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A New Type of S-S Dication. Preparation and Reactions with Alkenes and Dienes

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Abstract: The reaction of dimethyl sulfide ditriflate with dimethyl sulfide leads to the formation of tetramethyldisulfonium ditriflate **1a** representing a first example of acyclic S-S dication. Similarly was prepared S-S dication **1b** from tetrahydrothiophene. It was found that dications **1a** and **1b** react with arylalkenes. The reaction forms the corresponding 1,2-disulfonium salts. Conjugated dienes afford 1,4-disulfonium salts.

Structures with two adjacent positively charged heteroatoms are relatively rare. Investigation of these compounds as intermediates in electrophilic and redox reactions is of considerable theoretical interest. Structures containing such doubly charged heteroatomic fragments as N-N,[1] S-N,[2] Se-N,[3] S-S[4], Se-Se,[5] S-Se,[5] Te-Te [6] have been thoroughly investigated in recent years.

The most fully studied class of such structures are the S-S dications (dithia dication).[7] Their formation has been suggested as intermediates in several reactions of sulfides. For example, electrochemical oxidation of β-dithioacetals to the carbonyl compounds has been found to occur *via* dithia dications.[8] Formation of S-S dications by oxidation of cyclic and acyclic 1,5- or 1,6-bis-sulfide appears to be general.[9] Moreover, in the case of cyclic compounds, Musker and co-workers have isolated the first dication species as stable solid substances.[4] Earlier attempts to obtain dithia dications by alkylation of disulfides were unsuccessful.[10] Further progress in the synthesis and chemistry of S-S dications was achieved by Furukawa and co-workers [11] who found a convenient approach to dithia dications based on the reaction of cyclic monosulfoxides of bis-sulfides with trifluoromethanesulfonic anhydride.[12]

Now we have found that dimethylsulfoxide/triflic anhydride complex (dimethyl sulfide ditriflate, DMSD) reacts with dimethylsulfide in methylene chloride at -40 °C to form tetramethyldisulfonium ditriflate **1a** - a new type of S-S dication. Similarly, from tetrahydrothiophene and the corresponding sulfoxide/ trifluoromethanesulfonic anhydride complex dithia dication **1b** was prepared.

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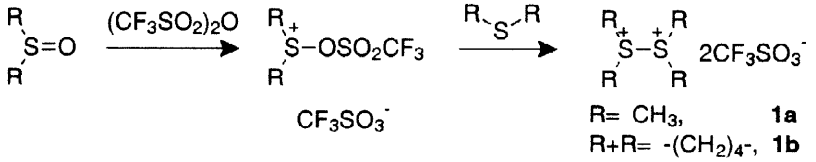
DMSD is known to be a highly reactive S-electrophile and an oxidant. It reacts with alkenes, alkynes and various aromatic compounds including benzene to afford vinyl or dimethylaryl sulfonium salts in high yield.[14-16]

When dimethyl sulfide was added to DMSD (-40 °C in CD_2Cl_2/CH_3NO_2 - 1/1) the signals of starting substances (2.04 ppm - SMe_2 and 3.14 ppm - DMSD[8]) disappeared and new singlets are observed at 3.16 ppm in ^1H NMR and 36.0 ppm in ^{13}C NMR. We believe that nucleophilic substitution of triflate anion in DMSD by dimethyl sulfide gives rise to the dithia dication **1a.**



Scheme 1

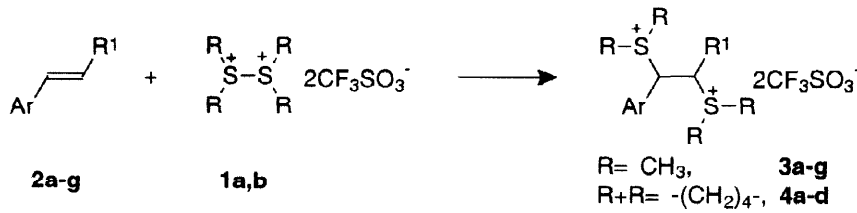
It was found earlier that S-S dications are oxidants (in the case of reaction with organometallics, alcohols, hydrazines, and mercaptans[16]) and electrophilic reagents (with such nucleophiles as water, bromide anion, and electron-rich aromatic compounds).[13] Recently we have found that S-S dication derivative of 1,4-dithiane 1-oxide reacts with arylalkenes to give bicyclic sulfonium salts. However, other dications formed from 1,5-dithiacyclooctane 1-oxide or 1,4- dithiacycloheptane 1-oxide did not react.[17]

Now we have investigated electrophilic addition of the dications **1a** and **1b** to the carbon-carbon double bond. Reactions proceed under mild conditions to give the products of 1,2-addition - 1,2-disulfonium salts. However, only alkenes having the double bond conjugated with an aromatic enter into the reaction to give clearly identifiable products. Other alkenes, such as 1-hexene or cyclohexene, form of a complex mixture of unidentified sulfonium salts. We suppose this to be due to their propensity to form products of elimination. It should be noted that alkenes with an electron-rich aromatic substituent, for example substrates **2b** and **f**, react very fast with both dications. However, reaction of dication **1b** with these alkenes results in complex mixture of sulfonium salts and our attempts to characterise it were unsuccessful.

