Photochemical Reaction of the Open-Cage Fullerene Derivative with Singlet Oxygen

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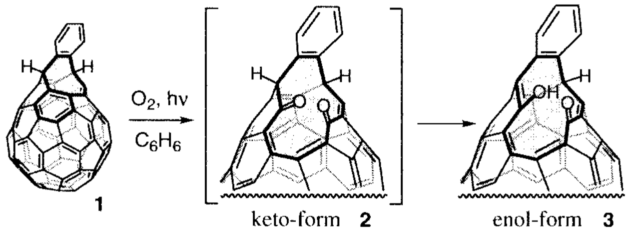
Photochemical reaction of open-cage fullerene **1** with singlet oxygen gave oxidation product **3**, which was shown to have an enol and a carbonyl groups on the 12-membered-ring orifice on the fullerene cage by spectroscopic method and density functional calculations.

Transformations of the fullerene cage are of great interest from the viewpoint of the chemical synthesis of endohedral metallofullerenes or heterofullerenes.[1] The reaction of fullerene derivatives with singlet oxygen is one of the most promising method for such purpose, although C_{60} itself simply affords epoxide, $C_{60}O$,[2] upon such oxidation. For example, Wudl and co-workers reported the reaction of azafulleroid with oxygen to give a ketolactam derivative[3] which is the precursor of the azafullerene dimer, $(C_{59}N)_2$.[4] Rubin and co-workers reported the reaction of bisazafulleroid with oxygen to yield a bisamide derivative of C_{60},[5] in which molecular hydrogen or helium atom can be incorporated.[6] In these reactions singlet oxygen generated by excited state of C_{60} is reported to play an important role and one of the double bond on the C_{60} cage is oxidatively cleaved. On the other hand, we recently reported the synthesis of an open-cage fullerene derivative having an eight-membered-ring orifice **1** by a thermal reaction of C_{60} with phthalazine in 1-chloronaphthalene.[7,8] In the present paper we report the structure and properties of the oxidation product obtained by the photochemical reaction of **1** with oxygen. A recent report by Murata and co-workers[9] prompted us to publish our own findings on the oxidation of an open-cage fullerene derivative.

The reaction of open-cage fullerene derivative **1**[7] with oxygen was conducted in a solution of air-saturated benzene under irradiation of room light at room temperature for 3 days (Scheme 1). The product, which was more polar than the starting material, was isolated in 32% yield as a brown powder[10] by column chromatography over silica gel. The molecular formula of this product was determined as $C_{68}H_6O_2$ by high-resolution mass spectroscopy, indicating that the product was formed by addition of O_2 to **1**. The structure of this product was shown to be not keto-form **2** but enol-form **3** as described below. The ^{1}H NMR exhibited four multiplets at δ 8.01, 7.94, 7.86, and 7.74 and two singlets at δ 6.98 and 6.79. The singlet at δ 6.98 disappeared upon addition of D_2O demonstrating that **3** has an acidic proton. The ^{13}C NMR spectrum displayed one signal corresponding to a carbonyl carbon at δ 193.67, one signal corresponding to an sp^3 carbon at 47.82 and 66 signals corresponding to sp^2 carbons at δ 148.67–120.20, indicating that **3** has the C_1 symmetry. The IR spectrum showed a strong band at 1706 cm^{-1} corresponding to a carbonyl group and a weak band at 3379 cm^{-1} corresponding to a hydroxy group. These spectra are in good agreement with the structure of **3**.

In order to determine the reaction site of the starting material **1**, the frontier orbitals of **1** calculated at B3LYP/6-31G(d) level[11] were studied. The HOMO is localized at the two double bonds of the eight-membered ring as shown in Figure 1(a) whereas the LUMO is delocalized over the C_{60} cage. Thus the oxidative cleavage is considered to take place on one of these bonds to afford, via a dioxetane intermediate, keto-form **2**, which would isomerize to enol-form **3** (Scheme 1).



Scheme 1.

