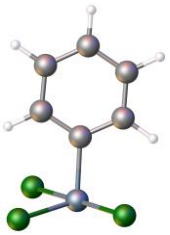
Supporting Information for

A New Polymorph of Phenylselenium Trichloride

Hannah R. Bloomfield & Jamie S. Ritch

Cartesian coordinates for DFT optimized structures (ωB97X–D/def2-TZVP) with Gibbs energy corrections for 273.15K:

$PhSeCl_3$ monomer

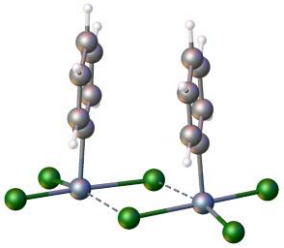


COORDINATES OF ALL ATOMS ARE (ANGS)

ATOM	CHARGE	X	Y	Z
SE	34.0	-0.8441370356	0.0544315097	0.4249646645
CL	17.0	-0.8459891495	-2.2628507997	0.7557595765
CL	17.0	-0.8788807993	2.3972544256	0.2048048789
CL	17.0	-1.7034519181	-0.1789949048	-1.5312701760
C	6.0	1.0493855903	0.0121133766	0.0252422169
C	6.0	1.8690509658	0.8127314740	0.8026928124
C	6.0	3.2395160566	0.7442661075	0.6042960282
C	6.0	3.7619291766	-0.0938259680	-0.3674440561
C	6.0	2.9197785216	-0.8797002699	-1.1411844945
C	6.0	1.5508256139	-0.8423231087	-0.9402907055
H	1.0	0.8926556501	-1.4743464619	-1.5200348283
H	1.0	3.3278386398	-1.5338872092	-1.9001963158
H	1.0	4.8319227976	-0.1345501646	-0.5250451497
H	1.0	3.8944876721	1.3594880160	1.2067585669
H	1.0	1.4566087175	1.4941588269	1.5338491064

Total ωB97X-D Energy: -4013.8967518094 Hartrees
Gibbs Energy Correction: 148.656 kJ mol^{-1}

$PhSeCl_2(\mu\text{-}Cl)_2SeCl_2Ph$, *syn* isomer

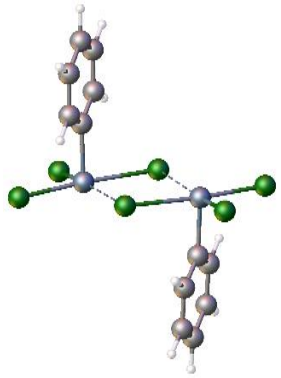


COORDINATES OF ALL ATOMS ARE (ANGS)

ATOM	CHARGE	X	Y	Z
SE	34.0	6.4037019450	3.7838180523	4.2477876448
SE	34.0	6.7552823433	7.7177986922	3.3277671891
CL	17.0	5.7047622610	6.4974676121	5.2700062704
CL	17.0	7.6262815787	5.0037693696	2.4100070309
CL	17.0	5.3039114609	2.8071909963	5.9707960748
CL	17.0	7.2889547825	1.9150519254	3.5853524784
CL	17.0	6.3652382089	9.6112403697	4.3144199665
CL	17.0	7.7706917150	8.6958603903	1.5552507846
C	6.0	4.8222444965	3.7557792669	3.1051190847
C	6.0	5.0615078662	7.5434288819	2.3784119863
C	6.0	3.8947868110	8.0196852021	2.9502494001
C	6.0	3.6442299450	4.2860942208	3.6022606807
C	6.0	4.9045776769	3.2137971967	1.8345795417
C	6.0	2.7105929675	7.8923571365	2.2437832246
C	6.0	2.5697752428	3.6954777303	1.5337021079
C	6.0	2.5150885074	4.2555676256	2.7991835389
C	6.0	5.0742371662	6.9247460216	1.1403335577
C	6.0	2.7012582434	7.2821886240	0.9992686315
C	6.0	3.7625539834	3.1791962119	1.0521628804
C	6.0	3.8771589921	6.7930717830	0.4554281017
H	1.0	3.8989587826	8.4786548475	3.9281778717
H	1.0	3.5975104509	4.7136799486	4.5929579067
H	1.0	5.8374306816	2.8246725004	1.4536103920
H	1.0	1.7930910480	8.2714441206	2.6743914323
H	1.0	1.6800477462	3.6658230934	0.9174860242
H	1.0	1.5891727755	4.6701649772	3.1749441130
H	1.0	5.9922303514	6.5496592764	0.7125159961
H	1.0	1.7715772053	7.1831401182	0.4534069543
H	1.0	3.8121935996	2.7455934578	0.0620079219
H	1.0	3.8728511651	6.3054803507	-0.5101687877

Total ωB97X-D Energy: -8027.8173235641 Hartrees
Gibbs Energy Correction: 356.324 kJ mol^{-1}

$PhSeCl_2(\mu\text{-}Cl)_2SeCl_2Ph$, *anti* isomer



COORDINATES OF ALL ATOMS ARE (ANGS)

