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Dimethyl Azo(bisisobutyrate) and C_{60} Produce 1,4- and 1,16-Di(2-carbomethoxy-2-propyl)-1,*x*-dihydro[60]fullerenes

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Thermal decomposition of dimethyl azo(bisisobutyrate) in a solution containing C_{60} produced 1,4- and 1,16-di(2-carbomethoxy-2-propyl)-1,*x*-dihydro[60]fullerenes in yields of 21% and 27%, respectively, based on reacted C_{60}. The structure of this first 1,16-dialkyl-1,16-dihydro[60]fullerene was assigned from ^{13}C 2D INADEQUATE NMR spectra. The 1,16-isomer has first and second electrochemical reduction potentials shifted positively by 0.18 V relative to those of the 1,4-isomer. From the close similarity of all spectral, chromatographic, and electrochemical data, the previously unassigned isomer of 1,*x*-di(2-cyano-2-propyl)-1,*x*-dihydro[60]fullerene, which was obtained from azo(bisisobutyronitrile) and C_{60}, is also a 1,16-isomer.

Introduction

Additions of radicals to C_{60} were investigated soon after gram amounts of C_{60} became available. Benzyl radicals, for example, add to give fullerene allyl and cyclopentadienyl radicals that were identified by ESR spectroscopy, and the FAB mass spectrum of the adducts showed as many as 15 benzyl groups per fullerene.[1−3] Addition of two radicals gives isomeric 1,*x*-dihydro[60]fullerenes, the 1,2-isomers of which are the major products when the radicals are small, and the 1,4-isomers are the major products when the radicals are large.[4−6] The only other isomer that has been reported is 1,16-di(trimethylsilyl)-1,16-dihydro[60]fullerene, which was produced by reaction of trimethylsilyllithium with C_{60} and identified by single-crystal X-ray analysis.[7,8]

The structures formed by addition of alkyl radicals to C_{60} are vital for understanding the structures of polymers produced from C_{60} and vinyl monomers.[9−21] During radical polymerizations of methyl methacrylate (MMA) and of styrene with C_{60} initiated by thermal decomposition of 2,2′-azo(bisisobutyronitrile) (AIBN), the C_{60} is incorporated into the polymer early, and the high-conversion polystyrene/C_{60}, but not the PMMA/C_{60}, contains molecules having large numbers of fullerene units.[9,21] Polymers made from a 5:1 molar ratio of AIBN/C_{60} contain an average of six 2-cyano-2-propyl groups per fullerene,[9] with the 2-cyano-2-propyl groups located both at the polymer chain ends and directly on the fullerenes.[9] At low conversion after attachment of 2.0−3.5 of the 2-cyano-2-propyl groups per C_{60} unit, 62−72% of the initiator groups are end groups of polymer chains, and 28−38% bond directly to fullerenes.[21]

Previously we reported three isomeric 1,*x*-di(2-cyano-2-propyl)-1,*x*-dihydro[60]fullerenes from the thermal decomposition of AIBN in a 1,2-dichlorobenzene (oDCB) solution of C_{60}.[22] The 1,2- and 1,4-isomers (**1** and **2**) were identified conclusively, but the structure of the third isomer (**3**) eluded us. Now we report that thermal decomposition of the analogous azo compound, dimethyl 2,2′-azo(bisisobutyrate) (DMAIB), produces only 1,4- and

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* To whom correspondence should be addressed.

(1) Krusic, P. J.; Wasserman, E.; Keizer, P. N.; Morton, J. R.; Preston, K. F. *Science* **1991**, *254*, 1183.

(2) 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.

(3) Morton, J. R.; Preston, K. F.; Krusic, P. J.; Hill, S. A.; Wasserman, E. *J. Phys. Chem.* **1992**, *96*, 3576.

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

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

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

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

(8) For the IUPAC numbering and nomenclature of fullerenes see: *Pure Appl. Chem.* **1997**, *69*, 1411−1434.

