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# Multifullerene compounds involving 2,5-dimethoxycarbonylpyrrolidinofullerene, from dumbbells to star shaped tris-, tetrakis- and hexakisfullerenes

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**Abstract**—The monoamidated derivative of 2,5-dimethoxycarbonylpyrrolidinofullerene with sebacoyl chloride can be attached to various multifunctional amines and alcohols to form multifullerene compounds. 

The synthesis of compounds with multifullerene cages has attracted great attention because of their unique structures and properties. Much progress has been made in the past few years. A number of $C_{60}$ dimers and dumbbell fullerene derivatives have been prepared.[1] Compared with the bisfullerenes, compounds with three or more $C_{60}$ subunits are still relatively rare. Diederich's group reported trimeric and tetrameric acetylenic macrocycles with three and four appended $C_{60}$ moieties.[2] Recently, Nierengarten et al. prepared a series of fullerene-containing dendrimers.[3] Almost all the known multifullerene compounds with more than two $C_{60}$ cages are derived from methanofullerenes involving the Bingel reaction. Pyrrolidinofullerene and methanofullerene are the two most frequently used fullerene derivatives in the investigation of potential applications of fullerenes.[4] In contrast to its wide application in many other areas, to our knowledge, pyrrolidinofullerene has not been applied to the synthesis of multifullerenes except the dumbbells.[1,5]

We have reported photochemical reactions between amino acid esters and $C_{60}$, which give pyrrolidinofullerenes such as 2,5-dimethoxycarbonylpyrrolidinofullerene **1** in high yield.[6] Compound **1** reacts with an excess of sebacoyl chloride to give the monoacylated sebacoyl acid derivative **2** quantitatively.[7] As a continuation of this work, we here report the synthesis of bis-, tris-, tetrakis- and hexakisfullerene compounds derived from **2**.

In the presence of DCC and BtOH compound **2** reacts with excess **1** to give **3**. Similarly, compounds with multifunctional bridging groups react with **2** to give multifullerene compounds, see Scheme 1. The bridging group, 1,2,3,4,5,6-hexakis(aminoethylsulfanylmethyl)benzene in **9** was prepared according to a procedure similar to the literature method.[8] The reaction time for assembly varies from four days for the bisfullerenes to three weeks for the hexakisfullerene. The major by-products of the reactions are unreacted **2** and dark materials stuck on the silica column. If commercial chloroform, which contains ethanol as the stablizer, is used directly as the eluent, unreacted **2** reacts with the ethanol to form the corresponding ethyl ester. This indicates that the carboxylic acid group of **2** is very reactive. Yields of the reaction range from 26% for **9** to 45% for **6**.[9] The solubility of the compounds decreases from more than 80 mg/mL for the bisfullerenes to about 10 mg/mL for the hexakisfullerene **9** in chloroform.

The composition of the acylated pyrrolidinofullerenes is established by elemental analysis and MALDI-TOF mass spectra. Most of the MALDI-TOF mass spectra show the molecular ion plus a sodium atom as the base

