Electronic Supporting Information for

Mesolysis of an asymmetric diphenyldisulfide radical anion studied by γ-ray and pulsed-electron radiolyses

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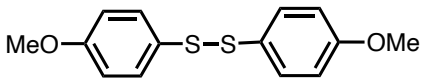
Contents

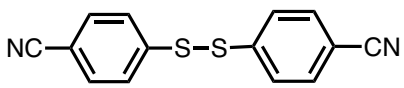
1. Synthetic procedure and ^{1}H NMR data for XSSX.

1-1. MeOSSOMe (bis(4-methoxyphenyl)disulfide).



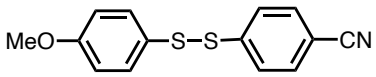
To a THF solution (20 mL) of 4-methoxyphenylthiol (0.50 ml, 4.1 mmol), aqueous H_2O_2 (30 %, 1.2 mL) was added at room temperature. The solution was kept stirring for 12 h at room temperature. The organic layer was separated, washed with brine, and dried with Na_2SO_4. The crude product was purified by silica chromatography with a mixture of hexane/chloroform (3:1 v/v) as an eluent to provide **MeOSSOMe** (290 mg, 52 %). ^{1}H 400 MHz NMR ($CDCl_3$) δ ; 3.79 (s, 6H), 6.82 (m, 4H), 7.38 (m, 4H). The ^{1}H NMR data was identical with those previously reported.[1]

1-2. NCSSCN (bis(4-cyanophenyl)disulfide).



Aerated THF solution (5 mL) of 4-cyanobenzenesulfonyl chloride (308 m g, 1.5 mmol) and PPh_3 (524 mg, 2.0 mmol) was kept stirring for 17 h at room temperature. The solution was washed with brine, and dried with Na_2SO_4. The crude product was purified by silica chromatography with a mixture of hexane/chloroform (1:9 v/v) as an eluent to provide **NCSSCN** (70 mg, 17 %). ^{1}H 400 MHz NMR ($CDCl_3$) δ; 7.55 (m, 4H), 7.60 (m, 4H). The NMR data was identical with that reported previousely.[1]

1-3. MeOSSCN (4-cyanophenyl)(4'-methoxyphenyl)disulfide).



Aerated THF solution (60 mL) of 4-methoxybenzenesulfonyl chloride (620 mg, 3.0 mmol), 4-cyanobenzenesulfonyl chloride (700 mg, 3.0 mmol) and PPh_3 (2.80 g, 10.7 mmol) was kept stirring under N_2 atmosphere for 7 h at room temperature. Three spots of the products were found on the TLC silica plate after evolved with benzene. Two of them were due to MeOSSOMe (Rf = 0.63) and NCSSCN (Rf = 0.25). The product with Rf = 0.49 was separated, and purified by silica chromatography with benzene as an eluent to provide yellowish solid **MeOSSCN** (120 mg, 7 %). **MeOSSOMe** (33 mg, 3% from 4-methoxybenzenesulfonyl chloride) and **NCSSCN** (50 mg, 6 % from 4-cyanobenzenesulfonyl chloride) were separated on the same chromatography. ^{1}H 400 MHz NMR ($CDCl_3$) δ; 3.77 (s, 3H), 6.83 (m, 2H), 7.40 (m, 2H), 7.58 (m, 2H), 7.63 (m, 2H). HRMS (FAB) *m/z* calcd. for $C_{14}H_{11}NOS_2$ 273.0282, found 273.0282.

2. ^{1}H NMR spectra of XSSX used in the present work.

