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# $C_{70}[NR_2]_2O$: The First $C_{70}$ Intramolecular Ethers Bearing Two Amine Groups

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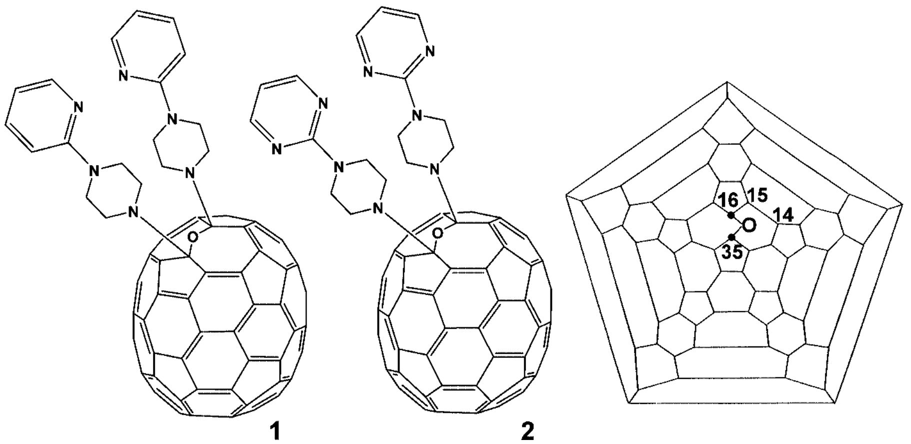
Photochemical reactions between [70]fullerene and *N*-substituted piperazines yield $C_{70}[NR_2]_2O$, the first isolated and characterized $C_{70}$-based aminofullerenes. Spectroscopic characterization revealed the presence of intramolecular ether moieties in the structures of these compounds.

## Introduction

Reactions between [60]fullerene and secondary amines have been studied quite extensively and the syntheses of a number of specific aminofullerene derivatives have been reported.[1] Our recent investigation of photoadditions of *N*-substituted piperazines to [60]fullerene resulted in the preparation of several new di- and tetraaminofullerenes; a comprehensive mechanism explaining the formation of these compounds was suggested.[2] Since some samples of the starting [60]fullerene used in that work contained 4–5% of $C_{70}$ as an impurity, we also observed the formation of very small quantities of aminated derivatives of $C_{70}$ along with the desired $C_{60}$-based aminofullerenes and thus succeeded for the first time in isolating and spectroscopically characterizing two unusual $C_{70}$-containing compounds **1** and **2** (Figure 1[3]), which we report in this work. To the best of our knowledge, **1** and **2** represent the first characterized $C_{70}$-based aminofullerenes.



**1** **2**

Figure 1. Molecular structures of the isolated ethers **1** and **2** and Schlegel diagram illustrating positions of the addends, see ref.[3] for the numbering scheme recommended for $C_{70}$ by IUPAC.

## Results and Discussion

Compounds **1** and **2** were also synthesized by starting from pure [70]fullerene, through photochemical reactions with the corresponding piperazines. In a typical procedure,

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$C_{70}$ (150 mg, 0.179 mmol) was dissolved in 1,2-dichlorobenzene (100 mL), and either *N*-(2-pyridyl)piperazine or 2-(piperazinyl)pyrimidine (416 mg, 2.57 mmol) was then added. The reaction mixture was stirred in an open flask and irradiated from above with a 60 W incandescent light bulb for 48 h. The course of the reaction was monitored by TLC, and the synthesis was stopped when the degree of $C_{70}$ conversion was about 50%. Chromatographic separation yielded compounds **1** and **2** (26–30% based on consumed $C_{70}$), followed by single fractions representing inseparable mixtures of polyamino[70]fullerenes as revealed by chemical analysis and NMR spectroscopy.

