Pergamon

SCIENCE DIRECT®

Tetrahedron Letters 44 (2003) 8649–8652

TETRAHEDRON
LETTERS

# Functionalization of azafullerene $C_{59}N$. Radical reactions with 9-substituted fluorenes

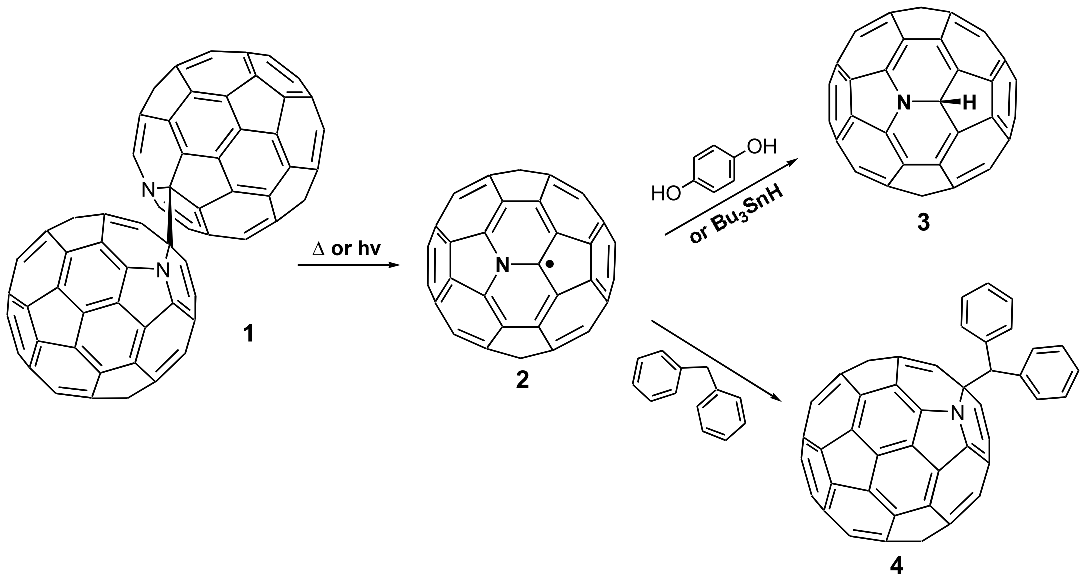
Georgios C. Vougioukalakis and Michael Orfanopoulos*

*Department of Chemistry, University of Crete, 71409 Iraklion, Crete, Greece*

Received 24 July 2003; revised 11 September 2003; accepted 19 September 2003

**Abstract**—An efficient reaction between the azafullerene dimer, $(C_{59}N)_2$ and 9-substituted fluorenes leads to the formation of four new azafullerene monoadducts.

Heterofullerenes together with exohedral and endohedral fullerene derivatives constitute the three basic groups of modified fullerenes. To date, the only known heterofullerene that can be synthesized in gram quantities as a pure substance, is azafullerene $C_{59}N$, which was isolated and characterized for the first time by Wudl and co-workers as its dimer, $(C_{59}N)_2$.[1] Soon thereafter the group of Hirsch reported an alternative synthetic route.[2] The dimeric nature of the compound hinders typical fullerene reactions that can take place at the heterofullerene core, because of the large number of possible isomeric products. However, Hirsch and co-workers isolated a tetrachlorinated azafullerene, which contains a pyrrole moiety in the fullerene cage,[3] as well as highly functionalized dimeric azafullerenes involving an octahedral $C_s$ symmetrical addition pattern.[4] Monomeric substitution products, where one azafullerene sphere ($C_{59}N$) is replaced by a substituent, can be synthesized after the thermal or photochemical homolytic cleavage of the interdimer C–C bond, which



**Scheme 1.** Reactions of azafullerene radical **2**.

---

*Keywords*: azafullerenes; radical reactions; fluorenes.

