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Self-Sensitized Photooxygenation of a C_{60}–Cycloheptatriene Dyad to Form Norcaradiene-Derived Endoperoxides

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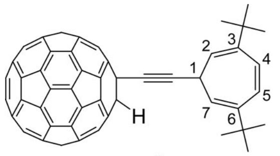
The [60]fullerene–cycloheptatriene dyad **1** readily underwent [4+2] cycloaddition of molecular oxygen at the cycloheptatriene moiety to give endoperoxides **5**-*exo* and **5**-*endo*. The involvement of singlet oxygen was verified by the complete inhibition of oxygenation on addition of 1,4-diazabicyclo[2.2.2]octane (DABCO), which is an efficient singlet-oxygen quencher. The observed facile oxygenation was attributed to both the strong photosensitizing ability of the fullerene cage and to the valence isomerization of **1** to the norcaradiene form, which was facilitated by the bulky *tert*-butyl groups. Competitive oxygenation of **1** and a related cycloheptatriene lacking the fullerenyl group (**2**) resulted in the formation of endoperoxides of the two molecules in comparable yields. This result demonstrates that the cycloaddition is not an in-cage reaction but occurs after the singlet oxygen has diffused from the solvent cage.

Introduction

It is well established that fullerenes C_{60}, C_{70}, and their derivatives are photosensitizers that produce singlet oxygen, based on studies of their photophysical characteristics[1] and reactions.[2–7] The high quantum yield of singlet oxygen production and its chemoselectivity in reactions with organic molecules make the process synthetically useful. Intramolecularly sensitized oxygenation of C_{60} and C_{70} derivatives, which occurs spontaneously by irradiation in the presence of molecular oxygen, allows the modification of attached structures that accept oxygen. Reported examples of such syntheses include [2+2][3] and [4+2][4] cycloadditions to give cyclic peroxides (dioxetanes and endoperoxides, respectively), ene reactions to give hydroperoxides,[5] and *N*- and *S*-oxygenation of amines[6] and sulfides.[7] When a cyclic peroxide is the product, it often undergoes additional transformations by cleavage of the O–O bond. However, the initially formed peroxide can be isolated if its stability is adequate, for example, self-sensitized photooxygenation of a C_{60} derivative bearing a 9-anthryl group allowed the isolation of a stable 9,10-endoperoxide.[4a]

In this study we investigated the self-sensitized photooxygenation of a C_{60}–cycloheptatriene dyad **1** (Scheme 1), which afforded a mixture of stable *endo*- and *exo*-endoperoxides derived from the corresponding norcaradiene isomers.



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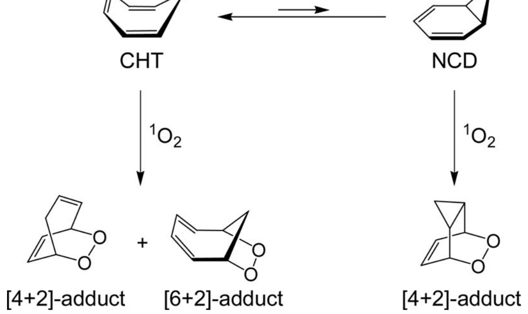
Scheme 1. C_{60}–cycloheptatriene dyad **1**.

Adam and Balci[8] previously reported that unsubstituted cycloheptatriene (CHT), which is in equilibrium with the energetically higher norcaradiene (NCD) tautomer,[9] is oxygenated to form a mixture of endoperoxides from both tautomers (Scheme 2).[10]



Scheme 2. Photooxygenation of the cycloheptatriene–norcaradiene equilibrium mixture.

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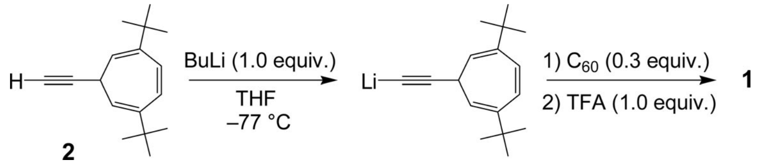
Although the CHT–NCD equilibrium mixture contains multiple reaction sites, its regioselectivity can be controlled with appropriate substituent(s). For instance, cycloheptatrienes with a π-electron-withdrawing substituent (CN, CHO or $COCH_3$) on the methylene carbon are oxygenated with singlet oxygen via the NCD form.[11] We previously reported that introduction of bulky alkyl substituents shifts the equilibrium towards the NCD form.[12,13] Based on this result, we hypothesized that dyad **1** would selectively give endoperoxides from the NCD isomer.

Results and Discussion

Synthesis of the [60]Fullerene–Cycloheptatriene Dyad

Dyad **1** was synthesized by nucleophilic addition of a cycloheptatrienylethynyllithium, prepared by lithiation of **2**, to C_{60} and subsequent quenching with an equimolar amount of trifluoroacetic acid (TFA; Scheme 3). The ^1H NMR spectrum of the product showed the disappearance of the ethynyl proton and the appearance of a proton attached to the C_{60} cage. All the protons, except the *tert*-butyl protons, were excessively broadened at room temperature (Figure 1, top spectrum) due to rapid valence tautomerism with the NCD isomer (see the next section). The ^{13}C NMR spectrum showed 30 sharp signals in the region between δ = 134.7 and 151.9 ppm, which were attributed to the sp^2 carbon atoms of the C_{60} core, indicating that the product was a 1,2 adduct of C_{60} with C_s symmetry. The sp^3 carbon atoms of the C_{60} core were observed at δ = 54.6 and 62.2 ppm. The cycloheptatrienyl ring exhibited four signals at 29.9 (C-1), 86.2 (C-2,7), 125.9 (C-4,5), and 143.8 (C-3,6) ppm, the last three signals also being extremely broadened. The ethynylene linker and the *tert*-butyl groups appeared at 83.4, 75.9, 34.4, and 29.4 ppm. The UV/Vis spectrum showed a narrow absorption band at 431 nm, which is characteristic of 1,2-adducts of C_{60}.[14] Each of these results is consistent with structure **1** in an equilibrium mixture with the NCD isomer.

