Photoinduced Inter- and Intra-molecular Electron Transfer Reactions of [60]Fullerene and a Tertiary Amine. Formation of the Cycloadduct *N*-Ethyl-*trans*-2′,5′-dimethylpyrrolidino[3′,4′ : 1,2][60]fullerene

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The photoreduction of [60]fullerene by triethylamine results in the formation of a cycloadduct *N*-ethyl-*trans*-2′,5′-dimethylpyrrolidino[3′,4′ : 1,2][60]fullerene, which is probably due to sequential intermolecular and intramolecular processes and argues strongly for the presence of ion pairs as intermediates in a room temperature toluene solution.

The photoreduction of aromatic systems by tertiary amines represents a class of reactions mechanistically important to an understanding of photoinduced electron transfer processes.[1–3] On the basis of extensive experimental studies of a number of systems,[3–5] especially the elegant work of Lewis *et al.* on photochemical addition of tertiary amines to *trans*-stilbene,[3,6–9] it has been established that oxidation of amines follows a sequential single electron transfer–proton transfer mechanism.

[60]Fullerene (C_{60}) and [70]fullerene (C_{70}) are excellent electron acceptors. Spectroscopic results show that electron transfer interactions of the fullerene molecules with aromatic and aliphatic amines are somewhat unusual.[10–20] Emissions of fullerene–amine exciplexes are extremely solvent sensitive. The intense exciplex fluorescence observed in nonpolar solvents such as hexane and cyclohexane are completely quenched in still nonpolar but polarizable solvents such as benzene and toluene. It has been proposed[15,16] that the quenching is due to the formation of ion pairs in a polarizable solvent environment. In this communication we report that C_{60} and triethylamine (TEA) undergo characteristic photoinduced electron transfer–proton transfer reactions in a room temperature toluene solution. It implies that there are indeed C_{60}–TEA ion pairs as intermediates in a nonpolar but polarizable solvent. Interestingly, the reactions result in the formation of a C_{60}–TEA cycloadduct.

Freshly prepared solutions of C_{60} in toluene (1 mg cm^{-3}) with 0.28 mol dm^{-3} TEA were irradiated for 0.5–2 h using a 450 W xenon source with a water filter and a 540 nm colour glass sharp-cut filter. The TEA concentration was optimized such that thermal reactions between C_{60} and TEA are negligible.[17,21] TLC analysis of the reaction mixture in toluene showed two major moving spots, corresponding to a product and unreacted C_{60}. The product was first isolated through a silica gel column (toluene as eluent), and then further purified using preparative HPLC (C_{18} column, a toluene–acetonitrile mixture with 55% *v*/*v* acetonitrile as mobile phase).

The structure of the product as a C_{60}–TEA cycloadduct *N*-ethyl-*trans*-2′,5′-dimethylpyrrolidino[3′,4′ : 1,2][60]fullerene (EDMP-C_{60}) was determined unambiguously from ^1H and ^{13}C NMR spectra. The proton spectrum (300.1 MHz, CS_2 solution, C_6D_6 internal lock) shows the CH protons at δ 4.81 (2 H, q, *J* 6.5 Hz), methyl protons at δ 1.84 (6 H, d, *J* 6.5 Hz) and 1.48 (3 H, t, *J* 7.1 Hz), and two methylene protons at δ 3.27 (H_a, 1 H, dq, *J* 7.4, 11.9 Hz) and 2.91 (H_b, 1 H, dq, *J* 6.9, 11.9 Hz). Experiments on selective homonuclear decoupling show that methylene protons H_a and H_b are coupled to each other and to the methyl protons. Inequivalence of the methylene protons indicates that methyl substituents at the tertiary carbons are *trans* with respect to the five-membered ring (Fig. 1).[22] The ^{13}C spectrum† further confirms the structure assignment. The signal at δ 74.36 (2C) due to the fullerene bridgehead sp^3 C atoms indicates that the compound has an σ-homoaromatic structure ('closed' transannular bond).[23,24] The number and intensity pattern of the signals in the fullerene region† correspond to an effectively C_2 symmetry. It is thus concluded that the bridging occurs at the 6–6 ring junction on the C_{60} cage.[24,25]

Molecular weight determination of the compound using matrix-assisted laser desorption ionization time-of-flight MS yields results (Fig. 1) that are consistent with the assignment of the NMR spectra. The product is a C_{60}–TEA mono-cycloadduct with no methine hydrogens on the cage (M_w = 819).

