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Tandem addition reactions of dialkoxyanthracenes with C_{60}. Thermal *vs.* electrochemical stability of Diels–Alder adducts

Maria Ángeles Herranz and Luis Echegoyen*

Department of Chemistry, Clemson University, Clemson, SC 29634, U.S.A.
E-mail: luis@clemson.edu; Fax: +1 (864) 656-6613; Tel: +1 (864) 656-0778

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In order to improve the ability to follow the events occurring in retro-cyclopropanation reactions, new methanofullerenes that incorporate fluorescent anthracene malonates were prepared using the Bingel cyclopropanation reaction. Since anthracene groups undergo thermal [4 + 2] cycloadditions with the [6,6] bonds of C_{60}, the formation of the corresponding side products, along with the Bingel adducts, was confirmed by ^{1}H NMR, HPLC, and cyclic voltammetric studies. When the anthracene malonates were reacted with C_{60} following a Diels–Alder protocol, the corresponding monoadducts were obtained. The mono-Diels–Alder derivative **5** was investigated under controlled potential electrolysis conditions and does not exhibit decomposition when approximately two electrons per C_{60} derivative were transferred. In contrast, upon heating to temperatures of 50 to 90 °C the monoadducts **5** and **6** decomposed to [60]fullerene and the corresponding anthracenes.

Introduction

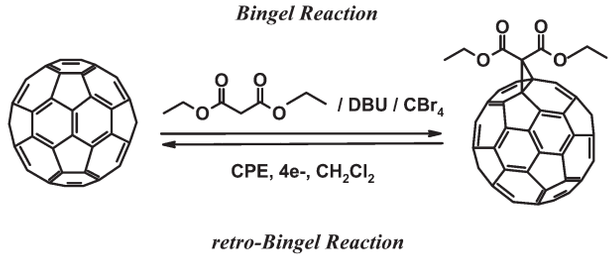
Of the many derivatization reactions involving C_{60}, the so-called Bingel–Hirsch reaction is one of the most commonly employed for the preparation of fullerene derivatives (Scheme 1).[1] The retro-cyclopropanation reaction, formally considered the reverse of a Bingel reaction, leads to the removal of cyclopropane addends under reductive conditions, either chemically[2–4] or electrochemically.[5–15] This process, initially called the retro-Bingel reaction, was discovered during controlled potential electrolysis (CPE) at the second reduction potential of diethyl-1,2-methano[60]fullerene-61,61-dicarboxylate (see Scheme 1)[5] and since then has been the object of intense investigation in our research group.[2,4–8,11–15] The electrochemical retro-cyclopropanation reaction has been applied to a large number of Bingel derivatives of C_{60}, C_{70}, C_{78} and C_{84},[5–8,11–13] spiromethanofullerenes[14,15] and other methanofullerenes.[16]

A major application of the cyclopropanation–retro-cyclopropanation strategy is the preparation of pure constitutional isomers of higher fullerenes, such as C_{2v}–C_{78}[6] and a new C_{84} isomer,[12] as well as enantiomerically pure chiral higher fullerenes such as ^{f}C– and ^{f}A–C_{76}[5] and ^{f}C– and ^{f}A–C_{84}.[12]

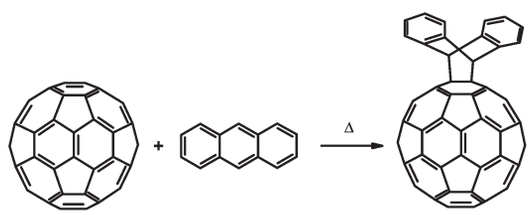
During the course of our investigations of these electrochemically induced retro-cyclopropanation reactions, we also discovered an isomerization reaction, the "walk-on-the-sphere" rearrangement.[7] Additionally, bisadducts with isomeric distributions different from that obtained *via* a synthetic route were isolated from the CPE of spiromethanofullerene monoadducts.[14]

We have recently proven how singly bonded dimers are formed as intermediates during retro-cyclopropanation reactions[16] and digital simulations have supplied detailed information about the mechanisms involved in these processes.[17] However, the fate of the organic addend was never the object of a detailed investigation until we decided to track the products obtained from retro-cyclopropanation reactions using highly fluorescent polycyclic aromatic compounds, such as pyrene and anthracene malonate derivatives. When pyrene malonates were added to C_{60} under Bingel conditions, product analyses of the electrolysis crude showed, for the first time, the presence of the malonate addends along with C_{60} after retro-cyclopropanation. These results have been discussed in a recent publication.[18]

Anthracene derivatives are known to undergo [4 + 2] cycloadditions with the [6,6] bonds of C_{60}.[19–21] Indeed, the reaction of [60]fullerene with anthracene to give a 1:1 addition product has been reported several times (Scheme 2).[22–25] The monoaddition product is unstable and rapidly undergoes a retro-Diels–Alder reaction to afford the starting materials. This easy removal of the anthracene addend has been used for the reversible template-directed activation of equatorial double bonds on the fullerene skeleton.[26,27] A solid state, topochemically controlled regioselective bisfunctionalization of C_{60} with anthracene was reported by Kräutler *et al.*[28] This unique



Scheme 1



Scheme 2

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and elegant approach resulted exclusively in the *trans*-1 regioisomer, in very high yield.