Irradiation of $C_{70}$ in the presence of *N*-substituted piperazines under vigorously deoxygenated argon over 1 week gave just traces of aminofullerenes ($C_{70}$ consumption below 0.5%); their attempted separation by column chromatography resulted in numerous badly resolved and unidentified fractions. The presence of oxygen is therefore very important for initiation of the reactions between $C_{70}$ and secondary amines; the same had previously been observed for similar reactions of [60]fullerene.[1]

The compositions of compounds **1** and **2** were initially deduced from the chemical analysis data, which revealed the presence of two piperazine addends on the fullerene cage. At the same time, the ESI mass spectrum of **1** (see Supporting Information) exhibited peaks at *m*/*z* = 1181.22 and 1018.11 amu, corresponding to $[C_{70}[4\text{-(2-pyridyl)piperazin-1-yl}]_2O + H]^+$ and $C_{70}[4\text{-(2-pyridyl)piperazin-1-yl}]O^+$, respectively. A number of solvent systems were tested in order to obtain this spectrum but only dichloromethane with ca. 0.01% of formic acid gave a satisfactory result.

Independent confirmation of the product composition came from analysis of the crude product formed in the photochemical reaction between $C_{70}$ and *N*-methylpiperazine. This material possesses quite basic amine groups on the fullerene cage and undergoes very strong absorption on the silica gel stationary phase, which prevented us from isolating and spectroscopically characterizing any specific compounds. However, the ESI mass spectrum of the crude product exhibited an intense signal at *m*/*z* = 955.1 amu, along with a very weak signal at 1055 amu, corresponding to the $C_{70}(\text{4-methylpiperazine-1-yl})O^+$ and $[C_{70}(\text{4-methylpiperazine-1-yl})_2O + H]^+$ ions. The presence of the ether moiety seems to be responsible for a facile fragmentation with elimination of one piperazinyl group under relatively mild ESI conditions, so these data constitute evidence of the formation of $C_{70}(\text{4-methylpiperazine-1-yl})_2O$, similarly to **1** and **2**.

The structures of compounds **1** and **2** were deduced from their $^1$H and $^{13}$C NMR spectra (Figures 2 and 3). The $^1$H NMR spectra of the two compounds are quite similar and each show signals from two nonequivalent piperazinyl groups (Figure 2).

The $^{13}$C NMR spectra each contain 39–40 signals representing sp$^2$ carbons, including peaks of pyridyl and pyrimidinyl groups that unambiguously establish either $C_2$ or $C_s$

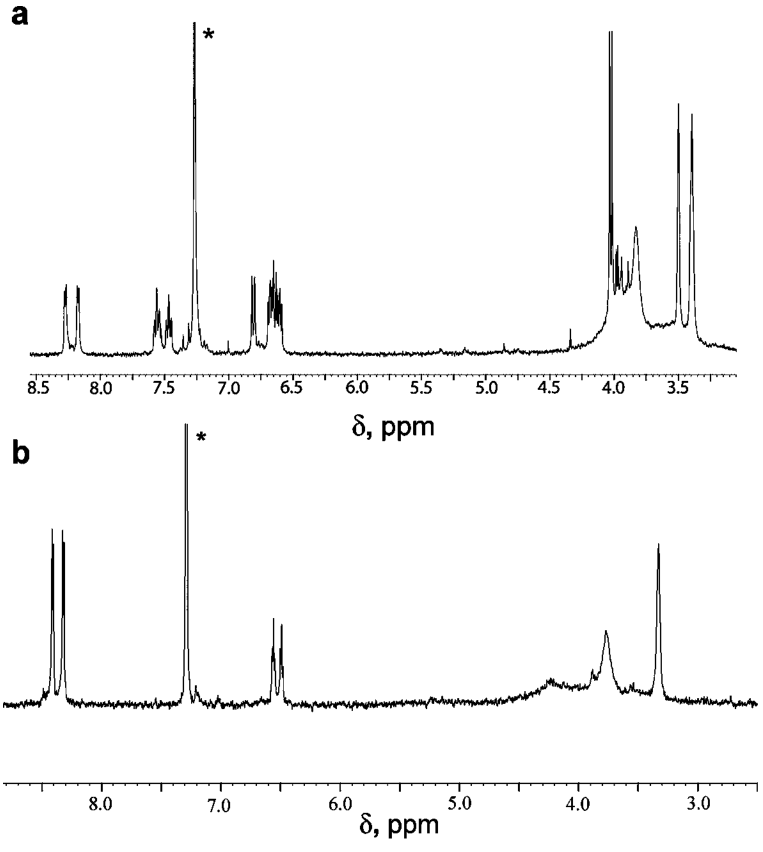


Figure 2. $^1$H NMR spectra of **1** (a) and **2** (b). Symbol “*” denotes $CHCl_3$ in $CDCl_3$.

