Cycloaddition of Functionalized Nitrile Oxides and Fulminic Acid to [60]Fullerene☆

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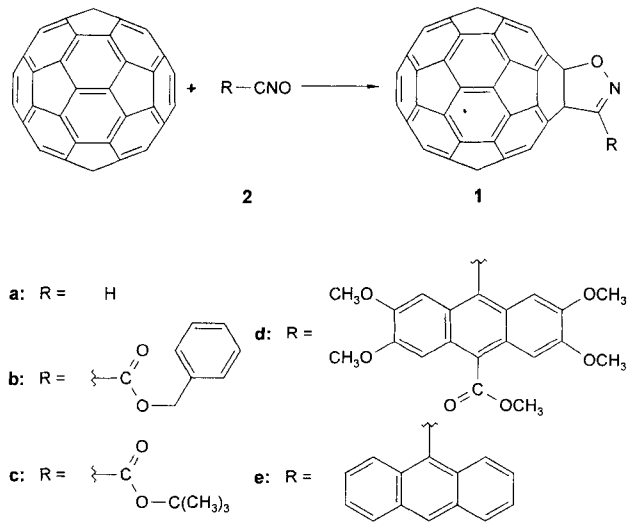
Cycloaddition of nitrile oxides to [60]fullerene led to [60]fullereno[1,2-*d*]isoxazole derivatives **1b–d**. [60]Fullereno[1,2-*d*]isoxazole (**1a**) is the corresponding cycloadduct with fulminic acid. X-ray structure analyses of compound **1b** and **1e** were determined.

Cycloadducts of nitrile oxides **2** with [60]fullerene bearing alkyl, aryl, and ethoxycarbonyl groups were already synthesized[1–4]. In this work we extend the area of functionalized substituents in compounds **1b–d** and we describe the synthesis of the parent compound [60]fullereno[1,2*d*]-isoxazole[5] (**1a**). The functionalized groups introduced here could make novel derivatives for further studies in the fullerene field.

Scheme 1

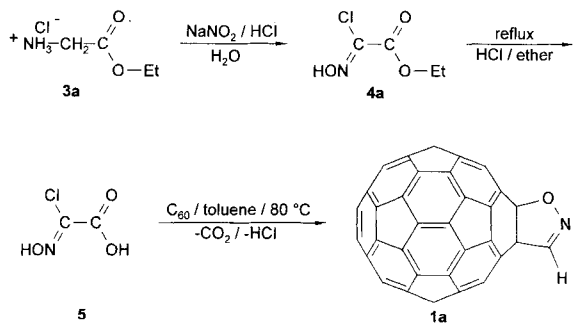


Results and Discussion

The parent compound of the fullereneisoxazoles **1a** was synthesized by heating a mixture of [60]fullerene and chlorooximidoacetic acid (**5**), which was prepared by known procedures via **3a** and **4a**[6,7]. Mono- and bisadducts were separated by chromatography on a silica gel column from the residual starting material. Obviously, the acid **5** decomposes at elevated temperature to produce fulminic acid. This is a new convenient method of in situ generation of this very reactive compound in nonpolar organic solvent[8,9].

Starting with the benzyl and *tert*-butyl ester of glycine hydrochloride **6b** and **6c**, we synthesized the corresponding esters of the chlorooximidoacetic acid **7b** and **7c** by a general procedure[6]. In situ elimination of hydrogen chloride from **7b** and **7c** furnished the nitrile oxides **2b** and **2c** which underwent 1,3-dipolar cycloaddition with an equimolar amount of [60]fullerene to afford the [60]fullereno[1,2-*d*]-isoxazoles **1b** and **1c**. The latter were separated from [60]fullerene and polyadducts by chromatography (SiO_2, toluene).

Scheme 2



In order to synthesize the [60]fullerene adduct **1d** veratrole (**8**) was treated with chloral and sulfuric acid to obtain the condensation product **9**. A second condensation step yielded the anthracene derivative **10**. The acid function was methylated with diazomethane to ester derivative **11**. Transformation of the aldehyde function with hydroxylamine hydrochloride furnished the oxime **12**. By oxidation of **12** with NBS the nitrile oxide **2d** was generated and the cycloaddition of **2d** to [60]fullerene was carried out in toluene. The cycloadduct **1d** could be purified by chromatography (SiO_2, toluene). 3-(9-Anthryl)-[60]fullereno[1,2-*d*]isoxazole (**1e**) is already known as CS_2 inclusion compound[3] and is now crystallized as a toluene clathrate. High-resolution FAB mass spectra for monoadducts **1b–1d** were recorded.

The ^{13}C-NMR spectra of **1a–d** indicate the addition of the nitrile oxides to the (6,6) bond of [60]fullerene since from the number of signals in the fullerene region mirror