In a recent report, Hirsch and coworkers described the preparation of several T_h symmetrical hexakisadducts of C_{60} bearing up to six 9,10-dialkoxyanthracene moieties *via* the Bingel reaction.[29] Under their reaction conditions, no apparent formation of [4 + 2] cycloaddition products between C_{60} and anthracene was detected. Indeed, significant differences in the reactivity between similarly substituted anthracenes have been found in other reports and are well-correlated with the ionization potentials.[30]

Here we report the synthesis of new methanofullerenes that incorporate anthracene malonate moieties. These structures were designed with the goal of performing further detailed product analysis after cyclopropanation–retro-cyclopropanation reactions for mechanistic insight. Several interesting observations were derived from the regioisomeric mixtures obtained from the Bingel reaction between anthracene malonates and C_{60}. Additionally, new Diels–Alder derivatives were synthesized and their thermal and electrochemical stabilities investigated under CV conditions. All of these results are summarized in the present work.

Results and discussion

Synthesis of Bingel adducts

Prior to performing the Bingel reaction, the malonates **1** and **2**[31] were obtained by the coupling of 9-anthracenemethanol with ethoxycarbonyl acetyl chloride or malonyl chloride, respectively (Scheme 3). These reactions were carried out using dilute solutions of the starting materials in methylene dichloride. The two malonates (**1** and **2**) were formed in 27% and 36% yields, respectively. Isolation was achieved by flash chromatography using a hexane–ethyl acetate (8:1) mixture as eluent and the compounds were completely characterized (see Experimental for details).

The corresponding cyclopropanation reactions were carried out under Bingel conditions, reacting **1** or **2** with C_{60} in the presence of CBr_4 or I_2 and DBU (diazabicyclo[4.2.0]undec-7-ene). The reactions progressed very rapidly and after 15 min, the formation of the expected derivatives was clearly completed. After purification by flash chromatography, using carbon disulfide (CS_2) initially to elute unreacted C_{60}, followed by chloroform, **3** and **4** were obtained in a 40% and 52% yield, respectively. The compounds appeared to be pure using TLC as a criterion, but ^{1}H NMR revealed the presence of multiple reaction products. Besides the disappearance of the methylenic protons at 3.42–3.45 ppm, indicative of the formation of the cyclopropane ring, two bridge hydrogens (5.60 and 5.99 ppm) and two different sets of protons, corresponding to the ethylenic fragment of malonate **1**, were observed in the ^{1}H NMR spectra of **3**. The situation was even more complicated for compound **4** and according to the ^{1}H NMR spectrum, at least three additional products, along with the Bingel derivative, were detected.

The formation of the methanofullerenes **3** and **4** was attempted several times with different dilution and temperature conditions, in the presence or absence of light, and with different bases. The results obtained were very similar to the ones initially observed. Although Bingel derivatives were obtained pure after column chromatography (according to TLC), additional Diels–Alder reactions between the anthracenes and C_{60} seem to occur even in the solid state and in the absence of light.

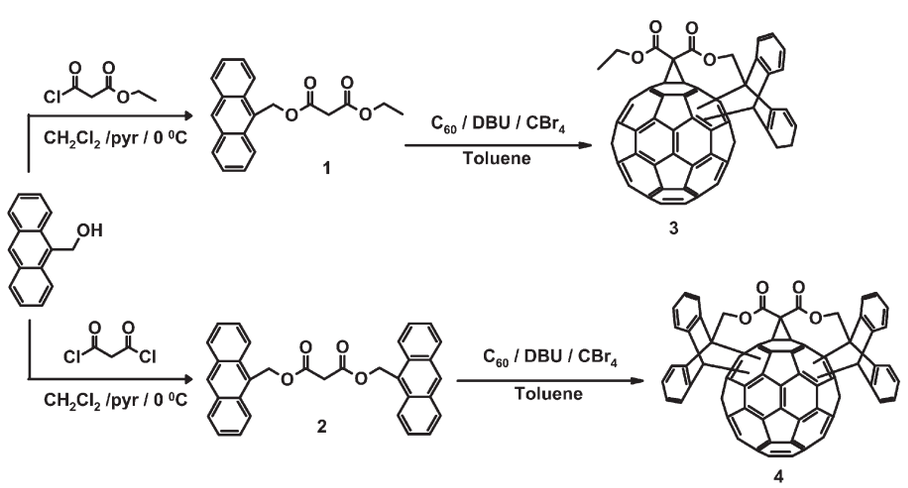
The HPLC chromatograms obtained for the regioisomeric mixtures of **3** and **4** are shown in Fig. 1, along with the HPLC for C_{60} under the same conditions. In the case of **3**, the different isomers have similar polarities and **3** shows a very broad peak when compared to C_{60}. The HPLC chromatogram of **4** shows a broad signal between 8 and 10 min, indicating the presence of additional products with similar polarity, in addition to the main peak and a small percent of C_{60}.

