Supplementary Information 1

A Novel Migrative Addition Reactions of Hydrazines to the Diketone Derivative of C_{60}

Sho-ichi Iwamatsu,* Fumiaoki Ono, and Shizuaki Murata

1. Experimental procedures and characterization data page 2-5
2. Computational procedures and Cartesian coordinate of **3a-I** page 6-8

General. All reactions were performed under argon atmosphere unless otherwise mentioned. Column chromatography was performed on silica gel (Merck, 230-400 mesh or Fuji silicia, FL-600) using indicated solvents. Thin layer chromatography was performed on glass plates coated with silica gel 60 F_{254} (Merck). Melting points were recorded in capillary tubes with SHIBATA MEL270 melting point apparatus and were uncorrected. All NMR studies were carried out on JEOL α 400 (^{1}H at 400 MHz, ^{13}C at 100 MHz), α 600 (^{1}H at 400 MHz, ^{13}C at 100 MHz, ^{15}N at 60.7 MHz) or Lambda 500 (^{1}H at 500 MHz, ^{13}C at 125 MHz) spectrometers. Inadequate 1D experiments were performed with J_{cc} set to 77, 57 or 37 Hz. ^{15}N chemical shifts are referenced relative to liquid ammonia by using the ^{15}N resonance of formamide at 85 ppm as an external reference. FT-IR spectra were recorded on a JASCO FT/IR-5300 instrument. UV/Vis spectra were recorded on a JASCO V-550 UV/Vis Spectrometer. Emission spectra were recorded on a JASCO FP-6600 Fluorescence Spectrometer. ES-Mass spectra were recorded in the negative ion modes on a micromass LCT instrument. Elemental analyses were performed by the microanalytical center of Kyoto University.

Materials. Pure C_{60} (99.5%), ^{13}C enriched (10-15%) C_{60} were obtained from Tokyo Progress System Co, Ltd. ^{15}N enriched hydrazine sulfate ($^{15}NH_2{}^{15}NH_2H_2SO_4$: 99% ^{15}N content for each nitrogen atom) was purchased from Aldrich Co, Ltd. The preparation of diketone derivative **1** was already reported.[1] ^{15}N enriched 2,4-dinitrophenylhydrazine **2b** was prepared according to the literature method.[2] Solvents were distilled under an inert atmosphere from sodium/benzophenone (toluene) or CaH_2 (pyridine). Other reagents and solvents were purchased reagent grade and used as received.

REFERENCES

1. H. Inoue, H. Yamaguchi, S.-i. Iwamatsu, T. Uozaki, T. Suzuki, T. Akasaka, S. Nagase, S. Murata, *Tetrahedron Lett.* 2001, **42**, 895.
2. C. F. H. Allen, *Org. Synth.* 1943, **2**, 228.

Typical procedure for the reaction of 1 with aromatic hydrazine.

(entry 1) In a 50 mL Schlenk tube, to a solution of **1** (20 mg, 0.019 mmol) in toluene (5 mL) was added **2a** (11 mg, 0.10 mmol), and the reaction mixture was stirred for 4 h at room temperature. The resulting mixture was subjected to chromatography (silica, 4% EtOAc/toluene) to give 18 mg (81%) of **3a** as a dark brown solid. **(entry 3)** In a 50 mL Schlenk tube, to a mixture of **2c**•HCl (17 mg, 0.097 mmol) and **1** (20 mg, 0.019 mmol) in toluene (5 mL) was added pyridine (16 μL, 0.20 mmol), and the mixture was stirred for 8 h at 60 °C. After cooling to room temperature, the resulting solution was washed with 2N HCl (×2) and brine, dried with $MgSO_4$, and subjected to chromatography (silica, 4% EtOAc/toluene) to give 19 mg (85%) of **3c** as a dark brown solid.

