Electronic Supplementary Material (ESI) for Chemical Communications

Relationship of charge to antiaromaticity in bis-fluorenyl dications and fluorenyl monocations: experimental support for theoretical calculations

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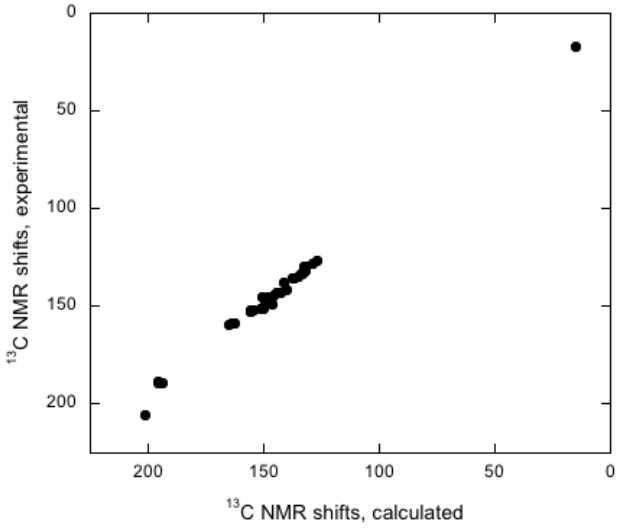
Electronic supplementary information

Plot of ^{13}C NMR shifts calculated[a] with solvent vs experimental shifts for **1a,b, 2a,** and **3.**



Plot of ΣNICS vs Σ^{13}C NMR shifts for **1a-c, 2a**,**b**, and **3**

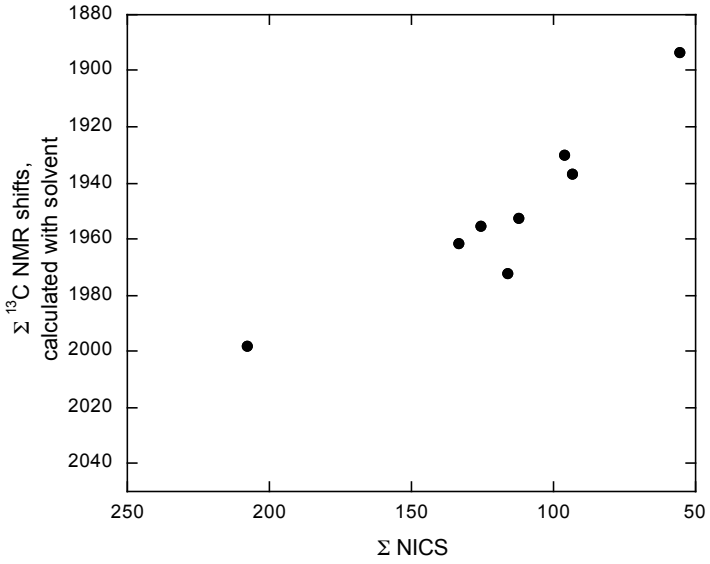


Table of calculated[1] charges for **1a-c, 2a**,**b**, and **3**

Charges for 1a, 2a, 3a

	1a		**2a**		**3**	
	C without H	C plus H	C without H	C plus H	C without H	C plus H
1	-0.0747	0.1556	-0.0868	0.1362	-0.1001	0.1245
2	-0.1956	0.0482	-0.1968	0.0389	-0.1967	0.0311
3	-0.0418	0.1967	-0.0644	0.1680	-0.0937	0.1301
4	-0.1441	0.0965	-0.1556	0.0788	-0.1681	0.0577
4a	0.0106	0.0106	0.0129	0.0129	0.0089	0.0089
4b	0.0106	0.0106	0.0129	0.0129	0.0089	0.0089
5	-0.1441	0.0965	-0.1556	0.0788	-0.1681	0.0577
6	-0.0418	0.1967	-0.0644	0.1680	-0.0937	0.1301
7	-0.1956	0.0482	-0.1968	0.0389	-0.1967	0.0311
8	-0.0747	0.1556	-0.0869	0.1362	-0.1001	0.1245
8a	-0.0985	-0.0985	-0.1094	-0.1094	-0.1061	-0.1061
9	0.1817	0.1817	0.2415	0.2414	0.2518	0.2518
9a	-0.0985	-0.0985	-0.1094	-0.1094	-0.1061	-0.1061
I			-0.0685	-0.0685	-0.1116	-0.1116
o			-0.1458	0.0881	-0.1374	0.0833
o			-0.1457	0.0881	-0.1374	0.0833
m/o			-0.0684	0.0881	-0.1851	0.0425
m/o			-0.1458	0.0881	-0.1851	0.0425
p/i			-0.1458	-0.0684	-0.1079	0.1160
Sum all C	-1.8129	2.0000	-2.6375	2.0000	-1.9241	1.0000
Sum fluorenyl C	-0.9065	1.0000	-0.9588	0.8923	-1.0596	0.7441
Sum phenyl			-0.7199	0.2154	-0.8645	0.2559
Fl system-6 ring		0.4092		0.3255		0.2462
Fl system-5-ring		0.0060		0.0486		0.0573
Stand. Dev.	0.108	0.091	0.123	0.106	0.124	0.100

