# $C_{60}$-Azacrown Ethers: the First Monoaminated Fullerene Derivatives

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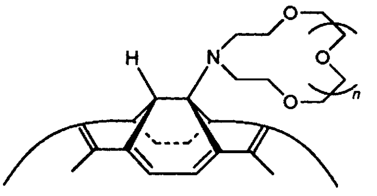
A family of $C_{60}$-azacrown ethers, the first examples of mono-aminated fullerenes, have been synthesised; spectroscopic evidence suggests that they may exist as two isomers probably arising from 1,2- and 1,4-addition.

In the study of the chemical modification of the fullerenes, investigations into the addition of nucleophiles, and particularly amines, have been of great interest.[1–9] Despite this, it has so far proved difficult to produce well-characterised derivatives, as multiple addition occurs readily, yielding mixtures of multiple addition products. However, Kampe *et al.*[1] have recently reported a method for the synthesis of di- and tetra-amino derivatives of $C_{60}$, while the addition of morpholine to $C_{60}$ by Wudl *et al.*[2,3] resulted in formation of the hexa-adduct.

All these reactions, however, involve multiple addition of amines to fullerenes. In this communication, we report the formation of a family of fullerene-azacrown ethers **1–3**, the first mono-amine derivatives of the fullerenes. (Fig. 1).



*n* = 1, $C_{60}$-1-aza-12-crown-4 ($C_{60}$-1A12C4), **1**
*n* = 2, $C_{60}$-1-aza-15-crown-5 ($C_{60}$-1A15C5), **2**
*n* = 3, $C_{60}$-1-aza-18-crown-6 ($C_{60}$-1A18C6), **3**

**Fig. 1** Diagram of the $C_{60}$-azacrown ether products showing addition at the most favourable site (by ZINDO calculations) of $C_{60}$

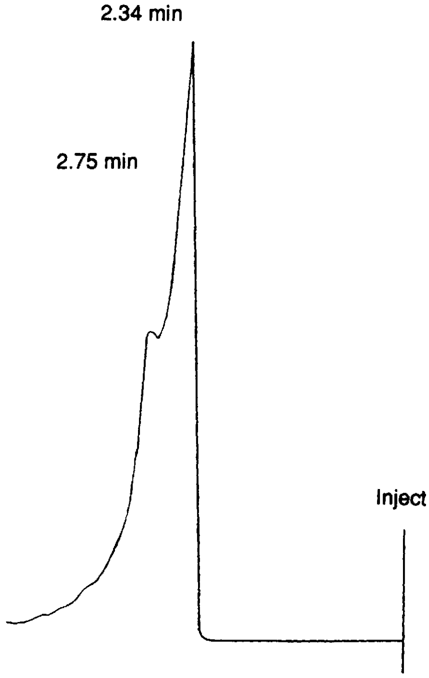


**Fig. 2** HPLC spectrum of **3**, showing evidence of two components. Separation on an octadecyl silica (5 μm) column, 25 cm × 4.6 mm I.D. Eluent, hexane(50):dichloromethane(10):ethanol(1); flow rate, 1 ml/min; detection, 254 nm.

The fullerene-azacrown ethers were formed by stirring 1 equiv. of azacrown ether with a toluene solution of $C_{60}$, at room temp. for up to 48 h. The reaction proceeded slowly, probably owing to the bulk of the amine, and could be terminated before multiple addition occurred. It is observed that addition of the larger azacrowns occurs more slowly than that of the smaller azacrowns.

The products were easily purified by column chromatography (silica, hexanes:dichloromethane:ethanol 25:10:1). Prior to this, any unreacted $C_{60}$ was removed by flash elution with toluene. The $C_{60}$-azacrown ethers were then isolated from any slower-running, multiple addition products and unreacted azacrown. The desired product was isolated in *ca.* 5% yield (76% based upon recovery of $C_{60}$).

