Synthesis, Stereochemistry and Adsorption Studies of New Spiranes and Polyspiranes Containing 1,2-Dithiolane Units

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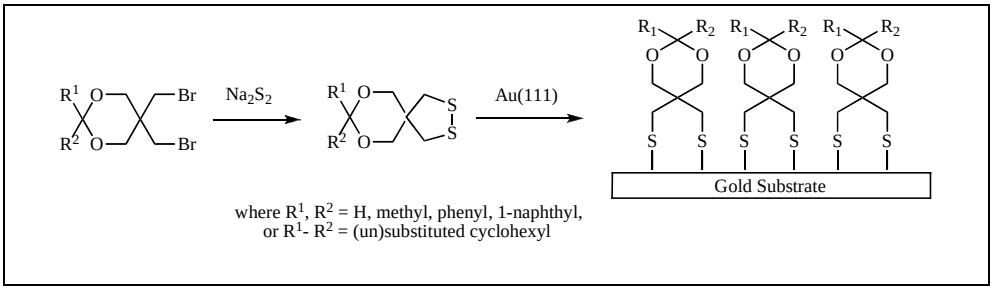

The synthesis and stereochemistry of a series of new cyclic disulfides containing (poly)spirane 1,2-dithiolane units are reported. Also included is a study of the self-assembled monolayers (*SAMs*) of these compounds on a gold surface. The characteristics of the resultant *SAMs* were determined by IR spectroscopy using molecular mechanics calculations.

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INTRODUCTION

The preparation and the characterization of *SAMs* from oriented organic molecules are of great interest particularly in those fields for which interface properties are important [1]. Studies in electrochemistry [2], vibrational spectroscopy [3], biological membranes [4], electrical conduction [5], catalysis [6], photolithography [7] and nanostructures [8] demonstrate just how important these highly organized *SAMs* can be.

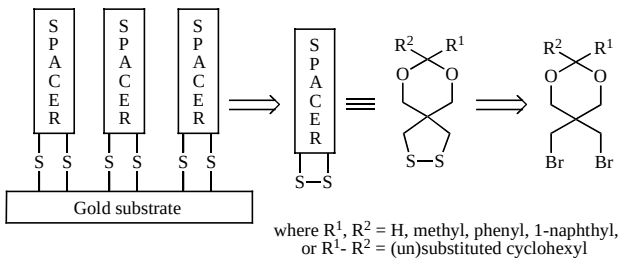
For those substrates having more than one anchor *per* molecule, a stronger interaction is observed between the organic species and the metal surface. This is particularly the case when sulfur atoms are chelated within a ring [9]. 1,2-Dithiane [10] and 1,2-dithiolane [11] rings were effectively bound as the disulfide in deposition experiments on gold. These *SAMs* were studied *via* IR spectroscopy and cyclic voltammetry.

These cyclic disulfides can be synthesized by two different pathways [12]. One involves the direct conversion of a dihalide or a ditosylate using sodium disulfide (prepared from sodium sulfide and sulfur [13]) or *via* tetrathiotungstates (as a sulfur transfer agent [14]). The second path is based on the oxidation of a dithiol with various oxidants [15].

Other methods for the synthesis of these cyclic disulfides involve a) the reaction of a 1,3-dielectrophile with S_4^{2-} (followed by the desulfurization with copper [16]), b) the cleavage of a bisthiocyanate with TBAF [17], or c) the steam distillation of an appropriate Bunte salt [18].

We were interested in obtaining *SAMs* from complex 1,2-dithiolane derivatives having a spirane skeleton since such structures combine common motifs of simple alkyl chain with cyclic disulfide and have a high degree of organization as well as being relatively flexible. Both of these properties are important if one wishes to obtain compact, uniform monolayers. When one considers the retro-synthesis of the target *SAMs*, the first step is the adsorption of a suitable disulfido-(poly)spirane onto the gold surface. A (poly)spirane having a terminal disulfide could potentially be prepared from the corresponding 5,5-bis(bromomethyl)-1,3-dioxane (Scheme I).

