Structure Determination and Electrochemistry of Products from the Radical Reaction of C_{60} with Azo(bisisobutyronitrile)

Warren T. Ford,*,[†] Takuya Nishioka,[†] Feng Qiu,[†] Francis D'Souza,[‡] Jai-pil Choi,[‡] Wlodzimierz Kutner,[§] and Krzysztof Noworyta[§]

Department of Chemistry, Oklahoma State University, Stillwater, Oklahoma 74078, Department of Chemistry, Wichita State University, Wichita, Kansas 67260, and Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warsaw, Poland

Thermal decomposition of azo(bisisobutyronitrile) in a 1,2-dichlorobenzene solution of C_{60} gave three regioisomeric 1,*x*-di(2-cyano-2-propyl)-1,*x*-dihydro[60]fullerenes in 12, 2, and 4% yields, assigned as the 1,4-, 1,2-, and a third isomer of still uncertain structure. The 1,4- and unidentified isomers underwent three reversible reduction steps by cyclic voltammetry, and UV−vis−NIR spectra of the mono- and dianions generated electrochemically were recorded. The first two redox potentials of the 1,4-isomer were the same as those of C_{60}, but those of the third isomer were positively shifted by 0.23 and 0.21 V from those of C_{60}, showing that it is an electron-deficient derivative of C_{60}.

During free-radical polymerizations of methyl methacrylate (MMA) and of styrene with C_{60} initiated by thermal decomposition of 2,2′-azo(bisisobutyronitrile) (AIBN) in 1,2-dichlorobenzene (oDCB) solution, the C_{60} is incorporated into polymer early, and the high conversion polystyrene/C_{60}, but not the PMMA/C_{60}, contains molecules having large numbers of C_{60} units.[1] High C_{60} content polymers formed with styrene and MMA by radical polymerization have been prepared in several laboratories.[2−15] Many alkyl radicals can add to one fullerene,[16−18] and the polymeric products from 1 wt %

C_{60} in styrene or MMA and a 5:1 mol ratio of AIBN/C_{60} contain an average of six to seven nitrogen atoms derived from AIBN per fullerene unit.[1,4] To understand the early stages of the polymerizations, we have examined reactions of C_{60} with AIBN but no monomer in oDCB. We have isolated pure 1,4-di(2-cyano-2-propyl)-1,4-dihydro[60]fullerene (**1**), identified 1,2-di(2-cyano-2-propyl)-1,2-dihydro[60]fullerene (**2**) in mixtures with the 1,4-isomer, and isolated pure but not identified a third isomer (**3**), as shown in Scheme 1. We have also investigated the reductions of **1** and **3** by cyclic voltammetry and characterized the one- and two-electron reduced products by UV−vis−NIR spectroscopy. The isomer **3** is more electron deficient than C_{60}, as evidenced by positively shifted first and second redox potentials.

Results

Compositions of the 2-Cyano-2-propyl Adducts of C_{60}.
Reaction of AIBN with C_{60} was carried out at 75 °C in oDCB at concentrations identical with those used previously for polymerizations of C_{60} with styrene and with MMA.[1] Over 60 min at 75 °C, 23% of the AIBN decomposes to 2-cyano-2-propyl radicals and dinitrogen, assuming a half-life of 160 min.[20] Three major fractions were isolated by silica chromatography: Red-brown fraction **A** contained **3**, and brown fraction **B** contained an 84/16 mixture of **1**/**2** from ^{1}H NMR peak areas. Although the third fraction **C** appeared as a single peak on reversed-phase HPLC, its ^{1}H NMR spectrum had many peaks in the 2 ppm region indicating a complex mixture, so it was not investigated further. After two more flash chromatographic purifications fraction **B** appeared as a single peak by reversed-phase HPLC, but subsequent analysis on a Buckyprep column resolved **1** and **2**.

Elemental analyses of fractions **A** and **B** are reported in Table 1. The contents of 2-cyano-2-propyl (C_4H_6N)