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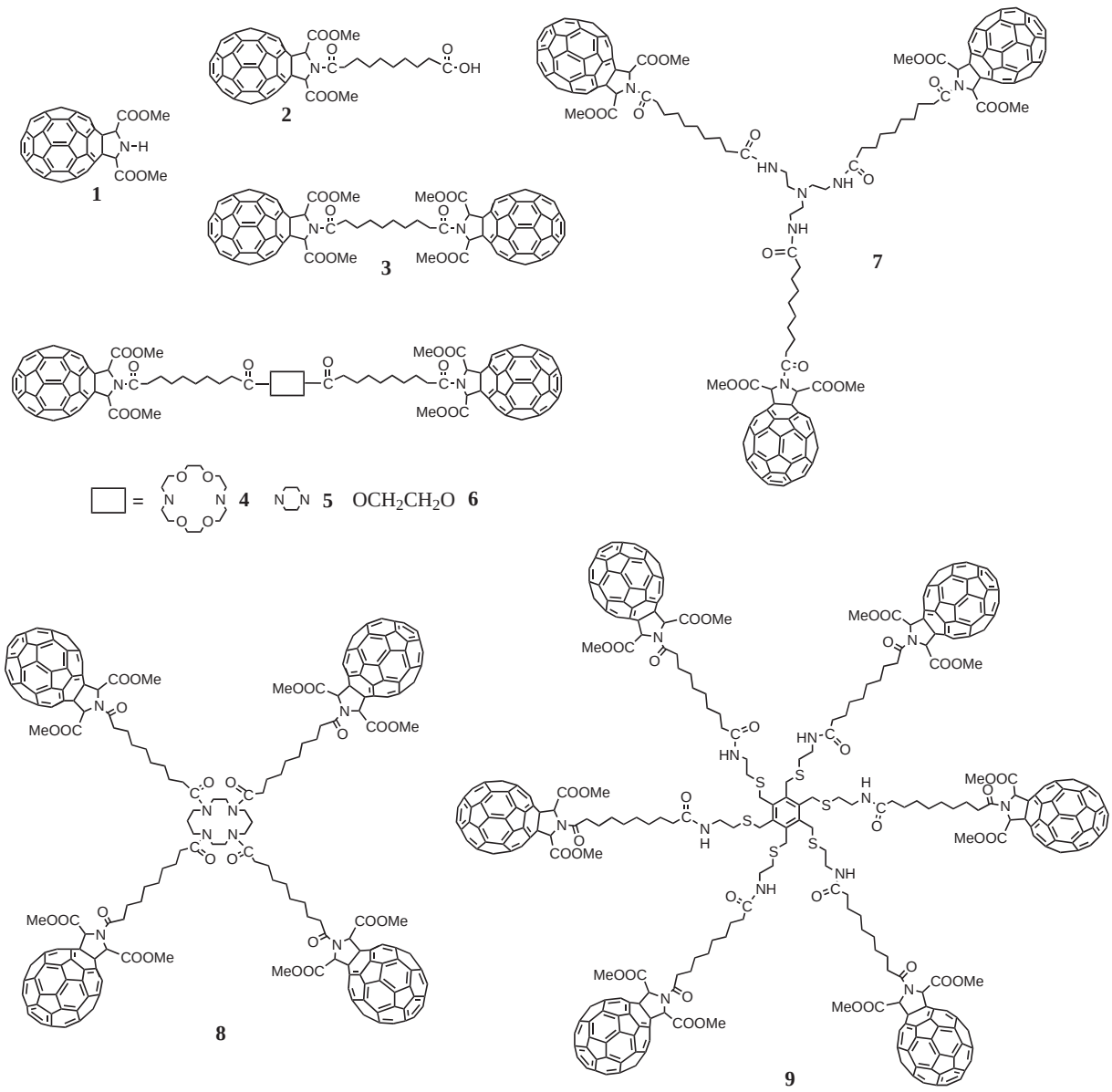


**Scheme 1.**

peak or at least a very strong peak. In the $^{13}C$ NMR spectra the fullerene carbons of all the multifullerenes are similar in terms of both their chemical shifts and number of signals. This indicates that the different bridges have no noticeable effect on the distant $C_{60}$ cage. The starting material **1** was previously assigned as the 2,5-*trans* isomer.[6] The present data suggest that the new products are not mixtures of 2,5-*cis*- and 2,5-*trans*-isomers since only one set of NMR signals are observed. But the data does not give conclusive information about the formation of diastereoisomers because of the weak interactions among the well-separated fullerene fragments, nor does it allow the assignment of the relative positions of the two methoxycarbonyl groups at the 2,5-positions due to overlapping $^{13}C$ NMR signals.

The $^{1}H$ NMR data indicates that steric hindrance increases as the number of $C_{60}$ cages increases in the molecule. The spectra of the bisfullerenes are well resolved. For the trisfullerene **7**, the three ethylene groups attached to the central nitrogen show broad signals at rt, while the other parts of the molecule still exhibit the same pattern as those of the bisfullerenes. For the tetrakisfullerene **8** all the signals are broad at rt, especially those of the azacrown and groups close to it. At 50°C, the methoxy and the methyne groups become sharp and the $CH_2$ adjacent to the $C_{60}$ becomes a clear triplet, all of which are at the less crowded outer edge of the molecule. The other groups remain broad. This indicates that the steric hindrance mainly originates from the center of the molecule. Heating the solution to 100°C did not produce any further change. For the hexakisfullerene **9** all the signals are broad at rt. At 50°C, the $CH_2$ adjacent to $C_{60}$ becomes a broad but recognizable triplet. MM2 modeling confirms that the center of the molecule is crowded but the $C_{60}$ cages are well separated from each other for these molecules.

