Thermal isomerisation of 25,26,27,28-tetrapropoxy-2,8,14,20-tetrathiacalix[4]arene: isolation of all four conformers

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25,26,27,28-Tetrapropoxy-2,8,14,20-tetrathiacalix[4]arene undergoes a thermal equilibration at elevated temperature yielding a mixture of conformers. The rate and equilibrium constants of this process were established using NMR spectroscopy. For the first time the equilibrating process was also used on a preparative scale for the isolation and characterisation of all four basic thiacalix[4]arene conformations.

Introduction

Calix[*n*]arenes, the well-known cyclic oligomers of *p*-substituted phenols and formaldehyde, have attracted great interest during the last decade.[1,2] Because of their simple one-pot preparation, enabling large-scale synthesis, and owing to their unique molecular structure with the possibility of "shaping" and "tuning", they became very popular as molecular scaffolds and/or useful building blocks in the construction of more elaborate molecular systems in supramolecular chemistry.[3]

Recently, the preparation of a new type of calix[4]arene derivative, thiacalix[4]arenes **1** (5,11,17,23-tetra-*tert*-butyl-2,8,14,20-tetrathiacalix[4]arene) and **2** (2,8,14,20-tetrathiacalix[4]arene) (Fig. 1), was reported.[4,5] Due to the presence of four sulfur atoms these compounds possess new chemical features as compared with "classical" calix[4]arenes. For instance, oxidation of the sulfur bridges to sulfoxide or sulfone moieties[6] leads to new types of ligands with potentially interesting complexation abilities. As we described recently, the direct alkylation of **1** or **2** with alkyl halides in the presence of K_2CO_3 or Cs_2CO_3 in refluxing acetone gave tetraalkylated products.[7] These compounds exhibit interesting behaviour both in the solid state[7] and in solution.[8] It is well known that the introduction of bulkier groups to the lower rim of calix[4]arene leads, in principle, to the formation of four stable isomers—*cone*, *partial cone*, *1,2-alternate* and *1,3-alternate*.[1] As we have found, the cavity of thiacalix[4]arene is larger than that of calix[4]arene.[7] Hence, we are interested in restrictions that govern the conformational behaviour of thiacalix[4]arenes.

The different conformers of thiacalix[4]arenes can be obtained by alkylation with ethyl bromoacetate in the presence of alkali metal carbonate as a base.[9–11] The template effect of the alkaline ion (Na^+, K^+, Cs^+) used results in formation of several conformers (*cone*, *partial cone*, *1,3-alternate*). However, alkylation using simple alkyl halogenides (propyl, butyl) leads to the *1,3-alternate* conformer almost exclusively.[7]

In this paper, we describe the kinetics of equilibration of the mixture of conformers of the tetrapropoxy derivative **3a**–**3d** (Fig. 2) in terms of interconversion rate constants and equilibrium constants utilising time-dependent ^{1}H NMR spectra. The experiment reveals that interconversion between the conformers is allowed exclusively at high temperature. This feature is used for preparative synthesis, providing four stable isomers **3a**–**3d** after separation at room temperature.

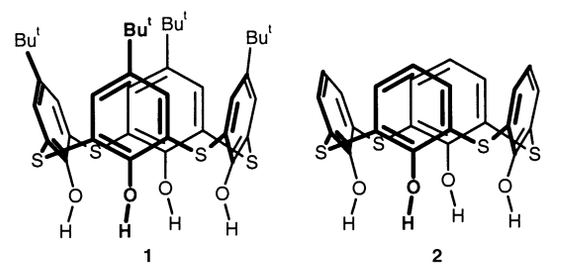

Fig. 1 Structures of compounds **1** and **2**.