Scheme I



RESULTS AND DISCUSSION

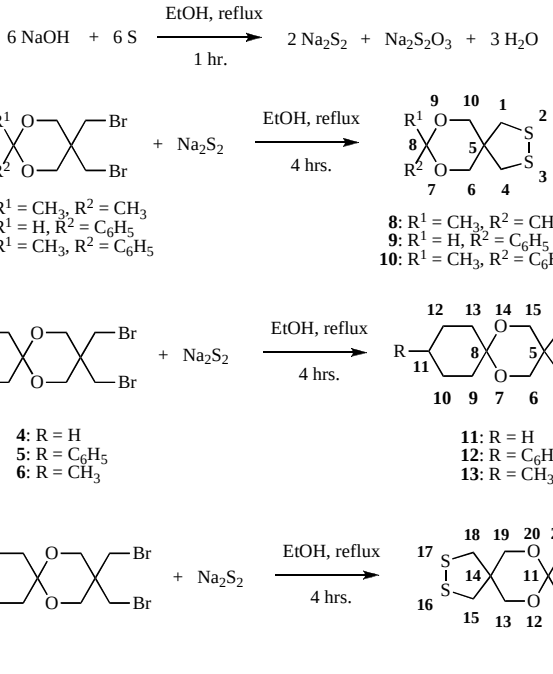
Synthesis of (poly)spiranes containing 1,2-dithiolane units. The starting 5,5-bis(bromomethyl)-1,3-dioxane

derivatives (**1**-**7**) were obtained by ketalization reaction of the appropriate carbonyl compound with 2,2-bis(bromomethyl)-1,3-propanediol [19].

We modified a procedure previously reported by Chorbadijev *et al* [20] for the synthesis of the 1,2-dithiolane (poly)spirane derivatives, **7-14**, (Scheme II). This group reported a synthesis for acyclic disulfides *via* substitution of a halide atom with disodium disulfide (previously generated from sulfur and sodium hydroxide). In order to increase the yield of the cyclic disulfide *via* suppression of polymer generation we greatly reduced the reagent concentrations (from 0.5 *M* to 0.03 *M*).

The desired (poly)spiranes were obtained in fair to good yields (35-74% for **8**-**13** and 27% for **14**) after separation with flash chromatography. Mass and NMR spectra of the products confirmed the assigned structures.

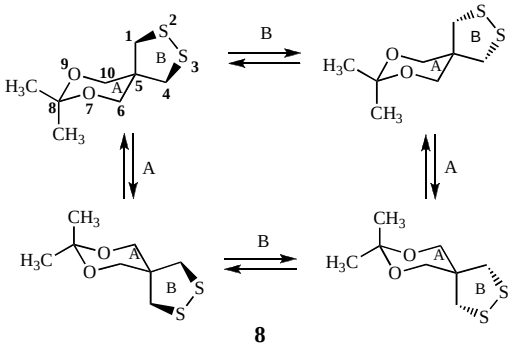
Scheme II



Stereochemistry of (Poly)spiranes Containing 1,2-Dithiolane Units. In order to better understand the structure of *SAMs* a stereochemistry study of these spiranes was carried out. Monospirane **8**, dispirane **11** and tetraspirane **14** all have symmetrically substituted six-membered rings and exhibit flexible structures. The six-membered rings prefer the chair conformation, while for the 1,2-dithiolane ring we propose (based on data published [21,22] for similar compounds) the envelope conformer with the spirane moiety out of the plane. The conformational equilibria are running between homomeric structures in **8** (Scheme III) and between *syn* and *anti* isomers in the cases of compound **11** (Scheme IV) and **14**. These isomers are due to the chirality of the spirane units with six-membered rings [23,24] and to the fact that the peripheral rings of the di or polyspirane skeleton may be in *syn* or *anti* positions [25-28]. The flipping of the 1,3-dioxane, cyclohexane and 1,2-dithiolane rings results in the conformational equilibration of all the possible isomers.