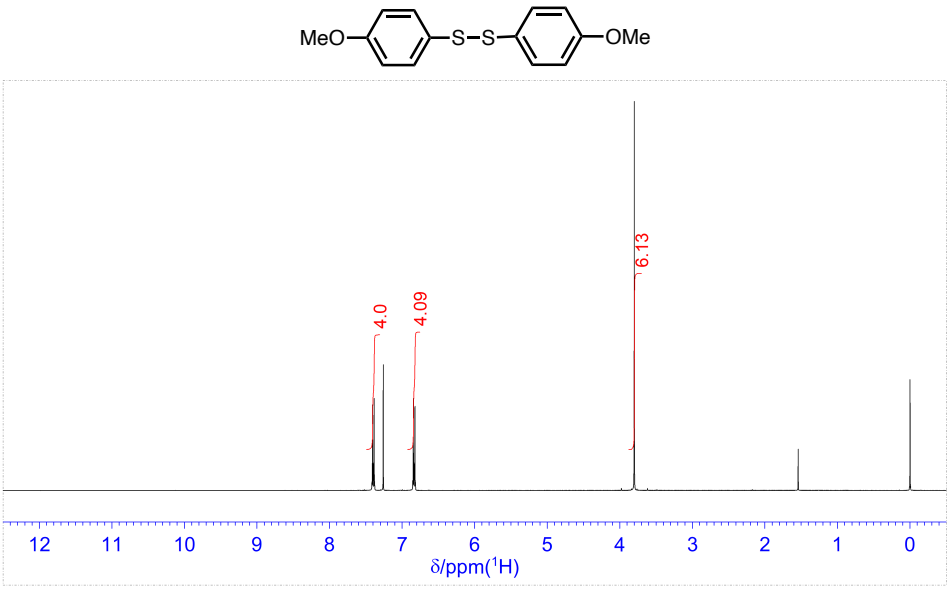


Fig. S1. ^{1}H (400 MHz, $CDCl_3$) NMR spectrum of **MeOSSOMe**.

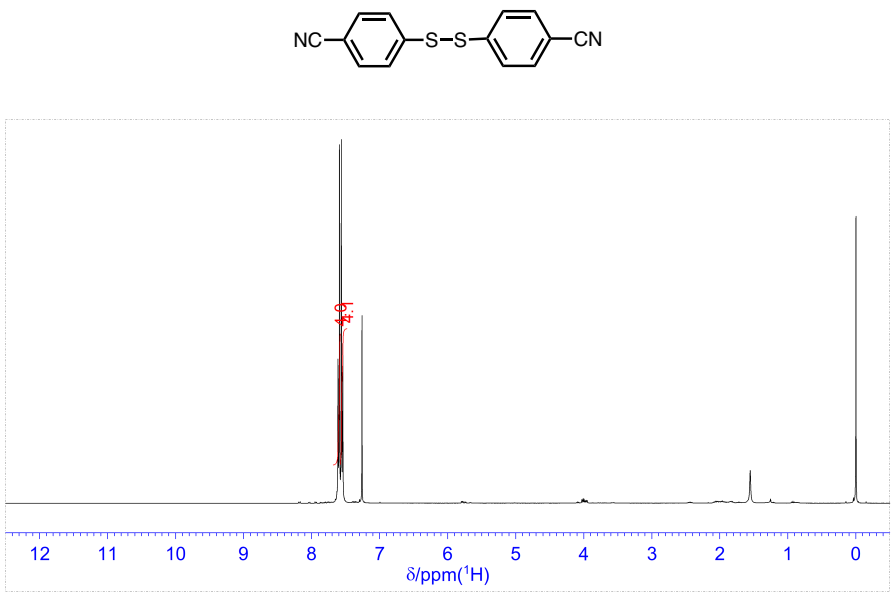


Fig. S2. ^{1}H (400 MHz, $CDCl_3$) NMR spectrum of **NCSSCN**.