(9) Ford, W. T.; Graham, T.; Mourey, T. H. *Macromolecules* **1997**, *30*, 6422.

(10) Cao, T.; Webber, S. E. *Macromolecules* **1995**, *28*, 3741.

(11) Bunker, C. E.; Lawson, G. E.; Sun, Y.-P. *Macromolecules* **1995**, *28*, 3744.

(12) Camp, A. G.; Lary, A.; Ford, W. T. *Macromolecules* **1995**, *28*, 7959.

(13) Sun, Y.-P.; Ma, B.; Bunker, C. E.; Liu, B. *J. Am. Chem. Soc.* **1995**, *117*, 12705.

(14) Cao, T.; Webber, S. E. *Macromolecules* **1996**, *29*, 3826.

(15) 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.

(16) 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.

(17) Stewart, D.; Imrie, C. T. *Chem. Commun.* **1996**, 1383.

(18) Kirkwood, K.; Stewart, D.; Imrie, C. T. *J. Polym. Sci., Part A: Polym. Chem.* **1997**, *35*, 3323.

(19) Nayak, P. L. Alva, S.; Yang, K.; Dhal, P. K.; Kumar, J.; Tripathy, S. K. *Macromolecules* **1997**, *30*, 7351.

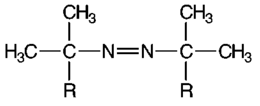
(20) Seno, M.; Fukunaga, H.; Sato, T. *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36*, 2905.

(21) Ford, W. T.; Nishioka, T.; McCleskey, S. C.; Mourey, T. H.; Kahol, P. *Macromolecules* **2000**, *33*, 2413.

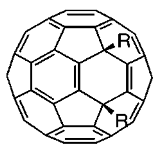
(22) Ford, W. T.; Nishioka, T.; Qiu, F.; D'Souza, F.; Choi, J.-p.; Kutner, W.; Noworyta, K. *J. Org. Chem.* **1999**, *64*, 6257.

10.1021/jo000686d CCC: $19.00

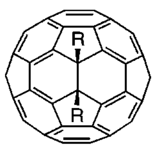
1,16-di(2-carbomethoxy-2-propyl)-1,*x*-dihydro[60]fullerenes (**4** and **5**), and that the structure of the previously unidentified product (**3**) from AIBN and C_{60} is also a 1,16-diadduct. The compounds **4** and **5** are models of the structures formed by the addition of two PMMA radicals to C_{60}.



AIBN, R = CN
DMAIB, R = CO_2CH_3



1, R = $C(CH_3)_2CN$
4, R = $C(CH_3)_2CO_2CH_3$



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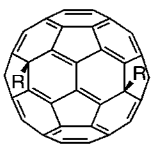

3, R = $C(CH_3)_2CN$
5, R = $C(CH_3)_2CO_2CH_3$

Experimental Section

Materials. C_{60} (99.5%) and ^{13}C-enriched C_{60} were from MER Corp. The enriched sample contained 90% of 16%-enriched C_{60} and 10% of natural abundance C_{60} by MALDI-TOF MS analysis. DMAIB was synthesized from AIBN by a literature method and recrystallized from pentane to give fine white needles in 61% yield.[23] All reagents and solvents were used without further purification.

Reaction of C_{60} with DMAIB. Natural abundance C_{60} (1.0 g, 1.4 mmol) was dissolved in 160 mL of oDCB and mixed with 40 mL of an oDCB solution containing 1.6 g (6.9 mmol) of DMAIB. After being stirred under nitrogen for 30 min, the mixture was heated to 75 °C for 75 min while being protected from light and then cooled quickly to 25 °C. The mixture was separated on Baker 40 μm flash chromatography silica gel with 60:40 toluene/hexane to give unreacted purple C_{60} (465 mg, 47%), an unidentified light brown band, a red-brown band containing 1,16-di(2-carbomethoxy-2-propyl)-1,16-dihydro[60]fullerene (**5**), and a brown band containing 1,4-di(2-carbomethoxy-2-propyl))-1,4-dihydro[60]fullerene (**4**). The eluant was changed to toluene, and a brown band containing a mixture of higher adducts of [60]fullerene was obtained. Both isomers were purified twice more by flash chromatography to yield 105 mg (8.2%) of **5** and 180 mg (14%) of **4**.

