1,3-Dipolar Cycloaddition of *N*-Methylazomethine Ylide to C_{70}

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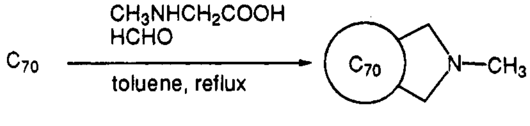
1,3-Dipolar cycloaddition of *N*-methylazomethine ylide to C_{70} affords a mixture of three isomeric monoadducts **1a–c**. The isomers were separated and appear to result from addition to 6,6-ring fusions of C_{70} at the 1,9-, 7,8-, and 22,23-bonds. Competition experiments indicate that C_{60} is slightly more than twice as reactive as C_{70} toward this reaction.

Organic chemical derivatization of fullerenes such as C_{60} and C_{70} by cycloaddition reactions has attracted intense interest from synthetic chemists. Although many derivatives of C_{60} have now been investigated,[1,2] only a few products of C_{70} have been isolated and characterized.[3] Unlike C_{60} where all carbons are equivalent, the elliptical C_{70} molecule poses unique regiochemical questions not raised with C_{60}. The lower symmetry of C_{70} gives rise to an array of distinct local substructures with potentially different reactivities at particular areas of the C_{70} fullerene surface. In C_{70}, 1,2-addition to two 6,6-ring fusion bonds closest to the poles (1,9- and 7,8-bond)[4] yields the lowest energy products by both theory and experiment,[5] suggesting that 1,9- and 7,8-bonds are the most reactive.

The 1,3-dipolar addition of azomethine ylides to C_{60} affording fulleropyrrolidines is an excellent and high-yield reaction of C_{60}.[6] In this paper, we report the first application of this reaction to C_{70} and the isolation and characterization of three isomeric pyrrolidines. The reaction was carried out by heating a mixture of *N*-methylglycine, paraformaldehyde, and C_{70} at 110 °C in toluene. After 2 h a mixture of *N*-methylfulleropyrrolidines monoadducts **1** was isolated in 45% yield after column chromatography.



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The presence of three distinct *N*-methyl resonances in the ^1H NMR of monoadducts **1** indicated three isomers **1a**, **1b**, and **1c** in a 46:41:13 ratio (Figure 1). Analysis of this monoadduct band by Buckyclutcher I HPLC[7] also suggested three components (Figure 2). These isomers were separated by semipreparative silica HPLC, and their electrospray ionization mass spectra (ESI-MS) confirmed that the three components are all *N*-methylpyrrolidine monoadducts of C_{70}.[8]

^1H NMR was used to assign the structure of isomers **1a–c**. Symmetry considerations proved critical in the correlation of ^1H NMR data with structure (Figure 3). The ^1H NMR spectrum of isomer **1a** is considerably simpler than the spectra of isomers **1b** and **1c**. Three singlets at δ 2.74, 3.58, and 3.92 in a 3:2:2 ratio are observed in the spectrum of **1a**, consistent with addition across the 1,9-bond. This structure has two nonequivalent methylenes with two equivalent hydrogens. One singlet at δ 2.60 and two doublets at δ 3.43 (J = 15.0 Hz) and 3.68 (J = 15.0 Hz) in a 3:2:2 ratio are observed in the spectrum of **1b**, consistent with addition across the 7,8-bond. This structure has two equivalent methylenes with two nonequivalent hydrogens coupled to each other. One singlet at δ 2.51 and four doublets at δ 2.27 (J = 1.0 Hz), 2.31 (J = 1.0 Hz), 3.99 (J = 1.2 Hz), and 4.04 (J = 1.2 Hz) in a 3:1:1:1:1 ratio are observed in the spectrum of **1c**, consistent with addition across the 22,23-bond. This structure has two nonequivalent methylenes with two nonequivalent hydrogens coupled to each other.

The chemical shifts of *N*-methyl resonances in **1a–c** are all downfield from typical aliphatic pyrrolidines (for example, δ 2.32 in *N*-methylpyrrolidine) because of ring currents on the surface of the C_{70} cage. It is interesting to compare the chemical shifts of the methyl resonances in the isomers **1**. The deshielding order of the methyl resonances is structure **1a** in which the methyl substituent is positioned the most closely over the apical region of C_{70}, structure **1b**, and structure **1c** in which the methyl substituent is positioned the most closely over the equatorial belt of C_{70}. This suggests that the influence

