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Impact of molecular chain length on polarizabilities of model acenes and oligomers

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Abstract: A systematic quantum chemical study of model linear oligomers and their ring-fused (condensed) analogues based on six-membered and five-membered aromatic units is presented. Static electric polarizabilities were calculated for optimal geometries. The dependence of electronic and vibrational polarizability contributions on the molecular size was discussed and polymer limits were estimated. The presence of a diradical electronic structure in fused six-membered compounds significantly increases the polarizability values.

Keywords: Electric properties; Organic molecules; Diradicals; B3LYP; Polymer limits

Introduction

Conjugated organic molecules with suitable electric and spectral characteristics have a prominent position in modern research because of their high-cost effectiveness, low dielectric constants, fast nonlinear optical response, and easy integration into passive and active devices (Brédas et al., 1994). Generally, polymeric structures are prepared as highly amorphous materials possessing thermal and chemical stability as well as specific mechanics (Szöcs et al., 2006; Skákalová et al., 1997). Smaller oligomers are of particular interest due to their relatively well-defined structure directly affecting their electronic structure (Lukeš et al., 2003) and simplifying manipulation, e.g., solubility, purification, film preparation of thiophene derivatives (Lukeš et al., 2002). Nevertheless, a large number of electrochemical (Prasad et al., 1991) and chemical coupling (Schuetz et al., 1971; Lukeš et al., 2021) reactions are employed for the preparation of the above-mentioned compounds. An alternative to oligomers is linear acenes (dos Santos, 2006). Conjugation as well as support of molecular packing are extended with linear fusion of aromatic rings (Lukeš et al., 2006). Additionally, a one-dimensional linear semiconductor possessing an open-shell singlet as the ground state can be obtained by linear fusion of benzene rings (Bendikov et al., 2004). Relatively stable radical systems can also be assembled through electrochemical oxidation or reduction of aromatic organic molecules containing nitrogen atoms (Matis et al., 2010; Lukeš et al. 2011).

Organic molecules used in optoelectronics exhibit low band gap that represents the energy difference between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) (Cagardová et al., 2020). Examples of organic molecules used in optoelectronics include aromatic benzene, pyrimidine, thiophene, furan, and pyrrole rings (Ostrovekhova, 2016). Solubility and chemical stability of molecules can be modified using side-chain substitutions (Kurach et al., 2011; Deming, 2016) and/or inclusion of specific bridges (Zhao et al., 1988; Zhao et al., 1989). These modifications significantly affect the off-planarity between the aromatic units (Lukeš et al., 2008; Breza et al., 2001).

An important microscopic electrical parameter for dielectrics is polarizability or coefficient of polarization (α), which expresses the ability of atoms, molecules, or groups of a dielectric material to be polarized in the presence of external electric field. In general, dipole moment of the molecule (μ_i) depends on components of electric field (E_i) (Prasad et al., 1991):

$$\mu_i(E) = \mu_i(0) + \alpha_{ij}E_j + \frac{1}{2}\beta_{ijk}E_jE_k + \frac{1}{6}\gamma_{ijkl}E_jE_kE_l \ldots \quad (1)$$

where μ_i is the component of the dipole moment vector in absence of external electric field, α_{ij} is polarizability component and β_{ijk} and γ_{ijkl} are, respectively, first and second hyperpolarizability tensors, which are components of polarizability. Electric field is expressed by the components of electric intensity vector ($\boldsymbol{E}$). Experimentally, the mean value of polarizability tensor $(\alpha_{xx}+\alpha_{yy}+\alpha_{zz})/3$ is usually determined from the refractive index or dielectric measurements. Additionally, polarizability appears in many formulas for low-energy processes involving the valence electrons of atoms or molecules. It is also widely used to describe the inductive and dispersive interactions of molecules or molecular systems (Petrucci et al., 2016).

