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Gas-Phase Photoelectron Spectroscopic and Theoretical Studies and 1,2-Dichalcogenins. Ionization Energies, Orbital Assignments, and an Explanation of Their Color

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Table 1Sa. Comparison of Various Methods and Basis Sets to Experimental Data for 1,2-Dithiin: Bond Lengths

Method	Basis Set	C=C (Å)	C-C (Å)	C-S (Å)	S-S (Å)
HF	6-31G*[a]	1.33	1.47	1.77	2.07
	6-311++G**	1.32	1.47	1.77	2.08
	LANL2DZ	1.33	1.48	1.82	2.24
B3PW91	6-31G*	1.35	1.46	1.77	2.09
	6-311++G**	1.34	1.45	1.77	2.10
	LANL2DZ	1.35	1.47	1.83	2.29
MP2	6-31G	1.36	1.47	1.85	2.29
	6-31+G	1.36	1.47	1.85	2.29
	6-31++G	1.36	1.47	1.85	2.29
	6-31G*	1.35	1.45	1.77	2.07
	6-31+G*	1.36	1.45	1.76	2.07
	6-31++G*	1.36	1.45	1.76	2.07
	6-31G**	1.35	1.45	1.77	2.07
	6-31+G**	1.36	1.45	1.76	2.07
	6-31++G**	1.36	1.45	1.76	2.07
	6-311G	1.35	1.47	1.85	2.28
	6-311+G	1.36	1.47	1.85	2.27
	6-311++G	1.36	1.47	1.85	2.27
	6-311G*	1.35	1.46	1.76	2.08
	6-311+G*	1.36	1.45	1.76	2.08
	6-311++G*	1.36	1.45	1.76	2.08
	6-311G**	1.36	1.45	1.76	2.08
	6-311+G**	1.36	1.45	1.76	2.08
	6-311++G**	1.36	1.45	1.76	2.08
	LANL2DZ	1.38	1.49	1.85	2.32
Experimental value		1.35	1.45	1.76	2.05

[a] These values taken from Mann, M.; Fabian, J. *J. Mol. Struct. (Theochem)* **1995**, *331*, 51-61.

Table 1Sb. Comparison of Various Methods and Basis Sets to Experimental Data for 1,2-Dithiin: Bond Angles

Method	Basis Set	C=C-C (°)	C=C-S (°)	C-S-S (°)
HF	6-31G*[a]	124.6	122.8	99.2
	6-311++G**	124.6	123.0	99.0
	LANL2DZ	126.3	124.6	98.7
B3PW91	6-31G*	124.7	122.5	98.9
	6-311++G**	124.7	122.2	98.6
	LANL2DZ	126.5	124.5	98.0
MP2	6-31G	125.8	123.8	96.5
	6-31+G	125.5	123.7	96.2
	6-31++G	125.5	123.7	96.1
	6-31G*	124.0	122.0	98.0
	6-31+G*	123.9	122.0	97.8
	6-31++G*	123.9	122.0	97.8
	6-31G**	124.0	122.1	97.9
	6-31+G**	123.8	122.0	97.8
	6-31++G**	123.9	122.1	97.7
	6-311G	125.5	123.8	95.8
	6-311+G	125.3	123.6	95.7
	6-311++G	125.3	123.6	95.7
	6-311G*	123.9	122.1	97.5
	6-311+G*	123.9	122.1	97.5
	6-311++G*	123.9	122.1	97.5
	6-311G**	123.8	122.1	97.5
	6-311+G**	123.8	122.1	97.5
	6-311++G**	123.8	122.1	97.5
	LANL2DZ	125.9	124.5	97.3
Experimental value		124.2	121.4	98.7

[a] These values taken from Mann, M.; Fabian, J. *J. Mol. Struct. (Theochem)* **1995**, *331*, 51-61.