3a: mp. >300 °C; ^{1}H NMR ($CDCl_3$) δ 13.86 (s, 1H), 7.71 (d, J = 8 Hz, 2H), 7.54 (t, J = 8 Hz, 2H), 7.3-7.2 (overlap, 1H), 5.30 (d, J = 20 Hz, 1H), 4.73 (d, J = 20 Hz, 1H), 4.26 (s, 3H), 3.93 (s, 3H), 3.88 (s, 3H), 3.74 (s, 3H); ^{13}C NMR/DEPT135 ($CDCl_3$) δ 190.52, 185.61, 170.25, 168.84, 167.15, 164.87, 154.48, 151.16, 150.43, 149.60, 149.54, 149.47, 149.34, 148.96, 148.53, 148.47, 148.15, 147.89, 147.70, 147.65, 147.59, 147.48, 147.23, 147.01, 146.93, 146.73, 146.21, 145.41, 145.35, 145.33, 144.92, 144.08, 143.94, 143.49, 142.93, 142.64, 142.60, 142.52, 142.50, 142.32, 141.06, 140.82, 140.41, 140.20, 138.00, 137.94, 137.85, 137.75, 137.28, 136.12, 136.01, 135.84, 135.67, 135.57, 135.22, 135.12, 133.87, 132.61, 131.64, 131.52, 129.90 (CH), 128.39, 128.21, 126.27, 125.71, 124.92 (CH), 115.34 (CH), 63.86, 55.86, 54.33 (CH_3), 54.20 (CH_3), 53.30 (CH_3), 52.88 (CH_3), 43.80 (CH_2); IR (KBr) 2940, 1744, 1686, 1537, 1478, 1433, 1260, 1225 cm^{-1}; UV/Vis (CH_2Cl_2) λ_{max} (ε) 253 (110,000), 329 (40,000), 438 (21,000), 536 (13,000), 681 (4,500) nm; ES-MS (neg.) 1144 (M^-); Anal calcd for $C_{78}H_{20}N_2O_{10}$: C. 81.82, H. 1.76, N. 2.45. found: C. 81.54, H. 2.05, N. 2.20.

3b: 50% yield; ^{1}H NMR (C_6D_6) δ 15.32 (s, 1H), 8.81 (d, J = 2 Hz, 1H), 7.95 (d, J = 9 Hz, 1H), 7.91 (dd, J = 9, 2 Hz, 1H), 5.23 (d, J = 20 Hz, 1H), 4.55 (d, J = 20 Hz, 1H), 4.37 (s, 3H), 3.62 (s, 3H), 3.40 (s, 3H), 3.19 (s, 3H); ^{15}N NMR (C_6D_6/C_6H_5Cl=1/4) δ 301 (d, J_{NN} = 12 Hz), 126 (dd, J_{NN} = 12, J_{NH} = 102

Hz); IR (KBr) ν (cm^{-1}) 2948, 1744, 1720, 1709, 1686, 1613, 1596, 1496, 1433, 1336, 1224; UV/Vis (CH_2Cl_2) λ_{max} (ε) 251 (100,000), 312 (40,000), 393 (27,000), 443 (26,000), 481 (26,000), 675 (2,700); ES-MS (neg.) 1234 (M^-); (Measurement of ^{13}C NMR spectrum has not been in success because of low solubility)

