Journal of Molecular Structure xxx (2014) xxx

Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: www.elsevier.com/locate/molstruc

Corrigendum

Corrigendum to "Molecular and solid state structure of 4,4′-bis(tetrahydrothiopyranyl)" [J. Mol. Struct. 1036 (2013) 115–120]

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The list of contributing authors has been published wrongly, it should read as above.
The corresponding author would like to apologize for any inconvenience caused.

DOI of original article: http://dx.doi.org/10.1016/j.molstruc.2012.09.068
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http://dx.doi.org/10.1016/j.molstruc.2014.02.049
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Journal of Molecular Structure 1036 (2013) 115–120

Contents lists available at SciVerse ScienceDirect

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journal homepage: www.elsevier.com/locate/molstruc

Molecular and solid state structure of 4,4′-bis(tetrahydrothiopyranyl)

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HIGHLIGHTS

- Molecular and solid state structure of a sulfur functionalized bicyclohexyl.
- Structure investigated by both X-ray diffraction and computational methods.
- The presence of sulfur atoms affects the conformational behavior.

ARTICLE INFO

Article history:
Received 20 July 2012
Received in revised form 25 September 2012
Accepted 25 September 2012
Available online 2 October 2012

Keywords:
Heterocyclic compounds
Organic synthesis
Conformational analysis
Crystal structure
MP2 calculations
DFT calculations

ABSTRACT

Single crystal X-ray diffraction reveals that 4,4′-bis(tetrahydrothiopyranyl) crystallizes in an equatorial–equatorial geometry with a gauche conformation along the central carbon–carbon bond. B3LYP/6-311G** and MP2/6-311G** calculations show that the antiperiplanar conformation is higher in energy than the gauche one because of sulfur induced stretching and widening of the cyclohexane-like rings. Calculations at various levels of theory suggest that in the antiperiplanar region the twisting coordinate of 4,4′-bis(tetrahydrothiopyranyl) exhibits a very shallow double-well potential. The gauche molecular structure of 4,4′-bis(tetrahydrothiopyranyl) thwarts efficient packing of its molecules in the solid state.

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1. Introduction

Molecules with a rod-like structure are of interest as functional building blocks for nanoscale architectures with specific and tunable properties [1]. One class of molecular rods is represented by oligo(cyclohexylidenes), which consist of cyclohexyl-type rings mutually connected at the 1- and 4-positions *via* olefinic bonds (Scheme 1) [2]. The σ–π–σ orbital topology in this class of compounds facilitates electronic interactions between suitable end groups *X* and *Y* [3,4], as has for instance been demonstrated by the occurrence of photoinduced charge transport in electron donor–acceptor substituted oligo(cyclohexylidenes) [5–7]. Interactions between the sulfur atoms of sulfide end-functionalized oligo(cyclohexylidenes), which result from through-bond coupling, are particularly substantial [3,8]. As sulfur atoms also bind to gold surfaces, the interactions allowed to exploit these compounds as active spacers in photoinduced charge transport between CdSe quantum dots and a gold electrode [9] and in molecular scale electronics [10–12].

Single crystal X-ray structure determinations of oligo(cyclohexylidene) derivatives have revealed that in the solid state they almost exclusively adopt an *anti* conformation with respect to the double bond [2,4,13]. Due to the anti-conformation and the chair conformation of the cyclohexane rings they possess a rod-like structure, leading to a brick-like stacking in the solid state. This rod-like structure enables the formation of self-assembled monolayers of sulfur functionalized oligo(cyclohexylidenes) on gold surfaces [14,15].

The replacement of the double bond(s) in oligo(cyclohexylidenes) by a single bond, leading to oligo(cyclohexyls), disrupts the σ–π–σ orbital topology and results in a substantial loss of through-bond orbital coupling [4]. Despite this loss, oligo(cyclohexyls) might

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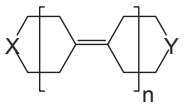
http://dx.doi.org/10.1016/j.molstruc.2012.09.068



Scheme 1. General structure of oligo(cyclohexylidenes).

still be a class of molecular rods with useful properties. They would for instance provide the opportunity to prepare mixed SAMs with alternating nonconducting–conducting domains by patterning saturated 4,4′-bis(tetrahydrothiopyranyl) (**1**) and unsaturated 4,4′-bis(tetrahydrothiopyranylidene (**2**) (Scheme 2). The monolayer forming properties are however expected to depend on the molecular geometry and packing pattern of these compounds, which makes it of interest to investigate their structures.

