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Synthesis and characterisation of C_{60} derivatives containing functionalised anthraquinone groups and an unusual fullerene-stabilised cation[1]

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Abstract

The *ortho*-anthraquinonedimethane dienophiles prepared in situ from 1,4-dihydroxy-2,3-bis(bromomethyl)-anthraquinone and 1,4-dimethoxy-2,3-bis(bromomethyl)anthraquinone respectively react with the fullerene C_{60} to give the anthraquinone derivatives: dihydroxy-anthraquinone-C_{60} and dimethoxy-anthraquinone-C_{60}. The former compound with sodium butoxide and 15-crown-5 gives the bis(sodium-15-crown-5)dioxo-anthraquinone-C_{60}. The dimethoxy-anthraquinone-C_{60} reacts with $[Ru(PPh_3)_2(NO)Cl]$ to form the bis-adduct $\{[\eta^2\text{-(dimethoxy-anthraquinone-}C_{60})][Ru(PPh_3)_2(NO)Cl]\}$. The electrochemistry of the dihydroxy- and dimethoxy-anthraquinone-C_{60} derivatives has been studied by cyclic voltammetry and, in contrast to 1,4-dihydroxy-2,3-dimethylanthraquinone, the compound dihydroxy-anthraquinone-C_{60} shows two separate one electron oxidations at lower potentials strongly suggesting a relatively rare example of a fullerene stablised cation. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Fullerenes; Anthraquinone derivatives; Ruthenium complexes; Electrochemistry

1. Introduction

Early studies of the reactions of the fullerene C_{60} showed the molecule behaved as an electron-poor 'superalkene' as indicated by its reactivity towards nucleophilic addition, radical addition, addition across the double bond, formation of exohedral transition metal complexes and cycloadditions [1–7]. The C_{60} molecule is very reactive but its derivatives are normally of low solubility [8–10] in common organic solvents and they often reversibly decompose to the very stable C_{60} [1–7]. Further, the C_{60} molecule has multiple reactive sites and mixtures of regio isomers and polyfunctional compounds are formed which, due to their instability and low solubility, are very difficult to separate and purify [11–13].

The electron withdrawing nature of the closed cage alkene C_{60} makes it an excellent dienophile for Diels–Alder [4 + 2] cycloaddition [1–7]. The [4 + 2] cycloaddition involves exclusive addition to the 6–6 bond [14–21]. However, many Diels–Alder C_{60}-adducts are often unstable and undergo retro-Diels–Alder reactions and hence are unsuitable for further reactions [14–21]. However, more stable, non-labile Diels–Alder C_{60}-adducts are formed when the adduct formation is accompanied by stabilisation energy gained by aromatisation. For example, stable C_{60} adducts are formed by *iso*-benzofurans [19] and *ortho*-quinodimethanes [20,21].

The objective of the work described below was to prepare relatively stable C_{60}-monoadducts, which could be used for further chemical reactions, for example to link C_{60} in a simple way through bridging groups with

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[1] Dedicated to Professor Bruce King on the occasion of his 65th birthday.

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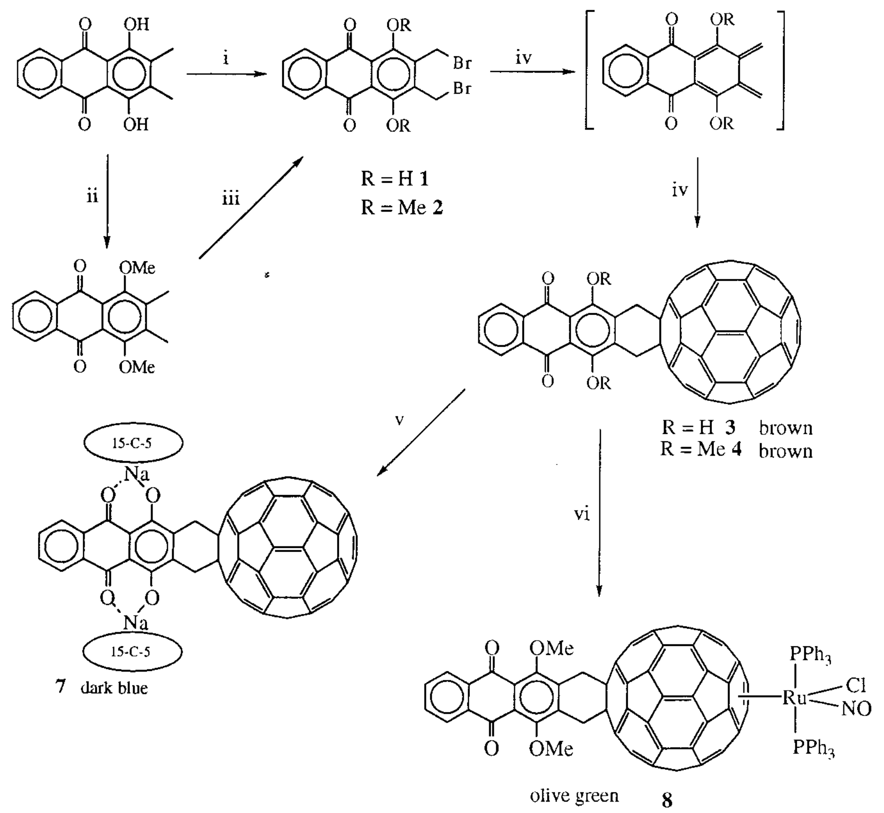


