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Synthesis of Sulfonamide Derivatives of Carboranyl Porphyrins Based on 5−(4−Aminophenyl)−10,15,20−triphenylporphyrin and Mercapto Carboranes

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New carboranyl substituted sulfonamide porphyrins were synthesized in good yields by the reaction of amino group of 5-(p-aminophenyl)-10,15,20-triphenylporphyrin with carboranylsulfonyl chlorides prepared in situ by oxidative chlorination of corresponding mercapto carborane with trichloroisocyanuric acid in MeCN–H_2O system. The reactions were carried out under mild conditions. The structure of all compounds obtained was confirmed by means of electronic, IR, ^{1}H and ^{11}B NMR spectroscopy and mass spectrometry. Quantum-chemical studies by DFT calculations were carried out for synthesized porphyrin derivatives.

Keywords: Porphyrins, metal complexes, carboranes, sulfonamide derivatives, DFT calculations.

Синтез сульфонамидных производных карборанилпорфиринов на основе 5−(4−аминофенил)−10,15,20−трифенилпорфирина и меркаптокарборанов

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Осуществлен синтез новых сульфонамидных карборанилзамещенных порфиринов реакцией аминогруппы 5-(п-аминофенил)-10,15,20-трифенилпорфирина с карборанилсульфонилхлоридами. Последние были получены in situ окислительным хлорированием соответствующих меркаптокарборанов трихлоризоциануровой кислотой.

Ключевые слова: Порфирины, металлокомплексы, карбораны, сульфонамидные производные, теория функционала плотности.

Introduction

Porphyrins and their analogues are a class of chemically and biologically important compounds that have found a variety of applications in different fields such as catalysis,[1-3] non-linear optics,[4] materials,[5] polymer synthesis[6] and energy conversions.[7,8] These macrocyclic compounds play also essential roles in biological systems in such processes as electron transfer, dioxygen transport,[9] substrate transformations[10] and photosynthesis.[11] Porphyrins have been extensively studied as potential photosensitizers in photodynamic therapy (PDT)[12,13] exhibiting characteristics desirable for drug preparations including chemical purity, high quantum yield of singlet oxygen production, significant absorption at longer wavelengths, preferential tumor location, minimal dark toxicity, stability and the ability to dissolve in injectable solvent systems. The structure of these compounds allows for a variety of modifications of their molecules along the periphery of macrocycles in order to optimize their antitumor characteristics. The observed preferential uptake of porphyrin macrocycles in tumors and their efficient use in PDT have led to their investigation as boron delivery agents for boron neutron capture therapy (BNCT).[14,15] Conjugates of porphyrins with carboranes are potential agents for use in PDT and BNCT. To continue our ongoing efforts on porphyrin functionalization,[16] we present herein the synthesis of sulphonamide substituted boronated porphyrins based on reactions of 5-(4-aminophenyl)-10,15,20-triphenylporphyrin with mercapto carboranes. The sulfonamide functional groups can be found in a variety of drugs which show broad spectrum of pharmacological activity such as antitumor,[17,18] anti-HIV,[19] antitubercular,[20] antimicrobial,[21] antileukemic,[22] anticonvulsant and analgesic.[23] In recent years sulfonamide substituted molecules have been investigated as inhibitors of carbonic anhydrase,[24] carboxypeptidase A,[25] HIV-1 integrase,[26] HIV-1 protease,[27] and as agonists of androgen receptor,[28] and β3-andrenergic receptor.[29] By considering the anticancer significance of porphyrins and dependence of the biological properties of porphyrins on their peripheric substituents it was contemplated to synthesize new porphyrin structures combining porphyrin macrocycle, carborane and sulfonamide moiety within one molecule.

