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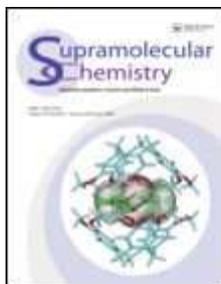
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Keywords:	Tr-podand, AM1d calculations, Potentiometric method, Stability constant

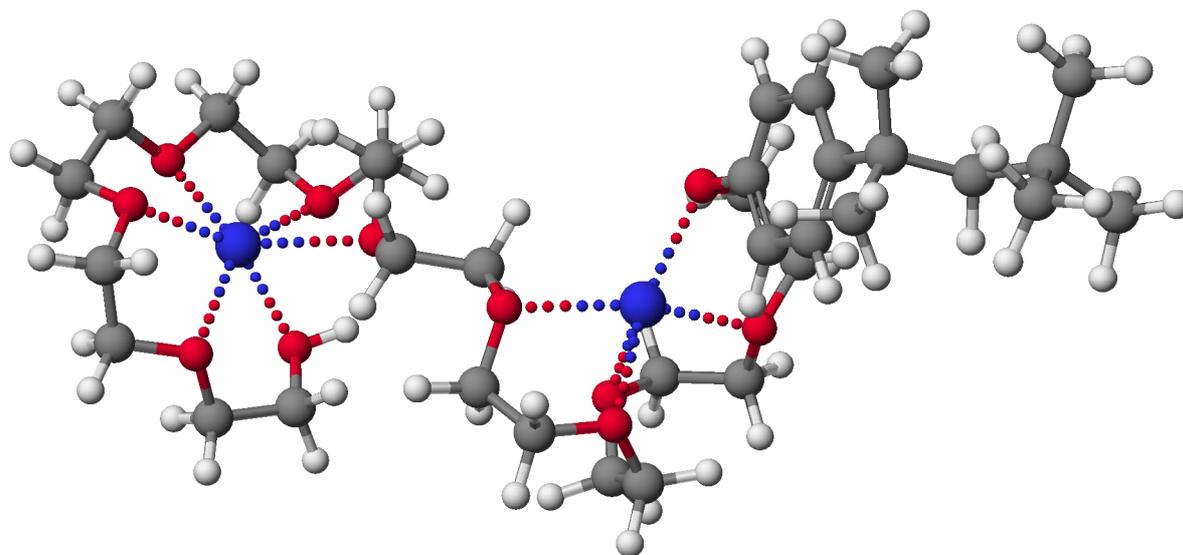
## Potentiometric and AM1d studies of a new class of Tr-podands — silver(I) complexes

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## Potentiometric and AM1d studies of a new class of Tr-podands — silver(I) complexes

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### Abstract

Formation of complexes of structurally comparable six silicon, boron and phosphorous Triton-X podands (Tr-podands) and silver (I) cations in propylene carbonate has been studied by the potentiometric and AM1d semi-empirical methods. Three types of these podands (**2-7**) form stable complexes with Ag<sup>+</sup> cations. The stability constants of the complexes including different number of silver (I) cations are determined. It has been shown that the number of Ag<sup>+</sup> cations complexed by the podands depends strongly on the number of oxaalkyl chains and on the type of central podand's atom (Si, B or P). The (**7**) podand (with six polyoxaalkyl chains) can complex as many as six silver(I) cations. The structures of these complexes are visualized by the AM1d semiempirical method.

**Keywords:** Supramolecular chemistry; Potentiometric method; Tr-podand; Silver(I) complexes; AM1d calculations; Stability constant

### 1. Introduction

The macrocyclic compounds both cyclic and acyclic are able to form complexes of different stoichiometry with some metal cations [1-4]. Podands are acyclic compounds characterized by a similar capability of complex formation with metal ions as crown ethers and cryptands [5, 6]. In earlier papers we have studied the complexes of various inorganic esters of ethylene glycols and their derivatives with monovalent cations such as Li<sup>+</sup>, Na<sup>+</sup> or K<sup>+</sup> using multinuclear NMR, FT-IR, calorimetric, potentiometric and semiempirical (PM3, PM5) methods [7–12]. We also shown

1  
2  
3 [13-15] that the silicon and phosphorus podands form stable complexes with silver (I) cations of  
4 various stoichiometry depending on the length of the oxaalkyl chains.

