Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

On the Reciprocal Relationship Between σ-Hole Boding and (Anti)aromaticity Gain in Ketocyclopolyenes

Hari Ram Paudel,[a] Lucas José Karas,[a] Judy I-Chia Wu*[a]

[a]Department of Chemistry, University of Houston, Houston, TX 77004, USA

Correspondence: jiwu@central.uh.edu

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1. Effects of σ-hole bonding on the cyclononatetraenone minimum structure

*Cyclononatetraenone (**3**$_{minima}$) adopts a tub-shaped minimum structure, and the computed planarization energy is –24 kcal/mol at the ωB97XD/def2-TZVP level. Like the tub-shaped minimum structure of cyclooctatetraene, distortion from prevents π-conjugative interactions among the ring double bonds, but hyperconjugative interactions between the CH/CC sigma bonds and the π-bonds are present (see J. Chem. Theory Comput. **2012**, 8, 1280). σ-Hole bonding has little to no effect on the ring bond lengths as shown in Figure S1 for **3**$_{minima}$ and the **3(a-d)**$_{minima}$ complexes*.

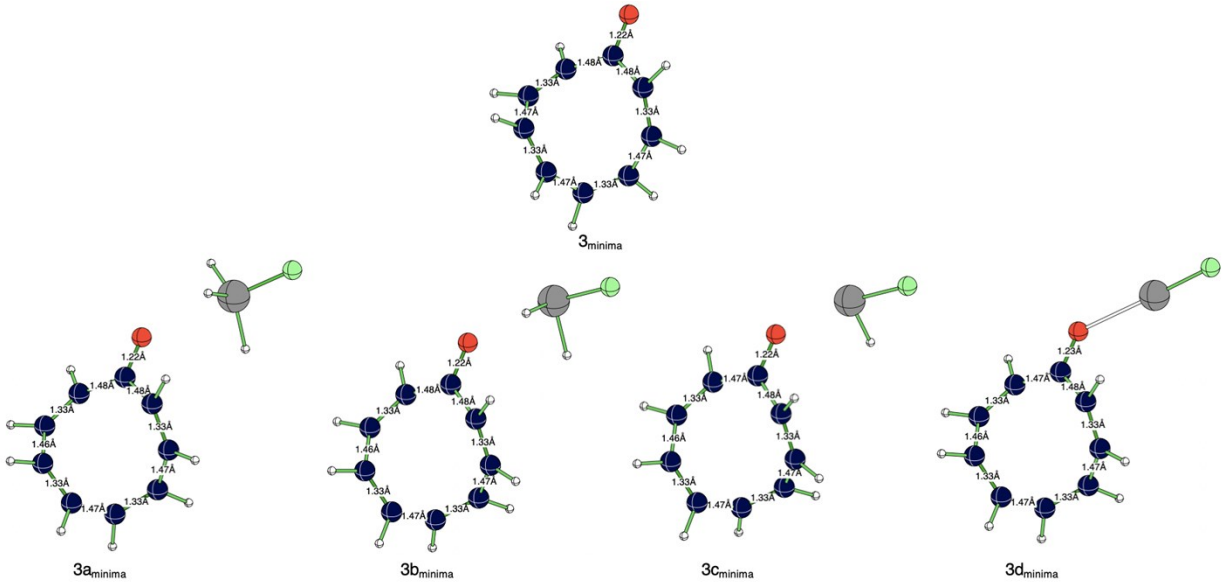

Figure S1. Optimized C=O and ring bond lengths of **3**$_{minima}$ compared to those of **3(a-d)**$_{minima}$.