When the acidic work-up was performed with excess TFA, the desired product **1** underwent an additional reaction to form allene **3** (Scheme 4). The structure of this product was determined on the basis of the two NMR doublet signals of the 1,3-disubstituted allene at δ = 7.29 and 7.60 ppm ($^4J_{H,H}$ = 6.0 Hz) and the aromatic proton signals corresponding to a 1,2,4-trisubstituted benzene. This result is consistent with our previous finding[15] that 7-ethynylcy-



Scheme 3. Synthesis of dyad **1**.

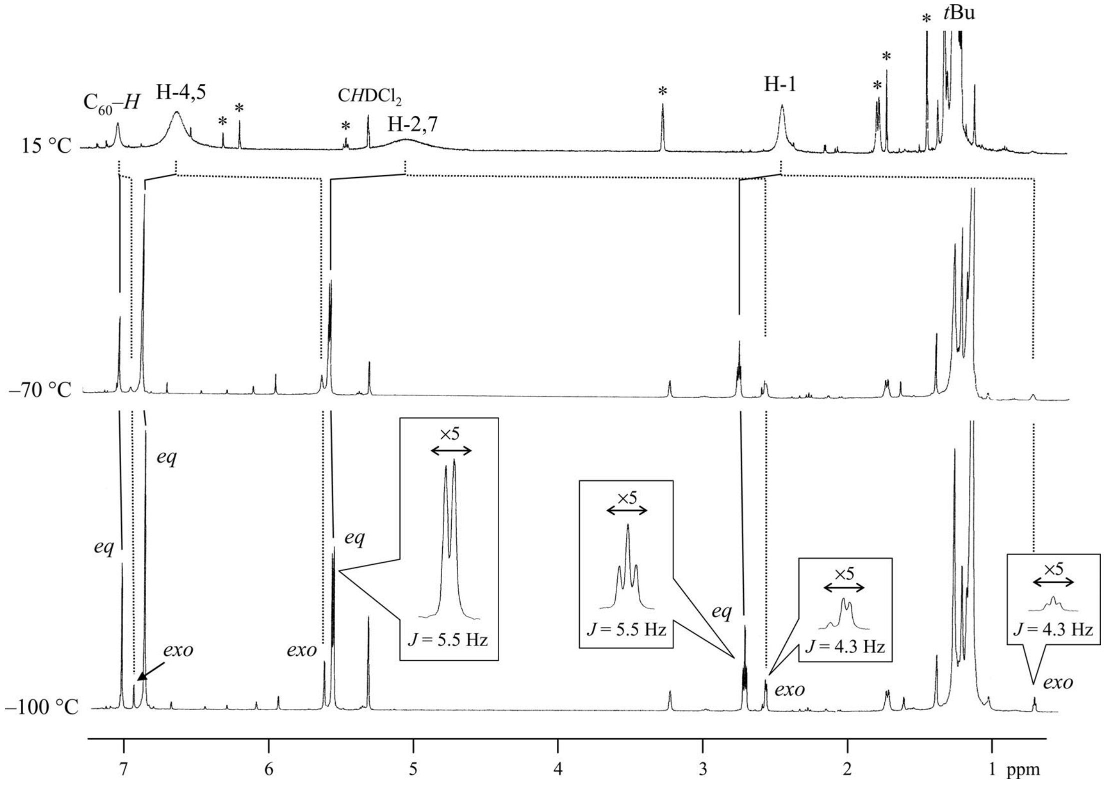
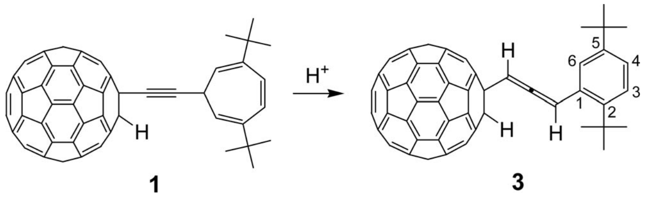


Figure 1. Variable-temperature ^1H NMR spectra (500 MHz) of **1** in CS_2/CD_2Cl_2 (4:1, v/v). The numbering of the carbon atoms is indicated in Scheme 1. * Impurity peaks.

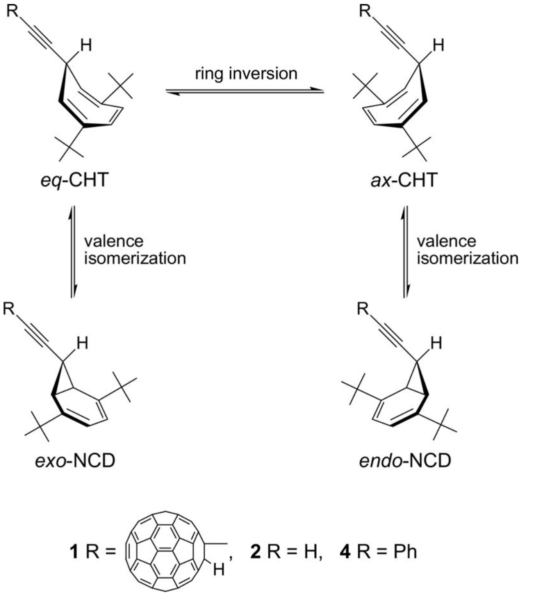
cloheptatrienes are isomerized to phenylallenes by an initial protonation of the ethynyl carbon under acidic conditions. Allene **3** was also formed by treatment of isolated **1** with TFA. Therefore the amount of acid used to quench the reaction must not exceed the amount of butyllithium for this synthesis.