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Scheme 3

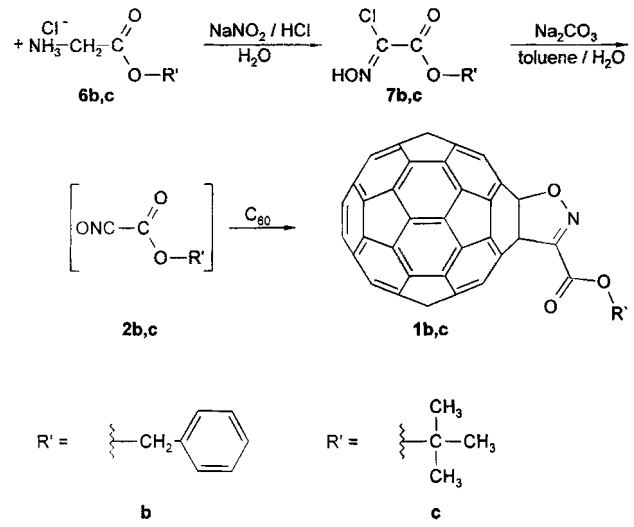
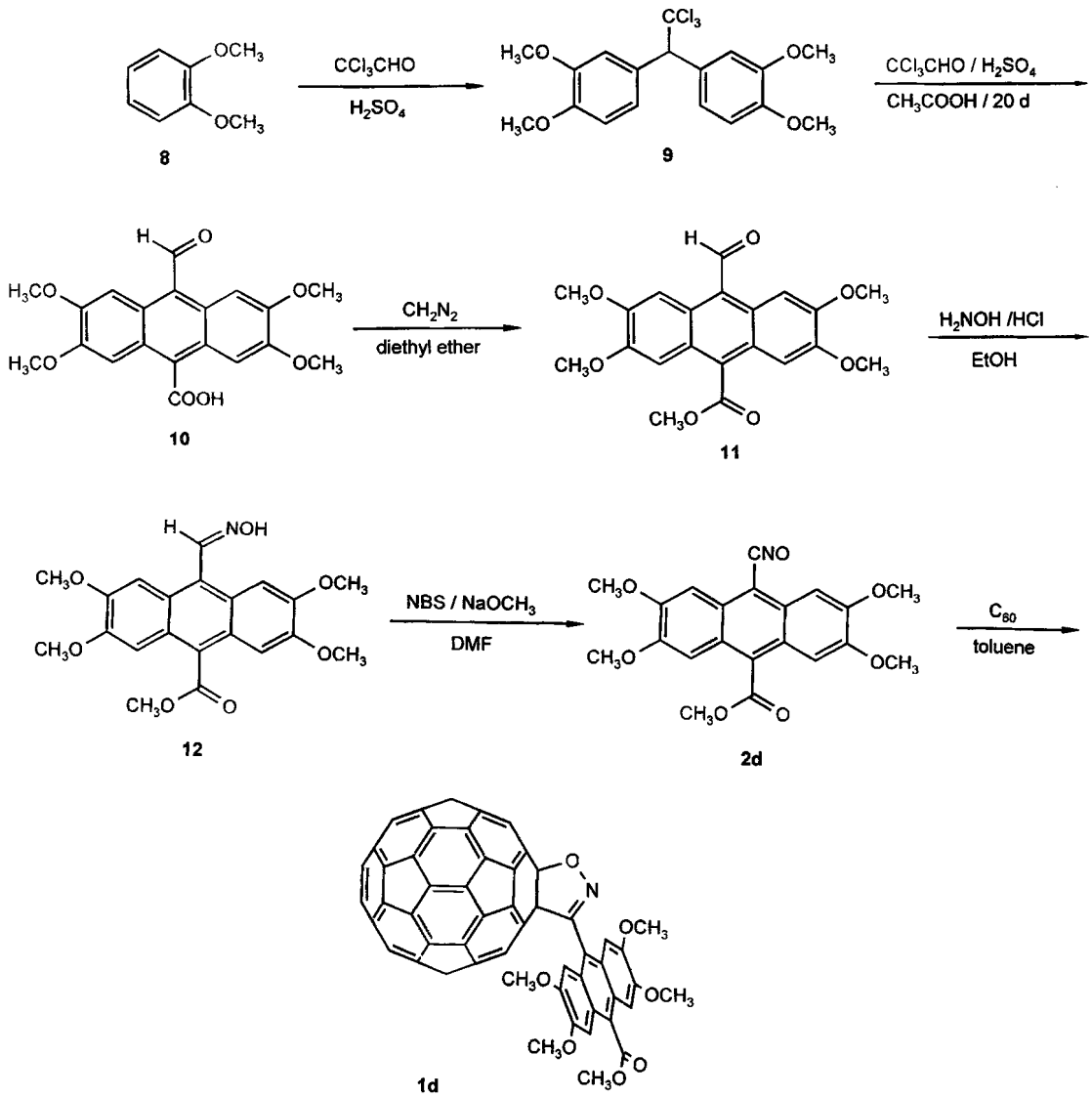


Table 1. ^{13}C-NMR spectra of **1a–d** (δ values, in 1-chloronaphthalene/2-chloronaphthalene/[D$_6$]acetone, 9:1:1[10] for **1a–1c**, and in $CDCl_3$ for **1d**)

	1a	1b	1c	1d
C(sp^2) fullerene (number of signals)	136.77-147.69 (30)	136.53-147.63 (24)	136.62-147.67 (24)	135.67-147.89 (26)
relative intensity	28×2C, 2×1C	6×4C, 16×2C 2×1C	1×6C, 4×4C 17×2C, 2×1C	1×6C, 2×4C 21×2C, 2×1C
C(sp^2) heterocycle	144.95	148.06	149.14	153.67
C(sp^3) heterocycle	79.15, 102.14	75.94, 106.67	76.31, 106.53	82.59, 119.80
substituents		68.80, 129.27 129.32, 129.35 135.27, 160.08 (C=O)	28.48, 85.38 159.27 (C=O)	52.64, 55.82 56.08, 102.74 103.85, 124.52 126.75, 128.23 129.04, 150.16 150.51, 170.24

Scheme 4



symmetry can be deduced (Table 1). Both signals for the sp^3 hybridized carbon atoms at the fusion of fullerene and isoxazoline are found upfield from the fullerene region. We assign the resonances at lower field (δ = 102–119, Table 1) to the carbon atoms bound to the oxygen atom in the heterocycle. Assignment of the signal at δ = 144.95 (within the fullerene region, Table 1) of compound **1a** could be confirmed by DEPT experiment. The absorption of the proton (δ = 8.39) in compound **1a** is deshielded by about 1 ppm compared to known isoxazolines[8,11] as revealed by the results for the methyl derivative of **1a**[12]. The remaining resonance of the ^{13}C-NMR and ^{1}H-NMR spectra and the absorption of the IR spectra of **1a–d** were detected in the expected region.

