Conformational analysis and molecular dynamics of glass-forming

aromatic thiacrown ethers

Supplementary materials

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1. Synthesis procedures of the analyzed thiacrown ethers

Synthesis procedure of 6-methyl-2,3-dihydro-1,4-benzodithiine (1).

Toluene-3,4-dithiol (5.4 g, 34.5 mmol), K₂CO₃ (10.8 g, 70 mmol), KI (0.1 g) and 200 ml of acetone were placed in a 0.5 L round-bottom flask equipped with a magnetic stirrer. 1,2-Dibromoethane (30 ml, 345 mmol) was quickly added in portions. As a result, the mixture became cloudy and warmed up. After stirring at r.t. overnight the mixture was filtrated, solvent and excess of dibromoethane were evaporated on a rotary evaporator. The crude product was distilled in vacuum (158 °C, approx 10 Tr), yielding 2.9 g (46.2%) of pure product, as slightly yellow liquid.

Cyclic thioether 1 (6-methyl-2,3-dihydro-1,4-benzodithiine)

NMR δH(400 MHz; DMSO-*d*6) 2.19 (3 H, s), 3.24 (4 H, m), 6.84 (1 H, dd), 6.98 (1 H, s), 7.01-7.08 (1 H, m). δC(101 MHz, DMSO-*d*6) 20.74, 28.88, 29.13, 126.65, 127.87, 128.96, 129.29, 131.20, 135.14. FT-IR (KBr) ν_{max} /cm⁻¹ 3043, 2949, 2917, 2862, 1590, 1467, 1413, 1374, 1290, 1274, 1256, 1115, 1043, 861, 805, 701, 679, 627, 541, 436. UV-Vis λ max(CH₃CN)/nm 243 and 271 (logε/dm³mol⁻¹cm⁻¹ 4.35 and 3.72).

Synthesis procedures of 2,3-(4'-methylbenzo)-1,4-dithia-7-oxacyclononane (2)

The thiacrown ether 2 was first obtained in low yield (0.54%) as a byproduct in synthesis of bis{4'[4"(5")]-methylbenzo}-tetrathia-18-crown-6 according to Pedersen method. However, its interesting properties led us to develop a better synthetic approach. Herein, we provide a synthesis procedures, which allowed to obtained this heterocyclic compound with better yields.

Method A. K₂CO₃ (17.3 g, 125 mmol) and 300 ml of dry DMF were placed in a 500 ml 2necked round-bottom flask, equipped with a dropping funnel containing solution of toluene-3,4-dithiol (2.87 g, 18.3 mmol) and bis(2-chloroethyl)ether (2.60 g, 18.3 mmol) in 100 ml dry DMF. The flask was fitted with a magnetic stirring assembly and with oil bath. Oil bath was heated up to 70°C. The solution from the dropping funnel was slowly added during 24 h with vigorous stirring at 70°C under argon atmosphere. The mixture was left stirring at 70°C for next 2 days. After cooling, DMF was evaporated in vacuum, the solid residue was extracted 4 times with DCM, and solvent from combined extracts was evaporated. Raw product was purified by column chromatography (SiO₂, DCM:hexane, 2:1), yielding 1.25 g (30%) of pure product in form of slightly orange oil (which solidifies after several days). Mp 59°C (58.7°C – DSC measurement).

Method B. Cs_2CO_3 (11.2 g, 34 mmol) and 300 ml of dry DMF were placed in a 2-neck 500 ml round-bottom flask equipped with a magnetic stirrer, thermostatic oil bath, argon balloon, and a dropping funnel. The mixture was heated to 70°C, and solution of toluene-3,4-dithiol (3.44 g, 22 mmol) and bis(2-chloroethyl)ether (3.15 g, 22 mmol) in 100 ml DMF was added within 15 h with vigorous stirring. The mixture was stirred additionally at 70°C for next 4 days. After cooling DMF was evaporated in vacuum, solid residue was extracted 4 times with DCM. Combined extracts were concentrated, and the pure product was isolated by column chromatography (SiO₂, DCM:hexane 2:1 v/v), yielding 2.15 g (43.2%) of pure product in form of almost colorless oil (which solidified after several days). Mp 59°C.

Thiacrown ether **2** (2,3-(4'-methylbenzo)-1,4-dithia-7-oxacyclononane)

NMR δ H(400 MHz; CDCl₃) 2.34 (3 H, s), 3.00 (2 H, t), 3.05 (2 H, t), 3.88 (4 H, t), 7.10 (1 H, dd), 7.56 (1 H, d), 7.61 (1 H, d). δ C(101 MHz; CDCl₃) 20.9, 39.4, 39.5, 73.7, 73.8, 130.4, 136.9, 137.6, 139.5, 139.6, 142.6. UV-Vis λ max(CH₃CN)/nm 202, 224 and 261 (logɛ/dm³mol⁻¹cm⁻¹ 4.62, 4.15 and 3.59). FT-IR (KBr) ν max/cm⁻¹ 2956, 2914, 2884, 2845, 2771, 1587, 1464, 1448, 1402, 1379, 1356, 1294, 1255, 1230, 1212, 1135, 1056, 1037, 1007, 900, 827, 786, 658, 556,

461. Raman v_{max} /cm⁻¹ 3280, 2913, 1118, 870, 684, 657, 626, 464, 429, 334, 103, 69. ESI-HRMS 249.03613 (M+Na)⁺; (calc. for C₁₁H₁₄OS₂Na: 249.03782).



