Density Functional Theory Studies of Semiquinone Radical Anions of Polychlorinated Biphenyls in the Syn- and Anti-like Conformation

SUPPORTING INFORMATION

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Table S1. Comparison of bond lengths calculated at the UB3LYP/6-311G** level of theory for PCB quinones (Q) and the corresponding semiquinone radicals ($SQ^{\bullet-}$) in the anti-like conformation.

Bond	2'-Cl-2,5-Q		3'-Cl-2,5-Q		2',5'-Cl-2,5-Q		3',4'-Cl-2,5-Q	
	Q	$SQ^{\bullet-}$	Q	$SQ^{\bullet-}$	Q	$SQ^{\bullet-}$	Q	$SQ^{\bullet-}$
C2-O2	1.217	1.258	1.218	1.258	1.217	1.258	1.218	1.259
C5-O5	1.219	1.260	1.220	1.259	1.219	1.259	1.220	1.259
C1-C2	1.505	1.470	1.508	1.472	1.505	1.470	1.508	1.471
C1-C6	1.347	1.380	1.350	1.385	1.345	1.381	1.351	1.387
C1-C1'	1.484	1.483	1.480	1.480	1.484	1.480	1.479	1.477
C2-C3	1.485	1.452	1.485	1.455	1.485	1.452	1.485	1.455
C3-C4	1.337	1.363	1.337	1.361	1.337	1.363	1.337	1.360
C4-C5	1.484	1.451	1.483	1.453	1.483	1.453	1.482	1.454
C5-C6	1.481	1.446	1.479	1.444	1.482	1.445	1.479	1.442
C1'-C6'	1.404	1.411	1.403	1.410	1.403	1.412	1.404	1.411
C1'-C2'	1.404	1.406	1.404	1.411	1.404	1.408	1.400	1.408
C2'-C3'	1.392	1.395	1.388	1.384	1.392	1.393	1.390	1.388
C3'-C4'	1.390	1.389	1.391	1.389	1.389	1.389	1.398	1.394
C4'-C5'	1.393	1.395	1.392	1.394	1.390	1.390	1.394	1.393
C5'-C6'	1.388	1.388	1.391	1.390	1.385	1.382	1.386	1.387
Cl-C[1]	1.763	1.774	1.759	1.782	1.759	1.770	1.747	1.765
					1.755	1.776	1.744	1.763

[1] The Cl-C bond lengths are listed in the following order: Cl-C2' and Cl-C5' for 2',5'-Cl-2,5-Q, Cl-C3' and Cl-C4' for 3',4'-Cl-2,5-Q, and Cl-C3, Cl-C4', and Cl-C6 for 3,4',6-Cl-2,5-Q.

Table S2. Selected bond angles (°) and dihedral angle averages calculated at the UB3LYP/6-311G** level of theory for PCB quinones (Q) and the corresponding semiquinone radicals ($SQ^{\bullet-}$) in the anti-like conformation.

Bond	2'-Cl-2,5-Q		3'-Cl-2,5-Q		2',5'-Cl-2,5-Q		3',4'-Cl-2,5-Q	
	Q	$SQ^{\bullet-}$	Q	$SQ^{\bullet-}$	Q	$SQ^{\bullet-}$	Q	$SQ^{\bullet-}$
O2-C2-C3	120.29	121.38	119.96	120.28	120.44	121.31	120.00	120.17
O2-C2-C1	122.04	123.47	122.26	124.21	121.93	123.40	122.18	124.19
O5-C5-C4	121.40	122.61	121.42	122.53	121.49	122.51	121.47	122.48
O5-C5-C6	121.22	122.47	121.31	122.62	121.11	122.48	121.23	122.58
C2-C1-C6	119.08	120.44	118.51	119.43	119.23	120.37	118.51	119.33
C2-C1-C1'	117.93	118.27	119.50	120.50	117.93	118.30	119.45	120.48
C6-C1-C1'	122.99	121.22	121.99	120.07	122.84	121.26	122.03	120.19
C1-C2-C3	117.68	115.15	117.78	115.51	117.62	115.29	117.82	115.64
C2-C3-C4	122.10	123.39	122.26	123.63	122.10	123.26	122.26	123.58
C3-C4-C5	120.76	122.08	120.71	121.79	120.77	122.09	120.71	121.76
C4-C5-C6	117.38	114.92	117.27	114.85	117.39	115.01	117.30	114.94
C5-C6-C1	122.07	123.95	123.46	124.77	122.85	123.90	123.40	124.72
C6'-C1'-C1	119.23	119.12	121.89	122.44	122.84	118.72	122.12	122.56
C6'-C1'-C2'	117.27	115.43	118.86	117.15	117.66	115.79	118.39	116.73
C1-C1'-C2'	123.50	125.45	119.23	120.41	123.49	125.49	119.48	120.71
C1'-C2'-C3'	121.51	122.69	119.94	120.46	121.25	122.47	121.22	121.79
C2'-C3'-C4'	119.87	119.99	121.39	122.51	120.28	120.53	119.80	120.45
C3'-C4'-C5'	119.87	119.10	118.63	117.27	118.96	117.76	119.40	118.74
C4'-C5'-C6'	119.84	120.15	120.95	121.50	121.06	122.12	120.71	120.89
C5'-C6'-C1'	121.63	122.60	120.23	121.10	120.77	121.29	120.47	121.38

