Supplementary Material (ESI) for Dalton Transactions

Supplementary Information for

Synthesis and reactivity of silylated tetrathiafulvalenes

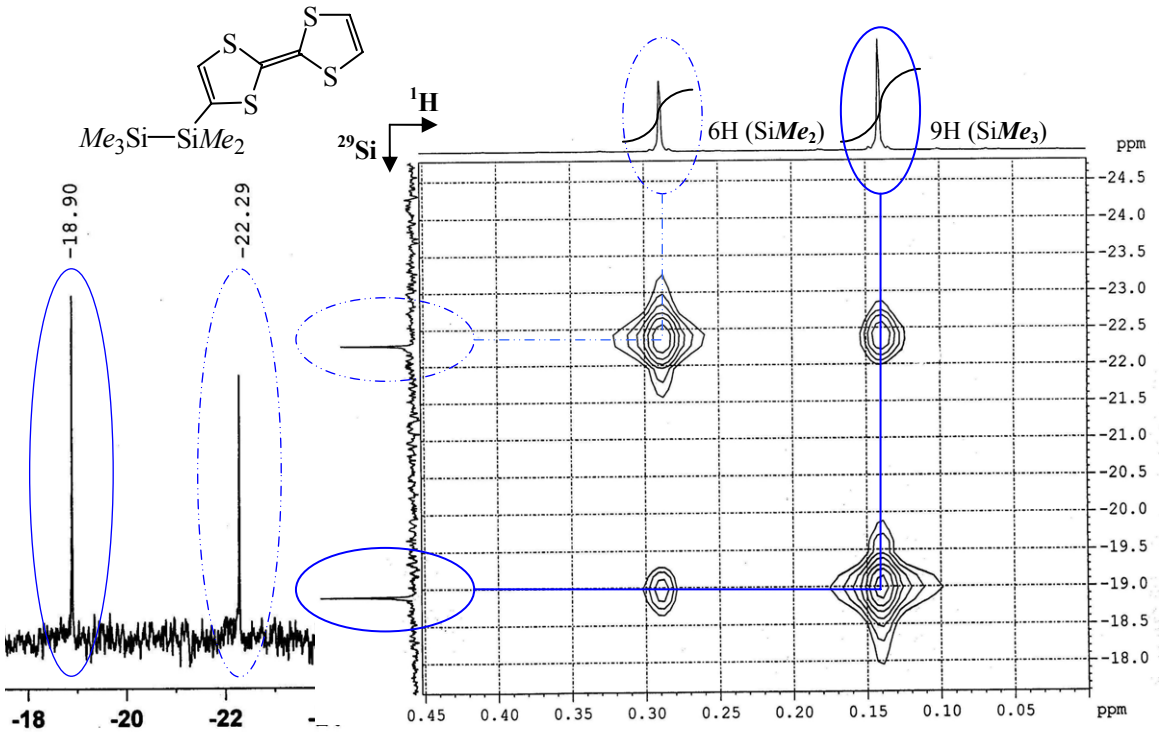
Aurélien Hameau,[a] Fabrice Guyon,*[a] Michael Knorr,[a] Christian Däschlein,[b] Carsten Strohmann,*[b] and Narcis Avarvari[c]

[a] *Institut UTINAM, UMR CNRS 6213, Université de Franche-Comté,*
Faculté des Sciences et des Techniques, 16, Route de Gray, 25030 Besançon, France.
E-mail: fabrice.guyon@univ-fcomte.fr

[b] *Institut für Anorganische Chemie der Universität Würzburg,*
Am Hubland, D-97074 Würzburg, Germany
E-mail: c.strohmann@mail.uni-wuerzburg.de

[c] *Laboratoire Chimie Ingénierie Moléculaire et Matériaux (CIMMA), UMR 6200, 2 boulevard Lavoisier, 49045 Angers, France*

Figure S1. $^{29}Si\{^{1}H\}$ and 2D-HMQC spectra of **8**



Computational Studies

All calculations were done with predetermined symmetry. Starting coordinates were taken from the crystal structure analysis of the TTF substituted silanes **11** and **12** prior to energy optimization at the B3LYP/6-31+G(d) level. Additional harmonic vibrational frequency analyses (to establish the nature of stationary point on the potential energy surface) were performed on the same level and showed no imaginary frequency. Table S2 lists the total and zero-point energy of **11** and **12**. Standard orientations of the model systems can be found in tables S3, S4, S5 and S6.