2. Optimized Cartesian coordinates for all structures at ωB97XD/def2-TZVP

$GeFH_3$, C_s

	X	Y	Z
F	-1.74425	0.00000	0.00000
Ge	0.00000	0.00000	0.00000
H	0.42866	0.73513	1.27248
H	0.42866	0.73513	-1.27248
H	0.42898	-1.46954	0.00000

Total Electronic Energy = -2178.7568621 a.u.
N_{im}= 0

$AsFH_2$, C_s

	X	Y	Z
F	1.75420	0.00000	0.00000
As	0.00000	0.00000	0.00000
H	-0.14744	1.05934	-1.09101
H	-0.14767	1.05929	1.09101

Total Electronic Energy = -2337.0046268 a.u.
N_{im}= 0

SeFH, C_s

	X	Y	Z
F	-2.43930	-1.38958	0.00000
Se	-1.03742	-0.33386	0.00000
H	-0.06550	-1.43904	0.00000

Total Electronic Energy = -2502.0471352 a.u.
N_{im}= 0

BrF, C_s

	X	Y	Z
Br	-0.10803	1.03922	0.00000
F	0.58811	2.64991	0.00000

Total Electronic Energy = -2674.0110041 a.u.
N_{im}= 0

1, C_{2v}

	X	Y	Z
O	1.23604	-0.48867	0.00000
C	0.53818	-1.46516	0.00000
C	0.98551	-2.90409	0.00000
C	-0.10824	-3.65877	0.00000
H	2.01973	-3.20894	0.00000
C	-1.32720	-2.78790	0.00000
H	-1.59160	-0.62886	0.00000
H	-0.14924	-4.73854	0.00000
H	-2.33543	-3.17669	0.00000
C	-0.96787	-1.50853	0.00000

Total Electronic Energy = -268.1119461 a.u.
N_{im}= 0

1a, C_s

	X	Y	Z
Ge	1.95518	-0.08585	0.00000
H	2.13906	-1.60011	0.00000
F	3.58914	0.56454	0.00000
O	-0.67663	-1.12981	0.00000
C	-1.68709	-0.47465	0.00000
C	-3.09545	-0.99944	0.00000
C	-3.90601	0.05323	0.00000
H	-3.34169	-2.04896	0.00000
C	-3.09807	1.31640	0.00000
H	-0.95742	1.69407	0.00000
H	-4.98628	0.03841	0.00000
H	-3.53745	2.30342	0.00000
C	-1.80193	1.02401	0.00000
H	1.33026	0.47692	-1.27851
H	1.33026	0.47692	1.27851

Total Electronic Energy = -2446.8771458 a.u.
N_{im}= 0

1b, C_s

	X	Y	Z
H	3.66783	2.81100	-1.09467
H	3.66817	2.81042	1.09467
As	3.38647	3.83583	0.00000
F	5.03188	4.49192	0.00000
O	1.19106	2.10803	0.00000
C	1.20097	0.90321	0.00000
C	0.00000	0.00000	0.00000
C	0.45026	-1.24990	0.00000
H	-1.01669	0.35834	0.00000
C	1.94978	-1.24953	0.00000
H	3.42072	0.35306	0.00000
H	-0.14428	-2.15197	0.00000
H	2.54473	-2.15136	0.00000
C	2.40203	0.00000	0.00000

Total Electronic Energy = -2605.1258029 a.u.
N_{im}= 0

1c, C_1

	X	Y	Z
O	-0.00735	1.07930	-0.03707
C	1.16948	0.81175	-0.02902
C	2.29966	1.79021	0.10844
C	3.42773	1.08958	0.06672
H	2.16031	2.85386	0.21379
C	3.11454	-0.36874	-0.09374
H	1.23408	-1.45791	-0.25660
H	4.43338	1.47836	0.13543
H	3.87202	-1.13714	-0.14818
C	1.79886	-0.54556	-0.15173
Se	-1.90294	-0.68765	-0.49294
F	-3.29348	-1.79261	-0.44362
H	-2.16743	-0.14949	0.84500

