Structures of Gas-Phase $(C_{60})_n(CN)_m$ Trianions from Reactions of C_{60} with NaCN in Solution

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Received: July 29, 1998; In Final Form: September 22, 1998

Negative ion electrospray mass spectra of solutions containing C_{60} and a 100-fold molar excess of NaCN display numerous polyanionic species of the general form $(C_{60})_n(CN)_m{}^{x-}$ where $n = 1-3$, $m = 1-7$, and $x = 1-3$. Collision-induced dissociation studies of selected di- and trianions reveal the structures of those ions; e.g., $(C_{60})_3(CN)_7{}^{3-}$ is shown to be $[C_{60}(CN)_2 \cdots C_{60}(CN)_3 \cdots C_{60}(CN)_2]^{3-}$. Simple electrostatic calculations indicate that the effective binding force ("$\cdots$" in the aforementioned example) between the components may result from a Coulomb barrier acting to prevent spontaneous dissociation of the components.

1. Introduction

Long-lived doubly charged negative ions in the gas phase have now been reported for a growing number of molecules. Several of these studies have been summarized in two recent review articles.[1,2] Many of the dianions have involved fullerene molecules or fullerene derivatives, e.g., $C_{60}{}^{2-}$ and $C_{70}{}^{2-}$,[3−5] $C_{84}{}^{2-}$,[6] $C_{60}F_{48}{}^{2-}$,[7,8] $C_{60}(C_nF_{2n+1})_m{}^{2-}$,[9] and $C_{60}F_{35}{}^{2-}$.[10] The publication by Khairallah and Peel[11] of the negative-ion mass spectrum of $C_{60}(CN)_n{}^{2-}$ ($n = 2-6$) represents a further addition to that series of publications. In that study, the spectrum was generated in situ by mixing solutions of C_{60} in 1,2-dichlorobenzene (DCB) and NaCN in dimethylformamide (DMF) and infusing the mixture into the electrospray source of a quadrupole mass spectrometer. Of particular interest to us was the assignment of *four* negative charges on a gas-phase cluster of fullerenes; namely, $(C_{60})_3{}^{4-}$ at *m/z* 540. Highly charged negative species generated by the abstraction of several protons from polyfunctional organic molecules are not uncommon in electrospray and ion spray mass spectrometry. For instance, the generation of polyanionic oligosacharides with up to seven negative charges has been reported.[12] However, the occurrence of relatively small quadruply charged clusters generated by the addition of electrons to molecules that already possessed complete "closed-shell" electron configurations was of considerable interest.

Our previous studies have firmly established the importance of the Coulomb barrier (CB) in providing increased stability for dianions (see refs 6 and 7). We term the effect "Coulomb barrier induced bound state" (CBIBS) to differentiate it from standard covalent or ionic bonds. It is natural to ask whether charged molecules could also be held together by CBs. The possibility that $(C_{60})_3{}^{4-}$ was long-lived suggested that a CBIBS might be instrumental in preventing a "Coulomb explosion" into separate C_{60} anions. Unfortunately, our replication (at somewhat higher resolution) of the experiment conducted by Khairallah and Peel indicated that the supposed $(C_{60})_3{}^{4-}$ had been misassigned. In this report we provide a corrected assignment for the ion cluster at *m/z* 540 and assign structures for other multiply charged anions not addressed by those authors. We also present the results of preliminary calculations involving only electron dipole and polarizability attraction, which indicate that the observed triply charged anion structures involving more than one C_{60} entity may result from CBIBS.

2. Experimental Section

Stock solutions of 1 mM C_{60} in 1,2-dichlorobenzene and 0.1 M NaCN in dimethylformamide were prepared from commercially available ingredients. C_{60} (99%) was obtained from Southern Chemical Group, LLC (Tucker, GA). All other chemicals were obtained from from Aldrich Chemical Co. (Milwaukee, WI). All reagents were used without further purification. Equal volumes of the stock solutions were mixed in a vial immediately prior to a mass spectrometric experiment. For the "degassed" experiment, ∼2 mL of each of the stock solutions was loaded into a separate septum-capped vial with a syringe needle left penetrating the septum. These vials were loaded into a glass container fitted with a three-way valve connected to a vacuum pump, and an argon cylinder. The glass container was subjected to three cycles of freeze (liquid N_2), evacuate, close valve, and thaw. After the last thaw, the container was filled with Ar. Upon opening the outer container, the syringe needles were removed from the septa, thus sealing the now oxygen-depleted solutions under an argon blanket. Equal volumes of the degassed solutions were mixed in an argon-filled, septum-capped vial prior to mass spectrometry.