Data for 4: UV−vis (THF) 252 (9.0×10^4), 292, 328, 448; IR (cm^{-1}) 1737, 528; ^1H NMR (400 MHz, $CDCl_3$) δ 2.10 (s, 12H), 3.85 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.0 (2C), 26.3 (2C), 51.8 (2C), 52.5 (2C), 64.1 (2C), 136.3 (2C), 138.5 (2C), 140.0 (1C), 141.1 (2C), 142.4 (2C), 142.7 (4C), 143.0 (2C), 143.1 (2C), 143.2 (2C), 143.3 (4C), 143.8 (2C), 144.0 (2C), 144.3 (4C), 144.5 (1C), 144.6_7 (2C), 144.7_4 (2C), 145.4 (2C), 145.7 (2C), 146.3 (2C), 146.4 (2C), 146.9 (2C), 147.1 (2C), 147.2 (2C), 148.7 (2C), 148.9 (2C), 151.4 (2C), 156.2 (2C), 175.7 (2C). Anal. Calcd for $C_{70}H_{18}O_4$: C, 91.10; H, 1.97. Found: C, 91.26; H, 2.08.

Data for 5: UV−vis (THF): 256 (7.6×10^4), 292, 400 sh; IR (cm^{-1}) 1731, 525; ^1H NMR (400 MHz, $CDCl_3$) δ 1.97 (s, 6H), 1.98 (s, 6H), 3.80 (s, 6H); ^{13}C (100 MHz, $CDCl_3$) 23.1 (2C), δ 23.2 (2C), 51.6 (2C), 52.3 (2C), 64.8 (2C), 135.2 (2C), 136.7 (2C), 137.6 (2C), 138.8 (2C), 141.1 (2C), 141.2 (2C), 141.4 (2C), 141.6 (2C), 142.1 (2C), 142.5 (2C), 142.7 (2C), 144.1 (2C), 144.3 (2C), 144.5 (2C), 144.6 (2C), 145.0 (2C), 145.2 (2C), 145.4 (2C), 145.5 (4C), 145.9 (2C), 146.6 (4C), 146.7 (2C), 147.8 (2C), 148.6 (2C), 150.8_7 (2C), 150.9_2 (2C), 160.4 (2C), 175.0 (2C); LSIMS (*m/z*) 922 (12), 821 (14), 721 (100); ESIMS in the Supporting Information. Anal. Calcd for $C_{70}H_{18}O_4$: C, 91.10; H, 1.97. Found: C, 90.90; H, 2.01.

The reaction of 640 mg of DMAIB with 400 mg of ^{13}C-enriched C_{60} was carried out similarly in 80 mL of oDCB at 65 °C for 75 min to yield 340 mg (84%) of unreacted C_{60}, 22 mg (4.3%) of **5**, and 18 mg (3.5%) of **4** after three flash chromatographic purifications.

Measurements. Elemental analyses were performed at Guelph Chemical Laboratories Ltd., Guelph, Ontario, Canada, using a catalyst at 1200 °C to promote combustion. ^{13}C NMR analyses at 100 MHz employed 0.5 mL of chloroform-*d* solutions containing 2 mg of $Cr(acac)_3$, 30 mg of sample, a 30° ^{13}C pulse, and a 6 s relaxation delay between acquisitions. IR spectra were obtained from KBr disks. LSIMS spectra with a Cs ion beam were obtained from samples in *m*-nitrobenzyl alcohol matrixes on a VG Analytical ZAB2-SE double-focusing mass spectrometer.