Total Electronic Energy = -2770.1710027 a.u.
N_{im}= 0

1d, C_s

	X	Y	Z
O	1.12618	-0.47344	0.00000
Br	0.17862	1.81365	0.00000
F	-0.50223	3.46240	0.00000
C	0.45300	-1.47707	0.00000
C	0.97616	-2.88279	0.00000
C	-0.07960	-3.68908	0.00000
H	2.02526	-3.12983	0.00000
C	-1.33991	-2.87468	0.00000
H	-1.70336	-0.72783	0.00000
H	-0.06860	-4.76930	0.00000
H	-2.32900	-3.30911	0.00000
C	-1.04284	-1.57950	0.00000

Total Electronic Energy = -2942.1368029 a.u.
N_{im}= 0

2, C_{2v}

	X	Y	Z
O	-0.21582	-1.26391	0.00000
C	0.85947	-0.68484	0.00000
C	2.09525	-1.47649	0.00000
C	0.87869	0.78263	0.00000
C	3.38679	-1.09307	0.00000
H	1.88757	-2.54129	0.00000
C	1.90966	1.64991	0.00000
H	-0.12463	1.19529	0.00000
C	3.96043	0.21881	0.00000
H	4.11364	-1.89944	0.00000

C	3.32068	1.40680	0.00000
H	1.63646	2.70058	0.00000
H	5.04446	0.24878	0.00000
H	3.94235	2.29537	0.00000

Total Electronic Energy = -345.5401717 a.u.
N_{im}= 0

2a, C_s

	X	Y	Z
Ge	-2.56748	-0.06297	0.00000
H	-2.74865	-1.57608	0.00000
H	-1.97535	0.52654	1.28211
H	-1.97535	0.52654	-1.28211
F	-4.22033	0.55930	0.00000
O	-0.05969	-1.07893	0.00000
C	1.06054	-0.57345	0.00000
C	2.22000	-1.46181	0.00000
C	1.19069	0.88111	0.00000
C	3.54021	-1.18416	0.00000
H	1.92680	-2.50585	0.00000
C	2.29017	1.66325	0.00000
H	0.22908	1.38168	0.00000
C	4.21759	0.07369	0.00000
H	4.19715	-2.04782	0.00000
C	3.67452	1.31065	0.00000
H	2.09960	2.73151	0.00000
H	5.30003	0.01616	0.00000
H	4.36447	2.14662	0.00000

Total Electronic Energy = -2524.3084243 a.u.
N_{im}= 0

2b, C_s

	X	Y	Z
C	-1.04638	-0.57314	0.00000
C	-2.21061	-1.45445	0.00000
C	-3.52930	-1.16870	0.00000
C	-4.19875	0.09300	0.00000
C	-3.64769	1.32662	0.00000
C	-2.26137	1.67017	0.00000
C	-1.16625	0.88138	0.00000
H	-0.20068	1.37496	0.00000
H	-2.06389	2.73720	0.00000
H	-4.33235	2.16695	0.00000
H	-5.28154	0.04232	0.00000
H	-4.19139	-2.02842	0.00000
H	-1.92370	-2.50022	0.00000
O	0.07040	-1.08912	0.00000
H	1.90991	0.63287	1.09770
H	1.90991	0.63287	-1.09770
As	2.58350	-0.18627	0.00000
F	4.06270	0.80504	0.00000

Total Electronic Energy = -2682.5573371 a.u.
N_{im}= 0

2c, C_1

	X	Y	Z
Se	-2.49607	-1.57356	-0.44416
H	-2.87397	-1.10597	0.89114
F	-3.55401	-3.01191	-0.34139
O	-1.23121	0.58240	-0.09107
C	-0.01366	0.77885	-0.04729
C	0.44555	2.15987	0.03345
C	0.90139	-0.35420	-0.06583
C	1.69573	2.66850	0.06457
H	-0.38181	2.86011	0.06434
C	2.25125	-0.38631	-0.05426
H	0.37888	-1.30471	-0.09437
C	2.95993	2.00725	0.03337
H	1.75538	3.75055	0.11921

