# Photoinduced reactions of tertiary amines with [60]fullerene; addition of an α-C–H bond of amines to [60]fullerene

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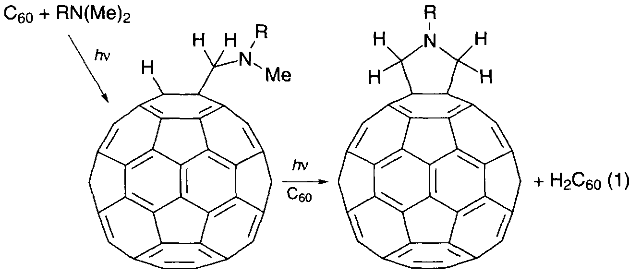
**The photochemical reaction of [60]fullerene with $RNMe_2$ (R = Ph and Me) gives an adduct (1, R = Ph; 2, R = Me) formed by the addition of an α-C–H bond of the amine to a 6/6 ring junction of [60]fullerene; 2 on further irradiation in the presence of [60]fullerene is converted to the pyrrolidine derivative 3 and 1,2-$H_2C_{60}$.**

Interaction of fullerenes with amines has recently been the subject of considerable interest.[1–6] A primary or secondary amine readily adds to [60]fullerene to give 1-H-2-(NR′R″)$C_{60}$–.[1] Due to the absence of an N–H bond, tertiary amines such as triethylamine, *N*,*N*-diethylaniline and *N*,*N*-dimethylaniline do not undergo the same type of addition, but form weak charge-transfer complexes with [60]fullerene in the ground state.[2] Photoexcitation of amine–[60]fullerene solutions leads to electron transfer from amines to the fullerene and the formation of $C_{60}^-$ amine$^+$ ion pairs.[3] For amines possessing α-hydrogens, evidence shows that proton transfer from amines to [60]fullerene occurs to eventually give photochemical products.[4,5] Recently, Sun and co-workers isolated a pyrrolidine derivative of [60]fullerene from the irradiation of triethylamine and [60]fullerene in toluene.[6] Apart from this cycloadduct, there appears to be no other report in the literature concerning the structures of the photochemical products. To shed light on the photochemistry of amines with [60]fullerene, we investigated the products of various tertiary amines with [60]fullerene. For *N*,*N*-dimethylaniline or trimethylamine, a new type of adduct involving an α-C–H bond addition of amine to the fullerene was isolated. The observation of this product is important to the understanding of the photochemistry of tertiary amines with fullerenes. Evidence shows that this adduct is the primary photochemical product which may be converted to the cyclic pyrrolidine derivative. Herein, we describe the preparation, characterization and photochemistry of this amine–[60]fullerene adduct.

Irradiation of [60]fullerene in the presence of an excess of *N*,*N*-dimethylaniline in toluene led slowly to the isolation of **1** in 25% yield (56.0% [60]fullerene was recovered). No cycloadduct similar to the [60]fullerene pyrrolidine obtained from the irradiation of triethylamine and [60]fullerene was detected.[6] No product was formed in the absence of light. The structure of **1** was determined from its mass, NMR and IR spectra.† Analysis of **1** by DCI$^-$ mass spectrometry showed the molecular ion at *m*/*z* 841 confirming its formulation as an adduct of a $NPh(CH_3)_2$ unit to [60]fullerene. The $^1H$ NMR spectrum of **1** reveals three characteristic singlets at δ 6.55, 5.40 and 3.55 for the proton bound to [60]fullerene and the methylene and the methyl protons attached to the nitrogen atom, respectively, as well as three resonances in the aromatic region for the phenyl group. In the $^{13}C$ NMR spectrum, 32 signals in the sp$^2$ region were observed with the resonances for the phenyl carbons appearing at δ 149.56, 129.68, 118.37 and 113.22. The other 28 peaks (30 are expected) in the range δ 155–135 are attributed to the quaternary sp$^2$ carbons on the fullerene moiety. Two of these resonances at δ 147.25 and 145.69 are significantly stronger than the others presumably due to overlapping signals. The observed $^{13}C$ NMR data of **1** suggests the presence of a $C_s$ symmetry and 1,2-addition across a 6/6 ring junction of [60]fullerene. In the sp$^3$ region of the $^{13}C$ NMR spectrum, the resonances at δ 68.18 and 58.57 are attributed to the quaternary and tertiary carbons, respectively, on the 6/6 ring junction of [60]fullerene, while the resonances at δ 67.72 and 41.45 are assigned to the methylene and methyl groups, respectively.



