

Cycloaddition of tetracyanoethene oxide with [60]fullerene

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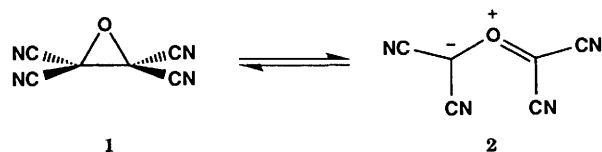
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A monoadduct of [60]fullerene having a tetracyanotetrahydrofuran structure has been isolated and characterized by FAB mass spectrometry and by ¹³C NMR spectroscopy.

The reactivity of [60]fullerene towards organic reagents has been largely investigated in recent years. Successful reactions of a variety of nucleophiles, dienes and 1,3-dipoles with [60]fullerene have been reported,^{1,2} leading to well-defined fullerene derivatives (for 1,3-dipolar cycloadditions, see refs. 3–6). Our interest in the functionalization of [60]fullerene led us to study the reactivity of tetracyanoethene oxide (TCNEO) with [60]fullerene.

A study of the reaction of TCNEO with olefins, acetylenes and aromatic compounds was reported in 1965 by Linn and Benson.⁷ This reaction was extended to naphthalene, anthracene and phenanthrene by Brown and Cookson in 1968.⁸ We have recently described the reactions of monosubstituted benzenes with TCNEO⁹ and we now report our results concerning the cycloaddition of TCNEO with [60]fullerene.

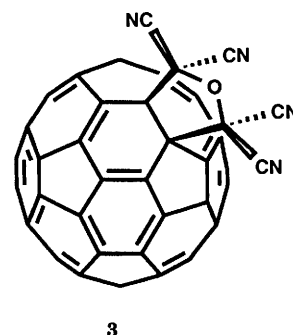
Activated at a temperature above 100 °C, the ring of tetracyanoethene oxide **1** (TCNEO) opens leading to the formation of a carbonyl ylide intermediate **2**. The intermediate



2 reacts with [60]fullerene by dipolar cycloaddition to yield the monoadduct **3**. The easy ring opening of the tetracyanotetrahydrofuran with loss of CO(CN)₂ observed in aromatic adducts could not occur in the fullerene series due to the absence of any protons.

The tetracyanotetrahydrofuran derivative **3** was characterized by FAB(+) mass spectrometry. Using EI spectrometry the fullerene adducts undergo a retro-cycloaddition and consequently the spectra show a weak abundance for the molecular peak and quite intense peak corresponding to the residue [60]fullerene. By use of FAB ionization, we obtained a FAB mass spectrum (positive ions) in which the abundance of the protonated molecule at *m/z* 865, (M + H)⁺ is higher than the abundance of the molecular ion M⁺ in the EI mass spectrum.

Diels–Alder, [3 + 2], [2 + 2], [1 + 2] and [1 + 3] cycloadditions always occur across a 6,6-ring fusion.¹⁰ Tetracyanoethene oxide **1** undergoes a [1 + 3] cycloaddition onto a double bond common to two six-membered rings of the [60]fullerene core. Evidence that the isolated cycloadduct was of the type [6 – 6] closed [60]fullerene **3**, was obtained by a ¹³C NMR spectrum recorded in CS₂. The presence of 16 carbon resonances in the fullerene region [150–130 ppm] is consistent with a high symmetry (C_{2v}) and the existence of a resonance at δ_C 65.3 attributed to sp³ fullerene carbons agrees with the assigned [6 – 6] isomer **3**. The typical cyano carbon signals appear at δ_C 108.9 and the IR spectrum shows an absorption band at ν_{max} 2240 cm⁻¹ characteristic of the cyano group. In the visible part of the electronic spectrum, recorded in CS₂, the fullerene derivative **3** has main absorption bands between



λ_{max} 510 and 440 nm (ε 1997–1719), while the spectrum of [60]fullerene shows two absorptions at λ_{max} 540 and 600 nm (ε 1075 and 950).

Experimental

1,2-(1',1',2',2'-Tetracyanomethanoxymethano)[60]fullerene

To a solution of [60]fullerene (200 mg, 2.78 × 10⁻⁴ mol) in toluene (150 cm³), TCNEO (40 mg, 2.78 × 10⁻⁴ mol) was added. The reaction mixture was stirred and heated to reflux for 15 h. The reddish solution was then evaporated to give a residue, which was dissolved in chloroform and filtered through Celite. Evaporation of the filtrate yielded the fullerene adduct **3** (54%); *m/z* (FAB) (JEOL SX102 spectrometer; matrix: 3-NOBA) 865 ([M + H]⁺, 15%) and 720 ([M – C₆N₄O], 100); δ_C(125 MHz; CS₂) 147.16, 146.15, 145.90, 145.77, 144.94, 144.35, 143.63, 143.59, 142.84, 142.44, 142.40, 141.77, 141.62, 140.79, 139.95, 136.70, 108.87 and 65.34; λ_{max}/nm 455 (ε/dm³ mol⁻¹ 1997), 480 (1719), 540 (1165) and 600 (720); ν_{max}(KBr)/cm⁻¹ 2240.

Acknowledgements

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