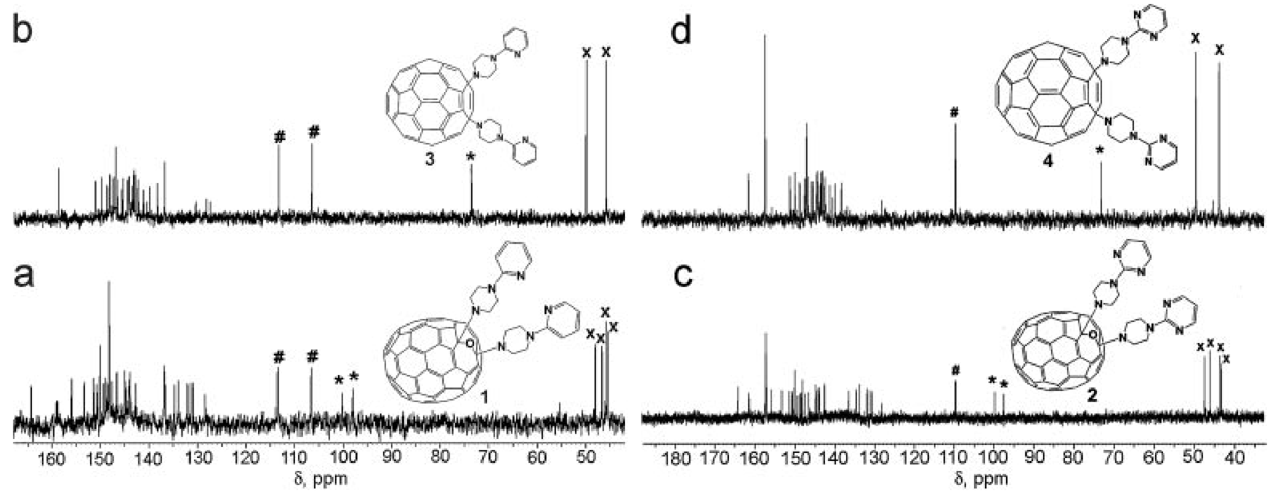


Figure 3. $^{13}$C NMR spectra of **1** (a) and **2** (c) compared with the spectra of $C_{60}$ derivatives **3** (b) and **4** (d). Symbol "*" denotes $sp^3$ fullerene cage carbons, "*x*" is for the piperazine ring carbons and "#" indicates the aromatic ring $sp^2$ carbons.

molecular symmetry for the title compounds (a few peaks were coincidentally overlapped). It appears impossible to draw any $C_2$ symmetry structure for $C_{70}[NR_2]_2O$ compounds because the amine groups are nonequivalent ($^1$H NMR spectroscopic data) and, as a consequence, must lie on the $C_2$-axis, so the title compounds must each have a $C_s$ symmetry structure with both amine groups lying in the symmetry plane. The oxygen atom must also be positioned in the plane and attached either as an epoxide or as an intramolecular ether.[4]

The assignment of the $sp^3$ carbon signals in the $^{13}$C NMR spectra becomes clearer if the spectra are compared with those of the similar $C_{60}$ derivatives (1,4-$C_{60}[NR_2]_2$).[2] Figure 3 shows the spectra of $C_{70}$-derived compounds **1** and **2**, together with the spectra of the corresponding $C_{60}$ derivatives **3** and **4**, respectively. The signals from the piperazine ring carbons ($CH_2$) thus appear at 43–48 ppm for **1** and **2**, in comparison with 44–51 ppm for **3** and **4**, while the signals due to the two equal fullerene cage $sp^3$ carbons in **3** and **4** were observed at 73.5–73.6 ppm, which is comparable with the 78.5 ppm observed for a tricyclic 1,2-diaminofullerene formed in the reaction between $C_{60}$ and unsubstituted piperazine. The $sp^3$ fullerene cage carbons of various methano- and pyrrolidinofullerenes derived from $C_{60}$ and possessing no strongly electron-withdrawing groups typically appear in the 70–85 ppm range,[5] which means that addition of amine groups to the [60]fullerene cage does not result in any significant downfield shifts of the $sp^3$ carbon signals. The lower electron affinity of $C_{70}$ seems to be responsible for the small upfield shift of the bridgehead $sp^3$ carbons in the spectra of its derivatives; they typically appear at 60–66 ppm.[6]

