

Energetic Preference in 5,6 and 6,6 Ring Junction Adducts of C₆₀: Fulleroids and Methanofullerenes

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The reaction of organic diazo compounds with C₆₀ is a versatile approach to fullerene functionalization.^{2–4} In the early publications, it was suggested that all diazomethane addition products had structure 3 (Figure 1). In this publication, employing a combination of spectroscopic techniques and MNDO calculations, we show (1) that the initial product of addition is a mixture of methanofullerene⁵ (1) and methanoannulene⁶ (fulleroid)⁵ (4) isomers^{7–14} and (2) that the lowest energy isomer of substituted

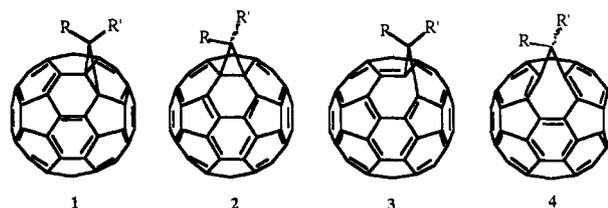
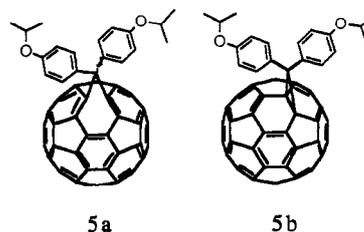


Figure 1. The four possible isomers from single addition of a diazomethane to C₆₀.

phenyldiazomethane and substituted diphenyldiazomethane addition has the structure 1.

The new structural assignments are based on the following: (a) the total number of ¹H and ¹³C resonances (for R = R') to distinguish between 5,6 (2, 4) and 6,6 (1, 3) junctions (5,6 junction = C_s and 6,6 junction = C_{2v} symmetry, respectively), (b) the assumption that chemical shifts of the bridgehead carbons for methanofullerenes (1 and 2) and fulleroids (3 and 4) appear in the δ 70–90 and 110–160 regions, respectively, and (c) the use of diagnostic 2D proton-detected ¹H–¹³C HETCOR spectroscopy.⁸

The R = R' (Figure 1) case was investigated with the adduct 5. Three different paradisubstituted benzene rings (in 2:2:1 ratio) are observed in the ¹H NMR spectrum of chromatographically pure 5.⁹ Based on the detection of NOE interactions between the respective ortho protons, two patterns (in fixed 1:1 ratio) are part of the same molecule. For this isomer, a number of ¹³C low-field resonances of the product mixture (32 from the fullerene sphere and 8 from the benzene rings) support the fulleroid structure with a 5,6 junction (5a, bridge carbon at δ 64.02). Heating the



mixture converted it quantitatively to the other, already present, isomer. The latter showed only one para-disubstituted benzene system and one 2-propoxy moiety in its ¹H NMR spectrum. The ¹³C NMR spectrum exhibited 16 fullerene sphere and 4 benzene ring resonances, one resonance at δ 79.58 (bridgehead), and 3 aliphatic resonances (bridge carbon at δ 57.35). This pattern is unambiguously diagnostic for a symmetric structure with a 6,6 junction (5b, above).

Next, we investigated the R ≠ R' case (Figure 1) with two unsymmetrical diazomethane adducts. Assuming (on the basis of MNDO level¹⁰ calculations) an energetic preference for isomers 1 and 4, at most three products can be anticipated. Indeed, the ¹H NMR spectrum of the chromatographically pure (*p*-methoxyphenyl)diazomethane addition product revealed three distinct isomers (in 4:2:1 ratio).

(11) The pulse sequence was "tuned" for a coupling constant $J_{CH} = 5$ Hz so that almost all correlations between protons and carbons 1, 2, or 3 bonds away could be identified.

(12) While the possibility of a methanofullerene–fulleroid equilibrium cannot be ruled out a priori, it was not observed for C₆₁H₂ (Smith, A. B., III; Strongin, R. M.; Brard, L.; Furst, G. T.; Romanow, W. J.; Owens, K. G.; King, R. C. *J. Am. Chem. Soc.* 1993, 115, 5829). No significant change was observed in the ¹³C spectra of our compounds in the –60/+20 temperature interval. Cf.: Günther, H.; Schmickler, H.; Bremser, W.; Straube, F. A.; Vogel, E. *Angew. Chem., Int. Ed. Engl.* 1973, 12, 570.

(13) Pasquarello, A.; Schluter, M.; Haddon, R. C. *Science* 1992, 257, 1660.

(14) A third species, detected in a very small amount, could not be characterized.