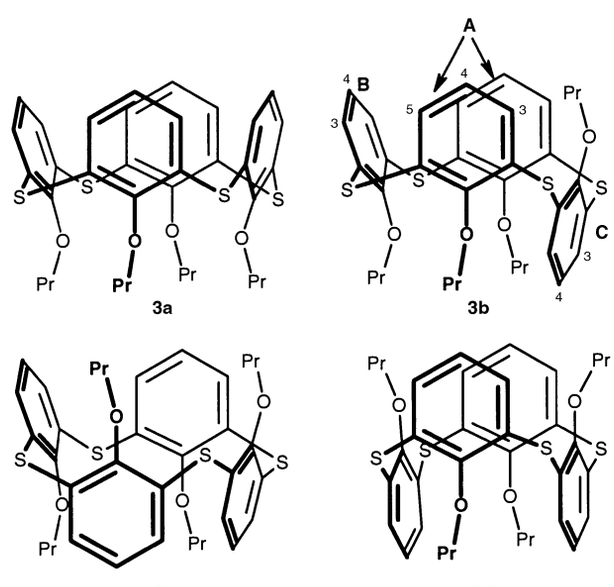

Fig. 2 Four basic conformations of thiacalix[4]arene **3**.

Results and discussion

Thermal equilibration of 3

It is known from our previous results[7] that alkylation of **2** with PrI–K_2CO_3 in acetone or acetonitrile gives 25,26,27,28-tetrapropoxy-2,8,14,20-tetrathiacalix[4]arene as the main product in the *1,3-alternate* conformation **3d** (67% yield). This conformer is accompanied by a smaller amount of the *partial cone* con-

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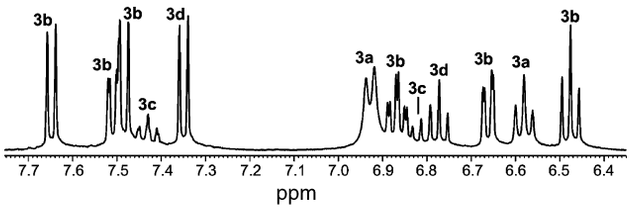


Fig. 3 Aromatic part of the ^{1}H NMR spectrum ($CDCl_2CDCl_2$, 393 K) of **3** close to equilibrium (after 65 days at 393 K).

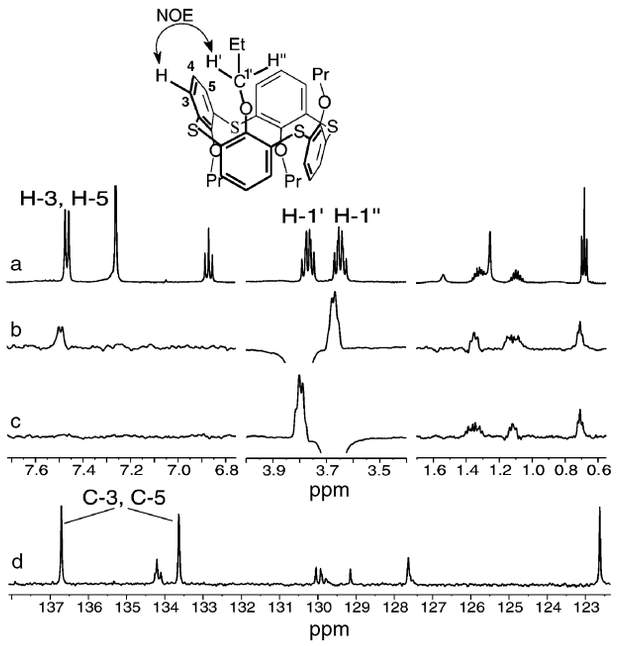


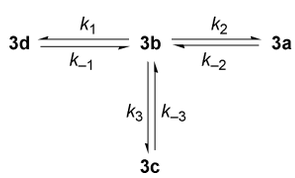
Fig. 4 Identification of the *1,2-alternate* conformer **3c**. a) ^{1}H NMR spectrum ($CDCl_3$, 303 K), b) DPFGSE-NOE spectrum with H-1′ irradiated, c) DPFGSE-NOE spectrum with H-1″ irradiated, d) aromatic part of the ^{13}C NMR spectrum.

formation **3b** (<25%), which makes these two conformers accessible. Unfortunately, all our attempts to prepare the other two conformations (*1,2-alternate* and *cone*) have failed. Both of the conformers that have been prepared are infinitely stable at room temperature and do not interconvert. Because it is known that the ethoxy derivative of **1** undergoes relatively fast conformational interconversion between the four conformers,[8] we investigated whether the transitions between the conformers of **3** can occur at increased temperature.