† Oklahoma State University.
‡ Wichita State University.
§ Polish Academy of Sciences.
(1) Ford, W. T.; Graham, T.; Mourey, T. H. *Macromolecules* **1997**, *30*, 6422−6429.
(2) Cao, T.; Webber, S. E. *Macromolecules* **1995**, *28*, 3741.
(3) Bunker, C. E.; Lawson, G. E.; Sun, Y. P. *Macromolecules* **1995**, *28*, 3744.
(4) Camp, A. G.; Lary, A.; Ford, W. T. *Macromolecules* **1995**, *28*, 7959.
(5) Sun, Y.-P.; Ma, B.; Bunker, C. E.; Liu, B. *J. Am. Chem. Soc.* **1995**, *117*, 12705.
(6) Cao, T.; Webber, S. E. *Macromolecules* **1996**, *29*, 3826.
(7) Sun, Y.-P.; Lawson, G. E.; Bunker, C. E.; Johnson, R. A.; Ma, B.; Farmer, C.; Riggs, J. E.; Kitaygorodskiy, A. *Macromolecules* **1996**, *29*, 8441.
(8) Bune, Ye. V.; Gromov, V. R.; Izumnikov, A. L.; Kardash, I. E. In *Recent Advances in the Chemistry and Physics of Fullerenes and Related Materials*; Kadish, K. M., Ruoff, R. S., Eds.; The Electrochemical Society: Pennington, NJ, 1994; pp 1550−1560.
(9) Stewart, D.; Imrie, C. T. *Chem. Commun.* **1996**, 1383−1384.
(10) Kirkwood, K.; Stewart, D.; Imrie, C. T. *J. Polym. Sci. A: Polym. Chem.* **1997**, *35*, 3323−3325.
(11) Mehrotra, S.; Nigam, A.; Malhotra, R. *Chem. Commun.* **1997**, 463−464.
(12) Nayak, P. L. Alva, S.; Yang, K.; Dhal, P. D.; Kumar, J.; Tripathy, S. K. *Macromolecules* **1997**, *30*, 7351−7354.
(13) Seno, M.; Fukunaga, H.; Sato, T. *J. Polym. Sci. Part A: Polym. Chem.* **1998**, *36*, 2905.
(14) Okamura, H.; Terauchi, T.; Minoda, M.; Fukuda, T. *Macromolecules* **1997**, *30*, 5279.
(15) Okamura, H.; Ide, N.; Minoda, M.; Komatsu, K.; Fukuda, T. *Macromolecules* **1998**, *31*, 1859.
(16) Krusic, P. J.; Wasserman, E.; Keizer, P. N.; Morton, J. R.; Preston, K. F. *Science* **1991**, *254*, 1183.
(17) Krusic, P. J.; Wasserman, E.; Parkinson, B. A.; Malone, B.; Holler, E. R., Jr.; Keizer, P. N.; Morton, J. R.; Preston, K. F. *J. Am. Chem. Soc.* **1991**, *113*, 6274.
(18) Morton, J. R.; Preston, K. F.; Krusic, P. J.; Hill, S. A.; Wasserman, E. *J. Phys. Chem.* **1992**, *96*, 3576.

(19) For the IUPAC numbering and nomenclature of fullerenes, see: *Pure Appl. Chem.* **1997**, *69*, 1411−1434.
(20) Brandrup, J., Immergut, E. H., Eds.; *Polymer Handbook*, 3rd ed.; Wiley: New York, 1989; p II/3−4.
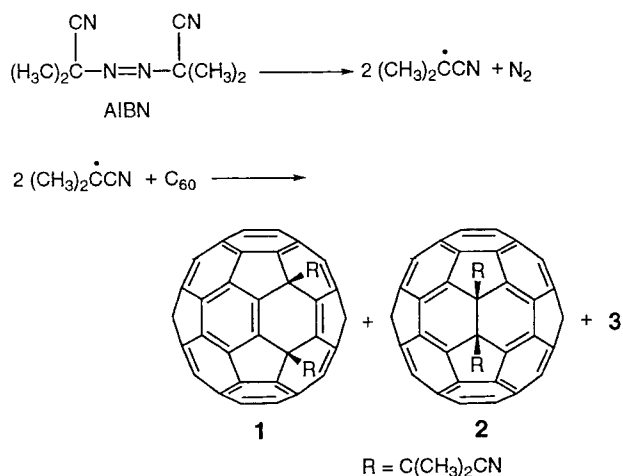
Scheme 1

R = C(CH₃)₂CN

Table 1. Elemental Analyses

fraction	%C	%H	%N	C_4H_6N/C_{60}
A	92.62, 92.81	1.28, 1.10	3.00, 2.90	1.87, 1.80
normalized	95.58, 95.86	1.32, 1.14	3.10, 3.00	
B	93.87, 93.83	1.50, 1.38	2.95, 3.02	1.81, 1.86
normalized	95.47, 95.53	1.52, 1.40	3.00, 3.07	
calcd[a]	95.33	1.40	3.27	2

[a] For $C_{60}(C_4H_6N)_2$.

groups and C_{60} were calculated by eqs 1–4. Since the total CHN analyses were <100.0%, the calculations were performed with both the experimental and normalized CHN data. The normalized data agree with theoretical values for $C_{60}(C_4H_6N)_2$. **A** and **B** contained two nitrogen atoms per C_{60} unit.

$$\% \text{ C from } C_4H_6N \text{ groups} = \% \text{ N } (48/14) \quad (1)$$

$$\% \text{ C from } C_{60} = \\ \% \text{ C}_{obs} - \% \text{ C from } C_4H_6N \text{ groups} \quad (2)$$

$$\text{mmol } C_4H_6N/g \text{ sample} = \% \text{ N}/1.4 \quad (3)$$

$$\text{mmol } C_{60}/g \text{ sample} = \% \text{ C from } C_{60}/72 \quad (4)$$