The molecular structure of compound **2** was resolved previously by single crystal X-ray diffraction [3]. In common with other oligo(cyclohexylidenes), **2** exhibits anti geometry at the double bond, with the cyclohexane rings adopting a chair conformation. Conformational mobility in **2** involves syn-anti interconversion at the double bond and chair–chair interconversion of the six-membered rings. Compound **1** has some more degrees of conformational freedom. Apart from changes within the rings, the cyclohexyl rings can adopt either an equatorial (e) or axial (a) position at the other ring. Furthermore, rotation around the central single bond is possible. Here we report the single crystal X-ray structure and packing pattern of **1**, while its conformational behavior is investigated with B3LYP/6-311G** and MP2/6-311G** calculations. To get more insight into this behavior it is compared with that of bicyclohexyl **3**. It is shown that the presence of sulfur atoms has a striking effect on the structure of these types of compounds.

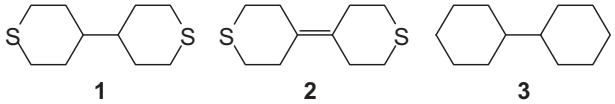
2. Results and discussion

2.1. Synthesis

4,4′-Bis(tetrahydrothiopyranyl) **1** was prepared as shown in Scheme 3 [16]. First, tetrahydrothiopyran-4-one (**4**) was reduced with $LiAlH_4$ to give tetrahydrothiopyran-4-ol (**5**). The hydroxyl group of alcohol **5** was replaced by action of phosphorus tribromide to give 4-bromotetrahydrothiopyran **6**. This compound was converted by magnesium mediated Wurtz coupling into **1**, which was isolated as an off-white crystalline compound.

2.2. Single crystal structure of 1

A single crystal of **1** was obtained by recrystallization from methanol. The single crystal X-ray structure (Fig. 1, Table 1) revealed that the compound crystallizes in the non-chiral space group *Fdd2* and that the molecule is located on a twofold axis; the asymmetric unit contains only half a molecule. The two rings occupy equatorial positions of the other ring. The central H*1*–C*1*–C*1*^{i}–H*1*^{i} torsion angle is −66.9(14)°, which represents an (ee) gauche conformation. This is another conformation as for instance found in simple 4,4-bipiperidine derivatives and 4,4-bipiperidinium salts, which invariably possess an antiperiplanar conformation around the central C–C bond [17,18].



Scheme 2. Molecular structures of 4,4′-bis(tetrahydrothiopyranyl) **1**, 4,4′-bis(tetrahydrothiopyranylidene) **2** and bicyclohexyl **3**.

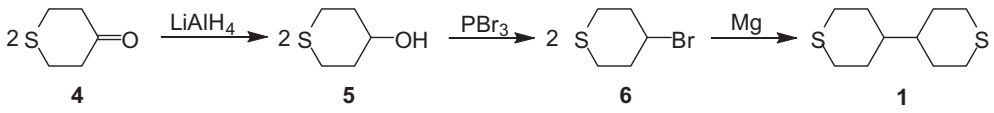
The inclusion of sulfide atoms in **1** (as well as in **2**) leads to the simultaneous stretching and widening of the ring as compared to other cyclohexane type rings, e.g. as found in bicyclohexyl **3**. The changes are manifested by the lengthening of the *S4*–*C3* and *S4*–*C5* bonds to 1.8101(13) and 1.8095(16) Å in **1** (1.8067(15) and 1.8071(15) Å in **2** [3]) compared to C–C distances of 1.532(2) Å in **3**. The latter value was determined by gas phase electron diffraction (GED) [19]. The through-space intramolecular C*1*···*S4* distances of 3.2480(12) Å in **1** and 3.2302(16) Å in **2** are also much longer than the related C*1*···*C4* distance in **3** (2.95 Å). The C1–C2–C3, C1–C6–C5 and C2–C1–C6 valence bond angles in **1** expand to 113.36(14), 113.64(10) and 111.49(12)° respectively, while the C*3*–*S4*–C*5* valence bond angle narrows to 97.21(7)°. Corresponding values for the C–C–C valence bond angles within the six-membered rings of **3** are 110.7(10)° [19]. The larger dimensions of the rings in **1** lead to the distortion from a perfect chair conformation. This can be expressed in a ring puckering analysis [20], which for **1** gives a puckering amplitude *Q* of 0.6460(14) Å, while θ and Φ angles (which locate the ring conformation on the puckering sphere surface) amount to 7.59(12)° and 7.5(11)°, respectively. For a perfect chair conformation these angles both are either 0° or 180°. For **2**, similar parameters of *Q* = 0.6461(14) Å, θ = 174.31(12)° and Φ = 187.1(13)° were found.