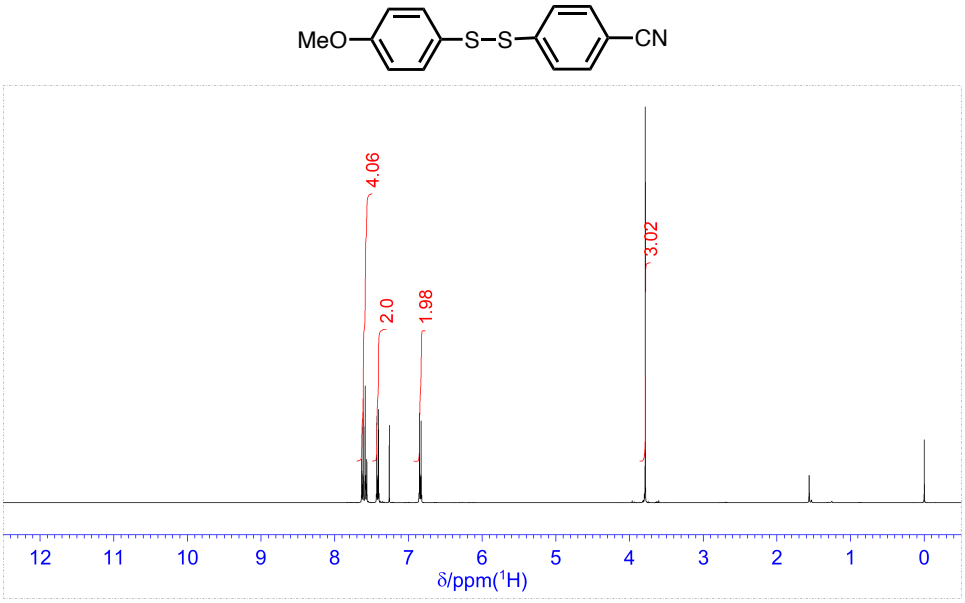


Fig. S3. ^{1}H (400 MHz, $CDCl_3$) NMR spectrum of **MeOSSCN**.

3. Results of DFT calculations for radicals and radical anions and atom coordinates in THF.

3-1. Heat of formation

The calculation was carried out at the DFT level, using the Gaussian 09 software package.[2] The geometries of the radical anions, anion and radicals were fully optimized by using the 6-31G(d) base set at the UB3LYP method considering a dielectric constant of tetrahydrofuran (THF) in the CPCM model.

Table S1. Calculated heats of formation for radical anions and radicals.

Species	$\Delta_f H$ / hartree
$MeOSSOMe^{\bullet-}$	-1488.589400
$NCSSCN^{\bullet-}$	-1444.114708
$MeOSSCN^{\bullet-}$	-1466.354009
$MeOPhS^{-}$	-744.358103
$MeOPhS^{\bullet}$	-744.220524
$NCPhS^{-}$	-722.129468
$NCPhS^{\bullet}$	-721.955231

3-2. Atom coordinates for the optimized geometries in THF for the used radical anions and radicals are listed in Tables S2-8.

Table S2. Atom coordinates for the optimized geometry of $MeOSSOMe^{\bullet-}$ in THF.

Atom	X	Y	Z
C	-3.609788	-1.158510	0.176006
C	-2.531777	1.194763	-1.074739
C	-1.777064	0.053882	-1.312297
C	-2.063742	-1.174569	-0.670050
C	-3.148498	-1.181603	0.229824
C	-3.915302	-0.041538	0.478965
S	-1.107053	-2.622569	-0.983040
S	1.088262	-2.506141	1.150019
C	2.135732	-1.175747	0.658661
C	3.269451	-1.388178	-0.161920

C	4.103044	-0.344086	-0.538055
C	3.835002	0.967262	-0.112749
C	2.716364	1.210653	0.694077
C	1.886944	0.150419	1.066267
O	-4.291761	2.334882	-0.011286
C	-5.388307	2.350695	0.894119
O	4.717509	1.925183	-0.536030
C	4.488145	3.270034	-0.134096
H	-2.302306	2.131220	-1.575927
H	-0.945086	0.100899	-2.009208
H	-3.395636	-2.104518	0.747026
H	-4.740741	-0.101317	1.179944
H	3.490062	-2.395931	-0.502500
H	4.972469	-0.520666	-1.165516
H	2.481275	2.212366	1.036846
H	1.022626	0.353562	1.692262
H	-5.780557	3.369068	0.873377
H	-5.070842	2.104771	1.915383
H	-6.176087	1.652092	0.584841
H	5.295345	3.857339	-0.575521
H	4.518555	3.374810	0.957876
H	3.524389	3.642181	-0.504035

Table S3. Atom coordinates for the optimized geometry of $NCSSCN^{\bullet-}$ in THF.

