Supplementary Table 4. P^2 and π for Phosphorus-Phosphorus Pairs in P_5S_2X (**1**)

Molecule			Coupling	Expt.	P^2	π
E_a	E_b	X		Coupling	$\times 10^3$	$\times 10^3$
S	S	Cl	$^1J(P_AP_B)$	–193.7	4.706	–2.286
S	Se	Cl		–190.3	4.747	–2.404
Se	S	Cl		–194.3	4.830	–2.401
Se	Se	Cl		–191.3	4.914	–2.487
S	S	Br		–191.8	4.665	–2.275
S	Se	Br		–188.4	4.692	–2.399
Se	S	Br		–192.4	4.789	–2.395
Se	Se	Br		–189.3	4.858	–2.478
S	S	Cl	$^1J(P_AP_E)$	–168.8	4.343	–2.726
S	Se	Cl		–173.4	4.409	–2.609
Se	S	Cl		–169.2	4.489	–2.852
Se	Se	Cl		–173.5	4.556	–2.732
S	S	Br		–169.1	4.251	–2.733
S	Se	Br		–174.0	4.330	–2.611
Se	S	Br		–169.4	4.409	–2.868
Se	Se	Br		–174.4	4.462	–2.742
S	S	Cl	$^1J(P_BP_E)$	–179.1	4.844	–1.900
S	Se	Cl		–177.4	5.055	–1.890
Se	S	Cl		–184.5	4.886	–1.788
Se	Se	Cl		–182.6	5.098	–1.778
S	S	Br		–173.5	4.692	–1.900
S	Se	Br		–171.1	4.872	–1.896
Se	S	Br		–178.9	4.706	–1.783
Se	Se	Br		–176.8	4.928	–1.786

S	S	Cl	$^{1}J(P_CP_D)$	–274.9	10.201	–2.853
S	Se	Cl		–282.1	10.241	–3.139
Se	S	Cl		–275.9	10.384	–3.017
Se	Se	Cl		–283.4	10.404	–3.310
S	S	Br		–265.2	9.960	–3.125
S	Se	Br		–272.7	10.000	–3.407
Se	S	Br		–266.1	10.140	–3.288
Se	Se	Br		–273.7	10.161	–3.575
S	S	Cl	$^{1}J(P_DP_E)$	–396.2	10.983	–4.228
S	Se	Cl		–393.1	10.795	–4.258
Se	S	Cl		–393.7	10.384	–4.724
Se	Se	Cl		–390.8	10.201	–4.752
S	S	Br		–386.0	10.837	–4.379
S	Se	Br		–382.2	10.630	–4.431
Se	S	Br		–383.3	10.241	–4.878
Se	Se	Br		–379.6	10.020	–4.921
S	S	Cl	$^{2}J(P_AP_C)$	73.5	2.107	4.438
S	Se	Cl		82.7	2.228	4.705
Se	S	Cl		64.3	1.452	3.634
Se	Se	Cl		73.0	1.529	3.844
S	S	Br		73.9	2.153	4.534
S	Se	Br		83.2	2.275	4.797
Se	S	Br		65.0	1.490	3.719
Se	Se	Br		73.5	1.568	3.924

S	S	Cl	$^2J(P_AP_D)$	15.3	0.973	2.398
S	Se	Cl		13.6	0.973	2.388
Se	S	Cl		21.3	1.109	2.668
Se	Se	Cl		18.9	1.102	2.636
S	S	Br		15.9	1.011	2.485
S	Se	Br		13.9	1.011	2.474
Se	S	Br		22.1	1.156	2.764
Se	Se	Br		19.8	1.149	2.726
S	S	Cl	$^2J(P_BP_C)$	59.5	1.858	3.959
S	Se	Cl		50.3	1.267	3.239
Se	S	Cl		65.5	1.945	4.149
Se	Se	Cl		55.3	1.325	3.388
S	S	Br		59.5	1.866	3.990
S	Se	Br		50.2	1.274	3.263
Se	S	Br		65.2	1.945	4.166
Se	Se	Br		55.1	1.325	3.406
S	S	Cl	$^2J(P_BP_D)$	–8.7	0.010	0.136
S	Se	Cl		–12.6	0.021	0.152
Se	S	Cl		–9.7	0.005	0.106
Se	Se	Cl		–13.0	0.014	0.118
S	S	Br		–8.7	0.012	0.150
S	Se	Br		–11.9	0.024	0.170
Se	S	Br		–9.5	0.006	0.118
Se	Se	Br		–12.6	0.016	0.133

S	S	Cl	$^2J(P_CP_E)$	43.5	1.391	3.888
S	Se	Cl		44.1	1.444	4.020
Se	S	Cl		48.6	1.467	4.065
Se	Se	Cl		49.8	1.521	4.199
S	S	Br		44.6	1.505	4.111
S	Se	Br		45.2	1.560	4.252
Se	S	Br		49.4	1.584	4.294
Se	Se	Br		50.7	1.640	4.433

P^2 (Equ. 5) and π (Equ. 6) are for products of coefficients of 3*s* NAOs obtained from *ab initio* calculations at the RHF/Ahlrichs pTZV level using RHF/Ahlrichs pVDZ geometries. Units of π are Hartree^{-1}; observed coupling constants are in Hz.