[1] The *in silico* dihedral angles are the average of the four dihedral angles involving the C1-C1' bond between the benzene and the quinone rings.

Table S3: Mulliken atomic spin densities in semiquinone radical anions in the syn-like conformation. Atoms highlighted in green are the carbon atoms in the benzoquinone ring and atoms highlighted in yellow are the oxygen atoms in the benzoquinone ring. These atoms have non-zero spin densities.[1]

2'-Cl-2,5-Q		**3'-Cl-2,5-Q**		**4-Cl-2,5-Q**		**2',5'-Cl-2,5-Q**		**3',4'-Cl-2,5-Q**		**3,4',6-Cl-2,5-Q**	
C1	0.08	C1	0.06	C1	0.06	C1	0.08	C1	0.06	C1	0.08
C2	0.05	C2	0.06	C2	0.07	C2	0.05	C2	0.06	C2	0.06
C3	0.08	C3	0.06	C3	0.06	C3	0.07	C3	0.06	C3	0.07
C4	0.07	C4	0.06	C4	0.07	C4	0.06	C4	0.06	C4	0.09
C5	0.05	C5	0.04	C5	0.04	C5	0.04	C5	0.03	C5	0.04
C6	0.13	C6	0.17	C6	0.16	C6	0.15	C6	0.18	C6	0.12
C1'	-0.01	C1'	-0.01	C1'	-0.01	C1'	-0.01	C1'	-0.01	C1'	-0.01
C2'	0.01	C2'	0.01	C2'	0.02	C2'	0.01	C2'	0.02	C2'	0.01
C3'	0.00	C3'	-0.01	C3'	-0.01	C3'	-0.01	C3'	-0.01	C3'	-0.01
C4'	0.01	C4'	0.02	C4'	0.02	C4'	0.01	C4'	0.02	C4'	0.01
C5'	0.00	C5'	-0.01	C5'	-0.01	C5'	0.00	C5'	-0.01	C5'	0.00
C6'	0.00	C6'	0.02	C6'	0.02	C6'	0.00	C6'	0.02	C6'	0.01
O2	0.26	O2	0.23	O2	0.24	O2	0.26	O2	0.23	O2	0.26
O5	0.29	O5	0.29	O5	0.29	O5	0.29	O5	0.29	O5	0.28
Cl2'	0.00	Cl3'	0.00	Cl4'	0.00	Cl2'	0.00	Cl3'	0.00	Cl3	0.00
H3	0.00	H3	-0.01	H3	-0.01	Cl5'	0.00	Cl4'	0.00	Cl6	0.00
H4	0.00	H4	-0.01	H4	-0.01	H3	0.00	H3	-0.01	Cl4'	0.00
H6	-0.01	H6	-0.01	H6	-0.01	H4	-0.01	H4	0.00	H4	-0.01
H3'	0.00	H2'	0.00	H2'	0.00	H6	-0.01	H6	-0.01	H2'	0.00
H4'	0.00	H4'	0.00	H3'	0.00	H3'	0.00	H2'	0.00	H3'	0.00
H5'	0.00	H5'	0.00	H5'	0.00	H4'	0.00	H5'	0.00	H5'	0.00
H6'	-0.01	H6'	0.00	H6'	0.00	H6'	0.00	H6'	0.00	H6'	0.00

[1] See Figure 1 for the atom numbering scheme.