We have also investigated the stereochemistry of the dication addition to a double bond. In the case of reactions dications **1a** and **1b** with 1,2-disubstituted alkenes both possible diastereomers were formed. Stereochemical data indicate the non concerted character of the reaction. We believe that the reaction proceeds *via* stepwise electrophilic addition: the first step is an attack on the double bond by the dithia dication resulting in carbocation intermediate, followed by trapping with sulfide.

The molecular mechanics (MM+) calculations shows that the *erythro* diastereomer is more stable than the *threo*. The *erythro* diastereomer of **3e** in it preferred conformation has torsion angle H-C(1)-C(2)-H about 180°, in contrast with the *threo* diastereomer which has an angle of about 60°. It seems likely that comparison of coupling constants $^3J_{HH}$ of this fragment may permit the assignment of configuration of sulfonium salts obtained: ^3J(H,H) 10.9 Hz for *threo* isomer > ^3J(H,H) 8.1 Hz for *erythro* isomer.

Interesting results were obtained in the reactions of S-S dications **1a, b** with indene. Both product **3g** and **4g** are formed as a single diastereomer with *trans* arrangement of sulfonium groups. It is evident that steric hindrance of the bulky sulfonium moieties makes the *cis* configuration considerably strained. The configurations were established using NOE experiments.



Scheme 2

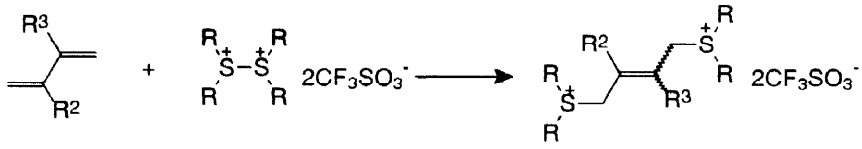
Table 1. Reaction of dithia dications **1a** and **1b** with arylalkenes

Substrate			Product			
entry	Ar	R^1	dication **1a**	yield	dication **1b**	yield
2a	C_6H_5	H	**3a**	88	**4a**	76
2b	2-thienyl	H	**3b**	81	-	
2c	$(CH_3)_3CC_6H_4$	H	**3c**	90	**4c**	81
2d	$CH_3OC_6H_4$	H	**3d**	91	**4d**	75
2e	C_6H_5	CH_3	**3e**	93	**4e**	67
2f	$CH_3OC_6H_4$	CH_3	**3f**	96	-	
2g	indene		**3g**	85	**4g**	43

- complex mixture of sulfonium salts was obtained

We have also found that dithia dications **1a, b** react with 1,3-dienes. The reaction proceeds to form unsaturated 1,4-disulfonium salts which are more unstable and should be kept at a low temperature. 1,4-Disubstituted linear dienes yielded complex mixtures of unidentified substances, in contrast to 1,3-cyclohexadiene which produces a moderate stable salt. Formation of the kinetically controlled products of 1,2-addition was not observed. S-S Dications of bicyclic structure (derivatives of 1,4-dithiane and 1,5-dithiacyclooctane) react with dienes to give unindentified mixtures of sulfonium salts.[17]

We have also studied the stereochemistry of the reaction with conjugated dienes. In all cases investigated the *E*-configuration of formed double bond predominates over the *Z*-configuration. The configuration of the products was established using the vicinal coupling constant $^3J_{HH}$ of vinyl protons determined by ^{13}C satellites of ^1H NMR spectra. As with the reaction with arylalkenes, we have observed formation of the thermodynamically more favourable products. In *E*-isomers van der Waals and Coulomb repulsion of the two methylenesulfonium moieties is minimal. Substitution of a vinyl hydrogen by the more bulky methyl group results in decreasing the energy difference between *E* and *Z* isomers and so increasing the *Z*-component in the isomer mixture.



5a-d **1a,b** **6a-d, 7a-d**

Scheme 3

Table 2. Reaction of dithia dications **1a** and **1b** with 1,3-dienes

Substrate			Product			
entry	R^2	R^3	dication **1a**	*E/Z* ratio, yield	dication **1b**	*E/Z* ratio, yield
5a	H	H	**6a**	*E*, 93	**7a**	*E*, 87
5b	CH_3	H	**6b**	6/1, 93	**7b**	9/1, 90
5c	CH_3	CH_3	**6c**	4/1, 95	**7c**	5/4, 86
5d	1,3-cyclohexadiene		**6d**	**a**, 72	**7d**	**b**, 48

a only isomer with *trans* arrangement of sulfonium group was isolated

b the ration of *trans/cis* isomers is 4/1

In summary we have prepared an acyclic S-S dication - tetramethyldisulfonium ditriflate for the first time. The reactions of S-S dications with alkenes and dienes have been investigated: the reactions proceed by 1,2- addition to give bis-sulfonium salts. The stereochemistry and reaction scope were studied.