The solution electrochemistry of mixtures **3** and **4** was also investigated by CV and Osteryoung square wave voltammetry (OSWV). Potentials *vs.* ferrocene are reported in Table 1 and the sequential CVs obtained are presented in Fig. 2.

The electrochemical behavior of **3** and **4** is very similar: four very broad waves, characteristic of the presence of several compounds in solution, were observed. Based on typical fullerene core reductions,[32] these compounds clearly exhibit three fullerene-based reductions (first, second, and fourth reduction waves). We assume that the third reduction is based on the addend, which has been recently observed for other Bingel derivatives.[16] Upon adduct formation, loss of conjugation leads to a higher LUMO energy than in C_{60} and to a consequent decreased electron affinity. This is reflected in cathodically shifted reduction potentials for **3** and **4**, when compared with those of C_{60} taken under the same experimental conditions (Table 1).

Synthesis of Diels–Alder adducts

Due to the difficulties encountered during the preparation of the new methanofullerenes **3** and **4** *via* the Bingel reaction, because of Diels–Alder tandem reactions, we decided to invert the reaction order. C_{60}-anthracene Diels–Alder adducts **5** and **6** were prepared by reacting the anthracene malonates **1** and **2** with C_{60} in a 1:1 molar ratio, in toluene at room temperature



Scheme 3

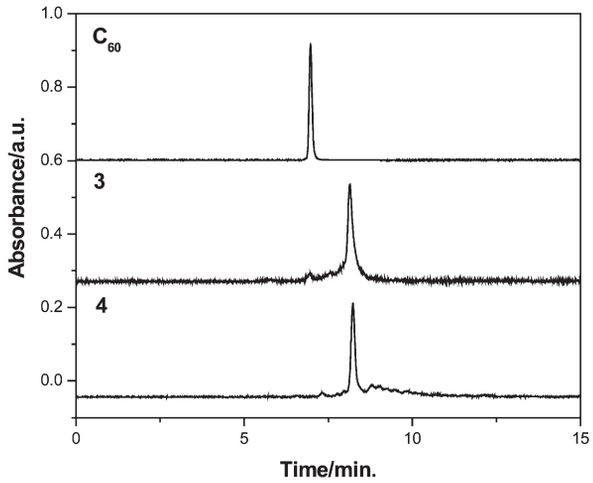


Fig. 1 HPLC chromatograms of the derivatives **3** and **4**, and C_{60}.

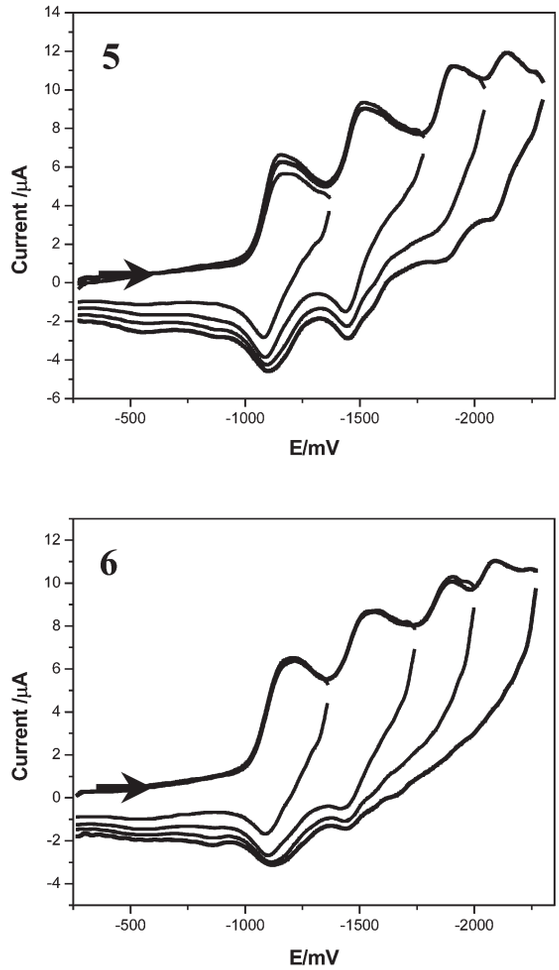


Fig. 2 Sequential cyclic voltammograms for **3** and **4** in *o*-DCB–$TBAClO_4$ (0.1 M). Scan rate 100 mV s^{-1}, $T = 20\,^{\circ}C$.

for 48 h (Scheme 4). Purification was accomplished by the use of column chromatography with CS_2 to elute the unreacted C_{60} and chloroform to elute the corresponding monoadducts **5** and **6**, which were obtained in 18% (36% based on recovered C_{60}) and 19% (44% based on recovered C_{60}) yield, respectively.