Although the size and shapes of the rings in disulfides **1** and **2** are comparable, their packing structures differ markedly. For **2** efficient packing is induced by the stacking of the rod-like molecules, leading to the formation of a highly ordered solid-state structure [3]. This is expressed by the density of ρ = 1.347 g/cm^3 and the Kitaigorodskii packing index K.P.I. [21] of 72.5%. For **1** the packing is less efficient (Fig. 2); a lower density and packing index values are obtained (ρ = 1.268 g/cm^3, K.P.I. 69.0%). There is little doubt that this is caused by the molecular geometry of **1**. Because of the gauche geometry around the central carbon–carbon bond the two rings are rotated with respect to each other, so that intermolecular interactions are less favorable than in **2**, where the normals to the planes through the six-membered rings are situated in the same direction.

2.3. Computational study

The structure of **1** was further investigated with B3LYP/6-311G** and MP2/6-311G** calculations. Data are compared to results obtained for bicyclohexyl **3** for reference. For both compounds the results of the two calculation methods are in qualitative agreement, but they differ in the actual numerical values. In the following, the results are discussed for the B3LYP/6-311G** method, with the MP2/6-311G** data given between parentheses.

As shown in Table 2, two minima were found for **1** with the cyclohexyl-type rings in an equatorial position (structures with axial substituents are about 5 kcal mol^{-1} higher in energy and are not supposed to play a role of importance). Without zero-point energy correction, one minimum occurs at a gauche H1–C1–C1^{i}–H1^{i} torsion angle Φ of 69.1° (68.8°), and another one at an antiperiplanar Φ angle of 165.4° (159.3°). Somewhat surprisingly, the latter torsion angle substantially deviates from the 'exact' antiperiplanar angle of 180°. The 180° geometry was found to represent a transition state, with an energy of only 0.05 (0.22) kcal mol^{-1} above that of the anti minimum. Taking zero point energy into account, the 165.4° (159.3°) stationary point becomes a fraction higher in energy than the 180° one. Thus, the first vibrational level is already positioned above the barrier. In order to shed more light on the nature of the stationary points in this region, structures were optimized at the CCSD/cc-pVDZ level of theory. With an energy of −1186.071631 a.u. the structure with a Φ angle of 162° was again slightly more stable (by 0.09 kcal mol^{-1}) than the 180° structure, which possesses an energy of −1186.071482 a.u. Also, CCSD(T)/



Scheme 3. Synthetic pathway to compound **1**.