Table 2. UV/Vis spectra of **1a–d** dissolved in chlorobenzene

	1a	**1b**	**1c**	**1d**
λ [nm]	423 (3.32)			
(lg ε [1000 cm²/mol])	453 (3.22)	452 (3.06)	450 (2.97)	455 (3.09)
	540 (2.96)	538 (2.82)	544 (2.71)	545 (2.88)
	602 (2.72)	600 (2.54)	595 (2.44)	610 (2.61)
	680 (2.34)	668 (2.12)	672 (2.01)	690 (2.16)

Compared with the UV/Vis spectrum of [60]fullerene a significant additional band at 450 nm was found for the derivatives **1a–d** (Table 2). By chromatography (SiO_2, toluene) a fraction of a mixture of isomeric bisadducts was also separated from cycloadducts of **2a–c** with [60]fullerene and analyzed by MALDI-TOF mass spectrometry.

X-ray Structure Analyses of 1b and 1e

The crystal and molecular structures of **1b** and **1e** were determined by X-ray diffraction (Figure 1). Both compounds crystallize from toluene as clathrates with toluene disordered around centers of symmetry. The structure of CS_2 inclusion crystals of **1e** is already known[3]. The fullerene derivative **1e** lies on a crystallographic mirror of symmetry (Figure 2). The $C(sp^3)-C(sp^3)$ single bond of the fullerene at the (6,6) bond where the addition has taken place is elongated [C1–C2 1.576(3) and 1.564(4) Å for **1b** and **1e**, respectively]. Besides other strain effects[13] the ecliptic orientation of all substituents of this bridging bond in a [4.4.3]propellane subunit may be the reason for this lengthening. The neighboring $C(sp^3)-C(sp^2)$ bonds [1.524(4/10)[14] **1b**, 1.523(3/7) Å **1e**] are also relatively long. The four (6,6) bonds adjacent to the cycloaddition site [1.369(4/8) **1b**, 1.366(3) Å **1e**] are shorter than the average of the other bonds of the same type in the fullerene. This observation is due to the effect of less conjugation. The remaining (6,6) bonds have a length of 1.390(4/9) Å for **1b** and 1.387(3/8) Å for **1e** on the average. The lengths of the $C(sp^2)-C(sp^2)$ (5,6) bonds are 1.447(4/11) **1b** and 1.447(3/10) Å **1e**.

The pyramidalization angles of the sp^2-hybridized fullerene carbon atoms were calculated as shown in Figure 3. The values for these angles around the C1–C2 bond (Figure 4) are significantly smaller than the average [**1b** 33.2(4/20)°; **1e** 31.7(2/5)°] of the remaining fullerene atoms.

