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CROWN COMPOUNDS CONTAINING A 1,3,4-THIADIAZOLE MOIETY: MICROWAVE ASSISTED SYNTHESIS, CRYSTAL STRUCTURE AND QUANTUM CALCULATIONS

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Abstract – A number of macrocyclic polyether compounds containing a 2,5-bis(2-hydroxyphenyl)-1,3,4-thiadiazole moiety are quickly prepared by a nucleophilic substitution reaction involving ethylene or polyethyleglycol ditosylate and a biphenol, the 2,5-bis(2-hydroxyphenyl)-1,3,4-thiadiazole, with solid anhydrous carbonate as a base under microwave irradiation. The quantum calculations at DFT level and the structure of different conformations of the 2,5-bis(2-hydroxyphenyl)-1,3,4-thiadiazole were performed both in vacuum and acetonitrile solvent using PCM method. The structures are ascertained by spectroscopic properties. The crystal structure of one of the crown compounds has been determined and shows the sufur atom to be inside the macroring cavity.

INTRODUCTION

Over the past decades, efforts toward the synthesis of heterocyclic coronands and particularly macrocyclic polyether have been conducted.[1-6] These new marcocyclic compounds are expected to show coordination behaviors toward cations and small molecules such as water, amines and urea.[1] As a part of a program directed to obtain heterocyclic molecules which can be used as corrosion inhibitors [7-9] and for the selective recognition of metal ions, [3,10] we have reported the synthesis of new 1,3,4-thiadiazoles containing macrocyclic polyethers.[11] These macrocycles (**2**) result from the heterocyclization of 2,5-bis(2-hydroxyphenyl)-1,3,4-thiadiazoles (**1**) (Scheme) [12] with ethylene or polyethylene glycol ditosylate in non-protic polar solvents such as acetone, acetonitrile, or dimethylformamide, with excess alkali metal carbonates as a base (Scheme). However, unfortunately, a good achievement of this reaction requires long reaction time (48 h) under classical heating; in this paper, we report that this reaction takes place in good yields and more rapidity under microwave irradiation.

In recent years, there has been a growing interest in microwave enhanced reactions because they are usually faster and give higher products yields than conventional heating.[13-16]

Microwave assisted organic reaction constitutes an emerging technology that makes experimentally and industrially important organic syntheses more effective and more eco-friendly than conventional reactions.

The number of publications and reviews that have advocated the advantages and the use of microwave irradiation over conventional technology have increased significantly. Remarkable decreases in reaction time and, in some cases, cleaner reaction and better yields have made this technique widely applicable in organic synthesis. MW irradiation leads to large reductions in reaction times and sometimes with enhancements in conversions and selectivity, with the advantage of an eco-friendly approach.[13,17-21] The most common benefits described are:

- rapid reactions brought about by high and homogeneous temperatures and combined with pressure effects (if conducted in closed vessels);
- higher degree of purity achieved due to short residence time at high temperatures;
- yields often better, obtained within shorter times and with purer products.

