

# Cyano adduct-anions of [60]fullerene observed by electrospray mass spectrometry

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**Negative-ion electrospray mass spectrometry of  $C_{60}$ -CN<sup>-</sup> solutions are used to study the cyano adduct-anions of [60]fullerene, revealing three abundant species, namely  $C_{60}(CN)_n^-$ ,  $n = 1, 3, 5$ , with  $C_{60}(CN)^-$  as the dominant anion.**

The nucleophilic addition reactions of [60]fullerene demonstrate its behaviour as an electron deficient polyalkene.<sup>1</sup> Thus  $C_{60}$  undergoes amination reactions such as with triethylamine,<sup>2</sup> where the intermediate radical anion,  $C_{60}^{\cdot-}$ , is thought to be involved. The  $C_{60}$  reaction with cyanide anion<sup>3</sup> forms the mono-adduct anion,  $C_{60}(CN)^-$ , as a soluble salt. Electrospray mass spectrometry (ESMS) examining both positive and negative ions has been demonstrated as a powerful technique in the study of fullerenes and their adducts. The study of  $C_{60}$  and  $C_{70}$  anions by negative-ion ESMS,<sup>4</sup> led to observation of higher fullerene anions.<sup>5</sup> Tagged fullerenes<sup>6</sup> and polyamine adducts of  $C_{60}$ <sup>7</sup> have been studied by positive-ion ESMS, and the methoxylated anions of  $C_{60}$  and  $C_{70}$  by negative-ion ESMS.<sup>5,8</sup>

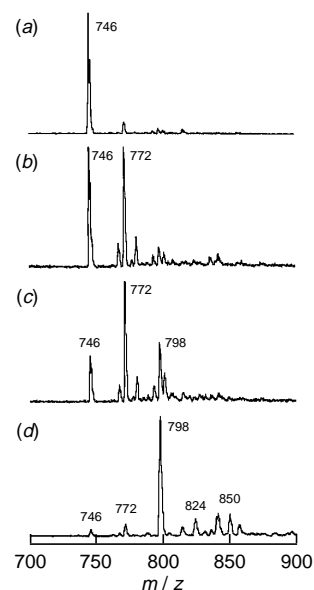
It has been noted that electrospray response varies according to source design as well as instrument conditions,<sup>8</sup> which offers an explanation for the different spectra observed for the methoxylated anions of  $C_{60}$  by Wilson and Wu<sup>8</sup> and by Hiraoka and coworkers.<sup>5</sup> The former observed only the even-electron species,  $C_{60}(OMe)_n^-$ ,  $n = 1, 3, 5$ , which are the more likely long-lived anions in solution, as confirmed by semi-empirical theoretical studies.<sup>9</sup> By contrast the latter workers observed one odd-electron species,  $C_{60}(OMe)_2^{\cdot-}$ , as well.<sup>5</sup> It is possible that this ion results from collision-induced dissociation of the stable higher ions within the electrospray source. However an electrospray source can also behave as an electrochemical cell,<sup>10,11</sup> and  $C_{60}^{\cdot-}$  is observed in the ESMS of  $C_{60}$  solutions.<sup>11</sup> Hence the odd-electron species  $C_{60}(OMe)_2^{\cdot-}$  is possibly resulting from electron attachment (reduction) of neutral  $C_{60}(OMe)_2$ .

We have used the reaction of  $C_{60}$  (MER Corporation) in dry 1,2-dichlorobenzene with NaCN in dry DMF to provide various solutions for examination by ESMS. Mass spectra were obtained with a VG BioQ triple-quadrupole system (VG Biotech, Altrincham, UK). The freshly prepared mixtures, which contained  $C_{60}$  total concentrations of ca. 0.5 mmol dm<sup>-3</sup> and NaCN of ca. 5–100 mmol dm<sup>-3</sup>, were injected directly into the spectrometer using a Rheodyne injector incorporating a 50 mm<sup>3</sup> loop. The mobile phase used was 1:1 propan-2-ol-water as recommended for its proven negative-ion sensitivity.<sup>12</sup> A flow rate of 5 mm<sup>3</sup> min<sup>-1</sup> was used and spectra were acquired in the negative-ion mode with the nozzle/skimmer (cone) voltage of 40 V. Scanning was from  $m/z$  700–900, with 25 scans being signal-averaged over a 120 s period to produce each mass spectrum.

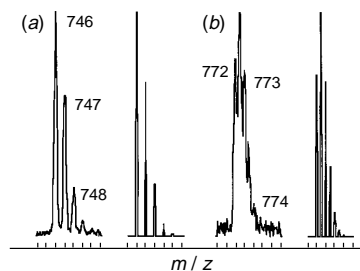
Visual observation of typical  $C_{60}$ -CN<sup>-</sup> solutions showed an initial olive green colour which changed progressively over a period of around an hour through dirty brown shades to a brown-yellow colour. The ESMS data presented here were obtained for solutions up to 1 h following mixing.

Typical spectra measured for various CN<sup>-</sup> concentrations and at various times, Fig. 1, exhibit strong peaks in the 740–800  $m/z$  range. The three peaks located at  $m/z$  values of 746, 798 and

850 indicate the presence of the even-electron cyano adduct-anions  $C_{60}(CN)_n^-$ ,  $n = 1, 3, 5$ . At higher resolution each peak clearly demonstrates the appropriate isotope ratios based on natural <sup>12</sup>C/<sup>13</sup>C as illustrated for the 746 peak in Fig. 2. The four discernible isotopes of  $C_{60}(CN)^-$ , of  $m/z$  746, 747, 748 and 749, have theoretical relative abundances of 100:68:23:5. However the peak at 772, of  $m/z$  corresponding to the odd-electron  $C_{60}(CN)_2^{\cdot-}$  species, as also shown in Fig. 2, exhibits an isotope distribution revealing 0.5 amu spacings, contrary to this formula. This pattern is suggestive of a doubly-charged ion containing two  $C_{60}$  units, and our conjecture is that it is an ion-molecule complex, namely  $C_{60}(CN)_4^{2-} \cdot C_{60}$ . This is supported by our observation that  $C_{60}(CN)_4^{2-}$  at  $m/z$  412 is also present in some  $C_{60}$ -CN<sup>-</sup> solutions.<sup>13</sup> Likewise the 824 peak is probably due to the analogous  $C_{60}(CN)_8^{2-} \cdot C_{60}$  species.



