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# New Simple and Selective Synthesis of the Mesitylene[4]arene and its Crystal Structure

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**A saddle conformer of mesitylene[4]arene has been synthesised and its crystal structure solved and refined using single crystal X-ray diffraction at 100 K and 293 K. The influence of selected Lewis acids and different solvents on the outcome of the synthesis has been studied.**

*Keywords:* Mesitylene; Calixarene; Lewis acid; X-ray

Calixarenes are one of the most important classes of supramolecular compounds. Synthesis and properties of calixarenes are well known and described in a couple of monographs and review papers [1–5]. However quite often synthesis of these compounds leads to a mixture of conformers. Additionally, most of the systems described in literature are based on *p*-*tert*-butylphenol or hydroxyphenol substrates.

Our previous studies [6–8] proved, that among many Lewis acids used in the synthesis of calixarenes, only SnCl<sub>4</sub> catalyses condensation reaction of 1,3-dimethoxybenzene with aliphatic aldehydes leading to a crown conformer of the octamethoxyresorcinarenes and permethoxypergalloarenes. In this contribution we have extended our previous studies on other benzene derivatives in order to exploit an interesting observation that when compounds such as mesitylene are catalyzed by SnCl<sub>4</sub> in the above reaction, it leads to a selective formation of new mesitylene[4]arene (see Scheme 1).

Although a large number of syntheses of such compounds have been reported [9–14], these syntheses have been much more complicated than the method we proposed.

As a result of reaction of mesitylene (1) with trioxane (2) in CHCl<sub>3</sub> in the presence of equimolar

amount of SnCl<sub>4</sub>, a saddle (1,3-alternate) conformer of mesitylene[4]arene was selectively obtained with 58% yield.

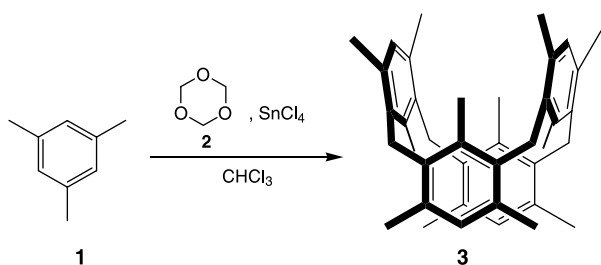
During the performance of the reaction according to Scheme 1, the influence of the amount of SnCl<sub>4</sub> catalyst on yield of mesitylene[4]arene has been analysed. The synthesis of calixarene has been checked in the presence of: 20%, 40%, 60%, 80% or 100% of SnCl<sub>4</sub> as catalyst. In the case of 20% SnCl<sub>4</sub> concentration, the desired product has not been obtained. Yields of mesitylene[4]arene formation in reactions accomplished are collected in Table I. The highest yield (58%) has been reached in the reaction with the equimolar ratio of SnCl<sub>4</sub> to mesitylene, while the smallest yield (26%) was in the case of the reaction with 40% SnCl<sub>4</sub> to mesitylene and trioxane.

In the next step of our studies we have checked a possibility of using some other catalysts of the Lewis acid type instead of SnCl<sub>4</sub> in the synthesis of mesitylene[4]arene (3). Therefore, the next condensation reactions of mesitylene with trioxane in chloroform were carried out in the presence of the following Lewis acids: BF<sub>3</sub>·Et<sub>2</sub>O, AlCl<sub>3</sub>, Al(OiPr)<sub>3</sub>, Ti(OiPr)<sub>4</sub>, TiCl<sub>4</sub>, LaCl<sub>3</sub>, Me<sub>2</sub>SiCl<sub>2</sub>, MeSiCl<sub>3</sub>. Only in the case of the synthesis with BF<sub>3</sub>·Et<sub>2</sub>O as catalyst mesitylene[4]arene (3) has been obtained with the yield of 39%. Experiments with other Lewis acids did not lead to any satisfactory results.

In all cases the reaction product was a complicated mixture of several compounds. Unfortunately, we were unable to separate them by applying column chromatography.

