Archive for
Organic Chemistry

The Free Internet Journal
for Organic Chemistry

Paper

Arkivoc **2017**, part v, 159-171

Solvent-free synthesis of (poly)thiacalix[*n*]arenes: the evaluation of possible mechanism based on semi-preparative HPLC separation and mass-spectrometric investigation of the reaction products

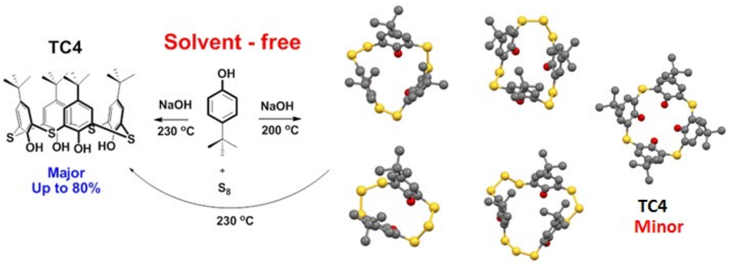
Igor S. Kovalev,[a,†] Matiur Rahman,[a,†] Leila K. Sadieva,[a] Dmitry E. Pavlyuk,[a] Kousik Giri,*[c] Sougata Santra,*[a] Dmitry S. Kopchuk,[a,b] Grigory. V. Zyryanov,[a,b] Adinath Majee,[d] Oleg N. Chupakhin,[a,b] and Valery N. Charushin[a,b]

[a] *Department of Organic and Biomolecular Chemistry, Chemical Engineering Institute, Ural Federal University, 19 Mira Street, Yekaterinburg, K-2, 620002, Russian Federation*
[b] *I. Ya. Postovskiy Institute of Organic Synthesis, Ural Division of the Russian Academy of Sciences, 22 S. Kovalevskoy Str., Yekaterinburg, 620219, Russian Federation*
[c] *Centre for Computational Sciences, School of Basic and Applied Sciences, Central University of Punjab, City Campus, Mansa Road, Bathinda-151001, India*
[d] *Department of Chemistry, Visva-Bharati (A Central University), Santiniketan-731235, India*
† Dr. Igor S. Kovalev and Dr. Matiur Rahman contributed equally to this article
Email: sougatasantra85@gmail.com, kousikgiri@gmail.com

Received 05-23-2017 **Accepted** 07-15-2017 **Published on line** 08-29-2017

Abstract

The interaction between *p-tert*-butylphenol and elemental sulfur (S_8) in alkaline condition in absence of solvent at 150-170 °C have been studied. (Poly)thiacalix[*n*]arenes with the phenol units connected by bi- and trisulfide bridges have been detected and characterized based on the MS data.



Keywords: (Poly)thiacalix[*n*]arenes, solvent-free synthesis, mechanistic investigation, mass-spectroscopic investigation, DFT-studies

Introduction

Thiacalix[4]arenes[1] are relatively new class of the family of calix[*n*]arenes.[2] Due to the presence of four sulfur atoms in their macrocycle and thus *c.a.* 15% larger cavity as compared to calix[4]arenes[3] these host molecules are of growing interest in terms of their advanced coordinations chemistry ("host-guest" complexes).[4] For instance, thiacalix[4]arenes exhibits advanced coordination ability towards *d*-elements, especially toward Hg^{2+},[5] and, more importantly, $^{226}Ra^{2+}$ cations.[6] Recently, some thiacalix[4]arene-supported heterodinuclear Ni(II)–Ln(III) (Ln = Gd, Tb, Dy) complexes have been reported and the magnetic relaxation behavior for some of them have been described.[7] In addition, thiacalix[4]arenes exhibit some physiological activity, for instance as potential inhibitors of protein tyrosine phosphatase 1B.[8]

The very first *p*-*tert*-butylthiacalix[4]arene synthesis was reported by Sone and co-authors[9] *via* stepwise reactions of *p*-*tert*-butylphenol and SCl_2. The most common approach for the thiacalix[4]arene synthesis so far reported is the condensation of *p*-R-phenol and elemental sulfur (S_8) under basic conditions in high boiling solvent at the temperature above 170 °C. According to the accepted mechanism reported by Patel *et al.*,[10] the formation of thiacalix[4]arenes occurs *via* their acyclic precursors (the kinetic products), *i.e.* polyphenolates, having one sulfur atom between the phenol moieties along with some less-stable polysulfide phenolates. As a last step the high-temperature cyclocondensation reaction affords the thiacalix[4]arene as a thermodynamic product.[10,11] The formation of larger thiacalix[*n*]arenes (*n* = 6, 8) as side-products has also been reported.[12-15] On the other hand disulfide- and polysulfide-bridged polymers are commonly obtained in the reaction of S_8 and polyenes.[16,17] In addition, the di- and tetrasulfide-bridged macrocycles are obtained in the reaction of substituted phenols with disulfur dichloride.[18] Recently, Dehaen and co-authors reported the preparation of disulfide-bridged [2^n]pillararene-like macrocyles in good yields.[19]

Herein, we report the synthesis of *p*-*tert*-butylthiacalix[4]arene as well as the formation of some di- and trisulfide-bridged macrocycles, *i.e. (*poly)thiacalix[*n*]arenes, *via* the one-pot solvent-free reaction of *p*-*tert*-butylphenol with S_8 in the presence of NaOH.

Results and Discussion

The reaction between phenol in a form of phenolate anion and S_8 affords linear oligomers with various degree of polysulfidity.[4] Subsequent homolytic cleavage of the -S-S- bonds in these oligomers affords monosulfide oligomers as well as some mercaptophenols. The chemical activity of polysulfide-containing macromolecules is stipulated by two main factors: (i) the mobility and electron donating ability of sulfur atoms in mercaptane end groups; (ii) the reduced bond energy in di- and polysulfide moieties compare to monosulfide ones, *i.e.* –S–S– *vs.* –C–S– bonds. The last factor sets the basic condition for exchange reactions in oligomer bulk and in the area of its contact with other compounds.[20] The (poly)sulfide bond chemistry in organic solutions is well reported with regard to dynamic combinatorial chemistry.[19,21-25]

Based on the proposed mechanism,[10] *tert*-butyphenol reacts with S_8 in a high-boiling solvent (tetraglyme or diphenyl ether) to afford a mixture of mono- and polysulfide bridged linear oligomers as kinetic products. While heating the reaction mixture to 230 °C affords the most thermodynamically stable thiacalix[4]arene. The use of lower-boiling solvents leads to lower yields of the thiacalix[4]arenes, and no solvent-free approaches have been reported so far.

