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ScienceDirect
Tetrahedron 63 (2007) 7070–7076
Tetrahedron

Sulfur-containing dihydro-pyrrolo [60]fullerene derivatives via 1,3-dipolar cycloadditions of glycine imine esters to C_{60}

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Received 2 October 2006; revised 14 April 2007; accepted 3 May 2007
Available online 8 May 2007

Abstract—C_{60} reacts thermally with 1,3-dipoles, formed in situ, from sulfide-bearing imines of glycine esters, and affords dihydro-pyrrolo [60]fullerene derivatives containing a vinylic sulfide group, which were isolated in good yields, and characterized with ^{1}H and ^{13}C NMR, FTIR, UV–vis spectroscopies, and with FAB, ESI mass spectrometries. The new derivatives contain a sulfide, an imine, and an ester functionality for further chemical transformations. Mechanistic considerations with regard to the loss of a mercaptan molecule in the course of the cycloaddition are deployed.

1. Introduction

Fullerene chemistry has established this novel allotropic form of carbon as a standard building block in organic synthesis.[1–3] In particular, the most abundant member of the fullerene family, C_{60}, has received the highest attention as C_{60}-based molecules display a wide range of interesting features, which include nonlinear optical properties and superconductivity.[4] The exceptionally hydrophobic nature and spheroidal shape of C_{60} make it very interesting for its potential use in medicinal chemistry.[5] A series of [60]fullerene derivatives display a wide range of biological properties, including neuroprotective, enzymatic, antiapoptotic, antibacterial, DNA photocleaving, nitric oxide synthase inhibiting, and chemotactic activities.[5] Among the different classes of derivatives, fullerene-based amino acids and peptides are particularly interesting, both for structural studies and biological applications.[5a] For example, C_{60}-based 3,4-fulleroproline (Fpr), which is the fullerene homologue of the natural proline residue, has been inserted into small peptides for studying its propensity to induce β-turn conformations and to influence the cis-trans equilibrium around the tertiary amide bond.[5a,6] Fulleroproline amino acid derivatives are also shown to interact with different hydrolytic enzymes in model transesterification reactions, and to form supramolecular complexes with, and selectively discriminate between, different size calix-[*n*]arenes, cyclodextrins, and other rationally designed peptides forming cavities.[7] Incorporation of the C_{60} moiety into biologically active peptides is thus desirable to alter both the structure and the biological activity of the parent peptide.[8] Sulfur-containing fullerene derivatives represent a growing area of fullerene chemistry. Some of these systems exhibit interesting electronic properties.[9] Among them are fullerene diads and triads such as C_{60}-oligothiophene/polythiophene, C_{60}-oligothiophene-C_{60}, and C_{60}-tetrathiofulvalene/π-extended tetrathiofulvalene, which have been intensively investigated.[10] Up to date, many reactions for the introduction of sulfur into [60]fullerene have been reported. The main types of sulfur reagents for fullerene functionalization are sulfones[11] and sultines,[12] which have been used to synthesize C_{60}-porphyrin derivatives,[11d,f] a C_{60}-chlorin dyad,[13] and a C_{60}-ZnP rotaxane.[11g] However, a number of other sulfur reagents for reaction with fullerene including: stabilized sulfonium ylides,[14] α,β-unsaturated thiocarbonyl reagents,[15] *o*-thioquinone methides,[16] thiocarbonyl ylides,[17] masked 1,3-dipoles of 5-imino-1,2,4-thiadiazolidine-3-ones,[18] disulfides,[19] sulfur trioxide,[20] hydrogen sulfide,[21] and sulfur[22] have been used. A new synthetic way to sulfur-containing C_{60} derivatives was recently reported, utilizing the reaction of C_{60} with amino acid ester hydrochlorides and CS_2 in the presence of triethylamine.[23] We have recently reported preliminary results on the synthesis of sulfur-containing dihydro-pyrrolo C_{60} derivatives utilizing 1,3-dipoles of sulfide-containing imines of methyl glycinate.[24] The continuing interest in the sulfur-fullerene chemistry prompted us to report here on novel dihydro-pyrrolo [60]fullerene derivatives that contain a vinyl sulfide substituent and an ester functionality.

