



Isolation and structure determination of a tetrameric sulfonyl dilithio methandiide in solution based on crystal structure analysis and $^6\text{Li}/^{13}\text{C}$ NMR spectroscopic data

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Abstract

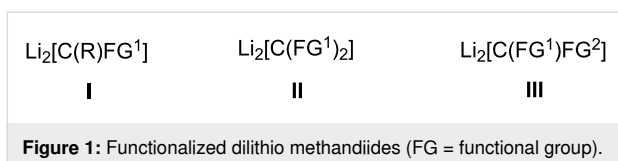
Dilithio sulfonyl methandiides are a synthetically and structurally highly interesting group of functionalized geminal dianions. Although very desirable, knowledge of the structure of dilithio methandiides in solution was lacking up to now. Herein, we describe the isolation and determination of the structure of tetrameric dilithio (trimethylsilyl)(phenylsulfonyl) methandiide in solution and in the crystal. The elucidation of the structure of the tetramer is based on crystal structure analysis and $^{13}\text{C}/^6\text{Li}$ NMR spectroscopic data. A characteristic feature of the structure of the tetramer is the C_2 symmetric C–Li chain, composed of four doubly Li-coordinated dianionic carbon and five Li atoms. Three Li atoms are devoid of a contact to a dianionic C atom. The tetramer, the dianionic C atoms of which undergo fast exchange, is in THF solution in fast equilibrium with a further aggregate, which is stable only at low temperatures.

Introduction

Functionalized dilithio methandiides **I–III** (Figure 1) are a fascinating class of compounds, whose reactivity, synthetic potential, and structure have received much interest in organic and metalorganic chemistry [1,2]. The most interesting aspects of compounds **I–III** are the likelihood of the formation of two new carbon–carbon and carbon–metal bonds, and the bonding

situation of the dianionic carbon atom, including its electronic structure and coordination geometry, together with the possibility of a coordination by two lithium atoms.

The sulfonyl dilithio methandiides **2**, carrying various substituents R^1 and R^2 , have attracted particular attention [1–6]. Reac-



tivity studies of **2** with carbon and metal-based electrophiles revealed a high synthetic potential, allowing, for example, the synthesis of carbo- and heterocycles [4,6], and transition-metal carbene complexes [1,2], carrying the synthetically versatile sulfonyl group [7,8].

Dilithio methandiides **2** are accessible from sulfonyl lithio methanides **1** [9] through α -deprotonation [1,2,4], and from arylsulfonyl dilithio methanides **3** [10,11] through *ortho*, α -transmetallation [10–13] (Scheme 1).

We had found that the α -deprotonation of the lithio methanide **1a** with *n*-butyllithium (*n*-BuLi) gave the stable silyl and sulfonyl-substituted dilithio methandiide **2a** [14,15]. The use of *n*-BuLi, inadvertently containing Li_2O , had yielded prismatic crystals of **2a**. An X-ray crystal structure analysis had shown a C_i symmetric hexamer, $(\mathbf{2a})_6 \cdot \text{Li}_2\text{O} \cdot (\text{THF})_6$, the dianionic C atoms of which are each coordinated by two Li atoms in a non-planar fashion (vide infra) [15]. Because of the general interest in dilithio methandiides that remains unabated to this day, crystal structure analysis has been carried out of a large number of derivatives [16–43]. They generally showed intricate aggregates with complex C–Li and C–Li–heteroatom chains, containing doubly lithiated C atoms. However, as much as there is now knowledge of the structure of dilithio methandiides in the crystal, as little is known about the structure and dynamics in solution [1,2,16–43]. The main obstacles at characterizing dilithio methandiides in terms of aggregate size, C–Li connectivity, Li coordination of the dianionic C atoms, and dynamics were poor solubility and problems to locate the ^{13}C signals of the dianionic C atoms or the detection of only broad ones. Knowledge of the solution structure of dilithio methandiides

would be, however, highly desirable in order to obtain a more complete understanding of the reactivity and coordination chemistry in general, and of the dianionic C atom in particular. During the structural investigation of **2a** it was observed that the Li_2O -free methandiide is in contrast to $(\mathbf{2a})_6 \cdot \text{Li}_2\text{O} \cdot (\text{THF})_6$ readily soluble in THF. ^6Li and ^{13}C NMR spectroscopy of **2a** had led to the detection of an aggregate, a substructure of which could be disclosed [15].

