Electronic Supplementary Material (ESI) for Photochemical & Photobiological Sciences

Computational and Experimental Evidence for the First Direct Spectroscopic Detection of the Pyrylogen Neutral Redox Partner

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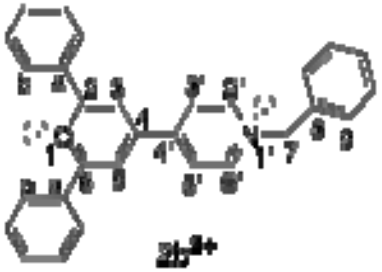
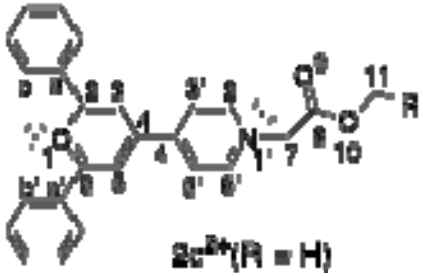
Supplementary Material



$2b^{2+}$



$2c^{2+}$(R = H)

Table. Computational and X-Ray Structural Parameters for Pyrylogen Dications.

	$\mathbf{2b}^{2+a}$	$\mathbf{2b}^{2+b}$	$\mathbf{2b}^{2+c}$	$\mathbf{2b}^{2+}$(X-Ray)	$\mathbf{2c}^{2+a}$ #1	$\mathbf{2c}^{2+b}$ #2	$\mathbf{2c}^{2+c}$ #2	$\mathbf{2c}^{2+}$(X-Ray)
E(a.u.)	-1248.39465653	-1248.72084769	-1244.39702827		-1245.19991910	-1245.20789247	-1241.32981259	
d_{12}	1.354Å	1.349Å	1.354Å	1.344Å	1.354Å	1.354Å	1.354Å	1.349Å
d_{16}	1.354Å	1.349Å	1.354Å	1.346 Å	1.354Å	1.354Å	1.354Å	1.345Å
$d_{44'}$	1.487Å	1.485Å	1.478Å	1.486Å	1.487Å	1.487Å	1.479Å	1.485Å
$d_{1'2'}$	1.348Å	1.343Å	1.352Å	1.348Å	1.355Å	1.355Å	1.355Å	1.344Å
$d_{1'6'}$	1.353Å	1.349Å	1.354Å	1.344Å	1.355Å	1.355Å	1.354Å	1.341Å
d_{2a}	1.446Å	1.445Å	1.444Å	1.459Å	1.446Å	1.446Å	1.443Å	1.459Å
$d_{6a'}$	1.446Å	1.445Å	1.444Å	1.459Å	1.445Å	1.446Å	1.444Å	1.455Å
>216	124.76°	124.44°	124.31°	123.08°	124.80°	124.78°	124.37°	123.44°
>2'1'6'	120.33°	120.27°	121.14°	121.22°	120.32°	120.49°	121.41°	121.25°
>344'3'	40.54°	41.61°	46.10°	33.86°	40.38°	41.45°	46.70°	40.29°
>12ab	-15.68°	16.68°	-23.92°	-9.76°	-15.70°	-15.67°	-23.60°	2.76°
>16a'b'	-15.46°	16.86°	-23.88°	14.74°	-15.72°	-16.23°	-23.88°	-3.48°
>3'2'N7	178.55°	178.62°	177.98°	178.78°	178.51°	176.88°	176.06°	174.30°
>1'789	95.25°	95.04°	97.83°	124.10°	153.89°	18.53°	15.51°	1.65°
>981011					0.76°	1.71°	1.50°	-4.41°
>2'1'78	14.14°	12.41°	23.39°	61.54°	98.32°	62.31°	66.60°	92.91°

a. B3LYP/6-31G(d). b. B3LYP/6-311+G(2d,p). c. MP2/6-31G(d).

2b^{2+} B3LYP/6-31G(d)

Geometry

C	-2.111365	0.581275	0.476129	C	-0.768049	0.578873	0.875000	C	0.030210	1.690737	0.623565
C	-1.810120	2.792786	-0.450463	C	-2.632394	1.701738	-0.184567	C	-2.977141	-0.596754	0.750367
C	-2.497247	-1.905580	0.597290	C	-3.325893	-2.987912	0.855661	C	-5.089512	-1.552723	1.422194
C	-4.309025	-0.438902	1.173083	H	-0.338456	-0.272202	1.385962	H	-3.665500	1.732601	-0.503490
H	-1.488195	-2.100618	0.251320	H	-3.005777	-4.017015	0.745092	H	-6.117848	-1.478218	1.758274
H	-4.738081	0.542963	1.339535	O	-0.524563	2.738519	-0.029897	C	-2.174094	4.021088	-1.121465
C	-3.363455	4.092919	-1.884112	C	-1.349307	5.165305	-1.018086	C	-3.712529	5.274509	-2.521947
H	-3.995983	3.220156	-2.010078	C	-1.712295	6.344264	-1.653945	H	-0.445601	5.130882	-0.420481
C	-2.891338	6.402438	-2.406389	H	-4.619203	5.319739	-3.116354	H	-1.082083	7.222805	-1.561520
H	-3.170137	7.326442	-2.903724	C	1.425241	1.862808	0.964281	C	2.038923	1.012424	1.913674
C	2.192487	2.878064	0.347337	C	3.379034	1.176872	2.233114	H	1.464399	0.249051	2.428205
C	3.534235	3.028234	0.668605	H	1.740387	3.523335	-0.397139	C	4.129902	2.181164	1.610494
H	3.841290	0.530481	2.971975	H	4.121703	3.801009	0.183589	H	5.179332	2.303968	1.860460
N	-4.598300	-2.803356	1.260970	C	-5.540091	-3.990606	1.519848	H	-6.057296	-3.733639	2.447445
H	-6.259848	-3.961126	0.696963	C	-4.851939	-5.318466	1.613005	C	-4.760624	-6.146374	0.482837
C	-4.320551	-5.754515	2.837557	C	-4.141044	-7.392679	0.576301	H	-5.193706	-5.827958	-0.463000
C	-3.702524	-7.000406	2.927127	H	-4.409546	-5.130580	3.724245	C	-3.612031	-7.818350	1.797049
H	-4.085704	-8.035587	-0.296603	H	-3.306723	-7.340340	3.879089	H	-3.140767	-8.793668	1.871687

Zero-point correction= 0.442895 (Hartree/Particle)
Thermal correction to Energy= 0.467484
Thermal correction to Enthalpy= 0.468428
Thermal correction to Gibbs Free Energy= 0.384423
Sum of electronic and zero-point Energies= -1247.951762

2b^{2+} B3LYP/6-311+G(2d,p)

Geometry and energies

C	-2.102543	0.585726	0.493074	C	-0.767313	0.592939	0.900102	C	0.027166	1.697886	0.637576
C	-1.802216	2.779092	-0.451702	C	-2.619229	1.692116	-0.183341	C	-2.966234	-0.589427	0.775170
C	-2.490495	-1.893374	0.621608	C	-3.316558	-2.970269	0.884871	C	-5.067128	-1.537328	1.459627
C	-4.289822	-0.429512	1.205497	H	-0.337677	-0.247804	1.422109	H	-3.647437	1.718959	-0.508949
H	-1.485983	-2.090962	0.272333	H	-2.995890	-3.996877	0.774620	H	-6.090412	-1.459024	1.802186
H	-4.716505	0.550341	1.372369	O	-0.522132	2.736167	-0.026893	C	-2.172960	3.997859	-1.132798
C	-3.341798	4.046267	-1.918393	C	-1.377486	5.154296	-1.012608	C	-3.698336	5.215610	-2.563932
H	-3.953749	3.164422	-2.056440	C	-1.748928	6.321739	-1.654212	H	-0.488602	5.140118	-0.397311
C	-2.906538	6.355778	-2.430985	H	-4.589028	5.242338	-3.178159	H	-1.141503	7.211185	-1.547584
H	-3.191826	7.271498	-2.933843	C	1.420581	1.868051	0.978670	C	2.023341	1.039727	1.946280
C	2.196097	2.855473	0.339660	C	3.359452	1.199513	2.263448	H	1.444093	0.295402	2.476814
C	3.534283	2.999960	0.657178	H	1.754180	3.485469	-0.419703	C	4.118258	2.175812	1.618478
H	3.813468	0.570501	3.018101	H	4.129024	3.751221	0.153860	H	5.165803	2.294653	1.866151
N	-4.581347	-2.784862	1.296198	C	-5.523355	-3.965956	1.563399	H	-6.009612	-3.723884	2.508004
H	-6.265448	-3.919691	0.765679	C	-4.846955	-5.298693	1.613993	C	-4.792675	-6.104478	0.472759
C	-4.292192	-5.760626	2.811861	C	-4.180547	-7.351527	0.526721	H	-5.247537	-5.769150	-0.453432
C	-3.680809	-7.006931	2.862756	H	-4.356875	-5.157420	3.711429	C	-3.623096	-7.800864	1.720053
H	-4.153076	-7.977631	-0.356094	H	-3.265617	-7.366645	3.795696	H	-3.157015	-8.777307	1.764118