Keywords: Fullerenes; Azomethine ylides; 1,3-Dipolar cycloadditions; Dihydro-pyrrole; Sulfides.
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doi:10.1016/j.tet.2007.05.011

2. Results and discussion

2.1. Synthesis of C_{60} derivatives

Amino acids react with C_{60} in the presence of carbonyl compounds in a 1,3-dipolar cycloaddition mode and give fullerene-containing pyrrolidine derivatives, known as the Prato reaction.[25] Already formed imines of amino acids or their derivatives react, through their 'in situ' generated 1,3-dipoles, with C_{60} and afford five-membered ring fullero-3,4-proline derivatives,[26] which then can be transformed into fullereno-peptides.[8] The reaction of bis[alkyl-(aralkyl)-sulfanyl]methylene glycinates **1** with C_{60} in refluxing toluene solution affords 3,4-dihydro-2*H*-pyrrolo [60]fullerene derivatives **2** as the products of 1,3-dipolar cycloaddition of the respective 1,3-dipoles, generated 'in situ' from their corresponding imines, to the fullerene surface (Scheme 1). The isolation of the above new fullerene derivatives in good yields (Table 1) is always accompanied with the loss of a thiol.

The product yields are comparatively low under neutral reaction conditions but increased considerably in the presence of acid and base. The influence of acid or base catalysis in 1,3-dipolar cycloadditions is well documented in the literature.[27] The structural characterization of the products **2a–f** was established by ^{1}H and ^{13}C NMR-, FTIR- and UV–vis spectroscopy, by mass spectrometry, and by elemental analysis. All FABMS spectra showed the correct molecular ion peak $[M]^+$. The UV–vis spectra display a characteristic absorption at 360–688 nm, typical for a 1,2-adduct to C_{60}.[2] The FTIR spectra of **2a–f** show characteristic vibrations at ~1740–1750 cm^{-1} for the carbonyl group, and ~1600 cm^{-1} for the imine bond. In the ^{1}H NMR spectra of **2a–f** besides signals for methoxy and sulfanyl groups, a singlet absorption peak for the methine hydrogen atom appears at ~6.5–6.6 ppm. A point to be mentioned is the diastereotopicity of the methylene hydrogen atoms α to the sulfur atom, due to the stereogenic center at position 5.

In addition, both imine and ester resonances (~170 ppm) were evident in ^{13}C NMR spectra, together with the methine carbon atoms (~85 ppm). The two sp^3 carbon atoms of the fullerene appeared right before (~73 ppm) and after (~83 ppm) the $CDCl_3$ signal.

One interesting feature is the loss of a thiol during the course of the reaction. In all the substrates of this study the only detected (prior to isolation) and isolated products were the final products **2a–f**. At present, we are lacking experimental evidence for the formation of the 'expected' products **3**, from a 1,3-dipolar cycloaddition between the azomethine 1,3-dipoles of substrates **1** to C_{60} (Fig. 1).

Table 1. Isolated yields of product **2**

Entry, R (Ar)	Isolated yield of product **2**[a] (%)/conditions		
	Neutral	Acidic (AcOH)[b]	Basic (Et_3N)[b]
1a, Me	9 (18)	50 (87)	35 (41)
1b, Et	2 (4)	35 (56)	20 (24)
1c, Pro	2 (5)	34 (46)	26 (35)
1d, *i*-Pr	2 (3)	19 (35)	18 (43)
1e, Bu	6 (11)	36 (82)	45[c]
1f, Bn	2 (8)	28 (36)	28[c]

[a] Yields in parenthesis are based on consumed C_{60}.
[b] AcOH (100 mol %) and Et_3N were used (stoichiometric to imine **1**).
[c] No noticeable C_{60} quantity was recovered.

The above-mentioned loss of a thiol suggests two mechanistic possibilities. Either the thiol departs from the 'in situ' formed azomethine 1,3-dipole, before the cycloaddition takes place, giving rise to a very reactive (albeit hard to form) nitrile ylide 1,3-dipole, or the cycloaddition takes place through an azomethine ylide 1,3-dipole and then a thiol molecule departs from the 'expected' but never detected or isolated product **3**. In addition, the formation of 1,4-dipole via a 1,4-$[H^+]$ shift could also be considered leading to a protonated sulfur. Then, thiol elimination could take place more easily. These mechanistic pathways are shown in Scheme 2.

The lower yields observed in the neutral reaction with bulkier sulfanyl substituents in **1a–f** do not allow the differentiation between the exposed reaction pathways, since this fact could be taken as evidence in favor of either the middle pathway (i.e., nitrile ylide 1,3-dipole formation prior to cycloaddition), where the MeS– is better leaving group with regard to the bulkier groups with increased +I inductive

