The first Diels–Alder adduct of [60]fullerene with a tetrathiafulvalene

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A Diels–Alder adduct of [60]fullerene and a tetrathiaful-valene (TTF) derivative is synthesised by direct reaction of [60]fullerene with a TTF diene precursor; the crystal structure of the formal intermediate 1,3-dithiole-2-thione derivative of [60]fullerene reveals short contacts between the [60]fullerene and 1,3-dithiole-2-thione moieties.

In the search for intramolecular energy and electron transfer phenomena in [60]fullerene donor-containing molecules, some electron donor fragments have been covalently linked to the fullerene core.[1–5] Only in very few cases has reliable evidence of thermal or photoinduced intramolecular electron-transfer processes been reported.[3–5] One of the strongest donors that can be attached to the [60]fullerene skeleton is tetrathiafulvalene (TTF). This attachament has been achieved for some compounds, in which the donor TTF moiety is linked by only one single bond to the [60]fullerene through a pyrrolidine bridge, but no electron transfer process has been observed.[6] With the aim of promoting an intramolecular electron transfer we sought to develop a novel type of TTF derivative of [60]fullerene in which the TTF core is directly attached by two σ-bonds to the ball giving rise to a different and more rigid spatial orientation of the HOMO of the TTF addend with respect to the LUMO of [60]fullerene.

Diels–Alder functionalisation of [60]fullerene was chosen in order to reach our goal, since it has been one of the most successful methods for a double attachment of a large variety of substituents[2,7] and it has recently been demonstrated that some Diels–Alder bichromophoric systems undergo energy and electron-transfer phenomena.[5] As a first approach, the thione 1 with a thermolabile sulfone group was used as a diene precursor. We synthesised the compound 1† by the same procedure used in the synthesis of the parent selenone,[8] and the adduct formation with [60]fullerene was achieved by refluxing a two-fold excess of [60]fullerene with 1 in chlorobenzene–benzonitrile (10 : 1). Chromatographic separation on silica gel (CS_2–$CHCl_3$, 10 : 1) afforded the target compound, the Diels–Alder adduct 2,† as a 1 : 1 clathrate with CS_2 in a 41% yield.

The crystallisation of 2·CS_2 by vapour diffusion of pentane into an o-dichlorobenzene solution surprisingly gave the 2·CS_2 clathrate back as brilliant dark plates, indicating the very high stability of this clathrate.‡ The crystal structure of thione 2 is