Negative-ion electrospray mass spectrometry was conducted on a Quattro-II (Micromass, Manchester, U.K.) instrument by direct infusion of the reaction mixture at 3 μL/min. Source temperature was maintained at 90 °C, and the nebulizing- and drying-gas flow rates were 30 and 300 L/h of N_2, respectively. The capillary and cone (nozzle to skimmer) voltages were 2250 and 30 V, respectively. Numerous scans were averaged over the acquisition times indicated in the figure captions. For collision-induced dissociation (CID) experiments, the precursor ion was selected in the first analyzer (MS1) of the triple quadrupole instrument, then allowed to collide with argon (3.4×10^{-3} mbar) in the rf-only collision quadrupole, and the resulting fragments were analyzed in the last quadrupole (MS2).

Because the relative intensities of the ions of interest are to some degree time-dependent,[11] a delay time was sometimes used between mixing of the stock solutions and the onset of data

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10.1021/jp983212f CCC: $15.00 © 1998 American Chemical Society
Published on Web 10/29/1998

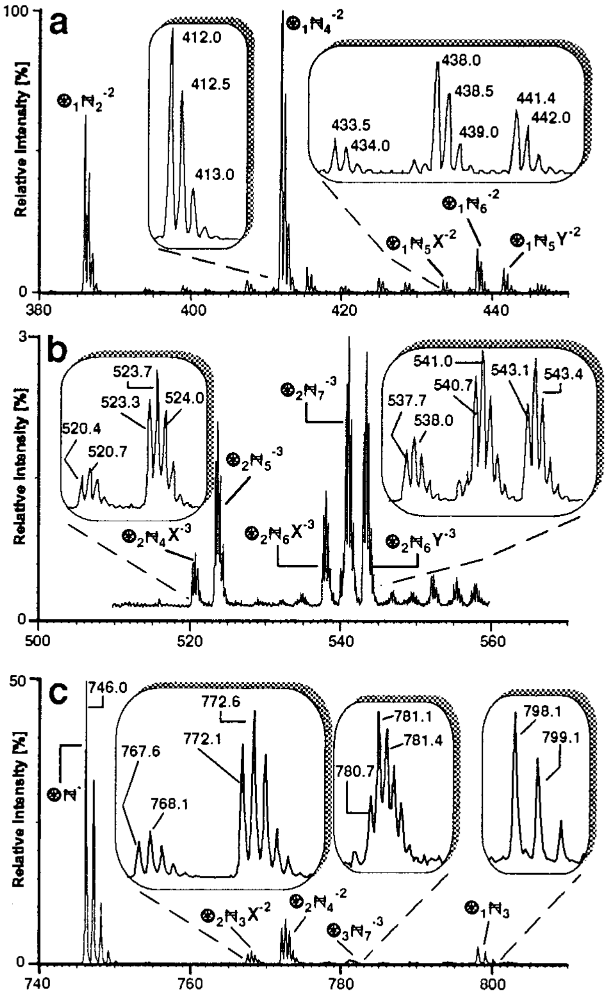


Figure 1. Three mass regions of the same negative-ion electrospray spectrum generated by spraying a mixture of C_{60} and NaCN in DMF/DCB for 15 min after a delay time of 2 min. Each region is normalized to the largest peak in that region. The "relative intensity" scales at the left indicate the approximate degree of magnification required to achieve this normalization. Thus, the intensity axis of part b has been magnified ~33× relative to that of part a, and part c is magnified ~2× relative to that of part a. All insets are expanded ×3 along the mass axis. The mass ranges below (down to *m*/*z* 50), above (up to *m*/*z* 2500), and between those depicted in Figure 1 were checked and did not contain salient peaks of interest. Structural assignments for peak clusters are in code: "circled asterisk" = "(C_{60})", "double-strikethrough N" = "(CN)", "X" = "OH", and "Y" = "OOH".

acquisition. Relatively long acquisition times were needed to compensate for the low absolute signal intensities resulting from the high resolutions needed to adequately identify the charge states of the polyanions. The duration of data acquisition and the delay time are recorded within the individual figure captions.

TABLE 1: Calculated Monoisotopic *m*/*z* Values for Structures Assigned in Figures 1−5

$(C_{60})_n(CN)_m(OH)_i(OOH)_j$				calcd *m*/*z* for		
n	*m*	*i*	*j*	$z = 1$	$z = 2$	$z = 3$
1	1			746.0		
1	1	1		763.0		
1	2			772.0	386.0	
1	3			798.0		
1	3	1		815.0		
1	3		1	831.0		
1	4			824.0	412.0	
1	4	1			420.5	
1	4		1	857.0	428.5	
1	5				425.0	
1	5	1			433.5	
1	5		1		441.5	
1	6				438.0	
2	3	1			767.5	
2	4				772.0	
2	4	1				520.3
2	5				785.0	523.3
2	5	1			793.5	
2	5		1		801.5	
2	6				798.0	
2	6	1				537.7
2	6		1			543.0
2	7					540.7
3	7					780.7