* Corresponding author. Fax: +30-2810-393601; e-mail: orfanop@chemistry.uoc.gr

0040-4039/$ - see front matter © 2003 Published by Elsevier Ltd.
doi:10.1016/j.tetlet.2003.09.158

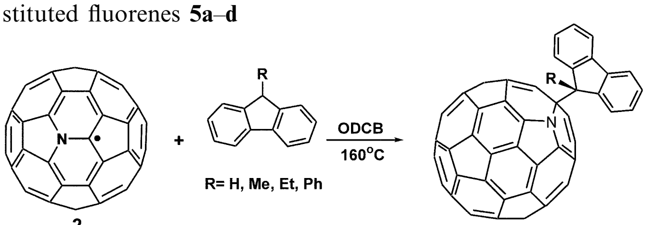
is relatively weak (18 kcal/mol).[5] When the thermal homolysis of the azafullerene dimer is followed by oxidation of the azafullerene radical $C_{59}N^{\bullet}$ to the azafulleronium cation $C_{59}N^+$, monomeric adducts with electron rich aromatics,[6] carbonyl compounds,[7] alcohols and olefins,[8] can be isolated. The proposed mechanism of these functionalizations involves nucleophilic trapping of the $C_{59}N^+$ cation by the corresponding nucleophile.

The first two reported azafullerene derivatives, both produced by trapping the azafullerene radical **2**, are the hydroazafullerene $C_{59}HN$ (**3**)[9] and the diphenylmethane adduct $C_{59}(CHPh_2)N$ (**4**),[10] shown in Scheme 1. To the best of our knowledge, these are the only isolated and characterized azafullerene adducts to date, whose formation involves a radical mechanism.

In our effort to study further the mechanism of this reaction by deuterium isotope effect measurements, we observed that apart from diphenylmethane,[10] none of its alkylated derivatives reacted with the azafullerene dimer. However, the corresponding fluorene alkyl derivatives, which are structurally similar to diphenylmethane, reacted smoothly with this compound.

Here we report an efficient preparation and characterization of four new azafullerene adducts **6a–d** (Table 1) by the thermal reaction between the azafullerene radical and: 9*H*-fluorene (**5a**), 9-methyl-9*H*-fluorene (**5b**), 9-ethyl-9*H*-fluorene (**5c**) and 9-phenyl-9*H*-fluorene (**5d**). Substituted fluorenes **5b–d** were synthesized quantitatively by reduction of the corresponding alcohols with the etherated boron trifluoride-triethylsilane system[11] (Scheme 2). Substrate **5a** is commercially available.

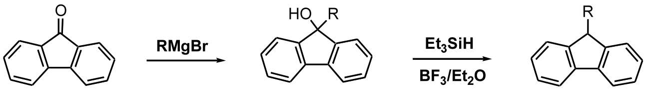
**Table 1.** Reactions of the azafullerene radical **2** with substituted fluorenes **5a–d**



**2** **5a-5d** **6a-6d**

| Adduct | R | Yield (%)[a] | Reaction time (h) |
|---|---|---|---|
| **6a** | H | 41 | 9 |
| **6b** | Me | 30 | 8 |
| **6c** | Et | 35 | 6 |
| **6d** | Ph | 20 | 4 |

[a] Based on the amount of isolated adduct.

