J Chem Crystallogr (2012) 42:165–172
DOI 10.1007/s10870-011-0219-z

ORIGINAL PAPER

Crystal Structures of 1,3,5-Tris(bromomethyl)-2,4,6-trimethylbenzene and 2,4,6-Trimethyl-1,3,5-tris(4-oxymethyl-1-formylphenyl)benzene

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Received: 4 June 2011 / Accepted: 17 November 2011 / Published online: 30 November 2011

Abstract The synthesis and X-ray crystal structure of 2,4,6-trimethyl-1,3,5-tris(4-oxymethyl-1-formylphenyl)benzene (**2**) and the crystal structure of its core molecule, 1,3,5-tris(bromomethyl)-2,4,6-trimethylbenzene (**1**) are reported. The compounds **1** and **2** crystallize in the triclinic system with space group $P\,\bar{1}$. The lattice parameters of **1** and **2** are $a = 9.454(2)$ Å, $b = 9.478(4)$ Å, $c = 9.573(2)$ Å, $\alpha = 116.53(2)°$, $\beta = 109.705(14)°$, $\gamma = 101.293(18)°$, $V = 658.5(4)$ and $a = 15.7707(6)$ Å, $b = 16.3646(5)$ Å, $c = 18.2805(6)$ Å, $\alpha = 83.202(2)°$, $\beta = 66.0120(10)°$, $\gamma = 73.704(2)°$, $V = 4137.2(2)$, respectively. In the crystals of **1** and **2**, there are one and three molecules in the asymmetric unit, respectively. The packing of the molecules in the solid is stabilized through van der Waals interactions in **1** and weak C–H···O and C–H···π interactions in **2**.

Keywords Crystal structure · Benzaldehyde · Tris(methyl)benzene · Hydrogen bonding

Introduction

In the recent years, design and construction of multidimensional metal-organic frameworks (MOFs) have attracted considerable attention in crystal engineering owing to their interesting properties and potential use as functional materials [1–5]. Important properties and functions of MOFs depend largely on their structures and topology and hence the selection of organic building blocks is key to the construction of desired frameworks [6]. In this article, we report the synthesis and crystal structure of 2,4,6-trimethyl-1,3,5-tris(4-oxymethyl-1-formylphenyl)benzene and the crystal structure of its core molecule, 1,3,5-tris(bromomethyl)-2,4,6-trimethylbenzene. 1,3,5-Tris(bromomethyl)-2,4,6-trimethylbenzene is a good core molecule due to the presence of three bromomethyl groups to synthesize different kinds of dendritic molecules.

Experimental

Physical Measurements

Elemental microanalyses were carried out using a Perkin-Elmer 2400 Series II CHNS/O Elemental Analyzer interfaced with a Perkin-Elmer AD 6 Autobalance. Helium was used as the carrier gas. Infrared spectra were recorded on a Perkin-Elmer Spectrum RX-I FT IR spectrometer in the range 4000–400 cm^{-1} using KBr pellets. NMR spectra were recorded on a Bruker AVANCE III 500 MHz (AV 500) multinuclear NMR spectrometer working at 500 MHz at 25 °C. Standard 5 mm probe was used for the ^{1}H and ^{13}C NMR measurements. The electrospray ionization mass spectra (ESI MS) were performed using a Micromass Quattro-II Triple Quadrupole mass spectrometer. The samples were dissolved in acetonitrile and introduced into the ESI capillary using a 5 μL syringe pump. The ESI capillary was set at 3.5 kV with the cone voltage of 40 V. The solvents were purified and dried using standard procedures [7].

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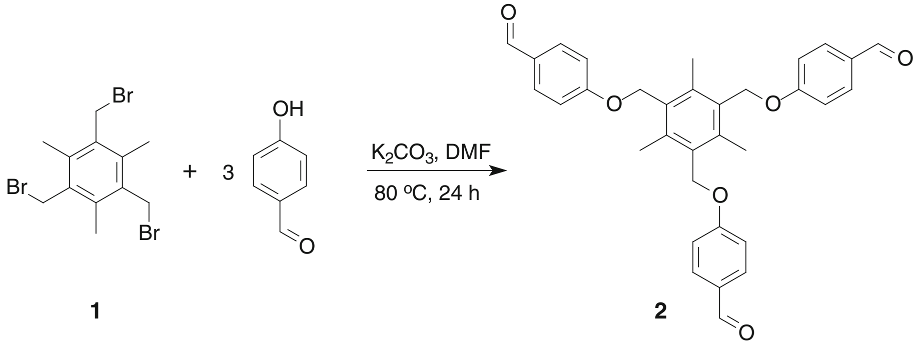
Scheme 1 Synthesis of 2,4,6-trimethyl-1,3,5-tris(4-oxymethyl-1-formylphenyl)benzene



