

^{19}F NMR-, ESR-, and vis-NIR-spectroelectrochemical study of the unconventional reduction behaviour of perfluoroalkylated fullerene: dimerization of the $\text{C}_{70}(\text{CF}_3)_{10}^-$ radical anion

Michal Zalibera,^{*a,b,c} Peter Machata,^{a,d} Tyler T. Clikeman,^e Marco Rosenkranz,^a Steven H. Strauss,^{*e} Olga V. Boltalina,^{*e} and Alexey A. Popov^{*a}

Supporting Information

Fast scan cyclic voltammetry of 70-10-1	2
Charge-to-spin ratio	3
^{19}F - ^{19}F 2D COSY NMR	4
NMR spectroelectrochemical cell	6
Mass spectrometry results	7
DFT results	8

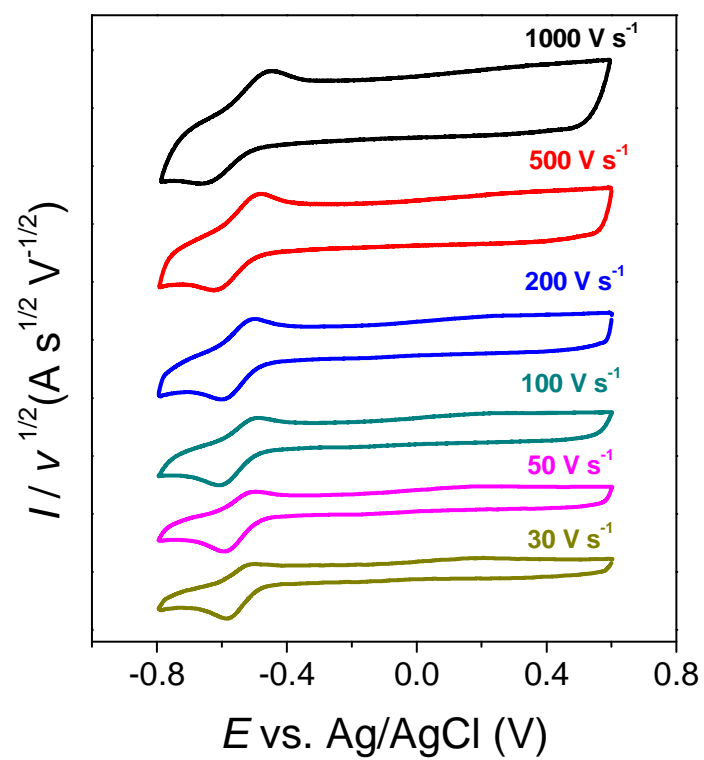


Figure S1. Cyclic voltammograms of **70-10-1** in *o*-DCB measured at different scan rates.