Experimental

All reactions were performed in an atmosphere of dry argon. All solvents were dried according to the standard protocols. ^{1}H and ^{11}B NMR spectra were recorded on a Bruker Avance-400 spectrometer operating at 400.13 MHz for ^{1}H NMR and 128.28 MHz for ^{11}B NMR. Chemical shifts (δ) were referenced to the residual solvent peak ($CDCl_3$, 1H: 7.26 ppm) for ^{1}H and external $BF_3{\cdot}OEt_2$ for ^{11}B. IR spectra were recorded on a Bruker FTIR spectrometer Tensor 37 in KBr tablets. Merck silica gel L 0.040–0.080 mesh was used for column chromatography. The identities of new compounds were verified by TLC on Sorbfil and Kieselgel 60 F254 (Merck) plates. The UV-Vis spectra were measured on a spectrophotometer Carl Zeis Specord M 40 in CH_2Cl_2. The mass spectra were obtained using VISION 2000 (MALDI) mass spectrometer, the most intense peaks were given for each compound.

*General procedure of synthesis of carboranylporphyrins **5**–**7**.* To a corresponding thiol **2**, **3** or **4** (14 mg, 0.08 mmol) in MeCN–H_2O mixture (4.0 ml, 1:1) TCCA (19.5 mg, 0.08 mmol) was added at 4 °C. The reaction was stirred for 15–20 min under argon to yield desired carboranylsulfonyl chlorides **8**, **9** or **10**. The completion of the reactions was confirmed by TLC (heptane–CH_2Cl_2, 1:1). The prepared carboranylsulfonyl chloride **8**, **9** or **10** was added to a mixture of porphyrin **1** (40 mg, 0.06 mmol) and NaOAc (26.2 mg, 0.32 mmol) in CH_2Cl_2 (5.0 ml) and the resulting mixture was stirred for 5–9 h under argon at 20 °C. The reaction mixture was poured into water (20 ml) and extracted with CH_2Cl_2 (2×5 ml). The organic solution was dried over Na_2SO_4 and evaporated *in vacuo*. Purification of the residue by silica gel (L 0.040–0.080 mesh) column chromatography, eluent CH_2Cl_2–hexane (1:1 v/v) afforded target compounds **5**–**7**.

*5-[4-(o-Carboran-9'-yl)sulfonamidophenyl]-10,15,20-triphenylporphyrin (**5**).* Yield 35 mg (70 %). *m/z* (MALDI): 836 $[M+H]^+$. IR (KBr) ν_{max} cm^{-1}: 3318 (NH), 3058 (carborane CH), 2606 (BH), 1337 (SO_2), 1156 (SO_2). UV-Vis ($CHCl_3$) λ_{max} (lgε) nm: 420 (4.83), 515 (4.11), 554 (3.88), 593 (3.66), 651 (3.78). ^{1}H NMR ($CDCl_3$) δ_H ppm: –2.77 (2H, br. s, pyrrole NH), 2.97 (2H, s, carborane CH), 7.79 (11H, m, Ph), 8.24 (8H, m, Ph), 8.63 (1H, s, $NHSO_2$), 8.87 (6H, s, β-H), 8.99 (2H, s, β-H). ^{11}B NMR ($CDCl_3$) δ_B ppm: 5.5 (1B, s), -2.5 (1B, d, *J*=158 Hz), –2.6 (2B, d, *J*=156 Hz), –14.5 (4B, d, *J*=154 Hz), –15.6 (2B, d, *J*=166 Hz).

*5-[4-(m-Carboran-9'-yl)sulfonamidophenyl]-10,15,20-triphenylporphyrin (**6**).* Yield 43 mg (86 %). *m/z* (MALDI): 835 $[M]^+$. IR (KBr) ν_{max} cm^{-1}: 3319 (NH), 3053 (carborane CH), 2606 (BH), 1350 (SO_2), 1157 (SO_2). UV-Vis ($CHCl_3$) λ_{max} (lgε) nm: 420 (4.52), 517 (4.49), 553 (4.22), 592 (4.03), 651 (4.11). ^{1}H NMR ($CDCl_3$) δ_H ppm: –2.68 (2H, br. s, pyrrole NH), 3.14 (2H, s, carborane CH), 7.57 (9H, m, Ph), 7.93 (2H, m, Ph), 8.29 (8H, m, Ph), 8.64 (1H, s, $NHSO_2$), 8.88 (6H, s, β-H), 8.97 (2H, s, β-H). ^{11}B NMR ($CDCl_3$) δ_B ppm: –0.9 (1B, s), –6.2 (2B, d, *J*=142 Hz), –9.6 (2B, d, *J*=148 Hz), –13.6 (4B, d, *J*=161 Hz), –17.2 (1B, d, *J*=179 Hz).