shown in Fig. 1.§ As for other adducts,[9] the cyclohexene ring formed by the cycloaddition of the diene derived from thione 1 to the reactive 6,6-ring junction of [60]fullerene shows a boat conformation [Fig. 1(a)]. Nevertheless, the angle determined by the two mean planes defined by C(1)–C(2)–C(61)–C(65) and C(61)–C(65)–C(62)–C(64) is smaller (109.2 (4)°) than those found (ca 130°) in three other related compounds for which the X-ray structure has been solved so far.[2,9] This small angle gives rise to short intramolecular S···C distances (3.915–4.036 Å) between the sulfur atoms S(1) and S(3) of the addend and C(1), C(2), C(3) and C(6) of the [60]fullerene moiety. If similar short
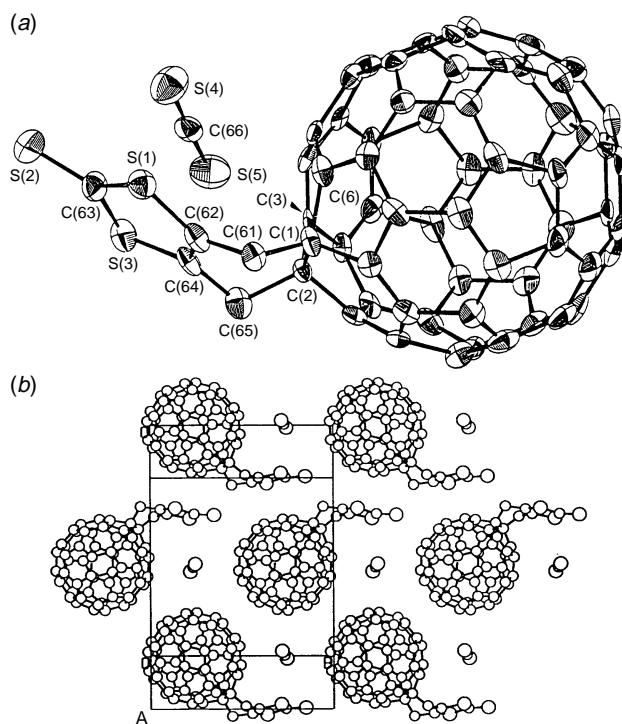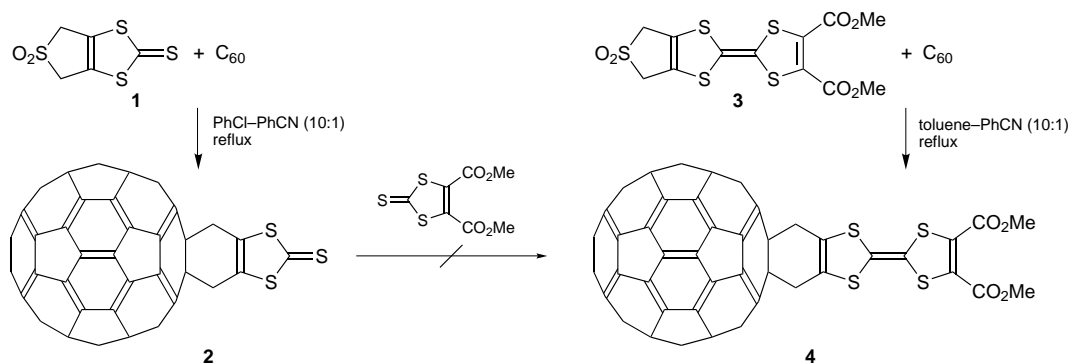

(a)

(b)

Fig. 1 Molecular and X-ray crystal structure of 2·CS_2: (a) asymmetric unit and, (b) crystal packing of 2·CS_2, view perpendicular to the bc plane

Scheme 1

Redox couple	$E^{0/1-}$	$E^{1-/2-}$	$E^{2-/3-}$	$E^{0/1+}$	$E^{1+/2+}$
C_{60}	-0.98	-1.36	-1.83	—	—
2	-1.03	-1.41	-1.93	—	—
4	-1.08	-1.46	-1.97	0.18	0.65
3	—	—	—	0.33	0.63

distances are maintained in the corresponding [60]fullerene–TTF derivatives an intramolecular electron-transfer phenomenon could be expected. The crystal packing of **2**·CS_2 consists of parallel intercalated planes (along *a*) of connected chains of molecules along the *b* axis formed by intermolecular close contacts [3.45(3) Å] between sulfur atoms of the thiocarbonyl group and carbon atoms of the contiguous [60]fullerene [Fig. 1(*b*)]. Solvent molecules show some short S···C contacts with two surrounding adduct molecules in addition to the contacts with the adduct inside the asymmetric unit.

Unfortunately, all attempts to perform a phosphite-mediated coupling of thione **2** in order to synthesise [60]fullerene–TTF derivatives have so far been unsuccessful.¶ So, we moved to the key compound **3** as a TTF diene precursor. The asymmetric TTF derivative **3**† was synthesised by a Wittig based methodology[10] in acceptable yield and the corresponding diene indeed undergoes a Diels–Alder addition to [60]fullerene yielding our target compound **4**† as a dark brown solid (47%).

All electroactive compounds here described were studied by cyclic voltammetry. The results are reported in Table 1. In the experimental conditions employed, compounds **2** and **4** show three one-electron reversible reduction waves due to the stepwise reduction of the fullerene moiety. The first reduction potentials of both compounds are slightly shifted cathodically compared to those of [60]fullerene, as observed in many [60]fullerene adducts in which one double bond has been saturated.[11] As expected, compound **4** shows two additional reversible oxidation processes corresponding to the formation of radical cation and dication of the TTF moiety.