Table S1 Results from Quantum Chemical Studies on the model systems..

model	total energy (Hartree)	zero point energy (Hartree)
11 (crystal)	–4385.026652	–4384.731717
conf-11	–4385.026811	–4384.731813
12 (crystal)	–4015.672340	–4015.452788
conf-12	–4015.673568	–4015.454053

Table S2 Standard Orientation of **11**.

atomic symbol	X	Y	Z
H	0.1779385364	–0.5627214558	–3.4064206888
H	1.6160721527	–0.5971252013	–2.3685321819
C	0.5386003187	–0.7976692088	–2.3969820542
H	8.4521919839	–1.3056002627	–2.2466856112
H	0.4033270805	–1.8727526424	–2.2291332239
H	–0.4617085194	2.3361539044	–2.4935518375
H	–2.1516000085	–1.9335512123	–2.4284292312
C	7.9362442243	–0.7812454396	–1.4500822648
C	–2.7358258879	–1.1994622188	–1.8831696963
S	–4.483723515	–1.442716043	–1.9089972726
H	9.3851247116	0.7411997051	–0.9916745904

C	8.4216380574	0.2833917682	–0.797149361
C	–0.1135349969	2.0996818676	–1.4802856591
C	–2.213921964	–0.1377549495	–1.2373448534
S	6.363983692	–1.4082223616	–0.9547870496
H	0.9476955233	2.3695894011	–1.4157847458
Si	–0.3599160632	0.2572837063	–1.1030291807
S	–7.4482429317	–0.9690895736	–0.5035341434
C	–4.8250660468	–0.1202477979	–0.7640961178
H	–0.6632794643	2.7424951382	–0.7823453546
C	–6.0325240295	0.0745086645	–0.1876335514
S	–3.414500195	0.9329969213	–0.4718596225
C	6.0325240295	–0.0745086645	0.1876335514
S	7.4482429317	0.9690895736	0.5035341434
C	–8.4216380574	–0.2833917682	0.797149361
S	3.414500195	–0.9329969213	0.4718596225
H	–9.3851247116	–0.7411997051	0.9916745904
C	4.8250660468	0.1202477979	0.7640961178
S	–6.363983692	1.4082223616	0.9547870496
H	0.6632794643	–2.7424951382	0.7823453546
C	–7.9362442243	0.7812454396	1.4500822648
H	–0.9476955233	–2.3695894011	1.4157847458
C	2.213921964	0.1377549495	1.2373448534
Si	0.3599160632	–0.2572837063	1.1030291807
H	–8.4521919839	1.3056002627	2.2466856112
C	0.1135349969	–2.0996818676	1.4802856591
S	4.483723515	1.442716043	1.9089972726
C	2.7358258879	1.1994622188	1.8831696963
H	2.1516000085	1.9335512123	2.4284292312
H	0.4617085194	–2.3361539044	2.4935518375
H	–0.4033270805	1.8727526424	2.2291332239
C	–0.5386003187	0.7976692088	2.3969820542

H	–1.6160721527	0.5971252013	2.3685321819
H	–0.1779385364	0.5627214558	3.4064206888

Table S3 Standard Orientation of **conf-11**.

atomic symbol	X	Y	Z
C	–0.0350583976	0.010840792	–0.0607302326
C	0.0987432542	0.0091935871	8.0971651382
C	1.6410432906	0.0526968613	–2.951196609
S	2.3346106049	–0.0663160761	–4.5702182207
C	–0.8460925313	0.9479307505	8.243231152
C	2.5603325145	–1.4057621166	0.9008871262
C	2.4355031554	–0.0669147896	–1.8692382371
S	1.2698333741	0.2104947253	6.7944216049
Si	1.8597706539	0.0684143561	–0.063817179
S	4.9512069886	0.2516404877	–6.5807538966
C	4.0216448277	–0.1026723097	–3.9964402471
C	5.0910019855	0.0292934327	–4.8132132048
S	4.1554554524	–0.3526487254	–2.2344434539
C	0.4587577032	1.6397163179	6.0915144969
S	–0.8406207348	2.3076867823	7.1208116024
C	6.6567709031	0.6360664135	–6.8103200706
S	2.1200747221	1.5233684895	3.8786165434
C	0.8045777876	2.170298249	4.8970451354
S	6.7781444703	–0.0149358906	–4.2254062901
C	7.4746615232	0.5164070969	–5.75578898
C	1.7338798645	2.4851106265	2.4302374938
Si	2.6399259426	2.1434138751	0.79568362
C	2.2225470619	3.5563507419	–0.3974948296
S	0.009836325	3.5996836738	4.18806567
C	0.7773369565	3.4173101497	2.6092842347
C	4.5044370296	2.1082251325	1.13875113

H	–0.4005824434	–0.9292071346	–0.4928427787
H	–0.4092857964	0.0742847864	0.9680636862
H	–0.4812419435	0.8403478783	–0.6222670428
H	0.2134314181	–0.8571667108	8.7390313433
H	0.566902256	0.2012754907	–2.9101067173
H	–1.6029670217	0.947300911	9.0196720795
H	2.1990612912	–2.3501045689	0.474529271
H	2.2486114656	–1.3659599601	1.9516503429
H	3.6563764894	–1.4294587024	0.8789164949
H	6.9710065097	0.927889096	–7.8062156671
H	8.5434163645	0.6978569239	–5.7790863947
H	1.1493821538	3.6194809555	–0.6137710531
H	2.7396146483	3.4036583207	–1.3524156368
H	2.5461620258	4.5232631301	0.0078458893
H	0.4409676189	4.1061637727	1.8412379811
H	4.7769346072	1.3295730879	1.8610641228
H	5.0645552058	1.9172074838	0.2154042146
H	4.838353588	3.0708366432	1.5461472847

