

Oxazolidinofullerene

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The first synthesis of the oxazolidinofullerene **2** has been achieved by cycloaddition of C_{60} with N_3CO_2Et , followed by the treatment of the product with BBr_3 at room temperature. The structure of **2** was unambiguously established by spectroscopic means (^{13}C NMR and MS). Methylcyclohexane solutions of aziridinofullerene **1a** and oxazolidinofullerene **2** exhibited, at ambient temperature, fluorescence emission at λ_{max} 686 and 691 nm, respectively, with vibronic fine structure. The fluorescence lifetimes and quantum yields for **1a** and **2** have been measured.

Cycloadditions have been extensively used for the synthesis of various fullerene derivatives,¹ the further transformation of which has been limited,² although ring opening of such cycloadducts is useful for their further elaboration.^{2c,d} Recently, we synthesized aziridinofullerene **1a** by the treatment of C_{60} with a large excess of EtO_2CN_3 in refluxing toluene.³ It is known that the thermal rearrangement of an *N*-acylaziridine will yield the corresponding oxazolidine derivative⁴ and, indeed, the corresponding *N*-aryloxycarbonylaziridinofullerene **1b** undergoes ring expansion when heated to give an oxazoline.⁵ Interestingly, **1a** was quite stable under refluxing toluene. Lewis acids can, however, promote the rearrangement of an aziridine to an oxazolidine,⁴ and here we describe such a rearrangement of **1a** leading to a convenient synthesis of the oxazolidinofullerene **2**.

Compound **1a** was treated with an excess of BBr_3 in toluene at room temperature for 10 h after which the reaction mixture was quenched with water and worked up as usual to give **2** (53%). The ^{13}C NMR exhibited 30 signals at δ 137–151 ppm due to sp^2 fullerene carbons. The two sp^3 carbons resonated at δ 98.75 and 90.45 clearly indicating their attachment to different heteroatoms. Both the ^{13}C NMR signal at δ 165.99 and the IR band at 1647 cm^{-1} supported the presence of an amide carbonyl group; in addition, amide NH absorption appeared at 3300

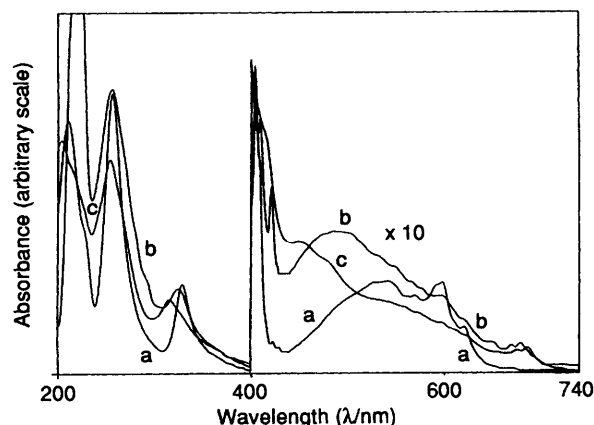
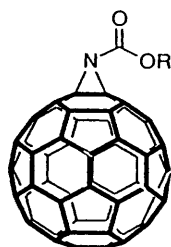


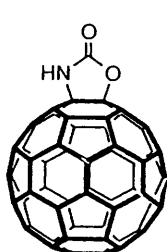
Fig. 1 The UV-VIS spectra of (a) C_{60} , (b) **1a**, and (c) **2** in methylcyclohexane. The molar absorptivities ($\times 10^3\text{ mol}^{-1}\text{ dm}^3\text{ cm}^{-1}$) are 211 at 223 nm, 133 at 256 nm, 40 at 324 nm, 2.4 at 408 nm, 1.7 at 428 nm and 1.3 at 491 nm in **1a**; 110 at 204 nm, 100 at 254 nm, 34 at 315 nm, 3.3 at 416 and 1.8 at 449 nm in **2**. Concentration of each compound: left panels, $1.0 \times 10^{-5}\text{ mol dm}^{-3}$; right panels, $5.0 \times 10^{-5}\text{ mol dm}^{-3}$



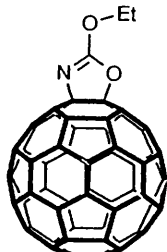
1a R = Et

1b R = 2, 4, 6- $Bu_3C_6H_2$

3 R = H



2



4

cm^{-1} . These data are consistent with the structure having a C_s symmetry and, therefore, the substituent on the C_{60} skeleton occurs at the junction of two six-membered rings.

