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Synthesis and Characterization of C_{60} Derivatives Possessing TEMPO Radicals

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Abstract: The sodium salt of TEMPON tosylhydrazone was pyrolyzed in chlorobenzene in the presence of C_{60} to give the adducts $C_{60}(TEMPO)_n$ (n = 1 - 3) [TEMPO = 2,2,6,6-tetramethylpiperidin-1-oxyl, TEMPON = 4-oxo-TEMPO]. The adducts were isolated by means of gel permeation chromatography, and characterized by mass, IR, UV/Vis, and ESR spectroscopies. The structure of C_{60}(TEMPO) was determined to be an open [5,6] adduct. The magnetic measurements ensured the radical purity. Copyright © 1996 Elsevier Science Ltd

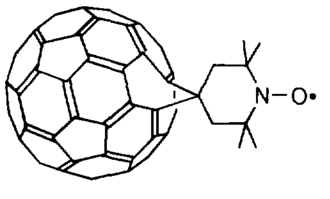
INTRODUCTION

The chemistry of fullerenes has been extensively studied[1] since the synthetic method of macroscopic quantities of fullerenes was discovered in 1990.[2] We have reported the reactions of C_{60} with dienes,[3a,b] carbenes,[3b,c] nitrenes,[3d] benzynes,[3e] and other organic reagents.[3a,f] Research on fullerene derivatives with new functionality attracts much attention as well as the chemistry and physics of fullerenes themselves do. Pharmacial studies such as the inhibition of HIV-1 protease by an application of molecular recognition[4] and DNA cleavage by photosensitizing effect under oxidative conditions[5] are important examples in the fullerene technology. For further development along this line, several interests may reside in problems on the structures of supra-molecular systems containing fullerenes. A variety of labels designed to be observed by spectroscopic techniques including fluorescence, optical absorption, and electron spin resonance (ESR) are known for probing local environment, molecular rotational motion, and bioorganic structure. Spin labeling was first introduced by McConnell in 1965,[6] and has rapidly progressed to be one of the most powerful and versatile tools.[7]

It has been reported that C_{60} was an efficient radical scavenger[8,9] or "radical sponge,"[10] and that the radicals in which the radical center is situated on the C_{60} sphere seem to be highly reactive.[8] Thus, sterically protected radicals are favorable for the spin center in fullerene spin labels. Among hindered nitroxide free radicals exhibiting chemical inertness,[11] TEMPO (2,2,6,6-tetramethylpiperidin-1-oxyl) has been widely investigated for the derivatization,[12] and a variety of TEMPO-based spin labels have been available.[7,12] We planned the synthesis, isolation, and characterization of fullerene derivatives having a TEMPO moiety as a functional group.[13]

RESULTS AND DISCUSSIONS

Synthesis

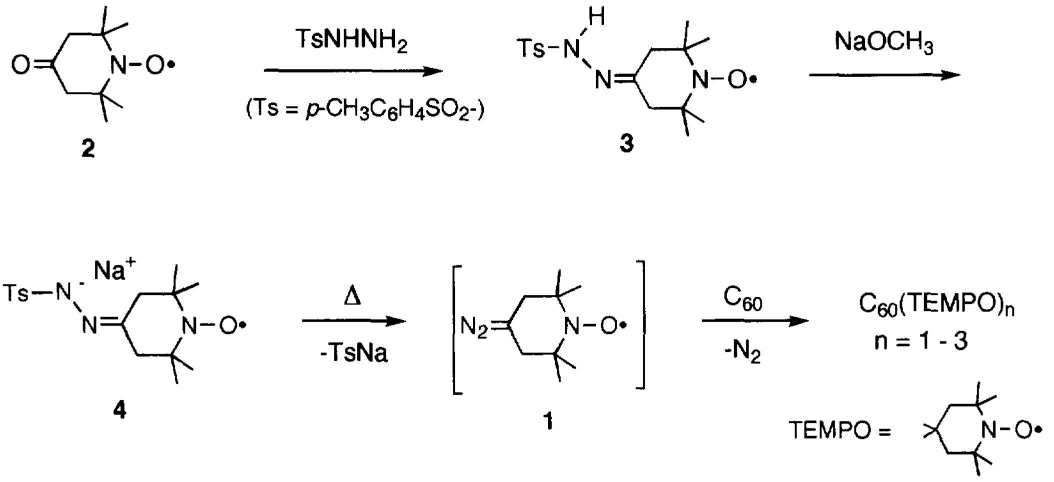


C_{60}(TEMPO)

Since steric and electronic perturbations must be as minimum as possible, C_{60}(TEMPO) seems to be a promising candidate for spin labels in which the C_{60} moiety covalently bonds to piperidine ring directly. We abbreviate 2,2,6,6-tetramethylpiperidin-1-oxyl-4,4-diyl as TEMPO in $C_{60}(TEMPO)_n$ hereafter.