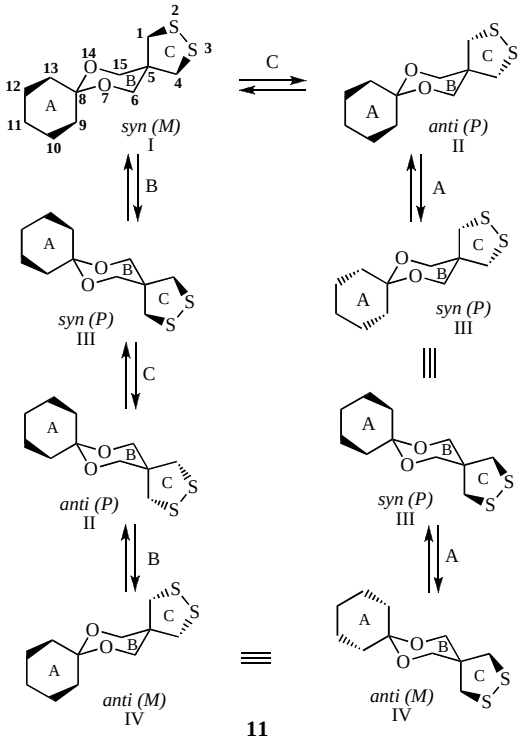
Spiranes **9** and **10** do not have the same substituents on the 1,3-dioxane units thus these rings are anancomeric. The flipping of the heterocycle shifts the conformational equilibrium towards that conformation having the most bulky substituent equatorial (Scheme V; Ph for **9** and Me for **10**; for similar cases see references [29-31]). Dispiranes **12** and **13** have semi-flexible structures (Scheme VI), the cyclohexane ring being rigid, its

Scheme III



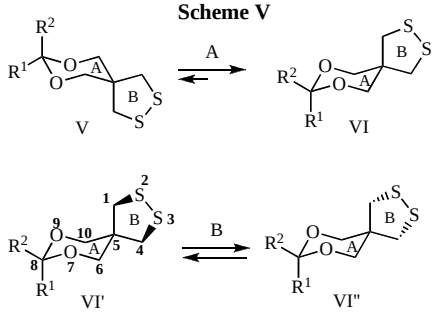
substituents are efficient "holding groups" while the 1,3-dioxane and 1,2-dithiolane moieties flip, equilibrating any possible stereoisomers (VII-X). The ^{1}H NMR spectra of **12** and **13** do not differentiate between the axial or equatorial protons of the heterocycles. Nonetheless, different signals (singlets) were observed for the diastereotopic positions at 6 and 15 (**12**: δ_6 = 3.81, δ_{15} = 3.85, $\delta_{1,4}$ = 3.04 ppm and **13**: δ_6 = 3.71, δ_{15} = 3.76, $\delta_{1,4}$ = 2.98 ppm).

Scheme IV



11

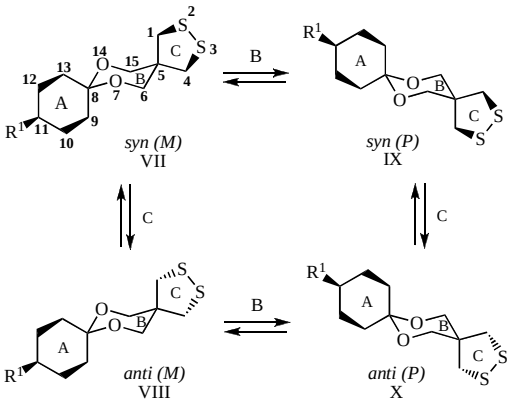
Scheme V



9: R^1 = H, R^2 = C_6H_5
10: R^1 = C_6H_5, R^2 = CH_3

The diastereotopicity of positions 6 and 15 was also observed in the ^{13}C NMR (**12**: δ_6 = 66.32, δ_{15} = 66.50 ppm and **13**: δ_6 = 66.34, δ_{15} = 66.61 ppm). Position 6 is *procis* while position 15 is *protrans* with respect to a substituent at 11.

