

The first synthesis of Diels–Alder adducts of [60]fullerene with sulfur containing heteroaromatic *o*-quinodimethanes

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Fullerene C_{60} undergoes cycloaddition reactions with substituted thieno-*o*-quinodimethanes yielding novel thiophene containing monoadducts. The spectroscopic data reveal C_s symmetry and the cyclic voltammetry studies show cathodically shifted reduction waves related to C_{60} .

The *o*-quinodimethane **1**, also named *o*-xylylene [5,6-bis(methylidene)cyclohexa-1,3-diene], has been widely used for synthetic applications as a highly reactive diene in cycloaddition reactions.¹ More recently, cycloadditions provided a powerful method for fullerene functionalization² and the reaction of C_{60} with *o*-quinodimethanes, which can be generated *in situ* by different routes, yields thermally stabilized cycloadducts showing different substitution patterns.³

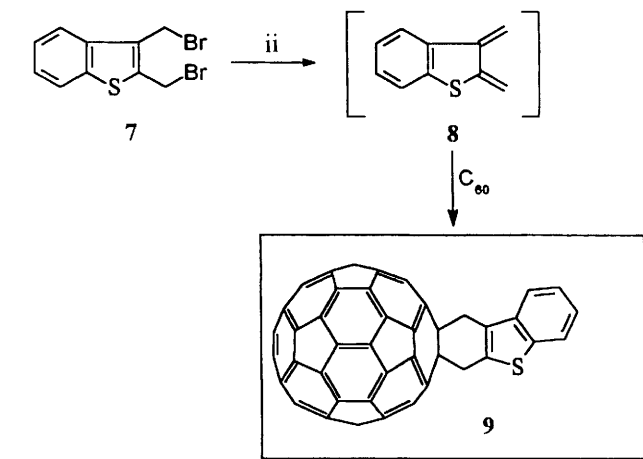
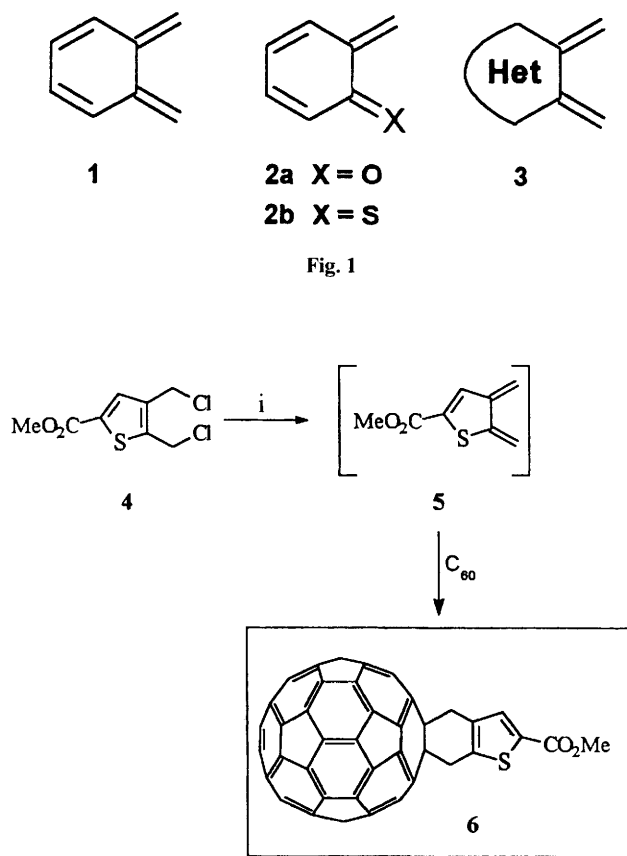
Hetero-Diels–Alder reactions of C_{60} with *o*-quinomethane **2a** and *o*-thioquinomethane **2b** have also been recently reported to form the respective cycloadducts with the heteroatom-bonded ring fusion to the C_{60} .⁴

In contrast, the heteroaromatic analogues of *o*-quinodimethane **3** as dienes have received much less attention despite their potential synthetic interest and, only recently, have been thoroughly reviewed^{1,5} (Fig. 1). Most studies involving heteroaromatic analogues of *o*-quinodimethane involve their generation and only few of them are related with their synthetic applications.⁵ Heteroaromatic *o*-quinodimethanes are not easy to prepare, particularly those bearing functionalities that can be altered during the generation process of the intermediate *o*-quinodimethane.⁵ Unlike the *o*-quinodimethane **1**, a specific precursor is required for the preparation of each particular heteroaromatic *o*-quinodimethane⁶ and this is one of the reasons that many of these reactive intermediates are still unknown.

