Supplementary Material (ESI) for Dalton Transactions

Supporting information for

Electrochemical, ESR, and theoretical studies of [6,6]-opened $C_{60}(CF_2)$, *cis*-2-$C_{60}(CF_2)_2$ and their anions

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Dalton Trans.

Table of contents

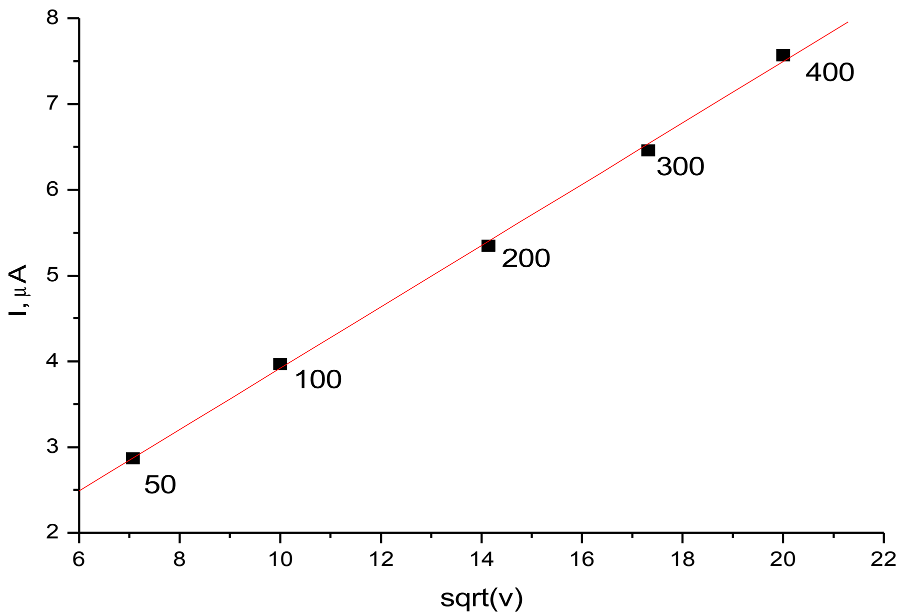


Figure S1. *Plot for dependence of peak current values (µA) on a square root of potential scan rates (mV$^{1/2}$·sec$^{-1/2}$) for $C_{60}(CF_2)$ reduction at Pt electrode in ODCB/0.15 TBABF*

Table S1. *First reduction potential values of some $C_{60}[CR^1R^2]$ compounds and calculated sums of σ_m and χ for substituents R^1 and R^2.*

N	**Compound, $C_{60}[C(R^1R^2)]$**		**E(I) *vs* C_{60}, mV**	**$\Sigma\sigma_m(R^i)^a$**	**$\Sigma\chi(R^i)^b$**	**Ref**
	R^1	**R^2**				
1	F	F	151	0.68	7.96	t.w.
2	CN	CN	156	1.12	6.66	[S3]
3	CN	CO_2Et	10	0.88	6.42	[S3]
4	Cl	Cl	4	0.74	5.88	t.w.
5	Br	Br	–7	0.78	–	[S3]
6	OMe	SO_2Et	–19	0.68	5.82	[S3]
7	H	NO_2	–40	0.71	4.00	[S3]
8	CO_2Et	CO_2Et	–41	0.64	6.18	[S3]
9	H	H	–82	0.00	–	[S3]
10	OMe	OMe	–86	0.24	6.12	[S3]
11	Ph	Ph	–87	0.12	3.86	[S3]

[a] Hammett constants [S1]; [b] Group electronegativity (Pauling Units) [S2] ; t.w. – this work

References

[S1] Gordon, A.J., Ford, R.A., "A Handbook of Practical Data, Techniques, and References", John Wiley & Sons, 1973

