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Cyanodihydrofullerenes and Dicyanodihydrofullerene: The First Polar Solid Based on C_{60}

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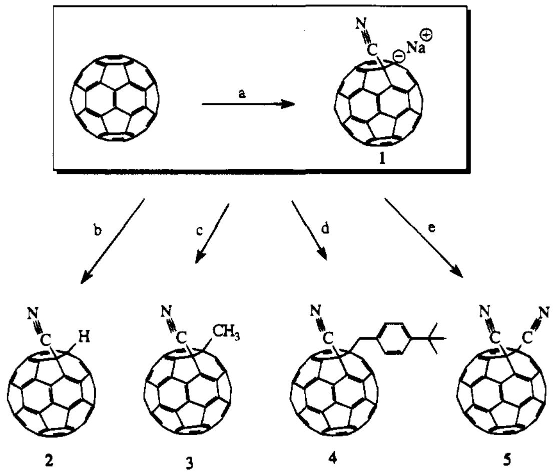
Buckminsterfullerene undergoes a variety of nucleophilic additions,[1] a characteristic reaction of an electron deficient olefin. However, the addition of nucleophiles to C_{60}, in most cases leads to a myriad of different polyadducts which are difficult to separate into isomerically pure single compounds.[1]

The controlled addition of lithium and Grignard reagents RM (R = alkyl,[2] phenyl,[3] alkynyl[4]) has been reported, and the corresponding anion RC_{60}^- has been quenched with acids. Surprisingly, the nucleophilicity and electronic properties of the RC_{60}^- anion have not yet been studied extensively, despite the fact that a variety of electrophiles can be introduced at the 2-position by this two-step, one-pot reaction.

We are interested in systematically increasing the electron affinity of C_{60} derivatives.[5,6] Saturation of one double bond of C_{60} in 1,2-dihydrofullerenes (58 π electrons) causes a negative shift of about 100−150 mV relative to C_{60} for the first three reduction waves. The logical way to compensate for this negative shift and possibly cause a positive shift is to introduce an electron-withdrawing group onto the buckminsterfullerene skeleton. Polyfluorofullerenes are reported to be relatively strong oxidizing agents, with the first reduction potential of $C_{60}F_{48}$ being 1.38 V more positive than that of C_{60}.[7]

In this communication, we report the controlled addition of an electron-withdrawing substituent, cyanide anion, and the quenching of the corresponding intermediate $C_{60}(CN)^-$ anion with different electrophiles. Earlier attempts to add cyanide or iodide to C_{60} under usual conditions failed, and the fullerene was recovered unchanged. Reinvestigation revealed that the addition of DMF solutions containing 1 equiv of MCN (M = Li or Na) to C_{60} in toluene at room temperature resulted in a black crystalline precipitate of a mixture of water-soluble polyadducts $(LiCN)_nC_{60}$ (n = 10, based on lithium ion, determined by atomic absorption spectroscopy). However, the addition of a 0.1 M solution of NaCN in DMF to a solution of C_{60} in 1,2-dichlorobenzene (ODCB) over a 3-min period at room temperature resulted in a deep green solution, which was subsequently quenched, after 15 min, with different electrophiles (Scheme 1).

Scheme 1[a]



[a] Reagents and conditions: (a) NaCN, ODCB/DMF, room temperature; (b) trifluoroacetic acid, room temperature, 29%; (c) methyl trifluoromethanesulfonate, room temperature, 10%; (d) 4-*tert*-butylbenzyl bromide, 70 °C, 11%; (e) *p*-toluenesulfonyl cyanide, room temperature, 61%.

Protonation of $C_{60}(CN)^-$ (**1**) with trifluoroacetic acid produced, upon chromatographic separation, **2** as the single isomer. Alkylation and benzylation of **1** with methyl triflate at ambient temperature and 4-*tert*-butylbenzyl bromide at 70 °C resulted in **3** and **4**, respectively, the former being rather insoluble and the latter being very soluble in most organic solvents, especially aromatic solvents. When anion **1** was treated with tosyl cyanide at room temperature, the 1,2-dicyano C_{60} (**5**) was formed, as a single isomer, in high yield, after chromatographic separation.

The 1,2-dihydrofullerene structures with C_s symmetry for compounds **2−4** and C_{2v} symmetry for compound **5** were assigned on the basis of ^1H NMR, ^{13}C NMR, UV−vis, and IR spectra.[2−4,8] The ^{13}C NMR of **5** (Figure 1) is in full accord with the structure.