Scheme VI



12, 13

Adsorption studies. Individual gold (111) surfaces were treated with one of each of the cyclic disulfides, **11**-**14,** in ethanol and the deposits were analyzed by IR spectroscopy. The collected data are presented in Table 1 and some details of the IR spectra of **11**-**14** are shown in Figure 1. The assignment of the vibrational bands and the direction and magnitudes of the vibrational dipole moments were obtained from Hartree-Fock calculations done with Gaussian 98® software. The widths of the bands at half-height in the IR spectra are in the range of 20-40 cm^{-1} which suggests that the molecules are disordered on the gold surface. Also, the methylene $\nu_a(CH_2)$ band at 2926-2930 cm^{-1} (that is present in all samples) is indicative of a liquid like monolayer. This disorder is probably due to the complex and relatively rigid structure of the molecules which results in a large distance between the adsorbed molecules and thus few stabilizing inter-adsorbate interactions that usually results in efficient self-assembly processes.

Although the monolayer is not very organized, some information on the orientation of the adsorbed molecules could be drawn from the IR investigations. Our analysis of the IR spectra are based on the direction of the vibrational dipole moments obtained from a computational chemistry calculation and the infrared surface selection rule for adsorbates on metallic substrates [32] which states that a vibrational mode is IR active if there is a component of its dipole moment perpendicular to the surface.

The analysis of the wave numbers and intensity of the vibrational bands of compounds **12** and **14** adsorbed on gold suggest that they adopt the orientations shown in Figures 2. Also, it is likely that both compounds bind to the surface *via* at least two of their sulfur atoms, as disulfides are known to dissociate upon adsorption on gold [33].

In the case of compound **12**, the absence of C-H deformation band for the aromatic ring in the range

1400-1500 cm^{-1}, suggests that the aromatic substituent in **12** is lying in either plane relatively parallel or perpendicular to the gold surface. Weak C-H aromatic stretches above 3000 cm^{-1} are observed for compound **12**. This makes it more likely that the aromatic group is in a plane perpendicular to the surface as is shown in Figure 2a. Also in this orientation, the methylene deformation bands (not observed in the range of 1200 to 1300 cm^{-1}) should be weaker than the methylene C-H stretching bands.

Table 1

IR wave numbers (ν/cm^{-1}) of the SAMs for each cyclic disulfide 11-14 on a gold (111) surface

Assignment	**11**	**12**	**13**	**14**
ν_a(=C-H, Ar)	-	3065 (weak)	-	-
ν_a(=C-H, Ar)	-	3031 (weak)	-	-
ν_a(=C-H, Ar)	-	3017 (weak)	-	-
$\nu_a(CH_3)$	2961[a] (weak)	2959[a]	2958	2958[a] (weak)
$\nu_a(CH_2)$	2928	2930	2926	2926
$\nu_s(CH_3)$	-	2874[a]	2869	-
$\nu_s(CH_2)$	2857	2856	2857	2857
ν_a(C-O-C)	1096	1131	1154	1130