Scheme 1. (i) Br_2 in C_2Cl_4, $PhCO_3H$, then irradiated with an IR lamp, 77%. (ii) K_2CO_3 in DMF and 2-butanone, add methyltosylate, 75%. (iii) 1,3-Dibromo-5,5-dimethylhydantoine and $PhCO_3H$ in CCl_4, 91%. (iv) C_{60}, 18-crown-6, and potassium iodide in toluene, reflux. R = H, 83%; R = Me, 89%. (v) **3** in toluene, add $NaOBu^t$ in THF with 15-crown-5 at r.t., 97%. (vi) **4** in benzene, add $[Ru(PPh_3)_2(NO)Cl]$ at r.t., 75%.

chromophoric, electrophoric, or ionophoric fragments. We identified the two functionalised anthraquinone dibromides 1,4-dihydroxy-2,3-bis(bromomethyl)-anthraquinone (**1**) and 1,4-dimethoxy-2,3-bis(bromomethyl)anthraquinone (**2**) as the precursors to unstable *ortho*-anthraquinonedimethanes dieneophiles which were likely to give stable functionalised C_{60} compounds. The synthesis and properties of new anthaquinone-C_{60} derivatives are described below. A communication of part of this work has appeared [22].

2. Results and discussion

The compounds **1** and **2** were prepared using substantially modified literature procedures [23,24] which are described in the Section 3 and Scheme 1. The published method to generate *ortho*-quinodimethanes is the iodide-induced 1,4-elimination at 1,2-bis(bromomethyl)-arene derivatives, which is usually performed in dimethylformamide (DMF) [25,26]. However, since C_{60} is almost insoluble in DMF, the synthesis was made in toluene using a suitable crown ether as phase transfer catalyst for the iodide salt. The analytical and spectroscopic data characterising **2**, and all the other new compounds described below, are given in the Table 1.

The new functionalised C_{60}-adducts, namely, dihydroxy-anthraquinone-C_{60} (**3**) and dimethoxy-anthraquinone-C_{60} (**4**) were prepared by adding a toluene solution of red 1,4-dihydroxy-2,3-bis(bromomethyl) anthraquinone **1** and yellow 1,4-dimethoxy-2,3-bis(bromomethyl)anthraquinone **2**, respectively, to a refluxing purple solution of C_{60}, 18-crown-6 and potassium iodide. After a period of heating, addition of acetone/water gave brown precipitates of **3** and **4** in excellent yields. Analytical and spectroscopic data showed no evidence for the formation of di-adducts. The solubility of dihydroxy-anthraquinone-C_{60} **3** is comparable to that of C_{60} and dimethoxy-anthraquinone-C_{60} **4** is significantly more soluble (ca. 17 mg in 5 ml benzene as compared with ca. 6 mg in 5 ml benzene).

The $^{13}C\{^1H\}$-NMR spectrum of **3** (Fig. 1) and **4** (Fig. 2) both showed the expected 17 fullerene signals consistent with the molecule having C_{2v} symmetry, as well as additional resonances for the sidechains. At 25°C the ^1H-NMR spectrum of **3** showed a broad singlet at 4.68 ppm due to the methylene protons (H_a, H_e), multiplets at 8.16 and 7.46 ppm due to the aromatic protons and a singlet at 13.42 ppm due to the two hydroxyl protons.