Recently, during our efforts to prepare pillar[*n*]arenes, we found that under the solvent-free conditions the reaction afforded mainly kinetic products, *i.e.* pillar[6]arenes as major products.[26] With this in mind that under the solvent-free conditions the kinetic products may be isolated, we studied the reaction between *tert*-butylphenol and S_8 using two different reaction conditions.

Table 1. ESI-MS data for the proposed linear oligomers

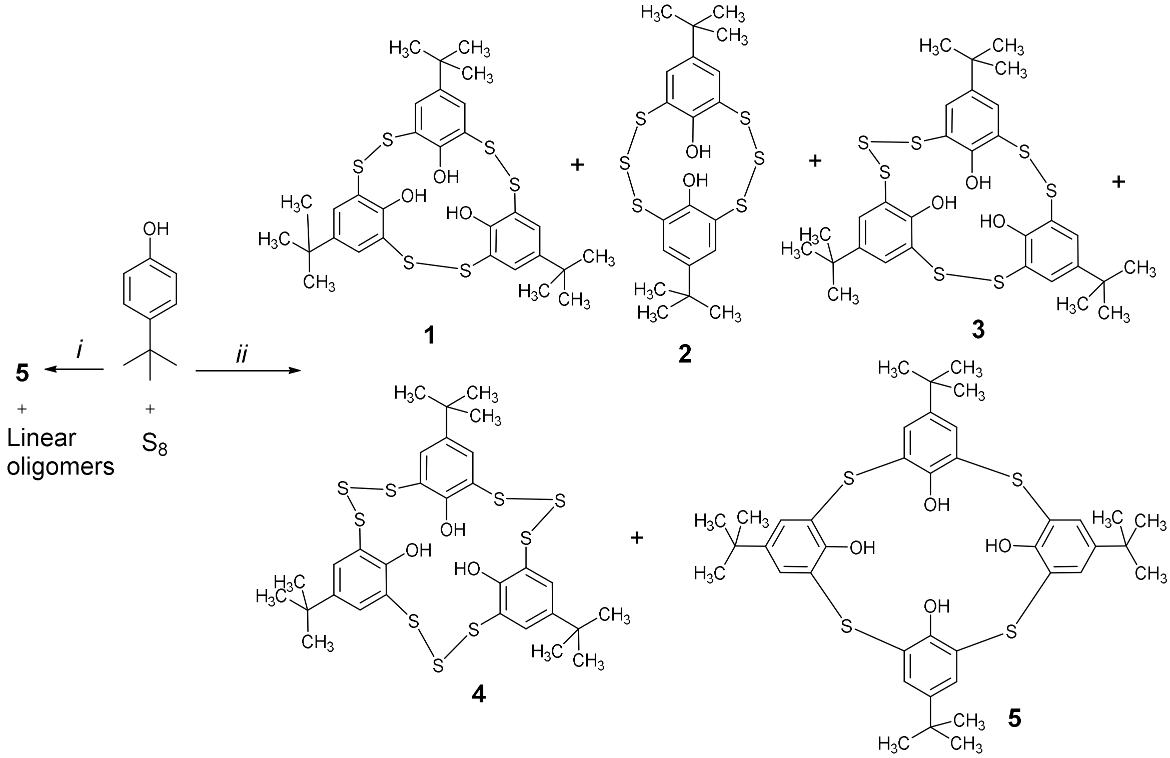
Entry	Proposed formula of the linear oligomer	Found [M-H]$^-$: *m/z* (%)	Calculated [M-H]$^-$, *m/z*
1	$H(C_{10}H_{12}OS)H$	181.0690 (10.15)	181.068162
2	$H(C_{10}H_{12}OS)SH$	213.0409 (14.15)	213.040233
3	$H(C_{10}H_{12}OS)S_2H$	245.0201 (0.69)	245.012304
4	$H(C_{10}H_{12}OS)_2H$	361.1325 (10.50)	361.129048
5	$H(C_{10}H_{12}OS)_3H$	541.1911 (29.52)	541.189934
6	$H(C_{10}H_{12}OS)_3SH$	573.1612 (16.54)	573.162005
7	$H(C_{10}H_{12}OS)_4H$	721.2503 (25.92)	721.250820
8	$H(C_{10}H_{12}OS)_4SH$	753.2199 (24.22)	753.222891
9	$H(C_{10}H_{12}OS)_4S_2H$	785.1877 (10.73)	785.194962
10	$H(C_{10}H_{12}OS)_4S_3H$	817.1558 (3.66)	817.167033
11	$(C_{10}H_{12}OS)_4(C_{10}H_{12}O)H_2$	869.3342 (8.02)	869.339635
12	$H(C_{10}H_{12}OS)_5H$	901.3097 (6.32)	901.311706

In our method, all reactions were carried out in the presence of 0.5 equiv. of NaOH as an important template. In a first case, to confirm the possibility of the formation of thiacalix[4]arenes the reaction mixture was heated at 170 °C for 3 h and then at 220-230 °C for 24 h (Scheme 1, way *i*) (a minimum amount of *o*-xylene was used to remove any trace of water from the reaction mass by slow distillation to make the reaction mass super dry and after that *o*-xylene was removed). According to our expectation the dynamic nature of di- and polysulfide bridges in initially formed linear oligomers was further explored in the transformation of the Ar-(S)$_n$–S-Ar′ bridges to a Ar-S–Ar′ bridge at higher temperature (230 °C). At this temperature the ease of homolytic cleavage of the di- and polysulfide bridges increases with the number of sulfur atoms in a bridge. At higher temperature thiacalix[4]arene should be formed preferably as it is a thermodynamic product. The ESI-MS-analysis of the reaction mixture after 24 h at 230 °C revealed the presence of only thiacalix[4]arene **5** as major product with the trace amounts of unreacted *tert*-butylphenol and some linear oligomers.

