_3H), which is one of the strongest simple protic acids and a good solvent for many organic compounds.[11]

Synthesis

Our standard procedure for the cyclocondensation was carried out at 70 °C with equal molar quantities of 2-bromoresorcinol (**1**) and an aldehyde **2** in acetonitrile–CF_3SO_3H (9:1 v/v), and the substrate concentration was set at 0.2 M. The product that precipitated during the reaction was collected and washed with hot methanol, and then characterized by ^{1}H NMR spectroscopy and FAB-mass spectrometry. In each case, a single stereoisomer was isolated (Scheme). Table 1 shows the isolated yields of the cyclic tetramers **3** and their configuration.



Scheme

The reaction with benzaldehydes **2a**–**c** gave the corresponding *rctt* (Figure 1) cyclic tetramers as precipitates in moderate to good yields. On the other hand, the benzaldehydes **2d**–**f** gave no or only negligible amount of precipitates, one of which was analyzed by ^{1}H NMR to be *rctt*-isomer. The ^{1}H NMR analysis of the soluble fractions showed that the products consisted of a complex mixture of lower linear oligomers. Interestingly, in the case of 4-methoxybenzaldehyde (**2f**), the condensation using 1.0 M concentration of the reactants gave the cyclic tetramer **3f** with *rctt* configuration in 44% yield. In other case, however, an appreciable increase in yield could not be obtained.

Two aliphatic aldehydes **2g** and **2h** also gave the cyclic tetramers under the standard conditions. Thus, the *rccc*-isomers **3g** and **3h** selectively precipitated from the reaction mixture. Moreover the resorcinarene having unsubstituted methylene bridges was prepared by the condensation with 1,3,5-trioxane. In this case, only the cyclic tetramer **3i** was obtained as a precipitate, while other cyclic oligomers with a larger ring size could not be isolated from the soluble fraction.

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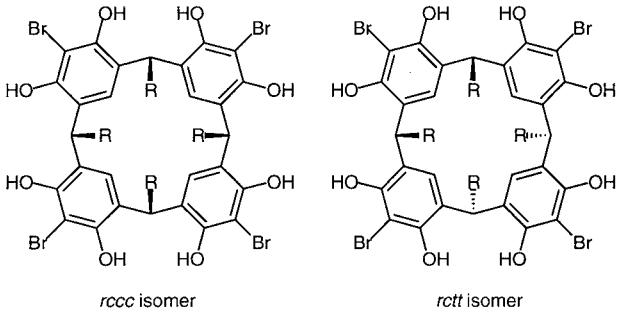

Figure 1

Table 1 Yields and Configurations of the Resorcin[4]arenes **3** by CF_3SO_3H-Catalyzed Reaction of 2-Bromoresorcinol with Aldehydes[a]

Compound	R	Yield (%)	Configuration
3a	Ph	65	*rctt*
3b	4-ClC_6H_4	29	*rctt*
3c	4-MeC_6H_4	45	*rctt*
3d	4-CNC_6H_4	<3[c]	*rctt*
3e	4-$NO_2C_6H_4$	0	–
3f[b]	4-$MeOC_6H_4$	44	*rctt*
3g	Me	56	*rccc*
3h	$PhCH_2CH_2$	49	*rccc*
3i	$H(CH_2O)_3$	58	–

[a] MeCN–CF_3SO_3H (9:1 v/v). Substrate concentration: 0.2 M.
[b] Substrate concentration: 1.0 M.
[c] Estimated by ^1H NMR spectroscopy.

Configuration and Conformational Properties in Solution

The stereochemistry of cyclic tetramers with aromatic substituents at the bridging positions was confirmed by ^1H NMR spectroscopy. Since most of the tetrabrominated resorcinarenes are practically insoluble in common solvents, their spectra were recorded in DMSO-d_6 at high temperature. The ^1H NMR spectrum (DMSO-d_6, 50 °C) of **3a** showed one singlet at $\delta = 5.67$ for the bridge methine protons (4 H) and two singlets at $\delta = 5.47$ and 6.20 for the intraannular aromatic protons H_{in} (each 2 H). These spectral patterns indicated that its configuration is *rctt*. A number of *rctt*-resorcinarenes with four aromatic substituents at the bridging position adopt the chair conformation, where all four aromatic groups are axial in solution[12] or solid state.[13] Based on the chemical shifts of H_{in} and the bridge methine protons, it is clearly indicated that the *rctt*-isomer **3a** also exists as the chair conformation stated above, which is shown in Figure 1. Since the ^1H NMR spectral features of the cyclic tetramers bearing aromatic substituents, **3b**,**c**,**d**, and **3f**, are very similar to that of **3a**, it is concluded that they also have the *rctt* configuration and exist in the chair conformation.