3. Results and Discussion

Newly Identified Products from the Reaction $C_{60} + CN^- \rightarrow (C_{60})_n(CN)_m^{x-}$. The negative-ion electrospray spectrum obtained from the solution of C_{60} + NaCN (under conditions essentially identical to those described by Khairallah and Peel, except for higher resolution) is displayed in Figure 1. The resolution was set to the highest practical level attainable on the Quattro-II quadrupole instrument without drastically compromising signal intensity. The measured resolution is ~0.2 Da (peak width at half-height = PWHH). To conserve space, structural assignments of isotope clusters are labeled in code in Figures 1−5, with the circled-asterisk and the double-strikethrough N symbols representing "(C_{60})" and "(CN)", respectively. The assignments were derived from the charge states of the individual clusters, combined with the *m*/*z*-value of the monoisotopic (=lowest mass) peak of each cluster. These values are readily discerned when spectrum resolution is adequate to separate the individual peaks of each ^{13}C cluster. Singly, doubly, and triply charged clusters produce peak spacings ($=\Delta^{13}C$) of 1.0, 0.5, and 0.33 Da, respectively. In cases where clusters are referenced in this text by their *m*/*z* values, the observed value of the monoisotopic peak is used. For the readers' convenience, the calculated monoisotopic *m*/*z*-values of all assigned structures discussed in this paper are listed in Table 1.

The first mass range (Figure 1a) contains exclusively doubly charged anions ($\Delta^{13}C = 0.5$ Da) encompassing a single C_{60}. The "satellite" clusters around $C_{60}(CN)_4^{2-}$ and $C_{60}(CN)_6^{2-}$ are oxygenated species presumably derived from the reaction of nitrilated intermediates with H_2O and/or O_2 dissolved in the solvents (see discussion below). All of the assigned clusters in Figure 1a have previously been identified.[11]

The second mass range (Figure 1b) contains exclusively triply charged species ($\Delta^{13}C = 0.3$ Da) encompassing two C_{60} entities. The major salient clusters, *m*/*z* 523.3 and 540.7, are assigned the compositions $(C_{60})_2(CN)_5^{3-}$ and $(C_{60})_2(CN)_7^{3-}$, respectively. One oxygenated satellite accompanies the former and two accompany the latter, indicating that the reactions leading to the formation of these oxygenated species are fundamentally different (see discussion below). The cluster assigned as $(C_{60})_2(CN)_7^{3-}$ in Figure 1b (*m*/*z* 540.7) was previously thought to be $(C_{60})_3^{4-}$.[11] The carbon isotope separations of 0.3 Da and the observed *m*/*z*-value of the monoisotopic peak unambiguously support the trianion assignment.

Within the last mass range (Figure 1c) three types of anion are present: monoanions comprising one C_{60} unit $\{C_{60}CN^-$ and $C_{60}(CN)_3^-\}$, dianions comprising two C_{60} units $\{(C_{60})_2(CN)_4^{2-}$ and $(C_{60})_2(CN)_3(OH)^{2-}\}$, and a trianion comprising three C_{60} units $\{(C_{60})_3(CN)_7^{3-}\}$. The singly and doubly charged $(C_{60})_n(CN)_m$ species have been previously identified,[13] and the

