A Novel Low Molecular Weight Chiral Gelator for Apolar Organic Solvents

Carina S. Snijder, Johannes C. de Jong, Auke Meetsma, Fré van Bolhuis, and Ben L. Feringa*

Abstract: The synthesis, molecular structure, and properties of a new chiral gel-forming agent **1** are described. Key structural features in **1** are a γ-alkoxybutyrolactone tetralin moiety and an angular phenylsulphone unit. The new low molecular weight gelator **1** can reversibly form stable gels in low concentrations (e.g., 1:800 for *n*-hexane) with isopropanol and a variety of apolar organic solvents. The gels were studied with differential scanning calorimetry and a combination of electron microscopy techniques, which revealed a highly ordered three-dimensional network of entangled fibers. X-ray analysis showed that the aggregation of **1** leads to a helical structure in the solid state. Nonchiral analogues **2** and **3** were unable to initiate gel formation.

Keywords
electron microscopy · gels · helices · self-assembly

Introduction

As the significance of gel formation in organic solvents is increasingly recognized[1] it also becomes evident that the self-assembly process in gel-forming systems of low molecular weight compounds is an example of molecular association par excellence.[2-4] Although gel formation in aqueous and nonaqueous solution by high molecular weight gelators is a widespread phenomenon and association processes of amphiphilic molecules have been well documented,[1, 5, 6] the study of gelation of organic solvents by low molecular weight gelators is still in its infancy.[2-5] Gelation by calixarenes[7] and depsipeptides[8] has been explained on the basis of aggregation processes through hydrogen-bond formation. Recently 2,3-bis-*n*-decyloxyanthracene[9] has been reported as a low molecular weight gelator, and the aggregation process has been attributed to the stacking of π systems in the gelator molecules. We report here on the discovery of a novel type of low molecular weight chiral gelator for organic solvents, **1**, which can reversibly gelate up to 800 molecules of hydrocarbon solvent.

Results and Discussion

The gel-forming agent **1** contains a γ-alkoxybutyrolactone annulated tetralin structure in a 1,2-arrangement with an angular phenylsulphone group and a menthyloxy moiety (Fig. 1). The synthesis of **1** is outlined in Scheme 1. The highly reactive dienophile (5*R*)-5-(L-menthyloxy)-4-phenylsulphonyl-2[5*H*]-furanone (**4**) was obtained from (5*R*)-5-(L-menthyloxy)-2[5*H*]-furanone as described elsewhere.[10] Cycloaddition of **4** and *o*-xylylene, generated in situ,[11] afforded enantiomerically pure **1** in 43% yield after chromatography (silica gel/CH_2Cl_2). According to 2D NMR (COSY, NOESY) and X-ray analysis (vide infra) cycloaddition occurred exclusively *anti* with respect to the menthyloxy substituent.[12]

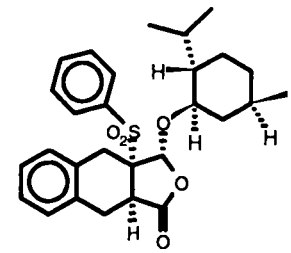
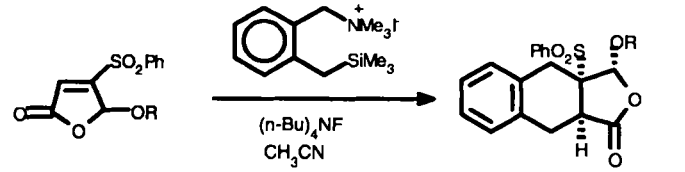


Fig. 1. Structure of **1**.

In order to examine the influence of the menthyloxy moiety, the cyclohexyl and methyl analogues **2** and **3**, respectively, were synthesized in an analogous manner, although in low yields (Scheme 1). It should be noted that the yields are low because of the extensive purification required to remove traces of impurities that might affect the gelation process.



4: OR = L-menthyloxy
5: R = C_6H_{11}
6: R = CH_3

1: OR = L-menthyloxy, 43 %
2: R = C_6H_{11}, 17%
3: R = CH_3, 8%

Scheme 1. Synthetic route to tetralins **1**, **2**, and **3**.