Atom	X	Y	Z
C	5.006393	0.169992	0.107741
C	4.070080	1.079335	0.639236
C	2.753733	0.688047	0.833323
C	2.315406	-0.615472	0.498604
C	3.267744	-1.509168	-0.046756
C	4.590077	-1.132511	-0.231625
S	0.653848	-1.116211	0.757175
S	-0.665306	0.568907	-1.271414
C	-2.321315	0.381958	-0.723850
C	-3.039363	-0.816132	-0.952316

C	-4.351449	-0.964313	-0.527246
C	-5.000338	0.092955	0.140989
C	-4.302922	1.294037	0.378535
C	-2.987412	1.427370	-0.040823
C	6.365093	0.565725	-0.085871
N	7.474250	0.888410	-0.243105
C	-6.353752	-0.051908	0.574498
N	-7.458474	-0.169879	0.927483
H	4.386036	2.084468	0.901528
H	2.040314	1.392016	1.249486
H	2.951755	-2.510701	-0.321454
H	5.306306	-1.835822	-0.645475
H	-2.547943	-1.632364	-1.472150
H	-4.884728	-1.891980	-0.711287
H	-4.797782	2.110195	0.896017
H	-2.452906	2.351850	0.153876
C	5.006393	0.169992	0.107741
C	4.070080	1.079335	0.639236
C	2.753733	0.688047	0.833323
C	2.315406	-0.615472	0.498604
C	3.267744	-1.509168	-0.046756
C	4.590077	-1.132511	-0.231625
S	0.653848	-1.116211	0.757175
S	-0.665306	0.568907	-1.271414
C	-2.321315	0.381958	-0.723850
C	-3.039363	-0.816132	-0.952316
C	-4.351449	-0.964313	-0.527246
C	-5.000338	0.092955	0.140989
C	-4.302922	1.294037	0.378535
C	-2.987412	1.427370	-0.040823
C	6.365093	0.565725	-0.085871
N	7.474250	0.888410	-0.243105
C	-6.353752	-0.051908	0.574498
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H	4.386036	2.084468	0.901528

H	2.040314	1.392016	1.249486
H	2.951755	-2.510701	-0.321454
H	5.306306	-1.835822	-0.645475
H	-2.547943	-1.632364	-1.472150
H	-4.884728	-1.891980	-0.711287
H	-4.797782	2.110195	0.896017
H	-2.452906	2.351850	0.153876

Table S4. Atom coordinates for the optimized geometry of $MeOSSCN^{\bullet-}$ in THF.

Atom	X	Y	Z
C	3.756103	-0.846095	-0.132277
C	3.968297	0.491577	-0.508798
C	3.075162	1.478424	-0.120559
C	1.935747	1.178123	0.664864
C	1.744217	-0.171198	1.027393
C	2.634048	-1.173922	0.641179
S	0.808425	2.430662	1.163327
S	-1.264615	2.449797	-1.037592
C	-2.231251	1.045899	-0.635926
C	-1.820001	-0.261743	-0.998603
C	-2.581467	-1.377014	-0.684517
C	-3.799459	-1.230767	0.010594
C	-4.227711	0.060271	0.382767
C	-3.456223	1.167946	0.067480
O	4.690662	-1.741488	-0.567301
C	4.521646	-3.112809	-0.222532
C	-4.588137	-2.374824	0.334472
N	-5.232497	-3.310473	0.599034
H	4.841195	0.730721	-1.109650
H	3.249223	2.506885	-0.423247
H	0.876764	-0.436504	1.624549
H	2.444586	-2.197305	0.945203
H	-0.884156	-0.385856	-1.534429
H	-2.244153	-2.368020	-0.973772
H	-5.163414	0.181191	0.920659

H	-3.793114	2.156662	0.363740
H	5.367563	-3.639336	-0.667442
H	3.586696	-3.516430	-0.630180
H	4.534197	-3.257349	0.864754

Table S5. Atom coordinates for the optimized geometry of $MeOPhS^-$ in THF.

