

Synthesis of [70]Azafulleroids: Investigations of Azide Addition to C₇₀

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Abstract: Treatment of C₇₀ with (2-methoxyethoxy)methyl azide gives rise to three out of a possible six triazoline isomers, showing chemoselectivity as well as regioselectivity. The major product arose from addition of azide to the double bond of C₇₀ possessing the greatest local curvature. Selective thermolysis of the least stable triazoline, the one resulting from addition to the least curved [6,6] double bond, allowed solution of the structure of the three isomers. Thermolysis of the triazoline isomers produced mixtures of C₇₀, azafulleroids, and fullereroaziridines.

Introduction

The chemistry of C₆₀ has been extensively investigated.¹ In comparison, there have been far fewer studies on the functionalization of C₇₀.^{2–5} Cycloadditions to C₇₀ present a greater challenge than to C₆₀; the lower symmetry of the former can, in principle, give rise to a large number of isomers. C₇₀ has five distinct types of carbon atoms⁶ (Figure 1) and eight different types of C–C bonds, four of which are [6,6] bonds. Similar to C₆₀, cycloaddition to C₇₀ occurs across the [6,6] bond, giving rise to a minimum of four possible isomers. The 1,3-dipolar addition of azide could, in principle, give rise to a maximum of six triazoline isomers, where addition across a [6,6] bond between two different types of carbon atoms gives rise to a pair of regioisomers^{3,7} (Scheme 1).

A number of cycloaddition reactions of C₆₀ have been the subject of intense investigation in our group over the past five years. Of these, the addition of SEM⁸ and MEM azide^{9,10} have been of particular interest because the latter led to the synthesis, in bulk quantity, of the heterofullerenes (C₅₉N)₂¹⁰ and C₅₉HN.¹¹ The reaction of alkyl azides with C₆₀ leads to the formation of a thermally labile triazoline which, upon loss of nitrogen, affords an azafulleroid (cf. **5**, **6**, and **8**). The [60]azafulleroids are attractive because to date they are the only fullerene derivatives which provide chemospecific cycloaddition reactions.^{9,12} These

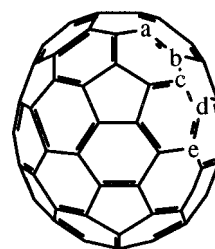


Figure 1. Five distinct sets of carbon atoms of C₇₀ are labeled a–e.

findings led us to investigate the formation of [70] fullerotriazoline(s) and their conversion to [70]azafulleroid(s), and here we report on the chemo- and regioselective addition of an alkyl azide to C₇₀.¹³

Results and Discussion

Treatment of C₇₀ with an excess of (2-methoxyethoxy)methyl azide (MEM-N₃) in *o*-dichlorobenzene (ODCB) at room temperature for 48 h afforded, upon chromatography, one band which contained a mixture of triazoline isomers **1**, **2**, and **3** (32% yield, 60% based on consumed C₇₀). Analysis of the mixture by high-performance liquid chromatography (HPLC) showed the apparent formation of only two isomers (62:38). However, ¹H NMR spectroscopy revealed the presence of three compounds, two with C_s symmetry and one with C₁ symmetry (Scheme 1); of these, it was later established that **2** and **3** were inseparable by HPLC. The percentage of **3** obtained in the product mixture was inversely proportional to the temperature of the reaction. Interestingly, when a mixture of **1**, **2**, and **3** was heated to 55 °C overnight, ¹H NMR spectroscopic analysis revealed the complete disappearance of **3**, with only **1**, **2**, **6**, and **7** remaining (cf. Scheme 3). HPLC analysis confirmed this observation as well as revealing a small amount of C₇₀ and trace amounts of other products, too minute to characterize. The fortunate, selective, thermal conversion of **3** allowed the separation and complete characterization of both **1** and **2**.

After separation of **1** and **2** by preparative HPLC, each was subjected to thermolysis. A dilute toluene solution of each isomer was heated to 80 °C until the disappearance of the triazoline was observed by TLC (Scheme 2a,b). In each case **1** or **2** gave rise to three separable bands by column chroma-

(13) While this work was in progress, a publication on the use of a [70]-bisazafulleroid appeared (Nuber, B.; Hirsch, A. *J. Chem. Soc., Chem. Commun.* **1996**, 1421).

[⊗] Abstract published in *Advance ACS Abstracts*, January 15, 1997.

