Energies of Low-lying Excited States and Reactivity of Giant Polycyclic Aromatic Hydrocarbons with a Hole Inside

Xia Yang, Balázs Hajgató, Megumi Yamada, and Koichi Ohno*
Department of Chemistry, Graduate School of Science, Tohoku University, Aramaki, Aoba-ku, Sendai

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By studying the lowest singlet and triplet excitations of a series of large polycyclic aromatic hydrocarbons (PAHs) by means of ZINDO and MO/8E methods, there appear blue shifts for those holed PAHs, in contrast to the ordinary π-conjugated systems with simple red shifts. In all investigated PAHs the even-layered holed PAHs show higher aromatic character. In addition, there is larger global softness in this kind of widely delocalized π-systems from reactivity indices.

Polycyclic aromatic hydrocarbons (PAHs) have long been in the focus of both theoretical and experimental research because of their important properties in connection with astrophysics of interstellar medium, molecular engineering of electronic devices, and environmental and biological chemistry.[1,2] In particular, large PAHs are very promising molecules for the manufacture of electronic devices, e.g., field effect transistors, solar cells, and electroluminescent diodes.[3] Recent progress in the chemistry of PAHs enabled the synthesis and physicochemical investigation of enormously large benzenoid systems and their derivatives.[4] However, the investigations on electronic spectra and structure-reactivity relations that in turn would aid in devising reaction mechanisms for these materials have been restricted to relatively few categories of polycyclic aromatic molecules and lower molecular weight range. Thus, it is necessary and interesting to investigate how larger PAHs behave.

In early theoretical work, Stein and Brown have reported some results using HMO calculations on several series of large condensed benzenoid polyaromatic molecules.[5] They showed that the edge structure has a significant influence on heats of formation.

In this study, we systematically investigated several homologous series of large, hexagonally symmetric benzenoid polyaromatic molecules, which were constructed entirely from condensed hexagon rings. The investigation was made to focus on the nature of low-lying excited states, aromaticity and reactivity as useful elucidation tools of PAHs, which further reveals more characters of π-conjugated systems.

All calculations were carried out by GAUSSIAN 03[6] and MO/8E[7] program packages. Geometrical structures of studied PAHs were fully optimized at ab initio HF/6-31G level (in Figure 1). The calculations of excited states were made by ZINDO[8] and MO/8E methods. Nucleus-independent chemical shifts (NICS)[9] were calculated using the GIAO-SCF/6-31G level of theory. Each molecule in Figure 1 can be labeled as (M, D), where the parameter M means the whole molecular size which is marked by the number of six-membered rings on the one of the outermost sides of the hexagon molecule; D denotes the donut layer when the whole molecule size is kept constant from the full-empty (D = 1) to the full-filled. In addition, the hole size H is defined as H = M − D − 1. For example, (6,4) represents the fourth molecule from the left at M = 6, its hole size is assigned as H = 1; (M, 1) (M = 2–6) corresponds to the full-empty systems where the hole size varies with H = M − 2, while (M, M − 1) (M = 2–6) means the full-filled systems where the hole size is thought as H = 0.

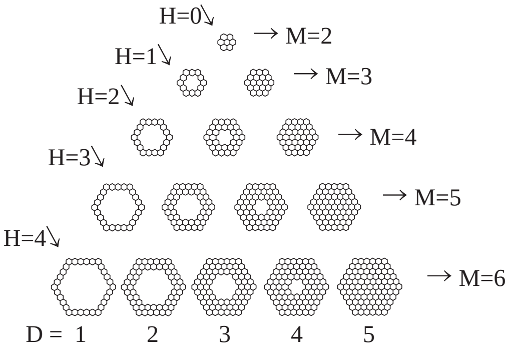

Figure 1. The investigated PAHs.

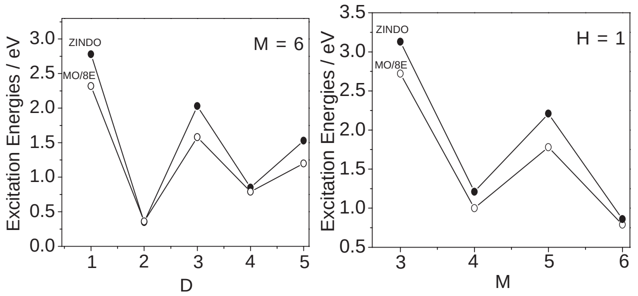

Figure 2. Calculated S_0–S_1 excitation energies as a function of D (the number of donut layers keeping molecular size constant M = 6) and of M (molecular size keeping hole size constant H = 1) by means of ZINDO (full-filled circle) and MO/8E (open circle) methods.