One possible reason for low analytical values is the presence of oxygen in the samples in the form of adducts of $C_{60}O^{21}$ or $C_{120}O,^{22,23}$ or some other oxygenated fullerene. Negative ion detected LSIMS showed sizable peaks for $[C_{60}OH]^-$ at m/z 737 and for $C_{60}(C_4H_6N)_2OH^-$ at m/z 873. However, the mass spectrum of the starting C_{60} also showed a 25% relative intensity $C_{60}O$ peak even though only a trace of $C_{60}O$ was detected by reversed-phase HPLC. We conclude that the negative ion LSIMS method is much more sensitive for detection of oxygen-containing ions than for ions lacking oxygen. If **A** and **B** were mainly compounds containing oxygen, many isomers would be possible. However, the ¹³C NMR spectra show no peaks

Table 2. Heats of Formation and LUMO Energies of $[(CH_3)_2C(CN)]_2C_{60}$ Regioisomers from Semiempirical Calculations at a PM3 Level

isomer	symmetry	ΔH, kcal mol^{-1}	LUMO energy, eV
1,4-	C_s	838.7	−2.911
1,16-	C_2	848.4	−3.135
1,19-	C_2	864.9	−3.253
1,15-	C_s	865.3	−3.614
1,2-	C_{2v}	867.6	−2.929
1,7-	C_s	886.6	−3.632

Chart 1
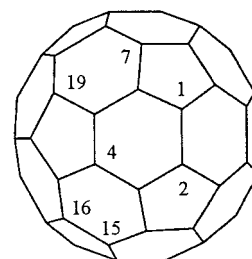
at 90–100 ppm for fullerene carbons bonded to oxygen,[21–24] and each major product has at least a plane or an axis of symmetry. One epoxide derivative of each of **1** and **3** has C_2 or C_s symmetry, and all other oxygen adducts of **1** and **3** have C_1 symmetry. Therefore, oxygen-containing compounds are not the principal components of fractions **A** and **B**.

Structures of the Adducts. PM3 semiempirical molecular orbital calculations of heats of formation and LUMOs of six isomers of $C_{60}(C_4H_6N)_2$ are reported in Table 2. They suggest that the 1,4- and 1,16-isomers are lowest in energy. The IUPAC numbering system for the isomers is shown in Chart 1.

We assign the structure of the major product **1** to the 1,4-isomer on the basis of its UV–vis absorption maximum at 446 nm[30,31] and its ¹³C NMR spectrum. The appearance of 25 2C, one 4C, and four 1C peaks in the 137–153 ppm region and one peak at 62.7 ppm for the fullerene unit in addition to the cyano carbon peak at 124.7 ppm, the quaternary carbon peak at 41.7 ppm, and diastereotopic methyl peaks at 26.8 and 27.8 ppm support a structure with a plane of symmetry. The ¹H NMR spectrum also has diastereotopic methyl peaks. The HMBC NMR spectrum of fraction **B** (84/16 **1**:**2**) shown in Figure 1 has cross-peaks between the methyl protons and the methyl, quaternary, nitrile, and fullerene sp³ carbons. The GOESY NMR spectrum shows a strong cross-peak between the two major methyl proton signals, as expected from a compound having diastereotopic geminal methyl groups.

(21) Creegan, K. M.; Robbins, J. L.; Robbins, W. K.; Millar, J. M.; Sherwood, R. D.; Tindall, P. J.; Cox, D. M., Smith, A. B., III; McCauley, J. P., Jr.; Jones, D. R.; Gallagher, R. T. *J. Am. Chem. Soc.* **1992**, *114*, 1103–1105.

(22) Lebedkin, S.; Ballenweg, S.; Gross, J.; Taylor, R.; Krätschmer, W. *Tetrahedron Lett.* **1995**, *36*, 4971–4974.

(23) Taylor, R.; Barrow, M. P.; Drewello, T. *Chem. Commun.* **1998**, 2497–2498.

(24) Elemes, Y.; Silverman, S. K.; Sheu, C.; Kao, M.; Foote, C. S.; Alvarez, M. M.; Whetten, R. L. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 351–353.

(25) Matusuzawa, N.; Dixon, D. A.; Fukuzawa, T. *J. Phys. Chem.* **1992**, *96*, 7594.

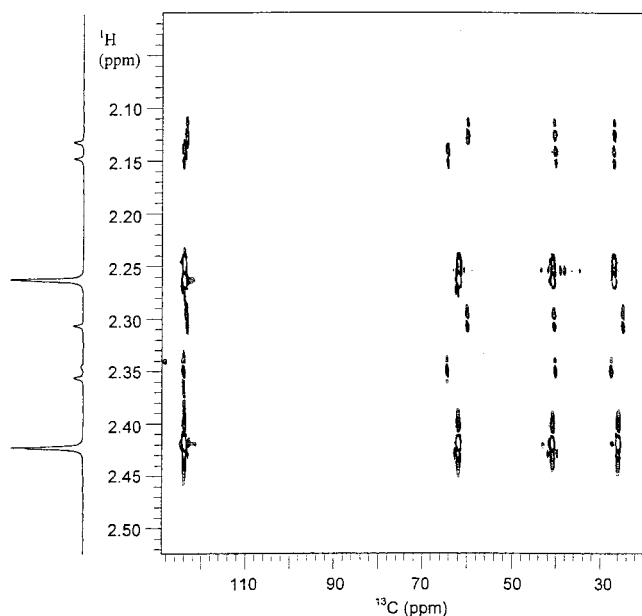(26) Hirsch, A. *The Chemistry of Fullerenes*; Georg Thieme Verlag: Stuttgart, 1994.