The chiral tetralin derivative **1** is an excellent gel-forming agent for a large variety of hydrocarbon solvents, as is shown by the results summarized in Table 1. Gelation was considered successful if the sample did not flow perceptibly when inverted under ambient conditions. Typically, when **1** dissolved in *n*-hexane at 69 °C (ratio **1**:*n*-hexane = 1:825) is cooled in air, it forms a stable gel which does not deteriorate for months.

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Table 1. Solvents gelated by **1**.

Solvent	Ratio of **1**: solvent [a]	Cooling method	Phase formation
n-pentane	1:200	air	gel
n-hexane	1:825	air	gel
n-heptane	1:294	air	gel
n-octane	1:228	air	gel
n-nonane	1:193	air	gel
n-decane	1:226	air	gel
cyclohexane	1:90	ice bath	gel
methylcyclohexane	1:292	ice bath	gel
isopropanol	1:420	air	gel
tetrachloromethane			solution
benzene			solution
cyclohexene			solution
n-butanol			solution
dichloromethane			solution
ethanol			solution
methanol			solution

[a] The ratios (mol:mol) were determined after preparation of the gel with an excess of solvent and removal of the excess after the gel had been formed.

Table 2. Collected data from the DSC experiments on the hexane gel.

Exp.	Conc. (mmol L^{-1})	T_{gel} [a] (°C)	ΔH_{gel} (kJ mol^{-1})	T_{melt} [a] (°C)	ΔH_{melt} (kJ mol^{-1})
1	3.21×10^{-2}	52.8	−8.4	68.1	8.2
2	2.20×10^{-2}	47.7	−11.8	66.0	n.d. [b]
3	1.90×10^{-2}	42.5	−10.3	57.5	11.2
4	1.32×10^{-2}	39.2	−5.5	56.5	10.0

[a] All measurements were performed at a cooling/heating rate of 5 °C min^{-1}; [b] n.d. = not determined.

It is interesting that polar solvents and solvents containing π systems do not show gel formation with **1**, although isopropanol is a notable exception.[13] The formation of a stable gel with various solvents depends on the amount of **1** and in some cases the cooling method employed. Remarkably, compounds **2** and **3** did not show any gel formation with the solvents given in Table 1.

Differential scanning calorimetry (DSC) was used to examine the gel-to-liquid phase transition at different concentrations (Table 2). The measurements on the hexane gel of **1** clearly show that the gelation process is thermally reversible and that the temperature of gelation decreases with decreasing concentration of **1**. Accordingly the enthalpy of gelation increases with higher concentrations of **1**; this points to enhanced association (network formation, vide infra) of gelator molecules and allows the formation of stable gels at temperatures as high as 52.8 °C, whereas in the reverse cycle gels show remarkable stability (T_{melt} = 68.1 °C) up to the boiling point of *n*-hexane.

As small amounts of **1** (usually 0.75–1 %) are sufficient to form stable gels with various linear and cyclic nonaromatic apolar (except for isopropanol) organic solvents, structural information on the self-aggregating behavior of the chiral tetralin derivative **1** is particularly interesting. Several electron microscopy (EM) techniques were used to investigate the aggregates formed by gelation. Figure 2, top left, shows a freeze-fracture electron microscopy (FF-EM) picture of the hexane gel in which the presence of fibers formed by **1** is clearly seen. These fibers are reminiscent of structures based on steroid/cyclohexane gels observed by Terech and coworkers[14] with FF-EM. Additional evidence for network formation was obtained by freeze-drying and cryo-EM. In Figure 2, top right, the solvent molecules have been partially evaporated by freeze-drying methods and the three-dimensional network of intertwined fibers of **1** remains. Apparently this three-dimensional array of associated molecules of **1** is responsible for the encapsulation of hexane molecules. The smallest observed diameter of a single fiber was established to be 50 nm by cryo-EM; this diameter corresponds to approximately 50 molecules of **1**. For the isopropanol gel, freeze-drying methods established that a more rigid network structure of **1** had been formed compared with the hexane gel (Fig. 2, bottom). Furthermore, DSC and EM measurements with different gels obtained from **1** (Table 1) showed that the domain size was dependent on the concentration and the solvent used. The elucidation of the network structure in organic gels from low molecular weight gelators with a combination of three different electron microscopy techniques as described here is, as far as we know, unprecedented.