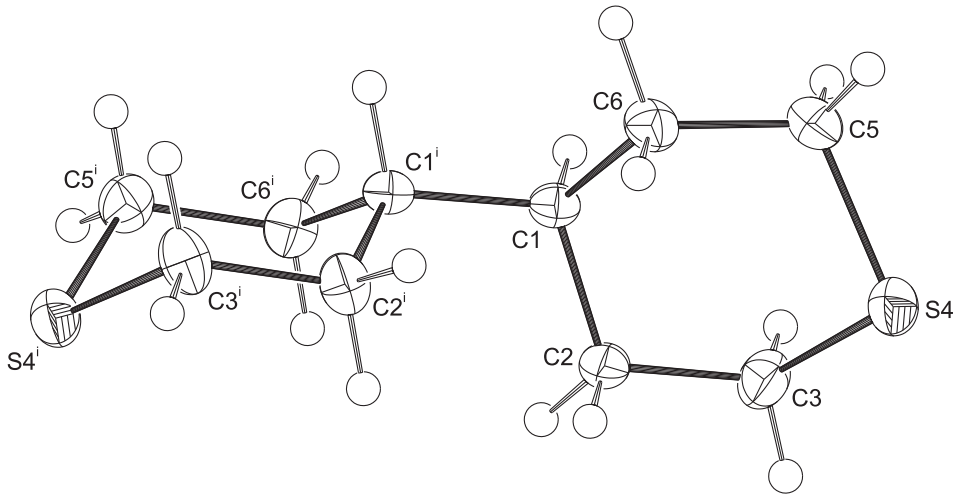


Fig. 1. Single crystal X-ray structure of 4,4′-bis(tetrahydropyranyl) **1**. Displacement ellipsoids are shown at the 50% probability level. Symmetry operation *i*: $-x$, $1-y$, z.

Table 1
Selected geometric parameters (Å and °) in the X-ray structure of 4,4-bis(tetrahydropyranyl) **1**. For atom numbering see Fig. 1. Standard deviations in the last digits are in parentheses.

Bond length		Valence angle		Torsion angle	
C1–C1[i][a]	1.547(2)	C1[i]–C1–C2	112.92(8)	H1–C1–C1[i]–H1[i]	−66.9(14)
C1–C2	1.535(2)	C1[i]–C1–C6	111.58(12)	C2–C1–C1[i]–C2[i]	55.24(15)
C1–C6	1.5331(16)	C1–C2–C3	113.36(14)	C2–C1–C1[i]–C6[i]	−71.28(17)
C2–C3	1.5247(18)	C1–C6–C5	113.64(10)	C6–C1–C1[i]–C6[i]	162.20(15)
C5–C6	1.5277(18)	C2–C3–S4	112.07(9)	C2–C3–S4–C5	−56.12(15)
S4–C3	1.8101(13)	C2–C1–C6	111.49(12)	C3–S4–C5–C6	55.36(11)
S4–C5	1.8095(16)	C3–S4–C5	97.21(7)	C1–C2–C3–S4	62.74(17)
C1–H1	0.987(17)	S4–C5–C6	112.64(11)		

[a] Symmetry operation *i*: $-x$, $1-y$, z.

cc-pVDZ single point calculations were performed on the CCSD/cc-pVDZ optimized geometries, which also indicated that the 162° structure is lower in energy than the 180° geometry. The difference was 0.08 kcal mol^{-1} (−1186.135543 vs. −1186.135417 a.u., respectively).

Hence, in the antiperiplanar region the system seems to consist of a very shallow double well potential, and the whole twisting coordinate in this region might best be regarded as a single broad minimum. Irrespective of the exact structure of **1** in its anti conformation, it is higher in energy than in the global gauche minimum. The energy difference between the two accessible conformations is small, though, and the barrier for rotation of 3.22 (3.70) kcal mol^{-1} is easily surpassed at room temperature. The compound will therefore spend most of the time in the gauche conformation.

In common with the X-ray structure, the rings in **1** are expanded and distorted. In both minima, bond angles are similar to those in the X-ray structure (Table 3). The calculated and X-ray geometry are thus fully in line, which rules out that packing effects are responsible for the characteristics of the X-ray structure.