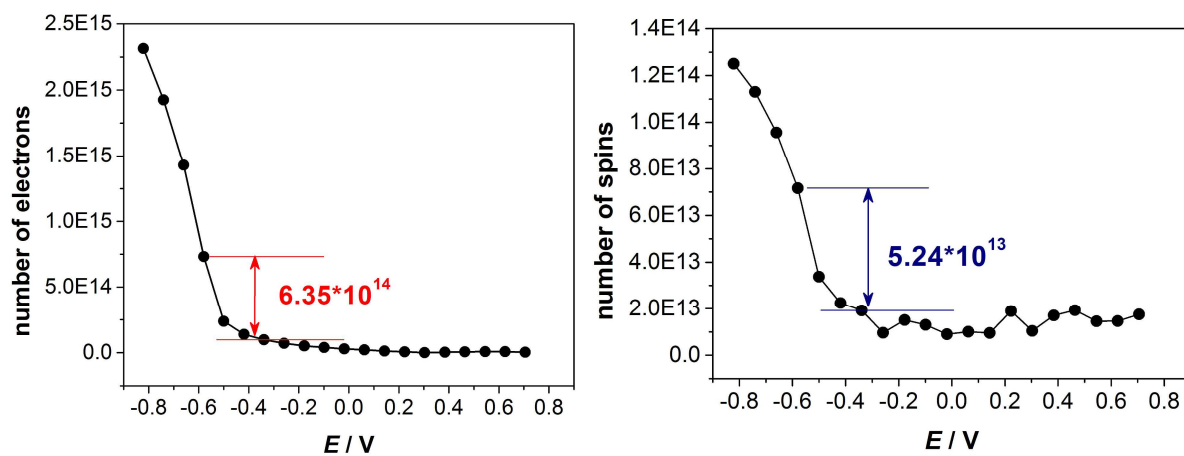


Figure S2. Number of transferred electrons (left) and formed spins (right) during the cyclic voltammetry of **70-10-1** at the first reduction step (scan rate 5 mV/s). At the beginning of the reduction process, the growth of the number of transferred electrons (6.35×10^{14}) to the number of unpaired spins observed (5.24×10^{13}) is 12:1. Measurements at later times gives less meaningful results due to the diffusion of radical out of the sensitive part of the ESR cavity.

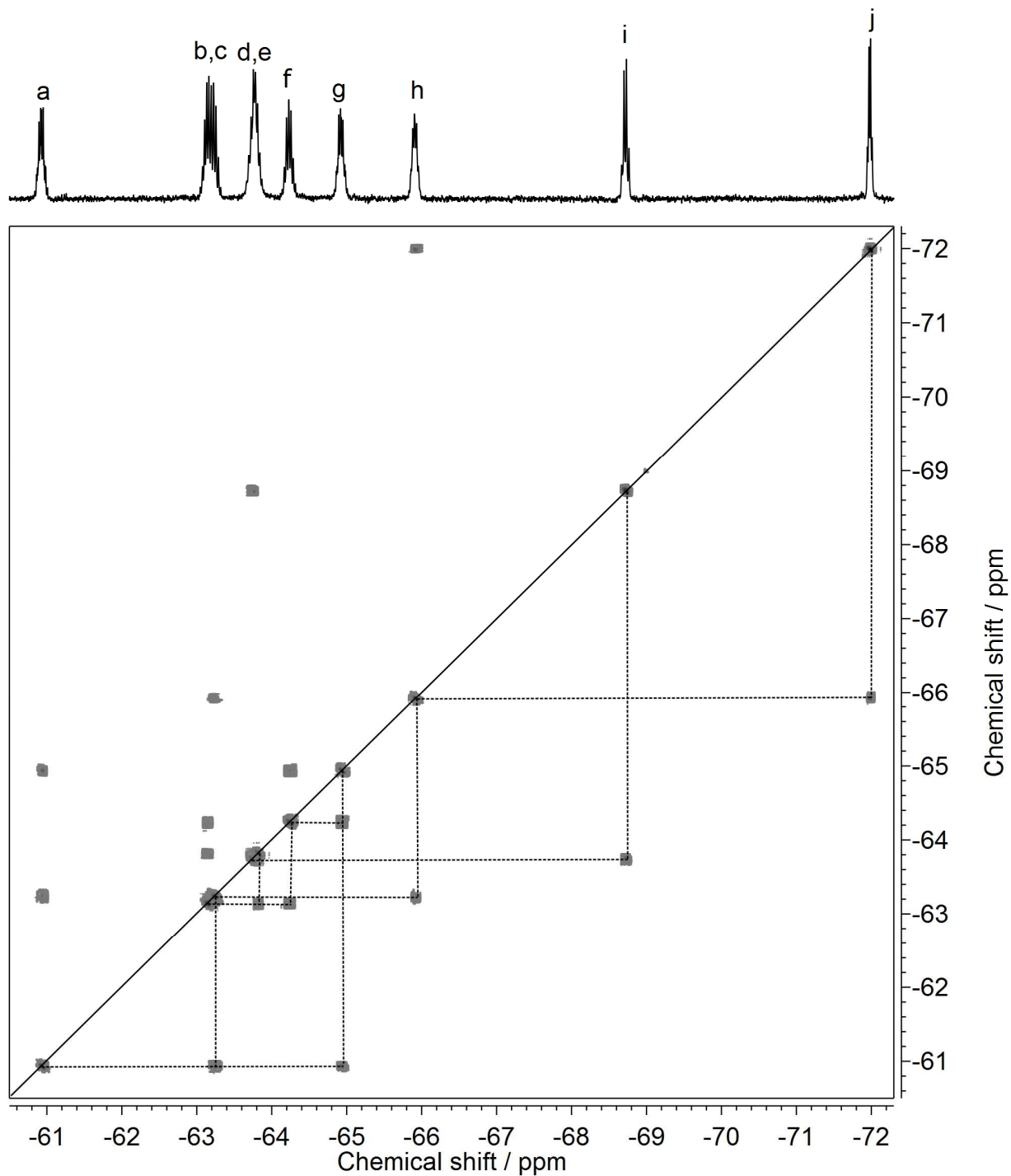


Figure S3. ^{19}F - ^{19}F 2D COSY NMR spectrum of **70-10-1** (470.59 MHz, *o*-DCB- d_4 , 298 K, C_6F_6 int. std. (δ -164.9)).