*5-[4-(o-Carboran-1'-yl)sulfonamidophenyl]-10,15,20-triphenylporphyrin (**7**).* Yield 30 mg (60 %). *m/z* (MALDI): 835 $[M]^+$. IR (KBr) ν_{max} cm^{-1}: 3314 (NH), 3053 (carborane CH), 2596 (BH), 1348 (SO_2), 1155 (SO_2). UV-Vis ($CHCl_3$) λ_{max} (lgε) nm: 420 (4.62), 515 (4.43), 553 (3.94), 593 (3.73), 651 (3.82). ^{1}H NMR ($CDCl_3$) δ_H ppm: –2.71 (2H, br. s, pyrrole NH), 3.98 (1H, s, carborane CH), 7.76 (11H, m, Ph), 8.21 (8H, m, Ph), 8.68 (1H, s, $NHSO_2$), 8.87 (6H, s, β-H), 8.96 (2H, s, β-H). ^{11}B NMR ($CDCl_3$) δ_B ppm: –1.6 (1B, d, *J*=153 Hz), –5.1 (2B, d, *J*=148 Hz), –8.9 (3B, d, *J*=147 Hz), –12.5 (3B, d, *J*=167 Hz), –13.6 (1B, d, *J*=171 Hz).

*General procedure of synthesis of carboranylporphyrins **11**, **12**.* To a solution of porphyrin **5** or **6** (30 mg, 0.04 mmol) in $CHCl_3$ (10 ml) and MeOH (4 ml) $Ni(OAc)_2{\cdot}4H_2O$ (18 mg, 0.07 mmol) or $Zn(OAc)_2{\cdot}2H_2O$ (16 mg, 0.07 mmol) was added. The resulting mixture was stirred under boiling for 4–6 h under argon and then was diluted with $CHCl_3$ (10 ml), washed with water (2×5 ml), dried over Na_2SO_4, and evaporated to dryness under *vacuo*. Purification of the residue by column chromatography on SiO_2 (eluent CH_2Cl_2–hexane 3:7) afforded target compounds **11**, **12**.

*5-[4-(o-Carboran-9'-yl)sulphonamidophenyl]-10,15,20-triphenylporphyrinatonickel(II) (**11**).* Yield 21 mg (59 %). *m/z* (MALDI): 892 $[M+H]^+$. IR (KBr) ν_{max} cm^{-1}: 3440 (NH), 3055 (carborane CH), 2615 (BH), 1331 (SO_2), 1139 (SO_2). UV-Vis ($CHCl_3$) λ_{max} (lgε) nm: 417 (5.37), 530 (4.21). ^{1}H NMR ($CDCl_3$) δ_H ppm: 3.14 (2H, br. s, carborane CH), 7.70 (11H, m, Ph), 7.86 (2H, d, Ph *J*=7.3 Hz), 7.94 (2H, d, Ph *J*=8.3 Hz), 8.01 (m, 4H, Ph), 8.75 (2H, s, β-H), 8.94 (6H, s, β-H), 9.10 (1H, s, $NHSO_2$). ^{11}B NMR ($CDCl_3$) δ_B ppm: 5.46 (1B, s), –2.8 (1B, d, *J*=158 Hz), –3.0 (2B, d, *J*=156 Hz), –15.8 (4B, d, *J*=154 Hz), –16.6 (2B, d, *J*=166 Hz).