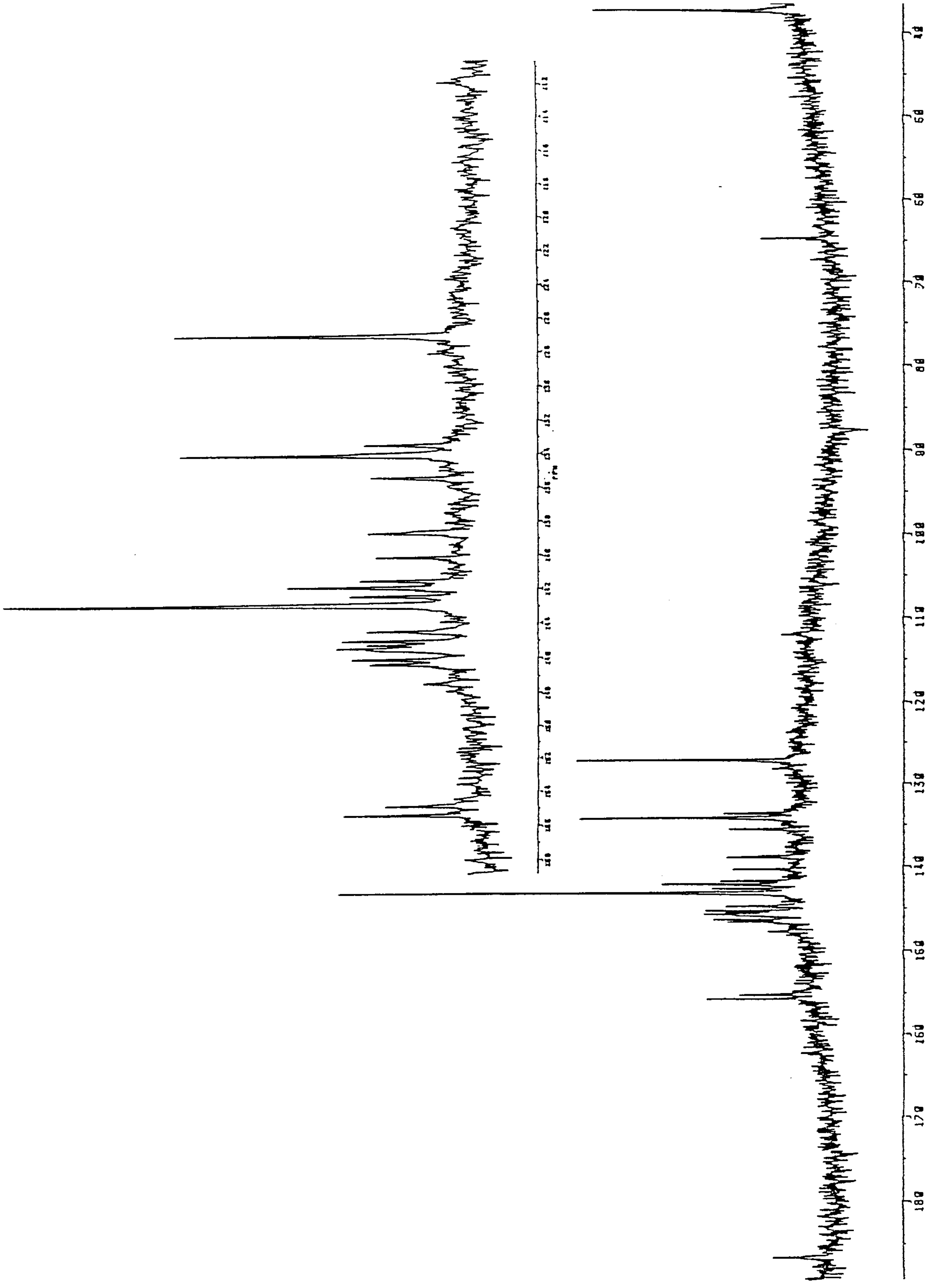


Fig. 1. ^{13}C-NMR (75.4 MHz) of dihydroxy-anthraquinone-C_{60} in $CS_2 + D_2O$ (external).

