

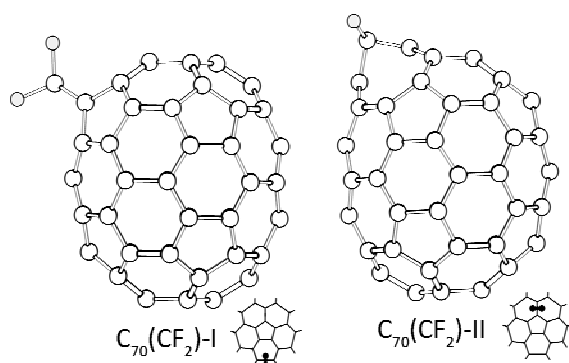
## CF<sub>2</sub>-derivatives of C<sub>70</sub>: synthesis and structure

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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 C<sub>60</sub>(CF<sub>2</sub>)<sub>n</sub>, 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 C<sub>70</sub> are reported in the present work for the first time.

Difluoromethylated derivatives C<sub>70</sub> were obtained by refluxing of fullerene C<sub>70</sub> 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 C<sub>70</sub>(CF<sub>2</sub>)<sub>n</sub>, where n is 1-4. Three isomers of C<sub>70</sub>(CF<sub>2</sub>) were isolated from prepared mixtures by means of HPLC. Structures of two major isomers of C<sub>70</sub>(CF<sub>2</sub>) were suggested on the basis of NMR spectroscopy data and quantum chemical calculations. Addition of CF<sub>2</sub> group occurs at [6,6]-double bonds of the polar region C<sub>70</sub> in both cases (see figures below). According to the quantum chemical calculations (DFT, PBE/TZ2P), distance between carbon atoms, carrying CF<sub>2</sub>-bridge, is 1.72 and 2.08 Å, correspondingly for isomers C<sub>70</sub>CF<sub>2</sub> **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 C<sub>70</sub>(CF<sub>2</sub>)-I and C<sub>70</sub>(CF<sub>2</sub>)-II; the fragments of corresponding top views (across former C<sub>5</sub> axe of C<sub>70</sub> 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).