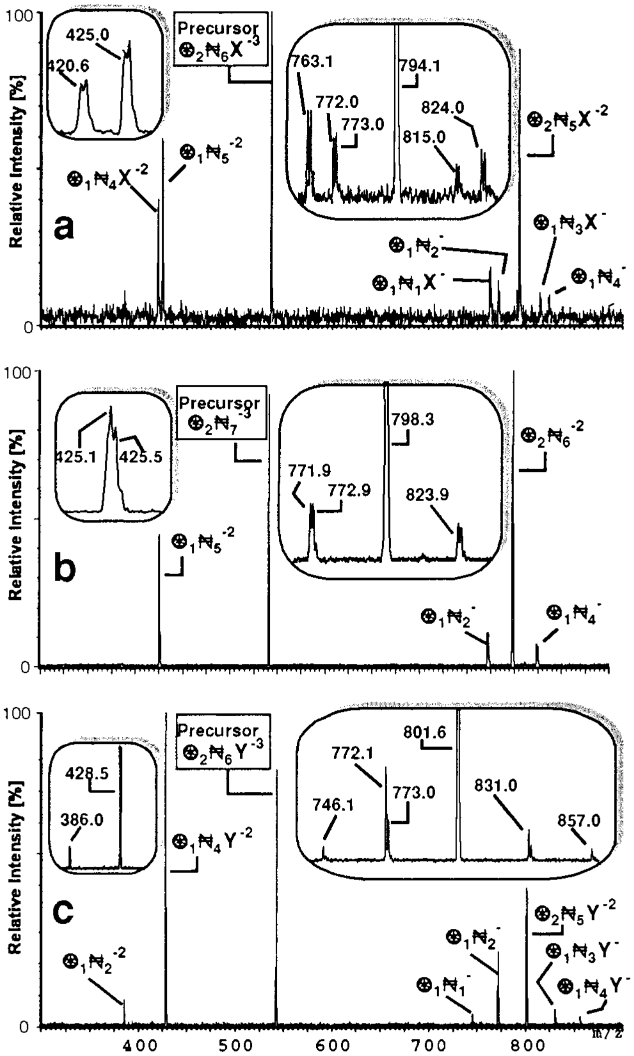


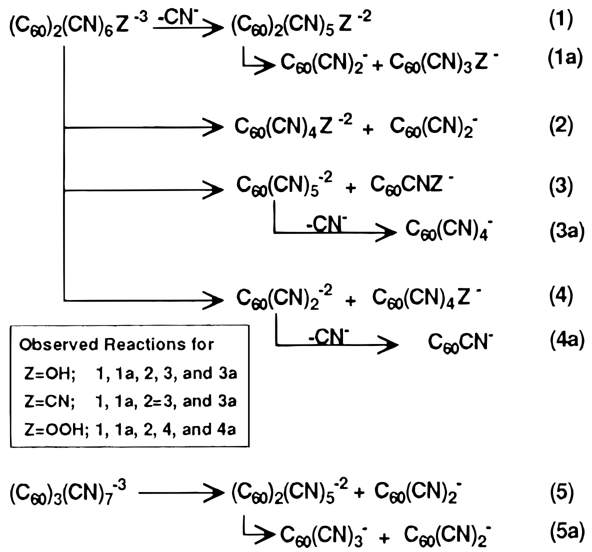
Figure 2. Collision-induced dissociation spectra of the three precursors indicated, acquired for 8 min after an initial delay of 15 min. Structural assignments for peak clusters are in code: "circled asterisk" = "(C_{60})", "double-strikethrough N" = "(CN)", "X" = "OH", and "Y" = "OOH". The resolution of MS1 was set sufficiently wide to sample all the major ^{13}C peaks of each precursor cluster. Resolution of MS2 was set sufficiently narrow to distinguish doubly from singly charged fragment ions. The insets are *not* expanded by equal amounts along the mass axis.

$(C_{60})_2(CN)_3(OH)^{2-}$ is analogous to the similar cluster starting at *m/z* 433.5 (Figure 1a). The very small $(C_{60})_3(CN)_7^{3-}$ cluster (abundance of ~1% of the base peak at *m/z* 412) turned out to be of special interest when attempting to discern the structure of the polybuckminsterfullerene adducts and the nature of the bond connecting the C_{60} moieties (see below).

The "new" (i.e., not previously assigned) ions in Figure 1 are therefore $(C_{60})_2(CN)_4(OH)^{3-}$, $(C_{60})_2(CN)_5^{3-}$, $(C_{60})_2(CN)_6(OH)^{3-}$, $(C_{60})_2(CN)_7^{3-}$, $(C_{60})_2(CN)_6(OOH)^{3-}$, and $(C_{60})_3(CN)_7^{3-}$. Quadruply charged anions were not observed.

Distribution of the Adducts on Individual C_{60} Units of Selected "New" Reaction Products. To determine the distribution of adducts on individual C_{60} entities of the di- and tri-"buckies", CID experiments were conducted on four such species. The results of the CID experiments for the precursors $(C_{60})_2(CN)_6(OH)^{3-}$, $(C_{60})_2(CN)_7^{3-}$, and $(C_{60})_2(CN)_6(OOH)^{3-}$ are presented in Figure 2. The resolution of MS1 is set at ~1.5 Da PWHH, i.e., sufficiently wide to transmit the various ^{13}C isotope peaks of each precursor cluster. Resolution of the fragment ions in Figure 2 is not as good as that of Figure 1 because the reduced intensity of the tandem mass spectrometry experiment dictates a lower resolution of MS2 in order to achieve sufficient sensitivity for detection. This applies especially to very weak precursor ions such as $(C_{60})_2(CN)_6(OH)^{3-}$. The resolution of MS2 is nevertheless sufficient to distinguish doubly from singly charged fragment clusters (see insets of Figure 2).