It was anticipated that additional information on the association process could be obtained from the three-dimensional structure of **1**. We were able to crystallize both compound **1** (gel former) and **2** (not a gel former), and their crystal and molecular structures were solved by X-ray diffraction (Figs. 3 and 4). When the structures of **1** and **2** are compared, the differences in

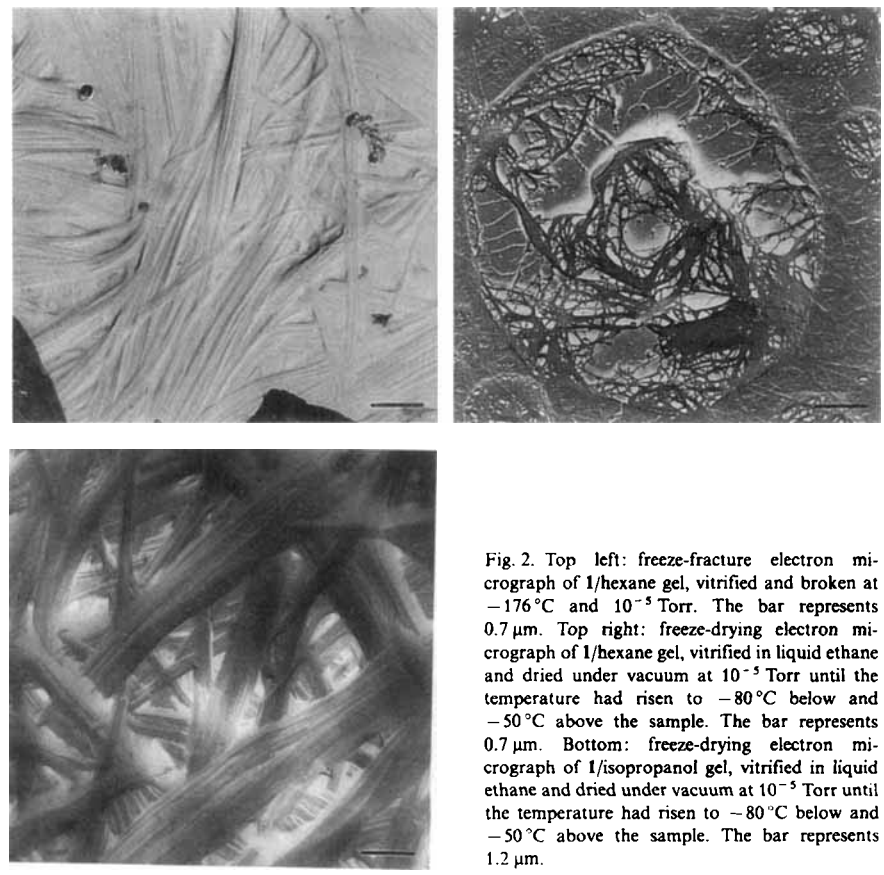

Fig. 2. Top left: freeze-fracture electron micrograph of **1**/hexane gel, vitrified and broken at −176 °C and 10^{-5} Torr. The bar represents 0.7 μm. Top right: freeze-drying electron micrograph of **1**/hexane gel, vitrified in liquid ethane and dried under vacuum at 10^{-5} Torr until the temperature had risen to −80 °C below and −50 °C above the sample. The bar represents 0.7 μm. Bottom: freeze-drying electron micrograph of **1**/isopropanol gel, vitrified in liquid ethane and dried under vacuum at 10^{-5} Torr until the temperature had risen to −80 °C below and −50 °C above the sample. The bar represents 1.2 μm.