Although many theoretical and experimental works deal with the dependence of optical or electric

properties on the molecular backbone elongation, a systematic theoretical study of electric polarizabilities for different sets of linear oligomers and their ring-fused analogues has not been performed yet. Neither the effect of diradical electronic structure in elongated oligoacenes on the polarizability has been theoretically analysed. In this work, DFT (Density functional theory) (Becke AD, 1993)) calculations of six series of representative model linear oligomers and their ring-fused (condensed) analogues modelled from aromatic monocycles (Fig. 1) are presented. The dependence of electronic and vibrational polarizability contributions on the molecular size are discussed and polymer limits have been estimated.



a) b)

Fig. 1. Aromatic monocycles for the study of fused and oligomeric molecules a) five-membered (X = N, S, Se, O) b) six-membered (X = C, N).

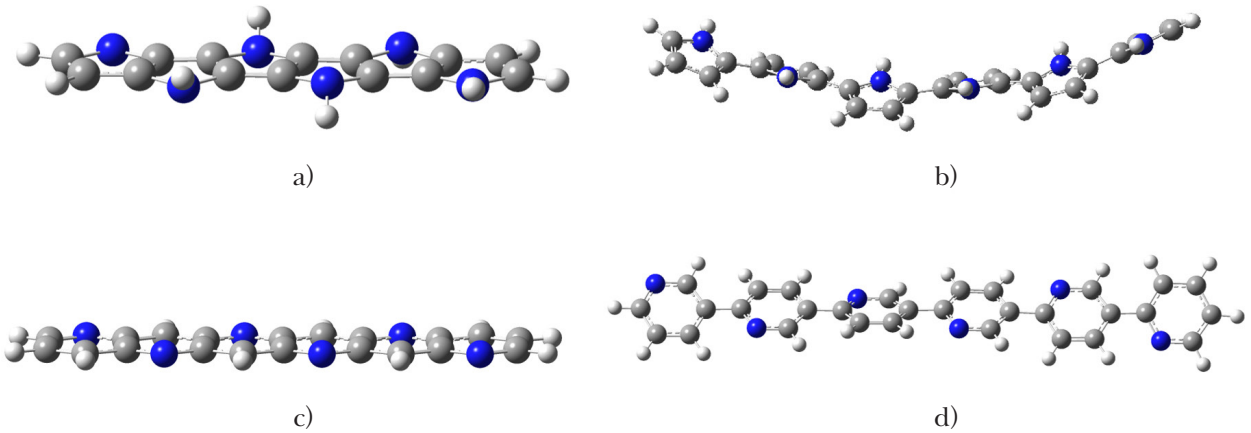
Calculation details

All calculations were performed using the Gaussian 16 program package (Frisch et al., 2016). The density functional theory with a three parameter hybrid B3LYP functional (Becke, 1993; Lee et al., 1988; Vosko et al., 1980; Stephens et al., 1994) and the basis set 6-31G(2d,p) (Pople et al., 1970) were used. This basis set is standardly used to calculate large organic molecules. The diradical systems were optimised using unrestricted broken-symmetry B3LYP. The process was performed applying tight optimization criteria and ultrafine DFT integration grid. True minima on the potential energy surface were confirmed through vibrational analysis (no imaginary frequencies present). For optimised geometries, the electronic and vibronic polarizabilities were computed by the Coupled-Perturbed Hartree-Fock (CP-HF) approach available for DFT functionals. All polarizabilities reported in this study are static and isotropic, meaning that they are the average of the diagonal elements of the polarizability tensor.

Results and Discussions

Because the oligomers under study can be found in many conformations, only geometries with all-trans arrangement of X-C-C-X dihedral angles (X denotes heteroatom) were investigated. These conformations correspond to the global minima at the potential energy surface (Maranas CD et al., 1994). Generally, the presence of one single inter-ring bond between planar aromatic moieties enables slight distortion (Fig. 2). Change of angles between X-C-C-X atoms of two neighbouring rings is from 10° to 30° depending on the type of the heteroatom and position of the oligomeric chain. Some molecules are deviated from planar symmetry, as depicted in Fig. 2. Trans orientations of heteroatoms in planar fused molecules were used in this study.