The UV–VIS spectra of compounds **2** and **4** clearly show a weak band around 430 nm characteristic of [60]fullerene cycloderivatives.[12] For compound **4** an additional weak and broad band appears at 482 nm (log ε = 3.43) which is not shifted significantly with the modification of the solvent polarity. The last result, together with the normal shift of the first reduction potential of **4** in relation with [60]fullerene, does not permit us to assign the extra band to an intramolecular electron-transfer process, as occurs in the case of 1,3-diphenylpyrazolo[4′,5′ : 1,2][60]fullerene.[3]

We have already synthesised some other TTF derivatives containing the sulfone group precursor of diene group on one side of the TTF core and different atoms (H, Me) on the other side. These compounds have better donor properties than compound **3**‖ and the synthesis and characterization of their corresponding [60]fullerene adducts has been recently performed in our laboratory with the aim of tuning the energy gap between the HOMO of the TTF addend and the LUMO of the [60]fullerene moiety. The study of the photoinduction of electron transfer in [60]fullerene adducts is being pursued.

Footnotes

† Satisfactory spectroscopic and analytical data were obtained for all new compounds: **1**, **2**, **3** and **4**. *Selected analytical and spectroscopic data* for **2**:

calc. for $C_{65}H_4S_3$: C, 88.6; H, 0.4; S, 10.9. Found: C, 88.1; H, 0.4; S, 10.8%. ¹H NMR (300 MHz, $CDCl_3$) δ 4.56. ¹³C NMR [75.42 MHz, CS_2–$CDCl_3$, 1 : 1, Cr(acac)₃] δ 40.33 (CH_2), 64.50 ([60]fullerene C_{sp}^3), 128.54 (C_{sp}^2), 135.42, 138.24, 139.97, 141.36, 141.77, 142.36, 142.71, 143.87, 144.28, 144.61, 145.20, 145.33, 145.98, 146.28, 147.53, 154.05, 219.25 (C=S). λ_{max}($CHCl_3$)/nm (log ε): 257 (5.02), 316 (4.41), 383 (4.41), 433 (3.58). *m/z* 880 (7%, M⁺), 720 (100, [M – $C_3H_4S_3$]⁺). For **4**: Calc. for $C_{72}H_{10}S_4O_4$: C, 81.0; H, 0.9; S, 12.0. Found: C, 81.0; H, 1.1; S, 11.9%. ¹H NMR (300 MHz, CS_2–$CDCl_3$, 1 : 1) δ 4.37 (s, 4 H, CH_2), 3.89 (s, 6 H, CH_3). ¹³C NMR (75.42 MHz, CS_2–$CDCl_3$, 1 : 1) δ 41.06 (CH_2), 53.25 (CH_3), 65.95 ([60]fullerene C_{sp}^3), 125.40 (C_{sp}^2), 132.38 (C_{sp}^2), 135.85, 140.34, 141.73, 142.16, 142.30, 142.78, 143.20, 144.71, 144.97, 145.59, 145.67, 145.81, 146.36, 146.64, 147.80, 155.04, 159.80 (C=O). λ_{max}($CHCl_3$)/nm (log ε): 256 (4.91), 313 (4.56), 432 (3.65), 482 (3.43). HRMS (FAB) calc. for $C_{72}H_{10}O_4S_4$: 1065.946. Found: 1065.951.

‡ Thermogravimetric analysis reveals that the loss of solvent takes place between 120 and 190 °C giving rise to the solvent free adduct **2** that is completely stable up to 390 °C.

§ *Crystal data* for **2**: $C_{68}H_3S_3$·CS_2, *M* = 956.9; monoclinic, $P2_1/n$, *a* = 15.167(2), *b* = 13.670(2), *c* = 17.701(2) Å; β = 105.76(2)°; *V* = 3532.0(8) Å³; *Z* = 4; D_c = 1.80 g cm⁻³; μ(Mo-Kα) = 3.9 cm⁻¹, $2\theta_{max}$ = 47.4°, giving 5342 unique reflections. A dark brown plate of dimensions 0.29 × 0.12 × 0.08 mm was used. The structure was solved by direct methods (SHELXS-86) yielding *R* = 0.056, R_w = 0.127 for 1838 independent reflexions with *F* > 4σ(*F*). Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/385.

