Computational and Theoretical Chemistry 1081 (2016) 44–48

Contents lists available at ScienceDirect

Computational and Theoretical Chemistry

journal homepage: www.elsevier.com/locate/comptc

Bisadducts of the C_{60} and C_{70} fullerenes with anthracene: Isomerism and DFT estimation of stability and polarizability

Denis Sh Sabirov [a,*], Anton O. Terentyev [a], Franco Cataldo [b,c]

[a] Institute of Petrochemistry and Catalysis, Russian Academy of Sciences, 450075 Ufa, Russia
[b] Actinium Chemical Research Institute, Via Casilina, 00182 Rome, Italy
[c] Università degli Studi della Tuscia, Dipartimento di Scienze Ecologiche e Biologiche, 01100 Viterbo, Italy

ARTICLE INFO

Article history:
Received 12 February 2016
Received in revised form 17 February 2016
Accepted 17 February 2016
Available online 23 February 2016

Keywords:
Fullerene adducts
Isomerism
Stability
Anisotropy of polarizability
Density functional theory

ABSTRACT

In the present work, stability and anisotropy of polarizability of possible regioisomeric C_{60}–anthracene (C_{60}ant$_2$) and C_{70}–anthracene (C_{70}ant$_2$) bisadducts have been studied by the PBE/3ζ density functional theory method (7 and 14 isomers, respectively) to indicate the most isotropic bisadducts, which are considered more appropriate for organic solar cells than their anisotropic counterparts. As found, anisotropy of polarizability is quadratically correlated with the interaddend distance in each isomeric set. The compounds C_{60}ant$_2$-*cis*-2 and C_{70}ant$_2$-*cc*$_1$*cc*$_2$ are characterized with the lowest calculated anisotropies and, hence, recommended for isolation, purification and further testing in photovoltaics.

1. Introduction

Reactions of C_{60} and C_{70} fullerenes with acenes attract researchers with opportunity of the synthesis of fullerene adducts with potential applications to nanoarchitecture, organic solar cells, and further synthetic transformations leading to other classes of fullerene derivatives (see review [1] and key original works [2–9]). In the case of anthracene, the fullerene–anthracene [2+4] cycloadducts C_{60}ant$_n$ with $n = 1–3$ [2–6], and C_{70}ant$_n$ with $n = 1$ and 2 [7] have been identified. According to the voltammetric measurements [7], such compounds may be useful as electron acceptors for organic solar cells (OSC). Indeed, the related C_{60} fullerene mono- and bisadducts with hydrocarbon moieties are widely tested for OSC applications [7,10–18], including bisnaphtho- [11–13] and bisanthracenofullerenes [12]. The mentioned fullerene derivatives are presented as hardly separable positional isomers (regioisomers). Hence, these species were tested in OSCs mostly used as the regioisomeric mixtures.

Recently, the isolated and purified bisadducts became available for OSC applications [19]. Moreover, as follows from the experimental works on the $C_{60}X_2$-based OSCs, their key output parameters (open-circuit voltages and power conversion efficiencies) depend on the arrangement of addends in $C_{60}X_2$. As is known, if X is a symmetric addend, $C_{60}X_2$ has 8 positional isomers [20]. In the case of unsymmetrical addends, the number of isomers becomes larger [21]. We have previously shown that anisotropy of polarizability maybe an index describing the dissimilarity of the regioisomeric fullerene bisadducts [21,22]. Indeed, this quantity perfectly reflects the mutual arrangement of the addends (it is quadratically correlated with the interaddend distance) and may be interpreted as unevenness of the electronic cloud of the molecule. As we found, the use of the most isotropic regioisomers of fullerene bisadducts allow obtaining higher power conversion efficiencies and open-circuit voltages as compared to their anisotropic isomers [22]. In this context, we pay attention to anthracene bisadducts due to the local symmetry of the anthracene addend. This leads to two advantages. First, it reduces the total number of possible regioisomers that should facilitate their chromatographic separation after the synthetic procedures. Second, symmetric addends may decrease anisotropy of polarizability of the anthracene–fullerene compounds as compared to other classes of bisadducts.

