Electron capture activation of the disulfide bond. The role of the asymmetry and electronegativity.

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Supporting Information (total of 5 pages)

Eigenvalues of the SOMO

Table S1. Eigenvalues (in au) of the HF HOMOs for the most stable anionic molecules

Compound	HSSH	CH_3SSCH_3	CH_3SSNH_2	CH_3SSOH	CH_3SSF
ε HF (au)	-0.12496	-0.11135	-0.10764	-0.13029	-0.15468

Relative Energy of the two stable anions of the CH_3SSOH and CH_3SSF systems

Table S2 shows that the *stretched* isomer is more stable than the *bent* one. However, this energy difference is not really large and actually for the CH_3SSF can be regarded as degenerate.

Table S2. ΔH and ΔG (in parenthesis) at 298 K between the two anionic isomers of CH_3SSOH and CH_3SSF for the process *bent* → *stretched*. Values in kJ mol^{-1}.

	QCISD	MP2	B3LYP	BH&HLYP	CASPT2	G3
CH_3SSOH	6 (13)	15 (21)	25 (27)	6 (10)	9 (16)	10 (15)
CH_3SSF	4 (0)	6 (4)	11 (9)	6 (8)	-1 (-3)	2 (-1)

Assessment of the performance of Perturbation Theory

The performance of the MP*n* approaches at describing two-center three-electron bonds was studied by Braïda and Hiberty (*J. Phys. Chem. A*, (2000), **104**, 4618). In this article, they provide a *thumb rule* to assess the good performance of perturbative treatments when describing this particular linkages: "*optimized geometries, vibrational frequencies and dissociation energies can be calculated at the MP2 and MP4 levels and deemed reliable provided the UHF and MP2 population analysis yield comparable results, say 10%, as regards the sharing out of the charges among the two fragments".* In the A∴B molecule, with the charge of the first and second fragment being q_A and q_B respectively, the sharing out of the charge between the two fragments can be measure by defining the following parameter:

$$S = \frac{q_A^{UHF} q_A^{UMP2} + q_B^{UHF} q_B^{UMP2}}{\sqrt{(q_A^{UHF})^2 + (q_B^{UHF})^2}\sqrt{(q_A^{UMP2})^2 + (q_B^{UMP2})^2}}$$

When the charge is equally distributed between both fragments at UHF and MP2 levels (as in symmetric systems), S = 1, and the more different the sharing out of electrons is described, the lower is S. Therefore, 1-S is a good indicator of the differences between the UHF and MP2 charge densities. The following table represents q_A^{UHF}, q_A^{UMP2} (notice that $q_A + q_B = 1$) and 1-S for each systems along the S-S and S-X linkages. As it can be seen, the *bent*-CH_3SSOH anion is the only one where 1-S is over 0.1 and, hence, is the only one in which MP2 is unadvisable.

Table S3. Charge analysis of the X and Y fragments at the UHF and MP2 levels with the 6-311++g(3df,2p) basis set.

	Along S-S bond A=SCH3; B=SX		Along S-X bond A=SSCH3; B=X			
	CH_3SSNH_2	Stetched-CH_3SSOH	Bent-CH_3SSOH	Stretched-CH_3SSOH	Bent-CH_3SSF	Stretched-CH_3SSF
q_A^{UHF} [a]	0.683	0.455	0.479	0.445	0.145	0.235
q_A^{UMP2} [b]	0.576	0.453	0.056	0.494	0.222	0.309
1-S	0.020	0.000	0.226	0.005	0.006	0.007

[a] Natural population analysis of the UHF wave function (as fraction of the charge of the electron). [b] Natural population analysis of the UMP2 wave function (as fraction of the charge of the electron)

NBO spin density

Table S4. NBO spin density analysis based on the QCISD density of the disulphides under study. S_1 is the sulfur atom link to the carbon while S_2 is bound to the X atom.

	HSSH	CH3SSCH3	CH3SSNH2	*bent-CH3SSOH*	*stretched-CH3SSOH*	*bent-CH3SSF*	*stretched-CH3SSF*
S1	0.5116	0.5042	0.3944	0.0257	0.2487	0.0649	0.1648
S2	0.5116	0.5042	0.5753	0.6339	0.6064	0.7588	0.7168
C	-0.0116	-0.0169	-0.0136	0.0052	-0.0095	-0.0001	-0.0094
X	-0.0116	-0.0169	0.0307	0.3300	0.1477	0.1694	0.1163

Cartesian Coordinates

Table S5. Cartesian coordinates (in angstroms) of the anionic derivatives of FSSF and OHSSF calculated with different methods and the 6-31++g(d,p) basis set (ANO S[4s3p2d1f]/C,N,O,F[3s2p1d]/H[2s1p] the CASSCF).

