Preparation and Isolation of Three Isomeric C_{70} Isoxazolines: Strong Deshielding in the Polar Region of C_{70}

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Abstract: The C_{70} fullerene reacts with acetonitrile oxide and with 4-methoxybenzonitrile oxide to form a mixture of three isomeric monoadducts in addition to small amounts of di- and triadducts. The three isomeric monoadducts were separated and were found to result from 1,3-dipolar addition to 6–6 ring fusions of C_{70} at the 1,9 position and at the 7,8 position. The 1,9 addition occurs in two different modes, while addition at the 7,8 positions results in an unseparated D,L pair of isomers. Proton NMR indicates that the fullerene moiety is strongly deshielding and that the deshielding is stronger over the poles of the fullerene than over the sides.

The chemistry of C_{60} has expanded a great deal in the few years since macroscopic quantities became available.[2-5] Representative reactions of C_{60} include Diels–Alder[6-14] and other cycloadditions[14-20] as well as the addition of electrophiles,[21,22] nucleophiles[5,23,24] and halogens.[25-27] However, the lower abundance, higher cost, and lower symmetry of C_{70} and higher fullerenes have limited the investigation of the chemical reactivity of other fullerenes. These fullerenes pose unique regiochemical questions not raised with C_{60}. Their lower symmetry gives rise to an array of distinct local substructures and potentially different reactivities at particular areas of the fullerene surface, and different isomers of derivatives of these fullerenes may show interesting differences in chemical or physical properties.

Some common patterns of reactivity between C_{60} and C_{70} can be identified from the limited data available. They share similar electrochemical[28-30] and photophysical[31,32] properties. Both C_{60} and C_{70} add nucleophiles,[33,34] 1,3-dienes,[35] disiliranes,[19,36] oxygen,[37] and hydrogen.[38-40] Reactions of C_{60} with electron-rich metal complexes are well-known,[41-45] and complexes of C_{70} with one[46] and two[47] metals have been isolated. The two most common fullerenes both react with OsO_4, and the mono-[48] and bisosmate[49] esters of C_{60} and the monoosmate ester of C_{70}[50] are known.

There is some indication that C_{60} and C_{70} differ in their rates of reaction with certain species. Hydroboration of C_{70} proceeds more slowly than that of C_{60},[51] and the addition of hydroxide to C_{70} is slower than to C_{60}.[33] We have investigated the reactivity

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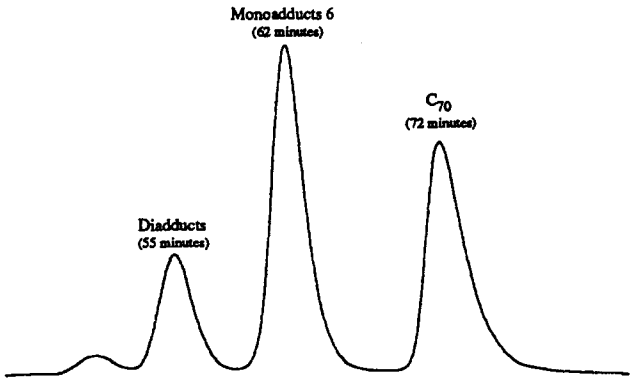
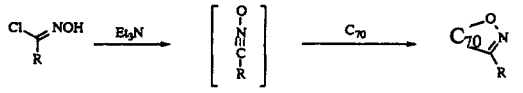


Figure 1. GPC chromatogram of the reaction mixture forming **6**. Conditions: 5-mL injection of the mixture in toluene, toluene mobile phase (5 mL/min), four GPC columns in a series as described in the Experimental Section, detection at 600 nm.

of C_{60} toward nitrile oxides,[52] and in this paper, we report the reactivity of C_{70} toward two of these reactive 1,3 dipoles.

Synthesis and Isolation

Treatment of C_{70} with acetonitrile oxide (**3**) leads to the formation of the corresponding isoxazoline **5**, albeit in low yield (13% yield of monoadduct, 31% based on recovered C_{70}). The yield was independent of the method of preparation of **3**: dehydration of nitroethane was only slightly more successful (20% yield of the monoadduct, 42% based on recovered C_{70}). This is in contrast to the reactivity of C_{60}, which undergoes the 1,3-dipolar addition of acetonitrile oxide in 63% yield based on unreacted C_{60}.[52] Much better yields were obtained from the reaction of C_{70} with 4-methoxybenzonitrile oxide (**4**).