Wudl *et al.* reported that the reactions of diazomethane derivatives and C_{60} gave the corresponding open [5,6] adduct "fulleroids."[14,15] The reaction mechanism has been intensively investigated.[15,16] We adopted this reaction for the introduction of TEMPO moiety to fullerene by use of 4-diazo-TEMPO (**1**). A part of the Bamford-Stevens reaction[17] was applied for the generation of **1** as described in Scheme 1. Because of the difficulty in isolation of **1**, the pyrolysis of the sodium salt was conducted in the presence of C_{60} by an *in-situ* trapping method.

Scheme 1.



TEMPON tosylhydrazone (**3**, tosyl = *p*-toluenesulfonyl) was easily obtained by condensation of TEMPON (**2**) and tosylhydrazine in aqueous media. Treatment of **3** with alcoholic sodium methoxide gave the sodium salt (**4**) as a hygroscopic orange solid. This solid was thoroughly washed with benzene and hexane and dried before being used to the next step. The suspension of **4** and C_{60} in chlorobenzene was heated to 125 - 132°C for 30 min to give $C_{60}(TEMPO)_n$ (n = 1 - 3). Tetra- and more-adducts were obtained in some cases.

The adducts are more soluble than C_{60} in ordinary organic solvents. In order to prevent the decomposition of radical sites, the reaction temperature was kept as low as possible. However, practically no reaction occurred below 120°C. The products were separated by means of gel permeation chromatography (GPC) eluted with toluene. The reaction conditions and the yields of the adducts $C_{60}(TEMPO)_n$ ($n = 1, 2$) are summarized in Table 1. $C_{60}(TEMPO)$ and $C_{60}(TEMPO)_2$ were obtained in comparable yields when two-equivalent amount of **4** was used. However, the yields of $C_{60}(TEMPO)$ did not increase by use of an equimolar amount of **4**. Higher reaction temperature (132°C) caused the conversion ratio of C_{60} and yields of $C_{60}(TEMPO)_n$ little higher than those at 125°C did.

Table 1. The reaction conditions and yields.

conditions			yields / %[a]		
temperature/°C	time/min	sodium salt/C_{60}	$C_{60}(TEMPO)$	$C_{60}(TEMPO)_2$	C_{60}
125	30	2	21	19	14
132	30	2	26	22	11
125	30	1	20	3	36
132	30	1	21	4	23

a) Isolated yields. The yield of $C_{60}(TEMPO)_2$ was indicated as the sum of possible isomers.

Spectral Characterization

The electrospray-ionization mass spectrum (ESI MS) of $C_{60}(TEMPO)$ showed only one signal at *m/z* 874 ascribable to the molecular ion (Fig. 1), which verifies the purity of the sample. The IR spectrum showed bands ascribable to the TEMPO moiety and C_{60} skeleton without any band due to an N=N group or

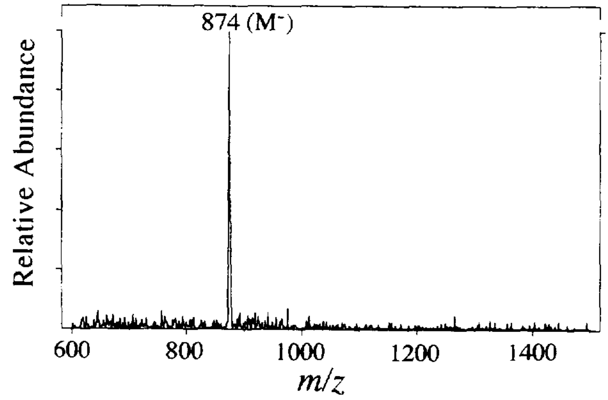


Fig. 1. Negative-ion electrospray-ionization mass spectrum of $C_{60}(TEMPO)$.

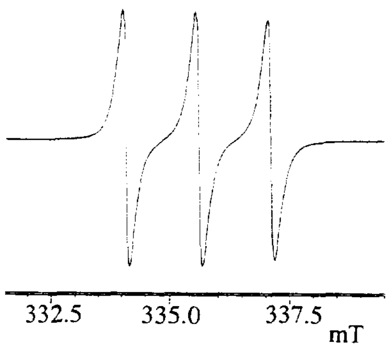


Fig. 2. X-Band ESR spectrum of $C_{60}(TEMPO)$ in non-degassed toluene at room temperature.