Taking into account the considerations described above, it is remarkable that there are no $sp^3$ carbon signals between 50 and 95 ppm in the $^{13}$C NMR spectra of compounds **1** and **2**. Only two $sp^3$ carbon signals were observed in the 97–101 ppm range, downfield shifted by 25–30 ppm in relation to the reference compounds **3** and **4**, so a strongly electron-withdrawing moiety such as ether oxygen must therefore be bonded to the $sp^3$ carbons bearing amine groups. For instance, in the $^{13}$C NMR spectrum of the epoxide 16,35-$C_{70}O$ (or 1,2-$C_{70}O$ according to the previously used nomenclature[7]) the signals of the $sp^3$ cage carbons are located at $\delta = 90.7$ and 92.2 ppm,[4] which is comparable with the values reported here for **1** and **2**. This conjecture is also consistent with the ESI MS data described above, which revealed the presence of oxygen in the molecule of **1**, and so the spectroscopic data established the intramolecular ether structures of compounds **1** and **2**. Among several possible isomers, only the annulene-like structure with the opened 16,35-bond (or 1,2-bond if following the numbering suggested by Taylor[7]) fits both the $^1$H and $^{13}$C NMR spectroscopic data obtained for $C_{70}[NR_2]_2O$. The cleavage of the 16,35-double bond in the cage is to be expected since it is the most reactive site in the $C_{70}$ molecule.[6]

The structures **1** and **2** deduced from the 1D $^1$H and $^{13}$C NMR spectra were also confirmed by 2D NMR; HH-COSY and HC-HSQC data were obtained for compound **2**.[8] The COSY spectrum allowed the attribution of the pyridyl ring proton signals, while the HSQC experiment unambiguously confirmed the assignment of the $^{13}$C NMR signals from the *N*-(2-pyridyl)piperazine residues. As was to be expected, the carbon signals observed at 97–101 ppm in the $^{13}$C NMR spectrum of **1** (marked with symbol "*") showed no correlations with protons (Figure 4), which corroborates their assignment to the bridgehead $sp^3$ carbons of the $C_{70}$ cage.

It is notable that compounds **1** and **2** have the same 68-electron π-system as other $C_{70}$ derivatives formed through addition across the 1,2-bond in the carbon cage, so the UV/Vis spectrum of **1** (Figure 5) fits very well with the previously reported spectra of 16,35-$C_{70}H_2$ and other substituted 1,2-dihydro[70]fullerenes.[9,10] At the same time, the absorption spectrum of **1** is quite different from the spectra