Zero-point correction= 0.440082 (Hartree/Particle)
Thermal correction to Energy= 0.464698
Thermal correction to Enthalpy= 0.465642
Thermal correction to Gibbs Free Energy= 0.381502
Sum of electronic and zero-point Energies= -1248.280766

2b^{2+} MP2/6-31G(d)

Geometry

C	-2.142792	0.558464	0.461722	C	-0.797016	0.532745	0.844680	C	0.005659	1.645143	0.610357
C	-1.825730	2.774087	-0.438391	C	-2.660727	1.692682	-0.173578	C	-3.013250	-0.606945	0.725773
C	-2.585173	-1.910332	0.435235	C	-3.416163	-2.992679	0.691539	C	-5.090262	-1.551700	1.514633
C	-4.293517	-0.442042	1.275978	H	-0.362492	-0.335627	1.329393	H	-3.702296	1.748320	-0.473360
H	-1.614413	-2.098474	-0.015942	H	-3.141074	-4.022523	0.487280	H	-6.084403	-1.480511	1.945674
H	-4.671802	0.539415	1.549546	O	-0.537969	2.707890	-0.027366	C	-2.177041	4.012523	-1.092052
C	-3.269077	4.046831	-1.983454	C	-1.433231	5.181831	-0.829507	C	-3.609421	5.244887	-2.602763
H	-3.813780	3.139582	-2.234994	C	-1.792963	6.372131	-1.452378	H	-0.605441	5.160094	-0.125872
C	-2.878130	6.407788	-2.335804	H	-4.439346	5.273230	-3.303112	H	-1.232556	7.279129	-1.243907
H	-3.151505	7.341619	-2.819876	C	1.400730	1.805295	0.946312	C	1.955874	1.053758	2.002326
C	2.201832	2.704933	0.212667	C	3.302578	1.205187	2.315724	H	1.334261	0.399389	2.609351
C	3.548062	2.837506	0.535679	H	1.779034	3.267849	-0.615087	C	4.100679	2.090489	1.582491
H	3.731386	0.641256	3.139238	H	4.173476	3.518768	-0.034325	H	5.153083	2.201565	1.829889
N	-4.643641	-2.796813	1.223480	C	-5.579202	-3.977083	1.464991	H	-6.129273	-3.723379	2.375203
H	-6.272133	-3.979742	0.617601	C	-4.846090	-5.269089	1.598202	C	-4.733131	-6.129214	0.495572
C	-4.261615	-5.617885	2.825380	C	-4.042673	-7.335867	0.623565	H	-5.212153	-5.875021	-0.449327
C	-3.572940	-6.823896	2.946678	H	-4.370202	-4.964676	3.690422	C	-3.460033	-7.680026	1.846111
H	-3.971050	-8.011361	-0.224409	H	-3.136565	-7.104742	3.901279	H	-2.933125	-8.624881	1.947604

Zero-point correction= 0.443039 (Hartree/Particle)
Thermal correction to Energy= 0.468241
Thermal correction to Enthalpy= 0.469185
Thermal correction to Gibbs Free Energy= 0.383822
Sum of electronic and zero-point Energies= -1243.953989

2c^{2+} B3LYP/6-31G(d) Isomer #1

Geometry

C	-2.075689	0.421927	-0.004070	C	-0.694391	0.331642	0.214034	C	0.081053	1.487879	0.224588

C	-1.862214	2.817727	-0.237505	C	-2.659841	1.676622	-0.223202	C	-2.915435	-0.805396	-0.006153
C	-2.467602	-1.992794	-0.608982	C	-3.274658	-3.116333	-0.612381	C	-4.952341	-1.972136	0.570477
C	-4.187947	-0.819798	0.590195	H	-0.215031	-0.622817	0.385010	H	-3.723112	1.777816	-0.394200
H	-1.507203	-2.046609	-1.109383	H	-2.973580	-4.046288	-1.080461	H	-5.929032	-2.032752	1.033937
H	-4.585655	0.053693	1.094627	O	-0.536189	2.670410	-0.006985	C	-2.289573	4.181580	-0.453218
C	-3.557974	4.452080	-1.019374	C	-1.447351	5.260504	-0.095937	C	-3.965919	5.762583	-1.220885
H	-4.208517	3.643307	-1.336245	C	-1.869449	6.567416	-0.294071	H	-0.481784	5.068338	0.357626
C	-3.125988	6.822035	-0.856592	H	-4.933652	5.964260	-1.668342	H	-1.224844	7.391823	-0.007105
H	-3.450885	7.846287	-1.012229	C	1.507828	1.582554	0.436280	C	2.219722	0.498004	1.001331
C	2.208892	2.756853	0.074990	C	3.589916	0.590414	1.197577	H	1.701233	-0.400369	1.320610
C	3.580843	2.834927	0.268206	H	1.679674	3.587244	-0.378222	C	4.273669	1.755558	0.829461
H	4.128849	-0.239017	1.643661	H	4.116135	3.733104	-0.022067	H	5.346755	1.822160	0.980848
N	-4.498768	-3.097140	-0.032651	C	-5.330084	-4.329192	-0.022675	H	-6.368252	-4.040345	-0.210177
H	-5.006883	-4.976334	-0.837648	C	-5.264785	-5.130694	1.292536	O	-5.475346	-6.313334	1.298475
O	-5.016690	-4.344038	2.341241	C	-5.020700	-5.012854	3.641002	H	-6.006366	-5.441944	3.826821
H	-4.264530	-5.799119	3.650397	H	-4.788680	-4.232139	4.362787				

Zero-point correction= 0.404687 (Hartree/Particle)
Thermal correction to Energy= 0.429229
Thermal correction to Enthalpy= 0.430173
Thermal correction to Gibbs Free Energy= 0.346051
Sum of electronic and zero-point Energies= -1244.795232

2c^{2+} B3LYP/6-31G(d) Isomer #2

Geometry

C	-2.255588	0.538999	0.069246	C	-0.891069	0.377720	0.342886	C	-0.044125	1.482116	0.308113
C	-1.881646	2.895194	-0.311336	C	-2.750887	1.809635	-0.252375	C	-3.170477	-0.632419	0.122403
C	-2.786736	-1.876842	-0.399807	C	-3.650465	-2.956680	-0.333022	C	-5.274304	-1.639799	0.746531
C	-4.448769	-0.532226	0.699182	H	-0.481262	-0.591602	0.593038	H	-3.799822	1.964335	-0.466690

H	-1.825904	-2.015913	-0.882369	H	-3.393641	-3.931878	-0.723365	H	-6.259711	-1.610474	1.196083
H	-4.800220	0.393517	1.140803	O	-0.576319	2.682406	-0.022190	C	-2.213710	4.265515	-0.631397
C	-3.438241	4.572713	-1.269971	C	-1.321991	5.313568	-0.304611	C	-3.756134	5.889208	-1.570984
H	-4.123356	3.784403	-1.565012	C	-1.654476	6.627607	-0.602394	H	-0.389547	5.094689	0.203068
C	-2.868558	6.918807	-1.235653	H	-4.690278	6.117820	-2.073501	H	-0.972711	7.429459	-0.338270
H	-3.123087	7.948172	-1.469086	C	1.377962	1.502442	0.566853	C	1.999164	0.415512	1.226199
C	2.164610	2.604653	0.158015	C	3.365251	0.435474	1.467147	H	1.413741	-0.426021	1.582377
C	3.531571	2.609882	0.396871	H	1.705061	3.434875	-0.366047	C	4.134438	1.528931	1.051179
H	3.834333	-0.394663	1.985060	H	4.132888	3.452082	0.070299	H	5.203960	1.538669	1.237995
N	-4.876694	-2.827560	0.229372	C	-5.742578	-4.022471	0.344029	H	-6.712986	-3.725618	0.741973
H	-5.898413	-4.444183	-0.653791	C	-5.070043	-5.078001	1.248719	O	-3.885752	-5.065055	1.499368
O	-5.973674	-5.956024	1.631801	C	-5.502646	-7.083786	2.433469	H	-4.761278	-7.649010	1.866749
H	-5.068220	-6.712563	3.362702	H	-6.392315	-7.679928	2.623979				

Zero-point correction= 0.404778 (Hartree/Particle)
Thermal correction to Energy= 0.429270
Thermal correction to Enthalpy= 0.430214
Thermal correction to Gibbs Free Energy= 0.346867
Sum of electronic and zero-point Energies= -1244.803114