1 R = CH_3
2 R = 4-C_6H_4OMe
3 R = CH_3
4 R = 4-C_6H_4OMe
5 R = CH_3 (42%)
6 R = 4-C_6H_4OMe (62%)

4-Methoxybenzonitrile oxide (**4**) was generated in toluene solution in the presence of C_{70} by dehydrochlorination of the corresponding hydroximinoyl chloride **2**.[53] After a 1-h reaction period, the mixture was washed with water and the components of the mixture were separated by preparative GPC using a toluene mobile phase (Figure 1).[52,54] FABS mass spectrometry indicated

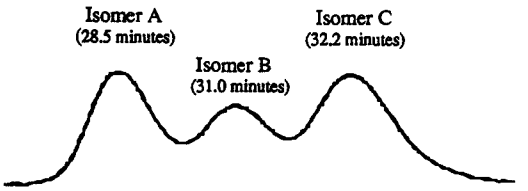


Figure 2. HPLC chromatogram of the mixture of isomeric monoadducts **6**. Conditions: 22- × 250-mm preparative "Buckyclutcher I" column, 50:50 hexane:toluene mobile phase (20 mL/min), 2-mL injection in toluene, UV/vis detection at 330 nm.

that the C_{70} isoxazolines **6** elute immediately before the unreacted C_{70}, consistent with our experience with the C_{60} analogs.[52] A mixture of monoadducts (**6**) was obtained in 62% yield (based on unreacted C_{70}), along with smaller quantities of higher adducts.

We cannot rule out the presence of other isomeric monoadducts **6** that may elute under other bands in the GPC, but we feel that it is unlikely that there are any other isomers present in significant quantities in the mixture. The mass spectrum of the diadduct band is nearly free of ions resulting from fragmentation to the monoadduct, giving us confidence that this band is not a mixture of di- and monoadducts.

The presence of three distinct $-OCH_3$ resonances in the ^1H NMR spectrum of the monoadduct **6** indicated that three isomers were present in a 34:26:40 ratio. Analysis of this monoadduct band on a "Buckyclutcher I" HPLC column (Figure 2) also suggested three components in virtually the same ratio, implying that the molar absorptivities of the isomers are similar. These were separated in several injections on a preparative "Buckyclutcher I" column using 50:50 hexane/toluene as the mobile phase.

As with **6**, monoadduct **5** is also formed as three isomers, but in a 1:1:1 ratio by ^1H NMR spectroscopy (Figure 4). The "Buckyclutcher" chromatogram also shows three different isomers (denoted as isomers **5A–C**). Interestingly, the retention times were *one-half as long* with **5** than with **6**. It appears that the interaction between the electron-rich side chain of **6** and the electron-deficient aromatic packing material in the "Buckyclutcher" column[55] is very important in determining the retention time, although separation of the isomers does not require an aromatic side chain.

Structural Characterization

A combination of ^{13}C and ^1H NMR was used to assign the structure of isomers **A–C** of adducts **5** and **6**. The ^{13}C NMR spectra of isomer **5A** and isomer **5C** are very similar and considerably more simple than the spectrum of isomer **5B**. In the aromatic region of the spectrum (130–160 ppm), a total of 33 lines of double intensity and two lines of single intensity are observed in the spectrum of **5C**, in addition to resonances due to the two fullerene sp^3 carbons. The same is observed in the spectrum of **5A**, except that one of the single intensity sp^2 lines is superimposed with one of the double intensity lines. The presence of two sp^3 fullerene carbons, two unique fullerene sp^2 carbons, and 33 *pairs* of fullerene sp^2 carbons indicates a plane of symmetry in the molecule. Addition to the 1,9 or to the 23,24 bonds[56] would provide such a structure, but the 23,24 product[36] should produce two single intensity fullerene sp^3 lines and eight single intensity fullerene sp^2 lines. The observed spectrum is most consistent with addition across the 1,9 double bond. Since addition of a nitrile oxide can occur in two different orientations, we believe that isomers **5A,C** are regioisomers resulting from addition of nitrile oxide **3** to the 1,9 double bond in two different orientations.