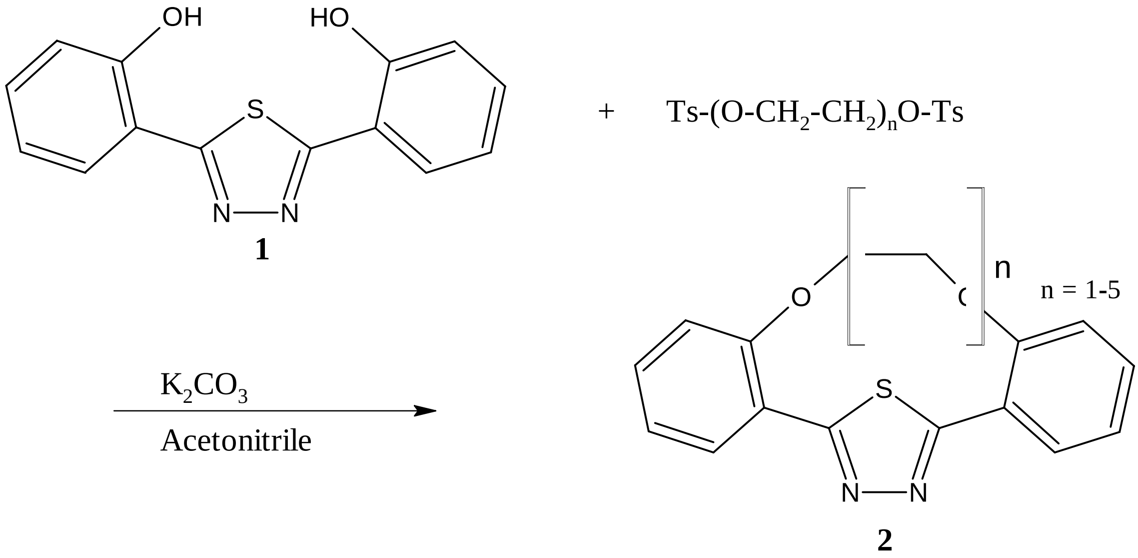
In the case of aromatic nucleophilic substitution, microwave irradiation produces specific effects both on reactivity and selectivity,[22] but very few is known concerning aliphatic nucleophilic substitutions under microwave irradiation. Finkelstein halogen exchange reaction using microwave energy has been recently studied; chloromethyltrimethylsilane was converted to the iodide by reacting with sodium iodide in the acetonitrile/cyclohexane mixture using conventional and microwave heating methods.[23] However; to our knowledge, nothing is reported concerning nucleophilic substitutions involving tosylates.

We present here the microwave assisted synthesis of crown compounds containing a 1,3,4-thiadiazole moiety, the quantum calculations at DFT level of potential intermediates and, in order to determine the conformation of **2d**, a structural study has been conducted.

The X-Ray crystal structure of **2d** is shown in Figure 2 and atomic parameters for the atoms are listed in Tables 3, 4, 5 and 6.

RESULTS AND DISCUSSION

Compounds (**2a-e**) were prepared by a nucleophilic substitution reaction involving a glycol ditosylate with the bisphenol (**1**) (Scheme).



Scheme. Synthesis of marcocyclic compounds.

Table 1. Data for the synthesis of macrocycles (**2a-e**) under microwave irradiation and classical heating

Compound	**Irradiation Yield (%)**	**Irradiation Mp (°C)**	**Heating Yield (%)**	**Heating Mp (°C)**	**Ref.**
2a (n = 1)	84	143-144	87	144	11
2b (n = 2)	63	210-212	55	210	11
2c (n = 3)	87	180	86	180	11
2d (n = 4)	65	151	62	150	11
2e (n = 5)	40	139-140	34	140	11

This reaction was easily achieved by microwave irradiation and the macrocycles (**2a-e**) are obtained in good yields and excellent state of purity. A good achievement of this synthesis requires longer times (48 h) (Table 1) using classical heating.[11] Under this experimental conditions, when the reaction is stopped after only 9 h of heating, as in the microwave experiments, important quantities of untransformed ethylene or polyethylene glycol ditosylate are detected by TLC and by ^{1}H NMR spectroscopy (about 50 %).

In order to understand reaction pathway that occur in the reaction of the ditosyl polyether with the thiadiphenol, quantum calculations at DFT level were performed, both in vacuum and acetonitrile solvent, using PCM method. The results are analyzed in term of electronic energy of the calculated molecule conformation.