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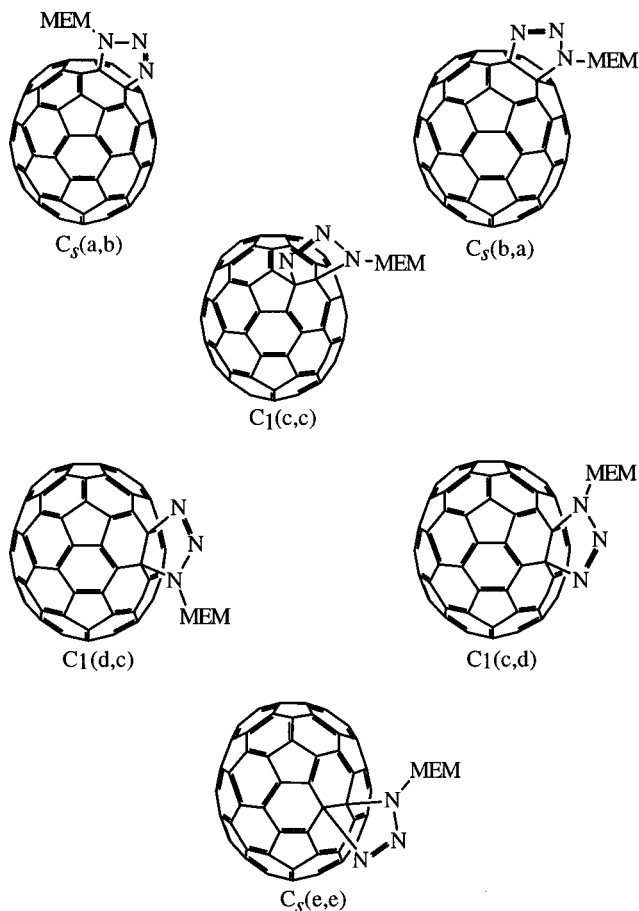
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Scheme 1. Six Possible Triazoline Isomers as a Result of Addition of MEM Azide to C_{70} and Their Point Group Assignments



tography (silica gel, toluene): C_{70} (64%), azafulleroid **5** or **6** (23%), respectively, and aziridine **4** (5%). Since **1** and **2** gave rise to the same aziridine, both isomers must arise from addition across the same double bond and are regioisomers. Therefore, **1** and **2** must result from addition across the [a,b] bond since their C_5 symmetry has already been established. Differentiation of **1** and **2** and characterization of **3** were accomplished by thermolysis of a solution of **2** and **3** in the same manner as described above (Scheme 3). The mixture of **2** and **3** afforded two different aziridines (**4** and **7**). However, only one azafulleroid (**6**) was formed, indicating that the MEM-bearing nitrogen atom of the nitrogen triad of **2** and **3** is attached to the same carbon atom in both compounds.

Thin layer chromatography R_f values and UV/vis absorption were used initially to differentiate azafulleroids from aziridines.⁸ An overlapped spectrum of **4**, **5**, and C_{70} suggested that **5** was an azafulleroid, having a UV/vis absorption pattern nearly identical with that of C_{70} , with only subtle differences. In contrast, the absorption maxima in **4** had a slight hypsochromic shift relative to C_{70} .

Fortunately the characterization of these labile C_{70} derivatives did not turn out to be as difficult as we assumed, because the simplicity of the ^1H NMR spectra in combination with low-temperature pyrolysis (see Schemes 2 and 3) allowed complete characterization of the three triazolines observed.

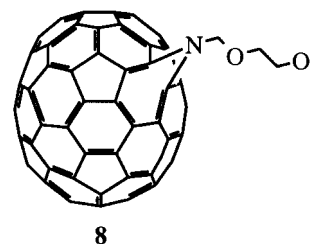
The following set of spectroscopic experiments confirms the above assignments. A combination of ^1H and ^{13}C NMR of **5** was indicative of an azafulleroid with C_5 symmetry, whereas azafulleroid **6** showed a ^1H NMR spectrum containing a doublet of doublets (AB pattern) at 4.92 ppm, corresponding to the

N-methylene protons. The ^{13}C NMR spectrum contained a minimum of 60 sp^2 resonances between 155 and 128 ppm. The ^1H NMR spectra of aziridines **4** and **7** were much alike; the difference was that the spectrum of **4** had its resonances shifted downfield relative to **7**. This observation was in accord with the theoretical deshielding effect in C_{70} , which increases as substituents get closer to the pole.⁴ Further structural evidence was seen in the ^{13}C NMR spectra, where aziridine **4** had two distinctive sp^3 resonances at 79.6 and 79.7 ppm and two sp^2 resonances at 150.8 and 145.8 ppm with a relative intensity of 1 carbon each. Aziridine **7** had only one sp^3 resonance at 73.5 ppm and four sp^2 resonances at 151.9, 149.1, 142.2, and 146.9 ppm, respectively, with a relative intensity of 1 carbon. An unusual feature of compound **7**'s NMR spectra was that the N-methylene proton resonance and the N-methylene carbon resonance were considerably broader than those of the other derivatives.