Table S4 Standard Orientation of **12**.

atomic symbol	X	Y	Z
S	0.0004213274	0.0039130535	0.0000041287
S	0.0004211825	0.0039133003	7.575068056
S	2.8954062521	0.0020220148	–1.6099458414
S	2.8954061575	0.0020220962	9.1850179372
C	–0.9355551219	0.4073449994	6.1376097488
C	–0.9355549992	0.407344811	1.4374624036
C	4.6098631786	0.4117704162	9.2336099883
C	4.6098632276	0.4117705187	–1.6585379803
C	1.3351370384	1.1215948282	7.1900854824
C	1.335137071	1.1215947656	0.3849865559
C	2.5188389102	1.120527638	–0.2683800749
C	2.5188389031	1.1205276228	7.8434520664

C	–3.1731794845	1.2001705213	3.7875359963
C	–0.5339000708	1.4146529052	2.2381126059
C	–0.5339001063	1.4146529741	5.3369594402
C	5.036347215	1.4173782418	–0.8825545434
C	5.0363472596	1.4173780054	8.4576264298
Si	–1.4561280863	1.9829874649	3.7875359997
S	0.9445826561	2.2512119593	1.7097920465
S	0.9445827034	2.2512119431	5.8652799028
S	3.8495624295	2.2464541066	7.4512285202
S	3.8495623157	2.2464543241	0.1238433026
C	–1.5549094382	3.8658225376	3.787535948
H	–1.8302126799	–0.1858419405	5.9786091716
H	–1.8302124974	–0.1858421996	1.5964630518
H	5.2377821217	–0.1554840654	9.911550949
H	5.2377822161	–0.1554839744	–2.336478892
H	–3.7367584353	1.5188719544	4.6724677296
H	–3.1425440422	0.1043968272	3.7875360151
H	–3.7367584086	1.5188719175	2.9026042327
H	6.0583316343	1.7777374817	–0.8446544664
H	6.058331718	1.777737128	8.4197262899
H	–0.5624419408	4.3320456087	3.7875359624
H	–2.087978543	4.225368645	4.6760738252
H	–2.0879784917	4.2253685985	2.8989980215

Table S5 Standard Orientation of **conf-12**.

atomic symbol	X	Y	Z
S	–0.4516146293	0.7412987386	–3.9555420999
S	–0.7570783904	0.4246314923	3.9555420999
S	2.6142411306	0.1192345061	–5.042615508
S	–0.0250319502	–2.6168391157	5.0426155081
C	–1.1499717287	1.52115929	2.6351491916
C	–1.5615775054	1.0944570601	–2.6351491917
C	0.2776153627	–4.3225283854	4.7146334929
C	4.329721218	–0.121803563	–4.7146334927
C	–1.0853327869	–1.0550723603	3.0156487718

C	1.0153110721	1.1226167516	–3.0156487718
C	2.2674749749	0.8671876143	–3.4567453751
C	–0.7849853465	–2.2972277044	3.4567453751
C	–3.9644978069	1.740410983	–0.4306180936
C	–1.090546584	1.6098133426	–1.4820973129
C	–1.6480344855	1.0318784738	1.4820973129
C	4.8296056221	0.3874351924	–3.5805718035
C	–0.2132949695	–4.8404237158	3.5805718036
Si	–2.1604955207	2.084058566	–0.0000000001
S	0.666180746	1.8814218587	–1.4378858801
S	–1.8562162674	–0.7334890358	1.4378858801
S	–1.1203941793	–3.7745886478	2.5087974959
S	3.731801692	1.2555710688	–2.5087974959
C	–1.8820235066	3.8992641321	0.4306180934
H	–0.9800575844	2.5746167856	2.832234264
H	–2.608234231	0.8867235519	–2.8322342641
H	0.8302080783	–4.8818240965	5.461290964
H	4.908550285	–0.6539006529	–5.4612909638
H	–4.6073195107	2.0165241665	0.4140642136
H	–4.144708562	0.6804158756	–0.6442356032
H	–4.2869427749	2.325323848	–1.3006602848
H	5.8698412051	0.3244709428	–3.2811142026
H	–0.1129180638	–5.8777178119	3.2811142028
H	–0.8292041357	4.1175229604	0.644235603
H	–2.4781666927	4.2004403575	1.3006602846
H	–2.1811023341	4.5317276392	–0.4140642138

Complete reference 30 of the publication:

Gaussian 03 (Revision B.04), M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Pittsburgh, PA, **2003**.

Figure S2. Illustration of the two energetically comparable conformers found in the flexible silyl bridged TTF's