

Synthesis and solubility properties of C₆₀ fullerene derivatives bearing carboxy groups

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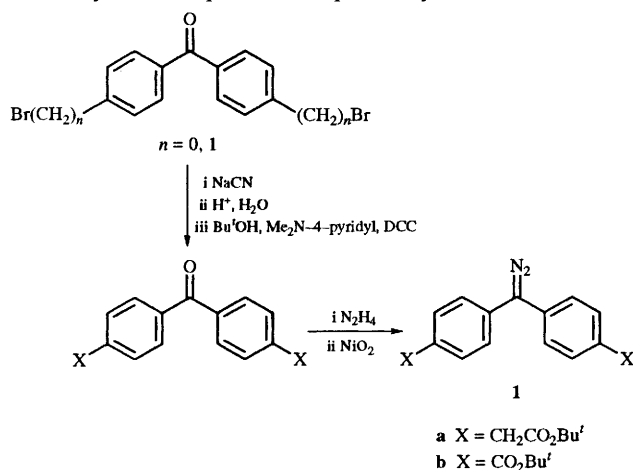
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Bis(4-*tert*-butoxycarbonylphenyl)diazomethanes have been prepared and treated with fullerene (C₆₀) to give the corresponding 1,2-methano derivatives which upon hydrolysis with CF₃CO₂H gave the title compounds. The solubility of the latter in aqueous THF has been measured.

Buckminsterfullerene, the C₆₀ molecule, is now known to be quite reactive chemically, in contrast to its physical stability, and fullerene functionalization has been attracting much interest.¹ Of the compounds thus far prepared, biological interest has focussed on the water-soluble derivatives²⁻⁷ since one of them has been shown to be active against the human immunodeficiency viruses.^{3,4} In this context, and in endeavouring to make an extremely hydrophobic molecule hydrophilic, the relationship between water solubility and the structure of the functional group is important. We report herein the preparation of C₆₀ carboxy derivatives and their solubilities in aqueous organic solvents.

Results and discussion

In order to introduce the carboxy moieties on C₆₀, we decided to use the diazomethane method developed by Wudl for the preparation of a series of fullerenes.⁸ Since the aliphatic diazomethanes are sensitive even to weak acids, the diazo compounds with appropriately protected acid groups were required. *tert*-Butoxycarbonyl groups were chosen as the protective group since they are stable to the hydrazine which is employed in the diazotisation step and easily cleaved under moderately acidic conditions where C₆₀ moieties are usually inert. Therefore, two diphenyldiazomethanes **1a** and **b** having *tert*-butoxycarbonyl groups were prepared according to the reactions summarized in Scheme 1 as a rather stable red oil or solid, respectively, and were used for the reaction with C₆₀ by essentially the same procedure reported by Wudl.

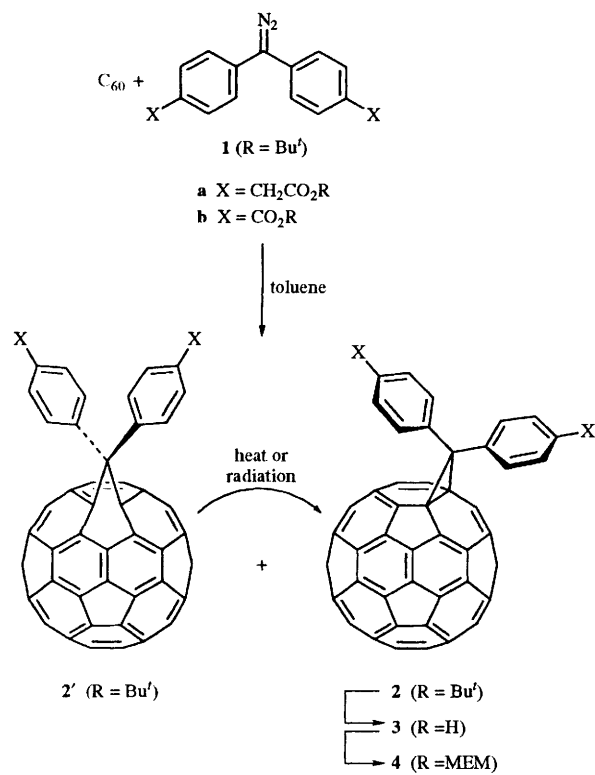


Scheme 1

Thus, in a typical run, a solution of C₆₀ and bis(4-*tert*-butoxycarbonylmethylphenyl)diazomethane **1a** in toluene was stirred at room temperature for 24 h. HPLC analysis of the

