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Structures of the Hexafluorocyclopropane, Octafluorocyclobutane and Decafluorocyclopentane Radical Anions Probed by Experimental and Computational Studies of Anisotropic ESR Spectra

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Supporting Information (1):
^{19}F anisotropic hyperfine couplings in molecular axis system calculated for *c*-$C_3F_6^-$.

Atom	Anisotropic *hf* dipole couplings/mT		Direction cosines: x, y, z system
1 C(13)	Baa	-0.826	1.0000 0.0000 0.0000
	Bbb	-0.490	0.0000 1.0000 0.0000
	Bcc	1.316	0.0000 0.0000 1.0000
2 C(13)	Baa	-0.826	-0.5000 0.8660 0.0000
	Bbb	-0.490	-0.8660 -0.5000 0.0000
	Bcc	1.316	0.0000 0.0000 1.0000
3 C(13)	Baa	-0.826	0.5000 0.8660 0.0000
	Bbb	-0.490	0.8660 -0.5000 0.0000
	Bcc	1.316	0.0000 0.0000 1.0000
4 F(19)	Baa	-4.901	0.0000 -0.3007 0.9537
	Bbb	-4.844	1.0000 0.0000 0.0000
	Bcc	9.745	0.0000 0.9537 0.3007
5 F(19)	Baa	-4.901	0.0000 0.3007 0.9537
	Bbb	-4.844	1.0000 0.0000 0.0000
	Bcc	9.744	0.0000 0.9537 -0.3007
6 F(19)	Baa	-4.901	-0.2604 -0.1503 0.9537
	Bbb	-4.844	-0.5000 0.8660 0.0000
	Bcc	9.744	0.8260 0.4769 0.3007
7 F(19)	Baa	-4.901	0.2604 0.1503 0.9537
	Bbb	-4.844	-0.5000 0.8660 0.0000
	Bcc	9.744	0.8260 0.4769 -0.3007
8 F(19)	Baa	-4.901	-0.2604 0.1503 0.9537
	Bbb	-4.844	0.5000 0.8660 0.0000
	Bcc	9.744	0.8260 -0.4769 0.3007
9 F(19)	Baa	-4.901	0.2604 -0.1503 0.9537
	Bbb	-4.844	0.5000 0.8660 0.0000
	Bcc	9.744	0.8260 -0.4769 -0.3007

- *Method/bases set (ESR//Geometry)*: B31YP/6-311+G(2df,p)//UHF/6-311+G(d,p).
- See Figure 4(a) for the numbering of ^{13}C and ^{19}F nucleus positions and the x, y, z system.

Supporting Information (2):
Anisotropic ^{19}F *hf* dipole couplings in molecular axis system calculated for *c*-$C_4F_8^-$.