An X-ray-quality single crystal of **5**·2ODCB[9] was grown from an ODCB solution, and the unit cell, without the disordered ODCB molecules, is shown in Figure 2. The X-ray data showed that the $C_{60}(CN)_2$ moieties are located on the 2-fold symmetry axes and oriented in the same direction, with all the molecules pointing along the b axis. The implication is that this solid should exhibit large second harmonic nonlinear optical properties. Unfortunately, it is deeply colored (absorption throughout the visible) and hence probably ineffectual for optical device fabrication, though other properties associated with ferroelectric solids (piezoelectricity, pyroelectricity) may be of interest and are being pursued.

As far as the molecular unit is concerned, the lengths of the 5−6 and 6−6 bonds averaged 1.40 and 1.46 Å, respectively, in agreement with the reported[10] values (1.39 and 1.43) for a Diels−Alder adduct.[10] The average angle on the sp^3 carbons is 108.8°, which is close to the ideal tetrahedral geometry. The average bond angles in the pentagons and hexagons are 107.2° and 116.2°, respectively, also in agreement with previously reported values.

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(9) Crystal data for $C_{62}N_2{\cdot}2C_6H_4Cl_2$: monoclinic, space group $C2$, d_{calc} = 1.75 g cm^{-3}, $Z = 2$, a = 16.028(3) Å, b = 12.539(3) Å, c = 10.357 Å, β = 102.029(3)°, V = 2035.9 Å^3. Data were collected at 298 K on a Huber four-circle automated diffractometer using Mo Kα radiation, λ = 0.710 69 Å. The unit cell was obtained from 15 reflections (2θ = 10−20°). The intensities were measured for 1688 unique reflections with $2\theta \le 45°$ and corrected for Lorentz and polarization effects. Three reflections were monitored every 2 h, and no crystal decay occurred during data collection. The structure was solved by direct methods and refined by using the UCLA package. For the refinement, 906 reflections were used with $I > 2\sigma(I)$. During the refinement of the structure, two possible orientations of ODCB were found with one of the Cl atoms occupying a single site, while the rest of the solvent molecule refined to the 0.6/0.4 ratio. Due to the limited number of data, only chlorine atoms together with cyano groups and sp^3 carbons were refined anisotropically, while the rest of the structure was refined with isotropic thermal parameters. The structure was refined to R = 0.084 and R_w = 0.097.

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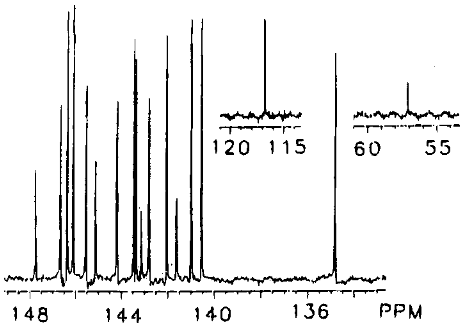

Figure 1. ^{13}C-NMR spectrum of 1,2-dicyano-1,2-dihydrofullerene in deuterium-labeled tetrachloroethane. Only the fullerene region is shown; other resonances are shown as insets.

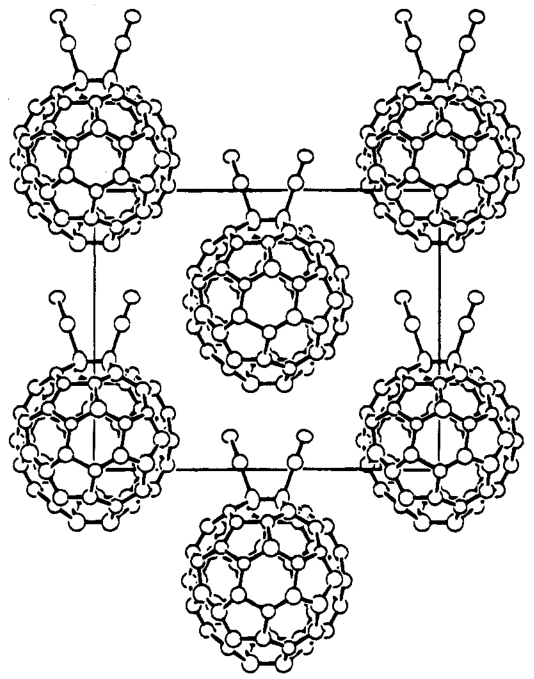

Figure 2. Crystal packing of compound **5** down the crystallographic *c* axis. The solvent molecules (ODCB) were left out for clarity. The molecules at the corners of the square are on one plane, and the other two are below the plane.