Table S4: Mulliken atomic spin densities in semiquinone radical anions in the anti-like conformation. Atoms highlighted in green are the carbon atoms in the benzoquinone ring and atoms highlighted in yellow are the oxygen atoms in the benzoquinone ring. These atoms have non-zero spin densities.[1]

2'-Cl-2,5-Q		**3'-Cl-2,5-Q**		**2',5'-Cl-2,5-Q**		**3',4'-Cl-2,5-Q**	
C1	0.06	C1	0.06	C1	0.06	C1	0.06
C2	0.07	C2	0.06	C2	0.07	C2	0.06
C3	0.07	C3	0.06	C3	0.07	C3	0.06
C4	0.08	C4	0.07	C4	0.07	C4	0.06
C5	0.04	C5	0.04	C5	0.04	C5	0.03
C6	0.15	C6	0.17	C6	0.17	C6	0.18
C1'	-0.01	C1'	-0.01	C1'	-0.01	C1'	-0.02
C2'	0.01	C2'	0.02	C2'	0.01	C2'	0.02
C3'	-0.01	C3'	-0.01	C3'	-0.01	C3'	-0.01
C4'	0.01	C4'	0.02	C4'	0.02	C4'	0.02
C5'	0.00	C5'	-0.01	C5'	0.00	C5'	-0.01
C6'	0.01	C6'	0.02	C6'	0.01	C6'	0.02
O2	0.25	O2	0.24	O2	0.24	O2	0.23
O5	0.30	O5	0.29	O5	0.30	O5	0.30
Cl1	0.00	Cl1	0.00	Cl1	0.00	Cl1	0.00
H3	-0.01	H3	-0.01	Cl2	0.00	Cl2	0.00
H4	-0.01	H4	-0.01	H3	-0.01	H3	-0.01
H6	-0.01	H6	-0.01	H4	-0.01	H4	-0.01
H3'	0.00	H2'	0.00	H6	-0.01	H6	0.00
H4'	0.00	H4'	0.00	H3'	0.00	H2'	0.00
H5'	0.00	H5'	0.00	H4'	0.00	H5'	0.00
H6'	0.00	H6'	0.00	H6'	0.00	H6'	0.00

[1] See Figure 1 for the atom numbering scheme.

Table S5: Linear polarizabilities (all units in a.u) {1 a.u = 0.148×10^{-30} m^3} of quinone and semiquinone radical anions in the syn-like conformation.

Congener	α_{xx}	α_{yy}	α_{zz}	α_{xy}	α_{yz}	α_{xz}	$\bar{\alpha}$	$\Delta\alpha$
2'-Cl-2,5-Q	191.895	138.92	96.2326	-2.81012	2.38643	-16.4952	142.349	88.01693
3'-Cl-2,5-Q	225.616	147.663	72.8103	-16.6603	1.66382	9.64476	148.696	136.5088
4-Cl-2,5-Q	244.383	144.416	69.0204	-19.2112	-6.76581	-2.66262	152.606	156.4633
2',5'-Cl-2,5-Q	205.224	158.282	102.811	-2.54029	11.2622	12.4883	155.439	93.55344
3',4'-Cl-2,5-Q	259.523	159.388	74.3489	18.3694	-1.34935	-8.75476	164.420	164.383
3,4',6-Cl-2,5-Q	246.559	185.63	91.5245	-15.3943	11.0706	2.61496	174.571	139.2878
2'-Cl-2,5-SQ	228.058	156.769	98.4028	4.03936	-7.46534	10.059	161.077	114.7576
3'-Cl-2,5-SQ	275.258	173.338	66.9607	0.592674	-0.92274	5.42974	171.852	180.6595
4-Cl-2,5-SQ	290.758	164.444	65.7119	-8.01	-3.89324	0.773213	173.638	195.9955
2',5'-Cl-2,5-SQ	248.587	176.837	105.124	-8.19884	14.8252	0.089757	176.849	127.6608
3',4'-Cl-2,5-SQ	316.362	181.701	68.7161	3.59375	-3.26268	-2.88588	188.926	214.9639
3,4',6-Cl-2,5-SQ	280.25	195.999	91.1821	-5.01103	11.5924	0.330957	189.144	165.513

Table S6: Linear polarizabilities (all units in a.u) {1 a.u = 0.148×10^{-30} m^3} of quinone and semiquinone radical anions in the anti-like conformation.

