

Prediction of UV-VIS Absorbance Data for Polycyclic Aromatic Hydrocarbons (PAHs). Performance of the LCOAO Procedure for Medium to Large Benzenoid Chromophores

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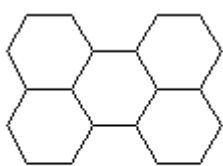
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Abstract

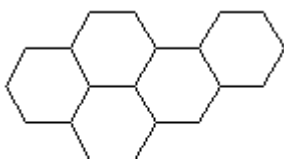
Polycyclic Aromatic Hydrocarbons (PAHs) constitute a large class of conjugated π electron systems of fundamental importance in many research areas of chemistry as well as in astrophysics and materials science. They are produced by the combustion of organic matter and are of great importance in environmental chemistry due to their carcinogenicity. Individual PAHs isolated by analytic procedures are generally identified by their characteristic UV-VIS absorption spectra, and an understanding of their electronic transitions is thus of considerable interest.

The semi-empirical LCOAO (Linear Combination of Orthogonalized Atomic Orbitals) [1] all-valence-electrons procedure is developed for the prediction of electronic transitions for this class of compounds. It is designed with particular attention to a satisfactory description of the observed electronic state pairing properties [1,2] for alternant conjugated hydrocarbons. The procedure is parameterized in such a manner [1,3] that the next-nearest-neighbor resonance integral between Löwdin-orthogonalized [4] π atomic orbitals just vanishes in the six-membered ring of benzene. In combination with a careful adjustment of penetration terms, the resulting model ensures near-perfect pairing symmetry for benzenoid PAHs. This is essential for an adequate description of the so-called minus-states [2] which are optically near-forbidden by the alternant pairing symmetry, such as the L_b state which frequently corresponds to the most longwave electronic absorption band. The LCOAO procedure has shown excellent results for PAHs where other procedures frequently fail [1,5]. The computer program has recently been expanded to deal with large molecules (100 atoms, 300 orbitals) [6], and we here present results for several benzenoid PAHs [7].

We first consider the spectra of a series of 10 benzenoid PAHs from the data base published by *Jinno Laboratory* [8], including perylene, benzo[*a*]pyrene, benzo[*ghi*]perylene, coronene, benzo[*a*]coronene, dibenzo[*bc,ef*]coronene, naphtho[*d*]coronene, benzo[*ghi*]naphtho[*cde*]perylene, benzo[*rst*]dinaphtho[*defg,ijkl*]pentaphene, and pyranthrene. The published spectra were recorded at room temp. in methanol solution [8]. The LCOAO calculations were based on planar molecular geometries computed with the PM3 method, and electronic transitions were predicted by CIS calculations with inclusion of π - π^* type excitations only [7]. [Click on the molecular diagrams](#) below to obtain graphical comparisons of the experimental and theoretical spectra; the transitions obtained with LCOAO are indicated by red columns for oscillator strength $f \geq 0.02$, weaker transitions are indicated by green dots [9]. It is apparent that LCOAO predicts excitation wavelengths close to the "centre of gravity" of the observed electronic band profiles, perhaps with a slight tendency to underestimation of wavelengths in the shortwave region (this trend is expected, see the discussion in [1b]).