**Table 1.** Electrochemical[a] and Langmuir film parameters. Values for $(E_pa+E_pc)/2$ (V) (versus $Fc/Fc^+$), $\Delta E_p$ (mV) (in parentheses), $n_p$ and limiting areas ($Å^2$) are given

| Compound | Reduction | | | | | Limiting area |
|---|---|---|---|---|---|---|
| | $E_1$ | $n_p$[d] | $E_2$ | $E_3$ | $E_4$ | |
| **2** | −1.01 (54) | | −1.42 (80) | −1.99 (79) | −2.45 (89) | 102 |
| **4** | −1.05 (83) | | −1.47 (98) | −2.07 (65) | −2.43 (95) | 177 |
| | −1.15 (74)[b] | 1.8 | −1.48 (120)[b] | | | |
| **6** | −1.05 (54) | | −1.45 (97) | −2.03 (53) | −2.48 (76) | 225 |
| | −1.09 (95)[b] | 2.0 | −1.47 (96)[b] | | | |
| **7** | −1.14 (105)[b] | 3.5 | −1.51 (133)[b] | | | 289 |
| **8** | −1.17[b,c] | 4.1 | −1.6[b,c] | | | 346 |
| **9** | −1.19 (120)[b] | 5.2 | | | | 509 |

[a] Cyclic voltammetry measurements: micro gold electrode, degassed toluene:acetonitrile = 4:1, 0.1 M $Bu_4NPF_6$, scan rate 1 V/s for **2**, **4**, **6** and 40 V/s for **7**–**9**.

[b] In degassed $CHCl_3$.

[c] Irreversible process, only $E_pc$ is observed.

[d] Number of electrons for the first wave, estimated error ±1.

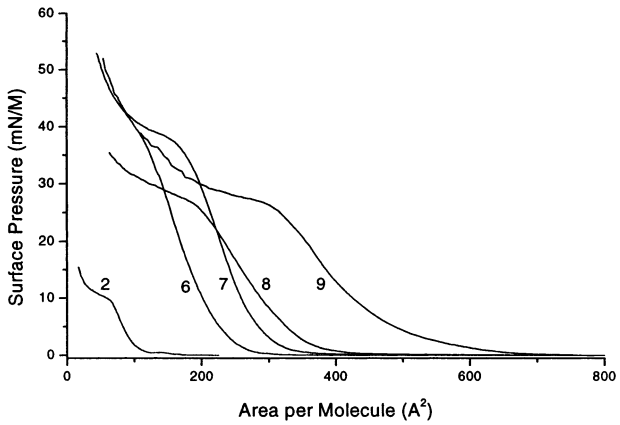


**Figure 1.** Area/pressure isotherms of the fullerene derivatives.

These temperature dependent NMR spectra effectively rule out the possibility that the broadness of the signals of the multifullerene derivatives is due to mixtures of 2,5-*cis*- and 2,5-*trans*-isomers.

The cyclic voltammograms show that the pyrrolidinofullerenes in the multifullerenes are independent. The redox potentials in Table 1 are virtually the same from the monofullerene **2** to the hexakisfullerene **9**. There is little interaction among the $C_{60}$ substituents. The number of electrons $n_p$ for the first wave (Table 1) can be estimated by using the Bard and Anson equation.[10] The results reflect well the number of $C_{60}$ substituents within the experimental error. The reversibility of the waves decreases as the number of $C_{60}$ substituents increases. A polystyrene star polymer with six $C_{60}$ end caps has been reported, which showed similar electrochemical behavior.[11]

Stable Langmuir films are observed for all the compounds on water surface, as shown in Fig. 1. The limiting area per molecule (Table 1) is close to the theoretical values of closely packed $C_{60}$ cages and confirms the number of $C_{60}$ subunits on each molecule. The structure of the film probably consists of hydrophobic fullerene fragments floating on the surface, which accounts for the observed limiting area per molecule. Introduction of metal ions in the subphase improves the Langmuir film in that the compression and expansion of the film becomes more reversible. Stable Langmuir films have been reported for fullerene containing dendrimers.[12]

