

Nitrogen derivatives of C₆₀ and C₇₀: Interaction of fullerenes with nitrogen in gas phase and with amines in solution phase

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Mass spectrometric studies show that contact-arc vaporization of graphite in a partial atmosphere of N₂ or NH₃ yields nitrogenous products tentatively assigned to species such as C₇₀N₂, C₅₉N₆, C₅₉N₄ and C₅₉N₂ involving addition of or substitution by nitrogen along with the species due to C₂ and C₄ losses. Mass spectrometry and other techniques have been employed to identify products of the nucleophilic addition of aliphatic amines to C₆₀ and C₇₀ in solution phase.

Research on C₆₀ has progressed at an enormous pace in the last few months. One of the important aspects of research in this area relates to the reactivity of C₆₀. It is known that C₆₀ readily produces singlet oxygen in high quantum yields¹ and reacts with oxygen². C₆₀ interacts strongly with nickel deposited on it as discussed in an earlier paper in this issue of the Journal. Our studies on the interaction of C₆₀ films with gaseous nitrogen³ by X-ray photoelectron spectroscopy showed evidence of strong binding with a sharp feature around 400 eV in the N(1s) spectrum⁴. (Note that graphite does not interact with N₂). Prompted by this observation and encouraged by the finding of Guo *et al.*⁵ that carbon can be replaced by boron in C₆₀, we sought to explore whether we can produce nitrogenous derivatives of C₆₀ and C₇₀ by carrying out the contact-arc vaporization of graphite in a partial atmosphere of gaseous N₂ or NH₃. We have indeed found that nitrogen containing derivatives of C₆₀ and C₇₀ involving the addition of nitrogen as well as substitution of carbon by nitrogen are formed in such a process. We report the results of our study in this article. In addition, we report results of our studies of the addition of aliphatic amines to C₆₀ and C₇₀. These fullerenes are shown to readily undergo nucleophilic additions of amines giving products involving the addition of 1,2,6,12 and even a larger number of amine molecules.

Materials and Methods

We carried out contact-arc vaporization of graphite in the presence of N₂ or NH₃ by leaking the gas at a rate of 1 cc sec⁻¹. Helium was simultaneously leaked at the same rate. The soot obtained was Soxhlet-extracted with toluene. After the solvent was evaporated from the toluene solution, the resulting product was light brown (in the case of N₂

reaction) or pale yellow (in the case of NH₃ reaction) in colour. Elemental analysis established the presence of nitrogen in the products. These products were subjected to mass spectrometric analysis and also other spectroscopic characterization. A JEOL direct inlet mass spectrometer (70 eV EI source) was used for the study.

C₆₀ (and C₇₀) were reacted with aliphatic amines such as CH₃NH₂ and (CH₃)₂NH in toluene solution at room temperature. Reaction took place instantaneously and the yellow products of the reactions were subjected to spectroscopic and mass spectrometric examination. Long chain amines were also reacted with C₆₀ in toluene solution under reflux.

Results and Discussion

Gas phase reactions with N₂ and NH₃

The product of the reaction between N₂ and the graphite vapour obtained after toluene extraction gave peaks in the mass spectrum at *m/z* 792, 764 and 736 along with the corresponding dication peaks (Fig. 1). Since the 792 peak is unlikely to arise from the substitution of 36 carbons of C₆₀ by nitrogen, we suggest that this is due to the addition of 5 nitrogen (N₅) and substitution of one carbon atom by nitrogen (N_s) giving a composition C₅₉N₆. Other possible alternatives are compounds with (5-n)N_a + (1+7n)N_s with n = 1, 2 or 3; even with n = 1, the formula works out to be C₅₂N₁₂ with more nitrogen than the structure can probably tolerate. We, therefore, feel that the assignment of the 792 peak to C₅₉N₆ may be reasonable; this is also justified by the internally consistent set of assignments of the other observed features that become possible on this basis. The 764 peak can be considered to be due to C₅₉N₄ (with 3N_a + 1N_s) arising from a loss of N₂ from C₅₉N₆ while the 736 feature is due to C₅₉N₂