Atom	Anisotropic *hf* dipole couplings/mT		Direction cosines: x, y, z system		
1 C(13)	Baa	-0. 524	1.0000	0.0000	0.0000
	Bbb	-0.287	0.0000	1.0000	0.0001
	Bcc	0.811	0.0000	-0.0001	1.0000
2 C(13)	Baa	-0. 524	1.0000	0.0000	0.0000
	Bbb	-0.287	0.0000	1.0000	-0.0001
	Bcc	0.811	0.0000	0.0001	1.0000
3 C(13)	Baa	-0. 524	0.0000	1.0000	0.0000
	Bbb	-0.287	1.0000	0.0000	0.0001
	Bcc	0.811	-0.0001	0.0000	1.0000
4 C(13)	Baa	-0. 524	0.0000	1.0000	0.0000
	Bbb	-0.287	1.0000	0.0000	-0.0001
	Bcc	0.811	0.0001	0.0000	1.0000
5 F(19)	Baa	-3.540	0.0000	-0.2659	0.9640
	Bbb	-3.482	1.0000	0.0000	0.0000
	Bcc	7.022	0.0000	0.9640	0.2659
6 F(19)	Baa	-3.538	0.0000	0.2653	0.9642
	Bbb	-3.480	1.0000	0.0000	0.0000
	Bcc	7.018	0.0000	0.9642	-0.2653
7F(19)	Baa	-3.540	0.0000	0.2659	0.9640
	Bbb	-3.482	1.0000	0.0000	0.0000
	Bcc	7.022	0.0000	0.9640	-0.2659
8 F(19)	Baa	-3.538	0.0000	-0.2653	0.9642
	Bbb	-3.480	1.0000	0.0000	0.0000
	Bcc	7.018	0.0000	0.9642	0.2653
9 F(19)	Baa	-3.538	0.2653	0.0000	0.9642
	Bbb	-3.480	0.0000	1.0000	0.0000
	Bcc	7.018	0.9642	0.0000	-0.2653
10 F(19)	Baa	-3.540	-0.2658	0.0000	0.9640
	Bbb	-3.482	0.0000	1.0000	0.0000
	Bcc	7.022	0.9640	0.0000	0.2658
11 F(19)	Baa	-3.538	-0.2653	0.0000	0.9642
	Bbb	-3.480	0.0000	1.0000	0.0000
	Bcc	7.018	0.9642	0.0000	0.2653
12 F(19)	Baa	-3.540	0.2658	0.0000	0.9640
	Bbb	-3.482	0.0000	1.0000	0.0000
	Bcc	7.022	0.9640	0.0000	-0.2658

- *Method/bases set (ESR//Geometry)*: B31YP/6-311+G(2df,p)//UHF/6-311+G(d,p).
- See Figure 4(b) for the numbering of ^{13}C and ^{19}F nucleus positions and the x, y, z system.

Supporting Information (3):
Anisotropic ^{19}F *hf* dipole couplings in molecular axis system calculated for *c*-$C_5F_{10}^-$ with D_{5h} structure.

Atom	Anisotropic *hf* dipole couplings	Direction cosines: x, y, z system
1 C(13)	Baa: -0.35 Bbb: -0.21 Bcc: 0.56	0.0000 0.9510 0.3092 -0.0001 -0.3092 0.9510 1.0000 0.0000 0.0001
2 C(13)	Baa: -0.35 Bbb: -0.21 Bcc: 0.56	0.0000 0.9510 -0.3092 0.0001 0.3092 0.9510 1.0000 0.0000 -0.0001
3 C(13)	Baa: -0.35 Bbb: -0.21 Bcc: 0.56	0.0000 -0.5879 0.8090 0.0000 0.8090 0.5879 1.0000 0.0000 0.0000
4 C(13)	Baa: -0.35 Bbb: -0.21 Bcc: 0.56	0.0000 0.5879 0.8090 0.0000 0.8090 -0.5879 1.0000 0.0000 0.0000
5 C(13)	Baa: -0.35 Bbb: -0.21 Bcc: 0.56	0.0000 0.0000 1.0000 -0.0002 1.0000 0.0000 1.0000 0.0002 0.0000
6 F(19)	Baa: -2.64 Bbb: -2.56 Bcc: 5.18	0.9717 -0.0728 0.2245 -0.0001 0.9510 0.3091 -0.2361 -0.3004 0.9242
7 F(19)	Baa: -2.64 Bbb: -2.56 Bcc: 5.18	0.9717 0.0728 -0.2245 0.0002 0.9510 0.3091 0.2361 -0.3004 0.9241
8 F(19)	Baa: -2.64 Bbb: -2.56 Bcc: 5.18	0.9717 0.0728 0.2245 0.0002 0.9510 -0.3091 -0.2361 0.3004 0.9241
9 F(19)	Baa: -2.64 Bbb: -2.56 Bcc: 5.18	0.9717 -0.0728 -0.2245 -0.0001 0.9510 -0.3091 0.2361 0.3004 0.9242
10 F(19)	Baa: -2.64 Bbb: -2.56 Bcc: 5.18	0.9717 0.1913 0.1383 0.0005 -0.5877 0.809□ -0.2361 0.7861 0.5712
11 F(19)	Baa: -2.64 Bbb: -2.56 Bcc: 5.18	0.9717 -0.1912 -0.1384 -0.0005 -0.5877 0.8091 0.2360 0.7861 0.5712
12 F(19)	Baa: -2.64 Bbb: -2.56 Bcc: 5.18	0.9717 -0.1912 0.1384 0.0005 0.5877 0.8091 0.2360 0.7861 -0.5712
13 F(19)	Baa: -2.64 Bbb: -2.56 Bcc: 5.18	-0.1383 -0.0005 0.5877 0.8091 -0.2361 0.7861 -0.5712
14 F(19)	Baa: -2.64 Bbb: -2.56 Bcc: 5.18	0.9717 -0.2361 0.0000 0.0000 0.0000 1.0000 0.2361 0.9717 0.0000
15 F(19)	Baa: -2.64 Bbb: -2.56 Bcc: 5.18	0.9717 0.2361 0.0000 0.0000 0.0000 1.0000 -0.2361 0.9717 0.0000