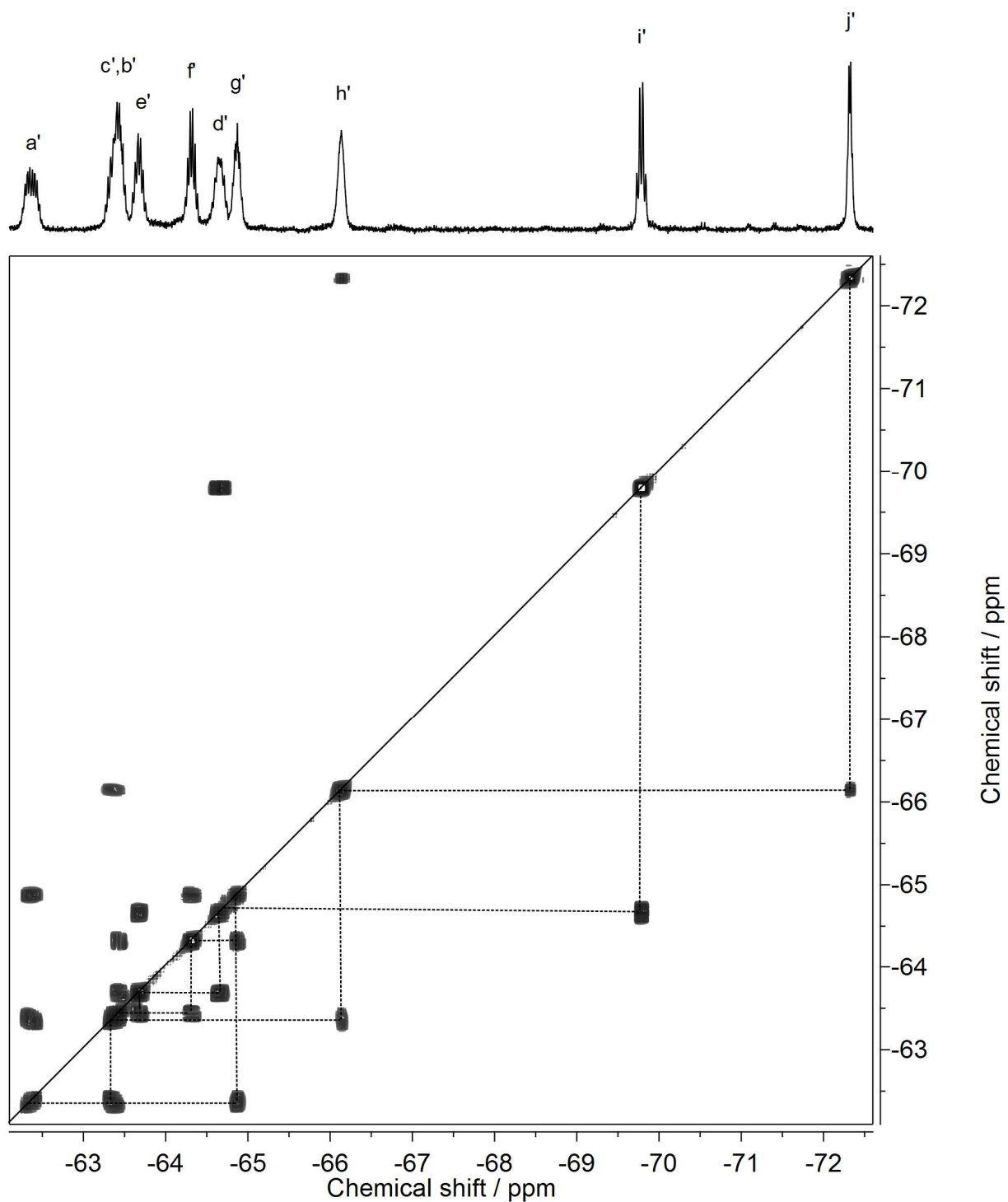


Figure S4. ^{19}F - ^{19}F 2D COSY NMR spectrum of $(70-10-1)_2^{2-}$ obtained by the reaction of **70-10-1** with CoCp_2 (470.59 MHz, *o*-DCB- d_4 , 298 K, C_6F_6 int. std. ($\delta -164.9$)).