2c^{2+} MP2/6-31G(d) Isomer #2

Geometries and Energies

C	-2.287169	0.536518	0.064665	C	-0.924399	0.359754	0.329103	C	-0.072014	1.459897	0.305173
C	-1.894308	2.886455	-0.308568	C	-2.775504	1.811066	-0.243901	C	-3.205039	-0.621546	0.114937
C	-2.873777	-1.830066	-0.514870	C	-3.738363	-2.911227	-0.441659	C	-5.266979	-1.647706	0.841906
C	-4.428647	-0.544017	0.796159	H	-0.514656	-0.617941	0.562126	H	-3.828568	1.982614	-0.442777
H	-1.952000	-1.940746	-1.079472	H	-3.529465	-3.867252	-0.907910	H	-6.216120	-1.645222	1.367971
H	-4.729616	0.358245	1.321643	O	-0.589796	2.666974	-0.021928	C	-2.209782	4.259273	-0.624129
C	-3.350674	4.553663	-1.398893	C	-1.381676	5.298009	-0.149832	C	-3.655279	5.878771	-1.692053

H	-3.963561	3.757732	-1.815981	C	-1.706420	6.617279	-0.446755	H	-0.515036	5.072297	0.465644
C	-2.839800	6.910761	-1.214055	H	-4.523364	6.110255	-2.302718	H	-1.080386	7.422607	-0.073000
H	-3.085371	7.944319	-1.443324	C	1.347752	1.473104	0.564513	C	1.921384	0.462371	1.363413
C	2.154280	2.489842	0.011650	C	3.291558	0.474358	1.602123	H	1.301061	-0.293784	1.839327
C	3.523428	2.481014	0.255255	H	1.715518	3.255782	-0.622086	C	4.094177	1.477151	1.046445
H	3.736147	-0.292257	2.230374	H	4.152078	3.253347	-0.178866	H	5.164759	1.478592	1.233460
N	-4.914229	-2.798534	0.221470	C	-5.764424	-4.000965	0.350089	H	-6.728135	-3.717681	0.776037
H	-5.936572	-4.421359	-0.645242	C	-5.037787	-5.016437	1.241915	O	-3.850239	-4.931780	1.504576
O	-5.895955	-5.950264	1.612282	C	-5.335359	-7.038728	2.418421	H	-4.553281	-7.541227	1.851151
H	-4.934979	-6.630031	3.344914	H	-6.178066	-7.697593	2.604919				

Zero-point correction= 0.406111 (Hartree/Particle)
Thermal correction to Energy= 0.431008
Thermal correction to Enthalpy= 0.431953
Thermal correction to Gibbs Free Energy= 0.348057
Sum of electronic and zero-point Energies= -1240.923701

Table. CIS Structural Data

	2b^{2+}a	**2b^{2+}**b
E(a.u.)	-1240.40425317	
d_{12}	1.352Å	1.351Å
d_{16}	1.352Å	1.351Å
$d_{44'}$	1.462Å	1.464Å
$d_{1'2'}$	1.339Å	1.337Å
$d_{1'6'}$	1.339Å	1.341Å
d_{2a}	1.429Å	1.430Å
$d_{6a'}$	1.429Å	1.430Å
>216	121.79^{o}	121.86^{o}
>2'1'6'	119.41^{o}	119.40^{o}
>344'3'	25.97^{o}	26.65^{o}

>12ab	-8.13°	-6.41°
>16a'b'	-8.25°	-6.54°
>3'2'N7	177.06°	177.00°
>1'789	109.18°	104.19°
>981011		
>2'1'78	41.05°	27.55°

a. CIS/6-31G(d). b. CIS/6-31+G(d)

2b^{2+} CIS/6-31G(d)

Geometry

C	-2.105097	0.488054	0.233657	C	-0.738408	0.481866	0.566767	C	0.037913	1.620184	0.449241
C	-1.821505	2.829859	-0.363441	C	-2.622298	1.710147	-0.233336	C	-2.938939	-0.705798	0.363565
C	-2.395611	-1.998129	0.300495	C	-3.204441	-3.094635	0.425061	C	-5.074575	-1.758264	0.677243
C	-4.326845	-0.619851	0.559025	H	-0.276923	-0.404918	0.943842	H	-3.647760	1.789179	-0.522759
H	-1.352969	-2.164871	0.119157	H	-2.817469	-4.091912	0.377524	H	-6.133515	-1.717616	0.836969
H	-4.827906	0.321721	0.659861	O	-0.516971	2.762185	-0.015116	C	-2.234809	4.115986	-0.830240
C	-3.519122	4.327976	-1.397635	C	-1.351384	5.220599	-0.729832	C	-3.888793	5.569955	-1.833077
H	-4.209287	3.515658	-1.514103	C	-1.736272	6.465153	-1.163963	H	-0.383268	5.087731	-0.292419
C	-3.000774	6.646917	-1.717297	H	-4.857727	5.721450	-2.269423	H	-1.064061	7.297401	-1.075503
H	-3.299247	7.620339	-2.060328	C	1.428302	1.731884	0.760926	C	2.133991	0.687569	1.414909
C	2.137151	2.909585	0.412816	C	3.464823	0.820705	1.697719	H	1.631476	-0.210409	1.716338
C	3.475556	3.029222	0.695549	H	1.629308	3.704415	-0.093696	C	4.144694	1.991295	1.338228
H	3.990266	0.031095	2.200320	H	4.005912	3.920939	0.420058	H	5.190994	2.087709	1.562431
N	-4.524968	-2.977746	0.612269	C	-5.404067	-4.201404	0.682190	H	-6.327960	-3.867761	1.130010
H	-5.606490	-4.492913	-0.338676	C	-4.791012	-5.330810	1.467229	C	-4.348025	-6.472138	0.812909
C	-4.697046	-5.252897	2.854735	C	-3.808061	-7.526495	1.535991	H	-4.438307	-6.553757	-0.256708
C	-4.156667	-6.301533	3.573840	H	-5.058519	-4.382100	3.374988	C	-3.710911	-7.439833	2.913328
H	-3.476436	-8.411024	1.024719	H	-4.094537	-6.241816	4.644640	H	-3.300146	-8.258269	3.475072

Zero-point correction= 0.472467 (Hartree/Particle)
Thermal correction to Energy= 0.495815
Thermal correction to Enthalpy= 0.496760
Thermal correction to Gibbs Free Energy= 0.414324
Sum of electronic and zero-point Energies= -1239.814354

2b^{2+} CIS/6-31+G(d)

Geometry

C	0.493945	-0.381559	-0.073257	C	0.933844	0.954329	-0.090817	C	2.281569	1.270145	-0.060321
C	2.838738	-1.023163	0.044648	C	1.498097	-1.364416	-0.009900	C	-0.927423	-0.728781	-0.117807
C	-1.916880	0.143616	0.355656	C	-3.240642	-0.213183	0.299501	C	-2.707593	-2.244329	-0.668519
C	-1.371587	-1.956503	-0.640004	H	0.229478	1.755251	-0.158340	H	1.240012	-2.400899	0.026691
H	-1.673603	1.086421	0.803681	H	-4.014003	0.432616	0.662128	H	-3.072924	-3.168299	-1.072334
H	-0.693976	-2.672768	-1.060289	O	3.197750	0.279315	0.012042	C	3.939308	-1.932166	0.124752
C	3.745009	-3.328882	0.303193	C	5.267983	-1.444811	0.022993	C	4.816728	-4.176547	0.371016
H	2.759429	-3.738957	0.405220	C	6.337357	-2.306804	0.086521	H	5.440611	-0.397903	-0.120051
C	6.120225	-3.671620	0.260712	H	4.662284	-5.229499	0.513542	H	7.338673	-1.928638	0.000663
H	6.956759	-4.344198	0.313083	C	2.842048	2.584984	-0.089569	C	2.036320	3.737739	-0.295644
C	4.237770	2.763102	0.093637	C	2.598841	4.984715	-0.312836	H	0.979995	3.649247	-0.457720
C	4.791342	4.021691	0.080547	H	4.864983	1.911402	0.259395	C	3.979899	5.135456	-0.122577
H	1.984809	5.850202	-0.476439	H	5.847669	4.146073	0.227908	H	4.413859	6.118515	-0.135504
N	-3.630532	-1.387149	-0.207344	C	-5.081225	-1.814930	-0.214253	H	-5.189177	-2.440201	-1.087969
H	-5.219778	-2.426106	0.666584	C	-6.055819	-0.668887	-0.245356	C	-6.744335	-0.306519	0.906249
C	-6.302694	0.011069	-1.436345	C	-7.662596	0.734984	0.873891	H	-6.582950	-0.841959	1.826428
C	-7.215346	1.051485	-1.468295	H	-5.797089	-0.279408	-2.342036	C	-7.895072	1.414657	-0.311233
H	-8.199195	1.002854	1.765345	H	-7.409911	1.565841	-2.391414	H	-8.611811	2.214750	-0.339628

Zero-point correction= 0.471628 (Hartree/Particle)
Thermal correction to Energy= 0.495072

Thermal correction to Enthalpy= 0.496016
Thermal correction to Gibbs Free Energy= 0.412527
Sum of electronic and zero-point Energies= -1239.836341