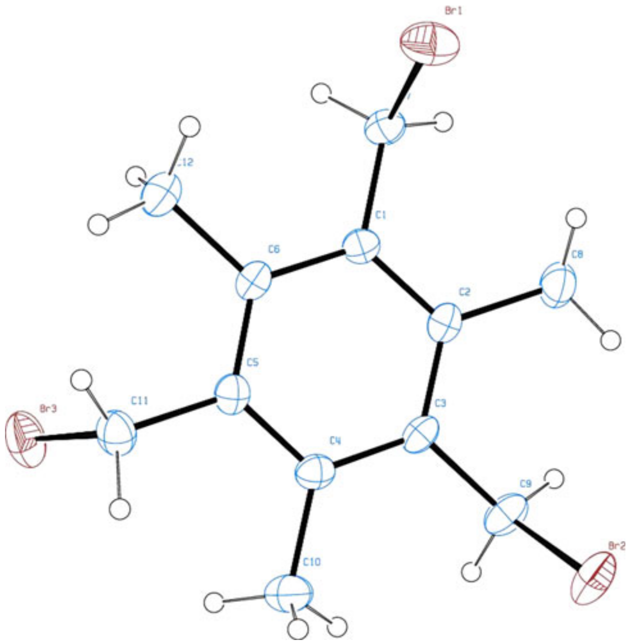
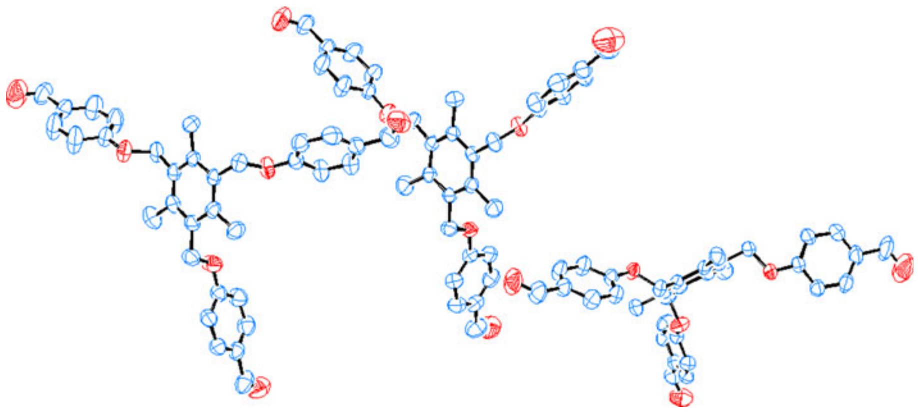


Fig. 1 ORTEP view of 1,3,5-tris(bromomethyl)-2,4,6-trimethylbenzene (**1**)

Synthesis of 1,3,5-Tris(bromomethyl)-2,4,6-trimethylbenzene (1)

Compound **1** was synthesized by the procedure reported by Zavada et al. [8]. To a mixture of mesitylene (4.16 mL, 30 mmol), paraformaldehyde (4.20 g, 140 mmol), and potassium bromide (19.20 g, 160 mmol) in acetic acid (32 mL) was added a mixture of concentrated sulfuric acid and acetic acid (1:1 v/v, 30 mL) dropwise, stirred at 90–95 °C for 6 h, allowed to stand overnight, and poured into water (1.6 L) at room temperature. The solid product that separated out was filtered, dried in vacuum, and recrystallized twice in ether-dichloromethane (1:1 v/v) to get colorless crystals suitable for X-ray diffraction. Yield 9.44 g (78%). mp 188–189 °C. Anal. Calcd. for $C_{12}H_{15}Br_3$: C 36.10, H 3.79. Found: C 36.00, H 3.69. IR (KBr, cm^{-1}): 3,039 ν_s(C–H) and 754 δ(C–H) (aromatic); 2,997 ν_{as}(C–H) and 2,920 ν_s(C–H) (aliphatic); 1,569 and 1,446 ν_s(C=C) (aromatic). ^{1}H NMR ($CDCl_3$, 298 K): δ 2.48 (s, 9H, –CH_3), 4.59 (s, 6H, –CH_2). ^{13}C NMR ($CDCl_3$, 298 K): δ 15.4, 29.9, 133.2, 137.9.

