Theoretical thermochemical studies of phenylacetylene scaffolds

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ABSTRACT

Phenylacetylene scaffolds are known to be an important component in electronic devices, but their thermochemistry has not been studied so far. In this paper, we systematically calculate the strain energies (SE) and the standard enthalpies of formation ($\Delta_f H_{298}^{\circ}$) of sixteen linear polyynes-substituted benzene (PSB) and seven cyclic [n]orthophenyleneacetylenes ([n]COPAs) (n = 2–8). The geometries and vibrational frequencies of PSB were calculated at B3LYP/6–31 + G(d,p), mPW1PW91/6–31 + G(d,p), and M06-2X/6–31 + G(d,p) levels of theory and for [n]COPAs, mPW1PW91/6-31G(d) was used. Isodesmic and homodesmotic reactions approach were used to calculate SE and $\Delta_f H_{298}^{\circ}$. The results show that $\Delta_f H_{298}^{\circ}$ of PSB increases steadily with the increasing the numbers of $-C\equiv C-$ linkage, and endothermic $\Delta_f H_{298}^{\circ}$ of these molecules are indicative of an acetylene substituent strain. The SE per-unit monomer (SE/n), and $\Delta_f H_{298}^{\circ}$ per-unit monomer ($\Delta_f H_{298}^{\circ}/n$) of [n]COPAs were calculated and results were compared with its *meta* and *para* counterpart. In addition, electronic properties such as HOMO, LUMO and HOMO-LUMO energy gap were calculated.

1. Introduction

The rapid developments of synthetic chemistry have been encouraging researchers to prepare and design carbons allotropes and carbon-rich compounds with an unusual structure, electronic, and optical properties [1,2]. The electronic and optoelectronic devices using carbon based π-conjugated organic materials, which include organic light-emitting diodes (OLEDs), organic photovoltaic devices (OPVs), organic field-effect transistors (OFETs), organic photorefractive devices, have recently attracted a great deal of attention and the major scientific challenges [3–12]. Shirakawa et al. [13] discovered the electrical conductivity of doped polyacetylene molecules in the use of π-conjugated organic materials in electronics devices. Much important progress has been made in their molecular design, synthesis, and the useful applications [13]. In the past few years, increasing interest has focused on conjugated triple-bond polyphenylacetylenes as a promising class of semiconductors due to their spatial and structural arrangements [14,15].

Many of these molecular and polymeric phenylacetylene allotropes (PPAs) are crucial in the field-effect transistor to enable low-cost, large area, and mechanically flexible devices. The acetylenic molecular designs with dimensions on the multi-nanometer scale have already been synthesized and are known to display some fascinating optoelectronic properties [1,2]. Malko et al. [16] reported the two-dimensional structures of graphynes, which are derived from graphite by replacing

the single C—C bond with −C≡C− linkage between every other hexagon. A more extended version of graphyne is graphdiyne, which has the buta-1, 3-diyne unit. Both graphyne and graphdiyne lend themselves into intercalation with a number of metals, leading to superconducting materials [14,15,17].

Cyclophynes are an another important class of PPAs, that are constructed by replacing ethano groups of *ortho*, *meta*, and *para* cycophanes [18,19] with single acetylenic linkage (−C≡C−) form a novel group of oligomer usually known as cyclic [n]orthophenyleneacetylenes ([n]COPAs]), cyclic[n]metaphenyleneacetylenes ([n]CMPAs), and cyclic [n]para-phenyleneacetylenes ([n]CPPAs]). Many experimental and theoretical studies of [n]COPAs, [n]CMPAs, and [n]CPPAs have been performed [16,17,20–22,] and it is known that these oligomer are a molecular model that can possibly form various new types of molecular electronic devices such as rectifiers [23–25], memory devices [26], switches [27], and transistors [28]. In our previous studies [21,22], we calculated strain energies (SE), standard enthalpies of formation ($\Delta_f H_{298}^{\circ}$), spectroscopic constants and electronic properties of [n]CMPAs [22] and [n]CPPAs [21]. The predicted SE, $\Delta_f H_{298}^{\circ}$ and electronic properties suggested that cyclic-phenyleneacetylenes (CPAs) are attracted a great interest because of their use in supramolecular chemistry, in the electronic devices, and also because they are precursor molecules of fullerenes and graphene [21,22].