As shown by the data in Table 4, for bicyclohexyl **3** two energy minima are found as well: at $\Phi = 67.7°$ (67.8°) and at $\Phi = 180.0°$ (180.0°). Hence, here a gauche minimum and a 'true' antiperiplanar minimum occur. When neglecting zero-point energy, the anti geometry is slightly higher in energy than the gauche one for both calculation methods, but with zero-point energy it is slightly lower in energy for the B3LYP case. This leads to the picture that the energy difference between the ee gauche and anti conformers of **3** is small, which is consistent with the experimental finding that **3** exists as a mixture of ee gauche and ee anti conformers with a ratio close to 1:1 [19,22]. The related compounds bicyclopropyl [23,24], bicyclobutyl [25], and 2,3-dimethylbutane [26] also have been shown to exhibit very small energy differences between the gauche and anti conformers and exist as mixtures of conformers at room temperature. Not unexpectedly, the ring bond angles all possess regular values in the 111° range (Table 5), although in the anti conformation somewhat more variation in the bond angles is found. With the exemption of the angle around the S4/C4 atom, in both the gauche and anti structures valence angles in **1** are consistently larger than in **3**.

The gauche conformation of **1** is thus more favored in comparison to the anti minimum than is the case for **3**. It may well be that this is the consequence of the sulfur induced ring expansion and distortion. In the anti conformation of **1**, the distorted ring leads to a somewhat stronger steric repulsion between equatorial hydrogen atoms at carbon atoms C6 and C2[i], and at C2 and C6[i]. In the $\Phi = 165.4$ (159.3)° conformation of **1**, the distance between these

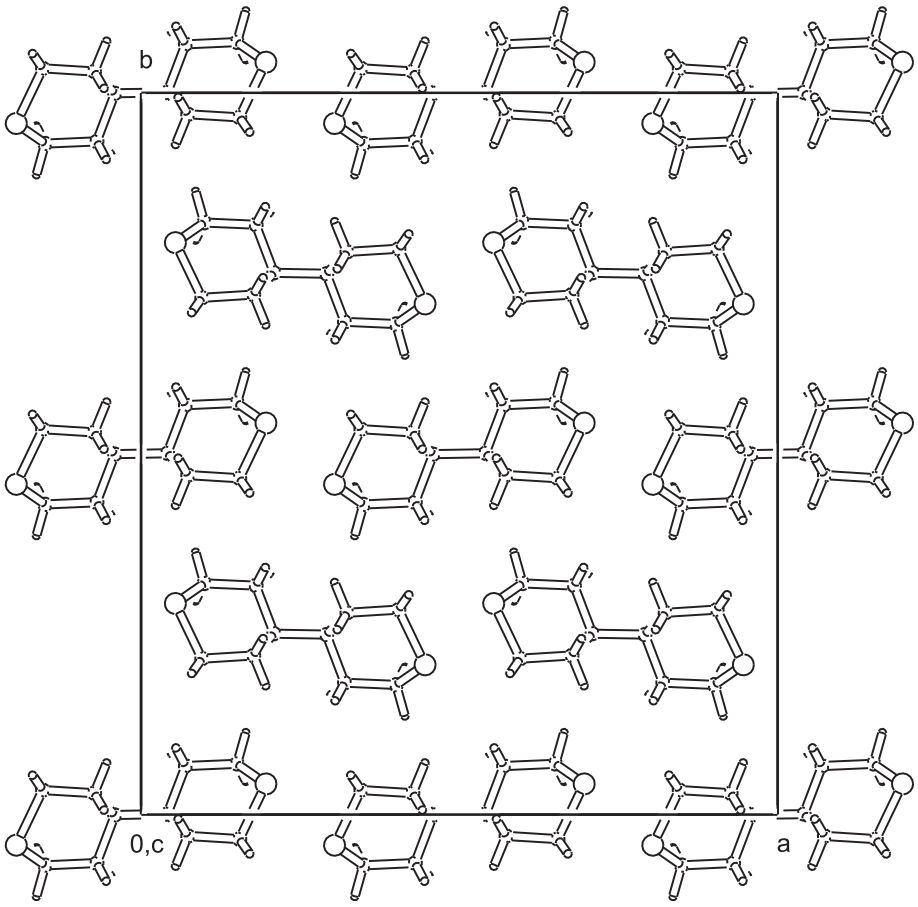


Fig. 2. Packing pattern of **1** as viewed along the *c*-axis.

Table 2
Values of the central H1–C1–C1^{i}–H1^{i} torsion angle Φ (°) at calculated stationary points for equatorial structures of 4,4-bis(tetrahydropyranyl) **1**. Energies without (E) and with zero-point contributions (E_{ZPE}) are given in kcal mol^{-1} relative to the gauche minimum.