The rearrangement appeared to be interesting since it is known that aziridine can rearrange to oxazolidinone upon treatment with CO_2 ,⁶ presumably, an *N*-carboxyaziridine intermediate is involved. The reaction of **1a** with BBr_3 may also yield a similar intermediate **3**, or the like, which undergoes conversion into **2**. Alternatively, acid-catalysed rearrangement of **1a** to give **4** may occur and this upon hydrolysis would lead to **2**.

The UV-VIS (Fig. 1) and the fluorescence emission spectra (Fig. 2) of **1a** and **2** were similar to those of many other C_{60} derivatives (Fig. 1). The fluorescence λ_{max} appeared at 686 and 691 nm for **1a** and **2**, respectively. Vibronic fine structure was observed for both compounds (**1a**: 659, 672, 686, 698 and 772 nm and **2**: 678, 691, 702, 727 and 742 nm).⁷ The fluorescence lifetimes were 1.3 ns and 1.7 ns for **1a** and **2**, respectively. Their respective fluorescence quantum yields were 4×10^{-5} and 3.7×10^{-3} . As can be seen from Fig. 2, the fluorescence intensity of **2** was much stronger than that of **1a** and C_{60} . Whereas **1a** has a more strained aziridine moiety and **2** has less rigid oxazolidinone skeleton, the fluorescence results suggested that the structural modification onto a C_{60} moiety would change to a significant degree the photophysical properties of C_{60} . Further investigation is in progress in this laboratory.

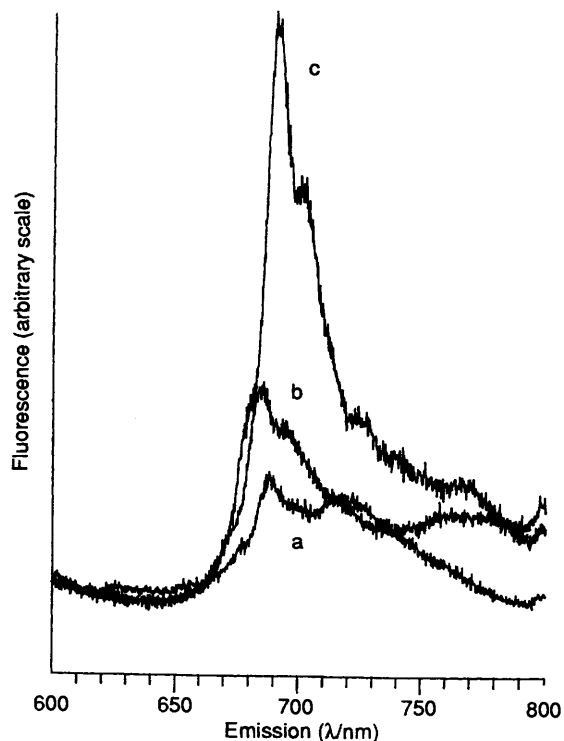


Fig. 2 Fluorescence emission spectra of (a) C_{60} , (b) **1a** and (c) **2** in methylcyclohexane at 25 °C. Excitation wavelength: (a) 328 nm, (b) 324 nm and (c) 314 nm with bandpass 8 nm and emission bandpass: 2 nm. Each curve was the average of four scans. All emission spectra were recorded by setting 450 nm long-pass filter in the emission pathway. Concentration of each compound: 1.0×10^{-5} mol dm^{-3}

Experimental

Preparation of 1a.—To a solution of C_{60} (72 mg, 0.10 mmol) in toluene (72 cm^3) was added ethyl azidoformate (690 mg, 6 mmol). The mixture was refluxed for 2 h during which time the colour turned from purple to reddish brown. The solvent was removed under reduced pressure and the residue was chromatographed on silica gel [toluene–hexane 1:1 (v/v)] to afford C_{60} , (20 mg, 28%) and **1a** (19 mg, 24%). $C_{60}NCO_2Et$: $\nu_{max}(KBr)/cm^{-1}$ 2917w, 2854w, 1738vs, 1424w, 1260s, 1226w, 1183w, 1036w, 807w and 710w; $\lambda_{max}(\text{methylcyclohexane})/nm$ 223, 256, 324, 408, 428 and 491 (b); $\delta_H(300 \text{ MHz}, CS_2, CDCl_3)$ 4.53 (q, J 7.1, 2 H), 1.52 (t, J 7.1, 3 H); $\delta_C[125 \text{ MHz}, CS_2, CDCl_3, 0.03 \text{ mol } dm^{-3} \text{ Cr}(\text{acac})_3]$ 155.37 (1, CO), 144.68 (4), 144.59 (4), 144.33 (4), 144.24 (2), 144.00 (4), 143.94 (4), 143.48 (2), 143.25 (4), 143.24 (4), 142.67 (4), 142.63 (4), 142.26 (2), 141.73 (4), 141.70 (4), 140.58 (4), 139.51 (4), 80.46 (2, $sp^3 C_{60}$), 63.89 (1, CH_2) and 14.28 (1, CH_3); m/z (DCI-MS) 807 (M^-), 779 ($[M-Et]^-$) and 720 (C_{60}^-).