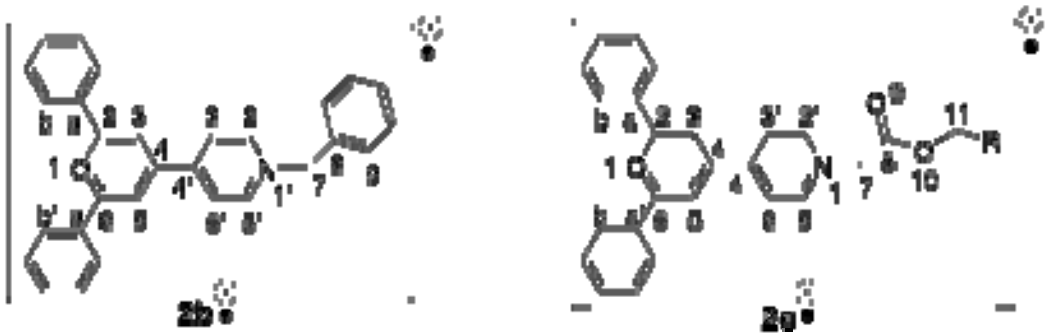


Table. Computational Structural Parameters for Pyrylogen Radical Cations.				
	2b$^{+.a}$	**2b**$^{+.b}$	**2c**$^{+.a}$	**2c**$^{+.b}$
E(a.u.)	-1248.70083745	-1249.03549791	-1245.51730424	-1245.86522090
d_{12}	1.366Å	1.363Å	1.365Å	1.362Å
d_{16}	1.366Å	1.363Å	1.365Å	1.362Å
$d_{44'}$	1.435Å	1.432Å	1.435Å	1.431Å
$d_{1'2'}$	1.369Å	1.364Å	1.371Å	1.366Å
$d_{1'6'}$	1.367Å	1.362Å	1.370Å	1.366Å
d_{2a}	1.464Å	1.463Å	1.464Å	1.463Å
$d_{6a'}$	1.464Å	1.463Å	1.464Å	1.463Å
>216	121.22°	120.99°	121.22°	121.01°
>2'1'6'	118.64°	118.64°	118.77°	118.73°
>344'3'	6.30°	3.45°	2.25°	4.00°
>12ab	21.48°	22.90°	21.60°	22.76°
>16a'b'	20.82°	22.43°	21.51°	23.00°
>3'2'N7	176.77°	177.46°	177.66°	175.91°

>1’789	67.54°	64.78°	16.32°	5.02°
>981011			1.11°	0.45°
>2’1’78	49.55°	53.08°	68.10°	92.65°
a. B3LYP/6-31G(d). b. B3LYP/6-311+G(2d,p)				

2b$^{+\cdot}$ B3LYP/6-31G(d)

C	-0.117072	0.205783	0.065255	C	0.441922	-0.927909	0.732469	C	1.585813	-0.829239	1.476330
C	1.764077	1.464828	0.985792	C	0.619906	1.419153	0.238884	C	-1.318835	0.132354	-0.716160
C	-1.940663	1.291931	-1.270763	C	-3.081835	1.204577	-2.019910	C	-3.129446	-1.157185	-1.725059
C	-1.975967	-1.105090	-0.991519	H	-0.031447	-1.900036	0.684211	H	2.009782	-1.680077	1.996151
H	2.344629	2.370728	1.107336	H	0.304849	2.340286	-0.234209	H	-1.548961	2.281077	-1.079810
H	-1.557483	-2.045170	-0.660918	C	3.470042	0.450461	2.477316	H	3.177082	0.953802	3.404898
H	3.742061	-0.577552	2.731226	C	-3.888047	-2.357344	-2.083698	C	-3.761238	-3.540548	-1.331552
C	-4.753993	-2.344009	-3.193299	C	-4.470839	-4.681818	-1.689590	H	-3.132914	-3.561454	-0.446339
C	-5.460395	-3.490270	-3.546270	H	-4.856589	-1.440856	-3.784413	C	-5.320614	-4.661684	-2.799033
H	-4.370478	-5.585473	-1.096002	H	-6.118765	-3.469997	-4.409526	C	-3.817041	2.314108	-2.630448
C	-3.175204	3.536325	-2.905363	C	-5.181076	2.172968	-2.947553	C	-3.883543	4.592150	-3.469067
H	-2.113636	3.652173	-2.709237	C	-5.884019	3.234389	-3.510423	H	-5.688304	1.238410	-2.735324
C	-5.240263	4.445992	-3.771127	H	-3.374634	5.526827	-3.684483	H	-6.938170	3.116533	-3.742657
N	2.259314	0.352571	1.611055	O	-3.668637	-0.010149	-2.234703	H	-5.790888	5.271350	-4.212533
H	-5.874634	-5.553725	-3.075739	C	4.620778	1.175515	1.818902	C	5.048444	2.412070	2.316002
C	5.280716	0.612258	0.717099	C	6.121975	3.079404	1.721413	H	4.550813	2.849797	3.178672
C	6.348393	1.279948	0.121632	H	4.962305	-0.351965	0.326975	C	6.770568	2.514893	0.623494
H	6.450400	4.035081	2.118973	H	6.857499	0.835043	-0.728265	H	7.606954	3.031019	0.161436

Zero-point correction= 0.441677 (Hartree/Particle)
Thermal correction to Energy= 0.466416
Thermal correction to Enthalpy= 0.467360
Thermal correction to Gibbs Free Energy= 0.382053
Sum of electronic and zero-point Energies= -1248.259161

2b$^{+\cdot}$ B3LYP/6-311+G(2d,p)

C	-0.133434	0.223130	0.077078	C	0.454752	-0.914679	0.701231	C	1.591563	-0.810854	1.446346
C	1.703255	1.496264	1.042778	C	0.565601	1.446627	0.295927	C	-1.328465	0.144576	-0.707266
C	-1.947765	1.296875	-1.268477	C	-3.081079	1.204182	-2.018313	C	-3.122801	-1.148196	-1.718955
C	-1.980240	-1.091316	-0.979621	H	0.015944	-1.896795	0.612048	H	2.038668	-1.667378	1.930552
H	2.251379	2.414026	1.199363	H	0.221516	2.375245	-0.133525	H	-1.555969	2.284997	-1.089776
H	-1.570205	-2.026966	-0.635965	C	3.441778	0.479613	2.480774	H	3.162278	1.001557	3.398148
H	3.706466	-0.542363	2.752063	C	-3.868871	-2.353799	-2.079235	C	-3.762053	-3.521622	-1.309697
C	-4.696838	-2.361232	-3.211140	C	-4.454611	-4.666608	-1.670704	H	-3.162336	-3.529334	-0.408296
C	-5.384656	-3.511797	-3.568774	H	-4.786269	-1.470371	-3.817671	C	-5.265483	-4.667007	-2.802869
H	-4.371393	-5.558365	-1.062134	H	-6.013310	-3.507497	-4.450461	C	-3.813680	2.312500	-2.630410
C	-3.168837	3.522922	-2.923833	C	-5.178574	2.182129	-2.925005	C	-3.873591	4.576202	-3.484923
H	-2.106957	3.633214	-2.743951	C	-5.878953	3.241694	-3.483237	H	-5.690917	1.256737	-2.699762
C	-5.231234	4.440632	-3.763689	H	-3.361536	5.501724	-3.716702	H	-6.934743	3.132122	-3.697390
N	2.228728	0.379709	1.624737	O	-3.663232	-0.008604	-2.234569	H	-5.779702	5.264770	-4.202671
H	-5.805713	-5.562843	-3.082790	C	4.596986	1.178819	1.807249	C	5.082857	2.380569	2.320038
C	5.208009	0.619716	0.681982	C	6.163975	3.018429	1.717613	H	4.624585	2.816805	3.201216
C	6.282450	1.258079	0.077804	H	4.848300	-0.320429	0.277308	C	6.762238	2.459284	0.595347
H	6.537537	3.948372	2.127986	H	6.752996	0.815724	-0.791575	H	7.604277	2.953068	0.126326

Zero-point correction= 0.438799 (Hartree/Particle)
Thermal correction to Energy= 0.463571
Thermal correction to Enthalpy= 0.464515
Thermal correction to Gibbs Free Energy= 0.379401
Sum of electronic and zero-point Energies= -1248.596699

2c$^{+\cdot}$ B3LYP/6-31G(d)