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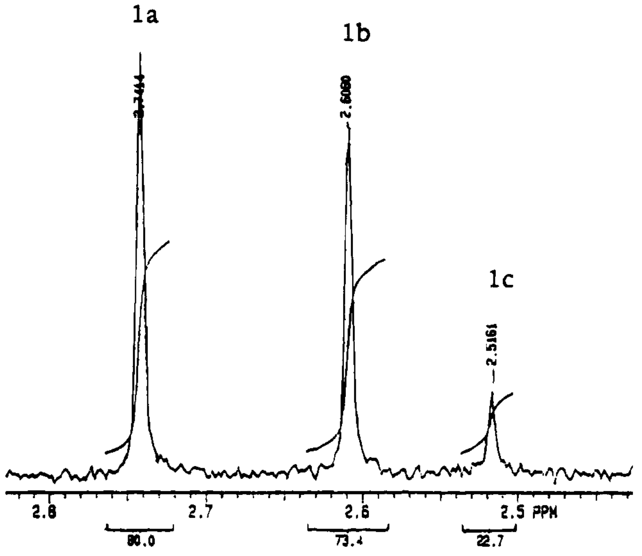


Figure 1. Methyl region of the ^1H NMR spectrum of the mixture of **1a−c**.

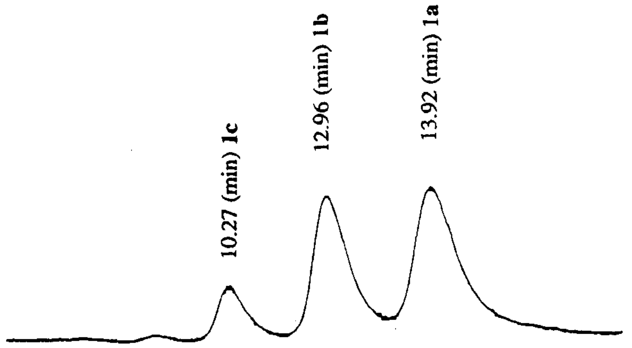
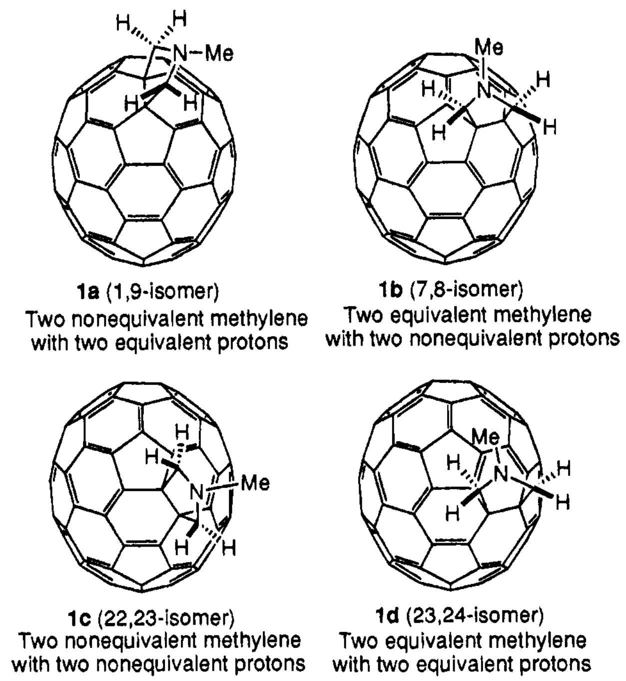


Figure 2. HPLC chromatogram of the mixture of isomeric monoadducts **1a−c**. Conditions: 250 x 4.6 mm Buckyclutcher I column, 40:60 hexane:toluene mobile phase (1 mL/min), 4 μL injection in toluene, UV/vis detection at 340 nm.



1a (1,9-isomer)
Two nonequivalent methylene
with two equivalent protons

1b (7,8-isomer)
Two equivalent methylene
with two nonequivalent protons

1c (22,23-isomer)
Two nonequivalent methylene
with two nonequivalent protons

1d (23,24-isomer)
Two equivalent methylene
with two equivalent protons

Figure 3. Symmetry-dependent NMR characteristics of the protons and skeletal pyrrolidine carbons for the four possible 6,6-isomers **1a−d**.

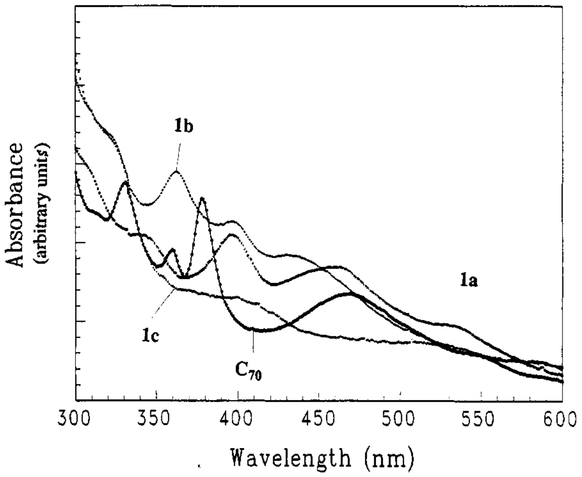


Figure 4. UV/vis spectra of C_{70} and **1a−c** in the 300−600 nm region. Relative intensities do not imply relative molar absorptivities.

of ring currents over the apical region of C_{70} is stronger than the influence of ring currents over the equatorial region of C_{70}. Deshielding on the surface of C_{70} may prove useful in the assignment of the structures of other C_{70} derivatives.