The ^1H NMR spectra of the new Diels–Alder adducts **5** and **6** show a single resonance at 5.84 ppm (**5**) or 5.73 ppm (**6**) for the bridge proton in the anthracene backbone, shifted significantly upfield from the corresponding resonance in anthracene.[21–23] The ^{13}C NMR spectra exhibit chemical shifts (δ_C 74.81, 74.42, 58.99 and 54.58 for **5** and 74.76, 74.38, 58.95 and 54.52 for **6**) than can reasonably be assigned to the corresponding bridging tetravalent carbons. In spite of the loss of full conjugation and formation of two saturated carbons on the original C_{60} surface, the electronic spectra of the adducts **5** and **6** exhibit UV absorptions similar to those of C_{60} and the visible absorption, which extends over 702 nm, are characteristic of [4 + 2] cycloadducts of C_{60}.[33,34] The MALDI spectra of the monoadducts **5** and **6** showed only weak signals due to the molecular ion, indicating efficient fragmentation of [4 + 2] cycloadducts of C_{60}, as noted elsewhere.[23,35,36]

Refluxing purified Diels–Alder cycloadducts **5** or **6** in toluene for several hours resulted in product degradation to C_{60} and anthracene malonates **1** and **2** *via* retro-Diels–Alder reactions. The 1:1 adduct **5** remained stable for months if stored in a freezer (−10 °C). However, cycloadduct **6** led to the formation of bisadducts and C_{60} in less than a week. Fig. 3 shows the HPLC chromatogram of derivatives **5** and **6** after purification and storage in the freezer (−10 °C) for 7 days.

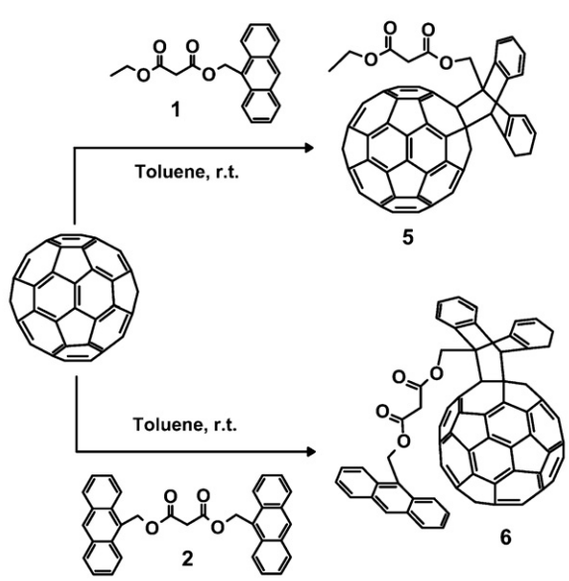
Further confirmation of a second Diels–Alder reaction taking place in cycloadduct **6** was obtained by CV. Fig. 4 depicts the sequential CVs obtained with samples of cycloadduct **5** and **6** after HPLC analyses. The redox potentials are listed in Table 1.

Table 1 Redox potentials of methanofullerenes **3** and **4**, and Diels–Alder derivatives **5** and **6**, *vs.* ferrocene in *o*-DCB (in mV) at a scan rate of 200 mV s^{-1}

Compound	$E^1_{1/2,red}$	$E^{1\prime}_{1/2,red}$	$E^2_{1/2,red}$	$E^{2\prime}_{1/2,red}$	$E^3_{1/2,red}$	$E^{3\prime}_{1/2,red}$
C_{60}	−1083	–	−1470	–	−1937	–
3	−1127	–	−1484	–	−1892[a]	–
4	−1154	–	−1508	–	−1884[a]	–
5	−1153	–	−1533	–	−2082	–
6	−1162	−1275	−1536	−1666	−1936	−2099

[a] Electrochemically irreversible reduction, cathodic peak potential.