Analogous to C_{60} chemistry,¹² azafulleroids can be produced directly from C_{70} by treatment with 1.25 equiv of MEM- N_3 in refluxing ODCB (180 °C). Column chromatography of the reaction mixture afforded two bands as the major products, after separation from C_{70} and higher fullerene adducts. The two fractions were subjected to HPLC analysis, where the first band showed formation of two azafulleroids **5** and **6** (49:51) and the second band consisted of aziridines **4** and **7** (60:40), respectively. Azafulleroid **8** was not observed, in accordance with previously reported diazomethane cycloaddition reactions of C_{70} .³

Conclusion

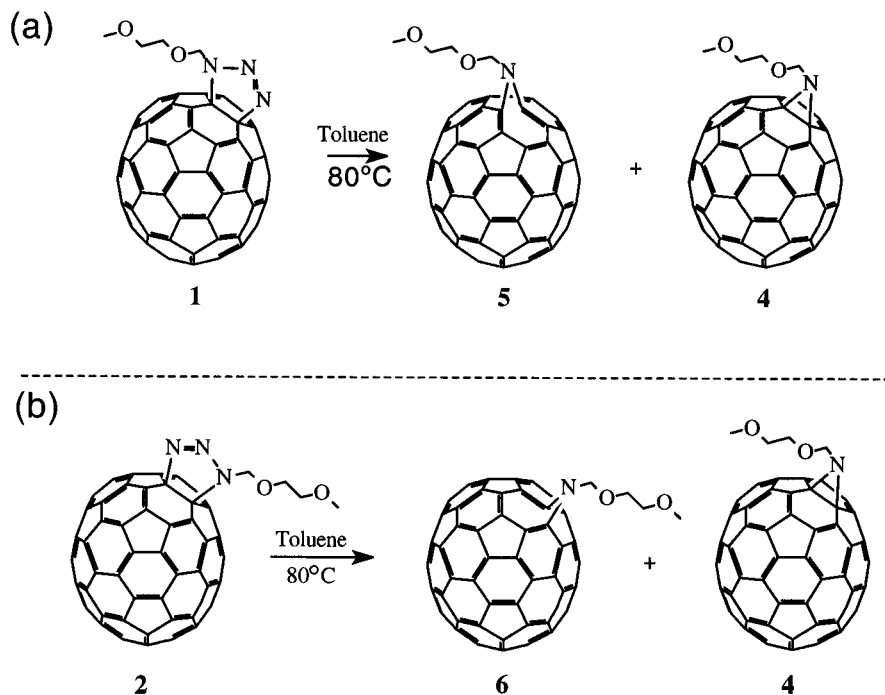
At moderate temperatures the addition of (2-methoxyethoxy)-methyl azide (MEM azide) to C_{70} gives rise to three triazoline isomers, where addition occurs to a greater extent across the [a,b] bond, the bond with greatest curvature, with preferential formation of **1**. Addition across the lower strain [c,c] bond also occurs but to a lesser extent, producing **3**. As a result and in accord with theory,¹⁴ structures C_1 (d,c), C_1 (c,d), and C_5 (e,e) (Scheme 1) are not observed. Also, by the same principle, azafulleroid **8** is not observed. At 55 °C triazoline **3**, a