Figure 1. Molecular structures of compounds **1b** and **1e** in the crystal

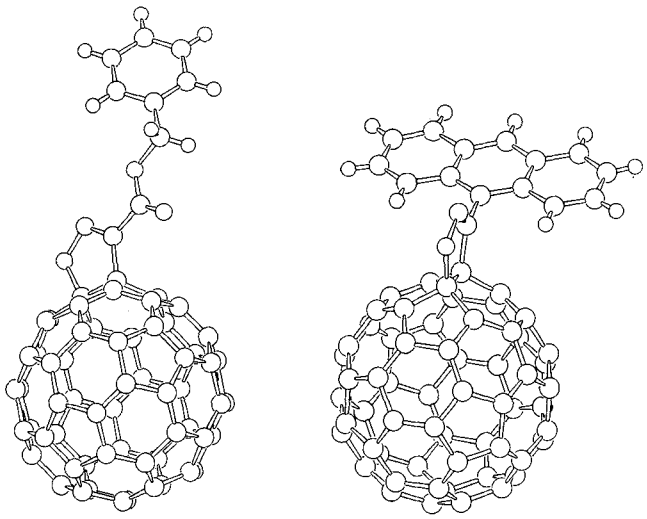


Figure 2. Packing arrangements of **1e**

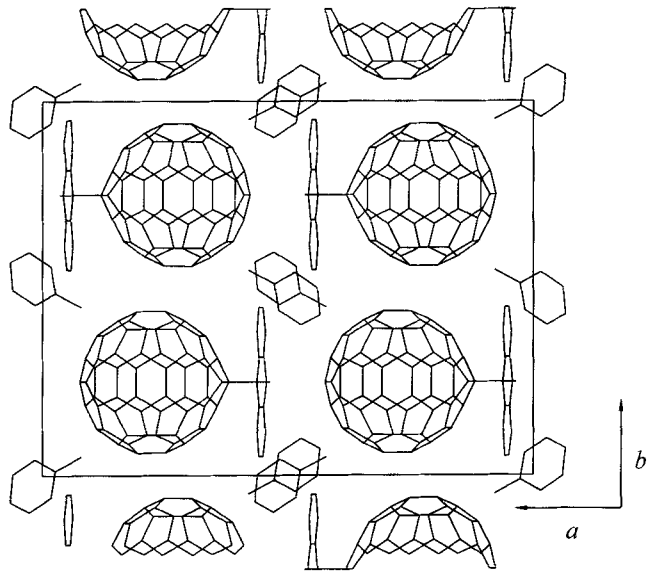
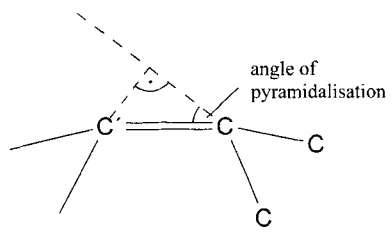
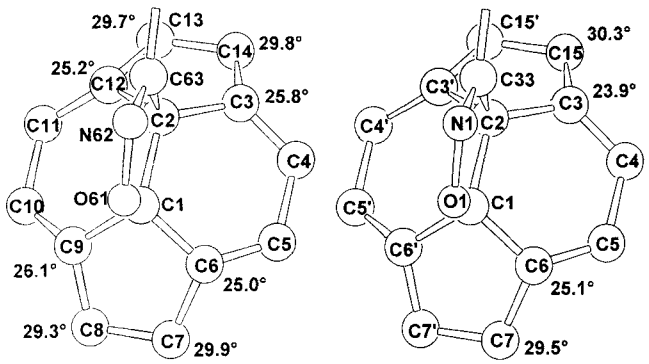


Figure 3. The shortest possible distance from C′ to the plane defined by the three C atoms was determined; with this length and the (6,6) bond distance the angle of pyramidalization was calcualted



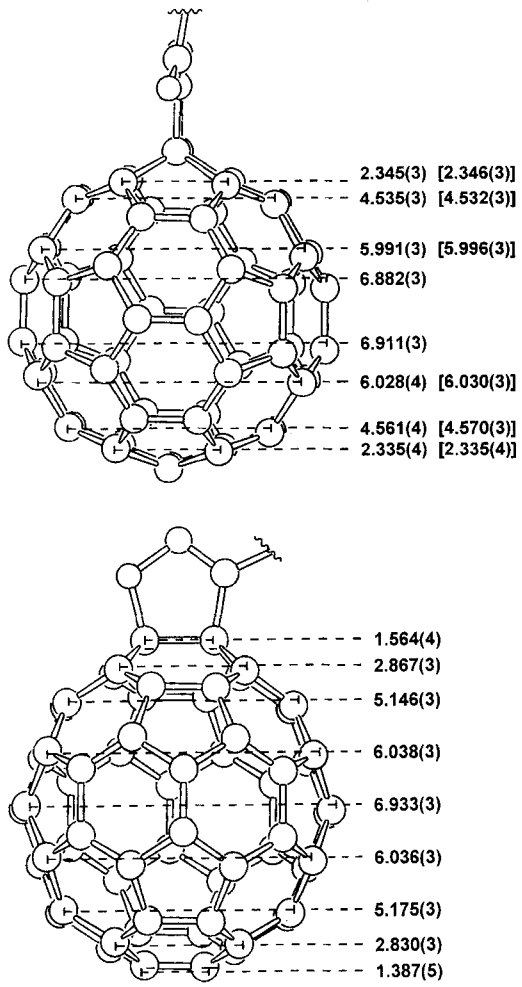
The deformation of the fullerene framework, which arises from the cycloaddition, is illustrated in Figure 5. The distances of the carbon atoms in the hemisphere of the cycloaddition tend to shorter values than the corresponding distances in the other hemisphere, except the C3–C6 distance

Figure 4. Cut-out from the compounds **1b** (left) and **1e** (right) at the position of addition with relevant pyramidalization angles



[2.867(3) compared with 2.830(3), Figures 4 and 5]. This exception is due to the elongation of the C1–C2 bond [1.564(4)]. We believe that the driving force for the unsymmetrical deformation is the global strain relief within the fullerene core.

Figure 5. Selected atomic distances in compound **1e** (in Å); the values in brackets are related to the corresponding atoms of the fullerene sphere on the opposite side of the projection



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Experimental

General: NMR: Bruker AC 200 (50 MHz for ^{13}C), Bruker AC 300 (300 MHz and 75 MHz, for ^{1}H and ^{13}C, respectively); chemical shifts are relative to the solvent signals ([D$_6$]acetone: δ_H = 2.04, δ_C = 29.8; C_6D_6: δ_H = 7.2; $CDCl_3$: δ_H = 7.26, δ_C = 77.0). – IR: Bruker IFS 66. – EI MS: Finnigan 3200. – FAB MS: JEOL JMS-RSX 102A, positive ion mode (matrix 3-nitrobenzyl alcohol/TFA, 99:1) and JEOL JMS-700, negative ion mode (matrix nitrobenzyl alcohol). – MALDI-TOF MS: Bruker Biflex, negative ion mode (matrix 9-nitroanthracene). – UV: HP 8452 (diode array). – Elemental Analyses: Heraeus CHN-O-Rapid.

Crystal-Structure Investigation: For crystal data see Table 3[16]. Data collection was performed with an Enraf Nonius CAD4 diffractometer (Mo-K_α radiation, graphite monochromator, ω-2Θ scan). The structures were solved by direct methods SIR92[17] (compound **1b**) and MULTAN[18] (compound **1e**). The structural parameters of the non-hydrogen atoms were refined anisotropically on F^2 by full-matrix least-squares technique. The disordered carbon atoms of the toluene molecules in **1b** and all hydrogen atoms were refined isotropically. All calculations were carried out with the MolEN[19] program for **1b** and with SHELXL-93[20] for **1e**.