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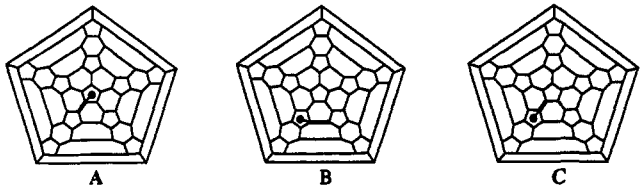


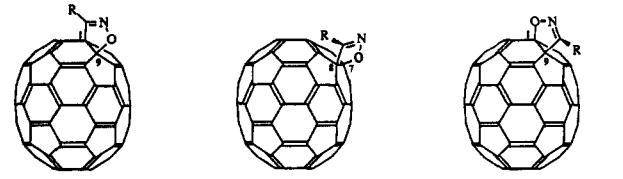
Figure 3. Schlegel diagrams of C_{70} isoxazolines resulting from addition to the 1,9 position (**A** and **C**) and to the 7,8 bond (**B**), showing the position of isoxazoline substituents (filled circles).

The ^{13}C NMR spectrum of isomer **5B** is quite complicated, showing a total of 58 single intensity lines and five double intensity lines, in addition to a line from the methyl and the two sp^3 lines from the heterocycle. Given the large number of peaks in a fairly narrow spectral window, we suspect that these double intensity lines result from accidental superposition of single intensity lines. This number of lines (70) implies a structure with no symmetry, and such a structure could result from addition across either the 7,8 or the 22,23 bond. The 7,8 double bond connects two five membered rings (a "6–6 ring fusion"), traditionally held to be the most reactive sites in fullerenes,[4,41] while the 22,23 double bond connects a five membered ring and a six-membered ring. We assign structure **5b** to isomer **5B**. This structure is consistent with the observed number of ^{13}C NMR lines as well as with the relative reactivity of different double bonds in C_{70} toward OsO_4 and toward BH_3·THF.[50,51]

Further consideration of the structures of isomers **5A–C** reveals that isomer **5A** is unique in that the methyl substituent is positioned over the apical five-membered ring, while in both **5B** and in **5C**, this substituent is positioned over one of the other five-membered rings. As shown in Figure 3, in isomers **5B,C**, the substituent is placed over the same ring.

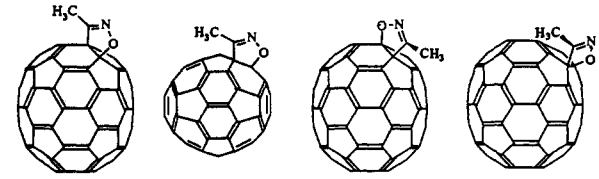
We expected that isomers **5B,C**, in which the methyl group is positioned over the same five membered ring, should show similar ^1H NMR shifts for that methyl, while the remaining isomer (**5A**) should be somewhat different. This is realized in practice: the methyl resonance of isomer **5A** appears at 2.90 ppm, of isomer **5B** appears at 2.39 ppm, and of isomer **5C** appears at 2.42 ppm. The methyl resonance of isomers **5B,C** are similar to each other ($\Delta\delta_{BC}$ = 0.03 ppm), while that of isomer **5A** is shifted downfield ($\Delta\delta_{AC}$ = 0.50 ppm). Based on the analysis above, we assign structures **5a–c** for isomers **5A–C**, respectively, and analysis of the ^{13}C and ^1H NMR spectra of the isomers of **6** by the same method allows the assignment of **6a–c**. The ^1H NMR spectrum of the **6a–c** mixture shows three distinct methyl singlets, with two being very similar ($\Delta\delta$ = 0.03 ppm) and one appearing 0.2 ppm farther downfield, consistent with the methyl group in one isomer being placed in a very different environment than in the other two. The deshielding of the $-OCH_3$ resonance of **6a** is less pronounced than the deshielding of the methyl resonance of **5a**, and the chemical shifts of the $-OCH_3$ resonances of **6b,c** are essentially unperturbed from values observed for the same resonances in non-fullerene analogs[57,58] and virtually identical to the chemical shift of anisole when measured under identical conditions. The $-OCH_3$ groups in **6a–c** are approximately 7 Å from the surface of the fullerene, and it is notable that the ring current in the apical ring is strong enough to perturb the resonance in **6a**.