Experimental Section

NMR spectra were recorded on Bruker AC 200, Bruker AMX 400 and Varian VXR-400 spectrometers with TMS as an internal standard. The IR spectra were obtained with UR-20 spectrometer as films. All solvents used were dried and distilled according to standard procedures. Triflic anhydride was prepared according to a literature method[18] from trifluoromethanesulfonic acid (Merck).

General procedure for the reaction of tetramethyldisulfonium ditriflate with alkenes and dienes: Trifluoromethanesulfonic anhydride (5 mmol, 1 equiv.) was added to a well-stirred solution of dimethylsulfoxide (5 mmol, 1 equiv.) in CH_2Cl_2 (20 mL) at - 40 °C. A solution of (5 mmol, 1 equiv.) of dimethyl sulfide in 10 mL of anhydrous dichloromethane was added dropwise. Over this period the solution become coloured yellow and then a white precipitate formed. The reaction mixture was allowed to warm to -20 °C followed by dropwise addition of an equimolar solution of the corresponding alkene (or diene) in 10 mL of dichloromethane. The resulting mixture was allowed to react at -20 °C for 1-5 h (TLC monitoring). Then 50 mL of ether was added followed by filtration of the precipitate. Crude products were washed three times by ether. The products should be kept at 0 °C.

[2-(1,1-Dimethylsulfonio)-2-phenylethyl](dimethyl)sulfonium bistrifluoromethanesulfonate (3a). Yield 88%, mp 136-137 °C (dec.); IR (Nujol): 1300-1140, 1040 cm^{-1}; ^1H NMR (400 MHz, CD_3CN): δ = 7.87-7.78 (m, 2H, C_6H_5), 7.70-7.61 (m, 3H, C_6H_5), 5.67 (q, X part of an ABX system, 1H, ^3J 6.1 Hz, ^3J 10.3 Hz), 4.85-4.60 (dq, AB part of an ABX system, 2H, ^2J 13.3 Hz, ^3J 10.3 Hz, ^3J 6.1 Hz), 3.26 (s, 6H, $(CH_3)_2S^+$), 3.17 (s, 3H, CH_3S^+), 2.92 (s, 3H, CH_3S^+); ^{13}C NMR (100 MHz, CD_3CN): δ = 132.32, 130.71, 130.60, 126.04, 120.00 (q, ^1J 320.0 Hz), 54.67, 43.45, 26.21 (CH_3S^+), 23.13 (CH_3S^+), 25.20 (CH_3S^+), 24.56 (CH_3S^+). Anal. Calcd. for $C_{14}H_{20}S_4F_6O_6$ (526.5): C 31.94, H 3.83. Found: C 31.41, H 3.85.

[2-(1,1-Dimethylsulfonio)-1-(2-thienyl)ethyl](dimethyl)sulfonium bistrifluoromethanesulfonate (3b). Yield 81%, mp 95-97 °C (dec.); IR (Nujol): 1300-1140, 1040 cm^{-1}; ^1H NMR (400 MHz, CD_3CN): δ = 7.73 (dd, 1H, C_4H_3S, ^3J 5.2 Hz, ^4J 1.2 Hz), 7.51 (dd, 1H, C_4H_3S, ^3J 3.7 Hz, ^4J 1.2 Hz), 7.21 (1H, C_4H_3S, ^3J 5.2 Hz, ^4J 3.7 Hz), 5.51 (q, X part of an ABX system, 1H, ^3J 5.5 Hz, ^3J 10.9 Hz), 4.25-4.09 (dq, AB part of an ABX system, 2H, ^3J 5.5 Hz, ^3J 10.9 Hz, ^2J 13.5 Hz), 2.91 (s, 3H, CH_3S^+), 2.85 (s, 3H, CH_3S^+), 2.82 (s, 3H, CH_3S^+), 2.60 (s, 3H, CH_3S^+); ^{13}NMR (100 MHz, CD_3CN): δ = 134.45, 132.85, 129.99, 128.83, 122.44 (q, ^1J 319.5 Hz), 51.35, 44.88, 26.99 (CH_3S^+), 26.09 (CH_3S^+), 25.31 (CH_3S^+), 23.30 (CH_3S^+). Anal. Calcd. for $C_{12}H_{18}S_5F_6O_6$ (532.6): C 27.06, H 3.41. Found: C 27.40, H 3.63.