[60]Fullereno[1,2-d]isoxazole (**1a**): Freshly prepared chlorooximidoacetic acid (**5**) (51 mg, 4.2 · 10^{-4} mol) was added to a stirred solution of C_{60} (100 mg, 1.4 · 10^{-4} mol) in 150 ml of toluene under nitrogen. The mixture was heated at 80 °C for 5 h. After cooling to room temp. the red-brown solution was concentrated in vacuo and the residue chromatographed on a silica gel column (toluene) to yield 19.2 mg (18% based on employed C_{60}) of the black monoadduct and 8.3 mg of the black bisadduct. – ^{1}H NMR (300 MHz, CS_2/[D$_6$]acetone, 10:1): δ = 8.39 (s). – ^{13}C NMR (75 MHz, 1-chloronaphthalene/2-chloronaphthalene/[D$_6$]acetone, 9:1:1): δ = 79.15 (1 C), 102.14 (1 C), 136.77 (2 C), 136.89 (2 C), 138.11 (toluene), 140.05 (2 C), 140.49 (2 C), 141.66 (2 C), 142.02 (2 C), 142.10 (2 C), 142.13 (2 C), 142.18 (2 C), 142.24 (2 C), 142.61 (2 C), 142.67 (2 C), 142.76 (2 C), 143.24 (2 C), 143.98 (2 C), 144.07 (2 C), 144.22 (2 C), 144.73 (2 C), 144.95 (CH, distinguished by DEPT experiment), 145.03 (2 C), 145.06 (2 C), 145.14 (2 C), 145.16 (2 C), 145.38 (2 C), 145.78 (2 C), 145.86 (2 C), 146.07 (2 C), 146.10 (2 C), 146.19 (2 C), 147.09 (1 C), 147.69 (1 C). – IR (KBr): $\tilde{\nu}$ = 3063 cm^{-1} (w, CH), 1599 (m, C=N), 1430 (m, fullerene), 1181 (m, fullerene), 839 (m), 526 (s, fullerene). – UV (chlorobenzene): λ_{max} (lg ε) = 423 nm (3.32), 453 (3.22), 540 (2.96), 602 (2.72), 680 (2.34). – FAB MS; *m/z* = 763.0 [M$^-$]. – $C_{61}HNO$ (763.7)[21]: calcd. C 95.94, H 0.13, N 1.83; found C 95.51, H 0.79, N 1.78. – MALDI-TOF MS (bisadducts); *m/z* (%): 807.2 (83) [M$^-$, $C_{61}{}^{13}CH_2N_2O_2$], calcd. 807.0; 806.2 (100) [M$^-$, $C_{62}H_2N_2O_2$], calcd. 806.0; 764.1 (32) [$C_{60}{}^{13}CHNO$], calcd. 764.0; 763.1 (43) [$C_{61}HNO$], calcd. 763.0.

Benzyl Chlorooximidoacetate (**7b**): Glycine ester hydrochloride (**6b**) (0.84 g, 4.2 · 10^{-3} mol) was dissolved in 3 ml of water and 0.35 ml of hydrochloric acid (d = 1.19 kg dm^{-3}, 4.2 · 10^{-3} mol HCl). The stirred solution was cooled to −15 °C, and a solution of $NaNO_2$ (0.29 g, 4.2 · 10^{-3} mol) in 0.42 ml of water was added dropwise during a period of 20 min. A second equivalent of HCl and a second equivalent of $NaNO_2$ were added in the same manner.

Stirring was continued for 30 min at −15 °C. The organic layer was separated and the aqueous layer extracted with ethyl ether. The combined organic layers were dried (Na_2SO_4) and concentrated in vacuo to yield a slightly yellow oil. The crude product was crystallized at −28 °C and then recrystallized from hexane to afford 0.28 g (32%) of a white solid, m.p. 91−93 °C. − ^{1}H NMR (300 MHz, [D$_6$]acetone): δ = 5.36 (s, 2H, OCH_2), 7.4−7.5 (m, 5H, aromatic), 12.43 (s, 1H, NOH). − ^{13}C NMR (75 MHz, [D$_6$]acetone): δ = 68.9 (CH_2), 129.2 (aromatic C), 129.3 (aromatic C), 129.4 (aromatic C), 131.0 (C=NOH), 136.3 (aromatic C), 159.5 (C=O). − IR (KBr): $\tilde{\nu}$ = 3305 cm^{-1} (m, OH), 3065 (w, CH), 3037 (w, CH), 3010 (w, CH), 1747 (s, C=O), 1411 (m), 1278 (m), 1088 (s), 1030 (s), 749 (m), 698 (m). − EI MS (70 eV); *m/z* (%): 215.0 (0.1) [M^+, $C_9H_8{}^{37}ClNO_3$], 213.0 (0.3) [M^+, $C_9H_8{}^{35}ClNO_3$], 197.9 (12.6) [$(M - OH)^+$, $C_9H_7{}^{37}ClNO_2$], 195.9 (39.4) [$(M - OH)^+$, $C_9H_7{}^{35}ClNO_2$], 106.9 (100) [$C_7H_7O^+$], 90.9 (100) [$C_7H_7^+$], 76.9 (86.8) [$C_6H_6^+$], 64.8 (100) [$C_5H_5^+$]. − $C_9H_8ClNO_3$ (213.6): calcd. C 50.60, H 3.77, Cl 16.60, N 6.56; found C 50.63, H 3.79, Cl 16.10, N 6.51.

tert-Butyl Chlorooximidoacetate (**7c**): The compound was synthesized in the same manner as described for chlorooxime **7b**. The crude product could not by purified. ^{1}H-NMR data indicated a very poor yield.