Electrochemistry.[22] Cyclic voltammetric experiments were performed by using a model 263A potentiostat/galvanostat of EG&G Princeton Applied Research (Princeton, NJ) and a 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 a sodium chloride saturated Ag/AgCl electrode served as the auxiliary and reference electrodes, respectively. Ferrocene/ferrocenium redox couple was used as an internal standard of potentials. Solutions were deaerated by N_2 purge prior to the experiments.

2D INADEQUATE ^{13}C NMR (150 MHz). The experiments were carried out at 30 °C on a Varian UNITY INOVA 600 MHz spectrometer equipped with a Varian broad-band probe. First a spectrum was obtained with spectral widths of 33 126 and 66 252 Hz in the directly and indirectly detected dimensions, respectively, with $^1J_{CC}$ set to 50 Hz and a *z*-axis relaxation delay of 1.5 s. Data were collected as an array of 2000 × 80 points (1024 scans per increment). After linear prediction and zero filling in t_1, the final data matrix was 2k × 2k. A second spectrum was acquired with spectral widths of 4694 and 9388 Hz, $^1J_{CC}$ set to 55 Hz, and a relaxation delay of 1.5 s, and the data were processed the same way, which folded the peaks of the 64.8 ppm signal into the spectrum.

Results

1,*x*-Di-(2-carbomethoxy-2-propyl)-1,*x*-dihydro[60]fullerenes 4 and 5.

During 75 min at 75 °C 24% of DMAIB decomposes to 2-carbomethoxy-2-propyl radicals and dinitrogen, assuming a half-life of 192 min.[24] Using a 5:1 molar ratio of azo compound to C_{60}, **4** and **5** were obtained pure after three flash chromatographic purifications in 26% and 15% yields, respectively, based on 53% of C_{60} reacted. Longer reaction times led to lower yields because of formation of higher adducts, which we isolated as a mixture and did not try to separate further. When a mixture of AIBN and C_{60} in oDCB at 75 °C was sampled and analyzed periodically by size exclusion chromatography, C_{60} steadily disappeared.[21] Amounts of diadducts increased over about 2 h and then decreased as higher adducts and low molar mass [60]fullerene oligomers formed.[21] Thus, C_{60} polymerizes slowly under the reaction conditions.

Compounds **4** and **5** eluted in the same order and had the same colors as the 1,4-isomer and an unidentified isomer of 1,*x*-di(2-cyano-2-propyl)-1,*x*-dihydro[60]fullerene (**1** and **3**, respectively).[22] None of the 1,2-isomer was detected from DMAIB, whereas flash chromatography of products from the AIBN failed to separate the 1,2- and 1,4-isomers, which were obtained as a 14:86 mixture.

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(23) Bizily, S.; Kelly, D. P.; Serelis, A. K.; Solomon, D. H.; White, K. E. *Aust. J. Chem.* **1985**, *38*, 1657.

(24) Brandrup, J., Immergut, E. H., Grulke, E. A., Eds. *Polymer Handbook*, 4th ed.; Wiley: New York, 1999; p II/10.