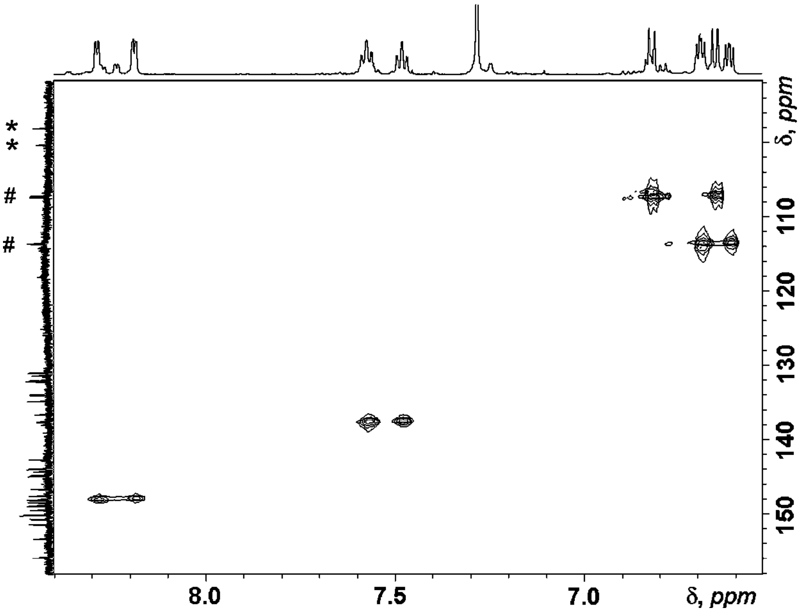


Figure 4. The part of the HC-HSQC 2D NMR spectrum of **1** demonstrating absence of C–H correlations for 98.03 and 100.20 ppm $^{13}$C NMR signals ascribed to the sp$^3$ carbons of the fullerene cage. Symbol “*” denotes sp$^3$ fullerene cage carbons, and “#” indicates the pyridine ring sp$^2$ carbons.

of 14,15-dihydro[70]fullerenes (or 5,6-dihydro[70]fullerenes according to the old numbering scheme[7]) that are usually formed together with the corresponding 16,35-isomers.[9,10]

A very similar structural moiety was recently suggested by Taylor et al. for the compound $C_{76}(CH_3)_2O$.[11] The $C_s$ symmetry of the molecule revealed by its $^1$H NMR spectrum also excluded other possible arrangements of oxygen and two methyl groups. It should also be noted that the structure of the oxohomofullerene with a 6–6 opened bond [in the -C(F)-O-C(F)- moiety] was determined unambiguously by single-crystal X-ray structure analysis for $C_{60}F_{18}O$.[12]

The formation of compounds **1** and **2** from $C_{70}$ correlates with a mechanism suggested for similar reactions of $C_{60}$.[2,13] The first stage of the reaction is the addition of amine to $C_{70}$ with the formation of the zwitterion **I**, a process known to occur in such systems (Scheme 1).[14] The amine most probably attacks the C16 carbon in the [70]fullerene cage, according to the previously reported data.[15] Quenching of anion **I** with oxygen can give **II**, which may undergo hydrogen transfer to yield hydroperoxide **III**. Similar hydroperoxides were observed by ESI MS when $C_{60}(CN)_n^{n-}$ anions were allowed to come into contact with air.[16] Possibly, the steric strain in the $C_{70}$ cage is responsible for the domination of the formal 1,2-addition of OOH and $R_2N$ groups, which contrasts with the 1,4-addition observed in the case of $C_{60}$.[2] Photoinduced reduction of **III** by another amine molecule may effect the elimination of