The UV/vis spectra (in CH_2Cl_2) of the three isomers (**1a, 1b,** and **1c**) are similar to that of C_{70} except for differences in the 300−600 nm region (Figure 4). The spectra for the 7,8- and 1,9-isomers **1a** and **1b** are in agreement with spectra recently reported by Cahill[9] for isomers of $C_{70}H_2$. This observation suggests that UV/vis spectra are also characteristic of the addition pattern and will be useful in future structure assignments.

There is some indication that C_{60} and C_{70} differ in their rates of reaction with certain species, although few common patterns of reactivity can be identified from the limited data available.[10] A competition experiment was carried out to establish the relative reactivity of C_{60} and C_{70} in the azomethine ylide addition reaction. A toluene solution of C_{60} and C_{70} (1:1) was heated at reflux with 1 equiv of sarcosine and 2 equiv of paraformaldehye. HPLC analysis of the reaction mixture indicates that the ratio for C_{60} and C_{70} is 32:68, virtually the same ratio of peak areas for C_{70} and C_{60} monoadducts. The product ratios are not time-dependent. Thus, for this reaction at least, C_{60} is approximately twice as reactive as C_{70}.

Most C_{70} reactions occur at the 1,9- and 7,8-bond. Ando et al.[11] recently proposed that the photocycloaddition of disilirane to C_{70} occurs across the equatorial 23,24-bond. To our knowledge, the structure proposed for **1c** is the

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first reported product of addition across the 22,23-bond in C_{70}. Thus, examples of all four possible addition modes are now found, although the 1,9- and 7,8-bonds are much more reactive than the 22,23- and 23,24-bonds.

Experimental Section

Preparation of 1a–c. A mixture of C_{70} (50 mg, 0.06 mmol), *N*-methylglycine (11 mg, 0.12 mmol), and parafomaldehyde (9 mg, 0.30 mmol) was heated at reflux in 75 mL of toluene under Ar for 2 h. The resulting brown solution was washed with water (2 × 50 mL), dried with Na_2SO_4, and concentrated in vacuo. The crude was purified by flash chromatography (silica gel, eluant toluene/triethylamine 100:1) affording 24 mg (45%) of monoadducts **1**. The monoadducts were separated using the semipreparative Econosil silica column (Altech) to produce **1a–c** (black solids), which were obtained in a 46:41:13 ratio.

1a. ^1H NMR (200 Hz, $CDCl_3/CS_2$): δ 3.92 (s, 2H), 3.58 (s, 2H), 2.74 (s, 3H); see spectrum 2 (supporting information). ESI-MS (TFA/toluene/MeOH) *m/z*: 898 ($M + H^+$); see spectrum 5 (supporting information). UV/vis (CH_2Cl_2): see Figure 4 in the text.

1b. ^1H NMR (200 Hz, $CDCl_3/CS_2$): δ 3.68 (d, $J = 15$ Hz, 2H), 3.43 (d, $J = 15$ Hz, 2H), 2.60 (s, 3H); see spectrum 3 (supporting information). ESI-MS (KOAc/toluene/MeOH) *m/z*: 1337 [$M + X + K^+$, X = C(Ph)Ph-18-crown-6, *m/e* for X = 401]; see spectrum 6 (supporting information). UV/vis (CH_2Cl_2): see Figure 4 in the text.

1c. ^1H NMR (200 Hz, $CDCl_3/CS_2$): δ 4.01 (d, $J = 1.2$ Hz, 1H), 3.99 (d, $J = 1.2$ Hz, 1H), 2.51 (s, 3H), 2.31 (d, $J = 1.0$, 1H), 2.27 (d, $J = 1.0$, 1H); see spectrum 4 (supporting information). ESI-MS (KOAc/toluene/MeOH) *m/z*: 1337 [$M + X + K^+$, X = C(Ph)Ph-18-crown-6, *m/e* for X = 401]; see spectrum 7 (supporting information). UV/vis (CH_2Cl_2): see Figure 4 in the text.

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Supporting Information Available: ^1H NMR spectra, ESI-MS spectra, and HPLC chromatograms (10 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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