The stereochemistry of the cyclic tetramers bearing alkyl substituents, **3g**[9] and **3h**,[14] was determined by comparison of their ^1H NMR spectra with those of authentic samples. Both cyclic tetramers showed one bridge methine signal and one intraannular aromatic signal, indicating the configuration to be *rccc*. These spectral features indicate that they exist in a cone conformation or in fast equilibrium among the conformational flexible species on the NMR time scale. Since the solubility of the samples is not adequate for the low temperature NMR spectroscopy, the conformational freezing could not be observed. Thus, the conformational properties of **3g** were examined on the basis of the ^1H NMR chemical shifts of the methyl protons (δ_{Me}). The cone conformers of the *rccc*-resorcinarenes display the methyl signals in the range of 1.7–1.9 ppm,[15–17] while the boat conformers display the methyl signals in the range of 1.2–1.5 ppm.[2,18,19] The upfield shifts of δ_{Me} observed for the boat conformers are the result of the anisotropic ring current effect of the horizontally oriented resorcinol units. Since the fast interconversion between two equal boat conformers at elevated temperatures affects only slightly the δ_{Me}. It is possible to use the δ_{Me} value as a criterion for the conformation analysis. Thus, the δ_{Me} for **3g** in DMSO-d_6 is 1.41 ppm, indicating the fast boat to boat interconversion. In the case of the phenylethyl derivative **3h**, no appropriate reference compounds could be available, therefore its conformational properties could not be determined at the present time.

The ^1H NMR spectrum in DMSO-d_6 showed that **3i** possesses a highly symmetrical structure. One singlet for the methylene protons (3.69 ppm), one singlet for the aromatic protons H_{in} (6.38 ppm), and a singlet for the OH protons (8.69 ppm) are compatible with a time-averaged D_{4h} conformation. Since the resorcinarenes **3i** has no substituents at the bridge methylene positions, the framework is very flexible and there are many possible stable conformers.[20] The high-field shift of H_{in} is remarkable and could be due to shielding of the adjacent aromatic rings. Thus, it is strongly suggested that the preferred conformation of **3i** is a 1,3-alternate conformation.

Stereoselectivity of Cyclic Tetramer. Study of Molecular Mechanics

The HCl-catalyzed cyclocondensation of resorcinol with aromatic aldehydes gave *rccc* and/or *rctt*-isomers. The isomer ratios depend on the nature of the resorcinols and/or aldehydes and the reaction time.[1,2] In this system, the reaction of resorcinol with benzaldehyde gives the *rccc*-isomer as a thermodynamically controlled product. On the other hand, the cyclocondensation of 2-methylresorcinol with benzaldehydes gave the *rctt*-isomers.[21] Hence, the bromine atom at the 2-position of resorcinol seems to play a role in the stereoselective formation of the *rctt*-isomer. Indeed, when the *rccc*-isomer of **3a** was treated with

CF_3SO_3H in acetonitrile, the isomerization to the *rctt*-isomer was observed.

To gain insight into the origin of the stereoselectivity, we performed molecular mechanics calculations. The most stable conformation of the eight compounds listed in Table 2 was searched by MacroModel V6.5 (MM2* force field).[22] The relative energies are calculated by comparison of the steric energies of the two isomers (*rccc*, *rctt*), and those of the more stable isomer are defined a 0.00 kJ mol^{-1}.

Table 2 MacroModel V6.5 (MM2* Force Field) Calculated Relative Energies/kJ mol^{-1}

R	X	*rccc*	*rctt*
Ph	Br	6.84	0.00
Ph	H	0.00	2.98
Me	Br	0.00	13.79
Me	H	0.00	9.66

The molecular mechanics calculation predicted that, for the brominated resorcinarene bearing phenyl substituents at the bridge methylene, the *rctt*-isomer is thermodynamically more stable than the *rccc*-isomer. The MM2 calculated lowest energy structure of *rctt*-**3a** is shown in Figure 2. It agrees very well with that predicted by the chemical shifts observed in solution. In other cases, the *rccc*-isomers are more stable than the *rctt*-isomers. The preferred conformation of *rccc*-**3g** is calculated to be a boat conformation, which is shown in Figure 3. This prediction is also compatible with the conformational properties that are suggested from the ^{1}H NMR spectrum of **3g**.