The kinetics of thermal equilibration starting from conformer **3d** (393 K, $CDCl_2CDCl_2$) was monitored using ^{1}H NMR over a period of 127 days. All four conformers **3a**–**3d** were identified in the ^{1}H NMR spectrum of the mixture close to equilibrium (Fig. 3), displaying a signal pattern similar to the spectrum of tetraethyl ether of thiacalix[4]arene.[8] The resonances of both *1,3-alternate* **3d** and *partial cone* **3b** were assigned unambiguously at room temperature. However, the broad aromatic signals of *cone* **3a**, indicating further conformational exchange between two *pinched cone*[8] conformations with C_{2v} symmetry, became sharper, and exhibited the characteristic multiplicity only at the elevated temperature of 393 K. The assignment of *1,2-alternate* **3c** was not so easy due to severe overlaps with the signals of the other, more populated conformers. Therefore, unambiguous determination was achieved only after preparative-scale synthesis and chromatographic separation of **3c**. The signal pattern in the ^{1}H NMR spectrum (measured in $CDCl_3$, Fig. 4a), corresponding to the expected low (C_2) symmetry of **3c**, was obvious only in the aliphatic region, where the methylene protons (H-1′ and H-2′) were nonequivalent. In the aromatic part, we observed only one degenerate aromatic doublet for protons H-3 and H-5. However, separate signals were found in the ^{13}C spectrum (Fig. 4d), and in the ^{1}H spectrum measured in $CDCl_2CDCl_2$. The final evidence for *1,2-alternate* conformation of **3c** was obtained from NOE spectra. Selective excitation of the methylene protons H-1′ or H-1″ gave rise to an NOE enhancement at H-3 only in the case of the first proton (Fig. 4b,c).

Measurements of the thermal equilibration process were carried out at room temperature initially, because there is no information on the observability of resonances of the *cone* conformation **3a**. This conformation is rather a time-average of two interconverting *pinched cones*. When a detectable amount of **3a** evolved, its resonances appeared heavily broadened at room temperature. Therefore, monitoring was continued at an increased temperature (393 K) when all the signals became sufficiently narrow.

After processing and integration of the spectra (24 in total), the conversion matrix describing how single nuclei of each individual conformer contribute to each integrated region was constructed, because some integral regions contained several overlapped peaks (and different peaks represent different numbers of equivalent nuclei). This method was adopted in order to use all the spectral information and to avoid errors due to overlap at the same time. The region integrals in each spectrum were normalised with respect to their sum in the whole spectrum. By this procedure, the 16 time-dependent sets of region integrals were obtained. The individual conformers are supposed to undergo a chemical reaction according to Scheme 1, controlled by the six rate constants k_1, k_{-1}, k_2, k_{-2}, k_3,



Scheme 1

k_{-3}. This interconversion pathway for calix[4]arenes has been well established by previous EXSY NMR experiments.[8,12] The kinetics of these coupled chemical reactions is described by the set of differential eqns. (1)–(3), where c_a, c_b, c_c, c_d denote the concentrations of the conformers **3a**, **3b**, **3c**, **3d**, respectively. The sum of the four concentrations must remain constant, and is equal to c_d at time $t = 0$ (c_d^0), eqn. (4).