B3LYP/6-311G**			MP2/6-311G**		
Φ	E	E_{ZPE}	Φ	E	E_{ZPE}
0.00[a]	8.42	8.01	0.00[a]	9.07	9.20
69.10[b]	0.00	0.00	68.83[b]	0.00	0.00
118.89[a]	3.22	2.86	117.61[a]	3.70	3.72
165.40[b]	1.14	0.67	159.31[b]	1.25	1.39
180.00[a]	1.19	0.63	180.00[a]	1.47	1.34

[a] Transition state.
[b] Minimum. See Supplementary Data for lowest vibrational frequencies.

hydrogen atoms is 2.06 (2.02) Å, while it amounts to 1.97 (1.97) Å in the Φ = 180° structure. These distances are less than twice the van der Waals radius of hydrogen (1.10 Å [26]). In the gauche structure, the shortest separation between hydrogen atoms bonded to these carbon atoms ranges from 2.25 (2.20) Å (calculated, for the axial–equatorial distance) to 2.29 Å (X-ray). This leads to the idea that there is steric congestion around the C1–C1′ bond in the anti minimum. In the calculated full antiperiplanar structure of **3** the spatial separation between the equatorial hydrogen atoms is 2.07 (2.04) Å. This value is very similar to the 2.06 (2.02) Å value in the calculated Φ = 165.4 (159.3)° structure of **1**, and apparently this distance guarantees sufficient space to accommodate the hydrogen atoms at C2 and C6. When **1** adopts a full antiperiplanar conformation, the shorter distance raises the energy.

Table 3
Selected bond angles in the B3LYP/6-311G** and MP2/6-311G** calculated gauche and anti geometries of 4,4′-bis(tetrahydrothiopyranyl) **1**. For numbering see Fig. 1.

	Gauche		Anti	
	B3LYP/6-311G**	MP2/6-311G**	B3LYP/6-311G**	MP2/6-311G**
C1–C2–C3	112.97	112.23	114.44	113.74
C1–C6–C5	113.47	112.50	113.97	112.91
C2–C3–S4	112.87	112.45	112.90	112.13
C2–C1–C6	111.39	111.20	110.38	110.44
C3–S4–C5	97.46	96.54	96.70	95.82
S4–C5–C6	112.98	112.38	113.63	113.37

Table 4
Values of the central H1–C1–C1^{i}–H1^{i} torsion angle Φ (°) at calculated stationary points for equatorial structures of bicyclohexyl **3**. Energies without (E) and with zero-point contibutions (E_{ZPE}) are given in kcal mol^{-1} relative to the lowest minimum.

B3LYP/6-311G**			MP2/6-311G**		
Φ	E	E_{ZPE}	Φ	E	E_{ZPE}
0.00[a]	7.38	7.51	0.00[a]	8.02	8.13
67.65[b]	0.00	0.50	67.84[b]	0.00	0.00
118.45[a]	3.05	3.20	118.53[a]	3.51	3.51
180.00[b]	0.13	0.00	180.00[b]	0.44	0.38

[a] Transition state.
[b] Minimum. See Supplementary Data for lowest vibrational frequencies.

MM3 molecular mechanics calculations on **1** show that the Van der Waals interaction in the 165° structure is 13.48 kcal mol^{-1}, while it is 13.78 kcal mol^{-1} in the 180° geometry. Despite the small margin, this lends support to the idea that steric strain is relieved

Table 5
Selected bond angles in the B3LYP/6-311G** and MP2/6-311G** calculated gauche and anti geometries of bicyclohexyl **3**. For numbering see Fig. 1, with the difference that S4 is replaced by C4.