Furthermore, the influence of the solvent type on the synthesis of mesitylene[4]arene (3) with SnCl<sub>4</sub>

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SCHEME 1 Reaction leading to the saddle conformer of mesitylene[4]arene.

TABLE I Yields of synthesis mesitylene[4]arene (3) with  $\text{SnCl}_4$  as catalyst

Amount of $\text{SnCl}_4$ in ratio to mesitylene [%]	Amount of $\text{SnCl}_4$ in ratio to 7.24 mmol mesitylene [mmol]	Yield of reaction [%]
100	7.24	58
80	5.79	49
60	4.30	40
40	2.89	26
20	1.44	–

TABLE II Yields of synthesis mesitylene[4]arene (3) performed in chosen solvents

Solvent	Yield of reaction [%]
$\text{CHCl}_3$	58
$\text{CH}_2\text{Cl}_2$	47
$\text{Et}_2\text{O}$	25
THF	–
Dioxan	–

catalyst has been investigated. Following solvents: methylene chloride, tetrahydrofuran, dioxane and diethyl ether have been used. The course of the reaction of mesitylene with trioxane performed in methylene chloride and in diethyl ether was alike the case of using  $\text{CHCl}_3$ , leading to mesitylene[4]arene (3) with reasonable yields collected in Table II. Other solvents do not give satisfactory results.

The possibility of using different aliphatic aldehydes (acetic, propionic, valeric and isovaleric) to

obtain mesitylene[4]arene with aliphatic groups attached to the methylene linker in the presence of  $\text{SnCl}_4$ , has also been checked. Unfortunately the products, which would be the desired calixarenes with different groups connected to the methylene bridge, have not been obtained.

The saddle structure of mesitylene[4]arene has been confirmed by the X-ray structure. A number of crystal structure of derivatives of this compound have been found in Cambridge Crystallographic Data Center [15]. However, the crystal structure of unsubstituted mesitylene[4]arene has not been found there.

The X-ray structure shows that the calixarene molecule exists in the solid state in the saddle conformation with—in the first approximation—noncrystallographic  $S_4$  symmetry axis (see Fig. 1). This is in line with  $^1\text{H}$  solution NMR characteristic methyl group peaks (C31, C39, C32, C37) appearing at ca.  $\delta = 1.18$  ppm. These signals are shifted towards stronger magnetic field due to the location of the methyl groups inside the calixarene voids. The rest of the methyl group signals in  $^1\text{H}$ -NMR spectrum appear at  $\delta = 2.34$  ppm.

In the solid state mesitylene[4]arene (3) crystallizes in the triclinic P-1 space group symmetry with the unit cell parameters defined in the **Experimental part**. The lengths of all the unit cell parameters, **a**, **b** and **c**, are larger at room temperature, although the increment is not the same in all three nonequivalent directions. The space group symmetry of crystals is the same at both 100 K and 293 K. One unit cell contains two molecules of 3 related by inversion centre. At room temperature, there is a disorder of atomic positions of the methyl groups in the crystal. There are two preferred positions of hydrogen atoms in the methyl groups (see Fig. 1(b)). No disorder of the methyl groups is observed at 100 K.

The packing of the molecules in the crystal lattice is governed by weak interactions. At 100 K two molecules of 3 are involved in three types of weak interaction, characterized by the following short