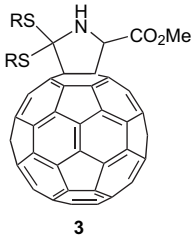

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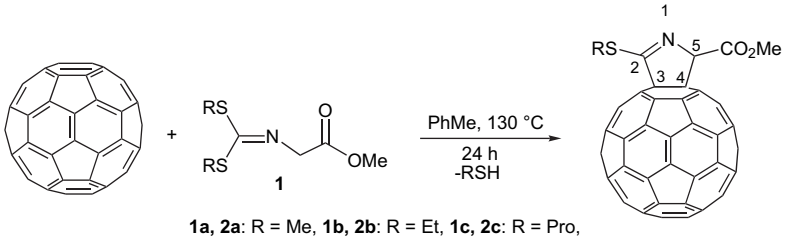
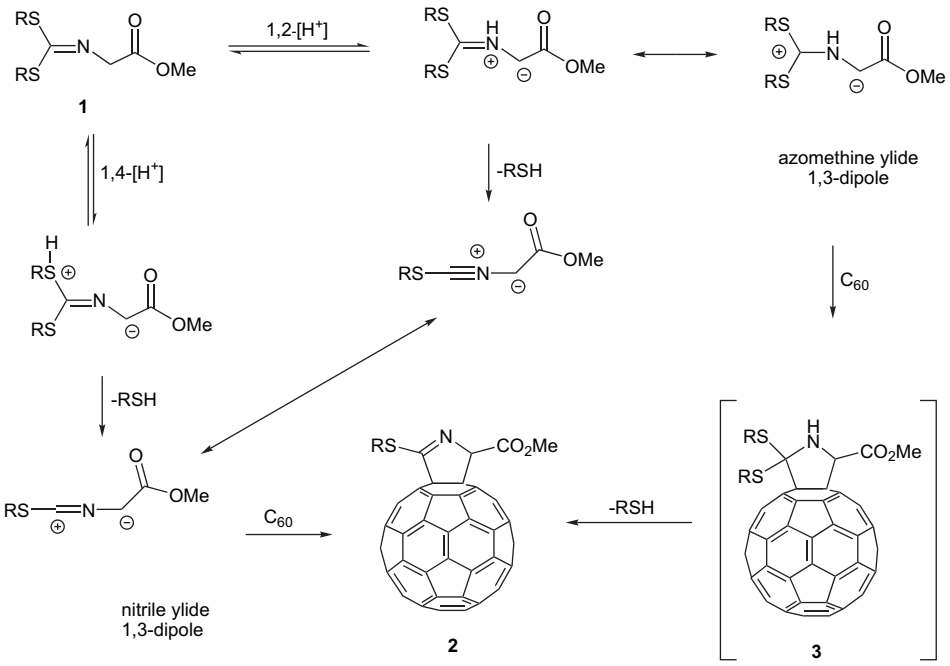
Figure 1. Expected product from the cycloaddition of 1,3-azomethine dipoles of **1a–f** to C_{60}.



1a, 2a: R = Me, **1b, 2b**: R = Et, **1c, 2c**: R = Pro,
1d, 2d: R = *i*-Pr, **1e, 2e**: R = Bu, **1f, 2f**: R = Bn

2

Scheme 1. Synthesis of [60]fullerene dihydro-pyrrolo derivative **2** via 1,3-dipolar cycloadditions of glycine ester imines **1** to C_{60}.



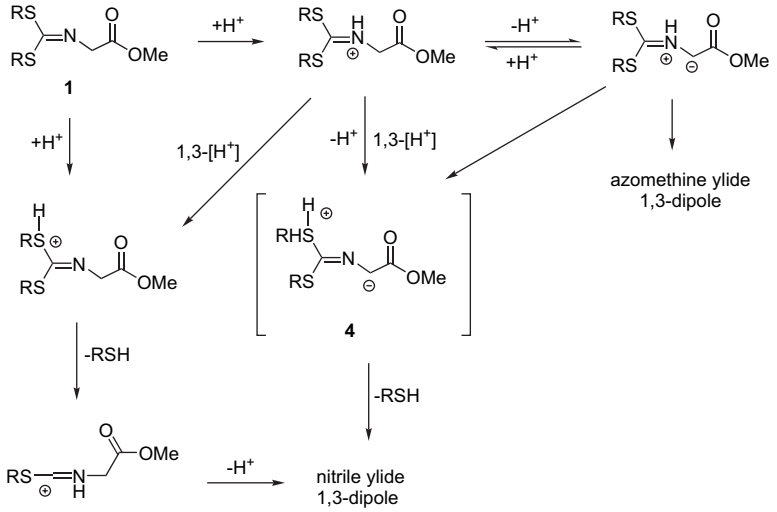
Scheme 2. Possible mechanistic paths for the formation of derivatives **2**.

effect, or the right pathway (azomethine ylide 1,3-dipole cycloaddition to C_{60}), where the steric hindrance for the reactants approach gets higher with bulkier sulfanyl substituents. In addition, the left-pathway, which proceeds via a 1,4-dipole, should favor larger sulfanyl substituents due to the stabilization of the protonated sulfur, through their increased +I inductive effect. This is clearly not the case, with the exception of **2e**, where R=Bu.