To the best of our knowledge, the reaction of a heteroaromatic analogue of *o*-quinodimethane with C_{60} has not been previously reported. In this communication we report our preliminary results on the cycloaddition reaction of thieno-*o*-quinodimethane derivatives to C_{60} .

The substituted thieno-*o*-quinodimethanes **5** and **8** were generated *in situ* by iodide-induced 1,4-elimination from the respective 2,3-bis(chloromethyl)thiophene **4**⁷ and 2,3-bis(bromomethyl)benzo[*b*]thiophene **7**⁸ (Scheme 1). The cycloaddition reaction is carried out in toluene to solubilize the fullerene C_{60} and, consequently, 18-crown-6 ether is required as a phase transfer catalyst.³ⁱ Thus, when C_{60} (125 mg, 0.17 mmol) was refluxed with argon atmosphere for a variable period of time (3 d for **6** and 17 h for **9**) with a slight excess of the thiophene derivative (**4**, **7**) (0.19 mmol), cycloadduct **6** was obtained in 23% yield (42% based on reacted C_{60}) and the benzo[*b*]thiophene derivative **9** in 43% yield (70% based on reacted C_{60}).[†] The isolation of compounds **6** and **9** was accomplished by column chromatography on silica-gel using cyclohexane as the eluent.

[†] Formation of the respective bisadducts could be observed by TLC.

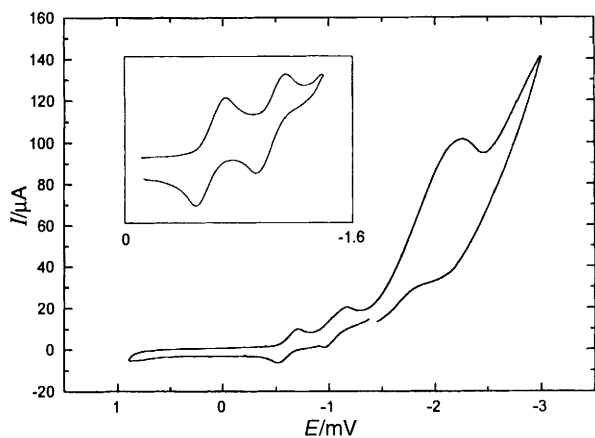


Scheme 1 Reagents and conditions: i, toluene, NaI (8.4 equiv.), 18-crown-6 (3.4 equiv.), reflux, 3 d; ii, toluene, NaI (4 equiv.), 18-crown-6 (3 equiv.), reflux, 24 h

Table 1 Peak potentials for reductions of C₆₀, **6** and **9**^a

Compound	E_{red}^1	E_{red}^2	E_{red}^3	E_{red}^4
C ₆₀	-0.60	-1.00	-1.52	-2.04
6	-0.66	-1.17	-1.89	-2.58
9	-0.70	-1.16	-2.25	—

^a All potentials in V vs. SCE; toluene-MeCN (5:1); 0.1 mol dm⁻³ Bu₄NClO₄; scan rate of 200 mV s⁻¹.

**Fig. 2**

Monoadducts **6** and **9** were isolated exclusively as adducts on 6/6 junctions. This finding is in good agreement with that observed for the cycloadducts resulting from the related homoaromatic *o*-quinodimethanes **1** and C₆₀.³ The structure of the products **6** and **9** was unambiguously determined from ¹H and ¹³C NMR spectra in addition to the UV-VIS and FTIR data. Thus, both monoadducts **6** and **9** showed the typical weak absorption band of most dihydrofullerenes in the UV-VIS spectrum at 432 and 434 nm respectively, together with the band around 700 nm.

The proton spectrum showed, in addition to the expected signals, the methylene protons which appear as singlets [**6**: δ 4.77 (2 H, CH₂), 4.62 (2 H, CH₂); **9**: δ 4.85 (2 H, CH₂), 4.80 (2 H, CH₂)]. The ¹³C NMR spectrum further confirms the structure assignment. The signals found for **6** and **9** are consistent with the C_s symmetry for both monoadducts. The fullerene bridgehead quaternary sp³ C atoms at δ 66.42 and 66.14 (for **6**) and δ 66.77 and 66.32 (for **9**) indicates the closed transannular bond,⁹ thus confirming the 6/6 ring junction on the C₆₀ cage. The methylene carbon atoms linking the C₆₀ and thiophene moieties appear at δ 41.24 and 41.07 (for **6**) and δ 41.37 and 39.46 (for **9**). This assignment was confirmed by comparison with the ¹³C NMR of the starting compounds **4** and **7**. The negative liquid secondary ion mass spectra (LSIMS) in 4-nitrobenzyl alcohol (NBA) matrix showed the molecular ions for **6** and **9** at *m/z* 888 and 880 respectively.