Fig. 2 ORTEP representation of the asymmetric unit of **2**. The atoms are not labeled for the sake of clarity



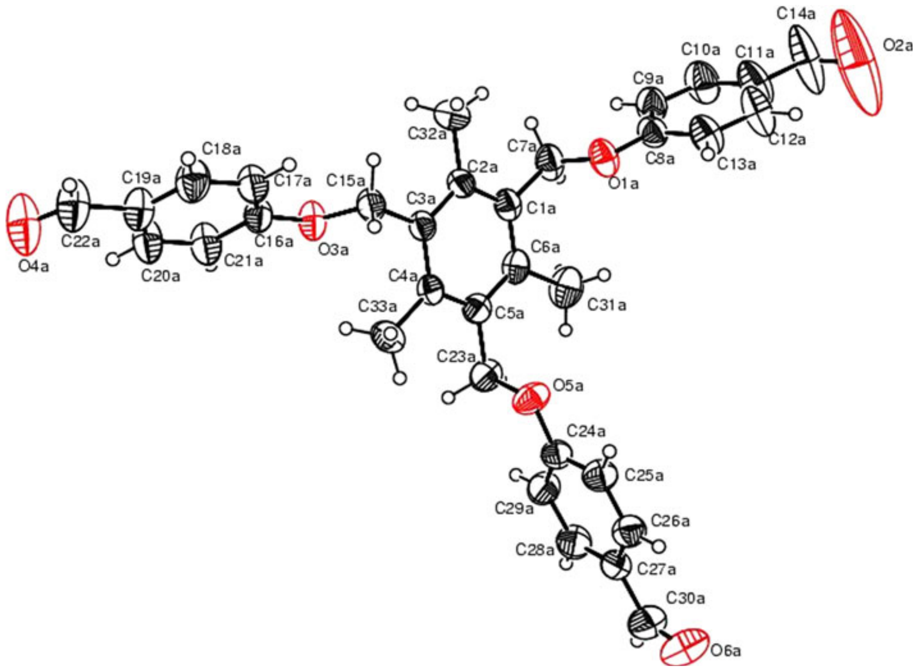


Fig. 3 ORTEP view of 2,4,6-trimethyl-1,3,5-tris(4-oxymethyl-1-formylphenyl)benzene (**2**) showing the atom labeling scheme of a molecule A of the asymmetric unit. The displacement *ellipsoids* are drawn at the 40% probability level. Molecules B and C are not drawn for the sake of clarity

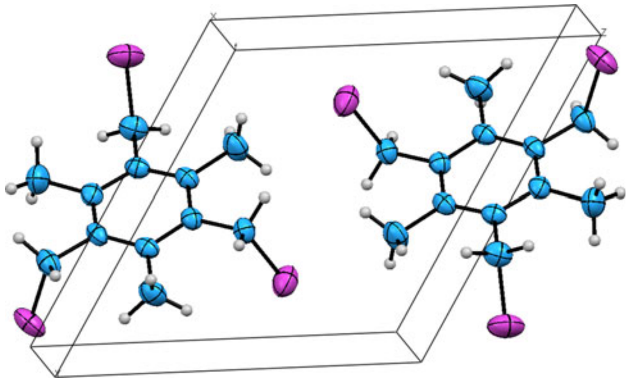


Fig. 4 Crystal packing of the molecule **1** in the unit cell

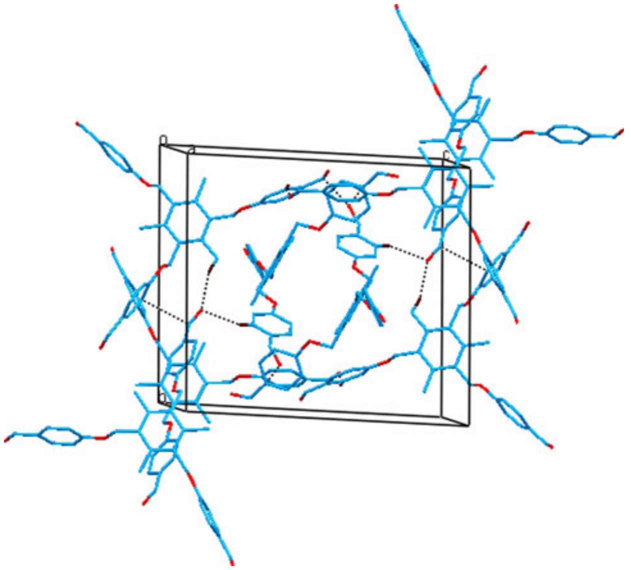


Fig. 5 Crystal packing of the molecule **2** in the unit cell. The intermolecular interactions are shown with *dotted lines*

Synthesis of 2,4,6-Trimethyl-1,3,5-tris(4-oxymethyl-1-formylphenyl)benzene (2)