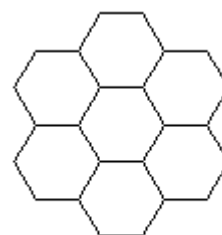
Perylene



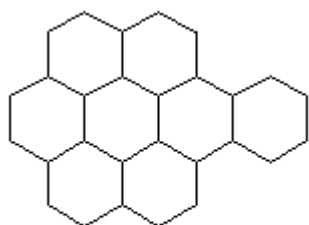
Benzo[*a*]pyrene



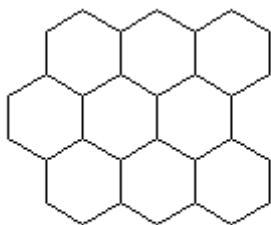
Benzo[*ghi*]perylene



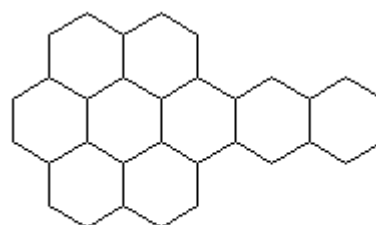
Coronene



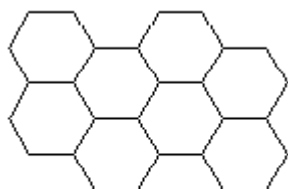
Benzo[a]coronene



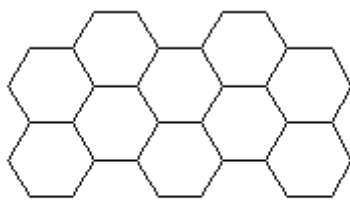
Dibenzo[bc,ef]coronene



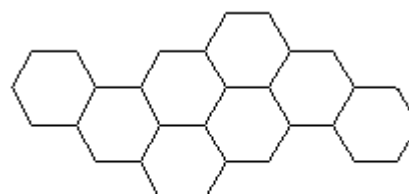
Naphtho[d]coronene



Benzo[ghi]naphtho[cde]-
perylene

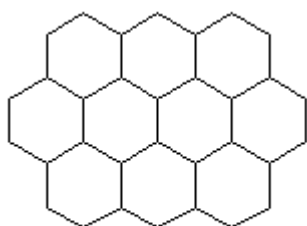


Benzo[rst]dinaphtho[defg,ijkl]-
pentaphene

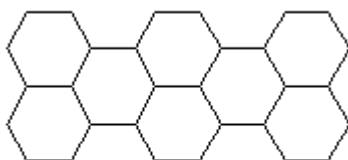


Pyranthrene

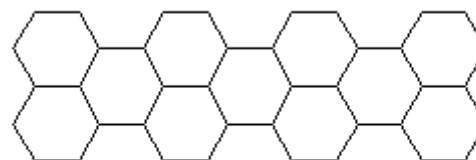
In addition, we consider the spectra of 5 large benzenoid PAHs published by Ruiterkamp *et al.* [10], namely ovalene, terrylene, quaterrylene, dicoronylene, and hexabenzoperopyrene. These spectra were recorded on samples isolated in cryogenic matrices (neon, 5 K). In this case, as a result of the influence of temperature and medium on the experimental spectra, LCOAO tends to predict slightly longer wavelengths than the observed band maxima, frequently coinciding with the onset of bands in the longwave region.



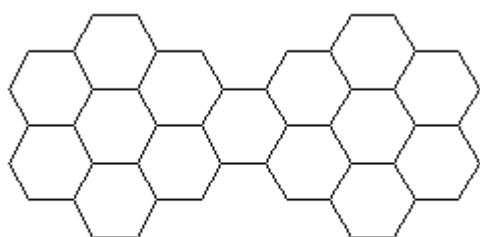
Ovalene



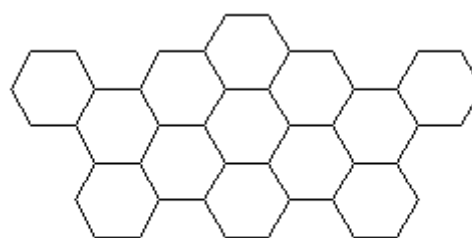
Terrylene



Quaterrylene



Dicoronylene



Hexabenzoperopyrene

In summary, the performance of the LCOAO procedure in the prediction of wavenumbers and relative intensities for the medium to large PAHs investigated here is very satisfactory. The LCOAO model should be useful as a theoretical tool in this field. The calculation time for the largest compounds considered in this investigation (*e.g.*, $C_{48}H_{20}$) amounts to a couple of minutes on a typical laptop PC. More advanced approaches like the popular TD-DFT procedure would require an exorbitant amount of cpu time for compounds of this size [11].

The electronic spectra of large PAHs are complicated, with a large number of overlapping bands. In order to unravel the complexity of these chromophores, the application of Linear Dichroism (LD) and Magnetic Circular Dichroism (MCD) spectroscopy has proved of great value [12]. LD and MCD spectroscopy provide information on transition moment directions and MCD B-terms, thereby frequently leading to resolution of otherwise overlapping transitions [12]. It should be noted that the LCOAO procedure successfully predicts electronic transition moment directions and MCD B-terms for PAHs, including a variety of aromatic as well as non-aromatic systems, and $[4N+2]$ - as well as $[4N]$ -perimeter π systems, where other semi-empirical procedures tend to fail [1,5].

PS: Contact [J. Spanget-Larsen](#) for a copy of the LCOAO Computer Program [6] with input instructions.

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[6] B.K.V. Hansen, J. Spanget-Larsen, *Computer Program LCOAO300*, Roskilde University 2006

[7] K.H. Swiatek, Student Project Report, Roskilde University 2009 (in Danish)

[8] Jinnō Laboratory, School of Materials Science, Toyohashi University of Technology, Toyohashi 441-8580, Japan: [Polycyclic Aromatic Hydrocarbons \(PAHs\) Data Base](#).

[9] Because of the high molecular symmetry (D_{6h}), coronene is a special case: The most longwave transitions are forbidden by symmetry, and the observed absorption is of vibronic origin.

[10] R. Ruiterkamp, T. Halasinski, F. Salama, B.H. Foing, L.J. Allamandola, W. Schmidt, P. Ehrenfreund, *Astronomy & Astrophysics* **390**, 1153 (2002)

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