[2-(1,1-Dimethylsulfonio)-1-(4-methoxyphenyl)ethyl](dimethyl)sulfonium bistrifluoromethanesulfonate (3c). Yield 91%, mp 118-119 °C (dec.); IR (Nujol): 1300-1140, 1030 cm^{-1}; ^1H NMR (400 MHz, CD_3CN): δ = 7.52 (d, 2H, ^3J 8.8 Hz), 7.11 (d, 2H, ^3J 8.8 Hz), 5.17 (dd, 1H, ^3J 5.6 Hz, ^3J 11.2 Hz), 4.31 (dd, 1H, ^3J 11.2, ^2J 13.2), 4.13 (dd, 1H, ^3J 5.6, ^2J 13.2), 3.84 (s, 3H), 2.94 (s, 3H, CH_3S^+), 2.91 (s, 3H, CH_3S^+), 2.82 (s, 3H, CH_3S^+), 2.59 (s, 3H, CH_3S^+); ^{13}C NMR (100 MHz, CD_3CN): δ = 162.18, 133.53, 132.67, 121.80 (q, ^1J 318.4 Hz), 116.74, 116.47, 56.46, 43.92, 26.90 (CH_3S^+), 25.77 (CH_3S^+), 25.11 (CH_3S^+), 25.06 (CH_3S^+), 23.55 (CH_3O). Anal. Calcd. for $C_{15}H_{22}S_4F_6O_7$ (556.6): C 32.37, H 3.98. Found: C 32.23, H 3.90.

[1-[4-(*tert*-Butyl)phenyl]-2-(1,1-dimethylsulfonio)ethyl](dimethyl)sulfonium bistrifluoromethanesulfonate (3d). Yield 90%, mp 150-151 °C (dec.); IR (Nujol): 1300-1140, 1040 cm^{-1}; ^1H NMR (400 MHz, CD_3CN): δ = 7.75 (d, 2H, C_6H_4, ^3J 8.6 Hz), 7.68 (d, 2H, C_6H_4, ^3J 8.6 Hz), 5.66 (dd, 1H, ^3J 10.6 Hz, ^3J 5.9 Hz), 4.78 (dd, 1H, ^3J 10.6 Hz, ^2J 13.4 Hz), 4.64 (dd, 1H, ^3J 5.9 Hz, ^2J 13.4 Hz), 3.24 (s, 3H, CH_3S^+), 3.22 (s, 3H, CH_3S^+), 3.15 (s, 3H, CH_3S^+), 2.90 (s, 3H, CH_3S^+), 1.32 (s, 9H, $(CH_3)_3C$); ^{13}C NMR (100 MHz, CD_3CN): δ = 155.30, 130.00, 127.20, 124.70, 119.2 (q, ^1J 320.0 Hz), 54.20, 43.20, 34.80, 30.50, 25.90 (CH_3S^+), 25.80 (CH_3S^+), 24.90 (CH_3S^+), 24.20 (CH_3S^+). Anal. Calcd. for $C_{18}H_{28}S_4F_6O_6$ (582.6): C 37.11, H 4.84. Found: C 36.97, H 4.84.

[2-(1,1-Dimethylsulfonio)-1-methyl-2-phenylethyl](dimethyl)sulfonium bistrifluoromethanesulfonate (3e) *erythro* and *threo* diastereomer mixture 4.6/1. Yield 93 %, mp 150-151 °C (dec.); IR (Nujol):

1300-1140, 1040 cm^{-1}; ^1H NMR (400 MHz, CD_3CN): δ = signals of *erythro* diastereomer 7.72-7.45 (m, 5H, C_6H_5), 5.16 (d, 1H, ^3J 10.9 Hz), 4.61 (dq, 1H, ^3J 10.9 Hz, ^3J 6.8 Hz), 2.82 (s, 3H, CH_3S^+), 2.66 (s, 3H, CH_3S^+), 2.53 (s, 3H, CH_3S^+), 2.52 (s, 3H, CH_3S^+), 1.78 (d, 3H, ^3J 6.8 Hz); signals of *threo* diastereomer 7.72-7.45 (m, 5H, C_6H_5), 5.15 (d, 1H, ^3J 8.1 Hz), 4.42 (dq, 1H, ^3J 8.1 Hz, ^3J 6.9 Hz), 3.06 (s, 6H, CH_3S^+), 2.79 (s, 3H, CH_3S^+), 2.76 (s, 3H, CH_3S^+), 1.48 (d, 3H, ^3J 6.9 Hz); ^{13}C NMR (100 MHz, CD_3CN): δ = signals of major diastereomer 133.23, 131.83, 131.30, 125.71, 121.80 (q, ^1J 318.3 Hz), 60.94, 49.94, 25.38 (CH_3S^+), 24.67 (CH_3S^+), 22.06 (CH_3S^+), 19.36 (CH_3S^+), 12.08 (CH_3). Anal. Calcd. for $C_{15}H_{22}S_4F_6O_6$ (540.6): C 33.33, H 4.10. Found: C 33.28, H 4.08.