[a] due to a small amount contaminant containing a methyl group

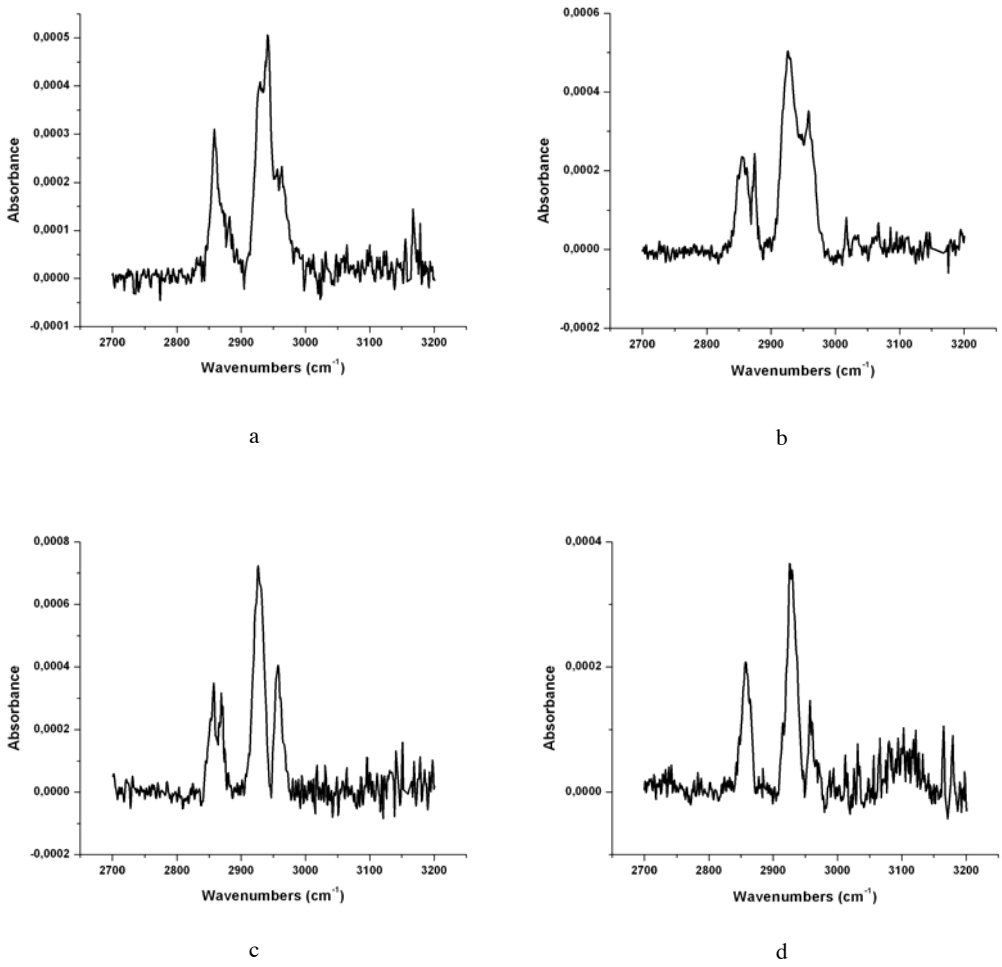
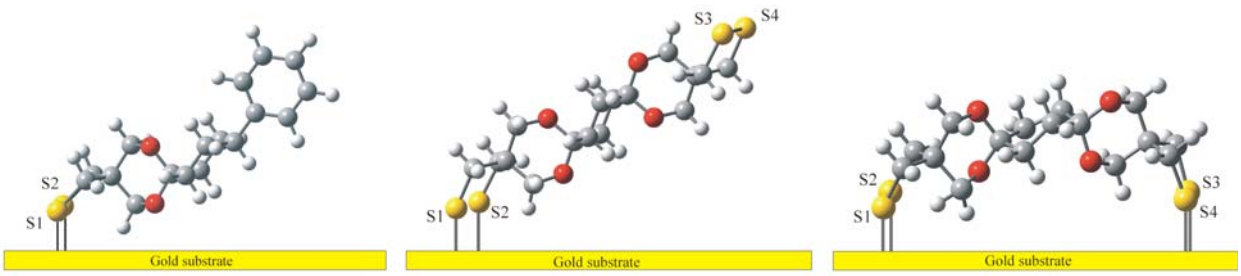


Figure 1. IR spectra (details) of compounds **11** (a), **12** (b), **13** (c) and **14** (d) adsorbed on Au (111).