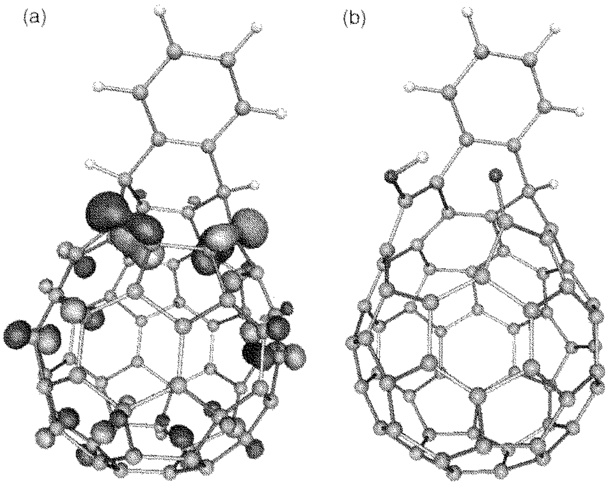


Figure 1. Optimized structures at B3LYP/6-31G(d) level of (a) **1** with HOMO and (b) **3**.

Theoretical calculations[11] also support the enolization to structure **3**. The relative energy of enol **3** was calculated to be lower than that of ketone **2** by 3.12 kcal mol^{-1} at the B3LYP/6-31G(d) level, although by calculations at AM1, PM3, and HF/6-31G(d) levels the energy of **2** was found to be lower than that of **3** by 1.44, 4.13, and 4.22 kcal mol^{-1}, respectively. Since in such a system the electron correlation plays a critical role, the results of DFT calculations are more reliable.[12] The optimized structure of **3** at the B3LYP/6-31G(d) level is shown in Figure 1(b). The enol group is supposed to be stabilized by intramolecular hydrogen bonding with the carbonyl group in close proximity. In order to further confirm the structure, the GIAO(SCF/6-31G(d)//B3LYP/6-31G(d)) calculations were conducted for both **2** and **3**.[13] The calculated chemical shifts of **3**, particularly those of a hydroxy proton at δ 7.04, a methine proton at δ 6.48, a carbonyl carbon at δ 198.26, enol carbons at δ 148.56 and 119.76, and an sp^3 carbon at δ 41.76, are in fairly good agreement with the experimental values while the calculated values for **2** are not.

Whereas the starting compound **1** is purple in $CHCl_3$ solution,[7] the color of the dilute solution of **3** in $CHCl_3$ is yellow and the UV–vis spectrum showed maximum absorptions at 257, 329, 453, 675, and 751 nm (Figure 2). This must be due to the perturbation of the π-conjugated system of the C_{60} part by cleavage of one double bond and replacement by a carbonyl and enol groups newly formed.

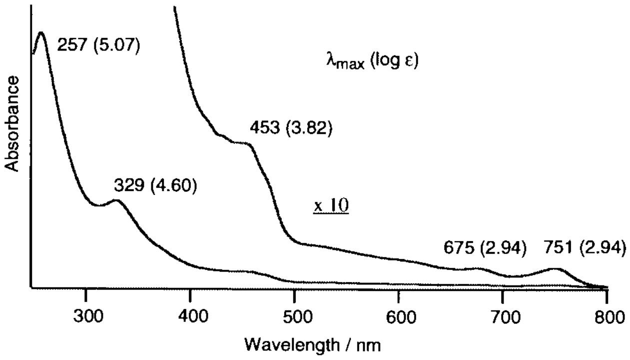


Figure 2. UV–vis spectra of **3** in $CHCl_3$.

The electrochemical behavior of **3** was investigated by cyclic voltammetry (CV).[14] Quasi-reversible five reduction waves were recorded at –1.07, –1.30, –1.41, –1.67, and –1.99 V vs ferrocene/ferrocenium couple upon CV of **3** whereas **1** showed only three reversible reduction waves at –1.29, –1.72, –2.20 V. C_{60} displayed three reversible reduction waves at –1.11, –1.51, and –1.97 V under the same conditions.[15] The multistep reduction of **3** is supposed to involve the reduction of enol and carbonyl groups along with reduction of the fullerene cage. Unfortunately the assignment of each of the reduction waves is not successful at the moment.