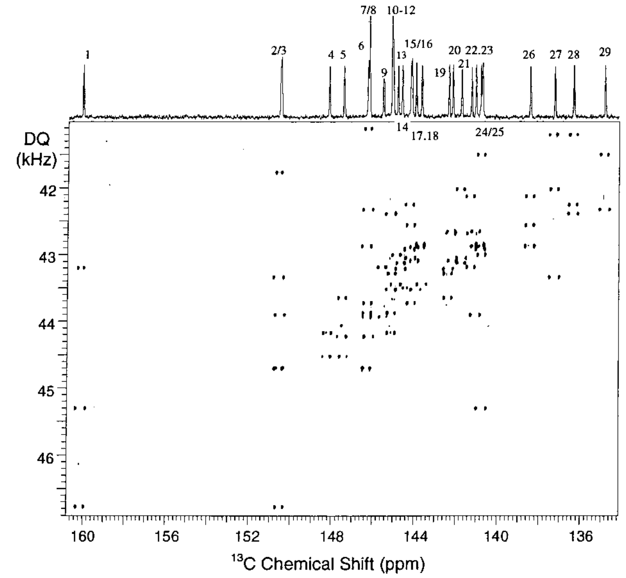

Figure 1. ^{13}C 2D INADEQUATE NMR spectrum of **5**. Peaks correlated to C(30) are not at correct positions in F1 because the spectral width did not include the C(30) frequency. On the vertical axis 150.567 MHz = 1 ppm.

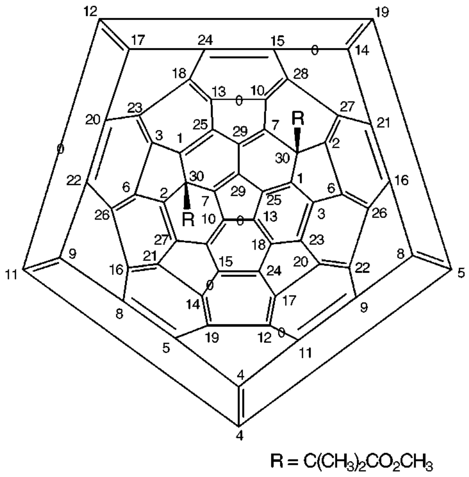

Figure 2. Schlegel diagram of correlations in the ^{13}C 2D inadequate NMR spectrum of **5**. Bonds between carbon atoms whose correlation peaks do not appear in the spectrum are marked 0. The chemical shifts of all such missing pairs differ by ≤90 Hz. The diagram is numbered in order of decreasing chemical shift as in Figure 1.

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

	$E_{1/2}$, V vs Ag/AgCl				
	0/−	−/2−	2−/3−	3−/4−	ref
C_{60}[a]	−0.44	−0.82	−1.25	−1.72	22
1	−0.41	−0.81	−1.32	−1.87[b]	22
3	−0.21	−0.61	−1.29	−1.78[b]	22
4	−0.55	−0.94	−1.41	−1.94[b]	*c*
5	−0.37	−0.76	−1.43	−1.97	*c*

[a] Agrees with literature values in benzonitrile.[27] [b] E_{pc} at 0.1 V/s. [c] This work.

When the DMAIB reaction was repeated with ^{13}C-enriched C_{60} at 65 °C for 75 min, the DMAIB was 7.4% decomposed (assuming a half-life of 680 min),[24] 84% of C_{60} was recovered, and the yields of **4** and **5** were 21% and 27%, respectively, based on reacted C_{60}.

The structures of **4** and **5** are supported by elemental analyses, and by mass, UV−vis, IR, and ^{1}H, and ^{13}C NMR spectra. The ^{1}H NMR spectrum of **4** showed two overlapping singlets for the diastereotopic *C*-methyl groups and one singlet for the *O*-methyl groups. The ^{13}C NMR spectrum of **4** had two diastereotopic *C*-methyl peaks, single peaks for *O*-methyl, quaternary aliphatic, and carbonyl carbons, one peak at 64 ppm for the substituted fullerene carbon atoms, and 28 two-carbon and 2 one-carbon peaks in the aromatic region. Its UV−vis spectrum had a peak at 448 nm characteristic of 1,4-adducts of C_{60}.[22]