resulting mixture showed the presence of two new peaks presumably due to the adducts, in addition to unchanged C₆₀. Silica gel chromatography of the mixture eluted with toluene resulted in the isolation of the major adduct products (43%; 57% based on consumed C₆₀) as a dark brown solid along with unchanged C₆₀ (24% recovery). NMR analysis of the products indicated that these adducts consisted of at least two isomers and the ¹H NMR spectrum (270 MHz, CDCl₃) of the mixture showed three signals at 3.58, 3.56 and 3.44 ppm assignable to the methylene protons, three sets of *para*-substituted aromatic proton signals at 8.05 and 7.37, 8.03 and 7.38 and 7.35 and 7.11 ppm and two *tert*-butyl signals at 1.45 and 1.40 ppm. ¹³C NMR (68 MHz, CDCl₃) indicated only one signal (δ_C 78.99) for the fullerene sp³ carbons. These spectra are interpreted in terms of the presence of 1,2- and 1,6-methano bridged fullerenes. Therefore, while a ring-closed 1,2-derivative such as **2a** should show only one *para*-disubstituted benzene and one *tert*-butoxycarbonylmethyl moiety in its ¹H NMR spectrum, a ring-open 1,6-derivative such as **2'a** should show two sets of those groups, one above a pentagon and one above a hexagon (Scheme 2). The assignment was further supported by the observations that when the mixture was heated in refluxing toluene for 12 h the **2'a** isomer was quantitatively converted into the other, already present C_{2v} isomer, **2a**. Similar thermal isomerization has been noted for related systems.⁹ This isomerization also occurred upon photoexcitation of the mixture, so that irradiation (λ > 300 nm) gave complete conversion of **2'a** into **2a**. The NMR spectra of **2a** obtained after the isomerization are consistent with the structure having two planes of symmetry. Thus, ¹H NMR showed one singlet at 3.58 ppm and the signals for one *para*-substituted benzene, and the ¹³C NMR spectrum showed five signals for aliphatic carbons, one signal at 170.74 ppm for carbonyl carbons and 18 signals for sp² carbons. The spectrum reveals formation of cyclopropane from the signals at 79.00 and 57.70 ppm, and C_{2v} symmetry from 18 signals in the sp² region.

The ester **2a** was easily hydrolysed using trifluoroacetic acid to give the corresponding carboxy derivative as a brown solid **3a** with the C₆₀ moiety intact.¹⁰ The electronic spectrum of **3a** (THF) exhibited maxima at 430, 328 and 258 nm, similar to that of C₆₀ and other cyclopropyl fullerenes. Since the acid was sparingly soluble in most organic solvents, its characterization by NMR was difficult. Therefore it was converted into the methoxyethoxymethoxy (MEM) ester **4**¹¹ by treating it with MEMCl and di(isopropyl)ethylamine in CH₂Cl₂ at 0 °C for 3 h. The product **4**, separated by TLC (silica gel-CH₂Cl₂) as a dark brown solid was characterized by NMR. *p*-Carboxyphenyl functionalized fullerenes (**2b**, **3b** and **4b**) were also prepared by using essentially the same procedure described above, using bis(4-*tert*-butoxycarbonylphenyl)diazomethane **1b** and were characterized by NMR.