In the second case the reaction mixture was heated at 170 °C for 3 h and then at 200 °C for 3 h (Scheme 1, way *ii*). The ESI-MS analysis of the reaction mixture after the first stage, *i.e.* heating at 170 °C for 3 h, reviled the presence of several types of linear oligomers (Scheme 1, Table 1).

After heating the reaction mixture for 200 °C for 3 h the ESI-MS-analysis of reaction mixture surprisingly revealed the unexpected cyclic oligomers with various ratios of aromatic fragments and sulfide moieties macrocycles **1-4** along with the "classic" thiacalix[4]arene **5** (Figures S1-S5, Tables S1-S5, ESI). The Table 2 indicates the detected products forming under these conditions.

The solvent-free condition's reaction for obtaining **5** was accomplished through *way ii* when the reaction continued at elevated up to 230 °C temperature (see Experimental Section, Method 3).



Scheme 1. Solvent-free synthesis of thiacalix[*n*]arenes **1-5**. Reagents and conditions: *i*: *p*-*tert*-butylphenol (1 equiv.), sulfur (2 equiv.), NaOH (0.5 equiv.), Ar, 150-170 °C, 3 h, then 230 °C, 24 h; *ii*: *p*-*tert*-butylphenol (1 equiv.), sulfur (2 equiv.), NaOH (0.5 equiv.), Ar, 150-170 °C, 3 h, then 200 °C, 3 h.

Table 2. ESI-MS data for the proposed cyclic oligomers

Entry	Macrocycles	Found $[M-H]^-$: *m/z* (%)	Calculated $[M-H]^-$, *m/z*	Proposed structure
1	$(C_{10}H_{12}OS_2)_2$	423.0585 (1.53)	423.057540	
2	$(C_{10}H_{12}OS_2)_2S$	455.0310 (4.35)	455.029611	
3	$(C_{10}H_{12}OS_3)_2$	487.0031 (58.30)	487.001682	**2**
4	$(C_{10}H_{12}OS_3)_2S$	518.9759 (2.10)	518.973753	
5	$(C_{10}H_{12}OS)_3$	539.1769 (2.74)	539.174284	
6	$(C_{10}H_{12}OS)_3S$	571.1505 (9.79)	571.146355	
7	$(C_{10}H_{12}OS)_3S_2$	603.1204 (56.88)	603.118426	
8	$(C_{10}H_{12}OS_2)_3$	635.0926 (100.00)	635.090497	**1**
9	$(C_{10}H_{12}OS_2)_3S$	667.0648 (78.07)	667.062568	**3**
10	$(C_{10}H_{12}OS_2)_3S_2$	699.0362 (11.19)	699.034639	
11	$(C_{10}H_{12}OS)_4$	719.2355 (7.35)	719.235170	**5**
12	$(C_{10}H_{12}OS_3)_3$	731.0074 (20.41)	731.006710	**4**
13	$(C_{10}H_{12}OS)_4S$	751.2071 (14.92)	751.207241	
14	$(C_{10}H_{12}OS)_4S_2$	783.1781 (11.76)	783.179312	
15	$(C_{10}H_{12}OS)_4S_3$	815.1491 (4.67)	815.151383	
16	$(C_{10}H_{12}OS_2)_4$	847.1196 (7.47)	847.123454	
17	$(C_{10}H_{12}OS_2)_4S$	879.0930 (3.42)	879.095525	

HPLC was then used to separate the reaction mixtures (Figures S6-S16, Tables S8-S9, ESI). We have achieved the separation of the reaction mixture to separate peaks in the analytical mode by using 70% acetonitrile and 30% 0.005 M citrate buffer as a mobile phase. Attempts to carry out the preparative separation to isolate the analytically pure samples failed: increasing the amount of the target components in the sample led to overlapping products peaks. However, by using the HPLC technique in manual semi-preparative mode we were able to collect the minimum number of fractions of the eluate containing sufficiently pure products **1-5** to evaluate their ratio in the starting reaction mixture. In addition the mass-spectra of eluates in the direct input mode have been measured. The results of the HPLC and ESI-MS analysis of the products are summarized in Table 3.