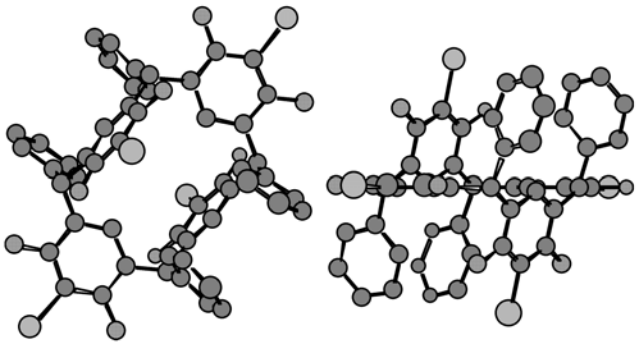

Figure 2 MM2 energy-minimized structure of *rctt*-**3a**. Hydrogen atoms are omitted for clarity, top view (left) and side view (right).

The cyclocondensation of 2-bromoresorcinol with some aldehydes proceeds in acetonitrile-CF_3SO_3H to give cyclic tetramers with high stereoselectivity. Molecular mechanics calculations predict that the isolated stereoisomers are the thermodynamically favored products. Furthermore, the reversibility of the C–C bond formation and the difference in the solubility of the isomers play an important role in the preparation of a single isomer.

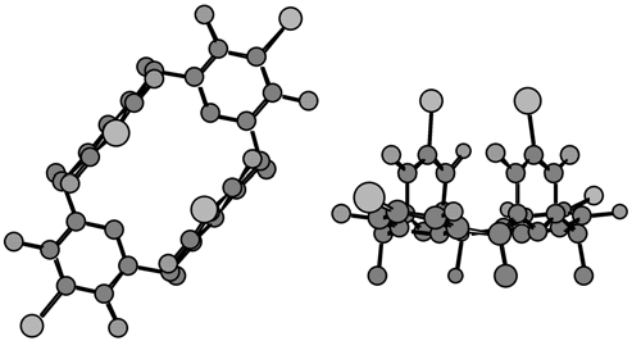

Figure 3 MM2 energy-minimized structure of *rccc*-**3g**. Hydrogen atoms are omitted for clarity, top view (left) and side view (right).

Melting points were taken on a MEL-Temp apparatus (Laboratory Devices) and are uncorrected. The ^{1}H and ^{13}C NMR spectra were recorded on a JEOL GX-270 spectrometer. IR spectra were taken with a Perkin-Elmer 1610 spectrophotometer. FAB mass spectra were recorded using xenon ionization techniques with *m*-nitrobenzyl alcohol (MNBA) as the matrix on a JEOL AX-505 spectrometer at the Faculty of Agriculture of Tottori University. Analyses were performed at the Microanalysis Center of Kyoto University. 2-Bromoresorcinol (**1**) was prepared according to the literature procedure.[23,24]

CF_3SO_3H-Catalyzed Cyclocondensation of 2-Bromoresorcinol (1) with Aldehydes; General Procedure

To a solution of 2-bromoresorcinol (**1**; 189 mg, 1 mmol) and an aldehyde (1 mmol) in MeCN (4.5 mL) was added CF_3SO_3H (0.5 mL) dropwise. The solution was stirred for 3 h at 70 °C. After cooling, the solid that precipitated during the reaction was collected by filtration. The crude product was stirred for 1 h in hot MeOH (10 mL) and filtered. The insoluble material was dried at 80 °C for 8 h under reduced pressure to give the cyclic tetramer.

***rctt*-5,11,17,23-Tetrabromo-2,8,14,20-tetraphenylpentacyclo-[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacosa-1(25),3,5,7(28),9,11,13(27),-15,17,19(26),21,23-dodecaene-4,6,10,12,16,18,22,24-octol (3a)**

White solid; yield: 65%; mp 239 °C (dec.).

IR (KBr): 3488 (OH), 1654, 1478, 1085 cm^{-1}.

^{1}H NMR (270 MHz, DMSO-d_6, 50 °C): δ = 5.47 (s, 2 H, H_{in}), 5.67 (s, 4 H, bridge H), 6.20 (s, 2 H, H_{in}), 6.63 (m, 8 H, C_6H_5), 6.91 (m, 12 H, C_6H_5), 8.14 (s, 4 H, OH), 8.17 (s, 4 H, OH).

