Research paper

(CH$_3$Br$\cdots$NH$_3$)@C$_{60}$: The effect of nanoconfinement on halogen bonding

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ABSTRACT

Halogen bonds resemble hydrogen bonds in many aspects. How do the properties of halogen bonds change when confined to nanoregion? In order to explore this, we have encapsulated a halogen bonded complex, CH$_3$Br$\cdots$NH$_3$ inside C$_{60}$ fullerene and studied their properties using density functional theory and quantum theory of atoms in molecule. Our findings show that the geometry of CH$_3$Br$\cdots$NH$_3$ complex is appreciably bent inside C$_{60}$, interaction becomes covalent with larger interaction energy, unlike free CH$_3$Br$\cdots$NH$_3$ complex, which is linear with closed shell interaction. Thus, the halogen bonded complexes show quite different properties at nanoscale.

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1. Introduction

Halogen bonds are characterized as non covalent interactions, which are paid much attention in last two decades. These bonds can be strong enough to control aggregation of organic molecules in solids [1], liquid [2], liquid crystals [3] and gas phase [4]. Halogen bonds can also be utilized in supramolecular architecture [5], molecular recognition [6] and solid state synthesis [7]. Halogen bonding (X-bond) resembles hydrogen bonding (H-bond) in many aspects [8,9]. These interactions are defined as, H-bond: D—H$\cdots$A and X-bond: D—X$\cdots$A, where D is an electron donor and A is acceptor, which is an electronegative atom or electron withdrawing group, i.e., it has lone pair of electrons. Lommerse et al. [10] performed a systematic study on the nature and geometry of intermolecular interactions between carbon bonded halogens (C—X, X = F, Cl, Br or I) and electronegative atoms (A = N, O and S). They found that the electronegative atoms in various hybridization states clearly prefer to form contacts with Cl, Br and I (but not F) in the direction of the extended C—X bond axis.

Buckminsterfullerene (C$_{60}$) [11] is a spherical empty nanocage of carbon, in which a variety of atoms, molecules and clusters can be encapsulated. Such fullerenes are termed as endohedral fullerenes [12,13] in which C$_{60}$ sphere works as a protective cover. The H$_2$ molecules encapsulated into C$_{60}$ have been reported [14–16], which suggests the hydrogen storage capacity of fullerene

nanocage [17]. The chemical bonding in the dimer of noble gas atoms inside C$_{60}$, Ng$_2$@C$_{60}$ (Ng = He, Ne, Ar, Kr and Xe) have been explored by Krapp and Frenking [18]. The properties of molecular clusters of various molecules, such as (H$_2$O)$_n$ [19,20], (HF)$_n$ [21] and (NH$_3$)$_n$ [22] inside C$_{60}$ have also been studied. It has been reported [19–21] that the geometries of hydrogen bonded (H$_2$O)$_2$ and (HF)$_2$ are significantly changed such that their interaction energy is increased. These findings motivated us to analyze the effect of confinement on halogen bonding inside C$_{60}$ nanocage. We have studied halogen bonding in molecular complex, CH$_3$-Br$\cdots$NH$_3$ encapsulated within C$_{60}$ using density functional theory (DFT) and quantum theory of atoms in molecules (QTAIM).

2. Computational methods

In order to choose appropriate DFT method for the system under study, we have performed test calculations on CH$_3$Br$\cdots$NH$_3$ complex using various functionals. In Table 1, we list the halogen bond distance and angle for comparison. We notice that the M06-2X [23,24] seems satisfactory due to performance equivalent to long range dispersion corrected ωB97xD method. Therefore, we have adopted M06-2X/6-311++G(d) scheme as implemented in GAUSSIAN 09 program [25]. The geometry optimization has been carried out without any symmetry constraint in the potential energy surface. The vibrational frequencies of optimized structures have been computed at the same level of theory. The partial atomic charges have been obtained using natural bonding orbital (NBO) scheme [26] available in the Gaussian 09 program. QTAIM calculations were carried out with AIMAll program [27].

