

The Absence of 'Globe-trotting' Hydrogen on the Surfaces of Aminated Fullerenes: 3-D Hydrogen Bonding between Aminated Fullerenes and Water Revealed

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Unusual temperature dependencies in the ^1H NMR spectra of aminated fullerenes, previously attributed to 'globe-trotting' hydrogen, are in fact due to temperature and dilution dependent hydrogen bonding interactions with water.

Soon after C_{60} became available in macroscopic quantities,¹ several groups worked to functionalize this novel form of carbon. Among the more interesting finds, Wudl *et al.* discovered² that C_{60} reacts readily and repeatedly with primary and secondary amines yielding aminated fullerene derivatives. Suggesting an electron transfer mechanism, it was reported² that each amination reaction is characterized by the

addition of R(R')N and H elements across a double bond of C_{60} , as one might expect upon the collapse of a $[\text{C}_{60}]^-$ $[\text{R(R')NH}]^+$ radical ion pair followed by (or subsequent to) proton transfer.³ Wudl *et al.* also reported² formation of a morpholine adduct of C_{60} , **1**, to which they assigned the structure $\text{C}_{60}\text{H}_6[\text{N}(\text{CH}_2\text{CH}_2)_2\text{O}]_6$,^{2b,c} and claimed^{2b} that the methine hydrogens readily 'globe-trot' about the aminated

fullerene surface *via* rapid, nearly degenerate [1,5]-sigma-tropic hydrogen shifts. Considering this dynamic process to be of tremendous interest, we sought to take a detailed look at hydrogen shifts on the surfaces of aminated fullerenes. In doing so, we discovered that the dynamic process observed is not due to 'globe-trotting' hydrogen, but instead results from reversible hydrogen bonding interactions between aminated fullerene and water.

Primary and secondary amine addition to C_{60} is facile.² Mixing the fullerene in neat amine at room temperature is sufficient to effect reaction in most cases. Thus, **1** was previously prepared^{2a,b} by adding C_{60} to neat morpholine. An unusual temperature dependence in the 1H NMR spectrum of a $CDCl_3$ solution of **1** was observed^{2b} and considered to be compelling evidence for rapid hydrogen migration about the aminated fullerene surface (*i.e.* 'globe-trotting' hydrogen). We reproduced such observations for solutions of **1**† in $CDCl_3$ and also observed similar temperature dependencies for the products of C_{60} and other amines including the corresponding dimethylamine addition product, **2**.‡ Room temperature 1H NMR spectra for separate solutions of **1** and **2** in $CDCl_3$ reveal in each case a broad, symmetrical signal resonating at δ 1.74§ and 1.72, respectively [Figs. 1(b) and (e); all chemical shifts are reported relative to $SiMe_4$ at 0 ppm]. Spiking the solutions with water causes the intensity of these signals to increase substantially and their chemical shifts to offset slightly. They remain broad and symmetrical but are now centred at δ 1.72 and 1.70, respectively [Figs. 1(c) and (f)]. Conversely, the addition of 3 Å molecular sieves removes these signals altogether [Figs. 1(d) and (g)]. Subsequent addition of water to dry solutions of **1** and **2** results in the reappearance of the original signals at *ca.* δ 1.7. These results conclusively demonstrate that the room temperature (RT) 1H NMR signals at *ca.* δ 1.7 are not indigenous to **1** and **2**, but are in fact due to water. As such, the temperature dependencies in the 1H NMR spectra of **1**^{2b}, **2** (Fig. 2), and other aminated fullerenes does not signal an intramolecular dynamic process (*e.g.* 'globe-trotting' hydrogen^{2b}), but rather an intermolecular one involving water-hydrogen bonding.

Alkyl amines are hygroscopic species. The hygroscopic nature of aminated fullerenes was confirmed *via* thermal gravimetric analysis (TGA) with FTIR detection of evolved gases, water in this case. Water also has some solubility in chloroform and most commercial sources of $CDCl_3$ contain water. In the absence of hydrogen bonding species, the water absorption in $CDCl_3$ is sharp and centred at *ca.* δ 1.52 [Fig. 1(a)]. Addition of alkyl amine causes this signal to broaden and move downfield [Figs. 1(b) and (e)] as a result of hydrogen bonding interactions.⁴ As expected, the protons on