It is interesting that the photochemical reaction actually results in the formation of a cycloadduct. This is unique to the fullerene system; there have been no reports of cycloadducts in reactions of non-fullerene acceptors such as *trans*-stilbene.[3,6–9] The cycloadduct is likely to be formed in a two-step process. In terms of the classical photoinduced electron transfer–proton transfer mechanism,[3–9] a simple photochemical addition yields the C_{60}–TEA mono-adduct **I** [Scheme 1(*a*)]. However, a special property of the fullerene system is that the mono-functionalized C_{60} can continue to serve as an electron acceptor, as demonstrated in multiple additions of a single C_{60} cage by up to two dozen primary or secondary amine molecules.[26] The mono-adduct **I** can undergo further electron transfer reaction intramolecularly [Scheme 1(*b*)]. The transfer might even be a thermal process because dark reactions between C_{60} and triethylamine (high concentration) have been observed.[17,21] A

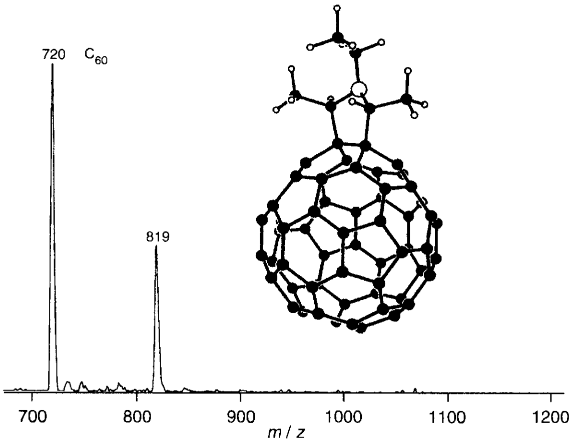
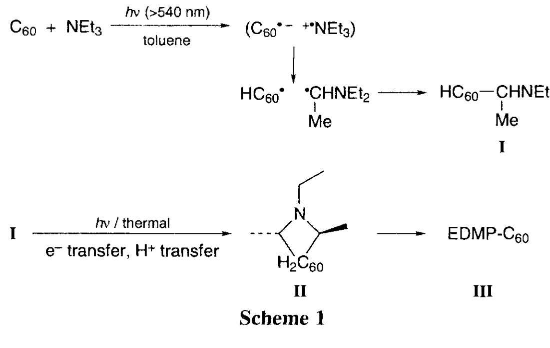


Fig. 1 Matrix-assisted laser desorption ionization time-of-flight mass spectroscopic study of EDMP-C_{60} in a matrix of α-cyano-4-hydroxycinnamic acid. The molecular structure is optimized by use of MM3 method.



Scheme 1

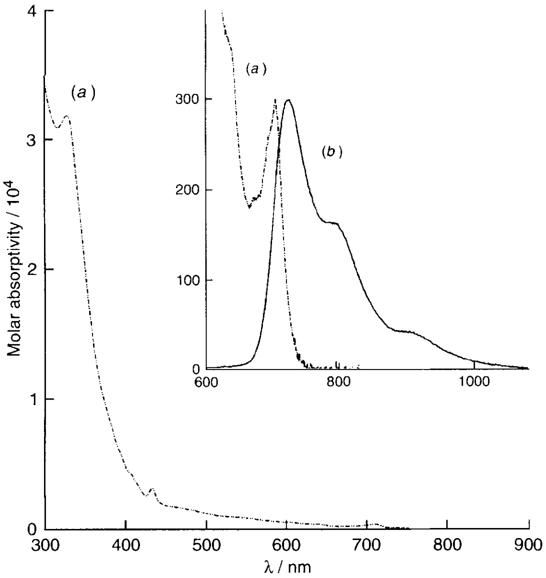


Fig. 2 (*a*) The absorption and (*b*) the uncorrected fluorescence spectra of EDMP-C_{60} in a toluene solution