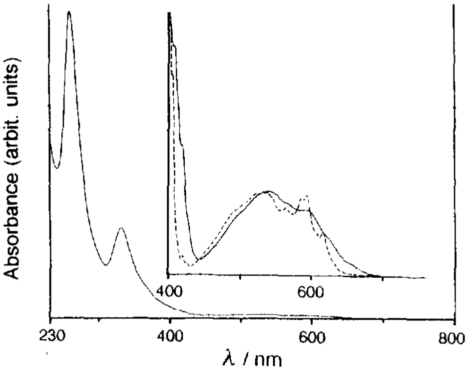


Fig. 3. UV/Vis absorption spectrum of C_{60}(TEMPO) in hexane. Inset: magnification of a selected region. Dotted line represents the absorption of C_{60} in hexane.

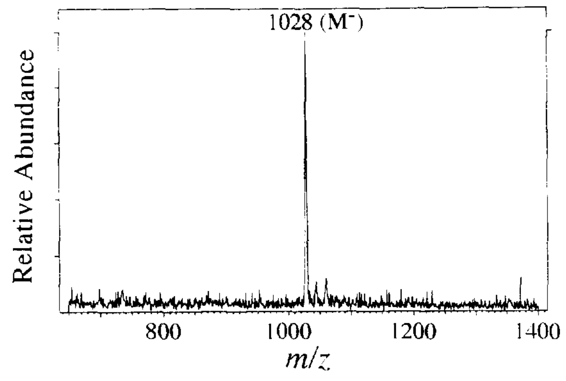


Fig. 4. Negative-ion electrospray-ionization mass spectrum of $C_{60}(TEMPO)_2$.

pyrazoline ring. These findings indicate that the elimination of N_2 completely occurred under these reaction conditions. The ESR spectrum of C_{60}(TEMPO) showed a triplet signal at $g = 2.0064$ with a_N of 1.49 mT in toluene (Fig. 2). These values are typical for nitroxide radicals, and the spectrum is quite similar to those of other TEMPO-based radicals. The UV/Vis absorption spectrum of C_{60}(TEMPO) in hexane is similar to that of C_{60} (Fig. 3), and this fact explains why C_{60} and C_{60}(TEMPO) have almost the same purple color in solution. The electronic structure of the C_{60} moiety in C_{60}(TEMPO) seems to be only slightly perturbed from that of C_{60}, strongly suggesting that C_{60}(TEMPO) has an open [5,6] structure with C_{60} conjugation retained.

In order to obtain a conclusive evidence of the structure, we synthesized and characterized other diamagnetic adducts suitable for NMR analysis.[18] A similar reaction starting from diethyl ketone instead of **2** gave the adducts $C_{60}(C(CH_2CH_3)_2)_n$ ($n = 1 - 3$). The ^1H NMR analysis of $C_{60}(C(CH_2CH_3)_2)$ revealed that two ethyl groups were nonequivalent with a large difference of the chemical shifts.[19] The ^{13}C NMR spectrum showed 31 signals with one signal unresolved in the aromatic region.[19] The structure was proved to be an open [5,6] adduct.

Several open [5,6] adducts were reported to be given through the 1,3-dipolar addition of diazo compounds to C_{60} followed by the liberation of N_2 under thermal conditions.[14,15] It has also been reported that carbenes likely react at [6,6] ring junctions to give closed [6,6] adducts.[1,3c] The reaction mechanism containing a carbene, TEMPO-4,4-diyl, generated from **1** (Scheme 1) is incompatible to our experimental results. Thus, the synthesis presented here should be understood to contain the 1,3-dipolar addition of **1** to C_{60}.

The multi-adducts $C_{60}(TEMPO)_2$ and $C_{60}(TEMPO)_3$ were characterized by mass, IR, UV/Vis and ESR spectroscopies. Their ESI mass spectra clearly indicated the molecular ions (the spectrum of $C_{60}(TEMPO)_2$ is shown in Fig. 4). Their UV/Vis absorption spectra were similar to that of C_{60}(TEMPO); $C_{60}(TEMPO)_2$ is purple and $C_{60}(TEMPO)_3$ is purplish brown in solution. These spectroscopic characteristics indicate that all of the addition sites have an open [5,6] structure, although positional isomerism seems to be possible. Their

ESR spectra showed typical nitrogen triplet signals with some broadening (the averaged peak-to-peak linewidths were 0.22, 0.23, and 0.24 mT for C_{60}(TEMPO), C_{60}(TEMPO)$_2$, and C_{60}(TEMPO)$_3$ respectively). These signal profiles indicate that the intramolecular exchange interaction should be negligible in comparison with the hyperfine interactions owing to the geometrical separation of the spin centers. However, the line broadening can be interpreted in terms of the intramolecular dipole-dipole interaction among the spins.