[S2] Campanelli et al, JPC A, 2004, 108

[S3] Keshavartz-K et al, Tetrahedron, 1996, 52, 5149

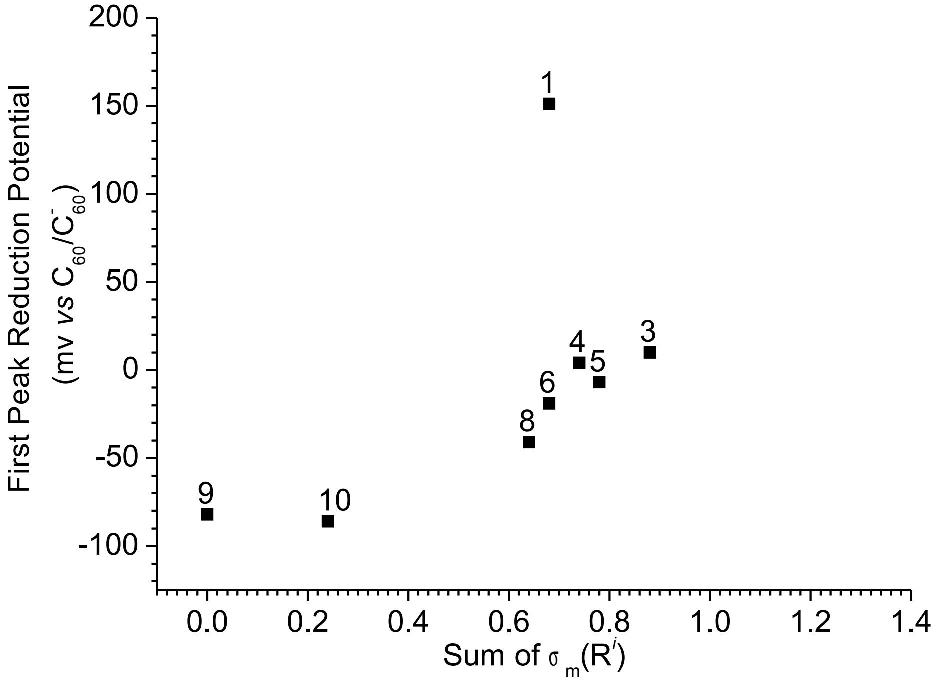


Figure S2. *A plot of first peak reduction potential versus the sum of σ_m values for substituents at the 61-position.*

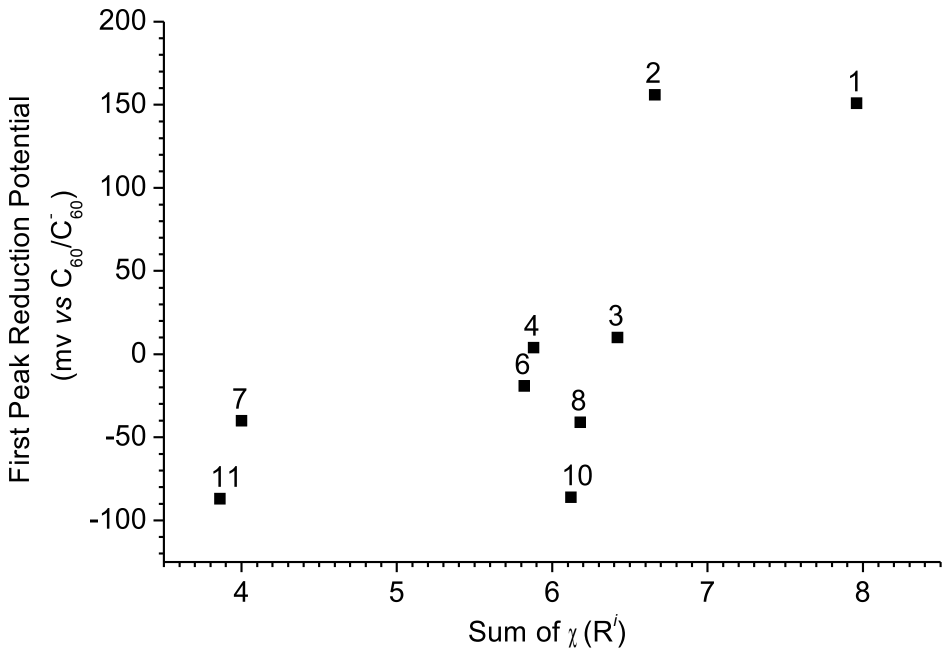


Figure S3. *A plot of first peak reduction potential versus the sum of χ values for substituents at the 61-position.*

Table S2. *DFT calculated charge and spin (shown in the parentheses) distributions*