The $C_{60}$-azacrown ethers **1–3** were characterised by FAB MS, IR, UV, $^{1}H$ and $^{13}C$ NMR spectroscopy.† The FAB MS confirmed that only mono-addition of the amine to the fullerene had taken place to produce the molecular ion corresponding to $[(M+H)\text{-}2H_2]^+$ (losses of $H_2$ molecules being common in MS of amines).[4] MS–MS studies also gave rise to the expected fragmentation products. Interestingly, exohedral metal ion complexation by each of the fullerene derivatives were also observed by FAB MS.[10]

Although the product appears clearly as one discrete spot by TLC, HPLC reproducibly demonstrated that this fraction consisted of two, as yet inseparable, major components (Fig. 2). There was no contamination by $C_{70}$ or higher fullerenes in our samples and no evidence of oxygenation or hydrogenation of the fullerene adducts. Therefore, as the spectroscopic evidence shows that only monoaddition had occurred, we believe these most likely represent the two different low-energy additions possible for the mono-adduct (Fig. 3).[11]‡

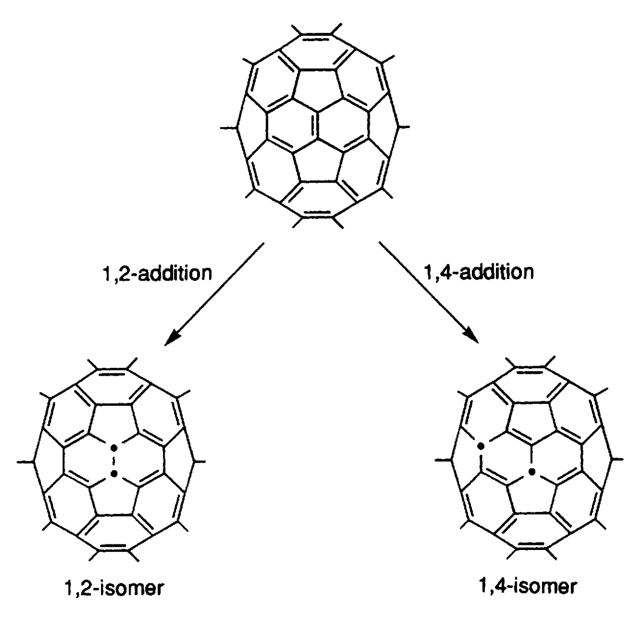


**Fig. 3** Diagram of the two most favoured isomers resulting from addition of the azacrown and the amine hydrogen[11]

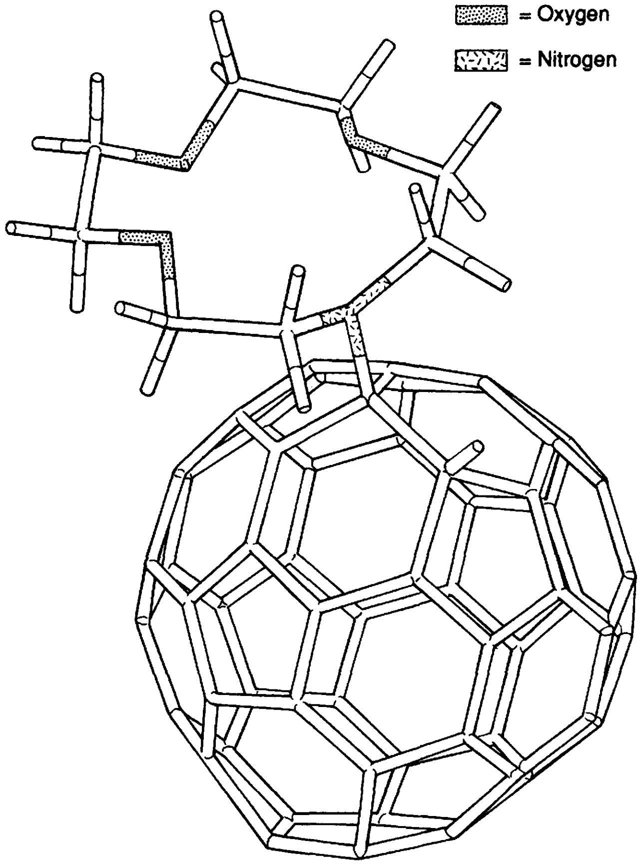


**Fig. 4** Semi-empirical minimised structure of the lowest energy isomer of $C_{60}$-1A12C4, **1**. Calculations were carried out on a Tektronix CAChe workstation using ZINDO.