Scheme 4. Acid-catalyzed isomerization of **1**.

CHT–NCD Isomerism

Dyad **1** demonstrated dynamic behavior in variable-temperature ^{1}H NMR measurements (Figure 1) that is typical of rapid CHT–NCD exchange.[9] Although **1** can exist as four structures, **1**-*eq*-CHT, **1**-*ax*-CHT, **1**-*exo*-NCD, and **1**-*endo*-NCD, which are interchangeable by valence isomerism and ring inversion (Scheme 5), the broad signals that were observed in the ^{1}H NMR spectrum at 15 °C split into only two signals at low temperatures. These signals were assigned to **1**-*eq*-CHT and **1**-*exo*-NCD in a molar ratio of 85.6:14.4 at –100 °C, whereas the concentrations of the *ax*-CHT and *endo*-NCD isomers were too low (<1%) to be detected. Based on the ^{1}H NMR spectroscopic data obtained at 15 and –100 °C, the values of $\Delta H°$ and $\Delta S°$ for the transformation of **1**-*eq*-CHT into **1**-*exo*-NCD were determined to be 0.10 ± 0.16 kcal mol^{-1} and -3.0 ± 1.0 cal mol^{-1} K^{-1}, respectively.[16]



Scheme 5. Valence isomerism and ring inversion of ethynylcycloheptatriene derivatives.

The DFT-calculated relative energies of the four possible isomers of **1** are listed in Table 1 along with those of the ethynyl (**2**) and phenylethynyl (**4**) derivatives. The lowest energy isomer of **1** was *eq*-CHT, which has a greater stability than **1**-*exo*-NCD by 1.35 kcal mol^{-1}. The relative energies of the other two isomers, **1**-*ax*-CHT and **1**-*endo*-NCD, were >3 kcal mol^{-1} higher than that of **1**-*eq*-CHT, which is consistent with the experimentally observed isomer distribution.

Table 1. Experimentally observed isomer populations, free energies, and DFT-calculated energies of 7-(R-ethynyl)-2,5-di-*tert*-butylcyclohepta-1,3,5-trienes.

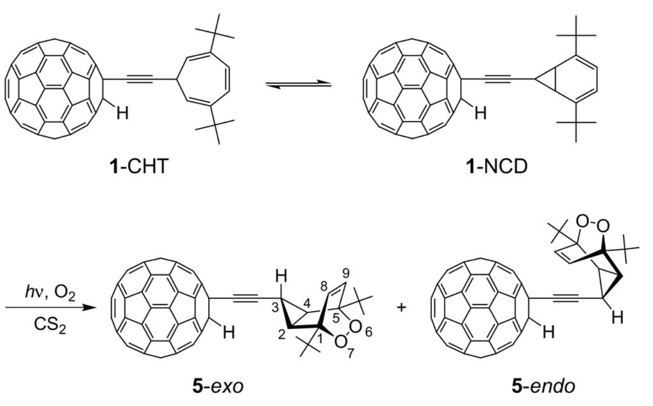
	Tautomer population[a] [%]	$\Delta G°_{25}$[b,c] [kcal mol^{-1}]	Energy by DFT calculations[b,d] [kcal mol^{-1}]
1 (R = HC_{60})			
eq-CHT	85.6[e]	0.00[e]	0.00
exo-NCD	14.4[e]	0.61[e]	1.35
endo-NCD	<1[e]	>1[e]	3.10
ax-CHT	<1[e]	>1[e]	3.09
2 (R = H)			
eq-CHT	79.5[f]	0.00[f]	0.00[g]
exo-NCD	16.9[f]	0.47[f]	1.17[g]
endo-NCD	3.6[f]	0.94[f]	3.44[g]
ax-CHT	<1[f]	>1[f]	3.47[g]
4 (R = Ph)			
eq-CHT	70.6[f]	0.00[f]	
exo-NCD	26.4[f]	0.30[f]	
endo-NCD	3.0[f]	0.96[f]	
ax-CHT	<1[f]	>1[f]	

[a] Obtained from variable-temperature NMR measurements. [b] Value determined relative to that of the *eq*-CHT isomer. [c] Experimental Gibbs free energy. [d] Electronic energy obtained at the B3LYP/6-311+G(2d,p)//B3LYP/6-31G(d) level of theory. [e] In CS_2/CD_2Cl_2 (4:1, v/v) at –100 °C. [f] In CS_2/CD_2Cl_2 (3:1, v/v) at –120 °C; ref.[13a] [g] Ref.[15a]

The proportion of the NCD form at equilibrium is negligible for unsubstituted cycloheptatriene.[9] The increased proportion (15–26%) of the *exo*-NCD form for **1**, **2**, and **4** is attributable to the presence of *tert*-butyl groups on C-3 and C-6. It is known that introduction of π-accepting substituent(s) on C-1 also lowers the energy of the NCD form.[9,13b,17] Although the π system of the C_{60} sphere is appreciably electronegative,[18] no increase in the NCD population was observed for fullerene derivative **1** relative to **2**. This result is mostly ascribed to the presence of an sp^3 carbon atom between the ethynyl group and the fullerene π-system, which inhibits the electron-withdrawing effect of the C_{60} π-system.

