The preparation and structures of non-hydrocarbon functionalised fullerene–diamine adducts†

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Addends based on C2-substituted piperazine are employed to generate C_{60} monoadducts by photochemical addition, representing the first introduction of non-hydrocarbon addend functionality to fullerenes *via* the oxidative dehydrogenation reaction of diamines with fullerenes.

The numerous chemical reactions of fullerenes[1] have been well documented over the last decade. The Bingel–Hirsch addition–elimination of halomalonates, Prato's dipolar cycloadditions of azomethine ylides and Diels–Alder reactions of quinodimethano-derivatives are some of the best examples of relatively general, substrate tolerant methods for addition to C_{60}, with typical yields of up to 45%.[2]

The oxidative dehydrogenation reactions of C_{60} with primary and secondary amines[3] and diamines[4] were established early in the story of fullerene chemistry. The reactions of primary and secondary amines with C_{60} are very difficult to control and give different products depending on substrate and conditions. These products include 1,2- and 1,4- monoadduct regioisomers,[1c] fullerene dimers and fullerene oxides,[5] in addition to the usual array of multiple-addition products. Indeed, when considering the monoadducts of amines or diamines, only the reaction of piperazine with C_{60} gives a synthetically useful yield of a single monoadduct (*ca.* 50% in the best case reported[4]). To the best of our knowledge, every other amine or diamine reagent and conditions give ≤20% yield of a fullerene monoadduct.[4,6] More significantly, no diamine reagent reported to date has contained non-hydrocarbon functionality. Consequently the oxidative dehydrogenation addition of secondary diamines (and amines) to C_{60} has not been exploited to any significant extent as a general method for the introduction of functionality to fullerene derivatives.

Recently, in a paper describing the assignment of the ^{1}H NMR spectrum of the piperazine–C_{60} adduct, we reported the photochemical reaction of 2-methylpiperazine with C_{60}.[7] This reaction gave the corresponding monoadduct in 41% yield, which compares favourably with the yield achieved by Kampe and others for the piperazine–C_{60} monoadduct.[4] We also reported an improved preparation for this latter adduct, obtaining a 72% yield by photochemical reaction of stoichiometric quantities of fullerene and diamine. The following is a report describing preparations of non-hydrocarbon functionalised C_{60}–piperazine adducts based on this method (Scheme 1), illustrating the potential of these reactions as a more general procedure for fullerene monoderivatisation.

A typical reaction‡ involved irradiation[8] of a degassed toluene solution of C_{60} (typically *ca.* 0.11 mmol) and 3 equivalents of a racemic piperazine derivative **1** under a nitrogen atmosphere for 64 hours. A summary of the reaction times and yields is given in Table 1, as well as the previously reported piperazine and methylpiperazine reactions for comparison. During the reaction, the solutions changed colour from deep purple to brown, as is generally observed in fullerene addition reactions. In all cases, reactions of substituted piperazines were found to be slower than that of unsubstituted piperazine **1h** (entry 8, Table 1).

Reactions of piperazine derivatives with alkyl, hydroxyl, ether and amide functionalities (**1a–e**, entries 1–5, Table 1) all proceed readily and no bis-addition products were isolated. The successful reaction of the amide derivatives **1d** and **1e** was surprising given that attempted photochemical reactions of C_{60} with the ester **1g** (entry 7, Table 1) gave no isolable products despite observation of the expected colour change. Significantly less than quantitative amounts of C_{60} were recovered from the latter reaction mixture, suggesting that the observed colour change is the result of some reaction of decomposition products with the fullerene. Irradiation of the ester under reaction conditions, but in the absence of C_{60}, gave no noticeable decomposition. Presumably the ester is unstable to the photochemical conditions only in the presence of the strongly electron accepting fullerene. As these reactions are proposed to proceed *via* an electron transfer step, forming radical anion–radical cation pairs, it seems likely that it is the radical cation of the piperazine ester which is decomposing. Similarly, an attempted reaction of a silyl ether derivative of **1b** also gave no isolable products, despite an observed colour change during photolysis.

The structures of adducts **2a–f** were confirmed by ^{1}H and ^{13}C NMR spectroscopy, as well as MALDI-TOF mass spectrometry.
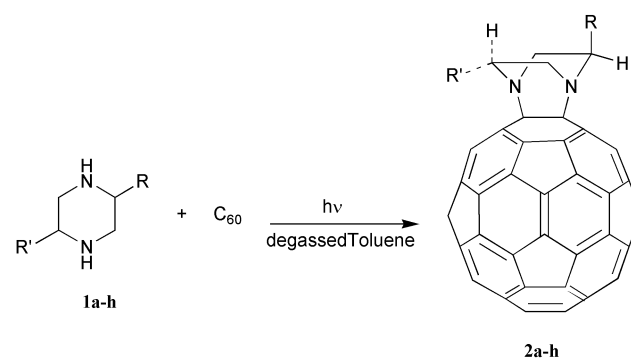
Scheme 1 Reaction of C_{60} with substituted piperazines **1a–h**.

Table 1 Yields of monoadducts **2a–h** from the photochemical reaction† of 3 equiv. of piperazines **1a–h** with C_{60} (80 mg) in toluene (80 ml)

Entry	Addend	Adduct	R	R′	t/h	Yield(%)
1	**1a**	**2a**	CH_3	H	64	41
2	**1b**	**2b**	CH_2OH	H	64	43
3	**1c**	**2c**	$CH_2OC_6H_{13}$	H	64	10
4	**1d**	**2d**	$CONH_2$	H	64	6
5	**1e**	**2e**	$CONHC_3H_7$	H	64	27
6	**1f**	**2f**	CH_3	CH_3	64	20[a]
7	**1g**	**2g**	CO_2Et	H	64	—[b]
8	**1h**	**2h**	H	H	18	72[c]

[a] Reaction employed 5 equivalents of **1f**. [b] Colour change observed, but no products isolated. [c] Reaction employed only 1 equivalent of piperazine **1h**.