ATOM	CHARGE	X	Y	Z
SE	34.0	6.2179739566	3.7730935159	4.4053695811
SE	34.0	6.6781797933	7.6995476438	3.5142546505
CL	17.0	5.4331826905	5.9197391788	5.5208754841
CL	17.0	7.5735718261	5.5520664961	2.4838209835
CL	17.0	4.9516029843	2.6293641461	5.7557007682
CL	17.0	6.8906862364	1.9415432467	3.2646491605
CL	17.0	5.9147460096	9.5392237177	4.5808226456
CL	17.0	7.8735291649	8.8487697160	2.1063209924
C	6.0	7.8171708266	3.8106104840	5.5231914960
C	6.0	5.0758835232	7.5289730485	2.4145060763
C	6.0	3.8403323226	7.6202898538	3.0324940284
C	6.0	9.0528499563	3.6737211291	4.9141187604
C	6.0	7.6885409730	4.0039542674	6.8877928895
C	6.0	2.7007031383	7.4637356776	2.2595433628
C	6.0	10.0831011724	3.9155566160	7.0735829087
C	6.0	10.1899265527	3.7316489266	5.7044859445
C	6.0	5.2019762989	7.2844383869	1.0579103281
C	6.0	2.8045395532	7.2281646662	0.8981192078
C	6.0	8.8351132418	4.0494781201	7.6626767536
C	6.0	4.0522921918	7.1404887580	0.2999658073
H	1.0	3.7574483229	7.8033366176	4.0933085664
H	1.0	9.1389071896	3.5298586819	3.8475422262
H	1.0	6.7176284562	4.1268745930	7.3450420855
H	1.0	1.7291825024	7.5295207021	2.7311722395
H	1.0	10.9756462972	3.9556425324	7.6846193853
H	1.0	11.1617976811	3.6300731690	5.2400470263
H	1.0	6.1736017868	7.1951625439	0.5946702503
H	1.0	1.9096765980	7.1107016857	0.3005626924
H	1.0	8.7468654293	4.1956583098	8.7309636782
H	1.0	4.1381733239	6.9529835697	-0.7621299795

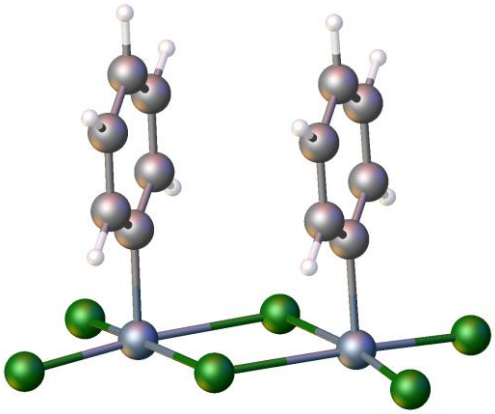
Total ωB97X-D Energy: -8027.8129400897 Hartrees
Gibbs Energy Correction: 349.564 kJ mol^{-1}

Dimerization energies (ωB97X–D/def2-TZVP)

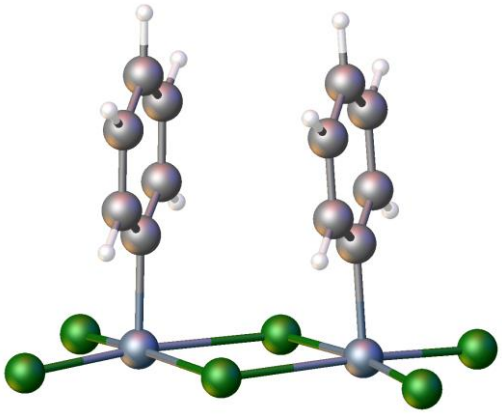
For the gas-phase processes: 2 $PhSeCl_3$ → $PhSeCl_2(\mu\text{-}Cl)_2SeCl_2Ph$

	***syn*-isomer**	***anti*-isomer**
ΔE	−62.5 kJ mol^{-1}	−51.0 kJ mol^{-1}
$\Delta H°$	−57.2 kJ mol^{-1}	−46.0 kJ mol^{-1}
$\Delta S°$	−179.9 J mol^{-1} K^{-1}	−158.5 J mol^{-1} K^{-1}
$\Delta G°$	−3.5 kJ mol^{-1}	+1.3 kJ mol^{-1}

Results of DFT optimization of $PhSeCl_2(\mu\text{-}Cl)_2SeCl_2Ph$ *syn* isomer using other density functionals:



B97–D3



PBE0–D3

Using the functions B97–D3 and PBE0–D3 resulted in similar converged geometries, featuring symmetrical bridging by two chlorides with d(Se–Cl) values of 2.69 and 2.65Å, respectively. The experimental structure exhibits asymmetric bridging, with noncovalent d(Se···Cl) distances of ca. 2.80 Å, thus these two models represent over-binding of the selenium-chlorine interactions.

The functional M06–2X was also utilized, however the SCF calculations failed to converge during the geometry search.