Furthermore, the higher product yields observed for the reactions under acidic conditions could be taken as an indication of the formation of both types of 1,3-dipoles through protonation of the iminic nitrogen atom. Alternatively, the S-atom could be protonated directly, and then the RSH leaves and the final step would be deprotonation of the methylene group (Scheme 3).

In this context, a reversal of the leaving group ability could be expected, since in the acidic environment a protonation of one sulfanyl substituent is reasonable making the larger substituents better leaving groups than MeSH, by more effective inductive stabilization in the protonated intermediate **4**. From the results we are unable to justify such a possibility.

Use of stronger, than AcOH, acids under the same conditions led to the isolation of product **2a** in very low yields. Indeed, with *p*-toluenesulfonic acid **2a** was isolated in 10% yield, whereas HCl gave **2a** in 8% yield. In the latter case a cycloaddition product through a 'decarboxylative' route was also isolated (12% yield), presumably through hydrolysis of the ester **2a** to give the corresponding acid, which then gave the cycloaddition with C_{60}. The spectroscopic data of the cycloadduct were identical to those reported in Ref. 24. A very



Scheme 3. Formation of 1,3-dipoles from imines **1** under acidic conditions.

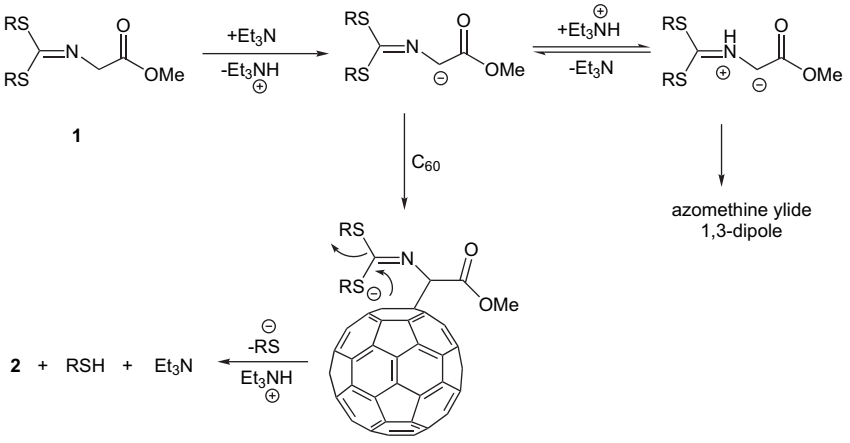
low yield of **2a** was also noticed with the use of trifluoroacetic acid (TFA).

On the other hand, when the reaction takes place under basic conditions the first step should be the α-hydrogen atom abstraction by the base, giving rise to a stabilized carbanion. This carbanion then could be added to C_{60} giving the opportunity for a nucleophilic substitution at the vinylic carbon atom of the imine functionality. In such a case the sulfanyl substituent should act as the leaving group where MeS– is the best one (although same behavior should be expected from the thiobenzyl group), Scheme 4.

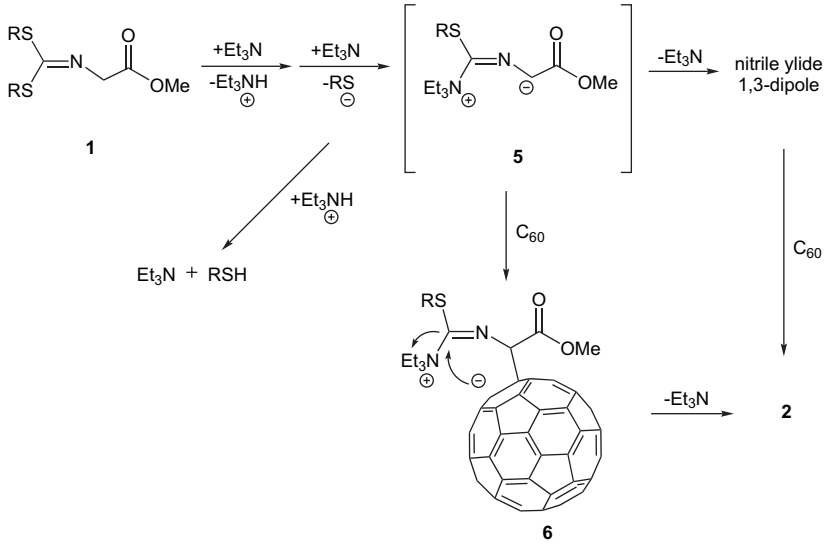
An alternative pathway for the reaction under basic conditions could be hydrogen abstraction, displacement of a –SR group by one molecule of the base, giving rise to the intermediate **5**. In the following step, electrophilic addition of C_{60} to **5** could be accompanied by liberation of Et_3N (Scheme 5).