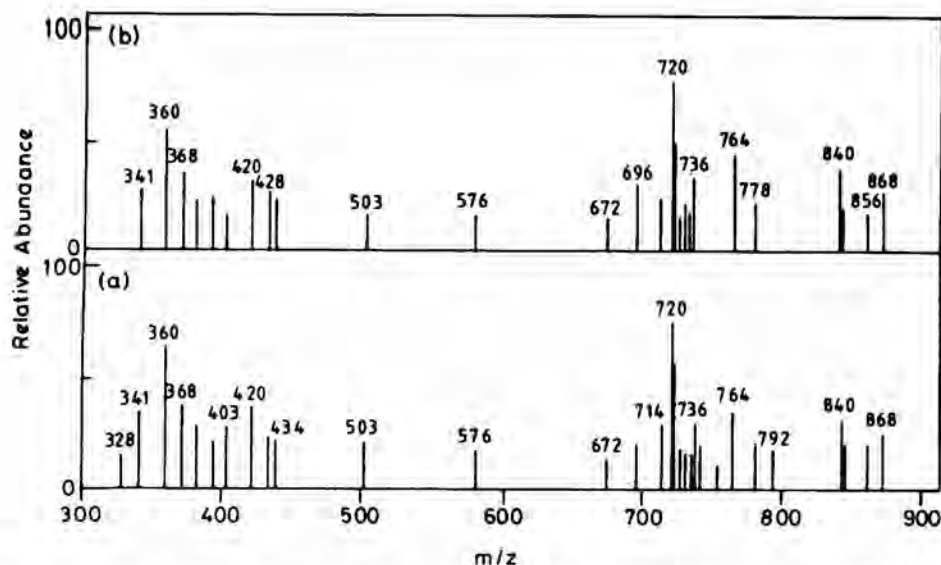


Fig. 1—Typical mass spectra of the toluene extract of the soot obtained from the contact-arc vaporization of graphite in a partial nitrogen atmosphere; (a) and (b) are spectra from different runs

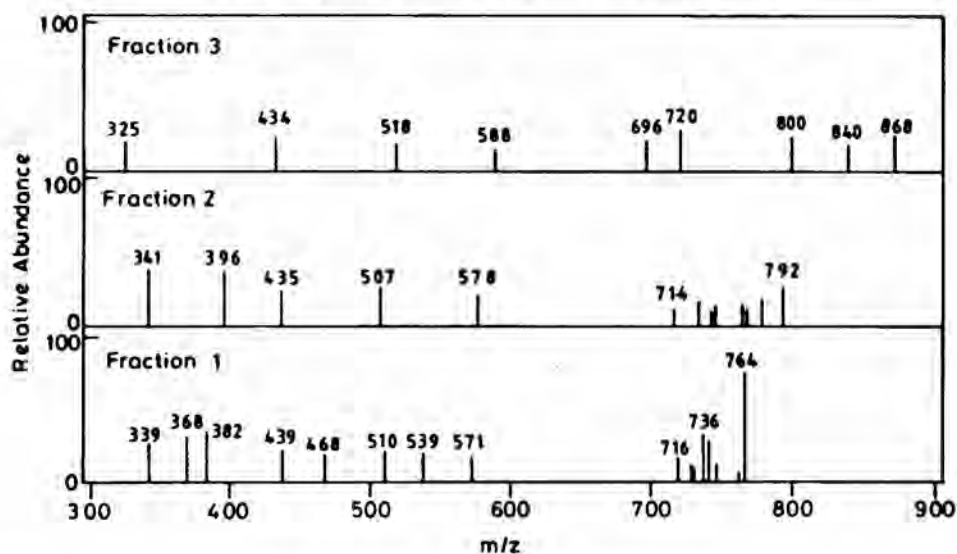


Fig. 2—Mass spectra of the chromatographic fractions of the toluene extract of the soot obtained from the contact-arc vaporization of graphite in a partial atmosphere of ammonia

(with $1 N_3 + N_5$) arising from a further N_2 loss. The other peaks in the mass spectra (Fig. 2) at m/z 778, 768 and 744 can be explained as due to loss of N , C_2 and C_4 respectively from $C_{59}N_6$. We also see peaks at m/z 722-728 which can be due to nitrogen substitution in C_{60} giving molecules in the range $C_{59}N-C_{56}N_4$. The m/z 868 peak (dication peak at 434) in the mass spectrum is clearly due to $C_{70}N_2$ with two N_3 ; the feature around 856 can also be due to $C_{69}N_2$ with 1 N_4 and 1 N_3 .