The chemical shifts of methyl resonances in **5a-c** are all farther downfield (as much as 1 ppm) than the corresponding resonances in typical aliphatic isoxazolines.[59–61] This seems reasonable in



5a (R = CH_3) **5b** (R = CH_3) **5c** (R = CH_3)
6a (R = 4-C_6H_4-OMe) **6b** (R = 4-C_6H_4-OMe) **6c** (R = 4-C_6H_4-OMe)

light of recent results that indicate that ^3He atoms in the interior of C_{70} are strongly shielded (29 ppm) relative to free helium.[62] It is interesting to compare the chemical shifts of the methyl resonances in the isomers of **5** and the methyl resonance in the C_{60} analog **7**.[52] In this series of compounds, the most deshielded methyl resonance is found in **5a**, then (in descending order) **7**, **5c**, and **5b**. This indicates that the influence of ring currents in C_{70} is strongest over the apical five-membered ring of the molecule and is less over the five membered rings on the sides. In addition, these results also suggest that the influence of ring currents over the apical five-membered rings of C_{70} is stronger than the influence of ring currents over the five-membered rings of C_{60}. This observation may prove highly useful in the assignment of the structures of other derivatives of C_{70}.



5a (2.90 ppm) **7** (2.74 ppm) **5c** (2.42 ppm) **5b** (2.39 ppm)

The UV/*vis* spectra of the two 1,9 isomers (**6a,c**) are similar, exhibiting absorption minima at 380 nm. The 7,8 isomer **6b** exhibits a maximum at 365 nm. These spectra are in good agreement with spectra recently obtained by Henderson and Cahill[51] for the 1,9 and 7,8 isomers of $C_{70}H_2$, in which there is a small maximum at ca. 375 nm for the 7,8 isomer **6b** and minima at ca. 380 nm for the 1,9 isomers.

Isoxazoline derivatives of C_{70} are stable to high temperatures, like their C_{60} congeners. Thermal gravimetric analysis (TGA) of the monoadduct mixture shows a loss of 5.2% of the mass of the sample over the temperature range 95–200 °C, probably due to loss of toluene occluded in the solid.[63] A loss of 13.2% of the mass occurred between 240–400 °C, corresponding well to the calculated loss of mass (15.3%) from fragmentation to the nitrile oxide and C_{70}. At 600 °C, the rest of the sample sublimed, leaving 30% of the mass as a nonvolatile residue at the end of the sublimation at 900 °C.

Electrochemistry

A number of papers[29,30,64–69] have been devoted to the electrochemistry of C_{60} and C_{70}, and there have been reports of

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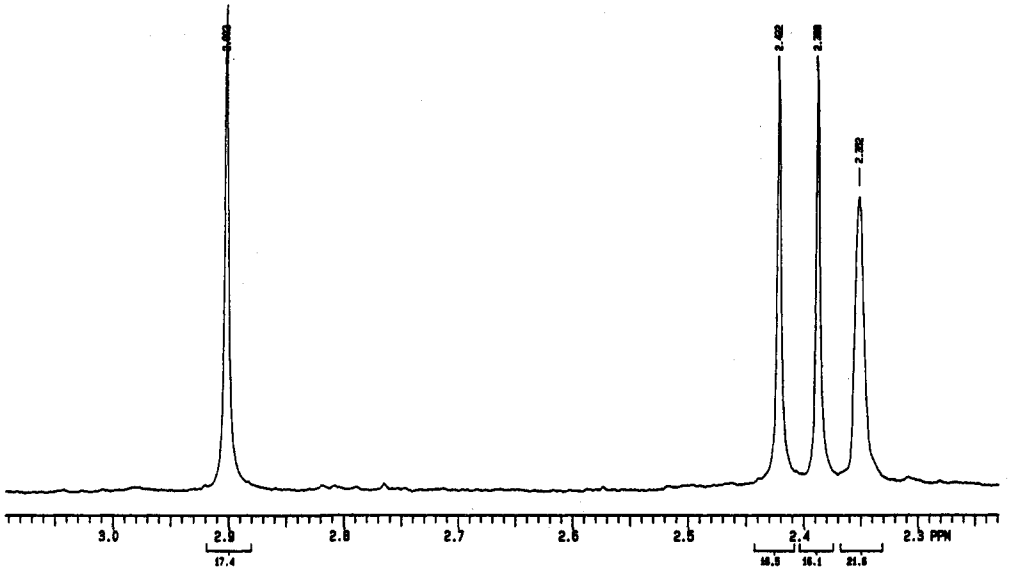

Figure 4. Methyl region of the ^1H NMR spectrum of a mixture of **5A–C**. The resonance at 2.35 ppm is due to residual toluene.