We describe in this paper the isolation of a tetramer of **2a** and the determination of its structure in solution based on crystal structure analysis and previously described NMR spectroscopic data.

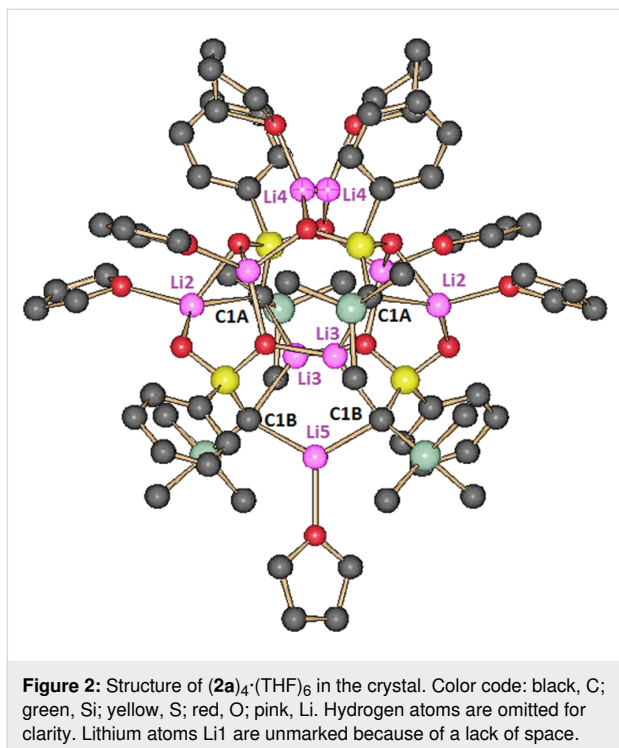
Results and Discussion

Crystal structure

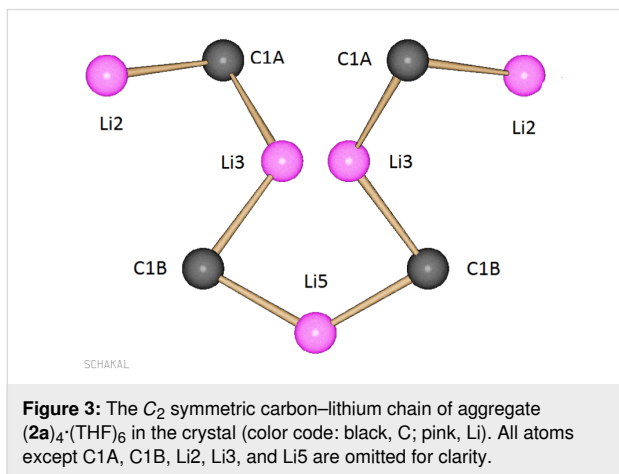
Treatment of sulfone **4** in a mixture of THF and *n*-hexane with Li_2O -free *n*-BuLi (1.88 equiv) in *n*-hexane at -90°C followed by warming the solution to room temperature gave octahedral crystals of **2a**. The use of two equivalents of the base led to a slower crystal growth. The X-ray crystal structure analysis showed a chiral C_2 symmetric tetramer, $(\mathbf{2a})_4 \cdot (\text{THF})_6$, containing six THF molecules (Figure 2) [44]. The lithium atom Li4 is not exactly located on the C_2 axis. It is resolved by two Li4 in general positions near the C_2 axis each with an occupancy of 0.5. Therefore, Figure 2 shows two positions for Li4 and the attached THF molecule (see the Supporting Information File 1 for details). The aggregate has two different types of dianionic carbon atoms, C1A and C1B, which are each coordinated by two Li atoms. Five Li atoms are coordinated by carbon atoms (2 Li2, 2 Li3 and Li5) and three Li atoms are without contact to a carbon atom and only coordinated by oxygen atoms (2 Li1 and Li4). Lithium atoms Li3 and Li5, which are each coordinated by two dianionic carbon atoms, have planar trigonal coordination geometry. The coordination geometry of C1A and C1B is characterized by τ_4 values [45] of 0.68 and 0.86, respectively, indicating seesaw geometry for C1A and a trigonal pyramidal one for C1B.



Scheme 1: Synthesis of sulfonyl dilithio methandiides **2**.