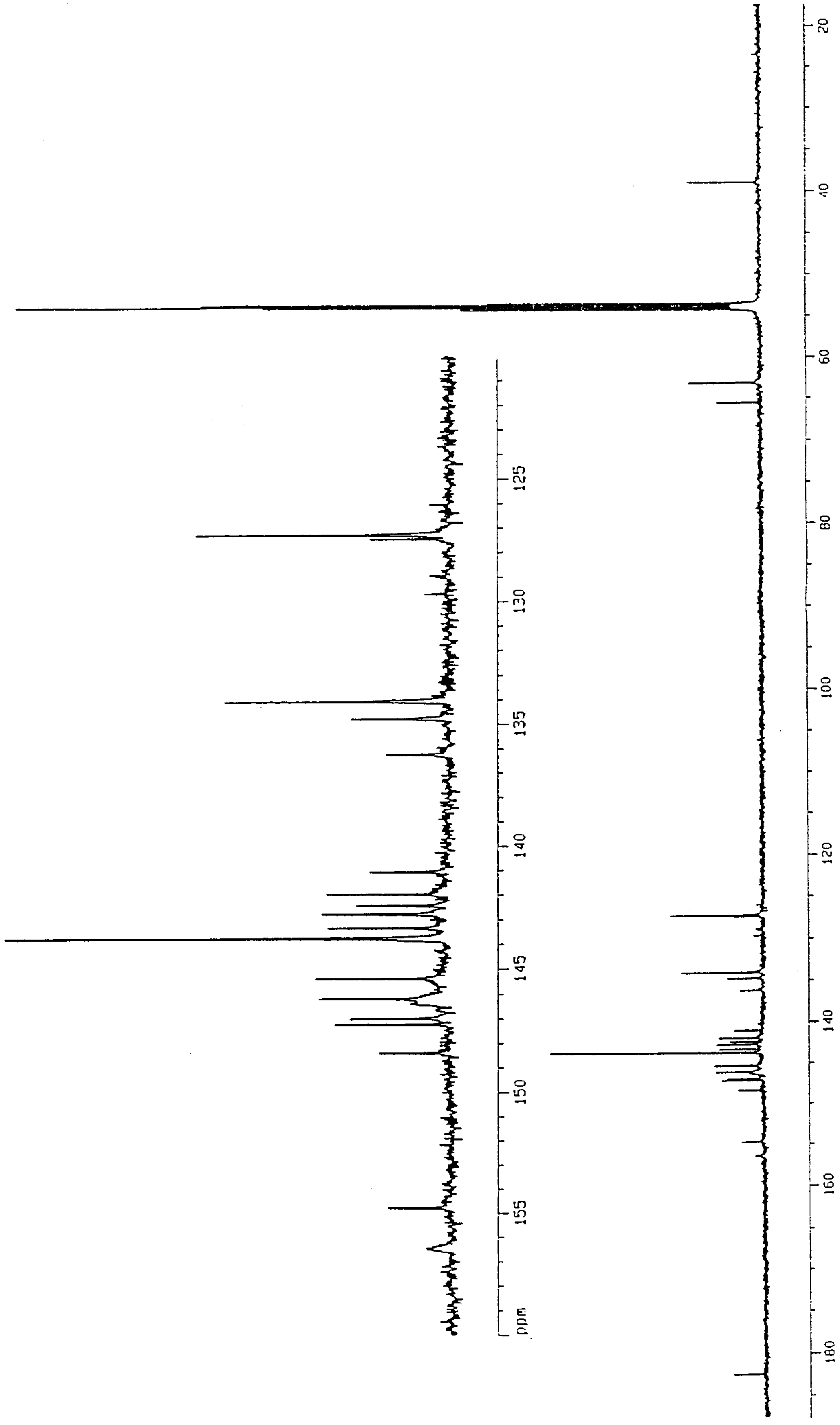


Fig. 2. ^{13}C-NMR (125 MHz) of dimethoxy-anthraquinone-C_{60} in $CS_2 + CD_2Cl_2$ (internal).

Table 1
Analytical and spectroscopic data[a]

Compound	Spectroscopic data
3	
C 92.2 (92.5), H: 1.0 (1.0). MS (FAB, NOBA matrix, toluene): expected [M$^+$ ion not found, only [C$_{60}$]$^+$. m.p.: >310°C (dec.)	^{1}H[b] 4.68 (s, br, C*H*$_2$); 7.46, 8.16 (m, arom. *H*, AA′BB′); 13.42 (s, O*H*). (CS$_2$ + C$_6$D$_5$CD$_3$, −38°C): 4.02 (d, $^{2}J = 14.5$, C*H*$_2$); 4.98 (d, ^{2}J = 14.5, C*H*$_2$); 7.43, 8.11 (m, arom. *H*, AA′BB′); 13.48 (s, O*H*). ^{13}C[c]: 37 (s, *C*H$_2$); 65 (s, sp^3 carbons C$_{60}$); 110–155 (s, 16 C$_{60}$ and 6 arene side chain signals); 186 (s, *C*O). IR[a]: 3450 (vw, $\nu_{(OH)}$), 1622 (m, $\nu_{(C=O)}$), 1585 (m), 1417 (s), 1339 (s), 1266 (s), 1183 (w), 810 (w), 775 (m), 732 (m), 723 (m), 578 (vw), 528 (s). UV–vis (CH$_2$Cl$_2$, nm): 229, 257, 328, 407, 437 (sh), 473, 489, 523 (sh).
4	
C 91.8 (92.3), H 1.6 (1.4), m.p.: >300°C (dec.). MS (FAB, NOBA matrix, toluene): 1014 (4.5%, [M]$^+$); 720 (58%, [C$_{60}$]$^+$); 292 (100%, [M-C$_{60}$H$_2$]$^+$).	^{1}H[b]: 4.33 (s, OC*H*$_3$); 4.61, 5.43 (s, br, C*H*$_2$); 8.08–8.10, 8.48–8.52 (m, arom. *H*, AA′BB′). (C$_6$D$_5$CD$_3$, −15°C): 4.00 (s, OC*H*$_3$); 3.91 (d, $^{2}J = 14.2$, C*H*$_2$); 4.93 (d, $^{2}J = 14.2$, C*H*$_2$); 7.09–7.11, 8.16–8.19 (m, arom. *H*, AA′BB′). (C$_6$D$_5$CD$_3$, 92°C): 3.99 (s, OC*H*$_3$); 4.52 (s, br, C*H*$_2$); 7.21–7.24, 8.12–8.15 (m, arom. *H*, AA′BB′). ^{13}C[d]: 39 (s, *C*H$_2$); 63 (s, O*C*H$_3$); 66 (s, sp^3 carbons C$_{60}$); 110–160 (s, 20 peaks for C$_{60}$ and arene side chain signals); 183 (s, *C*O). IR[a]: 1672 (vs, $\nu_{(C=O)}$), 1594 (m), 1567 (m),1317 (s), 1313 (s), 1255 (vs), 1083 (m), 1115 (w), 1061 (w), 1040 (m), 988 (m), 970 (vw), 952 (w), 800 (vw), 768 (w), 744 (m), 724 (m), 578 (m), 528 (vs). UV–vis (CH$_2$Cl$_2$, nm): 232, 255, 328, 431.
7	
C 80.6 (78.4), H 2.6 (3.3), Na 2.3 (3.1) MS (FAB, NOBA matrix, THF): expected [M]$^+$ ion not found, only 986 [M-2(Na-15C5)]$^+$ and 721 [C$_{60}$H]$^+$.	^{1}H[e]: 3.64 (s, OC*H*$_2$); 4.88, 5.20 (s, br, C*H*$_2$); 7.62, 8.39 (m, arom. *H*, AA′BB′). IR[a]: 1628 (vw), 1602 (w), 1580 (s), 1351 (s), 1299 (s), 1247 (m), 1119 (s), 950 (m), 860 (vw), 769 (w), 738 (m), 676 (vw), 578 (vw), 528 (s). UV–vis (THF, nm): 257, 288 (sh), 327, 404, 435, 489, 525, 573, 616.
8	
C 80.6 (80.3), H 2.6 (2.6), Cl 2.0 (2.1), N 0.7 (0.8)	^{1}H[f]: 3.98 (s, OC*H*$_3$); 3.54, 4.92 (s, br, C*H*$_2$); 7.12 (m, P(C$_6$*H*$_5$)$_3$); 7.63–7.82, 8.11–8.18 (m, arom. *H*, AA′BB′). ^{31}P-NMR (81 MHz, toluene-D$_8$, 25°C): 25.0 (s, br) IR[a]: 1785 (m, $\nu_{(NO)}$), 1756 (w, sh), 1672 (s, $\nu_{(C=O)}$), 1593 (w), 1568 (w), 1316 (s), 1255 (s), 1186 (vw), 1159 (vw), 1093 (w) 1040 (w), 988 (w), 970 (vw), 952 (vw), 768 (vw), 7.42 (s), 723 (s), 693 (m), 579 (vw), 527 (s), 521 (s).