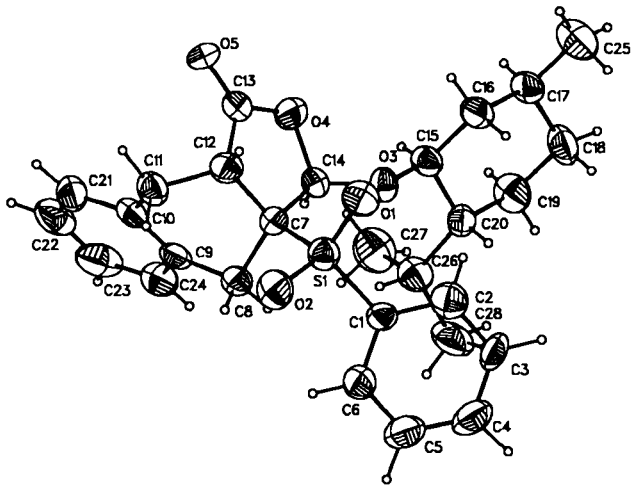

Fig. 3. X-ray structure of 1.

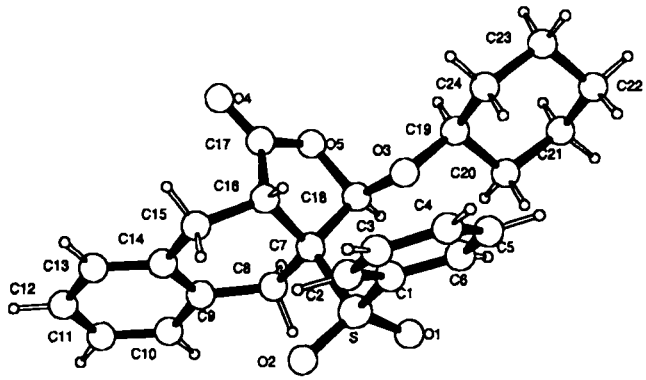

Fig. 4. X-ray structure of 2.

association (in the solid state) and the orientation of the phenylsulfonyl groups of both compounds are remarkable. For compound **1** the $PhSO_2$ moiety is bent towards the menthyl substituent (torsion angle $\measuredangle C_{14}$-C_7-S-C_1 = − 64.1(4)°). For compound **2** the $PhSO_2$ moiety is bent away from the cyclohexyl substituent (torsion angle $\measuredangle C_{18}$-C_7-S-C_1 = 72.4(0.3)°). Probably the phenylsulphonyl group is essential for the π−π stacking of molecules[9] in the first step of the gel-formation process. Furthermore, it appears that the chiral L-menthyloxy moiety is crucial for the gelating ability of **1**, since the racemic methoxy and cyclohexyloxy derivates (**3** and **2**) do not induce gel formation.

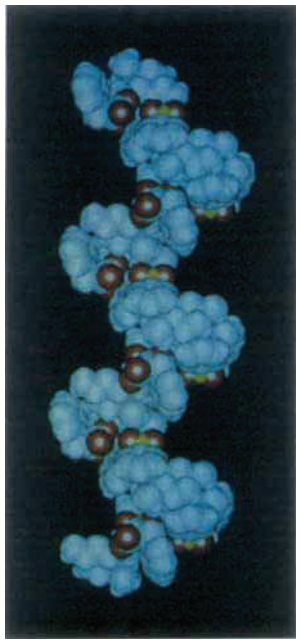

Fig. 5. Helical arrangement of molecules of **1**, based on molecular modeling and X-ray analysis.

Interestingly, the gel former **1** shows a helical array of associated molecules in its solid-state structure. Figure 5 depicts the helical organization of **1** from molecular-mechanics modeling[15] based on solid-state interactions (X-ray). The helical structure is the result of antiparallel π−π stacking of the phenylsulphonyl groups and antiparallel interaction of the hydrophobic menthyloxy moieties. Although the relationship between helical organization in the solid state and the association of **1** in the gel state needs further support, it is noteworthy that this helical organization was not observed in the crystal lattice of compound **2**, which was unable to form a gel. We propose that in apolar solution a single-stranded helix is formed by π−π stacking of the phenylsulphonyl moieties of **1**, after which the polar and apolar parts of the helices of **1** aggregate in multiple-stranded helices owing to solvophobic interactions, thereby forming a three-dimensional network. As solvents with π systems cannot be gelated by **1**, it is very possible that these solvents prevent intermolecular π−π stacking of the gelator.