For the Diels–Alder cycloadduct **5**, three perfectly reversible reduction processes were observed (Fig. 4), which, as expected, are negatively shifted compared with those of C_{60} (see Table 1).[32] In contrast, the CV obtained for **6** showed the presence of two different compounds (all the reduction processes appear



Scheme 4

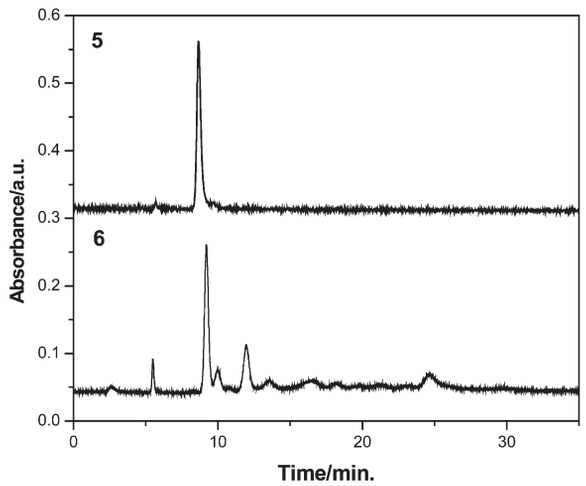


Fig. 3 HPLC chromatograms of the derivatives **5** and **6**.

split in two as shown on Fig. 4), which reduce approximately 100 mV apart. On the basis of the characterized structure of cycloadduct **6**, the HPLC results mentioned before, and the effect on the redox potentials of multiple functionalization on the C_{60} core,[37] these secondary reduction processes are attributed to regioisomeric bisadducts resulting from a second Diels–Alder reaction on cycloadduct **6**.

The stability of the Diels–Alder derivative **5** was further investigated by CV at different temperatures and by CPE experiments. In thermally controlled experiments [Fig. 5(a)], upon heating **5** to 50 °C, the redox waves became broader and the presence of additional species in the CV was evident [dotted line, Fig. 5(a)]. When the temperature was increased to 90 °C [dashed line, Fig. 5(a)], dissociation occurred and eventually the voltammogram corresponded to that of pure C_{60}. In contrast, the cyclic voltammetric behavior of cycloadduct **5** is very different after CPE [Fig. 5(b)]. Electrolysis of **5** was performed at the first and second electron reductions and consumed 1.0 and 2.0 electrons, respectively. The processes were fully reversible and no changes in the cyclic or OSWV voltammograms were observed. After re-oxidation the reaction mixture was purified by column chromatography and the Diels–Alder cycloadduct **5** was recovered in 98% yield. Although anticipated, we have now demonstrated that C_{60}-anthracene Diels–Alder derivatives are stable upon electrochemical reduction.

Additionally, Bingel reactions have been tried using cycloadduct **5** as starting material and considerable effort has been devoted to isolating and characterizing the multiple products resulting from these processes. Unfortunately, these involve tandem Diels–Alder/retro-Diels–Alder reactions for all the compounds in solution, leading to difficulties in controlling the reaction or tracking the products. We are presently trying

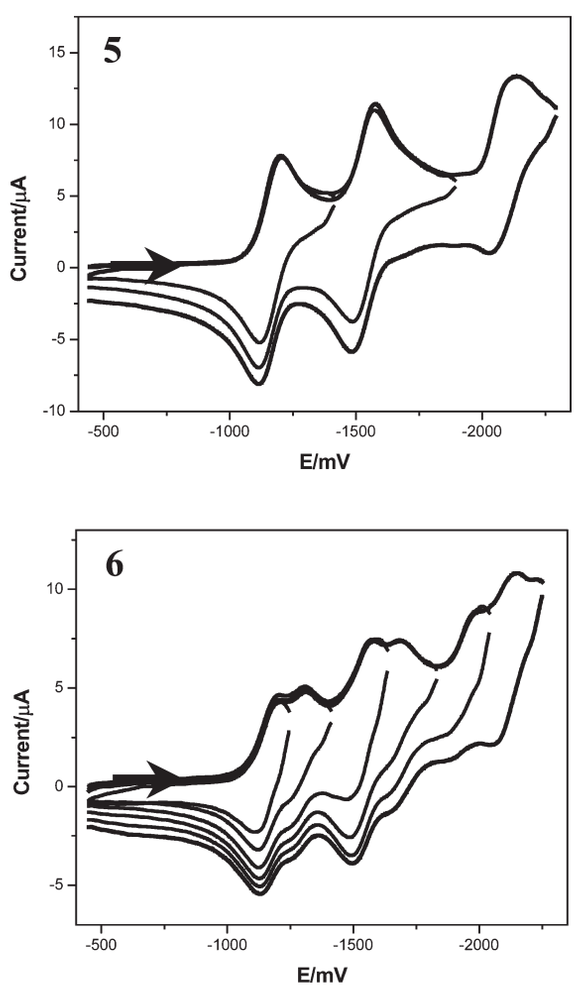


Fig. 4 Sequential cyclic voltammograms for **5** and **6** in *o*-DCB–TBA-ClO_4 (0.1 M). Scan rate 100 mV s^{-1}, $T = 20$ °C.

