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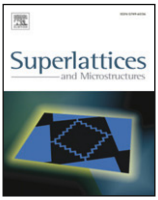

A DFT study of methylamine polyaddition to C_{80} fullerene

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ABSTRACT

We studied theoretically (GGA PW91 density functional theory in conjunction with the double-numerical basis set) the C_{80} functionalization by methylamine through successive reactions with up to three methylamine molecules. We calculated the energies of formation (relative to the level of separated reactants) of different isomers and, in accordance with these values, we defined the most probable site of reaction in each addition. The preferred addition sites are carbon atoms of the 5,6 bonds of the five-membered ring next to the pentagon of the previous addition. The pyramidalization angle θ_p can explain the reactivity of C atoms in pristine C_{80}, but not in the amine-functionalized C_{80}. At the same time, the higher reactivity is generally associated with shorter 5,6 C=C bond lengths.

1. Introduction

A low solubility of fullerenes in most solvents and especially in water limits many of their potential applications. The solubility problem can be resolved by means of chemical functionalization, which consists of the attachment of new chemical groups to the fullerene cage in order to increase its reactivity and affinity toward other compounds and/or media. Among these reactions, one of the first described was the addition of aliphatic amines. This reaction was performed by a variety of experimental methods, including the amination under solvent-free conditions proposed recently by us [1]. Theoretically the amine addition to C_{60} was studied by means of density functional theory (DFT) [1–3]. In particular, we found [3] a certain reaction pattern when adding successively methylamine ($H_3C–NH_2$) molecules onto C_{60}, which does not have a relation to the pyramidalization angle, θ_p [4]. This multiple nucleophilic addition preferentially takes place on 6,6 C=C bonds [3], where the $H_3C–NH$- fragment adds onto one C atom of each 6,6 C=C bond, and H adds onto the other carbon

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atom of the same bond. (The 6,6 bond is shared by two hexagonal rings. Another type of C=C bond in fullerenes is the 5,6 junction, shared by one pentagonal and one hexagonal ring.). C_{60} is the most common and thus best studied member of the fullerene family.

Another member of great interest in the present context is C_{80}. Therefore, the main goal of the present work was to study theoretically C_{80} functionalization by methylamine through successive reactions with up to three amine molecules. We calculated the energies of formation (relative to the level of separated reactants) of different isomers, and in accordance with these values, we defined the most probable site of reaction in each addition step. In this way, we tried to find an addition pattern. In addition, the interrelation between the pyramidalization angle θ_p and reactivity was analyzed.

2. Calculation method

All the results were obtained with the aid of the DMol^3 DFT module of the Materials Studio Modeling 3.1 package from Accelrys, Inc. [5,6]. One of the principal advantages of DMol^3 is the use of numerical functions, which are considered to be more exact compared to Gaussian functions of a comparable size. The DFT generalized gradient approximation (GGA) electronic structure calculations were performed by employing the PW91 functional [7], in conjunction with the double numerical basis set DN, with all-electron treatment. The convergence criteria were set to 'fine': the energy change, maximum force and maximum displacement were 10^{-5} Ha, 0.002 Ha Å^{-1} and 0.005 Å, respectively. The SCF tolerance and orbital cutoff were set to 'fine' as well, 10^{-5} and 3.7 Å, respectively.

The energies of formation ΔE_f of methylamine adducts were calculated in the following way:

$$\Delta E_{f(1)} = E_{\text{adduct}(1)} - (E_{C80} + E_{\text{methylamine}})$$
$$\Delta E_{f(2)} = E_{\text{adduct}(2)} - (E_{\text{adduct}(1)} + E_{\text{methylamine}})$$
$$\Delta E_{f(3)} = E_{\text{adduct}(3)} - (E_{\text{adduct}(2)} + E_{\text{methylamine}})$$

where E is total electronic energy and "adduct (i)" is a product of the addition of i methylamine molecules ($i = 1$–3) to C_{80}.

3. Results and discussion

One of the main differences between C_{60} and C_{80} (I_h) fullerenes is that the five-membered rings of the latter are isolated from each other, whereas they are directly connected in C_{60} to form pyracylene units together with two six-membered rings. Correspondingly, C_{80} has two sites where the amination can occur: the 6,6 bonds (unions between two hexagons) and 5,6 bonds (unions between hexagon and pentagon). The average bond length and pyramidalization angle θ_p for C atoms of the former are 1.43 Å and 8.78°, respectively, and for carbons of the latter type the corresponding values are 1.44 Å and 10.51°. Due to a shorter bond length, one can expect that the 6,6 bond in C_{80} is the preferential addition site. Nevertheless, the value of θ_p is much larger for the 5,6 bond; therefore, according to the theory of π-orbital axis vector (POAV1) [4] this should be the preferential addition site. Fig. 1 shows the optimized geometries for both possible monoaddition products. The formation energies calculated are -11.1 and -1.0 kcal mol^{-1} for the 5,6 and 6,6 adducts. While these values imply that both processes are exothermic, the isomer thermodynamically preferable is the 5,6 adduct. This observation correlates well with the higher value of pyramidalization angle.

For the further addition steps, a large number of isomers are possible in principle. In particular, for the addition of the second methylamine molecule to the monoadduct and for the third methylamine molecule to the diadduct, we analyzed 45 possible 5,6 reaction sites in each case. For the former process, the calculated formation energy spans from -11.8 to 4.6 kcal mol^{-1}, and for the latter, from -8.1 to 14.7 kcal mol^{-1}. For the overwhelming majority of isomers, negative values were obtained, which means that most options are thermodynamically feasible. Accounting for the lowest formation energies for each addition step (that is, -11.1, -11.8 and -8.1 kcal mol^{-1} for the monoadduct, diadduct and triadduct, respectively) implies that introducing the first methylamine moiety into the C_{80} cage slightly facilitates the second addition step, but the third one becomes less exothermic, apparently due to a growing steric hindrance. Optimized geometries for the most favorable addition