Scheme 2

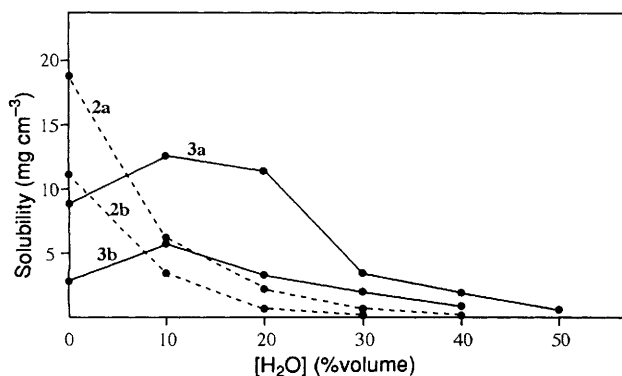


Fig. 1 Solubility curve of C_{60} derivatives in H_2O -THF co-solvent at $30^\circ C$

The solubility of these fullerene derivatives in aqueous THF was measured according to the procedures reported by Sivaraman *et al.*¹² The results shown in Fig. 1 show not only increased solubility of these functionalized C_{60} molecules over the parent compound ($41 \mu g cm^{-3}$ in dioxane) but also point to interesting structure-solubility relationships. Thus, although the increased solubility of **2a** in THF over **2b** is the result expected on going from CO_2H to CH_2CO_2H , the difference is unexpectedly high. C_{60} , which has been described as a van der Waals solid with little interaction between the molecules, is sparingly soluble, the energy required for the breaking of solvent bonds during the dissolution being inadequately compensated for by the interaction between the solute and the solvent. Thus, it may be that even small structural changes result in an unexpectedly large effect on the solute-solvent interaction. The solubility decreased quite sharply as the water content in the solvent was increased, a result understood in terms of less interaction between the solute and the solvent.

The solubility profiles of the C_{60} acid **3** are also worthy of comment. Thus, although the acid was less soluble in THF than the ester, both were more soluble than C_{60} itself. The relative solubilities of the acids **3a** and **3b** are the same as those observed for the C_{60} ester, indicating that the effect of an additional

methylene group on the interaction as noted above holds for the acid series. In contrast to the ester case, although the solubility increased as expected as water was added to the THF as a result of a better interaction between the solute and solvent, it decreased as the water content was increased to more than 20%, where the solute-solvent interaction became poorer again. We found, however, that the solubility of these C_{60} acids increased dramatically upon addition of triethylamine to aqueous solvents. Thus, **3** was soluble up to a concentration of $20 mg cm^{-3}$ in water containing 3% NEt_3 , although exact measurement was not possible due to deep colouration upon dissolution.†

Experimental

IR spectra were measured on a JASCO A-100 recording spectrometer. 1H and ^{13}C NMR spectra were run on a JEOL JNM-EX 270 spectrometer in $CDCl_3$ unless stated otherwise; J values are given in Hz. UV-VIS spectra were obtained with a JASCO V-560 spectrometer. GC-MS spectra were recorded on a Shimadzu QP-1000 mass spectrometer with a GC column prepared from 5% Silicone OV-17 on Diasolid L (5.0 mm \times 1.0 m). HPLC analyses were carried out on a JASCO Finapak C_{18} -T5 column. TLC was carried out on Merck Kieselgel 60 PF₂₅₄, and column chromatography on Fuji Davison silica gel BW-127ZH.

Preparation of bis(4-*tert*-butoxycarbonylmethylphenyl)diazomethane **1a**

To a stirred and heated solution of ditolyl ketone (2.0 g, 9.52 mmol, 1 equiv.) in CCl_4 (30 cm^3) at $75^\circ C$ was added dropwise a solution of bromine (1 cm^3 , 19.42 mmol, 2 equiv.) in CCl_4 (10 cm^3) over 4 h, the reaction mixture being irradiated with a 100 W tungsten lamp. After a further 30 min of heating and irradiation, the mixture was evaporated to afford crude bis(4-bromomethylphenyl) ketone (3.6 g) as a white solid. This was dissolved in dioxane (37 cm^3) and the solution heated to $70^\circ C$. A solution of KCN (1.4 g, 19.5 mmol, 2 equiv.) in water (18 cm^3) was then added to the mixture after which it was stirred at $70^\circ C$ for 30 min. After this, the reaction mixture was poured into water and extracted with Et_2O ($3 \times 20 cm^3$). The combined organic layers were dried (Na_2SO_4) and evaporated to leave a yellow solid, which was chromatographed on silica gel column using CH_2Cl_2 -hexane (5:1) as eluent to give bis(4-cyanomethylphenyl) ketone (0.78 g, 31%) as a white solid, mp 122.8 - $124^\circ C$; δ_H 3.87 (4 H, s), 7.49 (4 H, d, J 7.9) and 7.81 (4 H, d, J 7.9); $\nu_{max}(KBr)/cm^{-1}$ 2928w, 2912w, 2256w, 1648s, 1604s, 1408s, 1312m, 1288s, 1178w, 1144w, 1120w, 1016w, 968w, 928m, 848m and 738s.