Self-Sensitized Photooxygenation

Although **1** is stable in the dark, it was rapidly oxidized under exposure to light and air (Scheme 6). When a CS_2 solution of **1** (1.2×10^{-3} M) was irradiated for 30 min with a 500 W xenon lamp under oxygen, **1** was quantitatively converted into endoperoxide **5**. The MALDI-TOF mass spectrum of the product exhibited a molecular ion peak ($[M]^+$) at m/z = 980, which indicates the addition of two oxygen atoms to **1**. The ^{1}H and ^{13}C NMR spectra showed two sets of oxygenated norcaradiene signals due to the formation of *exo* and *endo* isomers. The ^{1}H NMR signals were assigned on the basis of the coupling constants between 2,4-H and 3-H [3.5 Hz (*exo*) and 7.4 Hz (*endo*)]. The *exo*/*endo* molar ratio was determined to be 60:40 based on signal integration. Attempts to separate the isomers by chromatography were not successful. The ^{13}C NMR spectrum of the mixture showed 30 large peaks between δ = 134 and 151 ppm that were attributed to the fullerene cage of **5**-*exo* and additional 29 peaks with lower intensities due to **5**-*endo*, which indicates that both isomers have C_s symmetry. The signals of the sp^3 carbon atoms of the fullerene cage appeared at δ = 54.3 and 61.9 ppm for **5**-*exo* and at δ = 54.7 and 61.2 ppm for **5**-*endo*. The carbon atoms of the dioxatricyclic moiety were observed at δ = 9.26 (**5**-*exo* C-3), 17.2 (**5**-*exo* C-2,4), 128.5 (**5**-*exo* C-8,9), 8.41 (**5**-*endo* C-3), 17.6 (**5**-*endo* C-2,4), and 131.1 ppm (**5**-*endo* C-8,9), and the ethynyl carbon atoms were detected at δ = 80.0 and 82.4 ppm (**5**-*exo*) and δ = 82.6 and 87.2 ppm (**5**-*endo*). The UV/Vis spectrum showed a narrow absorption band at 431 nm, which further confirmed the pattern of addition on the C_{60} sphere. This result is explained by the [4+2]-type addition of singlet oxygen $^1O_2$ to the NCD moiety.[19] Carbon disulfide is the solvent of choice because singlet oxygen has a prolonged lifetime (200–250 μs) in this solvent.[20]



Scheme 6. Photooxygenation of **1**.

Unlike the reported photooxygenation of the parent cycloheptatriene (Scheme 2),[8] no CHT-derived [4+2] and [6+2] cycloadducts were observed in the reaction of **1**. Adam and co-workers[11a] reported that 7-cyanocycloheptatriene, which contains an undetectable amount of the NCD isomer at equilibrium,[9] gave an endoperoxide only from the NCD tautomer. The exclusive formation of the NCD adduct **5** observed in this study is consistent with the greater proportion of the NCD tautomer of **1**.

The photooxygenation of **1** was effectively suppressed by the addition of 1,4-diazabicyclo[2.2.2]octane (DABCO). DABCO is a well-known singlet-oxygen quencher, which is frequently used to test the involvement of singlet oxygen in reaction sequences.[21] The most likely kinetic pathway for the self-sensitization reaction of **1** is shown in Scheme 7.

$$^1C_{60}\text{–CHT}\ (\mathbf{1}) \xrightarrow{h\nu} {}^1C_{60}^{*}\text{–CHT} \xrightarrow{\text{ISC}} {}^3C_{60}^{*}\text{–CHT}$$

$$^3C_{60}^{*}\text{–CHT} + {}^3O_2 \longrightarrow {}^1C_{60}\text{–CHT} + {}^1O_2$$

$$^1O_2 + \mathbf{1} \xrightarrow{k_a} \mathbf{5}$$

$$^1O_2 \xrightarrow[\text{quenching by solvent}]{k_d} {}^3O_2$$

$$^1O_2 \xrightarrow[\text{DABCO}]{k_q} {}^3O_2$$

Scheme 7. Elementary processes in the photooxygenation of **1**.

The steady-state treatment of the above process with respect to $^1O_2$ leads to a Stern–Volmer relationship [Equation (1)] that predicts a linear relationship between the overall rate of formation of **5** (k_{obs}) and the quencher concentration.[22] For rate measurement, **1** was photolyzed in benzene under exposure to air by using a 20 W tungsten lamp located 50 cm away. The yields of **5**-*exo* and **5**-*endo* were determined during the initial stage of the reaction. The total yield of the two isomers decreased as the concentration of DABCO added increased, giving the expected linear plot shown in Figure 2. Addition of 100 equiv. of DABCO resulted in the complete inhibition of the reaction even with irradiation using a 100 W tungsten lamp for 3 h.

$$\frac{k_{obs,0}}{k_{obs,[DABCO]}} = 1 + \frac{k_q}{k_d + k_a[\mathbf{1}]}[\text{DABCO}] \qquad (1)$$

