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Giant first hyperpolarizabilities of donor–acceptor substituted graphyne: An ab initio study

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ABSTRACT

Graphyne (Gy), a theoretically proposed material, has been utilized, for the first time, in a phenomenal donor–Gy–acceptor (D–Gy–A) structure to plan a superior nonlinear optical material. Owing to the extraordinary character of graphyne, this conjugate framework shows strikingly extensive static first hyperpolarizability (β_{tot}) up to 128×10^{-30} esu which is an enormous improvement than that of the bare graphyne. The donor–acceptor separation plays a key role in the change of β_{tot} value. The π-conjugation of graphyne backbone has spread throughout some of the D–A attached molecules and leads to a low band gap state. Finally, two level model clarifies that the molecule having low transition energy should have high first hyperpolarizability.

1. Introduction

Investigation of fascinating electronic properties of a few conjugated carbon atoms like graphene and its subordinates is turned into a current trend furthermore crucial since that could have open an extensive variety of applications. After a fruitful synthesis of graphene and its successors by mechanical cleavage [1] and a few chemical methods,[2] a flood of its application in molecular electronics [3,4], sensors [5,6], and energy storages [7,8] have come into sight. Carbon atom can stay in different hybridization which provides us the chance to think of different potential structure of it. As an example of another layered structure of carbon, dehydrobenzo(12)annulene (DBA-12) [9] named graphyne (Gy), containing sp^2 and sp^3 hybridization is turned into a potential member of the promising carbon family. Baughman et al. has hypothetically anticipated it in 1987 [10]. Among his few forecasts, the experimental realization of a few subunits of Gy by Haley and colleagues [11] and others [12,13] makes us confident. Graphyne framework was structurally developed by embeddings an acetylenic linkage between two reinforced carbons of graphene.

Molecules having large nonlinear optical property (NLO) have showed up as an essential class of material because of its enormous application in low cost, superior photonic applications [14–16]. The current period of trial studies is centered on the understanding of concepts and synthesis of new materials having extensive NLO property [17–22]. Quantum chemical studies play a principal part to anticipate the genuine structure–property relationship and give an extensive clue for approach to take after. The purpose of the paper is to predict the theoretical values of NLO properties, especially the static first hyperpolarizability of donor–acceptor (D–A) substituted graphyne structures. The essential feature is to predict the valid NLO molecule structure and study the impact of substitution on their first hyperpolarizability property. First hyperpolarizability is a measure of how effortlessly a dipole moment is induced in an atom in the vicinity of an electric field. 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

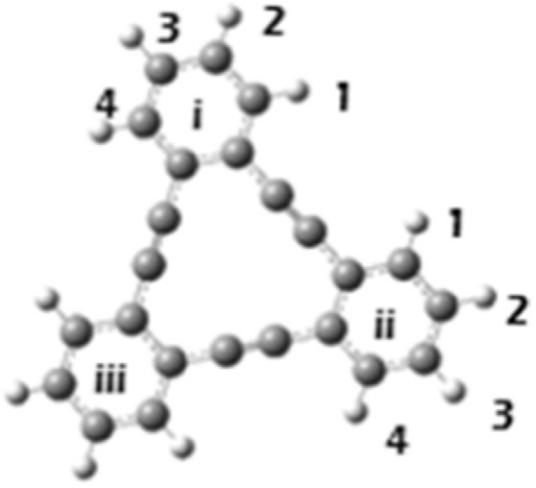

Fig. 1. Graphyne (dehydrobenzo[12]annulene (DBA-12)) with its substitution positions on each one ring demonstrated with numbers.

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hyperpolarizability. Numerous diverse mix of D and A can be utilized to get a good estimation of it. In NLO research, electron-donor amino (NH_2) group and an electron-acceptor nitryl (NO_2) group is well known and regularly use to do these estimations. Therefore, here in, we present donor–acceptor (D–A) substituted graphyne as an emergent NLO material utilizing electron push–pull mechanism.

2. Computational details

Geometry optimization and the static first hyperpolarizability estimation of all the graphyne structures were carried out by B3LYP/6–31 + G method [23,24]. This basis set is well used to reproduce the predicted geometry and the vibration frequency of graphyne. We found that the results turning out utilizing spin-restricted method just about correspond with those got using spin-unrestricted one. Again the spin-restricted technique gives better geometry optimization and impressively diminishes the computational expense. Considering all these main considerations, spin-restricted method was utilized as a part of this work. Absence of imaginary vibrational frequency guarantees the right geometry optimization of the structures. Electronic absorption property calculations were done utilizing CIS/6–31 + G basis set executed in TD-DFT formalism. All the calculations were performed utilizing Gaussian 09 software package [25]. Partial density of state (PDOS) and the information regarding the frontier molecular orbital's contributions to the excitations lead to the absorption maximum was extracted using GaussSum-2.2.5 package [26].