Congener	α_{xx}	α_{yy}	α_{zz}	α_{xy}	α_{yz}	α_{xz}	$\bar{\alpha}$	$\Delta\alpha$
2'-Cl-2,5-Q	195.097	149.377	86.0477	-22.8106	-2.50244	86.0477	143.507	181.0765
3'-Cl-2,5-Q	207.51	165.821	71.2827	16.7659	0.83388	-1.07335	148.205	124.3604
2',5'-Cl-2,5-Q	222.273	153.647	94.618	17.4873	6.87742	13.7552	156.846	117.7786
3',4'-Cl-2,5-Q	248.776	168.241	74.2395	-18.855	-1.91051	74.2395	163.752	201.2575
2'-Cl-2,5-SQ	238.575	167.353	86.0157	-15.3735	-7.07211	-4.88789	163.981	135.6911
3'-Cl-2,5-SQ	262.104	184.591	67.4944	14.7853	-1.03596	6.29309	171.396	171.9716
2',5'-Cl-2,5-SQ	270.532	178.05	92.2189	0.088222	13.4571	8.31371	180.267	156.8706
3',4'-Cl-2,5-SQ	308.374	187.132	69.5405	-12.1992	-3.5865	-2.94753	188.349	208.0758

Table S7: First order hyperpolarizabilities (all units in a.u) {1 a.u. = 3.206×10^{-53} C m^3 J^{-2}} of quinone and semiquinone radical anions in the syn-like conformation.

Congener	β_{xxx}	β_{yxx}	β_{xyy}	β_{yyy}	β_{zxx}	β_{xyz}	β_{xzz}	β_{zyy}	β_{yzz}	β_{zzz}	β
2'-Cl-2,5-Q	514.342	-7.262	-47.476	-103.950	5.590	24.417	-11.456	46.510	-28.166	20.148	481.709
3'-Cl-2,5-Q	-1451.880	-151.284	-34.812	72.136	-100.271	-32.446	-17.749	31.423	20.874	14.691	1506.542
4-Cl-2,5-Q	3015.000	-119.576	-46.394	28.113	-49.201	22.753	-6.469	0.083	-2.659	0.781	2964.026
2',5'-Cl-2,5-Q	378.421	-87.578	42.820	7.931	7.275	0.066	7.762	-0.851	-1.022	-2.347	436.540
3',4'-Cl-2,5-Q	-2796.640	135.453	-27.224	-85.747	136.158	-20.035	-22.269	-35.303	-18.865	-9.961	2847.751
3,4',6-Cl-2,5-Q	-2719.660	577.692	-12.308	-14.075	-47.366	28.332	32.691	-5.887	-6.150	8.962	2756.597
2'-Cl-2,5-SQ	2185.480	442.319	141.909	116.991	-171.851	18.921	25.250	57.315	27.782	19.264	2426.657
3'-Cl-2,5-SQ	2894.180	1169.520	367.542	155.703	34.739	35.286	-3.400	35.420	20.056	8.079	3525.983
4-Cl-2,5-SQ	-3367.940	-481.870	-29.054	23.124	-47.473	29.928	-5.023	0.135	-4.671	0.897	3433.749
2',5'-Cl-2,5-SQ	-3457.950	505.524	-111.548	22.473	-449.345	119.817	-38.496	-12.358	14.298	-0.490	3677.679
3',4'-Cl-2,5-SQ	4124.640	-990.582	92.882	-49.670	30.064	20.929	-17.693	-23.162	-14.282	-5.076	4330.197
3,4',6-Cl-2,5-SQ	1592.810	117.773	27.072	-6.896	-21.646	26.025	34.773	-10.721	-5.087	12.152	1658.157

Table S8: First order hyperpolarizabilities (all units in a.u) {1 a.u. = 3.206×10^{-53} C m^3 J^{-2}} of quinone and semiquinone radical anions in the anti-like conformation.