A novel PPAs network of fullerene, diamond, and graphite is yet to synthesize. Efforts directed towards its synthesis have generated a great variety of interesting molecules. Some of these molecules are useful in

photovoltaics cell because they have strong electron withdrawing character of the triple bond and their rod-like structure [29,30]. Although preparation of these novel compounds may not be straightforward, but the successful synthesis of some of PSB, [n]COPAs and their derivatives has been made [1,2,15–17,29,30]. Since only a little information about PSB and [n]COPAs are available in the literature therefore, it is important to advance a theoretical methods for predicting the thermodynamic properties of these oligomer analogs of π-conjugated organic materials before their laboratory synthesis. Electronic structure calculation has always proven to be very important tools to the experimentalist, in terms of both a prior expectation that cover the way for designing new experiments and explaining the experimental observation a posteriori.

Over the years, many different hypothetical chemical reactions have been proposed in efforts to correctly predict the $\Delta_f H_{298}^\circ$ and strain energies of organic molecules i.e. Pople bond separation, homodesmotic, hyperhomodesmotic, semihomodesmotic, isogeitonic, isoplesitoic [31–39], where experimental data have large uncertainties. In 2014, Ramabhadran et al. [31,32] have proposed connectivity based hierarchy (CBH) reaction schemes for the computation of $\Delta_f H_{298}^\circ$ of aliphatic organic molecules. The CBH method produces error less than 4.18 kJ mol^{-1} for these organic systems [31,32]. Wheeler et al. [35] proposed the homodesmotic reaction approach for the calculation of the $\Delta_f H_{298}^\circ$ for both aliphatic and aromatic hydrocarbon systems. The calculation of $\Delta_f H_{298}^\circ$ using isodesmic and homodesmotic reaction approaches were also tested by various research groups and the results were found to be in good agreements with experimentally measured value [21,35,36].

In this paper, we used similar approach i.e. bond separation isodesmic, ring conserved and homodesmotic reaction schemes coupled with density functional theory to analyze the trend of $\Delta_f H_{298}^\circ$ of PSB and [n]COPAs (n = 2–8). In addition, the highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO) and HOMO-LUMO energy gap usually defines the kinetic and thermodynamic stability [40] were also calculated. The results of this study can be used to improve the $\Delta_f H_{298}^\circ$ of other oligomer as well as aid in understanding the thermochemical properties of larger phenylacetylene scaffolds.

2. Computational methodology

All the density functional theory (DFT) calculations were carried out using the Gaussian 09 suite of programs [41]. The structure of polyynes-substituted benzene (PSB) and reference compounds were optimized using hybrid-DFT; B3LYP [42], mPW1PW91 [43], and M06-2X [44] methods with 6–31 + G(d,p) basis set. The optimized structures obtained using M06-2X/6–31 + G(d,p) are shown in Fig. 1. The structure of [n]COPAs (n = 2–8) were optimized using at the mPW1PW91/6-31G(d) level of theory and the optimized structure are shown in Fig. 2. Harmonic vibrational frequencies were calculated using the same level of theory to characterize the nature of the stationary point. The absence of imaginary frequency confirms that the obtained structure corresponds to a true minimum of the potential energy surface. In addition, the zero-point correction was used for the calculation of standard enthalpies of formation ($\Delta_f H_{298}^\circ$). The combination of B3LYP, mPW1PW91, and M06-2X with 6–31 + G(d,p) and 6–31G(d) basis set has been tested by various research groups [22,23,32,33] and shown to be reasonably accurate results.

The $\Delta_f H_{298}^\circ$ for PSB molecules were calculated using bond separation isodesmic (BSI), ring conserved isodesmic (RCI), and homodesmotic (HD) reaction schemes (refer to the Supplementary Material Information for their detailed description) and $\Delta_f H_{298}^\circ$ of [n]COPAs (n = 2–8) were calculated using HD reaction approach.