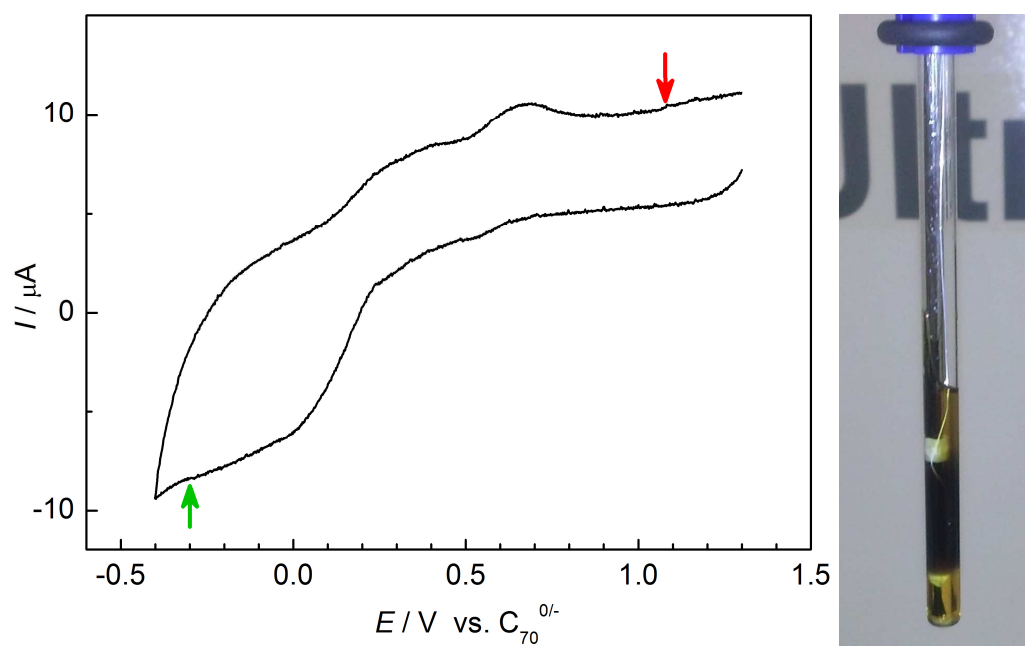


Figure S5. (Left) Cyclic voltammetry of **70-10-1** in *o*-DCB recorded at 0.003 V/s in the electrochemical-NMR cell; green/red arrows indicate the potentials of the reduction/reoxidation corresponding to Fig. 4 in the main text. (Right) Photograph of an *o*-DCB- d_4 solution of **70-10-1** in the spectroelectrochemical NMR cell after reduction at $-0.3 \text{ V vs. } C_{70}^{0/-}$ for 6 h.