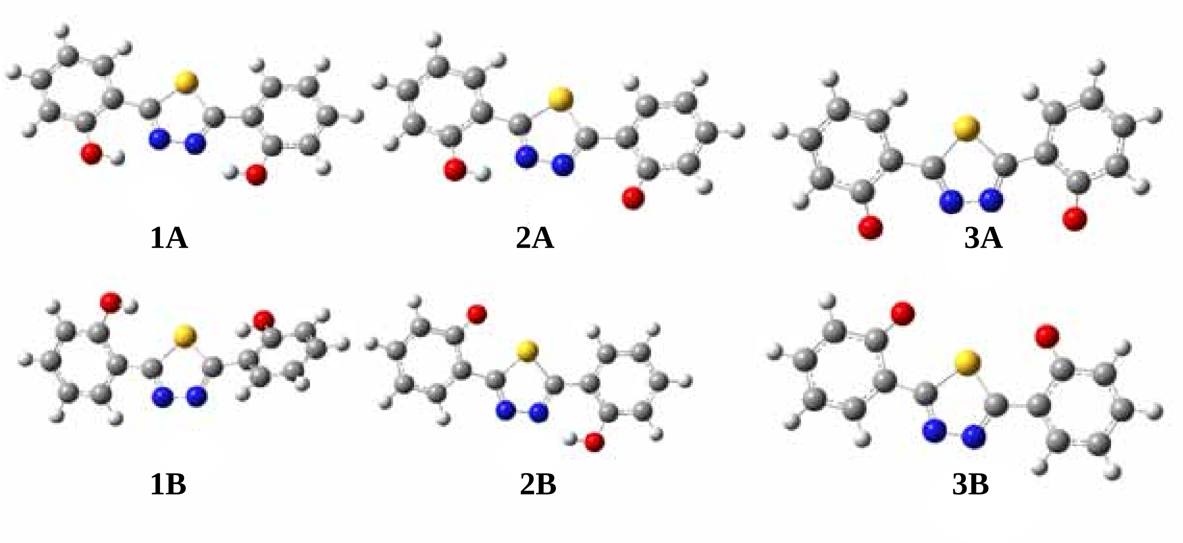


Figure 1. structure of different conformations of 2,5-bis(2-hydroxyphenyl)-1,3,4-thiadiazoles optimized at B3LYP/6-31+G(d,p) in acetonitrile solvent using PCM method.

As the reaction takes place in basic media to allow the deprotonation of the OH group, leading to both anion and dianion species, the calculations were performed with additional diffuse function that well describe such species. The energy values are given in Table 2.

For the protonated species, the most stable conformation results from the high stabilization of the structure by hydrogen bonding resulting from the position of OH group quite near the nitrogen atom of the thiadiazole ring (conformation **1A**) compared to the position of the OH groups close to the sulphur atom (conformation **1B**). This stabilization causes the conformation (**1A**) to have 19.2 kcal/mol in vacuum and 14.65 kcal/mol in the solvent less energy than the conformation (**1B**). The intermediary structure (**2B**) was found to be 9.4 kcal/mol more stable than the structure (**2A**). Increase in basicity by addition of K_2CO_3 leads to the formation of anionic or dianionic forms. In the case of the monoanionic form, the energy of the two conformations were calculated i.e. structures (**2A**) and (**2B**). It was found that the most stable structure found is **2B**, indicating that, after deprotonation, the electron clouds of the oxygen and nitrogen atoms are so close that they repel each other. This repulsion causes the structure (**2B**) to have 13.37 and 8.27 kcal/mol with solvent model, less energy than the structure (**2A**).

Another consideration is the enthalpy cost for the deprotonation in solvent from the higher stable hydrogen bonding structure (**1A**), to the monoanionic structure (**2B**), of 295.2 kcal/mol whereas the free energy at 298 K is 294.8 kcal/mol indicating a small entropic contribution.

These values explain that the deprotonation does not only occur with increase of pH in experimental conditions but also with heating the system to increase the entropic contribution. By the same ways the deprotonation of the second OH leads to a most stable structure that implies the rotation of the second oxygen atom to the sulphur side (structure **3B**), with an energy difference of 10.02 kcal/mol in vacuum and 1.15 kcal/mol in solvent and with an enthalpy of 304 kcal/mol and a free energy of 296 kcal/mol in solvent for the second deprotonation. These results seem to indicate that the cost in energy is closed for both protons to form the dianionic form.