Table 1Sc. Comparison of Various Methods and Basis Sets to Experimental Data for 1,2-Dithiin: Dihedral Angles[a]

Method	Basis Set	S-C=C-C (°)	C=C-C=C (°)	S-S-C=C (°)	C-S-S-C (°)
HF	6-31G*[b]	1.1	26.2	n/a[c]	49.7
	6-311++G**	1.1	26.3	-38.7	49.5
	LANL2DZ	1.2	24.4	-34.2	43.0
B3PW91	6-31G*	1.1	26.8	-39.5	50.7
	6-311++G**	1.3	26.8	-39.6	50.8
	LANL2DZ	1.3	25.4	-35.0	44.0
MP2	6-31G	1.1	28.6	-39.1	49.0
	6-31+G	1.0	29.2	-39.8	50.0
	6-31++G	1.3	28.9	-40.1	50.2
	6-31G*	1.7	27.6	-42.3	54.2
	6-31+G*	1.6	28.0	-42.6	54.8
	6-31++G*	1.8	27.7	-42.8	54.9
	6-31G**	1.7	27.6	-42.3	54.2
	6-31+G**	1.6	28.0	-42.6	54.7
	6-31++G**	1.8	27.7	-42.8	54.8
	6-311G	2.0	28.3	-40.8	50.6
	6-311+G	1.6	29.0	-41.2	51.3
	6-311++G	2.1	28.5	-41.5	51.5
	6-311G*	2.4	27.3	-43.2	55.1
	6-311+G*	2.3	27.3	-43.2	55.2
	6-311++G*	2.6	27.0	-43.4	55.3
	6-311G**	2.3	27.4	-43.2	55.4
	6-311+G**	2.3	27.4	-43.2	55.2
	6-311++G**	2.5	27.1	-43.3	55.2
	LANL2DZ	1.3	26.7	-36.8	46.2
Experimental value		0.3	29.0	-41.2	53.9

[a] When regarding a dihedral angle 1-2-3-4, if you look down the 2-3 bond, a positive sign indicates a clockwise rotation from 1 to 4, while a negative sign indicates counterclockwise rotation from 1 to 4.

[b] These values taken from Mann, M.; Fabian, J. *J. Mol. Struct. (Theochem)* **1995**, *331*, 51-61.

[c] Value not available.

Table 1Sd. Comparison of Various Methods and Basis Sets to Experimental Data for 1,2-Dithiin: Ionization Potentials and Spin-squared Values

Method	Basis Set	IP (eV)	$<S^2>$
HF	6-31G*	n/a	n/a
	6-311++G**	n/a	n/a
	LANL2DZ	n/a	n/a
B3PW91	6-31G*	n/a	n/a
	6-311++G**	n/a	n/a
	LANL2DZ	8.12	0.754
MP2	6-31G	8.31	0.811
	6-31+G	8.47	0.813
	6-31++G	8.47	0.813
	6-31G*	7.99	0.794
	6-31+G*	8.16	0.796
	6-31++G*	8.17	0.796
	6-31G**	8.03	0.793
	6-31+G**	8.20	0.795
	6-31++G**	8.20	0.795
	6-311G	8.48	0.809
	6-311+G	8.55	0.812
	6-311++G	8.56	0.813
	6-311G*	8.20	0.826
	6-311+G*	8.27	0.801
	6-311++G*	8.27	0.801
	6-311G**	8.25	0.798
	6-311+G**	8.32	0.800
	6-311++G**	8.32	0.800
	LANL2DZ	n/a	n/a
Experimental value		8.16	0.75[a]

[a] Theoretical expectation value for a pure doublet state.

Table 2S. Geometric Parameters[a] of Dimethyl Disulfide, Dithiirane and 1,2-Dithietane

Geometric Parameter	Dimethyl Disulfide	Dithiirane	1,2-Dithietane
S-S Bond Length (Å)	2.06	2.10	2.13
C-S Bond Length (Å)	1.81	1.80	1.84
C-C Bond Length (Å)	-	-	1.53
S-S-C Bond Angle (°)	102.1	54.1	78.0
S-C-C Bond Angle (°)	-	-	96.0
CSSC Dihedral Angle (°)[b]	84.0	-	21.8
SSCC Dihedral Angle (°)[b]	-	-	-26.0
SCCS Dihedral Angle (°)[b]	-	-	30.1

[a] Parameters obtained from a MP2/6-31+G* geometry optimization.