*5-[4-(m-Carboran-9'-yl)sulphonamidophenyl]-10,15,20-triphenylporphyrinatozinc(II) (**12**).* Yield 28 mg (78 %). *m/z* (MALDI): 835 $[M-Zn]^+$. IR (KBr) ν_{max} cm^{-1}: 3423 (NH), 3060 (carborane CH), 2580 (BH), 1337 (SO_2), 1178 (SO_2). UV-Vis ($CHCl_3$) λ_{max} (lgε) nm: 428 (5.28), 566 (3.99), 610 (3.89). ^{1}H NMR ($CDCl_3$) δ_H ppm: 3.32 (2H, s, carborane CH), 7.74 (11H, m, Ph), 8.21 (8H, m,

Ph), 8.56 (2H, s, β-H), 8.94 (6H, br. s, β-H), 8.82 (1H, s, $NHSO_2$). ^{11}B NMR ($CDCl_3$) δ_B ppm: –1.8 (1B, s), –6.3 (2B, d, *J*=159 Hz), –10.1 (1B, d, *J*=159 Hz), –13.2 (5B, d, *J*=168 Hz), -16.9 (1B, d, *J*=192 Hz).

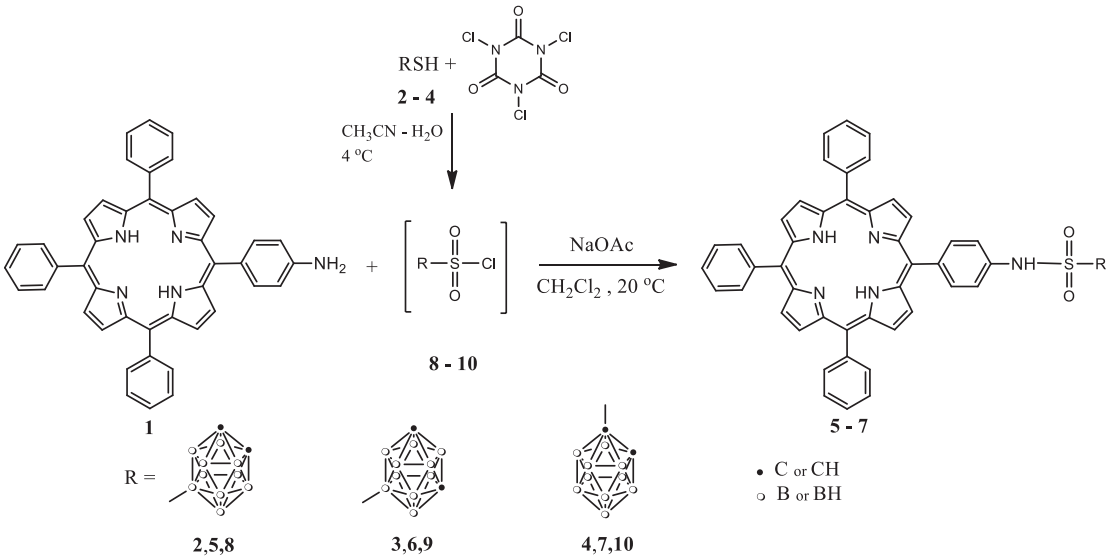
Results and Discussion

In the search for new compounds with potential biological activity in the present work we describe a convenient approach to the preparation of new sulfonamide-substituted carboranyl porphyrins **5**–**7** based on the one-stage reaction of 5-(*p*-aminophenyl)-10,15,20-triphenylporphyrin (**1**)[30] with 9-mercapto-*o*-carborane (**2**),[31] 9-mercapto-*m*-carborane (**3**) [32] and 1-mercapto-*m*-carborane (**4**).[33] Synthesis of boronated sulfonamide porphyrins **5**–**7** was carried out through the nucleophilic reaction of an amino group of porphyrin **1** with carboranylsulfonyl chlorides **8**–**10** in the presence of NaOAc in CH_2Cl_2 under argon by simple stirring at room temperature. In compounds **5**, **6** the porphyrin macrocycle is bound to the boron atom of carborane cluster *via* the $NHSO_2$ spacer while in compound **7**, it is attached to a carbon atom of carborane cluster (Scheme 1). Carboranylsulfonyl chlorides **8**–**10** were prepared *in situ* by oxidative chlorination[34] of corresponding mercapto carborane **2**–**4** with trichloroisocyanuric acid (TCCA) in MeCN–H_2O system.