a b c

Figure 2. Possible orientations of compounds **12** (a) and **14** (b and c) adsorbed on Au (111) suggested by the analysis of theirs IR spectra

The absence of CH deformation bands between 1300 and 1400 cm^{-1} suggests that **14** is not oriented perpendicular to the surface but is rather parallel to the surface. In this orientation the C-H deformation modes of methylenes will have a low intensity. It is thus possible that compound **14** is anchored to the surface by both 1,2-dithiolane rings (Figure 2c). However, this would require an important reorganization (the twisting of the middle cyclohexane ring) of the optimized structure shown in Figure 2b. Hence, it is more likely that compound **14** adopt the orientation shown in Figure 2b and adsorb *via* two sulfurs.

The more narrow bands (Figure 1) observed in the IR spectra of **13** (c) and **14** (d) as compared with those find in the spectra of **11** (a) and **12** (b) suggest a better organization of the monolayers for **13** and **14** than for **11** and **12**.

In the analysis of the monolayers generated by the deposit of our derivatives on gold surface we considered the compounds anchored by two sulfur atoms as the literature data [34,35,36,37] suggest for disulfides. The anchorage of the compounds on the gold surface by disulfides is more efficient than the fixation on gold in the case of the compounds anchored by only one sulfur atom (*e.g.* alkylmercaptanes [1b]) and cyclic disulfides showed to be efficient in the anchorage on gold of our spiro derivatives (other complex molecules as porphyrins [38] or catenanes [39] were successfully deposited on gold *via* cyclic disulfides). The degree of organization of the monolayers for our compounds is lower than in the case of the monolayers formed by the adsorbtion of more simple compounds (alkylmercaptanes [1b] or linear amides [40]). The relative flexible behavior of the absorbed spiro compounds determines a higher organization of the monolayers for our compounds than it was observed for the monoloyers obtained by the adsorbtion of the disulfides of rigid substrates (*e.g.* disulfides with aromatic groups [41]).

CONCLUSION

The synthesis by an original procedure of a series of new (poly)spiranes containing 1,2-dithiolane rings as cyclic disulfides leads to compounds with flexible or semi-flexible conformational behaviour. The adsorption of some of these derivatives on a gold surface and the structural behavior of the resultant *SAMs* were investigated using computational chemistry modeling as well as IR spectroscopy. They all appear to adopt a tilted orientation and a disorder of the molecules orientations in the monolayer was observed

EXPERIMENTAL

The solvents were purified according to standard procedures and were distilled prior to use. Column chromatography: silica gel 60 (Merck, Darmstadt). Thin layer chromatography (TLC): silica gel layered aluminium foil (60 F_{254} Merck, Darmstadt). Melting points (uncorrected) were taken using a Kleinfeld APOTEK apparatus. Starting materials 1-7 were synthesized according to a procedure reported in the literature [16]. NaOH and sulfur were purchased from Merck and used without further purification. The ^{1}H and ^{13}C NMR spectra were recorded with Varian Gemini 300 and Bruker ARX 300 (300 MHz for ^{1}H and 75 MHz for ^{13}C) spectrometers with $CDCl_3$ as solvent. The assignments of quaternary C (C_{quat}), CH, CH_2 and CH_3 were made on the basis of APT or DEPT spectra. Mass spectra (EI, 70 eV) were recorded using a Varian MAT 311 spectrometer.

The IR spectra were recorded on a Nicolet Nexus 670 FTIR spectrometer using a grazing angle ATR accessory. The incident angle of the IR beam was 85°. The number of scans per spectrum was 1000 and a resolution of 2 cm^{-1} was used. The background spectrum was that of an uncoated gold film. A 5 points baseline correction was done for all IR spectra.