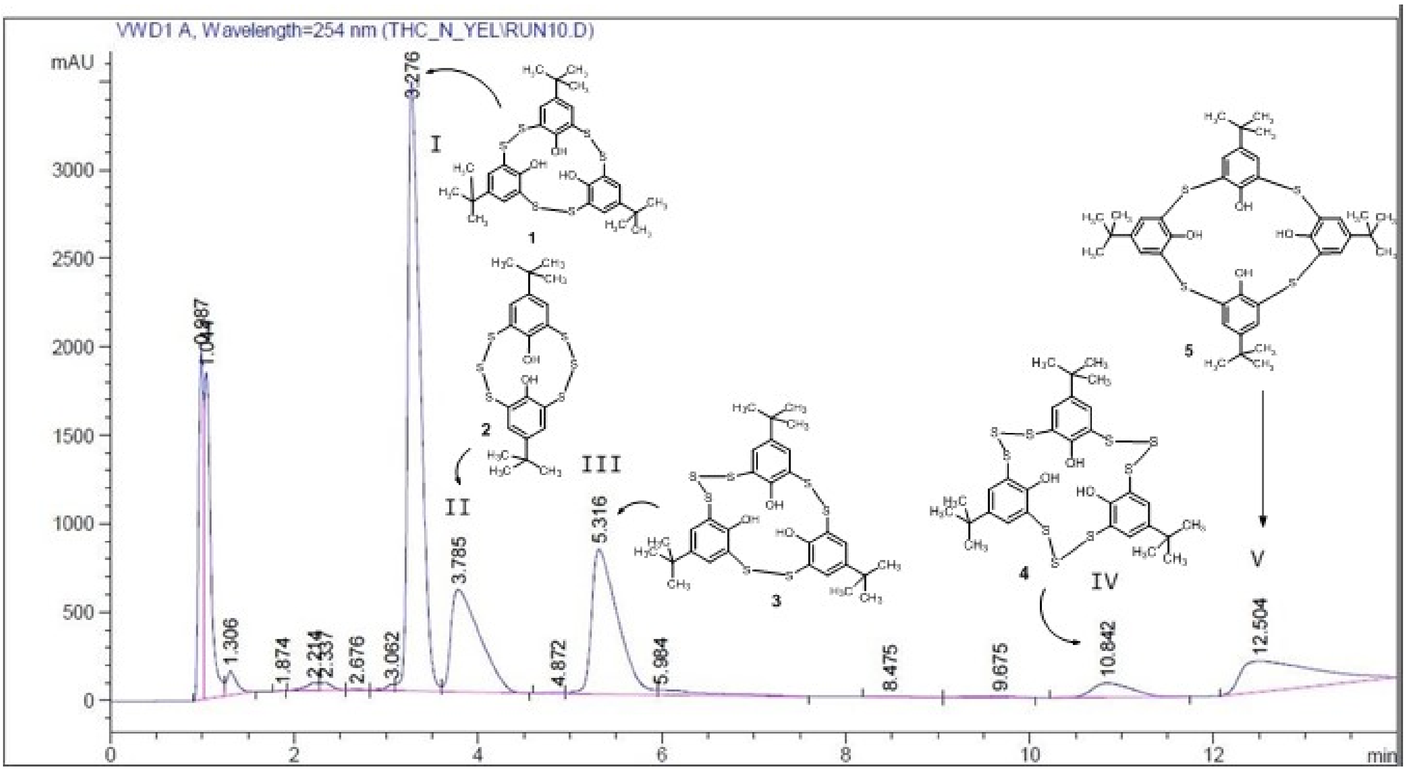


Figure 1. HPLC-analysis for the reaction mixture obtained according to way *ii*.

The stability of the obtained thiacalix[*n*]arenes **1-5** was computationally investigated using density functional theory (DFT) using dispersion corrected[27] B3LYP functional[28,29] and balanced polarized triple zeta basis set of Ahlrichs and co-workers.[30] The gas-phase thermodynamic enthalpies of formation were determined from harmonic frequency calculations in the same level. All the calculations were carried out using Gaussian 09[31] program.

Table 3. Chromatographic separation in a semi-preparative mode

Peak	Retention Time, min	Width, min	Area, [mAU*s]	Height, [mAU]	Area, %	Structure
1	0.987	0.0538	6918.50537	1976.63367	7.4215	N/A
2	1.044	0.0738	9140.85742	1844.36731	9.8054	N/A
3	1.306	0.1141	1088.99829	137.91559	1.1682	N/A
4	1.874	0.0644	9.02060	2.12894	0.0097	N/A

Table 3 (continued)

Peak	Retention Time, min	Width, min	Area, [mAU*s]	Height, [mAU]	Area, %	Structure
5	2.214	0.1368	413.54599	41.65092	0.4436	N/A
6	2.337	0.1216	351.53564	41.60085	0.3771	N/A
7	2.676	0.1353	40.40646	5.00056	0.0433	N/A
8	3.062	0.0916	227.94693	35.19339	0.2445	N/A
9	3.276	0.1448	32703.40101	3442.47095	35.0809	**1**
10	3.785	0.3361	12668.20012	577.17328	13.5891	**2**
11	4.872	0.1638	96.47369	8.67368	0.1035	N/A
12	5.316	0.2953	16156.90103	818.35370	17.3315	**3**
13	5.984	0.4400	1017.34076	28.46395	1.0913	N/A
14	8.475	0.3008	55.37892	2.61743	0.0594	N/A
15	9.675	0.3691	203.21167	7.92698	0.2180	N/A
16	10.842	0.5092	2420.69141	79.74023	2.5967	**4**
17	12.504	0.8030	9710.39648	173.75133	10.4163	**5**
Totals			93222.81179	9223.66275		

Table 4. Energy values calculated for thiacalix[*n*]arene macrocycles **1-5**

Comp.	E_0 (au)	ZPE (au)	H_{corr}(au)	Sum_$\Delta_f H°_0$ (x, 0 K), (kcal/mol)	Sum_x ε_0, (au)	$\Delta_f H°_0$ (M, 0 K), (kcal/mol)	$\Delta_f H°_{298}$ (M, 298 K), (kcal/mol)
1	-3780,5430288	0,5994770	0,6413930	7529,010	-3767,9449656	-0.22	-27.19
2	-3316,827497	0,402542	0,433677	5150,660	-3308,2280588	7.03	-11.05
3	-4178,771208	0,600485	0,643853	7594,670	-4166,0773398	5.96	-21.16
4	-4975,2310112	0,6039850	0,6515050	7725,990	-4962,3420882	17.07	-9.54
5	-3447,8116392	0.793272	0.843154	9776.040	-3431.3971240	-26.44	-61.98

From the calculations we can observe that among macrocycles **1-5** thiacalix[4]arene **5** is the mostly thermodynamically stable, which is at first confirmed by the literature data,[10] and, at second, can be seen from the DFT calculation on the basis of enthalpy calculations ($\Delta_f H°_0$ and $\Delta_f H°_{298}$) (Table 4, entry 5). The stability of four other thiacalixarenes, namely **1-4,** decreases in the following order **1** > **3** > **2** > **4**, *i.e.* macrocycle **1** is the most stable, which can be seen from the basis of enthalpy calculations ($\Delta_f H°_0$ and $\Delta_f H°_{298}$). We can also conclude that among the macrocycles **1-4** the macrocycles with three phenol units connected by two sulfur atoms, *i.e.* **1** and **3**, exhibit much lower enthalpy, which suggests these compounds to have higher stability than the macrocycles containing either two or three phenol units connected by three sulfur atoms. This observation is consistent with the experimental observations that show that the macrocycle with two phenol subunits, *i.e.* compound **2**, can be initially detected in the reaction mixture, but it readily decomposes upon standing in DMSO solution.

The proposed mechanism for the formation of products **1-4** is presented below. Thus, like in case of solvent-mediated method[10] the homolytic cleavage of -S-S- bond in S_8 affords the biradical **A**. Then interaction of **A** with phenolate anion and phenol affords connected by polysulfide bridges linear oligomers and their radicals, namely **B-E**, with various stoichiometry (Scheme 2).