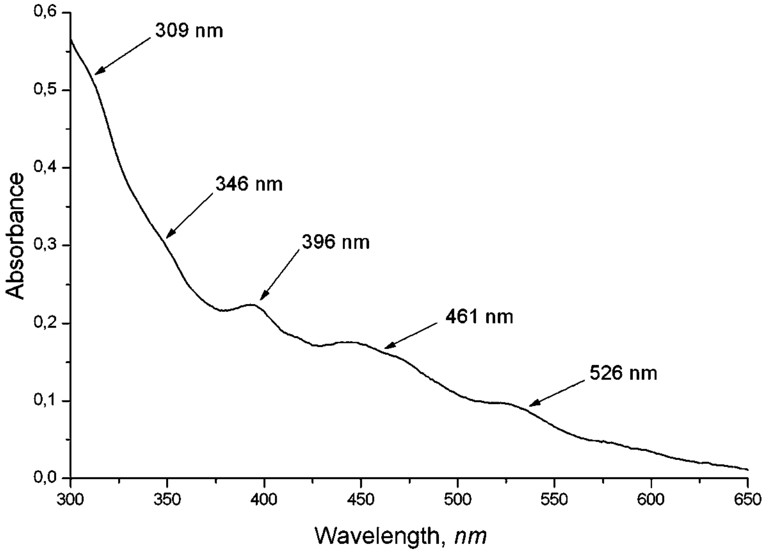
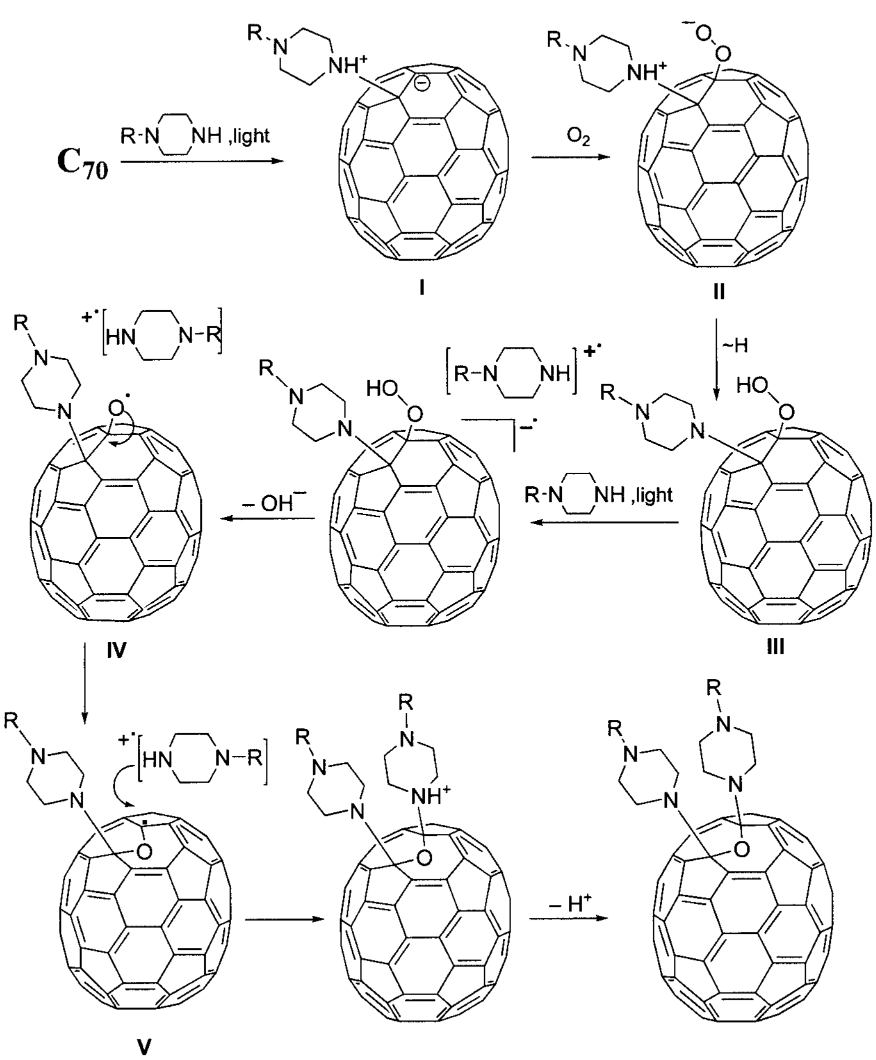


Figure 5. The UV/Vis spectrum of compound **1**.



Scheme 1.

hydroxide anion and the formation of **IV**; both events are known from the literature.[17,18] Subsequent rearrangement of **IV** leads to a rupture of the C16–C35 single bond and the release of some strain in the $C_{70}$-cage, giving rise to the intramolecular ether moiety in **V**. Recombination of radical **V** with $R_2NH^{+\cdot}$ and elimination of a proton yields the final product $C_{70}(NR_2)_2O$.

## Conclusions

We have succeeded in the preparation and spectroscopic characterization of the first aminated [70]fullerene derivatives possessing oxygen integrated into the carbon cage. Following studies will be focused on isolation of other derivatives of $C_{70}$ bearing higher numbers of amine groups and therefore potentially convertible into water-soluble salts, similarly to their $C_{60}$-based aminofullerene counterparts.