5  
6 Triton-X surfactants are used in numerous commercial and industrial products. Large amounts of  
7 such surfactants and their various residual biodegradation by-products are ultimately released into  
8 the environment. We have recently published a paper reporting the first synthesis of a group of  
9 Tr-polypodands (Triton-X polypodands) with different central atoms, such as Si, B or P. Results  
10 of this study demonstrate the application of these new compounds in some organic reactions in  
11 the phase transfer catalysis (PTC) conditions [16].

12  
13 In this paper we want to demonstrate the results of a study of complex formation between Triton-  
14 X (1) and new six Tr- podands (2-7) (Figure 1) including two or three oxaalkyl chains bonded  
15 with phosphorus, boron, sulphur or silica atoms or six polyoxaalkyl chains (7) and silver (I)  
16 cations and as well as their structures. This process has been studied by the potentiometric and  
17 AM1d methods.

## 28 **2. Experimental**

29  
30 The Tr-podands (2-7) were synthesized according to the method described in papers [16]. Triton  
31 X-100 was a commercial product (Aldrich). Propylene carbonate used as a solvent for  
32 potentiometric studies was from Merck.

### 37 **2.1. Potentiometric measurements**

38  
39 The potentiometric method used was described in Ref. [17]. The potentiometric titration was  
40 performed in propylene carbonate at 25<sup>0</sup>C using an OP-205 Radelkis pH-meter linked to a  
41 personal computer via a PCL-838 control card. The equilibrium constants were calculated using  
42 the program STOICHIO based on the non-linear least squares Gauss–Newton–Marquardt  
43 algorithm [18].

### 49 **2.2. AM1d semiempirical calculations**

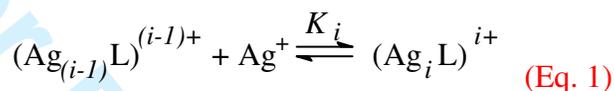
50  
51 AM1d semiempirical calculations were performed using the Win Mopac 2003 program. Full  
52 geometry optimization of the studied complexes of Si-podand with silver(I) cations was carried  
53 out without any symmetry constraints [19].  
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### 3. Results and discussion

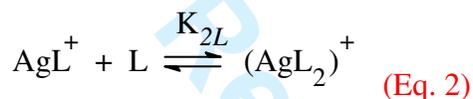
The formulae of the podands studied and their abbreviations are shown in Figure 1.

#### 3.1. Potentiometric measurements

The stability constants ( $K_i$ ) of  $i:1$  silver(I):Tr-podand complexes were calculated for the following equilibria Eq.1 and Eq. 2:



where  $i=1, 2, 3\dots$  and for 1:2 complexes of silver(I):Tr-podand the stability constants  $K_{2L}$  were calculated for the equilibrium:



The stability constants of silver(I) complexes with Triton-X podands in propylene carbonate at 25<sup>0</sup>C are collected in Table 1. The data given in Table 1 indicate the formation of two types of complexes in propylene carbonate as solvent, i.e.  $\text{Ag}_i\text{L}^{i+}$  ( $\log K_i$ ) and  $\text{AgL}_2^+$  ( $\log K_{2L}$ ).

We observed that with increasing number of the polyoxaalkyl chains and the same number of oxygen atoms in the molecule, the formation of the  $\text{Ag}_i\text{L}^{i+}$  complexes is favoured. This fact also determines the stoichiometry of the complexes, i.e. their structures. In all cases the most favourable structure of the complex made by silver(I) and Si-podand is the 1:1 stoichiometry. For the complexes of podands **1-6**, the type of the Tr-podand's central atom does not influence the value of stability constants of these complexes. The constants of complexation of silver with podand **7** containing 6polyoxaethylene chains are slightly higher than those of the complexes of the same stoichiometry but with different podands. For instance the highest value of the stability constant for the 1:1 complex with silver(I) for ligand **7** is  $\log K_1 = 6.89 \pm 0.06$ . The stability constants of the complexes with other stoichiometries decrease with increasing number of the complexed silver(I) cations (Table 1).

