

# Unexpected interconversion reaction of 1,4-diaminofullerenes†

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A facile substitution of amine groups attached to the fullerene cage occurs when 1,4-diaminofullerenes  $C_{60}[NR_2]_2$  are allowed to react with excess of another amine  $R'_2NH$ ; this reaction proceeds rapidly at room temperature without any additional initiators.

Fullerene  $C_{60}$  undergoes photochemical reactions with secondary amines to yield the corresponding aminofullerenes.<sup>1</sup> These reactions are mostly of low selectivity and yield complex mixtures of products; therefore, only a few types of individual derivatives have been isolated so far. They are single-bonded fullerene dimers 1,4- $[C_{60}NR_2]_2$ ,<sup>2</sup> tetraaminofullerenes  $C_{60}[NR_2]_4O^{2,3}$  bearing epoxide oxygen addends, and piperazinofullerenes formed from various  $N,N'$ -disubstituted 1,2-diamines.<sup>4</sup> In addition, two 1,4-diaminofullerenes  $C_{60}[NR_2]_2$  were previously isolated as minor byproducts in photochemical reactions of  $C_{60}$  with secondary amines.<sup>2,3</sup> We have developed recently an alternative approach to the synthesis of 1,4-diaminofullerenes using a reaction of  $C_{60}Cl_6$  with the corresponding secondary amines at elevated temperatures.<sup>5</sup> Here we employed an available diaminofullerene **1** as a substrate in photochemical reactions with other secondary amines, namely,  $N$ -substituted piperazines **2a–b**.

Since the reactions of **2a–b** with parent fullerene  $C_{60}$  result in the formation of tetraaminofullerenes  $C_{60}[NR_2]_4O$  as major products,<sup>6</sup> one can expect to obtain mixed tetraaminofullerenes (possessing different amine groups attached to the cage) starting from **1**. For this purpose, 50 mg (0.048 mmol) of **1** were dissolved in 50 ml of 1,2-dichlorobenzene and then 100 mg (0.610 mmol) of **2a** or 120 mg (0.645 mmol) of **2b** were added. Then the resulting mixtures were irradiated in air by a 60 W incandescent light bulb for 5 h (**2a**) and 20 h (**2b**). Chromatographic separation gave a single isolable product in each case, **3a** and **3b**, respectively.‡

The <sup>1</sup>H NMR spectra§ revealed the presence of only two or more symmetrically arranged residues of amines **2a–c** in molecular frameworks of **3a–b**; thus, 2-(pyridyl)piperazinyl groups were cleaved from the fullerene cage under the reaction conditions. The <sup>13</sup>C NMR spectra§ of **3a–b** were very similar to the spectrum of the starting diaminofullerene **1**. Particularly, both spectra exhibited single peaks at 73–74 ppm that correspond to the fullerene core sp<sup>3</sup> carbons bearing amine groups. Thus, both the <sup>1</sup>H and <sup>13</sup>C NMR spectra of **3a–b** were compatible only with the structures

of  $C_s$  symmetrical 1,4-diaminofullerenes as is shown in Scheme 1. Such a composition was also confirmed by chemical analysis data.

To rationalize the origin of such a facile substitution of  $N$ -(2-pyridyl)piperazinyl groups by residues of **2a–b**, we investigated the reverse reaction. For this purpose, **3a** was treated with an excess of  $N$ -(2-pyridyl)piperazine under photochemical conditions. The NMR spectroscopic characterization of the crude reaction product revealed that all (2-pyrimidinyl)piperazinyl groups were pushed out from the fullerene cage. However, a mixture of isomeric tetra- and even hexaaminofullerenes was formed in this case along with a small amount of diaminofullerene **1**.<sup>7</sup> The same product composition was obtained in a control experiment by irradiation of **1** with  $N$ -(2-pyridyl)piperazine. Conversion of **3a** to **3b** and *vice versa* were found to proceed smoothly and do not give much of the polyaddition side products.

Thus, it was shown that amine groups attached to the fullerene cage can be reversibly replaced by residues of other amines under irradiation with visible light (Scheme 2). Further studies revealed that this interconversion of 1,4-diaminofullerenes proceeds with the same efficiency at room temperature even in the absence of light and air.¶ Therefore, a participation of free radicals in this reaction must be ruled out.