Conclusion

A new low molecular weight chiral gelator for hydrocarbon solvents with excellent gel-forming properties at low concentrations has been developed. The presence of a network of entangled fibers in the gels has been unambiguously demonstrated by a combination of EM techniques, and indications of helical aggregation have been found. The influence of chirality on the gel-forming process and the far-reaching possibilities for organization of achiral organic solvents with small amounts of chiral additives are currently under investigation.

Experimental Procedure

General: Melting points (uncorrected) were determined on a Mettler FP-2 melting-point apparatus equipped with a Mettler microscope. ^1H NMR spectra were recorded on a Varian Gemini 200 (at 200 MHz) or a Varian VXR-300 spectrometer (at 300 MHz), and chemical shifts are denoted in δ units relative to $CDCl_3$ and converted to the TMS scale with $\delta(CHCl_3) = 7.26$. ^{13}C NMR spectra were recorded on a Varian Gemini 200 (at 50.32 MHz) or on a Varian VXR-300 spectrometer (at 75.48 MHz). Chemical shifts are denoted in δ units relative to $CDCl_3$ and converted to the TMS scale with $\delta(CHCl_3) = 76.91$. The splitting patterns are designated as follows: s (singlet), d (doublet), dd (double doublet), ddd (double double doublet), t (triplet), m (multiplet), and br (broad). Mass spectra were recorded on a AEI-MS-902 mass spectrometer by EI (acc. voltage 8 kV, voltage 70 eV). Rotations are measured on a Perkin-Elmer 241 MC polarimeter at room temperature at the Na D line. Elemental analyses were carried out in the Microanalytical Department of this laboratory. Molecular modeling was performed by A. R. van Buuren of the Biophysical Chemistry Department of our laboratory. All reagents and solvents were purified and dried where necessary according to standard procedures. Compounds **4** and **6** were synthesized as described previously [10, 16]. Compound **5** was prepared analogously with the route to **4** from 5-cyclohexyloxy-2[5*H*]-furanone by the following sequence: i) C_6H_5SH, Et_3N, CH_2Cl_2, 86%; ii) *N*-chlorosuccinimide, CCl_4, Et_3N, heat, 72%; iii) *m*-CPBA, CCl_4, 63%. [*o*-((Trimethylsilyl)methyl)-benzyl]trimethylammonium iodide was prepared in four steps (overall yield 77.5%) from *N*,*N*-dimethylbenzylamine according to Saegusa et al. [11a].

[3*R*-[3α(1*R,2*S**,5*R**),3aα,7aα]]-3a,4,9,9a-Tetrahydro-3-[5-methyl-2-(1-methylethyl)cyclohexyloxy]-3a-(phenylsulfonyl)-1(3*H*)-isonaphthofuranone (1)**: To a stirred solution of furanone **4** (5.5 g, 14.6 mmol) and [*o*-((trimethylsilyl)methyl)benzyl]trimethylammonium iodide (5.3 g, 14.6 mmol) in acetonitrile (280 mL) at room temperature was added very slowly (ca. 1 h) a solution of tetrabutylammonium fluoride (4.6 g, 14.6 mmol) in acetonitrile (280 mL). After evaporation of the solvent, a very small quantity of CH_2Cl_2 and ether was added until the solution became turbid. The solution was filtered through a short path of silica gel. The crude reaction product **1** (single diastereomer) was purified by radial chromatography (SiO_2/CH_2Cl_2) and, after evaporation of the solvent, recrystallized from CH_2Cl_2 to provide **1** in 43% yield. M.p. 95 °C. $[\alpha]_D^{20} = +153.8$ ($c = 1.00$, CH_2Cl_2). ^1H NMR ($CDCl_3$, 200 MHz): δ = 0.60–0.64 (d, J = 6.8 Hz, 3H), 0.73–0.88 (m, 3H), 0.77–0.81 (d, J = 6.8 Hz, 3H), 0.90–0.94 (d, J = 6.4 Hz, 3H), 1.20 (m, 2H), 1.61 (m, 2H), 1.72 (m, 1H), 1.86 (m, 1H), 3.00–3.09 (d, J = 15.8 Hz, 1H), 3.11 (dd, J = 6.6, 15.4 Hz, 1H), 3.28 (dd, J = 1.8, 15.7 Hz, 1H), 3.32 (dt, J = 4.4, 10.8 Hz, 1H), 3.71 (d, J = 15.8 Hz, 1H), 3.85 (dd, J = 2.6, 6.8 Hz, 1H), 5.20 (s, 1H), 7.15–8.03 (m, 9H); ^{13}C NMR ($CDCl_3$): δ = 14.94 (q), 20.82 (q), 22.04 (q), 22.62 (t), 24.74 (d), 28.37 (t), 31.18 (d), 31.94 (t), 34.03 (t), 39.10 (t), 42.09 (d), 47.26 (d), 70.88 (s), 79.03