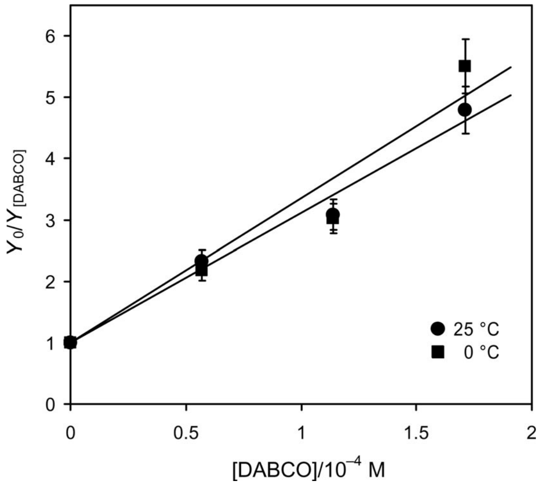
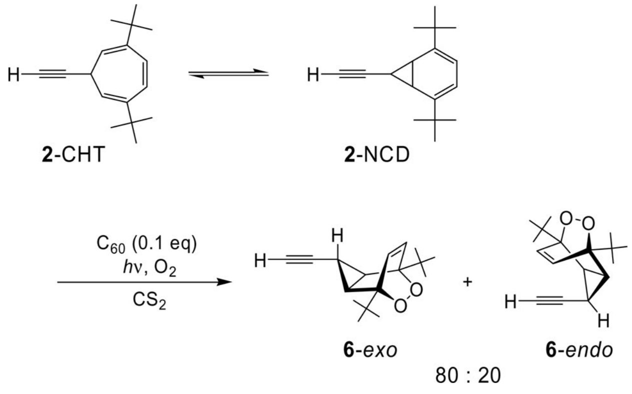


Figure 2. Stern–Volmer plot for DABCO quenching of the photooxygenation of **1**. Y_0 is the yield of **5** without quencher; $Y_{[DABCO]}$ is the yield of **5** with DABCO. Photolysis was carried out in CS_2 by irradiating the solution for 9 min with a 20 W tungsten lamp from a distance of 50 cm. Values of Y_0 were 22.5 and 24.2% at 25 and 0 °C, respectively.

Cycloheptatriene **2**, which lacks the C_{60} moiety, is stable in air and light. However, **2** was also converted into the endoperoxides **6**-*exo* and **6**-*endo* (80:20) when irradiated in the presence of 0.1 equiv. of pristine C_{60} (Scheme 8).[23] This demonstrates that C_{60}-sensitized oxygenation also occurs intermolecularly with an effectiveness similar to that of self-sensitized oxygenation, even at low C_{60} concentrations (ca. 10^{-4} M).



Scheme 8. C_{60}-sensitized photooxygenation of **2**.

Thus, it was of interest to determine whether sensitized oxygenation is enhanced by the connection of CHT and C_{60} through an ethynylene linker, as in **1**. This might allow an in-cage process in which the generated singlet oxygen could immediately attack the NCD moiety before escaping the cage. To examine this possibility, a competitive oxygenation reaction was carried out by irradiating a CS_2 solution containing equal concentrations of **1** and **2** (5.7×10^{-4} M) in the presence of air.[24] The yields of the oxygenated products **5** and **6** measured midway through the reaction were comparable (48 and 56%, respectively).[25] No preferred oxygenation of **1** was observed, which clearly indicates that the addition of singlet oxygen is not an in-cage reaction but occurs after its diffusion into the bulk solution. Consequently, in the present system, the close proximity of C_{60} is not responsible for the observed efficient oxygenation.

Conclusions

We have synthesized a new fullerene derivative **1** by nucleophilic addition of an organolithium to C_{60}. The connection of an oxygen-accepting cycloheptatrienyl group to the fullerene skeleton, which is an efficient photosensitizer, permitted self-sensitized photooxygenation leading to the stable endoperoxide **5** by irradiation in the presence of air. The photosensitivity of **1** was so high that even exposure to low light from a distant, low-power bulb was sufficient for complete oxygenation. The reaction was highly chemoselective such that the endoperoxide formed only from the norcaradiene tautomer, which was favored by the bulky *tert*-butyl groups. Competitive oxygenation of **1** and **2** demonstrated that the singlet oxygen, which was generated by photosensitization by the fullerene moiety of **1**, diffused into the bulk solution prior to cycloaddition.

Experimental Section

General: ^{1}H and ^{13}C NMR spectra were obtained by using JEOL JNM-Lambda500 (^{1}H, 500 MHz; ^{13}C, 125 MHz) and JNM-AL300 (^{1}H, 300 MHz; ^{13}C, 75 MHz) spectrometers. Peak assignments were based on DEPT, COSY, and/or H–C COSY measurements. UV/Vis spectra were recorded by using a JASCO V-670 spectrophotometer. High-resolution mass spectrometry was performed by using Applied Biosystems Voyager-DE PRO (MALDI-TOF) and JEOL JMS-600H (EI) spectrometers. Gel permeation chromatography (GPC) was carried out by using a Shodex H-2001 column. HPLC was performed by using Nacalai tesque Buckyprep and 5PBB columns with toluene and chloroform, respectively, as the eluents. 1,4-Di-*tert*-butyltropylium perchlorate was synthesized as previously reported.[26] THF was freshly distilled from sodium benzophenone ketyl prior to use. Compound **2** was synthesized according to the method described in our earlier reports[13a,15a] or by following the modified procedure described below.