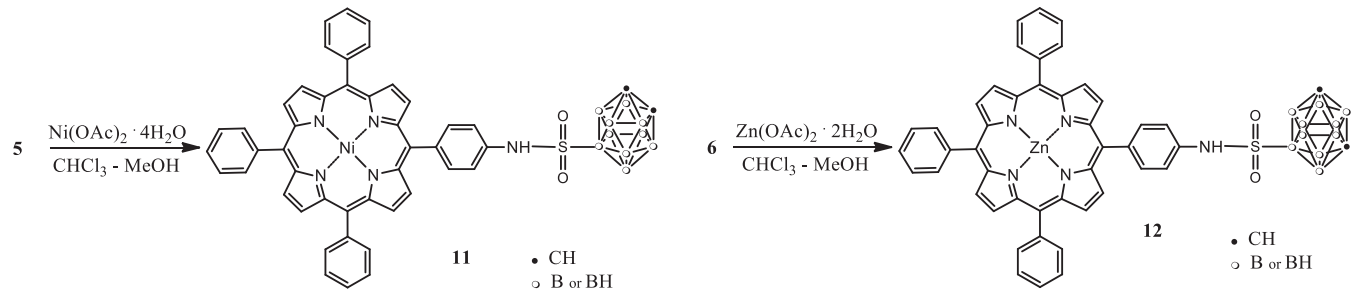
This synthetic approach allowed to obtain the desired sulfonamide porphyrins **5**–**7** in 60–86 % yields. It is known that the sulfonyl chlorides can be readily prepared[35] from the corresponding sulfonic/sulfinic acids under the treatment with $SOCl_2$, PCl_5 or $POCl_3$. It should be noted that previous studies of the oxidation of the SH-group of *o*- and *m*-carboranes with chlorine or bromine resulting in the formation of sulfinic and sulfonic acid derivatives have been reported.[36,37] Compared to these reaction conditions *in situ* oxidative chlorination of mercapto carboranes is more convenient since it is simple and allows to avoid harsh reaction conditions.

Nickel (**11**) and zinc (**12**) complexes of sulfonamide carboranylporphyrins were obtained in 59 and 78 % yields when porphyrins **5** and **6** reacted with $Ni(OAc)_2 \cdot 4H_2O$ and $Zn(OAc)_2 \cdot 2H_2O$, respectively, in $CHCl_3$–MeOH mixture under argon (Scheme 2).

All synthesized porphyrins **5**–**7**, **11**, **12** were isolated by column chromatography (elution with CH_2Cl_2–hexane 2:1, 3:7, or 1:1) as dark red powders. Structures of porphyrins **5**–**7**, and **11**, **12** were established by IR and ^1H, ^{11}B, $^{11}B\{^1H\}$ NMR spectroscopies and mass spectrometry. IR spectra of all porphyrins contain the intense absorption in the range of 2580–2606 cm^{-1} attributed to the BH stretching vibrations. The band at 3060–3053 cm^{-1} indicated the presence of the carborane CH groups. Stretching vibrations of the NH bonds of porphyrins **5**–**7**, and **11**–**12** are observed in the range of 3423–3319 cm^{-1}. The two IR bands for SO_2 group were observed in the range 1350–1337 cm^{-1} and 1178–1155 cm^{-1} as expected. ^1H NMR spectra of porphyrins **5**–**7**, **11**, **12**



Scheme 1. Synthetic route to the carboranyl substituted sulfonamide porphyrins **5**–7.