$$\frac{dc_d}{dt} = k_1 c_b - k_{-1} c_d \quad (1)$$

$$\frac{dc_a}{dt} = k_2 c_b - k_{-2} c_a \quad (2)$$

$$\frac{dc_c}{dt} = k_3 c_b - k_{-3} c_c \quad (3)$$

$$c_d^0 = c_a + c_b + c_c + c_d \quad (4)$$

The six rate constants were calculated using an iterative procedure involving numerical solution of eqns. (1)–(3). The calculated concentrations of the conformers were converted to theoretical integrals of the 16 regions using the conversion matrix. The sum of the squared differences was minimised by the iteration procedure. In this way, the calculation procedure employed all the available experimental data at once. The same absolute experimental error in the experimental data was anticipated without any regard to the actual size of the integral, *i.e.*, no weighting was applied. Fig. 5 shows the time dependence of the integrated intensities together with the fitted curves, and Fig. 6 shows the calculated time-dependent conformer concentrations. The equilibrium constants K_{bd}, K_{ba}, K_{bc} of the

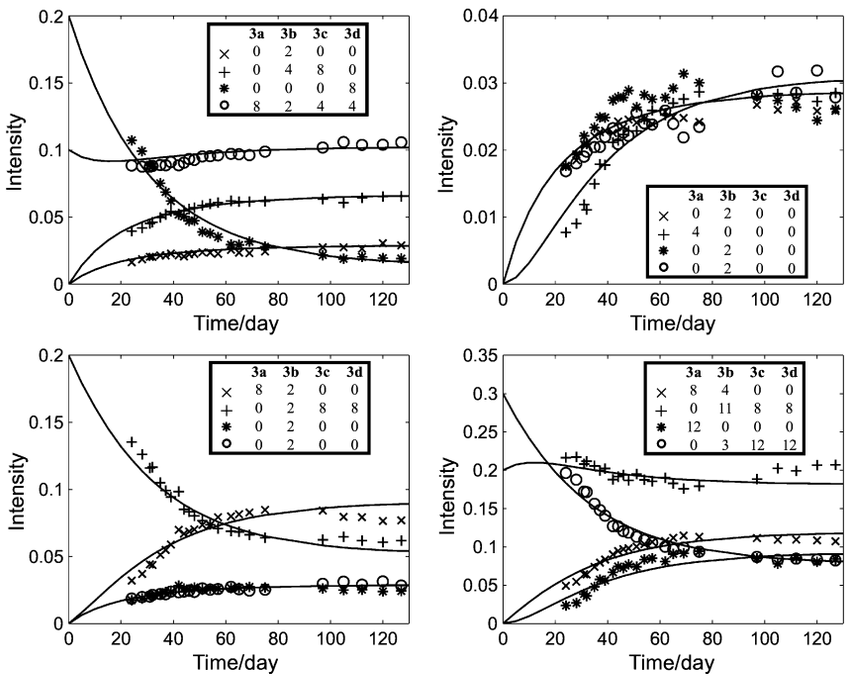


Fig. 5 Thermal equilibration of **3**. Time dependence of the 16 region integral intensities (in arbitrary units) with theoretical curves corresponding to the calculated reaction rate constants. The number of nuclei of each of the conformers **3a**–**3d** contributing to a particular region is indicated in the insets.

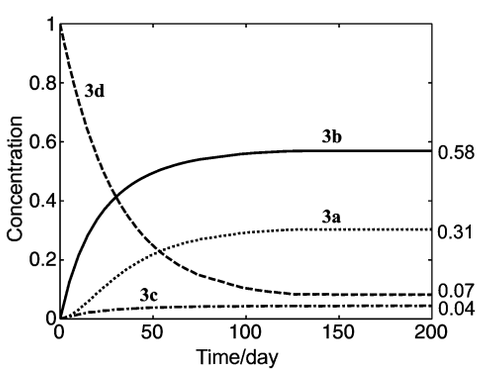


Fig. 6 The calculated time dependence of the relative concentrations of the conformers during equilibration at 393 K (**3a** dotted, **3b** solid, **3c** dash-dotted, **3d** dashed line), and the equilibrium populations.

