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New Route for [60]Fullerene Functionalisation in [4+2] Cycloaddition Reaction Using Indene

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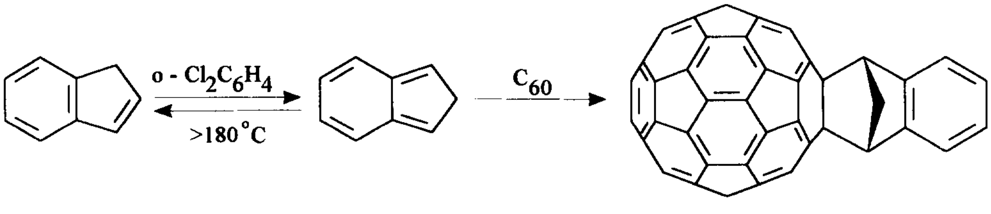
Abstract: The Diels-Alder [4+2] cycloaddition of isoindene, generated *in situ* from indene, to [60]fullerene, yielded the new [60]fullerene derivative **1**. The product was isolated by column chromatography and spectroscopically characterized. This method provides a new route to derivatives where functional groups can be rigidly attached to the [60]fullerene cage.

[60]Fullerene derivatives have become the current focus of research due to their important role in biological and materials science.[1] One of the most important methods for [60]fullerene functionalization involves formation of cycloadducts. The [4+2] cycloaddition is of special significance in this context. K.Müllen *et al* first demonstrated that [60]fullerene readily reacts with *ortho*-quinodimethanes, generated *in situ* from 1,2-bis(bromomethyl)benzene and 1,2,4,5-tetrakis(bromomethyl)benzene by iodine-induced 1,4-elimination, and forms energetically stabilized adducts.[2] This method was developed in other investigations and [60]fullerene cycloaddition products were prepared using *o*-quinodimethanes, generated from 1,2-bis(bromomethyl)benzenes by iodine-induced 1,4-elimination,[3] by thermolysis of 3-isochromanone and 1,3-dihydrobenzo[c]thiophene-2,2-dioxide and their derivatives,[4] 1,2-dihydrocyclobutabenzenes[5] and by microwave irradiation of sultines.[6] On the other hand [60]fullerene reacts with cyclopentadiene and forms cycloaddition products which are not energetically stabilized in comparison with [60]fullerene and *o*-quinodimethanes adducts.[7]



1

In this letter we describe the Diels-Alder [4+2] cycloaddition reaction of [60]fullerene with isoindene, generated thermally from indene *in situ* according to K. Alder *et al* who described a procedure for the isoindene reaction with maleic anhydride.[8] Isoindene formally reacts both as *o*-quinodimethane and as cyclopentadiene. This method provides a new route to derivatives where functional groups can be rigidly attached to the [60]fullerene cage using benzene-ring substituted indenes. The expected cycloaddition product 1 was obtained in 30-35% yield (based on reacted [60]fullerene).

Thus, the solution of [60]fullerene in *o*-dichlorobenzene was refluxed with a 12-fold excess of indene (10-12h). The reaction was monitored by TLC (silica gel, toluene) and when approximately 1/3 of [60]fullerene remained,[9] the solvent was partially evaporated under reduced pressure. Products were precipitated by ethanol and the mono-adduct 1 separated from [60]fullerene and higher adducts by column chromatography (silica gel, 1:7 benzene/hexane) and isolated as black microcrystals. Compound 1 is soluble in benzene, toluene, carbon disulfide and chloroform.

The ^{13}C NMR spectrum of 1 exhibited singlets at δ 75.45 (2C) corresponding to quaternary [60]fullerene cage carbons, at δ 53.70 (2C) and δ 58.23 (1C) - aliphatic bridge moiety carbons and at δ 124.01 (2C) and 127.50 (2C) - benzene ring carbons, together with 29 resonances in the δ 137.37 - 156.24 region[10] [4x1C, 22x2C, 3x4C (not fully resolved)] - the [60]fullerene and benzene ring carbons, comensurate with the C_s symmetry associated with [6,6] adduct.

There is significant chemical shift difference exhibited by the rigid CH$_2$ moiety protons in ^{1}H NMR spectra of 1.[10] The proton signal, which is located closer to benzene ring, is shifted 0.93 ppm upfield in comparison with the second geminal proton.