### 3.2. AM1d semiempirical calculations

The values of heats of formation of the complexes of triton and triton based podands and different numbers of silver(I) cations are collected in Table 2. This data show that the HOF (heat of formation) of the complex strongly depends on the number of silver cations complexed. The  $\Delta$ HOF is the difference between the HOF of the complex and the sum of HOFs of the isolated ligand and cations. For Triton (**1**) addition of up to 2 silver cations decreases the value of  $\Delta$ HOF, addition of another cation increases this value, making the complex unstable. This means that, for this complex, the stoichiometry of 1ligand:2Ag<sup>+</sup> is preferred. For the podands studied other stoichiometries are possible, the number of the complexed cations vary and strongly depend on the number of oxygen atoms in the host molecule. For podand (**2**) the preferred stoichiometry is 1:3, for podand (**7**) it is 1:6 and for all other podands (**3-6**) it is 1:4. The podands with tri pendant arms have the same number of oxygen atoms and differ only in the type of the central atom or when the central atom is Si, in the extra group on this atom. These differences for triton podands have only slight effect on its complexation ability, the  $\Delta$ HOFs change only by a few percent. This correlates well with the potentiometric data. In our previous study [15] with podands ending with alkyl groups the influence of the central atom was greater. We suggest that “marginalization of central atom” is the effect of the bulk ending of the triton chain. The visualisation of the energetically favourable structures of triton (**1**) with 2 Ag<sup>+</sup> cations and podand (**4**) with 4 Ag<sup>+</sup> cations are shown in Figs. 2 and 3, respectively. In Fig. 3, in addition the “bulk” effect of the triton ending group is shown.

It is interesting to note, that the formation of complexes of the 2:1 stoichiometry is indicated by the  $\log K_{2L}$  values. The value of this constant for complex (**5**) is significantly smaller ( $\log K_{2L} = 0.98$ ) than the corresponding values of the other Tr-podand complexes (2L) ( $\log K_{2L}$  of about 4.0). According to these values, the formation of complexes of compound (**5**) with B as the central atom with silver is less favourable than that of the same type of complexes with Si-ligands (compounds: **3** or **4**). The same tendency is observed for the heat of formation (HOF) of these complexes, calculated by AM1d. For the 2:1 complex of compound (**5**), the complex formation energy is about  $-444.07$  kJ, but for compound (**3**) it is about  $-579.38$  kJ. The difference follows from the structures of these complexes. In the process of formation of the complex composed of two ligands **5** and one silver ion, one chain from each ligand is involved, while the other chains

are not engaged in the complexation. In the process of formation of the complex of two ligands with Si as the central atom and one silver cation, two chains from each ligand are involved.

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Table 1 The stability constants ( $\log K_i$ ) and ( $\log K_{2L}$ ) of the complexes of Tr-podands with silver(I) cations in propylene carbonate at 25°C.

	$\log K_1$	$\log K_2$	$\log K_3$	$\log K_4$	$\log K_5$	$\log K_6$	$\log K_{2L}$
<b>1</b>	$5.46 \pm 0.03$	$4.22 \pm 0.05$	-	-	-	-	-
<b>2</b>	$6.12 \pm 0.05$	$5.16 \pm 0.09$	$4.63 \pm 0.12$	-	-	-	$3.26 \pm 0.17$
<b>3</b>	$6.03 \pm 0.05$	$5.66 \pm 0.08$	$4.94 \pm 0.10$	$4.62 \pm 0.11$	-	-	$3.55 \pm 0.18$
<b>4</b>	$5.94 \pm 0.03$	$5.45 \pm 0.05$	$4.91 \pm 0.09$	$4.29 \pm 0.12$	-	-	-
<b>5</b>	$5.73 \pm 0.04$	$5.48 \pm 0.07$	$4.86 \pm 0.10$	$4.45 \pm 0.13$	-	-	$0.98 \pm 0.26$
<b>6</b>	$6.09 \pm 0.05$	$5.61 \pm 0.08$	$4.48 \pm 0.11$	$4.11 \pm 0.14$	-	-	$3.95 \pm 0.20$
<b>7</b>	$6.89 \pm 0.06$	$6.14 \pm 0.14$	$5.53 \pm 0.10$	$5.15 \pm 0.18$	$4.95 \pm 0.13$	$4.35 \pm 0.26$	-

Table 2. The heat of formation (HOF) of podands and their energetically favourable complexes with Ag<sup>+</sup> cations.

