Functionalization of C_{60} with 1,3-Nitrilimine Dipole: Synthesis of 2-Pyrazoline Ring-Fused C_{60} Derivatives

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Pyrazoline ring-fused C_{60} derivatives (**1**, **2** and **3**) as an example of monofunctionalized C_{60} with heterocycle are synthesized by using the dipolar cycloaddition. The reaction of 1,3-nitrilimine with C_{60} takes place readily to provide the target monoadduct together with the di- and triadducts in good total yields. Based on the fluorescent and electrochemical characteristics, features of pyrazoline ring-fused C_{60} are briefly discussed.

Modification of C_{60} with heterocycle would be a promising area to develop a new chemistry of C_{60} and to find the novel functions of C_{60} derivatives leading eventually to biologically, chemically and/or physically interesting applications. As such a modified system, we have been interested in 2-pyrazoline ring-fused C_{60} in which the 58 π system of C_{60} sphere and the pyrazoline ring are fused in the non-conjugative manner. A special interest in the target compounds (**1**, **2** and **3**) will be their photophysical properties because pyrazolines[1] are strongly fluorescent in the 430 nm region, while C_{60} is only very weakly fluorescent in the 730 nm region.[2]

As a strategy for synthesis of 2-pyrazoline ring-fused C_{60} derivatives (**1**, **2** and **3**) we have adopted the 1,3-dipolar cycloaddition of 1-phenyl-3-R-substituted nitrilimine (substituent R : *t*-butyl-, *p*-methoxycarbonylphenyl- and *p*-methoxyphenyl-) generated *in situ*[3] as shown in Scheme 1. An example of the reaction conditions is as follows: A solution of C_{60} (0.05 mmol) and *N*-(α-chloro-neopentylidene or *p*-substituted benzylidene)-*N'*-phenylhydrazine[4] (0.05 mmol) in 45 ml of benzene was refluxed for 4 h in the presence of triethylamine (14 ml, 0.10 mmol); color of the solution changed from purple to dark brown. The reaction mixture was subjected to liquid chromatography (hexane-benzene / silica gel) to provide the target product (**1**, **2** or **3**), unreacted C_{60} and di- and triadducts with the following conversion.[5]

(1) Case of cycloaddition of 1-phenyl-3-*t*-butyl nitrilimine: monoadduct (**1**), $C_{60}(C_{11}H_{14}N_2)$, 31.3%, unreacted C_{60} 44.1%, di- and triadducts 24.6%.

(2) Case of cycloaddition of 1-phenyl-3-*p*-methoxycarbonylphenyl nitrilimine: monoadduct (**2**), $C_{60}(C_{15}H_{14}N_2O_2)$, 45.7%, unreacted C_{60} 29.1%, di- and triadducts 25.2%.

(3) Case of cycloaddition of 1-phenyl-3-*p*-methoxyphenyl nitrilimine: monoadduct (**3**), $C_{60}(C_{14}H_{12}N_2O)$, 24.7%, unreacted C_{60} 38.1%, di- and triadducts 37.2%.

The melting points were over 300 °C for **1**, **2** and **3**.

The structures of the target products (**1**, **2** and **3**) were elucidated by the MS, NMR and UV-Vis spectroscopic analyses.[6]

The molecular formulas of **1**, **2** and **3** were determined by the FABMS spectra [the parent peak (m/z) 894 for **1**, 972 for **2**, and 944 for **3**] and the exact FABMS spectra [found for **1** m/z (p+1) 895.1241, calcd for $C_{60}(C_{11}H_{15}N_2)$ 895.1240; found for **2** m/z (p+1) 973.0984, calcd for $C_{60}(C_{15}H_{13}N_2O_2)$ 973.0980; found for **3** m/z (p) 944.0958, calcd for $C_{60}(C_{14}H_{12}N_2O)$ 944.0950].