3-Benzyloxycarbonyl-[60]fullereno[1,2-d]isoxazole (**1b**): To a stirred two-phase mixture of C_{60} (85 mg, 1.2 · 10^{-4} mol) in 200 ml of toluene and Na_2CO_3 (125 mg, 1.2 · 10^{-3} mol) in 15 ml of H_2O a solution of chlorooxime **7b** (25.2 mg, 1.2 · 10^{-4} mol) in 30 ml of toluene was added dropwise under nitrogen during 3 h at room temp. A color change from violet to brown could be observed and stirring was continued for 15 h. After separation of the phases, the toluene phase was dried (Na_2SO_4) and concentrated in vacuo. The residue was chromatographed on a silica gel column (toluene) to furnish 35.2 mg (23.7%) of the black monoadduct **1b** R_f = 0.74 and 30.1 mg of the black bisadducts R_f = 0.65−0.54, − m.p. >320 °C. − ^{1}H NMR [300 MHz, CS_2/C_6D_6, 10/1 (v/v)]: δ = 5.36 (s, 2H, CH_2), 7.3−7.4 (m, 5H, aromatic H). − ^{13}C NMR (50 MHz, 1-chloronaphthalene/2-chloronaphthalene/[D$_6$]acetone[10], 9:1:1): δ = 68.80 (CH_2), 75.94 (1 C), 106.67 (1 C), 129.27 (aromatic C), 129.32 (aromatic C), 129.35 (aromatic C), 135.27 (aromatic C), 136.53 (2 C), 137.04 (2 C), 138.08 (toluene), 140.02 (2 C), 140.07 (2 C), 141.64 (2 C), 141.68 (2 C), 142.02 (2 C), 142.19 (2 C), 142.27 (2 C), 142.30 (4 C), 142.62 (4 C), 142.70 (2 C), 143.45 (2 C), 143.97 (4 C), 144.29 (2 C), 145.00 (4 C), 145.09 (2 C), 145.42 (2 C), 145.78 (4 C), 146.06 (2 C), 146.18 (4 C), 147.03 (1 C), 147.09 (2 C), 147.63 (1 C), 148.06 (1 C), 160.08 (C=O). − IR (KBr): $\tilde{\nu}$ = 2921 cm^{-1} (m, CH), 2851 (w, CH), 1720 (s, C=O), 1585 (m), 1335 (m), 1172 (m), 1143 (s), 1098 (w), 731 (m), 694 (m), 526 (s, fullerene). − HRFAB MS; *m/z* = 897.0409, $C_{69}H_7NO_3$ calcd. 897.0426 [M^+]. − UV (chlorobenzene): λ_{max} (lg ε) = 314 nm (4.53), 452 (3.06), 538 (2.82), 600 (2.54), 668 (2.12). − MALDI-TOF MS (bisadducts); *m/z* (%): 1075.4 (47) [M^-], calcd. 1075.0; 897.4 (22) [$M - C_9H_7NO_3]^-$, calcd. 897.8. − Single crystals were obtained by evaporation of toluene from a saturated solution within two weeks at room temperature. Crystallographic data for **1b**, see Table 3.

3-tert-Butyloxycarbonyl-[60]fullereno[1,2-d]isoxazole (**1c**): Mono- and bisadducts were prepared as described above. The crude precursor **7c** was employed. Yield 79.1 mg (1.5%, based on employed ester **6c**); m.p. >320 °C. − ^{1}H NMR (300 MHz, CS_2/[D$_6$]acetone, 10:1): δ = 1.68 (s). − ^{13}C NMR (75 MHz, 1-chloronaphthalene/2-chloronaphthalene/[D$_6$]acetone, 9:1:1): δ = 28.43 (CH_3), 76.31 (1 C), 85.38 [$C(CH_3)_3$], 106.53 (1 C), 136.62 (2 C), 137.03 (2 C), 138.11 (toluene), 140.01 (2 C), 140.13 (2 C), 141.69 (2 C), 141.72 (2 C), 142.12 (2 C), 142.25 (2 C), 142.32 (2 C), 142.34 (2 C), 142.67 (6 C), 142.74 (2 C), 143.89 (2 C), 144.04 (4 C), 144.37 (2 C), 145.06 (4 C), 145.17 (2 C), 145.50 (2 C), 145.83 (4 C), 146.08 (2 C), 146.22 (4 C), 147.08 (1 C), 147.23 (2 C), 147.67 (1 C), 149.14 (1 C), 159.27 (C=O). − IR (KBr): $\tilde{\nu}$ = 2976 cm^{-1} (w, CH), 2924 (w, CH), 2851 (w, CH), 1738 (s, C=O), 1714 (s, C=O), 1630 (m), 1593 (m), 1369 (m), 1347 (m), 1140 (s), 1003 (m), 825 (m), 527 (s, fullerene). − UV (chlorobenzene): λ_{max} (lg ε) = 315 nm (4.27), 450 (2.97), 544 (2.71), 595 (2.44), 672 (2.01). − HRFAB MS; *m/z*: 863.0590, $C_{66}H_9NO_3$ calcd. 863.0582 [M^+]. − $C_{66}H_9NO_3$ (863.8)[21]: calcd. C 91.77, H 1.05, N 1.62; found C 91.76, H 1.21, N 1.44. − MALDI-TOF MS (bisadducts); *m/z* (%): 1006.1 (94) [M^-, $C_{72}H_{18}N_2O_6$], calcd. 1006.1; 1007.1 (100) [$C_{71}{}^{13}CH_{18}N_2O_6$], calcd. 1007.1; 863.0 (44) [$M - C_6H_9NO_3]^-$, calcd. 863.1.

