

MOLECULAR SIZE EFFECT ON PHENYL OLIGOMERS ELECTRONIC AND VIBRATIONAL PROPERTIES

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A considerable amount of research has been devoted to organic materials, which have found their use in numerous applications in micro and optoelectronics [1, 2]. Their properties depend essentially on the level of material order, the changes of transport and optical properties of ParaSexiPhenyl (PSP) [3] upon the ordering in the needle like crystals, being a striking example. As the unit cells of various Phenyl crystals differ essentially only in the length of their longest edge [4, 5], the mixing of various crystallites during the PSP needles growth [6] is possible in principle. In this work we investigate electronic and vibrational properties of various Phenyl oligomers, using calculational capabilities of the HyperChem software package [7], in order to estimate energetic conditions for the process occurrence, and its consequence on electronic and optical properties of the material. All molecules were optimised and their vibrational and electronic spectra calculated at the semiempirical quantum mechanics (AM1) level. Electronic spectra and related properties, up to P4P, were calculated also at LCAO (RHF) level, using 6-31G* basis set. Parameters obtained from these calculations are presented in Table 1.

Table 1

Mol.	E_t [kcal/mol]	ΔH [kcal/mol]	MP2 [kcal/mol]	$h\nu_0$ [kcal/mol]	R [kcal/mol/Å]	I [eV]	d_M [Å]
Benzene	-19609.0 (-144766.2)	21.87	-479.7	64.2	0.00009 (9.12)	9.65 (8.98)	4.99
P2P	-38584.0 (-288805.1)	49.42	-963.2 -991.1*	116.8 114.1*	0.00032 (10.8)	8.79 (7.76)	9.32 9.39**
P3P	-57558.5 (-432844.7)	76.7	-1447.0	169.2	0.001 (11.21)	8.46 (7.24)	13.64 13.59**
P4P	-76533.0 (-576885.8)	104.0	-1697.6	221.6	0.001 (11.43)	8.30 (6.98)	17.96 17.81**
P5P	-95507.5	131.3		273.9	0.001	8.22	22.28 22.056**
P6P	-114482.0	158.6		326.3	0.006	8.16	26.60 26.241**

E_t —total energy, ΔH —enthalpy, MP2—second order Møller-Plesset correlation energy, $h\nu_0$ —zero point vibrational energy, *spin-unrestricted (UHF) values, R—energy gradient, I—first ionisation potential, (values from RHF calculations). d_M —molecular length, **experimental values.

The molecules lengths match the crystallographic data very well, PSP deviating the most. The ring elongation along the molecular axes, which originates from differences of C-C bond lengths is different for inner (2.859:2.770 Å) and terminal (2.825:2.780 Å) rings. Dipole moment of all molecules is zero. RHF calculations give larger charge transfer from H to C ($q_C = -0.20(1)$ except ring connecting C's with $q_C = 0.01(1)$, $q_H = 0.20(1)$) than the AM1 ($q_C = -0.12(1)$ except ring connecting C's with $q_C = -0.02(1)$, $q_H = 0.13(1)$ electrons). AM1 first ionisation potentials are higher than the RHF ones, both exceeding considerably the band gap of the materials (~3 eV) [5].

MP2 energy stabilises molecules notably, particularly according the UHF calculations, despite the fact that positions of energy levels remained unchanged. Unlike the RHF, UHF calculations allow the planar molecular conformations to transform out of plane, and sustained the degeneracy of many IR modes. All mentioned tell us that the effect of electrons delocalisation is important in Phenyl molecules. In Fig. 2. one can see that the increase of the oligomer length increases the number and intensity of IR modes around basic Benzene lines, shifted them slightly to higher frequencies. Together with observed differences of molecular stability and electronic levels (Table 1) this fact could be used for practical resolution of phases built of different oligomers.

References:

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Figures:

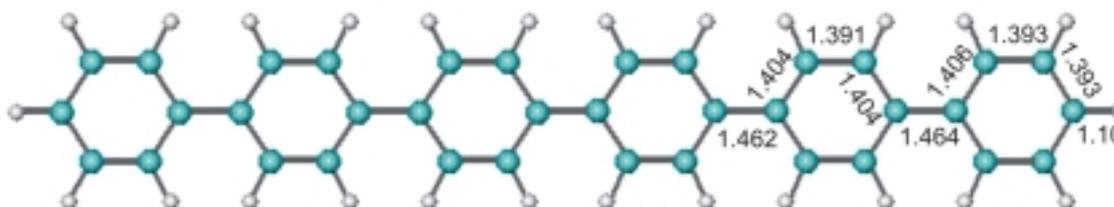


Fig.1. AM1 optimised PSP molecule. Bond lengths are in Å.

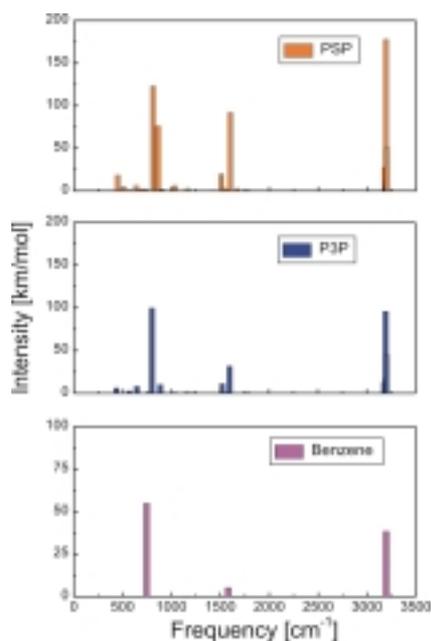


Fig.2. AM1 calculated IR spectra of Benzene and two Phenyl oligomers.