Geometric Parameters

C	-2.253264	0.512317	0.091147	C	-0.851375	0.406578	0.339898	C	-0.030112	1.499986	0.296004
C	-1.866430	2.891135	-0.298273	C	-2.719845	1.824364	-0.223772	C	-3.131429	-0.621397	0.153861
C	-2.665673	-1.946625	0.422762	C	-3.519319	-3.011336	0.480487	C	-5.360220	-1.610016	0.018499
C	-4.544129	-0.516808	-0.046329	H	-0.391565	-0.546216	0.559862	H	-3.767996	2.019229	-0.400392
H	-1.616646	-2.151830	0.590702	H	-3.179544	-4.015235	0.697932	H	-6.431342	-1.540974	-0.127725
H	-5.016160	0.435265	-0.250661	O	-0.538085	2.724549	-0.030510	C	-2.219971	4.274875	-0.621460
C	-3.394160	4.567273	-1.340872	C	-1.388291	5.334113	-0.212323	C	-3.732470	5.884912	-1.630112
H	-4.027291	3.763629	-1.704618	C	-1.734097	6.650450	-0.504045	H	-0.484068	5.122532	0.347398
C	-2.905497	6.930713	-1.210918	H	-4.636069	6.096635	-2.193729	H	-1.089255	7.459855	-0.175316
H	-3.171077	7.958616	-1.439186	C	1.413018	1.521526	0.542597	C	2.026457	0.508375	1.303583
C	2.207967	2.557261	0.016848	C	3.400262	0.524968	1.519519	H	1.426322	-0.275301	1.755989
C	3.582536	2.566235	0.235598	H	1.747855	3.340738	-0.574953	C	4.183032	1.551733	0.984457
H	3.860151	-0.257072	2.116070	H	4.187071	3.365432	-0.182544	H	5.255329	1.563208	1.155564
N	-4.865441	-2.863545	0.267579	C	-5.757741	-4.014910	0.387043	H	-6.745296	-3.747809	0.007519
H	-5.383031	-4.836137	-0.234214	C	-5.862307	-4.503750	1.839284	O	-5.085223	-4.199012	2.713386
O	-6.901926	-5.328353	1.954221	C	-7.096325	-5.931602	3.258755	H	-6.210685	-6.504228	3.541230
H	-7.285597	-5.155323	4.002808	H	-7.962009	-6.581979	3.145662				

Zero-point correction= 0.403307 (Hartree/Particle)
Thermal correction to Energy= 0.428082
Thermal correction to Enthalpy= 0.429026
Thermal correction to Gibbs Free Energy= 0.343013
Sum of electronic and zero-point Energies= -1245.113997

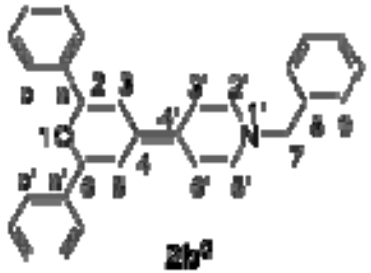
2c$^{+\cdot}$ B3LYP/6-311+G(2d,p)

Geometric Parameters

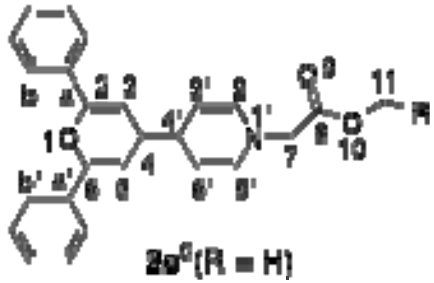
C	-2.211475	0.480335	0.080124	C	-0.811434	0.391157	0.318730	C	-0.009288	1.491759	0.280607

C	-1.862979	2.860097	-0.277829	C	-2.697430	1.784961	-0.214178	C	-3.070679	-0.663339	0.132925
C	-2.580282	-1.985161	0.346110	C	-3.416622	-3.056962	0.394436	C	-5.281715	-1.672517	0.036231
C	-4.485153	-0.571167	-0.022375	H	-0.338488	-0.554083	0.529149	H	-3.745785	1.966328	-0.386159
H	-1.526435	-2.181935	0.470240	H	-3.054896	-4.061145	0.562152	H	-6.355610	-1.610834	-0.067370
H	-4.974466	0.378105	-0.178357	O	-0.533259	2.711191	-0.024318	C	-2.243061	4.240375	-0.577162
C	-3.412757	4.521428	-1.298520	C	-1.443567	5.305913	-0.139012	C	-3.776011	5.832275	-1.564128
H	-4.024866	3.715326	-1.682972	C	-1.815104	6.615781	-0.404970	H	-0.541908	5.105703	0.423489
C	-2.980349	6.883762	-1.116317	H	-4.675405	6.035442	-2.131830	H	-1.194540	7.430320	-0.052927
H	-3.265909	7.907160	-1.325615	C	1.434125	1.524435	0.514443	C	2.058876	0.524371	1.274127
C	2.216549	2.554868	-0.026328	C	3.429686	0.549935	1.476549	H	1.470554	-0.257889	1.736957
C	3.588773	2.572084	0.176802	H	1.749709	3.330379	-0.618120	C	4.199535	1.571600	0.926401
H	3.898468	-0.221461	2.074585	H	4.183908	3.367718	-0.253644	H	5.270396	1.589950	1.086490
N	-4.765448	-2.922351	0.227966	C	-5.645544	-4.074862	0.375564	H	-6.569612	-3.900140	-0.174299
H	-5.172845	-4.954455	-0.063704	C	-5.967155	-4.360999	1.846321	O	-5.476683	-3.767926	2.769019
O	-6.846107	-5.355390	1.922813	C	-7.239690	-5.764574	3.259351	H	-6.367468	-6.109224	3.811484
H	-7.701097	-4.928010	3.780412	H	-7.950417	-6.571287	3.110972				

Zero-point correction= 0.400392 (Hartree/Particle)
Thermal correction to Energy= 0.425227
Thermal correction to Enthalpy= 0.426171
Thermal correction to Gibbs Free Energy= 0.339983
Sum of electronic and zero-point Energies= -1245.464829



2b'



2a'(R = H)

Table. Computational Parameters for Two Electron Reduced Pyrylogens.

	2b^0[a]	**2b^0**[b]	**2c^0**(R = H)[a]
E(a.u.)	-1248.87406284	-1249.22118095	-1245.69276860
d_{12}	1.386Å	1.383Å	1.385Å
d_{16}	1.386Å	1.383Å	1.385Å
$d_{44'}$	1.390Å	1.385Å	1.389Å
$d_{1'2'}$	1.390Å	1.382Å	1.390Å
$d_{1'6'}$	1.387Å	1.384Å	1.390Å
d_{2a}	1.470Å	1.468Å	1.470Å
$d_{6a'}$	1.470Å	1.468Å	1.470Å
>216	118.55^o	118.54^o	118.53^o
>2'1'6'	117.22^o	117.46^o	117.30^o
>344'3'	0.48^o	0.03^o	0.09^o
>12ab	19.28^o	19.57^o	19.32^o
>16a'b'	18.69^o	18.21^o	19.67^o
>3'2'N7	172.4^o	177.2^o	172.7^o
>1'789	46.53^o	25.06^o	2.37^o
>981011			0.15^o
>2'1'78	60.86^o	75.09^o	83.09^o

a. B3LYP/6-31G(d). b. B3LYP/6-311+G(2d,p)

2b^0 B3LYP/6-31G(d)

Geometric Coordinates

C	-0.166826	0.254160	0.105674	C	0.476363	-0.890926	0.733782	C	1.596554	-0.775053	1.485000
C	1.643810	1.569221	1.139816	C	0.522797	1.505363	0.384541	C	-1.314730	0.163969	-0.672415
C	-1.959893	1.309139	-1.285832	C	-3.074271	1.201808	-2.045336	C	-3.123909	-1.154206	-1.696636
C	-1.993498	-1.086096	-0.956399	H	0.066194	-1.886599	0.614406	H	2.067454	-1.631984	1.954781
H	2.159492	2.502179	1.336331	H	0.149799	2.439080	-0.019337	H	-1.565276	2.304540	-1.128179

H	-1.586342	-2.019993	-0.591252	C	3.337900	0.573540	2.640087	H	3.009684	1.119847	3.536583
H	3.593497	-0.439797	2.970141	C	-3.869039	-2.372746	-2.042712	C	-3.727152	-3.558349	-1.296560
C	-4.751100	-2.379414	-3.139394	C	-4.421163	-4.711392	-1.649607	H	-3.088298	-3.570320	-0.418641
C	-5.447797	-3.535622	-3.486177	H	-4.874347	-1.474762	-3.723761	C	-5.285838	-4.708579	-2.747930
H	-4.297536	-5.613432	-1.055784	H	-6.119164	-3.518735	-4.340996	C	-3.796928	2.304431	-2.694685
C	-3.171298	3.538015	-2.957496	C	-5.143566	2.148165	-3.072443	C	-3.873260	4.582189	-3.551480
H	-2.120568	3.671411	-2.718275	C	-5.841190	3.195510	-3.671523	H	-5.640115	1.204038	-2.879500
C	-5.213864	4.418668	-3.911772	H	-3.367246	5.523996	-3.747758	H	-6.882576	3.053975	-3.949387
N	2.229041	0.440291	1.699964	O	-3.690068	-0.021090	-2.258114	H	-5.758607	5.233111	-4.381551
H	-5.831813	-5.608360	-3.018221	C	4.566500	1.253464	2.058150	C	5.236385	2.237706	2.791974
C	5.068151	0.883245	0.803324	C	6.394253	2.836424	2.290233	H	4.849864	2.538219	3.763737
C	6.220705	1.482886	0.298370	H	4.545825	0.130805	0.218256	C	6.888692	2.459935	1.041662
H	6.902733	3.600663	2.871897	H	6.598446	1.188379	-0.677111	H	7.786226	2.927524	0.646037

Zero-point correction= 0.439221 (Hartree/Particle)
Thermal correction to Energy= 0.464346
Thermal correction to Enthalpy= 0.465290
Thermal correction to Gibbs Free Energy= 0.379037
Sum of electronic and zero-point Energies= -1248.434842