(27) Hirsch, A.; Grösser, T. Skiebe, A.; Soi, A. *Chem. Ber.* **1993**, *126*, 1061.

(28) Murata, Y.; Komatsu, K.; Wan, T. S. M. *Tetrahedron Lett.* **1996**, *37*, 7061.

(29) Kusukawa, T.; Ando, W. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1315–1317.

(30) D'Souza, F.; Caron, C.; Subramanian, R.; Kutner, W.; Jones, M. T.; Kadish, K. M. In *Recent Advances in the Chemistry and Physics of Fullerenes and Related Materials*; Kadish, K. M., Ruoff, R. S., Eds.; The Electrochemical Society: Pennington, NJ, 1994; pp 768–778.
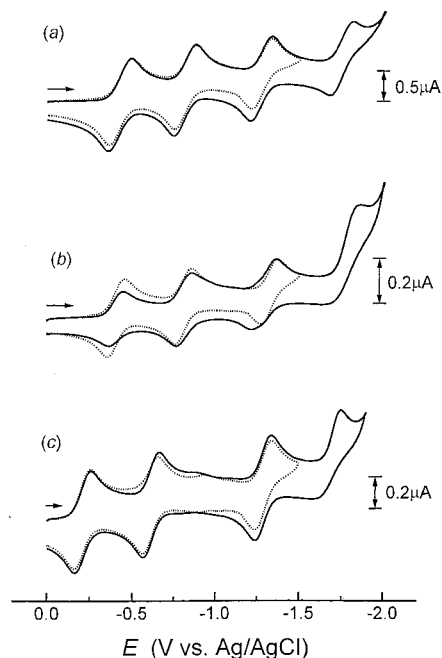
(31) Kadish, K. M.; Gao, X.; Van Caemelbecke, E.; Hirasaka, T.; Suenobu, T.; Fukuzumi, S. *J. Phys. Chem. A* **1998**, *102*, 3898–3906.

Figure 1. 600 MHz HMBC NMR spectrum of fraction **B**, an 84:16 mixture of **1:2**.

Figure 2. Cyclic voltammograms of (a) C$_{60}$, (b) **1**, and (c) **3** in 1,2-dichlorobenzene, 0.1 M (TBA)ClO$_4$. Potential scan rate 0.1 V s^{-1}.

Table 3.   Formal Redox Potentials for C$_{60}$ and C$_{60}$ Derivatives in 1,2-Dichlorobenzene, 0.1 M (TBA)ClO$_4$

	$E_{1/2}$, V vs Ag/AgCl			
	0/−	−/2-	2-/3-	3-/4-
C$_{60}$[a]	−0.44	−0.82	−1.25	−1.72
1	−0.41	−0.81	−1.32	−1.87[b]
3	−0.21	−0.61	−1.29	−1.78[b]

[a] Agrees with literature values in benzonitrile.[32]   [b] E_{pc} at 0.1 V/s.

We assign the structure of the minor component of fraction **B** to the 1,2-isomer (**2**) on the basis of a weak UV−vis band at 434 nm that is present in a 25/75 **1:2** mixture but absent in purified **1**, and on the basis of the NMR spectra of **B**. UV spectra of many 1,2-diadducts of C$_{60}$ have sharp peaks at 435 nm.[30] The four minor methyl peaks of equal area in the ^{1}H spectrum of **B** show no sign of coalescence even when heated to 150 °C in oDCB-d_4, although they do shift downfield by different amounts. For **2** to have four nonequivalent methyl signals, the tertiary alkyl groups must be locked into a single gearlike conformation that prevents rotation about the fullerene sp^3 to quaternary carbon bonds. A GOESY NMR spectrum of fraction **B** shows strong NOE interaction with the 2.14 ppm peak and a weak interaction with the 2.12 ppm peak during irradiation of the 2.35 ppm methyl peak, weak interaction with the 2.14 ppm peak, and weak interaction with the 2.12 ppm peak during irradiation of the 2.30 ppm peak. The strong interactions are due to two methyls on the same 2-cyano-2-propyl group and the weak interactions to methyls on different 2-cyano-2-propyl groups. The GOESY spectrum indicates that the four minor methyl peaks from fraction **B** all come from one compound and support the close proximity of the two 2-cyano-2-propyl groups of the 1,2-isomer **2**. The ^{13}C NMR spectrum of the 25/75 **1:2** mixture has four methyl peaks at 25.8−29.7 ppm, two quaternary carbon peaks at 41.1 and 41.4 ppm, and two aliphatic fullerene peaks at 60.8 and 65.5 ppm. Most importantly, there is no evidence of peaks at 90−100 ppm expected from fullerene carbons bonded to oxygen.[21−24] Although a 1,2-dihydro-fullerene with freely rotating bonds would have C_{2v} symmetry and 13 4C and three 2C peaks in the aromatic region of the ^{13}C NMR spectrum, the nonequivalent methyl peaks for **2** mean that the structure lacks symmetry, and the aromatic region could have as many as 58 peaks. The aromatic carbon peaks due to **2** were not distinguishable in the presence of 84% of **1** in fraction **B**.