The optimisation of the structures and calculation of the IR spectra were done with the Gaussian 98 software. A restricted Hartree-Fock calculation using a 6-31G basis set was done on the electronic ground states. The optimisation of the structures was done using the Berny algorithm. Once the structure was optimized, the IR spectrum was calculated. A correction was done on the calculated wavenumbers. This consisted in multiplying the numbers by a factor of approx. 0.9 as suggested in the Gaussian manual because the IR wavenumbers are usually overestimated. These calculations were used for qualitative purposes to help in the interpretation of the IR spectra of absorbed monolayers on gold. A complete study of the stability of numerous structures of spiro compounds is beyond the scope of this study.

The monolayers of all compounds were formed as follow: a solution of 10^{-3} *M* concentration of the compounds in ethanol was done. A gold substrate from Arrandee was annealed in a natural gas flame in order to remove organic impurities and to remove surface imperfections. The gold substrate was then immersed in the adsorbate solution overnight. The adsorption of disulfide compounds on gold is known to cause their dissociation. It is thus expected that the compounds adsorb *via* its two sulfur atoms. The resulting monolayers were then rinsed with ethanol and dried before recording their IR spectra.

The elemental analyses were performed at IRCOF, University of Rouen, France, and are in good agreement with the assigned structures.

General method for the synthesis of the cyclic disulfides. A mixture of 0.6 g of sodium hydroxide (15 mmol) and 0.48 g sulfur (15 mmol) in 10 cm^3 of 96% ethanol was refluxed for 1 h, and was added over a solution of 5 mmol of starting material in 150 ml of 96% ethanol. After 4 h of reflux the reaction mixture was cooled to *rt* and was added to a mixture of 200 cm^3 of water and 50 cm^3 of methylene chloride. The aqueous layer was separated, extracted with 2x50 cm^3 of methylene chloride, the organic layers were combined, washed with 100 cm^3 of water followed by 100 cm^3 of brine and finally dried over sodium sulfate. The residue was adsorbed on silica gel and was separated (petroleum ether-methylene chloride = 1:1) to afford the products.

8,8-Dimethyl-7,9-dioxa-2,3-dithiaspiro[4.5]decan (8). Yellow solid, m.p.=51-2°C, yield 74%. Rf=0.55. ^{1}H nmr: δ = 1.37 (6H, s, 8-CH_{3ae})**,** 2.94 (4H, s, H-1, H-4), 3.71 (4H, s, H-6, H-10). ^{13}C nmr: δ = 23.65 (CH_3), 45.08 (CH_2), 50.30 (C_{quat}), 66.98 (CH_2), 97.39 (C_{quat}). ms: m/z 206 (M^+). *Anal.* Calcd. for $C_8H_{14}O_2S_2$: C, 46.57; H, 6.84; S, 31.08. Found: C, 46.79; H, 7.03; S, 30.95.

8-Phenyl-7,9-dioxa-2,3-dithia-spiro[4.5]decan (9). Yellow solid, m.p.=67-69°C yield 52%. ^{1}H nmr and ^{13}C nmr spectra were found to be identical with the one described in Ref. [15].

8-Methyl-8-phenyl-7,9-dioxa-2,3-dithia-spiro[4.5]decan (10). Yellow solid, m.p.=63°C, yield 60%. Rf=0.40. ^{1}H nmr: δ = 1.53 (3H, s, 8-CH_3)**,** 2.45 (2H, s, H-1), 3.71 (2H, s, H-4), 3.68 (2H, d, *J*=11.1 Hz, H-6ax, H-10ax), 3.75 (2H, d, *J*=11.1 Hz, H-6eq, H-10eq), 7.35-7.46 (5H, overlapped peaks, phenyl protons). ^{13}C nmr: δ = 31.89 (CH_3), 47.21 (CH_2), 50.19 (C_{quat}), 67.99 (CH_2), 101.04 (C_{quat}), 126.69 (CH) 128.07 (CH) 128.90 (CH) 139.90 (C_{quat}). ms: m/z 322 (M^+). *Anal.* Calcd. for $C_{13}H_{16}O_2S_2$: C, 58.18; H, 6.01; S, 23.89. Found: C, 58.31; H, 6.17; S, 23.72.