## Experimental Section

**General Synthetic Procedure:** In a typical procedure, $C_{70}$ (150 mg, 0.179 mmol) was dissolved in 1,2-dichlorobenzene (100 mL), and either *N*-(2-pyridyl)piperazine or 2-(piperazinyl)pyrimidine (416 mg, 2.57 mmol) was then added. The reaction mixture was stirred in an open flask and irradiated from above with a 60 W incandescent light bulb for 48 h. The course of the reaction was monitored by TLC; the synthesis was stopped when the degree of $C_{70}$ conversion was about 50%.

The reaction mixture was diluted with toluene (300 mL) and hexane (300 mL) and was then filtered and loaded onto a silica gel column (30–75 µ, 90 Å). Unreacted [70]fullerene was washed out with toluene; the recovery of $C_{70}$ in the syntheses of **1** and **2** was 60 mg (40%) and 85 mg (57%), respectively. Elution with a toluene/MeOH mixture resulted in single distinct fractions of **1** (61 mg, 29%) or **2** (55 mg, 26%), followed by badly resolved fractions of other aminated derivatives of $C_{70}$.

**Compound 1:** Eluent: toluene/MeOH 99.2:0.8 vv. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 3.20–4.25 (broad m, 16 H), 6.65 (m, 3 H), 6.81 (d, 1 H), 7.47 (t, 1 H), 7.56 (t, 1 H), 8.18 (d, 1 H), 8.27 (d, 1 H) ppm. $^{13}C$ NMR (100 MHz, $CS_2/C_6D_{12}$ 10:1): $\delta$ = 45.38 ($CH_2$), 45.68 ($CH_2$), 46.51 ($CH_2$), 47.9 ($CH_2$), 97.77 (fullerene $sp^3$ C), 99.99 (fullerene $sp^3$ C), 106.37 ($sp^2$ C of pyridyl unit), 113.24 ($sp^2$ C of pyridyl unit), 128.24, 130.86, 131.2, 131.86, 131.96, 133.8, 134.6, 136.5, 136.65, 136.75, 142.36, 142.5, 142.6, 143.73, 143.84, 143.91, 144.11, 144.62, 144.8, 146.44, 147.42, 147.89, 148.01, 148.25, 148.62, 148.76, 149.28, 149.96, 150.05, 150.46, 150.64, 151.23, 153.18, 155.79, 158.63, 158.84, 164.08 ppm. $C_{88}H_{24}N_6O$ (1180.2): calcd. C 89.48, H 2.05, N 7.11; found C 89.73, H 2.19, N 7.85.

**Compound 2:** Eluent: toluene/MeOH 99:1 vv. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 3.33 (broad s, 4 H), 3.38–4.60 (broad m, 12 H), 6.49 (t, 1 H), 6.56 (t, 1 H), 8.32 (d, 2 H), 8.41 (d, 2 H) ppm. $^{13}$C NMR (150 MHz, $CS_2/C_6D_{12}$ 10:1): $\delta$ = 43.71 ($CH_2$), 44.04 ($CH_2$), 46.52 ($CH_2$), 47.91 ($CH_2$), 97.83 (fullerene sp$^3$ C), 100.02 (fullerene sp$^3$ C), 109.26 (sp$^2$ C of pyrimidinyl unit), 109.81 (sp$^2$ C of pyrimidinyl unit), 128.17, 130.69, 130.76, 131.10, 131.77, 131.86, 133.69, 134.52, 136.41, 142.42, 143.64, 143.72, 143.80, 144.02, 144.52, 144.67, 144.71, 146.35, 147.31, 147.89, 147.92, 148.16, 148.50, 148.66, 149.18, 149.86, 149.94, 150.36, 150.53, 151.12, 151.16, 153.06, 155.64, 156.94, 157.04, 161.02, 161.24, 163.97 ppm. $C_{86}H_{22}N_8O$ (1182.2): C 87.30, H 1.87, N 9.47; found C 87.54, H 2.11, N 9.58.

**Supporting Information** (see also the footnote on the first page of this article): $^1$H and $^{13}$C NMR spectra of a mixture of polyaddition products, HH-COSY and HC-HSQC 2D NMR spectra for compound **1**, high-resolution ESI MS spectra for **1** and crude $C_{70}$/*N*-methylpiperazine reaction product.