3c: 85% yield; mp. >300 °C; ^1H NMR ($CDCl_3$) δ 14.00 (s, 1H), 7.68 (d, *J* = 9 Hz, 2H), 7.09 (d, *J* = 9 Hz, 2H), 5.30 (d, *J* = 20 Hz, 1H), 4.70 (d, *J* = 20 Hz, 1H), 4.24 (s, 3H), 3.92 (s, 3H), 3.91 (s, 3H), 3.88 (s, 3H), 3.73 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 190.46, 185.48, 170.30, 168.90, 167.14, 164.91, 157.58, 154.56, 151.13, 150.42, 149.65, 149.52, 149.48, 149.36, 148.87, 148.63, 148.57, 148.08, 147.94, 147.75, 147.70, 147.64, 147.51, 147.48, 147.14, 147.05, 146.97, 146.76, 146.27, 145.44, 145.37, 145.10, 144.90, 144.10, 144.00, 142.82, 142.70, 142.62, 142.18, 141.07, 140.83, 140.49, 140.14, 138.82, 138.27, 137.98, 137.95, 137.93, 137.57, 137.20, 136.19, 136.18, 136.04, 135.87, 135.85, 135.11, 135.08, 134.96, 133.88, 132.65, 131.32, 131.11, 128.43, 128.25, 126.28, 125.72, 116.77, 115.33 55.74, 54.32, 54.19, 53.27, 52.86, 43.69 (two sp^3 quaternary carbons assigned to the fulleroid bridge positions could not be detected because of low solubility); IR (KBr) ν (cm^{-1}) 2949, 1744, 1723, 1686, 1537, 1512, 1480, 1435, 1244, 1229; UV/Vis (CH_2Cl_2) λ_{max} (ε) 254 (110,000), 331 (38,000), 448 (19,000), 550 (13,000), 699 (7,600) nm; ES-MS (neg.) 1174 (M^-); Anal calcd for $C_{79}H_{22}N_2O_{11}$: C. 80.75, H. 1.89, N. 2.38. found: C. 80.22, H. 2.04, N. 2.11.

3d: 89% yield; mp. >300 °C; ^1H NMR ($CDCl_3$) δ 13.83 (s, 1H), 7.65 (d, *J* = 9 Hz, 2H), 7.59 (d, *J* = 9 Hz, 2H), 5.25 (d, *J* = 20 Hz, 1H), 4.68 (d, *J* = 20 Hz, 1H), 4.23 (s, 3H), 3.93 (s, 3H), 3.88 (s, 3H), 3.74 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 190.57, 185.76, 170.21, 168.76, 166.91, 164.83, 154.39, 151.10, 150.44, 149.58, 149.56, 149.49, 149.36, 149.00, 148.54, 148.37, 148.20, 147.89, 147.79, 147.73, 147.62, 147.48, 147.23, 147.01, 146.93, 146.75, 146.20, 145.50, 145.39, 145.34, 144.91, 144.11, 143.97, 143.57, 143.01, 142.61, 142.47, 142.41, 141.68, 141.49, 141.06, 140.84, 140.35, 140.23, 138.03, 137.95, 137.89, 137.35, 137.18, 136.46, 136.10, 136.01, 135.55, 135.31, 135.30, 135.09, 133.84, 132.89, 132.55, 131.95, 131.61,

128.35, 128.28, 128.21, 126.25, 125.70, 117.39, 116.73, 54.36, 54.24, 53.28, 52.91, 43.88 (two sp^3 quaternary carbons assigned to the fulleroid bridge positions could not be detected because of low solubility); IR (KBr) ν (cm^{-1}) 2948, 1744, 1723, 1688, 1588, 1537, 1474, 1433, 1256, 1225; UV/Vis (CH_2Cl_2) λ_{max} (ε) 253 (110,000), 328 (41,000), 439 (22,000), 537 (14,000), 682 (5,000) nm; ES-MS (neg.) 1223 (M^--H+2, 34), 1221 (M^--H, 20), 1036(100); Anal calcd for $C_{78}H_{19}BrN_2O_{10}$: C. 76.55, H. 1.56, N. 2.29. found: C. 75.90, H. 1.44, N. 2.04.