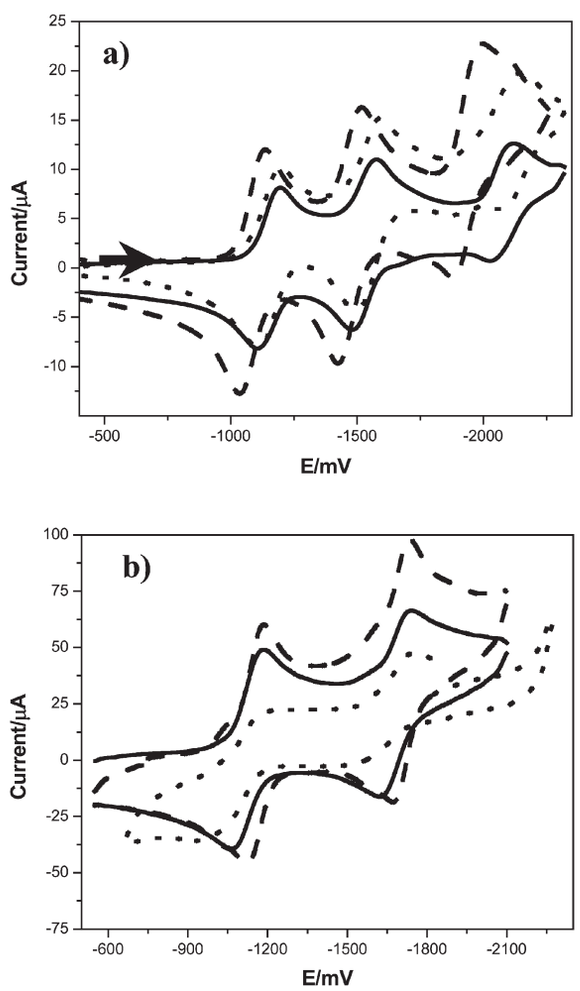


Fig. 5 Thermal *vs.* electrochemical behavior in derivative **5**. (a) CV at room temperature (solid line), CV at 50 °C (dotted line), CV at 90 °C (dashed line); (b) initial CV (solid line), CV after $2e^-$ reduction (dotted line), CV after $2e^-$ reduction and re-oxidation (dashed line).

to isolate some of these new derivatives, which include interesting dimeric structures.

Conclusions

In this work, we have reported the preparation of new anthracene malonates (**1** and **2**), which were initially reacted with C_{60} following a Bingel protocol. The reaction led to the preparation of regioisomeric mixtures (**3** and **4**), which besides the expected Bingel adducts, contain Diels–Alder cycloaddition products between anthracene and C_{60}.

The malonates **1** and **2** were also reacted with C_{60} *via* a Diels–Alder reaction. The cycloadducts obtained (**5** and **6**) were fully characterized and detailed CV analyses of **5** established the stability of this Diels–Alder cycloadduct under electroreductive conditions.

Experimental

General methods

All reagents were of commercial quality and were used as supplied unless otherwise specified. Solvents were dried using standard procedures. Column chromatography was performed on silica gel (60 Å, 32–63 μm). ^{1}H NMR and ^{13}C NMR were recorded using a 300 or a 500 MHz instrument; samples were prepared in deuterated chloroform with TMS as internal reference. MS spectra were obtained using EI or MALDI. A Varian ProStar high-performance liquid chromatography (HPLC) system, equipped with a ProStar 330 photodiode array detector, was used to determine the purity of the compounds synthesized. A semipreparative SiO_2 column (column dimensions, 25 cm × 10 mm; flow rate, 2.0 mL min^{-1}; injection volume, 20 μL; mobile phase, toluene) was employed. The retention time (t_R) and the peak area (PA) reported were determined at a wavelength of 310 nm.

Electrochemistry

Electrochemical measurements at different temperatures were performed in *o*-DCB with a three-electrode configuration containing 0.1 M tetrabutylammonium perchlorate ($TBAClO_4$) as the supporting electrolyte, which was recrystallized twice from ethanol and dried under vacuum. A glassy carbon (3 mm ϕ) was used as the working electrode; a platinum wire and a silver wire were employed as the counter and the reference electrodes, respectively. Solutions were stirred and deaerated by bubbling argon for a few minutes prior to each voltammetric measurement. The potentials were corrected against ferrocene, used as an internal standard, added after each measurement. Bulk electrolysis under high vacuum conditions of derivative **7** was carried out using a two-compartment cell designed to carry out CPE experiments.[38] A 4 mg sample of the fullerene Diels–Alder adduct **7** and 600 mg of the supporting electrolyte, tetrabutylammonium hexafluorophosphate ($TBAPF_6$), were added into the electrolysis cell. The cell was degassed and pumped to 10^{-6} Torr, and the solvent, methylene dichloride, which had also been degassed and pumped to the same pressure in the presence of calcium hydride, was then vapor-transferred into the cell. CPE at 293 K was performed on a Pt mesh working electrode. After reductive electrolysis, the solution was deoxidized at 0 V and the crude of the electrolytic reaction was analyzed by HPLC.