[b] When regarding a dihedral angle 1-2-3-4, if you look down the 2-3 bond, a positive sign indicates a clockwise rotation from 1 to 4, while a negative sign indicates counterclockwise rotation from 1 to 4.

Table 3S. Molecular Orbital Energies[a]: Selected Disulfides

Molecular Orbital	1,2-Dithiin	3,6-Dimethyl-1,2-dithiin	Dimethyl Disulfide	Dithiirane	1,2-Dithietane
LUMO+2	0.08023	0.07640	0.08696	0.08716	0.08675
	B	B	B	A_1	A
LUMO+1	0.07340	0.07406	0.07779	0.06092	0.06363
	A	A	B	A_1	A
LUMO	0.04750	0.06248	0.07224	0.04406	0.05218
	B	B	A	B_2	B
HOMO	-0.30589	-0.29525	-0.35132	-0.33892	-0.32239
	A	A	A	A_2	A
HOMO-1	-0.38338	-0.36638	-0.36205	-0.42524	-0.41124
	A	A	B	B_1	B
HOMO-2	-0.38475	-0.37632	-0.43980	-0.45546	-0.43624
	B	B	A	A_1	A
HOMO-3	-0.46415	-0.44346	-0.49254	-0.46287	-0.45688
	B	B	B	B_2	B
HOMO-4	-0.47838	-0.46782	-0.53497	-0.57852	-0.53072
	A	A	A	A_1	A
HOMO-5	-0.52472	-0.50024	-0.58110	-0.65676	-0.55362
	A	B	B	B_1	A
HOMO-6	-0.52837	-0.50598	-0.59886	-0.85212	-0.62798
	B	A	A	B_2	A
HOMO-7	-0.61184	-0.53484	-0.60140	-0.86370	-0.65920
	B	A	B	A_1	B
HOMO-8	-0.61957	-0.57025	-0.61431	-1.15714	-0.76970
	A	B	A	A_1	B
HOMO-9	-0.68875	-0.57763	-0.78979	-6.66768	-0.93546
	B	B	B	A_2	B

[a] The orbital energy (in hartrees) is followed by the orbital symmetry.
The dithiins, dimethyl disulfide, and 1,2-dithietane were found to possess C_2 symmetry, while dithiirane was found to possess C_{2v} symmetry.

Table 4Sa. Electronic Transitions: Symmetries, Energies, Oscillator Strengths, and Contributing Molecular Orbitals for 1,2-Dithiin and Dimethyl Disulfide

Compound	Transition Symmetry	Transition Energy (nm)[a]	Oscillator Strength	Contributing MOs and Coefficients[b]
1,2-dithiin	^{3}B	605	0	**HOMO → LUMO, 0.57454**
	^{3}B	357	0	**HOMO-1 → LUMO, 0.44537**
				HOMO → LUMO, 0.23075
				HOMO → LUMO+10, -0.27665
	^{1}B	**354**	0.0078	**HOMO → LUMO, 0.64505**
	^{3}A	332	0	**HOMO-2 → LUMO, 0.45346**
	^{3}A	244	0	HOMO-3 → LUMO, -0.26057
				HOMO-2 → LUMO, 0.36667
				HOMO-2 → LUMO+10, -0.25713
	^{1}B	**237**	0.0389	**HOMO-1 → LUMO, 0.50774**
				HOMO → LUMO+5, 0.21902
	^{3}B	226	0	**HOMO-4 → LUMO, 0.34956**
				HOMO-1 → LUMO, -0.35430
				HOMO → LUMO+5, 0.20515
	^{1}A	**225**	0.0430	**HOMO-2 → LUMO, 0.57423**
	^{3}A	215	0	**HOMO → LUMO+4, 0.45933**
				HOMO → LUMO+22, 0.25511
	^{1}A	**200**	0.0005	**HOMO → LUMO+1, 0.48717**
				HOMO → LUMO+4, 0.36569
	^{1}A	**196**	0.0005	**HOMO → LUMO+1, 0.43917**
				HOMO → LUMO+4, -0.37091
	^{1}B	**193**	0.0361	HOMO-1 → LUMO, -0.36013
				HOMO → LUMO+2, 0.29102
				HOMO → LUMO+5, 0.40951
dimethyl disulfide	^{3}B	273	0	**HOMO → LUMO+2, 0.34598**
				HOMO → LUMO+8, -0.32650
				HOMO → LUMO+14, 0.30545
	^{3}A	255	0	**HOMO-1→ LUMO+2, 0.34567**
				HOMO-1 → LUMO+8, -0.30903
				HOMO-1 → LUMO+14, 0.31408
	^{1}B	**224**	0.0141	HOMO → LUMO+1, -0.30706
				HOMO → LUMO+2, 0.33436
				HOMO → LUMO+8, -0.31222
	^{1}A	**215**	0.0013	HOMO-1 → LUMO+1, -0.31122
				HOMO-1 → LUMO+2, 0.32460
				HOMO-1 → LUMO+8, -0.31212
	^{3}B	201	0	**HOMO → LUMO+2, 0.22990**
	^{3}A	198	0	**HOMO → LUMO, 0.29286**
	^{3}B	197	0	**HOMO-2 → LUMO+2, 0.28672**
	^{1}B	**175**	0.0110	**HOMO → LUMO+2, 0.38501**
	^{1}A	**174**	0.0017	**HOMO → LUMO, 0.31152**
				HOMO → LUMO+3, -0.32836
	^{1}A	**167**	0.0211	HOMO → LUMO, 0.37589
				HOMO → LUMO+3, 0.47975