Charges for 1b, substituted, and unsubstituted, 2b

	1b, substituted ring		**1b, unsubstituted ring**		**2b**	
	C without H	C plus H	C without H	C plus H	C without H	C plus H
1	-0.07538	0.15929	-0.06406	0.17475	-0.07855	0.15395
2	-0.01719	-0.01719	-0.20334	0.03341	-0.20538	0.02579
3	-0.06184	0.16559	-0.05777	0.17287	-0.08144	0.14476
4	-0.14578	0.09308	-0.15151	0.08838	-0.16758	0.06691
4a	0.01107	0.01107	0.01685	0.01685	0.01671	0.01671
4b	0.01107	0.01107	0.01685	0.01685	0.01469	0.01469

5	-0.14578	0.09308	-0.15151	0.08838	-0.16537	0.06917
6	-0.06184	0.16559	-0.05777	0.17287	-0.08161	0.14469
7	-0.01719	-0.01719	-0.20334	0.03341	-0.20551	0.02567
8	-0.07538	0.15929	-0.06406	0.17475	-0.07738	0.15716
8a	-0.08409	-0.08409	-0.09212	-0.09212	-0.11019	-0.11019
9	0.20088	0.20088	0.20612	0.20612	0.27904	0.27904
9a	-0.08409	-0.08409	-0.09212	-0.09212	-0.11223	-0.11223
CH_3	-0.59194	0.07461			-0.60009	0.07448
i					-0.0774	-0.0774
o-CH_3					0.03816	0.0382
o					-0.14344	0.08868
Sum fluorenyl C	-0.54554	0.85638	-0.89778	0.9944	-0.9748	0.87612
Stand. Dev.	0.088	0.101	0.109	0.101	0.128	0.110

Charges for **1c**, substituted and unsubstituted fluorenyl systems, and **5**

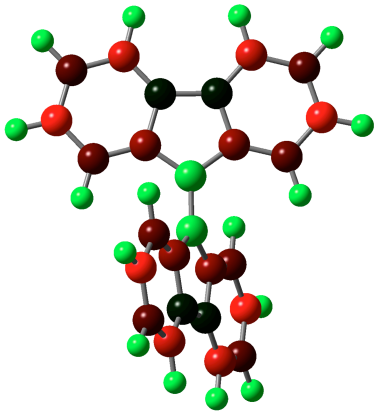
	1c, substituted ring		**1c**, unsubstituted ring		**5**	
	C without H	C plus H	C without H	C plus H	C without H	C plus H
1	-0.07335	0.16383	-0.06571	0.17262	-0.14452	0.08281
2	-0.21150	0.02192	-0.20355	0.03263	-0.15026	0.08301
3	0.13087	0.13087	-0.06000	0.17018	-0.11162	0.12073
4	-0.15704	0.07919	-0.15291	0.08641	-0.1591	0.07094
4a	0.02424	0.02424	0.01673	0.01673	0.01374	0.01374
4b	0.02424	0.02424	0.01673	0.01673	-0.10559	0.12437
5	-0.15704	0.07919	-0.15291	0.08641	-0.10559	0.12437
6	0.13087	0.13087	-0.06000	0.17018	0.01374	0.01374
7	-0.21150	0.02192	-0.20355	0.03263	-0.1591	0.07094
8	-0.07335	0.16383	-0.06571	0.17262	-0.11163	0.12072
8a	-0.09042	-0.09042	-0.09378	-0.09378	-0.15026	0.08301
9	0.17068	0.17068	0.21461	0.21461	-0.14452	0.08281
9a	-0.09042	-0.09042	-0.09378	-0.09378	-0.05632	-0.05632
CH_3	-0.60900	0.09293			0.12144	0.12144
Sum fluorenyl C	-0.58372	0.82994	-0.90383	0.98419	-0.05632	-0.05632
St. Dev.	0.136	0.079	0.111	0.102	0.081	0.061