The thermal isomerization of the open adducts is stated briefly. The color of TEMPO adducts turned from purple to brown in solution after long heating in the evaporating process. We examined the isomerization by ^{1}H NMR experiments again using a diamagnetic model compound $C_{60}(C(CH_2CH_3)_2)$. New signals due to the ethyl protons of the corresponding closed isomer[20] appeared after refluxing in *o*-dichlorobenzene. The solution was heated to reflux for 5 h, giving the relative intensity ratio (open isomer : closed isomer) of 83 : 17. Thus, the thermal isomerization was confirmed to occur. Very recently Smith *et al.* reported similar results on a dimethyl analogue $C_{60}C(CH_3)_2$.[21]

Magnetic Measurements

The elemental analysis of the samples recrystallized from CS_2 indicated the composition formula C_{60}(TEMPO)•1.3CS$_2$. The temperature dependence of the magnetic susceptibilities on these samples obeyed the Curie-Weiss relation ($\chi = C / (T - \theta)$, where C and θ stand for Curie and Weiss constants respectively). Figure 5 shows the temperature dependences of the magnetic susceptibility and reciprocal magnetic susceptibility of the sample prepared by the pyrolysis at 125°C. We obtained $C = 3.86 \times 10^{-4}$ and 3.53×10^{-4} cm^3 K g^{-1} with $\theta = -0.25$ K for the samples prepared by the pyrolysis at 125 and 132°C respectively. The purities of the specimens were estimated to be 100±2 and 92±2%, respectively, based on the above composition, by the comparison with the theoretical value of the Curie constant for S = 1/2 species (0.375 cm^3 K mol^{-1}). The experimental error was mainly due to the composition formula determined by elemental analysis. The purity of C_{60}(TEMPO) were proved to be very high; the introduction of the TEMPO group to C_{60} was accomplished without appreciable destruction of the radical sites.

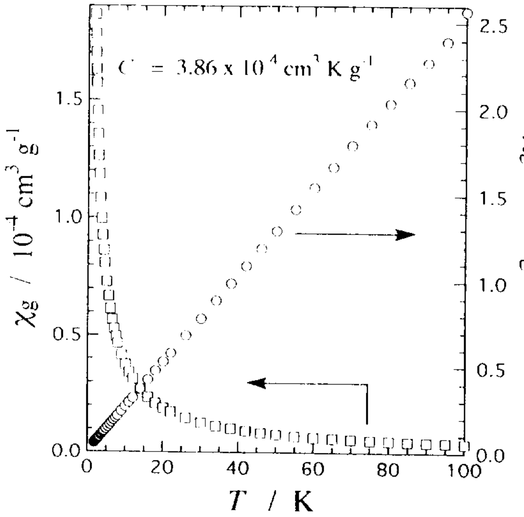


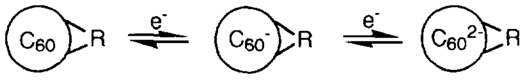
Fig. 5. Temperature dependences of the magnetic susceptibility and reciprocal magnetic susceptibility of C_{60}(TEMPO)•1.3CS$_2$.

Several TEMPO derivatives were reported to exhibit intermolecular ferromagnetic interaction,[22] and we have reported that some of them were purely organic ferromagnets with T_c of *ca.* 0.4 K.[23] However, C_{60}(TEMPO)•1.3CS$_2$ showed intermolecular antiferromagnetic interaction indicated by the negative Weiss constant (-0.25 K). The bulky substituent C_{60} seems to be unfavorable for the molecular arrangement exhibiting ferromagnetic coupling.

Electrochemical Measurements

The reduction and oxidation potentials were determined by cyclic voltammetry. The half-wave redox potentials are summarized in Table 2. C_{60}(TEMPO) was proved to possess both the electron-donating and -accepting sites. The redox wave at 0.62 V *vs.* Ag/Ag$^+$ can be assigned to the oxidation-reduction process of the nitroxide site as described in eq. (1) and the others to those of C_{60} moiety as described in eq. (2).

(1)



(2)

Table 2. Half-wave potentials[a)] of C_{60}(TEMPO), C_{60}, and TEMPON.

	E_{ox} / V	$E_{red}(1)$ / V	$E_{red}(2)$ / V
C_{60}(TEMPO)	0.62	-0.88	-1.29
C_{60}		-0.84	-1.24
TEMPON	0.56		

a) Measured in *o*-dichlorobenzene by using 0.05 M $Bu_4N^+BF_4^-$ as a supporting electrolyte, Pt working and counter electrodes, and Ag/Ag$^+$ reference electrode.

