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BELONGING TO THE PAPER

AB INITIO CALCULATIONS ON *2,6*-DIMETHYLPHENOL AND *4*-(*2'*,*6'*-DIMETHYLPHENOXY)-*2,6*-DIMETHYLPHENOL. EVIDENCE FOR AN IMPORTANT ROLE OF THE PHENOXONIUM CATION IN THE COPPER CATALYSED OXIDATIVE PHENOL COUPLING REACTION

by

Patrick J. Baesjou, Willem L. Driessen, Ger Challa and Jan Reedijk.

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Table S1 - Calculated Carthesian coordinates for *2,6*-dimethylphenol.

	x	y	z
O1	-2.0049524	-0.0211942	-0.1275564
C2	-0.6502795	-0.0069898	-0.0235410
C3	2.1087183	0.0225717	0.0519295
C4	-0.0084724	-0.0069898	1.2100777
C5	0.0577472	0.0075618	-1.2235336
C6	1.4410233	0.0222002	-1.1627745
C7	1.3813233	0.0081019	1.2254812
C8	-0.8040542	-0.0228528	2.4963803
C9	-0.6862038	0.0069599	-2.5364671
H10	2.0035109	0.0335595	-2.0800225
H11	1.8929630	0.0083755	2.1721582
H12	3.1833240	0.0340561	0.0800189
H13	-2.4143568	-0.0310483	0.7244534
H14	-1.4299301	-0.9094105	2.5776380
H15	-1.4493830	0.8486807	2.5872217
H16	-0.1432958	-0.0202441	3.3539358
H17	-1.3154839	-0.8718316	-2.6307919
H18	0.0079193	0.0193252	-3.3687379
H19	-1.3345719	0.8728122	-2.6207909

Table S2 - Calculated Carthesian coordinates for *2,6*-dimethylphenolate anion.

	x	y	z
O1	-2.0184514	-0.0090895	-0.0496734
C2	-0.7671293	-0.0033292	-0.0188779
C3	2.0966390	0.0097813	0.0515988
C4	-0.0329003	-0.0070695	1.2172883
C5	0.0269591	0.0074977	-1.2174375
C6	1.4037830	0.0136144	-1.1561248
C7	1.3452774	-0.0005956	1.2237818
C8	-0.8398870	-0.0184593	2.4904436
C9	-0.7164848	0.0113587	-2.5287380
H10	1.9636101	0.0216772	-2.0819092
H11	1.8589378	-0.0037190	2.1759862
H12	3.1739154	0.0147836	0.0781096
H13	-1.3700135	0.8772071	-2.6112162
H14	-1.4881453	-0.8907138	2.5409061
H15	-1.4973608	0.8462356	2.5505690
H16	-0.1975439	-0.0199896	3.3703668
H17	-1.3616792	-0.8597466	-2.6208766
H18	-0.0316903	0.0193681	-3.3760159

Table S3 - Calculated Carthesian coordinates for *2,6*-dimethylphenoxy radical.

	x	y	z
O1	-1.9850753	-0.0090282	-0.0488038
C2	-0.7385962	-0.0033678	-0.0181533
C3	2.0716425	0.0093609	0.0509176
C4	-0.0420264	-0.0074316	1.2558920
C5	0.0196743	0.0072614	-1.2564398
C6	1.4057200	0.0135106	-1.1888508
C7	1.3456675	-0.0010131	1.2564773
C8	-0.8549482	-0.0186110	2.5230292
C9	-0.7300731	0.0115389	-2.5619646
H10	1.9826441	0.0215438	-2.0966602
H11	1.8773510	-0.0039834	2.1915320
H12	3.1463026	0.0142248	0.0773446
H13	-1.3730712	0.8815733	-2.6384421
H14	-1.4937517	-0.8939346	2.5677086
H15	-1.5022730	0.8498575	2.5776255
H16	-0.2094694	-0.0204169	3.3934949
H17	-1.3667754	-0.8622263	-2.6477464
H18	-0.0426603	0.0185502	-3.3996753

Table S4 - Calculated Carthesian coordinates for *2,6*-dimethylphenoxonium cation (singlet state).