similar process of proton transfer and radical pair combination [Scheme 1(*a*)] following the formation of an intramolecular ion pair results in the ring-closed product **II**. However, it is not clear how the two methine hydrogens on the cage are eliminated for the final product **III**. We suspect that it is due to an oxidation process similar to the one observed in the formation of phenanthrene from dihydrophenanthrene in the photocyclization reaction of *cis*-stilbene.[27–30] Despite a careful deoxygenation of the solution for photoirradiation, the oxidation process could hardly be prevented due to the possible existence of trace oxidants as solvent impurities and/or the fact that separation and characterization of the reaction mixture was carried out in an air-saturated environment.

The photoinduced electron transfer in the C_{60}–TEA system is surprisingly efficient. For *trans*-stilbene and other aromatic acceptors, photooxidation of simple trialkylamines typically requires a polar solvent environment.[3][‡] The fact that C_{60} and TEA undergo the characteristic photoinduced electron transfer–proton transfer reactions argues strongly for the suggestion[15,16] that the complete quenching of fullerene–amine exciplex emissions in polarizable solvents is due to the formation of ion pairs as an effective competing decay pathway.

The absorption and fluorescence spectra of EDMP-C_{60} are shown in Fig. 2. The absorption spectral profile is essentially the same as that of the *N*-methylpyrrolidine derivative of C_{60},[24,32] with a structured band at *ca.* 700 nm. The transition probability of the C_{60}–TEA cycloadduct is larger, which is probably responsible for a significant increase in the fluorescence quantum yield from that of C_{60}. The fluorescence spectrum and quantum yield of EDMP-C_{60} are independent of excitation wavelength. The yield is also not affected by the presence of oxygen in an air-saturated solution. The compound is stable with respect to photoirradiation due to excitations in repeated fluorescence measurements in an emission spectrometer equipped with a 450 W xenon source.

It is particularly interesting that EDMP-C_{60} consists of a covalently linked redox pair. Investigations on the redox properties of EDMP-C_{60} and related compounds are in progress.

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Footnotes

[†] ^{13}C spectrum (75.5 MHz, CS_2 solution, C_6D_6 internal lock) was accumulated overnight in the presence of 0.04 mol dm^{-3} $Cr(acac)_3$ (50000 scans). Resonances in the aliphatic region: δ 14.16 ($\mathrm{CH_2}\mathit{Me}$, 1C), 15.10 (2 × CH*Me*, 2C), 40.77 (*C*$\mathrm{H_2Me}$, 1C), 65.43 (*C*HMe, 2C), and 74.36 (bridgehead, 2C); and in the fullerene region: δ 155.85 (2C), 153.39 (2C), 146.95 (2C), 146.30 (2C), 146.01 (2C), 145.95 (2 × 2C), 145.71 (2 × 2C), 145.32 (2C), 145.15 (2C), 145.01 (2C), 144.98 (2C), 144.87 (2C), 144.27 (2C), 144.25 (2C), 142.85 (2C), 142.38 (2C), 142.32 (2C), 141.99 (2C), 141.89 (2C), 141.82 (2 × 2C), 141.52 (2C), 141.42 (2C), 139.91 (2C), 139.51 (2C), 136.79 (2C) and 135.84 (2C).

[‡] A noticeable exception is the photoaddition of tertiary amines to styrenes, in which polar solvents are not required.[31]

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