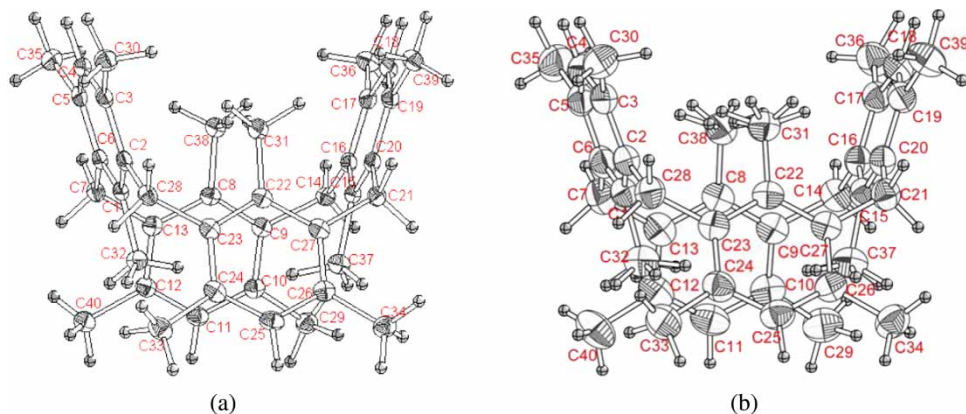


FIGURE 1 Atom labels and thermal ellipsoids (on 50% probability level) for one molecule of mesitylene[4]arene (3) at 100 K (a) and at 293 K (b).

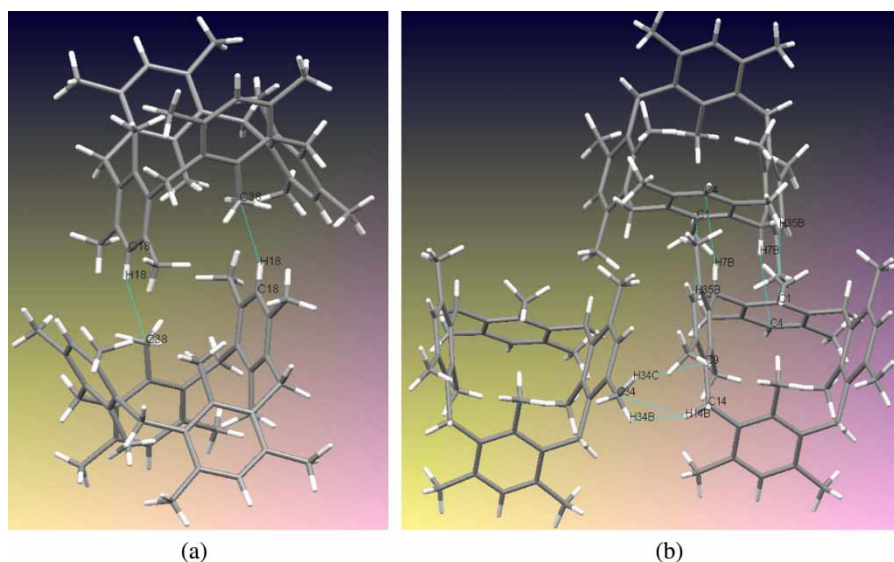


FIGURE 2 Examples of the shortest intermolecular contacts for **3** at 100 K: (a) C(18)H(18)...C(38), (b) C(34)H(34C)...C(9) and C(34)H(34B)...C(14).

TABLE III Geometry of the shortest intermolecular contacts closer than the sum of the van der Waals radii

Temperature	D–H...A	Symm	D–H [Å]	H...A [Å]	D...A [Å]	D–H...A °
T = 100 K	CC(35)H(35B)...C(1)	1 – X, 1 – Y, – Z	0.98	2.84	3.707(2)	148.6(12)
	C(7)H(7B)...C(4)	1 – X, 1 – Y, – Z	0.98	2.87	3.760(2)	150.8(11)
	C(34)H(34C)...C(9)	1 + X, Y, Z	1.03	2.88	3.718(2)	138.6(11)
	C(29)H(29A)...C(19)	1 – X, 2 – Y, 1 – Z	0.95	2.77	3.424(2)	129.1(13)
	C(18)H(18)...C(38)	1 – X, 1 – Y, 1 – Z	0.99	2.82	3.698(2)	146.9(11)
	C(39)H(39B)...C(29)	1 – X, 2 – Y, 1 – Z	0.98	2.83	3.424(2)	120.1(12)
	C(14)H(14B)...C(34)	X – 1, Y, Z	1.04	2.85	3.711(2)	139.7(11)
	C(34)H(34A)...C(17)	1 – X, 1 – Y, 1 – Z	0.96	2.83	3.506(4)	129(2)
T = 293 K	C(34)H(34A)...C(17)	1 – X, 1 – Y, 1 – Z	0.96	2.83	3.506(4)	129(2)