	x	y	z
O1	-1.9332963	-0.0083900	-0.0476816
C2	-0.7487765	-0.0032046	-0.0184602
C3	2.0097899	0.0090592	0.0495333
C4	-0.0218036	-0.0078967	1.3090025
C5	0.0426756	0.0078724	-1.3084892
C6	1.3912937	0.0137528	-1.2230883
C7	1.3293739	-0.0013699	1.2901554
C8	-0.8544473	-0.0188986	2.5449331
C9	-0.7281112	0.0112933	-2.5839431
H10	2.0082514	0.0215629	-2.1009436
H11	1.9023843	-0.0040341	2.1973403
H12	3.0859173	0.0137793	0.0760644
H13	-1.3771596	0.8800349	-2.6212834
H14	-1.4967000	-0.8934572	2.5502017
H15	-1.5053887	0.8490956	2.5597822
H16	-0.2348549	-0.0206878	3.4298121
H17	-1.3697134	-0.8625251	-2.6303604
H18	-0.0657243	0.0186148	-3.4372397

Table S5 - Calculated Carthesian coordinates for *2,6*-dimethylphenoxonium cation (triplet state).

	x	y	z
O1	-2.0526172	-0.0081473	-0.0492555
C2	-0.7783533	-0.0033528	-0.0186894
C3	2.0864889	0.0073221	0.0500138
C4	-0.0869271	-0.0564267	1.2286589
C5	-0.0283131	0.0552215	-1.2314694
C6	1.4125649	0.0587053	-1.1520710
C7	1.3561151	-0.0489940	1.2184431
C8	-0.8129974	-0.1192107	2.5341643
C9	-0.6914171	0.1138812	-2.5702322
H10	1.9654248	0.1032732	-2.0734965
H11	1.8644896	-0.0894052	2.1653236
H12	3.1588216	0.0113000	0.0757396
H13	-0.3928347	1.0214547	-3.0878971
H14	-0.5264003	-1.0195475	3.0707204
H15	-1.8814546	-0.1160928	2.3918930
H16	-0.5319548	0.7292640	3.1519497
H17	-1.7653390	0.0946844	-2.4797427
H18	-0.3681670	-0.7267876	-3.1778597

Table S6 - Calculated Carthesian coordinates for *4-(2',6'*-dimethylphenoxy)-*2,6*-dimethylphenol.

	x	y	z
O1	-4.2482191	0.2586023	1.2133021
C2	-2.9002461	0.1990275	1.0215500
C3	-0.1511187	0.0935006	0.7771750
C4	-2.1084135	0.3041809	2.1659605
C5	-2.3341348	0.0433410	-0.2308812
C6	-0.9439108	-0.0089423	-0.3445163
C7	-0.7368734	0.2495176	2.0262247
C8	-2.7588607	0.4733339	3.5165174
C9	-3.2034369	-0.0691734	-1.4637860
H10	-0.5003582	-0.1297597	-1.3144049
H11	-0.0975874	0.3273250	2.8862868
O12	1.2151635	0.0534861	0.7647634
H13	-3.8174011	0.8173877	-1.6080411
H14	-3.4145995	-0.3613767	3.7400523
H15	-3.3659491	1.3717975	3.5463537
H16	-2.0105456	0.5395330	4.2970377
H17	-3.8678732	-0.9292075	-1.4130191
H18	-2.5970869	-0.1859288	-2.3526378
C19	1.9059447	-0.1007554	-0.4121510
C20	3.3917889	-0.4048691	-2.7031647
C21	2.3109508	1.0364294	-1.1005542
C22	2.2403665	-1.3848779	-0.8248233
C23	2.9887799	-1.5179911	-1.9870881
C24	3.0581346	0.8619239	-2.2581088
C25	1.9559441	2.4114351	-0.5877764
C26	1.8102368	-2.5869055	-0.0186684
H27	3.2615488	-2.5012835	-2.3276436
H28	3.3847127	1.7262571	-2.8090053
H29	3.9731925	-0.5239535	-3.6000448
H30	2.2467577	-3.4923954	-0.4230561
H31	0.7313582	-2.7036505	-0.0232830
H32	2.1189204	-2.4912705	1.0161332
H33	2.4396321	3.1764048	-1.1834320
H34	2.2670466	2.5336314	0.4434957
H35	0.8853897	2.5852047	-0.6237877
H36	-4.7135714	0.1812435	0.3942693

Table S7 - Calculated Carthesian coordinates for *4*-(*2'*,*6'*-dimethylphenoxy)-*2*,*6*-dimethylphenolate anion.