The yellow product of the NH_3 reaction with graphite vapours gave three fractions in column chromatography (with neutral alumina) which could be

eluted out with CH_2Cl_2 , leaving one band at the top of the column. Mass spectra of the three fractions showed the total absence of the m/z 720 peak due to C_{60} (Fig. 2), but instead showed peaks which can be assigned to nitrogenous products similar to those obtained in the vaporization of graphite in the presence of N_2 . Accordingly, the mass spectrum of fraction 1 showed peaks at m/z 764 and 736 (along with the corresponding dication peaks at m/z 382 and 368) due to $C_{59}N_4$ and $C_{59}N_2$. The peaks at m/z 740 and 716 are considered to be due to C_2 and C_4 loss respectively from $C_{59}N_4$; the other peaks in the mass spectra can also be interpreted in terms of si-

milar combinations of N_a and N_s. Fraction 2 showed peaks at *m/z* 792 and 764 due to C₅₉N₆ and C₅₉N₄ (Fig. 2); peaks at *m/z* 778, 768 and 744 are likely to be due to loss of N, C₂ and C₄ respectively from C₅₉N₆ while the other peaks in the *m/z* 714-742 range can be interpreted as due to combinations of N_a and N_s. Fraction 2 also showed peaks at *m/z* 868 and 434 due to C₇₀N₂; the peak at *m/z* 842 could be due to C₆₉N with one carbon substituted by nitrogen. Fraction 3 showed a peak at *m/z* 868 due to C₇₀N₂.

The compounds present in these fractions only show absorption in the ultraviolet region (Fig. 3). The infrared spectra are completely different from those of C₆₀ and C₇₀. While there could be some hydrogenation, we have not found evidence for C-H or N-H bonds. Contact-arc vaporization of graphite in a partial atmosphere of CH₃NH₂ also gives similar nitrogenous products, completely transforming C₆₀; C₅₉N₄, C₅₉N₂ and the associated peaks have been found by us in the mass spectrum.

In summary, the present study demonstrates that C₆₀ interacts strongly with nitrogen⁶. The reaction products of the contact-arc vaporization of graphite in a partial atmosphere of N₂ or NH₃ can be identified by mass spectrometry. In Table 1, we list the approximate description of the nitrogenous products; the exact characterization of these products, however, has to await more detailed mass spectrometric and chemical studies. It is possible that C₇₀N₂, C₅₉N₆ and C₅₉N₄ and possibly some of the species with mass numbers in the range 722-728 (C₅₆N₄-C₅₆N with only N_s) are bonafide compounds formed in the vaporization of graphite while the others are fragmentation features⁶. We are not able to comment on the nature of the nitrogen added to C₆₀ or C₇₀ at this stage, although one pos-

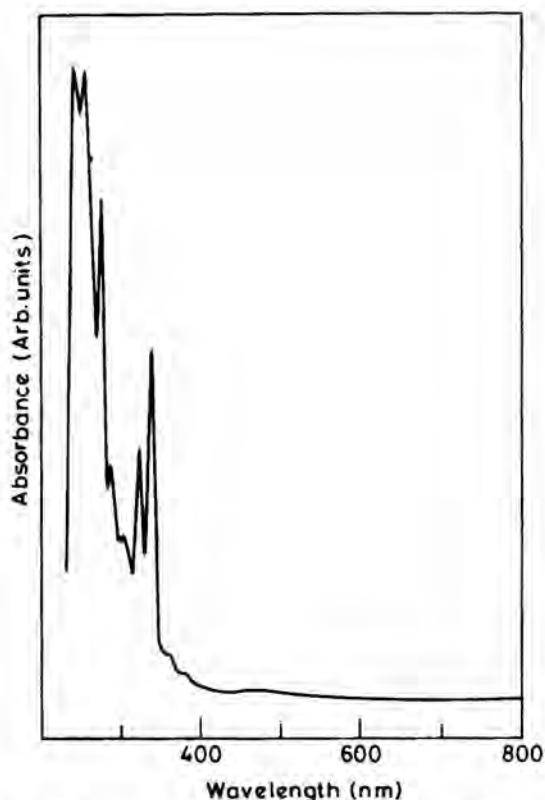


Fig. 3—Electronic absorption spectrum of fraction 1 from the NH₃ reaction

sibility is the formation of 3- or 4-membered rings. A noteworthy feature is that they seem to eliminate N₂ (e.g. C₅₉N₆ → C₅₉N₄ → C₅₉N₂). The likely reason that we have found formation of nitrogenous derivatives in the present study is because we did not backfill the reactor completely with N₂, but only leaked N₂ gas at a slow rate. On backfilling, we found a polymeric product.

