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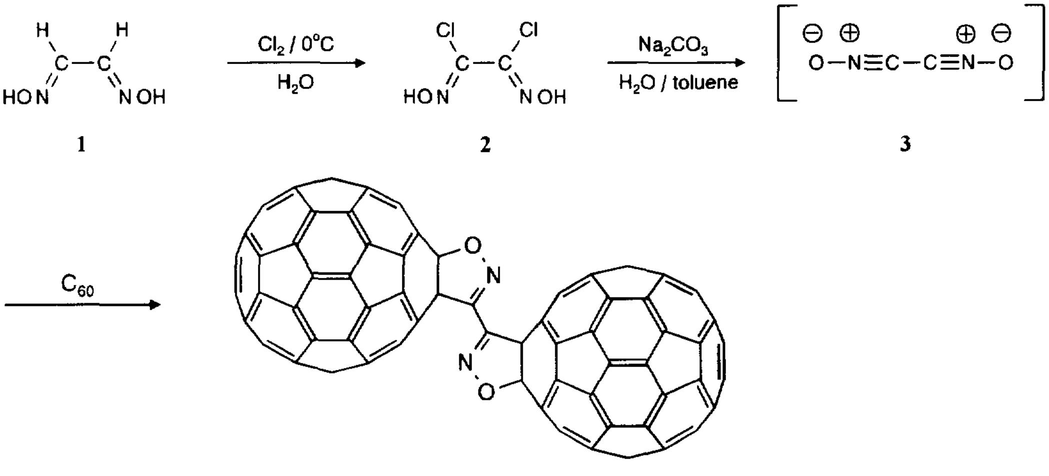
Twofold Cycloaddition of [60]Fullerene to a Bifunctional Nitrile Oxide*

Hermann Irngartinger* and Anton Weber

Organisch-Chemisches Institut der Universität, Im Neuenheimer Feld 270, D-69120 Heidelberg, Germany.

Abstract: Bi-([60]fullereno[1,2-d]isoxazole-3-yl)[1] (4) was synthesised by twofold 1,3-dipolar cycloaddition of [60]fullerene to cyanogen di-*N*-oxide (3) and characterised by ^{13}C NMR, IR, UV/VIS and MALDI-TOF mass spectrometry. Isomeric mixtures of higher molecular copolymerisation products 5 could be detected by MALDI-TOF MS. Copyright © 1996 Elsevier Science Ltd

Bifunctional cycloadditions to [60]fullerene were described for diazo compounds[2] and dienes.[3,4a] Oligomers, containing [60]fullerene in the main-chain, could be characterised for bis-*o*-chinodimethane adducts.[4b] Cyclic oligomers have been synthesised by oxidative cyclisation of diethynyl methanofullerenes.[5] In this paper we present the double 1,3-dipolar cycloaddition of [60]fullerene to cyanogen di-*N*-oxide (3) generating bi-([60]fullereno[1,2-d]isoxazole-3-yl) (4). Cycloadditions of monofunctional nitrile oxides to [60]- and [70]fullerene have been reported.[6,7,8]



The precursor dichloroglyoxime (**2**) was synthesised by chlorination of glyoxime (**1**).[9] Cyanogen di-*N*-oxide (**3**) has been generated in situ as follows: A solution of one equivalent of **2** in toluene/ether (5/1, v/v) was added dropwise under nitrogen to a two-phase system of toluene/water (20/1, v/v) containing four equivalents of C_{60} and Na_2CO_3, respectively. The mixture was stirred vigorously for 15 hours at room temperature. After separating, washing and drying the red-brown toluene phase was concentrated under reduced pressure and filtered through a silica-gel column (mobile phase toluene). The C_{60} product mixture was concentrated once more and separated by HPLC on the Buckyclutcher® I column[10] yielding 57% of compound **4** (based on employed dioxime **2**) as a black powder.