The oxidation potentials of the nitroxide site in TEMPO derivatives are reported to be susceptible to the substituent effect.[24] The oxidation potentials of TEMPON (**2**) and unsubstituted TEMPO were 0.44 and 0.27 V *vs.* Ag/Ag$^+$ in acetonitrile.[24] We obtained 0.56 V *vs.* Ag/Ag$^+$ for the former in *o*-dichlorobenzene. The oxidation potential of C_{60}(TEMPO) was larger than that of **2**, indicating the electron-withdrawing nature of the C_{60} moiety as a substituent effect at 4-position in the piperidine ring. The fullerene moiety was actually electron-withdrawing as previously reported on the fluoren-9-ylidene-C_{60} system.[25] However, the fact that the fullerene was more electron-demanding than a carbonyl group is not valid in the case of the fluorenylidene system.[25]

Slight negative shifts of the reduction potentials were observed for C_{60}(TEMPO) relative to those of C_{60}. This finding is in good agreement with the open [5,6] structure of C_{60}(TEMPO), as often discussed on open fulleroid derivatives.[14,15] The decrease of electron affinity must be due to electron-donating properties of the alkyl moieties in the TEMPO substituent.

SUMMARY

The fullerene spin labels, $C_{60}(TEMPO)_n$ (n = 1 - 3), were synthesized and characterized. These molecules were designed to be environmentally stable, electronically unperturbed, and easily available. These labeled reagents seem to be applicable in studies on molecular systems, especially on bioorganic systems, containing fullerenes. Furthermore, application of electron-accepting properties is of great interest from the viewpoint of studies on magnetic and conducting properties of the charge-transfer complexes.

EXPERIMENTAL

Instruments. GPC separation was performed on a LC 908 (Japan Analytical Industry) by using gel permeation columns (Jaigel 1H+1H) and toluene as an eluent with a flow rate of 3.5 ml/min. The elution was monitored by absorption at 254 nm. ESI mass spectra were recorded on a Finigan MAT TSQ 700 mass spectrometer. Samples were ionized from a 10^{-5} molar solution of benzene / methanol / 1,2-dimethoxyethane (6:3:1).[26] Fast-atom-bombardment (FAB) ionization was conducted by a xenon beam with an energy of 8 kV from a matrix of *m*-nitrobenzyl alcohol on the same mass spectrometer. EI-mass spectra were obtained on a Shimadzu GCMS QP-1000 spectrometer. UV/Vis and IR absorption spectra were recorded on a Shimadzu UV-250 and JASCO IR-810 spectrophotometers respectively. ESR spectra were recorded on a JEOL JES-TE300 spectrometer. Magnetic measurements were carried out on a Quantum Design MPMS-7 SQUID magnetometer at a magnetic field of 0.5 T. The diamagnetic contribution (-1.1×10^{-6} cm^3 g^{-1}) of $C_{60}(TEMPO)\bullet1.3CS_2$ was estimated by best fit to the equation of $\chi_{exp} = C / (T - \theta) + \chi_{dia}$. Electrochemical data were obtained in *o*-dichlorobenzene by using 0.05 M $Bu_4N^+BF_4^-$ as a supporting electrolyte, Pt working and counter electrodes, and Ag/Ag^+ reference electrode with a scan rate of 200 mV/s on a Hokuto Denko HA-501 and HB-104 system.

Materials. TEMPON (**2**) and tosylhydrazone were purchased from Tokyo Kasei Corp. and sodium methoxide (28% methanol solution) was from Wako Pure Chemical industry, and they were used without purification.

TEMPON tosylhydrazone (**3**). A solution of 1.68 g of **2** in 50 ml of H_2O was added to a solution of 1.86 g of tosylhydrazine in 250 ml of water and the mixture was stirred for one day at room temperature. Orange crystals precipitated were collected on a suction filter, washed with a small amount of water, and dried under vacuum, giving 1.84 g of of **3** (55%). Mp. 130°C, EI-MS *m/z* 338 (M^+, 4%), 322 (M^+-O, 3%), 183 (M^+-tosyl, 15%), 101 (100%), IR (KBr disk) 3200, 1395, 1175, 1165, 680, 540 cm^{-1}. The magnetic measurement of **3** gave Curie and Weiss constants of 0.375 cm^3 K mol^{-1} and -4.1 K respectively, which confirmed the radical purity.

