Electronic Supplementary Material (ESI) for Chemical Communications

Supproting Information for

First Synthesis and Aggregation Behaviour of Periconjugated Triazoliumfullerene

Naohiko Ikuma,* Saori Inaba, Ken Kokubo and Takumi Oshima

Synthesis of 1,3-diphenylfullerotriazolium hexafluorophosphate (3^+•PF_6^-):

To a solution of 1,3-diphenyltriazene (12mg, 0.06 mmol), C_{60} (36 mg, 0.05 mmol) and potassium hexafluorophosphate (14 mg, 0.08 mmol) in dry CH_2Cl_2/Toluene (15 mL/35mL) under N_2 atmosphere, *tert*-butyl hypochlorite (65 mg, 0.6 mmol) was dropwisely added at –78 ºC. The solution maintained stirring 16h with gradually increasing temperature to rt. Solvent was removed in vacuo, and the residue was washed with ether, toluene (twice), and small amount of methanol to remove unreacted C_{60} and KPF_6 byproduct. The residue was dried in vacuo, to give $\mathbf{3}^+$•PF6$^-$ as dark brown powder (27mg, 50%). 1H-NMR (270 MHz, DMSO-d_6) d 8.45 (m, 4H), 7.86 (m, 6H).13C-NMR (67.8 MHz, DMSO-d6): d 147.4, 146.3, 146.2, 145.7, 144.9, 144.6, 143.6, 142.6, 142.0, 141.8, 140.9, 140.1, 138.6, 136.1, 134.3, 132.8, 130.7, 128.9, 128.2, 127.2. MALDI-TOF-MS, positive *m/z* = 916.1 [$\mathbf{3}^+$].

Synthesis of N,N-dimethylpyrrolidiniumfullerene iodide

For the reference compound of typical ionic fullerene in CV measurement, N,N-dimethylpyrrolidiniumfullerene iodide was prepared from the similar method as shown in ref.1b.