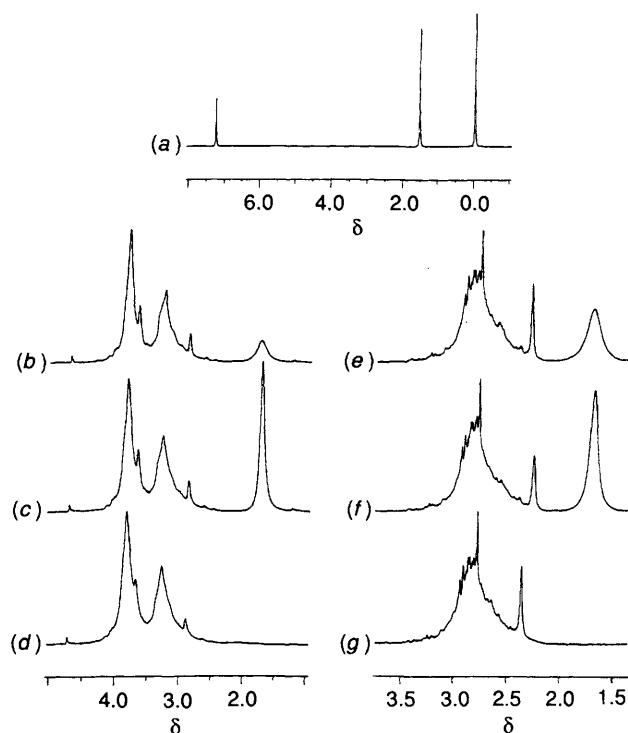


Fig. 1 1H NMR spectra of (a) $CDCl_3$ containing H_2O (δ 1.52), TMS $SiMe_4$ (0.0 ppm) and residual $CHCl_3$ (δ 7.24), (b) solution of **1** in $CDCl_3$ containing some H_2O , (c) **1** in $CDCl_3$ spiked with additional H_2O , (d) **1** in $CDCl_3$ after treatment with 3 Å molecular sieves to remove all H_2O , (e) solution of **2** in $CDCl_3$ containing some H_2O , (f) **2** in $CDCl_3$ spiked with additional H_2O and (g) **2** in $CDCl_3$ after treatment with 3 Å molecular sieves to remove all H_2O . Spectra were recorded on a 360 MHz Bruker FT-NMR at room temperature.

water rapidly exchange with deuterium upon addition of either CH_3OD ^{2b} or D_2O at RT.¶ Such exchange does not require the presence of aminated fullerene although if present, **1** and **2** can assist exchange *via* reversible protonation (deuteriation).

Unlike any intramolecular process (*e.g.* 'globe-trotting' hydrogen), intermolecular hydrogen bonding is long known to be both temperature and dilution dependent.⁴ Thus, the signals corresponding to hydrogen-bonded water in the 1H NMR spectra of **1** and **2** move downfield as the temperature of the sample, and consequently the rate of proton exchange, is decreased (Fig. 2). At $-40^\circ C$, the water signals are shifted *ca.* 1 ppm downfield [Figs. 2(c) and (g)] from their respective RT absorptions. At $-60^\circ C$, the water signals have moved even further and distinct sets of absorptions are observed for **1** corresponding to 'frozen' structures|| [Fig. 2(d)]. Dilution shifts the water absorptions to higher field (closer to the 1.52 ppm chemical shift observed for water in the absence of

† The orange-brown morpholine adduct of C_{60} , **1**, readily precipitates out of an all soluble C_{60} -neat morpholine solution ensuring that the product we prepared is identical to that prepared in ref. 2(b). Moreover, our IR and TGA characterization of **1** matches that reported in ref. 2(b).

‡ Quantitative ^{13}C NMR spectra of **2** indicate the addition of 10 dimethylamino groups to C_{60} . **2** was prepared by adding a 40 wt.% solution of dimethylamine in water (Aldrich Chemical Co.) to a solution/suspension of C_{60} in $CHCl_3$. The biphasic mixture was stirred for three days at RT during which time the $CHCl_3$ soluble product, **2**, was concentrated in the organic layer. Separation of the $CHCl_3$ layer followed by $MgSO_4$ drying, gravity filtration and evaporation of solvent at $50^\circ C$ under reduced pressure afforded the red-brown solid **2**. IR ν/cm^{-1} (KBr): 2964w, 2941s, 2860m, 2821m, 2776m, 1654br, m, 1452br, s, 1404w, 1381w, 1263s, 1221w, 1186w, 1157w, 1093br, s, 1022br, s, 862w, 801s, 753m, 662w, 579m, 557w, 528s, 392br, m.