Scheme 2. Synthesis of metal complexes of sulfonamide carboranylporphyrins **11** and **12**.

exhibit singlet signals of the β-pyrrole protons at δ 8.75–8.99 ppm, aromatic multiplet signals at δ 7.08–8.29 ppm and broadened singlets at δ 2.77–(–2.68) ppm associated with two pyrrolic NH-protons in the core of the free base porphyrin for compounds **5**–**7**. Singlet signals at δ 8.63–9.10 ppm corresponded to the protons of sulfonamide group of prepared compounds. The protons of the carborane CH groups of **5**–**7**, **11**, **12** appeared as broad singlets in the interval δ 2.97–3.98 ppm. It should be noted that signals of all protons in ^{1}H NMR spectra of metallocomplexes **11**, **12** shifted downfield relatively corresponding signals in the spectra of free base porphyrins **5** and **6** that reflects influence of central metal ion on electronic structure both porphyrin and carboran moieties. The ^{11}B{^{1}H}NMR spectra were sufficiently well-resolved to allow integration and contained set of signals between δ_B 5.46–(–17.20) ppm for compounds **5**–**7**, **11, 12** indicative of the *closo*-structure of carborane polyhedra.

To predict a number of molecular properties (molecular geometry, total energy, electron structure and dipole moment) quantum-chemical studies were carried out for porphyrins **5**–**7**, **11**, **12**. Such parameters as geometry optimization, calculation of vibrational mode frequencies, electron density distribution, full energies, transformation energies, transformation entropy were computed at DFT B3LYP/6-31G* level using GAUSSIAN-09 program suite[38-41] under LINUX. The absence of imaginary frequencies indicates that optimized configurations correspond to the minima on the potential energy hypersurfaces.

The optimized geometries of molecules **5** and **11** in gas phase are given for example in Figures 1 and 2. The structures of **5** and **11** are similar in general. Two phenyl rings situated opposite each other *via* porphyrin ring (one of them with -NH-SO_2-carboranyl fragment) are located in the same plane which is perpendicular to the plane of porphyrin ring. The planes of other two phenyl rings are crossed at about 70° to the plane of porphyrin ring (Figure 3). In compound **5** interatomic distance between nitrogen atoms N…N in porphyrin fragment is 4.078 while in NH…NH it is 4.223. The insertion of nickel into the porphyrin ring leads to decrease of interatomic distances between nitrogen atoms to 3.876 thus causing the contraction of porphyrin cycle.

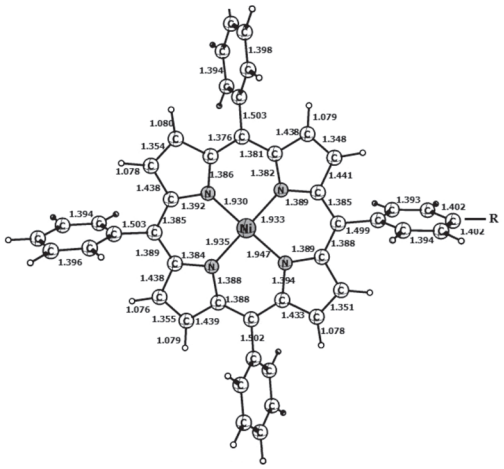


Figure 2. DFT-optimized geometry of porphyrin **11**.

Simultaneously, C–N distance in triad CNC increases on *ca*. 0.02 , while C–C in triad CCC diminishes on the same 0.02. Bond angle (CNC) in **5** is 105.4°, while in **11** it is 103.2°. Table 1 shows the calculated energy characteristics.

The HOMO energy characterizes the electron donating ability and the LUMO energy characterizes the electron accepting ability, while HOMO–LUMO energy gap is very important molecular description to predict stability and reactivity of molecule. Our calculations (Table 2) show that compounds prepared should to be stable both in gas phase and in solution and thus are expected to be successfully used in various applications including antitumor therapy.