To test further such an alternative we performed three parallel cycloaddition reactions, of **1b** (R=Et) using Et_3N, DBU {1,8-diazabicyclo[5.4.0]undecene}, DIPEA (*N*,*N*-diisopropylethylamine) as the base, in the presence of C_{60} in toluene solutions, at 130 °C for 24 h. The idea was to follow the reaction with respect to the influence of the increased steric hindrance of the base upon the possible nucleophilic displacement. After the first two hours the reaction in the presence of DBU gave baseline spots on the TLC plate, accompanied with total consumption of C_{60}, and upon chromatographic purification no product was eluted from the column. The DIPEA reaction showed after 24 h a weak product spot on TLC and after column purification gave product **2b** (R=Et) in ~4% yield (based on consumed C_{60}). From the reaction with Et_3N product **2b** was isolated in 19%. From the above result it is clear that the use of the more sterically hindered base (DIPEA) (upon nucleophilic displacement of the sulfide substituent) led to a five-fold drop in the product yield.

Results of the same direction were also obtained with the use of 1,4-diazabicyclo[2,2,2]octane (DABCO), tripropyl-, and tributyl-amine as bases in the cycloaddition reaction of **1a**, under the same conditions. Product **2a** was isolated in 26%



Scheme 4. 1,3-Dipolar cycloaddition of imines **1** to C_{60} under basic conditions.



Scheme 5. Alternative proposed path for the formation of derivatives **2** under basic conditions.

(after 7 h reaction time, because after 24 h a 4% yield of the product yield was found), 50%, and 36% yields, respectively. These results are very close to the one obtained with Et_3N (Table 1). From the yields it follows that aliphatic tertiary amines gave closely related yields of the product, while the weaker base, DABCO, gave the lower yield.

The results so far obtained for the reaction under basic conditions with **1a** and **1b** may be taken also as a qualitative indication about the effect of the sulfide substituent bulkiness, since lower product yields were observed with the larger substituent. In general the above results for the catalyzed reaction may be taken as a qualitative evidence in favor of the mechanism in Scheme 5.

3. Conclusions

We reported in this study a new mode of functionalization of C_{60} utilizing 1,3-dipolar cycloaddition reactions of sulfur-containing imines of methyl glycinate. The resultant dihydro-pyrrolo [60]fullerenes were isolated in synthetically useful yields and contain three functional groups, i.e., a sulfide, an iminic double bond, and an ester functionality, allowing for further derivatization. Possible mechanistic schemes are qualitatively discussed. Such C_{60} derivatives **2** could be of biological interest since in principle, they could act as antioxidants and also as amino acid mimics. Study on further chemical transformations and biological studies of the products is in progress.

4. Experimental

4.1. General

All NMR spectra were taken in $CDCl_3$ 98% D, and in mixtures of $CS_2/CDCl_3$ as indicated, on a Bruker-Spectrospin, Avance spectrometer. ESI MS spectra were taken on a Agilent Technologies model 1100 LC/MSD trap SL. FABMS were taken on a MICROMASS ZABSPEC spectrometer (FAB modus, with 3-nitrobenzylalcohol as matrix). FTIR spectra were taken on a Perkin–Elmer Spectrum GX, FTIR System, spectrometer. UV–vis spectra were recorded on a Hitachi U-2001 spectrophotometer. All reagents and solvents were obtained from commercial suppliers and used without further purification. Dry quality solvents were obtained according to the literature procedures[28] and stored over MS 4Å under Ar atmosphere. Thus, PhMe distilled from Na with benzophenone as an indicator; Et_3N pre-dried with KOH and then distilled from BaO. DBU and DIEA were dried according to the literature procedures.[28] Substrates **1a–f** were synthesized according to the literature procedures.[29] We were unable, though, to synthesize imines with sulfide substituents R=Ph, and R=*t*-Bu, probably due to steric hindrance reasons.

4.2. Typical synthetic procedure for the preparation of compounds 2 by the 1,3-dipolar cycloaddition reaction of imines 1 with C_{60}

A C_{60} solution (72 mg, 0.1 mmol in ~70 mL of toluene) was prepared in a 150 mL round-bottom flask equipped with a reflux condenser and a magnetic stirrer bar. To this solution, 2 mmol of imine **1** was added with a help of a small quantity of toluene (~5 mL) and the mixture set in reflux (~130 °C) for 24 h. Then ~15 mL of hexanes were added and the solution placed on the top of a SiO_2 column (pre-washed with toluene/hexanes 80:20 v/v). Unreacted C_{60} was eluted first. Additional quantities of the toluene/hexanes mixture were added until all the remaining C_{60} was eluted. Then toluene was passed through the column and products **2** were eluted. Depending on the product polarity, mixtures of toluene/EtOAc may be used (starting with 99:1 v/v). After the desired product fraction was collected, the solvent was removed in a rotary evaporator and high vacuum pump. Then the remaining amorphous brown solid was dissolved in CS_2 and precipitated by the addition of sufficient *n*-hexanes. After centrifugation, the supernatant was discarded and the above precipitation–centrifugation procedure was repeated for additional two times (by this sequence the excess of imine **1** was completely removed from products **2**). Isolated yields along with the recovered C_{60} are listed in Table 1.