	Gauche		Anti	
	B3LYP/6-311G**	MP2/6-311G**	B3LYP/6-311G**	MP2/6-311G**
C*1*–C*2*–C*3*	111.72	111.04	112.99	112.70
C*1*–C*6*–C*5*	112.09	111.35	112.99	112.70
C*2*–C*3*–C*4*	111.64	110.96	111.91	111.36
C*2*–C*1*–C*6*	109.72	109.57	109.27	109.33
C*3*–C*4*–C*5*	111.21	110.93	110.64	109.95
C*4*–C*5*–C*6*	111.58	110.89	111.91	111.36

in the 165° conformation. MM3 predicts that the 180° structure (E = 19.89 kcal mol^{-1}) is more stable than the 165° geometry (E = 20.55 kcal mol^{-1}), because of decreased torsional strain. Thus, steric strain presumably is the reason that Φ can be twisted from 180°, but this goes at the cost of some torsional energy, and in the end the energy difference is very small. The steric interactions however have the consequence that the anti-conformation is less stable in comparison to the gauche structure.

3. Conclusions

The ee gauche molecular structure of 4,4′-bis(tetrahydrothiopyranyl) **1** has been resolved by single crystal X-ray diffraction, and is supported by both B3LYP/6-311G** and MP2/6-311G** calculations. These calculations also reveal the existence of an antiperiplanar structure. In the antiperiplanar conformation the compound is subject to steric interactions, caused by the distortion and expansion of the six-membered rings by the sulfur atom. This also has the consequence that the antiperiplanar minimum is relatively high in energy, and in this way the presence of the sulfur atoms favors the gauche structure. Because of this gauche structure the intermolecular interactions in **1** are less favorable than in **2**, and this results in a less dense packing structure. It might therefore be expected that monolayer formation for **1** is more difficult than for **2**.

4. Experimental

4.1. General

Melting points were determined with a Mettler-Toledo DSC 821^e apparatus. NMR spectra were recorded on a Bruker AC 300 spectrometer (^{1}H at 300 MHz and ^{13}C at 75 MHz) at 25 °C. Solid-state FT-IR was recorded on a Perkin Elmer Spectrum One spectrometer equipped with a Universal ATR sampling accessory (resolution 1 cm^{-1}).

4.2. Synthesis

4.2.1. Tetrahydrothiopyran-4-ol **5**

$LiAlH_4$ (1.13 g, 30 mmol) was suspended in anhydrous diethyl ether (200 mL). A solution of tetrahydrothiopyran-4-one (**4**, 5.28 g, 45 mmol) in anhydrous diethyl ether was added dropwise in 1 h. After the addition, the reaction mixture was heated at reflux temperature for 90 min and then stirred at room temperature overnight. The reaction mixture was subsequently placed in an ice-bath and carefully quenched with excess water. The aqueous phase was extracted with diethyl ether (2 × 100 mL), and the organic phase dried with $MgSO_4$. The solvent was evaporated to give 4.45 g (38 mmol, 84%) of **5**. δ_H ($CDCl_3$) 3.66 (m, 1H, C*H*OH), 2.78 (m, 2H, CH_2S), 2.59 (m, 2H, CH_2S), 2.17 (m, 2H, SCH_2CH_2), 1.73 (m, 2H, SCH_2CH_2), 1.45 (s, 1H, OH). δ_C ($CDCl_3$) 68.2 (COH), 36.2 (SC*C*), 26.5 (S*C*).

4.2.2. 4-Bromotetrahydrothiopyran **6**

Phosphorus tribromide (3.9 g, 14 mmol) was added dropwise in 30 min to a solution of alcohol **5** (3.73 g, 32 mmol) in CH_2Cl_2 (50 mL) at ambient temperature. Upon completion of the addition, the reaction mixture was slowly heated to the boiling point and stirred overnight. After cooling to room temperature the mixture was quenched with water and extracted with diethyl ether (2 × 100 mL). The organic phase was washed with a saturated solution of $NaHCO_3$, dried over anhydrous $MgSO_4$ and evaporated to yield 3.37 g (19 mmol, 59%) of a yellow oil. δ_H ($CDCl_3$) 4.32 (m, 1H, C*H*Br), 2.90 (m, 2H, SCH_2), 2.55 (m, 2H, SCH_2), 2.38 (m, 2H, SCH_2CH_2), 2.23 (m, 2H, SCH_2CH_2). δ_C ($CDCl_3$) 45.3 (CBr), 36.9 (SC*C*), 26.9 (S*C*).