To a solution of 4-hydroxybenzaldehyde (1.47 g, 12 mmol) in dry DMF (100 mL) was added potassium carbonate (1.93 g, 14 mmol) and stirred for 15 min under an atmosphere of argon. 1,3,5-Tris(bromomethyl)-2,4,6-trimethylbenzene (1.60 g, 4 mmol) in dry DMF (40 mL) was added dropwise over a period of 15 min, heated at 80 °C for 24 h, cooled to room temperature, and flash evaporated. The resulting crude product was dissolved in chloroform (100 mL), washed with water (3 × 100 mL), the organic layer was dried over sodium sulfate overnight, and filtered. The chloroform extract was flash evaporated and the resulting solid product was recrystallized in hot ethanol to get pale yellow crystals suitable for X-ray diffraction. The reaction is illustrated in Scheme 1. Yield 1.76 g (84%). Anal. Calcd. for $C_{33}H_{30}O_6$: C 75.84, H 5.79. Found: C 75.77, H 5.72. IR (KBr, cm^{-1}): 2,926 $\nu_{as}(CH_2)$, 1,690 $\nu_s(C{=}O)$, 1,600 $\nu_s(C{=}C)$ (aromatic), 1,508 ν_s(C–C), 1,311 $\tau(CH_2)$, 1,244 ν_{as}(C–O–C), 830 τ(C–H). ^1H NMR ($CDCl_3$, 298 K): δ 2.47 (s, 9H, –C*H₃*), 5.23 (s, 6H, –O–CH_2–), 7.15 (d, 6H, $J = 8.5$ Hz, Ph-*H*), 7.90 (d, 6H, $J = 7$ Hz, Ph-*H*), 9.92 (s, 3H, –C*H*O). ^{13}C NMR ($CDCl_3$, 298 K): δ 16.0,

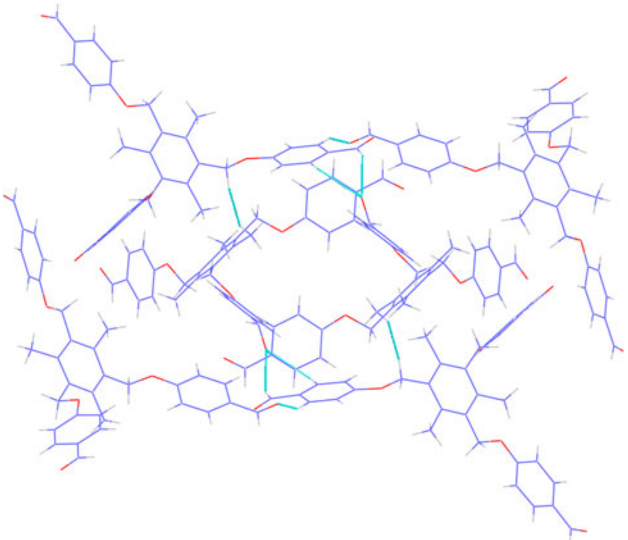


Fig. 6 The 3D supramolecular structure of **2** via hydrogen bonding interactions

65.2, 114.8, 130.3, 131.2, 132.1, 139.7, 163.9, 190.7. ESI MS: *m/z* 546 $[M+Na]^+$, 523 $[M]^+$, 375 $[M-(C_9H_{10}O_2)]^+$, 102 $[M-(C_{26}H_{28}O_5)]^+$.

Single-Crystal X-ray Diffraction

X-ray diffraction studies were carried out using Bruker axs kappa Apex II single crystal X-ray diffractometer equipped with graphite monochromated Mo($K\alpha$) ($\lambda = 0.7107$ Å) radiation and CCD detector. Crystals were cut to suitable size and mounted on a glass fiber using cyanoacrylate adhesive. The unit cell parameters were determined from 36 frames measured (0.5° phi-scan) from three different crystallographic zones using the method of difference vectors. The intensity data was collected with an average four-fold redundancy per reflection and optimum resolution (0.80 Å). The intensity data collection, integration of frames, LP and decay corrections were carried out using

Table 1 The crystal structure data and structure refinement parameters of **1** and **2**