The structure of the smaller fraction **A** separated by column chromatography could be the 1,16-isomer on the basis of its low energy from PM3 calculations and its NMR spectra. It lacks the peaks at 434 and 446 nm in the UV−vis spectrum characteristic of 1,2- and 1,4-dihydro[60]fullerenes. The ^{1}H NMR spectrum has only one methyl peak. The ^{13}C NMR spectrum has two methyl peaks at 24.2 and 24.5 ppm, one quaternary carbon peak at 41.7 ppm, one fullerene sp^3 carbon peak at 64.2 ppm, one cyano carbon peak at 122.6 ppm, and 29 peaks of equal intensity at 136−159 ppm consistent with C_2 symmetry. However, correlations of redox potentials and LUMO energies do not support assignment of the 1,16 structure to **3**.

Electrochemistry. The cyclic voltammograms of C$_{60}$, **1**, and **3** in 1,2-dichlorobenzene, 0.1 M tetrabutylammonium perchlorate [(TBA)ClO$_4$] recorded between 0.0 and −2.0 V vs Ag/AgCl are shown in Figure 2. The first three reductions are reversible, and the last one is quasireversible for both **1** and **3**. No oxidation is observed between 0 and +1.5 V when the scan is reversed at a potential more negative than that of the third reduction peak. However, a new oxidation peak at 0.21 V is seen in case of **1** when the potential scan is reversed after the fourth electroreduction peak. Redox potentials of C$_{60}$, **1**, and **3** are listed in Table 3. Redox potentials of the first two reductions of the 1,4-isomer **1** are almost the same as those of C$_{60}$, while the potentials for the third and fourth reductions are shifted more negatively by 0.07 and 0.05 V, respectively. In contrast, the first
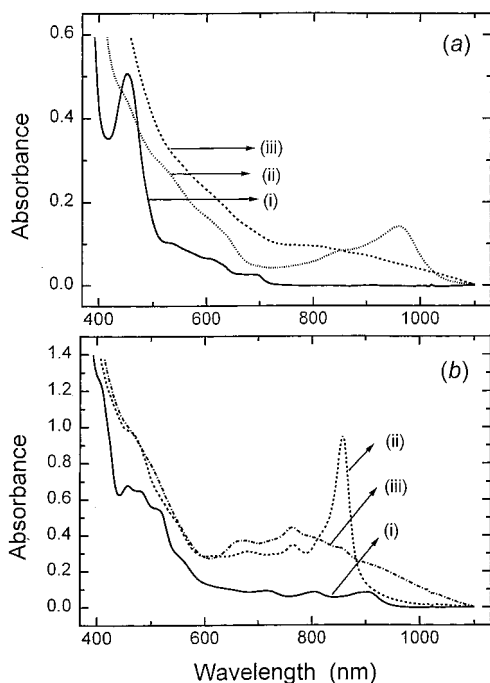
Figure 3. Visible spectra of (i) neutral, (ii) monoanionic, and (iii) dianionic species of (a) **1** and (b) **3** in 1,2-dichlorobenzene, 0.1 M (TBA)ClO$_4$.

Table 4. UV−Vis Data for Neutral, Monoanionic, and Dianionic C$_{60}$ and C$_{60}$ Derivatives Generated Electrochemically in 1,2-Dichlorobenzene, 0.1 M (TBA)ClO$_4$

	oxidation state	λ_{max}, nm	ref
C$_{60}$[a]	0	213, 257, 329, 404, 568	30
	−1	1075	33
	−2	840, 950	33
1	0	450, 542, 616, 700	b
	−1	850sh, 960	b
	−2	808	b
3	0	456, 713, 804, 904	b
	−1	463, 616, 682, 765, 858	b
	−2	667, 763, 840sh	b

[a] In hexane. [b] This work.

two redox potentials of isomer **3** are 0.23 and 0.21 V more positive than those of C$_{60}$, while the third and fourth redox potentials are 0.06 and 0.04 V more positive, respectively.

The reversibility of the first two reduction steps enabled recording of the UV−vis−NIR spectra of the monoanions and dianions of **1** and **3**, which are shown in Figure 3. Spectral features are compared with those of C$_{60}$ in Table 4. The monoanion radical of isomer **1** exhibits a strong absorption band at 960 nm similar to that reported for the one-electron reduced product of the xylyl C$_{60}$ derivatives.[31] Interestingly, the one-electron reduced product of the isomer **3** is blue shifted by over 100 nm, which might be due to the electron-deficient nature of the C$_{60}$ as indicated by the redox potentials. Generally, the two-electron reduced products of isomers **1** and **3** follow a trend similar to that reported for the two-electron reduced products of bis-alkylated C$_{60}$ derivatives.[31] Such spectral trends have been assigned earlier to the splitting of the triply degenrate t_{1u} and t_{1g} orbitals of C$_{60}$, caused by the reduction in symmetry in C$_{60}$R$_2$ derivatives.[31]

Discussion

The reaction of C$_{60}$ with AIBN and identification of a product were reported by Zhu and co-workers.[34] Their mass spectrum had a major peak at $m/z = 856$, and their IR spectrum showed a nitrile stretching band, but otherwise their results are inconsistent with ours. For example, they reported a ^{1}H NMR signal at 1.58 ppm for the methyl group of the product, while we observe two signals at 2.27 and 2.43 ppm for isomer **1**, four signals at 2.14, 2.16, 2.32, and 2.37 ppm for isomer **2**, and a singlet at 2.14 ppm for isomer **3**.