[a] Wavelengths in bold indicate allowed transitions.

[b] All contributions from MOs with coefficient magnitudes of less than 0.2 for dithiin or 0.3 for dimethyl disulfide not listed (except that the largest contributing MO is always listed); major positively contributing MO is listed in bold.

Table 4Sb. Electronic Transitions: Symmetries, Energies, Oscillator Strengths, and Contributing Molecular Orbitals for Dithiirane and 1,2-Dithietane

Compound	Transition Symmetry	Transition Energy (nm)[a]	Oscillator Strength	Contributing MOs and Coefficients[b]
dithiirane	$^3B_1$	534	0	**HOMO → LUMO, 0.60600**
	$^1B_1$	**393**	0.0010	**HOMO → LUMO, 0.61335**
	$^3B_2$	265	0	**HOMO → LUMO, 0.59208**
	$^3A_2$	265	0	**HOMO-1 → LUMO, 0.51236**
	$^3A_2$	235	0	**HOMO → LUMO+1, 0.38432**
	$^1A_2$	233	0	**HOMO-1 → LUMO, 0.47538**
				HOMO → LUMO+1, 0.31015
	$^3B_1$	217	0	**HOMO → LUMO+3, 0.42897**
				HOMO → LUMO+14, 0.33079
	$^1A_2$	204	0	**HOMO → LUMO+1, 0.41926**
	$^1B_1$	**188**	0.0198	**HOMO → LUMO+3, 0.52629**
	$^1A_2$	180	0	**HOMO → LUMO+2, 0.54934**
1,2-dithietane	^3B	513	0	**HOMO → LUMO, 0.56191**
	^1B	**380**	0.0010	**HOMO → LUMO, 0.57922**
	^3A	295	0	**HOMO-1 → LUMO, 0.33499**
				HOMO → LUMO+1, 0.32769
	^1A	253	0	HOMO-1 → LUMO, 0.30409
				HOMO → LUMO+1, 0.37363
	^3B	253	0	**HOMO-2 → LUMO, 0.53212**
	^3A	237	0	**HOMO-1 → LUMO, 0.45022**
	^1A	**204**	0.0002	**HOMO-1 → LUMO, 0.47660**
				HOMO → LUMO+2, 0.34979
	^3B	203	0	**HOMO → LUMO+18, 0.31107**
	^1A	**184**	0.0136	HOMO → LUMO+1, 0.38352
				HOMO → LUMO+2, 0.46252
	^1B	**179**	0.0819	**HOMO → LUMO+3, 0.41745**

[a] Wavelengths in bold indicate allowed transitions.

[b] All contributions from MOs with coefficient magnitudes of less than 0. 3 are not listed (except that the largest contributing MO is always listed); major positively contributing MO is listed in bold.

