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Synthesis of a phthalonitrile derivative of fullerenopyrrolidine

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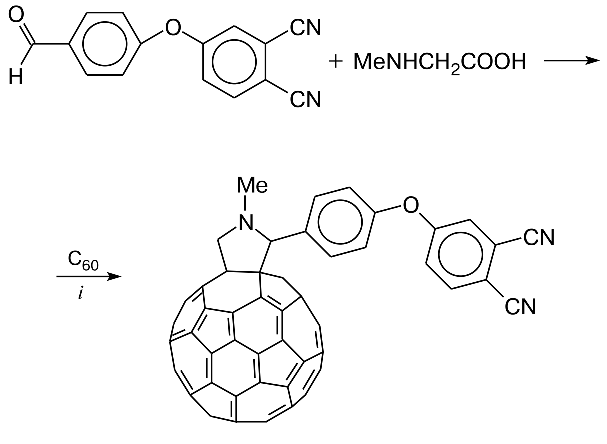
The Prato reaction was used to synthesize 2-[4-(3,4-dicyanophenoxy)phenyl]-*N*-methyl-3,4-[60]fullerenopyrrolidine.

Key words: [60]fullerene, cycloaddition reaction, phthalonitrile.

Interest in the photophysical properties of fullerene derivatives is based on rather easy excitation of fullerene (acceptor)—linkage—electron donor systems producing states with charge separation. The lifetime of the excited state can vary in a wide range depending on the type of functional groups on fullerene and the donor properties of the second component.[1,2] Fullerene—phthalocyanine supramolecular systems in which strong donor-acceptor interactions result in long-lived excited states with charge separation are intensively used now.[3–6] Reactions of cycloaddition of formylphthalocyanines to fullerene are mainly used for the preparation of systems of this type.[4] The purpose of this work is to synthesize fullerene-containing phthalonitrile for the further formation of the fullerene-containing phthalocyanine macrocycle.

2-[4-(3,4-Dicyanophenoxy)phenyl]-*N*-methyl-3,4-fullerenopyrrolidine was synthesized by the 1,3-dipolar cycloaddition reaction of fullerene C$_{60}$ with azomethine formed upon the interaction of 4-(4-formylphenoxy)phthalonitrile with sarcosine (Scheme 1).

Scheme 1



i. Toluene

The reaction affords a mixture of cycloaddition products from which the mono- and diaddition products were isolated by column chromatography. The both compounds are brown solids stable in air and soluble in organic solvents (toluene, chloroform). The ESI mass spectra were obtained for both compounds. The mass spectra of these substances contain the main peaks of molecular ions 995 [M]$^{-\bullet}$ for monosubstituted and 1270 [M]$^{-\bullet}$ for disubstituted fullerenopyrrolidine phthalonitriles. The presence in the ^{1}H NMR spectrum of the monosubstituted product of signals with δ = 5.02, 5.01, and 4.31 assigned to the pyrrolidine ring proves its formation. The IR spectrum exhibits a band at 2230 cm^{-1} characteristic of the cyano group. The electronic absorption spectrum of the synthesized fullerene derivative is characteristic of fullerenopyrrolidines.[7]

The ^{1}H NMR spectrum was recorded on a Bruker Avance DPX-200 instrument. Electrospray mass spectra (ESI) were measured on a Bruker Esquire LC instrument. The electronic absorption spectrum was obtained on a Perkin—Elmer Lambda 25 spectrometer in a 1.0-cm quartz cell. The IR spectrum was recorded on a Perkin—Elmer Spectrum 1000 spectrometer, using KBr as an emission medium. The cycloaddition products were separated on silica gel 60 (Merck). Sarcosine (Aldrich) was used without additional purification. 4-(4-Formylphenoxy)phthalonitrile was synthesized by a known procedure.[8]

2-[4-(3,4-Dicyanophenoxy)phenyl]-*N*-methyl-3,4-fullerenopyrrolidine. Sarcosine (0.111 g, 1.247 mmol) and 3-formyl-4-phenoxyphthalonitrile (0.103 g, 0.416 mmol) were added to a solution of fullerene C$_{60}$ (0.3 g, 0.416 mmol) in toluene (200 mL). The reaction mixture was stirred for 20 h with boiling, cooled to room temperature, and filtered. The resulting solution of the reaction products was separated on a column packed with silica gel. Toluene was used as eluent for the isolation of unreacted fullerene, and the desired monoaddition product was isolated with a toluene—chloroform (1 : 1) system. After the solvents were removed *in vacuo*, a solid brown product (0.109 g)

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was obtained. The yield was 30% (based on reacted fullerene), m.p. > 300 °C. Found (%): C, 92.85; H, 1.21. $C_{78}H_{14}N_2O$. Calculated (%): C, 93.05; H, 1.11. ^{1}H NMR ($CDCl_3$), δ: 2.88 (s, 3 H, N—CH_3) 4.31, 5.02 (both d, 1 H, pyrrolidine, *J* = 9.4 Hz); 5.01 (s, 1 H, pyrrolidine); 7.08—7.21 (m, 4 H, Ar); 7.69 (d, 1 H, Ar, *J* = 9.0 Hz); 8.02—7.82 (m, 2 H, Ar). UV (toluene), λ_{max}/nm: 430. IR (KBr, 4000—400 cm^{-1}), ν/cm^{-1}: 2922, 2851, 2230, 1590, 1562, 1500, 1484, 1462, 1425, 1353, 1331, 1307, 1277, 1247, 1201, 1177, 1163, 1122, 1089, 1030, 1015, 949, 908, 869, 850, 831, 796, 787, 746, 728, 600, 563, 525. MS (ESI—MS, in CH_2Cl_2—MeOH, 1 : 10), *m/z*: 995 $[M]^{-\bullet}$.

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References

1. G. Possamai, M. Maggini, *Appl. Physics A*, 2004, **79**, 51.
2. E. A. Katz, *Phys. Solid State*, 2002, **44**, 647.
3. J. Drechsel, D. Gebeyehe, M. Pfeiffer, K. Leo, Y. Hoppe, *Organic Electronics*, 2004, **5**, 175.
4. D. M. Guldi, A. Gouloumis, P. Vazquez, T. Torres, V. Georgakilas, M. Prato, *J. Am. Chem. Soc.*, 2005, **127**, 5811.
5. A. Gouloumis, Sh. Lio, A. Sastre, P. Vazquez, L. Echegoyen, T. Torres, *Chem. Eur. J.*, 2000, **6**, 3600.
6. M. A. Loi, P. Denk, H. Hoppe, H. Neugebaner, D. Metssener, C. Winder, C. J. Brabes, N. S. Sariciftci, A. Gouloumis, P. Varquez, T. Torres, *Synthetic Metals*, 2003, **137**, 1491.
7. M. Maggini, G. Scorrano, M. Prato, *J. Am. Chem. Soc.*, 1993, **115**, 9798.
8. D. Woehle, N. Iskander, G. Graschew, H. Sinn, E. Friedrich, W. Maier-Borst, J. Stern, P. Schlag, *Photochem. Photobiol.*, 1990, **51**, 351.

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