Since C₆₀ shows a weak electron-accepting ability, there is great interest in the preparation of novel organofullerenes exhibiting a more electropositive or electronegative behaviour.¹⁰ Recently, we have reported the redox properties of monoadducts^{3a} involving C₆₀ and *o*-quinodimethanes **1**. The effect of the thiophene fragment on the electronic properties of fullerene C₆₀ has been studied by cyclic voltammetry (Table 1). Both compounds **6** and **9** show quasi-reversible electrochemical behaviour with the reduction waves cathodically shifted in comparison with that observed for the unsubstituted C₆₀ (Fig. 2). Consequently, monoadducts **6** and **9** show a poorer acceptor ability than the parent C₆₀. This fact has been accounted for by the loss of conjugation due to the saturation of a double bond in the C₆₀ cage,¹¹ in addition to the lack of conjugation between C₆₀ and the thiophene fragment. However, substitution of the benzene-fused ring for the methoxycarbonyl group on the thiophene ring leads to an additional shift to the more negative

values of the cathodic peaks (Table 1), thus indicating some electronic interaction between the two partners.¹²

In summary, we have described the first reaction of a heteroaromatic *o*-quinodimethane with C₆₀, a novel and promising procedure for the functionalization of fullerene C₆₀. The current chemistry on the generation of unknown heteroaromatic *o*-quinodimethanes will open up an alternative route for the preparation of novel organofullerenes bearing heterocyclic units. In addition, we have also carried out the cyclic voltammetry of the novel adducts which showed a slightly poorer electron acceptor ability.

Experimental

Typical procedure for the preparation of [60]fullerene adducts

To a refluxing toluene solution (90 cm³) of [60]fullerene (0.125 g, 1.7 mmol), sodium iodide [0.215 g, 1.4 mmol (for **6**) and 0.104 g, 0.7 mmol (for **9**)] and 18-crown-6 [0.151 g, 0.6 mmol (for **6**) and 0.138 g, 0.52 mmol (for **9**)], a toluene solution (20 cm³) of the respective thiophene derivative (1.9 mmol) was added dropwise. The resulting brown reaction mixture was refluxed for a variable period of time (72 h for **6** and 24 h for **9**). The solid obtained by evaporation to dryness was chromatographed on silica-gel using cyclohexane-toluene. Further purification was accomplished by washing the obtained solid three times with methanol.

Adduct 6. ν_{max} (KBr)/cm⁻¹ 2964, 2927, 2841, 1708, 1461, 1264, 1104, 1015, 800, 526; ¹H NMR (300 MHz; CDCl₃) δ 8.09 (1 H, s), 4.77 (2 H, s), 4.62 (2 H, s), 3.98 (3 H, s); ¹³C NMR (75 MHz; CDCl₃) δ 162.89, 156.29, 155.78, 153.83, 147.74, 146.57, 146.27, 145.74, 145.53, 145.09, 144.70, 144.14, 143.15, 142.63, 142.09, 141.64, 140.21, 139.40, 135.47, 132.96, 66.42, 66.14, 52.29, 41.24, 41.07; *m/z* 888 (M⁺), 720 (C₆₀).

Adduct 9. ν_{max} (KBr)/cm⁻¹ 1511, 1424, 766, 748, 726, 569, 526; ¹H NMR (300 MHz; CDCl₃) δ 8.08–7.99 (2 H, m), 7.56–7.44 (2 H, m), 4.85 (2 H, s), 4.80 (2 H, s); ¹³C NMR (75 MHz; CDCl₃) δ 156.62, 150.25, 147.77, 146.58, 146.30, 145.79, 145.54, 145.30, 145.23, 144.72, 143.16, 142.65, 142.35, 142.28, 142.15, 141.67, 140.24, 139.70, 138.41, 137.39, 135.75, 135.59, 135.51, 133.23, 124.72, 124.44, 123.19, 120.86, 66.77, 66.32, 41.37, 39.46; *m/z* 880 (M⁺), 720 (C₆₀).