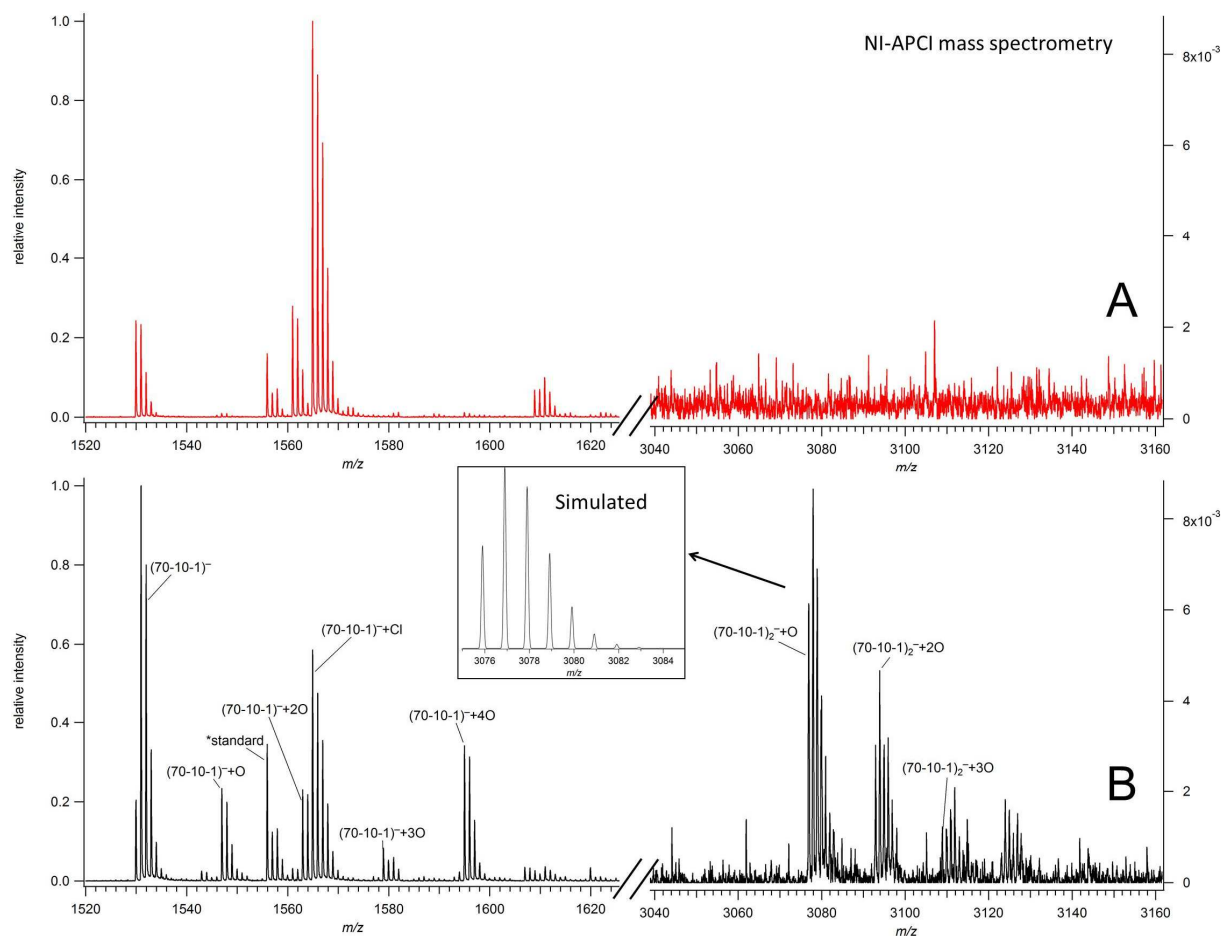
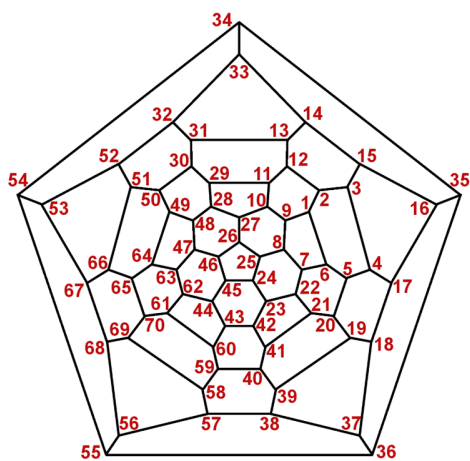


Figure S6. NI-APCI mass spectra of **70-10-1** (upper spectrum) and **70-10-1** reduced with CoCp₂ (lower spectrum). In the upper spectrum, the M⁺ molecular anion (**70-10-1**)⁻ at *m/z* 1530 and its (M+Cl)⁻ adduct with a Cl atom (from CH₂Cl₂) at *m/z* 1565 are present. In the bottom spectrum, in the lower mass range, anionic species due to hydrogenated and oxidized monomer, as well as the adduct with a Cl atom, are present; in the higher mass region, mono- and multiply-oxidized dimeric species are present (note the ca. two orders of magnitude lower intensities of the peaks for the dimeric species).