A mixture of the dinitrile (780 mg, 3.0 mmol) in conc. H_2SO_4 (5 cm^3) and water (7 cm^3) was refluxed for 15 h and then poured into ice-water. The precipitate was filtered off and dissolved in sat. aq. $NaHCO_3$ and the solution was washed with Et_2O and acidified with aq. HCl (2 mol dm^{-3}). The resulting precipitate was filtered off, washed with water and dried *in vacuo* to afford bis(4-carboxymethylphenyl) ketone (0.62 g, 69%), mp 172.3 - $173.9^\circ C$; $\nu_{max}(KBr)$ 2928m, 2640w, 1728m, 1688s, 1640s, 1608m, 1424m, 1408m, 1392m, 1352w, 1280m, 1248m, 928m, 856w, 832w, 752m and 696m.

N,N' -Dicyclohexylcarbodiimide (DCC; 1.8 g, 8.6 mmol, 2.4 equiv.) was added to a cooled mixture of the dicarboxylic acid (1.0 g, 3.6 mmol, 1 equiv.), 2-methylpropan-2-ol (2.0 cm^3 , 24.0 mmol, 6.5 equiv.) and 4-(dimethylamino)pyridine (1.0 g, 8.6 mmol, 2.4 equiv.) in CH_2Cl_2 (20 cm^3) at $0^\circ C$ and the mixture was stirred at room temperature for 5 h. It was then filtered, and

† During the course of this study, we found that essentially similar procedures had been employed for the preparation of fullerenes incorporating a 4-carboxyphenyl moiety, which were converted into fullerene peptides.⁷

the filtrate was washed with aq. HCl (0.5 mol dm⁻³) and sat. aq. NaHCO₃, dried (Na₂SO₄) and evaporated to afford a yellow viscous liquid. The crude product was chromatographed on silica gel column using CH₂Cl₂ to afford bis(4-*tert*-butoxycarbonylmethyl)phenyl ketone (0.81 g, 59%) as a colourless oily liquid (0.81 g, 59%); δ_{H} 1.46 (18 H, s), 3.62 (4 H, s), 7.39 (4 H, d, *J* 8.2) and 7.77 (4 H, d, *J* 8.3); ν_{max} (neat)/cm⁻¹ 2976m, 2928m, 1728s, 1656s, 1608s, 1416w, 1368m, 1272s, 1140s, 928m, 872w, 832w and 760s.

A solution of the diester (750 mg, 1.83 mmol, 1 equiv.), hydrazine monohydrate (3.3 cm³, 68 mmol, 37.2 equiv.) and hydrazine dihydrochloride (1.1 g, 10 mmol, 5.7 equiv.) in ethanol (15 cm³) was refluxed for 2 h. The solution was diluted with Et₂O, poured into water, the aqueous phase was separated and extracted with Et₂O and the combined organic layers were washed with water, dried (Na₂SO₄) and evaporated. The residue was dried *in vacuo* to afford bis(4-*tert*-butoxycarbonylmethyl)phenyl ketone hydrazone (665 mg, 86%) as a white solid, mp 111.5–112.8 °C; δ_{H} 1.42 (9 H, s), 1.47 (9 H, s), 1.47 (9 H, s), 3.50 (2 H, s), 3.61 (2 H, s), 5.79 (2 H, s), 7.16–7.25 (4 H, m) and 7.39–7.44 (4 H, m); ν_{max} (KBr)/cm⁻¹ 3392w, 3280w, 2976w, 2928w, 1728s, 1512w, 1368m, 1344m, 1232m, 1144s, 944w, 972w, 824w, 760w and 712w.