The most interesting structural feature of tetramer $(2a)_4 \cdot (THF)_6$ is the linear carbon–lithium chain shown in Figure 3, which has C_2 symmetry and contains the four dianionic carbon atoms and five lithium atoms. It will be shown later that the presence of this chain is the key to the assignment of the structure of the aggregate in solution (vide infra).



The tetramer $(2a)_4 \cdot (THF)_6$ shows besides the C–Li chain a number of further interesting structural features. Lithium atom Li5 bridges an eight-membered (C–Li–O–S)₂ ring at the carbon atoms, while Li4 overpasses an eight-membered (O–S–O–Li)₂ ring at the oxygen atoms. Eight-membered (O–S–O–Li)₂ rings of this type are also found as typical structural element of

dimeric sulfonyl lithio methanides **1** in the crystal [46–50]. The atoms C1A, Li2, O1A, and S1 are embedded in two four-membered rings, while two lithium atoms, a sulfur atom, and three oxygen atoms form two six-membered rings. Because of the presence of C–Li and O–Li bonds in $(2a)_4 \cdot (THF)_6$, the dicarbanions are both C,C- and O,Li-dilithiated species.

The C–Li, C–S, and O–Li bond lengths (Table 1) of the tetramer $(2a)_4 \cdot (THF)_6$ are in the range of those found in the hexamer $(2a)_6 \cdot Li_2O \cdot (THF)_6$ and functionalized dilithio sulfonyl methandiides [40,43].

Table 1: Selected bond lengths, bond angles, and dihedral angles of $(2a)_4 \cdot (THF)_6$.

bond lengths ^a	bond angles ^b
C1A–S 156.8(6)	C1A–S–C2A 115.4(3)
C1B–S 158.7(6)	C1A–Li3–C1B 120.9(5)
C1A–Li2 222.2(11)	O1F–Li5–C1B 118.6(4)
C1A–Li3 222.7(11)	C1B–Li5–C1B 122.8(7)
C1B–Li3 224.2(11)	O2B–Li3–C1A 117.2(5)
C1B–Li5 209.8(9)	O2B–Li3–C1B 121.4(5)
O1–Li2 216.7(12)	S–C1A–Si 125.4(4)
O1–Li1 196.7(10)	C1B–S–C2B 115.3(3)
O2–Li4 187(4)	Li2–C1A–Li3 86.2(4)
O1B–Li2 189.1(11)	S–C1A–Li2 85.2(4)
O2B–Li1 195.6(10)	Li5–C1B–Li3 91.4(4)
C1A–Si 179.3(6)	S–C1B–Si 117.9(3)
C1B–Si 180.9(6)	
dihedral angles ^b	
Li2–C1A–Li3–C1B 35.2(6)	C2A–S–C1A–Si 51.2(5)
Li3–C1B–Li5–C1B 33.6(3)	C2B–S–C1B–Si 78.6(4)

^aIn pm. ^bIn degree.

Solution structure

The synthesis of **2a** from sulfone ⁶Li and ¹³C-labelled **4** with Li₂O-free *n*-BuLi had yielded the methandiide, being readily soluble in THF. ¹³C and ⁶Li NMR spectroscopy of ¹³C,⁶Li-**2a** in [D₈]THF [15,51–53] had shown an aggregate, **2a-I**, which is present in the whole temperature range from 22 °C to –103 °C. The formation of a further equilibrium aggregate, **2a-II**, was detected from –50 °C downwards. The equilibrium between the aggregates lies at –103 °C on the side of **2a-II**. Interestingly, formation of **2a-II** in THF could not be detected when diglyme was present.

According to the ¹³C and ⁶Li NMR spectroscopic experiments of **2a-I** at –103 °C, the aggregate contains a C_2 symmetric linear carbon–lithium chain composed of the four dianionic carbon and five lithium atoms (Figure 4).

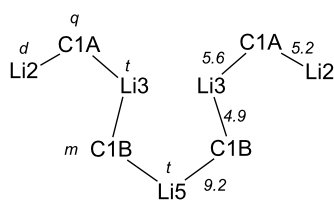


Figure 4: C_2 Symmetric carbon–lithium chain of **2a-I** in THF, showing the carbon–lithium connectivities, multiplicities of the NMR signals (left), and magnitudes of $^1J(^{13}\text{C}, ^6\text{Li})$ couplings in Hz (right) [15].

