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On accuracy of the ^{13}C NMR chemical shift GIAO calculations of fullerene C_{60} derivatives at PBE/3ζ approach

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ABSTRACT

The correlation analysis of the calculated by means of GIAO PBE/3ζ method and experimental (2D NMR INADEQUATE) ^{13}C NMR chemical shifts of C_{60} derivatives was performed. It was shown that the computational method with sufficient accuracy (r.m.s. ~ 5 ppm) reproduces the experimental ^{13}C NMR chemical shifts of the sp^2-fullerene carbon atoms uncoupled with the sp^3-fullerene carbons. By quality description the GIAO method in PBE/3ζ approach best reflects the experimental ^{13}C NMR chemical shifts of studied in this work fullerene derivatives such as hydrofullerene $C_{60}H_2$, methanofullerenes, fullerene adducts of [2 + 2]- and [2 + 3]-cycloaddition, as well as azaheterofullerene.

1. Introduction

Since the discovery of fullerene C_{60} in 1985 [1] and at a moment when it became available in bulk quantities in 1990 [2] the number of fullerene derivatives is growing. They are prospective in various fields of medicine [3], optics [4,5] and technical equipment [6]. The NMR, IR- and UV-spectroscopy, mass-spectrometry, and X-ray techniques are attributed to the identification methods of the newly obtained fullerene derivatives. However, the NMR spectroscopy occupies a central position among mentioned above methods, since an NMR chemical shift δ is very sensitive to an electron environment of magnetic nuclei [7]. In such a case the structure elucidation may be almost completely performed even there are no the crystal and enriched by ^{13}C isotope samples of fullerene derivatives.

The literature contains only few examples demonstrating the full assignments of ^{13}C NMR fullerene frame resonances by means of 2D NMR INADEQUATE technique. Using the direct $^{13}C–^{13}C$ coupling constants produced with this experiment, it is managed to assign all the ^{13}C NMR fullerene signals. So, the structure elucidation of hydrofullerenes $C_{60}H_2$ and $C_{60}H_6$ [8], [60]fullerenyldihydropyrrole [9], *bis*-methano[60]fullerenyl amino acid derivatives [10], methanofullerene $C_{61}H_2$ [11], benzene adduct [12,13], N-triphenylmethyl-pyrrolidine[60]fullerene [14], osmylated tetraoxide adduct [15], 1,16-di(2-carbomethoxy-2-propyl)-1,*x*-dihydro[60]fullerene [16] and 1,2-methano[60]fullerene 61,61-dicarboxylate [17] was

successfully carried out. However, a performing of these experiments is not commonly possible for the cases of the absence of enriched samples in view of the fact that they are commercially confined.

At the same time, the quantum chemistry methods are widely and successfully employed for structure elucidation, in order to determine the thermodynamically stable isomers, to reveal their reactivity and to calculate some NMR parameters such as ^{13}C chemical shifts of fullerene derivatives [18]. Thus, there are several works revealed the ^{13}C NMR chemical shift calculations by means of various quantum chemistry approaches, for instance in application to fullerene C_{84} [19,20], azafullerenes $(C_{59}N)_2$ and $C_{59}HN$ [21,22], hydroxylated fullerenes [23] and to high fullerenes [24–26].

Rather recently the quantum chemistry package PRIRODA [27] with implemented PBE/3ζ method [28–30] has been developed. Judicious application of computational approaches has ensured the high speed with an acceptable accuracy of calculations performed in the PRIRODA program. As consequence, it allowed modeling the structural and physicochemical properties of large organic compounds including the substituted fullerenes. So, earlier we have carried out the experimental ^{13}C NMR chemical shift assignments of *spiro*-homo- and methano[60] fullerenes by means of GIAO PBE/3ζ embracing the statistical analysis at the comparing experimental and calculated ^{13}C NMR chemical shift values [31].