## Acknowledgments

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[1] K. D. Kampe, N. Egger, M. Vogel, *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1174; H. Isobe, A. Ohbayashi, M. Sawamura, E. Nakamura, *J. Am. Chem. Soc.* **2000**, *122*, 2669; H. Isobe, N. Tomita, E. Nakamura, *Org. Lett.* **2000**, *2*, 3663; N. X. Wang, *Tetrahedron* **2002**, *58*, 2377; C. P. Butts, M. Jazdzyk, *Chem. Commun.* **2003**, 1530; C. P. Butts, R. W. A. Havenith, M. Jazdzyk, T. Drewello, S. Kotsiris, *Tetrahedron Lett.* **2003**, *44*, 3565; H. Isobe, T. Tanaka, W. Nakanishi, L. Lemiègre, E. Nakamura, *J. Org. Chem.* **2005**, *70*, 4826.

[2] O. A. Troshina, P. A. Troshin, A. S. Peregudov, V. I. Kozlovskiy, R. N. Lyubovskaya, *Chem. Eur. J.* **2006**, *12*, 5569.

[3] W. H. Powell, F. Cozzi, G. P. Moss, C. Thilgen, R. J.-R. Hwu, D. A. Yerin, *Pure Appl. Chem.* **2002**, *74*, 629.

[4] D. Heymann, S. M. Bachilo, R. B. Weisman, *J. Am. Chem. Soc.* **2002**, *124*, 631.

[5] T. Ohno, N. Martin, F. Wudl, T. Suzuki, H. Yu, *J. Org. Chem.* **1996**, *61*, 1306; T. Hino, K. Kinbara, K. Saigo, *Tetrahedron Lett.* **2001**, *42*, 5065.

[6] Y. Wang, D. I. Schuster, S. R. Wilson, *J. Org. Chem.* **1996**, *61*, 5198.

[7] R. Taylor, *J. Chem. Soc., Perkin Trans. 2* **1993**, 813.

[8] The 2D NMR spectra were requested by a referee of this paper and were acquired several months after the 1D NMR spectroscopic data. Therefore, a small amount of admixture due to its oxidation in air (ca. 7–8%) appeared in the sample. However, the presence of this impurity does not significantly affect the quality and reliability of the given 2D NMR spectroscopic data. The isolation and structural characterization of the oxidation product will be reported elsewhere.

[9] C. C. Henderson, C. M. Rohfing, K. T. Gillen, P. Cahil, *Science* **1994**, *264*, 397.

[10] Z. Wang, M. S. Meier, *J. Org. Chem.* **2003**, *68*, 3043.

[11] A. D. Darwish, N. Martsinovich, R. Taylor, *Org. Biomol. Chem.* **2004**, *2*, 1364.

[12] O. V. Boltalina, B. Vaissiere, P. W. Fowler, P. B. Hitchcock, J. P. B. Sandall, P. A. Troshin, R. Taylor, *Chem. Commun.* **2000**, 1325.

[13] O. A. Troshina, P. A. Troshin, A. S. Peregudov, R. N. Lyubovskaya, *Org. Biomol. Chem.* **2006**, *4*, 1647.

[14] A. Hirsch, Q. Li, F. Wudl, *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 1309.

[15] P. N. Keizer, J. R. Morton, K. F. Preston, *J. Chem. Soc., Chem. Commun.* **1992**, 1259; Z. Xiao, F. Wang, S. Huang, L. Gan, J. Zhou, G. Yuan, M. Lu, J. Pan, *J. Org. Chem.* **2005**, *70*, 2060.

[16] A. A. Tuiman, R. N. Compton, *J. Phys. Chem. A* **1998**, *102*, 9791.

[17] D. V. Konarev, A. Yu. Kovalevsky, A. L. Litvinov, N. V. Drichko, B. P. Tarasov, P. Coppens, R. N. Lyubovskaya, *J. Solid State Chem.* **2002**, *168*, 474.

[18] S. Huang, Z. Xiao, F. Wang, J. Zhou, G. Yuan, S. Zhang, Z. Chen, W. Thiel, P. von R. Schleyer, X. Zhang, X. Hu, B. Chen, L. Gan, *Chem. Eur. J.* **2005**, *11*, 5449.

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