LSIMS (liquid secondary ion mass spectroscopy) of **5** gave a molecular ion at $m/z = 922$, a peak for loss of one alkyl group at $m/z = 821$, and C_{60} at $m/z = 720$. MALDI-TOF MS gave a similar result. The ^{1}H NMR spectrum had two diastereotopic *C*-methyl peaks and one *O*-methyl peak. The ^{13}C NMR spectrum had two diastereotopic *C*-methyl, one *O*-methyl, one quaternary aliphatic, one fullerene aliphatic, one carbonyl, and the fullerene unsaturated carbon peaks described below. Its UV−vis spectrum closely resembled that of the previously unidentified isomeric 1,*x*-di-(2-cyano-2-propyl)-1,*x*-dihydro[60]fullerene.[22]

2D INADEQUATE ^{13}C NMR Spectrum of 5. Two spectra were obtained: one at a spectral width that included both the saturated and the unsaturated fullerene carbons, and the one in Figure 1 that covers only the unsaturated region. The 1D spectrum has one saturated and 26 unsaturated fullerene carbon peaks, one of which corresponds to two carbon atoms and one corresponds to three carbon atoms, to give a total of 29 unsaturated carbon atoms and one saturated carbon atom, which is consistent with an isomer of C_2 symmetry. Starting with the saturated fullerene peak, the connectivity of carbon atoms is consistent only with the 1,16-isomer (**5**), and not with the 1,2-, 1,4-, 1,7-, 1,15-, or 1,19-isomers. The correlations are listed in the Schlegel diagram of C_{60} in Figure 2.

Electrochemistry. Electrochemical data for the first four reductions of C_{60}, **1**, **3**, **4**, and **5** are given in Table 1, and Figure 3 shows cyclic voltammograms of C_{60}, **4**, and **5** in 0.1 M (TBA)ClO$_4$ and oDCB. The first two peaks of the 1,4-isomer (**4**) are shifted to negative potential by 0.11−0.12 V relative to those of C_{60}, whereas those of the analogous cyano compound **1** are nearly the same as those of C_{60}. The first two peaks of the 1,16-isomer (**5**) are shifted by 0.06−0.07 V to more positive potential relative to those of C_{60}, a smaller amount but in the same direction as those of the corresponding cyano compound **3**. The unusual shifts of the reduction peaks of **5** and **3** to positive potential suggests that they are the same regioisomeric diadducts of C_{60}. Only the first two peaks of the 1,16-isomers are shifted to positive potential: The third and fourth reduction peaks of both **3** and **5** are 0.16−0.25 V more negative than those of C_{60}.

UV−vis spectra of the neutral and the electrogenerated monoanionic and dianionic 1,*x*-di-(2-carbomethoxy-2-propyl)-1,*x*-dihydro[60]fullerenes are shown for **5** in Figure 4a and for **4** in Figure 4b, and the peak maxima are reported in Table 2. The peak at 448 nm in the spectrum of the neutral compound **4** is characteristic of 1,4-adducts of C_{60}, and the band at 953 nm in the spectrum of its monoanion is at about the same wavelength but much less intense than that in the spectrum of the analogous

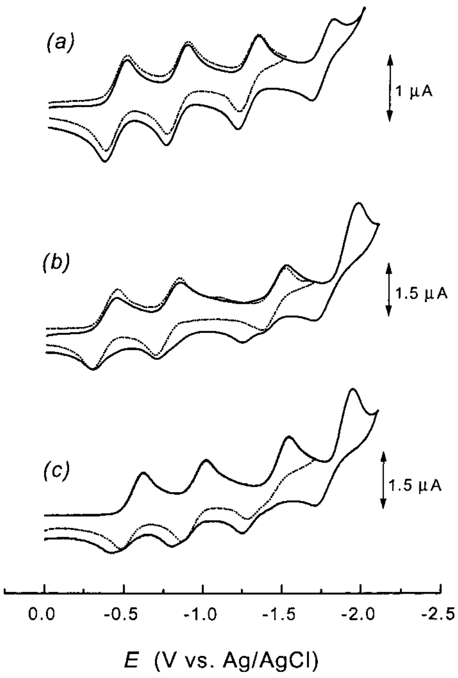

Figure 3. Cyclic voltammograms of (a) C_{60}, (b) **5**, and (c) **4** in 1,2-dichlorobenzene and 0.1 M $(TBA)ClO_4$. Scan rate 0.1 V s^{-1}.