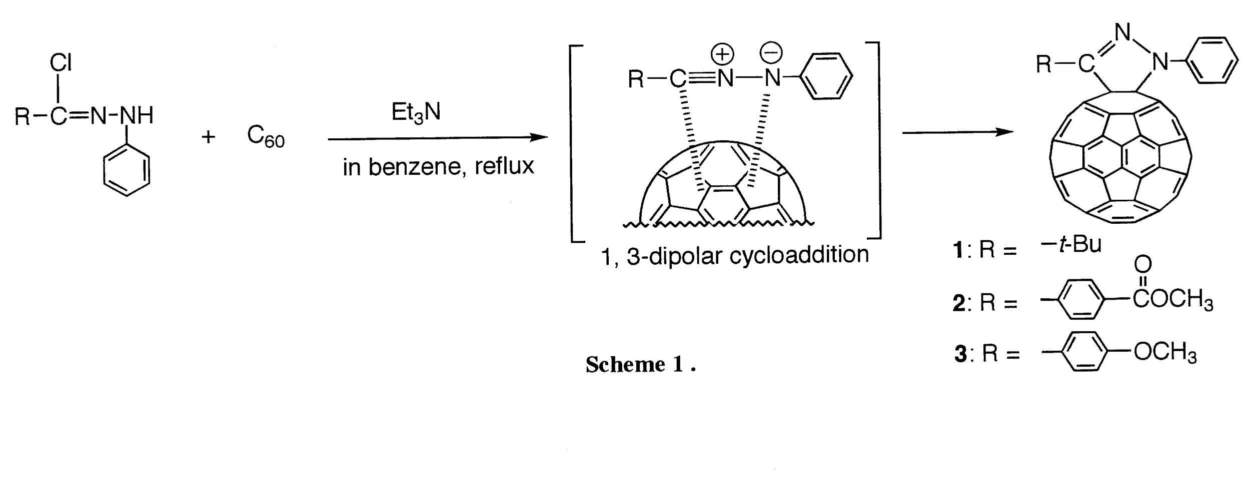
Although we have already proved that cycloaddition of 1,3-diphenylnitrilimine takes place at the 6/6 bond of C_{60},[3] it was also confirmed for **1** ~ **3** by observing the characteristic sharp absorption at 425-430 nm of 6/6 bond addition products.[6]

To examine the electrochemical characteristics of **1**, **2** and **3**, their reduction potentials were measured together with C_{60}, $C_{60}H_2$[7] and 1,3-diphenyl-2-pyrazoline ring-fused C_{60}(**4**)[3] as the reference material by cyclic voltammetry[8] (Table 1).

Table 1. CV data of C_{60} derivatives[a]

Compound	$E^1_{1/2}$/V	$E^2_{1/2}$/V	$E^3_{1/2}$/V
C_{60}	-0.94	-1.37	-1.81
$C_{60}H_2$	-1.08	-1.52	-2.08
1 (*t*-Bu/ Ph)	-1.29	-1.74	-2.23
2 (*p*-CH_3OCO-C_6H_4/ Ph)	-1.28	-1.71	-2.23
3 (*p*-CH_3O-C_6H_4/ Ph)	-1.30	-1.73	-2.27
4 (Ph/ Ph)	-1.17	-1.58	-2.11

[a]Conditions: *n*-Bu_4NBF_4 (0.05 mol dm^{-3}), benzonitrile, 25 °C, Pt working and Pt counter electrodes, 100 mV s^{-1}. Potentials were measured vs Fc/Fc^+ using Ag/Ag^+ reference electrode.



Scheme 1.

The products **1**, **2** and **3** show reversible three one-electron reductions corresponding mono-, di-, and trianions, respectively. From this table we can find the following electrochemical characteristics:
(1) The corresponding reduction potentials for **1**, **2** and **3** are very close to each other and are shifted to the negative side by 0.2V compared with those of $C_{60}H_2$ (58π system). Noteworthy is a significant difference between the reduction potentials for **1** ~ **3** and those for **4**, suggesting a possibility of the different structure of the radical anion species formed by the reduction of the former (**1** ~ **3**) and the latter (**4**). (2) The characteristic reduction waves (irreversible) of 2-pyrazolines (Ep -1.13 ~ -1.56V) are not observed for **1**, **2** and **3**, suggesting the occurrence of some kind of interaction between the pyrazoline system and the 58π system of C_{60} sphere both of which are non-conjugatively fused to each other.