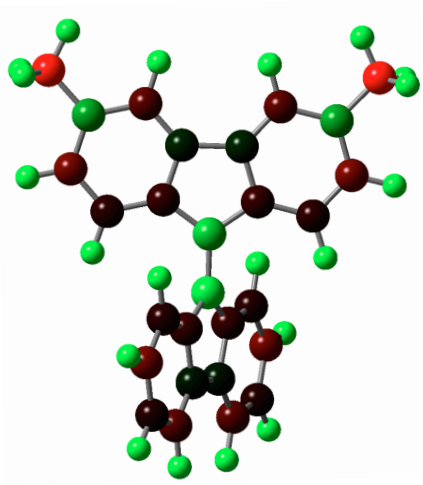
Graphical presentation of charge distribution, geometries optimized at the B3LYP/6-31g(d) level, charge calculated with natural population analysis with basis set B3LYP/6-311g(d,p) with the inclusion of solvent (DMSO as the model solvent) via the polarization continuum method

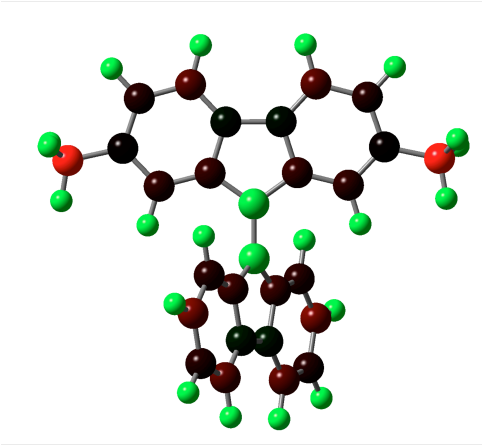
Figure 1 shows the variation in charge for **1a**. The charge distribution for the carbons of the fluorenyl system ranges from -0.203 to 0.203, red indicates the negative end of the range, green the positive end. Charge alternation is apparent in the variation colors of the carbons of the fluorenyl ring as shown in the alternation between atoms that have more green coloration and those that are more reddish. The charge alternation is mirrored between both halves of the fluorenyl system.

Figure 2 shows the variation in charge for **1c**. The charge distribution for the substituted fluorenyl system ranges from -0.024 to 0.171. The charge alternation continues to be visible in the fluorenyl ring system. Because the range is smaller, the difference in the colors is also smaller.

Figure 3 shows the variation in charge for **1b**. The charge distribution for the substituted fluorenyl system ranges from -0.201 to 0.111. In comparison to **1a** and **1c**, there is markedly less charge alternation suggesting that the delocalization is more complete throughout the fluorenyl system of the substituted ring. Although the range of charge is greater, the similarity of the colors of the carbons of the fluorenyl system indicate greater alternation.