Table 2. The energy values of different conformations of 2,5-bis(2-hydroxyphenyl)-1,3,4-thiadiazoles

Structure	**B3LYP 6-31+G(d,p) in-vacuum (hartree)**	**B3LYP 6-31+G(d,p) PCM solvent (hartree)**
1A	-1197,704587650	-1197,702373000
1B	-1197,673970560	-1197,679001000
	ΔΔH=19.2 kcal/mol	ΔΔH=14.5 kcal/mol
2A anion	-1197,149220570	-1197,218133000
2B anion	-1197,170553650	-1197,231574000
	ΔΔH=13.37 kcal/mol	ΔΔH=8.2 kcal/mol
3A dianion	-1196,485965600	-1196,743582000
3B dianion	-1196,512456550	-1196,745419000
	ΔΔH=10.02 kcal/mol	ΔΔH=1.15 kcal/mol

X-Ray crystallographic analysis was carried out for the compound (**2d**). Figure 2 shows a perspective view of this compound with the numbering scheme, while in Table 5 bond distances and angles in the molecule are reported.

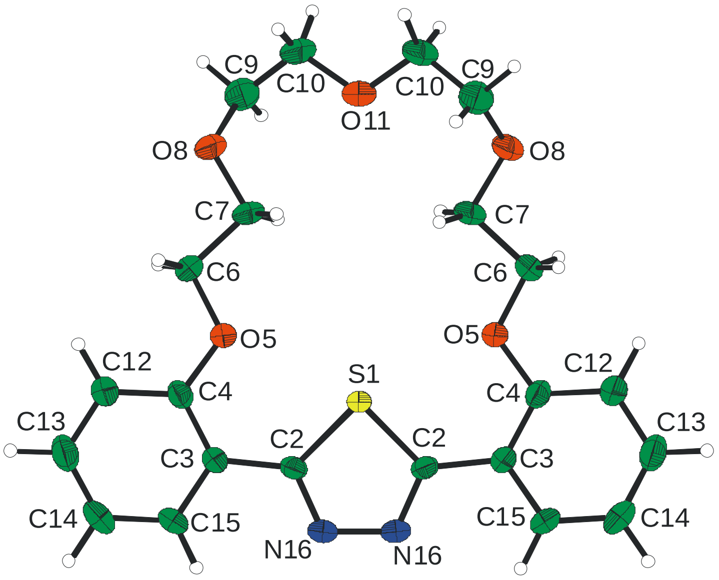


Figure 2. Perspective view of **2d**.

This very symmetric molecule is obtained through the specific symmetry elements of C2/c space group, running through the S1 and O11 atoms (**4e** crystallographic sites).

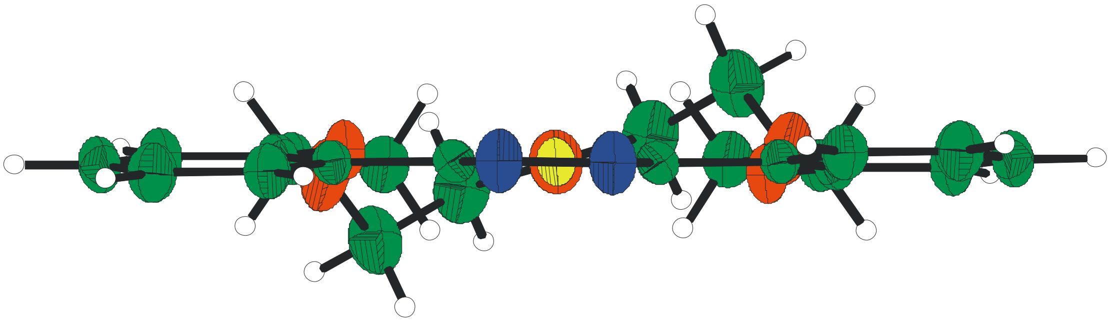


Figure 3. Projection view of **2d**.

Mean plane calculations show that the central thiadiazole ring impose the global planeity with the following: Atoms(out of plane distance (Å)) plane definition:

C2(-0.003); S1(0.0); C2^{i}(0.003); N16(0.005); N16^{i}(-0.005)

where (i) stands for symmetry related atoms through (1-x, y, 0.5-z) operation. The plane normal is :m1= 0.691; m2= 0.0; m3= -0.723, and the distance from origin is 5.59(1) Å.