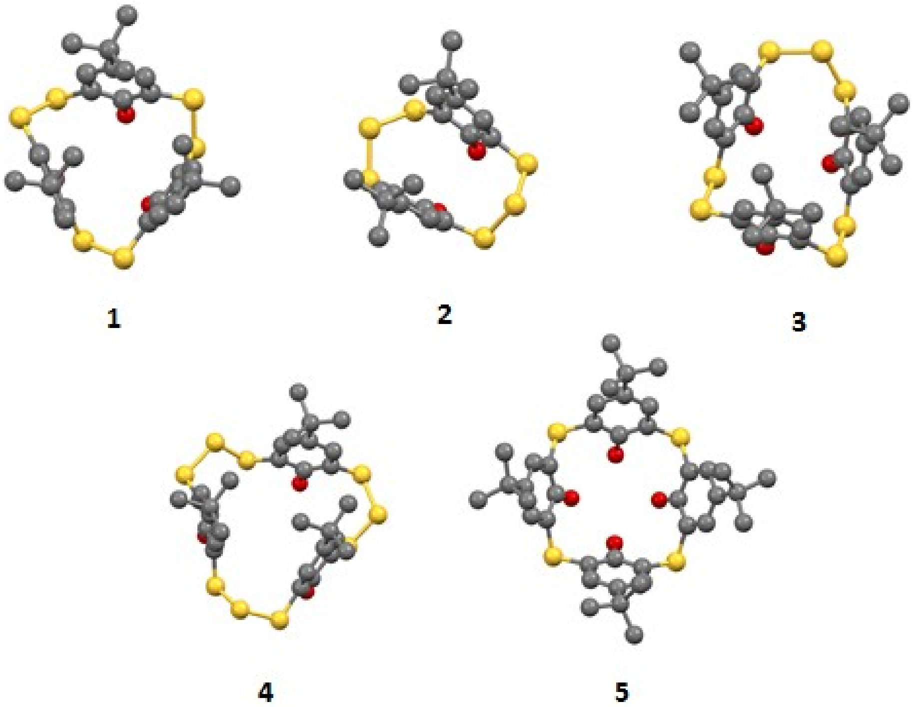
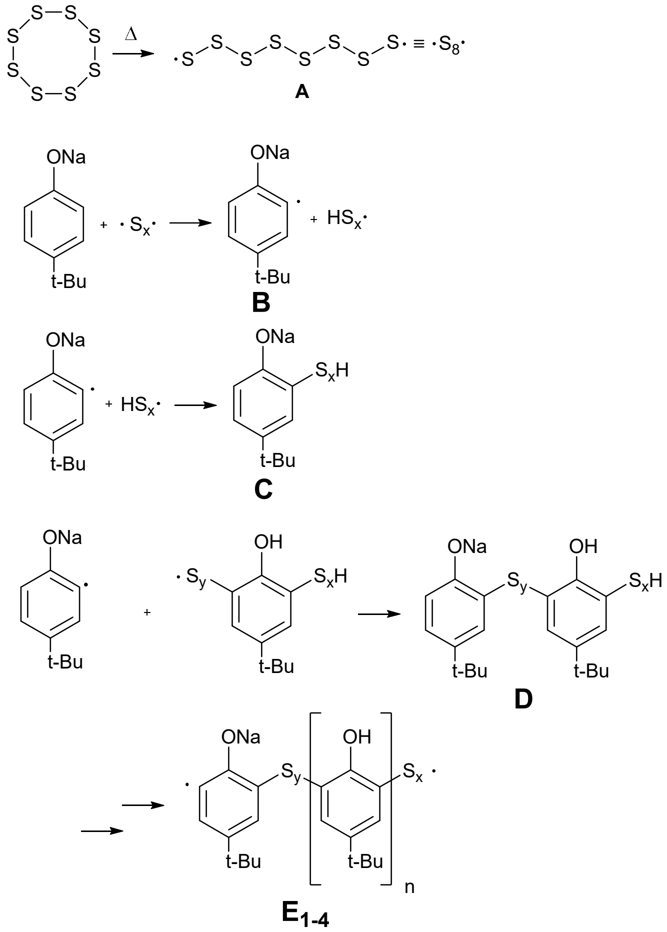
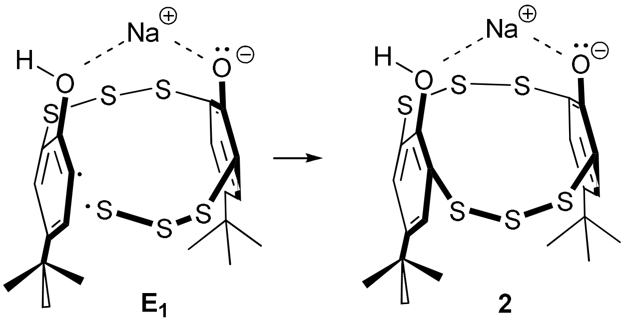


Figure 2. Computed (B3LYP-D3/def2-TZVP) most stable geometries for thiacalixarenes **1-5**.



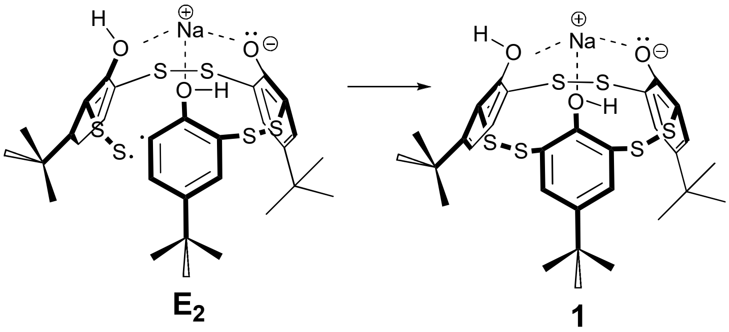
Scheme 2. The proposed pathway for the formation of radicals **A-E** under the solvent-free conditions.

At the next step depending on (*n* = 1, 2…) the cyclocondensation of biradicals **E$_{1-4}$** under the solvent-free conditions affords thiacalix[*n*]arenes **1-4**. The most important factor of this cyclocondensation is the template effect of sodium atom. Each of the biradicals **E$_{1-4}$** folds over the sodium atom to afford the cyclic products. Thus, the shortest biradical **E$_1$** (6 sulfur atoms, 2 phenol units) (*n* = 1, x = y = 3) affords thiacalix[*n*]arene **2** (Scheme 3).