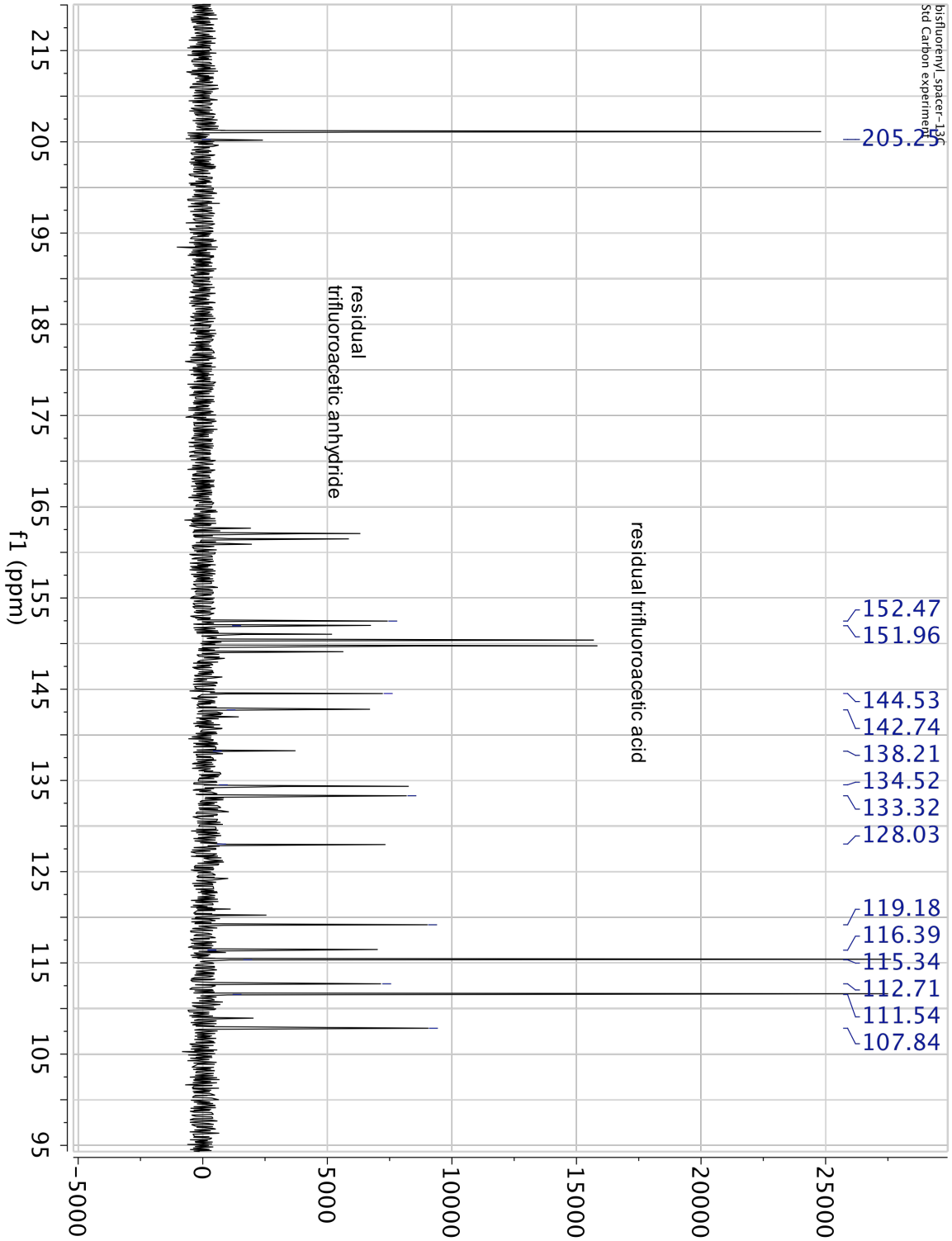






Details of the synthesis of the precursors to **1a**, **1b**, **1c**, **2a**, and **3** can be found in the chemical literature, along with their NMR shifts. The report of **1c** did not contain ^{13}C NMR data because we were unable to obtain it for the dication prepared by oxidation of the unsaturated precursor in Magic Acid®. Similarly, we were unable to obtain ^{13}C NMR data for **2a** when it was prepared by ionization with Magic Acid®; but have been able to obtain it for the dication when prepared by ionization under more stabilizing conditions. Because the data has not previously been reported, we include it here, see next page.

^{13}C NMR spectrum for **2a**, details of preparation[2]



Cartesian coordinates[1], total energies for **1a-c, 2a**,**b**, and **3**

1a , Total energy, -999.809426 Hartrees

H	-0.72309	1.18159	-4.98482
C	-0.87033	1.42753	-3.93779
C	-1.32111	2.16346	-1.22164
C	-0.38218	0.63497	-2.92769
C	-1.59136	2.60341	-3.58629
C	-1.81399	2.96435	-2.25526
C	-0.59321	1.00576	-1.5603
H	-1.50312	-2.43134	0.18538
H	-1.98351	3.23188	-4.3806
H	-2.37679	3.86265	-2.02565
C	0.	0.	-0.73047
H	-1.50312	2.43134	-0.18538
C	0.	0.	0.73047
C	0.59321	-1.00576	-1.5603
C	0.59321	1.00576	1.5603
C	-0.59321	-1.00576	1.5603
C	1.59136	-2.60341	-3.58629
C	1.32111	-2.16346	-1.22164
C	0.38218	-0.63497	-2.92769
C	0.87033	-1.42753	-3.93779
C	1.81399	-2.96435	-2.25526
H	1.50312	-2.43134	-0.18538
H	-2.37679	-3.86265	2.02565
H	0.72309	-1.18159	-4.98482
H	2.37679	-3.86265	-2.02565
H	1.98351	-3.23188	-4.3806
C	1.59136	2.60341	3.58629
C	0.38218	0.63497	2.92769
C	1.32111	2.16346	1.22164
C	1.81399	2.96435	2.25526
C	0.87033	1.42753	3.93779
H	-0.72309	-1.18159	4.98482
H	1.50312	2.43134	0.18538
H	2.37679	3.86265	2.02565
H	0.72309	1.18159	4.98482
H	1.98351	3.23188	4.3806
C	-1.59136	-2.60341	3.58629
C	-0.38218	-0.63497	2.92769
C	-1.32111	-2.16346	1.22164
C	-1.81399	-2.96435	2.25526
C	-0.87033	-1.42753	3.93779
H	-1.98351	-3.23188	4.3806