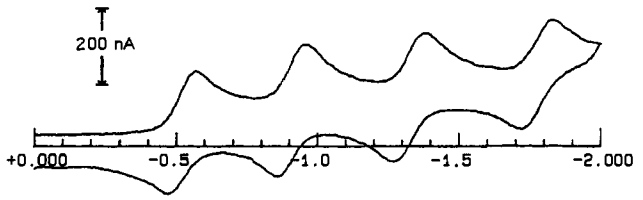

Figure 5. Cyclic voltammogram of **6c** in 80:20 toluene/acetonitrile using a 125-μm Pt disk as the working electrode. Scan rate was 5 V/s.

the electrochemical behavior of fullerene derivatives[40,70] and fulleroids.[71,72] Fullerene isoxazolines show reduction potentials that are virtually identical to those of the parent fullerene. Cyclic voltammetry of **6** in toluene/acetonitrile solution using a Pt electrode shows up to four quasireversible reduction waves at high scan rates (>1 V/s). No oxidative processes were observed out to a potential of +1.3 V versus Fc/Fc^+ reference. For example, **6c** shows quasireversible reductions at –0.98, –1.37, –1.79, and –2.24 V (Figure 5), while the first four reductions of underivatized C_{70} occur at –0.97, –1.34, –1.78, and –2.21 V in the same solvent system.[29]

We believe that two opposing factors are responsible for the similarity in reduction potentials: a shift to more negative potentials due to the loss of a double bond from the fullerene moiety and a compensating shift to less negative potentials due to an electronic interaction, such as periconjugation, between the heterocycle and the fullerene.[73] This interaction may also be partially responsible for the diminished chemical reactivity of the heterocycle.[74]

No significant differences in the reduction potentials of **6a–c** were observed. Compound **6a** was substantially less soluble in the toluene/acetonitrile solvent system than the other two isomers, leading to a poor quality voltammogram. We are currently investigating the use of this phenomenon to improve the chromatographic separation of the isomers.

Additional waves appear at lower scan rates, and electrode fouling occurs in some cases. In the cyclic voltammetry of $C_{60}H_2$, we observed the appearance of reoxidation waves due to C_{60} anions, resulting from expulsion of H_2 from $C_{60}H_2$ upon reduction.[70] We would not be able to detect such a reaction of **6**, since the potentials of **6a-c** and C_{70} are virtually identical. However, the appearance of new waves clearly indicates a reaction occurs upon reduction, and we are currently investigating this process.

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Conclusions

The C_{70} fullerene participates in 1,3-dipolar addition reactions with nitrile oxides, although at a somewhat slower rate than does the C_{60} fullerene. Three isomeric monoadducts are formed, corresponding to addition to the 1,9 bond (in two different orientations) and to the 7,8 bond (two equivalent orientations). Product ratios suggest that the 1,9 bond is the more reactive of the two, with relative yields of 74:26 for 1,9 versus 7,8 adducts. There is essentially no preference for one orientation of addition to the 1,9 position over the other. One of the adducts places a substituent over the apical five-membered ring, while the other two of the adducts place a substituent over one of the other five-membered rings. The apical ring is strongly deshielding, more so than other five-membered rings in C_{70} and more so than the five-membered rings in C_{60}.