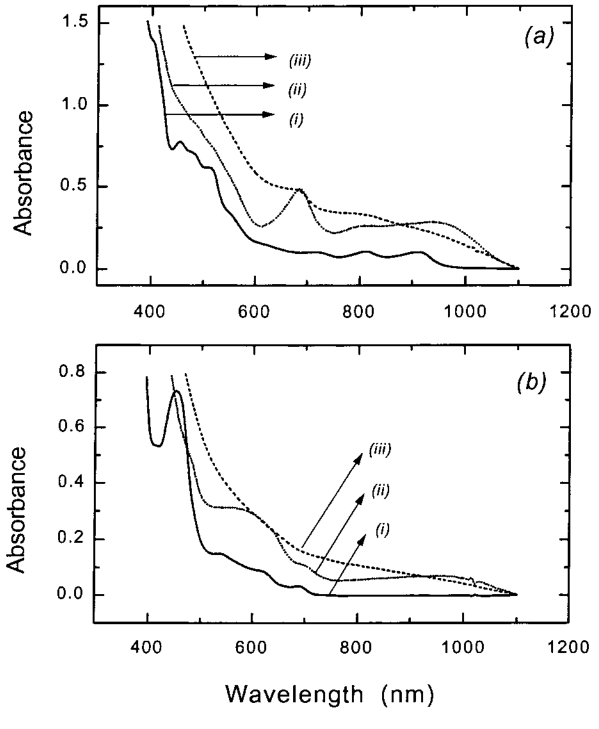

Figure 4. Vis−near-IR spectra of (i) neutral, (ii) monoanionic, and (iii) dianionic species of (a) **5** and (b) **4** in 1,2-dichlorobenzene and 0.1 M $(TBA)ClO_4$.

cyano compound **1**. The neutral 1,16-isomers (**3** and **5**) exhibit split near-UV bands and additional characteristic bands in the wavelength range of 700−950 nm. The absorption peak maxima are red shifted by 6−8 nm in the case of **5** as compared to the peak positions of the more electron deficient **3**. The spectrum of the monoanion of the 1,16-isomer (**5**) lacks the intense peak of the corresponding monoanion of cyano compound **3**, and instead has less intense peaks at 685 and 985 nm. Further reduction of compounds **4** and **5** to their doubly reduced states resulted in broader bands; hence, no further analysis is offered.

Table 2. UV−Vis Data for Neutral, Monoanionic, and Dianionic C_{60} and C_{60} Derivatives Generated Electrochemically in 1,2-Dichlorobenzene, and 0.1 M $(TBA)ClO_4$

	oxidation state	λ_{max}, nm	ref
C_{60}[a]	0	213,257, 329, 404, 568	28
	−1	1075	29
	−2	840, 950	29
4	0	451, 549, 626, 687	*b*
	−1	441, 484, 630, 953	*b*
	−2	no peaks	*b*
5	0	407, 454, 484, 520, 712, 813, 912	*b*
	−1	685, 936, 985	*b*
	−2	684	*b*

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

Discussion

The spectra firmly establish the structures of the diadducts of C_{60} and DMAIB as **4** and **5**. Compound **5** is the first example of a 1,16-dialkyl-1,16-dihydro[60]-fullerene. Similar results were obtained with AIBN except that a small amount of the 1,2-isomer (**2**) was mixed with the 1,4-isomer (**1**). Identification of the 1,16-diadduct (**5**) from DMAIB establishes the structure of the previously unidentified diadduct from AIBN and C_{60} also as the 1,16-isomer (**3**), because both compounds elute from silica gel before the 1,4-isomers, have 30 ^{13}C NMR peaks indicative of C_2 symmetry, have similar UV−vis spectra, and have first and second redox potentials shifted positively by about 0.2 V from those of the 1,4-isomers.