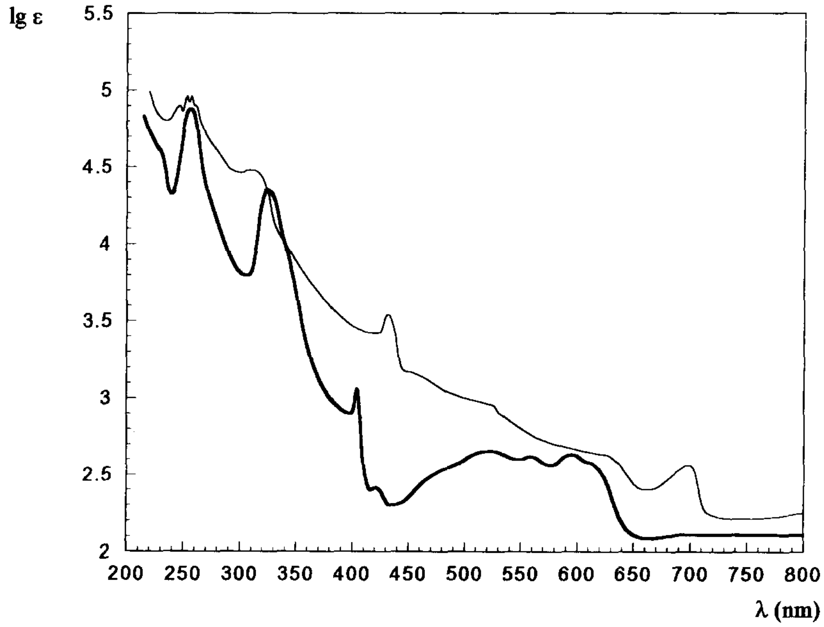


Fig. 1 UV-VIS spectra of [60] fullerene (——) and 1 (—) in hexane, c = 1x10^{-5} mol/l.

The UV-VIS spectra of 1 (Fig. 1) has some significant differences in comparison with [60]fullerene. The band at 255 nm is split and a new weak band at 700 nm appears. The band at 325 nm is hypsochromicly shifted. Very characteristic for the spectra of the Diels - Alder cycloadducts of [60]fullerene is a new sharp band with λ_{max} near 430 nm.[1d] The spectrum of 1 is much more structured in the 450-650 nm region in comparision with [60]fullerene.

The electrono-acceptor properties of compound 1 are slightly weaker in comparison with [60]fullerene. The reversible electroreduction values of 1 by cyclic voltammetry are approximately by 0.1 V higher than [60]fullerene.[11]

In summary the successful addition of isoindene to [60]fullerene demonstrates that this route could be used for [60]fullerene functionalization. [60]Fullerene derivatives with electrondonors functional groups, rigidly attached to the fullerene cage, obtained using this method can be especially attractive as new advanced materials for optics and electronics. Investigation of [60]fullerene reactions with another indene derivatives is under progress.

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9. In the case of larger excess of indene or of longer period of the reaction was, the yield of mono-adduct decreased.
10. NMR spectral data: ^{1}H NMR ($CDCl_3$), δ 2.92 (dt, 1H, $^2J=10Hz$, $^3J=1.5Hz$), 3.84 (dt, 1H), 4.89 (t, 2H, CH), 7.36 - 7.67 (m, 4H, AA`BB`system of the arene).

    ^{13}C NMR (125.76 Mhz, $CS_2/CDCl_3$ 1:1, $Cr(acac)_3$ as relaxation agent), δ 156.24(2), 154.89(2), 147.19(2), 146.27(2), 146.14(2), 146.05(4), 145.98(4), 145.67(2), 145.38(4), 145.20(2), 145.08(2), 144.57(2), 144.38(2), 143.06(2), 142.85(1),142.64(2), 142.50(2), 142.38(1), 142.27(2), 142.17(2), 142.05(2), 141.97(2), 141.87(2), 141.58(1), 141.47(1), 140.16(2), 139.67(2), 137.60(2), 137.37(2).
11. Cyclic voltammetry data $E_{red.}/E_{ox.}$ for **1**: (benzonitrile with TBAP as supporting electrolyte, glass carbon electrode, Ag/AgCl reference electrode, scan rate 200 mV/s) -0.56/-0.48, -0.97/-0.89, -1.54/-1.45; for [60]fullerene: -0.45/-0.32, -0.87/-0.75, -1.35/-1.25, -1.85/-1.72.

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