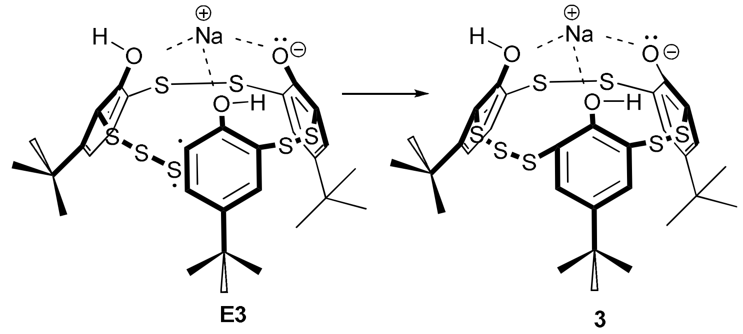
Scheme 3. Formation of thiacalixarene **2**.

The linear oligomers with longer chains afford other thiacalixarenes under the same conditions. Thus, if n = 2, x = y = 2 (6 sulfur atoms, 3 phenol units) the cyclocondensation of biradical **E$_2$** affords the macrocycle **1**. Due to its C$_{3v}$-symmetry the formation of this macrocycle is preferred based on the DFT calculations (Table 1) and thus thiacalixarene **1** has the highest content in the reaction mixture (Scheme 4).



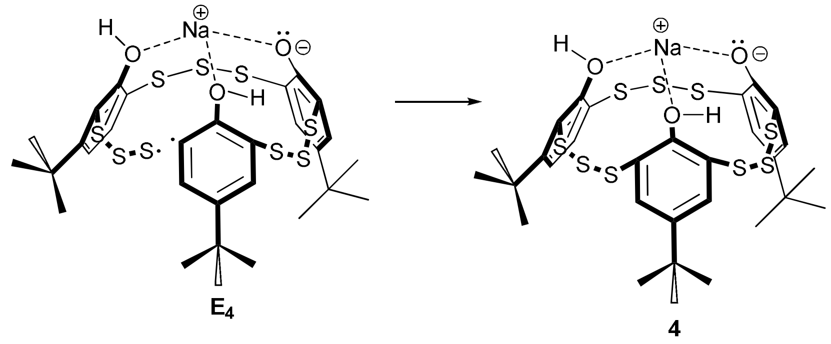
Scheme 4. Formation of thiacalixarene **1**.

Oligomer **E$_3$** (7 sulfur atoms, 3 phenol units) (n = 2, x = 3) and its cyclization product **3** are less symmetrical compare to oligomer **E$_2$** and **1**. Due to the presence of one extra sulfur atom in the polysulfide bridge, macrocycle **3** is less stable than macrocycle **1** (Table 4). Worthy of note is that this macrocycle is geometrically very similar to macrocycle **1**, but the template effect of sodium atom on the formation of the macrocycle **3** is less pronounced than for the macrocycle **1** (Scheme 5).



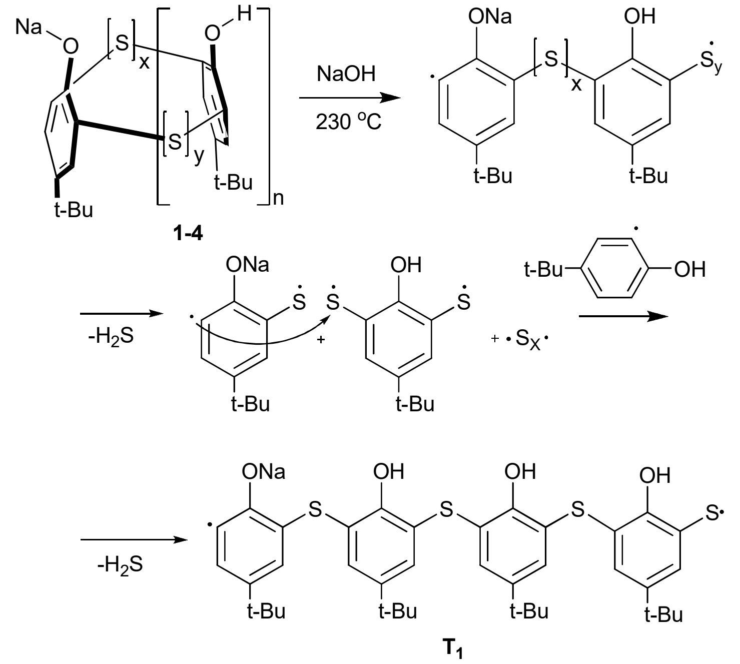
Scheme 5. Formation of thiacalixarene **3**.

Finally, oligomer **E₄** (n = x = 3) (9 sulfur atoms, 3 phenol units) affords macrocycle **4**, which is also highly symmetric. However the sodium atom is less suitable as a template atom for the cyclization **E₄** into **4**, therefore this cyclic product was observed as a minor product, which was confirmed based on both the experimental data and the theoretical calculations (Scheme 6).



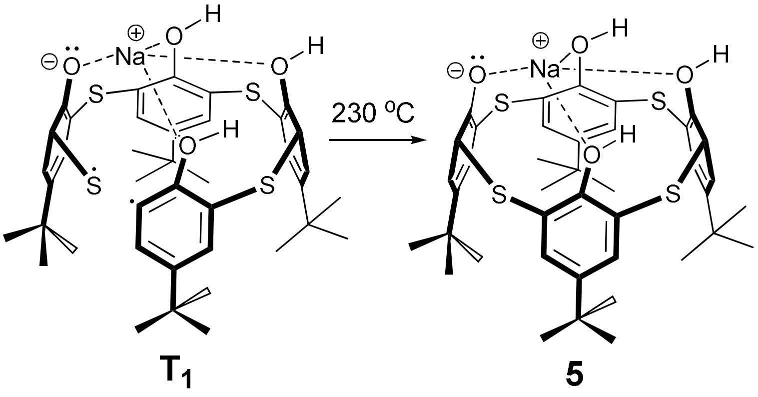
Scheme 6. Formation of thiacalixarene **4**.

As kinetic products all these macrocycles **1-4** were observed in the reaction mixture at temperatures below 200 °C. To confirm the kinetic control for the formation of **1-4** at the final step we have increased the temperature of the reaction mixture to 230 °C.