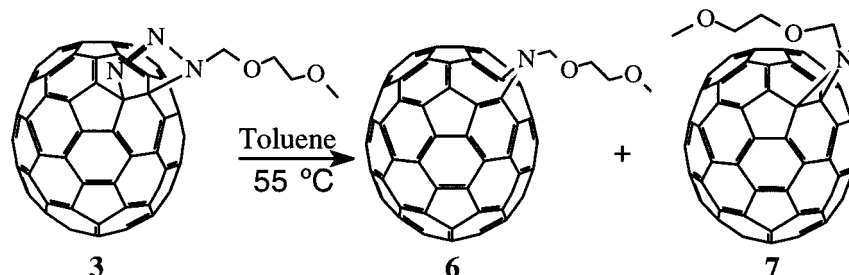
chemoisomer of regioisomers **1** and **2**, was readily and selectively transformed to azafulleroid **6** and aziridine **7** as well as a small quantity of C_{70} , showing the varied stability of the isomers. In comparing the thermal stability of **1**, **2**, and **3**, the reduced stability of **3** is very likely due to the higher strain in its polar region; i.e., **1** and **2** have a lower total strain energy than **3** because, in the former, two of the polar carbon atoms are pyramidal and introduction of sp^3 carbons in the poles is expected to alleviate some of the polar strain of the C_{70} cluster.

At the higher temperature of 180 °C, we observed that the preference of addition across the bond containing the greatest local curvature (a-b) (reflected in formation of **4**), as opposed to addition across the bond with the shortest bond order (c-c) (reflected in formation of **7**), decreased from 4:1 to 3:2. This result reflects that (1) at this temperature the MEM azide also

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Scheme 2. Thermolysis of MEM-Triazolines^a

^a (a) Thermolysis of **1**. ^b Thermolysis of **2**.

Scheme 3. Thermolysis of MEM-Triazoline Isomer **3**

decomposes to MEM nitrene, which is expected to exhibit lower selectivity due its higher energy content, and (**2**) at more elevated temperature the selectivity of the 1,3-dipolar addition is also expected to decrease. This study is the first step toward a full understanding of addition of azide to C₇₀ and allows for easy characterization of the subsequent transformation to azafulleroids. The addition of MEM azide to C₇₀ shows a wider range of selectivity than previously reported reactions of C₇₀ such as osylation² and addition of diazomethane.³

Experimental Section

[6,6]-(1-N-MEM-triazoline)-C₇₀ 1 and 2. To a degassed solution of C₇₀ (150 mg, 0.18 mmol) in HPLC grade ODCB (10 mL) was added MEM-N₃ (330 mg, 2.5 mmol, 14 equiv). The resulting mixture was stirred at 50 °C for 48 h under nitrogen. The crude product was chromatographed over a silica gel column (toluene as eluant) and concentrated to afford 67 mg of unreacted C₇₀ (45%) and 55 mg of a 7:3 mixture of **1** and **2** (32%; 60% based on consumed C₇₀). The isomers were separated by HPLC (semipreparative Cosmosil Buckyprep column, UV/326 nm, 50% CHCl₃, 50% hexane, 5 mL/min; retention times 21.82 and 23.82 min, respectively). **1**: UV/vis (toluene) λ_{max} 532, 462, 400, 340, 312, 286 nm; IR (DRIFT) 2912 (m), 2860 (m), 2816 (w), 1501 (m), 1457 (s), 1359 (w), 1258 (m), 1215 (w), 1143 (m), 1112 (s), 1070 (s), 1042 (s), 941 (w), 876 (w), 811 (m), 778 (w), 709 (m), 697 (m), 641 (m), 577 (m), 548 (w), 467 (w) cm⁻¹; ¹H NMR (CS₂/D₂O, 500 MHz) 6.02 (s, 2H), 3.89 (t, *J* = 4.8 Hz, 2H), 3.63 (t, *J* = 4.8 Hz, 2H), 3.39 (s, 3H) ppm; ¹³C NMR (CS₂/D₂O, 125 MHz) 153.9, 151.3, 151.1 (1C), 150.8, 150.7, 150.5, 150.4, 150.0, 149.6, 149.4,

