Letters to the Editor

Cycloaddition of [60]fullerene to stable benzenedicarbonitrile oxides

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When studying the chemistry of [60]fullerene, a major effort generally went into the functionalization of the C_{60} molecule by adding one or (more rarely) several substituents followed by their transformations.[1] At the same time, in connection with the unusual chemical and physical properties of the [60]fullerene nucleus, it is of interest to construct substrates containing several fullerene nuclei in the molecule, including polymeric compounds. For this purpose, we studied interactions of [60]fullerene with bifunctional tetrachloro-*p*- and -*m*-benzenedicarbonitrile oxides. Previously, it has been established that [60]fullerene reacts with nitrile oxides to form the corresponding isoxazoline derivatives as a result of [3+2]-cycloaddition at the double (6,6) bond of the C_{60} molecule.[2–6]

The reaction of [60]fullerene with 2,3,5,6-tetrachlorobenzene-1,4-dicarbonitrile oxide[7] (**1**) (Scheme 1) was carried out by portionwise addition of dinitrile oxide **1** (30 mg, 0.1 mmol) to a stirred hot (100 °C) solution of [60]fullerene (288 mg, 0.4 mmol) in *o*-dichlorobenzene (40 mL) for 4 h. The reaction mixture was kept at this temperature for 2 h. The solvent was removed *in vacuo* and the residue was chromatographed on silica gel. Unconsumed [60]fullerene (140 mg, 48% with respect to the initial amount) was eluted with benzene. 2,3,5,6-Tetrachloro-1,4-phenylene-3,3′-bis([60]fullereno[1,2-*d*]isoxazole) (**2**) (44 mg, 25%) was eluted with a 1 : 1 benzene—*o*-dichlorobenzene mixture. The band of polymeric products remained at the start. This band was partially eluted with pure *o*-dichlorobenzene.

After removal of the solvents from the fraction containing compound **2**, the residue was dried *in vacuo* at 80 °C for 2 h. The structure of compound **2** was confirmed by the mass spectrum (*m/z*: 1738 $[M]^+$), which was obtained by the TOF-PDMS method with ionization with ^{252}Cf decay fragments, and by the data of elemental analysis. Found (%): C, 87.73; Cl, 8.71; N, 1.93. $C_{128}Cl_4N_2O_2$. Calculated (%): C, 88.40; Cl, 8.15; N, 1.61. The compound under study contained a small amount of hydrogen (0.04%), which apparently appeared due to the solvent sorbed (most probably, *o*-dichlorobenzene), along with the above-mentioned elements. The results of calculations for this sample, $C_{128}Cl_4N_2O_2 \cdot 0.2C_6H_4Cl_2$ (calculated (%): C, 87.74; H, 0.05; Cl, 8.82; N, 1.58), agree much more closely with the experimental data.

In the IR spectrum (KBr) and in the visible region of the electronic spectrum (a solution in toluene) of compound **2**, the most intense bands at 529, 578, 856, 1212, 1332, and 1423 cm^{-1} and at 334, 538, and 599 nm, respectively, are caused by absorption of fullerene nuclei.[1] In addition, the IR spectrum has a strong absorp-

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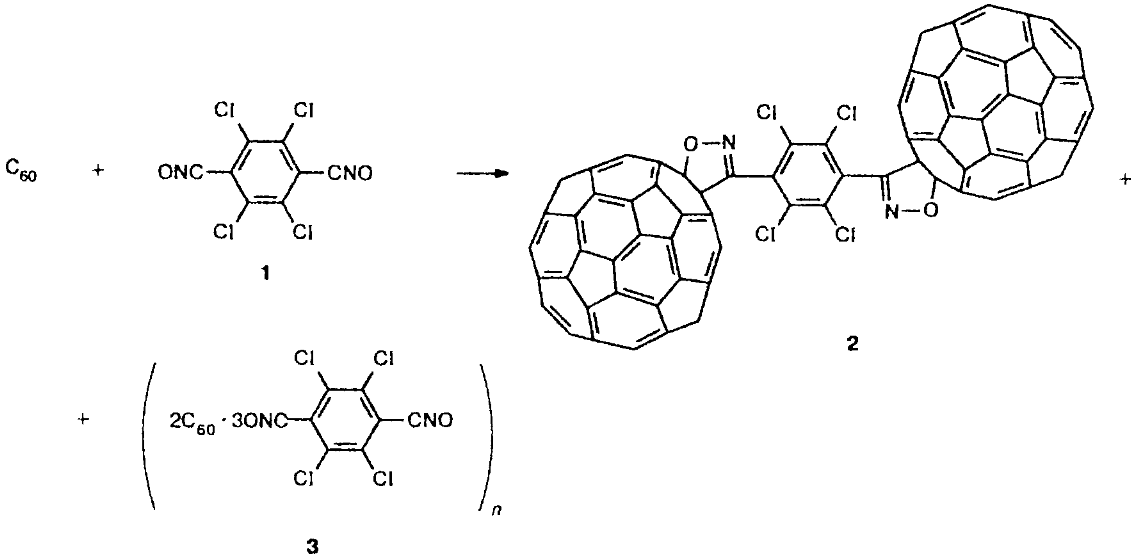
Scheme 1



tion band at 752 cm^{-1}, which apparently corresponds to C—Cl stretching vibrations,[8] while no noticeable absorption in the 1500—1600 cm^{-1} region expected for the C=N bond is observed. Note that of all the isoxazoline derivatives of [60]fullerene synthesized,[2—6] only the compound that does not contain substituents in the isoxazoline ring gives the absorption band corresponding to C=N stretching vibrations (1599 cm^{-1}).[5] The very low solubility of compound **2** in solvents commonly used did not allow us to record its ^{13}C NMR spectrum.

The yield of compound **2** decreases and the amount of the polymeric product increases (see Scheme 1) as the excess of [60]fullerene with respect to dinitrile oxide **1** decreases. In this case, the reaction was performed by adding a solution of dinitrile oxide **1** (30 mg, 0.1 mmol) in *o*-dichlorobenzene (5 mL) to a solution of [60]fullerene (72 mg, 0.1 mmol) in *o*-dichlorobenzene (20 mL). The reaction mixture was kept at room temperature for 20 h. The precipitate that formed was washed with *o*-dichlorobenzene and dried *in vacuo* at 80 °C for 3 h. Product **3** was obtained in a yield of 68 mg. Found (%): C, 71.56; H, 0.55; Cl, 21.66; N, 3.23. If, as we assumed, the presence of H is associated with *o*-dichlorobenzene sorbed, the data of elemental analysis of compound **3** correspond to a combination of two [60]fullerene molecules, three molecules of dinitrile oxide **1**, and two *o*-$Cl_2C_6H_4$ molecules. For this composition, $C_{144}Cl_{12}N_6O_6 \cdot 2C_6H_4Cl_2$, calculated (%): C, 71.27; H, 0.31; Cl, 21.58; N, 3.20. The IR spectrum (KBr) of compound **3**, like the spectrum of compound **2**, has absorption bands of fullerene nuclei at 528, 556, 856, 1212, 1328, and 1432 cm^{-1}. The most intense band at 752 cm^{-1} and the relatively weak band at 1604 cm^{-1} apparently correspond to stretching vibrations of the C—Cl and C=N bonds, respectively. The yield of product **3** was ~77%. We defined compound **3** as a polymer based on the fact that binding of two fullerene nuclei through three above-mentioned bridges is unlikely.

Analogously, the reactions of [60]fullerene with 2,4,5,6-tetrachlorobenzene-1,3-dicarbonitrile oxide[7] in both cases afforded only polymeric products of variable compositions.

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