1,1-Bis(3′,4′-dimethoxyphenyl)-2,2,2-trichloroethane (**9**) was prepared by a literature procedure[22]. − ^{1}H NMR (300 MHz, C_6D_6): δ = 3.37 and 3.44 each (s, 6H, OCH_3), 4.95 (s, 1H, 1-H), 6.57 (d, *J* = 8.4 Hz, 2H, 5′-H), 7.15−7.21 (m, 4H, aromatic). − ^{13}C NMR (75 MHz, C_6D_6): δ = 55.47 and 55.78 (OCH_3), 70.58 ($CHCCl_3$), 103.39 ($CHCCl_3$), 111.91 (aromatic C), 114.86 (aromatic C), 122.93 (aromatic C), 131.41 (1′-C), 149.99 and 150.21 (3′-C, 4′-C).

10-Formyl-2,3,6,7-tetramethoxyanthracene-9-carboxylic Acid (**10**) was synthesized by the known literature procedure[23]. − ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 4.70 and 4.78 each (s, 6H, OCH_3), 7.94 and 8.15 each (s, 2H, aromatic), 12.13 (s, 1H, CHO), (proton of the acid not detectable). − ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 55.17 and 55.57 (OCH_3), 101.23 and 102.40 (C-1, C-4, C-5, C-8), 121.13 (q, aromatic), 122.21 (q, aromatic), 127.67 (q, aromatic), 133.38 (q, aromatic), 149.45 and 151.61 (C-2, C-3, C-6, C-7), 170.08 (COOH), 193.88 (CHO).

Methyl 10-Formyl-2,3,6,7-tetramethoxyanthracene-9-carboxylate (**11**) was prepared by the general method described in ref.[24]. − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.01 (s, 6H, OCH_3), 4.07 (s, 6H, OCH_3), 4.17 (s, 3H, $COOCH_3$), 7.03 (s, 2H, aromatic), 8.23 (s, 2H, aromatic), 11.29 (s, 1H, CHO). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 52.68 ($COOCH_3$), 55.66 (OCH_3), 55.98 (OCH_3), 101.06 (aromatic, C-H), 102.62 (aromatic, C-H), 122.42 (q), 123.94 (q), 128.25 (q), 131.26 (q), 149.99 (q), 151.96 (q), 169.98 ($COOCH_3$), 192.44 (CHO).

Methyl 10-Hydroximidomethyl-2,3,6,7-tetramethoxyanthracene-9-carboxylate (**12**) was prepared from 0.50 g (1.2 · 10^{-3} mol) of the aldehyde **11** in 150 ml of ethanol at 70 °C by the addition of a solution of 2.00 g (2.9 · 10^{-2} mol; 28 equiv.) of hydroxylamine hydrochloride in 20 ml of water. The mixture was neutralized with $NaHCO_3$. After the suspension had been heated for 30 min at reflux, it was diluted with 100 ml of water. The precipitate was filtered and washed several times with water. Yield: 450 mg (91.7%) of orange-yellowish crystals, m.p. 264 °C. − ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 3.91 (s, 6H, OCH_3), 3.93 (s, 6H, OCH_3), 4.13 (s, 3H, $COOCH_3$), 7.06 (s, 2H, aromatic), 7.65 (s, 2H, aromatic), 9.10 (s, 1H, CHN), 11.71 (s, 1H, OH). − ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 52.65 ($COOCH_3$), 55.27 (OCH_3), 55.29 (OCH_3), 102.05 (aromatic CH), 102.88 (aromatic CH), 123.09 (q), 123.37 (q), 124.83 (q), 125.19 (q), 146.88 (CHN), 149.66 and 149.89 (C-2, C-3, C-6, C-7), 169.48 ($COOCH_3$). − IR (KBr): $\tilde{\nu}$ = 3429 cm^{-1} (br, OH), 3114 (w, CH), 2997 (w, CH), 2954 (w, CH), 2832 (w, CH), 1717 (m, C=O), 1690 (m), 1637 (w), 1532 (m), 1498 (s), 1464 (m), 1436 (s), 1357 (m), 1283 (m), 1247 (s, C−O), 1206 (m), 1164 (m), 1071 (m), 1042 (m), 983 (m), 930 (m), 833 (w), 573 (w). − UV ($CHCl_3$): λ_{max} (lg ε) = 278 nm (4.50), 386 (3.80). − EI MS (70 eV); *m/z* (%): 400 (100) [MH^+], 399 (45) [M^+], 383 (13), 382 (45),

368 (10). – $C_{21}H_{21}NO_7$ (399.4): calcd. C 63.15, H 5.30, N 3.51; found C 62.90, H 5.30, N 3.44.