4.2.3. 4,4′-Bis(tetrahydrothiopyranyl) **1**

A solution of **6** (3.3 g, 18.4 mmol) in anhydrous diethyl ether (40 mL) was added dropwise to a mixture of activated magnesium turnings (0.96 g, 40 mmol) in diethyl ether (40 mL). Upon completion of the addition, the mixture was kept at reflux temperature overnight. The mixture was then quenched with 1 M HCl and extracted with diethyl ether. The organic phase was washed with a saturated solution of $NaHCO_3$, dried with anhydrous $MgSO_4$ and evaporated. It was recrystallized twice from methanol and repeatedly washed with acetonitrile to yield **1** as an off-white crystalline compound (0.79 g, 3.9 mmol). Yield 42%. mp 116 °C; δ_H ($CDCl_3$) 2.58–2.72 (m, 8H, SCH_2), 1.88–1.93 (m, 4H, equatorial SCH_2CH_2), 1.44–1.57 (m, 4H, axial SCH_2CH_2), 1.15–1.23 (m, 2H, CH). δ_C ($CDCl_3$) 43.8 (CH), 31.1 (SC*C*), 29.4 (S*C*). Spectral data are in agreement with those previously reported [16].

4.3. Crystallography

A single crystal of **1** was prepared by recrystallization from a minimum amount of methanol. $C_{10}H_{18}S_2$, F.w. = 202.36, colorless needle, 0.60 × 0.09 × 0.09 mm^3, orthorhombic, *Fdd2* (no. 43), a = 18.7964(4), b = 21.3135(5), c = 5.2910(1) Å, V = 2119.67(8) Å^3, Z = 8, D_{calc} = 1.268 g/cm^3, μ = 0.449 mm^{-1}. 7067 reflections were measured at a temperature of 150(2) K up to a resolution of $(\sin\theta/\lambda)_{max}$ = 0.65 Å^{-1} on a Nonius KappaCCD diffractometer with rotating anode and graphite monochromator (λ = 0.71073 Å). An absorption correction was not considered necessary. 1189 reflections were unique (R_{int} = 0.0337). The structure was solved with Direct Methods [27] and refined with SHELXL-97 [28] on F^2 of all reflections. Non-hydrogen atoms were refined freely with anisotropic displacement parameters. All hydrogen atoms were located in the difference Fourier map and refined freely with isotropic displacement parameters. 91 parameters were refined with one restraint. $R1/wR2$ ($I > 2\sigma(I)$): 0.0208/0.0536. $R1/wR2$ (all refl.): 0.0228/0.0548. S = 1.063. Flack parameter [29] x = −0.03(8). Residual electron density between −0.14 and 0.21 e/Å^3. Geometry calculations, drawings and checking for higher symmetry were performed with the PLATON package [30].

4.4. Computational methods

The energy minima and saddle points of **1** and **3** for rotation around the central C*1*–C*1*^{i} bond were optimized at both the B3LYP/6-311G** and MP2/6-311G** levels of theory with the GAMESS-UK [31] program. Convergence criteria for geometry optimization were 0.0001 au, which resulted in convergence of energy on average of 0.00027 kcal mol^{-1} (see Supplementary Data). Hessian matrices for all B3LYP/6-311G** and MP2/6-311G** stationary points were calculated. MM3 calculations were per-

formed with the Tinker package [32], and the CCSD/cc-pVDZ and CCSD(T)/cc-pVDZ calculations were run with the DALTON program [33].

Acknowledgements

Dr. R. Dabirian (Utrecht University, NL) is acknowledged for synthetic contributions. R.W.A.H. acknowledges fruitful discussions with Prof. R. Broer (University of Groningen, NL) and the Zernike Institute for Advanced Materials for financial support (“Diepte-strategie” program).

Appendix A. Supplementary material

CCDC 859046 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Coordinates, convergence energies, zero point energies and lowest vibrational frequencies of B3LYP/6-311G** and MP2/6-311G** calculated stationary points of **1** and **3** are given in the Supplementary data. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.molstruc.2012.09.068.

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