^{13}C NMR (67.8 MHz, DMSO-d_6, 50 °C): δ = 44.2, 101.4, 101.5, 122.6, 123.2, 124.9, 126.6, 127.2, 128.6, 129.4, 141.6, 148.9, 149.1.

FAB-MS (MNBA), *m*/*z* = 1104.0 (M^+).

Anal. Calcd for $C_{52}H_{36}Br_4O_8 \cdot 2H_2O$: C, 54.57; H, 3.52; Br, 27.93. Found: C, 54.20; H, 3.52; Br, 27.81.

***rctt*-5,11,17,23-Tetrabromo-2,8,14,20-tetra(4-chlorophenyl)-pentacyclo-[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacosa-1(25),3,5,7(28),9,-11,13(27),15,17,19(26),21,23-dodecaene- 4,6,10,12,16,18,22,24-octol (3b)**

White solid; yield: 29%; mp 315 °C (dec.).

IR (KBr): 3507 (OH), 1609, 1478, 1337, 559 cm^{-1}.

^{1}H NMR (270 MHz, DMSO-d_6, 130 °C): δ = 5.46 (s, 2 H, H_{in}), 5.74 (s, 4 H, bridge H), 6.16 (s, 2 H, H_{in}), 6.65 (d, 8 H, *J* = 7.9 Hz, ArH), 7.01 (d, 8 H, *J* = 7.9 Hz, ArH), 7.90 (br s, 8 H, OH).

FAB-MS (MNBA): *m*/*z* = 1239.8 (M^+).

Anal. Calcd for $C_{52}H_{32}Br_4Cl_4O_8 \cdot 2H_2O$: C, 48.71; H, 2.83. Found: C, 48.62; H, 2.63.

***rctt*-5,11,17,23-Tetrabromo-2,8,14,20-tetra(4-methylphenyl)-pentacyclo- [19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacosa-1(25),3,5,7(28),-9,11,13(27),15,17,19(26),21,23-dodecaene- 4,6,10,12,16,18,-22,24-octol (3c)**

White solid, yield: 45%; mp 285 °C (dec.).

IR (KBr): 3496 (OH), 3018, 2920, 1610, 1428, 1335, 562 cm^{-1}.

^{1}H NMR (270 MHz, DMSO-d_6, 130 °C): δ = 2.18 (s, 12 H, CH_3), 5.59 (s, 2 H, H_{in}), 5.61(s, 4 H, bridge H), 6.19 (s, 2 H, H_{in}), 6.51 (d, 8 H, *J* = 7.9 Hz, ArH), 6.75 (d, 8 H, *J* = 7.6 Hz, ArH), 8.10 (s, 8 H, OH).

FAB-MS (MNBA): *m*/*z* = 1160.1 (M^+).

Anal. Calcd for $C_{56}H_{44}Br_4O_8 \cdot H_2O$: C, 56.88; H, 3.92. Found: C, 57.10; H, 3.93.

***rctt*-5,11,17,23-Tetrabromo-2,8,14,20-tetra(4-cyanophenyl)pentacyclo-[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacosa-1(25),3,5,7(28),9,-11,13(27),15,17,19(26),21,23-dodecaene- 4,6,10,12,16,18,22,24-octol (3d)**

White solid; yield: 3%; mp 280 °C (dec.).

^{1}H NMR (270 MHz, DMSO-d_6, 130 °C): δ = 5.20 (s, 2 H, H_{in}), 5.84 (s, 4 H, bridge H), 6.14 (s, 2 H, H_{in}), 6.82 (d, 8 H, *J* = 7.9 Hz, ArH), 7.36 (d, 8 H, *J* = 7.9 Hz, ArH), 8.11 (br s, 8 H, OH).

***rctt*-5,11,17,23-Tetrabromo-2,8,14,20-tetra(4-methoxyphenyl)-pentacyclo-[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacosa-1(25),3,5,7(28),9,-11,13(27),15,17,19(26),21,23-dodecaene-4,6,10,12,16,18,22,24-octol (3f)**

The reaction of 2-bromoresorcinol (189 mg, 1 mmol) and 4-methoxybenzaldehyde (136 mg, 1 mmol) was carried out according to the general procedure using MeCN (0.9 mL) and CF_3SO_3H (0.5 mL; light tan solid; yield: 44%; mp 305 °C (dec.).

IR (KBr): 3484 (OH), 1609, 1511, 1475, 1248, 1179, 1084 cm^{-1}.