149.2, 148.9, 148.6, 148.5, 148.0, 147.3, 147.2, 147.1 (1C), 146.9, 146.1, 146.0, 143.9, 143.7, 143.5, 143.2, 140.6, 140.3, 140.0, 138.0, 133.6, 133.4, 131.9, 131.2, 101.4 (bridgehead C), 78.0, 74.0 (bridgehead C), 72.2, 68.0, 59.0 ppm; -FAB-MS (chloroform/NBA) *m/z* 971 (M)⁺, 840 (C₇₀)⁺. **2**: UV/vis (toluene) λ_{max} 534, 462, 400, 382, 338, 312, 286 nm; IR (DRIFT) 2976 (m), 2904 (m), 1453 (m), 1444 (m), 1437 (s), 1374 (w), 1153 (m), 1120 (m), 1092 (m), 1070 (m), 1050 (m), 820 (w), 806 (w), 777 (w), 674 (w), 640 (w), 579 (w), 536 (w), 469 (w), 431 (w), 420 (m) cm⁻¹; ¹H NMR (CS₂/D₂O, 500 MHz) 5.51 (s, 2H), 3.66 (t, *J* = 4.8 Hz, 2H), 3.39 (t, *J* = 4.8 Hz, 2H), 3.18 (s, 3H) ppm; ¹³C NMR (CS₂/D₂O, 125 MHz) 155.1, 151.0, 150.7 (1C), 150.4, 150.3, 150.2, 150.1, 149.4, 148.9, 148.7, 148.2, 148.1, 147.3, 147.0, 146.9, 146.8, 146.7 (1C), 146.4, 145.6, 145.5, 143.6, 143.2, 143.1, 142.9, 140.1, 139.8, 139.4, 137.1, 133.2, 132.2, 131.6, 130.9, 130.8, 101.1 (bridgehead C), 77.2, 73.3 (bridgehead C), 71.6, 67.3, 58.4 ppm; -FAB-MS (chloroform/NBA), *m/z* 971 (M)⁺, 840 (C₇₀)⁺.

A General Procedure for the Decomposition of N-MEM-fulleretriazoline to N-MEM-azafulleroid and N-MEM-fulleroaziridine.

A dilute, degassed solution of triazoline **1** (10 mg, 10.3 μmol) in toluene (30 mL) was heated overnight at 80 °C under nitrogen with stirring. The disappearance of triazoline and the concomitant formation of three products, C₇₀ (5 mg, 64%), fulleroaziridine **4** (0.4 mg, 5%), and azafulleroid **5** (2 mg, 23%), were detected by TLC (toluene; silica gel). The fractions were collected after chromatography (toluene, silica gel), concentrated, and precipitated with hexane. The precipitate was centrifuged, washed with hexane (3 × 10 mL), and dried *in vacuo*. **[6,6]-(1-N-MEM-fulleroaziridine)-C₇₀ 4**: UV/vis (toluene) λ_{max} 574, 464, 378, 330, 286 nm; IR (DRIFT) 2948 (m), 2890 (m), 1477 (s), 1383 (m), 1315 (w), 1154 (s), 1119 (s), 1025 (w), 999 (w), 807 (m),

681 (w), 678 (w), 675 (m), 644 (w), 589 (m), 571 (w), 559 (w), 543 (w), 538 (m), 453 (w) cm^{-1} ; ^1H NMR ($\text{CS}_2/\text{D}_2\text{O}$, 500 MHz) 4.76 (s, 2H), 4.16 (t, $J = 4.8$ Hz, 2H), 3.68 (t, $J = 4.8$ Hz, 2H), 3.40 (s, 3H) ppm; ^{13}C NMR ($\text{CS}_2/\text{D}_2\text{O}$, 125 MHz): 153.9, 150.8 (1C), 150.7, 150.7, 150.1, 150.1, 148.9, 148.6, 148.6, 148.1, 148.0, 147.9, 147.5, 147.5, 147.1, 147.0, 146.6, 145.8 (1C), 145.6, 145.3, 143.7, 143.6, 143.4, 143.4, 143.0, 142.7, 142.2, 141.8, 140.9, 136.8, 132.9, 131.9, 130.5, 130.5, 130.4, 130.2, 127.2, 82.3, 79.7 (bridgehead C), 79.6 (bridgehead C), 72.1, 69.2, 58.6 ppm; $-\text{FAB-MS}$ (chloroform/NBA), m/z 943 (M^+), 841 (C_{70}^+). **[5,6]-(1-*N*-MEM-azafulleroid)- C_{70} 5:** UV/vis (toluene) λ_{max} 468, 392, 336, 288 nm; IR (DRIFT) 2969 (m), 2928 (m), 2889 (w), 1598 (w), 1578 (w), 1426 (m), 1446 (s), 1325 (w), 1244 (w), 1125 (s), 816 (m), 687 (m), 583 (m), 554 (m), 504 (m) cm^{-1} ; ^1H NMR ($\text{CS}_2/\text{D}_2\text{O}$, 500 MHz) 5.27 (s, 2H), 4.29 (t, $J = 4.8$ Hz, 2H), 3.77 (t, $J = 4.8$ Hz, 2H), 3.45 (s, 3H) ppm; ^{13}C NMR ($\text{CS}_2/\text{D}_2\text{O}$, 125 MHz) 151.8, 150.4, 149.8, 148.5, 148.3 (1C), 148.0, 147.8, 147.7, 147.5, 147.2, 147.0, 146.8, 146.0, 145.7, 144.8, 144.3, 144.1, 144.0, 143.9, 143.5, 143.3, 143.2, 142.7, 141.6, 139.6, 139.5, 136.5 (1C), 135.3, 134.8 (1C), 132.2, 132.2, 131.2, 130.9, 128.1, 128.0 (1C), 127.9, 84.8, 72.2, 68.4, 58.6 ppm; $-\text{FAB-MS}$ (chloroform/NBA) m/z 943 (M^+), 840 (C_{70}^+). **[5,6]-(1-*N*-MEM-azafulleroid)- C_{70} 6:** UV/vis (toluene) λ_{max} 468, 384, 340, 286 nm; IR (DRIFT) 2945 (m), 2890 (m), 1557 (w), 1442 (s), 1397 (w), 1108 (m), 809 (w), 688 (m), 650 (w), 631 (m), 581 (m), 561 (m), 531 (w), 459 (m) cm^{-1} ; ^1H NMR ($\text{CS}_2/\text{D}_2\text{O}$, 500 MHz) 4.95 (2H, AB, $\delta_{\text{A}} = 4.97$, $\delta_{\text{B}} = 4.92$, $J_{\text{AB}} = 9.5$ Hz), 4.02 (2H; dt, AB(M_2), $\delta_{\text{A}} = 4.02$, $\delta_{\text{B}} = 4.01$, $J_{\text{AB}} = 2$ Hz, $J_{\text{AM}} = J_{\text{BM}} = 5$ Hz), 3.61 (t, $J = 5$ Hz,