3e: 85% yield; mp. >300 °C; ^{1}H NMR ($CDCl_3$) δ 7.8-7.2 (br, 10H), 4.88 (d, *J* = 20 Hz, 1H), 4.70 (d, *J* = 20 Hz, 1H), 4.33 (s, 3H), 3.93 (s, 3H), 3.92 (s, 3H), 3.74 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 190.20, 183.25, 170.47, 169.33, 168.35, 164.95, 163.73, 155.62, 150.23, 149.79, 149.44, 149.42, 149.40, 149.22, 148.44, 148.41, 148.24, 147.75, 147.60, 147.51, 147.47, 147.39, 147.37, 146.85, 146.77, 146.72, 146.33, 145.83, 145.43, 145.36, 145.34, 144.66, 144.07, 143.80, 143.71, 143.57, 142.80, 142.61, 142.45, 141.91, 140.87, 140.68, 140.61, 138.84, 138.13, 138.00, 137.87, 137.79, 137.77, 137.50, 136.90, 136.30, 136.02, 135.72, 135.56, 134.98, 134.60, 133.82, 132.71, 131.74, 131.22, 129.37, 129.28, 128.59, 128.36, 126.63, 125.76, 63.73, 56.02, 54.34, 54.13, 53.16, 52.83, 40.83; IR (KBr) ν (cm^{-1}) 2948, 1734, 1718, 1694, 1530, 1487, 1433, 1271, 1223; UV/Vis (CH_2Cl_2) λ_{max} (ε) 255 (110,000), 329 (40,000), 439 (13,000), 546 (10,000), 678 (5,100) nm; ES-MS 1220 (M^-); Anal calcd for $C_{84}H_{24}N_2O_{10}$: C. 82.62, H. 1.98, N. 2.29. found: C. 82.60, H. 1.98, N. 2.16.

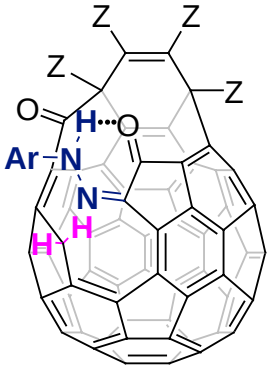
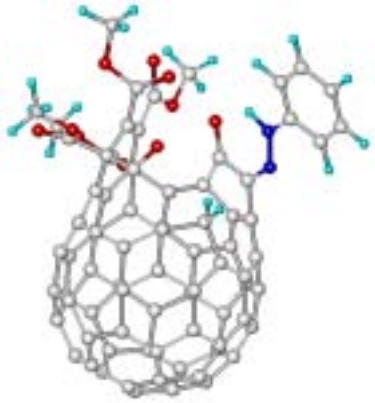
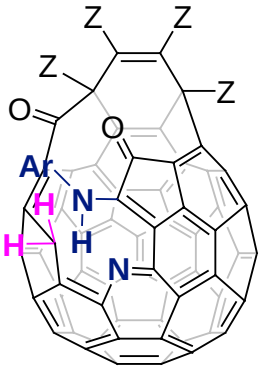
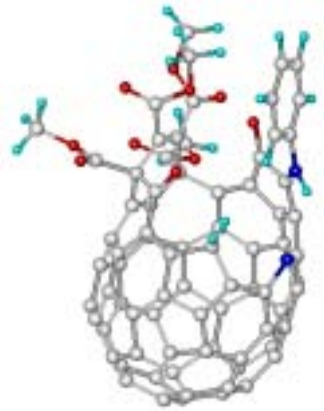
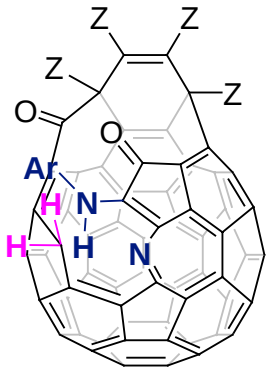
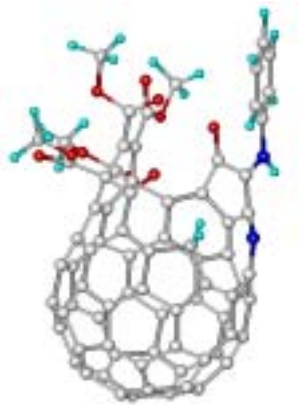
Calculations. All calculations were carried out using Hyper Chem 6.0[3] and GAUSSIAN 98 (Revision A.11)[4] set of programs. Possible structures **3a-I**, **3a-II** and **3a-III** were optimized at the AM1 level. Structure **3a-I** was further optimized at the B3LYP/6-31G* level.