The substituted phenyl ring intrinsic planeity is obtained from:

C3^{i}(-0.006); C4^{i}(0.008); C12^{i}(-0.005); C13^{i}(-0.001); C14^{i}(0.004); C15^{i}(0.000).

The plane normal is :m1= 0.670; m2= -0.082; m3= -0.737; the distance from origin is 5.23(2) Å. From these definitions, the angle between the two planes is 7.93(8)°, which means that the substituted phenyl ring is slightly rotated out of the previous plane by +4.93°on one side , and –4.93° on the symmetrically opposite side. A comparison with the 2,5-bis(phenyl)-1,3,4-thiadiazole crystal structure,[24] shows the rotation of the phenyl ring out of the central thia diazole central plane to be much more important at 16.41°; in compound (2**d**), the limited twisting is related to the macrocycle ring linkage. Most of this macrocycle belongs to the described mean plane, except the C9-C10 part and its symmetry generated equivalent, both bonded to the terminal O11 linking atom. When viewed along the b direction, a layer-like packing is organized parallel to (-2 0 1) and characterizes the tridimensionnal crystal structure. In-plane packing occurs via C13-HC13…..O8 (D= 3.505 Å; d=2.527 Å; Θ = 165.9°) weak hydrogen bonds [25] thus linking one molecule to its four in plane neighbors (Figure 4).

The coordination behavior of these compounds as well as the formation of change transfer complexes with TCNQ remain to be carried out and are under progress.