Methyl 2,3,6,7-Tetramethoxy-10-oxycyanoanthracene-9-carboxylate (**2d**): In a 25-ml round-bottomed flask, fitted with a dropping funnel, 150 mg ($3.8 \cdot 10^{-4}$ mol) of the oxime **12** and 20.3 mg ($3.8 \cdot 10^{-4}$ mol) of $NaOCH_3$ were dissolved in 1 ml of DMF and the solution was cooled down to 5°C. To this solution a solution of 66.9 mg ($3.8 \cdot 10^{-4}$ mol) of NBS in 1 ml of DMF was added dropwise. The temperature should not exceed 10°C. After stirring for 1 h at 10°C the mixture was diluted with 20 ml of ice-cold water causing precipitation of a yellowish compound. This precipitate was filtered and washed several times with ice-cold water. Thus, 140 mg of a yellow powder could be isolated. The crude product showed the characteristic band of nitrile oxides in the IR spectrum at 2288 cm^{-1}.

3-(2',3',6',7'-Tetramethoxy-10-methoxycarbonyl-9-anthryl)-[60]fullereno[1,2-d]isoxazole (**1d**): Under argon 100 mg ($1.4 \cdot 10^{-4}$ mol) of C_{60} was dissolved in 200 ml of toluene in a 500-ml flask sealed with a septum. By means of a syringe a solution of 40 mg of crude **2d** in 40 ml of $CHCl_3$ was added dropwise. The red-brown solution was stirred for 24 h and afterwards concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (toluene/acetonitrile, 9:1; R_f = 0.5). 60 mg of unreacted C_{60} and 35 mg (31.1% based on the pure oxime **12**) of **1d** could be isolated, m.p. >300°C. – ^1H NMR (300 MHz, $CDCl_3$): δ = 4.02 (s, 6H, OCH_3), 4.15 (s, 6H, OCH_3), 4.19 (s, 3H, $COOCH_3$), 7.18 (s, 2H, aromatic), 7.75 (s, 2H, aromatic). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.24 (COO), 153.67 (C=N), 150.51 (2 C, $COCH_3$), 150.16 (2 C, $COCH_3$), 147.89 (1 C), 147.26 (1 C), 146.40 (6 C), 146.35 (2 C), 146.06 (2 C), 145.96 (2 C), 145.79 (2 C), 145.19 (4 C), 145.09 (2 C), 144.90 (2 C), 144.81 (2 C), 144.48 (2 C), 144.27 (2 C), 144.08 (2 C), 143.04 (2 C), 142.90 (2 C), 142.78 (2 C), 142.45 (2 C), 142.40 (2 C), 142.16 (4 C), 141.76 (2 C), 141.62 (2 C), 140.84 (2 C), 140.34 (2 C), 136.10 (2 C), 135.67 (2 C), 129.04 (1 C), 128.23 (1 C, aromatic), 126.75 (2 C, aromatic), 124.52 (2 C, aromatic), 119.80 (1 C, sp^3-fullerene), 103.85 (2 C, aromatic), 102.74 (2 C, aromatic), 82.59 (1 C, sp^3-fullerene), 56.08 (2 C, OCH_3), 55.82 (2 C, OCH_3), 52.64 ($COOCH_3$). – IR (KBr): $\tilde{\nu}$ = 2947 cm^{-1} (w, CH), 1723 (m, CO), 1496 (s), 1432 (m), 1246 (s, C–O), 1139 (m), 840 (w), 831 (w), 527 (m, fullerene). – UV (chlorobenzene): λ_{max} (lg ε) = 455 nm (3.09), 545 (2.88), 610 (2.61), 690 (2.16). – HRFAB MS; *m/z*: 1118.1217 ($C_{81}H_{19}NO_7$), calcd. 1118.1240 [MH^+].

3-(9-Anthryl)-[60]fullereno[1,2-d]isoxazole (**1e**): This compound was synthesized according to procedures reported in ref.[3] Single crystals were obtained from a saturated toluene solution (45°C) within one week at room temp. Crystallographic data for **1e**, see Table 3.

Table 3. Crystallographic data of **1b** and **1e**

Compound	**1b**	**1e**
Empirical formula	$C_{69}H_7NO_3 \cdot C_7H_8$	$C_{75}H_9NO \cdot C_7H_8$
Molecular mass [g/mol]	897.8	1032.0
Crystal size [mm]	0.5 x 0.45 x 0.2	0.5 x 0.3 x 0.3
Crystal color	black	black
Crystal shape	prism	irregular
Space group	$P2_1/n$	Pnma
a [Å]	16.937(3)	24.137(2)
b [Å]	22.270(3)	18.150(1)
c [Å]	10.191(1)	9.858(2)
V [$Å^3$]	3842(2)	4319(1)
$D_{calcd.}$ [Mg/m^3]	1.55	1.59
Z	4	4
F(000)	1808	2096
Temperature [K]	293	253
$h_{min.}$ / $h_{max.}$	0 / 22	0 / 31
$k_{min.}$ / $k_{max.}$	-29 / 29	0 / 23
$l_{min.}$ / $l_{max.}$	-13 / 13	0 / 13
$(\sin\Theta/\lambda)_{max.}$ [$Å^{-1}$]	0.61	0.66
μ [mm^{-1}]	0.09	0.79
Refl. collected	14278	5519
Refl. unique	9196	4335
Refl. observed [$I > 2.5\,\sigma(I)$]	4035	2889
Variables	682	450
$(\Delta/\sigma)_{max.}$	0.02	<0.01
R	0.046	0.039
R_w^2	0.108	0.097
S (Gof)	2.20	1.20
$(\Delta\rho)_{max.}$ [e $Å^{-3}$]	0.35	0.16
$(\Delta\rho)_{min.}$ [e $Å^{-3}$]	-0.05	-0.24

☆ Dedicated to Professor *Klaus Weinges* on the occasion of his 70th birthday.

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