The antitumor characteristics of porphyrins **5** and **12** were assessed by measuring the dark toxicity and the ability to cause light-induced death of cultured human tumor cells (HCT116 colon cancer and K562 leukemia cell lines). [42] The porphyrin free base **5** which contains the *o*-carborane substituent, exhibited a low dark cytotoxicity against HCT116 line (IC_{50}>50 μM), so this compound can be used for PDT. The porphyrin zinc complex **12** exhibited a cytotoxic effect against HCT116 cell line (IC_{50}=10 μM) and K562 (IC_{50}=5.2 μM). These agents can be promising as anticancer drug candidates.

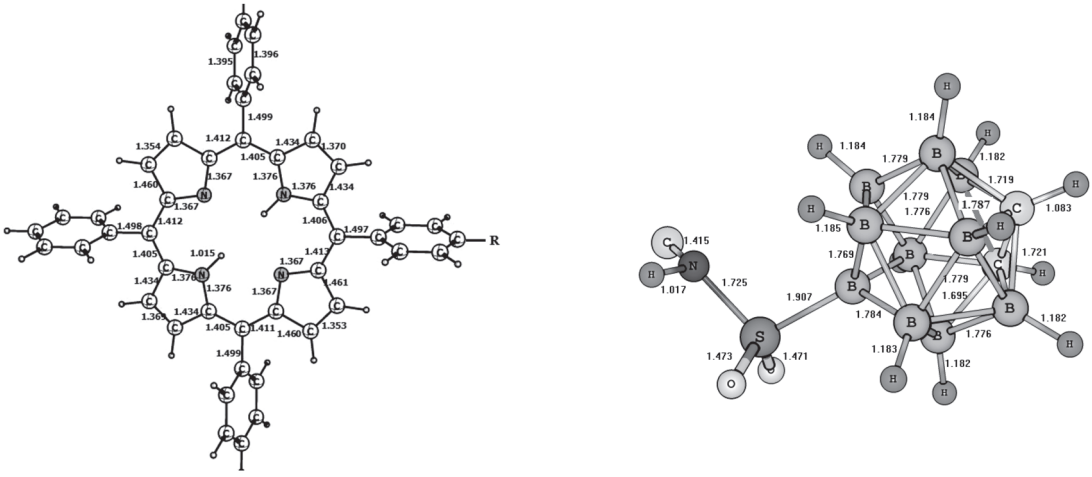


Figure 1. DFT-optimized geometry of porphyrin **5** (left) and carboranyl sulfonamide substituent R (right).