^{1}H NMR (270 MHz, DMSO-d_6, 50 °C): δ = 3.65 (s, 12 H, OCH_3), 5.53 (s, 2 H, H_{in}), 5.61 (s, 4 H, bridge H), 6.15 (s, 2 H, H_{in}), 6.52 (m, 16 H, ArH), 8.12 (s, 8 H, OH).

FAB-MS (MNBA), *m*/*z* = 1223.9 (M^+).

Anal. Calcd for $C_{56}H_{44}Br_4O_{12} \cdot 2H_2O$: C, 53.19; H, 3.83. Found: C, 53.18; H, 3.74.

***rccc*-5,11,17,23-Tetrabromo-2,8,14,20-tetramethylpentacyclo-[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]-octacosa-1(25),3,5,7(28),9,11,13(27),-15,17,19(26),21,23-dodecaene-4,6,10,12,16,18,22,24-octol (3g)**

White solid; yield: 56%; mp 270 °C (dec.).

IR (KBr): 3395 (OH), 2968, 1610, 1475, 862 cm^{-1}.

^{1}H NMR (270 MHz, DMSO-d_6, 50 °C): δ = 1.41 (d, 12 H, *J* = 7.3 Hz, CH_3), 4.61 (q, 4 H, *J* = 7.3 Hz, bridge H), 6.82 (s, 4 H, H_{in}), 8.24 (br s, 8 H, OH).

^{13}C NMR (67.8 MHz, DMSO-d_6, 50 °C): δ = 20.8, 30.9, 101.7, 123.3, 125.4, 148.4.

FAB-MS (MNBA), *m*/*z* = 856.0 (M^+).

***rccc*-5,11,17,23-Tetrabromo-2,8,14,20-tetrakis(2-phenylethyl)-pentacyclo- [19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacosa-1(25),3,5,7(28),9,-11,13(27),15,17,19(26),21,23-dodecaene- 4,6,10,12,16,18,22,24-octol (3h)**

White solid; yield: 49%; mp 270 °C (dec.).

IR (KBr): 3450 (OH), 2936, 1617, 1474, 1096 cm^{-1}.

^{1}H NMR (270 MHz, DMSO-d_6, 50 °C): δ = 2.05 (m, 16 H, CH_2CH_2), 4.42 (m, 4 H, bridge H), 7.10–7.19 (m, 20 H, C_6H_5), 7.50 (s, 4 H, H_{in}), 9.10 (br s, 8 H, OH).

^{13}C NMR (67.8 MHz, DMSO-d_6, 50 °C): δ = 30.4, 34.0, 35.5, 101.0, 123.3, 125.3, 125.4, 127.9, 128.1, 141.4, 148.4.

FAB-MS (MNBA): *m*/*z* = 1216.1 (M^+).

Anal. Calcd for $C_{60}H_{52}Br_4O_8$: C, 59.04; H, 4.29; Br, 26.18. Found: C, 58.86; H, 4.19; Br, 25.97.

5,11,17,23-Tetrabromopentacyclo[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacosa-1(25),3,5,7(28),9,11,13(27),15,17,19(26),21,23-dodecaene-4,6,10,12,16,18,22,24-octol (3i)

Light-tan solid; yield: 58%; mp 223 °C.

IR (KBr): 3380 (OH), 2886, 1616, 1480, 1096 cm^{-1}.

^{1}H NMR (270 MHz, DMSO-d_6, 50 °C): δ = 3.69 (s, 8 H, bridge CH_2), 6.38 (s, 4 H, H_{in}), 8.69 (s, 8 H, OH).

^{13}C NMR (67.8 MHz, DMSO-d_6, 50 °C): δ = 29.4, 101.6, 120.1, 128.8, 149.4.

FAB-MS (MNBA): *m*/*z* = 799.8 (M^+).

Anal. Calcd for $C_{28}H_{20}Br_4O_8$: C, 41.82; H, 2.51. Found: C, 41.83; H, 2.55.

Molecular Mechanics Calculations

The molecular mechanics calculations were performed with MacroModel V6.5 using the implemented MM2* force field on an SGI Octane workstation at the Center for Instrumental Analysis, Tottori University. Energy optimization was carried out using Polak-Ribiere conjugated gradient minimization. The conformational search on the resorcinarenes was divided in two steps. In the first one, the analysis of the macrocyclic core was undertaken by the Monte Carlo Multiple Minimum (MCMM) module. The eight bridging C–C bonds were selected as the rotatable bonds. In the second step, each structure that was obtained in the first step was energy-minimized by the MCMM module for the rotation of the four substituents at the bridging positions and the eight OH groups.

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