SCHEME 1



The CID spectra are compatible with the following two generalized modes of dissociation, best illustrated with reference to Figure 2b and Scheme 1. In the first mode, the trianionic precursor loses CN^- to produce an even-electron dianion still comprising two C_{60} units $\{(C_{60})_2(CN)_7^{3-} \rightarrow (C_{60})_2(CN)_6^{2-}$; Figure 2b}. This in turn fragments into two odd-electron (i.e., radical) monoanions $\{(C_{60})_2(CN)_6^{2-} \rightarrow C_{60}(CN)_2^- + C_{60}(CN)_4^-$; Figure 2b}. In the second mode of reaction the even-electron trianion separates into two odd-electron fragments carrying one and two charges, respectively, and including one C_{60} each $\{(C_{60})_2(CN)_7^{3-} \rightarrow C_{60}(CN)_5^{2-} + C_{60}(CN)_2^-$; Figure 2b}. All of the observed CID product ions in Figure 2b are thus accounted for by these two modes of fragmentation.

The generalized reactions described above, applied to the three precursors of Figure 2 and adapted to the observed CID fragments of each, are depicted in Scheme 1, reactions 1−4. Reactions 1 and 1a, common to all the precursors, do not unequivocally identify the distribution patterns on the individual C_{60} units because it is impossible to say from which C_{60} the original loss of CN^- occurs. However, reactions 2−4 show a consistent pattern of fragmentation into a di- and a monoanion containing one C_{60} unit each, with one unit carrying five substituents and the other carrying two substituents. The OOH-containing precursor differentiates itself from the other two in that the less substituted C_{60} may become the dianion on fragmentation of the original trianion (reaction 4), whereas for Z = OH or Z = CN, only the more highly substituted C_{60} units become dianions (reactions 2 and 3). Because the "extra" electrons may be highly mobile during the fragmentation process, differences in charge distribution probably have more to do with the relative stabilities of the final CID fragments than with the structures of the trianionic precursors. Therefore, the structural assignments made below do not attribute specific charge states to the individual C_{60} units.

The energy-resolved CID spectrum of another trianion, $(C_{60})_3(CN)_7^{3-}$, is presented in Figure 3. Only the mass range from 760 to 810 Da is displayed, but scanning from 100 to

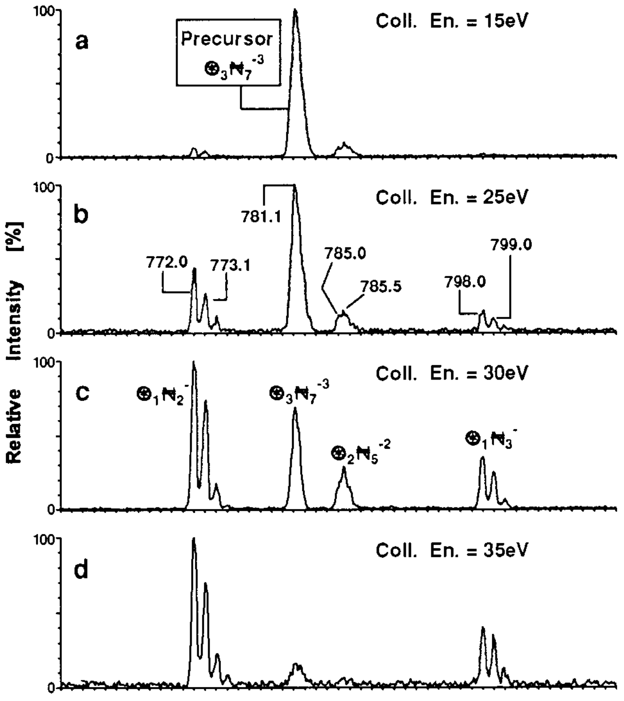


Figure 3. Collision-induced dissociation spectra of $(C_{60})_3(CN)_7^{3-}$ at the different collision energies listed on the spectra; data acquisition for 10 min after an initial delay of 30 min. Structural assignments for peak clusters are in code: "circled asterisk" = "(C_{60})" and "double-strikethrough N" = "(CN)".

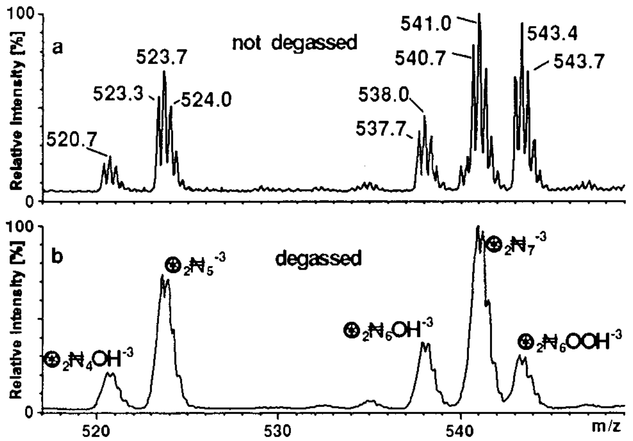


Figure 4. Comparison of spectra derived from (a) the "normal" (nondegassed) and (b) the degassed mixtures of C_{60} and NaCN in DCB/DMF. Spectrum in part b was acquired for 6 min after a 2 min delay, whereas that in part a is an expanded view of Figure 1a. The resolution of the spectrum in part b is lower than that of part a because of instrument settings, not because of the lower oxygen content of the solution. Structural assignments for peak clusters are in code: "circled asterisk" = "(C_{60})" and "double-strikethrough N" = "(CN)".