- *Method/bases set (ESR//Geometry)*: B31YP/6-311+G(2df,p)//UHF/6-311+G(d,p).
- See Figure 7(a) for the numbering of ^{13}C and ^{19}F nucleus positions and the x, y, z system.

Supporting Information (4):
Anisotropic ^{19}F *hf* dipole couplings in molecular axis system calculated for $cC_5F_{10}^-$ with C_s structure.

Atom	Anisotropic *hf* dipole couplings	Direction cosines: x, y, z system
1 C(13)	Baa: -0.37 Bbb: -0.24 Bcc: 0.60	0.0310 0.9427 0.3323 0.1709 -0.3326 0.9275 0.9848 0.0281 -0.1714
2 C(13)	Baa: -0.37 Bbb: -0.24 Bcc: 0.60	0.0310 0.9427 -0.3323 -0.1709 0.3326 0.9275 0.9848 0.0281 0.1714
3 C(13)	Baa: -0.40 Bbb: -0.26 Bcc: 0.66	0.0300 -0.6001 0.7993 -0.0636 0.7969 0.6007 0.9975 0.0689 0.0142
4 C(13)	Baa: -0.40 Bbb: -0.26 Bcc: 0.66	-0.0300 0.6001 0.7993 -0.0636 0.7969 -0.6007 0.9975 0.0689 -0.0142
5 C(13)	Baa: -0.35 Bbb: -0.22 Bcc: 0.57	0.0000 0.0000 1.0000 0.2138 0.9769 0.0000 0.9769 -0.2138 0.0000
6 F(19)	Baa: -2.02 Bbb: -1.97 Bcc: 3.99	0.9989 0.0444 0.0150 -0.0468 0.9519 0.3027 -0.0009 -0.3031 0.9530
7 F(19)	Baa: -3.67 Bbb: -3.53 Bcc: 7.19	0.8524 0.1318 -0.5059 0.0472 0.9443 0.3256 0.5207 -0.3015 0.7987
8 F(19)	Baa: -3.67 Bbb: -3.53 Bcc: 7.19	0.8524 0.1318 0.5059 0.0472 0.9443 -0.3256 -0.5207 0.3015 0.7987
9 F(19)	Baa: -2.02 Bbb: -1.97 Bcc: 3.99	0.9989 0.0444 -0.0150 -0.0468 0.9519 -0.3027 0.0009 0.3031 0.9530
10 F(19)	Baa: -3.28 Bbb: -3.18 Bcc: 6.46	0.9240 0.3284 0.1958 0.0481 -0.6078 0.7926 -0.3793 0.7230 0.5774
11 F(19)	Baa: -2.61 Bbb: -2.53 Bcc: 5.14	0.9835 -0.1504 -0.1006 -0.0025 -0.5673 0.8235 0.1809 0.8096 0.5583
12 F(19)	Baa: -2.61 Bbb: -2.53 Bcc: 5.14	0.9835 -0.1504 0.1006 0.0025 0.5673 0.8235 0.1809 0.8096 -0.5583
13 F(19)	Baa: -3.28 Bbb: -3.18 Bcc: 6.46	0.9240 0.3284 -0.1958 -0.0481 0.6078 0.7926 -0.3793 0.7230 -0.5774
14 F(19)	Baa: -3.74 Bbb: -3.59 Bcc: 7.33	0.8230 -0.5681 0.0000 0.0000 0.0000 1.0000 0.5681 0.8230 0.0000
15 F(19)	Baa: -1.81 Bbb: -1.77 Bcc: 3.58	0.9976 -0.0690 0.0000 0.0000 0.0000 1.0000 0.0690 0.9976 0.0000