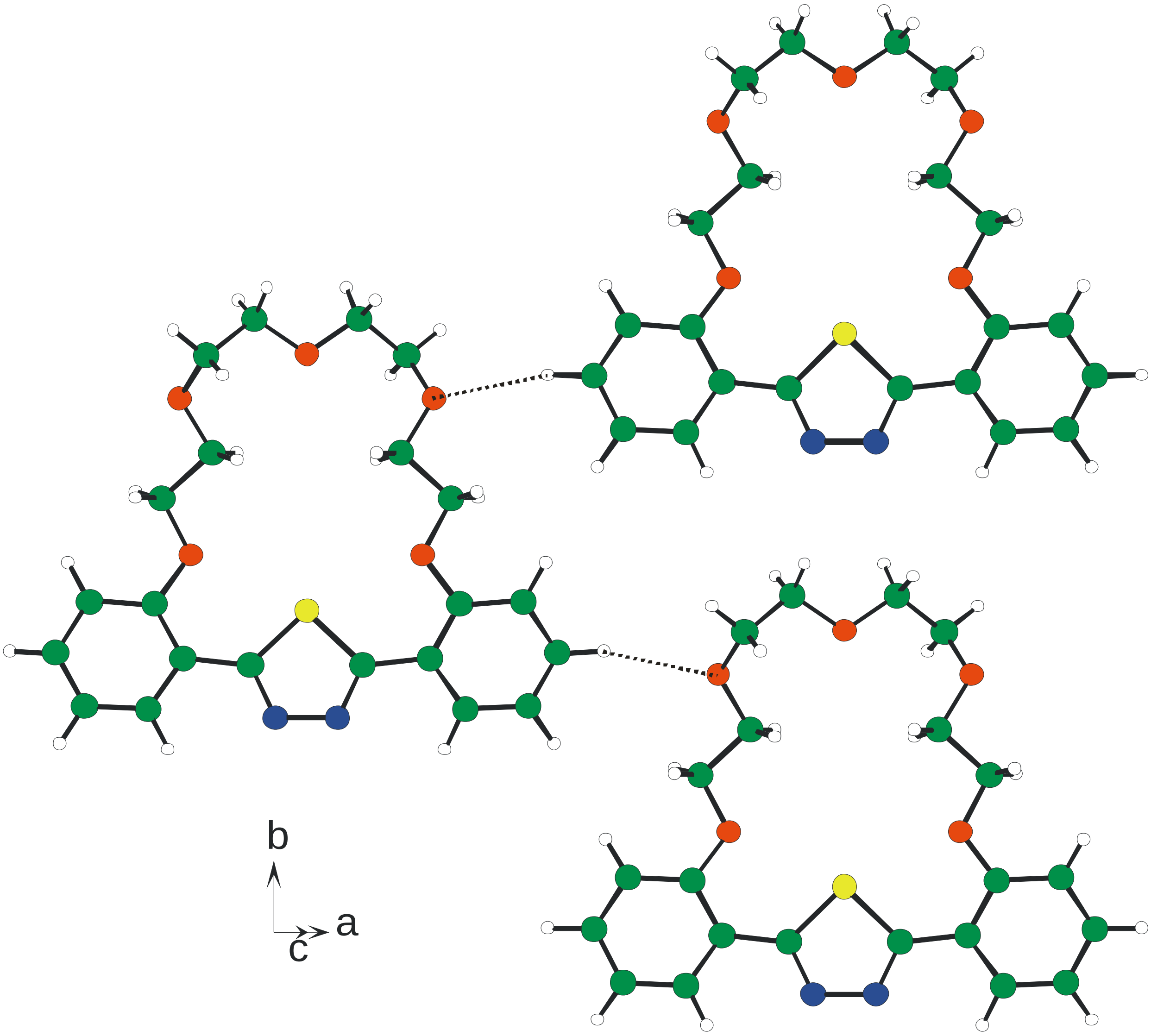


Figure 4. The hydrogen bonds between the molecules of **2d**.

Table 3. Summary of the crystal data and structure refinement for **2d**

Empirical formula	$C_{22}N_2SO_5H_{24}$
Formula weight	428.50
Temperature	295 K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	C2/c
Unit cell dimensions	a = 21.267(4) Å
	b = 12.495(3) Å β= 104.44(1)°.
	c = 8.050(2) Å.
Volume	2071.6(1) $Å^3$
Z	4
Density (calculated)	1.3735 g/cm^3
Absorption coefficient	0.193 mm^{-1}
F(000)	904
Crystal size	0.30 x 0.30 x 0.01 mm^3
Theta range for data collection	3.03 to 28.53°.
Index ranges	-28<=h<=27, -16<=k<=16, -10<=l<=10
Reflections collected	6689
Independent reflections	2213 [R(int) = 0.0479]
Completeness to theta = 24.89°	95.0 %
Absorption correction	SADABS[a]
Refinement method	Full-matrix least-squares on F
Data / restraints / parameters	2213 / 0 / 137
Weighting scheme	$w=1/\sigma^2$
Final R indices [I>3sigma(I)]	R = 0.0583, wR = 0.0470
R indices (all data)	R_{all} = 0.1311, wR_{all} = 0.0507
Largest diff. peak and hole	0.44 and -0.32 e.Å-3

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[a] SADABS, Sheldrick, G.M. “Program for Absorption Correction of Area Detector Frames”, BRUKER AXS Inc., 5465 East Cheryl Parkway, Madison, WI 53711-5373 USA