Experimental Section

All reactions were carried out under argon in deoxygenated solution, unless otherwise noted. NMR spectra were measured in $CDCl_3/CS_2$ solution at 200 MHz (^1H) or 100 MHz (^{13}C). Fullerenes (C_{60} and C_{70}) were obtained by GPC purification[54] of the toluene extract of fullerene soot. Cyclic voltammograms and differential pulse polarograms were obtained using a BAS 100A electrochemical analyzer equipped with a low-current preamplifier and Faraday cage. Preparative GPC was performed using a bank of four 19- × 300-mm GPC columns (1, Jordigel E-277 (500 Å); 2 and 3, Waters Ultrastyragel (500 Å); 4, Waters Ultrastyragel (100 Å)) using toluene as the mobile phase at a flow rate of 5 mL/min. Injections of up to 5 mL of saturated solutions in toluene were made. Preparative HPLC was performed using a 22- × 250-mm "Buckyclutcher 1" column obtained from Regis, Inc. ^1H NMR spectra are referenced to internal TMS, and ^{13}C NMR spectra are referenced to the $CDCl_3$ solvent. Mass spectral data were obtained by fast atom bombardment of the samples in nitrobenzyl alcohol.

Preparation of 5a–c. These compounds were prepared by two different methods. Method 1: A mixture of C_{70} (42 mg, 0.05 mmol), $CH_3CClNOH$ (ca. 9.35 mg, 0.1 mmol, in 0.5 mL of CH_2Cl_2), and Et_3N (10.1 mg, 0.1 mmol) was stirred in toluene (50 mL) for 1 h. The resulting red-brown solution was diluted with toluene, and extracted with deionized water (3 × 50 mL), dried ($MgSO_4$), and concentrated *in vacuo* to a final volume of 25 mL. This final solution was filtered through a 0.2 μm Teflon HPLC filter and purified by GPC[52,54] to produce 6 mg of monoadduct (0.0067 mmol, 31% based on recovered C_{70}) and 24 mg (0.0286 mmol) of unreacted

C_{70}. Method 2: C_{70} (42 mg, 0.05 mmol), nitroethane (18.76 mg, 0.25 mmol), and triethylamine (14 μL, 0.01 mmol) were dissolved in 32 mL of deoxygenated toluene. To this mixture was added dropwise phenyl isocyanate (59.56 mg, 0.5 mmol) in 5 mL of toluene. The mixture was heated for 15 h under argon and worked up and purified as above to produce 9 mg of monoadducts (0.01 mmol, 42% based on recovered C_{70}) and 22 mg of C_{70} (0.026 mmol). In each case, the monoadducts were separated using the preparative Buckyclutcher column to produce **5a–c**, which were obtained in a 1:1:1: ratio (14% yield each).

5a. ^{1}H NMR data (200 MHz, $CDCl_3/CS_2$): δ 2.90 (s, CH_3). ^{13}C NMR data (100 MHz, $CDCl_3/CS_2$ + Cr(acac)$_3$): δ 14.13 (CH_3), 73.71 (isoxazoline, C-4, 1), 98.05 (isoxazoline, C-5, 1), 131.25 (2), 131.29 (2), 132.14 (2), 133.02 (2), 133.30 (2), 137.60 (2), 140.28 (2), 140.30 (2), 142.03 (2), 143.18 (2), 143.37 (2), 143.46 (2), 143.70 (2), 145.68 (2), 145.82 (2), 146.43 (2), 146.81 (3), 147.09 (2), 147.16 (2), 147.22 (2), 148.17 (2), 148.47 (2), 148.81 (2), 148.90 (2), 149.39 (2), 149.65 (2), 149.77 (2), 150.20 (2), 150.29 (2), 150.39 (2), 150.71 (2), 151.09 (1), 151.18 (2), 154.11 (isoxazoline C-3, 1), 154.79 (2). FABS-MS: *m/z* 898 (MH^+).