No. of compound	Compound	Mixture	HOF [kJ/mol]	ΔHOF [kJ/mol]
1	Triton	Tr	-2144.21	
		Tr:Ag <sup>+</sup> (uncomplexed)	-1128.70	
		Tr:Ag <sup>+</sup> (complexed)	-1535.71	-407.01
		Tr:2Ag <sup>+</sup> (uncomplexed)	-113.19	
		Tr:2Ag <sup>+</sup> (complexed)	-768.30	-655.11
		Tr:3Ag <sup>+</sup> (uncomplexed)	902.32	
		Tr:3Ag <sup>+</sup> (complexed)	386.05	-516.27
2	Si2Me	Si2Me	-4517.90	
		Si2Me:2Ag <sup>+</sup> (uncomplexed)	-2486.88	
		Si2Me:2Ag <sup>+</sup> (complexed)	-3274.95	-788.07
		Si2Me:3Ag <sup>+</sup> (uncomplexed)	-1471.37	
		Si2Me:3Ag <sup>+</sup> (complexed)	-2277.43	-806.06
		Si2Me:4Ag <sup>+</sup> (uncomplexed)	-455.86	
		Si2Me:4Ag <sup>+</sup> (complexed)	-1205.06	-749.20
3	SiVin	SiVin	-6593.82	
		SiVin:2Ag <sup>+</sup> (uncomplexed)	-4562.80	
		SiVin:2Ag <sup>+</sup> (complexed)	-5285.23	-722.43
		SiVin:3Ag <sup>+</sup> (uncomplexed)	-3547.29	
		SiVin:3Ag <sup>+</sup> (complexed)	-4453.29	-906.00
		SiVin:4Ag <sup>+</sup> (uncomplexed)	-2531.78	
		SiVin:4Ag <sup>+</sup> (complexed)	-3563.99	-1032.21
4	SiPh	SiPh	-6553.02	
		SiPh:2Ag <sup>+</sup> (uncomplexed)	-4522.00	
		SiPh:2Ag <sup>+</sup> (complexed)	-5258.49	-736.49
		SiPh:3Ag <sup>+</sup> (uncomplexed)	-3506.49	
		SiPh:3Ag <sup>+</sup> (complexed)	-4441.21	-934.72
		SiPh:4Ag <sup>+</sup> (uncomplexed)	-2490.98	
		SiPh:4Ag <sup>+</sup> (complexed)	-3534.83	-1043.85
5	B	B3	-6630.45	
		B3:2Ag <sup>+</sup> (uncomplexed)	-4599.43	
		B3:2Ag <sup>+</sup> (complexed)	-5318.25	-718.82
		B3:3Ag <sup>+</sup> (uncomplexed)	-3583.92	
		B3:3Ag <sup>+</sup> (complexed)	-4492.76	-908.84
		B3:4Ag <sup>+</sup> (uncomplexed)	-2568.41	
		B3:4Ag <sup>+</sup> (complexed)	-3580.30	-1011.89
6	PO	B3:5Ag <sup>+</sup> (uncomplexed)	-1552.90	
		B3:5Ag <sup>+</sup> (complexed)	-2355.01	-802.11
		PO	-6852.14	
		PO:2Ag <sup>+</sup> (uncomplexed)	-4821.12	
		PO:2Ag <sup>+</sup> (complexed)	-5492.96	-671.84
		PO:3Ag <sup>+</sup> (uncomplexed)	-3805.61	
		PO:3Ag <sup>+</sup> (complexed)	-4674.12	-868.51
7	Si2	PO:4Ag <sup>+</sup> (uncomplexed)	-2790.10	
		PO:4Ag <sup>+</sup> (complexed)	-3757.62	-967.52
		PO:5Ag <sup>+</sup> (uncomplexed)	-1774.59	
		PO:5Ag <sup>+</sup> (complexed)	-2658.79	-884.20
		2Si2	-13372.70	
		Si2:4Ag <sup>+</sup> (uncomplexed)	-9310.68	
		Si2:4Ag <sup>+</sup> (complexed)	-10651.20	-1340.55
		Si2:6Ag <sup>+</sup> (uncomplexed)	-7279.66	
		Si2:6Ag <sup>+</sup> (complexed)	-8860.62	-1580.96
		Si2:8Ag <sup>+</sup> (uncomplexed)	-5248.64	
		Si2:8Ag <sup>+</sup> (complexed)	-6465.94	-1217.30