The carbon–lithium chain includes three different types of lithium atoms, Li2, Li3, and Li5 and two different types of dianionic atoms, C1A and C1B. The ^{13}C NMR spectrum of $^{13}\text{C}, ^6\text{Li}$ -**2a-I** at -103°C showed a quintet (q) for C1A ($\delta = 49.9$ ppm) and a multiplet (m) for C1B ($\delta = 51.4$ ppm) due to $^6\text{Li}, ^{13}\text{C}$ spin coupling. The ^6Li NMR spectrum of **2a-I** at -103°C displayed three signals split by $^6\text{Li}, ^{13}\text{C}$ spin coupling. Selective $^6\text{Li}\{^{13}\text{C}\}$ double resonance and two-dimensional double quantum based shift correlation experiments had served to establish the ^6Li – ^{13}C connectivity. In addition, ^6Li spin echo spectroscopy with gated ^{13}C decoupling had confirmed the multiplicities of the ^6Li signals. All together these experiments had established a triplet (t) structure for the signals of Li3 ($\delta = 2.62$ ppm) and Li5 ($\delta = 2.86$ ppm) and a doublet (d) structure for the signal of Li2 ($\delta = 1.17$ ppm) [15,51–53]. Essential for the success of the NMR spectroscopic investigation of **2a** was the $^{13}\text{C}, ^6\text{Li}$ labelling of the dilithio methandiide. It allowed the detection of the otherwise low intensity signals of the dianionic carbon atoms of the aggregates and the attainment of signals with a small line width [54].

The complete connectivity of the carbon–lithium chain of **2a-II** could not be revealed, since the determination of the multiplicities of all ^6Li and ^{13}C signals failed.

Undoubtedly, the C_2 symmetric linear C–Li chain is the most revealing structural feature of tetramer **2a-I**, since it contains besides Li atoms the four dianionic C atoms. A chain having these carbon–lithium connectivities is contained in tetramer $(\mathbf{2a})_4\cdot(\text{THF})_6$ in the crystal. The excellent agreement between the two C–Li chains shows that **2a-I** is a tetramer, adopting in solution the same structure as the tetramer $(\mathbf{2a})_4\cdot(\text{THF})_6$ in the crystal. Although the lithium oxygen bonds of **2a-I** evaded a direct detection by NMR spectroscopy, the $^{13}\text{C}, ^6\text{Li}$ shift correlation experiments of **2a-I** had shown two ^6Li signals, lacking correlation with ^{13}C signals [15]. Thus, there is good reason to believe that the lithium oxygen bonds of $(\mathbf{2a})_4\cdot(\text{THF})_6$ are retained in **2a-I** in solution. Most likely, six lithium atoms of **2a-I** are coordinated by THF molecules in a similar way as in tetramer $(\mathbf{2a})_4\cdot(\text{THF})_6$.

The aggregate **2a-I** is fluxional in THF with an estimated barrier of $\Delta G^\ddagger = 12.0 \pm 0.5$ kcal/mol (248 K) for the exchange of the dianionic C atoms C1A and C1B [53]. An intra-aggregate exchange seems to be less probable, because it would require an extensive carbon lithium and oxygen lithium bond reorganization (cf. Figure 2). A more likely scenario for the exchange would be the existence of a THF-assisted tetramer–dimer equilibrium.

Bonding of the dianionic C atoms

^6Li NMR spectroscopy of tetramer **2a-I** had revealed a dianionic carbon atom, C1B, carrying two different Li atoms, a bonding situation which is reflected by the two different $^6\text{Li}, ^{13}\text{C}$ coupling constants. It was thus of particular interest to see whether this feature is mirrored by the bonding situation of C1B of $(\mathbf{2a})_4\cdot(\text{THF})_6$. An inspection of the tetramer shows for C1B different carbon–lithium bond lengths, while those of C1A are similar in length. The shorter C1B–Li5 bond corresponds to a larger and the longer C1B–Li3 bond to a smaller $^6\text{Li}, ^{13}\text{C}$ coupling constant (Table 2). Accordingly, the similar coupling constants of C1A in **2a-I** are matched by similar carbon lithium bond lengths of C1A in $(\mathbf{2a})_4\cdot(\text{THF})_6$. It is generally accepted that the carbon lithium interaction in dilithio methandiides is ionic in nature [1,2]. The observation of $^6\text{Li}, ^{13}\text{C}$ couplings shows, however, that the carbon lithium bonds in **2a-I** have a covalent contribution as generally observed for organolithiums [55].