Formation of the 1,4-isomer **1** is expected from AIBN and C$_{60}$ because of steric hindrance to formation of the 1,2-isomer **2**. The 1,4-isomer is the major product from the addition of two benzoyloxy radicals to C$_{60}$,[14,15] from the addition of two polystyryl radicals to C$_{60}$,[14,15] and from the reaction of the dianion of C$_{60}$ with two molar equivalents of benzyl bromide.[31] Of the simplest dihydro-[60]fullerenes C$_{60}$H$_2$, the 1,2-isomer has the lowest heat of formation,[25] but nonbonded repulsions between the tertiary alkyl groups raise the heat of formation of 1,2-disubstituted fullerenes such as **2**. Previous structure determinations of dihydro[60]fullerenes have shown that 1,2-isomers are the major products of reactions when the substituents are small, and 1,4-isomers are the major products when the substituents are large.[26−28] The only other regioisomer ever reported is 1,16-bis(trimethylsilyl)-1,16-dihydro[60]fullerene, which was prepared by reaction of trimethylsilyllithium with C$_{60}$, and its structure was established by single-crystal X-ray analysis. [29]

Cyclic voltammograms of the 1,4-isomer **1** have the first and second redox potentials similar to those of C$_{60}$ and the third and fourth redox potentials shifted more negatively. For comparison, the first three redox potentials of 1,4-dibenzyl-1,4-dihydro[60]fullerene all are more negative by 0.09, 0.15, and 0.17 V than those of C$_{60}$.[31] Similar negative shifts of the first redox potentials, −0.05 to −0.13 V, and second redox potentials, −0.02 to −0.11 V, with respect to those of C$_{60}$ occur for 1,2-dialkyl and 1,2-methano adducts, respectively, and the potentials correlate with LUMO energy levels calculated by the AM1 method.[35] We attribute the lesser first and second redox potentials of **1**, compared with other 1,4-dialkyl-1,4-dihydro[60]fullerenes, to the electron-withdrawing effect of cyano groups in conformations having the cyano π-orbitals strongly interacting with the fullerene π-orbitals. Among seven derivatives of C$_{60}$ having cyano groups attached either directly to the fullerene or one C−C bond away, only 1,2-dicyano-1,2-dihydro[60]fullerene,[36] dicyanomethano-1,2-dihydro[60]fullerene,[37] and 1,1′,3,3′-tetracyano-2-oxa-1′,3′-propano-1,2-dihydro[60]fullerene[38] have substantially more positive redox potentials than C$_{60}$ itself. Six more fullerenes containing cyano groups at the same positions or in spiro conjugation to the fullerene

(32) Dubois, D.; Kadish, K. M. *J. Am. Chem. Soc.* **1991**, *113*, 4364.
(33) Khaled, M. M.; Carlin, R. T.; Trulove, P. C.; Eaton, G. R.; Eaton, S. S. *J. Am. Chem. Soc.* **1994**, *116*, 3465.
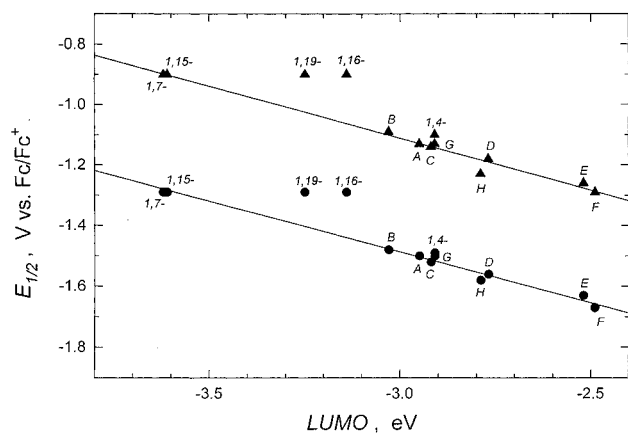(34) Li, Y.; Xu, Y.; Mo, Y.; Bai, F.; Li, Y.; Wu, Z.; Han, H.; Zhu, D. *Solid State Commun.* **1994**, *92*, 185.
(35) Suzuki, T.; Maruyama, Y.; Akasaka, T.; Ando, W.; Kobayashi, K.; Nagase, S. *J. Am. Chem. Soc.* **1994**, *116*, 1359−1364.
(36) Keshavarz-K, M.; Knight, B.; Srdanov, G.; Wudl, F. *J. Am. Chem. Soc.* **1995**, *117*, 11371−11372.
(37) Keshavarz-K, M.; Knight, B.; Haddon, R. C.; Wudl, F. *Tetrahedron* **1996**, *52*, 5149−5159.
(38) Fan, L.; Li, Y.; Li, F.; Zheng, D.; Xu, J.; Li, Y.; Zhu, D. *Fullerene Sci. Tech.* **1998**, *6*, 963−980.