Although no 1,16-dialkyl adduct of C_{60} has been reported before, 1,16-disilyl adducts are known. Reaction of trimethylsilyllithium with C_{60} produced 1,16-di(trimethylsilyl)-1,16-dihydro[60]fullerene, which was identified by single-crystal X-ray analysis.[7] Bissilylated fullerenes are produced also by photolysis of disilanes in a solution of C_{60} under conditions where the disilane dissociates homolytically into silyl radicals.[26] Photolysis of 1,1,2,2-tetraphenyl-1,2-di-*tert*-butyl-1,2-disilane gave a 58% yield of a [60]fullerene that was assigned the 1,16-isomer structure on the basis of spectral properties that did not correspond with those of known 1,2- and 1,4-bistrialklysilyl-1,*x*-dihydro[60]fullerenes and a heat of formation of 1,16-$(H_3Si)_2C_{60}$ (calculated at the AM1 level) that was only 4.6 kcal/mol higher than that of the 1,2-isomer.[26]

The electrochemical redox and the optical absorption spectral studies reveal interesting properties of the 1,-16-adducts. The most important observation is the easier electroreductions of 1,16-isomers by 0.2 V compared with the corresponding 1,4-isomers. Earlier, easily reducible functionalized fullerenes were synthesized by either halogen addition or appending one or more electron-withdrawing or positively charged substituents on the fullerene spheroid.[30] Formation of 1,16-adducts offers a

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(25) Bax, A.; Freeman, R. *J. Magn. Reson.* **1980**, *41*, 507.

(26) Akasaka, T.; Suzuki, T.; Maeda, Y.; Ara, M.; Wakahara, T.; Kobayashi, K.; Nagase, S.; Kako, M.; Nakadaira, Y.; Fujitsuka, M.; Ito, O. *J. Org. Chem.* **1999**, *64*, 566.

(27) Dubois, D.; Kadish, K. M.; Flanagan, S.; Haufler, R. E.; Chibante, L. P. F.; Wilson, L. J. *J. Am. Chem. Soc.* **1991**, *113*, 4364.

(28) D'Souza, F.; Caron, C.; Subramamian, 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.

simple and elegant way of making electron-deficient organofullerenes, although this approach needs to be verified on other 1,16-adducts. Also, the optical absorption spectra of the 1,16-adducts have a characteristic split near-UV band and three absorption bands in the spectral range of 700−950 nm. Higher level theoretical calculations are needed to understand the electron-deficient nature of 1,16-adducts and their resulting optical transitions.

The stimulus for this investigation was to determine the sites of addition of polymer radical chains to C_{60} during its copolymerization with styrene and with methyl methacrylate (MMA). The 2-carbomethoxy-2-propyl radical is a model of a PMMA radical, and since the PMMA radical is bulkier, the PMMA radicals probably form more of the 1,16-adducts relative to the 1,4-adducts. Polystyryl radicals are somewhat less hindered, and probably form less of the 1,16-adduct. Copolymerization of C_{60} with styrene and with MMA produces macromolecules containing short polymer chains and many fullerenes after 30−120 min of reaction. The polymers contain fullerene−fullerene carbon−carbon bonds, which are labile and react further over longer polymerization times.[21] Compounds containing fullerene−fullerene bonds are likely also formed during the reactions of AIBN and DMAIB with C_{60}, but we have not isolated them.

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Supporting Information Available: ^{13}C NMR spectra of **4** and ESIMS spectrum of **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(29) Khaled, M. M.; Carlin, R. T.; Trulove, P. C.; Eaton, G. R.; Eaton, S. S. *J. Am. Chem. Soc.* **1994**, *116*, 3465.

(30) Martín, N.; Sánchez, L.; Illescas, B.; Pérez, I. *Chem. Rev.* **1998**, *98*, 2527 and references therein.