The organic fullerene derivative **4**, which contains no hydrogen, is nearly insoluble in common organic solvents including toluene, poorly soluble in CS_2, chlorobenzene and *o*-dichlorobenzene but well in 1-chloronaphthalene/2-chloronaphthalene 9/1 (v/v), which allows the determination of the molecular structure by recording a ^{13}C NMR spectrum (Fig. 1). As expected the cycloaddition occurs at the [6-6]-ring fusion of the fullerene. The number of signals indicates a C_s symmetry of the molecule. A total of 31 resonances are observed (33 signals are expected). Twenty-four of them are of double intensity, two are of quadruple intensity by accidental overlap of two signals with double intensity and five are of single intensity arising from the carbon-atoms lying in the mirror plane.

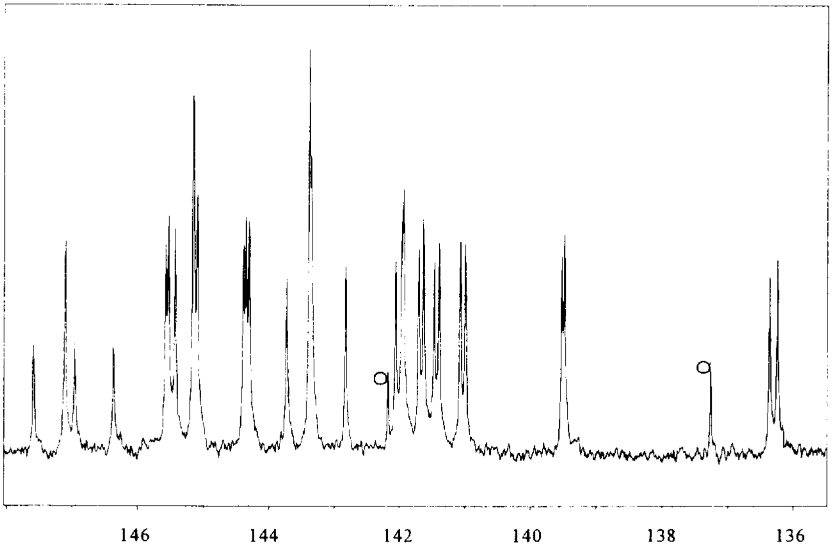
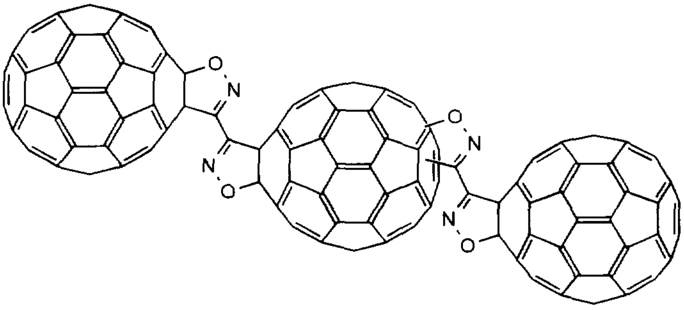


Fig. 1. 75 MHz, ^{13}C NMR spectrum recorded in 1-chloronaphthalene/2-chloronaphthalene[11] 9/1 (v/v) of compound **4** (sp^2 region). The two sp^3 carbon-atoms are appearing at δ 104.93 and δ 76.99. The marked resonances originate from a small impurity of C_{60} (δ 142.18)[12] and toluene (δ 137.26).

The UV/VIS spectrum (*o*-dichlorobenzene) shows a significant additional band at 450 nm compared with the spectrum of [60]fullerene, like other nitrile oxide adducts.[13]

In the IR spectrum the characteristic fullerene band at 527 cm^{-1} is observed.

The MALDI-TOF mass spectrum (matrix 9-nitroanthracene, negative mode) indicates the molecular ion peak at *m/z* 1525.3 (calculated 1525.4) and fragmentation peak $[M\text{-}C_{60}]^-$ at 804.5 (calculated 804.7).