contacts: (a) [C–H... $\pi$  electrons] hydrogen bond like interactions of the C–H dipoles from the methyl groups with the  $\pi$  electrons of the aromatic rings from the neighbouring molecules, (b) repulsive C–H...C contacts between hydrogen atoms attached to the aromatic carbons and some methyl groups [for example, C(18)–H(18)...C(38), see Fig. 2(a)], and (c) C–H...C between methylene hydrogens and the methyl carbon atoms. The third type of interactions is a consequence of the first one [C–H... $\pi$ , see Fig. 2(b)]. For example, C(34)–H(34C) interacts with aromatic carbon C(9) due to the close proximity of C(14) to C(34)–H(34B) atoms (for numerical details see Table III). Because of applying the riding model of the hydrogen atom refinement, the C–H and H...Acceptor bond lengths and intermolecular contacts were not refined and were set at the averaged neutron values.

As one can see the number of close contacts at room temperature are significantly lower than at 100 K.

The most spectacular fragment of the studied compound is its molecular void enclosed in aromatic fragments (see Fig. 3 and Table IV for details). In general, the geometry of the void at room temperature does not differ much from this at

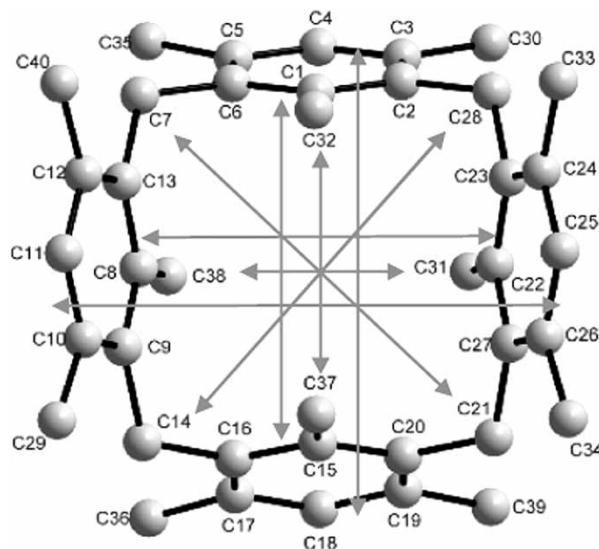


FIGURE 3 Interatomic distances defining the size of the void (for numerical details see (Table IV), and the definition of the best least-squares planes and angles between them: plane 1: C1,C2,C3,C4,C5, C6; plane 2: C8,C9,C10,C11,C12,C13; plane 3: C15,C16,C17, C18, C19, C20; plane 4: C22,C23,C24,C25,C26,C27. Angles between planes [°] at T = 100 K/T = 293 K: (1;2) 83,3/83,6; (2;3) 82,4/84,5; (3;4) 84,8/82,7; (1;4) 83,7/83,0; (1;3) 35,1/35,8; (2;4) 43,9/43,4.



TABLE IV Dimensions of the molecular void

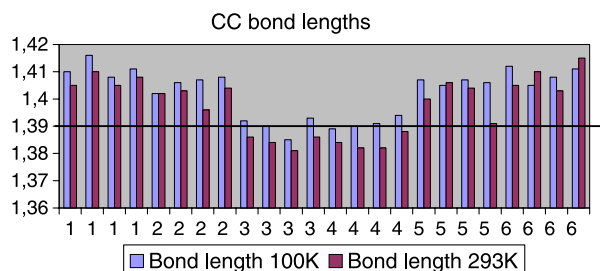
Structural Parameter	Void distances [Å] at:	
	T = 100	T = 293 K
C(4)–C(18)	6.831	6.86
C(11)–C(25)	7.209	7.208
C(31)–C(38)	4.383	4.416
C(32)–C(37)	4.509	4.526
C(8)–C(22)	5.176	5.196
C(1)–C(15)	5.185	5.196
C(7)–C(21)	7.217	7.244
C(14)–C(28)	7.252	7.218

100 K. The cavity is closed by planar aromatic fragments. These fragments can be used to define the best least-squares planes (see Fig. 3). It appears that the pairs of planes based on the neighbouring fragments form angles from 82° up to 85°, whereas the planes based on fragments which face each other form angles *ca.* 35° and 43°. An approximate size of the cavity is *ca.* 5 Å by 5 Å with the shortest interatomic distance equal to 4.4 Å.