In the case of excitation energies, the size of the CI space employed was 200 × 200 in ZINDO and 20 × 20 in the MO/8E. This was found to be sufficient for convergence of the lowest allowed (most intense) electronic transition. Two methods give the similar results in the transition energies. The singlet S_0–S_1 excitations considered here are all of the π(HOMO)–π^*(LUMO) types. For (M, 1) and (M, M − 1) systems, the excitation energies progressively decrease with increasing number of electrons in π-systems, which shows the same red shifted trend as other series of PAHs such as acenes and zigzag phenes.[10] However, it is interesting that the excitation energies of holed PAHs except for the (M, 1) systems show fluctuating nature with an increase of the number of π-electrons when the global molecular size or the hole size is kept constant, as shown in Figure 2. As a

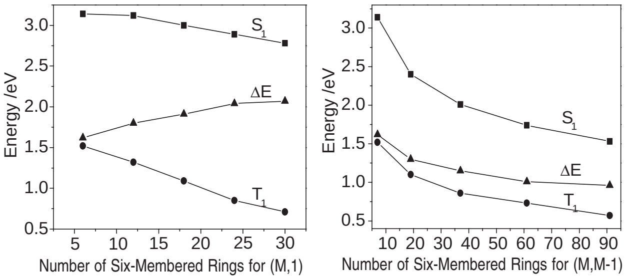

Figure 3. The vertical S_1 and T_1 energy and S_1–T_1 energy difference (ΔE) calculated by ZINDO plotted against the number of six-membered rings for (M, 1) and (M, M-1) systems.

consequence there appear blue shifts within this series, in contrast to the ordinary π-conjugated systems with simple red shifted character. This result is in agreement with a recent report.[11]

The trend in the lowest triplet states is, in general, similar to those in the singlet excited state. S_0–T_1 excitation energies also show an oscillatory trend as a function of the number of carbon atoms for those PAHs with a hole. There are lower transition energies in the even-layered holed PAHs. Figure 3 shows the vertical S_1 and T_1 energies as a function of the number of six-membered rings for (M, 1) and (M, M-1) systems, together with the energy difference between S_1 and T_1. The energy difference between S_1 and T_1 is a measure of the exchange energy, a parameter of interest for the efficiency of electroluminescence from organic materials.[12] The decrease in the transition energy of S_1 for the series (M, 1) and of T_1 for the series (M, M-1) with increasing system size are relatively slow, which is indicative of a more localized nature of singlet exciton for (M, 1) systems and of triplet exciton for (M, M-1) systems, respectively. It is clear that the calculated exchange energy smoothly increases with molecular size for (M, 1) systems and decreases for (M, M-1) systems, and then tends to respective saturation (converging to around 2.0 eV for (M, 1) and 1.0 eV for (M, M-1), respectively).

Here all investigated PAHs are overall aromatic by calculated NICS values. In particular, the center of even-layered holed PAHs shows higher aromatic character (NICS values from -14 to -23) with respect to odd-layered holed PAHs (NICS values from 1 to 7). π-Electrons within this series move almost freely in the whole molecular framework, which arises from the migration of the aromatic sextet, as proposed by Clar.[13] The even-layered holed PAHs correspond to an aromatic sextet resonance system[10] while odd-layered holed PAHs are similar to an aromatic sextet alternation system[10] because π-electrons within this series have a tendency to localize in a particular portion of the molecular framework.

In order to predict global chemical reactivity trends of the involved molecules, the global reactivity descriptors —the electronegativity χ, the absolute hardness η and electrophilicity ω— can be computed applying the finite difference method.[14] The electrophilicity is defined as

$$\omega = \mu^2/2\eta. \tag{1}$$

In Eq 1, $\mu \approx -(\mathrm{I}+\mathrm{A})/2$ and $\eta \approx (\mathrm{I}-\mathrm{A})/2$ are the electronic chemical potential and the absolute hardness of molecules, respectively, approximated in terms of the vertical ionization potential (I) and electron affinity (A). The electrophilicity is an index of reactivity that allows a quantitative classification of the global electrophilic nature of a molecule within a relative scan.[15]

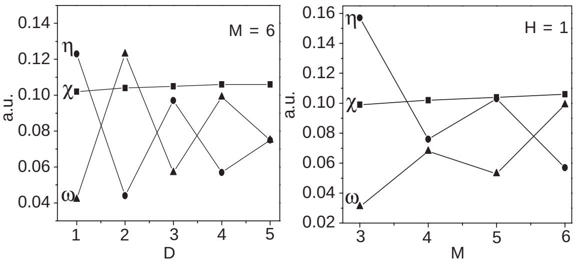

Figure 4. Dependence of reactivity indices (the absolute hardness η, electronegativity χ, and electrophilicity ω) on D (the number of donut layers keeping molecular size constant $M = 6$) and on M keeping hole size constant $H = 1$ at HF/6-31G level.

Our results show that there is a progressively enhancing reactivity as the system size grows for (M, 1) and (M, M-1) systems, which is similar to acenes and zigzag phenes.[10] However, a clear oscillatory correlation between the number of layers and reactivity is found for the holed PAHs consisting of a sequence of increasing hexagon ring layers, as shown in Figure 4. The electronegativity shows small change because of the symmetric HOMO–LUMO levels in alternant PAHs. No matter keeping the same molecular size or hole size, even-layered holed PAHs show higher electrophilicity in comparison with the odd-layered. Consequently, aromatic sextet resonance systems would be chemically soft compounds, while aromatic sextet alternation systems would have chemical hardness.

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