5

Another small fraction could be isolated by HPLC from the reaction mixture.[11] We propose that the black solid is a mixture of isomers **5**. The molecular ions of the compounds **5** and all expected fragmentation peaks could be detected by MALDI-TOF MS (Fig. 2), within the mass accuracy utilising external calibration: $[M]^-$ **5** *m/z* 2332.1 (calc. 2330.1), $[M\text{-}C_{60}]^-$ *m/z* 1610.8 (calc. 1609.4), $[M\text{-}C_{62}N_2O_2]^-$ **4** *m/z* 1526.4 (calc. 1525.4), $[M\text{-}C_{120}]^-$ *m/z* 889.3 (calc. 888.7), $[M\text{-}C_{122}N_2O_2]^-$ *m/z* 804.9 (calc. 804.7). In a separate measurement with internal calibration[14] molecular ions of **5** were detected at *m/z* 2330.2.

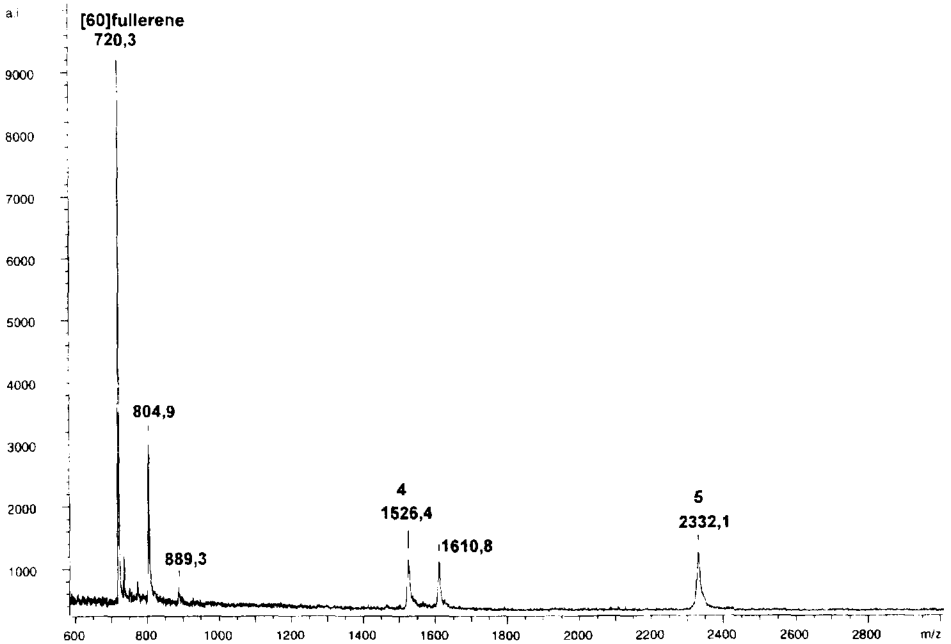


Fig.2. MALDI-TOF MS of the isomeric mixture **5**. The spectrum was observed in the negative mode using 9-nitroanthracene as matrix.

The presented new compounds **4**, **5** can be regarded as parts of a copolymer of [60]fullerene and the bifunctional nitrile oxide.

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REFERENCES AND NOTES

[*] Dedicated to Prof. Horst Prinzbach on the occasion of his 65th birthday.

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10. Preparative column (250×21.1 mm), mobile phase toluene, flow 10 ml/min, UV detection at 330 nm. Order of elution: 1. C_{60}, 7.73 min; 2. **4**, 10.30 min; 3. **5**, 15.53 min.
11. The spectrum was calibrated by the high field signal of 1-chloronaphthalene δ 123.9. Addition of other solvents (e.g. C_6D_6, *o*-$C_6Cl_2D_4$) decreased the solubility of compound **4** drastically.
12. A sample of C_{60} measured in 1-chloronaphthalene/2-chloronaphthalene/$CDCl_3$ 9/1/1 (v/v/v) showed a signal at δ 142.16.
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14. Calibrated by peaks which originate from the matrix (9-nitroanthracene): $[NO_2]^-$ *m/z* 45.99, $[C_{14}H_9O]^-$ *m/z* 193.07, $[C_{28}H_{16}N_2O_4]^-$ *m/z* 444.11 and by $[C_{60}]^-$ *m/z* 720.00.

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