[a] Analytical data given as found (calc.)%. NMR data given as: chemical shift (ppm) [multiplicity (*J* in Hz), assignment]. Infrared data, in Nujol mull, cm^{-1}.

[b] 300 MHz, CS$_2$ + C$_6$D$_5$CD$_3$, 25°C.

[c] 75.4 MHz, CS$_2$ (D$_2$O, external), 25°C.

[d] 125 MHz, CS$_2$ + CD$_2$Cl$_2$, 25°C.

[e] In THF-d$_8$, 50°C.

[f] 250 MHz, toluene-D$_8$, 25°C.

The broad singlet for the methylene protons H$_a$, H$_e$ suggested a low conformational inversion barrier on the ^{1}H-NMR time scale (Fig. 3). Indeed, variable temperature experiments showed the two signals for H$_a$ and H$_e$ coalesced at ca. 6°C and on cooling to −40°C resolved into two doublets at 4.98 and 4.02 ppm with a geminal coupling constant of 14.5 Hz (Fig. 3). At r.t., the ^{1}H-NMR spectrum of dimethoxy-anthraquinone-C$_{60}$ **4** showed two separate peaks for the methylene protons (H$_a$, H$_e$) at 4.93 and 3.91 ppm which resolved on cooling to −15°C into two doublets with a geminal coupling constant of 14.2 Hz. On heating the NMR sample, the coalesce temperature occurred at ca. 50°C and on heating to 90°C, the methylene protons showed a broad singlet at 4.52 ppm.

The UV–vis spectra (CH$_2$Cl$_2$) of dihydroxy-anthraquinone-C$_{60}$ **3** and dimethoxy-anthraquinone-C$_{60}$ **4** all exhibit typical peaks assignable to the fullerene moiety at ca. 220, 255 and 330 nm. In addition, there is a broad absorption at 450–600 nm which exhibits different fine structure for the adducts.

Cyclic voltammetry investigations were undertaken on **3** and **4** as well as the related analogues **5** and **6** shown in Scheme 2. The experiments were conducted in dichloromethane solvent containing 0.1 M tetrabutylammonium perchlorate as the supporting electrolyte using platinum electrodes in the form of either microdisc electrodes (of radius ca. 30 μm) or flag electrodes of traditional dimensions (3 mm).