Sodium salt of TEMPON tosylhydrazone (**4**). To a suspension of 663 mg of **3** in 3 ml of methanol was added 0.4 ml of 28% methanolic solution of sodium methoxide at room temperature under argon. After stirring for 70 min the solvent of the resulting orange solution was removed under reduced pressure to give an orange solid. The solid was suspended in benzene and the solvent was evaporated again. A small amount of benzene was added to the solid and the mixture was treated by sonicator and the supernatant containing impurity was removed with a pipet. The resultant orange solid was dried under vacuum to give 676 mg of **4** (96%) as a very hygroscopic solid. The IR spectrum had no absorption due to N-H stretching. The magnetic measurement of **4** gave Curie and Weiss constants of 0.329 cm^3 K mol^{-1} and -1.4 K respectively. The Curie constant was somewhat lower than theoretical value, probably because the sample was wet or contaminated with washing solvents.

C_{60}(TEMPO)$_n$. A mixture of 51.7 mg of **4**, 53.2 mg of C_{60}, and 10 ml of chlorobenzene was gently refluxed (bp. 132°C) with stirring under argon for 30 min. The mixture was filtered on a silica-gel short column. A hexane-toluene-ethanol mixed solvent was used for the eluent with a gradual increase of the content of polar solvents. The elution was concentrated under reduced pressure below 45°C, and addition of methanol gave brown powder. It was collected, dissolved in a small amount of CS_2, and reprecipitated with hexane to give 67.4 mg of brown powder. The solid (61.9 mg) was dissolved in 5 ml of toluene and the products were separated by means of GPC. The isolated products were as follows in the order of the retention time: 7.5 mg (9%) of C_{60}(TEMPO)$_3$ at 57 min, 16.6 mg (22%) of C_{60}(TEMPO)$_2$ at 65 min, 16.5 mg (26%) of C_{60}(TEMPO) at 65 min, and 6.3 mg (12%) of C_{60} recovered at 103 min. All of the products are dark brown powder (mp > 350°C). C_{60}(TEMPO) and C_{60}(TEMPO)$_2$ are purple and other adducts are brown in solution. Reaction conditions and yields are summarized in Table 1.

C_{60}(TEMPO) : ESI MS *m/z* 874 (M^-). FAB MS *m/z* 875 (M^-+1), 720 (C_{60}^-). IR (KBr disk) 2960, 2910, 1240, 525, 510 cm^{-1}. UV/Vis (hexane) λ_{max} 260, 332, 540(br), 600(sh) nm. ESR (toluene, room temperature) g = 2.0064, a_N = 1.49 mT, ΔH_{pp} = 0.23, 0.22, and 0.22 mT. Anal. for the samples recrystallized from CS_2. Calc. for C_{60}(TEMPO)•1.3CS_2: C, 86.70; H, 1.66; N, 1.44; S, 8.56%. Found: 1) C, 86.68; H, 2.47; N, 1.61; S, 8.18% (prepared by the pyrolysis at 132°C). 2) C, 86.10; H, 2.33; N, 1.88; S, 8.73% (prepared by the pyrolysis at 125°C).

C_{60}(TEMPO)$_2$: ESI MS *m/z* 1028 (M^-). FAB MS *m/z* 1030 (M^-+2), 720 (C_{60}^-). IR (KBr disk) 2960, 2910, 1240, 525, 510 cm^{-1}. UV/Vis (THF) λ_{max} 260, 340, 540(br) nm. ESR (toluene, room temperature) g = 2.0063, a_N = 1.49 mT, ΔH_{pp} = 0.24, 0.23, 0.23 mT.

C_{60}(TEMPO)$_3$: ESI MS *m/z* 1182 (M^-). FAB MS *m/z* 1185 (M^-+3), 720 (C_{60}^-). IR (KBr disk) 2960, 2910, 1240, 525, 510 cm^{-1}. UV/Vis (THF) λ_{max} 270, 340(sh), 550(br) nm. ESR (toluene, room temperature) g = 2.0061, a_N = 1.49 mT, ΔH_{pp} = 0.25, 0.24, 0.23 mT.

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REFERENCES AND NOTES

1. For reviews, see, *Acc. Chem. Res.* **1992**, *25*, 97-176; Taylor, R.; Walton, D. R. M. *Nature* **1993**, *363*, 685-693; Hirsch, A. "The Chemistry of the Fullerenes," Thieme Medical Publishers, New York, 1994; Sliwa, W. *Fullerene Sci. Technol.*, **1995**, *3*, 243-281.
2. Krätshmer, W.; Lamb, L. D.; Fostiropoulos, K.; Huffman, D. R. *Nature* **1990**, *347*, 354-358.