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Table 1
Comparison of halogen bond distance and angle in $CH_3Br\cdots NH_3$ at various DFT levels.

DFT level	$d(Br\cdots N)$	$A(C-Br\cdots N)$
B3LYP/6-311++G(d)	3.121 Å	179.9°
CAM-B3LYP/6-311++G(d)	3.102 Å	179.9°
ωB97xD/6-311++G(d)	3.096 Å	179.9°
M06/6-311++G(d)	2.985 Å	179.9°
M06-2X/6-311++G(d)	3.075 Å	179.9°

3. Results and discussion

The equilibrium structure of $(CH_3Br\cdots NH_3)@C_{60}$ is displayed in Fig. 1. The hexagon–hexagon and hexagon–pentagon C—C bonds are calculated to be 1.411–1.467 Å and 1.426–1.469 Å, respectively. The corresponding bonds in empty C_{60} cage are obtained to be 1.385 Å and 1.450 Å, respectively at the same level of theory. The root mean square of deviation (RMSD) of bond lengths is only 0.075 Å. This suggests that encapsulated molecular complex does not affect the geometry of C_{60} appreciably. The structure of encapsulated $CH_3Br\cdots NH_3$ has been displayed in Fig. 2 and compared with that of free (gas phase) $CH_3Br\cdots NH_3$ complex. One can note that in free complex, both CH_3Br and NH_3 molecules are almost linear (bond angle ∼180°) and linked by a halogen bond (C—Br⋯N) with the bond distance of 3.075 Å. When the complex is encapsulated in C_{60}, the molecules rearrange themselves such that the bond angle and distance are reduced to 77° and 1.800 Å, respectively. Likewise, C—Br bond length inside C_{60} is also reduced from 1.944 Å to 1.839 Å. Thus, the pressure exerted by C_{60} brings the molecules closer and reorients them. This feature resembles that of $(H_2O)_2@C_{60}$ in which two hydrogen bonded H_2O molecules become perpendicular inside C_{60} [19,20]. In order to further explore the effect of confinement on halogen bonding, we have listed some parameters corresponding to halogen bond in free $CH_3Br\cdots NH_3$ complex and that inside C_{60} in Table 2, along with their geometry. The stretching vibration of Br⋯N halogen bond is calculated at 121.9 cm^{-1} for free complex, which is shifted to higher wavenumber (228.3 cm^{-1}) when the complex is encapsulated within C_{60}. Note that the blue shift of stretching frequencies has already been reported for a variety of molecules inside C_{60} [28].
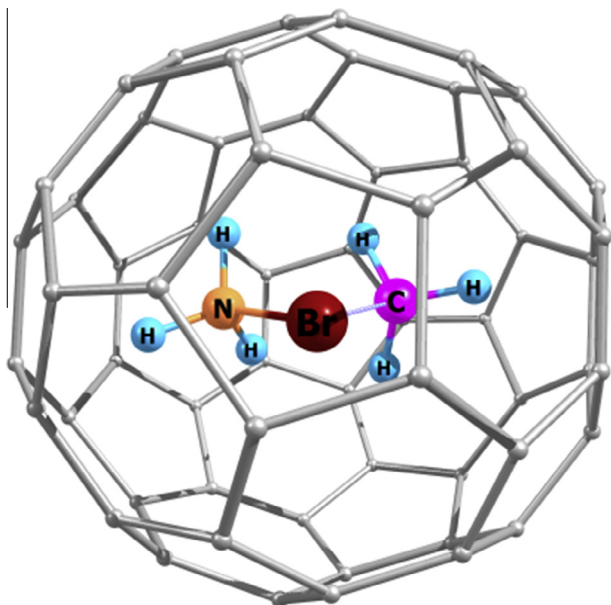

Fig. 1. The optimized structure of $(CH_3Br\cdots NH_3)@C_{60}$ at M06-2X/6-311++G(d) level.