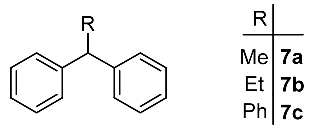


R= Me, Et, Ph **5b-5d**

**Scheme 2.** Synthesis of substituted fluorenes **5b–d**.

Substituted azafullerenes **6a–d** were obtained by the reaction of the azafullerene radical **2** with the corresponding fluorenes **5a–d** (Table 1). In a typical experiment, 300 equiv. of the substituted fluorene were added to a degassed (5 vacuum/argon cycles) solution of 1 (20 mg) in 40 ml HPLC grade 1,2-dichlorobenzene (ODCB). The mixture was heated at 160°C for 4–9 h under argon and the reaction was monitored by HPLC, equipped with a Separon C18 reverse phase column, at 326 nm. After distillation of ODCB, the crude mixture was washed 4–6 times with acetonitrile and/or acetone (centrifugation) in order to remove the remaining fluorene. Flash chromatographic purification on $SiO_2$ using hexane as eluent (the crude reaction mixture was loaded with $CS_2$), afforded **6a–d** as black solids (yields 20–41%, as shown in Table 1). The remaining azafullerene dimer elutes first, followed by the more polar, green colored azafullerene adducts **6a–d**. All adducts were characterized by $^1H$ NMR, $^{13}C$ NMR, COSY and HMQC experiments, as well as with UV-VIS, FT-IR spectroscopy and mass spectrometry. A representative $^1H$ NMR spectrum of the adduct between the azafullerene radical 2 and 9-methyl-9*H*-fluorene is presented in Figure 1. The assignment of the aromatic hydrogen absorptions of the azafullerene adducts was based on the COSY and HMQC experiments. In Figure 2 the $^{13}C$ NMR spectrum of **6c** is also presented, which like all the adducts **6a–d**, shows a similar absorption pattern to those previously reported for other azafullerene adducts.[12]

The solutions of adducts **6a–d** are green and their UV-VIS spectra are identical to that of $(C_{59}N)_2$. These adducts, as well as all the azafullerene monoadducts reported so far, have characteristic absorptions at 380, 450, 595, 730 and 817 nm. The FT-IR spectra of **6a–d** are also very similar with strong characteristic absorptions at 524 and 1510 $cm^{-1}$.



**Scheme 3.** Substituted diphenylmethanes **7a–c**.

It is worth mentioning here that diphenylmethane reacts slower than fluorene with the azafullerene radical. For example after 48 h heating at 180°C the reaction with diphenylmethane gave the adduct in 42% yield, whereas in the case of fluorene the same yield was obtained only after 9 h heating at 160°C. However, substituted diphenylmethanes **7a–c** (Scheme 3), which are structurally similar to the corresponding fluorenes **6a–c**, gave no adducts with azafullerene under the same experimental conditions. Instead, progressive decomposition of the azafullerene dimer was observed and no further investigation of its fate was attempted. Apparently, the observed dramatic change in reactivity