3. a) Tsuda, M.; Ishida, T.; Nogami, T.; Kurono, S.; Ohashi, M.*J. Chem. Soc., Chem. Commun.* **1993**, 1296-1298; *idem Fullerene Sci. Technol.* **1993**, *1*, 275-285; b) *idem ibid.* **1994**, *2*, 155-164; c) *idem Tetrahedron Lett.* **1993**, *34*, 6911-6912; Ishida, T.; Furudate, T.; Nogami, T.; Kubota, M.; Hirano, T.; Ohashi, M. *Fullerene Sci. Technol.* in press; d) Ishida, T.; Tanaka, K.; Nogami, T. *Chem. Lett.* **1994**, 561-562; Kuwashima, S.-y.; Kubota, M.; Kushida, K.; Ishida, T.; Ohashi, M.; Nogami, T. *Tetrahedron Lett.* **1994**, *35*, 4371-4374; e) Tsuda, M.; Ishida, T.; Nogami, T.; Kurono, S.; Ohashi, M. *Chem. Lett.* **1992**, 2333-2334; Ishida, T.; Shinozuka, K.; Nogami, T.; Sasaki, S.; Iyoda, M. *ibid.* **1995**, 317-318; f) Ishida, T.; Tanaka, K.; Furudate, T.; Nogami, T.; Kubota, M.; Kurono, S.; Ohashi, M. *Fullerene Sci. Technol.* **1994**, *3*, 85-92.
4. Friedman, S. H.; DeCamp, D. L.; Sijbesma, R. P.; Srdanov, G.; Wudl, F.; Kenyon, G. L. *J. Am. Chem. Soc.* **1993**, *115*, 6506-6509; Sijbesma, R.; Srdanov, G.; Wudl, F.; Castoro, J. A.; Wilkins, C.; Friedman, S. H.; DeCamp, D. L.; Kenyon, G. L. *ibid.* **1993**, *115*, 6510-6512.
5. Tokuyama, H.; Yamago, S.; Nakamura, E.; Shiraki, T.; Sugiura, Y. *J. Am. Chem. Soc.* **1993**, *115*, 7918-7919.
6. Stone, T. J.; Buckman, T.; Nordio, P. L.; McConnell, H. M. *Proc. Natl. Acad. Sci. U. S. A.* **1965**, *52*, 1010-1017; Ohnishi, S.; McConnell, H. M. *J. Am. Chem. Soc.* **1965**, *87*, 2293.
7. Griffith, O. H.; Waggoner, A. S. *Acc. Chem. Res.* **1969**, *2*, 17-24.; Keana, J. F. W. *Chem. Rev.* **1978**, *78*, 37-64.
8. Krusic, P.; Wasserman, E.; Keizer, P. N.; Morton, J. M.; Preston, K. F. *Science* **1991**, *254*, 1183-1185.
9. Brizzolara, D.; Ahlemann, J. T.; Roesky, H. W.; Keller, K. *Bull. Soc. Chim. Fr.* **1993**, *130*, 745-747.
10. McEwen, C. N.; McKay, R. G.; Larsen, B. S. *J. Am. Chem. Soc.* **1992**, *114*, 4412-4414.
11. Rozantsev, E. G.; Sholle, V. D. *Synthesis* **1971**, 190-202; *idem ibid.* **1971**, 401-414; Rozantsev, E. G. "Free Nitroxyl Radicals," Plenum Press, New York-London, 1970.
12. Dagonneau, M.; Kagan, E. S.; Mikhailov, V. I.; Rozantsev, E. G.; Sholle, V. D. *Synthesis* **1984**, 895-916.
13. Preliminary communications: Ishida, T.; Shinozuka, K.; Kubota, M.; Ohashi, M.; Nogami, T. *J. Chem. Soc., Chem. Commun.*, in press.
14. Suzuki, T.; Li, Q.; Khemani, K. C.; Wudl, F.; Almarsson, Ö. *Science* **1991**, *254*, 1186-1188.
15. Suzuki, T.; Li, Q; Khemani, K. C.; Wudl, F. *J. Am. Chem. Soc.* **1991**,*114*, 7301-7302; Smith III, A. B.; Strongin, R. M.; Brard, L.; Furst, G. T.; Romanow, W. J.; Owens, K. G.; King R. C. *ibid.* **1993**, *115*, 5829-5830.
16. Prato, M.; Lucchini, V.; Maggini, M.; Stimpfl, E.; Scorrano, G.; Eiermann, M.; Suzuki, T.; Wudl, F. *J. Am. Chem. Soc.* **1993**, *115*, 8479-8480; Isaacs, L.; Wehrsig, A.; Diederich, F. *Helv. Chim. Acta* **1993**, *76*, 1231-1250; Diederich, F.; Isaacs, L.; Philp, D. *Chem. Soc. Rev.* **1994**, 243-255.
17. Shapiro, R. H. *Org. React.* **1976**, *23*, 405-507.
18. Kawasumi, M.; Ishida, T.; Nogami, T. *Fullerene Sci. Technol.*, submitted.
19. ^{1}H NMR (500 MHz, 1:4 acetone-d_6-CS_2) δ 3.85 (2H, q, J = 7.3 Hz), 1.52 (3H, t, J = 7.3 Hz), 1.52 (2H, q, J = 7.3 Hz), 0.98 (3H, t, J = 7.3 Hz). The residual proton signal of acetone-d_6 (δ 2.05 ppm) was used for the reference. ^{13}C NMR (126 MHz, 1:4 acetone-d_6-CS_2) δ_C 147.70 (2C), 145.48 (2C), 145.05 (2C), 144.69 (1C), 144.32 (2C), 144.17 (2C), 143.99 (2C), 143.96 (1C), 143.92 (2C), 143.77 (2C), 143.40 (2C), 143.36 (2C), 143.30 (2C), 143.25 (2C), 143.09 (2C), 142.86 (2C), 142.45 (2C), 142.28 (2C),