(1) ERASMUS Visting Student from the University of Innsbruck, Austria.
(2) Suzuki, T.; Li, Q.; Khemani, K. C.; Wudl, F.; Almarsson, O. *Science* 1991, 254, 1186.

(3) (a) Wudl, F. *Acc. Chem. Res.* 1992, 25, 157. (b) Suzuki, T.; Li, Q.; Khemani, K. C.; Wudl, F. *J. Am. Chem. Soc.* 1992, 114, 7300. (c) Suzuki, T.; Li, Q.; Khemani, K. C.; Wudl, F. *J. Am. Chem. Soc.* 1992, 114, 7301. (d) Shi, S.; Li, Q.; Khemani, K. C.; Wudl, F. *J. Am. Chem. Soc.* 1992, 114, 10656.

(4) For other examples of stable single organic C₆₀ derivatives, see: (a) Fagan, P. J.; Krusic, P. J.; Evans, D. H.; Lerke, S.; Johnston, E. *J. Am. Chem. Soc.* 1992, 114, 9697. (b) Hoke, S. H., II; Molstad, J.; Dilettato, D.; Jay, M. J.; Carlson, D.; Kahr, B.; Cooks, R. G. *J. Org. Chem.* 1992, 57, 5069. (c) Vasella, A.; Uhlmann, P.; Waldruff, C. A. A.; Diederich, F.; Thilgen, C. *Angew. Chem., Int. Ed. Engl.* 1992, 31, 1388. (d) Hirsch, A.; Soi, A.; Karfunkel, H. R. *Angew. Chem., Int. Ed. Engl.* 1992, 31, 766. (e) Morton, J. R.; Preston, K. F.; Krusic, P. J.; Hill, S. A.; Wasserman, E. *J. Am. Chem. Soc.* 1992, 114, 5454. (f) Birkett, P. R.; Hitchcock, P. B.; Kroto, H. W.; Taylor, R.; Walton, D. R. M. *Nature* 1992, 357, 479. (g) Creegan, K. M.; Robbins, J. L.; Robbins, W. K.; Millar, J. M.; Sherwood, R. D.; Tindall, P. J.; Cox, D. M.; Smith, A. B., III; McCauley, J. P., Jr.; Jones, D. R.; Gallagher, R. T. *J. Am. Chem. Soc.* 1992, 114, 1103. (h) Elmes, Y.; Silverman, S. K.; Sheu, C.; Kao, M.; Foote, C. S.; Alvarez, M. M.; Whetten, R. R. *Angew. Chem., Int. Ed. Engl.* 1992, 31, 351. (i) Rubin, Y.; Khan, S.; Freedberg, D. I.; Yeretzian, C. *J. Am. Chem. Soc.* 1993, 115, 344. (j) Belik, P.; Gügel, A.; Spickermann, J.; Müllen, K. *Angew. Chem., Int. Ed. Engl.* 1993, 32, 78. (k) Prato, M.; Li, Q.; Wudl, F.; Lucchini, V. *J. Am. Chem. Soc.* 1993, 115, 1148–1150. (l) Prato, M.; Suzuki, T.; Foroudian, H.; Li, Q.; Khemani, K. C.; Wudl, F.; Leonetti, J.; Little, R. D.; White, T.; Rickborn, B.; Yamago, S.; Nakamura, E. *J. Am. Chem. Soc.* 1993, 115, 1594–1595.

(5) In conformity with recent IUPAC rules, the terms *methanofullerene* and *fulleroid* are used to indicate the ring-closed (cyclopropane) and ring-open (methanoannulene) structures, respectively, of C₆₀ derivatives.

(6) Vogel, E. *Pure Appl. Chem.* 1982, 54, 1015.

(7) In the case of unsubstituted diphenyldiazomethane or phenyldiazomethane addition, three isomers are observed in the isolated product of monoaddition (see below and refs 2 and 3a, above). The third isomer is a very minor one which, so far, has eluded isolation and characterization.

(8) Otting, G.; Wütherich, J. *J. Magn. Reson.* 1988, 76, 569.

(9) Please refer to supplementary material.

(10) *Spartan 2.1* program running on an IBM RS/6000 workstation.