Interestingly fluorescence spectra of **1** and **3** in cyclohexane at room temperature appeared in the both regions at around 430 nm and 760 nm.[9] The former corresponds to the emission due to the pyrazoline part, and the latter due to the C_{60} sphere as is obvious from the following data. Fluorescence (λmax and quantum yield ϕ_f) for **1** and reference materials: 423 nm (ϕ_f 4.91×10^{-4} at 363 nm excitation) and 765 nm (ϕ_f 1.37×10^{-4} at 363 nm excitation) for **1**, 427 nm (ϕ_f 7.4×10^{-1} at 357 nm excitation) for 1,3-diphenyl-2-pyrazoline (reference material for the pyrazoline part), 737 nm (ϕ_f 4.7×10^{-5} at 370 nm excitation) for C_{60} (reference material for C_{60} sphere). It is to be noted that the 1-phenyl-3-*t*-butyl-2-pyrazoline ring fusion results in the decreasing in ϕ_f for fluorescence of the pyrazoline part but the increasing in ϕ_f for fluorescence of the C_{60} sphere compared with those of the parent systems. Although the reliable emission spectra due to the C_{60} sphere in **2** was not obtained because of incomplete elimination of the overtone of the excitation Raman, the fluorescence emission (764 nm, ϕ_f 3.17×10^{-6} at 362 nm excitation) due to the C_{60} sphere in **3** was remarkably weakened by the fusion of 1-phenyl-3-*p*-methoxyphenyl-2-pyrazoline ring, the quantum yield of fluorescence emission (424 nm, ϕ_f 2.46×10^{-4} at 362 nm excitation) due to the pyrazoline part in **3** being close to that of **1**. The drastic change in the quantum yield of 760 nm fluorescence emission for **1** and **3** might presumably be interpreted in terms of difference in the photophysical process (intramolecular energy transfer or electron transfer) in **1** and **3**. Intensive investigation (including low temperature fluorescence of pyrazoline ring-fused C_{60}) is currently underway to elucidate this photophysical process.

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References and Notes

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4 This reactant can be easily prepared by the condensation of the corresponding carboxylic acid (or chloride) with phenyl hydrazine, and the subsequent chlorination of the condensation product with PCl_5 (or PPh_3-CCl_4).

5 From the amounts of unreacted C_{60}, the reactivity of 1-phenyl-3-R-substituted nitrilimine is demonstrated to be the following order; R: *p*-CH_3OCO-C_6H_4- > *p*-CH_3O-C_6H_4- > *t*-Bu-.