	x	y	z
O1	-4.2454237	-0.2194987	1.1842270
C2	-3.0164616	-0.0257184	1.0372041
C3	-0.2233754	0.4017854	0.7039870
C4	-2.1005703	-0.0544880	2.1426380
C5	-2.4304466	0.2387224	-0.2446285
C6	-1.0721635	0.4528769	-0.3879381
C7	-0.7488503	0.1516388	1.9595154
C8	-2.6825664	-0.3243095	3.5057208
C9	-3.3638711	0.2788160	-1.4269141
H10	-0.6684933	0.6517101	-1.3683195
H11	-0.0762785	0.1249553	2.8026574
O12	1.1572469	0.6575423	0.6089460
H13	-4.1303625	1.0389378	-1.2959630
H14	-3.1972121	-1.2818440	3.5299399
H15	-3.4271905	0.4230493	3.7685886
H16	-1.9136002	-0.3281058	4.2763373
H17	-3.8931871	-0.6642173	-1.5409778
H18	-2.8303498	0.4860083	-2.3530315
C19	1.8622848	0.1635405	-0.4369391
C20	3.4291164	-0.7291508	-2.5396897
C21	2.4316844	1.0881659	-1.3116482
C22	2.0821479	-1.2062926	-0.5886083
C23	2.8661506	-1.6304479	-1.6536816
C24	3.2143951	0.6253300	-2.3599762
C25	2.1928917	2.5633251	-1.0952788
C26	1.5020021	-2.2017859	0.3867706
H27	3.0425778	-2.6850069	-1.7823592
H28	3.6537514	1.3336998	-3.0419264
H29	4.0343448	-1.0796122	-3.3579543
H30	1.9571582	-3.1769934	0.2438698
H31	0.4299738	-2.2994731	0.2643750
H32	1.6756895	-1.8889760	1.4097193
H33	2.6513833	3.1462741	-1.8879676
H34	2.6071431	2.8911613	-0.1474449
H35	1.1332912	2.7895925	-1.0706150

Table S8 - Calculated Carthesian coordinates for *4-(2′,6′*-dimethylphenoxy)-*2,6*-dimethylphenoxy radical.

	x	y	z
O1	-4.2375666	0.2251850	1.1088895
C2	-2.9957466	0.1856427	1.0106112
C3	-0.1971899	0.0958214	0.7806456
C4	-2.1623630	0.2970403	2.1924477
C5	-2.3698300	0.0278738	-0.2865711
C6	-0.9847607	-0.0136542	-0.3752563
C7	-0.7893705	0.2495387	2.0489047
C8	-2.8272928	0.4603308	3.5331808
C9	-3.2506044	-0.0861539	-1.5026556
H10	-0.5157442	-0.1302686	-1.3336195
H11	-0.1404229	0.3287833	2.9016166
O12	1.1623210	0.0646902	0.7798823
H13	-3.8740897	0.7942388	-1.6139180
H14	-3.4806125	-0.3785106	3.7467986
H15	-3.4407192	1.3543898	3.5554774
H16	-2.0888214	0.5305275	4.3228019
H17	-3.9165839	-0.9381278	-1.4204990
H18	-2.6554262	-0.2009301	-2.4007294
C19	1.8725588	-0.0834528	-0.3895012
C20	3.4007385	-0.3757223	-2.6721216
C21	2.2818957	1.0670387	-1.0722922
C22	2.2228218	-1.3745234	-0.7991876
C23	2.9928308	-1.5007352	-1.9587791
C24	3.0508409	0.8971931	-2.2269893
C25	1.9098442	2.4384835	-0.5632351
C26	1.7884133	-2.5804578	-0.0019367
H27	3.2768637	-2.4811990	-2.2976295
H28	3.3794958	1.7639130	-2.7724557
H29	3.9946891	-0.4895414	-3.5611216
H30	2.2537964	-3.4793011	-0.3882362
H31	0.7124061	-2.7197450	-0.0422802
H32	2.0615291	-2.4772349	1.0421215
H33	2.4143729	3.2066340	-1.1368695
H34	2.1847119	2.5557541	0.4788619
H35	0.8413386	2.6160076	-0.6376112

Table S9 - Calculated Carthesian coordinates for *4-(2',6'*-dimethylphenoxy)-*2,6*-dimethylphenoxonium cation (singlet state).