Preparation of 2.—To a solution of $C_{60}NCO_2Et$ (42 mg, 0.052 mmol) in dry toluene (52 cm^3) was added boron tribromide (130 mg, 0.52 mmol). The mixture was stirred at room temperature for 10 h and then quenched with water (30 cm^3). The organic layer was washed with 5% aqueous $NaHCO_3$ (25 cm^3) and brine (25 $cm^3 \times 2$), dried ($MgSO_4$) and evaporated under reduced pressure and the residue was chromatographed on silica gel [toluene–hexane 1:1 (v/v)] to afford **2** (22 mg, 53%); $\nu_{max}(KBr)/cm^{-1}$ 3300m, 1647s, 1367w, 1324s, 1141w and 985s; $\lambda_{max}(\text{methylcyclohexane})/nm$ 204, 254, 315, 416, 449, 483, 560, 675 and 686; $\delta_C[75 \text{ MHz}, CS_2, [^2H_6]\text{acetone}, 0.03 \text{ mol } dm^{-3} \text{ Cr}(\text{acac})_3]$ 165.99 (1), 150.69 (2), 149.84 (1), 149.46 (1), 148.01 (2), 147.98 (2), 147.79 (2), 147.71 (2), 147.65 (2), 147.29 (2), 147.06 (2), 146.91 (2), 146.81 (2), 146.64 (2), 146.32 (2), 146.24 (2), 145.91 (2), 145.31 (2), 144.37

(2), 144.32 (2), 144.25 (2), 143.95 (2), 143.89 (2), 143.85 (2), 143.72 (2), 143.57 (2), 143.36 (2), 141.88 (2), 141.10 (2), 139.70 (2), 137.50 (2), 98.75 (1) and 90.45 (1); m/z (DCI-MS) 779 (M^-).

Fluorescence Study.—The fluorescence excitation and emission spectra of compounds **1a** and **2** were measured in a scanning luminescence spectrometer (SLM-Aminco Model AB2, Urbana, IL 61801, USA) equipped with a red-extended photomultiplier detector (R928, Hamamatsu Co., Japan). The excitation spectra were corrected from 200 to 600 nm, and the emission spectra from 250 to 900 nm. In order to resolve the spectral details, a wavelength stepping size of 0.2 nm and a scanning speed of 0.4 and 0.2 $nm s^{-1}$ for the excitation and emission spectra were employed, respectively. The slits were 2 and 8 nm for the scanning and the non-scanning monochromator, respectively. Each spectrum reported was the average of at least four scans. For the emission spectral measurements, a 450 nm long-pass filter was placed in the emission path to eliminate the interference from the solvent and the stray light. The quantum yield was determined by a comparative method using quinine bisulfate as the standard. A quantum yield of 0.56 for quinine bisulfate solution (5.4×10^{-8} mol dm^{-3} in 0.05 mol dm^{-3} sulfuric acid) is assumed. The fluorescence lifetime was measured in a time-correlated single-photon counting instrument (Model FL-900, Edinburgh Instrument, UK). The excitation source was a nitrogen flash lamp regulated by a fast-switching thyatron. The pulse width (full width half maximum) was ca. 1.5 ns. The lamp was typically operated at a repetition rate of 30 KHz. The excitation wavelength was 335 nm. The entrance slit was removed from the excitation monochromator and replaced with a 650 nm long-pass filter in the sample compartment in order to increase the intensity of incident light. Fluorescence was measured at the emission maxima with an extended red wavelength photomultiplier (R955, Hamamatsu) operated at 1.1 kV. All samples were degassed just prior to the measurement. Fluorescence lifetimes were extracted from the composite single-photon counting decay curve by the deconvolution technique using a nonlinear least-squares curve-fit method with the software provided by the instrument vendor. Routinely, the decay curves were fitted with 1 to 3 exponentials and the goodness of fit was judged by a number of standard statistical tests, e.g. weighted residual and chi-squares analyses. Employing the deconvolution technique provided the time resolution to 0.1 ns.

Acknowledgements

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