[2-(1,1-Dimethylsulfonio)-1-methyl-2-(4-methoxyphenyl)](dimethyl)sulfonium bistrifluoromethanesulfonate (3f) *erythro* and *threo* diastereomer mixture ~1/1. Yield 96 %, mp 111-112 °C (dec.); IR (Nujol): 1300-1140, 1030 cm^{-1}; ^1H NMR (400 MHz, CD_3CN): δ = 7.50-7.40 (m, 2H, C_6H_5), 7.15-7.10 (m, 3H, C_6H_5), 5.17 (d, 1H, ^3J 4.8 Hz, *threo*), 5.14 (d, 1H, ^3J 1.6 Hz, *erythro*), 4.63 (dq, 1H, ^3J 4.8 Hz, ^3J 7.2 Hz, *threo*), 4.43 (dq, 1H, ^3J 1.6 Hz, ^3J 6.8 Hz, *erythro*), 3.84 (s, 3H, CH_3O), 3.00 (s, 3H), 2.89 (s, 3H), 2.86 (s, 3H), 2.66 (s, 3H), 2.60 (s, 3H), 2.59 (s, 3H), 2.57 (s, 3H), 2.55 (s, 3H), 1.82 (d, 3H, ^3J 6.8 Hz, *erythro*), 1.53 (d, 3H, ^3J 7.2 Hz, *threo*); ^{13}C NMR (100 MHz, CD_3CN): δ = 158.35, 133.72, 133.02, 119.58 (q, ^1J 319.4 Hz), 117.84, 116.59, 61.28, 61.35, 56.57, 50.71, 50.02, 25.42, 25.12, 24.97, 24.53, 23.81, 21.78, 20.93, 19.18, 12.12 (CH_3), 11.4 (CH_3). Anal. Calcd. for $C_{16}H_{24}S_4F_6O_7$ (570.6): C 33.68, H 4.24. Found: C 33.51, H 4.20.

***trans*-[1-(1,1-Dimethylsulfonio)-2,3-dihydro-1*H*-inden-2-yl](dimethyl)sulfonium bistrifluoromethanesulfonate (3g).** Yield 85 %, mp 117-118 °C (dec.); IR (Nujol): 1300-1140, 1040 cm^{-1}; ^1H NMR (400 MHz, CD_3CN): δ = 7.61-7.56 (m, 2H, C_6H_5), 7.51-7.46 (m, 2H, C_6H_5), 5.54 (bs, 1H, CH-1), 4.76 (dd, 1H, CH-2, ^3J 7.2 Hz, ^3J 0.7 Hz), 3.79 (dd, 1H, ^2J 19.5 Hz, ^3J 7.2 Hz), 3.49 (d, 1H, ^2J 19.5 Hz), 2.94 (s, 3H, CH_3S^+), 2.89 (s, 3H, CH_3S^+), 2.78 (s, 3H, CH_3S^+), 2.65 (s, 3H, CH_3S^+); ^{13}C NMR (100 MHz, CD_3CN): δ = 141.99, 132.60, 129.79, 129.23, 127.33, 126.38, 119.82 (q, ^1J 319.7 Hz), 59.75, 55.10, 33.67, 23.76 (CH_3S^+), 23.52 (CH_3S^+), 23.02 (CH_3S^+), 22.36 (CH_3S^+). Anal. Calcd. for $C_{15}H_{20}S_4F_6O_6$ (538.5): C 33.45, H 3.74. Found: C 33.32, H 3.73.

1-(2-Phenyl-2-tetrahydro-1-thiopheniumylethyl)tetrahydrothiophenium bistrifluoromethanesulfonate (4a). Yield 76 %, mp 149-150 °C (dec.); IR (Nujol): 1300-1140, 1040 cm^{-1}; ^1H NMR (400 MHz, CD_3CN): δ = 7.61-7.59 (m, 5H, C_6H_5), 5.01 (dd, 1H, ^3J 5.6 Hz, ^3J 11.2 Hz), 4.17 (dd, ^3J 11.2 Hz, ^2J 13.6 Hz), 4.00 (dd, ^3J 5.6 Hz, ^2J 13.6 Hz), 3.77-3.70 (m, 2H), 3.63-3.52 (m, 2H), 3.42-3.29 (m, 2H), 3.17-3.00 (m, 2H), 2.42-2.00 (m, 8H); ^{13}C NMR (100 MHz, CD_3CN): δ = 132.90, 131.54, 130.73, 129.53, 121.92 (q, ^1J 318.8 Hz), 55.43, 46.59, 46.01, 45.25, 44.55, 44.28, 29.81, 29.57, 29.50, 29.44. Anal. Calcd. for $C_{18}H_{24}S_4F_6O_6$ (578.6): C 37.36, H 4.18. Found: C 37.32, H 4.12.