Scheme 7. Formation of tetramer **T₁** containing 4 sulfur atoms.

As expected, the most thermodynamically stable thiacalix[4]arene **5** was isolated as the only product in up to 80% yield (Scheme 7, Figure S17, Table S10, ESI). In this case the high-temperature cyclocondensation of the most geometrically suitable tetramer $\mathbf{T_1}$ (4 sulfur atoms, 4 phenol units) affords the thiacalixarene **5** (Schemes 7 & 8).



Scheme 8. Formation of thiacalix[4]arene **5** from tetramer $\mathbf{T_1}$.

It is worthy to mention that, as we assumed, under the solvent-free conditions at lower temperature, *i.e.* less than 230 °C, the formation of macrocycles **1-4** was more favorable than thiacalix[4]arene **5**. In this case the reaction mixture is enriched with S_8 while it is poor in *tert*-butylphenol due to its continuous sublimation from the reaction mixture and that makes possible the formation of linear oligomers $\mathbf{E_1}$-$\mathbf{E_4}$ along with small amount of $\mathbf{T_1}$. The following sodium atom-mediated cyclization of $\mathbf{E_1}$-$\mathbf{E_4}$ and $\mathbf{T_1}$ affords the corresponding macrocycles **1-4** alone with small amount of classic thiacalix[4]arene **5**.

Conclusions

Several di- and trisulfide-bridged thiacalix[*n*]arenes have been synthesized by means of solvent-free condensation between *tert*-butylphenol and sulfur in the presence of NaOH. The existence of these products was supported by mass-spectrometry (ESI-MS and semi-preparative HPLC) and DFT-studies. These macrocycles are suggested to form under the kinetically-controlled reaction conditions and their further conversion into the thermodynamically stable *tert*-butylthiacalix[4]arene is possible.

Experimental Section

General. HPLC grade DMSO and DCM were used for preparing (poly)thiacalix[*n*]arenes (TCAs) mixture solutions. Acetonitrile HPLC grade and deionized water were used for separations. For the standard buffer solutions were used reagent grade tri-sodium citrate 5,5-hydrate, ammonium acetate, ammonium hydroxide solution, sodium hydroxide, formic acid, hydrochloric acid and deionized water.

Modular HPLC chromatograph Agilent 1200 (USA), water purification system Simplicity (Merck Millipore, USA), ultrasonic bath «Sapphire» (Russia), centrifuge vortex Microspin FV-2400 (Biosan, Latvia), mass-spectrometer

Bruker micrOTOF-Q II (Bruker, Germany). All ESI-MS studies were performed in the negative ion mode due to the presence of the NaOH in almost all the samples.

General procedure for the synthesis of macrocycles 1-4 and thiacalix[4]arene (5)

Method 1 (way *i*): Finely ground dry *p*-*tert*-butylphenol (20 g, 133.1 mmol), sulfur (8.54 g., 266.2 mmol) and NaOH (2.66 g, 66.6 mmol) were placed in flame-dried 250 mL Shlenk flask equipped with argon line and descending condenser. Under the constant flow of argon *o*-xylene (30 mL) was added to the reaction mixture and the reaction mixture was heated 165-170 °C for 4 h, and then to 230 °C for additional 24 h. Distillation of water and *o*-xylene was observed over this period. After that the reaction mixture was cooled down and the obtained brownish tar was triturated with DCM (30 mL). The resulted suspension was filtered, washed with DCM (3 x 10 mL), 3% aqueous HCl (30 mL), water (10 mL) and air-dried to afford fine yellowish crystalline powder. For the obtaining of analytically pure sample the reaction mixture was subject to column chromatography (SiO_2, eluent: 0.5% acetic acid in toluene) to afford thiacalix[4]arene[1] **5** as an off-white solid., m.p. >300 °C; Yield 80%. ^1H NMR ($CDCl_3$, 400 MHz): δ 9.60 (s, 4H, -OH), 7.63 (s, 8H, ArH), 1.22 (s, 36H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 155.68 (Ar$\underline{C}$-OH), 144.70 (Ar$\underline{C}$), 136.39 (Ar$\underline{C}$H), 120.63 (Ar$\underline{C}$-S-), 34.20 (-$\underline{C}(CH_3)_3$), 31.24 (-$\underline{C}H_3$).

Method 2 (way *ii*): Finely ground dry *p*-*tert*-butylphenol (3.2 g, 21.3 mmol), sulfur (1.68 g, 52.5 mmol) and NaOH (0.44 g, 11 mmole) were placed in flame-dried 50 mL Shlenk flask equipped with argon line. Constant flow of argon was used during all experiments. The flask was heated to 165-170 °C for 3 h and then to 200 °C for additional 3 h. The partial sublimation of starting *p*-*tert*-butylphenol was observed on the inner cold wall of reaction flask. Residue was triturated with diethyl ether and the resulted suspension was filtered off, washed with diethyl ether and air-dried to afford fine yellowish crystalline powder.

Method 3. Conversion of compounds 1-4 into thiacalix[4]arene 5. The reaction mixture obtained according to method 2 (1.0 g) was finely ground with NaOH (0.5 g), placed into 5 mL Shlenk flask and gradually heated up to 230 °C for 3 h and then to 230 °C for additional 24 h. After the cooling down to room temperature the reaction mixture was subject to workup according to the method 1.

Acknowledgements

K. Giri acknowledges financial support from DST, Govt. of India (Ref. # YSS/2014/000060). This work was supported by the Russian Science Foundation (Ref. # 16-43-02020) and, for A. Majee by DST-RSF Major Research Project (Ref. No. INT/RUS/RSF/P-08).

Supplementary Material

Additional supporting information can be found in the online version of this article at the publisher's website.