2500 Da uncovered no further fragment peaks. The collision energies employed range from 15 eV, at which very little fragmentation occurs, to 35 eV, at which the precursor ion abundance is all but depleted in the collision cell. As in Figure 2, the resolution of fragment ions is less than adequate to resolve the 0.33 Da spacing of the precursor cluster peaks but sufficient to distinguish the 0.5 Da spacing of the $(C_{60})_2(CN)_5^{2-}$ fragment cluster. The proposed CID fragmentation reactions for this precursor are presented in Scheme 1, reactions 5 and 5a.

From the reactions of Scheme 1 the substitution patterns of the four precursors can be deduced as

$$(C_{60})_2(CN)_6(OH)^{3-} = [C_{60}(CN)_2\cdots C_{60}(CN)_4(OH)]^{3-} + [C_{60}(CN)(OH)\cdots C_{60}(CN)_5]^{3-}$$

$$(C_{60})_2(CN)_7^{3-} = [C_{60}(CN)_2\cdots C_{60}(CN)_5]^{3-}$$

$$(C_{60})_2(CN)_6(OOH)^{3-} = [C_{60}(CN)_2\cdots C_{60}(CN)_4(OOH)]^{3-}$$

$$(C_{60})_3(CN)_7^{3-} = [C_{60}(CN)_2\cdots C_{60}(CN)_3\cdots C_{60}(CN)_2]^{3-}$$

where "$\cdots$" designates a bond that might be covalent or, as we will discuss below, the adhesion of the "spheres" might be a CBIBS between two charged clusters. Note that $C_{60}(CN)_2$ is a constituent of each of the four precursors. It is manifested in each of the CID spectra of Figures 2 and 3 as a monoanion. It is therefore demonstarted that the monoanion is stable in the gas phase, at least on the time scale of the mass spectrometric experiment (~160 μs). However, this monoanion (*m/z* 772, $\Delta^{13}C = 1.0$) does not appear in the mass spectra (as opposed to CID spectra in Figures 2 and 3) displayed and discussed in ref 13 or in Figure 1c above. Instead, the "dimeric dianion", $(C_{60})_2(CN)_4^{2-}$, is the only cluster seen at *m/z* 772 in these mass spectra. We propose that $C_{60}(CN)_2^-$, which is a radical anion and stable in the gas phase, is unviable as an isolated entity in the reaction solution. It seeks out a partner in the solution with which to complex or bond. That partner may be another of its kind—to form the even-electron $(C_{60})_2(CN)_4^{2-}$—or one of the more highly adducted species, e.g., the radical dianion $C_{60}(CN)_5^{2-}$—to form the even-electron $(C_{60})_2(CN)_7^{3-}$. It is precisely the nature of the complexing or covalent bond thus formed that interests us from the theoretical point of view. It may very well be a CBIBS.

Oxygenated Species. To gain insight into the mode of formation of the oxygenated C_{60} species, "degassed" solutions of C_{60} in DCB and NaCN in DMF were prepared and mixed in an inert atmosphere (see the Experimental Section). This mixture behaved differently than the "standard" mixture in that the green coloration attained upon mixing was retained for up to 2 h instead of immediately beginning the transition "to a dirty brown and then an earthy yellow".[11,13] A comparison of part of the spectra obtained with "normal" and degassed solutions is presented in Figure 4. The $(C_{60})_2(CN)_6(OOH)^{3-}$ abundance is obviously significantly reduced relative to the $(C_{60})_2(CN)_7^{3-}$ cluster, indicating that this species is derived from molecular oxygen (presumably with the H atom derived from the solvent). Conversely, the nondiminution of $(C_{60})_2(CN)_6(OH)^{3-}$ and $(C_{60})_2(CN)_4(OH)^{3-}$ relative to $(C_{60})_2(CN)_7^{3-}$ and $(C_{60})_2(CN)_5^{3-}$, respectively, implies that the OH groups observed in the spectra are derived from traces of water that would not have been eliminated in the degassing procedure.