In addition, as a previous experience, attributed to the structure investigations of fullerene derivatives, shows that there are no published studies concerned to the ^{13}C NMR chemical shift

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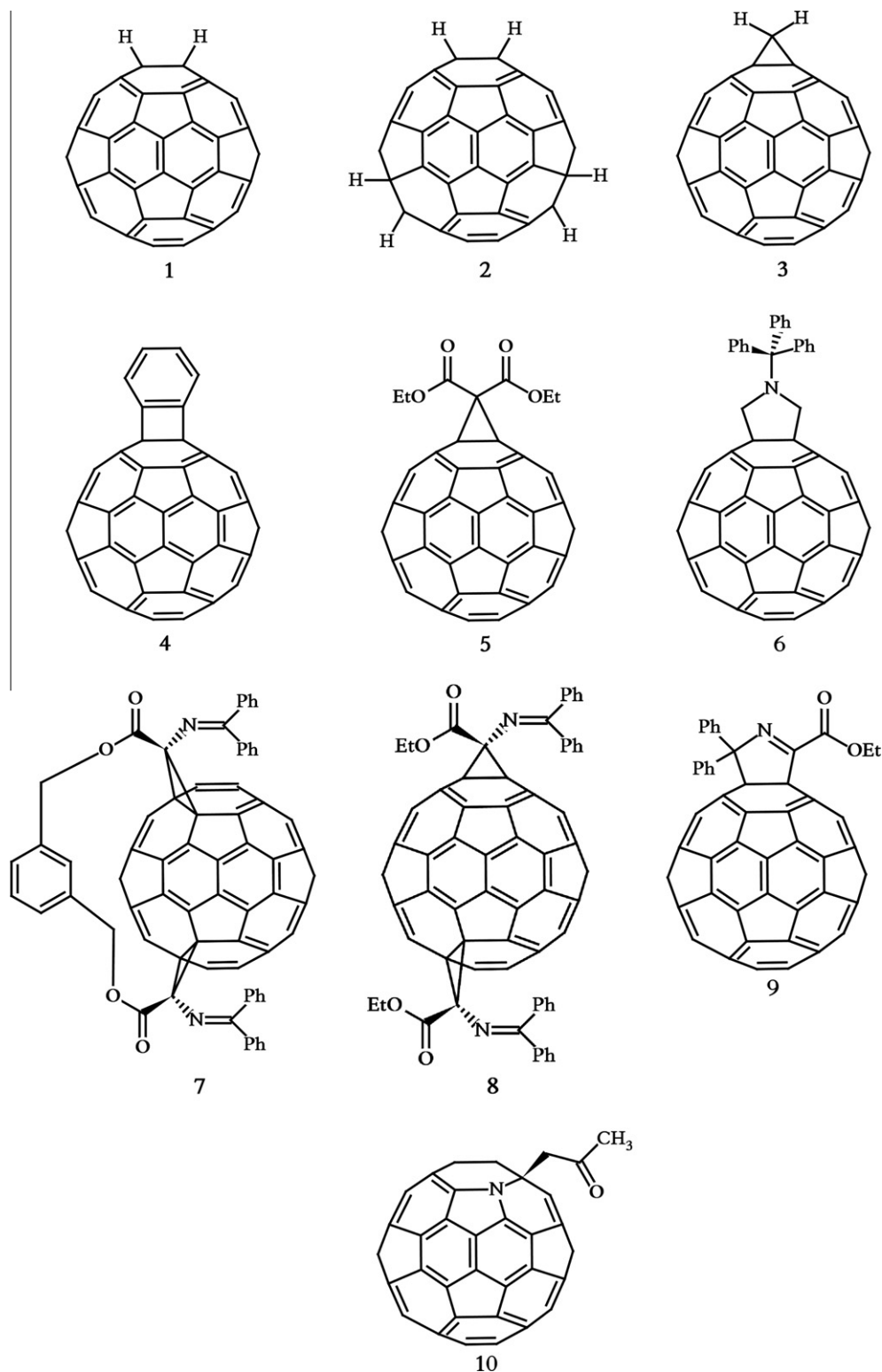 *E-mail address:* tulebeich@gmail.com (A.R. Tulyabaev).

Fig. 1. The test fullerene derivatives structures **1–10**.

calculations accompanying by the detailed statistical analysis at the comparing of the calculated and experimental data obtained by means of 2D NMR INADEQUATE. In this regard, the statistical analysis of the calculated with the GIAO PBE/3ζ method and experimental (2D NMR INADEQUATE) ^{13}C NMR chemical shifts of fullerene derivatives containing various substituents is the goal of our present work.

2. Computational details

Full geometry optimization and vibrational frequencies analysis of fullerene derivatives have been performed by using of the PBE/3ζ approach [27–30] (PRIRODA program [29]). The ^{13}C NMR chemical shifts have been calculated for the thermodynamically stable conformations of derivatives by means of GIAO method [32]