Effect of Solvents on the Electronic Properties of Fullerene Based Systems: Molecular Modelling

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Abstract

Density functional theory (DFT) was utilized as a backup for the experimental study. Solvent effects on the molecular structure and electronic properties of fullerene C60 and its derivatives were estimated by performing the DFT with B3LYP/3-21G** calculations using the polarized continuum model (PCM) developed by Tomasi. Overall, different forms of quantum-chemistry were used based on performed calculations, including dipole moments (total dipole moment, X, Y, and Z components) and finally, orbital energies, EHOMO, ELUMO; HL gap (gap between EHOMO and ELUMO).

Keywords: Computational methods; Fullerene; Solubility; DFT; polarized continuum model; Molecular modeling; Electronic properties

Introduction

Fullerenes are allotropes of carbon and possess various novel properties that make them useful in the area of nanotechnology and pharmaceuticals. Fullerenes are currently being widely investigated and have potential for various technical applications [1]. In particular, for biomedical testing, water-soluble forms of fullerenes are of outstanding interest.

Numerous efforts have been formed to explain the trends in room-temperature solubility of the fullerenes [2-4]. There are many different approaches to calculate and predict C60 solubility in organic solvents. Some of them are fully mechanistic [5-9], developed from the thermodynamical point of view; others are statistically based, with good correlation coefficients, but not transparent and complicated in interpretation [10-16].

In this work, we aspired to discover simple, transparent relationship and computationally fast approach to predict the solubility of C60 in various solvents. The exact description of solvation phenomena presents a substantial challenge to theoretical chemistry. Two typical approaches are employed to contain the solvent effects. One is the so-called supermolecular approach or the discrete model, where explicit solvent molecules are added and treated at the same level of theory as that employed for the solute. Nevertheless, this supermolecular approach does come with a significant increase in computational expense. Some other approach is the polarizable continuum model (PCM).

Previously, the structures of Fullerenes c60 had been studied in the gas phase by means of the B3LYP/3-21G** level of calculation [17,18]. We made geometry optimization in vacuo, and the calculation was based along the gas-phase optimized geometries. The solvent effects were identified through the polarizable continuum model (PCM) of Tomasi et al. [19] because the PCM model offers a balanced and theoretically sound treatment of all solute–solvent interactions at a very reasonable computational cost.

Computational Methods

All the calculations use the polarizable continuum model (PCM) were utilized to describe the thermodynamics of solvation of the fullerenes C60 and its derivatives in some solvents. Solvent effects were evaluated using the (Gaussian 98 w) [20] implementation of the thermodynamically based polarized continuum model (PCM) the level of calculations is b3lyp/3-21g** for the ground state.

Results and Discussions

Solubility of fullerene C60

The bond lengths and bond angles of the studied compound, C60, were optimized in the gas phase, water, Methanol, Heptane, Acetonitrile, Toluene and Pyrrolidine. Table 1 establishes the important changes of bond length and bond angle for C60 from gas to solute.

- a) Minimal value of bond length between carbon atoms;
- b) Maximal value of bond length between carbon atoms;
- c) Minimal value of bond angle between carbon atoms;
- d) Maximal value of bond angle between carbon atoms

From Table 1, we can see little changes in the bond lengths of C60 when C60 was optimized with water, Methanol, Heptane, Acetonitrile and Toluene and compared within the gas phase. The great change of bond length and angle value of C60 in the Pyrrolidine compared within the gas phase, water, Methanol, Heptane, Acetonitrile and Toluene. The same bond length and angle in water, Heptane, Acetonitrile and Toluene (slight modifications in the attachment angle of C60 in Methanol).

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HOMO and LUMO energy gaps for C60 calculated at the DFT level (HOMO), the lowest unoccupied molecular orbital (LUMO) and might imply that the solvent (Pyrrolidine) is in favor of the C-C bond. The solvent (Pyrrolidine) can reduce the intensity of the max. C–C bond, which is smaller than that in a vacuum, and the solvents (water, Methanol, Heptane, Acetonitrile and Toluene), these results indicate that the solvent effect has a minor influence on these geometrical parameters, the smaller changes for the bond lengths and angles. Our simulation predicts a lengthening of the max C–C bond (≈-0.873 Å and 7.3 degrees, respectively), whereas the Methanol-solvent results predict a narrowing of the min. bond length and angle (≈-0.873 Å and 7.3 degrees, respectively), whereas the Methanol-solvent results predict smaller changes for the bond lengths and angles.