Congener	β_{xxx}	β_{yxx}	β_{yxy}/β_{xyy}	β_{yyy}	β_{zxx}	β_{xyz}	β_{zxz}	β_{zyy}	β_{zyz}	β_{zzz}	β
2'-Cl-2,5-Q	-775.940	34.670	46.220	-107.301	-41.630	27.536	15.338	-28.628	-27.014	-26.285	727.731
3'-Cl-2,5-Q	-1385.650	-301.607	-99.856	101.050	-11.514	-16.370	-3.856	24.371	18.721	16.066	1500.700
2',5'-Cl-2,5-Q	631.164	-111.216	44.564	8.278	71.201	-18.514	9.342	-8.103	-5.235	6.509	697.042
3',4'-Cl-2,5-Q	-2733.340	364.101	-65.788	-122.880	-13.708	-6.157	-13.286	-27.349	-16.148	-12.215	2821.908
2'-Cl-2,5-SQ	2716.750	279.817	67.286	-91.759	-296.945	32.069	33.356	-25.653	-20.270	-26.613	2843.906
3'-Cl-2,5-SQ	3591.710	314.407	-31.160	72.577	242.202	49.522	17.038	23.897	13.791	11.098	3610.622
2',5'-Cl-2,5-SQ	3113.870	1299.690	-519.489	185.853	216.462	-35.251	18.622	-4.920	-6.304	10.221	3010.832
3',4'-Cl-2,5-SQ	4556.930	69.573	-103.970	-79.802	-176.916	31.494	-8.610	-15.415	-7.841	-6.621	4448.837

Table S9: Octupole moments (all units in Debye Å^2) {1 Debye Å^2 = 3.336 × 10^{-50} C m^3} of quinone and semiquinone radical anions in the syn-like conformation.

Congener	**Ω_{xxx}**	**Ω_{xxy}**	**Ω_{yyz}**	**Ω_{yyy}**	**Ω_{xxz}**	**Ω_{xyz}**	**Ω_{zzz}**	**Ω_{xzz}**	**Ω_{xyy}**	**Ω_{yzz}**
2'-Cl-2,5-Q	-47.789	30.849	5.834	-0.034	28.472	-0.875	-6.814	2.887	-9.987	0.162
3'-Cl-2,5-Q	22.311	-37.447	3.584	8.230	26.168	-1.141	-3.585	-1.098	10.972	-1.930
4-Cl-2,5-Q	37.742	58.335	-0.189	-2.860	9.689	3.240	0.139	0.475	-32.208	0.096
2',5'-Cl-2,5-Q	12.312	48.528	5.250	10.351	32.826	-13.321	-3.266	-3.094	-22.989	-0.990
3',4'-Cl-2,5-Q	-2.235	64.993	-2.172	-6.959	-25.696	-6.190	2.337	4.164	22.591	1.062
3,4',6-Cl-2,5-Q	-62.916	-18.217	-1.583	-8.417	3.664	9.500	-0.027	3.038	28.596	-0.358
2'-Cl-2,5-SQ	122.405	-54.638	1.997	-2.090	34.372	-15.085	-10.153	7.730	22.352	1.980
3'-Cl-2,5-SQ	132.040	-49.910	-0.394	18.136	28.702	-8.413	-3.202	2.720	29.315	-3.441
4-Cl-2,5-SQ	-57.115	79.342	0.010	-9.818	10.036	-3.098	-0.302	-2.968	-69.796	-0.077
2',5'-Cl-2,5-SQ	-76.018	91.052	10.272	24.712	26.522	-30.979	-7.900	-21.317	-49.413	-1.362
3',4'-Cl-2,5-SQ	172.143	90.257	-0.466	-15.604	-24.498	-13.641	2.183	9.990	54.208	1.926
3,4',6-Cl-2,5-SQ	-24.323	-10.229	-0.117	-19.431	0.453	5.900	-0.207	3.985	73.845	-0.337

Table S10: Octupole moments (all units in Debye Å^2) {1 Debye Å^2 = 3.336 × 10^{-50} C m^3} of quinone and semiquinone radical anions in the anti-like conformation.