Atom	X	Y	Z
C	-0.773062	-0.993713	-0.000011
C	0.620094	-1.132111	-0.000008
C	1.496394	-0.027452	-0.000006
C	0.876885	1.246109	0.000001
C	-0.505975	1.400997	-0.000001
C	-1.348089	0.280792	-0.000008
S	3.263611	-0.215403	0.000007
O	-2.703927	0.538153	-0.000012
C	-3.582757	-0.574580	0.000018
H	-1.390912	-1.886067	-0.000015
H	1.041965	-2.134245	-0.000008
H	1.505774	2.133127	0.000008
H	-0.954330	2.391847	0.000003
H	-4.594736	-0.163596	0.000035
H	-3.447548	-1.200054	-0.892885
H	-3.447509	-1.200035	0.892928

Table S6. Atom coordinates for the optimized geometry of $MeOPhS^{\bullet}$ in THF.

Atom	X	Y	Z
C	-0.756896	-1.015117	-0.000007
C	0.620104	-1.155181	-0.000005
C	1.488837	-0.027360	0.000002
C	0.885693	1.266912	0.000001
C	-0.482861	1.416036	-0.000002
C	-1.322064	0.276950	-0.000004
S	3.197412	-0.218981	0.000003
O	-2.643014	0.532225	-0.000009

C	-3.568912	-0.560505	0.000013
H	-1.385540	-1.897296	-0.000014
H	1.057622	-2.148212	-0.000009
H	1.527753	2.141723	0.000004
H	-0.945180	2.397874	0.000000
H	-4.558642	-0.104244	0.000032
H	-3.446966	-1.177184	-0.896441
H	-3.446928	-1.177180	0.896464

Table S7. Atom coordinates for the optimized geometry of $NCPhS^-$ in THF.

Atom	X	Y	Z
C	1.213637	0.782191	0.000000
C	1.207218	-0.602657	0.000000
C	0.000001	-1.355106	0.000000
C	-1.207216	-0.602657	0.000000
C	-1.213635	0.782191	0.000000
C	0.000001	1.503784	0.000000
S	0.000001	-3.102517	0.000000
C	0.000001	2.927111	0.000000
N	-0.000007	4.094959	0.000000
H	2.156835	1.321807	0.000000
H	2.152330	-1.138597	0.000000
H	-2.152329	-1.138598	0.000000
H	-2.156834	1.321807	0.000000

Table S8. Atom coordinates for the optimized geometry of $NCPhS^{\bullet}$ in THF.

Atom	X	Y	Z
C	-0.775763	1.215193	-0.000001
C	0.612797	1.217499	0.000000
C	1.318582	0.000000	0.000001
C	0.612796	-1.217499	0.000000
C	-0.775764	-1.215190	-0.000001
C	-1.483068	0.000002	0.000001
S	3.081946	-0.000001	0.000000

C	-2.913703	0.000002	0.000001
N	-4.078001	-0.000003	0.000000
H	-1.315966	2.156338	-0.000002
H	1.145776	2.162856	0.000000
H	1.145774	-2.162856	0.000001
H	-1.315969	-2.156334	-0.000002

3-4. S-S Bond length in XSSX$^{\bullet-}$.

Figs. S4-6 show bond lengths in the Å unit between bonded atoms in XSSX$^{\bullet-}$.

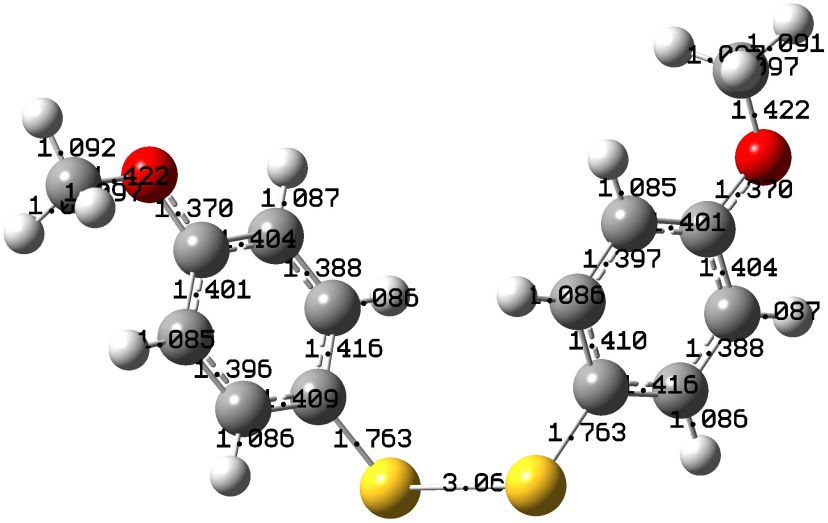

Fig. S4. Bond lengths between bonded atoms in MeOSSOMe$^{\bullet-}$.