The solvents (water, Methanol, Heptane, Acetonitrile and Toluene) effect has a minor influence on these geometrical parameters, the calculations do not evidence any significative effect on the lengths and angles, the only observable change is of C60 in the Pyrrolidine.

Also, Table 1 shows a slight lengthening of the maximum bond length and angle of C60 in Pyrrolidine (a widening of the maximum bond length and angle), and a narrowing of minimum bond length and angle. Our simulation predicts a lengthening of the max C-C bond and the max. C-C-C angle (≈+0.11Å and 4.6 degrees, respectively) and a narrowing of the min. bond length and angle (≈-0.873 Å and 7.3 degrees, respectively), whereas the Methanol-solvent results predict smaller changes for the bond lengths and angles.

The solvents (water, Methanol, Heptane, Acetonitrile and Toluene) also found that the C–C bond in C60 is also decreased by 0.017 Å compared with that in the pristine cage. It is well-known that there are two kinds of C–C bond in the C59X (X=C, B, Al, Ga, In, P, As, Sb) cages in pyrrolidine solvent, the bond lengths and bond angles in pyrrolidine solvent are listed in Table 4. From Table 4, we can see that all the doped cages in pyrrolidine solvent undergo some distortions due to the dopant atoms, though they still preserve closed cage structures.

### Table 1: Selected structural parameters of the optimized C60 in gas and different solvents, bond distance (Å) and bond angles (°). Obtained by the B3LYP method with 3-21G* basis set method which described through the polarizable continuum model (PCM).

| Solvent     | Geometry | Optimization | C – C a) | C – C b) | C - C – C c) | C - C – C d) |
|-------------|----------|--------------|----------|----------|-------------|-------------|
| Gas phase   |          |              | 1.385    | 1.464    | 108         | 120         |
| Water       |          |              | 1.389    | 1.461    | 108         | 120         |
| Methanol    |          |              | 1.393    | 1.457    | 107.9       | 120.2       |
| Heptane     |          |              | 1.389    | 1.461    | 108         | 120         |
| Acetonitrile|          |              | 1.389    | 1.461    | 108         | 120         |
| Toluene     |          |              | 1.389    | 1.461    | 108         | 120         |
| Pyrrolidine |          |              | 1.011    | 1.571    | 100.7       | 124.6       |

From Table 2, one can see that the solvent sequence with low to high HOMO/LUMO gap is (energy gap of C60 in Pyrrolidine-energy gap of C60 in the gas phase, water, Methanol, Heptane, Acetonitrile and Toluene solutions).

The HOMO–LUMO gaps had been studied in the gas phase, water, Methanol, Heptane, Acetonitrile and Toluene solutions, show no effect and the energy gap remains the same. Based on the above description, it is easy to understand why the water, Methanol, Heptane, Acetonitrile and Toluene solutions are suspension of C60.

The results reported in Table 3, show that C60 in the gas phase, water, Methanol, Heptane, Acetonitrile and Toluene solvents possess the lowest dipole moment compared with C60 in Pyrrolidine solvent.

By knowing the value of dipole moment we can conclude that the clusters having a higher dipole moment can be treated as a good solvent.

As expected, the molecule becomes more polarized in the presence of the Pyrrolidine solvent (Table 3), and the molecular dipole moment increases with solvent polarity.

### Solubility of specific fullerene derivatives

The optimized structures of the C59X (X=C, B, Al, Ga, In, P, As, Sb) cages in pyrrolidine solvent, the bond lengths and bond angles in pyrrolidine solvent are listed in Table 4. From Table 4, we can see that all the doped cages in pyrrolidine solvent undergo some distortions due to the dopant atoms, though they still preserve closed cage structures.