To a cooled solution of the hydrazone (815 mg, 1.92 mmol, 1 equiv.) in Et₂O (20 cm³) at 0 °C, was added nickel(IV) oxide (700 mg, 7.72 mmol, 4 equiv.), and the mixture was stirred at 0 °C for 30 min. The reaction mixture was filtered, and the filtrate was evaporated under reduced pressure to afford bis(4-*tert*-butoxycarbonylmethyl)phenyl diazomethane **1a** (582 mg, 72%) as a red viscous liquid; δ_{H} 1.45 (18 H, s), 3.53 (4 H, s), 7.23 (4 H, d, *J* 8.6) and 7.28 (4 H, d, *J* 8.6); ν_{max} (neat)/cm⁻¹ 2974w, 2912w, 2032s, 1729s, 1510m, 1366m, 1254w and 1139s.

Preparation of 1',1'-bis(4-*tert*-butoxycarbonylmethyl)phenyl)-1,2-methano[60]fullerene **2a**

A solution of C₆₀ (115 mg, 0.16 mmol, 1 equiv.) and the diazomethane **1a** (68 mg, 0.16 mmol, 1 equiv.) in toluene (20 cm³) was stirred under Ar at room temperature for 24 h. The mixture was evaporated and the crude product was chromatographed on a silica gel column using toluene as eluent to afford unchanged C₆₀ (28 mg, 24% recovery) and a mixture of mono-adducts **2a** and **2'a** (78 mg) as a dark brown solid; δ_{H} 1.40 and 1.45 (CH₃), 3.44, 3.56 and 3.58 (3 × s, CH₂), 7.11 and 7.35, 7.38 and 8.03 and 7.37 and 8.05 (3 sets of ArH). A solution of the mixture in toluene (50 cm³) was refluxed for 12 h, to give **2a** (78 mg, 43%, 57% based on consumed C₆₀) as a dark brown solid. Irradiation of the mixture of **2a** and **2'a** (1 mg) in CDCl₃ (0.5 cm³) with a filtered light ($\lambda > 300$ nm) from a 300 W high-pressure Hg lamp for 10 min also resulted in the complete conversion of **2'a** into **2a**; δ_{H} 1.45 (18 H, s), 3.58 (4 H, s), 7.34 (4 H, d, *J* 8.1) and 8.04 (4 H, d, *J* 8.0); δ_{C} 28.01, 42.23, 57.70, 78.97, 81.06, 129.58, 131.03, 134.54, 137.41, 138.11, 140.79, 142.01, 142.21, 142.87, 143.05, 143.78, 144.20, 144.58, 144.65, 145.03, 145.12, 145.33, 148.25 and 170.67; ν_{max} (KBr)/cm⁻¹ 2960w, 2928w, 1728s, 1360m, 1256m, 1136s, 960w, 832w, 552w and 528s.

Preparation of 1',1'-bis(4-carboxymethyl)phenyl)-1,2-methano[60]fullerene **3a**

A solution of the ester **2a** (40 mg, 0.036 mmol, 1 equiv.) and trifluoroacetic acid (5 cm³) in CH₂Cl₂ (20 cm³) was stirred at room temperature for 5 h. The reaction mixture was evaporated and then diluted with water to give a precipitate, which was filtered off, washed with water and acetone and dried *in vacuo* to afford **3a** (32 mg, 88%) as a dark brown solid; δ_{H} (C₅D₅N) 3.92 (4 H, s), 7.74 (4 H, d, *J* 8.2) and 8.41 (4 H, d, *J* 8.2); ν_{max} (KBr)/cm⁻¹ 3440s, 2944m, 2912m, 1712s,

1432m, 1224w, 1184w, 1152w, 1120w, 1024w, 800m, 752m, 552m and 528s.