three reactions are calculated as ratios of the respective pairs of rate constants, eqns. (5)–(7). The values are shown in Table 1.

$$K_{bd} = \frac{k_1}{k_{-1}} = \frac{[\mathbf{3d}]}{[\mathbf{3b}]} \quad (5)$$

$$K_{ba} = \frac{k_2}{k_{-2}} = \frac{[\mathbf{3a}]}{[\mathbf{3b}]} \quad (6)$$

$$K_{bc} = \frac{k_3}{k_{-3}} = \frac{[\mathbf{3c}]}{[\mathbf{3b}]} \quad (7)$$

To establish the errors of the determined chemical rate and equilibrium constants, a Monte Carlo (MC) simulation was carried out. Experimental integrals were varied randomly. The standard deviation of the variation was equal to the standard deviation obtained from the fit. The standard deviations of the exchange rate constants and the equilibrium constants obtained from the MC simulations are given in Table 1. The relative error in the rate constants for the interconversion between **3a**, **3b**, **3c** is just a few percent. The rate constants for **3d** include a larger error of 30% due to the very low concentration of the compound in the mixture. However, the corresponding equilibrium

Table 1 The determined rate constants k_i, their errors Δk_i, activation free energies G^{+}_{0i}, equilibrium constants K, and their errors ΔK

i	$10^7 k_i$/ s^{-1}	$10^7 \Delta k_i$/ s^{-1}	G^{+}_{0i}/ kcal mol^{-1}	K	ΔK
1	0.43	0.04	23.9	0.117[a]	0.011
−1	3.60	0.05	22.2		
2	3.74	0.18	22.2	0.531[b]	0.009
−2	6.93	0.40	21.7		
3	8.4	2.5	21.6	0.077[c]	0.007
−3	108	33	19.6		

[a] K_{bd}. [b] K_{ba}. [c] K_{bc}.

constant K_{bc} was determined with a relative error of 9%. The MC simulation provides realistic error estimates of the dynamic parameters that include a contribution from the fact that the spectra were acquired over a very long period of time, and it was not always possible to make sure that some experimental conditions (*e.g.*, magnetic field homogeneity) did not vary to a certain extent.

Table 1 also summarises the activation free energies of the interconversion ΔG^{+}_{0i} at 393 K calculated from the rate constants $[(k_i = (k_B T/h)\exp(-\Delta G^{+}_{0i}/(RT))$, k_B, h, R are the Boltzmann, Planck and gas constants, respectively, T is absolute temperature, $i = \pm1, \pm2, \pm3]$.[13]

The calculated equilibrium molar ratios of the four isomers **3a**, **3b**, **3c** and **3d** are 31 : 58 : 4 : 7, which provide free energies for the isomers **3a**, **3c** and **3d**, relative to **3b** of 0.48, 1.99 and 1.66 kcal mol^{-1}, respectively, according to the Boltzmann distribution.

Despite the fact that the preparative synthesis provides the conformer **3d**, the thermodynamically most stable conformers (at 393 K) are **3b** and **3a**. The alternate conformers **3c** and **3d** occur only in minor amounts.

The opportunity to obtain all four conformers by the equilibration procedure was utilised on a preparative scale. The derivative **3d** (400 mg) was refluxed for 15 days in 1,1,2,2-tetrachloroethane (bp 147 °C), and the resulting mixture was then subjected to preparative chromatographic purification (column, TLC). By this procedure the conformers **3a**–**3d** were

isolated in 27, 52, 8 and 11%, yields, respectively. All the propyl-substituted conformers **3a**–**3d** are infinitely stable at room temperature and no mutual interconversion either in solution or in the solid state was observed.