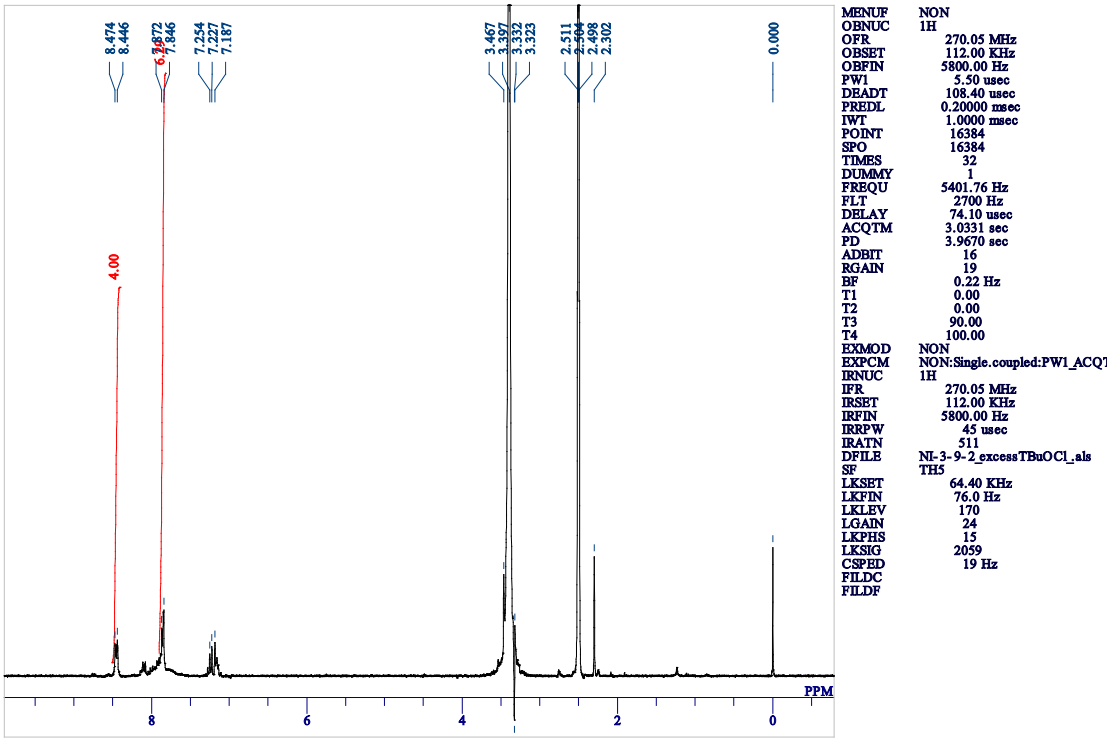


Figure S1. ^{1}H and ^{13}C NMR charts of $\mathbf{3}^{+}\bullet PF6^{-}$ in DMSO-d6 (with small contamination of toluene in 1H NMR).