2b⁰ B3LYP/6-311+G(2d,p)

Geometric Coordinates

C	-0.278995	0.473035	0.286551	C	0.411397	-0.636489	0.920548	C	1.485649	-0.459154	1.718040
C	1.378761	1.884563	1.423265	C	0.301845	1.761589	0.620689	C	-1.374535	0.319678	-0.546490
C	-2.056938	1.426764	-1.179216	C	-3.111950	1.258878	-2.000239	C	-3.022158	-1.095732	-1.684219
C	-1.951414	-0.964943	-0.877127	H	0.076739	-1.652637	0.771110	H	1.995878	-1.290460	2.185744
H	1.811519	2.846798	1.661126	H	-0.122663	2.674926	0.230027	H	-1.738282	2.440300	-0.991486
H	-1.513690	-1.872973	-0.492228	C	3.196814	0.962209	2.808845	H	3.020520	1.766098	3.530455
H	3.324180	0.048116	3.395000	C	-3.658532	-2.356232	-2.085790	C	-3.493514	-3.531686	-1.337138

C	-4.450884	-2.415052	-3.241498	C	-4.077142	-4.722166	-1.742607	H	-2.923249	-3.509910	-0.417095
H	-5.035906	-3.609899	-3.642964	H	-4.594608	-1.519581	-3.830030	C	-4.851104	-4.770335	-2.900294
H	-3.939216	-5.615581	-1.144810	H	-5.638839	-3.632357	-4.543347	C	-3.866006	2.322111	-2.675603
C	-3.322239	3.603303	-2.857132	C	-5.160136	2.079969	-3.158813	C	-4.052453	4.606521	-3.475121
H	-2.310352	3.811396	-2.533378	C	-5.887679	3.087976	-3.780254	H	-5.596355	1.098816	-3.033139
C	-5.342096	4.356472	-3.939814	H	-3.608328	5.586160	-3.607949	H	-6.888459	2.878826	-4.139988
N	2.004265	0.791331	1.997449	O	-3.625417	0.002886	-2.268200	H	-5.909247	5.140178	-4.427498
H	-5.310600	-5.700459	-3.212409	C	4.474214	1.254029	2.036214	C	5.528774	1.900423	2.682656
C	4.636727	0.861131	0.708934	C	6.727619	2.139860	2.021150	H	5.410977	2.222363	3.712559
C	5.835162	1.103646	0.043919	H	3.822695	0.372329	0.187654	C	6.884300	1.740413	0.697441
H	7.536239	2.644631	2.536537	H	5.946245	0.795816	-0.989061	H	7.815550	1.930551	0.177507

Zero-point correction= 0.436390 (Hartree/Particle)
Thermal correction to Energy= 0.461548
Thermal correction to Enthalpy= 0.462492
Thermal correction to Gibbs Free Energy= 0.376039
Sum of electronic and zero-point Energies= -1248.784791

2c^0 B3LYP/6-31G(d)

Geometric Coordinates

C	-2.197154	0.429385	0.093993	C	-0.764617	0.383595	0.317827	C	0.018440	1.486115	0.278285
C	-1.862683	2.841642	-0.263298	C	-2.680207	1.765843	-0.196968	C	-3.019033	-0.689150	0.149496
C	-2.536541	-2.031815	0.440012	C	-3.353489	-3.108458	0.470983	C	-5.234384	-1.750545	-0.033435
C	-4.456914	-0.645435	-0.075532	H	-0.274233	-0.562074	0.508548	H	-3.736631	1.940267	-0.354400
H	-1.487233	-2.206097	0.645566	H	-2.990412	-4.105680	0.694236	H	-6.305792	-1.712343	-0.197575
H	-4.951616	0.294941	-0.286704	O	-0.503819	2.734451	-0.017457	C	-2.265129	4.225658	-0.550965
C	-3.470483	4.515338	-1.218219	C	-1.443842	5.300806	-0.164050	C	-3.850549	5.830696	-1.466104
H	-4.101386	3.703792	-1.568293	C	-1.826647	6.616506	-0.418657	H	-0.511073	5.095416	0.348735
C	-3.031503	6.890755	-1.067062	H	-4.783920	6.029218	-1.986646	H	-1.179278	7.431598	-0.105263

H	-3.326821	7.917103	-1.267416	H	1.472155	1.530911	0.490112	C	2.144419	0.504259	1.180177
C	2.229508	2.613019	0.004591	C	3.524161	0.546542	1.354600	H	1.579006	-0.319584	1.605335
C	3.610817	2.653183	0.185982	H	1.727038	3.413701	-0.526118	C	4.267302	1.621038	0.857559
H	4.020412	-0.255915	1.894355	H	4.176574	3.496091	-0.202755	H	5.343907	1.655704	1.000642
N	-4.713846	-3.018037	0.200282	C	-5.582706	-4.149726	0.393489	H	-6.462881	-4.058801	-0.252649
H	-5.071503	-5.069880	0.087198	C	-6.060474	-4.326433	1.840894	O	-5.735851	-3.638629	2.778077
O	-6.901388	-5.378937	1.911836	C	-7.422666	-5.667046	3.223176	H	-6.608707	-5.898352	3.914981
H	-7.984702	-4.811671	3.606456	H	-8.075487	-6.530459	3.094618				

Zero-point correction= 0.400977 (Hartree/Particle)
Thermal correction to Energy= 0.426065
Thermal correction to Enthalpy= 0.427009
Thermal correction to Gibbs Free Energy= 0.340994
Sum of electronic and zero-point Energies= -1245.291791

2b^{2+} February 5, 2009

Crystallographic Data. The X-ray diffraction data were measured at 150 K on a Bruker SMART APEX II CCD area detector system equipped with a graphite monochromator and a Mo Kα fine-focus sealed tube operated at 1.50 kW power (50 kV, 30 mA). A yellow trigonal prismatic crystal of $[BzPyPh_2OPy](BF_4)_2$ approximate dimensions 0.47 mm × 0.35 mm × 0.26 mm glued to a Hampton Research cryoloop using Paratone N oil. The detector was placed at a distance of 6.12 cm from the crystal during the data collection.

A series of narrow frames of data were collected with a scan width of 0.5º in ω or ϕ and an exposure time of 10 s per frame. The frames were integrated with the Bruker SAINT Software package[1] using a narrow-frame integration algorithm. The integration of the data using a monoclinic unit cell yielded a total of 18821 reflections in the 2θ range of 3.34 – 57.40˚ of which 7425 were independent with $I \geq 2\sigma(I)$ (R_{int}= 0.0261). The data were corrected for absorption effects by the multi-scan method (SADABS). The compound crystallizes in a centro-symmetric monoclinic space group, namely, *C2/c*. Crystallographic data collection parameters and refinement data are collected in Table 1. The structure was solved by direct methods using the Bruker Software Package.[1] The non-hydrogen atoms were located in successive Fourier maps and refined anisotropically. All hydrogen atoms were also located, and refined isotropically. The final refinement parameters are R_1 = 0.0549 and *wR2* = 0.1488 for data with $F > 4\sigma(F)$ giving the data to parameter ratio of 14.8. The refinement data for all data are R_1 = 0.0696 and *wR2* = 0.1612.

The asymmetric unit consists of **2b^{2+}**, two tetrafluoroborate anions and a solvated acetonitrile molecule. The contents of the unit cell are well ordered. Both borates appear to interact with the oxopyrilium cation. One of the borate is located close to the oxopyrilium oxygen atom with the associated F···O distance being 2.933(2) Å, whereas the other is located close to an oxopyrilium C-H group with the associated F···C distance being 2.946(2) Å. The dication is non-planar as the oxopyrilium and pyridinium rings are twisted at 33.94(7)˚. The two phenyl rings also deviate from the mean plane of the oxopyrilium ring. But the angles are comparatively smaller at 10.32(8) and 14.79(7)˚.

Acknowledgment. Financial support by the NSF (CHE 0619920) for the purchase of the Bruker Apex II Diffractometer is gratefully acknowledged.