Syntheses

Synthesis of malonates. A solution of 9-anthracenemethanol (209 mg, 1 mmol) in methylene dichloride (60 mL) was prepared under an argon atmosphere. Pyridine (0.08 mL, 1 mmol) was added to the solution dropwise and the resulting mixture was cooled in an ice bath. Ethoxycarbonyl acetic acid chloride (0.13 mL, 1 mmol) for **1** or malonic acid dichloride (0.005 mL, 0.9 mmol) for **2** was added dropwise. The ice bath was removed after the solution was stirred for a 2 hour period. The reaction was then stirred overnight at room temperature. Water was added and the residue was extracted with CH_2Cl_2. The combined extracts were dried ($MgSO_4$) and filtered, and the solvent was removed under reduced pressure. Purification of products was achieved by column chromatography on silica gel using hexane–ethyl acetate (8:1) as eluent.

Malonic acid anthracen-9-yl methyl ester ethyl ester (**1**). 27% yield. Mp: 89–91 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.75 (1H, s), 8.33 (2H, d, J = 8.58 Hz), 7.99 (2H, d, J = 8.58 Hz), 7.54 (4H, m), 6.20 (2H, s), 4.13 (2H, q, J = 7.14 Hz), 3.42 (2H, s), 1.15 (3H, t, J = 7.14 Hz). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 166.73, 166.22, 131.12, 130.86, 129.23, 128.92, 126.55, 125.25, 124.94, 123.63, 61.34, 59.64, 41.40, 13.72. FTIR [polyethylene glycol (PE)]: 1728, 1751, 1558, 1519, 1458, 1404, 1373, 1327, 1265, 1196, 1134, 1026, 980, 734, 602 cm^{-1}. UV-vis ($CHCl_3$): λ_{max} (log ε) 387 (3.89), 367 (3.93), 349 (3.76), 333 (3.48), 318 (3.18), 253 (4.78) nm. MS (EI): m/z 322 (M^+). Anal. calcd for $C_{20}H_{18}O_4$: C: 74.51, H: 5.63; found C: 73.64, H: 5.72.

Malonic acid dianthracen-9-yl methyl ester (**2**).[31] 36% yield. Mp: 178–182 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.51 (1H, s), 8.23 (2H, m), 8.02 (2H, m), 7.49 (4H, m), 6.16 (4H, s), 3.45 (2H, s). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 166.70, 131.26, 131.00, 129.39, 129.03, 126.72, 125.30, 125.09, 123.72, 59.92, 41.43. FTIR (PE): 1743, 1651, 1535, 1458, 1388, 1334, 1265, 1172, 1141, 987, 902, 733, 671, 602 cm^{-1}. UV-vis ($CHCl_3$): λ_{max} (log ε) 388 (4.22), 368 (4.26), 350 (4.09), 332 (3.79), 320 (3.52), 254 (5.05) nm. MS (EI): m/z 484 (M^+). Anal calcd for $C_{33}H_{14}O_4$: C: 81.79, H: 5.00; found: C: 80.82, H: 4.98.

Synthesis of Bingel adducts. A solution of C_{60} (50 mg, 0.069 mmol) was prepared in toluene (50 mL) under an argon atmosphere. The corresponding malonate **1** or **2** (0.090 mmol), CBr_4 or I_2 (0.090 mmol), and diazabicyclo[4.2.0]undec-7-ene (DBU; 0.17 mL, 1.13 mmol) were added in this order. The reaction progressed rapidly and the mixture was loaded into a column less than 15 min after adding DBU. CS_2 was first added to elute unreacted C_{60}, then chloroform was added to elute the mixtures **3** or **4**. An overall yield of 40% and 52%, respectively (based on recovered C_{60}), was obtained for the product mixtures.

Regioisomeric mixture **3**. 40% yield. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.48 (s), 8.41 (d, J = 9.20 Hz), 7.98 (d, J = 8.75 Hz), 7.54 (m), 7.44 (m), 7.25 (m), 6.51 (s), 5.99 (s), 5.60 (s), 5.23 (s), 4.33 (q, J = 6.90), 4.23 (q, J = 7.30 Hz), 1.14 (t, J = 6.90 Hz), 1.09 (t, J = 7.30 Hz). UV-Vis ($CHCl_3$): λ_{max} (log ε) 519 (3.33), 426 (3.58), 414 (3.64), 390 (4.02), 368 (4.18), 324 (4.52), 261 (4.82).