As far as bond lengths are concerned (Scheme 2), the average numerical values are shown in Fig. 4 (at both temperatures, bold values for 100 K). On average there is a certain small increase of the bond lengths with temperature.

Variation of the bond lengths at both temperatures is shown in Scheme 2. Again almost all bonds at the higher temperature are a bit longer than those at 100 K. The line drawn at 1.39 Å illustrates the average bond lengths in the benzene molecule. Comparing to this value, most of the bond lengths in the compound studied are a bit longer. Of course bonds 1 and 6, 2 and 5 or 3 and 4 (Scheme 2) have similar values. However, the charge in this compound seems to be localised only in bonds 3 and 4 which are becoming significantly shorter.

In conclusions we describe a simple and efficient synthesis of a saddle conformer of mesitylene[4]arene. There is a significant influence of a chosen Lewis acids and solvents on the yield of mesitylene[4]arene (3) and formation of monocrystals. The crystal structure showed that there was a disorder of atomic



SCHEME 2 The CC bond distribution. The average bond length in benzene displayed as a constant line at 1.39 Å.

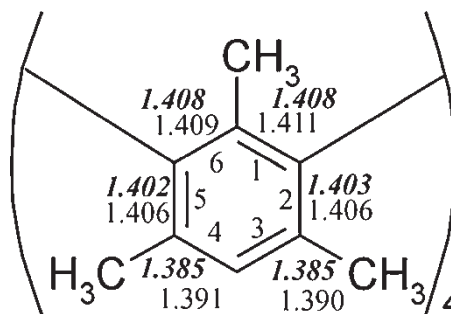


FIGURE 4 The definition of bonds (see Scheme 2) and the average bond lengths for the aromatic fragments.

positions in room temperature. We hope that this simple reaction could be a very useful and general way to produce synthesise other calixarenes.

## EXPERIMENTAL PART

### Synthesis of Mesitylene[4]arene (3)

To a solution of mesitylene (1.00 ml, 7.24 mmol) and trioxane (0.65 g, 7.24 mmol) in  $\text{CHCl}_3$  (15 ml)  $\text{SnCl}_4$  (0.77 ml, 7.24 mmol) was added and the reaction mixture was stirring for 2 h at room temperature. Then methanol (30 ml) was added. The precipitated white solid was collected and washed with methanol. The crude product was purified by column chromatography with  $\text{CHCl}_3/\text{CH}_3\text{OH}$  (1/5) as eluent to give pure mesitylene[4]arene (1.21 g, 58%) as white crystals: m.p. > 300°.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 303 K, 400 MHz,  $\delta$ [ppm]): 1.18 (s, 12 H,  $\text{CH}_3$ ), 2.34 (s, 24 H,  $\text{CH}_3$ ), 3.88 (s, 8 H,  $\text{CH}_2$ ), 6.70 (s, 4 H, ArH);  $^{13}\text{C}$  NMR (100 MHz) ( $\text{CDCl}_3$ , 303 K, 100 MHz,  $\delta$ [ppm]): 17.93, 21.39, 31.89, 130.29, 133.20, 135.87, 137.60; IR [ $\text{cm}^{-1}$ ]: (756, 860, 944, 1024, 1216, 1448, 2936); HR-MS (70 eV): m/z (%): calc 528.3756, found 528.3785.

### Both X-ray Diffraction Measurements

(at 293 K and 100 K) were carried out on a single crystal X-ray  $\kappa$ -axis KM4CCD diffractometer [16] with graphite-monochromated  $\text{MoK}\alpha$  radiation using the omega scan technique. Both crystals were positioned at 65 mm from the CCD 1024 × 1024 pix. Camera. The  $2\theta$  angle range goes from *ca.* 3° up to 50°. Each frame was measured with 1° angle interval and counting time 24 s and 26 s for the normal and low temperatures, respectively. Due to the relatively low absorption coefficient in both measurements no absorption correction was applied. Data reduction and analysis were carried out with the CRYSTALIS RED. The structure was solved by direct methods [17] and refined using SHELXL [18]. The refinement was based on  $F^2$  for all reflections except those with very negative  $F^2$ . Most of the hydrogen atoms were

located in idealized averaged geometrical positions. Scattering factors were taken from Tables 6.1.1.4 and 4.2.4.2 in ref. [19].