Molecule	Method							
	B3LYP				MP2			
FSSF	S	-0.0578	-0.0699	0.1202	S	-0.0535	-0.0622	0.1304
	S	0.0699	0.0578	2.0465	S	0.0622	0.0535	2.0363
	F	1.7062	0.0629	2.4459	F	1.6994	0.0526	2.4201
	F	-0.0629	-1.7062	-0.2792	F	-0.0526	-1.6994	-0.2534
Bent-FSSF anion	S	-0.0125	-0.0036	-0.0118	S	0.0025	-0.0243	-0.0105
	S	1.7941	0.0141	-0.7080	S	1.7887	0.0227	-0.6845
	F	2.9201	-1.3779	0.1063	F	2.8347	-1.3428	0.1396
	F	-0.0536	0.0275	1.9544	F	0.0222	0.0045	1.8964
Stretched-FSSF anion	S	0.1992	-0.3386	-0.0128	S	-0.0393	0.0357	-0.0026
	S	0.3446	-0.1887	1.9476	S	0.0137	0.0513	1.9742
	F	1.6604	0.5996	3.1159	F	1.3585	-0.0614	3.2032

	F	-0.5481	-1.6780	-1.1811	F	-1.1101	-0.7855	-1.2316

Table S5. (*Cont.)*

Molecule	Method						
	QCISD				CASSCF		
FSSF	S	0.0068	0.0143	-0.0007	S	-0.8334	0.4705	0.3970
	S	-0.0141	-0.0073	1.9355	S	0.8334	-0.4705	0.3970
	F	1.5957	-0.0184	2.4003	F	1.7654	0.2136	-0.7051
	F	0.0676	-1.5944	-0.4655	F	-1.7654	-0.2136	-0.7051
Bent-FSSF anion	S	-0.0093	-0.0234	-0.0198	S	-0.5823	1.7195	-1.3939
	S	1.7925	0.0318	-0.6958	S	0.5823	-1.7195	-1.3939
	F	2.8507	-1.3561	0.1411	F	-0.3158	-3.4053	1.6578
	F	0.0142	0.0079	1.9154	F	0.3158	3.4053	1.6578
	B3LYP				MP2		
Stretched-FSSF anion	S	0.0163	0.0584	0.0108	S	-0.7603	1.6989	-0.2602
	S	-0.0452	0.0404	1.9607	S	0.7608	-1.6993	-0.2605
	F	1.3981	-0.0561	3.2258	F	-0.4524	-4.9366	0.4699
	F	-1.1463	-0.8024	-1.2542	F	0.4519	4.9370	0.4698
OHSSF	S	0.1476	-0.6822	-0.0646	S	0.1344	-0.6891	-0.0619
	S	-0.0657	-0.5964	1.8967	S	-0.0453	-0.6052	1.8800
	O	1.5335	0.2004	-0.4879	O	1.5120	0.2030	-0.4756
	H	1.2689	1.1158	-0.6782	H	1.2385	1.1206	-0.6433
	F	-1.0024	0.7789	2.2075	F	-0.9576	0.7872	2.1742
Bent-OHSSF anion	S	0.1019	0.0024	-0.0534	S	-0.1306	-0.2608	0.0098
	S	-0.0265	-0.0025	1.9518	S	-0.8494	-0.8620	1.7494
	O	1.5925	-0.0023	-0.5623	O	1.4071	0.0757	0.0394
	H	1.8664	0.0004	-2.0132	H	2.0478	1.2882	0.6414
	F	2.0857	0.0034	-2.9834	F	2.5151	2.0874	0.9775
Stretched-OHSSF anion	S	0.3320	-0.7702	-0.2839	S	0.3801	-0.8428	-0.1997
	S	-0.1878	-0.3729	1.6493	S	-0.1114	-0.3811	1.6855
	O	1.7508	0.1800	-0.7592	O	1.7179	0.1753	-0.7170
	H	1.4765	1.1065	-0.6778	H	1.3664	1.0803	-0.7007
	F	-1.4896	0.6730	2.9451	F	-1.4710	0.7848	2.8054

Table S5. (*Cont.)*

Molecule		Method		
		QCISD		
OHSSF	S	-0.0191	-0.0073	-0.0051
	S	0.0119	-0.0130	1.9670
	O	1.5968	0.0130	-0.5054
	H	1.8773	0.9355	-0.5994
	F	0.0607	1.6192	2.3778
Bent-OHSSF anion	S	-0.0102	0.0001	0.0118
	S	0.0097	-0.0002	2.0002
	O	1.4421	0.0002	-0.5908
	H	1.6424	0.0002	-2.0833
	F	1.7991	0.0010	-3.0510
Stretched-OHSSF anion	S	-0.0172	-0.0107	-0.0311
	S	-0.0200	-0.0680	1.9886
	O	1.6479	0.0190	-0.5661
	H	2.0231	0.8409	-0.2197
	F	-0.1408	1.1866	3.7466