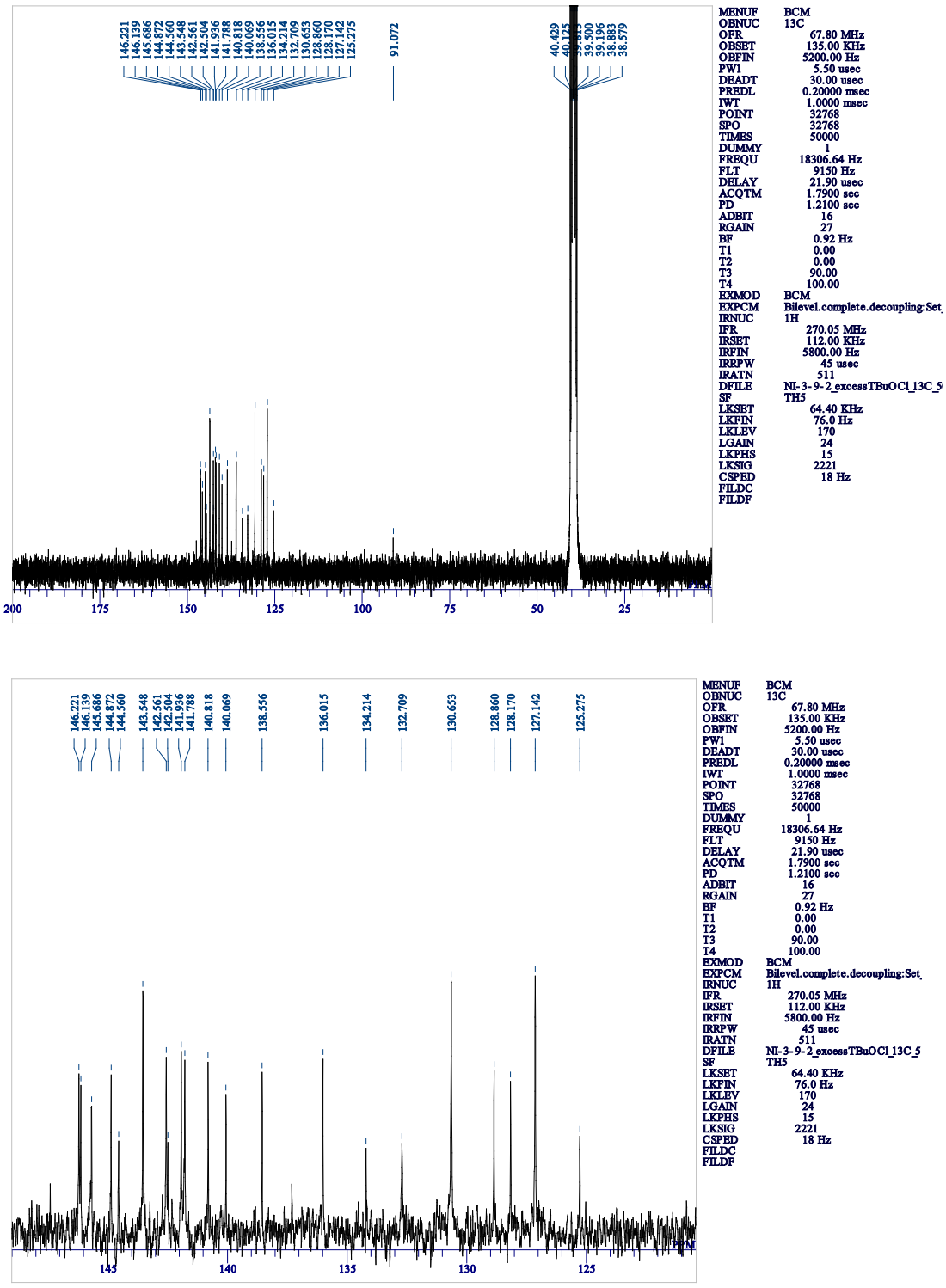


Figure S1 (continued)

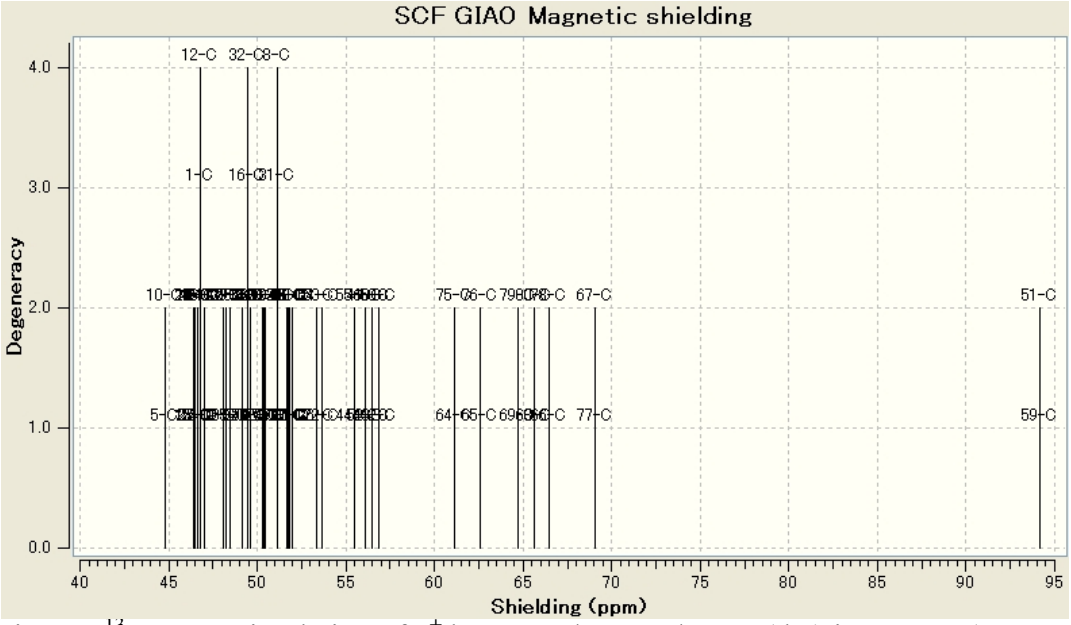


Fig. S2. ^{13}C NMR simulation of **3**$^{+}$ by GIAO/B3LYP/6-31G(d,p) in DMSO (IEFPCM). TMS is 190.17 ppm by the same method, then the relative shielding of two sp^3 carbons (59C and51C) is 96.0 ppm.