Preparation of 1',1'-bis(4-methoxyethoxymethoxycarbonylmethyl)phenyl)-1,2-methano[60]fullerene **4a**

A solution of **3a** (15.0 mg, 0.015 mmol, 1 equiv.), MEMCl (4.4 mg, 0.035 mmol, 2.3 equiv.) and di(isopropyl)ethylamine (14.5 mg, 0.035 mmol, 2.3 equiv.) in CH₂Cl₂ (5 cm³) was stirred at 0 °C for 3 h. The reaction mixture was evaporated to afford a crude product, which was separated by TLC using CH₂Cl₂ as eluent to afford **4a** as a brown solid (10.3 mg, 58%); δ_{H} 3.35 (6 H, s), 3.38–3.40 (4 H, m), 3.71–3.76 (8 H, m), 5.36 (4 H, s), 7.42 (4 H, d, *J* 8.25) and 8.06 (4 H, d, *J* 8.25); δ_{C} 41.10, 57.45, 59.06, 69.59, 71.46, 78.90, 89.85, 129.77, 131.14, 133.60, 137.90, 138.15, 140.90, 142.17, 142.24, 142.96, 143.02, 143.84, 144.27, 144.60, 144.67, 144.74, 145.20, 145.21, 145.33, 148.12 and 170.83.

Preparation of bis(4-*tert*-butoxycarbonyl)phenyl)diazomethane **1b**

A mixture of bis(4-bromophenyl) ketone (5.65 g, 20 mmol, 1 equiv.) and CuCN (5.00 g, 60 mmol, 3 equiv.) in DMF (20 cm³) was heated at 140 °C for 24 h. The solution was poured into ice-water to give a precipitate, which was filtered off and dissolved in 50% aq. ethylenediamine. The aqueous solution was extracted with toluene (3 × 30 cm³) and the toluene extracts were washed with 20% aq. NaCN and water, dried (Na₂SO₄) and evaporated to give bis(4-cyanophenyl) ketone (1.62 g, 35%) as a yellow solid, mp 159.2–160.7 °C; δ_{H} 7.82 (4 H, d, *J* 8.2) and 7.87 (4 H, d, *J* 8.2); ν_{max} (KBr)/cm⁻¹ 2912w, 2848w, 2224m, 1654s, 1600m, 1400m, 1312m, 1272s, 1176w, 1136w, 1112w, 1016w, 928m, 768m and 680m. The dicyano compound was converted into the diazomethane **1b** by a similar procedure to that described above for **1a** by way of the following compounds.

Bis(4-carboxyphenyl) ketone. Grey solid (78%), mp 355.7–357.0 °C; ν_{max} (KBr)/cm⁻¹ 3008s, 2672m, 2544m, 1688s, 1648s, 1594s, 1424s, 1264s, 1112m, 1014m, 936s, 872m, 800m and 720s.

Bis(4-*tert*-butoxycarbonyl)phenyl) ketone. White solid (47%), mp 118.5–120.0 °C; δ_{H} 1.63 (18 H, s), 7.81 (4 H, d, *J* 6.9) and 8.10 (4 H, d, *J* 6.9); ν_{max} (KBr)/cm⁻¹ 2976m, 2928w, 1704s, 1656s, 1496w, 1456w, 1392m, 1368m, 1296s, 1256s, 1160s, 1120s, 1016m, 928m, 872w, 848m and 720s.

Bis(4-*tert*-butoxycarbonyl)phenyl) ketone hydrazone. White solid (98%), mp 148.1–149.1 °C; δ_{H} 1.58 (9 H, s), 1.63 (9 H, s), 5.58 (2 H, s), 7.35 (2 H, d, *J* 8.6), 7.46 (2 H, d, *J* 8.6), 7.89 (2 H, d, *J* 8.6) and 8.15 (2 H, d, *J* 8.6); ν_{max} (KBr)/cm⁻¹ 3376s, 3216w, 2976w, 2928w, 1712s, 1608w, 1576w, 1552w, 1448w, 1392w, 1368w, 1296s, 1256m, 1160s, 1120s, 1016w, 944w, 848m, 776w and 712w.