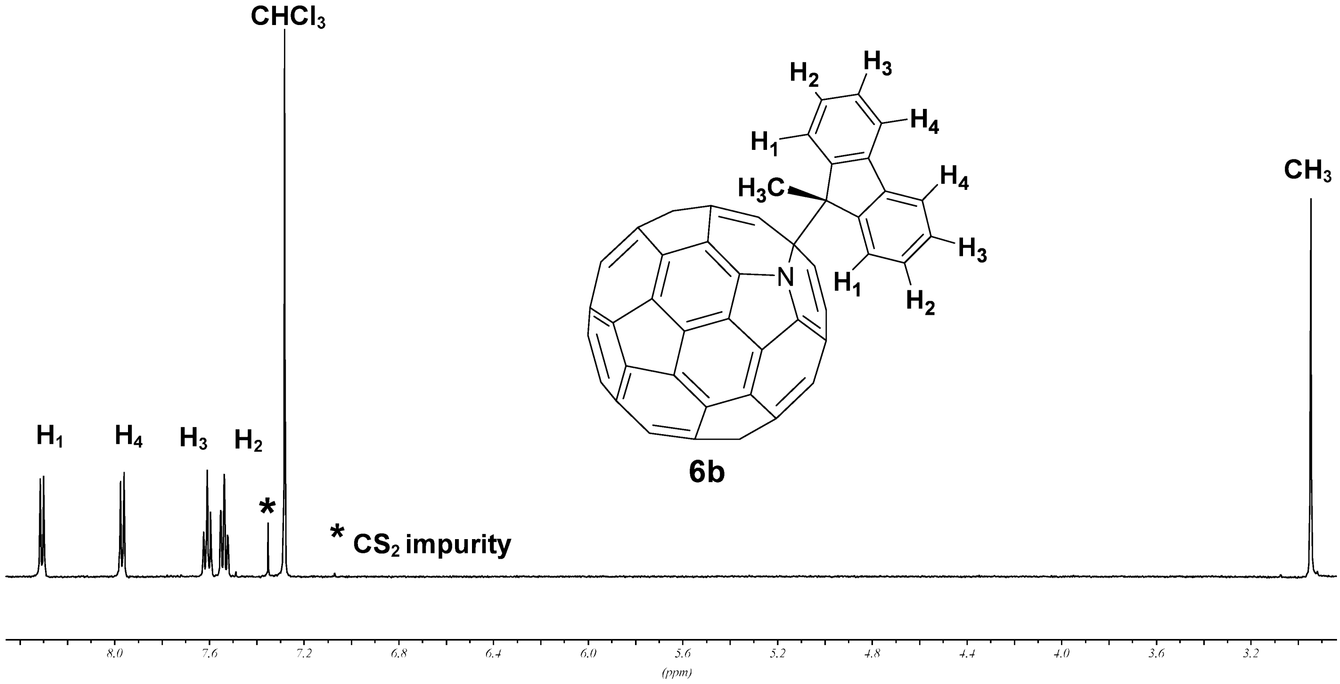


**Figure 1.** 500 MHz $^{1}$H NMR spectrum of the azafullerene adduct **6b** in $CDCl_3/CS_2$.

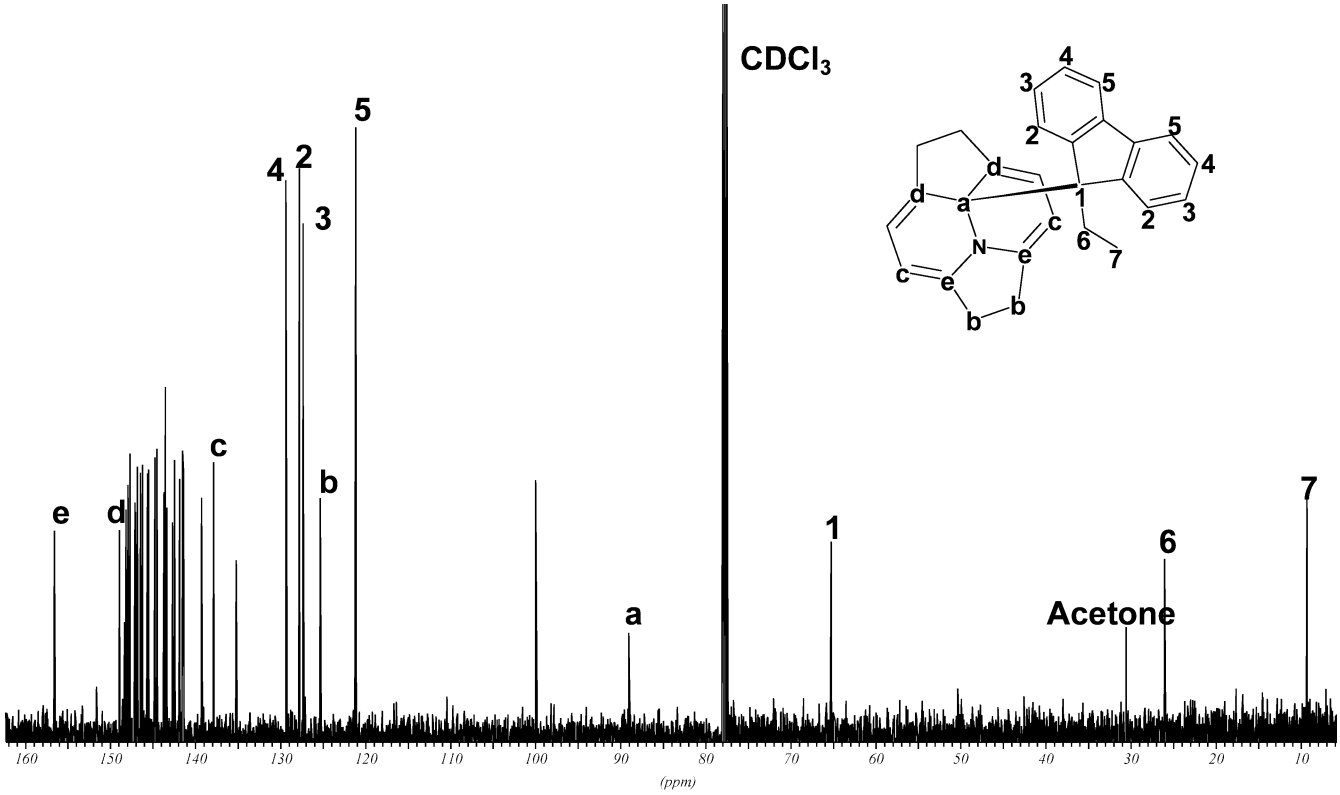


**Figure 2.** 125 MHz $^{13}$C NMR spectrum of the azafullerene adduct **6c** in $CDCl_3/CS_2$.

between fluorenes and the corresponding diphenylmethanes towards azafullerene, may be due to the rigid planar structure of fluorenes. The methine hydrogen abstraction to form the substituted fluorene radical is much easier than the corresponding abstraction from the substituted diphenylmethane, where free rotation of the phenyl rings sterically hinders the attack of the azafullerene radical to the benzylic hydrogen.

In conclusion, the reaction between the azafullerene radical and substituted fluorenes **5a**–**d** is particularly valuable because easily separable, well defined monoadducts are obtained. Unlike fluorenes, the structurally similar substituted diphenylmethanes show minimal, if any, reactivity towards azafullerene radicals. Investigations on the mechanistic aspects of this reaction are currently underway.

## Acknowledgements

G.C.V. thanks Professor K. Prassides for financial support during his three months stay at Sussex University on a Socrates-Erasmus research graduate program, as well as the Greek National Scholarships Foundation (IKY) for a research fellowship. M.O. thanks the British Council and the Greek Ministry of Education for financial support