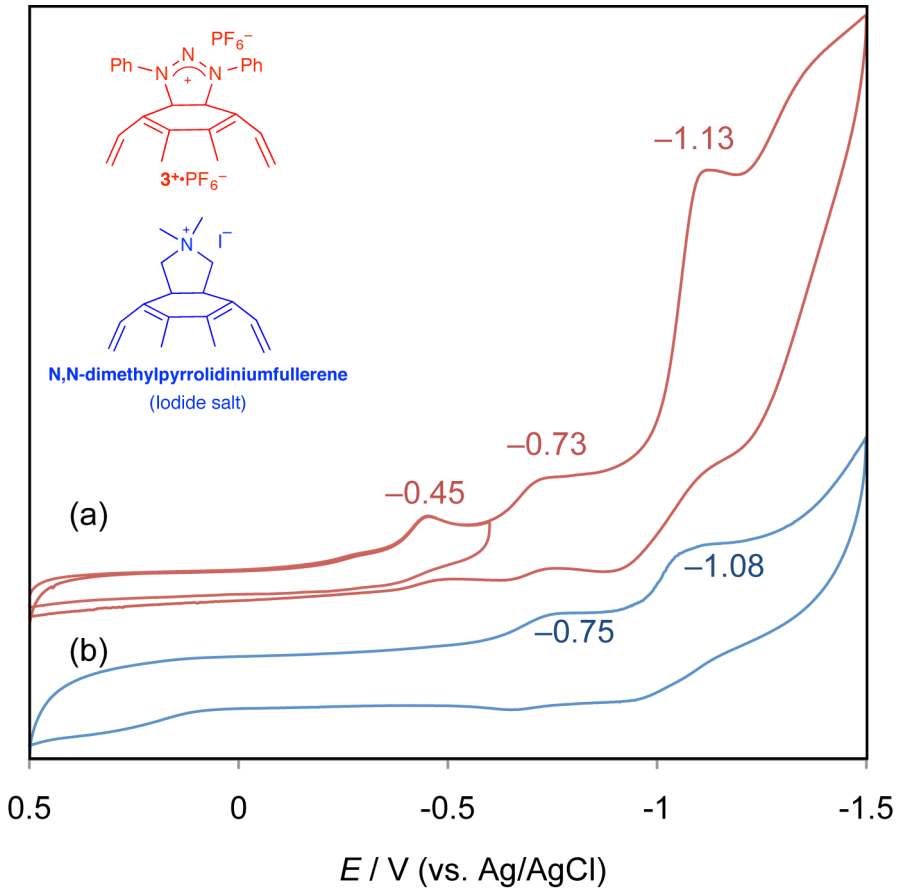


Fig. S3. CV curves and E_p values for (a) $\mathbf{3}^{+\bullet}PF_6^-$ and (b) N,N-dimethylpyrrolidiniumfullerene iodide (0.1 mM PhCN solution, with 0.1 M $^nBu_4PF_6$ electrolyte).