Table 5S. Calculated S-S Bond Lengths and Stretching Frequencies for Ground State and Electronic Excited States of Dimethyldisulfide, Dithiirane, 1,2-Dithietane, and 1,2-Dithiin.

Compound (State)	S-S Bond Length (Å)	S-S Stretch (cm^{-1})
Dimethyl disulfide		
(S_0)	2.06	554.9
(S_1)	2.59	304.7
(T_1)	2.63	286.5
Dithiirane		
(S_0)	1.80	521.2
(S_1)	2.44	337.5
(T_1)	2.53	308.5
1,2-Dithietane		
(S_0)	2.13	515.6
(S_1)	2.48	347.6
(T_1)	2.59	313.9
1,2-Dithiin		
(S_0)	2.07	556.1
(S_1)	2.66	284.1
(T_1)	2.65	287.4

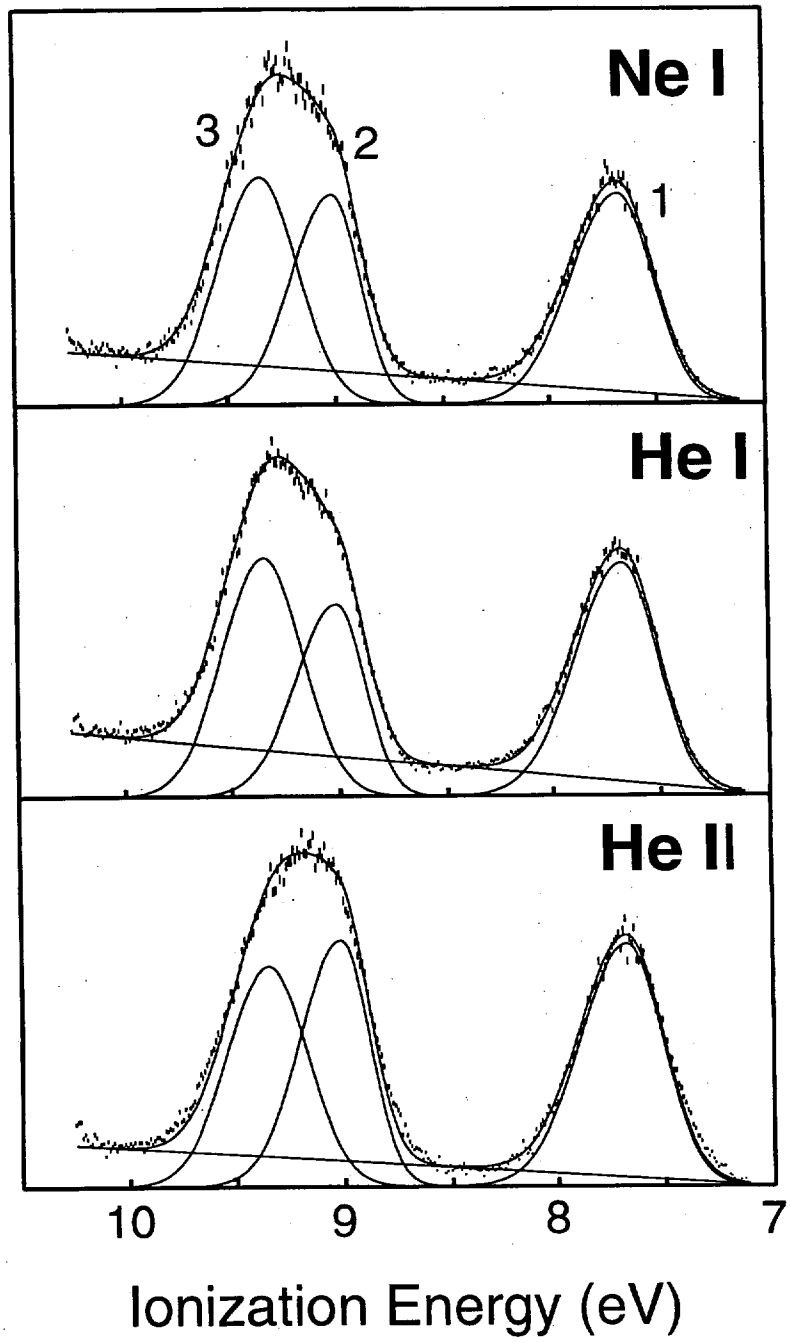

Figure S1. Ne I, He I, and He II photoelectron spectra of 3,6-diisopropyl-1,2-dithiin.