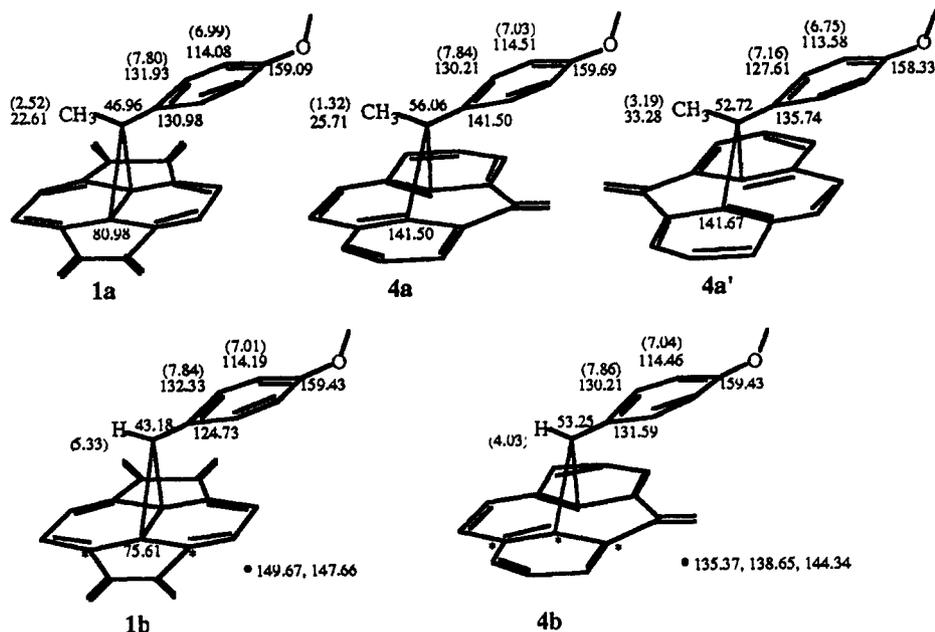


Figure 2. Chemical shifts of addition products of (*p*-methoxyphenyl)diazoethane (**1a**, **4a**, and **4a'**) and (*p*-methoxyphenyl)diazomethane (**1b**, **4b**) to C_{60} . The 1H NMR shifts are in parentheses.

The inseparable mixture was subjected to HETCOR analysis.¹¹ Inspection of the connection nets allowed the 1H (in parentheses) and ^{13}C assignments reported in Figure 2 (partial structures **1a**, **4a**, **4a'**, only the relevant moiety of the C_{61} molecule is drawn). In one isomer the methyl proton resonance at δ 2.52 correlates with the fullerene carbon resonance at δ 80.98, providing corroborating evidence for a methanofullerene structure for this compound. In the other two isomers, the bridgehead carbons resonate in the low-field region, supporting fulleroid structures.¹² Theoretically, strong paramagnetic currents flow within the 5-membered rings in buckminsterfullerene, while weaker diamagnetic currents are associated with 6-membered rings.¹³ These currents, albeit reduced, may be operative within the homorings of the structures **4a** and **4a'** and offer a rationale for the observed chemical shifts and the proposed stereochemistry. Upon refluxing overnight in toluene, the mixture converged cleanly to the methanofullerene **1a**.

Two major isomers (in 1:1 ratio) were found in the NMR spectrum of the (*p*-methoxyphenyl)diazomethane adduct.¹⁴ The HETCOR analysis (Figure 2, structures **1b** and **4b**) shows a correlation between the methine 1H resonance at δ 5.33 and the ^{13}C resonance at δ 75.61. The assignment of the methanofullerene structure **1b** to this compound is strengthened by the observed methine $^1J_{CH} = 163.7$ Hz, typical of cyclopropane rings.¹⁵ For the other isomer, the methine 1H resonance at δ 4.03 ($^1J_{CH} = 142.0$ Hz, characteristic of open 1,6-methano[10]annulenes¹⁵)

couples only with four ^{13}C low-field resonances (one of them correlates also with phenyl protons). This result, combined with UV-vis spectroscopy (identical to C_{60}) and spectroscopic similarities with the homolog **4a** point to the fulleroid **4b** structure for this isomer. Heating the mixture produced **1b** quantitatively.

The energetic preference observed in 5,6 and 6,6 adducts appears to be governed by the general propensity of buckminsterfullerene and fullerene derivatives for structures with the greatest number of doubly bonded 6,6 junctions (as in **1** and **4**), which also implies the greatest number of 5-radialene rings.¹⁶ We are actively pursuing the addition reaction mechanism and rearrangements as well as computations.

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Supplementary Material Available: Detailed experimental procedures and analytical data with copies of 1H and ^{13}C NMR spectra of the mixtures and of the single-component heated samples (23 pages). Ordering information is given on any current masthead page.

(15) Arnz, R.; Carneiro, J. W. M.; Klug, W.; Schmickler, H.; Vogel, E.; Breuckmann, R.; Klärner, F.-G. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 683.

(16) (a) Kroto, H. W. *Nature* **1987**, *329*, 529. (b) Taylor, R. *Tetrahedron Lett.* **1991**, *32*, 3731. (c) Matsuzawa, N.; Dixon, D. A.; Fukunaga, T. *J. Phys. Chem.* **1992**, *96*, 7594.