7,14-dioxa-2,3-dithia-dispiro[4.2.5.2]pentadecan (11). Yellow solid, m.p.=84-6°C, yield 46%. Rf=0.45. ^{1}H nmr: δ = 1.38-1.73 ppm (10H, overlapped peaks), 2.96 (4H, s, H-1, H-4), 3.74 (4H, s, H-6, H-15). ^{13}C nmr: δ = 22.52 (CH_2), 25.65 (CH_2), 32.45 (CH_2), 45.21 (CH_2), 50.52 (C_{quat}), 66.14 (CH_2), 98.90 (C_{quat}). ms: m/z 246 (M^+). *Anal.* Calcd. for $C_{11}H_{18}O_2S_2$: C, 53.62; H, 7.36; S, 26.03 Found: C, 53.88; H, 7.54; S, 25.88.

11-Phenyl-7,14-dioxa-2,3-dithia-dispiro[4.2.5.2]pentadecan (12). Yellow solid, m.p.=118-9°C, yield 56%. Rf=0.40. ^{1}H nmr: δ = 1.48-2.36 (8H, overlapped peaks), 2.53-2.63 (1H, m), 3.04 (4H, s, H-1, H-4), 3.81 (2H, s, H-6), 3.85 (2H, s, H-15), 7.18-7.33 (5H, m, phenyl protons). ^{13}C nmr: δ = 30.04 (CH_2), 32.46 (CH_2), 43.83 (CH), 45.23 (CH_2), 50.58 (C_{quat}), 66.32 (CH_2), 66.50 (CH_2), 98.90 (C_{quat}), 126.20 (CH) 126.90 (CH) 128.43 (CH), 146.38 (C_{quat}). ms: m/z 322 (M^+). *Anal.* Calcd. for $C_{17}H_{22}O_2S_2$: C, 63.32; H, 6.88; S, 19.89. Found: C, 63.50; H, 7.01; S, 19.75.

11-Methyl-7,14-dioxa-2,3-dithia-dispiro[4.2.5.2]pentadecan (13). Yellow solid, m.p.=99-101°C, yield 61%. Rf=0.45. ^{1}H nmr: δ = 0.87 (3H, d, *J*=6.6 Hz, 11-CH_3), 1.09-1.67 (7H, overlapped peaks), 2.13-2.18 (2H, overlapped peaks), 2.98 (4H, s, H-1, H-4), 3.71 (2H, s, H-6), 3.76 (2H, s, H-15). ^{13}C nmr: δ = 21.73 (CH_3), 30.76 (CH_2), 31.87 (CH_2), 31.92 (CH), 45.21 (CH_2), 50.52 (C_{quat}), 66.34 (CH_2), 66.61 (CH_2), 98.47 (C_{quat}). ms: m/z 240 (M^+). *Anal.* Calcd. for $C_{12}H_{20}O_2S_2$: C, 55.35; H, 7.74; S, 24.62. Found: C, 55.57; H, 7.92; S, 24.45.

7,12,20,23-Tetraoxa-2,3,16,17-tetrathia-tetraspiro[4.2.2.2.4.2.2.2]tetracosan (14). Yellow solid, m.p.=151-2°C, yield 27%. Rf=0.35. ^{1}H nmr: δ = 1.87 (8H, s, H-9, H-10, H-21, H-22)**,** 3.00 (8H, s, H-1, H-4, H-15, H-18), 3.76 (8H, s, H-6, H-13, H-19, H-24). ^{13}C nmr: δ = 28.22 (CH_2), 45.21 (CH_2), 50.52 (C_{quat}), 66.60 (CH_2), 98.47 (C_{quat}). ms: m/z 408 (M^+). *Anal.* Calcd. for $C_{16}H_{24}O_4S_4$: C, 47.03; H, 5.92; S, 31.39. Found: C, 47.21; H, 6.19; S, 31.30.

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