The energy of Br⋯N halogen bond in free $CH_3Br\cdots NH_3$ complex can be estimated as:

$$\Delta E = E[CH_3Br] + E[NH_3] - E[CH_3Br\cdots NH_3] \qquad (1)$$

which is calculated to be 2.3 kcal/mol. In order to check whether the basis set superposition error (BSSE) affects this interaction energy value, we have applied counterpoise procedure [29]. The BSSE corrected value is same as 2.3 kcal at M06-2X/6-311++G(d) level of theory. This is expected as BSSE reduces with the increase in the size of basis set [30] and becomes insignificant for sufficiently large basis set as in the present case. Therefore, we have excluded BSSE for our further calculations. The stabilization energy of C_{60} by encapsulation of $CH_3Br\cdots NH_3$ complex is calculated as below:

$$\Delta E_1 = E[(CH_3Br\cdots NH_3)@C_{60}] - E[C_{60}] - E[CH_3Br\cdots NH_3] \qquad (2)$$

Likewise, the stabilization energy of the cage encapsulating two isolated CH_3Br and NH_3 molecules without any intermolecular interaction can be estimated as follows:

$$\Delta E_2 = E[(CH_3Br\cdots NH_3)@C_{60}] - E[C_{60}] - E[CH_3Br] - E[NH_3] \qquad (3)$$

The calculated ΔE_1 and ΔE_2 values at M06-2X/6-311++G(d) level are 1059.9 kcal/mol and 1050.5 kcal/mol, respectively. Therefore, the intermolecular interaction energy between CH_3Br and NH_3 inside C_{60} can be obtained as below:

$$\Delta E = \Delta E_1 - \Delta E_2 \qquad (4)$$

which is 9.4 kcal/mol, as listed in Table 2. Although molecular complex tends to destabilize the C_{60} cage, intermolecular interaction becomes stronger than that in free complex. This feature can be explained on the basis of the polarization of C_{60} by charge transfer from encapsulated molecules. Note that NH_3 possesses a lone pair of electrons and acts as a good nucleophile. It is believed [31] that nucleophiles generally interact coaxially with the C—X bond in organic molecules (X = Cl, Br and I). This is due to the fact that the electropositive potential region lies at the end of X atom in CH_3Br [32]. In Fig. 3, we have displayed the electrostatic potential (ESP) surface of $CH_3Br\cdots NH_3$ complex. Recently, the importance of ESP surfaces in the study of X-bonds has been highlighted [33]. It is evident that NH_3 approaches CH_3Br along the axis of C—Br bond, i.e., electron deficient region of Br. This is also reflected in the NBO charge on Br, which is 0.02e (see Table 2). In case of $(CH_3Br\cdots NH_3)@C_{60}$, the cage is polarized mainly due to electron transfer from Br atom, which is accredited to its larger size responsible for high polarizing power. One can see that the NBO charges on Br and N atoms inside C_{60} are found to be +1.07e and −1.76e, respectively. This increases the electropositive potential in the vicinity of Br, which is reflected in the ESP surface (see Fig. 3). Consequently, the strength of interaction of Br⋯N increases.

In order to get insights into interaction of molecular complex with C_{60}, we have performed QTAIM [34] analysis. The interaction between two atoms is described by the presence of a bond critical point (BCP) [35]. The nature and strength of interaction are quantified on the basis of some topological parameters at BCP. According to Rozas et al. [36], H-bonds are characterized as strong (covalent) for $\nabla^2\rho_{BCP} < 0$ and $H_{BCP} < 0$, medium (partially covalent) for $\nabla^2\rho_{BCP} > 0$ and $H_{BCP} < 0$, and weak (electrostatic) $\nabla^2\rho_{BCP} > 0$ and $H_{BCP} > 0$. The strength of interaction can be estimated as suggested by Espinosa et al. [37]:

$$E_{int} = -\frac{1}{2}V_{BCP} \qquad (5)$$

QTAIM method has also been applied on the physical nature and characteristics of X-bonds [38,39] and it has been found that X-bonds can be classified as closed shell for relatively low values of ρ_{BCP} and positive sign of $\nabla^2\rho_{BCP}$, whereas H_{BCP} is negative for strong X-bonds, reflecting the increase in covalent character. A