For the OOH-containing precursor (Figure 2c) each CID fragment harbors both or none of the oxygen atoms, thus supporting the conclusion reached above that this moiety is derived from dissolved oxygen, as opposed to trace water contamination of the solvents. Furthermore, OOH is contained only on those fragments that also carry three or more nitrile substituents. It appears that under the conditions of the chemical reaction $C_{60} + CN^- + O_2 \rightarrow$ products, the oxygen reacts with an intermediate only after several nitriles have done so previously. These observations can be rationalized as follows. The presence of nitrile substituents on an organic molecule is known to increase its propensity to undergo radical addition reactions.[14] Elemental oxygen (O_2) is a diradical. The presence of several CN groups on C_{60} therefore encourages the reaction $C_{60}(CN)_m^-$

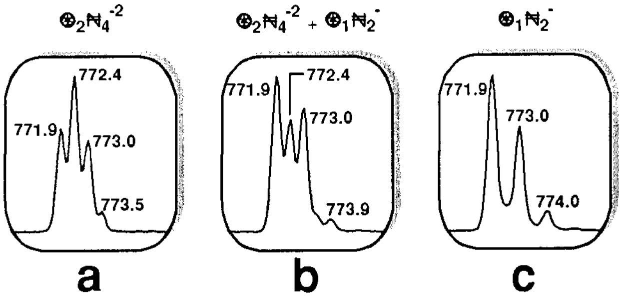


Figure 5. Collision-induced dissociation spectra of $(C_{60})_2(CN)_4^{2-}$ at collision energies (a) 10 eV, (b) 35 eV, and (c) 50 eV with data acquisition for 5 min after a 20 min delay. Structural assignments for peak clusters are in code: "circled asterisk" = "(C_{60})" and "double-strikethrough N" = "(CN)".

$+ O_2 \rightarrow C_{60}(CN)_m(OO)^-$ (for $m > 2$), which can then abstract a hydrogen atom (e.g., from the DMF cosolvent) to form $C_{60}(CN)_m(OOH)^-$. This hypothesis for the formation of the OOH-containing species also rationalizes our preference for writing "OOH" rather than "(O)(OH)" as used by Peel.[13] However, there is no direct mass spectrometric evidence to support either of these terminologies.

The genesis of the OH-containing species (all those containing "X" in Figure 1) is more difficult to fathom. Attachment of the elements of water to an organic molecule is usually induced by partial cationic character of an atom on the molecule; i.e., the molecule reacts as an electrophile. However, in this reaction we are dealing with highly anionic systems, i.e., nucleophiles, and attachment to the oxygen of water is unexpected. At this time we have no rational explanation for the nearly ubiquitous OH-containing satellites of the $(C_{60})_n(CN)_m^{x-}$ clusters observed in Figure 1.

Simplest Product Containing Two C_{60} Units. The simplest $(C_{60})_2(CN)_m$ anion, $(C_{60})_2(CN)_4^{2-}$, was previously assumed to be an ion−molecule complex formulated as $C_{60}(CN)_4^{2-}\cdot C_{60}$.[13] To empirically establish the distribution pattern of nitriles on the two C_{60} units of this ion, further CID experiments were undertaken with the cluster at *m/z* 772 as precursor. At low collision energy (Figure 5a; CE = 10 eV) essentially no fragmentation occurs, i.e., $\Delta^{13}C = 0.5$ Da, and the intensity of the major ^{13}C peak is consistent with C_{124} (calculated intensity ratio for $^{12}C_{123}{}^{13}C_1/{}^{12}C_{124} = 1.39$; observed value is ∼1.5). At high collision energy (Figure 5c; CE = 50 eV) the precursor is completely dissociated in the collision cell to $C_{60}(CN)_2^-$ ($\Delta^{13}C = 1.0$ Da, and the ^{13}C cluster is consistent with a C_{62} composition). The CID spectrum with intermediate collision energy (Figure 5b; CE = 35 eV) is clearly a mixture of the two. No further fragmentation products were observed at any of these collision energies between *m/z* 300 and 850. From these data it is apparent that

$$(C_{60})_2(CN)_4^{2-} = [C_{60}(CN)_2\cdots C_{60}(CN)_2]^{2-}$$

where once again "⋯" represents a bond that might be covalent, or it might be a CBIBS. The rationale favoring it being a CB is presented below.

Approximation of the Coulomb Barrier. Previously,[6,7] we have discussed the stability of doubly charged anions in terms of the interaction of an electron with a polarizable negative ion. Classically, any highly negatively charged conducting sphere can bind an additional electron. The repulsive (positive) Coulomb potential falls asymptotically to zero as $1/r$, while the attractive (negative) polarization increases more steeply as $-1/r^2$. They combine to provide a maximum in the potential curve (the Coulomb barrier) at some distance r_{CB}. At distances greater than r_{CB} the extra electron is "free", while at distances smaller than r_{CB} it is "bound"; i.e., a CBIBS. Although C_{60}^{2-} is calculated to be less stable by 0.2−0.4 eV than C_{60}^- plus a free electron, it is very long-lived (>1 s) as a result of the CB.[3] Likewise, the stabilities of C_{84}^{2-} (ref 7) and $C_{60}F_{48}^{2-}$ (ref 6) are effectively increased as a result of the CB. It is therefore reasonable to pose the question "Can a CB act to effectively bind two charged clusters together into a bound state or into a long-lived metastable state?" The interaction potential between two charged clusters of dipole moments μ_1 and μ_2, charges q_1 and q_2, and polarizabilities α_1 and α_2 can be approximated as