Table 4. Atomic coordinates and equivalent displacement parameters for **2d**

Atom	x	y	z	Ueq
S1	0.5	0.00506(8)	0.25	0.0431(4)
C2	0.44869(14)	0.1043(2)	0.1431(4)	0.0423(12)
C3	0.38640(14)	0.0924(2)	0.0178(4)	0.0445(13)
C4	0.36100(13)	-0.0060(3)	-0.0454(4)	0.0476(12)
O5	0.39660(9)	-0.09495(16)	0.0169(2)	0.0571(9)
C6	0.36736(14)	-0.1963(2)	-0.0280(4)	0.0544(14)
C7	0.41228(14)	-0.2790(2)	0.0743(4)	0.0610(14)
O8	0.37951(11)	-0.37799(17)	0.0251(3)	0.0816(11)
C9	0.38607(17)	-0.4550(3)	0.1522(5)	0.0874(19)
C10	0.44406(17)	-0.5214(3)	0.1841(4)	0.0798(17)
O11	0.5	-0.4584(2)	0.25	0.0740(15)
C12	0.30174(14)	-0.0111(3)	-0.1671(4)	0.0611(14)
C13	0.26814(16)	0.0820(3)	-0.2205(4)	0.0711(18)
C14	0.29261(17)	0.1788(3)	-0.1566(4)	0.0745(18)
C15	0.35115(15)	0.1845(2)	-0.0387(4)	0.0592(15)
N16	0.47147(11)	0.19993(18)	0.1896(3)	0.0647(13)
H1c6	0.3623	-0.2093	-0.1532	0.065322
H2c6	0.3247	-0.1989	0.0029	0.065322
H1c7	0.4542	-0.2788	0.0395	0.073258
H2c7	0.4169	-0.2666	0.1995	0.073258
H1c9	0.3467	-0.5018	0.1274	0.104849
H2c9	0.3828	-0.4203	0.2617	0.104849
H1c10	0.4411	-0.5787	0.2686	0.095808
H2c10	0.4474	-0.5559	0.0746	0.095808
Hc12	0.2834	-0.0814	-0.2159	0.073364
Hc13	0.2253	0.0794	-0.3069	0.085332
Hc14	0.2675	0.2456	-0.1964	0.089396
Hc15	0.3682	0.2562	0.0063	0.071054

Table 5. Select bond distances and bond angles for **2d**

Bond angles		**Bond distances**	
C2-S1-C2^i	88.6(2)	S1-C2	1.732(3)
S1-C2-C3	128.4(2)	C2-C3	1.459(3)
S1-C2-N16	111.6(2)	C2-N16	1.308(3)
C3-C2-N16	119.9(2)	C3-C4	1.388(4)
C2-C3-C4	123.2(2)	C3-C15	1.386(4)
C2-C3-C15	117.7(2)	C4-O5	1.367(4)
C4-C3-C15	119.1(2)	C4-C12	1.392(3)
C3-C4-O5	117.1(2)	O5-C6	1.418(3)
C3-C4-C12	120.0(3)	C6-C7	1.505(3)
O5-C4-C12	122.9(3)	C7-O8	1.427(3)
C4-O5-C6	117.7(2)	O8-C9	1.386(5)
O5-C6-C7	107.2 (2)	C9-C10	1.455(6)
C6-C7-O8	104.1 (2)	C10-O11	1.414(4)
C7-O8-C9	116.4(2)	C12-C13	1.377(5)
O8-C9-C10	116.8(4)	C13-C14	1.366(5)
C9-C10-O11	110.2(3)	C14-C15	1.367(5)
C10-O11-C10^i	112.4(3)	N16-N16^i	1.352(3)
C10^i-O11-C10	112.4(3)		
C4-C12-C13	119.3(3)		
C12-C13-C14	120.7(3)		
C13-C14-C15	120.2(3)		
C3-C15-C14	120.6(3)		
C2-N16-N16^i	114.1(2)		

i=1-x, y,0.5-z

Table 6. Anisotropic displacement parameters for **2d**

	U11	**U22**	**U33**	**U12**	**U13**	**U23**
S1	0.0414(6)	0.0281(6)	0.0542(7)	0	0.0015(5)	0
C2	0.0427(19)	0.0321(17)	0.052(2)	0.0057(15)	0.0111(16)	0.0033(16)
C3	0.041(2)	0.042(2)	0.048(2)	0.0051(15)	0.0052(16)	0.0046(17)
C4	0.0380(18)	0.050(2)	0.0519(19)	0.0075(18)	0.0067(15)	0.006(2)
O5	0.0504(14)	0.0364(13)	0.0724(17)	-0.0013(11)	-0.0072(12)	0.0010(12)
C6	0.051(2)	0.043(2)	0.062(2)	-0.0084(17)	0.0021(17)	-0.0036(18)
C7	0.069(2)	0.034(2)	0.074(3)	-0.0140(19)	0.0070(18)	0.002(2)
O8	0.0938(18)	0.0413(15)	0.087(2)	-0.0192(14)	-0.0194(15)	0.0074(14)
C9	0.074(3)	0.066(3)	0.112(3)	-0.021(2)	0.005(2)	0.024(3)
C10	0.092(3)	0.042(2)	0.095(3)	-0.018(2)	0.004(2)	0.006(2)
O11	0.079(2)	0.039(2)	0.096(3)	0	0.006(2)	0
C12	0.050(2)	0.055(2)	0.070(2)	0.0018(19)	-0.0001(18)	0.005(2)
C13	0.049(2)	0.083(3)	0.073(3)	0.009(2)	-0.0018(19)	0.013(2)
C14	0.068(3)	0.068(3)	0.079(3)	0.026(2)	0.002(2)	0.020(2)
C15	0.060(2)	0.041(2)	0.070(3)	0.0129(18)	0.004(2)	0.0105(19)
N16	0.067(2)	0.0317(15)	0.083(2)	0.0024(13)	-0.0052(15)	0.0013(15)