Description	1	2
Empirical formula	$C_{12}H_{15}Br_3$	$C_{33}H_{30}O_6$
Formula weight	398.97	522.57
Color	Colorless	Yellow
Crystal description	Block	Prism
Crystal size/mm	0.3 × 0.25 × 0.2	0.2 × 0.16 × 0.16
Diffractometer	Bruker axs kappa apex2 CCD	Bruker axs kappa apex2 CCD
Radiation type	Mo$K\alpha$	Mo$K\alpha$
Crystal system	Triclinic	Triclinic
Space group	$P\,\bar{1}$	$P\,\bar{1}$
a (Å)	9.454(2)	15.7707(6)
b (Å)	9.478(4)	16.3646(5)
c (Å)	9.573(2)	18.2805(6)
α (°)	116.530(2)	83.202(2)
β (°)	109.705(14)	66.0120(10)
γ (°)	101.293(18)	73.704(2)
V (Å^3)	658.5(4)	4137.2(2)
Z	2	6
ρ_{calcd} (mg cm^{-3})	2.012	1.258
λ (Å)	0.71073	0.71073
T (K)	293(2) K	293(2) K
Absorption correction	Multi-scan	Multi-scan
Absorption correction range	0.1698–0.2618	0.9830–0.9864
2θ range (°)	2.51–28.56	1.30–24.44
F(000)	384	1,656
No. of reflections collected	14,861	73,977
No. of independent reflections	3,337	13,594
No. of parameters	140	1,065
Goodness-of-fit on F^2	1.045	1.020
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0342$, w$R2 = 0.0781$	$R1 = 0.0582$, w$R2 = 0.1689$
R[a] indices, all data	$R1 = 0.0598$, w$R2 = 0.0853$	$R1 = 0.1003$, w$R2 = 0.2121$
Largest diff. peak and hole	0.836 and −0.814	0.656 and −0.225
Absorption coefficient	9.156	0.086

[a] $R = \sum ||F_o| - |F_c|| / \sum |F_o|$. $R_w = \left[\sum \left\{w\left(F_o^2 - F_o^2\right)^2\right\} / \sum \left\{w\left(F_o^2\right)^2\right\}\right]^{1/2}$

Table 2 Hydrogen bonds for 2,4,6-trimethyl-1,3,5-tris(4-oxymethyl-1-formylphenyl)benzene (**2**) (Å and °)

D–H···A	d(D–H)	d(H···A)	d(D···A)	<(DHA)
C(31B)–H(31D)···O(4C)#1	0.960	2.535	3.447	158.68
C(26B)–H(26B)···O(6C)#2	0.930	2.523	3.342	147.0
C(10A)–(10A)···O(4C)#3	0.930	2.580	3.368	143.0

Symmetry transformations used to generate equivalent atoms: $^{\#1}-x+1, -y+1, -z$; $^{\#2}-x+1, -y, -z+1$; $^{\#3}-x+2, -y+1, -z$

SAINT-NT (version 7.06a) software [9]. Empirical absorption correction (multi-scan) was performed using SADABS (1999) program [10]. The structure was solved using SIR92 [11] and refined using SHELXL-97 [12] programs. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were geometrically fixed at chemically meaningful positions and were allowed to ride over the parent atoms during refinement.

Results and Discussion

Compound **1** was synthesized by the bromomethylation of mesitylene with potassium bromide and paraformaldehyde [8]. Compound **2** was synthesized by the *O*-alkylation of 4-hydroxybenzaldehyde (3 equiv) with 1,3,5-tris(bromomethyl)-2,4,6-trimethylbenzene (1 equiv) in DMF. In **2**, three oxybenzaldehyde moieties are covalently appended at the 1,3,5-positions of 1,3,5-tris(methylene)-2,4,6-trimethylbenzene.

The ^{1}H NMR spectrum of **2** in $CDCl_3$ shows five resonances. The methyl ($-CH_3$) and the methylene ($-CH_2-$) protons resonate at 2.47 and 5.23 ppm, respectively. The phenyl protons resonanate at 7.15 and 7.90 ppm. The aldehyde (–C*H*O) protons resonate at 9.92 ppm. The ^{13}C NMR spectrum of **2** in $CDCl_3$ shows nine resonances for nine different types of carbon atoms. The methyl carbons and the methylene carbons resonate at 16.0 and 65.2 ppm, respectively. The aryl carbons resonate at 114.8, 130.3, 132.1, and 163.9 ppm. The aldehyde (–*C*HO) carbons resonate at 190.7 ppm.