Reactions with amines in solution phase

Addition of methylamine to C₆₀ was carried out by passing dry methylamine gas into a solution of C₆₀ in toluene at 298K. Such an addition gave rise to a yellow product almost instantaneously. This product was studied by mass spectrometry. A typical mass spectrum is shown in Fig. 4. The mass spectra showed a large number of addition products involving multiple addition of the amine to C₆₀. The intense peak with *m/z* around 751 corresponds to the addition of one CH₃NH₂ to C₆₀. Peaks with *m/z* of 727 and 703 could arise from C₂ and C₄ losses. The weaker peak at *m/z* of 782 could be assigned to the product with two MeNH₂ units. More interestingly, we see features which correspond to the addition of six CH₃NH₂ at *m/z* of 906 with associated fragmentation loss peaks at *m/z* of 882 and 858. Features

Table 1—Nitrogen derivatives of C₆₀ and C₇₀ identified by mass spectrometry

Mass No.	Molecular formula	Approximate description ^a
868	C ₇₀ N ₂	2 N _a
856	C ₆₉ N ₂	1 N _a + 1 N _s
842	C ₆₉ N	1 N _s
792	C ₅₉ N ₆	5 N _a + 1 N _s (4 N _a + 8 N _s) ^b
764	C ₅₉ N ₄	3 N _a + 1 N _s (2 N _a + 8 N _s) ^b
736	C ₅₉ N ₂	1 N _a + 1 N _s (8 N _s) ^b
728 to 722	C ₅₉ N ₄ to C ₅₉ N	4 N _s to 1 N _s

(a) N_a and N_s stand for addition of nitrogen and substitution of a carbon by nitrogen respectively. Alternative combinations of N_a and N_s are possible.

(b) Alternative descriptions of *m/z* 792, 764 and 736 features shown in parentheses would be C₅₂N₁₂, C₅₂N₁₀ and C₅₂N₈, but these seem unlikely.

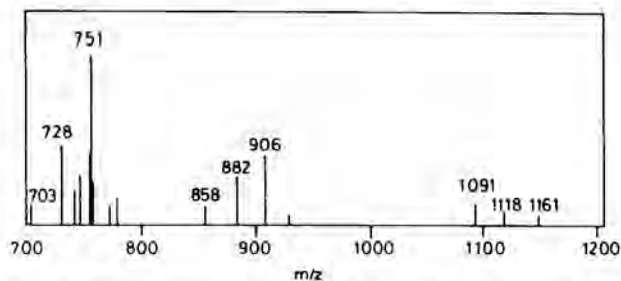


Fig. 4—Mass spectrum of the addition product of C_{60} with methylamine

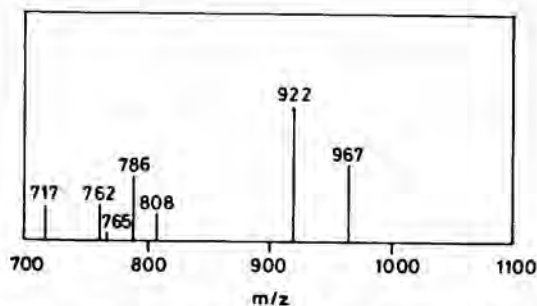


Fig. 6—Mass spectrum of the addition product of C_{60} with dimethylamine

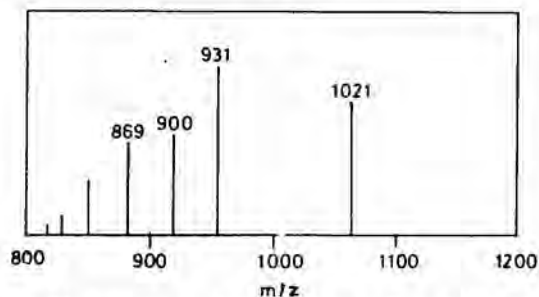


Fig. 5—Mass spectrum of the addition product of C_{70} with methylamine

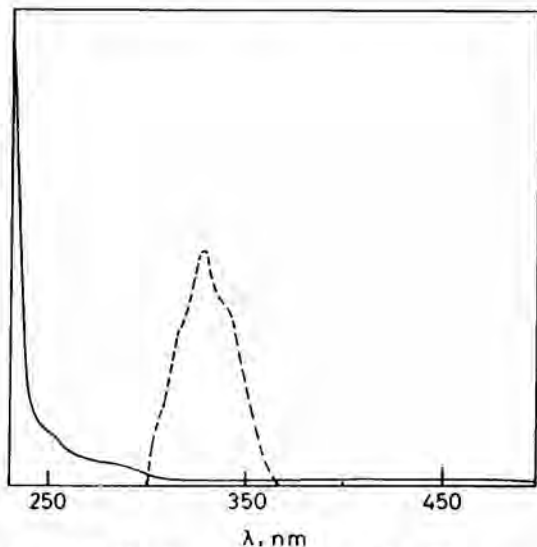


Fig. 7—UV-visible absorption (solid curve) and fluorescence (broken curve) spectra of the addition product of C_{60} and methylamine in methanol solution