REFERENCES

3. HyperChem (TM), Hypercube, Inc., 1115 NW 4th Street, Gainesville, Florida 32601.

4. Gaussian 98, Revision A.11, Frisch, M. J., Trucks, G. W., Schlegel, H. B., Scuseria, G. E., Robb, M. A., Cheeseman, J. R., Zakrzewski, V. G., Montgomery, Jr., J. A.,Stratmann, R. E., Burant, J. C., Dapprich, S., Millam, J. M., Daniels, A. D., Kudin, K. N., Strain, M. C., Farkas, O., Tomasi, J., Barone, V., Cossi, M., Cammi, R., Mennucci, B., Pomelli, C., Adamo, C.,Clifford, S., Ochterski, J., Petersson, G. A., Ayala, P. Y., Cui, Q., Morokuma, K., Malick, D. K., Rabuck, A. D., Raghavachari, K., Foresman, J. B., Cioslowski, J., Ortiz, J. V., Stefanov, B. B., Liu, G., Liashenko, A., Piskorz, P., Komaromi, I., Gomperts, R., Martin, R. L., Fox, D. J., Keith, T., Al-Laham, M. A., Peng, C. Y., Nanayakkara, A., Gonzalez, C., Challacombe, M., Gill, P. M. W., Johnson, B., Chen, W., Wong, M. W., Andres, J. L., Gonzalez, C., Head-Gordon, M., Replogle, E. S. & Pople, J. A. Gaussian, Inc., Pittsburgh PA, 1998.

Table S1. Calculated heats of formation and relative energies for the possible structures **3a-I**, **3a-II** and **3a-III**.

3a-I		
AM1 (rel. to **3a-I)**	585.89 kcal/mol (±0)	
3a-II		
AM1 (rel. to **3a-I)**	561.33 kcal/mol (-24.6)	
3a-III		
AM1 (rel. to **3a-I)**	562.16 kcal/mol (-23.7)	

Cartesian coordinate of **3a-I** optimized at the B3LYP/6-31G(d) level.

E(UB+HF-LYP) = -3845.8753 au.