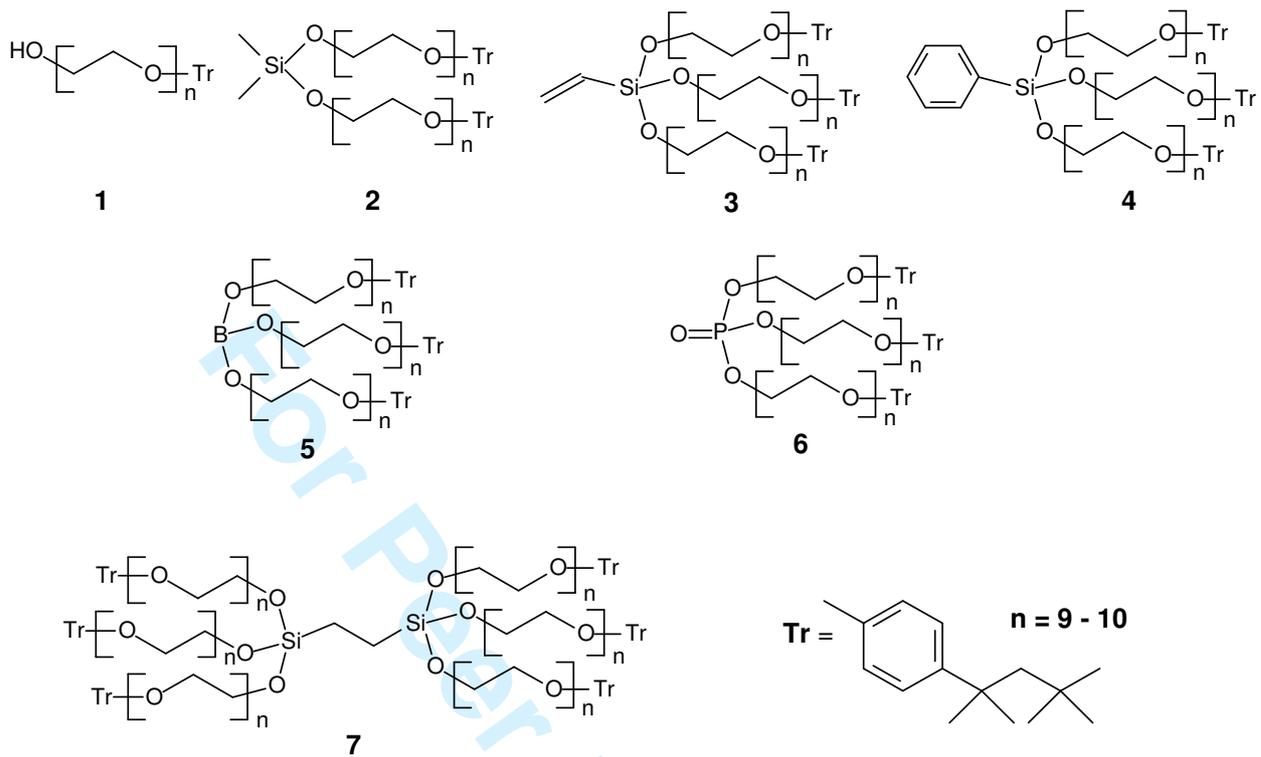
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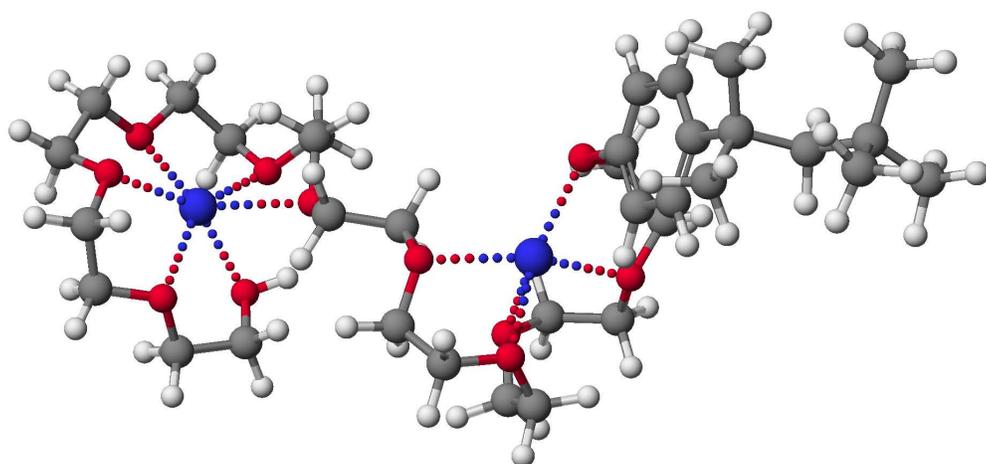
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## Figure captions