5b. ^{1}H NMR data (200 MHz, $CDCl_3/CS_2$): δ 2.39 (s, CH_3). ^{13}C NMR data (100 MHz, $CDCl_3/CS_2$ + Cr(acac)$_3$): δ 12.38 (CH_3), 70.85 (isoxazoline, C-4, 1), 94.58 (isoxazoline, C-5, 1), 130.28 (1), 130 43 (1), 130.73 (1), 131.02 (1), 131.68 (1), 132.04 (1), 132.08 (1), 132.18 (1), 140.11 (1), 140.54 (1), 141.93 (1), 142.90 (1), 143.28 (1), 143.31 (1), 143.91 (2), 143.97 (1), 144.05 (2), 144.35 (1), 144.40 (1), 144.62 (1), 144.83 (1), 144.91 (1), 144.95 (1), 145.14 (1), 145.38 (1), 145.47 (1), 145.48 (1), 145.53 (1), 145.76 (1), 145.92 (1), 146.02 (1), 146.25 (1), 146.28 (1), 146.30 (1), 146.33 (1), 146.73 (1), 146.75 (2), 146.77 (1), 146.89 (1), 146.96 (1), 147.05 (1), 147.09 (1), 147.46 (1), 147.65 (1), 147.74 (1), 147.97 (1), 148.31 (1), 148.43 (1), 148.58 (1), 148.62 (1), 148.82 (1), 148.84 (1), 148.90 (2), 148.95 (1), 149.18 (1), 149.27 (1), 149.33 (2), 149.37 (1), 149.39 (1), 149.98 (1), 151.47 (1), 151.53 (1), 154.26 (1), 154.34 (isoxazoline C-3, 1). FABS-MS: *m/z* 898 (MH^+).

5c. ^{1}H NMR data (200 MHz, $CDCl_3/CS_2$): δ 2.42 (s, CH_3). ^{13}C NMR data (100 MHz, $CDCl_3/CS_2$ + Cr(acac)$_3$): δ 13.22 (CH_3), 74.20 (isoxazoline, C-4, 1), 98.72 (isoxazoline, C-5, 1), 130.73 (2), 130.95 (2), 131.48 (2), 132.66 (2), 133.27 (2), 138.88 (2), 139.55 (2), 139.86 (2), 141.50 (2), 143.06 (2), 143.27 (2), 143.33 (2), 143.75 (2), 145.69 (2), 145.90 (2), 146.77 (2), 146.94 (2), 146.99 (2), 147.06 (1), 147.47 (2), 148.25 (2), 148.53 (2), 148.77 (2), 148.91 (2), 149.23 (2), 149.43 (2), 149.62 (2), 150.05 (2), 150.44 (2), 150.70 (2), 150.85 (1), 150.89 (2), 151.11 (2), 151.72 (isoxazoline, C-3, 1), 153.44 (2), 154.28 (2). FABS-MS: *m/z* 898 (MH^+).

Preparation of 6a–c. Solutions of *p*-$CH_3OC_6H_4CClNOH$ (9.25 mg, 0.05 mmol) and Et_3N (5.05 mg, 0.05 mmol), each in 10 mL of toluene, were added simultaneously by syringe to a solution of C_{70} (42 mg, 0.05 mmol) in 40 mL of toluene. The resulting red-brown solution was stirred for 1 h, then extracted with deionized water (3 × 50 mL), dried ($MgSO_4$), and concentrated *in vacuo* to a final volume of 25 mL. This final solution was filtered through a 0.2-μm Teflon HPLC filter and purified by GPC,[52,54] to produce 8.6 mg (0.007 mmol, 26% yield based on recovered C_{70}) of diadducts (FABS, nitrobenzyl alcohol matrix, *m/e* 1139, MH^+), 16.4 mg (0.017 mmol, 63% yield based on recovered C_{70}) of monoadducts (*m/e* 990, MH^+), and 19.6 mg (0.023 mmol) of unreacted C_{70}, in addition to a small quantity of material believed to be triadducts. ^{1}H NMR analysis of the monoadduct band showed **6a-c** in a 34:26:40 ratio, respectively, on the basis of integration of the $-OCH_3$ resonances, corresponding to yields of 21%, 16%, and 25%, respectively. Separation of the isomers on a Buckyclutcher column (toluene/hexane (50:50), 20 mL/min) produced three bands which were isolated to produce **6a-c**, respectively.