Reference

1. APEX2 Software Suite V. 2.2, Bruker AXS Inc.: Madison, WI, 2007.

Table 1. Crystallographic Data for $[BzPyPh_2OPy](BF_4)_2$

compound	$[BzPyPh_2OPy](BF_4)_2$	chemical formula	$C_{31}H_{26}B_2F_8N_2O$
fw	616.16	T, K	150(2)
λ, Å	0.71073	space group	*C2/c*
a, Å	30.0651(5)	*b*, Å	13.6116(2)
c, Å	15.4512(2)	β, ˚	114.351(1)
V, Å^3	5760.63(15)	*Z*	8
D_{calc}, Mg m^{-3}	1.421	μ, mm^{-1}	0.121
$R1[I > 2\sigma(I)]^a$	0.0549	wR2[I > 2σ(I)]b	1488

$^aR1 = \sum| |F_o| - |F_c| |/\sum |F_o|$; $^bwR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum w(F_o^2)^2]\}^{1/2}$

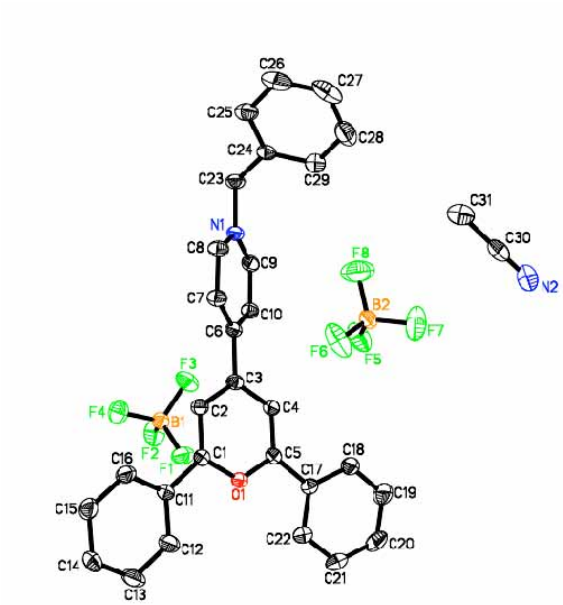


Fig. 1. View of the contents of the unit cell in the crystals of $[BzPyPh_2OPy](BF_4)_2$. Hydrogen atoms are omitted for clarity. The thermal ellipsoids are drawn at the 50% probability.

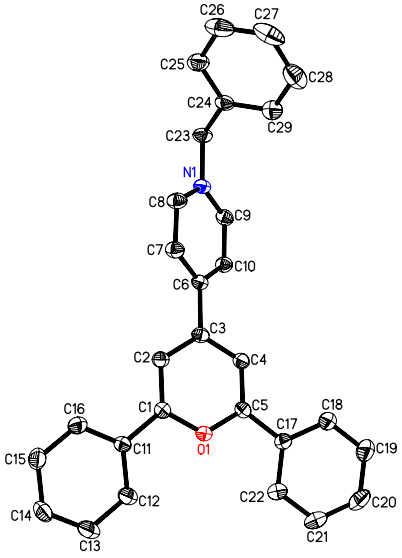


Fig. 2. View of the $[BzPyPh_2OPy]^{2+}$ cation. Hydrogen atoms are omitted and the thermal ellipsoids are drawn at the 50% probability.

Table 1. Crystal data and structure refinement for **2b**$^{2+}$.

Identification code	tt01	
Empirical formula	C31 H26 B2 F8 N2 O	
Formula weight	616.16	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 30.0651(5) Å	α= 90°.
	b = 13.6116(2) Å	β= 114.351(1)°.
	c = 15.4512(2) Å	γ = 90°.
Volume	5760.63(15) Å^3	
Z	8	
Density (calculated)	1.421 Mg/m^3	
Absorption coefficient	0.121 mm^{-1}	
F(000)	2528	
Crystal size	0.47 x 0.35 x 0.26 mm^3	
Theta range for data collection	1.67 to 28.70°.	
Index ranges	-40<=h<=40, -18<=k<=13, -17<=l<=20	
Reflections collected	18821	
Independent reflections	7425 [R(int) = 0.0261]	
Completeness to theta = 28.70°	99.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9696 and 0.9450	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7425 / 0 / 501	
Goodness-of-fit on F^2	1.035	
Final R indices [I>2sigma(I)]	R1 = 0.0549, wR2 = 0.1488	
R indices (all data)	R1 = 0.0696, wR2 = 0.1612	
Largest diff. peak and hole	1.078 and -0.550 e.Å^{-3}	

Table 2. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for tt01. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	367(1)	3840(1)	4292(1)	21(1)
C(1)	606(1)	4682(1)	4648(1)	21(1)
C(2)	1092(1)	4645(1)	5269(1)	22(1)
C(3)	1330(1)	3741(1)	5472(1)	21(1)
C(4)	1072(1)	2888(1)	5063(1)	22(1)
C(5)	584(1)	2953(1)	4484(1)	21(1)
C(6)	1855(1)	3663(1)	6121(1)	20(1)
C(7)	2068(1)	4290(1)	6898(1)	24(1)
C(8)	2551(1)	4166(1)	7501(1)	25(1)
N(1)	2818(1)	3449(1)	7344(1)	21(1)
C(9)	2623(1)	2843(1)	6594(1)	23(1)
C(10)	2141(1)	2938(1)	5969(1)	22(1)
C(11)	303(1)	5556(1)	4306(1)	22(1)
C(12)	-163(1)	5486(1)	3564(1)	33(1)
C(13)	-447(1)	6319(2)	3240(2)	39(1)
C(14)	-272(1)	7222(1)	3642(2)	34(1)

C(15)	187(1)	7299(1)	4384(2)	32(1)
C(16)	474(1)	6470(1)	4719(1)	28(1)
C(17)	255(1)	2134(1)	4042(1)	23(1)
C(18)	402(1)	1176(1)	4360(2)	32(1)
C(19)	89(1)	398(2)	3952(2)	41(1)
C(20)	-367(1)	564(2)	3222(2)	39(1)
C(21)	-512(1)	1509(2)	2899(1)	32(1)
C(22)	-206(1)	2298(1)	3311(1)	26(1)
C(23)	3345(1)	3348(1)	8004(1)	26(1)
C(24)	3414(1)	3127(1)	9005(1)	24(1)
C(25)	3707(1)	3740(2)	9742(1)	33(1)
C(26)	3789(1)	3517(2)	10671(2)	44(1)
C(27)	3582(1)	2697(2)	10870(2)	47(1)
C(28)	3287(1)	2091(2)	10143(2)	45(1)
C(29)	3201(1)	2302(2)	9208(2)	34(1)
F(1)	914(1)	4062(1)	3112(1)	39(1)
B(1)	1374(1)	4235(2)	3140(1)	26(1)
F(2)	1384(1)	3958(1)	2278(1)	45(1)
F(3)	1721(1)	3692(1)	3874(1)	41(1)
F(4)	1491(1)	5220(1)	3296(1)	48(1)
B(2)	1677(1)	1244(2)	7141(2)	29(1)
F(5)	1655(1)	905(1)	6282(1)	54(1)
F(6)	1445(1)	2137(1)	7024(1)	61(1)
F(7)	1491(1)	566(1)	7562(1)	67(1)
F(8)	2162(1)	1387(2)	7729(1)	74(1)
N(2)	1626(1)	-1148(1)	9183(1)	43(1)
C(30)	1914(1)	-552(2)	9463(1)	34(1)
C(31)	2292(1)	197(2)	9810(2)	44(1)

$2c^{2+}$ (20i) February 19, 2009

Crystallographic Data. The X-ray diffraction data were measured at 150 K on a Bruker SMART APEX II CCD area detector system equipped with a graphite monochromator and a Mo Kα fine-focus sealed tube operated at 1.50 kW power (50 kV, 30 mA). A yellow rectangular prismatic crystal of 20i approximate dimensions 0.34 mm × 0.31 mm × 0.14 mm glued to a MiTeGen micromount using Paratone N oil. The detector was placed at a distance of 5.12 cm from the crystal during the data collection.

A series of narrow frames of data were collected with a scan width of 0.5º in ω or ϕ and an exposure time of 10 s per frame. The frames were integrated with the Bruker SAINT Software package[1] using a narrow-frame integration algorithm. The integration of the data using a triclinic unit cell yielded a total of 16479 reflections in the 2θ range of 4.70 – 57.40˚ of which 8187 were independent with $I \geq 2\sigma(I)$ (R_{int}= 0.0294). The data were corrected for absorption effects by the multi-scan method (SADABS).[1] The compound crystallizes in the centro-symmetric triclinic space group $P\bar{1}$. Crystallographic data collection parameters and refinement data are collected in Table 1. The structure was solved by direct methods using the Bruker Software Package.[1] The non-hydrogen atoms were located in successive Fourier maps and refined anisotropically. The asymmetric unit consists of a pyrilogen dication, two tetrafluoroborate anions and two solvated acetic acid molecules (Figure 1). The hydrogen atoms of the carboxylate ethyl group belonging to the cation were placed in calculated positions and refined isotropically by adopting a riding model. The rest of the hydrogen

atoms of the cation were located in the Fourier maps and refined isotropically. The carboxylic acid hydrogen atoms of the acetic acid molecules was located and refined isotropically with fixed positional and thermal parameters, whereas their methyl hydrogen atoms were placed in calculated positions and refined isotropically by adopting a riding model.

The cation (Figure 2) is non-planar as the oxopyrilium and pyridinium rings are twisted at 39.99(9)°. But the two phenyl rings are nearly coplanar with the oxopyrilium ring with the angles between the respective phenyl mean planes and the oxopyrilium ring's mean plane being at 3.97(13)° and 3.80(13)°. The cation and one of the anions exhibit weak inter-ionic interaction with the associated N1···F3A inter-atomic distance of 2.901(3) Å. The other borate ion is well separated from the cation. Consequently, both of the borates are disordered. The disorder in one of the borate is modeled by assigning two sets of positions for three of its fluorine atoms, and that in the other borate is modeled by assigning two sets of positions for all of its fluorine atoms. The two acetic acid molecules are reasonably well ordered as they are hydrogen bonded to each other. The final refinement parameters are R_1 = 0.0603 and *wR2* = 0.1586 for the data with $F > 4\sigma(F)$ giving the data to parameter ratio of 14. The refinement data for all data are R_1 = 0.1088 and *wR2* = 0.1876.