References

1. Kumagai, H.; Hasegawa, M.; Miyanari, S.; Sugawa, Y.; Sato, Y.; Hori, T.; Ueda, S.; Kamiyama, H.; Miyano, S. *Tetrahedron Lett*. **1997**, *38*, 3971–3972.
   https://doi.org/10.1016/S0040-4039(97)00792-2
2. Gutsche, C. D. In *Calixarenes Revisited*; J. F. Stoddart, Ed.; RSC: Cambridge, 1998.
3. Akdas, H.; Bringel, L.; Graf, E.; Hosseini, M. W.; Mislin, G.; Pansanel, J.; De Cian, A.; Fischer, J. *Tetrahedron Lett*. **1998**, *39*, 2311–2314.
   https://doi.org/10.1016/S0040-4039(98)00067-7
4. Kumar, R.; Lee, Y. O.; Bhalla, V.; Kumar, M.; Kim, J. S. *Chem. Soc. Rev*. **2014**, *43*, 4824-4870.
   https://doi.org/10.1039/c4cs00068d
5. Miao, F.; Zhan, J.; Zou, Z.; Tian, D.; Li, H. *Tetrahedron* **2012**, *68*, 2409-2413.
   https://doi.org/10.1016/j.tet.2012.01.010
6. Leeuwen, F. W. B. van; Beijleveld, H.; Velders, A. H.; Huskens, J.; Verboom, W.; Reinhoudt, D. N. *Org. Biomol. Chem*. **2005**, *3*, 1993-2001.
7. Ge, J.-Y.; Xie, J.-Z.; Zhao, Z.-Y.; Ru, J.; Song, Y.; J.-L. *RSC Adv*. **2016**, *6*, 1143-1150.
   https://doi.org/10.1039/C5RA23697E
8. Trush, V. V.; Kharchenko, S. G.; Tanchuk, V. Yu.; Kalchenko, V. I.; Vovk, A. I. *Org. Biomol. Chem*. **2015**, *13*, 8803-8806.
   https://doi.org/10.1039/C5OB01247C
9. Sone, T.; Ohba, Y.; Moriya K.; Kumada, H. *Abstract Book of Workshop on Calixarenes and Related Compounds*, Fukuoka, Japan, **1993**, PS/B-36.
10. Patel, M. H.; Patel, V. B.; Shrivastav, P. S. *Tetrahedron Lett.* **2008**, *49*, 3087–3091.
    https://doi.org/10.1016/j.tetlet.2008.03.052
11. Asfari, Z.; Bohmer, V.; Harrowfield, J.; Vicens J., Eds., *Calixarenes 2001*, Kluwer Academic: Dordrecht 2001.
12. Patel, M. H.; Shrivastav, P. S. *Chem. Commun*. **2009**, 586–588.
    https://doi.org/10.1039/B817415F
13. Kon, N.; Iki, N.; Miyano, S. *Tetrahedron Lett*. **2002**, *43*, 2231–2234.
    https://doi.org/10.1016/S0040-4039(02)00214-9
14. Kondo, Y.; Endo, K.; Iki, N.; Miyano, S.; Hamada, F. *J. Inclusion Phenom. Macrocyclic Chem*. **2005**, *52*, 45–49.
    https://doi.org/10.1007/s10847-004-2384-6
15. Kondo, Y.; Hamada, N. *J. Inclusion Phenom. Macrocyclic Chem*. **2007**, *58*, 123–126.
    https://doi.org/10.1007/s10847-006-9133-y
16. Saunders, K. J. *Organic Polymer Chemistry: An Introduction to the Organic Chemistry of Adhesives, Fibres, Paints, Plastics, and Rubbers*; Springer Science & Business Media, 2013.
17. Crockett, M. P.; Evans, A. M.; Worthington, M. J. H.; Albuquerque, I. S.; Slattery, A. D.; Gibson, C. T.; Campbell, J. A.; Lewis, D. A.; Bernardes, G. J. L.; Chalker, J. M. *Angew. Chem. Int. Ed.* **2016**, *55*, 1714-1718.
    https://doi.org/10.1002/anie.201508708
18. Ariyan, Z. S.; Martin, R. L. *J. Chem. Soc., Perkin Trans. 1* **1972**, 1687-1691.
    https://doi.org/10.1039/p19720001687
19. Sonawane, M. P.; Jacobs, J.; Thomas, J.; Van Meervelt, L.; Dehaen, W. *Chem. Commun*. **2013**, *49*, 6310-6312.
    https://doi.org/10.1039/c3cc42984a

20. *Polysulfide Oligomer Sealants: Synthesis, Properties and Applications*, Khakimullin, Y. N.; Minkin, V. S.; Deberdeev, T. R. *CRC Press*, **2015**, p. 304.
21. Kieran, A.; Bond, A.; Belenguer, A.; Sanders, J. *Chem. Commun*. **2003**, 2674-2675.
22. Otto, S.; Furlan, R. L. E.; Sanders, J. K. M. *J. Am. Chem. Soc*. **2000**, *122*, 12063-12064. https://doi.org/10.1021/ja005507o
23. Otto, S.; Furlanand, R. L. E.; Sanders, J. K. M. *Science* **2002**, *297*, 590-593. https://doi.org/10.1126/science.1072361
24. Carnall, J. M. A.; Waudby, C. A.; Belenguer, A. M.; Stuart, M. C. A.; Peyralans, J. J.-P.; Otto, S. *Science* **2010**, *327*, 1502-1506. https://doi.org/10.1126/science.1182767
25. Stefankiewiez, A. R.; Sambrook, M. R.; Sanders, J. K. M. *Chem. Sci*. **2012**, *3*, 2326-2329. https://doi.org/10.1039/c2sc20347b
26. Santra, S.; Kopchuk, D. S.; Kovalev, I. S.; Zyryanov, G. V.; Majee, A.; Charushin, V. N.; Chupakhin, O. N. *Green Chem.* **2016**, *18*, 423-426. https://doi.org/10.1039/C5GC01505G
27. Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. *J. Chem. Phys.* **2010**, *132***,** 154104-154122. https://doi.org/10.1063/1.3382344
28. Bardez, E.; Devol, I.; Larrey, B.; Valeur, B. *J. Phys. Chem. B* **1997**, *101*, 7786-7793. https://doi.org/10.1021/jp971293u
29. Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785-789. https://doi.org/10.1103/PhysRevB.37.785
30. Weigend, F.; Ahlrichs, R. *Phys. Chem. Chem. Phys*. **2005**, *7*, 3297-3305. https://doi.org/10.1039/b508541a
31. Gaussian 09, Revision D.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr. J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian, Inc.*, Wallingford CT, **2009**.