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(d), 102.39 (d), 127.34 (d), 127.42 (d), 128.05 (d), 128.34 (d), 128.41 (d), 130.88 (d), 131.48 (s), 133.75 (s), 133.84 (d), 137.43 (s), 173.60 (s); HRMS could not be determined as M^+ was not observed; Anal. calcd for $C_{28}H_{34}O_5S$: C, 69.68; H, 7.10; S, 6.64. Found: C, 69.69; H, 7.22; S, 6.69.

3a,4,9,9a-Tetrahydro-3-(cyclohexyloxy)-3a-(phenylsulfonyl)-1(3*H*)-isonaphthofuranone (2): Pure compound **2** was obtained by the procedure described for **1**, starting from **5** (1.0 g, 3.1 mmol), in 17% yield after repeated crystallization from *n*-hexane. ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 1.16–1.87 (m, 10H), 3.00–3.08 (m, 2H), 3.24–3.32 (dd, J = 2.1, 15.4 Hz, 1H), 3.45–3.62 (m, 2H), 3.93–3.98 (dd, J = 2.1, 6.8 Hz, 1H), 5.15 (s, 1H), 7.08–8.05 (m, 9H); ^{13}C NMR ($CDCl_3$): δ = 23.98 (t), 24.09 (t), 25.26 (t), 25.26 (t), 28.72 (t), 31.23 (t), 32.37 (t), 32.82 (t), 42.58 (d), 71.22 (s), 80.27 (d), 104.07 (d), 127.54 (d), 127.68 (d), 128.27 (d), 128.50 (d), 128.58 (d), 131.02 (d), 131.73 (s), 134.04 (s), 134.18 (d), 137.37 (s); Anal. calcd. for $C_{24}H_{26}O_5S$: C, 67.58; H, 6.15; S, 7.52. Found: C, 67.28; H, 6.18; S, 7.55.

3a,4,9,9a-Tetrahydro-3-methoxy-3a-(phenylsulfonyl)-1(3*H*)-isonaphthofuranone (3): From the procedure described for **1** but with **6** (1.1 g, 2.91 mmol) as starting material, compound **3** was isolated in 8% yield as a slightly yellow oil. ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 2.91 (d, J = 7.12 Hz, 1H), 3.03 (m, 1H), 3.24 (dd, J = 2.14, 15.58 Hz, 1H), 3.42 (s, 3H), 3.56 (m, 2H), 3.77 (m, 1H), 4.94 (s, 1H), 7.07–8.00 (m, 9H); ^{13}C NMR ($CDCl_3$): δ = 28.63 (t), 32.78 (t), 41.76 (q), 57.66 (d), 71.02 (s), 106.75 (d), 127.54 (d), 127.67 (d), 128.17 (d), 128.49 (d), 128.75 (d), 130.75 (s), 133.92 (s), 134.30 (d), 137.35 (s), 173.84 (s).

Preparation of the gel: A weighed amount of **1** (approximately 62 mmol L^{-1} hexane) was heated in solvent until it had dissolved completely. The mixture was left to cool to ambient temperature. The gel was stored in a closed flask in the refrigerator. The solvents used had been purified and dried by distillation from P_2O_5 and stored over 4 Å molecular sieves. Isopropanol of pa grade was used as received.

DSC measurements: A weighed amount of **1** was put into a small aluminium DSC pan and the pan was filled with *n*-hexane. The pan was closed and weighed on a five-decimal-place balance. For gel formation the pan was heated to 100 °C and then cooled to the required temperature. The cooling and heating curves were recorded at rates of 5 °C min^{-1} by a Perkin–Elmer DSC-7 apparatus.