2,5-Di-*tert*-butyl-7-(trimethylsilylethynyl)cyclohepta-1,3,5-triene: Butyllithium (2.6 M in hexane, 2.13 mL, 5.54 mmol) was added dropwise to a THF solution (50 mL) of trimethylsilylacetylene (1.01 mL, 7.15 mmol) at –66 °C over 5 min. 1,4-Di-*tert*-butyltropylium perchlorate (1.40 g, 4.63 mmol) was added and the mixture was stirred at room temperature for 30 min. Aqueous work-up afforded a pale-yellow oil (1.30 g), which was purified by flash column chromatography (SiO_2, hexane) to afford 2,5-di-*tert*-butyl-7-(trimethylsilylethynyl)cyclohepta-1,3,5-triene (223 mg, 16%) as colorless crystals; m.p. 91.6–92.7 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.16 [s, 9 H, $Si(CH_3)_3$], 1.10 (s, 18 H, *t*Bu), 1.89 (br. t, J = 5.5 Hz, 1 H, 7-H), 4.25 (br. s, 2 H, 1,6-H), 6.36 (br. s, 2 H, 3,4-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 0.28 [$Si(CH_3)_3$], 29.40 [$C(CH_3)_3$], 30.86 (C-7), 34.74 [$C(CH_3)_3$], 65.82 (C≡C), 84.08 (C≡C), 109.03 (br., C-1,6), 124.92 (br., C-3,4), 143.92 (br., C-2,5) ppm. IR (KBr): $\tilde{\nu}$ = 2176 (C≡C) cm^{-1}. HRMS (EI, 70 eV): calcd. for $C_{20}H_{32}Si$ $[M]^+$ 300.2273; found 300.2280. Further elution gave the 1,5-di-*tert*-butyl isomer (525 mg, 38%) as a pale-yellow oil and the 1,4-di-*tert*-butyl isomer (309 mg, 22%) as colorless crystals.

2,5-Di-*tert*-butyl-7-ethynylcyclohepta-1,3,5-triene (2): A 0.88 M solution of KOH in ethanol (18 mL, 16 mmol) was added to a solution of 2,5-di-*tert*-butyl-7-(trimethylsilylethynyl)cyclohepta-1,3,5-triene (162 mg, 0.538 mmol) in ethanol (50 mL). The mixture was heated at reflux for 10 min and stirred for an additional 30 min at room temperature. After aqueous work-up, the solvent was evaporated to give a pale-yellow oil (116 mg). Purification by GPC ($CHCl_3$) afforded **2** (81.6 mg, 66%), which showed a ^{1}H NMR spectrum identical to that reported in ref.[15a,27].

1-[(3,6-Di-*tert*-butylcyclohepta-2,4,6-trien-1-yl)ethynyl]-1,2-dihydro[60]fullerene (1): The reaction and purification were carried out in the dark. Butyllithium (2.64 M in hexane, 0.097 mL, 0.26 mmol) was added dropwise to a solution of **2** (58.4 mg, 0.256 mmol) in THF (1 mL) at –77 °C over 5 min and the mixture was stirred for 25 min at room temperature. The solution was added dropwise to a suspension of C_{60} (62 mg, 0.085 mmol) in THF (60 mL) over 10 min, during which the solution turned dark bluish-brown due to the formation of the conjugate base of **1**, R–C≡C–C_{60}^-. After stirring the mixture for 50 min, a 0.05 M solution of TFA (5.1 mL) was added. The solvent was removed under vacuum and the residue was extracted with CS_2. The solvent was evaporated and the remaining solid was purified by GPC (toluene) to afford a dark-brown solid of **1** (33.5 mg, 41% based on C_{60}) as a rapidly exchanging mixture of *eq*-CHT and *endo*-NCD isomers (84.2:15.8 at 15 °C, 85.6:14.4 at –100 °C). The ^{1}H and ^{13}C NMR spectra showed time-averaged signals at room temperature. ^{1}H NMR (500 MHz, CS_2/

CD_2Cl_2, 4:1, v/v, 15 °C): δ = 1.25 (s, 18 H, *t*Bu), 2.45 (br. s, 1 H, 1-H), 5.05 (br. s, 2 H, 2,7-H), 6.63 (br. s, 2 H, 4,5-H), 7.04 (s, 1 H, C_{60}-H) ppm. ^{13}C NMR (125 MHz, CS_2/CD_2Cl_2, 4:1, v/v, 24 °C): δ = 29.38 (CH_3), 29.87 (C-1), 34.41 [$C(CH_3)_3$], 54.55, 62.17 (sp^3, fullerene), 75.91, 83.38 (-C≡C-), 86.19 (br., C-2,7), 125.85 (br., C-4,5), 143.75 (br., C-3,6), 134.69, 135.94, 140.09, 140.15, 141.40, 141.48, 141.75, 141.80, 141.84, 141.93, 142.36, 142.38, 143.00, 144.34, 144.48, 145.13, 145.18, 145.27, 145.39, 145.47, 145.60, 145.98, 145.99, 146.15, 146.16, 146.50, 147.10, 147.37, 151.53, 151.90 (sp^2, fullerene) ppm. IR (neat): $\tilde{\nu}$ = 2233 (C≡C) cm^{-1}. UV/Vis: λ_{max} (ε [M^{-1}cm^{-1}]) = 211 (127000), 255 (102000), 306 (32600), 325 (32000), 431 (3670), 701 (734) nm. HRMS (MALDI-TOF): calcd. for $C_{77}H_{23}$ [M – H]$^+$ 947.1794; found 947.1784.

At –100 °C, the exchange was frozen. **1**-*eq*-CHT: ^{1}H NMR: δ = 1.14 (s, 18 H, *t*Bu), 2.70 (t, *J* = 5.5 Hz, 1 H, 1-H), 5.55 (d, *J* = 5.5 Hz, 2 H, 2,7-H), 6.86 (s, 2 H, 4,5-H), 7.02 (s, 1 H, C_{60}-H) ppm. **1**-*exo*-NCD: ^{1}H NMR: δ = 0.70 (t, *J* = 4.3 Hz, 1 H, 1-H), 1.26 (s, 18 H, *t*Bu), 2.55 (d, *J* = 4.3 Hz, 2 H, 2,7-H), 5.61 (s, 2 H, 4,5-H), 6.93 (s, 1 H, C_{60}-H) ppm.