142.20 (2C), 142.09 (2C), 142.01 (2C), 141.69 (3C), 141.59 (2C), 141.12 (2C), 140.41 (2C), 139.97 (2C), 138.99 (2C), 138.96 (2C), 137.99 (2C), 137.16 (2C), 135.97 (1C), 135.27 (2C), 54.06 (1C), 30.31, 22.05, 10.20, 8.92. The CS_2 signal (δ_C 192.80) was used for the reference. The relative carbon abundances shown in parentheses were estimated by the signal integrals. The signal at δ_C 141.69 was resolved in benzene-d_6-CS_2.

20. ^{1}H NMR (500 MHz, 1:4 acetone-d_6-CS_2) δ 2.76 (2H, q, J = 7.3 Hz), 1.58 (3H, t, J = 7.3 Hz). The residual proton signal of acetone-d_6 (δ 2.05 ppm) was used for the reference.
21. Smith III, A. B.; Strongin, R. M.; Brard, L.; Furst, G. T.; Romanow, W. J.; Owens, K. G.; Goldschmidt, R. J.; King, R. C. *J. Am. Chem. Soc.*, **1995**, *117*, 5492-5502.
22. Kobayashi, T.; Takiguchi, M.; Amaya, K.; Sugimoto, H.; Kajiwara, A.; Harada, A.; Kamachi, M. *J. Phys. Soc. Jpn.* **1993**, *62*, 3239-3243; Chouteau, C.; Veyret-Jeandey, C. *J. Physique* **1981**, *42*, 1441-1444; Tomioka, K.; Ishida, T.; Nogami, T.; Iwamura, H. *Chem. Lett.* **1993**, 625-626.
23. Nogami, T.; Tomioka, K.; Ishida, T.; Yoshikawa, H.; Yasui, M.; Iwasaki, F.; Iwamura, H.; Takeda, N.; Ishikawa, M. *Chem. Lett.* **1994**, 29-32; Ishida, T.; Tsuboi, H.; Nogami, T.; Yoshikawa, H.; Yasui, M.; Iwasaki, F.; Iwamura, H.; Takeda, N.; Ishikawa, M. *ibid.* **1994**, 919-922; Nogami, T.; Togashi, K.; Tsuboi, H.; Ishida, T.; Yoshikawa, H.; Yasui, M.; Iwasaki, F.; Iwamura, H.; Takeda, N.; Ishikawa, M. *Synth. Met.*, **1995**, *71*, 1813-1814; Nogami, T.; Ishida, T.; Tsuboi, H.; Yoshikawa, H.; Yamamoto, H.; Yasui, M.; Iwasaki, F.; Iwamura, H.; Takeda, N.; Ishikawa, M. *Chem. Lett.*, **1995**, in press; Nogami, T.; Ishida, T.; Yasui, M.; Iwasaki, F.; Iwamura, H.; Takeda, N.; Ishikawa, M. *Mol. Cryst. Liq. Cryst.*, in press.
24. Sümmermann, W.; Deffner, U. *Tetrahedron* **1975**, *31*, 593-596.
25. Wudl, F.; Suzuki, T.; Prato, M. *Synth. Met.*, **1993**, *59*, 297-305.
26. Hiraoka, K.; Kudaka, I.; Fujimaki, S. *Rapid Commun. Mass Spectrom.* **1992**, *6*, 254-256.

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