These correspond to the 1,2-isomer and 1,4-isomer, of which the most favourable, from ZINDO calculations, is 1,2-addition (Fig. 4). The UV absorption spectra experimentally obtained are in excellent agreement with those predicted by ZINDO calculations for the 1,2- and 1,4-addition isomers.

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## Footnotes

† Data for **1**: brown solid, mp > 400°C; IR (KBr) $\nu$ cm$^{-1}$ 3300, 2920, 2860, 1465, 1360, 1290, 1250, 1220, 1140, 1085, 1025, 945, 910, 835, 800, 590, 555, 530; UV-VIS ($\lambda_{max}$, $CH_2Cl_2$) 275, 365; FAB MS: *m/z* = 892 $(M + H - 2H_2)^+$; FAB MS-MS: precursor ion *m/z* 892, fragment ions *m/z* 792 $[C_{60}\text{-}N(CH_2)_2OCH_2]^+$, 734 $[C_{60}N]^+$ and/or $[C_{60}CH_2]^+$, 172 [azacrown-$H_2$]$^+$, 128 $[(N(CH_2CH_2O)_2CH_2CH_2)\text{-}H_2]^+$; $^1$H NMR (300 MHz, $CS_2/CDCl_3$ 4:1) $\delta$ 5.87 and 5.83 (s) (fullerenyl-H of 1,2 and 1,4 isomers), 3.65 (m) (crown ether-H), 3.58 (m) (crown ether-H) ppm; $^{13}$C NMR-sample insufficiently soluble for satisfactory characterisation.

Data for **2**: brown solid, mp > 400°C; IR (KBr) $\nu$ cm$^{-1}$ 3460, 3400, 2910, 2865, 1745, 1670, 1445, 1385, 1290, 1245, 1220, 1205, 1170, 1135, 1090, 1040, 1020, 995, 980, 960, 915, 855, 835, 740, 660, 590, 570, 525; UV-VIS ($\lambda_{max}$, $CH_2Cl_2$) 260, 340; FAB MS: *m/z* = 936 $(M + H - 2H_2)^+$; $^1$H NMR (300 MHz, $CS_2$;$CDCl_3$ 4:1) $\delta$ 5.85 (b,s) (fullerenyl-H of 1,2 and 1,4 isomers), 3.5 (m) (crown ether-H), 3.35 (m) (crown ether-H); $^{13}$C NMR — sample insufficiently soluble for satisfactory characterisation.

Data for **3**: brown solid, mp > 400°C; IR (KBr) $\nu$ cm$^{-1}$ 2920, 2860, 1720, 1670, 1465, 1380, 1350, 1290, 1250, 1180, 1110, 945, 835, 575, 525; UV-VIS ($\lambda_{max}$, $CH_2Cl_2$) 255, 330; FAB MS: *m/z* = 982 $(M + H - H_2)$, 1005 $(M + Na)^+$; $^1$H NMR (300 MHz, $CS_2/CDCl_3$ 4:1) $\delta$ 5.8 (b,s) (fullerenyl-H of 1,2 and 1,4 isomers), 4.2 (b) (crown ether-H), 4.05 (b) (crown ether-H), 3.85 (s,b) (crown ether-H); $^{13}$C NMR (75 MHz, $CS_2/CDCl_3$ 4:1) $\delta$ 147–144 (15 peaks), 142–137 (21 peaks), 72.4–68.8 (13 peaks), 58.6 ($C_{60}$-H), 53.2 ($C_{60}$-H).

Satisfactory elemental analysis could not be obtained for any of **1–3**, probably because of incomplete combustion of the fullerene (%C obtained were always *ca.* 10% less than expected) or because of the observation of very tight binding of the crown ether fullerene derivatives to solvents of crystallisation, such as toluene and chloroform.

‡ Temperature dependent shifts in the NMR spectra of aminated fullerene derivatives, previously attributed to 'globe-trotting' hydrogens have recently been shown to be caused by H-bonding of the amines to water (ref. 5).

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