Congener	Ω_{xxx}	Ω_{xxy}	Ω_{yyz}	Ω_{yyy}	Ω_{xxz}	Ω_{xyz}	Ω_{zzz}	Ω_{xzz}	Ω_{xyy}	Ω_{yzz}
2'-Cl-2,5-Q	34.0625	-36.1602	-6.6529	5.2663	20.5239	-0.9428	5.5451	-3.2399	11.0124	0.5772
3'-Cl-2,5-Q	-31.974	52.281	5.208	8.756	-8.897	-2.917	-4.194	-3.404	37.869	-2.071
2',5'-Cl-2,5-Q	-24.098	-11.460	3.698	1.159	-43.837	1.457	-0.773	-5.335	3.389	1.532
3',4'-Cl-2,5-Q	-41.538	-54.714	-3.962	-3.654	21.100	-7.708	2.350	2.932	39.382	1.683
2'-Cl-2,5-SQ	91.450	-40.932	-10.043	19.846	28.567	-14.742	6.111	4.146	29.044	2.798
3'-Cl-2,5-SQ	44.095	68.815	2.316	9.879	-4.212	-11.491	-3.011	1.132	71.944	-3.607
2',5'-Cl-2,5-SQ	-131.913	1.821	14.015	16.736	-62.401	-9.580	-1.213	-18.257	-9.371	5.556
3',4'-Cl-2,5-SQ	107.741	-71.260	-2.784	-0.076	16.777	-16.261	1.489	9.427	81.441	2.576

Table S11: Properties of PCB congeners in the syn-like conformation, calculated at the UB3LPY / 6-311++G** level of theory.

Linear Polarizabilities (a.u. = 0.148 × 10^{-30} m^3)

Congener	α_{xx}	α_{yy}	α_{zz}	α_{xy}	α_{yz}	α_{xz}	$\bar{\alpha}$	$\Delta\alpha$
2'-Cl-2,5-Q	205.874	152.046	115.398	-5.43988	-17.8695	5.2306	157.77	85.686
2',5'-Cl-2,5-Q	218.607	172.784	124.806	-5.80916	13.5012	-13.8382	172.07	88.446
2'-Cl-2,5-SQ	244.665	175.577	129.559	-1.50709	-11.7648	14.2753	183.27	105.373
2',5'-Cl-2,5-SQ	260.724	196.382	139.667	-11.8429	19.0313	-4.76156	198.92	112.165

First order hyperpolarizabilities (a.u. = 3.206 × 10^{-53} C m^3 J^{-2})

Congener	β_{xxx}	β_{yxx}	β_{xyy}	β_{yyy}	β_{zxx}	β_{xyz}	β_{xzz}	β_{zyy}	β_{yzz}	β_{zzz}	β
2'-Cl-2,5-Q	627.681	-26.6319	-61.6763	-115.556	-11.546	2.36186	-41.632	33.186	-36.9498	56.5939	559.6
2',5'-Cl-2,5-Q	460.048	-121.211	71.3835	-0.450389	-20.1325	-12.5064	-11.3003	-0.0368342	6.77094	-1.97266	533.1
2'-Cl-2,5-SQ	1554.49	366.382	149.814	133.177	-133.486	-2.86043	66.9646	30.5581	36.3101	71.8327	1850.8
2',5'-Cl-2,5-SQ	-2454.19	325.161	-44.7145	30.3732	-353.889	82.2029	-38.1504	-3.2391	29.3877	15.7668	2588.7

Octupole moments (Debye $Å^2$ = 3.336 × 10^{-50} C m^3)

Congener	Ω_{xxx}	Ω_{xxy}	Ω_{yyz}	Ω_{yyy}	Ω_{xxz}	Ω_{xyz}	Ω_{zzz}	Ω_{xzz}	Ω_{xyy}	Ω_{yzz}
2'-Cl-2,5-Q	-47.789	30.849	5.834	-0.034	28.472	-0.875	-6.814	2.887	-9.987	0.162
2',5'-Cl-2,5-Q	12.312	48.528	5.250	10.351	32.826	-13.321	-3.266	-3.094	-22.989	-0.990
2'-Cl-2,5-SQ	122.405	-54.638	1.997	-2.090	34.372	-15.085	-10.153	7.730	22.352	1.980
2',5'-Cl-2,5-SQ	-76.018	91.052	10.272	24.712	26.522	-30.979	-7.900	-21.317	-49.413	-1.362