Comparison with other alkylated thiacalix[4]arenes and calix[4]-arenes

The effect of variable length of the lower rim substituent can be estimated by comparison with the equilibrium mixture of tetraethyl ether of thiacalix[4]arene (17 : 56 : traces : 26 for conformers **a**, **b**, **c**, **d** respectively) at 303 K.[8] Populations of the conformers of **3** according to the Boltzmann distribution at 303 K, derived from the above presented free energies, would be 29 : 65 : 2 : 4 (**3a**–**3d**) (if we do not consider the existence of large interconversion barriers that, in fact, do not allow for equilibration at this temperature). The *1,3-alternate* conformer **3d** is strongly disfavoured while population of *cone* **3a** is significantly enhanced compared to the ethoxy derivative.

Similar attempts to achieve thermal equilibration of tetrabutoxythiacalix[4]arene failed and only the starting *1,3-alternate* conformation was isolated. This indicates that the *n*-butyl groups are just bulky enough to hinder the rotation of the alkylated phenolic rings through the main annulus of the thiacalix[4]arene under ordinary conditions (up to 413 K). The thermal equilibration of **3d** reflects also the fact that the cavity of the thiacalix[4]arene is larger than that of the corresponding "classical" calix[4]arene. The distances between the two distal and the two proximal sulfur atoms[7] are approximately 7.8 and 5.5 Å, respectively, while the typical distances between corresponding CH_2 groups in *1,3-alternate* calix[4]arene are 7.1 and 5.0 Å. In the case of the tetraethoxy derivative of the "classical" *p-tert*-butylcalix[4]arene, equilibrium was reached in 12 hours at 405 K yielding a ratio of the conformers of 7 : 47 : 43 : 3.[14] Taking into account the high interconversion barrier, this compound can be considered as an acceptable "classical" analogue of **3**.

Conclusion

It was proved that propyl groups on the lower rim of thiacalix[4]arene **3** are not bulky enough to immobilise the conformation. Thermal equilibration of the tetrapropoxy derivative **3d** yields all four of the basic conformers **3a**–**d** with the *partial cone* **3b** as the most stable isomer. Using this procedure on a preparative scale, all the conformations including *1,2-alternate* **3c** were isolated and characterised for the first time.

Experimental

Synthesis

25,26,27,28-Tetrapropoxy-2,8,14,20-tetrathiacalix[4]arene (3d). A mixture of derivative **2** (2.00 g), potassium carbonate (5.00 g) and propyl iodide (8 ml) was stirred under reflux in 50 ml of dry acetone for 3 days. The reaction mixture was poured into diluted hydrochloric acid and extracted with chloroform. The organic layer was washed with water, dried over $MgSO_4$ and evaporated to yield crude product. Precipitation from an MeOH–$CHCl_3$ mixture gave pure derivative **3d** (67%) as white crystals, mp 257–258 °C (ethyl acetate).

Thermal equilibration of 3d. The solution of **3d** (400 mg) in 30 ml of 1,1,2,2-tetrachloroethane was heated to reflux for 15 days under a nitrogen atmosphere. The resulting mixture was then evaporated to dryness under reduced pressure and the residue was subjected to column chromatography on silica gel to afford crude fractions of the product. Pure conformers **3a**–**3d** were obtained using preparative TLC on silica gel using a petroleum ether–$CHCl_3$ (10 : 1) mixture as eluent.

Compound ***3a***. (27%), mp 174–176 °C (ethyl acetate); NMR ($CDCl_2CDCl_2$, 393 K) δ_H 0.99 (12H, t, *J* 7.4, -$CH_2CH_2CH_3$), ~1.85 (8H, m, -$CH_2CH_2CH_3$), 4.09 (8H, t, *J* 6.6, -$CH_2CH_2CH_3$), 6.58 (4H, t, *J* 7.7, 4-H arom.), 6.93 (8H, t, *J* 7.7, 3,5-H arom.); δ_C 10.32 (-$CH_2CH_2CH_3$), 23.14 (-$CH_2CH_2CH_3$), 77.15 (-$CH_2CH_2CH_3$), 123.12 (4-C arom.), 132.25 (2,6-C arom.), 134.30 (3,5-C arom.), ~160 (1-C arom.). EA for $C_{36}H_{40}O_4S_4$: calcd./found, C 65.03/64.84, H 6.06/6.00, S 19.29/19.05%.