6a. ^{1}H NMR data (200 MHz, $CDCl_3/CS_2$): δ 3.98 (s, OMe, 3H), 7.15–7.19, 8.41-8.45 (AA'BB' phenyl ring, 4H). ^{13}C NMR data (100 MHz, $CDCl_3/CS_2$ + Cr(acac)$_3$): δ 55.39 (OMe), 72.66 (isoxazoline, C-4, 1), 100.10 (isoxazoline, C-5, 1), 114.44 (phenyl), 121.48 (phenyl), 130.62 (phenyl), 131.33 (4), 132.20 (2), 133.17 (2), 133.32 (2), 137.50 (2), 140.14 (2), 140.29 (2), 142.42 (2), 143.34 (2), 143.41 (4), 143.71 (2), 145.66 (2), 145.81 (2), 146.41 (2), 146.60 (2), 146.81 (1), 146.89 (2), 147.11 (2), 147.25 (2), 148.15 (2), 148.49 (2), 148.81 (2), 148.90 (2), 149.17 (2), 149.42 (2), 149.66 (2), 150.08 (2), 150.24 (2), 150.28 (2), 150.78 (2), 151.11 (1), 151.18 (2), 154.82 (2), 155.70 (isoxazoline, C-3, 1), 161.45 (phenyl). FABS-MS: *m/z* 990 (MH^+).

6b. ^{1}H NMR data (200 MHz, $CDCl_3/CS_2$): δ 3.82 (s, OMe, 3H), 6.87–6.92, 7.84-7.88 (AA'BB' phenyl ring, 4H). ^{13}C NMR data (100 MHz, $CDCl_3/CS_2$ + Cr(acac)$_3$): δ 55.28 (OMe), 70.17 (isoxazoline, C-4, 1), 96.70 (isoxazoline, C-5, 1), 114.27 (phenyl), 121.01 (phenyl), 130.07 (phenyl), 130.71 (1), 130.78 (2), 131.26 (1), 131.88 (1), 132.27 (1), 132.34 (1), 132.38 (1), 140.37 (1), 140.82 (1), 141.96 (1), 142.60 (1), 143.16 (1), 143.42 (2), 144.07 (1), 144.18 (2), 144.29 (1), 144.31 (1), 144.64 (1), 144.94 (1), 145.02 (1), 145.09 (1),145.23 (1), 145.55 (1), 145.57 (1), 145.59 (1), 145.64 (1), 145.70 (1), 145.92 (1), 146.12 (1), 146.23 (1), 146.39 (1), 146.42 (1), 146.55 (1), 146.57 (1), 146.63 (1), 146.67 (1), 146.79 (1), 146.91 (1), 146.99 (1), 147.16 (2), 147.24 (1), 147.39 (1), 147.81 (1), 147.92 (1), 148.03 (1), 148.20 (1), 148.49 (1), 148.57 (1), 148.74 (1), 148.85 (1), 149.03 (1), 149.05 (1), 149.07 (1), 149.12 (1), 149.34 (1), 149.50 (1), 149.53 (2), 149.59 (1), 149.62 (1), 150.16 (1), 151.64 (1), 154.66 (1), 154.56 (1), 155.83 (isoxazoline, C-3, 1), 161.27 (phenyl). FABS-MS: *m/z* 990 (MH^+).

6c. ^{1}H NMR data (200 MHz, $CDCl_3/CS_2$): δ 3.79 (s, OMe, 3H), 6.87–6.91, 7.82-7.87 (AA'BB' phenyl ring, 4H). ^{13}C NMR data (100 MHz, $CDCl_3/CS_2$ + Cr(acac)$_3$): δ 55.26 (OMe), 73.56 (isoxazoline, C-4, 1), 100.85 (isoxazoline, C-5, 1), 114.23 (phenyl), 120.95 (phenyl), 130.11 (phenyl), 130.94 (2), 131.18 (2), 131.60 (2), 132.32 (2), 133.49 (2), 139.13 (2), 139.78 (2), 139.99 (2), 141.55 (2), 143.33 (2), 143.51 (2), 143.63 (2), 144.03 (2), 145.91 (2), 146.15 (2), 146.94 (2), 147.21 (2), 147.28 (2), 147.31 (1), 148.02 (2), 148.40 (2), 148.72 (2), 148.40 (2), 149.00 (2), 149.39 (2), 149.66 (2), 150.07 (2), 150.32 (2), 150.71 (2), 150.92 (2), 151.06 (1), 151.12 (2), 151.30 (2), 153.72 (isoxazoline, C-3, 1), 153.97 (2), 154.42 (2), 161.29 (phenyl). FAS-MS: *m/z* 990 (MH^+).

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Supplementary Material Available: The ^{13}C and ^{1}H NMR spectra and FABS-MS of **5a–c** and **6a–c**, the absorption spectra of **6a–c**, and the TGA of **6** are available as supplementary material (28 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microform version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.