1Pp065 Strange Properties of Novel Series of Giant Polycyclic Aromatic Hydrocarbons

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Introduction: Polycyclic aromatic hydrocarbons (PAHs) are important group of environmental pollutants, which structures consist of two or more condensed aromatic rings and composed entirely from carbon and hydrogen. They occur in the nature mostly in traces in different matrices and their origin both anthropogenic and natural. PAHs exist not only in the Earth but they are thought to be an important reservoir of carbon in the universe and presumably also responsible of some of the Diffuse Interstellar Bands and the Unidentified Emission Bands in the mid–IR range [1]. Since large PAHs are practically insoluble in any solvent, the available structure elucidation methods are limited. One of the available methods is the UV/visible spectroscopy. Normally in a certain series of PAHs as the size of π -system extending, the whole

spectra are progressively red shifted and this trend is most easily observed in the stronger absorption β -bands [2] (Figure 1).

Computational methods: In this computational study a novel series of PAHs with hollow sites have been investigated by molecular orbital and functional density methods. optimized Geometries were bv CNDO method, and the excitation calculated energies were using



Figure 1: Excitation energies of linear acenes

MO/8–CI, ZINDO–CI, and TD–BLYP/{STO–3G, 3–21G, 6–31G} levels of theory. Nucleus–Independent Chemical Shifts (NICS) were calculated at the GIAO–SCF level of theory using 3–21G and 6–31G basis sets. In this abstract the ZINDO–CI and GIAO–SCF/6–31G results have been shown.

Results and discussion: One of the interesting groups of investigated PAHs is shown in Figure 2. The excitation energies strongly correlate with the energies of the HOMOs. In this series with contrast to the normal PAHs in some cases the excitation energies shift blue as the number of π electrons are increasing. This effect is the most conspicuous in cases of **2**,**3** and **5**,**6**. The excitation energies of **2** and **5** seem to be smaller than the tendency suggested values. Surprisingly the homodesmotic stabilization energies of these compounds are relatively smaller compared to the others in this group. The smaller specific aromatic stabilization somewhat contradict



Figure 2: Excitation energies of invesigated new series of giant PAHs

the lower excitation energy. However, an analysis of the local ring aromaticity using NICS values changes the picture a bit. All the PAHs show benzenoid structure and the extraordinary PAHs also have annulenoid character (Scheme 1).



Scheme 1 Benzenoid and annulenoid PAH Rings marked with O have lower than -8 NICS value.

Another interesting group of PAHs is shown in Figure 3. It can be seen as the number of electrons is

increasing in the π -system the energies of the first excited states are slightly blue



shifted and the β -bands are only hardly red shifted. An analisis of NICS values found that the π -system of the "super" rings are more or less separated because the junction rings (which have three neighboring condensed rings) are non-aromatic (NICS values of circa +1).

Conclusion: We have investigated several PAHs with hollow sites and also some related "replete" PAHs.

The bathochromic shift of the electronic spectra is the consequence of the extending π -system. Nevertheless, the amount of red shift strongly depends on the local and global aromaticity. In some cases we have found that the increasing number of electrons in the π -system does not mean overall extended π -system.

[1] Chillier et al., J. Chem. Phys., 2001 (115) 1769.

[2] Dötz et al., J. Am. Chem. Soc., 2000 (122) 7707.