The compounds **1** and **2** crystallize in the triclinic system with the space group $P\bar{1}$. In the crystal of **1** there is one molecule in the asymmetric unit, whereas in **2** there are three molecules in the asymmetric unit. The ORTEP representation of **1** is shown in Fig. 1. The ORTEP representation of the asymmetric unit of **2** and the atom labeling scheme are depicted in Figs. 2 and 3, respectively. The displacement *ellipsoids* are drawn at 40% probability level. The crystal packing of the molecules **1** and **2** in the unit cell are shown in Figs. 4 and 5, respectively. In **2**, the packing is stabilized mostly through the C–H···O interactions and van der Waals forces. The mean plane of all the three oxybenzaldehyde moieties are nearly perpendicular to the mean plane of the tris(methyl)benzene core. The corresponding angle between the mean planes of *p*-oxybenzaldehyde moieties considerably differ among the three molecules in the asymmetric unit. This shows that the three

Table 3 Summary of selected bond lengths (Å), bond angles (°), and torsion angles (°) with e.s.d. in parentheses for **2**

Bond	Angle	Bond	Length
O(1A)–C(7A)–C(1A)	106.9(2)	C(1A)–C(7A)	1.501(4)
C(8A)–O(1A)–C(7A)	118.4(2)	C(2A)–C(32A)	1.510(4)
O(2A)–C(14A)–C(11A)	117.6(8)	C(3A)–C(15A)	1.501(4)
O(5A)–C(23A)–C(5A)	106.5(2)	C(4A)–C(33A)	1.505(4)
C(24A)–O(5A)–C(23A)	118.9(2)	C(5A)–C(23A)	1.504(4)
O(6A)–C(30A)–C(27A)	125.8(4)	C(6A)–C(31A)	1.513(4)
O(3A)–C(15A)–C(3A)	108.0(2)	C(7A)–O(1A)	1.435(3)
C(16A)–O(3A)–C(15A)	117.0(2)	C(8A)–O(1A)	1.353(3)
O(4A)–C(22A)–C(19A)	125.6(4)	C(14A)–O(2A)	1.336(12)
		C(15A)–O(3A)	1.444(3)
C(9A)–C(8A)–O(1A)–C(7A)	5.8(5)	C(16A)–O(3A)	1.361(3)
C(13A)–C(8A)–O(1A)–C(7A)	−172.6(3)	C(22A)–O(4A)	1.187(5)
C(1A)–C(7A)–O(1A)–C(8A)	167.3(3)	C(23A)–O(5A)	1.435(3)
C(17A)–C(16A)–O(3A)–C(15A)	13.8(4)	C(24A)–O(5A)	1.363(3)
C(21A)–C(16A)–O(3A)–C(15A)	−166.0(3)	C(30A)–O(6A)	1.179(4)
C(3A)–C(15A)–O(3A)–C(16A)	169.1(2)		
C(29A)–C(24A)–O(5A)–C(23A)	2.9(4)		
C(25A)–C(24A)–O(5A)–C(23A)	−177.9(3)		
C(5A)–C(23A)–O(5A)–C(24A)	−167.7(2)		