Table S1. DFT-predicted relative energies of (70-10-1)(CH₃)⁻ monoanions and (70-10-1)₂²⁻ dimeric dianions (kJ/mol)

C# ^a	(70-10-1)(CH ₃) ⁻	(70-10-1) ₂ ²⁻	
	PBE/TZ2P	PBE/TZ2P	PBE-D3/TZ2P
34	0.0	0.0	0.0
33	9.1	19.7	17.5
13	17.7	58.1	29.0
35	18.2	37.4	30.7
54	18.9	39.8	33.8
32	24.1	52.6	38.7
14	26.8	58.8	43.2
55	25.3	52.5	45.1
36	25.8	56.1	48.8
53	4.4	81.4	58.5
15	8.9	88.1	61.0
16	5.1	84.4	61.5
46	13.4	100.2	66.2
56	10.1	96.1	68.3
44	8.4	109.9	69.3
52	16.2	106.5	81.4
37	10.5	119.6	92.2
29	14.1		
47	29.6		
45	30.7		
38	34.5		
31	34.5		
57	37.2		
63	39.3		
7	40.0		
62	47.7		
22	48.1		
23	50.8		
30	57.7		
12	64.7		
28	65.8		



^a see the Schlegel diagram for the IUPAC numbering system of cage C atoms in 70-10-1; positions adjacent to CF₃ groups were not considered because they are sterically hindered from dimerization

Table S2. Cartesian coordinates for DFT-optimized (70-10-1)₂²⁻ with a C34–C34 bond.

C	0.046751440	0.923913000	3.503676870
C	-3.075469950	0.972552410	0.694566180
C	-1.372059810	0.956539040	-3.139363110
C	2.790461580	0.944136670	-2.739975650
C	3.584031920	0.909560430	-1.534065210
C	2.820523870	0.935308180	2.592782740
C	-1.328907160	0.928836220	3.061601550
C	-3.079433150	0.979720790	-0.747707770
C	-0.005625530	0.953656540	-3.589939350
C	3.603970870	0.916297180	1.386328650
C	0.780805460	-0.262632330	3.424942150
C	-3.053660900	-0.321323550	1.507136100
C	-1.930666040	-0.225144340	-2.636070070
C	2.269043040	-0.344372130	-3.350132530
C	3.763957680	2.105209990	0.640217750
C	0.840293600	2.219617160	3.720880160
C	-2.754832870	2.145432350	1.383295530
C	-2.131360000	2.252280830	-2.852959430
C	2.160686470	2.150501520	-3.089197120
C	3.755005720	2.103480070	-0.783915170
C	2.197825350	2.133666260	2.965023160
C	-2.084457700	2.226403750	2.785497750
C	-2.772640160	2.156006750	-1.435109220
C	0.785268600	2.244051760	-3.809407850
C	3.769332860	-0.290227560	-0.781231390
C	2.317230210	-0.359587160	3.212789850
C	-1.904551050	-0.238467420	2.560139370
C	-3.055345940	-0.309332840	-1.564702570
C	0.734355940	-0.227522070	-3.508610950
C	3.750554100	-0.286791350	0.618305200
C	0.182714880	-1.445361650	2.926484190
C	-2.552755370	-1.486265630	0.650465000
C	-1.170418590	-1.412513970	-2.589035510
C	2.367506050	-1.544756840	-2.375373830
C	3.182281010	3.356290810	1.071943280
C	0.192792990	3.388936960	2.976546540
C	-2.448842440	3.328469580	0.675740970
C	-1.157627930	3.413753950	-2.634236260
C	2.366472890	3.344225130	-2.352683210
C	3.165929600	3.358470700	-1.197379180
C	2.399855040	3.334344650	2.240973470
C	-1.118943540	3.395768510	2.573491380