The calculations of $\Delta_f H_{298}^\circ$ are based on the following two steps: (1) enthalpy of reaction ($\Delta_{rxn} H_{298}^\circ$) was computed from these schemes and

(2) $\Delta_{rxn} H_{298}^\circ$ was used with the experimental enthalpies of formations on the reference molecules. For example, the $\Delta_f H_{298}^\circ$ of unknown molecule *A* of reaction type $mA + nB \rightarrow rC + sD$ is given by:

$$m\Delta_f H_{298}^\circ(A) = \{[r\Delta_f H_{298}^\circ(C) + s\Delta_f H_{298}^\circ(D)] - n\Delta_f H_{298}^\circ(B) - \Delta_{rxn} H_{298}^\circ\}.$$

The $\Delta_{rxn} H_{298}^\circ$ were calculated using;

$$\Delta_{rxn} H_{298}^\circ = \{[r(\varepsilon_0 + H_{corr})_{(C)} + s(\varepsilon_0 + H_{corr})_{(D)}] - [m(\varepsilon_0 + H_{corr})_{(A)} + n(\varepsilon_0 + H_{corr})_{(B)}]\}$$

where $(\varepsilon_0 + H_{corr})$ is the sum of electronic energies and thermal correction for each species were obtained from Gaussian 09 thermochemistry output.

The calculations were done for sixteen PSB molecules namely; Phenylacetylene

(**1**), Buta-1,3-diyn-1-ylbenzene (**2**), Hexa-1,3,5-triyn-1-ylbenzene (**3**), Octa-1,3,5,7-tetrayn-1-ylbenzene (**4**), 1,2-Diethynylbenzene (**5**), 1-(Buta-1,3-dienyl)-2-ethynylbenzene (**6**),1-Ethynyl-2-(hexa-1,3,5-triynyl)benzene (**7**), 1-Ethynyl-2-(octa-1,3,5,7-tetraynyl)benzene (**8**), 1,3-Diethynylbenzene (**9**), 1-(Buta-1,3-diyn-1-yl)-3-ethynylbenzene (**10**), 1-Ethynyl-3-(hexa-1,3,5-triyn-1-yl)benzene (**11**), 1-Ethynyl-3-(octa-1,3,5,7-tetraenyl)benzene (**12**), 1,4-Diethynylbenzene (**13**), 1-(Buta-1,3-diyn-1-yl)-4-ethynylbenzene (**14**), 1-Ethynyl-4-(hexa-1,3,5-triyn-1-yl)benzene (**15**) and 1-Ethynyl-4-(octa-1,3,5,7-tetrayn-1-yl)benzene (**16**) as shown in Fig. 1 and [n]COPAs (n = 2–8) molecules as shown in Fig. 2.

All of the geometrical parameters, vibrational frequencies needed to reproduce the calculations are given in the Supporting Information. Strain energies and enthalpies of formation are expressed in units of kJ mol^{-1}, vibrational frequencies in units of cm^{-1} and HOMO, LUMO and HOMO-LUMO gap energies in units of (eV).

3. Results and discussion

3.1. Geometries and vibrational frequencies

The geometries of polyynes-substituted benzene (PSB), designated as **1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15,** and **16** were optimized using B3LYP, mPW1PW91, and M06-2X functional with 6–31 + G(d,p) basis set. The optimized geometries using B3LYP/6–31 + G(d,p), mPW1PW91/6–31 + G(d,p), and M06-2X/6–31 + G(d,p) levels are given in the Supplementary Material Table S1–S3. The optimized geometries of the molecules **1, 2, 3, 4, 5, 9, 14, 15,** and **16** have the point group symmetry C$_{2v}$, molecules **7, 8, 10, 11,** and **12** have C$_s$ symmetry and molecule **13** has point group symmetry D$_{2h}$. The vibrational analysis was carried out at the same level of theory to obtain zero-point correction. The calculated vibrational frequencies of PSB are given in Supplementary Material Table S4–S6.

To gain more confidence in the performance of the B3LYP/6–31 + G(d,p), mPW1PW91/6–31 + G(d,p), and M06-2 × 6–31 + G(d,p), the normal modes of vibrations of 1,4- diethynyl-benzene (**13**) were compared with experimentally observed values [45]. The comparison between theory and experiment are given in Supplementary Material Table S7. The estimated errors for most of the normal modes are in the range of ∼ ± 1–6%, but the errors in the lower frequency modes are higher. The calculated vibrational frequencies were scaled by a factor of 0.96, 0.95, and 0.95, the agreement between the fundamental (experimentally determined) and theoretically computed frequencies are good indeed [46].

The geometries of cyclic [n]orthophenyleneacetylenes ([n]COPAs (n = 2–8) were calculated using mPW1PW91/6-31(d) and the optimized structures are shown in Fig. 2. The optimized geometries and vibrational frequencies are tabulated in Supplementary Material Table S8–S9. The optimized structure for [2]COPA and [3]COPA, with atom labels are shown in Fig. 3 and selected bond lengths and bond angles are listed in Table 1. The comparison between the calculated values and