CONCLUSIONS

Macrocyclic polyether compounds containing a 1,3,4-thiadiazole moiety were prepared in good yields under microwave irradiation. Non-thermal microwave specific effect was observed in all the cases. Quantum calculations at DFT level were performed and the results seem to indicated that the reaction intermediate is a dianionic form where the two oxygen atoms are closed to the heterocyclic sulfur. The crystal structure of one the crown compounds (**2d**) shows that the sulfur atom is situated inside the macroring cavity. The macrocyclic compounds have rather flexible polyethylene glycol unit that forms a cavity. The transport of cations by these crown compounds as well as their inhibiting properties for metal corrosion in acidic media remain to be carried out and are under progress.

EXPERIMENTAL

Melting points were determined using an IA 9000 series Electrothermal apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker F.T. AC 200 spectrometer (200 MHz for ^{1}H NMR and 50 MHz for ^{13}C NMR) using chloroform-d$_1$ ($CDCl_3$). Matrix assisted laser desorption ionization (MALDI) and time-of-flight mass spectrometry (TOF-MS) are used to record the MS spectra of the macrocyclic polyether compounds. Elemental analyses were performed by the Elemental Analysis service of CNRS, Vernaison, France. All starting materials were of reagent grade and used as purchased.

A mixture of 2,5-bis(2-hydroxyphenyl)-1,3,4-thiadiazole (**1**) (0.75 g, 2.77 mmol), anhydrous potassium carbonate (1.65 g, 12 mmol) and ethylene or polyethylene glycol ditosylate (2.78 mmol) in 30 mL of nonprotic polar solvent (acetonitrile, acetone …) was introduced into a fluoropolymere cylindrical flask placed in a MARS5 XP-1500 PLUS CEM multimode microwave and irradiated for 9 h (300 W) at 100°C with vigorous stirring. The solvent was evaporated *in vacuo* and the solid residue was heated under reflux with 20 mL of a potassium hydroxide solution for 1 h. After cooling, the crude product was filtered, washed with water, recrystallized from ethanol and dried. Pale yellow solids were obtained. The ^{1}H and ^{13}C NMR spectra are in good agreement with those reported previously.[11]

Computation chemistry calculations were performed using DFT B3LYP formalism using 6-31+G(d,p) basis set. The structure were fully optimized with tight SCF both in vacuum and solvent (acetonitrile) using polarized continuum method (PCM). All calculations were performed with Gaussian 03 software.

Single crystal of **2d** was mounted on a Brucker AXS SMART three-circle diffractometer using graphite monochromated MoKα radiation (λ=0.71073Å), equipped with a CCD two dimensional detector.[26] Data (Table 3) were corrected for Lorentz, polarization, background and decomposition effects. Atomic positions were determined using SHELXS [27] and refined using full matrix least squares.[28] Hydrogen positions were calculated and included in the final cycles of refinement in constrained positions and with fixed isotropic thermal parameters. Absorption corrections were not made due to the small value of the absorption coefficients (Table 3). Extinction was refined for all three structures but was minimal. Table 5 presents the bond angles and distances for **2d**.

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