

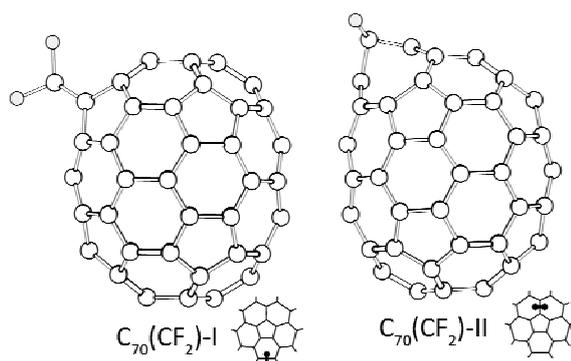
CF₂-derivatives of C₇₀: synthesis and structure

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Fine tuning of electron properties of fullerene derivatives is an actual problem for the nowadays. One of the possible ways of such tuning is insertion of electron withdrawing units into fullerene cage. Impressive example of it is difluoromethylene homofullerenes C₆₀(CF₂)_n, n=1-3, which were synthesized [1] and found as prospective materials for organic electronic applications [2]. The synthesis and structure of the difluoromethylated derivatives of fullerene C₇₀ are reported in the present work for the first time.

Difluoromethylated derivatives C₇₀ were obtained by refluxing of fullerene C₇₀ and sodium difluorochloroacetate solution. Product composition and dynamic of the reaction were monitored by means of HPLC and MALDI mass spectrometry. We observe formation of C₇₀(CF₂)_n, where n is 1-4. Three isomers of C₇₀(CF₂) were isolated from prepared mixtures by means of HPLC. Structures of two major isomers of C₇₀(CF₂) were suggested on the basis of NMR spectroscopy data and quantum chemical calculations. Addition of CF₂ group occurs at [6,6]-double bonds of the polar region C₇₀ in both cases (see figures below). According to the quantum chemical calculations (DFT, PBE/TZ2P), distance between carbon atoms, carrying CF₂-bridge, is 1.72 and 2.08 Å, correspondingly for isomers C₇₀CF₂ **I** and **II**. Thus, isomer **I** is a methanofullerene, while isomer **II** demonstrates homofullerene features (also it was justified by UV/Vis spectroscopy).



Structures of the C₇₀(CF₂)-I and C₇₀(CF₂)-II; the fragments of corresponding top views (across former C₅ axe of C₇₀ fullerene) are shown on insets.

- [1] A.S. Pimenova, A.A. Kozlov, A.A. Goryunkov, V.Yu. Markov, P.A. Khavrel, S.M. Avdoshenko, I.N. Ioffe, S.G. Sakharov, S.I. Troyanov, L.N. Sidorov, *Chem. Commun.* 374 (2007).
[2] K. Tokunaga, S. Ohmori, H. Kawabata, *Thin Solid Films* **518**, 477 (2009).