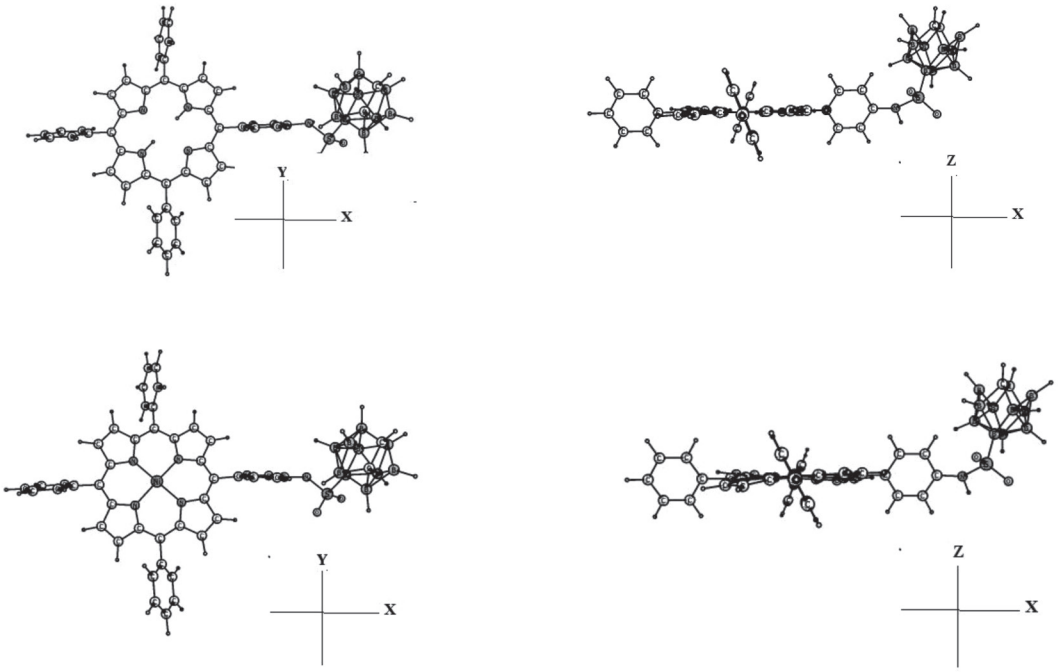


Figure 3. Projections of porphyrin **5** (up) and **11** (bottom).

Table 1. Computed energy and entropy data for compounds **5**-**7**, **11** and **12** in gas phase and in CH_2Cl_2 solution.

Compound	E_t, a.u.	E_{zpc}, a.u.	E_G*), a.u.	S, kcal·M^{-1} grad^{-1}
5	–2848.5872295	–2847.782338	–2847.870512	292.078
6	–2848.6060351	–2847.800703	–2847.880995	269.489
7	–2848.5823005	–2847.778440	–2847.865545	289.206
11	–4355.6506864	–4354.865832	–4354.948808	276.590
12	–4626.6219318	–4625.839633	–4625.929217	297.105
5 + solv	–2848.6117504	–2847.807199	–2847.894658	290.575
6 + solv	–2848.6276585	–2847.822650	–2847.903500	270.963
7 + solv	–2848.5984504	–2847.795077	–2847.882300	289.621
11 + solv	–4355.6844009	–4354.900034	–4354.987936	290.537
12 + solv	–4626.6526262	–4625.870595	–4625.958865	294.086

E_t, – total energy, E_{zpc} – zero point corrected total energy, E_G*) – Gibbs free energy, computation of E_G was carried out at 298.15 K, S – entropy.

Table 2. Computed dipole moments (μ), diagonal tensor elements of polarizability (P_{xx}, P_{yy}, P_{zz}), HOMO and LUMO energies for compounds **5**–**7**, **11** and **12** in gas phase and in CH_2Cl_2 solution.

Compound	μ, D	P_{xx}, Bohr^3	P_{yy}, Bohr^3	P_{zz}, Bohr^3	HOMO, a.u.	LUMO, a.u.
5	7.2988	1089.6	938.6	445.8	–0.1776	–0.0785
6	6.3076	1087.2	936.1	445.3	–0.1763	–0.0794
7	3.0082	1093.3	936.9	440.7	–0.1835	–0.0841
11	6.8384	1052.0	905.6	454.6	–0.1844	–0.0725
12	7.3803	1081.2	933.4	453.4	–0.1800	–0.0756
5 + solv	9.5987	1413.1	1312.9	597.3	–0.1887	–0.0899
6 + solv	8.0890	1409.7	1307.1	596.3	–0.1890	–0.0900
7 + solv	3.2480	1418.9	1312.1	590.3	–0.1903	–0.0913
11 + solv	9.3466	1344.9	1263.4	623.4	–0.1941	–0.0836
12 + solv	9.3891	1399.2	1307.9	607.7	–0.1876	–0.0840

1 Bohr=0.529177 A

Conclusions

In summary, the one step *in situ* sulfonamidation of 5-(*p*-aminophenyl)-10,15,20-triphenylporphyrin with mercapto carboranes proposed in this paper is a convenient route to prepare pure and stable boronated sulfonamide porphyrin derivatives in good yields. The minimum energy conformations were subjected to the full range of calculations, including the peripheral phenyl and carborane groups and the solvent. Because of the readily available starting compounds, and reasonable biological characteristics, this synthetic approach might be applicable in material science and medicine.

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