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Donor-Acceptor Substituted Graphyne: A Promising Nonlinear Optical Material

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Abstract

Graphyne (Gy) has been modified to prepare an extraordinary donor-Gy-acceptor structure to plan a better nonlinear optical material. Extraordinary character of conjugate graphyne backbone leads to a huge static first hyperpolarizability (β_{tot}) up to 128 × 10^{-30} esu which is an enormous improvement than that of the bare graphyne. Amusingly, we have discovered two groups of site of substitution in graphyne having two separate symmetries although they all are energetically equivalent. Besides the colossal static first hyperpolarizability, it can be used over a wide range of electromagnetic spectrum.

Introduction

Study of attractive electronic properties of conjugated carbon family is turned into a current trend furthermore important since that could have opened an extensive variety of applications. After a few successful attempts to synthesis of graphene and its successors by mechanical cleavage [1] and a few chemical methods, [2,3] a bunch of its application in molecular electronics [4,5], sensors [6,7], and energy storages [8,9] have come into realization. The most interesting part of a carbon molecule is its stay in different hybridization which leads to different fascinating properties of it. Recently another layered structure of carbon, dehydrobenzo(12)annulene (DBA-12) [10] named graphyne (Gy), containing sp^2 and sp^3 hybridization is turned into a potential member of the promising carbon family. Baughman et al was hypothetically anticipated it in 1987 [11]. Among his few predictions, the experimental realization of a few subunits of Gy by Haley and colleagues [12] and others [13,14] makes us convinced. Graphyne framework was structurally stabilized by embeddings an acetylenic linkage between two reinforced carbons of graphene.

Molecules having large nonlinear optical property (NLO) are very important because of its massive application in low cost, superior photonic applications [15-17]. The current period of studies are concentrated on the understanding of concept and synthesize new materials having extensive NLO property [18-23]. Quantum chemical studies play a principal part to predict the structure-property relationship and give an extensive clue for the further approach. The purpose of the communication is to predict the right NLO molecule structure and study the impact of substitution on their first hyperpolarizability property as well as some other electronic properties. First hyperpolarizability is a measure of how effortlessly a dipole is induced in an atom by an electric field in its vicinity. The molecules having a Π-network motif end capped with an electron donating (D) and electron accepting (A) group has a place with an established class of NLO material having large first hyperpolarizability by electron push-pull mechanism. Here, electron-donor amino (NH_2) group and an electron-acceptor nitryl (NO_2) group are used to do these estimations.

Computational Details

Geometry optimization and the static first hyperpolarizability estimation of all the graphyne structures were carried out by B3LYP/6-31+g method [24,25]. Electronic absorption property calculations were done utilizing B3LYP/6-31+g basis set executed in TD-DFT formalism. All the calculations were performed utilizing Gaussian 09 software package [26]. Absorption spectrum was extracted utilizing Gausssum-2.2.5 package [27].

The energy (E) of a molecular system in a uniform electric field (F) can be written as equation (1):

$$E = E(0) - \mu_i F_i - \frac{1}{2}\alpha_i \beta F_i F_j - \frac{1}{6}\beta_{ijk} F_i F_j F_k \qquad (1)$$

Where, E (0) is the energy of the framework without the electric field F; and μ, α and β are the dipole moment, polarizability and the first hyperpolarizability respectively. The subscript i, j and k was used to name the x, y and z parts individually. It is quite clear that α, β can be obtained by differentiating E with respect to F. Total static first hyperpolarizability (βtot), is characterized by equation (2)

$$\beta_{tot} = \left(\beta_X^2 + \beta_Y^2 + \beta_Z^2\right)^{\frac{1}{2}} \qquad (2)$$

Where, $\beta_i = \frac{3}{5}(\beta_{iii} + \beta_{ijj} + \beta_{ikk})$; i,j,k=x,y,z.

Results and Discussion

The optimized structure of graphyne (DBA-12) [1] is shown in Figure 1 [2]. It has three benzene rings (i, ii and iii) and having four substitution positions (1, 2, 3 and 4) in each of them.

Symmetry of graphyne allows us to see that, every benzene ring-(i) is symmetrically situated with respect to the other two. This same symmetry is reflected in ring-(ii) and ring-(iii). Owing to the symmetry, the donor and acceptor substitutions were carried out in any two of the rings separately. This work basically utilized ring-(i) for electron acceptor (-NO_2) and ring-(ii) for electron donor (-NH_2) substitution. The relative position of donor and acceptor was changed and the relevant estimations were carried out on every framework (Figure 2) to discover the suitable substitution site. It is interesting to note that, every one of them is energetically equivalant with energy -1181.23 ev.