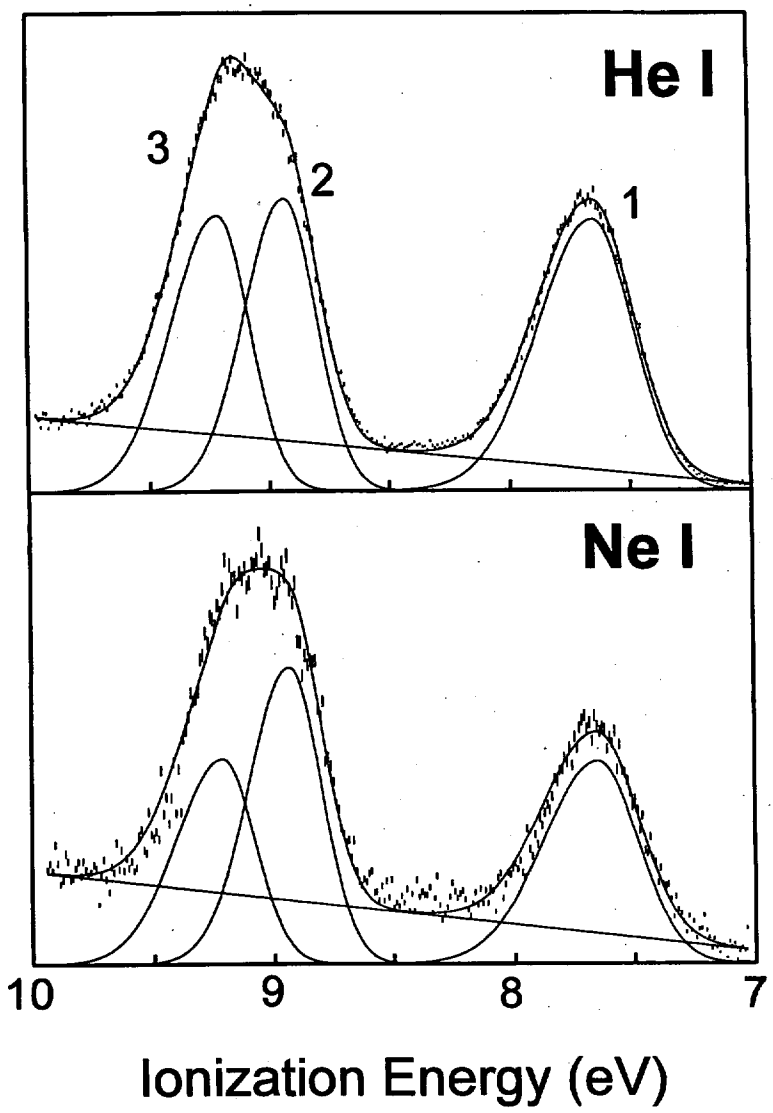

Figure S2. He I and Ne I photoelectron spectra of 3,6-di-*tert*-butyl-1,2-dithiin.