Dihydroxy-anthraquinone-C$_{60}$ **3** was found to show two separate one electron oxidations at potentials of +0.49 and +0.82 V (vs SCE), respectively. However, the related analogue **5** showed a single two electron oxidation wave with a halfwave potential of +1.51 V (vs SCE). This may be attributed to the reaction shown in Scheme 2. The cyclic voltammetry studies confirmed the production of H$^+$. Tafel analysis showed the oxidation to be electrochemically irreversible (Tafel slope 120 mV per decade). The contrast in the oxidation behaviour with **3** is intriguing. The significant decrease in

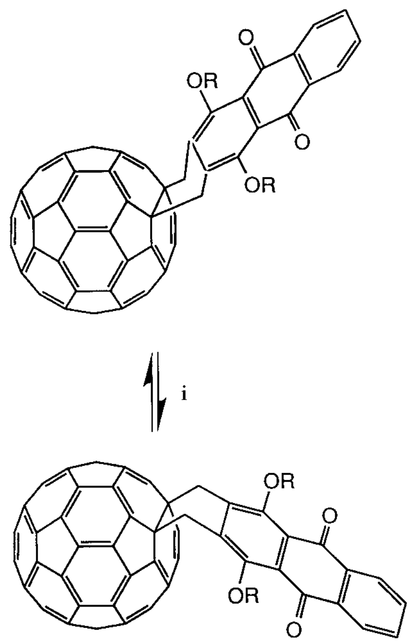


Fig. 3. The two possible boat conformers of the anthraquinone-C_{60} derivatives with their coalescence temperature (T_c). (i) R = H. T_c = 6°C; R = Me. T_c = 50°C.

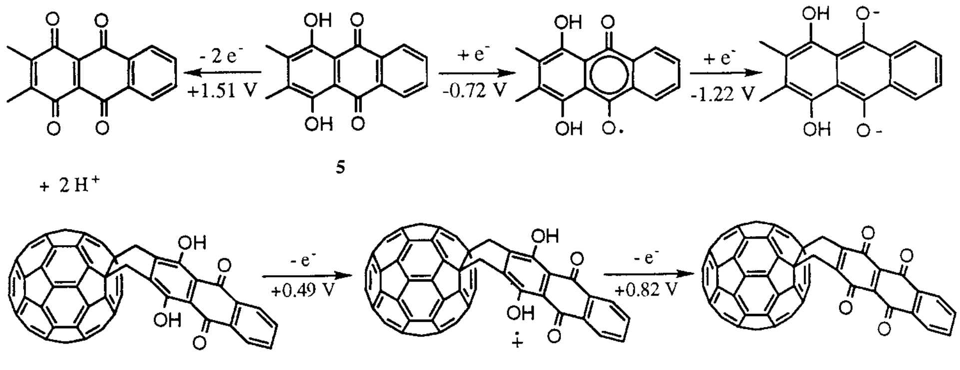
the potentials suggests there is an appreciable stabilisation of the intermediate radical cation and the product quinonoid forms, presumably due to a through-space overlap of molecular orbitals of the C_{60} unit with those on the aromatic ligand. Under cathodic conditions two reversible one-electron waves were seen at potentials of − 0.72 and − 1.22 V (vs SCE), respectively.

The dimethoxy analogues were also investigated. Compound **4** displayed reduction peaks which are a superposition of 1,4-dimethoxy-2,3-dimethylanthraquinone (**6**) and pure C_{60}. These show a one electron reduction with a halfwave potential at − 1.05 V (vs SCE) and at − 0.49, − 0.88 and − 1.33 V (vs SCE), respectively. That the reduction potential of the anthraquinone unit is essentially unchanged between the ligand and the C_{60} adduct may arise if the methyl groups cause a greater distance between the 9, 10 positions in the anthraquinone unit and the C_{60} fragment. In consequence, there would be a reduced through-space electronic interactions. Neither compounds **4** nor **6** display any oxidative voltammetry.

The compounds **3** and **4** could not be chromatographed on silica gel or silylated silica gel and chromatography on alumina led to an irreversible formation of a bright red material. However, dimethoxy-anthraquinone-C_{60} **4** could be converted quantitatively into dihydroxy-anthraquinone-C_{60} **3** by ether cleavage using BBr_3 in *o*-dichlorobenzene.

Treatment of dihydroxy-anthraquinone-C_{60} **5** with two equivalents of sodium *tert*-butoxide in toluene gave a insoluble dark blue precipitate presumed to be bis(-sodium)dioxo-anthraquinone-C_{60},which is sparingly soluble in THF. Addition of 15-crown-5 increased the solubility and the dark blue compound bis(sodium-15-crown-5)dioxo-anthraquinone-C_{60} **7** could be precipitated by addition of pentane. The ^{1}H-NMR spectrum of **7** at 50°C showed bands assignable to the methylene protons at 5.20 and 4.88 ppm which indicated that the conformational inversion does not occur below this temperature. No reaction was observed between **3** and an excess of 1,8-bis(dimethylamino)naphthalene ('proton sponge').