Acid-Catalyzed Isomerization of 1 to 3: TFA (5 µL, 0.067 mmol) was added to a solution of **1** (15.9 mg, 0.0168 mmol) in $CDCl_3$ (0.6 mL) in an NMR tube. After 30 min, the solvent was evaporated and the residue was purified by flash column chromatography (SiO_2, CS_2) to afford 5.3 mg (33%) of 1-[3-(2,5-di-*tert*-butylphenyl)propa-1,2-dien-1-yl]-1,2-dihydro[60]fullerene (**3**) as a dark-brown solid. ^{1}H NMR (300 MHz, $CS_2/CDCl_3$, 4:1, v/v): δ = 1.29 (s, 9 H, *t*Bu), 1.54 (s, 9 H, *t*Bu), 6.89 (s, 1 H, C_{60}-H), 7.18 (dd, *J* = 8.3, 2.3 Hz, 1 H, 4-H), 7.29 (d, *J* = 5.9 Hz, 1 H, C_{60}-C=C=C-H), 7.31 (d, *J* = 8.1 Hz, 1 H, 3-H), 7.60 (d, *J* = 6.1 Hz, 1 H, C_{60}-C-H), 7.81 (d, *J* = 2.4 Hz, 1 H, 6-H) ppm. ^{13}C NMR (125 MHz, $CS_2/CDCl_3$, 4:1, v/v): δ = 31.08 (CH_3), 31.44 (CH_3), 33.66 [$C(CH_3)_3$], 34.63 [$C(CH_3)_3$], 59.09, 63.75 (sp^3, fullerene), 102.27, 103.70 (-CH=), 124.87, 126.08, 127.27, 130.28, 133.71, 135.00, 135.18, 135.88, 135.92, 140.027, 140.032, 140.16, 140.18, 141.35, 141.36, 141.39, 141.41, 141.61, 141.70, 141.71, 141.75, 141.76, 141.77, 141.78, 141.93, 141.94, 142.28, 142.29, 142.31, 142.96, 143.80, 144.277, 144.283, 144.41, 144.42, 145.08, 145.10, 145.11, 145.21, 145.23, 145.28, 145.30, 145.50, 145.51, 145.63, 145.900, 145.908, 145.917, 145.923, 146.07, 146.08, 146.11, 146.61, 146.62, 147.01, 147.21, 148.34, 152.73, 152.77, 153.95, 154.10 (sp^2 carbons), 204.40 (=C=) ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 1942 (C=C=C) cm^{-1}. UV/Vis: λ_{max} (ε [M^{-1}cm^{-1}]) = 211 (117000), 256 (88300), 309 (32700), 432 (3100), 704 (535) nm. HRMS (MALDI-TOF): calcd. for $C_{77}H_{24}$ [M]$^+$ 948.1873; found 948.1879.

Photooxygenation of 1 to Form the Endoperoxide 5: A solution of **1** (17.6 mg, 0.0185 mmol) in CS_2 (15 mL) in a Pyrex vessel was irradiated with a 500 W xenon lamp under bubbling oxygen for 30 min. The solvent was evaporated to give a dark-brown solid (14.3 mg), which was shown to be an essentially pure mixture of **5**-*exo* and **5**-*endo* (60:40) by NMR spectroscopy. Although this solid was further purified by flash column chromatography (SiO_2, Et_2O/CS_2, 1:1) to give dark-brown crystals (8.8 mg, 50%), the isomers could not be separated even by recycle chromatography by using a Buckyprep (Nacalai tesque) or GPC H-2001 (Shodex) column. ^{1}H NMR (300 MHz, $CS_2/CDCl_3$, 4:1, v/v): **5**-*exo*: δ = 1.08 (t, *J* = 3.5 Hz, 1 H, 3-H), 1.18 (s, 18 H, *t*Bu), 2.11 (d, *J* = 3.5 Hz, 2 H, 2,4-H), 6.26 (s, 2 H, 8,9-H), 6.89 (s, 1 H, C_{60}-H) ppm; **5**-*endo*: δ = 1.20 (s, 18 H, *t*Bu), 1.77 (t, *J* = 7.4 Hz, 1 H, 3-H), 2.04 (d, *J* = 7.4 Hz, 2 H, 2,4-H), 6.49 (s, 2 H, 8,9-H), 6.81 (s, 1 H, C_{60}-H) ppm. ^{13}C NMR (125 MHz, $CS_2/CDCl_3$, 4:1, v/v): δ = 8.41 (**5**-*endo*, C-3), 9.26 (**5**-*exo*, C-3), 17.19 (**5**-*exo*, C-2,4), 17.63 (**5**-*endo*, C-2,4), 24.87 (**5**-*exo*, CH_3), 24.94 (**5**-*endo*, CH_3), 34.23 [**5**-*exo*, $C(CH_3)_3$], 34.29 [**5**-*endo*, $C(CH_3)_3$], 54.33, 61.87 (**5**-*exo*, sp^3, fullerene), 54.69, 61.20 (**5**-*endo*, sp^3, fullerene), 80.02, 82.39, 82.55, 82.65, 83.37, 87.23 (**5**-*exo*/**5**-*endo*, C-1,5 and -C≡C-), 128.47 (**5**-*exo*, C-8,9), 131.06 (**5**-*endo*, C-8,9), 134.71, 135.83, 140.04, 140.06, 141.35, 141.41, 141.57, 141.72, 141.77, 141.80, 142.31, 142.34, 142.95, 144.23, 144.41, 145.07, 145.13, 145.21, 145.28, 145.36, 145.48, 145.92, 145.94, 146.10, 146.11, 146.31, 147.03, 147.31, 151.19, 151.22 (**5**-*exo*, sp^2, fullerene), 134.33, 135.70, 140.09, 140.26, 141.35, 141.43, 141.679, 141.684, 141.78, 141.84, 142.34, 142.36, 142.98, 144.26, 144.43, 144.91, 145.10, 145.15, 145.25, 145.27, 145.45, 145.96 (2 C), 146.10, 146.12, 146.33, 147.08, 147.34, 151.06, 151.36 (**5**-*endo*, sp^2, fullerene) ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 2233 (C≡C) cm^{-1}. UV/Vis: λ_{max} (ε [M^{-1}cm^{-1}]) = 212 (119000), 255 (105000), 307 (34800), 324 (34600), 431 (4000), 701 (558) nm. HRMS (MALDI-TOF): calcd. for $C_{77}H_{24}O_2$ [M]$^+$ 980.1771; found 980.1731.