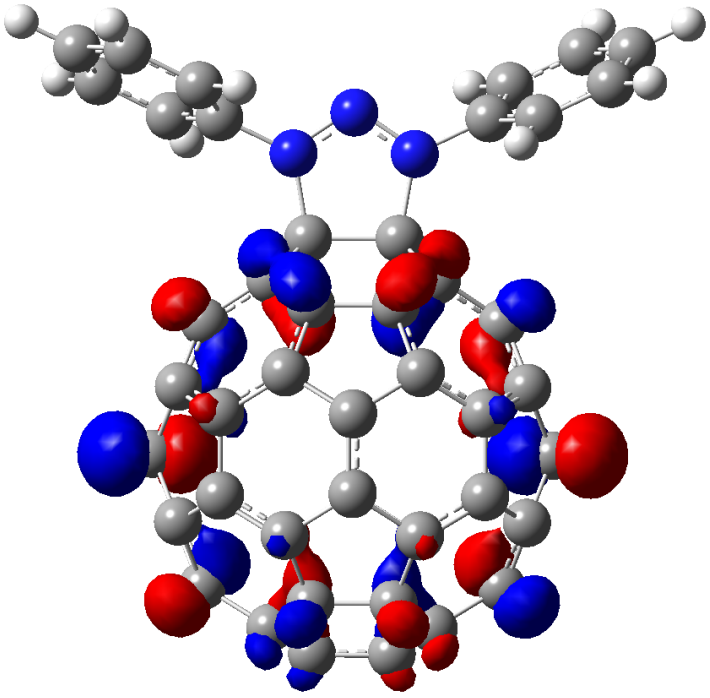
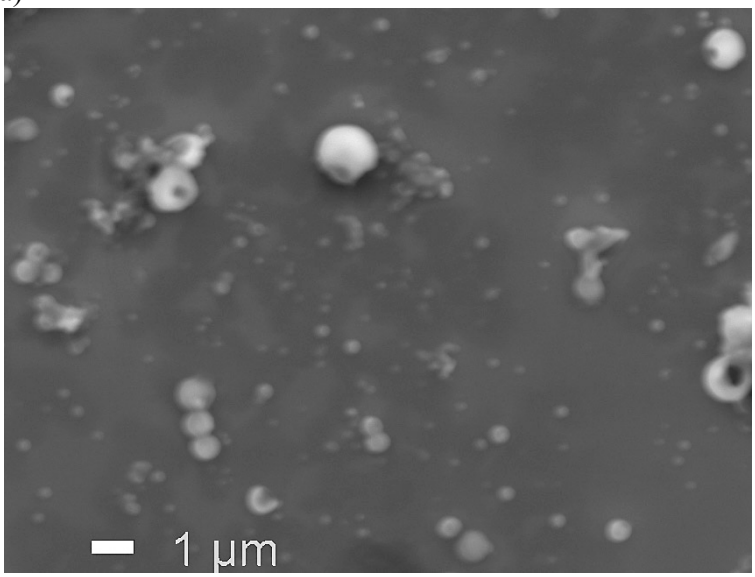


Fig. S4. HOMO orbital of **3**$^{+}$ (BHandHLYP/6-31G(d), IEFPCM=toluene)

a)



(b)

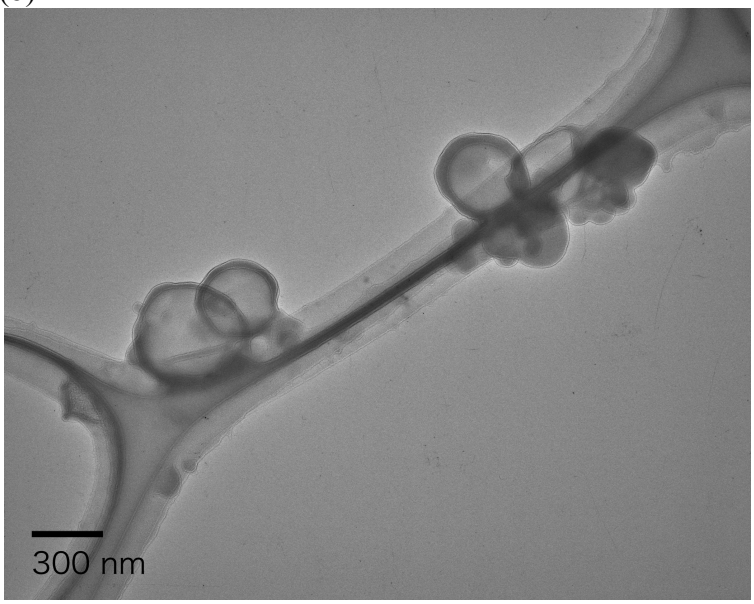


Fig. S5. (a) SEM image (magnified) from THF solution and (b) TEM image (magnified) from MEOH solution

Full Citation of Spartan'08:

J. Kong, C. A. White, A. I. Krylov, D. Sherrill, R. D. Adamson, T. R. Furlani, M. S. Lee, A. M. Lee, S. R. Gwaltney, T. R. Adams, C. Ochsenfeld, A. T. B. Gilbert, G. S. Kedziora, V. A. Rassolov, D. R. Maurice, N. Nair, Y. H. Shao, N. A. Besley, P. E. Maslen, J. P. Dombroski, H. Daschel, W. M. Zhang, P. P. Korambath, J. Baker, E. F. C. Byrd, T. Van Voorhis, M. Oumi, S. Hirata, C. P. Hsu, N. Ishikawa, J. Florian, A. Warshel, B. G. Johnson, P. M. W. Gill, M. Head-Gordon and J. A. Pople, *J. Comput. Chem.*, 2000, **21**, 1532.