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10 Spectroscopic data of **3**: mp >300 °C; IR (KBr) ν 3379, 3070, 3043, 2949, 2918, 1706, 1563, 1541, 1510, 1481, 1457, 1440, 1423, 1351, 1284, 1264, 1252, 1232, 1205, 1186, 1158, 1141, 1104, 1088, 1062, 1007, 940, 931, 868, 849, 817, 787, 760, 745, 731, 657, 637, 621, 605, 580, 551, 522, 488 cm^{-1}; UV–vis ($CHCl_3$) λ_{max} (log ε) 257 nm (5.07), 329 (4.60), 453 (3.82), 675 (2.94), 751 (2.94); ^{1}H NMR (300 MHz, CS_2–$CDCl_3$ (1:1)) δ 8.01 (dd, *J* = 7.5 and 1.2 Hz, 1H), 7.94 (dt, *J* = 7.8 and 0.6 Hz, 1 H), 7.86 (td, *J* = 7.5 and 1.5 Hz, 1H), 7.74 (td, *J* = 7.5 and 1.2 Hz, 1H), 6.98 (s, 1H), 6.79 (s, 1H); ^{13}C NMR (100 MHz, CS_2–CD_2Cl_2 (3:1)) δ 193.67, 148.67, 148.31, 148.14, 148.01, 147.97, 147.79, 147.17, 147.04, 147.02, 146.90, 146.64, 146.42, 146.34, 146.22, 146.20, 146.01, 145.84, 145.58, 145.14, 145.03, 144.81, 144.77, 144.71, 144.66, 144.63, 144.35, 144.00, 143.62, 143.58, 143.17, 143.11, 142.93, 142.62, 142.47, 142.31, 141.85, 140.73, 140.53, 140.45, 140.06, 140.00, 139.80, 139.46, 139.35, 138.97, 138.44, 138.40, 137.33, 136.90, 135.76, 135.57, 135.34, 135.09, 134.85, 134.81, 134.45, 132.76, 131.76, 131.23, 130.59, 130.01, 129.75, 128.54, 128.31, 124.66, 120.20, 47.82; HR MS (+FAB) calcd for $C_{68}H_6O_2$ (M^+), 854.0368; found, 854.0330.
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13 The calculated NMR chemical shifts of **2** and **3** by GIAO (SCF/6-31G(d)//B3LYP/6-31G(d)) relative to calculated chemical shifts of tetramethylsilane at the same level are as follows. ^{1}H NMR of **2**: δ 8.76 (Ar), 8.18 (Ar), 8.10 (Ar), 8.06 (Ar), 6.45 (CH), 5.45 (CH). ^{13}C NMR of **2**: δ 199.98 (C=O), 196.47 (C=O), 189.68, 156.73, 153.38, 153.26, 152.76, 152.71, 152.50, 152.19, 152.18, 152.13, 151.93, 151.79, 151.66, 151.63, 151.55, 151.54, 151.20, 151.18, 150.81, 150.80, 150.71, 150.51, 150.47, 150.39, 150.34, 149.52, 149.07, 148.81, 148.60, 148.01, 147.63, 147.31, 147.10, 146.67, 146.10, 146.00, 145.87, 145.52, 145.50, 145.36, 144.14, 143.70, 143.46, 143.08, 142.34, 142.31, 141.89, 141.60, 141.07, 139.81, 139.09, 137.32, 137.05, 136.86, 136.61, 136.54, 135.77, 133.40 (CH), 133.10, 132.78, 132.76, 128.92 (CH), 128.77 (CH), 128.30 (CH), 46.58 (CH), 39.73 (CH). ^{1}H NMR of **3**: δ 8.45, 8.19, 8.16, 8.02, 7.04 (OH), 6.48 (CH). ^{13}C NMR of **3**: δ 198.26 (C=O), 153.52, 152.69, 152.29, 152.21, 152.02, 151.94, 151.90, 151.90, 151.84, 151.81, 151.75, 151.63, 151.37, 151.29, 150.95, 150.92, 150.18, 150.15, 150.08, 150.08, 150.03, 149.84, 149.71, 149.61, 149.56, 148.89, 148.83, 148.76, 148.56 (C–OH), 147.93, 147.32, 147.13, 146.89, 145.97, 145.76, 145.71, 145.51, 145.50, 145.40, 144.86, 144.66, 142.94, 142.63, 142.36, 141.67, 141.29, 141.29, 141.28, 141.27, 141.12, 140.43, 139.43, 139.19, 139.01, 138.87, 137.31, 136.89, 135.42, 135.28, 133.91, 130.62, 129.87 (CH), 129.33 (CH), 129.19 (CH), 128.28 (CH), 119.76 (*C*=COH), 41.76 (CH),
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