1b, Total energy, -1078.4536114 Hartrees

C	0.	0.	0.88547
C	0.	0.	-0.57506
C	0.02425	1.16847	-1.40416
C	-0.02425	-1.16847	-1.40416
C	0.0108	2.53557	-1.06335
C	-0.0108	-2.53557	-1.06335
C	0.00719	3.50418	-2.07867
C	-0.00719	-3.50418	-2.07867
C	0.00498	3.05563	-3.41016
C	-0.00498	-3.05563	-3.41016
C	0.00438	1.68097	-3.7695
C	-0.00438	-1.68097	-3.7695
C	0.00758	0.74055	-2.7683
C	-0.00758	-0.74055	-2.7683
C	1.03427	0.54106	1.71634
C	-1.03427	-0.54106	1.71634
C	2.26341	1.13841	1.37686
C	-2.26341	-1.13841	1.37686
C	3.10804	1.55337	2.41028
C	-3.10804	-1.55337	2.41028
C	2.73086	1.36116	3.74135
C	-2.73086	-1.36116	3.74135
C	1.4969	0.74602	4.09345
C	-1.4969	-0.74602	4.09345
C	0.66058	0.33621	3.08357
C	-0.66058	-0.33621	3.08357
H	-0.00278	2.84862	-0.02313
H	0.00278	-2.84862	-0.02313
H	-0.00373	3.79365	-4.20837
H	0.00373	-3.79365	-4.20837
H	-0.00101	1.40431	-4.81936
H	0.00101	-1.40431	-4.81936
H	2.55621	1.27239	0.34007
H	-2.55621	-1.27239	0.34007
H	4.06095	2.01752	2.18013
H	-4.06095	-2.01752	2.18013
H	3.39833	1.68355	4.53524
H	-3.39833	-1.68355	4.53524
H	1.24382	0.61179	5.14054
H	-1.24382	-0.61179	5.14054
C	0.	4.97909	-1.76336
H	-0.0773	5.16032	-0.68825
H	0.91685	5.46075	-2.12232
H	-0.84207	5.48116	-2.25182
C	0.	-4.97909	-1.76336

H	0.0773	-5.16032	-0.68825
H	-0.91685	-5.46075	-2.12232
H	0.84207	-5.48116	-2.25182

1c, total energy, -1078.4631406 Hartrees

C	0.	0.	1.14675
C	0.	0.	-0.31365
C	0.02776	1.16605	-1.14136
C	-0.02776	-1.16605	-1.14136
C	0.01504	2.53862	-0.81927
C	-0.01504	-2.53862	-0.81927
C	0.01266	3.46802	-1.85347
C	-0.01266	-3.46802	-1.85347
C	0.00905	3.06359	-3.20313
C	-0.00905	-3.06359	-3.20313
C	0.00597	1.66676	-3.52063
C	-0.00597	-1.66676	-3.52063
C	0.00868	0.74175	-2.50856
C	-0.00868	-0.74175	-2.50856
C	1.02067	0.56585	1.97897
C	-1.02067	-0.56585	1.97897
C	2.23623	1.19014	1.64062
C	-2.23623	-1.19014	1.64062
C	3.07079	1.62449	2.67439
C	-3.07079	-1.62449	2.67439
C	2.69773	1.42387	4.00528
C	-2.69773	-1.42387	4.00528
C	1.47871	0.7801	4.35648
C	-1.47871	-0.7801	4.35648
C	0.65222	0.3521	3.3459
C	-0.65222	-0.3521	3.3459
H	0.00283	2.87394	0.2134
H	-0.00283	-2.87394	0.2134
H	0.00479	4.52842	-1.62083
H	-0.00479	-4.52842	-1.62083
H	-0.00066	1.36645	-4.5644
H	0.00066	-1.36645	-4.5644
H	2.52682	1.32937	0.60396
H	-2.52682	-1.32937	0.60396
H	4.01295	2.11024	2.44457
H	-4.01295	-2.11024	2.44457
H	3.35733	1.76151	4.79938
H	-3.35733	-1.76151	4.79938
H	1.22879	0.63832	5.40333
H	-1.22879	-0.63832	5.40333
C	0.	4.08397	-4.29811