Substitution of tertiary amine groups by stronger nucleophiles is well-known for aliphatic substrates. According to the known mechanism, it starts from the protonation of the nitrogen atom followed by elimination of  $R_2NH$  and formation of the corresponding carbocation.<sup>8</sup> The addition of  $R'_2NH$  to this carbocation and the following elimination of a proton can result in formal substitution of  $R_2N$  group by  $R'_2N$  at the fullerene cage (Scheme 3, route I).

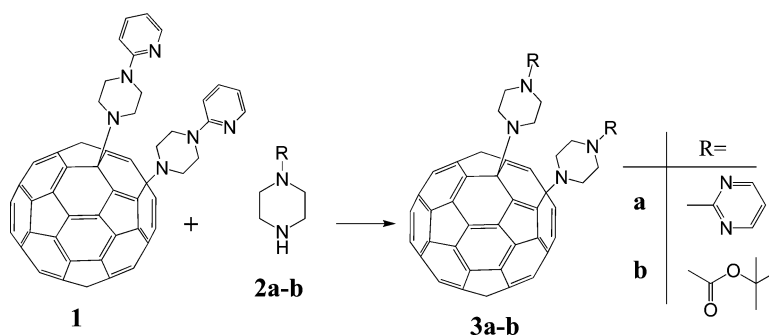
If the observed interconversion of 1,4-diaminofullerenes really obeys such a mechanism, all other known types of aminated fullerenes, in particular, compounds **4** and **5** (Scheme 3), should also be reactive under the given conditions. In contrast, we observed no exchange of amine groups in **4** and **5** even under continuous irradiation in air.

Therefore, some peculiarities of the molecular structure of 1,4-diaminofullerenes are presumably responsible for the facile substitution of amine groups. We believe that the first step of the reaction is addition of  $R_2NH$  to 1,4- $C_{60}(NR_2)_2$  that gives “allyl-like” intermediate **A**.<sup>9</sup> The formation of a similar intermediate from **4** is not possible because two amine groups are attached to adjacent carbons in this molecule (1,2- but not 1,4-addition pathway); tetraaminofullerene **5** already has a stabilizing cyclopentadienyl moiety in its molecular framework that makes this compound quite inert towards further additions.<sup>10</sup> Following hydrogen transfer may convert **A** to **B**; the following elimination of  $R_2NH$  accomplishes the substitution of one amine group by another (Scheme 3, route II). All stages of the suggested mechanism are reversible, so an excess of the reagent (corresponding amine) shifts it to the desired direction.

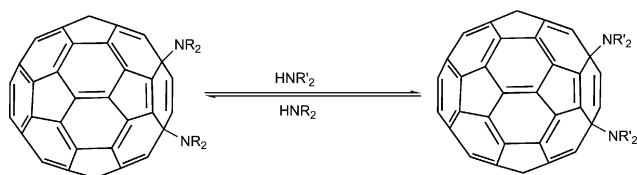
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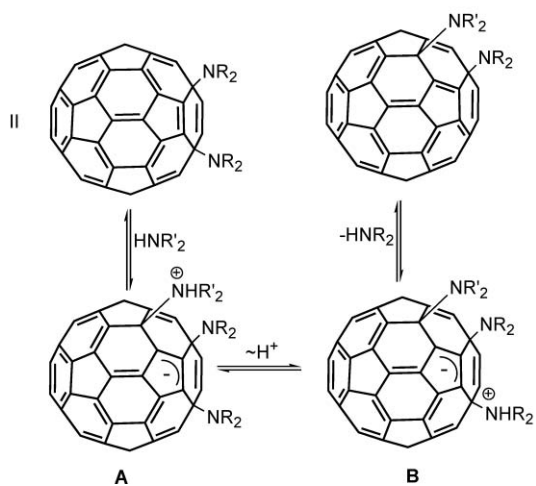
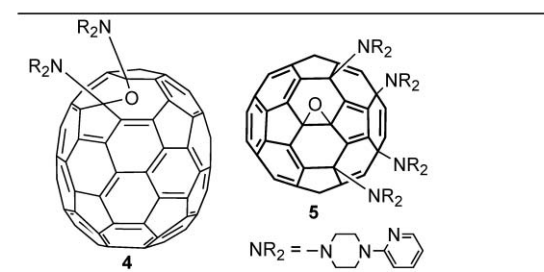
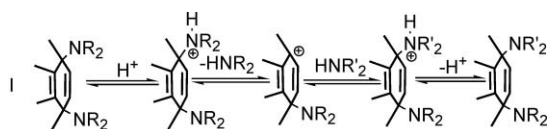
† Electronic supplementary information (ESI) available: Spectral data for compounds **1**, **3a–b** and polyaminofullerenes formed as by-products with **1**. See DOI: 10.1039/b601880g