Table 4 Atomic coordinates and thermal parameters for **2**

	x	*y*	*z*	U(eq)
C(1A)	11977(2)	4847(2)	3595(2)	56(1)
C(2A)	11053(2)	5141(2)	3597(2)	53(1)
C(3A)	10394(2)	4652(2)	3974(2)	50(1)
C(4A)	10655(2)	3868(2)	4338(2)	50(1)
C(5A)	11583(2)	3580(2)	4313(2)	53(1)
C(6A)	12243(2)	4072(2)	3959(2)	57(1)
C(7A)	12704(2)	5360(2)	3216(2)	70(1)
C(8A)	13376(2)	6221(2)	3689(2)	62(1)
C(9A)	14099(2)	6252(2)	2946(2)	79(1)
C(10A)	14787(3)	6651(3)	2867(2)	97(1)
C(11A)	14773(3)	7018(3)	3508(3)	105(1)
C(12A)	14056(3)	6970(3)	4253(3)	103(1)
C(13A)	13355(2)	6580(2)	4346(2)	79(1)
C(14A)	15548(4)	7415(5)	3378(4)	179(3)
C(15A)	9381(2)	4957(2)	4026(2)	61(1)
C(16A)	8329(2)	4469(2)	3639(2)	61(1)
C(17A)	7566(2)	5147(2)	3995(2)	69(1)
C(18A)	6676(2)	5161(2)	4035(2)	80(1)
C(19A)	6529(2)	4510(2)	3724(2)	78(1)
C(20A)	7303(3)	3829(2)	3372(2)	87(1)
C(21A)	8194(2)	3801(2)	3333(2)	80(1)
C(22A)	5575(3)	4541(3)	3766(3)	107(1)
C(23A)	11886(2)	2742(2)	4692(2)	66(1)
C(24A)	12097(2)	2309(2)	5926(2)	57(1)
C(25A)	11873(2)	2534(2)	6704(2)	64(1)
C(26A)	12216(2)	1971(2)	7192(2)	65(1)
C(27A)	12804(2)	1174(2)	6910(2)	65(1)
C(28A)	13021(3)	966(2)	6141(2)	81(1)
C(29A)	12667(3)	1520(2)	5641(2)	73(1)
C(30A)	13201(3)	569(3)	7415(3)	89(1)
C(31A)	13233(2)	3779(3)	3977(2)	87(1)
C(32A)	10765(3)	5979(2)	3207(2)	78(1)
C(33A)	9931(2)	3353(2)	4747(2)	69(1)
O(1A)	12666(1)	5835(1)	3844(1)	71(1)
O(2A)	15710(9)	7529(17)	4016(8)	211(9)
O(2A′)	15310(20)	8138(15)	3771(15)	147(11)
O(3A)	9245(1)	4389(1)	3560(1)	66(1)
O(4A)	5387(2)	4038(3)	3477(2)	140(1)
O(5A)	11720(2)	2927(1)	5494(1)	71(1)
O(6A)	13052(2)	678(2)	8087(2)	119(1)
C(1B)	6194(2)	3590(2)	101(2)	55(1)
C(2B)	6481(2)	2923(2)	−428(2)	56(1)
C(3B)	6428(2)	2105(2)	−134(2)	56(1)
C(4B)	6065(2)	1955(2)	691(2)	57(1)
C(5B)	5824(2)	2618(2)	1217(2)	55(1)
C(6B)	5893(2)	3440(2)	921(2)	56(1)
C(7B)	6208(2)	4470(2)	−237(2)	68(1)
C(8B)	7389(2)	5206(2)	−1065(2)	63(1)
C(9B)	6737(3)	5839(2)	−1270(2)	78(1)
C(10B)	7048(4)	6494(2)	−1772(2)	90(1)
C(11B)	7990(4)	6521(3)	−2060(2)	93(1)
C(12B)	8625(3)	5875(3)	−1855(2)	98(1)
C(13B)	8330(3)	5230(2)	−1361(2)	79(1)
C(14B)	8341(5)	7208(4)	−2580(3)	136(2)
C(15B)	6772(2)	1397(2)	−719(2)	68(1)
C(16B)	6198(2)	911(2)	−1570(2)	62(1)
C(17B)	7074(2)	381(2)	−1983(2)	81(1)
C(18B)	7164(3)	−133(2)	−2564(2)	90(1)
C(19B)	6405(3)	−138(2)	−2737(2)	74(1)
C(20B)	5543(3)	386(3)	−2325(3)	98(1)
C(21B)	5426(3)	917(3)	−1743(2)	97(1)
C(22B)	6539(4)	−716(3)	−3350(2)	102(1)
C(23B)	5544(2)	2435(2)	2097(2)	67(1)
C(24B)	6387(2)	1868(2)	2959(2)	62(1)
C(25B)	7258(3)	1622(2)	3039(2)	79(1)
C(26B)	7321(3)	1281(2)	3737(2)	84(1)
C(27B)	6506(3)	1190(2)	4392(2)	78(1)
C(28B)	5637(3)	1458(2)	4314(2)	80(1)
C(29B)	5563(2)	1792(2)	3608(2)	71(1)
C(30B)	6553(4)	796(3)	5136(3)	104(1)
C(31B)	5654(3)	4139(2)	1497(2)	80(1)
C(32B)	6838(3)	3084(3)	−1324(2)	84(1)
C(33B)	5911(3)	1085(2)	1010(2)	85(1)
O(1B)	7185(1)	4521(1)	−588(1)	69(1)
O(2B)	7909(4)	7761(3)	−2826(3)	192(2)
O(3B)	6019(1)	1446(1)	−980(1)	75(1)
O(4B)	5944(3)	−828(3)	−3518(2)	152(1)
O(5B)	6417(1)	2175(1)	2228(1)	71(1)
O(6B)	7297(3)	480(2)	5231(2)	136(1)
C(1C)	1079(2)	−1534(2)	337(2)	62(1)
C(2C)	1221(2)	−763(2)	−35(2)	57(1)
C(3C)	1024(2)	−61(2)	430(2)	57(1)
C(4C)	603(2)	−109(2)	1270(2)	61(1)
C(5C)	399(2)	−871(2)	1631(2)	64(1)
C(6C)	658(2)	−1594(2)	1173(2)	66(1)
C(7C)	1450(2)	−2326(2)	−156(2)	78(1)
C(8C)	892(2)	−3310(2)	−592(2)	74(1)
C(9C)	1787(3)	−3810(3)	−960(3)	114(2)
C(10C)	1912(3)	−4559(3)	−1311(3)	120(2)
C(11C)	1183(3)	−4817(2)	−1313(2)	87(1)
C(12C)	286(3)	−4333(3)	−903(4)	135(2)
C(13C)	136(3)	−3576(3)	−552(3)	131(2)
C(14C)	1371(4)	−5613(3)	−1718(3)	118(2)
C(15C)	1335(2)	729(2)	47(2)	67(1)
C(16C)	2538(2)	1380(2)	52(2)	67(1)
C(17C)	2344(3)	2040(2)	−434(2)	81(1)