6 All new compounds reported here were fully characterized by the spectroscopic analysis. The UV-Vis and NMR data are as follows.
1: UV-vis (cyclohexane) λ max (log ε) 217(4.81), 255(4.84), 310(4.30), 426(3.27), 461(3.14); ^{1}H NMR (CS_2 / acetone-d_6) δ 8.89 (d, 2H, N-*o-Ph*), 8.49(t, 2H, N-*m-Ph*), 8.27(t, 1H, N-*p-Ph*), 1.20(s, 9H, CH_3); ^{13}C NMR(CS_2 / acetone-d_6): 39 signals, (δ 82.73, 92.86, for two sp^3 carbons of C_{60} formed by the cycloaddition; 124.03, 125.11, 129.54, for phenyl CH groups; 31.72, 38.13, for *t*-Bu groups; 128.79, 136.17, 136.47, 140.12, 140.27, 142.20, 142.61, 142.69, 142.74, 142.81, 142.94, 143.23, 143.37, 143.56, 143.64, 144.65, 144.68, 145.54, 145.57, 145.72, 145.85, 146.10, 146.26, 146.29, 146.33, 146.55, 146.61, 146.71, 147.50, 147.84, 147.91, 151.89, for (1) one phenyl carbons without hydrogen, (2) one sp^2 carbon of pyrazoline >C=N- group and (3) 58 sp^2 carbons of C_{60} skeleton).
2: UV-vis (cyclohexane) λ max (log ε) 219(4.71), 254(4.80), 336(4.47), 425(3.20), 465(3.10); ^{1}H NMR (CS_2 / acetone-d_6) δ 3.90(s, 3H, ester methyl), 7.92(d, 2H, N-*o-Ph*), 7.46(t, 2H, N-*m-Ph*), 7.24(t, 1H, N-*p-Ph*), 8.10(d, 2H, C-*o-Ph*), 8.42(d, 2H, C-*m-Ph*); ^{13}C NMR (CS_2 / acetone-d_6):43 signals, (δ 52.19, one sp^3 carbon of ester methyl; 81.75, 92.85, for two sp^3 carbons of C_{60} formed by the cycloaddition; 128.84, 130.21, 130.37, 130.66, 130.71, for both phenyl CH groups; 130.75, 131.09, 132.99, 136.76, 136.82, 140.14, 140.72, 142.34, 142.62, 142.75, 142.80, 142.87, 142.90, 143.29, 143.35, 144.69, 144.51, 144.73, 144.75, 145.11, 145.37, 145.60, 145.68, 145.84, 146.29, 146.35, 146.42, 146.50, 146.60, 146.68, 146.80, 146.95, 147.61, 148.01 for (1) three phenyl carbons without hydrogen, (2) one sp^2 carbon of pyrazoline >C=N- group and (3) 58 sp^2 carbons of C_{60} skeleton; 167.67, one sp^2 carbon of carbonyl) .
3: UV-vis (cyclohexane) λ max (log ε) 212(4.94), 255(4.91), 314(4.49), 430(3.45), 467(3.27); ^{1}H NMR(CS_2 / acetone-d_6): δ 3.87(s, 3H, methoxy), 7.89(d, 2H, N-*o-Ph*), 7.41(t, 2H, N-*m-Ph*), 7.18 (t, 1H, N-*p-Ph*), 6.99 (d, 2H, C-*m-Ph*), 8.17(d, 2H, C-*o-Ph*); ^{13}C NMR(CS_2 / acetone-d_6) 42 signals, (δ 55.57, one sp^3 carbon of methoxy; 82.50, 92.41, for two sp^3 carbons of C_{60} formed by the cycloaddition; 114.82, 125.33, 128.87, 129.29, 129.58, for both phenyl CH groups; 129.95, 130.66, 136.83, 136.89, 140.19, 140.79, 142.42, 142.71, 142.83, 142.90, 142.94, 142.99, 143.37, 143.42, 143.67, 143.73, 144.81, 144.84, 145.68, 145.70, 145.73, 145.82, 145.91, 146.30, 146.36, 146.42, 146.49, 146.65, 146.76, 146.89, 147.18, 147.66, 148.07 for (1) two phenyl carbons without hydrogen, (2) one sp^2 carbon of pyrazoline >C=N- group and (3) 58 sp^2 carbons of C_{60} skeleton; 161.11, one sp^2 carbon of C-*p-Ph*).

7 $C_{60}H_2$ was prepared by modifying the Cahill's method (C. C. Henderson, P. R. Cahill, *Science*, **259**, 1885 (1993)).

8 Cyclic and differential pulse voltammograms were recorded using BAS-100W electrochemical analyzer.

9 Fluorescence and absorption spectra were recorded using HITACHI 850 fluorescence spectrophotometer and SHIMADZU UV-Visible recording spectrophotometer 160A, respectively. A 350 nm cutoff filter was used for fluorescence measurement.