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Infrared vibrational and electronic transitions in the dibenzopolyacene family

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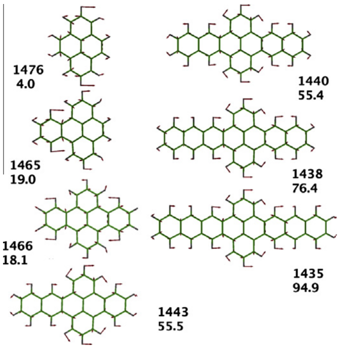
HIGHLIGHTS

- Experimental spectra in the mid- and near-IR and DFT calculations for the vibrational and electronic spectra are reported.
- Good agreement between theory and experiment for the vibrational frequencies of the neutral species.
- The intensity of the 1440 cm^{-1} band grows with molecular size.
- B3LYP fails for ions, BP86 is in reasonable agreement with experiment.
- The large molecules show electronic transitions in the mid-IR and theory gives insight into these transitions.

GRAPHICAL ABSTRACT



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ABSTRACT

We report experimental spectra in the mid-infrared (IR) and near-IR for a series of dibenzoacenes isolated in Ar matrices. The experiments are supported by Density Functional Theory (DFT) and Time-Dependent DFT (TD-DFT) calculations with both vibrational and electronic transitions studied. For the neutrals, we find good agreement between the experimental and B3LYP and BP86 results for all species studied. The band at about 1440 cm^{-1} carries more intensity than in typical PAHs and increases in intensity with the size of the dibenzoacene molecule. For the ions the B3LYP approach fails to yield reasonable IR spectra for most systems and the BP86 approach is used. Electronic transitions dominate the vibrational bands in the mid-IR region for the large dibenzoacene ions. In spite of the very strong electronic transitions, there is still reasonable agreement between theory and experiment for the vibrational band positions. The experimental and theoretical results for the dibenzoacenes are also compared with those for the polyacenes.

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Introduction

Over the past several years Polycyclic Aromatic Hydrocarbons, better known as PAHs, have witnessed a resurgence in research interest due to their applicability to diverse fields such as environmental science [1,2], health science [2,3], materials science [4–6] and astrophysics [7,8]. As a by-product of combustion, PAHs

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represent an environmental contaminant at many hazardous waste sites [1]. PAHs' carcinogenic properties make them of interest to health sciences [3]. Their aromatic and extended structures can potentially serve as building blocks to carbonaceous compounds ranging from carbon nanotubes to graphene, thus they are of considerable use in materials science [5]. Astronomical observations have shown that most interstellar and circumstellar objects in the Galaxy and many extra-galactic objects are emitting an infrared spectrum that is dominated by a family of highly vibrationally excited PAHs [7]. Thus PAHs are also of great interest to the astrophysical community.

One subset of the PAH family consists of the polyacene molecules (see Fig. 1, molecules I to O) composed of linearly annulated benzene subunits. The polyacenes unique structure has fascinated organic chemists for over a century [6,9–11], while their unique electronic structure has generated considerable interest from materials scientists, resulting in numerous investigations [11,12]. The π systems in the polyacene molecules have smaller highest occupied molecular orbital-lowest unoccupied molecular orbital (HOMO–LUMO) gaps than typically observed for similar-sized PAHs, with the energy gap decreasing with increasing polyacene length [13]. The changing electronic structure with increasing polyacene length eventually causes the polyacenes to shift from being insulators to p-type semiconductors. Unfortunately this also causes the polyacenes to become chemically reactive as well, with hexacene (composed of 6 benzene rings) slowly decomposing at room temperature. Although Clar reported [14] the synthesis of hexacene in 1942, its existence remained controversial until 2006, when its synthesis was finally reproduced in stabilizing matrices [13,15]. In 2009, the polyacene series from pentacene through heptacene was produced and investigated in a matrix-isolation study by Mondal et al. [13] In 2010 Tönshoff and Bettinger [16] reported the production, ultraviolet (UV) and infrared (IR) spectroscopic characterization of octacene and nonacene in an argon matrix.