4.2.1. Methyl 2-methylsulfenyl-3,4-dihydro-2*H*-pyrrolo-[60]fullerene-5-carboxylate, 2a. R_f (PhMe/EtOAc 99:1, v/v) 0.33; ^{1}H NMR (250 MHz, $CS_2/CDCl_3$ 3:1, v/v): δ 6.58 (s, 1H), 3.89 (s, 3H, OMe), 2.97 (s, 3H, SMe); ^{13}C NMR (62.9 MHz, $CS_2/CDCl_3$ 3:1, v/v): δ 174.2 (C=O), 169.2 (C=N), 152.7 (2C), 149.2 (2C), 147.7, 147.5, 146.9, 146.7, 146.3, 146.2, 146.0, 145.9 (2C), 145.8, 145.6 (4C), 145.2 (3C), 145.1, 145.0 (4C), 144.9, 143.9 (4C), 142.8 (2C), 142.5, 142.4 (2C), 141.9 (4C), 141.7, 141.6, 141.5 (2C), 140.2 (2C), 140.1, 139.4, 135.8, 135.3, 134.8, 134.2, 85.1 (CH), 83.0 (1C, sp^3, C_{60}), 73.5 (1C, sp^3, C_{60}), 52.1 (OMe), 14.9 (SMe); FTIR (KBr) ν_{max}: 2915, 2849, 1738 (C=O), 1604 (C=N), 1428, 1348, 1166, 1111, 1075, 526 cm^{-1}; UV–vis ($CHCl_3$): λ_{max} 257, 313, 427, 458, 692, 756, 797 nm; MS (FAB$^+$) *m/z*: 866 (M)$^+$; MS (ESI$^+$) *m/z*: 866.7 (MH)$^+$; Elemental Analysis for $C_{65}H_7NO_2S$ requires: C, 90.26; H, 0.82; N, 1.62; S, 3.71%; found: C, 90.60; H, 0.84; N, 1.63; S, 3.70%.

4.2.2. Methyl 2-ethylsulfenyl-3,4-dihydro-2*H*-pyrrolo-[60]fullerene-5-carboxylate, 2b. R_f (PhMe/EtOAc 99:1, v/v) 0.39; ^{1}H NMR (250 MHz, $CS_2/CDCl_3$ 3:1, v/v): δ 6.56 (s, 1H), 3.89 (s, 3H, OMe), 3.53 (qd, J_1=7.3 Hz, J_2=13.0 Hz, 1H), 3.63 (qd, J_1=7.4 Hz, J_2=13.0 Hz, 1H), 1.65 (t, J=7.4 Hz, 3H); ^{13}C NMR (62.9 MHz, $CS_2/CDCl_3$ 3:1, v/v): δ 174.3 (C=O), 170.3 (C=N), 153.0, 149.6, 148.2, 147.9, 147.2, 147.1, 146.6 (2C), 146.2, 146.3 (2C), 146.1, 146.0 (4C), 145.6, 145.5 (2C), 145.4 (2C), 145.3 (3C), 145.2, 144.3 (2C), 144.2 (2C), 143.1 (2C), 142.7 (4C), 142.2 (3C), 142.1 (2C), 142.0 (2C), 141.8 (2C), 141.7, 140.5 (2C), 140.4, 139.8, 136.1, 135.6, 135.1, 134.6, 85.6 (CH), 83.7 (1C, sp^3, C_{60}), 73.4 (1C, sp^3, C_{60}), 52.7 (OMe), 26.8 (SCH_2), 14.2 (CH_3); FTIR (KBr) ν_{max}: 2915, 2863, 1750 (C=O), 1601 (C=N), 1428, 1384, 1259, 1168, 1104, 1077, 986, 526 cm^{-1}; UV–vis ($CHCl_3$): λ_{max} 257, 312, 427, 444, 458, 692, 760, 788 nm; MS (FAB$^+$) *m/z*: 880 (M)$^+$, 919 (M+K)$^+$; MS (ESI$^+$) *m/z*: 880.7 (MH)$^+$. Elemental Analysis for $C_{66}H_9NO_2S$ requires: C, 90.10; H, 1.03; N, 1.59; S, 3.64%; found: C, 90.45; H, 1.05; N, 1.60; S, 3.62%.