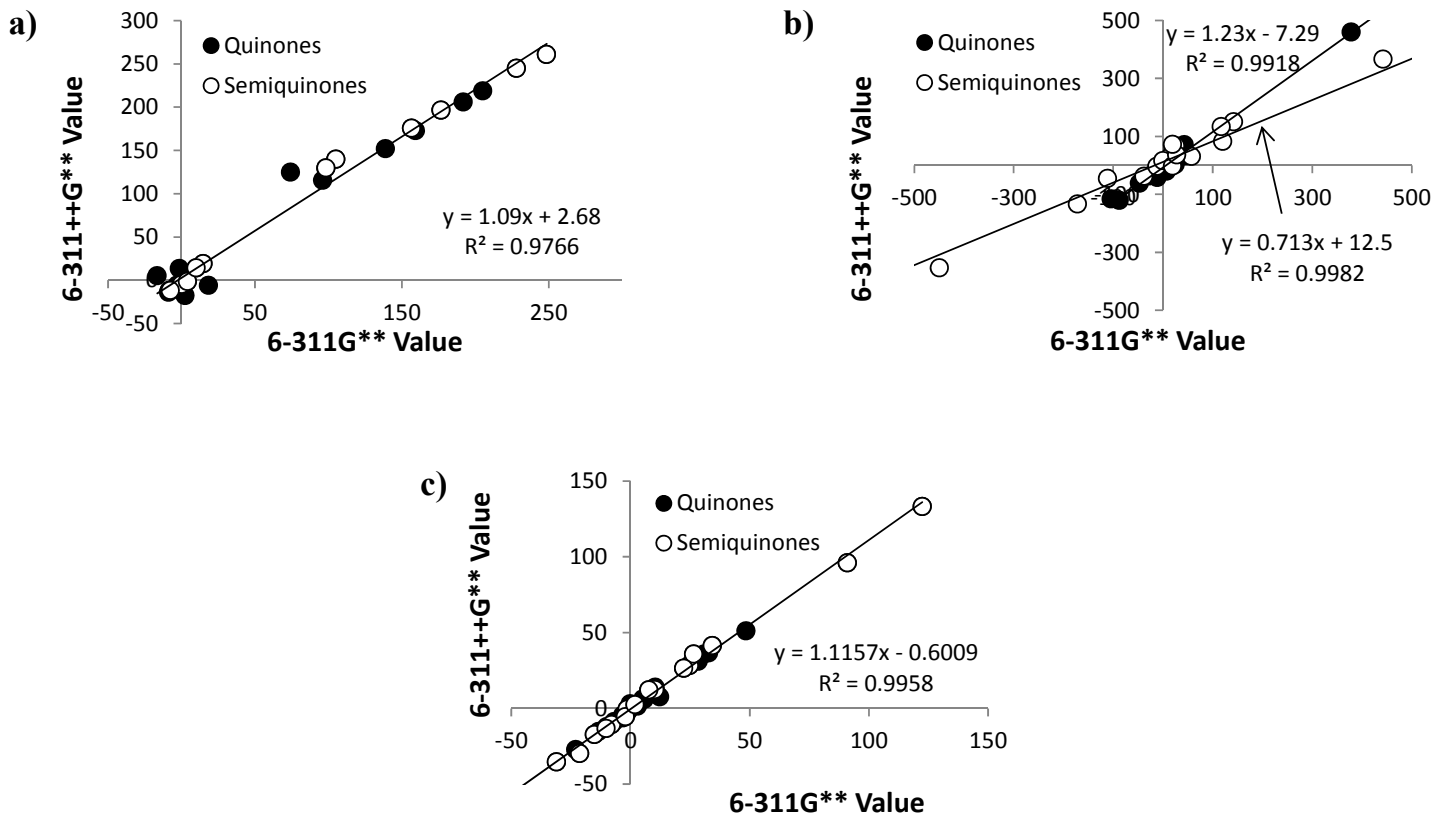

Figure S1. Comparison of (a) polarizabilities, (b) first-order hyperpolarizabilities, and (c) octupole moment values calculated using the UB3LYP method and either the 6-311G** basis set or the 6-311++G** basis set. Lines are best fits to either all of the data (parts a and c) or individual fits to quinone and semiquinone values (part b).