H	-0.879	4.73616	-4.20972
H	0.87728	4.73992	-4.22119
H	-0.00551	3.62905	-5.29055
C	0.	-4.08397	-4.29811
H	0.879	-4.73616	-4.20972
H	-0.87728	-4.73992	-4.22119
H	0.00551	-3.62905	-5.29055

2a, total energy, -1230.9145386 Hartrees

C	0.00171	-0.50001	-0.00111
C	0.00171	-0.50001	1.39734
C	1.2091	-0.50001	2.09774
C	2.45939	-0.49032	1.42786
C	2.46428	-0.49989	0.05236
C	3.56389	-0.46587	-0.93871
C	4.93247	-0.45974	-0.80058
C	5.7286	-0.45526	-1.97456
C	5.15757	-0.47584	-3.24809
C	3.76677	-0.4919	-3.39335
C	2.96801	-0.45978	-2.2377
C	1.53704	-0.49997	-2.08258
C	1.2344	-0.52711	-0.67514
C	0.56012	-0.51126	-3.1669
C	-0.54523	-1.38977	-3.13049
C	-1.45844	-1.42035	-4.17536
C	-1.33208	-0.53314	-5.26713
C	-0.24236	0.3652	-5.28959
C	0.70217	0.35613	-4.27253
C	-2.77096	1.98168	-6.65976
C	-3.50394	2.90865	-7.40748
C	-4.36563	2.47144	-8.41483
C	-4.53393	1.09331	-8.70548
C	-3.80782	0.17844	-7.97894
C	-3.76424	-1.30148	-8.00278
C	-4.40187	-2.23212	-8.78983
C	-4.11604	-3.60498	-8.57646
C	-3.19925	-4.02167	-7.60982
C	-2.54141	-3.0786	-6.81385
C	-2.84387	-1.71794	-6.99183
C	-2.30901	-0.54444	-6.35146
C	-2.90242	0.61599	-6.96337
H	-0.93687	-0.46293	-0.54442
H	-0.93763	-0.48685	1.93958
H	1.19583	-0.49225	3.18368
H	3.37905	-0.46851	2.0043
H	5.41035	-0.46539	0.17417

H	6.81006	-0.45064	-1.87489
H	5.79464	-0.4925	-4.12584
H	3.32441	-0.54493	-4.38279
H	-0.6577	-2.08345	-2.3041
H	-2.30326	-2.09895	-4.12503
H	-0.11147	1.03553	-6.13239
H	1.52855	1.05801	-4.30653
H	-2.12944	2.32029	-5.85272
H	-3.41317	3.96876	-7.19639
H	-4.93515	3.20074	-8.9834
H	-5.22906	0.78753	-9.48124
H	-5.10426	-1.94249	-9.56525
H	-4.61469	-4.34664	-9.19348
H	-2.98774	-5.07827	-7.48545
H	-1.80202	-3.40124	-6.08812

2b, total energy, -1309.5452787 Hartrees

C	3.39174	1.74456	-1.83773
C	4.43067	2.39378	-2.51212
C	5.75916	2.10693	-2.19402
C	6.09844	1.15517	-1.19849
C	5.07975	0.52108	-0.52594
C	5.07974	-0.5211	0.52592
C	6.09845	-1.15512	1.19851
C	5.75919	-2.10692	2.19402
C	4.43069	-2.39376	2.51213
C	3.39174	-1.74457	1.83773
C	3.7159	-0.82652	0.82448
C	2.87303	0.00001	-0.00001
C	3.71586	0.82651	-0.82447
C	1.41349	0.	-0.00001
C	0.69389	1.21527	-0.01419
C	-0.69385	1.21529	0.01465
C	-1.4135	-0.00001	0.
C	-0.69384	-1.21528	-0.01467
C	0.69389	-1.21529	0.01417
C	-3.39174	-1.74378	-1.83846
C	-4.43067	-2.39266	-2.51314
C	-5.7592	-2.10598	-2.19493
C	-6.09844	-1.15463	-1.199
C	-5.07975	-0.52089	-0.52615
C	-5.07974	0.52087	0.52617
C	-6.09845	1.15464	1.19898
C	-5.75924	2.10597	2.19492
C	-4.43069	2.39268	2.51316
C	-3.39174	1.74377	1.83848