Photooxygenation of 2 to Form the Endoperoxide 6: A solution of **2** (27.9 mg, 0.122 mmol) and C_{60} (8.8 mg, 0.0122 mmol) in CS_2 (90 mL) in a Pyrex vessel was irradiated with a 500 W xenon lamp under bubbling oxygen for 30 min. The solvent was evaporated and the residue was extracted with diethyl ether. Removal of the ether gave a mixture of **6**-*exo* and **6**-*endo* (80:20) as colorless crystals (25.2 mg). Flash column chromatography (SiO_2, hexane) gave a fraction consisting of pure **6**-*exo* (7.9 mg) followed by mixtures of **6**-*exo* and **6**-*endo* [10.8 mg (91:9) and 4.9 mg (46:54)]. Total yield: 23.6 mg (74%). **6**-*exo*: Colorless crystals; m.p. 104.9–105.9 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.72 (m, 1 H, 3-H), 1.09 (s, 18 H, *t*Bu), 1.80 (d, *J* = 2.0 Hz, 1 H, -C≡CH), 1.876 (d, *J* = 3.3 Hz, 2 H, 2,4-H), 6.20 (s, 2 H, 8,9-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 8.76 (C-3), 16.89 (C-2,4), 24.99 (CH_3), 34.72 [$C(CH_3)_3$], 65.07 (-C≡C-), 83.09 (-C≡C-), 128.76 (C-8,9) ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3307 (H–C≡C), 2122 (C≡C) cm^{-1}. HRMS (EI, 20 eV): calcd. for $C_{17}H_{24}$ [M – O_2]$^+$ 228.1878; found 228.1879. **6**-*endo*: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.12 (s, 18 H, *t*Bu), 1.43 (td, *J* = 7.5, 2.6 Hz, 1 H, 3-H), 1.879 (d, *J* = 7.3 Hz, 2 H, 2,4-H), 2.01 (d, *J* = 2.6 Hz, 1 H, -C≡CH), 6.32 (s, 2 H, 8,9-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 7.85 (C-3), 16.97 (C-2,4), 25.03 (CH_3), 34.80 [$C(CH_3)_3$], 73.05 (-C≡C-), 83.23 (-C≡C-), 131.35 (C-8,9) ppm.

Photooxygenation of 1 in the Presence of DABCO: Compound **1** was dissolved in CS_2 (5.7×10^{-4} M) containing a known concentration of DABCO in a Pyrex tube. The solution was irradiated with a 20 W tungsten lamp from a distance of 50 cm for 9 min at 25 or 0 °C under air. The solvent was removed under vacuum and the remaining mixture was analyzed by ^{1}H NMR to determine the yield of **5**. The results are given in Figure 2.

Competitive Photooxygenation of 1 and 2: A solution containing both **1** and **2** in CS_2 (5.7×10^{-4} M each) in a Pyrex tube was irradiated with a 20 W tungsten lamp from a distance of 50 cm for 1 h at 0 °C under air. The solvent was removed under vacuum and the remaining mixture was analyzed by ^{1}H NMR to determine the yield of **5** (48%) and **6** (56%).

Calculations: Density functional theory (DFT) calculations[28] were performed by using the Gaussian 03 program.[29] The molecular structures of the isomers of **1** were optimized at the B3LYP/6-31G(d) level of theory starting from the B3LYP/3-21G-optimized geometries, which were verified by frequency calculations to have no imaginary frequencies. The B3LYP/6-31G(d)-optimized structures were found to be similar to those obtained at the B3LYP/3-21G level of theory. The energies were computed by B3LYP/6-311+G(2d,p) single-point calculations using the B3LYP/6-31G(d) geometries and are summarized in Table S1 of the Supporting Information.

Supporting Information (see also the footnote on the first page of this article): NMR spectra of all new compounds and DFT-calculated energies and Cartesian coordinates of the optimized structures of the isomers of **1**.

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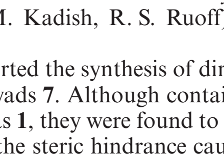

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[24] Because **1** and **2** contain similar proportions of the NCD isomer (Table 1), their rates of oxygenation are expected to reflect the relative probabilities of encountering singlet oxygen.

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