$C_{60}(CR_2)$	Uncharged			Anion			
	$\delta(C_2CR_2)$		δ(C_{60} cage)	$\delta(C_2CR_2)$			δ(C_{60} cage)
	$\delta(C_{bridge})$	δ(2R)		$\delta(C_{bridge})$	δ(2R)	$\delta(2C_{hold})$	
	[6,6]-$C_{60}(CR_2)$			[6,6]-$C_{60}(CR_2)^-$			
H	–0.06	0.12	0.02	–0.08 (0.00)	0.09 (0.00)	0.03 (0.00)	–0.92 (1.00)
F	0.16	–0.19	0.11	0.15 (0.01)	–0.25 (0.00)	–0.06 (0.16)	–0.81 (0.99)
Cl	0.04	–0.05	0.08	0.04 (0.00)	–0.12 (0.00)	0.00 (0.00)	–0.83 (0.99)
CN	0.04	–0.22	0.25	0.04 (0.01)	–0.28 (0.00)	0.00 (0.15)	–0.69 (0.98)
	1-C_{60}–(CR_2)			1-C_{60}–$(CR_2)^-$			
H	–0.06 (0.73)	0.08 (0.10)	0.06 (1.16)	–0.11 (0.63)	0.04 (0.09)	–0.10 (0.05)	–0.85 (0.28)
F	0.13 (0.66)	–0.15 (0.23)	0.09 (1.11)	0.11 (0.63)	–0.20 (0.21)	–0.12 (0.03)	–0.82 (0.16)
Cl	0.01 (0.59)	–0.01 (0.31)	0.07 (1.10)	0.00 (0.57)	–0.11 (0.27)	–0.12 (0.05)	–0.81 (0.16)
CN	0.05 (0.49)	–0.21 (0.50)	0.23 (1.08)	–0.02 (0.23)	–0.45 (0.28)	–0.04 (0.22)	–0.45 (0.49)

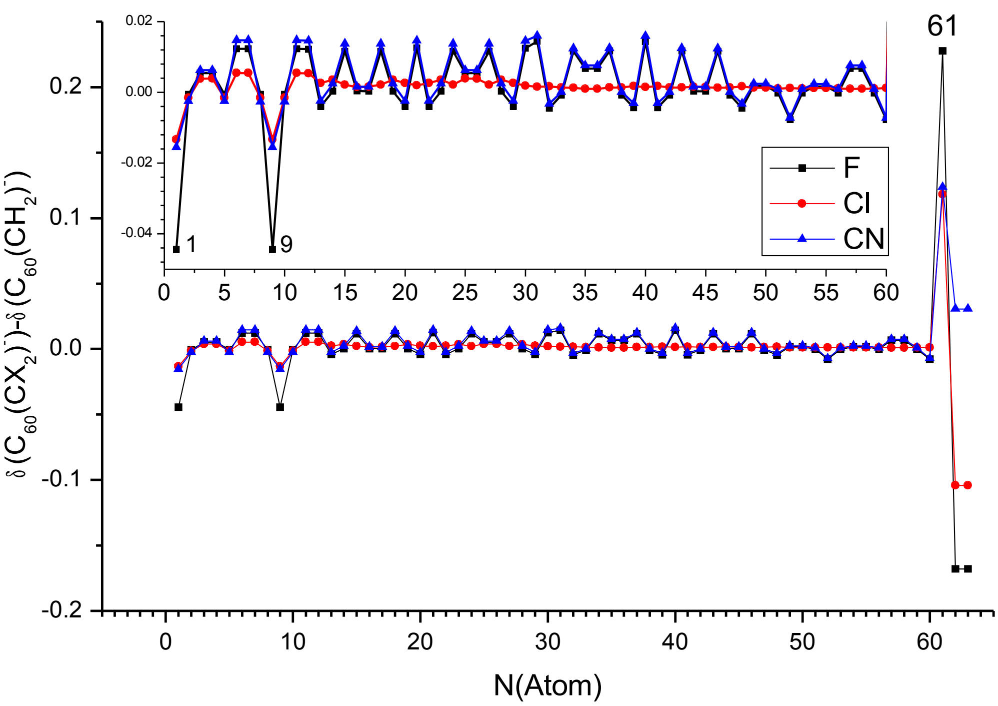


Figure S4. *Charge distribution in [6,6]-$C_{60}(CX_2)^-$ (X=F, Cl, CN) vs [6,6]-$C_{60}(CH_2)^-$. Locant indexation is given in accordance with IUPAC recommendation [36]*