The UV−vis absorption spectra are similar to those of the other 1,2-dihydrofullerenes.[2,3,8] The UV−vis of **2**, in nonpolar solvents, was almost identical to that of **3**−**5**. However, when **2** was dissolved in toluene−DMSO, it was partially dissociated to give a greenish solution. Deprotonation of **2** with NaH, NaOAc, TEA, TBA triflate, etc. yielded a deep green solution which exhibited broad absorption peaks at 599 and 952 nm (DMF) in the VIS−near-IR region.[11] From the changes in the absorption spectra of **2**, upon titration with mild bases, a pK_a of 2.5 was determined in ODCB for $C_{60}(CN)H$.[12]

Cyclic voltammetry[13] showed that each of the cyanodihydrofullerenes undergoes four well-defined, single-electron, quasi-reversible processes. However, the cyclic voltammograms of **2** and **3** are complicated by the presence of a tiny prewave just prior to the first reduction and the presence of an extra anodic wave on the return. The prewave occurs at a potential some 200 mV more positive than the initial reduction peak and is likely due to adsorption on the surface of the electrode.[14] We attribute the extra anodic wave to the oxidation of a deprotonated species because the peak anodic current increases in the presence of base. The half-cell potentials (defined as $E_x = 0.5[E_{p,c} - E_{p,a}]$) for the quasi-reversible waves of cyanodihydrofullerenes **2**−**5**, versus Fc/Fc$^+$, are given in Table 1 and Figure 3. The corresponding values[15] for C_{60} are included for comparison.

Table 1

compd	half-cell potentials (mV) E_1	E_2	E_3	E_4
2	−1058	−1438	−1925	−2380
3	−1073	−1458	−1943	−2410
4	−1090	−1495	−1986	−2435
5	−935	−1330	−1800	−2225
C_{60}	−1056	−1451	−1906	−2384

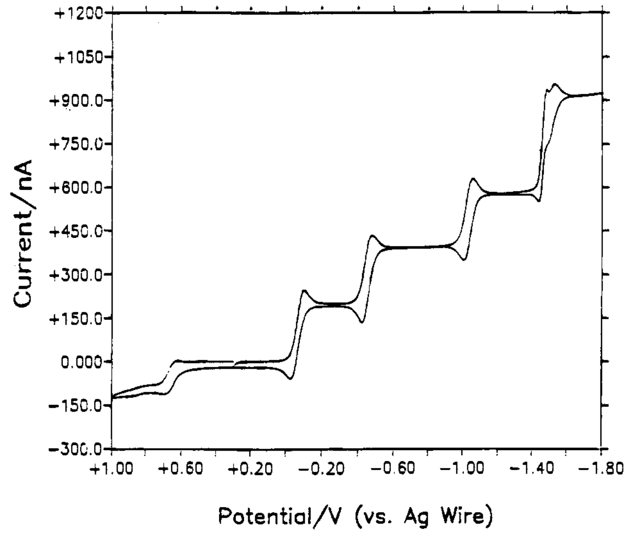

Figure 3. Low-temperature (−72 °C) cyclic voltammogram of **5** in 2/3 DMF/toluene: Pt working and counter electrodes; Bu_4NBF_4, electrolyte; Ag wire external reference and Fc/Fc$^+$ internal reference (cycle at +0.6 V); scan rate, 2 mV/s.

In summary, by producing a cyanodihydrofullerene anion and quenching with various electrophiles, we are able to prepare, in a two-step process, C_{60}-based electron acceptors with controlled redox potentials. First, the inclusion of one cyano group in the dihydrofullerenes increases the electron affinity of the dihydrofullerene such that compound **2** is very nearly as good an electron acceptor as C_{60} itself (Table 1). In addition, we may "fine-tune" the electron-accepting ability of the cyanodihydrofullerenes by the judicious selection of an electrophile; we are able to vary the first reduction of the cyanodihydrofullerene from ca. 30 mV more negative than C_{60} to an exceptional 120 mV more positive than C_{60}.

Acknowledgment. We thank the National Science Foundation for support through the Materials Research Laboratory as well as Grants DMR-91-22536, DMR-9500888, and CHE 93-00954.

Supporting Information Available: Experimental details for the preparation, purification, and characterization of **1**−**5** (40 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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