C	3.20123	0.67822	-0.01861
H	2.69000	-1.37854	-0.07702
H	3.82492	2.65998	0.05855
H	4.24074	0.37128	-0.03063

Total Electronic Energy = -2847.603576 a.u.
N_{im}= 0

2d, C_s

	X	Y	Z
O	-0.21963	-1.16784	0.00000
C	0.87514	-0.59115	0.00000
C	2.06429	-1.42980	0.00000
C	0.93406	0.86140	0.00000
C	3.37298	-1.09626	0.00000
H	1.81579	-2.48509	0.00000
C	2.00163	1.68939	0.00000
H	-0.04783	1.32034	0.00000
C	3.99557	0.18657	0.00000
H	4.06432	-1.93238	0.00000
C	3.39795	1.39958	0.00000
H	1.76334	2.74787	0.00000
H	5.07931	0.17593	0.00000
H	4.05014	2.26516	0.00000
Br	-2.39977	-0.20136	0.00000
F	-4.06339	0.48083	0.00000

Total Electronic Energy = -3019.5703045 a.u.
N_{im}= 0

3, C_{2v}

	X	Y	Z
C	-2.1281	0.6722	0.0000
C	-2.0973	-0.7766	0.0000
C	-1.2847	1.7169	0.0000
C	-1.2103	-1.7846	0.0000
C	0.1420	2.0003	0.0000
C	0.2271	-2.0071	0.0000
C	1.3322	1.3891	0.0000
C	1.3903	-1.3460	0.0000
C	1.9411	0.0339	0.0000
O	3.1614	0.0598	0.0000
H	-3.1159	-1.1533	0.0000
H	-3.1617	1.0053	0.0000
H	-1.7128	-2.7470	0.0000
H	-1.8275	2.6571	0.0000
H	0.4071	-3.0788	0.0000
H	0.2764	3.0786	0.0000
H	2.2556	-1.9997	0.0000
H	2.1689	2.0789	0.0000

Total Electronic Energy = -422.8711784 a.u.
N_{im}= 2 (154*i* cm^{-1}, 69*i* cm^{-1})

3, C_1

	X	Y	Z
C	-3.42182	0.36468	0.32627
C	-3.30081	-0.17245	-1.03385
C	-2.55356	1.18830	0.90526
C	-2.39845	-1.06577	-1.42778
C	-1.39963	1.80984	0.24508
C	-1.45758	-1.76977	-0.54866
C	-0.25871	1.29183	-0.20299
C	-0.39699	-1.33841	0.12948
C	0.33376	-0.04934	0.03237
O	1.54161	-0.09688	0.15857
H	-4.05241	0.15025	-1.74900
H	-4.32764	0.10723	0.86818
H	-2.45351	-1.43915	-2.44645
H	-2.78855	1.57309	1.89361
H	-1.66478	-2.83604	-0.47327
H	-1.50325	2.88835	0.13723

H	0.17090	-2.06624	0.69851
H	0.46925	1.96866	-0.63657

Total Electronic Energy = -422.9094337 a.u.
N_{im}= 0

3a, C_s

	X	Y	Z
C	-0.41391	-1.36571	0.00000
C	-1.59192	-2.00049	0.00000
C	-3.02518	-1.75104	0.00000
C	-3.89122	-0.72578	0.00000
C	-3.89219	0.72410	0.00000
C	-3.02686	1.74988	0.00000
C	-1.59362	2.00043	0.00000
C	-0.41577	1.36578	0.00000
C	0.16105	-0.00035	0.00000
O	1.38578	0.00918	0.00000
H	-4.91710	-1.08164	0.00000
H	-4.91846	1.07874	0.00000
H	-3.54529	-2.70365	0.00000
H	-3.54785	2.70207	0.00000
H	-1.43316	-3.07543	0.00000
H	-1.43533	3.07543	0.00000
H	0.43102	-2.04461	0.00000
H	0.43442	2.03868	0.00000
Ge	3.54457	-1.80846	0.00000
F	4.91846	-2.90764	0.00000
H	4.16633	-0.41538	0.00000
H	2.78302	-2.16277	-1.27887
H	2.78302	-2.16277	1.27887