It is exceptionally intriguing that, with the change of position of -NH_2 and -NO_2 the band gap demonstrates a very nearly oscillatory behavior as delineated in Figure 3.
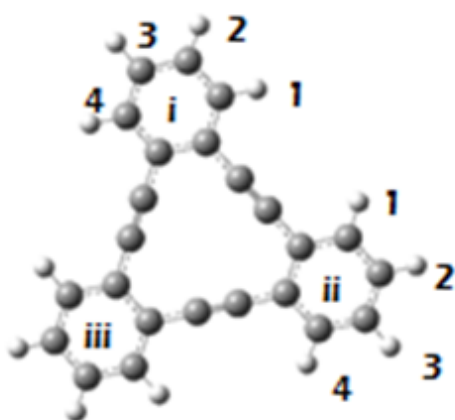
Figure 1: Graphyne (dehydrobenzo(12)annulene (DBA-12)) with its substitution positions on each ring demonstrated with numbers.

Band gap variety can give an insight of two classes of sites of substitution in graphyne. One group constitutes of 1-1, 2-1, 3-2 and 4-2 and other one has 1-3, 2-3, 3-3 and 4-3. Substitution at these two sites prompts two different symmetry and subsequently exhibit differing band gaps. From Figure 3, it can be infer that the oscillation width is almost periodic.

Static first hyperpolarizability

Static first hyperpolarizability (β_{tot}) variation of molecules was depicted in the inset of Figure 4. It shows that the substitution has an enormous effect on the first hyperpolarizability of Gy. The β_{tot} of substituted graphyne 3-3 is improved significantly in compare to the unsubstituted one. The sum of the first hyperpolarizability of Gy-A and Gy-D is not equivalent to that of any individual donor-acceptor substituted Gy which discard the cooperative –effect. It is intriguing to notice that the first hyperpolarizability climbs to the highest value (127.956×10^{-30} esu) at a most extreme DA-separation, graphyne 3-3 (molecule no 11), of 12.55 Å. Although there could be some other factors responsible for this large improvement of β_{tot} of the molecule 3-3.
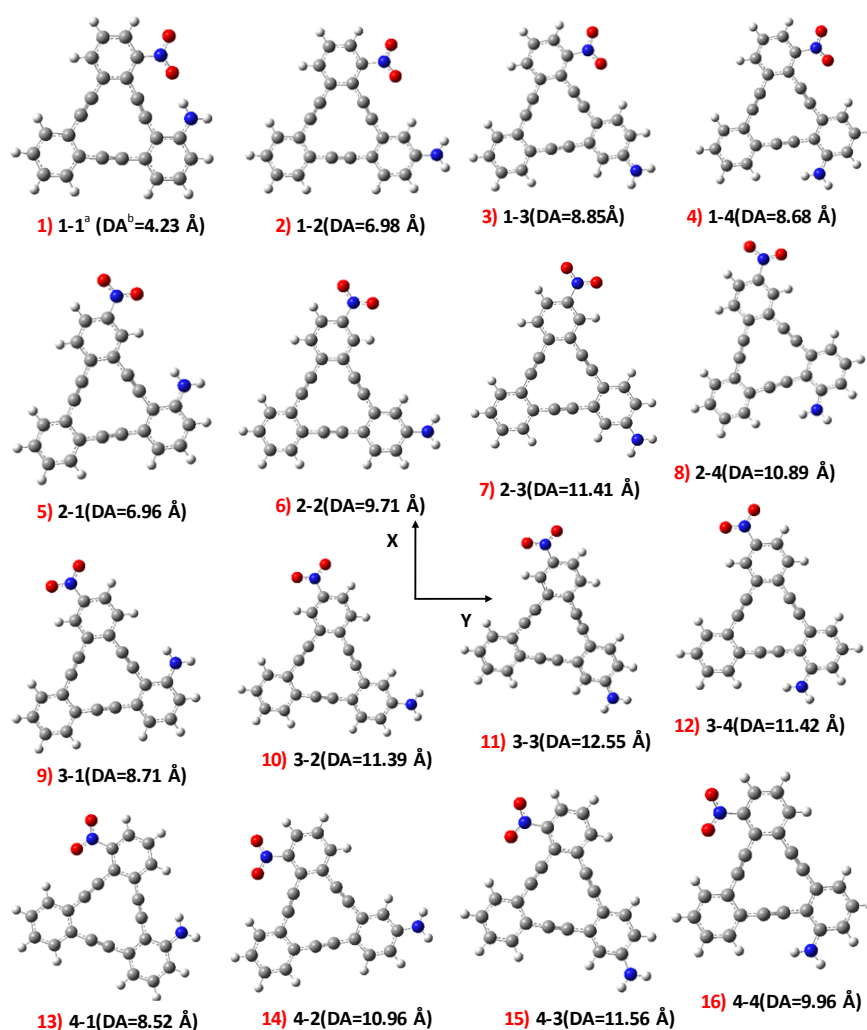

Figure 2: Donor-acceptor substituted graphyne structures. Each row corresponds to a particular position of acceptor group in ring (i) and varying position of donor group in ring (ii) with respect to the acceptor one.

[a] the name of the structures reflects the donor-acceptor positions; [b] DA=Donor-acceptor distance in angstrom.