2. NMR spectra

Fig. S1. ¹H NMR spectrum of compound **1**. *Solvent DMSO-d6 (2.50 ppm), *H₂O (3.33 ppm)



Fig. S2. ¹³C NMR spectrum of compound 1. *Solvent DMSO-d6 (39.52 ppm)



Fig. S3. ¹H NMR spectrum of compound 2. *Solvent CDCl₃ (7.28 ppm), *H₂O (1.64 ppm)



3. IR and Raman spectra



Fig. S5. IR spectrum of compound 1.



Fig. S6. IR spectrum of compound 2.



Fig. S7. Raman spectrum of compound 2.

4. Thermal evolution of refractive index

The refractive index, n, measured for thiacrown ethers 1 and 2 with the resolution of 0.0001, increases with temperature decrease in a linear manner. Therefore, the data were refined with linear functions, which allowed to characterize the thermal evolutions of n. The obtained equations, as well as fit parameters are shown in Fig. S8.



Fig. S8. Thermal evolution of refractive index for thiacrown ethers 1 and 2.

5. Calculations of Kirkwood-Fröhlich factor

The values of dipole moment and polarizability of the thiacrown ethers were determined on the basis of DFT calculations carried out using the Gaussian09 program on b3pw91/6-311g++ level. The B3PW91 functional was chosen because it is recommended to describe the properties of the organic molecules.

Table S1. Values of polarizability, dipole moment and molar mass for the energetically privileged conformers of thiacrown ethers 1 and 2.

Thiacrown ether	Polarizability	Dipole moment	Molar mass
	$[C^2 m^2 J^{-1}]$	[D]	[g mol ⁻¹]
1 (conformer I)	2.20•10 ⁻³⁹	0.55	182.31
1 (conformer II)	2.20•10 ⁻³⁹	0.78	182.31
2	2.66•10 ⁻³⁹	2.32	226.36

The values of refractive index, *n*, for the thiacrown ethers **1** and **2** were calculated according to the obtained equations form Fig. S8 characterizing the thermal evolutions of *n*. The permittivity at infinite frequencies, ε_{∞} , was estimated on the basis of n(T) dependences according to the formula $\varepsilon_{\infty} \approx n^2$. For the determination of the density according the Lorentz-Lorenz formula we used the polarizability from the DFT calculations

Temperature **Refractive index** Density **€**∞ $[g cm^{-3}]$ [K] 197 1.7017 2.8956 1.414 199 1.7006 2.89218 1.412 201 1.6998 2.88914 1.411 203 1.6987 2.88572 1.410 205 1.6978 2.88268 1.408 207 1.6968 2.87927 1.407

Table S2. Thermal evolution of refractive index, ε_{∞} and density in the temperature range of 197 - 207 K for thiacrown ether **1**.

Table S3. Thermal evolution of refractive index, ε_{∞} and density in the temperature range of 236 - 275 K for thiacrown ether **2**.

Temperature	Refractive index	${oldsymbol{\mathcal{E}}}_\infty$	Density
[K]			$[g \text{ cm}^{-3}]$
236	1.6473	2.7136	1.3622
239	1.6460	2.7095	1.3602
242	1.6448	2.7054	1.3581
245	1.6436	2.7014	1.3560
248	1.6423	2.6973	1.3540
251	1.6410	2.6929	1.3517
254	1.6398	2.6888	1.3497
257	1.6385	2.6848	1.3476
260	1.6373	2.6807	1.3455
263	1.6361	2.6766	1.3434
266	1.6348	2.6726	1.3413
269	1.6336	2.6686	1.3392
272	1.6323	2.6645	1.3372
275	1.6311	2.6605	1.3351

The Kirkwood–Fröhlich factor, g_k , has been calculated according to the equation:

$$g_k = \frac{9k_B\varepsilon_0 MT(\varepsilon_s - \varepsilon_\infty)(2\varepsilon_s + \varepsilon_\infty)}{\rho N_A \mu^2 \varepsilon_s (\varepsilon_\infty + 2)^2}$$

where k_B is Boltzmann's constant, *M*- molar mass, ε_0 - permittivity of a vacuum, *N*_A- Avogadro number, ρ - density, and μ is molecular dipole moment.

Table S4. Thermal evolution of Kirkwood factor in the temperature range of 197 – 207 K forthiacrown ether 1.

Temperature	Kirkwood factor	Kirkwood factor	Kirkwood factor
[K]	(conformer I)	(conformer II)	(mean value)
197	1.29(2)	0.64(2)	0.97(4)
199	1.30(2)	0.65(2)	0.97(4)
201	1.32(2)	0.66(2)	0.99(4)
203	1.33(2)	0.66(2)	1.00(4)
205	1.35(2)	0.67(2)	1.01(4)
207	1.35(2)	0.67(2)	1.01(4)

Temperature	Kirkwood factor	
[K]		
236	0.60(4)	
239	0.61(4)	
242	0.62(4)	
245	0.62(4)	
248	0.63(4)	
251	0.63(4)	
254	0.64(4)	
257	0.65(4)	
260	0.65(4)	
263	0.66(4)	
266	0.66(4)	
269	0.67(4)	
272	0.68(4)	
275	0.68(4)	

Table S5. Thermal evolution of Kirkwood factor in the temperature range of 236 – 275 K forthiacrown ether 2.

6. Dipole moments directions in the low and high energy conformers



Fig. S9. Dipole moment direction for the most energetically favored conformation of compounds 1 (a) and 2 (c) and the most stressed conformers of thiacrown ethers 1 (b) and 2 (d).

7. DSC thermograms for the analyzed thiacrown ethers



Fig. S10. DSC thermograms for compounds 1 (a) and 2 (b) registered while heating and cooling with a rate of 10 K/min.