which can be attributed to seven and eight CH_3NH_2 units were also seen in some scans. The highest m/z seen by us could be assigned to 12, 13 and 14 CH_3NH_2 units at m/z of around 1091, 1118 and 1148 respectively.

We carried out a similar reaction with C_{70} . A typical mass spectrum is shown in Fig. 5. Here we see peaks at m/z of 869, 900, 931 and 1021 which could be assigned to products with one, two, three or five CH_3NH_2 additions. We did not see evidence for the addition of a large number of amine molecules.

We carried out a reaction of C_{60} with dimethylamine in the same fashion. The mass spectra do not show strong molecular ion peaks (Fig. 6). However, based on fragmentation loss peaks at m/z 717 and 762, we assign the peaks at m/z of 765 and 808 to mono- and di-adducts. Peaks at m/z of 922 and 967 are considered to arise from the penta- and hexa-adducts respectively. In Fig. 7, we show the UV spectrum of the mixture of adducts with CH_3NH_2 along with the fluorescence spectrum. In Fig. 8, we show the infrared spectra of the amine adducts. The CH_3NH_2 adduct shows the N-H stretching band (3400 cm^{-1}) absent in the $(CH_3)_2NH$ adduct.

Mass spectrometry of the product of reaction of C_{60} with methylamine shows that we get a mixture of addition products, the predominant ones being the mono- and hexa-adducts. We attempted a separation of the components by thin-layer chromatography on silica using ethyl acetate-petroleum ether (40:60, v/v). We obtained separation into three

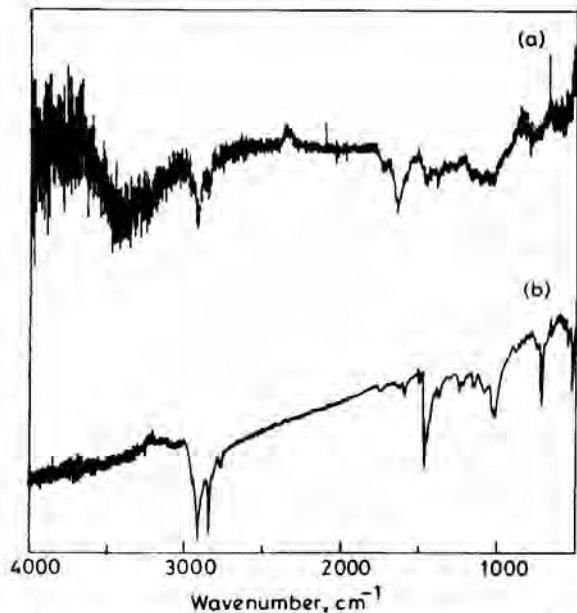


Fig. 8—IR spectra of the adducts of (a) CH_3NH_2 and (b) $(CH_3)_2NH$ with C_{60} . Notice the NH stretching band in (a)

bands 1, 2 and 3 with R.F. values of 0.61, 0.73 and 0.94. The highest mass peaks in the mass spectrum of 1 corresponds to the addition of 4 to 6 CH₃NH₂ units, although peaks corresponding to the addition of 8 to 11 amine units are occasionally seen. Fraction 2 seemed to give, predominantly, features corresponding to addition of 6 to 8 CH₃NH₂ units and some weak features due to the addition of up to 12 units. Fraction 3 was predominantly composed of products from the addition of 9 to 18 CH₃NH₂ units with a few of the lower adducts. We did not see these large adducts in the mass spectrum of the as-reacted product (Fig. 4) probably due to poor volatization.

We have been able to prepare an essentially pure mono adduct of C₄H₉NH₂ with C₆₀ by refluxing a 2:1 mixture in toluene solution. The UV spectrum of the product shows peaks at 328, 286, 271, 265

and 257 nm in the THF solution. The compound shows a fluorescence maximum at 394 nm (excitation maximum 330 nm). The mass spectrum showed the expected molecular ion peak at *m/z* 793.

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