Compound ***3b***. (52%), mp 224–226 °C (ethyl acetate); NMR ($CDCl_2CDCl_2$) δ_H 0.65 (3H, t, *J* 7.4, -$CH_2CH_2CH_3$ B), 1.12 (6H, t, *J* 7.4, -$CH_2CH_2CH_3$ A), 1.13 (3H, t, *J* 7.4, -$CH_2CH_2CH_3$ C), 1.08 (2H, m, *J* 7.4, -$CH_2CH_2CH_3$ B), 1.81 (4H, m, *J* 7.4, -$CH_2CH_2CH_3$ A), 2.00 (2H, m, *J* 7.4, -$CH_2CH_2CH_3$ C), 3.45 (2H, m, *J* 7.4, -$CH_2CH_2CH_3$ B), 3.59 (2H, dt, *J* 6.6, 8.5, -$CH'H''CH_2CH_3$ A), 4.02 (2H, dt, *J* 6.6 and 8.5, -$CH'H''CH_2CH_3$ A), 4.07 (2H, t, *J* 7.4, -$CH_2CH_2CH_3$ C), 6.47 (2H, t, *J* 7.7, 4-H arom. A), 6.65 (2H, dd, *J* 1.8 and 7.7, 5-H arom. A), 6.87 (1H, t, *J* 7.7, 4-H arom. B), 6.88 (1H, t, *J* 7.7, 4-H arom. C), 7.45 (2H, dd, *J* 1.8 and 7.7, 3-H arom. A), 7.47 (2H, d, *J* 7.7, 3,5-H arom. B), 7.59 (2H, d, *J* 7.7, 3,5-H arom. C); δ_C 9.19 (-$CH_2CH_2CH_3$ B), 10.66 (-$CH_2CH_2CH_3$ C), 10.78 (-$CH_2CH_2CH_3$ A), 21.03 (-$CH_2CH_2CH_3$ B), 23.59 (-$CH_2CH_2CH_3$ A), 23.94 (-$CH_2CH_2CH_3$ C), 74.21 (-CH_2-CH_2CH_3 B), 75.36 (-$CH_2CH_2CH_3$ C), 77.38 (-$CH_2CH_2CH_3$ A), 122.38 and 122.57 (C4 arom. B and C), 122.49 (4-C arom. A), 127.20 (6-C arom. A), 129.74 (2,6-C arom. C), 130.89 (2-C arom. A), 132.80 (2,6-C arom. B), 135.18 (3,5-C arom. B), 135.49 (5-C arom. A), 137.32 (3,5-C arom. C), 137.76 (3-C arom. A), 160.21 (1-C arom. A), 160.48 (1-C arom. A), 162.73 (1-C arom. A). EA for $C_{36}H_{40}O_4S_4$: calcd./found, C 65.03/64.71, H 6.06/5.91, S 19.29/19.08%.

Compound ***3c***. (8%), mp 200–203 °C (ethyl acetate); NMR ($CDCl_3$) δ_H 0.68 (12H, t, *J* 7.3, -$CH_2CH_2CH_3$), 1.09 (4H, m, *J* 7.3, -$CH_2CH'H''CH_3$), 1.33 (4H, m, *J* 7.3, -$CH_2CH'H''CH_3$), 3.65 (4H, dt, *J* 6.4 and 8.2, -$CH'H''CH_2CH_3$), 3.77 (4H, dt, *J* 6.4 and 8.2, -$CH'H''CH_2CH_3$), 6.87 (4H, t, *J* 7.8, 4-H arom.), 7.47 (8H, d, *J* 7.8, 3,5-H arom.); δ_C 10.31 (-$CH_2CH_2CH_3$), 22.81 (-$CH_2CH_2CH_3$), 75.43 (-$CH_2CH_2CH_3$), 122.61 (4-C arom.), 129.91 and 130.04 (2-C and 6-C arom.), 133.62 and 136.69 (3-C and 5-C arom.), 160.20 (1-C arom.). MS FAB ($C_{36}H_{40}O_4S_4$) calcd. 664.18, found 665.3 ($M + H^+$). EA for $C_{36}H_{40}O_4S_4$: calcd./found, C 65.03/64.75, H 6.06/5.89%.