during his visit to Sussex University (Greek-United Kingdom collaborative scientific visit under cultural programme, 2003). He also thanks Professor K. Prassides for his generous hospitality. The FAB-MS were taken at Michigan State University by Professor J. Allison who is gratefully acknowledged.

## References

1. Hummelen, J. C.; Knight, B.; Pavlovich, J.; Gonzalez, R.; Wudl, F. *Science* **1995**, *269*, 1554–1556.
2. Nuber, B.; Hirsch, A. *Chem. Commun.* **1996**, 1421–1422.
3. Reuther, U.; Hirsch, A. *Chem. Commun.* **1998**, 1401–1402.
4. Hauke, F.; Hirsch, A. *Chem. Commun.* **2001**, 1316–1317.
5. Andreoni, W.; Curioni, A.; Holczer, K.; Prassides, K.; Keshavarz, K. M.; Hummelen, L. C.; Wudl, F. *J. Am. Chem. Soc.* **1996**, *118*, 11335–11336.
6. Nuber, B.; Hirsch, A. *Chem. Commun.* **1998**, 405–406.
7. Hauke, F.; Hirsch, A. *Chem. Commun.* **1999**, 2199–2200.
8. Hauke, F.; Hirsch, A. *Tetrahedron* **2001**, 3697–3708.
9. Keshavarz, K. M.; Gonzalez, R.; Hicks, R. G.; Srdanov, G.; Srdanov, V. I.; Collins, T. G.; Hummelen, J. C.; Bellavia-Lund, C.; Pavlovich, J.; Wudl, F.; Holczer, K. *Nature* **1996**, *383*, 147–150.
10. Bellavia-Lund, C.; Gonzalez, R.; Hummelen, J. C.; Hicks, R. G.; Sastre, A.; Wudl, F. *J. Am. Chem. Soc.* **1997**, *119*, 2946–2947.
11. Orfanopoulos, M.; Smonou, I. *Synth. Comm.* **1988**, *18*, 833–839.
12. Bellavia-Lund, C.; Keshavarz, K. M.; Collins, T.; Wudl, F. *J. Am. Chem. Soc.* **1997**, *119*, 8101–8102.