Electronic absorption

Theoretical electronic absorption spectra were calculated to find out the reason of this polarizability improvement. It was found that the absorption of the molecule 3-3 at 265nm was due to the transition from HOMO to LUMO+1. Huge number of donor and acceptor contribution including all the more near degenerate orbitals in the excitation process leads to a gigantic charge transfer process which bring this streak improvement of first hyperpolarizability (β_{tot}).

Two level model [3,4] was used to further understanding this improvement of β_{tot}. As indicated by this model the first hyperpolarizability (β_{tot}) is inversely corresponding to the third power of the transition energy (i.e., $\alpha\ \Delta E^3$) and so it is stand out to be a strong parameter. Consequently the molecule having low transition energy should have high first hyperpolarizability. Using two level model, the term for all the molecules (1 to 16) was plotted in Figure 5 which depicts the almost same variation as first hyperpolarizability (β_{tot}) (inset of Figure 5).

Again the absorption spectrum of molecule 3-3 shows a wide range of spectrum coverage compared to the bare graphyne (Figure 6). This will make it useful in a broad wavelength range from ultra-violet to near infrared.
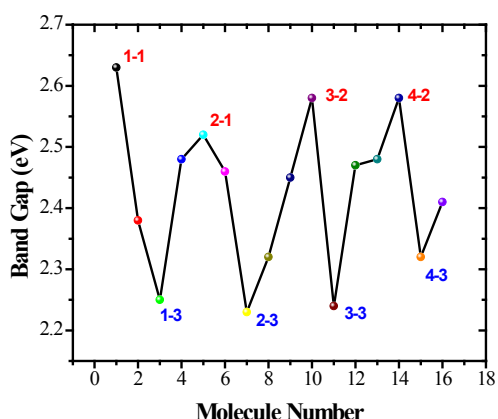

Figure 3: Variation of band gap of graphyne after donor-acceptor substitution.
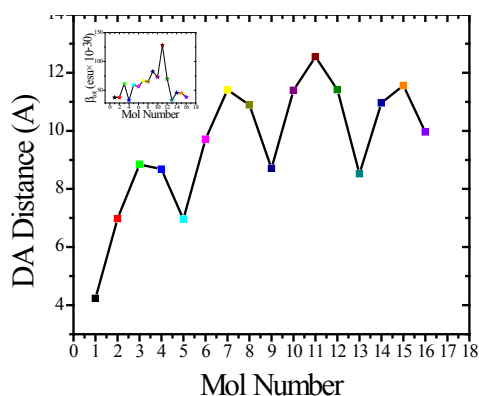

Figure 4: Change of donor-acceptor separation in different stable graphyne structures after substitution. Inset: First hyperpolarizability change of the molecules after donor-acceptor attachment.
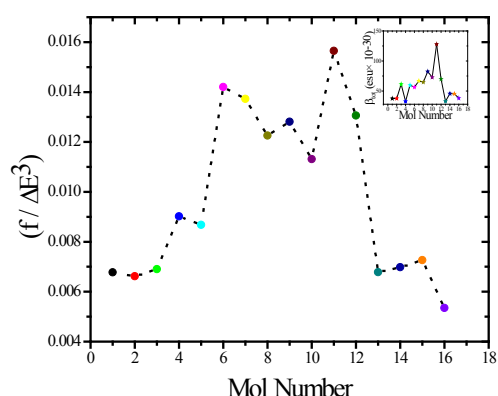

Figure 5: Depicting the variation of the term $\left(\frac{f}{\Delta E^3}\right)$ in all the donor-acceptor substituted graphyne structures (1to 16). Inset: first hyperpolarizability variation of the molecules.
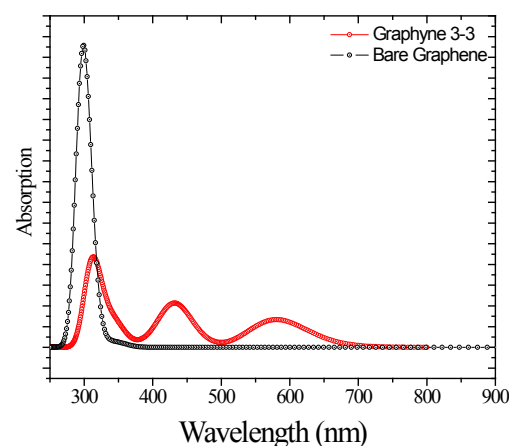

Figure 6: Absorption spectra of molecule 3-3 and bare graphene (see the legends).

Conclusion

From first principles, the geometry structure, electronic properties of a donor acceptor substituted graphyne small cluster was estimated and altogether researched. From band gap perspective, two groups of symmetries were found in the substituted structures despite the fact that they all are energetically comparable. Fascinatingly there is a giant improvement in first hyperpolarizability (β_{tot}) in the structure 3-3 in contrast with the bare graphyne. It can absorb light from near 300 nm to 700 nm covering a wide range of electromagnetic spectrum which makes it very useful in application purpose. So, this designed donor -acceptor substituted graphyne structure has great potential to become a versatile member for nonlinear optics (NLO) applications.

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