1-{1-[4-(*tert*-Butyl)phenyl]-2-tetrahydro-1-thiopheniumylethyl}tetrahydrothiophenium bistrifluoromethanesulfonate (4c). Yield 81 %, mp 115-117 °C (dec.); IR (Nujol): 1300-1140, 1040 cm^{-1}; ^1H

NMR (400 MHz, CD_3CN): δ = 7.63 (d, 2H, ^3J 5.6 Hz), 7.53 (d, 2H, ^3J 5.6 Hz), 4.97 (dd, 1H, ^3J 5.6 Hz, ^3J 10.8 Hz), 4.13 (dd, ^3J 10.8 Hz, ^2J 13.6 Hz), 3.97 (dd, ^3J 5.6 Hz, ^2J 13.6 Hz), 3.74-3.70 (m, 2H), 3.61-3.51 (m, 2H), 3.41-3.30 (m, 2H), 3.17-3.02 (m, 2H), 2.36-2.11 (m, 8H); ^{13}C NMR (100 MHz, CD_3CN): δ = 156.64, 130.42, 128.47, 126.31, 121.98 (q, ^1J 318.9 Hz), 55.35, 46.50, 45.98, 45.19, 44.53, 44.08, 35.70, 31.27 ($3CH_3$), 29.79, 29.58, 29.50, 29.43. Anal. Calcd. for $C_{22}H_{32}S_4F_6O_6$ (634.7): C 41.63, H 5.08. Found: C 41.51, H 4.96.

1-[1-(4-Methoxyphenyl)-2-tetrahydro-1-thiopheniumylethyl]tetrahydrothiophenium bistrifluoromethanesulfonate (4d). Yield 75 %, mp 131-132 °C (dec.); IR (Nujol): 1300-1140, 1040 cm^{-1}; ^1H NMR (400 MHz, CD_3CN): δ = 7.55 (d, 2H, ^3J 8.8 Hz), 7.10 (d, 2H, ^3J 8.8 Hz), 4.97 (dd, 1H, ^3J 5.2 Hz, ^3J 11.2 Hz), 4.15 (dd, ^3J 11.2 Hz, ^2J 13.2 Hz), 3.96 (dd, ^3J 5.2 Hz, ^2J 13.2 Hz), 3.83 (s, 3H, CH_3O), 3.78-3.66 (m, 2H), 3.58-3.30 (m, 4H), 3.18-3.04 (m, 2H), 2.40-2.12 (m, 8H); ^{13}C NMR (100 MHz, CD_3CN): δ = 163.24, 162.18, 123.17, 121.80 (q, ^1J 318.6 Hz), 120.66, 118.05, 116.82, 53.53, 46.53, 45.83, 45.11, 44.63, 43.98, 29.80, 29.53, 29.48, 29.41, 27.34 (CH_3O). Anal. Calcd. for $C_{19}H_{26}S_4F_6O_7$ (608.6): C 37.50, H 4.31. Found: C 37.47, H 4.35.

1-(1-Phenyl-2-tetrahydro-1-thiopheniumylpropyl)tetrahydrothiophenium bistrifluoromethanesulfonate (4e) *erythro* and *threo* diastereomer mixture 3.7/1. Yield 67 %, mp 162-163 °C (dec.); IR (Nujol): 1300-1140, 1040 cm^{-1}; ^1H NMR (400 MHz, CD_3CN): δ = signals of major diastereomer 7.59-7.40 (m, 5H, C_6H_5), 5.14 (d, 1H, ^3J 6.8 Hz), 4.64 (dq, 1H, ^3J 6.8 Hz, ^3J 6.4 Hz), 3.90-3.42 (m, 4H), 3.20-2.78 (m, 4H), 2.36-2.11 (m, 8H), 1.72 (d, 3H, ^3J 6.4 Hz); ^{13}C NMR (100 MHz, CD_3CN): δ = signals of major diastereomer 132.76, 131.60, 130.85, 128.86, 121.74 (q, ^1J 318.1 Hz), 62.13, 53.72, 46.82, 45.04, 44.59, 39.44, 30.24, 29.66, 29.59, 27.32, 14.14 (CH_3). Anal. Calcd. for $C_{19}H_{26}S_4F_6O_6$ (592.6): C 38.51, H 4.42. Found: C 38.01, H 4.37.

1-(1-Tetrahydro-1-thiopheniumyl-2,3-dihydro-1*H*-inden-2-yl)tetrahydrothiophenium bistrifluoromethanesulfonate (4g). Yield 43 %, mp 130-132 °C (dec.); IR (Nujol): 1300-1140, 1040 cm^{-1}; ^1H NMR (400 MHz, CD_3CN): δ = 7.71-7.49 (m, 4H, C_6H_5), 5.42 (s, 1H, CH-1), 4.68 (d, 1H, CH-2, ^3J 5.6 Hz), --3.85-3.82 (m, 2H), 3.70-3.62 (m, 4H), 3.48-3.39 (m, 4H), 2.46-2.12 (m, 8H); ^{13}C NMR (100 MHz, CD_3CN): δ = 142.77, 133.56, 131.80, 130.16, 128.59, 127.79, 120.13 (q, ^1J 320.2 Hz), 61.91, 61.85, 58.82, 53.51, 46.01, 45.47, 35.76, 29.95, 29.69, 29.61, 27.34. Anal. Calcd. for $C_{19}H_{24}S_4F_6O_6$ (590.6): C 38.64, H 4.10. Found: C 38.52, H 3.97.