- *Method/bases set (ESR//Geometry)*: B31YP/6-311+G(2df,p)//MP2/6-311+G(d,p) (method B).
- See Figure 7(b) for the numbering of ^{13}C and ^{19}F nucleus positions and the x, y, z system.

Supporting Information (5):
Electronic excitation energies and oscillator strengths (*f*) of *c*-$C_3F_6^-$, *c*-$C_4F_8^-$ and *c*-$C_5F_{10}^-$ anions computed by TD-DFT methods. The data related to the first ten excited states are given.

Perfluorocycloalkane radical anion [state(symmetry)]	Excitation energies/nm	Oscillator strengths: *f*	Main electron transition: state to state (contribution)
c-$C_3F_6^-$ [$^2A_2''$ (D_{3h})]	1: 561.41	0.0233	37A □ 38A (0.9940) [$5a_2''$ □ $7a_1'$]
	2: 407.86	0.0000	37A □ 39A (1.0027
	3: 407.83	0.0000	37A □ 40A (1.0027
	4: 323.96	0.0000	37A □ 41A (0.9973
	5: 291.97	0.0580	37A □ 42A (1.0032)
	6: 291.97	0.0580	37A □ 43A (1.0031)
	7: 285.29	0.0000	37A □ 44A (1.0025)
	8: 285.28	0.0000	37A □ 45A (1.0024)
	9: 271.23	0.0209	37A □ 46A (0.9893) 37A □ 50A (-0.1155)
	10: 229.25	0.0000	37A □ 47A (1.00331)
c-$C_4F_8^-$ [$^2A_{2u}$ (D_{4h})]	1: 535.11	0.0261	49A □ 50A (0.9945) [$5a_{2u}$ □ $6a_{1g}$]
	2: 404.19	0.0000	49A □ 51 A (1.0023)
	3: 404.19	0.0000	49A □ 52 A (1.0023)
	4: 339.17	0.0000	49A □ 53 A (1.0035)
	5: 311.82	0.0000	49A □ 54 A (0.9986)
	6: 301.32	0.0907	49A □ 55A (0.9990)
	7: 301.31	0.0907	49A □ 56A (0.9990)
	8: 283.69	0.0000	49A □ 57 A (1.0021)
	9: 255.31	0.0322	49A □ 59A (0.9811) 49A □ 62A (0.1828)
	10: 253.76	0.0000	49A □ 58 A (1.0068)
c-$C_5F_{10}^-$ [$^2A_2$" (D_{5h})]	1: 535.13	0.0298	61A □ 62A (0.9941) [$6a_2''$ □ $8a_1'$]
	2: 412.82	0.0000	61A □ 63A (1.0010)
	3: 412.81	0.0000	61A □ 64A (1.0010)
	4: 339.76	0.0000	61A □ 65A (1.0032)
	5: 339.76	0.0000	61A □ 66A (1.0032)
	6: 331.21	0.1606	61A □ 67A (0.9829)
	7: 331.14	0.1607	61A □ 68A (0.9829)
	8: 308.50	0.0000	61A □ 69A (0.9998
	9: 272.41	0.0150	61A □ 74A (0.3563) 61A □ 75A (0.9324)
	10: 254.30	0.0000	61A □ 70A (1.0066)

Time-dependent (TD) B3LYP/6-311+G (d,p)// UHF/ 6-311+G (d,p) methods were used.