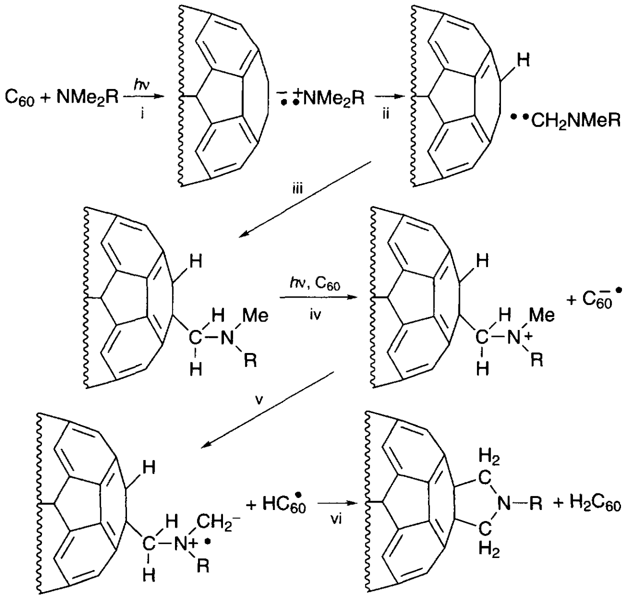
**1** R = Ph
**2** R = Me
**3** R = Me

Irradiation of [60]fullerene and trimethylamine in toluene with 350 nm light for 12 h led to the isolation of **2**‡ in 18% yield. If the irradiation was extended to 60 h, products **2** and **3** were isolated in 16 and 12% yields, respectively, (eqn. 1) in addition to the recovered [60]fullerene (58%) and a small amount of 1,2-$H_2C_{60}$.[7] The DCI$^-$ mass spectrum of **2** showed the molecular ion at *m*/*z* 779 supporting the formulation of a trimethylamine and a [60]fullerene unit. In the $^1H$ NMR spectrum of this product, only three characteristic singlets at δ 7.04, 4.31 and 2.99 for the proton directly attached to the fullerene moiety, and the methylene and methyl protons of the amine fragment, respectively, were observed. The $^{13}C$ NMR spectrum shows 29 signals in the sp$^2$ region and 4 signals in the sp$^3$ region confirming **2** as an adduct to the double bond across a 6/6 ring junction of [60]fullerene. These spectral results indicate that **2** is analogous to **1** in structure.

The $^1H$ NMR spectrum of **3** is surprisingly simple exhibiting only two signals with a ratio of 4 : 3 at δ 4.39 and 3.00 assigned to the methylene and methyl protons of the amino group, respectively. Based on comparison with the NMR data reported previously,[8] we proposed that **3** is a cycloadduct similar in structure to the [60]fullerene pyrrolidine from irradiation of triethylamine and [60]fullerene.[6] The proposed structure is further supported by the DCI$^-$ mass spectrum of **3** showing the molecular ion at *m*/*z* 777 in agreement with a $MeN(CH_2)_2$ fragment and [60]fullerene unit.

Product **1** is stable in 350 nm and visible light. However, photolysis of **2** in toluene in the presence of [60]fullerene converted **2** into **3**. A dihydrogen derivative, 1,2-$H_2C_{60}$, was also formed during the reaction. Product **3** was not observed on heating the same solution at 50–70 °C in the absence of light indicating that the transformation is photoinduced. These observations suggest that **2** is an intermediate for **3**. In accordance with this notion, the effect of irradiation time for the reaction of [60]fullerene with trimethylamine on product distribution shows that **2** was produced in the early period of irradiation, while **3** started to form only after a substantial amount of **2** was present in the solution.

For the formation of **1** and **2**, evidence provided by previous investigations[3–6] suggests that a photoinduced electron transfer from the amine to [60]fullerene to yield a radical ion pair is the first step. This is followed by deprotonation of the amine cation by the [60]fullerene anion to give an α-aminoalkyl and $HC_{60}$ radical pair.[4] Subsequent combination of the radical pair led to the final product.[6] Scheme 1 outlines this electron- and proton-transfer mechanism. It is noteworthy that similar photochemical addition products for amines and stilbene were observed by F. D. Lewis *et al.*[9] and a mechanism similar to steps i–iii shown in Scheme 1 was proposed by them to account for the photoinduced reactions. Based on the requirement of light and the observed products, the formation of **3** is likely to be initiated by a photoinduced electron transfer from **2** to [60]fullerene. This is then followed by successive intermolecular proton transfer, hydrogen attraction and ring closure to give $1,2\text{-}H_2C_{60}$ and **3** (Scheme 1).



Scheme 1

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## Footnotes

† Compound **1** was synthesized according to the following procedure. To a 250 ml side-arm flask containing [60]fullerene (0.072 g, 0.10 mmol) and *N,N*-dimethylaniline (0.61 g, 5.0 mmol) under one atmosphere of nitrogen was added toluene (50 ml). The system was then stirred at ambient temperature until [60]fullerene was dissolved. The solution was irradiated with 350 nm light (Rayonet) for 12 h and was then filtered through a short silica-gel column to remove coloured material. Concentration, followed by separation on a silica-gel column using toluene/hexane ($v/v$ = 1/4) as eluent recovered [60]fullerene (0.040 g, 0.056 mmol) in 56% yield and afforded compound **1** (0.0210 g, 0.0250 mmol) in 25% yield. $^1H$ NMR (300 MHz, $CD_2Cl_2/CS_2$ = 1/2) δ 3.55 (s, 3 H, $NCH_3$), 5.40 (s, 2 H, $CH_2$), 6.55 (s, 1 H, CH), 6.61 (t, *J* 7.28 Hz, 1 H, CH), 7.21 (d, *J* 8.36 Hz, 2 H, CH) and 7.32 (t, *J* 7.68 Hz, 1 H, CH); $^{13}C$ {$^1H$} NMR (150 MHz, $CD_2Cl_2/CS_2$ = 1/2) δ 41.45 ($CH_3$), 58.57 ($CH_2$), 67.72 (CH), 68.18, 113.22 (CH), 118.37 (CH), 129.68 (CH); $DCI^-$-MS *m/z* 841.

‡ Compound **2** was prepared by following a procedure similar to that described for **1**. Aqueous trimethylamine (45% in water, 5.0 ml) was used. *Selected spectral data* for **2**: $^1H$ NMR (300 MHz, $CDCl_3/CS_2$ = 1/2) δ 2.99 (s, 6 H, $NCH_3$), 4.31 (s, 2 H, $CH_2$), 7.04 (s, 1 H, CH); $^{13}C$ {$^1H$} NMR (150 MHz, $CDCl_3/CS_2$ = 1/2) δ 47.70 ($CH_3$), 57.80 (CH), 66.98, 72.88 ($CH_2$); $DCI^-$-MS *m/z* 779.

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