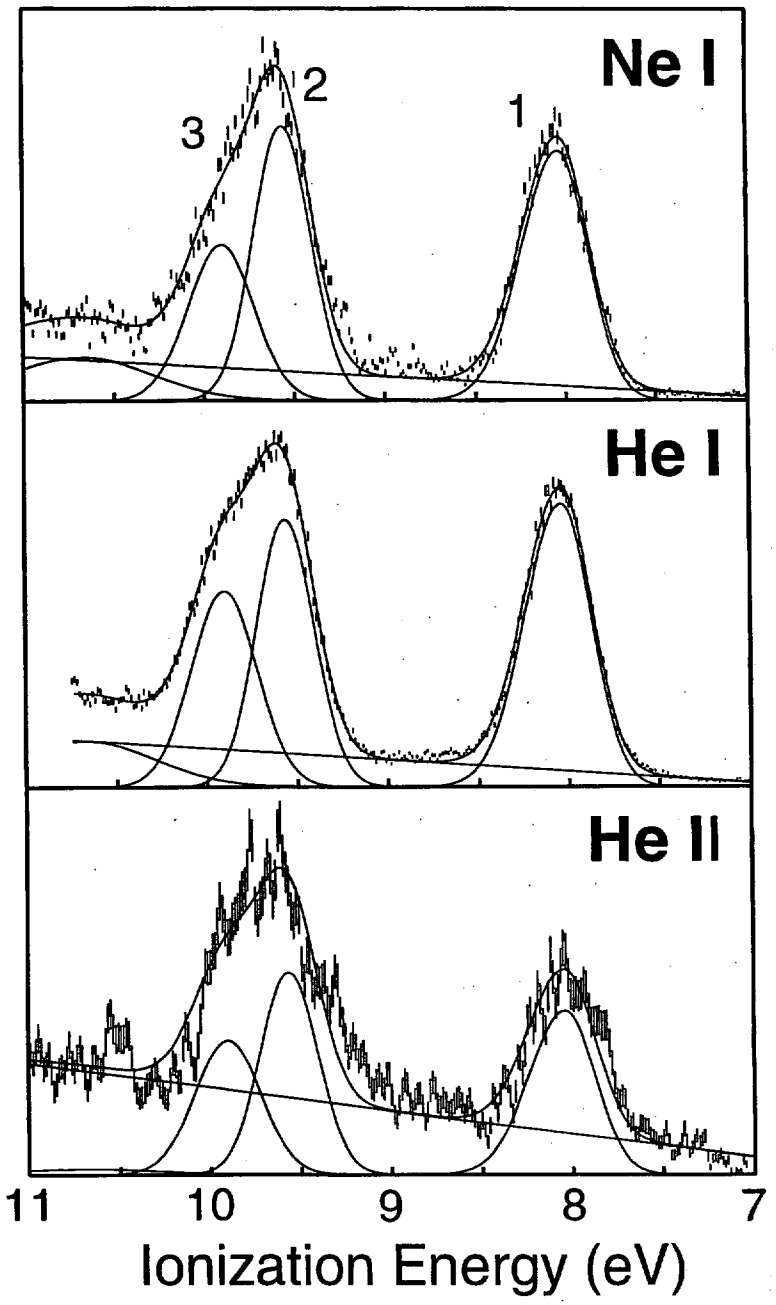

Figure S3. Ne I, He I and He II photoelectron spectra of 2-selenathiin.