Scheme 1



Scheme 2



Scheme 3

1,4-diaminofullerene substrate makes possible formation of a relatively stable zwitterionic allyl-type intermediate that provides a possible route for substitution of amine groups at the fullerene surface. It can be expected that the reported novel reaction will find many applications, particularly, when a wider range of nucleophiles is introduced in the reactions with 1,4-diaminofullerenes.

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## Notes and references

‡ After irradiation the reaction mixtures were diluted with toluene and n-hexane (1 : 3 : 3 v/v ratio). The resulting solution was filtered and poured on the top of a silica gel column (Acros Organics, 30–75  $\mu$ , 90 Å) pre-eluted with 1 : 1 v/v hexane : toluene mixture. Passing toluene: MeOH 99 : 1 v/v mixture through the column yielded a single fraction that was concentrated *in vacuo* to serve **3a** and **3b** with 50 and 30% yields, respectively. A further increase in polarity of the eluent (going from 99 : 1 to 90 : 10 toluene: MeOH) did not result in any distinct fractions though the material was monotonously washed out from the column. The NMR spectroscopy revealed it to be a complex mixture of products.

§ **Compound 1**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 3.40–4.20 (broad m; 8H), 6.70 (t, 1H), 6.81 (d, 1H), 7.56 (t, 1H), 8.27 (d, 1H) ppm.  $^{13}\text{C}$  NMR (100 MHz,  $\text{CS}_2\text{-C}_6\text{D}_{12}$  10 : 1):  $\delta$  = 45.82, 49.89, 73.52, 106.43, 113.29, 127.36, 128.17, 130.36, 136.75, 138.20, 139.78, 140.38, 141.11, 142.09, 142.25, 142.53, 142.97, 143.03, 143.16, 143.41, 143.50, 144.06, 144.16, 144.22, 144.32, 144.39, 145.37, 145.60, 146.47, 146.88, 147.00, 147.35, 148.00, 148.61, 149.75, 150.98, 158.67 ppm. **Compound 3a**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 3.72–4.07 (broad m, 8H), 4.22 (broad s, 8H), 6.56 (t, 2H), 8.39 (d, 4H) ppm.  $^{13}\text{C}$  NMR (100 MHz,  $\text{CS}_2\text{-C}_6\text{D}_{12}$  10 : 1):  $\delta$  = 44.31, 50.02, 73.57, 109.85, 138.19, 139.78, 140.35, 141.10, 142.09, 142.25, 142.53, 142.97, 143.01, 143.17, 143.41, 143.50, 143.69, 144.05, 144.16, 144.22, 144.31, 145.36, 145.59, 146.47, 146.87, 146.99, 147.34, 148.60, 149.76, 150.99, 157.08, 157.16, 157.25, 161.27 ppm. **Compound 3b**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 1.55 (s, 9H), 3.60–3.90 (broad m, 8H) ppm.  $^{13}\text{C}$  NMR (100 MHz,  $\text{CS}_2\text{-C}_6\text{D}_{12}$  10 : 1):  $\delta$  = 28.30, 30.09, 49.90, 73.35, 78.61, 138.15, 139.67, 140.37, 141.07, 142.05, 142.23, 142.47, 142.91, 142.96, 142.98, 143.12, 143.19, 143.35, 143.43, 143.60, 144.02, 144.12, 144.17, 144.25, 145.33, 145.59, 146.13, 146.46, 146.64, 146.74, 146.86, 146.97, 147.23, 148.59, 149.52, 150.68, 153.09 ppm.

¶ Typically, the starting diaminofullerene (**1**, **3a** or **3b**) was treated with 6–8 equivalents of another amine under stirring in an argon atmosphere and dark environment for 4–5 h at room temperature. Then the reaction mixtures were processed as described above for photochemical reactions.‡

To the best of our knowledge, we have serendipitously observed the first example of a very easy substitution of one amine group by another in carbocyclic systems. The structure of the

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