§ Our δ 1.74 absorption for **1** in $CDCl_3$ [Fig. 1(b)] corresponds to the δ 1.84 absorption for **1** in ref. 2(b). The exact chemical shift of the water absorption is a function of the water : amine molar ratio as well as the temperature and extent of dilution.

¶ The only observation in ref. 2(b) that cannot be reconciled *via* a consideration of hydrogen bonding interactions with water is the appearance of a 2240 cm^{-1} C_{60} -D stretching frequency in the IR spectrum of deuterium exchanged **1**. Using the identical procedure outlined in ref. 2(b), we did not observe any IR bands that might be attributed to C_{60} -D stretching.

|| The 1H - 1H COSY 2D NMR spectrum of **1** at $-60^\circ C$ reveals several crosspeaks for each large, broad absorption. Thus, several distinct hydrogen bonding structures are frozen out at low temperature. **2** behaves differently from **1** to the extent that at $-60^\circ C$, a distinct set of 'frozen' structures is not observed [Fig. 2(h)]. Substantial increases in the viscosity of $CDCl_3$ preclude us from moving to lower temperatures. The differences in the low temperature spectra of **1** and **2** demonstrate that changes in amine basicity and/or structure impact the dynamic hydrogen bonding interactions observed.

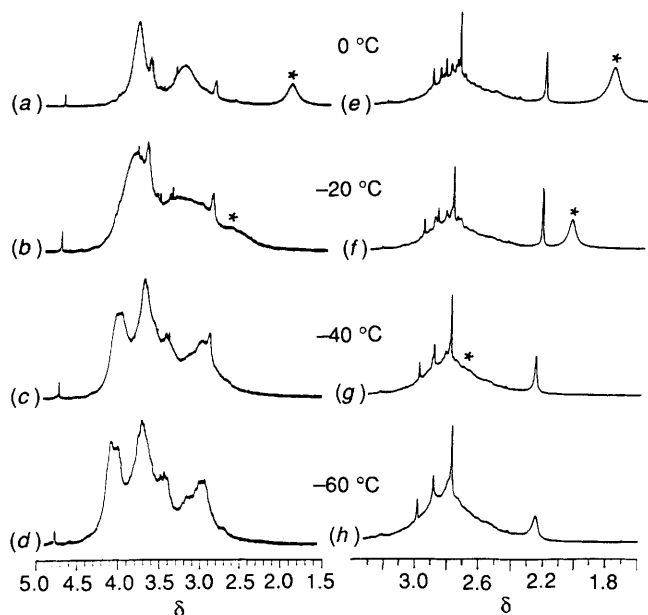


Fig. 2 Variable temperature ^1H NMR spectra of **1**, (a)–(d), and **2**, (e)–(h) in CDCl_3 containing some H_2O ; * denotes, where determinable, the locations of the H_2O absorptions. Spectra were recorded on a 300 MHz Varian FT-NMR.

aminated fullerene) and decreases their respective linewidths. For example, the δ 1.72 water absorption in Fig. 1(e) has a linewidth at half-height ($\Delta W_{1/2}$) of 37 Hz, while the same sample diluted 340-fold has a new chemical shift of δ 1.53 and a $\Delta W_{1/2}$ of less than 5 Hz. Non-fullerene containing tertiary amines behave similarly. Thus, trace water in a CDCl_3 solution of tripropylamine resonates at δ 1.70 at RT, δ 2.10 at -10°C , δ 2.75 at -40°C and δ 3.40 at -60°C . Likewise,

dilution shifts the water absorption to higher field (ultimately reaching δ 1.52) and decreases its $\Delta W_{1/2}$.

In summary, unusual temperature dependencies in the ^1H NMR spectra of aminated fullerenes do not, as previously reported, signal hydrogen migration about the aminated fullerene surface (*i.e.* 'globe-trotting' hydrogen). Pronounced temperature and dilution dependent hydrogen bonding interactions between aminated fullerenes and trace water fully account for such observations. Hydrogen bonding interactions between aminated fullerenes and other proton-donors are currently under investigation and will be reported in due course. Indeed, aminated fullerenes represent unique molecular templates upon which 3-D hydrogen bonding networks can be grown.

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