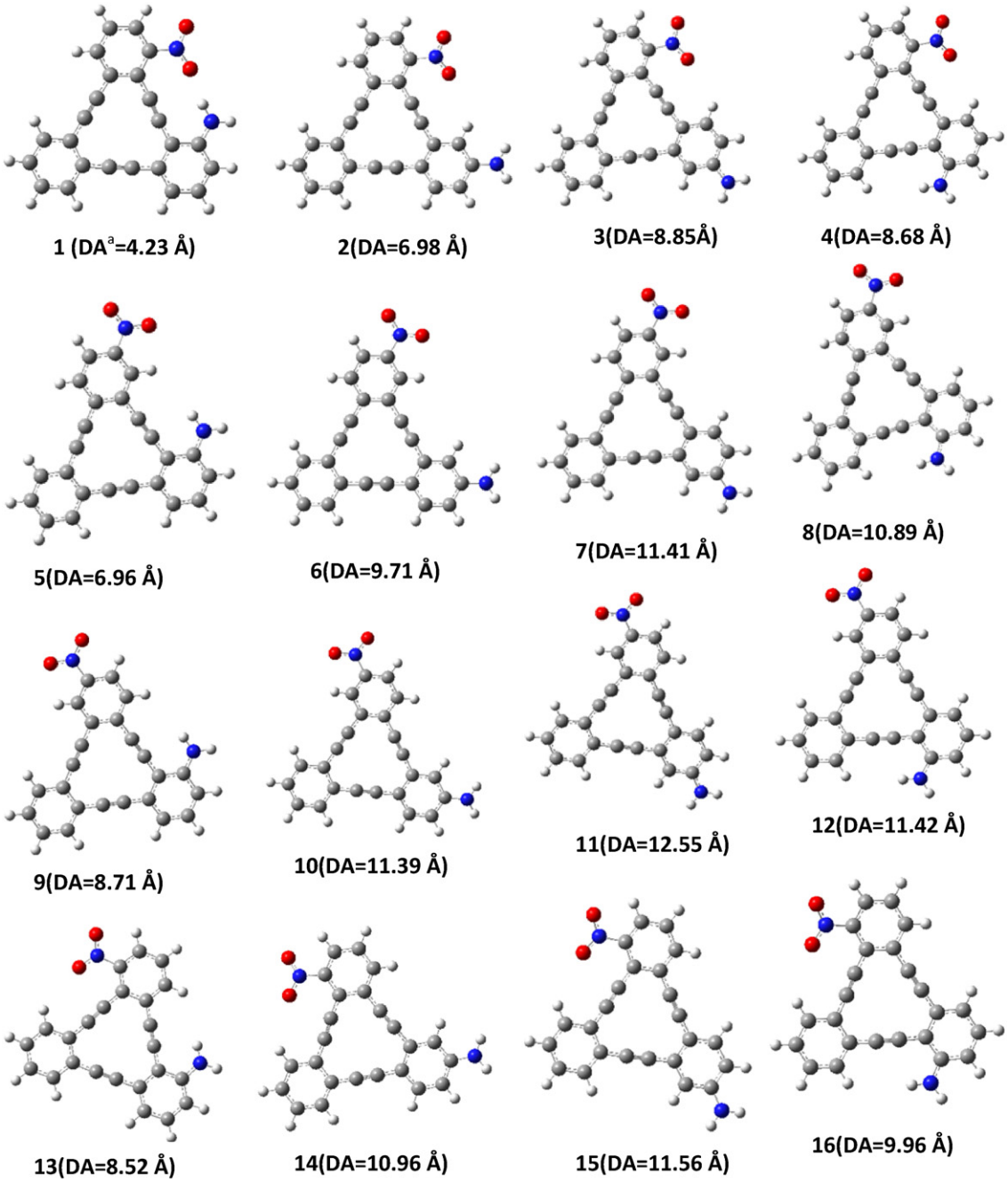

Fig. 2. Donor–acceptor substituted graphyne structures. [a]DA = donor–acceptor distance is in Angstrom.