[(*E*)-4-(1,1-Dimethylsulfonio)-2-butenyl](dimethyl)sulfonium bistrifluoromethanesulfonate (6a). Yield 93 %, mp 75-77 °C; IR (Nujol): 1300-1140, 1040 cm^{-1}; ^1H NMR (400 MHz, CD_3CN): δ = 6.12-6.09 (m, 2H, CH=), 4.04-4.02 (m, 4H), 2.79 (s, 12H, CH_3S^+); ^{13}C NMR (100 MHz, CD_3CN): δ = 129.03 (C=C), 121.88 (q, ^1J 318.4 Hz), 43.90, 24.36 (CH_3S). Anal. Calcd. for $C_{10}H_{18}S_4F_6O_6$ (476.5): C 25.21, H 3.81. Found: C 25.28, H 3.85.

[4-(1,1-Dimethylsulfonio)-3-methyl-2-butenyl](dimethyl)sulfonium bistrifluoromethanesulfonate (6b) mixture *E/Z*= 6/1. Yield 93 %, mp 106-108 °C (dec.); IR (Nujol): 1300-1140, 1040 cm^{-1}; ^1H NMR (400 MHz, CD_3CN): δ = signals of major isomer 5.85 (t, 1H, CH=,^3J 7.85 Hz), 4.07-4.03 (m, 2H), 2.84 (s, 6H, CH_3S^+), 2.81 (s, 6H, CH_3S^+), 1.91 (bs, 3H, CH_3); ^{13}C NMR (100 MHz, CD_3CN): δ = signals of major isomer 136.90 (*C*=CH), 121.02 (C=*C*H), 120.90 (q, ^1J 320.2 Hz), 51.43, 44.41, 24.18 (CH_3S^+), 23.32 (CH_3S^+), 16.05 (CH_3). Anal. Calcd. for $C_{11}H_{20}S_4F_6O_6$ (490.5): C 26.94, H 4.11. Found: C 27.23, H 4.16.

[4-(1,1-Dimethylsulfonio)-2,3-dimethyl-2-butenyl](dimethyl)sulfonium bistrifluoromethanesulfonate (6c) mixture *E/Z*= 4/1. Yield 95 %, mp 120-122 °C (dec.); IR (Nujol): 1300-1140, 1040 cm^{-1}; ^1H NMR (400 MHz, CD_3CN): δ = signals of *E* isomer 4.58 (s, 4H), 3.15 (s, 12H, CH_3S^+), 2.05 (s, 6H); signals of *Z* isomer 4.49 (s, 4H), 3.17 (s, 12H, CH_3S^+), 2.16 (s, 6H); ^{13}C NMR (100 MHz, CD_3CN): δ = signals of *E* isomer 130.26 (C=C), 121.91 (q, ^1J 319.7 Hz), 47.94, 24.52 (CH_3S^+), 19.53 (CH_3); signals of *Z* isomer 130.22 (C=C), 121.91 (q, ^1J 319.7 Hz), 48.49, 25.10 (CH_3S^+), 19.53 (CH_3). Anal. Calcd. for $C_{12}H_{22}S_4F_6O_6$ (504.5): C 28.57, H 4.39. Found: C 29.00, H 4.51.

[4-(1,1-Dimethylsulfonio)-2-cyclohexenyl](dimethyl)sulfonium bistrifluoromethanesulfonate (6d). Yield 72 %, mp 149-150 °C (dec.); IR (Nujol): 1300-1140, 1040 cm^{-1}; ^1H NMR (400 MHz, CD_3CN): δ = 6.34 (s, 2H, CH=), 4.36 (bs, 2H), 2.87 (s, 6H, CH_3S^+), 2.82 (s, 6H, CH_3S^+), 2.35-2.32 (m, 2H), 2.07-2.04 (m, 2H); ^{13}C NMR (100 MHz, CD_3CN): δ = 128.78 (C=C), 121.96 (q, ^1J 319.1 Hz), 49.98, 23.72, 22.57 (CH_3S^+), 22.23 (CH_3S^+). Anal. Calcd. for $C_{12}H_{20}S_4F_6O_6$ (502.51): C 28.68, H 4.01. Found: C 28.93, H 4.24.