Regioisomeric mixture **4**. 52% yield. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.45 (s), 8.41 (d, J = 8.25 Hz), 8.30 (d, J = 8.70 Hz), 8.22 (d, J = 8.25 Hz), 7.95–7.93 (m), 7.43–7.37 (m), 6.34 (s), 6.00 (s), 5.95 (s), 5.46 (s), 5.43 (s), 4.23–4.21 (m), 1.14–1.12 (m). UV-Vis ($CHCl_3$): λ_{max} (log ε) 507 (3.51), 426 (3.70), 388 (4.15), 369 (4.27), 350 (4.35), 323 (4.52), 261 (4.31).

Synthesis of Diels–Alder adducts. A 1:1 ratio solution of C_{60} (200 mg, 0.028 mmol) and diesters **1** or **2** (0.028 mmol) in 20 mL of toluene, was allowed to stand at room temperature for 48 h. The solvent was then evaporated below 50 °C and the resulting dark brown solid was purified by column chromatography on SiO_2. CS_2 was used to elute the unreacted C_{60} and monoadducts **5** or **6** were obtained when the polarity was changed to chloroform.

Monoadduct **5**. 18% yield (36% based on recovered C_{60}). Mp: > 300 °C. HPLC (analytical): t_R = 8.66 min, PA = 98%. ^{1}H

NMR ($CDCl_3$, 500 MHz): δ 7.72 (2H, m), 7.71 (2H, m), 7.46 (4H, m), 6.18 (2H, s), 5.84 (1H, s), 4.16 (2H, q, $J = 7.10$ Hz), 3.55 (2H, s), 1.23 (3H, t, $J = 7.10$ Hz). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 167.03, 166.34, 155.91, 152.50, 147.71, 147.55, 146.58, 146.49, 146.31, 146.24, 145.52, 145.50, 145.43, 145.35, 145.28, 145.14, 144.72, 144.60, 143.19, 142.99, 142.71, 142.28, 142.26, 142.09, 142.03, 141.72, 141.54, 141.27, 140.25, 139.69, 138.94, 137.39, 136.62, 129.22, 127.64, 127.41, 126.88, 126.09, 125.26, 124.75, 123.93, 74.81, 74.42, 65.87, 61.91, 58.99, 54.58, 41.83, 14.17. FTIR (PE): 1751, 1735, 1620, 1558, 1520, 1458, 1188, 1149, 748, 532 cm^{-1}. UV-vis ($CHCl_3$): λ_{max} (log ε) 701 (2.81), 484 (3.22), 432 (3.43), 326 (3.79), 271 (4.48) nm. MS (MALDI): m/z 1012 ($M^+ - CH_2CH_3$), 720 (C_{60}), 322 (**3**).

Monoadduct **6**. 19% yield (44% based on recovered C_{60}). Mp: $> 300\,^{\circ}C$. HPLC (analytical): $t_R = 9.21$ min, PA = 67%. ^1H NMR ($CDCl_3$, 500 MHz): δ 8.45 (1H, s), 8.18 (2H, d, $J = 8.70$ Hz), 7.95 (2H, d, $J = 8.70$ Hz), 7.67 (2H, d, $J = 7.35$ Hz), 7.49–7.36 (10H, m), 6.14 (2H, s), 6.01 (2H, s), 5.73 (1H, s), 3.47 (2H, s). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 166.87, 166.65, 155.89, 152.52, 147.69, 147.54, 146.55, 146.47, 146.29, 146.22, 145.68, 145.50, 145.42, 145.34, 145.24, 145.12, 144.70, 144.57, 143.17, 142.94, 142.69, 142.27, 142.23, 142.08, 142.00, 141.71, 141.49, 141.21, 140.22, 139.65, 138.88, 137.34, 136.60, 131.45, 131.15, 130.64, 129.70, 129.56, 129.26, 129.19, 128.11, 127.95, 127.82, 127.55, 127.38, 127.00, 126.88, 126.00, 125.31, 125.25, 124.63, 123.87, 74.76, 74.38, 65.84, 60.33, 58.95, 54.52, 41.76. FTIR (PE): 1758, 1740, 1459, 1412, 1183, 1144, 756, 563, 528 cm^{-1}. UV-vis ($CHCl_3$): λ_{max} (log ε) 702 (2.40), 563 (2.84), 433 (3.44), 387 (3.80), 332 (4.20) nm. MS (MALDI): m/z 1205 (M^+), 720 (C_{60}).

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