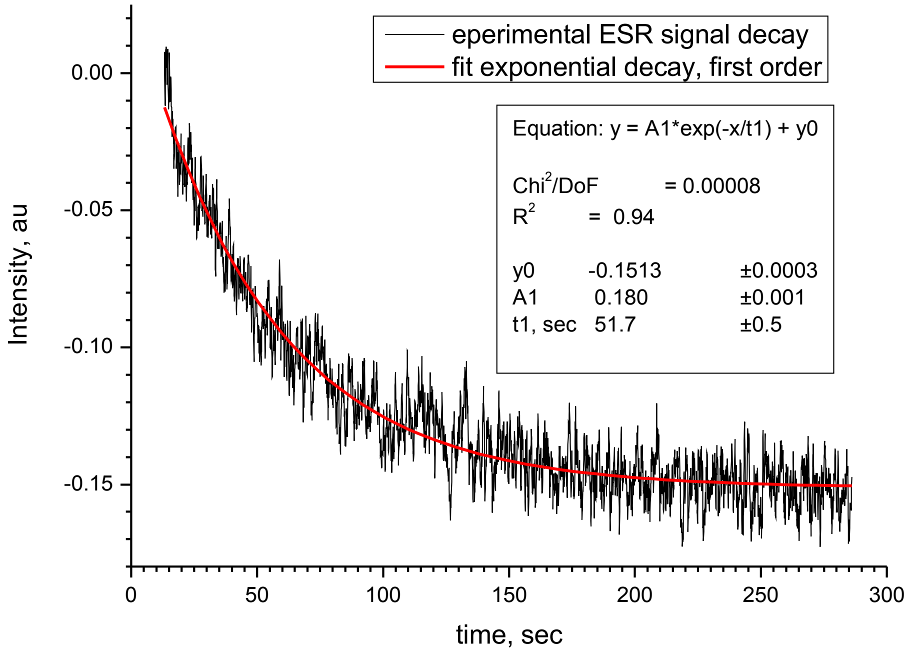


Figure S5. *ESR signal decay of electrochemically generated $C_{60}(CF_2)^{-\cdot}$ anion-radical*

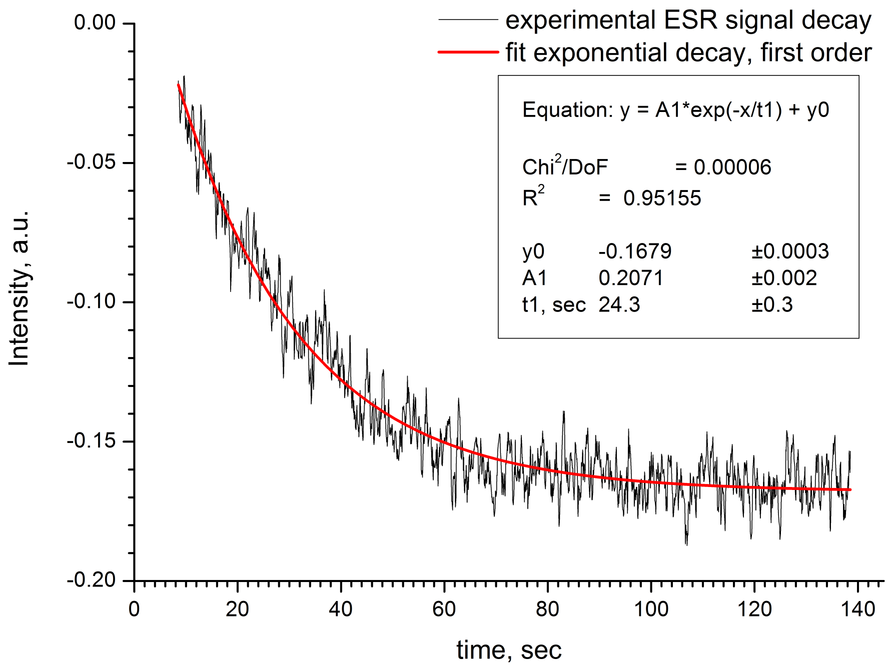


Figure S6. *ESR signal decay of electrochemically generated anion-radical of cis-2-$C_{60}(CF_2)_2$*

Table S3. *Schlegel diagram, relative DFT energies, and DFT predicted EA values of some $C_{60}(CF_2)_2$*