Total Electronic Energy = -2601.6367706 a.u.
N_{im}= 2 (158*i* cm^{-1}, 64*i* cm^{-1})

3b, C_s

	X	Y	Z
C	-0.2705	-1.3380	0.0000
C	-1.4486	-1.9728	0.0000
C	-2.8821	-1.7239	0.0000
C	-3.7484	-0.6989	0.0000
C	-3.7495	0.7511	0.0000
C	-2.8842	1.7769	0.0000
C	-1.4509	2.0275	0.0000
C	-0.2729	1.3931	0.0000
C	0.3035	0.0269	0.0000
O	1.5291	0.0388	0.0000
H	-4.7742	-1.0549	0.0000
H	-4.7758	1.1056	0.0000
H	-3.4018	-2.6767	0.0000
H	-3.4052	2.7291	0.0000
H	-1.2895	-3.0477	0.0000
H	-1.2927	3.1025	0.0000
H	0.5746	-2.0171	0.0000
H	0.5773	2.0660	0.0000
As	3.7105	-1.6863	0.0000
F	4.7758	-3.1025	0.0000
H	2.7945	-2.2259	-1.0952
H	2.7945	-2.2259	1.0952

Total Electronic Energy = -2759.8854298 a.u.
N_{im}= 2 (157*i* cm^{-1}, 61*i* cm^{-1})

3c, *C_1 (ring atoms constrained to planar symmetry)*

	X	Y	Z
C	0.00000	0.00000	0.00000
H	1.08471	0.00000	0.00000
C	-0.52128	1.23262	0.00000
H	0.27700	1.96990	0.00000
C	-1.79364	1.93865	0.00000
H	-1.59994	3.00656	0.00000
C	-3.11131	1.68482	0.00000

H	-3.68660	2.60571	0.00000
C	-4.02192	0.55625	0.00000
H	-5.04367	0.92369	0.00000
C	-3.99111	-0.78521	0.00000
H	-4.99373	-1.20087	0.00000
C	-3.03087	-1.87849	0.00000
H	-3.58132	-2.81531	0.00000
C	-1.71549	-2.12374	0.00000
H	-1.47618	-3.18113	0.00000
C	-0.41113	-1.42029	0.00000
O	0.53348	-2.20507	0.00000
Se	3.12727	-1.98626	0.31566
F	4.89697	-2.10228	0.19884
H	2.90379	-2.75443	-0.91253

Total Electronic Energy = -2924.930676 a.u.
N_{im}= 2 (157*i* cm^{-1}, 63*i* cm^{-1})

3d, C_s

	X	Y	Z
C	-0.20335	-1.36427	0.00000
C	-1.38309	-1.99660	0.00000
C	-2.81737	-1.75083	0.00000
C	-3.68582	-0.72813	0.00000
C	-3.68903	0.72220	0.00000
C	-2.82403	1.74762	0.00000
C	-1.39020	1.99650	0.00000
C	-0.21119	1.36392	0.00000
C	0.36368	-0.00120	0.00000
O	1.59347	0.02792	0.00000
H	-4.71092	-1.08606	0.00000
H	-4.71552	1.07604	0.00000
H	-3.33437	-2.70502	0.00000
H	-3.34392	2.70030	0.00000
H	-1.22313	-3.07134	0.00000
H	-1.23136	3.07134	0.00000
H	0.63812	-2.04704	0.00000
H	0.63742	2.03835	0.00000
Br	3.37895	-1.68023	0.00000
F	4.71552	-2.86170	0.00000

Total Electronic Energy = -3096.8963081 a.u.
N_{im}= 2 (158*i* cm^{-1}, 61*i* cm^{-1})