In the present work, dipole polarizability and relative stability of all possible isomers of the bisadducts of C_{60} and C_{70} fullerenes with anthracene have been studied by the DFT method PBE/3ζ.

2. Calculation details

The PBE/3ζ density functional theory method (Priroda program [23,24]) were used for calculations because it successfully describes thermodynamic and kinetic parameters of fullerene

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* Corresponding author. Fax: +7 (347) 284 27 50.
E-mail address: diozno@mail.ru (D.S. Sabirov).

http://dx.doi.org/10.1016/j.comptc.2016.02.012
2210-271X/

reactions [25–32], IR, NMR spectra, [33–36] and the measured mean polarizabilities of fullerenes and their derivatives (see review [37] and original works [16,22,27,28,31,33,34,38–40]).

After standard DFT-optimizations and vibration modes solving (to prove that all the stationary points, respective to the molecules under study, are minima of the potential energy surfaces), the components of polarizability tensors $\boldsymbol{\alpha}$ have been calculated in terms of the finite field approach as the second order derivatives of the total energy E with respect to the homogeneous external electric field $\boldsymbol{F}$:

$$\alpha_{ij} = -\frac{\partial^2 E}{\partial F_i \partial F_j} \quad (1)$$

Tensors α have been calculated in the arbitrary coordinate system and then diagonalized. Their eigenvalues α_{ii} ($i = x$, y, and z) allow calculating the mean polarizability α and its anisotropy a^2:

$$\alpha = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \quad (2)$$

$$a^2 = \frac{1}{2}\left((\alpha_{yy} - \alpha_{xx})^2 + (\alpha_{zz} - \alpha_{yy})^2 + (\alpha_{zz} - \alpha_{xx})^2\right) \quad (3)$$

Thermochemical parameters of the reaction between C_{60} and anthracene

$$C_{60} + \text{ant} \rightarrow C_{60}\text{ant} \quad (4)$$

was previously studied experimentally (kinetic studies [4,5]) and theoretically (in terms of the incremental approach for calculation of thermodynamic reaction parameters [8]). Our calculations lead to the Gibbs energy $\Delta G°_r$ of reaction (4) equal to +61.0 kJ mol^{-1} (this has been performed as the energy difference between the product and reactants taking into account their zero-point vibration energies, and thermal corrections for $T = 298$ K). Thus, the DFT calculations shows that the reaction above is endothermic as stated in the previous incremental study (+8.6 kJ mol^{-1} [8]). Note that the compared values have been obtained within very different approaches, so we compare these estimates only in qualitative aspect.

3. Results and discussion

3.1. Bisanthraceno[60]fullerenes

Bis[60]anthracene has 8 inequivalent double bonds, to which the attachment of another addend is possible (Fig. 1). The attachment occurs *via* 9 and 10 carbon atoms of the anthracene molecule, so the attached moieties became nonplanar [1]. Counting the theoretically achievable structures of bisanthraceno[60]fullerenes, we took into account the volume of the anthracene addends that leads to appearance of the steric constraints when the addends are in the *cis*-1 position. This remains only 7 possible regioisomeric bisanthraceno[60]fullerenes. Their calculated energetic, structural, and polarizability characteristics are shown in Table 1.