## Acknowledgements

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## References

1. (a) Taylor, R. *Lecture Notes on Fullerene Chemistry*; Imperial College Press, Imperial College, London, 1999; pp. 223–240 and references cited therein; (b) Segura, J. L.; Mattin, N. *Chem. Soc. Rev.* **2000**, *29*, 13.
2. (a) Timmerman, P.; Witschel, L. E.; Diederich, F.; Boudon, C.; Gisselbrecht, J. P.; Gross, M. *Helv. Chim. Acta* **1996**, *79*, 6; (b) Isaacs, L.; Diederich, F.; Haldimann, R. F. *Helv. Chim. Acta* **1997**, *80*, 317.
3. (a) Nierengarten, J. F.; Schall, C.; Nicoud, J. F. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 1934; (b) Armaroli, N.; Boudon, C.; Felder, D.; Disselbrecht, J. P.; Gross, M.; Marconi, G.; Nicoud, J. F.; Nierengarten, J. F.; Vicinelli, V. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 3730; (c) Nierengarten, J. F.; Felder, D.; Nicoud, J. F. *Tetrahedron Lett.* **2000**, *41*, 41 and references cited therein.
4. Prato, M.; Maggini, M. *Acc. Chem. Res.* **1998**, *31*, 519.
5. Sun, Y. P.; Drovetskaya, T.; Bolskar, R. D.; Bau, R.; Boyd, P. D. W.; Reed, C. A. *J. Org. Chem.* **1997**, *62*, 3642.
6. (a) Gan, L. B.; Zhou, D. J.; Luo, C. P.; Tan, H. S.; Huang, C. H.; Lu, M. J.; Pan, J. Q.; Wu, Y. *J. Org.*

*Chem*. **1996**, *61*, 1954; (b) Gan, L. B.; Jiang, J. F.; Zhang, W.; Su, Y.; Shi, Y. R.; Huang, C. H.; Pan, J. Q.; Lu, M. J.; Wu, Y. *J. Org. Chem*. **1998**, *63*, 4240.

7. Zhang, S.; Gan, L. B.; Huang, C. H. *Proceedings of the 197th ECS Meeting, Fullerenes 2000 Vol. 9: Functional Fullerenes*, pp. 156–160, Maggini, M.; Martin, N.; Guldi, D. M. Eds. Toronto, Canada.
8. Comba, P.; Ensling, J.; Gutlich, P.; Kuhner, A.; Peters, A.; Prtzkow, H. *Inorg. Chem*. **1999**, *38*, 3316.
9. The data of **7** is shown as an example: $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 1.35–1.52 (m, 30H), 1.85–1.95 (m, 6H), 2.24 (t, 6H, $J=7.2$ Hz), 2.56 (broad, 6H), 2.82 (t, 6H, $J=7.2$ Hz), 3.29 (broad, 6H), 3.94 (s, 18H), 6.59 (s, 6H). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 173.68, 172.40, 168.92, 153.47, 150.08, 147.42, 146.33, 146.27, 146.06, 146.01, 145.64, 145.54, 145.42 (broad), 145.26, 145.23, 144.37, 144.32, 144.20, 143.11, 143.03, 142.66, 142.58, 142.18, 142.00, 141.96, 141.75 (broad), 141.70, 140.10, 139.53, 137.30, 134.01, DEPT 135: 70.14 (CH), 54.58 ($CH_2$), 53.02 ($CH_3$), 37.68 ($CH_2$), 36.56 ($CH_2$), 34.38 ($CH_2$), 29.46 ($CH_2$), 29.42 ($CH_2$), 29.36 ($CH_2$), 29.31 ($CH_2$), 25.83 ($CH_2$), 25.62 ($CH_2$). MS (MALDI-TOF): $m/z$ (%) 3321 (14) [$M^+$+K, requires 3320], 2753 (14), 720 (100) [$C_{60}^+$]. Anal. calcd for $C_{234}H_{87}O_{18}N_7\cdot(2H_2O)$: C, 84.65; H, 2.76; N, 2.95; found: C, 84.48; H, 2.63; N, 2.82%.
10. Flagan, J. B.; Margel, S.; Bard, A. J.; Anson, F. C. *J. Am. Chem. Soc*. **1978**, *100*, 4248.
11. Cloutet, E.; Gnanou, Y.; Fillaut, J. L.; Astruc, D. *Chem. Commun*. **1996**, 1565.
12. Felder, D.; Gallani, J. L.; Guillon, D.; Heinrich, B.; Nicoud, J. F.; Nierengarten, J. F. *Angew. Chem., Int. Ed. Engl*. **2000**, *39*, 201.