4.2.3. Methyl 2-propylsulfenyl-3,4-dihydro-2*H*-pyrrolo-[60]fullerene-5-carboxylate, 2c. R_f (PhMe/EtOAc 99:1, v/v)

0.50; ^{1}H NMR (250 MHz, CS_2/$CDCl_3$ 3:1, v/v): δ 6.55 (s, 1H), 3.88 (s, 3H, OMe), 3.6 (td, J_1=7.2 Hz, J_2=12.8 Hz, 1H), 3.51 (td, J_1=7.2 Hz, J_2=12.8 Hz, 1H), 2.03 (sextet, J=7.2 Hz, 2H), 1.21 (t, J=7.2 Hz, 3H); ^{13}C NMR (62.9 MHz, CS_2/$CDCl_3$ 3:1, v/v): δ 174.5 (C=O), 170.4 (C=N), 153.0 (2C), 150.4, 149.6, 148.2, 147.9, 147.2, 147.1, 146.7, 146.6, 146.3 (2C), 146.2, 146.0 (4C), 145.6, 145.5 (2C), 145.4 (3C), 145.3 (4C), 145.2, 144.3 (2C), 144.2 (2C), 143.1 (2C), 142.7 (4C), 142.6, 142.3, 142.2, 142.1, 142.0, 141.9, 141.8 (2C), 141.7, 140.5 (2C), 140.4, 139.8, 136.1, 135.6, 135.1, 134.5, 85.5 (1C, CH), 83.7 (1C, sp^3, C_{60}), 73.4 (1C, sp^3, C_{60}), 52.7 (OMe), 34.4 (SCH_2), 22.4 (CH_2), 13.7 (CH_3); FTIR (KBr) ν_{max}: 2952, 2915, 2856, 1742 (C=O), 1602 (C=N), 1425, 1384, 1167, 1100, 1067, 986, 526 cm^{-1}; UV–vis ($CHCl_3$): λ_{max} 257, 312, 427, 462, 657, 692, 733, 752, 770, 795 nm; MS (FAB^+) *m/z*: 894 $(M)^+$, 933 $(M+K)^+$; MS (ESI^+) *m/z*: 894.7 $(MH)^+$. Elemental Analysis for $C_{67}H_{11}NO_2S$ requires: C, 90.02; H, 1.24; N, 1.57; S, 3.59%; found: C, 90.37; H, 1.26; N, 1.58; S, 3.58%.

4.2.4. Methyl 2-*iso*-propylylsulfenyl-3,4-dihydro-2*H*-pyrrolo-[60]fullerene-5-carboxylate, 2d. R_f (PhMe/EtOAc 99:1, v/v) 0.50; ^{1}H NMR (250 MHz, CS_2/$CDCl_3$ 3:1, v/v): δ 6.59 (s, 1H), 4.39 (septet, J=6.8 Hz, 1H), 3.89 (s, 3H, OMe), 1.72 (d, J=6.8 Hz, 3H), 1.65 (d, J=6.8 Hz, 3H); ^{13}C NMR (62.9 MHz, CS_2/$CDCl_3$ 3:1, v/v): δ 173.9 (C=O), 170.4 (C=N), 153.0, 149.7, 148.3, 147.9, 147.2, 147.1, 146.6 (2C), 146.3 (2C), 146.2, 146.1, 146.0 (4C), 145.6, 145.5 (2C), 145.4 (2C), 145.3 (2C), 145.2, 144.3 (2C), 144.2 (2C), 143.1 (2C), 142.7 (4C), 142.2 (2C), 142.1 (2C), 142.0, 141.9 (2C), 141.8, 141.7, 140.5 (2C), 140.4, 139.7, 136.1, 135.5, 135.0, 134.6, 85.7 (CH), 83.9 (1C, sp^3, C_{60}), 73.1 (1C, sp^3, C_{60}), 52.7 (OMe), 38.3 [$SCH(Me)_2$], 23.3 (CH_3), 23.0 (CH_3); FTIR (KBr) ν_{max}: 2952, 2922, 2856, 1753 (C=O), 1602 (C=N), 1428, 1384, 1167, 1067, 525 cm^{-1}; UV–vis ($CHCl_3$): λ_{max} 257, 312, 427, 455, 692, 755, 789 nm; MS (FAB^+) *m/z*: 894 $(M)^+$; MS (ESI^+) *m/z*: 894.7 $(MH)^+$. Elemental Analysis for $C_{67}H_{11}NO_2S$ requires: C, 90.02; H, 1.24; N, 1.57; S, 3.59%; found: C, 90.33; H, 1.25; N, 1.58; S, 3.58%.