Our computational results suggest the decrease in thermodynamic favorability of the second addition of anthracene to C_{60}. The calculated Gibbs energies of the second addition:

$$C_{60}\text{ant} + \text{ant} \rightarrow C_{60}\text{ant}_2 \quad (5)$$

lie in the range 71.5–106.2 kJ mol^{-1} that is more endothermic as compared with the first step (reaction (4)). The calculated relative stabilities ΔE, heat effects $\Delta H°_r$, and Gibbs energies $\Delta G°_r$ demonstrate the decrease in favorability of the bisadduct formation in the following order: *trans*-3 ⩾ *e* > *trans*-2 > *trans*-4 ⩾ *trans*-1 > *cis*-3 > *cis*-2. Moreover, the calculated values are symbate with the measured yields of the C_{60}–anthracene bisadducts taken from the synthetic work [2]. The last sentence is demonstrated by the plot of their relative energies against the yields (Fig. 2).

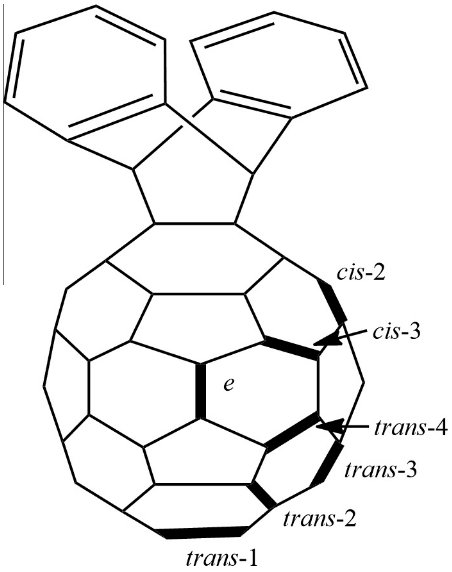

Fig. 1. Designation of the addition of the second addend in the $C_{60}\text{ant}_2$ bisadducts.

Bisanthraceno[60]fullerenes are characterized with different anisotropies of polarizability a^2. The a^2 *vs.* L plot (Fig. 3) shows that anisotropy correlates with the interaddend distances L, *i.e.* distances between the middle points of two C–C bonds keeping the anthracene addends. The correlation is well described with a quadratic polynomial similar to the previously studied case of the [2+1]-cycloadducts of C_{60} [16]. Its minimum corresponds to the *cis*-2 isomer, which has the lowest value of anisotropy of polarizability, so this compound is expected to be the most efficient electron-acceptor for the OSC application as compared with the other compounds of the isomeric set (Fig. 4). Its antipode, bis-[60] anthracene-*trans*-1 demonstrate the highest a^2 value (Fig. 4). Unfortunately, $C_{60}\text{ant}_2$-*cis*-2 has not been isolated and characterized experimentally as one of the thermodynamically unfavorable isomers. As for the more abundant isomers (*trans*-3 and *e*), the equatorial isomer should demonstrate higher output OSC parameters as it is ~1.5 times less anisotropic than $C_{60}\text{ant}_2$-*trans*-3 (Table 1).

3.2. Bisanthraceno[70]fullerenes

Less symmetric than C_{60}, the C_{70} fullerene provides two ways of the Diels–Alder reaction with anthracene, *via ab* and *cc* bonds (Fig. 5). The first additions

$$C_{70} + \text{ant} \rightarrow C_{70}\text{ant-}ab + 65.9\ \text{kJ mol}^{-1} \quad (6)$$

$$C_{70} + \text{ant} \rightarrow C_{70}\text{ant-}cc + 80.61\ \text{kJ mol}^{-1} \quad (7)$$

are characterized with the calculated Gibbs energies (shown in the thermochemical equations above) close to the value of the C_{60} case. Their comparison shows that addition to the *ab* bonds, placed at the poles of the C_{70} skeleton, should be more favorable as the addition to the *cc* bons is more endothermic. The next addition leads to one of three type of the C_{70} bisadducts: *abab*, *cccc*, and mixed *abcc*. To distinguish these isomers numerically, we designate isomeric bisanthraceno[70]fullerenes by numbering the bonds, to which the addends are attached. These are five *ab* and five *cc* bonds, numbered from 1 to 5 on the first pole of the C_{70} molecule and from 1′ to 5′ on the other (Fig. 5).