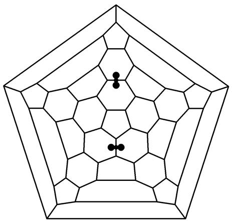
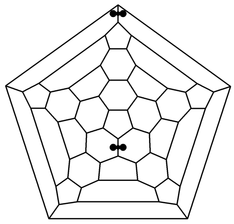
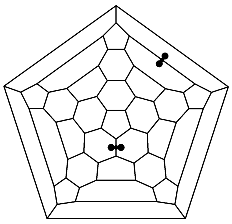
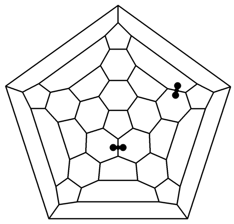
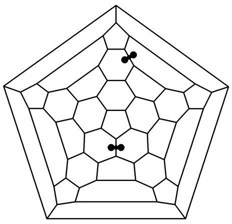
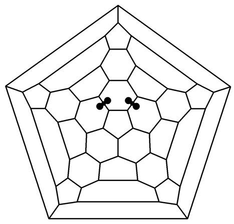
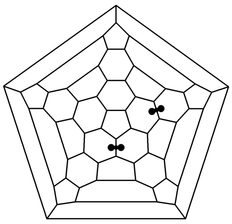
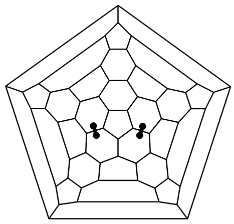
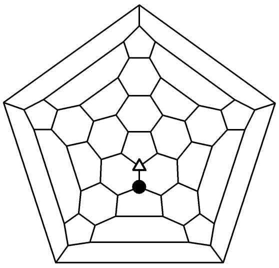
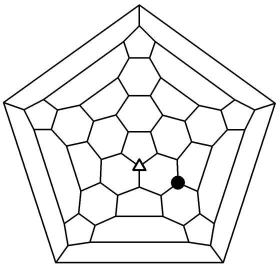
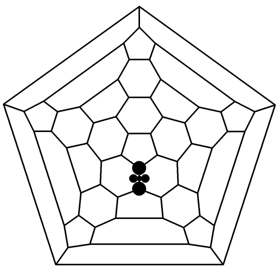
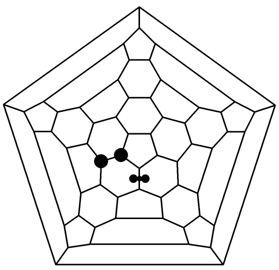
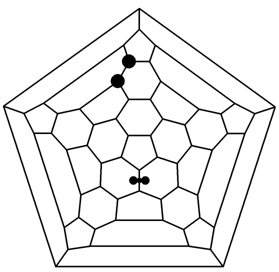
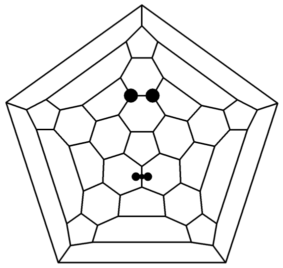
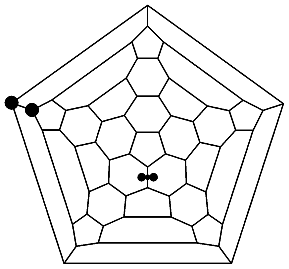
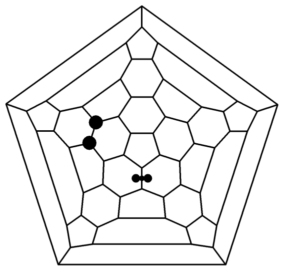
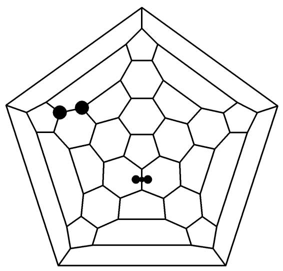
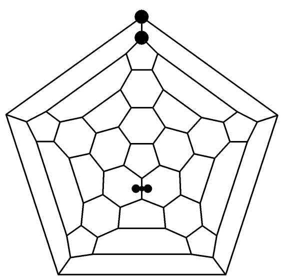
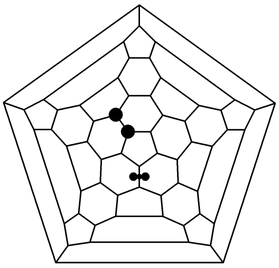
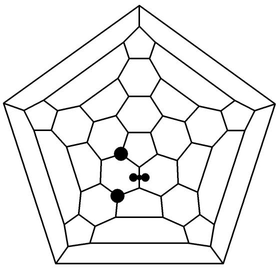
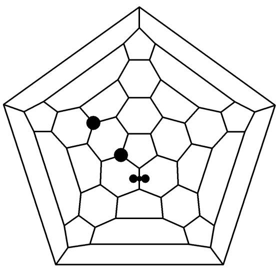
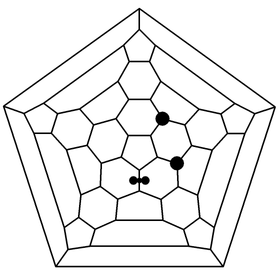
№	$C_{60}(CF_2)_2$	ΔE, $kJ \cdot mol^{-1}$	EA, eV	Lowest Locant	№	$C_{60}(CF_2)_2$	ΔE, $kJ \cdot mol^{-1}$	EA, eV	Lowest Locant
1		0.0	2.9	*e*-1,9:16,17	5		6.9	2.9	*trans*-1-1,9:52,60
2		2.2	2.9	*trans*-2-1,9:49,59	6		11.4	2.9	*trans*-4-1,9:32,33
3		2.4	2.9	*trans*-3-1,9:34,35	7		19.2	3.3	*cis*-1-1,9:2,12
4		3.8	3.0	*cis*-3-1,9:13,14	8		24.4	2.7	*cis*-2-1,9:3,15