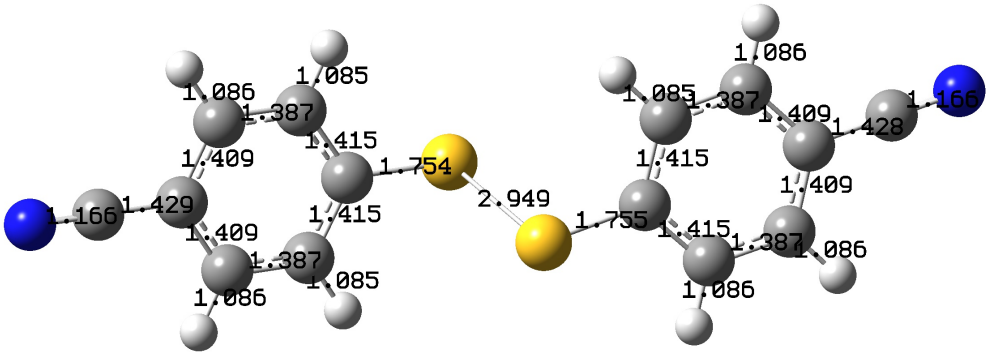

Fig. S5. Bond lengths between bonded atoms in NCSSCN$^{\bullet-}$.

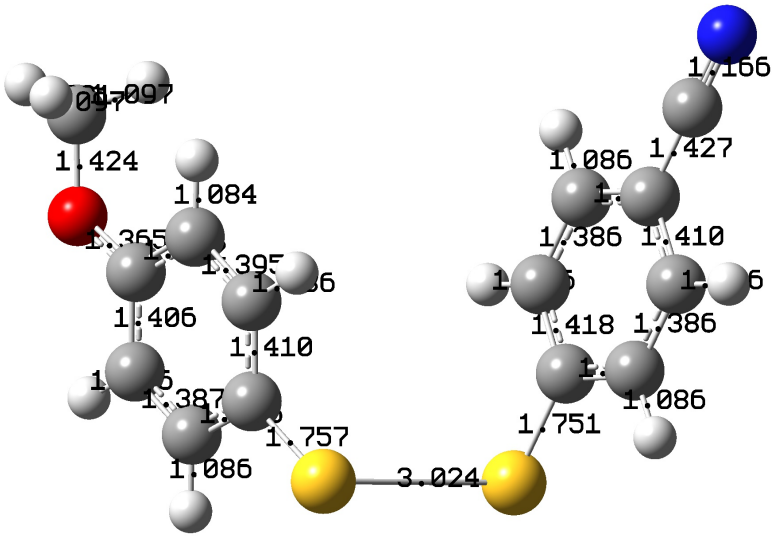

Fig. S6. Bond lengths between bonded atoms in MeOSSCN$^{\bullet-}$.

3-5. Charge distribution on the atoms in XSSX$^{\bullet-}$.

Figs. S7-9 show charge distribution on the atoms of XSSX$^{\bullet-}$.