**Fig. 1** Negative-ion electrospray mass spectra for  $m/z = 700$ – $900$  of  $C_{60}$ -CN<sup>-</sup> solutions (a) [CN<sup>-</sup>] = ca. 5 mmol dm<sup>-3</sup>, (b) [CN<sup>-</sup>] = ca. 50 mmol dm<sup>-3</sup> at 25 min, (c) [CN<sup>-</sup>] = ca. 50 mmol dm<sup>-3</sup> at 50 min, and (d) [CN<sup>-</sup>] = ca. 100 mmol dm<sup>-3</sup>



**Fig. 2** Comparison of experimental and theoretical <sup>12</sup>C/<sup>13</sup>C isotope distributions for the negative-ion mass spectra of (a)  $C_{60}(CN)^-$  and (b)  $C_{60}(CN)_4^{2-} \cdot C_{60}$

The spectra of fresher and lower concentration solutions are dominated by  $C_{60}(CN)^-$  in agreement with the observation of this species as the intermediate in the reactions described by Majid *et al.*<sup>3</sup> For older and more concentrated solutions the relative abundance of  $C_{60}(CN)_3^-$  increases and then  $C_{60}(CN)_5^-$  likewise, with all three ( $n = 1, 3, 5$ ) present in some cases in comparable amounts. There are various other weak peaks in this mass region, and these can be assigned to species containing oxygen indicative of some degree of oxidation.

A comparison with the ESMS data reported<sup>5,8</sup> for  $C_{60}(OMe)_n^-$  shows that the same even-electron species ( $n = 1, 3, 5$ ) are dominant. However the  $C_{60}^-$  observed in the  $C_{60}-OMe^-$  mixtures is not observed here with the  $C_{60}(CN)_n^-$  species.

The results of semi-empirical molecular orbital calculations obtained using the AM1 approximation with the MOPAC program<sup>14</sup> are presented in Table 1. On the basis of earlier calculations<sup>9</sup> on the OMe<sup>-</sup> adducts the likely isomers for the  $C_{60}(CN)_n^-$  ( $n \geq 2$ ) species are relatively few in number. An analysis of the charge distribution for  $C_{60}(CN)^-$  shows that the negative charge is located mostly on and near the CN group, analogous to the case of  $C_{60}OMe^-$ .<sup>9</sup> So for the higher isomers the structures with reasonably localized CN groups should adequately support the excess negative charge in their vicinity.

The calculated ionization energies and heats of formation, and the derived mean binding energies per CN of the chosen isomeric structures for each  $C_{60}(CN)_n^-$  for  $n = 1, 3, 5$  are given in Table 1. The latter parameters offer a simple quantitative comparison of the relative stabilities of the respective anion species.

**Table 1** MOPAC/AM1 results for selected isomers of  $C_{60}(CN)_n^-$ ,  $n = 1, 3, 5$ ; calculated ionization energies, IE (in eV) and heats of formation,  $\Delta H_f$  with mean binding energies per CN,  $\Delta H_b$  (kJ mol<sup>-1</sup>)

Molecule	Structure <sup>a</sup>	IE	$\Delta H_f$	$\Delta H_b^b$
$C_{60}$		9.64	4072	
$C_{60}^-$		3.31	3771	
$CN^-$		3.13	184	
$C_{60}(CN)^-$		4.99	3817	439
$C_{60}(CN)_3^-$	1,4,11-	5.37	3950	197
	1,4,55-	5.13	3994	182
	1,4,15-	5.19	4016	175
$C_{60}(CN)_5^-$	1,4,11,15,30-	6.09	4042	157
	1,2,39,57,60-	5.31	4169	131
	1,4,39,53,57-	5.31	4176	130

<sup>a</sup> The numbering system used is that given in ref. 15. <sup>b</sup>  $\Delta H_b$  is given by  $\Delta H/n$  for the reaction  $C_{60} + n CN^- \rightarrow C_{60}(CN)_n^-$ .

Since the ionization energies (IEs) of the anions are significantly positive and increasing with increasing  $n$ , it is not surprising that the strong ionic environment is able to support the negative charge state of these species. So  $C_{60}^-$ , with its much lower calculated IE of 3.31 eV, is not supported in this environment, while  $C_{60}(CN)^-$  with its higher IE of 4.99 eV is present at moderate  $CN^-$  concentration. Hence the favoured isomers of  $C_{60}(CN)_3^-$  and  $C_{60}(CN)_5^-$  with their higher IEs of 5.37 and 6.09 eV, respectively, are formed at higher  $CN^-$  concentration and over time. However the  $CN^-$  concentration may not be high enough to produce the  $C_{60}(CN)_7^-$  species, possibly because of an unfavourable equilibrium with  $C_{60}(CN)_6$ , which, with a structure likely to be the same as  $C_{60}Cl_6$ ,<sup>15</sup> is expected to be the most stable of the neutral species considered. Overall these results show good correspondence with the ESMS observation of the dominance of  $C_{60}(CN)^-$  represented in the spectra of Fig. 1.

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