Table S4. *Schlegel diagrams, relative energies (at the DFT and AM1 levels of theory), and IUPAC lowest-locant abbreviation for the most stable isomers of $C_{60}(CF_2)H_2$ within the gap of 40 kJ·mol^{-1}. All possible isomers (436) of addition of 2 H atoms to [6,6]-$C_{60}(CF_2)$ without opening $(C_2)CF_2$ fragment, 1,7- and 1,9-$C_{60}(CF_2H)H$ were considered at the AM1 level of the theory. The best isomers (28) within 87 kJ·mol^{-1} AM1 energy gap were refined at the DFT theory.*

№№	**Schlegel Diagrams of $C_{60}(CF_2)H_2$**	**$\Delta\Delta_f H_0^o$ kJ·mol^{-1}**		**IUPAC lowest-locant abbreviation for $C_{60}(CF_2)H_2$ and C(1)-C(9) distances, Å**
		DFT	**AM1**	
1		-29.2	-26.0	1,9-$C_{60}(CF_2H)H$ r(C-C)=1.59
2		-0.4	-8.9	1,7-$C_{60}(CF_2H)H$
3		0.0	9.4	1,9-$C_{60}(CF_2)H_2$ Opened: r(C-C)=2.59
4		24.9	0.0	2, 12-$C_{60}(CF_2)H_2$ Closed: r(C-C)=1.64
5		39.3	2.9	34, 35-$C_{60}(CF_2)H_2$ Opened: r(C-C)=2.07

№№	Schlegel Diagrams of $C_{60}(CF_2)H_2$	$\Delta\Delta_f H_0^o$ kJ·mol^{-1}		IUPAC lowest-locant abbreviation for $C_{60}(CF_2)H_2$ and C(1)-C(9) distances, Å
		DFT	AM1	
6		39.5	1.0	16, 17-$C_{60}(CF_2)H_2$ Opened: r(C-C)=2.04
7		40.4	3.5	49, 59-$C_{60}(CF_2)H_2$ Opened: r(C-C)=2.08
8		41.7	10.0	13, 14-$C_{60}(CF_2)H_2$ Opened: r(C-C)=2.14
9		41.9	2.5	32, 33-$C_{60}(CF_2)H_2$ Opened: r(C-C)=2.08
10		42.7	3.4	52, 60-$C_{60}(CF_2)H_2$ Opened: r(C-C)=2.06

№№	Schlegel Diagrams of $C_{60}(CF_2)H_2$	$\Delta\Delta_f H_0^o$ kJ·mol^{-1}		IUPAC lowest-locant abbreviation for $C_{60}(CF_2)H_2$ and C(1)-C(9) distances, Å
		DFT	AM1	
11		45.3	12.3	3, 15-$C_{60}(CF_2)H_2$ Opened: r(C-C)=2.13
12		48.1	19.7	2, 10-$C_{60}(CF_2)H_2$ Closed: r(C-C)=1.66
13		55.0	11.9	2, 14-$C_{60}(CF_2)H_2$ Closed: r(C-C)=1.66
13		59.7	6.3	6, 18-$C_{60}(CF_2)H_2$ Closed: r(C-C)=1.65