- a) Minimal value of bond length between carbon atoms;
- b) Maximal value of bond length between carbon atoms;
- c) Minimal value of bond angle between carbon atoms;
- d) Maximal value of bond angle between carbon atoms

It is well-known that there are two kinds of C–C bond in C60 cage, the [6] bond and the [5,6] bond. In pyrrolidine solvent, the bond lengths are 1.011 Å and 1.571 Å for [6] and [5,6] bonds, respectively based on our DFT calculations. When the carbon cage is doped by the dopant atom, the C–X bonds are presented. From Table 4, it can be determined that the C–X bond lengths are in the orbit of 1.011 to 2.143Å. The bond lengths increased obviously for X= B, Al, Ga and In, ranging from 1.087Å to 2.143Å and for X= P, As, and Sb, ranging from 1.087Å to 2.013Å. Nevertheless, the C–N bonds in CSN9 are 1.084 and 1.554Å, and therefore the original [5,6] bond (max. bond length) is even decreased by 0.017 Å compared with that in the pristine cage. It is also found that the C–X bond lengths increase more significantly for the larger dopant atoms.

For example, the C–B bonds are 1.087 and 1.603 Å, while the C–X bonds (X =P, As, Sb) are estimated to be within 1.087–2.013Å. Hence it is clearly that the cage with larger dopant atom gives more obvious distortion.

The bond angles are also listed in Table 4, for fullerene and substituted fullerene in pyrrolidine solvent. From the table it is found that the bond angles are about unchanged for doping with the atoms compared with that of the pristine cage.

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Table 2: Calculated HOMO/LUMO energy gap as (ev) for C60, which described through the polarizable continuum model (PCM) and calculated by B3LYP methods with 3-21G* basis set.

| Solvent     | Energy Gap (ev) |
|-------------|-----------------|
| HOMO        | LUMO            |
| Gas phase   | -6.531          | -3.523          | 3.007  |
| Water       | -6.531          | -3.523          | 3.007  |
| Methanol    | -6.531          | -3.523          | 3.007  |
| Heptane     | -6.531          | -3.523          | 3.007  |
| Acetonitrile| -6.531          | -3.523          | 3.007  |
| Toluene     | -6.531          | -3.523          | 3.007  |
| Pyrrolidine | -6.06           | -3.359          | 2.7    |
It is well-known that the frontier orbitals, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), act as an important role in chemical reaction for the reactant molecule. so, the frontier orbital analysis of the doped cages is necessary. In Table 5, the HOMO and LUMO energy levels of the substituted fullerene were summarized. It can be seen that HOMO and LUMO levels of the doped cages are all decreased and for substituted fullerenes, which described through the polarizable continuum model (PCM) by using Pyrrolidine and calculated by B3LYP methods with 3-21G** basis set.

Clusters | Geometry Optimization | Calculated bond lengths (Å) and bond angles (°) for C60 and some substituted fullerenes, which described through the polarizable continuum model (PCM) by using Pyrrolidine and calculated by B3LYP methods with 3-21G** basis set.
|---|---|---|---|---|---|---|---|
| C60 | 1.9692 | 0 | -1.2089 | 2.3106 |
| C60_B | -0.7839 | -0.0001 | -2.5694 | 2.6863 |
| C60_Ai | -2.3374 | 0.0004 | -1.3346 | 2.6916 |
| C60_Ga | 2.6356 | -1.0881 | 0.0002 | 2.8514 |
| C60_In | 3.0786 | 0.7356 | 0 | 3.1653 |
| C60_N | 0.3106 | 0 | -1.6342 | 1.6635 |
| C60_P | 0.4219 | 0 | -1.8398 | 1.8875 |
| C60_As | 1.0084 | 0.0011 | -1.6833 | 1.9622 |
| C60_Sb | -1.5629 | -1.538 | 0.0011 | 2.1928 |

C60 cage. So the kinetic stability of the cage is increased by substitution from viewpoint of HOMO-LUMO gap.