	x	y	z
O1	-4.1549112	0.2522232	1.1650594
C2	-2.9756029	0.2051284	1.0516527
C3	-0.2014501	0.0908476	0.7580311
C4	-2.0811114	0.3151256	2.2589771
C5	-2.3516507	0.0330230	-0.3140370
C6	-1.0194646	-0.0188117	-0.4254925
C7	-0.7603760	0.2564322	2.0822996
C8	-2.7484720	0.4846226	3.5871557
C9	-3.2900865	-0.0700427	-1.4736170
H10	-0.5341578	-0.1398795	-1.3732806
H11	-0.0591256	0.3272145	2.8915416
O12	1.0639230	0.0504898	0.7259352
H13	-3.9077169	0.8191774	-1.5308809
H14	-3.4099857	-0.3521141	3.7808982
H15	-3.3594423	1.3801461	3.5852021
H16	-2.0171772	0.5528421	4.3800004
H17	-3.9592434	-0.9118018	-1.3352763
H18	-2.7485926	-0.1909140	-2.4010245
C19	1.8424542	-0.1056321	-0.4602815
C20	3.4224398	-0.3962738	-2.6369553
C21	2.2605278	1.0503070	-1.0960035
C22	2.1903307	-1.3957663	-0.8202950
C23	2.9954840	-1.5168475	-1.9456730
C24	3.0640197	0.8723038	-2.2149630
C25	1.8807426	2.4251375	-0.5979905
C26	1.7364377	-2.6017094	-0.0314705
H27	3.2966013	-2.4949741	-2.2723260
H28	3.4178704	1.7346158	-2.7490767
H29	4.0491531	-0.5117131	-3.5017190
H30	2.2352523	-3.4916356	-0.3895915
H31	0.6670138	-2.7693185	-0.1279675
H32	1.9644746	-2.4927268	1.0229056
H33	2.4255998	3.1834967	-1.1429668
H34	2.1105137	2.5411305	0.4552721
H35	0.8216207	2.6267218	-0.7346141

Table S10 - Calculated Carthesian coordinates for *4*-(*2'*,*6'*-dimethylphenoxy)-*2*,*6*-dimethylphenoxonium cation (triplet state).

	x	y	z
O1	-4.1225720	-0.6060411	1.6680130
C2	-3.0092444	-0.2618313	1.2134717
C3	-0.5418161	0.4555312	0.2072069
C4	-1.8996969	-0.0386163	2.1220820
C5	-2.8413766	-0.0804407	-0.2166592
C6	-1.5921521	0.2906275	-0.6991055
C7	-0.6694279	0.3318553	1.5928939
C8	-2.1220387	-0.2029850	3.6015088
C9	-4.0246970	-0.2869251	-1.1236128
H10	-1.4276655	0.4579827	-1.7477645
H11	0.1734440	0.5295569	2.2293667
O12	0.6833475	0.9381456	-0.2948050
H13	-4.8290103	0.3906388	-0.8627019
H14	-2.4515565	-1.2094761	3.8310670
H15	-2.8935800	0.4734836	3.9495176
H16	-1.2130467	-0.0019936	4.1545211
H17	-4.4113811	-1.2946675	-1.0276071
H18	-3.7539727	-0.1173013	-2.1582514
C19	1.7289578	0.3221820	-0.7011590
C20	4.1413635	-0.6745175	-1.6442561
C21	2.7697078	1.2452883	-1.1352483
C22	1.9104569	-1.1202555	-0.7461482
C23	3.1241445	-1.5564485	-1.2216424
C24	3.9510170	0.7181389	-1.5958543
C25	2.5101489	2.7258780	-1.0608867
C26	0.8702897	-2.1273014	-0.3131364
H27	3.3068294	-2.6128636	-1.2741558
H28	4.7351322	1.3745375	-1.9215680
H29	5.0687123	-1.0761762	-2.0062394
H30	1.2699105	-3.1216493	-0.4549653
H31	-0.0379944	-2.0476686	-0.8954051
H32	0.6110286	-2.0188127	0.7315396
H33	3.3733168	3.2685584	-1.4194917
H34	2.3065689	3.0354583	-0.0422809
H35	1.6532937	3.0025425	-1.6642048

Table S11 - Calculated (UHF; 6-31G* basis) energies in hartree of *2,6*-dimethylphenol (monomer DMP) and *4-(2',6'*-dimethylphenoxy)-*2,6*-dimethylphenol (dimer DMP), as phenol, phenolate anion, phenoxy radical and phenoxonium cation (both singlet and triplet state). The overall spin state is given between brackets.

	monomer DMP	dimer DMP
phenol (S=0)	-383.631575	-766.099759
anion (S=0)	-383.046186	-765.516768
radical ($S=^1/_2$)	-383.053089	-765.526165
cation (S=0)	-382.768448	-765.280205
cation (S=1)	-382.762098	-765.272832