Acknowledgements

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References

- 1 For a recent review on *o*-quinodimethane chemistry see, N. Martín, C. Seoane and M. Hanack, *Org. Prep. Proced. Int.*, 1991, **23**, 237.
- 2 A. Hirsch, *Synthesis*, 1995, 895.
- 3 (a) B. Illescas, N. Martín, C. Seoane, P. de la Cruz, F. Langa and F. Wudl, *Tetrahedron Lett.*, 1995, **36**, 8307; (b) A. Kraus, A. Gügel, P. Belik, M. Walter and K. Müllen, *Tetrahedron*, 1995, **51**, 9927; (c) P. Belik, A. Gügel, A. Kraus, M. Walter and K. Müllen, *J. Org. Chem.*, 1995, **60**, 3307; (d) H. Imahori, K. Hagiwara, T. Akiyama, S. Taniguchi, T. Okada and Y. Sakata, *Chem. Lett.*, 1995, 265; (e) A. Gügel, A. Kraus, J. Spickermann, P. Belik and K. Müllen, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 559; (f) M. Iyoda, F. Sultana, S. Sasaki and M. Yoshida, *J. Chem. Soc., Chem. Commun.*, 1994, 1929; (g) W. Bidell, R. E. Douthwaite, M. L. H. Green, A. H. Stephens and J. F. C. Turner, *J. Chem. Soc., Chem. Commun.*, 1994, 1641; (h) X. Zhang and C. S. Foote, *J. Org. Chem.*, 1994, **59**, 5235; (i) P. Belik, A. Gügel, J. Spickermann and K. Müllen, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 78; (j) P. Belik, A. Gügel, A. Kraus, J. Spickermann, V. Enkelmann, G. Frank and K. Müllen, *Adv. Mater.*, 1993, **5**, 854.
- 4 M. Ohno, T. Azuma and S. Eguchi, *Chem. Lett.*, 1993, 1833; M. Ohno, S. Kojima, Y. Shirakawa and S. Eguchi, *Tetrahedron Lett.*, 1995, **36**, 6899.

- 5 T.-S. Chou, *Rev. Heteroat. Chem.*, 1993, **8**, 65; T.-S. Chou and R.-C. Chang, *J. Org. Chem.*, 1993, **58**, 493; M. L. Chaloner, A. P. A. Crew, P. M. O'Neill, R. C. Storr and M. Yelland, *Tetrahedron*, 1992, **48**, 8101.
- 6 For some recently reported heteroaromatic *o*-quinodimethanes see: W. Danikiewicz, K. Wojciechowski and M. Olejnik, *Tetrahedron Lett.*, 1995, **36**, 1099; P. R. Carly, F. Compennolle and G. J. Hoornaert, *Tetrahedron Lett.*, 1995, **36**, 2113; L. A. White, P. M. O'Neill, B. K. Park and R. C. Storr, *Tetrahedron Lett.*, 1995, **36**, 5983.
- 7 D. J. Zwanenburg, H. de Haan and H. Wynberg, *J. Org. Chem.*, 1966, **31**, 3363.
- 8 G. Dyker and R. P. Kreher, *Chem. Ber.*, 1988, **121**, 1203.
- 9 M. Maggini, G. Scorrano and M. Prato, *J. Am. Chem. Soc.*, 1993, **115**, 9798; L. Isaaks, A. Wehrsig and F. Diederich, *Helv. Chim. Acta*, 1993, **76**, 1231.
- 10 M. Eiermann, R. C. Haddon, B. Knight, Q.-Ch. Li, M. Maggini, N. Martín, T. Ohno, M. Prato, T. Suzuki and F. Wudl, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1591.
- 11 R. C. Haddon, *Science*, 1993, **261**, 1545; F. Arias, Q. Xie, Y. Wu, Q. Lu, R. S. Wilson and L. Echegoyen, *J. Am. Chem. Soc.*, 1994, **116**, 6388; E. Beer, M. Feuerer, A. Knorr, A. Mirlach and J. Daub, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 1097; M. Maggini, A. Karlsson, G. Scorrano, G. Sandona, G. Farnia and M. Prato, *J. Chem. Soc., Chem. Commun.*, 1994, 589.
- 12 T. Suzuki, Y. Maruyama, T. Akasaba, W. Ando, K. Kobayashi and S. Nagase, *J. Am. Chem. Soc.*, 1994, **116**, 1359.

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