† Electronic supplementary information (ESI) available: full synthetic and spectroscopic details. See http://www.rsc.org/suppdata/cc/b3/b303952h/

The ^{1}H NMR spectra of **2a–f** show all of the expected signals derived from their corresponding starting materials **1a–f**, albeit shifted significantly downfield in **2a–f** as is expected for addends on a C_{60} cage. The structures of the adducts **2a–e** are presumed to be bicyclic DABCO analogues, as illustrated in Scheme 1, similar to that of the known **2h**.[9] However for these C2-substituted examples, there are two possible arrangements for the C2-substituents, either *exo* or *endo* to the fullerene cage, as shown schematically in Fig. 1. In all photochemical reactions reported here, only one monoadduct was isolated. Our previous report[7] demonstrated that the methyl substituent in adduct **2a** occupies an *exo*-position and that *exo* protons give rise to ^{1}H NMR signals upfield of those corresponding to *endo* protons. This matched conclusions drawn elsewhere[10] for fullerene Diels–Alder adducts, in which resonances corresponding to *endo* groups in similar structures are observed downfield of the corresponding *exo* protons.
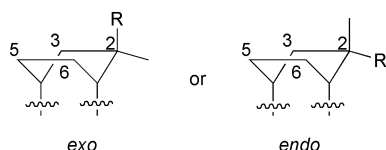

Fig. 1 Schematic diagram of addend conformations.

It is presumed that the C2-substituent in all of the mono-substituted adducts **2b–2e** also occupies an *exo* position. Indeed, the ^{1}H NMR spectra of **2b–e** were all substantially similar to that of the methyl derivative **2a** with the ^{1}H chemical shifts of *exo* and *endo* protons fitting the trend of **2a** and **2h** if the C2-substituent was assumed to be *exo* in all of these cases.[11] Analysis of COSY and NOE experiments supported these assignments although the crucial '1,3-diaxial' NOE between the C2-substituent and H6$_{exo}$ was not observed in the adducts **2b** and **2c** and cannot exist in amides **2d** and **2e** as there are no C2-methylene protons present.

In the case of the *trans*-2,5-dimethylpiperazine adduct **2f**, one methyl group must be *exo* to the cage, while the other methyl group must be *endo* to the cage. This is shown by the loss of symmetry in the ^{1}H NMR spectrum of **2f** compared to **1f**, with 2 independent resonances being observed for the methyl groups and 6 independent resonances for the ring protons in the former. While the loss of symmetry in the ^{1}H NMR spectrum of **2f** might also be explained by formation of an adduct with only one C_{60}–N bond, the lack of any resonance corresponding to a C_{60}–H in the ^{1}H NMR spectrum, and the identified mass of the protonated parent ion (m/z = 833) by MALDI-TOF mass spectrometry do not support this. The observed ^{1}H chemical shifts of the methyl group resonances also support the proposed configuration, with one resonance arising at δ 1.82 (*exo*-CH$_3$) and the other at δ 1.97 (*endo*-CH$_3$). The chemical shift of the more upfield resonance is comparable to that observed for the *exo* configured methyl group in adduct **2a** (δ 1.78), while the resonance at δ 1.97 fits the trend of signals arising from *endo* substituents being downfield shifted. There is also an observed NOE (*ca.* 2.5%) between the resonance at δ 1.82 and a resonance (δ 4.15) which, according to the COSY spectrum, is not in the same ^{1}H coupling system of adduct **2f**. This suggests a '1,3-diaxial' relationship between the two nuclei, thus assigning them both to *exo* positions.

The incorporation of the *endo* substituent does appear to have some energy cost, as the photochemical reaction of **1f** with C_{60} was much slower than those of the monosubstituted substrates and consequently 5 equivalents of substrate were employed for this reaction.

In the ^{13}C NMR spectra of all adducts, the most upfield resonances correspond to the piperazine adduct carbons (δ 10–62) and the sp[3] hybridised fullerene carbons (δ 77–81). The amide carbonyl resonances at *ca.* δ 171 are also observed for both adducts **2d** and **2e**. The remaining observed resonances (δ 136–154) correspond to sp[2] hybridised fullerene carbons. While not all of the expected ^{13}C resonances for the fullerene cage carbons in adducts **2a–f** are fully resolved, numeric analysis based on the smallest peak in the appropriate region suggests that all of the expected carbon resonances are indeed present, albeit overlapping in some cases.

In conclusion, we have developed methods for the first efficient monoaddition of diamines containing non-hydrocarbon functionality to C_{60}. Good yields of the corresponding monoadducts are achieved for cases where the piperazine substituents are stable to the photochemical conditions. For all monosubstituted piperazine adducts, the C2-substituent appears to preferentially occupy an *exo* position on the piperazine ring, however *endo* arrangements are energetically acceptable, albeit less so, as demonstrated by the *trans*-2,5-dimethylpiperazine adduct **2f**. We are currently exploring methods of preparing other polyfunctionalised examples and the synthetic potential of adduct **2b**, which can be used to access a wide variety of C_{60} derivatives by simple transformations of the hydroxyl functional group.

Notes and references

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11 The only exception to the trend was the H3$_{exo}$ protons of adducts **2d** and **2e**, which were observed at > 4.20 ppm. This is readily explained by a through-space deshielding effect of the adjacent C2-carbonyl group.