It has been previously shown that C_{60} reacts with $[Ru(PPh_3)_2(NO)Cl]$ to give the crystalline adduct $\{(\eta^2\text{-}C_{60})[Ru(PPh_3)_2(NO)Cl]\}$ [27] and attempts were made to prepare analogues with **4**. $[Ru(PPh_3)_2(NO)Cl]$ was found to react with **4** in benzene to give olive green $\{[\eta^2\text{-(dimethoxy-anthraquinone-}C_{60})][Ru(PPh_3)_2(NO)Cl]\}$**8** which was moderately soluble in aromatic solvents. The spectroscopic properties of **8** were very similar to those of **4** and $\{(\eta^2\text{-}C_{60})[Ru(PPh_3)_2(NO)Cl]\}$. Thus the ^{1}H-NMR spectrum of **8** showed broad singlets for the methylene protons (H_a, H_e) at 3.54 and 4.92 ppm, a singlet at 3.98 ppm due to the methoxy protons, a multiplet at 7.12 ppm due to the PPh_3 protons and multiplets between 7.63–7.83 and



Scheme 2. Electrochemical processes for **3** and **5**.

8.11–8.18 ppm. The $^{31}P\{^1H\}$-NMR spectrum showed a broad band at 25.0 ppm due to the PPh_3 groups in the mixed substituted C_{60} compound. The IR spectrum of **6** showed a broad peak at 1785 cm^{-1} assignable to $\nu_{(NO)}$ which is at exactly the same frequency as that for for $\{(\eta^2\text{-}C_{60})[Ru(PPh_3)_2(NO)Cl]\}$. The relative positions of attachment of the anthraquinone and ruthenium moieties on the fullerene cage could not be ascertained as low solubility prevented successful acquisition of ^{13}C-NMR data or crystal growth.

3. Experimental

3.1. General

All operations were carried out under an atmosphere of dinitrogen using standard Schlenk-line techniques or in a dinitrogen glove box. Solvents were dried and freshly distilled before use. All solvents were thoroughly degassed by repeated evacuation and re-admission of the inert gas on the Schlenk-line.

NMR spectra were recorded either on a Bruker AM 300, Bruker AC 250 or a Bruker AMX 500 spectrometer. Spectra were referenced internally using the residual protio solvent relative to tetramethylsilane ($\delta = 0$ ppm). All chemical shifts are quoted in ppm and coupling constants are in Hz. Infrared spectra were recorded on a Perkin-Elmer 1510 F.T. Interferometer in the range 4000–400 cm^{-1}. All samples were prepared as Nujol mulls between KBr plates. FAB-Mass spectra were recorded in the EPSRC Mass Spectrometry Service Centre, University of Wales, Swansea. UV–vis spectra were recorded on a Lambda 6 Perkin Elmer spectrometer in 1 cm quartz cells. Melting points were recorded on a Gallenkamp melting point apparatus and are uncorrected. Elemental analyses were performed by the Microanalytical Department of Inorganic Chemistry Laboratory, University Oxford. The fullerene C_{60} was synthesised using the arc evaporation of graphite in a dynamic atmosphere of helium ca. 150 mmHg using variable power supply at ca. 40 V/200 A DC).Separation of the C_{60} and the higher fullerenes from the amorphous carbon matrix (soot) generated during evaporation (ca. 15 g) was achieved by column chromatography of the soot with hexane using an adapted Soxhlet method. After evaporation of the solvent of the hexane-C_{60}, was extracted with CS_2, filtered and evaporated to dryness. The black C_{60} was sonicated five times in ca. 25 ml pentane, filtered and dried in high vacuo (10^{-4}–10^{-5} Torr) at 200°C for 48 h. The yield of C_{60} was typically 2–4% and a typical experiment gave ca. 100–150 mg. For all reactions the isolated C_{60} or its derivatives were dissolved overnight in the chosen solvent and the solution was filtered (typically there was ca. 5% insoluble material).

The compounds $[Ru(PPh_3)_2(NO)Cl]$ [28–31] 1,4-dihydroxy-2,3-dimethylanthraquinone [23,24] and 1,4-dimethoxy-2,3-dimethylanthraquinone [23,24] were prepared as described. The published procedures [23,24] for **1** and **2** have been modified.

*3.2. Synthesis of 1,4-dihydroxy-2,3-bis(bromomethyl) anthraquinone **1***

A solution of bromine (2.00 ml, 38.82 mmol) in tetrachloroethylene (15 ml) was added dropwise to a hot solution (110°C) of 1,4-dihydroxy-2,3-dimethylanthraquinone (2.50 g, 9.32 mmol) in tetrachloroethylene (120 ml) containing benzoyl peroxide (100 mg) under irradiation with an IR lamp. Irradiation and heating were continued for 36 h, at the end of which, upon cooling, the dibromide was separated as dark red crystals. These were extracted with cold chloroform (in total 1.5 l). The volume of the extract was reduced and cooled to − 80°C to give 1,4-dihydroxy-2,3-bis(bromomethyl)anthraquinone as dark red crystals. Yield, 3.06 g (77%).