Figure 4. Dependence of the redox potential of the first (▲) and second (•) electroreduction for 1,4-isomer **1** as well as 1,7-, 1,15-, 1,16-, and 1,19-isomers, considered as **3**, vs LUMO energy from Table 2. Data for other 1,2-diadducts of C$_{60}$ are from ref 35: A, C$_{60}$; B, C$_{60}$O; C, C$_{60}$[C(O)CH=CH]; D, C$_{61}$Ph$_2$; E, C$_{60}$Si(2,6-diisopropylphenyl)$_2$; F, C$_{60}$[(mesityl)$_2$SiCH$_2$Si-(mesityl)$_2$]; G, C$_{60}$[OC(CH$_3$)$_2$O]; H, C$_{60}$[(CH$_2$)$_3$]; All $E_{1/2}$ values are for 1,2-dichlorobenzene, 0.1 M tetrabutylammonium perchlorate.

via a methano bridge have first and second redox potentials about the same as that of C$_{60}$.[36,37,39]

The 0.2 V positive shift of the first and second redox potentials and the blue-shifted absorption bands of the one- and two-electron reduced products of the unidentified isomer **3** are unprecedented. Advantageously, **3** may be promising as an acceptor for charge-transfer complexes. Previous investigations have found good correlations between $E_{1/2}$ and LUMO energies. The PM3 calculations performed for the different isomers (Table 2) and the determined $E_{1/2}$ values for **1** and **3** along with literature data are correlated in Figure 4. The larger the distance between addends attached to the C$_{60}$ cage, the higher is the LUMO energy of the isomer. The calculated LUMO energies of the 1,7- and 1,15-di(2-cyano-2-propyl)-1,x-dihydro[60]fullerenes correlate with the observed redox potentials of isolated compound **3**, but the LUMO energies of the 1,16- and 1,19-isomers do not. However, the 1,7- and 1,15-isomers have C_s symmetry, and the ^{13}C NMR spectrum of **3** supports C_2 symmetry, which fits the 1,16- and 1,19-isomers, so the structure of compound **3** cannot be assigned. So far, efforts to grow single crystals of **3** for X-ray structure determination have not succeeded.

Experimental Section

Materials. C$_{60}$ (99.5%) was obtained from MER Corp. AIBN from Aldrich was recrystallized from ethanol at ≤50 °C. Hexane from Pharmaco and toluene and oDCB from Fisher were used without further purification.

Measurements. Elemental analyses were performed at Guelph Chemical Laboratories Ltd., Guelph, Ontario, Canada, using a catalyst at 1200 °C to promote combustion. HPLC analyses were performed on a C$_{18}$ column (J. T. Baker Inc., 250 mm long, 4.6 mm i.d.) and a Cosmosil Buckyprep column (Nacalai Tesque Co., 250 mm long, 4.6 mm i.d.) at a flow rate of 1.0 mL min^{-1} at 25 °C monitored by absorbance at 340 or 350 nm. Chloroform/methanol (50:50 v/v) was the eluant for the C$_{18}$ column and toluene/hexane (70:30 v/v) for the Bucky

(39) Knight, B.; Martin, N.; Ohno, T.; Orti, E.; Rovira, C.; Veciana, J.; Vidal-Gancedo, J.; Viruela, P.; Viruela, R.; Wudl, F. *J. Am. Chem. Soc.* **1997**, *119*, 9871–9882.

column. UV/vis spectra were taken at 30 °C. Liquid secondary ion mass spectra (LSIMS) were obtained from samples in a 3-nitrobenzyl alcohol matrix using negative ion detection. 1D NMR spectra were recorded in CDCl$_3$ solutions at ^{1}H frequencies of 300 or 400 MHz and a ^{13}C frequency of 100.6 MHz, and 2D spectra were recorded at a ^{1}H frequency of 600 MHz. For 1D[13]C NMR experiments 2 mg of Cr(acac)$_3$ was added as a relaxation reagent to 0.5 mL of solution, and a 6 s delay was used between acquisitions.

Electrochemistry. The cyclic voltammetric experiments were performed by using a Model 263A potentiostat/galvanostat of EG&G Princeton Applied Research (Princeton, NJ) and a typical three-electrode electrochemical cell. A 1.6 mm diameter disk platinum electrode of Bioanalytical Systems (West Lafayette, IN) was used as the working electrode, while a platinum wire and sodium chloride saturated Ag/AgCl electrode served as the auxiliary and reference electrodes, respectively. A ferrocene/ferrocenium redox couple was used as an internal standard of potentials. Bulk electrolyses of about 0.05 mM fullerene derivatives in 0.1 M (TBA)PF$_6$ in oDCB were carried out by using an EG&G Model 377A coulometry cell. Solutions were deaerated by nitrogen purge prior to experiments.