Full Citation of Gaussian 09:

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

Coordinates of the transition state geometry and the vibration mode of imaginary frequency

Coodinates of TS

1	C	-4.551	-1.690	-0.743	41	C	1.024	-0.084	2.393
2	C	-3.828	-2.694	0.001	42	C	1.456	-1.048	1.511
3	C	-3.830	-2.306	1.393	43	C	1.465	-1.679	-0.743
4	C	-4.554	-1.062	1.507	44	C	1.029	-1.309	-1.996
5	C	-5.000	-0.681	0.187	45	C	-0.139	0.318	-3.206
6	C	-4.129	-0.095	2.397	46	C	-0.835	1.507	-3.097
7	C	-2.714	-2.530	2.174	47	C	-1.564	3.141	-1.594
8	C	-2.710	-3.290	-0.548	48	C	-1.564	3.511	-0.264
9	C	-4.124	-1.325	-2.004	49	C	-0.839	2.894	1.869
10	C	-5.004	0.649	-0.185	50	C	-0.144	1.935	2.581
11	C	-4.133	1.297	2.008	51	C	1.944	-0.675	0.193
12	C	-4.562	1.660	0.746	52	C	1.024	0.090	-2.388
13	C	-4.129	0.067	-2.394	53	C	-0.393	2.518	-2.169
14	C	-4.560	1.032	-1.504	54	C	-0.395	3.278	0.552
15	C	-2.954	-1.945	-2.577	55	C	1.020	1.315	2.001
16	C	-2.263	-2.907	-1.867	56	C	0.725	2.295	-1.388
17	C	-1.542	-3.522	0.268	57	C	0.725	2.684	0.004
18	C	-1.544	-3.151	1.598	58	C	1.450	1.056	-1.506
19	C	-2.961	-0.327	3.211	59	C	1.939	0.687	-0.188
20	C	-2.270	-1.518	3.104	60	C	1.454	1.688	0.748
21	C	-0.826	-1.513	3.102	61	N	4.296	1.043	-0.435
22	C	-0.378	-2.521	2.173	62	N	4.805	0.015	0.003
23	C	-2.962	0.308	-3.207	63	N	4.303	-1.016	0.441
24	C	-2.234	-0.936	-3.322	64	C	4.875	2.287	-0.209
25	C	-0.819	-2.900	-1.865	65	C	5.877	4.824	0.157
26	C	-0.373	-3.281	-0.548	66	C	5.781	2.522	0.829
27	C	-3.845	2.669	0.002	67	C	4.464	3.316	-1.056
28	C	-3.844	2.281	-1.389	68	C	4.972	4.586	-0.868
29	C	-2.968	1.925	2.581	69	C	6.281	3.793	1.003
30	C	-2.241	0.921	3.326	70	H	6.080	1.715	1.477
31	C	-2.731	3.272	0.552	71	H	3.764	3.103	-1.845
32	C	-2.283	2.892	1.871	72	H	4.666	5.389	-1.517
33	C	-2.729	2.512	-2.171	73	H	6.983	3.990	1.795
34	C	-2.278	1.503	-3.100	74	H	6.272	5.815	0.302
35	C	-0.855	-0.932	-3.321	75	C	4.889	-2.256	0.215
36	C	-0.130	-1.936	-2.576	76	C	5.906	-4.787	-0.152
37	C	0.742	-2.680	0.002	77	C	4.485	-3.287	1.062
38	C	0.739	-2.291	1.393	78	C	5.795	-2.485	-0.825
39	C	-0.862	0.926	3.326	79	C	6.302	-3.754	-0.998
40	C	-0.138	-0.319	3.211	80	C	5.000	-4.555	0.873