*3.3. Synthesis of 1,4-dimethoxy-2,3-bis(bromomethyl) anthraquinone **2***

A suspension of 1,4-dimethoxy-2,3-dimethylanthraquinone (2.00 g, 6.75 mmol), 1,3-dibromo-5,5-dimethylhydantoine (2.00 g, 7.00 mmol) and benzoyl peroxide (100 mg) in carbontetrachloride (100 ml) was refluxed under irradiation, using an IR lamp, for 12 h. After the mixture cooled, the succinimide was filtered off, and the solvent was removed from the yellow solution under reduced pressure. The yellow residue was extracted with carbontetrachloride (10 × 10 ml) to separate the succinimide. Evaporation of solvent from the extract and crystallisation of the resulting yellow residue from CH_2Cl_2 (50 ml) and pentane (150 ml) at − 80°C gave bright yellow needles. Yield, 2.79 g (91%).

*3.4. Synthesis of dihydroxy-anthraquinone-C_{60} **3***

A purple toluene solution of C_{60} (500 mg, 0.695 mmol), 18-crown-6 (1.84 g, 6.95 mmol) and potassium iodide (254 mg, 1.53 mmol) under reflux was treated very slowly with a red toluene solution of 1,4-dihydroxy-2,3-bis(bromomethyl)-anthraquinone (326 mg, 0.765 mmol). The resulting brown reaction mixture was refluxed for 8 h, the volume of the solution reduced in vacuo (to ca. 150 ml) and the product was precipitated by addition of 500 ml of an acetone-water mixture (20:1). The resulting brown precipitate was washed with acetone (3 × 500 ml), then pentane (2 × 100 ml) and dried in vacuo. Yield, 569 mg (83%). The compound is soluble in CS_2, toluene and benzene, sparingly soluble in CH_2Cl_2 and insoluble in polar solvents.

3.5. Synthesis of dimethoxy-anthraquinone-C_{60} **4**

A purple solution of C_{60} (235 mg, 0.326 mmol), anhydrous potassium iodide (117 mg, 0.705 mmol) and 18-crown-6 (860 mg, 3.26 mmol) in toluene (200 ml) under reflux was treated in a dropwise manner with a yellow toluene solution (50 ml) of 1,4-dimethoxy-2,3-bis(bromomethyl)anthraquinone (160 mg). The resulting dark brown reaction mixture was refluxed for 12 h. The solvent was concentrated to 50 ml giving a colourless precipitate. This was filtered off and addition of acetone (250 ml) to the filtrate gave a brown precipitate. This was washed with acetone (5 × 250 ml), then with pentane (3 × 100 ml) and dried in vacuo. Yield, 295 mg (89%). The compound is soluble in CS_2, *o*-dichlorobenzene, toluene and benzene, and moderately soluble in CH_2Cl_2 and insoluble in THF, ether, acetone and water. Compared with dihydroxy-anthraquinone-C_{60} the solubility is much greater, in aromatic solvents, CS_2 and CH_2Cl_2.

3.6. Synthesis of bis(sodium-15-crown-5)dioxo-anthraquinone-C_{60} **7**

A reddish brown solution of dihydroxy-anthraquinone-C_{60} (100 mg, 0.101 mmol) in toluene (250 ml) was treated with a THF solution (50 ml) of sodium *tert*-butoxide (20 mg, 0.208 mmol) and 0.1 ml (0.5 mmol) of 15-crown-5 at r.t. and the mixture was stirred overnight. During the addition, the colour of the reaction mixture changed from reddish brown over deep red to dark blue. The solvent was evaporated in vacuo, the dark blue residue was extracted with ca. 300 ml THF. The extract was filtered and the filtrate was concentrated under reduced pressure. Addition of pentane (200 ml) precipitated the dark blue product. This was washed with pentane (3 × 100ml) and dried in vacuo. Yield, 144 mg (97%). The compound is slightly soluble in THF, very sparingly soluble in acetonitrile and insoluble in aromatic solvents, CS_2, CH_2Cl_2 and pentane.

3.7. Reaction of dimethoxy-anthraquinone-C_{60} with bis(triphenylphosphine)nitrosylchlororuthenium **8**

To a dark brown benzene solution (75 ml) of dimethoxy-anthraquinone-C_{60} (85 mg, 0.084 mmol) was added dropwise at r.t. a green benzene solution (20 ml) of bis(triphenylphosphine) ruthenium nitrosyl chloride (58 mg, 0.084 mmol). The resulting black olive green solution was stirred for 48 h at r.t. The reaction mixture was then reduced in volume and pentane was added giving an olive green precipitate. This was washed with pentane and dried in vacuo. Yield, 108 mg (75%). The compound is fairly soluble in aromatic solvents.

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