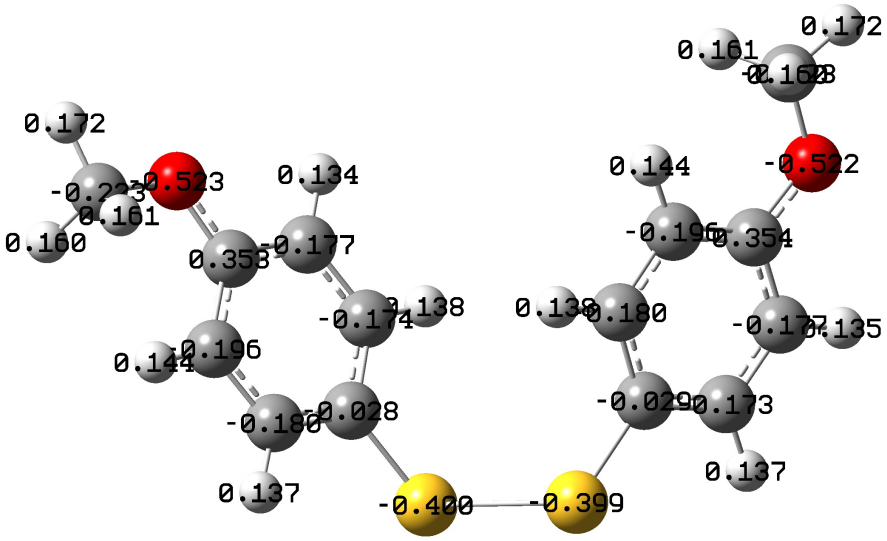

Fig. S7. Charge distribution on the atoms of MeOSSOMe$^{\bullet-}$.

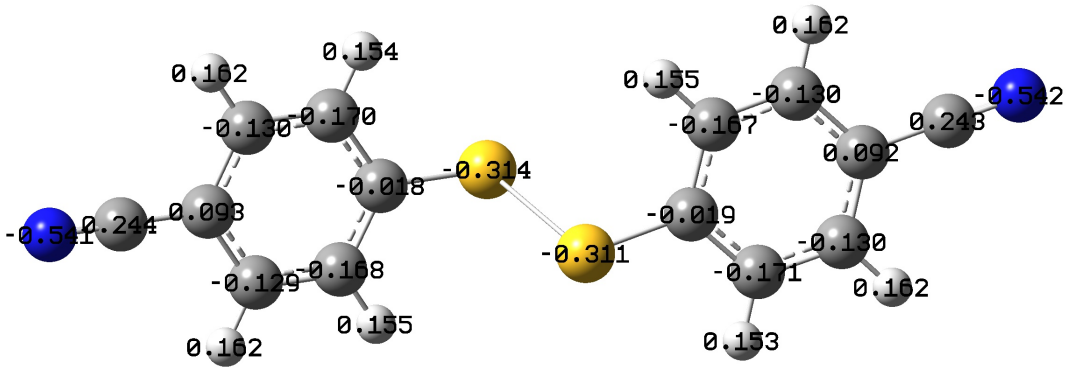

Fig. S8. Charge distribution on the atoms of $NCSSCN^{\bullet-}$.

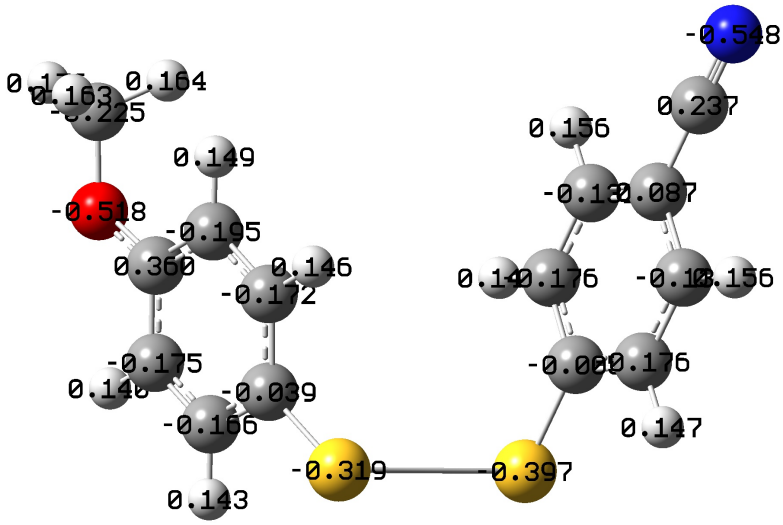

Fig. S9. Charge distribution on the atoms of $MeOSSCN^{\bullet-}$.

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