C	-2.461150030	3.334879150	-0.722910980
C	0.147753910	3.409649280	-3.054725510
C	3.433335120	-1.690721980	-1.315270100
C	2.393934230	-1.545588410	2.234941720
C	-1.146914850	-1.429785090	2.492862650
C	-2.557041010	-1.485179490	-0.722970880
C	0.156595530	-1.405143940	-3.005657810
C	3.157749270	-1.531240390	1.079706180
C	0.788840640	-3.001933210	1.092923360
C	-0.588398060	-2.962904110	0.644081520
C	-0.619424780	-2.999548070	-0.772764730
C	0.798509110	-3.270045980	-1.318483890
C	1.780528550	5.215722270	-0.047404020
C	0.833780420	4.918876290	1.140511930
C	-0.519259990	4.865843520	0.694908280
C	-0.529904510	4.871757980	-0.757229860
C	0.817212780	4.926118740	-1.221157970
C	1.648160000	-3.064090620	-0.052901420
C	1.163534750	-2.243237050	2.212841560
C	-1.545962630	-2.212095550	1.345519070
C	-1.548873460	-2.211063880	-1.430863410
C	1.176447810	-2.196085470	-2.319495140
C	2.861207730	4.154349800	-0.059391350
C	1.174839920	4.118333640	2.230900740
C	-1.473371460	4.116282060	1.394804260
C	-1.495355460	4.128683810	-1.449100690
C	1.142634040	4.130541690	-2.319660130
C	2.815083600	-2.334259000	-0.059257480
C	3.123056830	-0.736656630	4.487766670
C	1.008344570	2.568528530	5.249636480
C	-3.093896570	2.563063090	3.916213420
C	-4.452696910	-0.700751380	2.136765700
C	-4.448692670	-0.651238740	-2.159435820
C	-3.169899110	2.627459710	-3.982021190
C	0.900473640	2.593587410	-5.317734180
C	2.967832040	-0.743147730	-4.720842310
C	4.750918510	-2.414963090	-1.728477880
C	0.885015040	-4.692410110	-1.919625600
F	1.595444140	3.743328970	-5.509427850
F	1.523326800	1.618964590	-6.031364230
F	-0.331071590	2.761469150	-5.878048170
F	3.726672410	0.255344670	-5.225729140
F	3.790194640	-1.822993950	-4.576946640
F	2.054852430	-1.096567770	-5.670175100

F	-3.463472040	1.577223820	-4.794010160
F	-2.703970150	3.619680010	-4.784857450
F	-4.340748860	3.079744780	-3.452241410
F	-5.325208420	0.334932430	2.144062350
F	-4.321916360	-1.148095000	3.416744290
F	-5.054389030	-1.710311650	1.443282140
F	-5.354953780	-0.891339470	-1.172317540
F	-4.953936900	0.345822390	-2.923895670
F	-4.392324240	-1.771156390	-2.936492080
F	-3.801799140	3.688345690	3.625539690
F	-3.993318910	1.564722780	4.125533850
F	-2.460927650	2.772789980	5.099224990
F	2.227943250	3.106231160	5.508993770
F	0.085753700	3.478060810	5.665209660
F	0.861755320	1.476895340	6.051470770
F	4.404551910	-1.070411830	4.157759970
F	3.195117440	0.269385680	5.389664310
F	2.580663040	-1.817391910	5.126184530
F	5.519517210	-1.647657650	-2.543386920
F	5.508539370	-2.698193010	-0.629125040
F	4.515902200	-3.591968190	-2.362929560
F	2.137736700	-5.005880220	-2.329800340
F	0.058494180	-4.816400620	-2.997947010
F	0.507491410	-5.636342340	-1.010929620
C	2.319981140	6.726639030	-0.044633190
C	4.101688310	10.987560620	3.520286430
C	7.185298190	10.963891410	0.668482890
C	5.430230290	11.013149540	-3.141761450
C	1.273515330	11.021451960	-2.685916090
C	0.496369050	11.045390540	-1.469117820
C	1.316196220	10.983661350	2.646105330
C	5.471221690	10.986669490	3.059498000
C	7.169768340	10.969315040	-0.773712010
C	4.057810640	11.019777460	-3.573738500
C	0.516187070	11.013089290	1.450905280
C	3.366563440	12.174721240	3.462219940
C	7.174599420	12.250575310	1.492595650
C	5.995579460	12.190462690	-2.635744320
C	1.786573730	12.315342920	-3.291761020
C	0.345954990	9.830714280	0.696792460
C	3.311153650	9.689853210	3.736554820
C	6.874097900	9.784992600	1.351184150
C	6.193358460	9.715059520	-2.877001690
C	1.898533330	9.818265940	-3.054151140