Table 4 continued

	x	*y*	*z*	U(eq)
C(18C)	2842(3)	2673(2)	−600(2)	91(1)
C(19C)	3508(3)	2629(2)	−284(2)	78(1)
C(20C)	3672(3)	1971(2)	214(3)	90(1)
C(21C)	3197(3)	1354(2)	379(3)	88(1)
C(22C)	4057(3)	3273(3)	−481(3)	105(1)
C(23C)	−53(2)	−923(3)	2526(2)	80(1)
C(24C)	504(2)	−1214(2)	3601(2)	72(1)
C(25C)	−395(2)	−898(2)	4173(2)	74(1)
C(26C)	−511(3)	−903(2)	4962(2)	78(1)
C(27C)	238(3)	−1213(2)	5199(2)	76(1)
C(28C)	1138(3)	−1532(3)	4612(3)	92(1)
C(29C)	1274(3)	−1526(3)	3822(2)	90(1)
C(30C)	36(4)	−1212(3)	6064(3)	107(1)
C(31C)	1569(2)	−684(2)	−933(2)	81(1)
C(32C)	386(3)	653(2)	1764(2)	85(1)
C(33C)	495(3)	−2429(2)	1564(3)	101(1)
O(1C)	674(2)	−2554(1)	−229(2)	82(1)
O(2C)	776(3)	−5887(3)	−1747(3)	176(2)
O(3C)	2131(2)	719(1)	243(2)	76(1)
O(4C)	4032(3)	3849(2)	−911(2)	133(1)
O(5C)	717(2)	−1222(2)	2799(1)	89(1)
O(6C)	615(3)	−1525(3)	6329(2)	149(1)

Equivalent isotropic *U*eq defined as one-third of the trace of the orthogonalized **U***ij* tensor

molecules are crystallographically and conformationally nonequivalent. The spacial orientations of the three *p*-oxybenzaldehyde moieties with respect to the core differ within the molecule and among the molecules. One of the aldehyde oxygens of molecule A is disordered. The C–Br bond length in **1** is 1.958 Å and the C–O bond, formed by replacing the bromine atom in **1** by *p*-oxybenzaldehyde moiety, in **2** is 1.438 Å.

There has been significant interest in structures with Z′ > 1 [13–16]. Among the structures published in the Cambridge Structural Database, 8.8% of all structures and 11.5% of organic structures had Z′ > 1 [16]. Steed and his co-workers have identified several types of intermolecular interactions which can lead to crystal structures with Z′ > 1. They termed this as ‘‘synthon frustration’’ [13]. The compound **2** has an unusual Z′ value of 3. The 3D supramolecular structure of **2** via hydrogen bonding interactions is shown in Fig. 6. The crystal data and the structure refinement parameters of **1** and **2** are summarized in Table 1. The C–H···O hydrogen bonding interactions between the molecules in **2** are presented in Table 2. Selected bond lengths (Å), bond angles (°), and torsion angles (°) for **2** are listed in Table 3. Atomic coordinates and thermal parameters of the non-hyrdrogen atoms of the **2** are listed in Table 4.

Conclusions

In summary, 1,3,5-tris(bromomethyl)-2,4,6-trimethylbenzene and 2,4,6-trimethyl-1,3,5-tris(4-oxymethyl-1-formylphenyl) benzene have been successfully synthesized and characterized. The 3D network structure of **2** is stabilized by the C–H···O hydrogen bonding interactions. The title compound **2** has an unusual Z′ value of 3. This compound could be used as a supramolecular synthon to construct polynucleating ligands by exploiting the reactivity of the benzaldehyde moiety.

Supplementary Material

CCDC #765840 and CCDC # 708245 contain the supplementary crystallographic data for this article. This data can be obtained free of charge at http://www.ccdc.cam.ac.uk/data_request/cif [or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44(0)1223-336033; email: deposit@ccdc.cam.ac.uk].

Acknowledgments This research work was carried out with the financial support from the Department of Science and Technology (DST), Government of India, New Delhi. We thank Dr. Babu Varghese, Sophisticated Analytical Instrumentation Facility (SAIF), IIT Madras, Chennai, for his help in solving the crystal structures. Thanks are due to Dr. M. S. Moni, SAIF, IIT Madras, Chennai, for recording the NMR spectra and to the SAIF, CDRI, Lucknow, for recording the mass spectra.

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