Table 2: $^1J(^{13}\text{C}, ^6\text{Li})$ coupling constants of **2a-I** and bond lengths of $(\mathbf{2a})_4\cdot(\text{THF})_6$.

bond	2a-I $^1J^a$	$(\mathbf{2a})_4\cdot(\text{THF})_6$ lengths ^b
C1B–Li5	9.2	209.8(11)
C1B–Li3	4.9	224.2(11)
C1A–Li3	5.2	222.7(11)
C1A–Li2	5.6	222.2(11)

^aIn Hz. ^bIn pm.

Three mechanisms most likely contribute to the stabilization of the negative charge of the carbon atoms of tetramer $(\mathbf{2a})_4\cdot(\text{THF})_6$ and hexamer $(\mathbf{2a})_6\cdot\text{Li}_2\text{O}\cdot(\text{THF})_6$, electrostatic interaction with and charge polarization by the positively charged sulfur atom [56] and silicon atom [57], and negative $n_{\text{C}}-\sigma^*_{\text{SPh}}$ hyperconjugation [56,58]. The anions of $(\mathbf{2a})_4\cdot(\text{THF})_6$ and $(\mathbf{2a})_6\cdot\text{Li}_2\text{O}\cdot(\text{THF})_6$ adopt conformations around the carbon sulfur bond, which would allow for stabilization by negative hyperconjugation. Density functional theory and natural bond order calculations of dilithio methandiides of type **II** [32,43] suggest that the two lone pairs at the dianionic

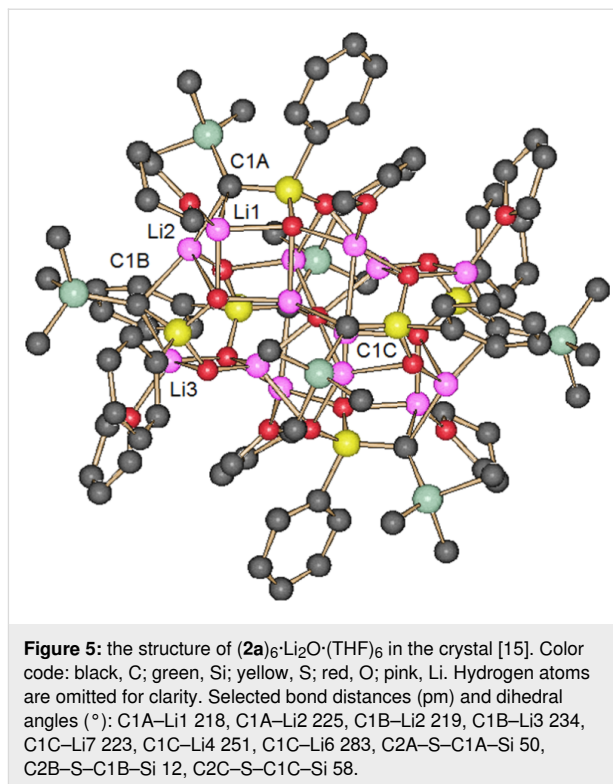
carbon atom of $(2a)_4 \cdot (THF)_6$ and $(2a)_6 \cdot Li_2O \cdot (THF)_6$ are perhaps located in an sp^2 hybridized orbital and p orbital. However, the importance and quantification of the three stabilizing factors as well as the electronic structure of **2a** have to await investigation by quantum chemical calculation. It seems appropriate in this context to have a look at the bonding situation of the corresponding sulfonyl lithio methanides **1**. Their anion is stabilized by electrostatic interaction, polarization, and negative $n_C-\sigma^*_S$ hyperconjugation, with electrostatic interaction as dominating mechanism [56,58]. The lithio methanides **1** are monomeric or dimeric in THF solution and the solid state, depending on Lewis basic ligands of the lithium atom [46–50]. A characteristic feature of **1** is the formation of O–Li bonds in solution and in the crystal. The NMR spectroscopic investigation of **1**, including **1a** [53], gave no indication for the existence of a species with a C–Li bond. However, the failure to detect a 6Li , ^{13}C coupling is no proof for the not existence of a C–Li-bonded species, because of the possibility of a fast C,Li exchange process, even at low temperatures. While the anion of **1** carries one lone pair at the carbon atom, the anion **2** bears two lone pairs. The higher negative charge density of the carbon atom of **2** seems to be a decisive factor for the formation of C–Li bonds in the crystal and in solution.