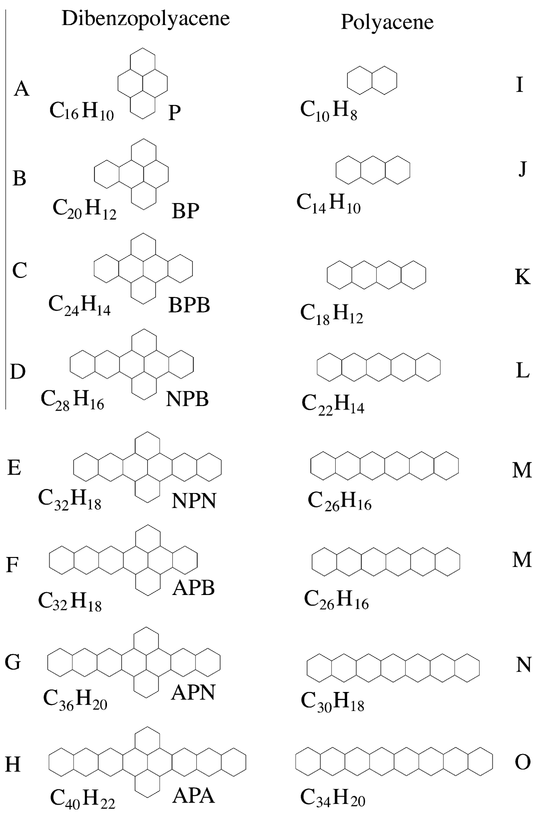

Fig. 1. Dibenzopolyacenes studied in this work and their polyacene analogs. The dibenzopolyacenes are denoted P through APA using the shorthand notation explained in Section 'Methods'.

Though the polyacene molecules are reactive, their derivatives seem to be more stable [17–19]. Payne et al. [17], Chun et al. [18], and Kaur et al. [19] have reported the synthesis of heptacene derivatives. Weisman et al. [20] have reported a theoretical and spectroscopic study of dibenzopolyacene molecules up to the dibenzo[jk,a1b1]octacene range. In their matrix-isolated study, Weisman et al. reported the remarkable finding of the presence of strong electronic transitions in the mid-IR for the radical cation and anions of dibenzo[jk,a1b1]octacene and dibenzo[hi,uv]hexacene.

The current work presents a mid-IR spectroscopic study of the neutral molecules from pyrene (dibenzonaphthlene) through dibenzo[jk,a1b1]octacene and a mid-IR and near IR (NIR) spectroscopic study of the radical cation and anions for dibenzo[fg,op]tetracene through dibenzo[jk,a1b1]octacene. This expands on the Weisman et al. study in several ways: first, we report the results for some less symmetric dibenzopolyacene molecules; second, we analyze the experiments in more detail to extract IR vibrational band positions and intensities; and third, we compare theory and experiment for the allowed IR vibrational transitions. The inclusion of the less symmetric species allows an understanding of the effect of both size and shape on the results. Finally, we note that we compute the electronic transitions using a different basis set and functional than used by Weisman et al. This allows an evaluation of the effect of basis set and functional on the results.

Methods

The dibenzopolyacene molecules studied here are shown in the left-hand column of Fig. 1. Their polyacene counterparts are shown in the right-hand column. All of the dibenzopolyacene molecules can be described as containing a pyrene core with side groups added to one or two sides. The side groups are benzo, naphtho, or anthro. Because the names are quite long, we use an XPY abbreviation, where the P denotes the pyrene central unit and the X and Y are the wings, of which B denotes benzo, N denotes naphtho and A denotes anthro.

Experimental techniques

The matrix-isolation mid-IR and NIR spectroscopic techniques employed in these studies have been described in detail elsewhere [20–24] and are briefly summarized here. Matrix isolated dibenzopolyacene samples were prepared by vapor co-deposition of the species of interest with an over abundance of argon (Ar) onto a 14 K CsI window suspended in a high-vacuum chamber ($p < 10^{-7}$ Torr). The deposition conditions produced an Ar/polyacene ratio in excess of 1000:1. After accumulation of a sufficient amount of neutral material, an IR spectrum of the sample was recorded.

Once the neutral spectra were recorded, cation and anion molecular species were generated *in situ* via vacuum UV photolysis of the PAH/Ar matrix. Photolysis was accomplished with the combined 120 nm Lyman α/160 nm very broad molecular hydrogen emission bands (10.1 and 7.77 eV, respectively) from a microwave-powered flowing H_2 discharge lamp with a dynamic pressure of 150 mTorr. An upper limit to the ionization efficiency can be obtained by measuring the percent decrease in the neutral band integrated areas that accompany photolysis, assuming that all neutral PAH molecules that disappear are converted into ions. For the pure Argon matrix experiments, ionization results in the formation of both cation and anion species. For the determination of the molecular absorbance (A values), we assume that one cation and