1-[(*E*)-4-Tetrahydro-1-thiopheniumyl-2-butenyl]tetrahydrothiophenium bistrifluoromethanesulfonate (7a). Yield 87 %, mp 102-104 °C; IR (Nujol): 1300-1140, 1040 cm^{-1}; ^1H NMR (400 MHz, CD_3CN): δ = 6.13-6.10 (m, 2H, CH=), 3.92-3.90 (m, 4H), 3.51-3.46 (m, 4H, $C_4H_8S^+$), 3.38-3.33 (m, 4H, $C_4H_8S^+$), 2.32-2.20 (m, 8H, $C_4H_8S^+$); ^{13}C NMR (100 MHz, CD_3CN): δ = 129.69, 121.95 (q, ^1J 319.0 Hz), 43.68 (double), 29.45. Anal. Calcd. for $C_{14}H_{22}S_4F_6O_6$ (528.6): C 31.81, H 4.20. Found: C 32.27, H 4.35.

1-[2-Methyl-4-tetrahydro-1-thiopheniumyl-2-butenyl]tetrahydrothiophenium bistrifluoromethanesulfonate (7b) mixture *E/Z*=9/1. Yield 90 %, mp 121-122 °C (dec.); IR (Nujol): 1300-1140, 1040 cm^{-1}; ^1H NMR (400 MHz, CD_3CN): δ = signals of major isomer 5.85 (t, 1H, CH=,^3J 8.00 Hz), 3.91 (d, 2H,^3J 8.00 Hz), 3.87 (s, 2H), 3.54-3.47 (m, 4H, $C_4H_8S^+$), 3.37-3.25 (m, 4H, $C_4H_8S^+$), 2.34-2.22 (m, 8H, $C_4H_8S^+$), 1.92 (s, 3H, CH_3); ^{13}C NMR (100 MHz, CD_3CN): δ = signals of major isomer 138.16 (*C*=CH), 122.90 (C=*C*H), 121.51 (q, ^1J 319.2 Hz), 51.13, 44.18, 43.68, 39.90, 29.48, 29.30, 16.80 (CH_3). Anal. Calcd. for $C_{15}H_{24}S_4F_6O_6$ (542.6): C 33.21, H 4.46. Found: C 33.56, H 4.73.

1-(2,3-Dimethyl-4-tetrahydro-1-thiopheniumyl-2-butenyl)tetrahydrothiophenium bistrifluoromethanesulfonate (7c) mixture *E/Z*= 5/4. Yield 86 %, mp 135-137 °C (dec.); IR (Nujol): 1300-1140, 1040 cm^{-1}; ^1H NMR (400 MHz, CD_3CN): δ = signals of *E* isomer 3.97 (s, 4H), 3.55-3.49 (m, 4H, $C_4H_8S^+$), 3.32-3.25 (m, 4H, $C_4H_8S^+$), 2.41-2.21 (m, 8H, $C_4H_8S^+$), 1.95 (s, 6H); signals of *Z* isomer 4.02 (s, 4H), 3.55-3.49 (m, 4H, $C_4H_8S^+$), 3.32-3.25 (m, 4H, $C_4H_8S^+$), 2.41-2.21 (m, 8H, $C_4H_8S^+$), 1.91 (s, 6H); ^{13}C NMR (100 MHz, CD_3CN): δ = signals of *E* isomer 130.50 (C=C), 121.99 (q, ^1J 318.6 Hz), 47.04, 44.20, 29.54, 19.26 (CH_3); signals of *Z* isomer 130.38 (C=C), 121.99 (q, ^1J 318.6 Hz), 47.11, 44.17, 29.43, 19.70 (CH_3). Anal. Calcd. for $C_{16}H_{26}S_4F_6O_6$ (556.6): C 34.53, H 4.71. Found: C 34.76, H 4.87.

1-(4-Tetrahydro-1-thiopheniumyl-2-cyclohexenyl)tetrahydrothiophenium bistrifluoromethanesulfonate (7d) *trans* and *cis* isomer 4/1. Yield 48 %, mp 145-147 °C (dec.); IR (Nujol): 1300-1140, 1040 cm^{-1}; ^1H NMR (400 MHz, CD_3CN): δ = signals of *trans* isomer 6.34 (d, 2H, CH=, ^3J 2.0 Hz), 4.27 (bs, 2H), 3.61-3.42 (m, 4H, $C_4H_8S^+$), 2.39-2.22 (m, 6H); signals of *cis* isomer 6.31 (d, 2H, CH=, ^3J 1.6 Hz), 4.27 (bs, 2H), 3.61-3.42 (m, 4H, $C_4H_8S^+$), 2.39-2.22 (m, 6H); ^{13}C NMR (100 MHz, CD_3CN): δ = signals of *trans* isomer 129.59 (C=C), 121.94 (q, ^1J 318.6 Hz), 49.24, 44.04, 42.10, 29.92, 29.50, 22.60; signals of *cis* isomer 129.59 (C=C), 121.94 (q, ^1J 318.6 Hz), 49.58, 43.72, 42.20, 29.83, 29.58, 23.34. Anal. Calcd. for $C_{16}H_{24}S_4F_6O_6$ (554.6): C 34.65, H 4.36. Found: C 35.11, H 4.42.

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