Comparison of tetramer and hexamer

It seems interesting to compare the carbon lithium connectivity and lithium coordination of the dianionic carbon atoms of tetramer $(2a)_4 \cdot (THF)_6$ and Li_2O -containing hexamer $(2a)_6 \cdot Li_2O \cdot (THF)_6$. The hexamer has an octahedral cluster of lithium atoms with an oxygen atom in the center of symmetry and three different types of strongly distorted tetrahedral dianionic carbon atoms (C1A: $\tau_4 = 0.66$, C1B: $\tau_4 = 0.75$, C1C: $\tau_4 = 0.61$) (Figure 5). It contains two linear Li1–C1A–Li2–C1B–Li3 chains and two dianionic carbon atoms, C1C, outside of the chains, which are each coordinated by three Li atoms. In hexamer $(2a)_6 \cdot Li_2O \cdot (THF)_6$ all lithium atoms are coordinated by dianionic carbon atoms, while three lithium atoms of tetramer $(2a)_4 \cdot (THF)_6$ are without contact to the dianionic C atoms. Interestingly, the structure of $(2a)_6 \cdot Li_2O \cdot (THF)_6$ is in contrast to that of $(2a)_4 \cdot (THF)_6$ characterized by a large number of four-membered Li–C–S–O and Li–O–Li–O chelate rings. The dianions of hexamer $(2a)_6 \cdot Li_2O \cdot (THF)_6$ are as those of the tetramer both C,C- and O,Li-dilithiated species.

Comparison of $(2a)_4 \cdot (THF)_6$ and $(2a)_6 \cdot Li_2O \cdot (THF)_6$ with functionalized sulfonyl dilithio methanides

Besides the crystal structures of $(2a)_4 \cdot (THF)_6$ and $(2a)_6 \cdot Li_2O \cdot (THF)_6$ those of the sulfonyl dilithio methanides **IIIa** ($FG^1 = SO_2Ph$, $FG^2 = P(S)Ph_2$) [36] and **IIIb** ($FG^1 =$



SO_2Ph , $FG^2 = P(NSiMe_3)Ph_2$) [43] have been determined. Methandiides **IIIa** and carbanion **IIIb** have in contrast to **2a** a further lithium atom coordinating and stabilizing heteroatom-substituent. Both methandiides are tetramers, featuring dilithiated dianionic carbon atoms with a coordination geometry, which strongly deviates from tetrahedral and O–Li, S–Li, and N–Li bonds. They are, however, devoid of C–Li chains of the type found in $(2a)_4 \cdot (THF)_6$ and $(2a)_6 \cdot Li_2O \cdot (THF)_6$. The bonding situation of tetramer $(2a)_4 \cdot (THF)_6$ and hexamer $(2a)_6 \cdot Li_2O \cdot (THF)_6$ indicates that the dominating structure building factor is the interaction between the charged carbon, oxygen and lithium atoms and not between orbitals. A similar conclusion was reached in the case of the dilithio methandiides **IIIa** and **IIIb**.

Conclusion

The determination of the structure of tetramer **2a-I** in both the solution and solid state, which is the first of a dilithio methandiide, was achieved based on X-ray crystal structure analysis and 6Li , ^{13}C NMR spectroscopic data. The tetramer **2a-I** in THF solution has the same structure as the tetramer $(2a)_4 \cdot (THF)_6$ in the crystal. A characteristic feature of the structure of the tetramer is the C_2 symmetric linear C–Li chain, composed of the four dianionic C atoms and five Li atoms. Each dianionic C atom is coordinated by two Li atoms. While one dianionic C atom has seesaw coordination geometry, the other dianionic C atom has a trigonal bipyramidal one. As a

consequence of the C–Li chain three Li atoms are without a contact to a dianionic C atom. The tetramer is fluxional leading to an exchange of the dianionic C atoms. It stands in THF in equilibrium with a second aggregate, which is only stable at low temperatures.

Supporting Information

Supporting Information File 1

Experimental details, crystal data, and parameters of data collection for tetramer (**2a**)₄(THF)₆.

[<https://www.beilstein-journals.org/bjoc/content/supplementary/1860-5397-16-172-S1.pdf>]

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