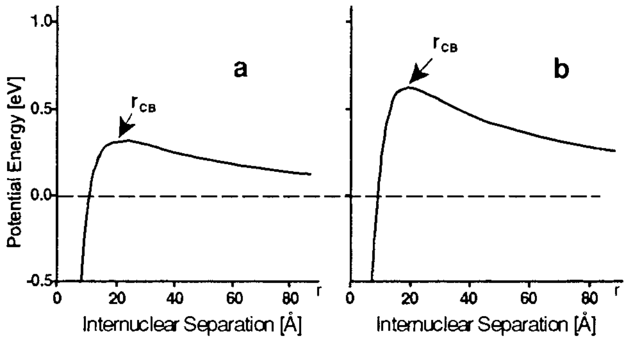


Figure 6. Translational potential energy of (a) two charged ($q_1 = q_2 = e$) "polar" spheres as defined by eq 6 and (b) a single "polar" sphere ($q_1 = e$) and two collinear "polar" spheres ($q_2 = q_3 = e$) held at a distance of 8 Å from one another. In each case the internuclear separation "r" denotes the distance between the centers of the two nearest approaching spheres, and "r_{CB}" indicates the distance at which "bonding" reverts to "nonbonding".

$$V(r) = \frac{q_1q_2}{r} - \frac{q_2\mu_1 + q_1\mu_2}{r^2} - \frac{\alpha_1{q_2}^2 + \alpha_2{q_1}^2}{2r^4} - \frac{2\mu_1\mu_2}{r^3} \quad (6)$$

where we have assumed that the dipole−dipole orientation provides attraction. The first term represents the Coulomb repulsion, the second the ion−dipole attraction, the third the polarizability attraction, and the last term represents the dipole−dipole interaction

$$\frac{\vec{\mu}_1\cdot\vec{\mu}_2}{r^3} - \frac{3(\vec{\mu}_1\cdot\vec{r})(\vec{\mu}_2\cdot\vec{r})}{r^5}$$

For purposes of calculation let us first consider the $C_{60}(CN)_2^-\cdots C_{60}(CN)_2^-$ dianion, for which we estimate a dipole moment of 5.4 D (mm3 molecular modeling calculation; Serena software) and a polarizability of 85 Å^3.[15] Figure 6a presents the classical interaction potential as a function of the distance between the centers of the $C_{60}(CN)_2$ spheres. Taking the radius of C_{60} to be 3.5 Å, it is clear that the interaction potential becomes negative before the van der Waals radii "touch". The CB seems to be of a shape and magnitude to provide binding. Thus, we conclude that dianions such as $(C_{60}(CN)_2)_2^{2-}$ could be made stable with respect to dissociation as a result of a CB acting to prevent the two singly charged anion clusters from separating. In other words, a Coulomb barrier induced bound state—a CBIBS—may account for the stability of cluster dianions such as $(C_{60}(CN)_2)_2^{2-}$. These simple classical arguments can be extended to the case of three $C_{60}(CN)_m^-$ entities aligned in a linear array. Figure 6b shows the translational interaction potential of a single $C_{60}(CN)_2^-$ with two similar species separated by a distance where "binding" occurs between the two (~8 Å separation). Again, attraction between the three charged spheres is observed before the van der Waals radii touch. For each of the calculations, a CB of ~0.7 eV is found. Placing more than one charge on any entity increases the CB without changing the point at which the potential energy becomes negative (i.e., bound).

4. Conclusions

Numerous species of the general structure $(C_{60})_n(CN)_m(OH)_u(OOH)_v^{x-}$ (where $n = 1-3$, $m = 1-7$, $u + v = 0$ or 1, and $x = 1-3$) are formed in the solution of C_{60} and a 100-fold excess of NaCN in DCB + DMF. Oxygen atoms for the OOH moiety are derived from dissolved O_2, and those of the OH moiety derive from water. Where $n > 1$ and $x > 1$, these species are composed of "building blocks" such as $C_{60}(CN)_2^-$, which can be separated into the individual components by collision-induced dissociation. The force holding these components together may arise from a Coulomb barrier generated by the combination of classical electrostatic repulsion and polarization attraction.

Acknowledgment. This research was supported by the National Science Foundation (CHE-9724435).

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