81	H	3.784	-3.079	1.852
82	H	6.089	-1.677	-1.473
83	H	7.005	-3.946	-1.791
84	H	4.700	-5.359	1.523
85	H	6.307	-5.776	-0.297

Frequency Calculation:

Frequencies -- -102.2798
Red. masses -- 9.1655
Frc consts -- 0.0565
IR Inten -- 354.7922

Atom	AN	X	Y	Z
1	6	0.03	0.00	0.00
2	6	0.03	0.00	0.00
3	6	0.03	0.00	0.00
4	6	0.03	0.00	0.00
5	6	0.04	0.00	0.00
6	6	0.04	0.00	0.00
7	6	0.03	0.00	0.00
8	6	0.03	0.00	0.00
9	6	0.04	0.00	0.00
10	6	0.04	0.00	0.00
11	6	0.04	0.00	0.00
12	6	0.03	0.00	0.00
13	6	0.04	0.00	0.00
14	6	0.03	0.00	0.00
15	6	0.04	0.00	0.00
16	6	0.04	0.00	0.00
17	6	0.03	0.00	0.00
18	6	0.03	0.00	0.00
19	6	0.04	0.00	0.00
20	6	0.04	0.00	0.00
21	6	0.04	0.00	-0.01
22	6	0.04	0.00	0.00
23	6	0.04	0.00	0.00
24	6	0.04	0.00	0.01
25	6	0.04	0.00	0.01
26	6	0.04	0.00	0.00
27	6	0.03	0.00	0.00
28	6	0.03	0.00	0.00
29	6	0.04	0.00	0.00
30	6	0.04	0.00	-0.01
31	6	0.03	0.00	0.00
32	6	0.04	0.00	0.00
33	6	0.03	0.00	0.00
34	6	0.04	0.00	0.00
35	6	0.04	0.00	0.01
36	6	0.04	0.00	0.01
37	6	0.04	0.01	0.00
38	6	0.04	0.01	0.00
39	6	0.04	0.00	-0.01
40	6	0.04	0.00	-0.01
41	6	0.04	-0.01	-0.01
42	6	0.05	-0.01	0.00
43	6	0.06	-0.01	0.00
44	6	0.04	0.00	0.01
45	6	0.04	0.00	0.01
46	6	0.04	0.00	0.01
47	6	0.03	0.00	0.00
48	6	0.03	0.00	0.00
49	6	0.04	0.00	-0.01
50	6	0.04	0.00	-0.01
51	6	0.15	-0.03	0.01
52	6	0.04	0.01	0.01
53	6	0.04	0.00	0.00
54	6	0.04	0.00	0.00
55	6	0.04	0.00	-0.01
56	6	0.04	-0.01	0.00
57	6	0.04	-0.01	0.00
58	6	0.05	0.01	0.00
59	6	0.15	0.03	-0.01
60	6	0.06	0.01	0.00
61	7	-0.32	0.00	0.10
62	7	-0.16	0.00	0.00
63	7	-0.32	-0.01	-0.10
64	6	-0.25	0.00	0.05
65	6	-0.01	-0.06	-0.05
66	6	-0.21	-0.03	0.02
67	6	-0.16	0.01	0.03
68	6	-0.04	-0.02	-0.02
69	6	-0.08	-0.07	-0.03
70	1	-0.27	-0.04	0.05
71	1	-0.18	0.05	0.03
72	1	0.02	-0.02	-0.05
73	1	-0.04	-0.11	-0.05
74	1	0.08	-0.09	-0.09
75	6	-0.25	0.00	-0.05

76	6	-0.01	0.06	0.05
77	6	-0.16	-0.01	-0.03
78	6	-0.21	0.03	-0.02
79	6	-0.08	0.07	0.03
80	6	-0.04	0.02	0.02
81	1	-0.17	-0.06	-0.03
82	1	-0.27	0.03	-0.05
83	1	-0.05	0.11	0.05
84	1	0.02	0.02	0.05
85	1	0.08	0.09	0.09