Fluorenone, C_{2v}

	X	Y	Z
C	0.00000	-0.74037	0.00000
C	0.00000	0.74037	0.00000
C	1.32326	1.18672	0.00000
C	1.32326	-1.18672	0.00000
C	1.63543	2.52839	0.00000
C	1.63543	-2.52839	0.00000
C	0.58888	3.44591	0.00000
C	0.58888	-3.44591	0.00000
C	-1.03849	1.64911	0.00000
C	-1.03849	-1.64911	0.00000
C	-0.72839	3.00758	0.00000
C	-0.72839	-3.00758	0.00000
H	2.66968	2.84908	0.00000
H	2.66968	-2.84908	0.00000
H	0.80013	4.50737	0.00000
H	0.80013	-4.50737	0.00000
H	-2.07137	1.32392	0.00000
H	-2.07137	-1.32392	0.00000
H	-1.53031	3.73526	0.00000
H	-1.53031	-3.73526	0.00000
C	2.23615	0.00000	0.00000
O	3.43923	0.00000	0.00000

Total Electronic Energy = -575.4374684 a.u.
N_{im}= 0

Fluorenone-GeH_3F, C_s

	X	Y	Z
C	-2.22092	0.76767	0.00000
C	-2.23709	-0.71281	0.00000
C	-0.91765	-1.17482	0.00000
C	-0.62360	-2.52136	0.00000
C	-1.68174	-3.42544	0.00000
C	-3.28584	-1.60799	0.00000
C	-2.99264	-2.97071	0.00000
H	0.40319	-2.86286	0.00000
H	-1.48241	-4.48894	0.00000
H	-4.31439	-1.26985	0.00000
H	-3.80355	-3.68820	0.00000
C	-0.89218	1.19735	0.00000
C	-0.56042	2.53439	0.00000
C	-1.59505	3.46532	0.00000
C	-3.24681	1.68942	0.00000
C	-2.91762	3.04391	0.00000
C	0.00064	0.00208	0.00000
H	0.47776	2.84172	0.00000
H	-1.36999	4.52376	0.00000
H	-4.28394	1.37858	0.00000
H	-3.70965	3.78221	0.00000
O	1.20853	0.00281	0.00000
Ge	3.36839	-1.77306	0.00000
H	2.61127	-2.13591	-1.27917
H	2.61127	-2.13591	1.27917
H	3.98588	-0.37856	0.00000
F	4.74862	-2.86603	0.00000

Total Electronic Energy = -2754.2036495 a.u.
N_{im}= 1 (10*i* cm^{-1})

Fluorenone-AsH_2F, C_s

	X	Y	Z
C	-2.21780	0.77585	0.00000
C	-2.24034	-0.70448	0.00000
C	-0.92279	-1.17289	0.00000
C	-0.63526	-2.52115	0.00000
C	-1.69841	-3.41958	0.00000
C	-3.29343	-1.59433	0.00000
C	-3.00698	-2.95856	0.00000
H	0.39024	-2.86722	0.00000
H	-1.50418	-4.48404	0.00000
H	-4.32023	-1.25096	0.00000
H	-3.82150	-3.67198	0.00000
C	-0.88723	1.19939	0.00000
C	-0.54894	2.53480	0.00000
C	-1.57923	3.47051	0.00000
C	-3.23939	1.70231	0.00000
C	-2.90377	3.05526	0.00000
C	0.00016	0.00037	0.00000
H	0.49074	2.83702	0.00000
H	-1.34926	4.52790	0.00000
H	-4.27796	1.39636	0.00000
H	-3.69232	3.79728	0.00000
O	1.20859	0.00049	0.00000
As	3.41499	-1.65784	0.00000
H	2.51191	-2.21612	-1.09610
H	2.51191	-2.21612	1.09610
F	4.50762	-3.05454	0.00000

Total Electronic Energy = -2912.4522597 a.u.
N_{im}= 1 (7*i* cm^{-1})