Formula  $C_{40}H_{48}$ ;  $fw = 528$ ,  $\lambda = 0.71073 \text{ \AA}$ ,  $T = 293 \text{ K}$ , crystal system triclinic, space group, P-1, unit cell dimensions:  $a = 10.518(4) \text{ \AA}$ ,  $b = 10.855(4) \text{ \AA}$ ,  $c = 14.325(5) \text{ \AA}$ , cell volume =  $1538.41 \text{ \AA}^3$ ,  $Z = 2$ ; calculated density =  $1.142 \text{ Mg/m}^3$ . Max.  $2\theta$  equal to  $50^\circ$  because of relatively weak higher angle reflection intensities. The data collection range gave 29602 reflections collected and 7490 unique with  $R_{\text{int}} = 0.0476$  and  $R_{\text{sig}} = 0.0310$ . The refinement was based on  $F^2$  for all reflections. The  $R_1$  factor for  $F_0^2 > 4\sigma(F_0^2)$  reflections is equal to  $R_1 = 0.0571$ ,  $\text{GooF} = 0.991$  and for all reflections  $R_1 = 0.077$ .  $wR2 = 0.179$ ;  $\text{Weight} = 1/[\sigma^2(F_o^2) + (0.1224*P)^2]$  where  $P = (\text{Max}(F_o^2, 0) + 2*F_c^2)/3$ ;  $F(000) = 576.0$ ; calculated absorption coefficient =  $0.06 \text{ mm}^{-1}$ ; largest diff. peak and hole:  $0.30$  and  $-0.24 \text{ e\AA}^{-3}$ . The extinction coefficient was refined and is equal to  $0.022144$ .

$T = 100 \text{ K}$ , crystal system triclinic, space group, P-1, unit cell dimensions:  $a = 10.431(1) \text{ \AA}$ ,  $b = 10.728(1) \text{ \AA}$ ,  $c = 14.209(1) \text{ \AA}$ , cell volume =  $1500.3 \text{ \AA}^3$ ,  $Z = 2$ ; calculated density =  $1.170 \text{ Mg/m}^3$ . Max.  $2\theta$  equal to  $50^\circ$ . The data collection range gave 27748 reflections collected and 5051 unique with  $R_{\text{int}} = 0.0291$  and  $R_{\text{sig}} = 0.0272$ . The refinement based on  $F^2$  for all reflections.  $R_1 = 0.0394$ ,  $\text{GooF} = 1.065$  for  $F_0^2 > 4\sigma(F_0^2)$  reflections are and for all reflections  $R_1 = 0.0518$ .  $wR2 = 0.1246$ ;  $\text{weight} = 1/[\sigma^2(F_o^2) + (0.0840*P)^2]$  where  $P = (\text{Max}(F_o^2, 0) + 2*F_c^2)/3$ ; largest diff. peak and hole:  $0.19$  and  $-0.23 \text{ e\AA}^{-3}$ .  $F(000) = 576.0$ ;  $Z = 2$ ; calculated absorption coefficient =  $0.07 \text{ mm}^{-1}$ . The extinction coefficient was refined and is equal  $0.01029$ .

### Acknowledgements

The X-ray measurements were undertaken in the Crystallographic Unit of the Physical Chemistry Lab. at the Chemistry Department of the University of Warsaw.

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### SUPPORTING INFORMATION AVAILABLE

Full crystallographic data (excluding structure factors) for the structures reported in this work have been deposited with the Cambridge Crystallographic Data Center and allocated the deposition numbers: CCDC 285312 & 285313. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EW, UK (Fax: Int code + (1223)336-033; E-mail: deposit @ ccdc.cam.ac.uk).