Acknowledgment. Financial support by the NSF (CHE 0619920) for the purchase of the Bruker Apex II Diffractometer is gratefully acknowledged.

Reference

1. APEX2 Software Suite V. 2.2, Bruker AXS Inc.: Madison, WI, 2007.

Table 1. Crystallographic Data for 20i

Compound	20i	chemical formula	$C_{30}H_{31}B_2F_8NO_7$
fw	691.18	T, K	150(2)
λ, Å	0.71073	space group	$P\bar{1}$
a, Å	8.7453(2)	*b*, Å	14.2435(3)
c, Å	14.7221(3)	α, °	118.767(1)
β, °	91.692(1)	γ, °	95.485(1)
V, Å^3	1594.15(6)	*Z*	2
D_{calc}, Mg m^{-3}	1.440	μ, mm^{-1}	0.130
$R1[I > 2\sigma(I)]^a$	0.0603	wR2[I > 2σ(I)]b	0.1586

$^aR1 = \sum| |F_o| - |F_c| | / \sum |F_o|$; $^bwR2 = \{\sum[w(F_o^2 - F_c^2)^2] / \sum w(F_o^2)^2]\}^{1/2}$

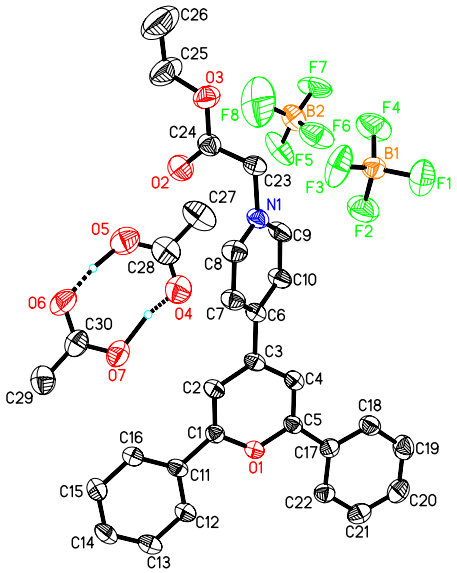


Figure 1. View of the contents of the unit cell in the crystals of 20i. The second set of atoms of the two disordered borate anions is omitted, and all hydrogen atoms except for those involved in hydrogen bonding are omitted for clarity. The thermal ellipsoids are drawn at the 50% probability.

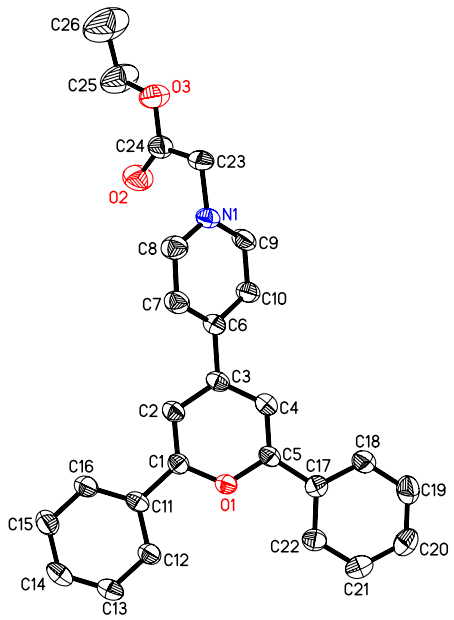


Figure 2. View of the cation in the crystals of 20i. Hydrogen atoms are omitted and the thermal ellipsoids are drawn at the 50% probability.

Table 1. Crystal data and structure refinement for 20i.

Identification code	tt03a	
Empirical formula	C30 H31 B2 F8 N O7	
Formula weight	691.18	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 8.7453(2) Å	α= 118.767(1)°.
	b = 14.2435(3) Å	β= 91.692(1)°.
	c = 14.7221(3) Å	γ = 95.485(1)°.
Volume	1594.15(6) $Å^3$	
Z	2	
Density (calculated)	1.440 Mg/m^3	
Absorption coefficient	0.130 mm^{-1}	
F(000)	712	
Crystal size	0.34 × 0.31 × 0.14 mm^3	
Theta range for data collection	2.35 to 28.70°.	
Index ranges	-11<=h<=11, -14<=k<=19, -19<=l<=19	
Reflections collected	16479	
Independent reflections	8187 [R(int) = 0.0294]	
Completeness to theta = 28.70°	99.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9825 and 0.9575	
Refinement method	Full-matrix least-squares on F^2	

Data / restraints / parameters	8187 / 0 / 569
Goodness-of-fit on F^2	1.036
Final R indices [I>2sigma(I)]	R1 = 0.0603, wR2 = 0.1586
R indices (all data)	R1 = 0.1088, wR2 = 0.1876
Largest diff. peak and hole	0.423 and -0.378 e.Å^{-3}

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å$^2 \times 10^3$) for 20i. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	7908(2)	942(1)	550(1)	32(1)
C(1)	8833(2)	1705(2)	1378(2)	30(1)
C(2)	8838(2)	2770(2)	1633(2)	33(1)
C(3)	7915(2)	3032(2)	1024(2)	31(1)
C(4)	6974(2)	2219(2)	182(2)	33(1)
C(5)	6978(2)	1165(2)	-46(2)	30(1)
C(6)	7917(2)	4170(2)	1261(2)	32(1)
C(7)	9268(3)	4877(2)	1572(2)	39(1)
C(8)	9214(3)	5925(2)	1793(2)	42(1)
N(1)	7859(2)	6271(1)	1723(1)	36(1)
C(9)	6537(3)	5600(2)	1410(2)	42(1)
C(10)	6544(3)	4540(2)	1161(2)	40(1)
C(23)	7836(3)	7425(2)	2062(2)	42(1)
C(24)	7762(3)	8049(2)	3222(2)	42(1)
O(2)	7761(3)	7659(2)	3782(1)	62(1)
O(3)	7746(2)	9083(1)	3517(1)	53(1)
C(25)	7610(5)	9797(2)	4621(2)	81(1)
C(26)	8056(7)	10912(3)	4858(3)	126(2)
C(11)	9745(2)	1260(2)	1890(2)	32(1)
C(12)	9658(3)	143(2)	1487(2)	35(1)
C(13)	10546(3)	-271(2)	1970(2)	39(1)
C(14)	11496(3)	411(2)	2853(2)	41(1)
C(15)	11576(3)	1517(2)	3263(2)	45(1)
C(16)	10704(3)	1943(2)	2784(2)	41(1)
C(17)	6072(2)	220(2)	-893(2)	33(1)
C(18)	5012(3)	346(2)	-1537(2)	41(1)
C(19)	4171(3)	-548(2)	-2350(2)	49(1)
C(20)	4368(3)	-1569(2)	-2538(2)	48(1)
C(21)	5407(3)	-1705(2)	-1903(2)	44(1)
C(22)	6262(3)	-825(2)	-1078(2)	37(1)
B(1)	7660(3)	6893(2)	-508(2)	39(1)
F(1)	7664(2)	6520(2)	-1555(1)	71(1)
F(2)	7199(4)	5963(2)	-428(2)	72(1)
F(3)	9040(3)	7331(3)	13(2)	75(2)
F(4)	6521(6)	7538(4)	-102(4)	75(1)
F(2A)	8552(12)	7921(6)	-247(8)	100(4)
F(3A)	8610(13)	6453(9)	-97(6)	97(5)
F(4A)	6428(10)	7145(12)	-2(8)	75(4)
B(2)	3214(3)	7502(3)	2360(3)	52(1)
F(5)	2709(10)	6754(7)	2636(8)	77(2)
F(6)	4080(9)	7144(6)	1550(7)	77(2)

F(7)	1972(10)	7902(6)	2264(7)	79(2)
F(8)	4324(6)	8210(6)	3069(5)	140(2)
F(5A)	3030(30)	6839(15)	2793(17)	70(5)
F(6A)	3650(30)	6797(19)	1301(16)	98(7)
F(7A)	1830(20)	7673(16)	1890(19)	93(7)
F(8A)	3742(15)	8624(6)	3103(9)	83(3)
C(27)	4844(4)	5907(3)	3795(3)	80(1)
C(28)	5988(3)	5446(3)	4170(3)	64(1)
O(4)	6508(3)	4595(2)	3537(2)	72(1)
O(5)	6425(3)	5940(2)	5142(2)	73(1)
C(29)	9683(4)	3667(3)	5648(2)	65(1)
C(30)	8757(3)	4209(2)	5235(2)	53(1)
O(6)	8566(2)	5187(2)	5821(2)	67(1)
O(7)	8153(2)	3664(2)	4309(1)	63(1)