0	1			
C	0	-3.920753	5.347721	-1.139771
C	0	-4.372207	4.032291	-0.964174
C	0	-5.625634	3.780126	-0.386766
C	0	-6.424775	4.848979	0.009799
C	0	-5.985477	6.164075	-0.161006
C	0	-4.732644	6.403386	-0.73345
C	0	3.152558	-2.985989	1.105963
C	0	1.718282	-2.957208	1.219601
C	0	0.881266	-2.903705	0.097792
C	0	1.475727	-2.793348	-1.231213
C	0	2.883238	-2.850885	-1.328955
C	0	3.728291	-2.939013	-0.152956
C	0	3.722812	-2.228853	2.205096
C	0	2.618162	-1.734611	2.995008
C	0	1.384755	-2.1975	2.403885
C	0	0.211296	-1.447222	2.431695
C	0	-0.475601	-2.449529	0.309384
C	0	0.719529	-2.007613	-2.21918
C	0	1.476109	-1.255004	-3.136646
C	0	2.917932	-1.251917	-3.177053
C	0	3.618481	-2.062193	-2.304042
C	0	4.849777	-1.588556	-1.700272
C	0	4.925852	-2.142469	-0.367091
C	0	5.46257	-1.388433	0.680799
C	0	4.849448	-1.433591	1.996963
C	0	2.663909	-0.462558	3.548595
C	0	3.831667	0.37324	3.333093
C	0	4.901908	-0.099078	2.567579
C	0	5.540371	0.775078	1.597915
C	0	5.897818	-0.024209	0.438124
C	0	5.798688	0.522464	-0.844031
C	0	5.286097	-0.279204	-1.941291
C	0	4.516546	0.589025	-2.80982
C	0	3.373937	0.107324	-3.440245
C	0	-0.662447	-1.604676	-1.949414
C	0	0.912136	2.622363	-2.181963
C	0	-0.275386	1.906053	-2.430794
C	0	-1.680626	1.952665	-2.020321
C	0	-0.508613	3.03377	0.843015
C	0	0.873448	3.445569	0.327731
C	0	2.8789	3.399766	-1.058775
C	0	3.299677	2.653096	-2.215691
C	0	2.116926	2.157452	-2.867071
C	0	2.196364	0.934326	-3.543316
C	0	1.059139	0.07565	-3.462187
C	0	-0.112547	0.556076	-2.948431
C	0	-2.237176	0.562342	-2.071472
C	0	-1.893708	0.436706	1.709211
C	0	-0.635246	0.892169	2.349378
C	0	-0.144572	2.159911	2.039118
C	0	1.14909	2.55611	2.478918
C	0	1.764452	3.395374	1.468886
C	0	3.150455	3.415533	1.365152
C	0	3.727683	3.438528	0.054629
C	0	4.48976	1.912815	-2.21385
C	0	5.310364	1.880245	-1.0197
C	0	4.94174	2.639745	0.087271
C	0	5.078379	2.08518	1.426254
C	0	3.967542	2.568319	2.219666
C	0	3.365026	1.733561	3.16218
C	0	1.922747	1.721334	3.281033
C	0	1.476989	0.368169	3.508305
C	0	0.258857	-0.081912	2.963358
C	0	-1.078471	-0.341941	-2.373272
C	0	-0.808115	-1.77896	1.461799
C	0	1.414464	3.37525	-0.959119
C	0	-2.146034	-1.113824	1.680205
C	0	-3.168361	-1.472078	0.610796
C	0	-2.82803	-2.068534	-0.544528
C	0	-1.404347	-2.484713	-0.911657
C	0	-2.68142	-1.570624	3.073173
C	0	-4.619893	-1.107144	0.894831
C	0	-3.918208	-2.40008	-1.522821
C	0	-1.44508	-3.968438	-1.404974
O	0	-2.677242	1.206598	1.185038
O	0	-3.428717	0.288661	-1.952441
N	0	-2.350068	3.04159	-1.713123
O	0	-3.386529	-0.588739	3.66003
O	0	-2.481992	-2.657513	3.555423
O	0	-0.83843	-4.429403	-2.34082
O	0	-2.22471	-4.691122	-0.580495
O	0	-5.171869	-2.054609	1.680717
O	0	-5.186677	-0.104519	0.535979
O	0	-3.413097	-2.696155	-2.73597
O	0	-5.102615	-2.434931	-1.266045
N	0	-3.609798	2.926182	-1.357704
C	0	-3.972908	-0.925447	4.932067
C	0	-6.57109	-1.870713	1.956688
C	0	-4.378971	-2.990387	-3.758087
C	0	-2.312032	-6.095986	-0.880936
H	0	-2.951565	5.522954	-1.59236
H	0	-5.948729	2.753449	-0.233076
H	0	-7.393572	4.650826	0.459923
H	0	-6.612421	6.995051	0.149022
H	0	-4.384677	7.423653	-0.871073
H	0	-1.101548	2.493476	0.123855
H	0	-1.10072	3.913673	1.132041
H	0	-4.015043	1.987426	-1.280975
H	0	-3.193363	-1.200712	5.646387
H	0	-4.666926	-1.760879	4.814446
H	0	-4.496387	-0.026241	5.255844
H	0	-7.135255	-1.883002	1.021122
H	0	-6.74114	-0.92127	2.471291
H	0	-6.855762	-2.711835	2.589522
H	0	-5.006416	-2.114145	-3.93898
H	0	-5.01042	-3.830483	-3.458366
H	0	-3.795497	-3.239642	-4.644155
H	0	-1.322415	-6.556478	-0.827543
H	0	-2.724559	-6.245877	-1.881779
H	0	-2.97425	-6.512361	-0.122327