4.2.5. Methyl 2-butylsulfenyl-3,4-dihydro-2*H*-pyrrolo-[60]fullerene-5-carboxylate, 2e. R_f (PhMe/EtOAc 99:1, v/v) 0.56; ^{1}H NMR (250 MHz, $CDCl_3$): δ 6.52 (s, 1H), 3.87 (s, 3H, OMe), 3.61 (td, J_1=7.2, J_2=12.8 Hz, 1H), 3.5 (td, J_1=7.2, J_2=12.8 Hz, 1H), 1.97 (quintet, J=7.7 Hz, 2H), 1.63 (sextet, J=7.2 Hz, 2H), 1.08 (t, J=7.2 Hz, 3H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 173.9 (C=O), 169.6 (C=N), 152.8, 149.4, 148.0, 147.7, 147.0, 146.8, 146.5, 146.1, 146.0, 145.9, 145.7 (4C), 145.4, 145.3 (2C), 145.2 (2C), 145.1, 145.0 (2C), 144.1 (2C), 144.0 (2C), 142.9, 142.6, 142.5 (2C), 142.1, 142.0 (2C), 141.9 (2C), 141.8 (2C), 141.7 (2C), 141.6 (2C), 140.3, 140.2, 139.5, 135.9, 135.3, 134.7, 134.3, 128.8, 128.0, 85.4 (CH), 83.4 (1C, sp^3, C_{60}), 73.2 (1C, sp^3, C_{60}), 52.2 (OMe), 32.2 (SCH_2), 31.1 (CH_2–C–S), 22.2 (CH_2–C–C–S), 13.8 (CH_3); FTIR (KBr) ν_{max}: 2945, 2922, 2856, 1749 (C=O), 1602 (C=N), 1425, 1384, 1167, 1063, 990, 526 cm^{-1}; UV–vis ($CHCl_3$): λ_{max} 257, 312, 427, 691, 763 nm; MS (FAB+) *m/z*: 908 $(M)^+$. Elemental Analysis for $C_{68}H_{13}NO_2S$ requires: C, 89.96; H, 1.44; N, 1.54; S, 3.53%; found: C, 90.31; H, 1.46; N, 1.55; S, 3.52%.

4.2.6. Methyl 2-benzylsulfenyl-3,4-dihydro-2*H*-pyrrolo-[60]fullerene-5-carboxylate, 2f. R_f (PhMe/EtOAc 99:1, v/v) 0.58; ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.4 (m, 5H, aromatics), 6.6 (s, 1H), 4.9 (d, J=13.0 Hz, 1H, benzylic), 4.77 (d, J=13.0 Hz, 1H, benzylic), 3.9 (s, 3H, OMe); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 174.2 (C=O), 170.3 (C=N), 152.9, 149.5, 148.0, 147.6, 147.2, 147.1, 146.6, 146.4, 146.3, 146.2, 146.1, 145.9 (4C), 145.5 (3C), 145.4, 145.3 (2C), 145.2, 145.0, 144.3 (2C), 144.2 (2C), 143.1 (2C), 142.8, 142.7 (2C), 142.2 (4C), 142.1, 142.0 (2C), 141.8 (2C), 141.7 (2C), 140.5 (2C), 140.4, 139.8, 136.1, 136.0 (2C), 135.7, 135.2, 134.6, 85.5 (CH), 83.5 (1C, sp^3, C_{60}), 73.6 (1C, sp^3, C_{60}), 52.8 (OMe), 36.8 (CH_2, benzylic); FTIR (KBr) ν_{max}: 3018, 2922, 2841, 1741 (C=O), 1598 (C=N), 1428, 1384, 1168, 1071, 901, 728, 699, 526 cm^{-1}; UV–vis ($CHCl_3$): λ_{max} 257, 312, 427, 692, 743, 788 nm; MS (FAB^+) *m/z*: 942 $(M)^+$. Elemental Analysis for $C_{71}H_{11}NO_2S$ requires: C, 90.53; H, 1.18; N, 1.49; S, 3.40%; found: C, 90.89; H, 1.19; N, 1.50; S, 3.41%.

Acknowledgements

The NMR and MS Centres of The University of Ioannina, Greece and The Friedrich Alexander University of Erlangen-Nürnberg, Germany are gratefully acknowledged for the spectra. We thank Dr. Y. Fiamegos and Dr. G. Kostakis from the Department of Chemistry, University of Ioannina, for the UV–vis spectra. Y.E. thanks the Department of Chemistry, The University of Ioannina, for an absence of leave for a sabbatical stay at the University of Elangen-Nürnberg, Germany, for the period February–July, 2005.

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