Bis(4-*tert*-butoxycarbonyl)phenyl)diazomethane **1b.** Red solid (93%), mp 108.2–109.5 °C; δ_{H} 1.60 (18 H, s), 7.32 (4 H, d, *J* 8.6), 7.99 (4 H, d, *J* 8.6); ν_{max} (KBr)/cm⁻¹ 2974m, 2928w, 2048s, 1701s, 1596s, 1366m, 1290s, 1253m, 1158s, 1110s, 1028w, 932w, 860w, 845m, 780m and 700w.

Preparation of 1',1'-bis(4-*tert*-butoxycarbonyl)phenyl)-1,2-methano[60]fullerene **2b**

A solution of C₆₀ (115 mg, 0.16 mmol, 1 equiv.) and diazomethane **1a** (63 mg, 0.16 mmol, 1 equiv.) in toluene (120 cm³) was stirred under Ar at room temperature for 24 h after which the mixture was evaporated. The crude product was chromatographed on a silica gel column using toluene as eluent

to afford unchanged C₆₀ (31 mg, 30% recovery) and a mixture of mono-adducts **2b** and **2'b** (78 mg) as a dark brown solid; δ_{H} 1.54, 1.57, 1.60 (3 × s, CH₃), 7.51 and 7.86 (2 × d, ArH). A solution of the mixture in toluene (50 cm³) was refluxed for 12 h to give **2b** (43%, 55% based on consumed C₆₀) as a dark brown solid; δ_{H} 1.59 (18-H, s), 8.10 (4 H, d, *J* 8.5) and 8.17 (4 H, d, *J* 8.5); δ_{C} 28.19, 57.07, 78.26, 81.38, 130.08, 130.83, 132.07, 138.17, 141.03, 142.17, 142.68, 143.00, 143.18, 143.84, 144.58, 144.72, 144.78, 145.21, 145.24, 147.46 and 165.12; $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 2960w, 2928w, 1712s, 1600m, 1360m, 1288s, 1248m, 1160m, 1112m, 1016w, 848w, 760w, 712w, 552w and 528m.

Preparation of 1',1'-bis(4-carboxyphenyl)-1,2-methano[60]-fullerene **3b**

A solution of the ester **2b** (14 mg, 0.013 mmol, 1 equiv.) and trifluoroacetic acid (1 cm³) in CH₂Cl₂ (5 cm³) was stirred at room temperature for 5 h, after which it was evaporated and added to water to give a precipitate. This was filtered off, washed with water and acetone and dried *in vacuo* to afford **3b** as a dark brown solid (11 g, 87%); $\delta_{\text{H}}(\text{C}_5\text{D}_5\text{N})$ 8.50 (8 H, s); $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 3480m, 1688s, 1600m, 1408m, 1264m, 1168m, 1104m, 1016w, 752m, 552m and 528s.

Preparation of 1',1'-bis(4-methoxyethoxymethoxycarbonylphenyl)-1,2-methano[60]fullerene **4b**

A solution of **3b** (13.8 mg, 0.014 mmol, 1 equiv.), MEMCl (4.4 mg, 0.035 mmol, 2.5 equiv.) and di(isopropyl)ethylamine (4.5 mg, 0.035 mmol, 2.5 equiv.) in CH₂Cl₂ (5 cm³) was stirred at 0 °C for 3 h after which it was evaporated to afford a crude product. This was separated by TLC using CH₂Cl₂ as eluent to afford **4b** (9.2 mg, 57%) as a brown solid; δ_{H} 3.39 (6 H, s), 3.58 (4 H, t, *J* 4.6), 3.87–3.91 (4 H, m), 5.60 (4 H, s) and 8.22 (8 H, s); δ_{C} 56.78, 59.12, 69.74, 71.50, 77.97, 90.19, 130.49, 131.12, 138.13, 141.04, 142.12, 142.98, 143.02, 143.39, 143.83, 144.42, 144.53, 144.76, 145.12, 145.19, 145.24, 147.19 and 165.42.

Solubility measurements

An excess of the fullerenes was added to the solvent under study in an equilibration tube that was maintained at a constant temperature of 303 K in a water-bath. The contents of the tube were stirred for a period of 5 h. A sample of the solution phase

was withdrawn, filtered (Millipore Millex-GV, 0.22 μm) and diluted with dioxane after which its absorption spectrum was measured.

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