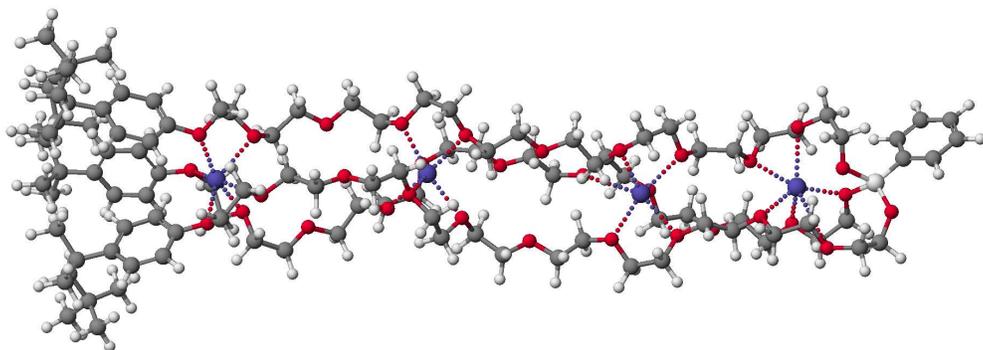
1. Compounds studied.
2. Calculated structure of triton (**1**) with 2 Ag<sup>+</sup> cations.
3. Calculated structure of podand (**4**) with 4 Ag<sup>+</sup> cations

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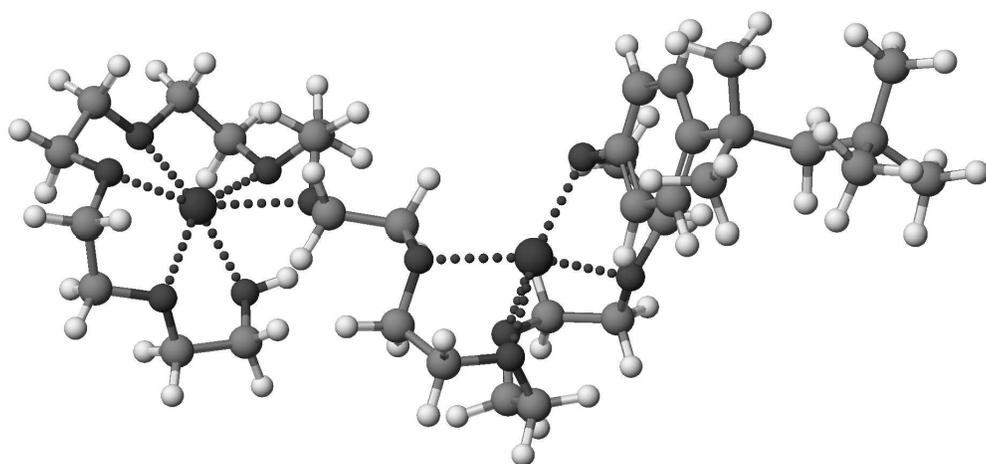


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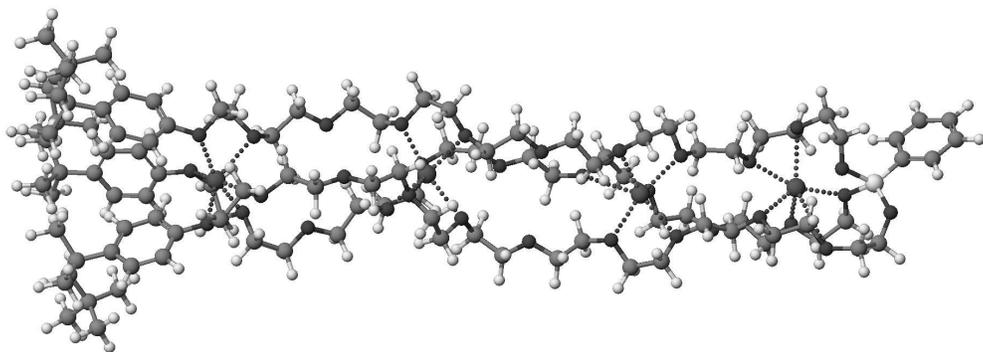


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