Fluorenone-SeHF, C_1

	X	Y	Z
C	-1.89194	0.31428	0.14705
C	-0.95838	-0.72866	-0.33484
C	0.33996	-0.20773	-0.32722
C	1.42508	-0.96277	-0.72004
C	1.19606	-2.27184	-1.13468
C	-1.18389	-2.0247	-0.74602

C	-0.09037	-2.79086	-1.14725
H	2.42341	-0.54343	-0.7016
H	2.02699	-2.8895	-1.44908
H	-2.18137	-2.44549	-0.75892
H	-0.24851	-3.81116	-1.47353
C	-1.15606	1.46236	0.44773
C	-1.75596	2.60857	0.92119
C	-3.13637	2.59831	1.09874
C	-3.25967	0.30357	0.32206
C	-3.87299	1.45989	0.80202
C	0.283	1.19896	0.1636
H	-1.16261	3.48609	1.14499
H	-3.64036	3.48126	1.46927
H	-3.8503	-0.57495	0.095
H	-4.94613	1.4701	0.94579
O	1.19296	1.9835	0.31239
Se	3.73426	2.10557	-0.3236
H	3.64886	2.276	1.1298
F	5.50199	2.29039	-0.35317

Total Electronic Energy = -3077.4975545 a.u.
N_{im}= 0

9-Fluorenone-BrF, C_s

	X	Y	Z
C	-2.19805	0.81860	0.00000
C	-2.24712	-0.66049	0.00000
C	-0.93759	-1.15529	0.00000
C	-0.67928	-2.51045	0.00000
C	-1.76224	-3.38505	0.00000
C	-3.31812	-1.52732	0.00000
C	-3.06053	-2.89748	0.00000
H	0.33712	-2.88073	0.00000
H	-1.58964	-4.45314	0.00000
H	-4.33714	-1.16170	0.00000
H	-3.88987	-3.59360	0.00000
C	-0.85968	1.21591	0.00000
C	-0.49313	2.54394	0.00000
C	-1.50465	3.49987	0.00000
C	-3.20051	1.76500	0.00000
C	-2.83706	3.11107	0.00000
C	0.00105	0.00151	0.00000
H	0.55232	2.82508	0.00000
H	-1.25347	4.55234	0.00000
H	-4.24505	1.48035	0.00000
H	-3.61056	3.86874	0.00000
O	1.21394	0.00230	0.00000
Br	2.96662	-1.72681	0.00000
F	4.27838	-2.93731	0.00000

Total Electronic Energy = -3249.4632352 a.u.
N_{im}= 0

9-Fluorenone complexed to two BrF's, C_s

	X	Y	Z
C	1.92559	-1.32542	0.00000
C	0.44772	-1.32542	0.00000
C	0.00000	0.00000	0.00000
C	-1.34593	0.30401	0.00000
C	-2.25697	-0.74820	0.00000
C	-0.45390	-2.36637	0.00000
C	-1.81465	-2.06225	0.00000
H	-1.68425	1.33084	0.00000
H	-3.31825	-0.53827	0.00000
H	-0.12279	-3.39700	0.00000
H	-2.53873	-2.86722	0.00000
C	2.37331	0.00000	0.00000
C	3.71924	0.30401	0.00000
C	4.63028	-0.74820	0.00000
C	2.82721	-2.36637	0.00000
C	4.18796	-2.06225	0.00000
C	1.18665	0.89698	0.00000

H	4.05756	1.33084	0.00000
H	5.69156	-0.53827	0.00000
H	2.49610	-3.39700	0.00000
H	4.91203	-2.86722	0.00000
O	1.18665	2.11706	0.00000
Br	-0.70157	3.92121	0.00000
F	-1.94684	5.18324	0.00000
Br	3.07488	3.92121	0.00000
F	4.32015	5.18324	0.00000

Total Electronic Energy = -5923.4844724 a.u.

N_{im}= 1 ($2i$ cm^{-1})