C	-3.71588	0.82617	0.82483
C	-2.87305	-0.00001	0.
C	-3.71586	-0.82615	-0.82482
H	2.36016	1.94114	-2.11105
H	4.20488	3.11208	-3.2929
H	6.55711	2.61216	-2.73025
H	7.14242	0.94078	-0.9919
H	7.14243	-0.94073	0.99191
H	6.55713	-2.61218	2.73023
H	4.20488	-3.11206	3.29292
H	2.36016	-1.94116	2.11104
H	1.22718	2.15976	0.00297
H	-1.22718	2.15977	-0.00213
H	-1.22718	-2.15977	0.00214
H	1.22719	-2.15975	-0.00295
H	-2.36016	-1.94024	-2.1119
H	-4.20489	-3.11066	-3.29425
H	-6.55715	-2.61097	-2.73136
H	-7.14241	-0.94032	-0.99233
H	-7.14242	0.94032	0.99232
H	-6.55714	2.61097	2.73135
H	-4.2049	3.11064	3.29428
H	-2.36017	1.94025	2.11189

3, total energy, -731.6239583 Hartrees

C	0.01651	2.53459	-0.27012
C	0.02584	3.46552	-1.31519
C	0.03525	3.03362	-2.64163
C	0.02193	1.6588	-2.96926
C	0.02592	0.73899	-1.94258
C	-0.02592	-0.73899	-1.94258
C	-0.02193	-1.6588	-2.96926
C	-0.03525	-3.03362	-2.64163
C	-0.02584	-3.46552	-1.31519
C	-0.01651	-2.53459	-0.27012
C	-0.05157	-1.16907	-0.58412
C	0.	0.	0.27354
C	0.05157	1.16907	-0.58412
C	0.	0.	1.71186
C	-0.79517	-0.92687	2.43515
C	0.79517	0.92687	2.43515
C	0.80692	0.90832	3.82232
C	-0.80692	-0.90832	3.82232
C	0.	0.	4.5185
H	-0.03818	2.87471	0.75817
H	0.00973	4.52701	-1.09191

H	0.03249	3.76695	-3.44254
H	-0.00231	1.35001	-4.00981
H	0.00231	-1.35001	-4.00981
H	-0.03249	-3.76695	-3.44254
H	-0.00973	-4.52701	-1.09191
H	0.03818	-2.87471	0.75817
H	-1.45309	-1.60154	1.89851
H	1.45309	1.60154	1.89851
H	1.44589	1.59663	4.36631
H	-1.44589	-1.5966	4.36631
H	0.00000	0.0000	5.60438

(1)Gaussian 09, R. A.; M. J. Frisch, G. W. T., H. B. Schlegel, G. E. Scuseria, ; M. A. Robb, J. R. C., G. Scalmani, V. Barone, B. Mennucci, ; G. A. Petersson, H. N., M. Caricato, X. Li, H. P. Hratchian, ; A. F. Izmaylov, J. B., G. Zheng, J. L. Sonnenberg, M. Hada, ; M. Ehara, K. T., R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, ; Y. Honda, O. K., H. Nakai, T. Vreven, J. A. Montgomery, Jr., ; J. E. Peralta, F. O., M. Bearpark, J. J. Heyd, E. Brothers, ; K. N. Kudin, V. N. S., R. Kobayashi, J. Normand, ; K. Raghavachari, A. R., J. C. Burant, S. S. Iyengar, J. Tomasi, ; M. Cossi, N. R., J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, ; V. Bakken, C. A., J. Jaramillo, R. Gomperts, R. E. Stratmann, ; O. Yazyev, A. J. A., R. Cammi, C. Pomelli, J. W. Ochterski, ; R. L. Martin, K. M., V. G. Zakrzewski, G. A. Voth, ; P. Salvador, J. J. D., S. Dapprich, A. D. Daniels, ; O. Farkas, J. B. F., J. V. Ortiz, J. Cioslowski, ; and D. J. Fox, G., Inc., Wallingford CT, 2009.

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