C	0.335555080	9.844900140	-0.727244300
C	1.943673170	9.782237870	2.999679230
C	6.222929000	9.691651690	2.761636280
C	6.853765080	9.799041220	-1.467161860
C	3.264050240	9.731225580	-3.793749990
C	0.321273380	12.238566200	-0.703399030
C	1.827454340	12.272990520	3.270466380
C	6.039973870	12.158409550	2.560457150
C	7.134650320	12.265426460	-1.578992650
C	3.318977450	12.200105610	-3.472052690
C	0.359116610	12.222887650	0.695647600
C	3.957811040	13.361806970	2.965748930
C	6.662086170	13.422869190	0.653023130
C	5.236013500	13.377259660	-2.567996100
C	1.701346840	13.507136910	-2.305259700
C	0.933531570	8.576045560	1.109680020
C	3.948545750	8.527149320	2.973373010
C	6.558679460	8.608112040	0.637545080
C	5.222741360	8.551554020	-2.655261070
C	1.702754520	8.618088080	-2.325432280
C	0.919050820	8.593653190	-1.159561310
C	1.731744290	8.587848400	2.268125410
C	5.254686960	8.524017180	2.552526170
C	6.552034480	8.613924330	-0.761150700
C	3.911774330	8.559171720	-3.057951770
C	0.649970160	13.643740070	-1.229624160
C	1.737449120	13.467741470	2.304829600
C	5.281433360	13.350158030	2.513880610
C	6.647758670	13.433774470	-0.720308300
C	3.903483140	13.373345450	-2.966650910
C	0.958030970	13.463361200	1.159923730
C	3.326846660	14.934193350	1.153996210
C	4.697868120	14.899275400	0.686193710
C	4.709679160	14.948273700	-0.730581060
C	3.284485420	15.223323080	-1.254653010
C	3.282766760	7.013264820	1.132840730
C	4.629648420	7.070300570	0.669435300
C	4.620584420	7.077067720	-0.782730320
C	3.267271070	7.026599720	-1.228782690
C	2.452083150	15.006239360	0.020490910
C	2.967415070	14.165703810	2.272273040
C	5.664829300	14.142466100	1.368019120
C	5.630110900	14.165695270	-1.408105180
C	2.893034130	14.158115420	-2.259818180

C	1.239154310	7.787885520	-0.032799080
C	2.956501800	7.804129910	2.234730990
C	5.593132830	7.813851960	1.362881730
C	5.576524450	7.826337570	-1.481099810
C	2.926980960	7.831738500	-2.315779210
C	1.285160860	14.276365940	0.023514600
C	1.037358970	12.637838930	4.558953190
C	3.163533360	9.327404940	5.264183100
C	7.248108620	9.345133180	3.875108300
C	8.582170340	12.624681830	2.106272180
C	8.519838730	12.612701060	-2.189482380
C	7.216535390	9.349878470	-4.023213290
C	3.128215540	9.394920650	-5.303374700
C	1.069212650	12.726000810	-4.649324510
C	-0.673088870	14.371404180	-1.618615570
C	3.189790730	16.650881930	-1.842124650
F	2.431001710	8.246626330	-5.495591120
F	2.495231060	10.375509370	-5.999647390
F	4.351977110	9.232350230	-5.882004470
F	0.303461150	11.731930620	-5.152460150
F	0.249003440	13.804555730	-4.484840310
F	1.969225810	13.087673230	-5.607891090
F	7.499838950	10.407373630	-4.829396930
F	6.739421120	8.365246490	-4.828800040
F	8.394095770	8.892271760	-3.513206050
F	9.455094680	11.589433690	2.091477260
F	8.469156520	13.059780600	3.392148630
F	9.173743600	13.641120970	1.414104080
F	9.439320670	12.844442010	-1.212629630
F	9.014834080	11.622359980	-2.969224540
F	8.452922600	13.739270220	-2.956009220
F	7.951408720	8.222188290	3.564820060
F	8.150813130	10.341422660	4.080023840
F	6.632014720	9.125485850	5.065190440
F	1.948265500	8.785368680	5.534594560
F	4.092934720	8.415873120	5.659733090
F	3.318826140	10.412224540	6.073564770
F	-0.248368720	12.973583860	4.248057970
F	0.977228960	11.623613700	5.452507680
F	1.586969930	13.713171530	5.200366590
F	-1.452667710	13.611130530	-2.429678510
F	-1.415729060	14.644970780	-0.506665540
F	-0.446690420	15.553910550	-2.245927740
F	1.931554710	16.967795810	-2.232315510

F	4.001425720	16.784348740	-2.930563990
F	3.579765990	17.586886690	-0.930494440