X-ray diffraction: The X-ray data collection was performed on Enraf-Nonius CAD-4F diffractometer equipped with a graphite monochromator and interfaced to a VAX-11/730 computer. Crystal data for **1**: $C_{28}H_{34}O_5S$, M = 482.64, orthorhombic, $p2_12_12_1$, a = 11.523(1), b = 11.641(1), c = 18.598(1) Å, V = 2494.7(3) Å^3, Z = 4, ρ_{calcd} = 1.285 g cm^{-3}, $\mu(Mo_{K\alpha})$ = 1.6 cm^{-1}, T = 295 K. Total reflections 3060, unique data 2761 of which 1779 were observed ($I > 2\sigma(I)$). 410 refined parameters. R = 0.067, wR = 0.040 ($w = 1/\sigma^2(F)$), residual electron density in final difference Fourier map 0.31 e Å^{-3}. Crystal data for **2**: $C_{24}H_{26}O_5S$, M = 426.54, triclinic, $p-1$, a = 8.317(1), b = 11.229(1), c = 11.991(1) Å, V = 1052.0(2) Å^3, Z = 2, ρ_{calcd} = 1.346 g cm^{-3}, $\mu(Mo_{K\alpha})$ = 1.78 cm^{-1}, T = 295 K. Total reflections 5047, unique data 5047 of which 3480 were observed ($I > 3\sigma(I)$); 326 refined parameters. R = 0.061, wR = 0.079, residual electron density in final difference Fourier map 0.28 e Å^{-3}. Structures were solved by Patterson methods and extension of the model was accomplished by direct methods applied to difference structure factors with the program Dirdif (P. T. Beurkens, G. Admiraal, G. Beurskens, W. P. Bosman, S. Garcia-Granda, R. O. Gould, J. M. M. Smits, C. Smykalla, *The Dirdif Program System, Technical Report of the Crystallography Laboratory*, University of Nijmegen, The Netherlands, **1992**), and the positional and anisotropic thermal displacement parameters for non-hydrogen atoms refined with block-diagonal least-squares procedure Crylsq (*XTAL 3.0 reference manual*, Eds.: S. R. Hall, J. M. Stewart, Universities of Western Australia and Maryland, lamb. Perth, **1990**) minimizing the function $Q = S_h[w(|F_o| - k|F_c|^2]$.

Freeze-Fracture Electron Microscopy: Freeze-fracture replicas were made by placing a little gel between two small copper holder plates and immersing this rapidly in a nitrogen slush (a mixture of solid and liquid nitrogen). The vitrified sample was broken at −176 °C under low pressure ($< 10^{-5}$ Torr). A platinum/carbon shadow layer of approximately 20 Å was then deposited at a 45° angle, followed by a carbon support of approximately 200 Å at normal incidence, by a Balzers EVM 052 A electron beam evaporation device with evaporator head EK 552. Film thickness was measured on a Baltzers crystal quartz thin film monitor QSG 201 D. The replica was washed with water and chromic acid [17]. These replicas were examined in a Philips EM 300 electron microscope operating at 80 kV.

Freeze-Drying Electron Microscopy: Replicas were made by placing a small volume of gel on Formvar carbon grids and immersing these rapidly in liquid ethane. The vitrified sample was placed in a holder equipped with a thermometer and held under high vacuum ($< 10^{-5}$ Torr) until the temperature had risen to −80 °C below and −50 °C above the sample. Subsequently the holder was opened (under vacuum) and the replicas were shadowed with a platinum/carbon layer. These replicas were examined in a Philips EM 300 electron microscope or a Philips EM 201 electron microscope operating at 80 kV. Samples of hexane and isopropanol gel were prepared this way.

Cryo-Electron Microscopy: Replicas were prepared by placing a small volume of the gel on Formvar carbon grids and immersing these rapidly in liquid ethane. They were subsequently transfered to liquid nitrogen. The vitrified samples were observed in this condition in a Philips CM 20 microscope operating at 200 kV.

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