2H), 3.35 (s, 3H) ppm; ^{13}C NMR ($\text{CS}_2/\text{D}_2\text{O}$, 125 MHz) 154.2, 150.0, 149.6, 149.5, 149.2, 149.1, 148.7, 147.6, 147.58, 147.4, 147.35, 147.2, 147.1, 147.0, 146.9, 146.8, 146.7, 146.5, 146.4, 146.3, 146.26, 146.2, 145.7, 145.6, 145.2, 144.9, 144.0, 143.5, 143.4, 143.2, 143.1, 143.0, 142.6, 142.5, 142.3, 142.1, 141.7, 141.5, 140.7, 140.3, 139.9, 139.3, 138.6, 135.5, 134.5, 134.4, 134.3, 132.6, 130.9, 130.0, 129.6, 129.2, 128.8, 128.0, 127.6, 127.3, 126.7, 126.6, 125.5, 124.4, 123.2, 121.5, 82.7, 71.3, 67.3, 57.8 ppm; $-\text{FAB-MS}$ (chloroform/NBA) m/z 943 (M^+), 840 (C_{70}^+). **[6,6]-(1-*N*-MEM-fulleroaziridine)- C_{70} 7:** UV/vis (toluene) λ_{max} 450, 376, 316, 288 nm; IR (DRIFT) 2959 (m), 2920 (m), 2893 (m), 1462 (s), 1386 (w), 1156 (s), 1119 (m), 1092 (w), 1015 (w), 803 (m), 687 (w), 680 (w), 672 (m), 651 (m), 586 (m), 564 (w), 529 (w), 456 (w) cm^{-1} ; ^1H NMR ($\text{CS}_2/\text{D}_2\text{O}$, 500 MHz) 4.69 (s, 2H), 4.11 (t, $J = 4.6$ Hz, 2H), 3.70 (t, $J = 4.6$ Hz, 2H), 3.44 (s, 3H) ppm; ^{13}C NMR ($\text{CS}_2/\text{D}_2\text{O}$, 125 MHz) 151.9 (1C), 150.8, 149.4, 149.1 (1C), 148.5, 148.4, 148.2, 147.9, 147.8, 147.7, 147.1, 146.92 (1C), 146.86, 146.6, 146.6, 145.7, 145.5, 145.1, 144.6, 144.3, 144.1, 143.4, 142.2 (1C), 131.7, 131.4, 131.4, 130.8, 82.7, 73.5 (bridgehead C), 71.9, 69.0, 58.5 ppm; $-\text{FAB-MS}$ (chloroform/NBA), m/z 943 (M^+), 840 (C_{70}^+).

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