Compound ***3d***. (12%), mp 257–258 °C (ethyl acetate); NMR ($CDCl_2CDCl_2$) δ_H 0.64 (12H, t, *J* 7.7, -$CH_2CH_2CH_3$), 1.16 (8H, m, *J* 7.7, -$CH_2CH_2CH_3$), 3.82 (8H, t, *J* 7.4, -$CH_2CH_2CH_3$), 6.86 (4H, t, *J* 7.7, 4-H arom.), 7.37 (8H, d, *J* 7.7, 3,5-H arom.); δ_C 9.95 (-$CH_2CH_2CH_3$), 22.15 (-$CH_2CH_2CH_3$), 70.57 (-$CH_2CH_2CH_3$), 122.70 (4-C arom.), 128.61 (2,6-C arom.), 131.67 (3,5-C arom.), 159.61 (1-C arom.). EA for $C_{36}H_{40}O_4S_4$: calcd./found, C 65.03/65.24, H 6.06/6.50, S 19.29/19.35%.

NMR Spectroscopy

The sample of **3d** was dissolved in $CDCl_2CDCl_2$ (99.8% D, Eurorad, Germany), degassed by the freeze–pump–thaw procedure (three times), and flame-sealed in a 5 mm NMR tube. The solvent was used as purchased without further purification or stabilisation. During the equilibration, the sample was kept in an oil bath at 393 K controlled by a thermostat over a period of 127 days. A total number of 24 ^1H spectra were acquired on a Bruker AMX 400 spectrometer (^1H resonance frequency of 400.1 MHz) at 393 K in order to determine the chemical reaction rate constants. The size of the spectrum was 16 K data points, the number of scans was 16, the recycle time was 10 s. The typical π/2-pulse length was 6 μs. The spectra were processed, phased and baseline-corrected in absolute terms piece by piece. The signals of the entire spectrum were divided into 16 regions that could always be integrated separately without the introduction of a significant error due to signal overlap. The assignment was carried out on a Bruker DRX 500

Avance spectrometer working at 500.1 MHz for ^{1}H and 125.8 MHz for ^{13}C. Experiments were performed at 303 K; only those concerning the compound **3a** were carried out at 393 K. Chemical shifts in ppm are referenced to Me_4Si, *J* values are in Hz. ^{1}H NMR spectra were measured with a spectral width of 7500 Hz, size 32 K data points, the recycle time 3.1 s, and 16 scans. ^{13}C NMR spectra were measured with a spectral width 26.5 kHz, size 32 K data points, the recycle time 2.6 s, and 3000 scans. The spin systems were identified by 2D COSY (128 t_1-increments of 1024 data points, 16 scans, spectral width 3000 Hz), ^{1}H–^{13}C HMQC (128 t_1 increments, spectral widths 3000 Hz in ^{1}H and 23.7 kHz in ^{13}C dimensions, respectively, 16 scans, the delay for polarisation transfer 3.5 ms), ^{1}H–^{13}C HMBC (128 t_1 increments, spectral widths 3000 Hz in ^{1}H and 23.7 kHz in ^{13}C dimensions, respectively, 128 scans, the delay for polarisation transfer 60 ms). A 1D ^{1}H DPFGSE-NOE experiment[15] was performed using a selective q3-gaussian-cascade of 79.2 ms, the mixing time was 2 s. Typical π/2-pulses were 9.5 μs for ^{1}H, and 12 μs for ^{13}C. Calculation of the rate constants was carried out using a home-made program running on a PC.

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