Reaction of C$_{60}$ with AIBN. C$_{60}$ (1.0 g, 1.4 mmol) was dissolved in 80 mL of oDCB and mixed with 20 mL of oDCB solution containing 1.1 g (6.9 mmol) of AIBN. The mixture was purged with nitrogen for 30 min and submerged in a 75 °C oil bath for 60 min while protected from light. The reaction mixture was cooled to room temperature immediately, mixed with 250 mL of hexane, and separated using 200 cm^3 of Baker 40 μm flash chromatography silica gel. The column was prepared in toluene/hexane (60:40 v/v) that was degassed by sonication and kept in nitrogen atmosphere. Unreacted C$_{60}$ (45%, magenta) eluted first, followed by four light brown bands. Next, the eluent was changed to 80:20 v/v toluene/hexane, and a reddish brown band (fraction **A**) and a brown band (fraction **B**) were collected. Then the eluent was changed to 98:2 v/v toluene/acetic acid, and a brown band (fraction **C**) was obtained. Fractions **A** and **B** were flash chromatographed twice more to yield 32 mg (2.4%) of **3** and 180 mg (14%) of a mixture of **1** and **2** that had retention times of 6.4 and 5.4 min, respectively, and accounted for >97% of the peak areas of each sample by reversed-phase HPLC. Pure 1,4-isomer (**1**) and a sample containing 75/25 **2/1** were isolated from fraction **B** by repeated HPLC on the Cosmosil Buckyprep column. Retention times and relative areas at 340 nm were 13.6 min (74%) **1** and 15.2 min (26%) **2**.

1,4-Di(2-cyano-2-propyl)-1,4-dihydro[60]fullerene (1). UV (THF): 271 nm ($\epsilon = 7.1 \times 10^4$), 330sh, 446 ($5.1 \times 10^3$). IR: 2238, 529 cm^{-1}. ^{1}H NMR: δ 2.27 (s, 6H) 2.43 (s, 6H). ^{13}C NMR: δ 26.8 (2C), 27.8 (2C), 41.7 (2C), 62.7 (2C), 124.7 (2C), 137.4 (2C), 138.8 (2C), 140.8 (1C), 141.5 (2C), 142.3 (2C), 142.5 (1C), 142.8 (2C), 142.9 (1C), 143.2 (2C), 143.3 (2C), 143.4 (2C), 143.5 (2C), 143.8 (4C), 144.1 (2C), 144.2 (2C), 144.3 (2C), 144.4 (2C), 144.5 (1C), 144.6 (2C), 145.1 (2C), 145.9 (2C), 146.3 (2C), 147.0 (2C), 147.1 (2C), 147.4 (2C), 148.4 (2C), 148.9 (2C), 149.8 (2C), 152.7 (2C). LSIMS: m/z 873 [C$_{60}$+H+C$_8$H$_{12}$N$_2$ + O] (21), 857 [C$_{60}$ + H + C$_8$H$_{12}$N$_2$] (27), 788 [C$_{60}$ + C$_4$H$_6$N] (19), 737 [C$_{60}$ + H + O] (24), 720 [C$_{60}$] (100).

1,2-Di(2-cyano-2-propyl)-1,2-dihydro[60]fullerene (2). From mixtures with **1**. UV: 434 nm, 452sh. ^{1}H NMR: δ 2.14 (s, 3H), 2.16 (s, 3H), 2.32 (s, 3H), 2.37 (s, 3H). ^{13}C NMR: δ 25.8 (1C), 27.9 (1C), 28.5 (1C), 29.7 (1C), 41.1 (1C), 41.4 (1C), 60.8 (1C), 65.5 (1C); peaks at >100 ppm were not identified.

1,x-Di(2-cyano-2-propyl)-1,x-dihydro[60]fullerene (3). UV (THF): 254 nm ($\epsilon = 5.9 \times 10^4$), 320sh, 350sh, 410sh, 454, 480sh, 514sh. IR: 2234, 525 cm^{-1}. ^{1}H NMR: δ 2.14 (s,12H). ^{13}C NMR: δ 24.2 (2C), 24.5 (2C), 41.7(2C), 64.2 (2C), 122.6 (2C), 136.0 (2C), 136.9 (2C), 138.6 (2C), 139.5 (2C), 141.6 (2C), 141.7 (2C), 142.0 (2C), 142.2 (2C), 142.3 (2C), 142.8 (2C), 143.0 (2C), 144.3 (2C), 144.7$_0$ (2C), 144.7$_3$ (2C), 144.9 (2C), 145.0$_2$ (2C), 145.0$_7$ (2C), 145.1$_2$ (2C), 145.2 (2C), 145.7 (2C), 145.8 (2C), 146.0 (2C), 146.5 (2C), 146.9 (2C), 148.1 (2C), 148.2 (2C), 148.8 (2C), 150.9 (2C), 158.4 (2C). LSIMS: m/z 873 [C$_{60}$ + H +

$C_8H_{12}N_2 + O$] (13), 856 [$C_{60} + C_8H_{12}N_2$] (24), 788 [$C_{60} + C_4H_6N$] (17), 737 [$C_{60} + H + O$] (23), 720 [C_{60}] (100).

Supporting Information Available: ^{13}C NMR spectra of **1** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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