¶ Besides homocoupling of **2**, heterocoupling with distinct thiones and ketones similar to **1** using a variety of different phosphites and solvents, have been performed. In all cases compound **2** was recovered almost quantitatively.

‖ First oxidation potentials (*vs* Fc⁺/Fc) are $E^{1/2}$ = 0.01 V for the donor with Me substituents and $E^{1/2}$ = 0.02 V for the donor with no substituents.

References

1 T. Drovestkaya, Ch. A. Reed and P. Boyd, *Tetrahedron Lett.*, 1995, **36**, 7971; M. Maggini, A. Karlsson, G. Scorrano, G. Sandonà, G. Farina and M. Prato, *J. Chem. Soc., Chem. Commun.*, 1994, 598.

2 J. M. Lawson, A. M. Oliver, D. F. Rothenfluh, Y-Z. An, G. A. Ellis, M. G. Ranasinghe, S. I. Khan, A. G. Franz, P. S. Ganapathi, M. J. Shephard, M. N. Paddon-Row and Y. Rubin, *J. Org. Chem.*, 1996, **61**, 5032.

3 Y. Matsubara, H. Tada, S. Nagase and Z. Yoshida, *J. Org. Chem.*, 1995, **60**, 5372.

4 H. Imahori, K. Hagiwara, T. Akiyama, S. Taniguchi, T. Okada and Y. Sakata, *Chem. Lett.*, 1995, 265; R. M. Williams, J. M. Zwier and J. W. Verhoeven, *J. Am. Chem. Soc.*, 1995, **117**, 4093; Y. Nakamura, T. Minowa, S. Tobita, H. Shizuka and J. Nishimura, *J. Chem. Soc., Perkin Trans. 2*, 1995, 2351.

5 R. M. Williams, M. Kroeberg, J. M. Lawson, Y.-Z. An, Y. Rubin, M. N. Paddon-Row and J. W. Verhoeven, *J. Org. Chem.*, 1996, **61**, 5055.

6 M. Prato, M. Maggini, C. Giacometti, G. Scorrano, G. Sandonà and G. Farina, *Tetrahedron*, 1996, **52**, 5221; N. Martín, L. Sánchez, C. Seoane, R. Andreu, J. Garín and J. Orduna, *Tetrahedron Lett.*, 1996, **33**, 5979.

7 A. Hirsch, *The Chemistry of the Fullerenes*, Thieme, Stuttgart, 1994; F. Diederich and C. Thilgen, *Science*, 1996, **271**, 317

8 J. Veciana, C. Rovira and D. O. Cowan, *Tetrahedron Lett.*, 1988, **29**, 3467.

9 Y. Rubin, S. Khan, D. I. Freedberg and C. Yeretzian, *J. Am. Chem. Soc.*, 1993, **115**, 334; F. Diederich, U. Jonas, V. Gramlich, A. Hermann, H. Ringsdorf and C. Thilgen, *Helv. Chim. Acta*, 1993, **76**, 2445; P. Belik, A. Gügel, A. Kraus, J. Spikermann, V. Enkelmann, G. Frank and K. Müllen, *Adv. Mater.*, 1993, **5**, 854.

10 A. J. Moore and M. R. Bryce, *Synthesis*, 1991, 26.

11 T. Suzuki, Y. Maroyama, T. Akasaba, W. Ando, K. Kobayashi and S. Nagasane, *J. Am. Chem. Soc.*, 1994, **116**, 1359.

12 M. Ohno, T. Azuma and S. Eguchi, *Chem. Lett.*, 1993, 1833; T. G. Linssen, K. Dürr, M. Hanack and A. Hirsch, *J. Chem. Soc., Chem. Commun.*, 1995, 103.