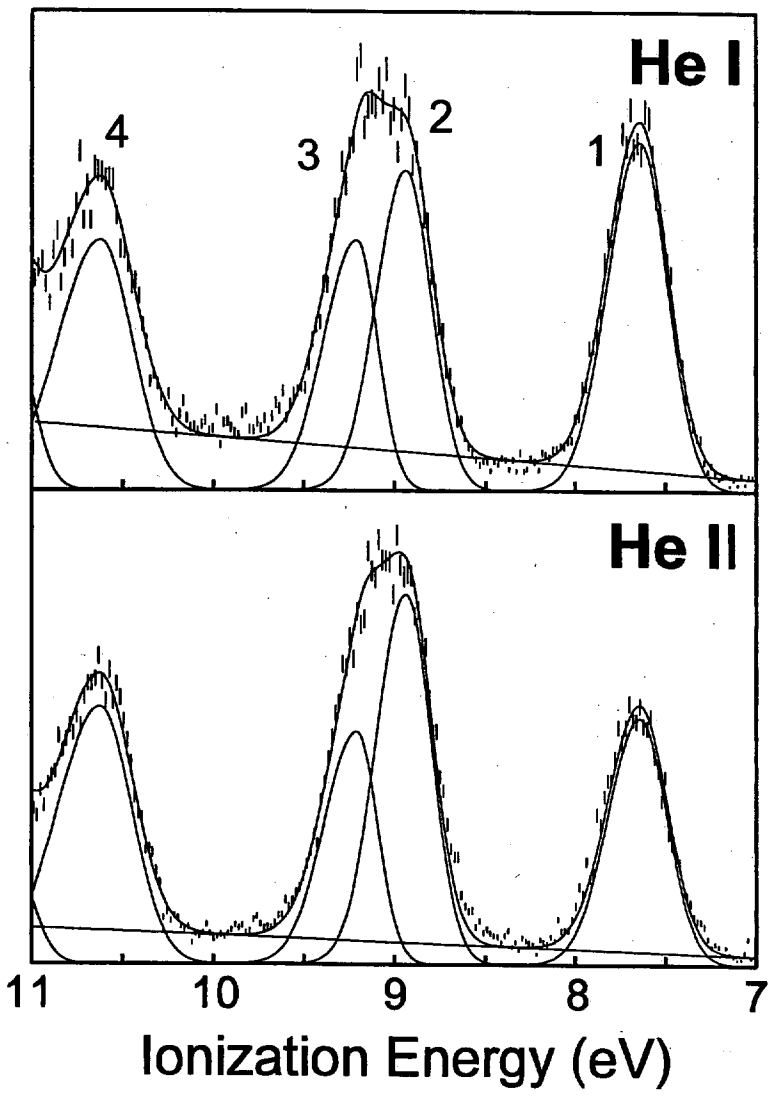

Figure S4. He I and He II photoelectron spectra of 3,6-dimethyl-1,2-diselenin.

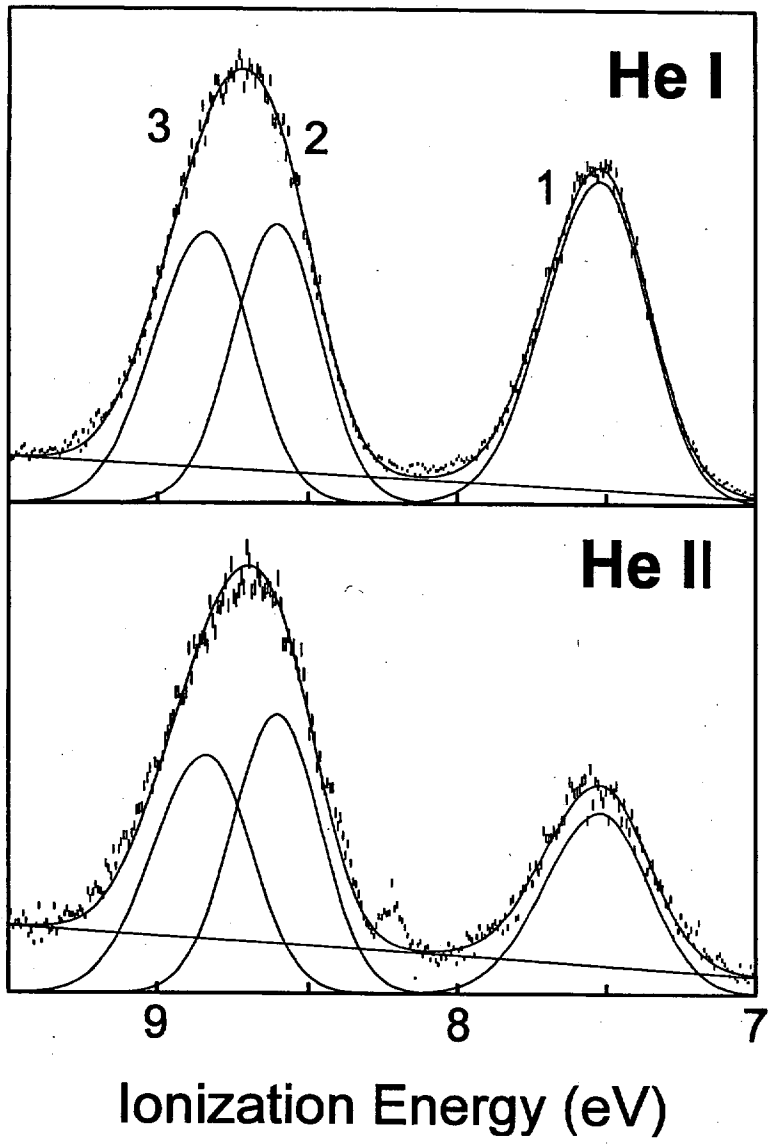

Figure S5. He I and He II photoelectron spectra of 3,6-di-*tert*-butyl-1,2-diselenin.