Lastly, we have also worked out the dipole moments of the C60 and some substituted fullerenes, which described through the polarizable continuum model (PCM) by using Pyrrolidine and calculated by B3LYP methods with 3-21G** basis set (Table 6).

The dipole moment is defined as the first derivative of the energy with respect to an electric field. The calculated dipole moment can be conveyed in terms of vector in three directions X, Y and Z as indicated in Table 6. The negative mark of both X, Y and Z-axis indicates that doping has an outcome on the dipole moment, which can cause subsequent changes in the electrical properties of the molecular species.

Table 5: Calculated HOMO/LUMO energy gap as (ev) for C60 and some substituted fullerenes, which described through the polarizable continuum model (PCM) by using Pyrrolidine and calculated by B3LYP methods with 3-21G** basis set.

Clusters | Geometry Optimization | Calculated bond lengths (Å) and bond angles (°) for C60 and some substituted fullerenes, which described through the polarizable continuum model (PCM) by using Pyrrolidine and calculated by B3LYP methods with 3-21G** basis set.
|---|---|---|---|---|---|---|---|
| C60 | | | | | | | |
| C60_B | | | | | | | |
| C60_Ai | | | | | | | |
| C60_Ga | | | | | | | |
| C60_In | | | | | | | |
| C60_N | | | | | | | |
| C60_P | | | | | | | |
| C60_As | | | | | | | |
| C60_Sb | | | | | | | |

The dipole moment is increased for C59X (X= N, P, As, Sb) with respect to an electric field. The calculated dipole moment can be conveyed in terms of vector in three directions X, Y and Z as indicated in Table 6. The negative mark of both X, Y and Z-axis indicates that it points in X, Y and Z direction. Regarding Table 5, one can conclude that, the total dipole moment and the net contribution of charge in the directions X, Y and Z are completely exchanged.

As listed in Table 5 the dipole moment is computed. Regarding C60, the total dipole moment is 2.3106 Debye distributed as 1.9692, -0.0000 and -1.2089 contributions in the x, y, and z-directions, respectively. As the effect of doping the change in the dipole moment of C60 and C59X was being discussed. The value of dipole moment is increased for C59X (X= B, Al, Ga, In) and it is increased as compared with that of C60. And also, The value of dipole moment is increased for C59X (X= N, P, As, Sb) and it is decreased as compared with that of C60.

The C60 and doped-C60 indicate that doping has an outcome on the dipole moment, which can cause subsequent changes in the electrical properties of the molecular species.

Conclusions

The solubility of C60 in the solvents is important to enable purification and chemical change. In universal, the solubility in the majority of solvents is very depressed, because C60 exhibit a high tendency for aggregation. On the other hand the interaction between the solvent molecules and C60 is usually very light, since the fullerene is a nonpolar molecule, which is hardly polarizable due to the large HOMO-LUMO gap. In summary, the solubility of C60 in polar solvents

Table 6: Calculated dipole moment as Debye for C59 and some substituted fullerenes, which described through the polarizable continuum model (PCM) by using Pyrrolidine and calculated by B3LYP methods with 3-21G** basis set.

Clusters | Geometry Optimization | Calculated bond lengths (Å) and bond angles (°) for C60 and some substituted fullerenes, which described through the polarizable continuum model (PCM) by using Pyrrolidine and calculated by B3LYP methods with 3-21G** basis set.
|---|---|---|---|---|---|---|---|
| C60 | | | | | | | |
| C60_B | | | | | | | |
| C60_Ai | | | | | | | |
| C60_Ga | | | | | | | |
| C60_In | | | | | | | |
| C60_N | | | | | | | |
| C60_P | | | | | | | |
| C60_As | | | | | | | |
| C60_Sb | | | | | | | |

The dipole moment is increased for C59X (X= B, Ga, In) and it is decreased as compared with that of C60. And also, The value of dipole moment is increased for C59X (X= N, P, As, Sb) and it is decreased as compared with that of C60.
such as methanol and water is about zero. This low solubility can also be considered in the case of, Heptane, Acetonitrile and Toluene as solvents. The best solubilities are obtained in Pyrrolidine, which makes these solvents to the standard solvents for preparative use.

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