Energetical stability of diradicals for longer oligoacenes was obtained in accordance with the theoretical work of Bendikov et al. (2004). Energy differences of electronic energies for closed-shell and open-shell diradical state for six-membered acenes are collected in Table 1. Molecules composed of fused five-membered rings do not prefer diradical state and the energy differences are not presented.



a) b)

c) d)

Fig. 2. Optimal geometries of closed-shell oligomeric hexamers in side-view perspective: a) five-membered ring acenes, b) five-membered ring oligomers, c) six-membered ring acenes, d) six-membered ring oligomers.

Tab. 1. Electron energy differences between closed- and open-shell molecules kJ · mol^{-1}, spin contamination for open-shell diradicals (<S^2>).

Molecule	Δ*E*(OS–CS)	<S^2>	Molecule	Δ*E*(OS–CS)	<S^2>
fPh2	261.76	2.02	**fP2**	358.15	2.03
fPh3	174.33	2.02	**fP3**	283.61	2.02
fPh4	115.26	2.03	**fP4**	200.06	2.03
fPh5	73.78	2.03	**fP5**	141.48	2.03
fPh6	44.11	2.03	**fP6**	70.41	2.04
fPh7	22.05	2.04	**fP7**	48.29	2.04
fPh8	5.51	2.04	**fP8**	31.60	2.04
fPh9	–6.83	2.04	**fP9**	18.81	2.04
fPh10	–16.54	2.04	**fP10**	8.91	2.05
fPh11	–24.15	2.05	**fP11**	1.16	2.05
fPh12	–29.93	2.05	**fP12**	–4.94	2.05
fPh13	–33.08	2.05	**fP13**	–9.78	2.05
fPh14	–28.36	2.05	**fP14**	–13.63	2.05
fPh15	–24.68	2.05	**fP15**	–16.81	2.11

Tab. 2. Parameters *a*, *b* and *c* for fitted dependences of the difference ($\alpha_{n+1} - \alpha_n$) on increasing number *n* of aromatic rings in polymeric molecules. Symbol *R* denotes correlation coefficient.

Series	*a*/Bohr^3	*b*/Bohr^3	*c*	*R*	Series	*a*/Bohr^3	*b*/Bohr^3	*c*	*R*
fPh(n)	178.954	–147.694	–0.098	0.9994	**oPh(n)**	95.930	–43.894	–0.504	0.9988
fP(n)	229.250	–201.067	–0.062	0.9958	**oP(n)**	103.650	–63.701	–0.480	0.9994
fFu(n)	240.818	–223.675	–0.023	0.9997	**oFu(n)**	121.306	–90.607	–0.258	0.9975
fTh(n)	135.550	–103.691	–0.057	0.9973	**oTh(n)**	171.827	–134.621	–0.236	0.9989
fSe(n)	226.887	–188.187	–0.032	0.9951	**oSe(n)**	236.204	–199.415	–0.201	0.9988
fPy(n)	142.052	–120.531	–0.043	0.9989	**oPy(n)**	90.806	–56.585	–0.416	0.9960
fPh(n)-dir	226.887	–188.186	–0.032	0.9951	**fP(n)-dir**	135.550	–103.691	–0.057	0.9973

Diradical state is preferred for acenes **fPh**9 and larger, inclusion of nitrogen atom shifts preference for **fP1**2 and larger. With the increase of the number of aromatic rings, the calculated Δ*E* is –6.95 kJ · mol^{-1} for **fPh**9 and –4.94 kJ · mol^{-1} for **fP12**. Yet, the sudden change in trend of Δ*E* at **fPh1**3 suggest that the diradicals may become less preferred. Spin contamination for diradicals is relatively low. For example, the <S^2> value is 2.04 for **fPh**9 and 2.05 for **fP10**. The correct theoretical value is 2.00.

Generally, polarizability is proportional to the molecular size and thus equivalently proportional to the number of aromatic rings. Such increase of isotropic electronic polarizability with molecular length is shown in Fig. 3. Parameters of the evaluated exponential dependence are shown in Table 2.

$$\alpha_{n+1} - \alpha_n = a + b \times \exp(c/n) \qquad (2)$$

where *n* is the number of aromatic rings in molecules, while individual indices *a*, *b* and *c* are used for trend determination of the studied dependence and they do not correspond to any physical value (Champagne et al., 1992).

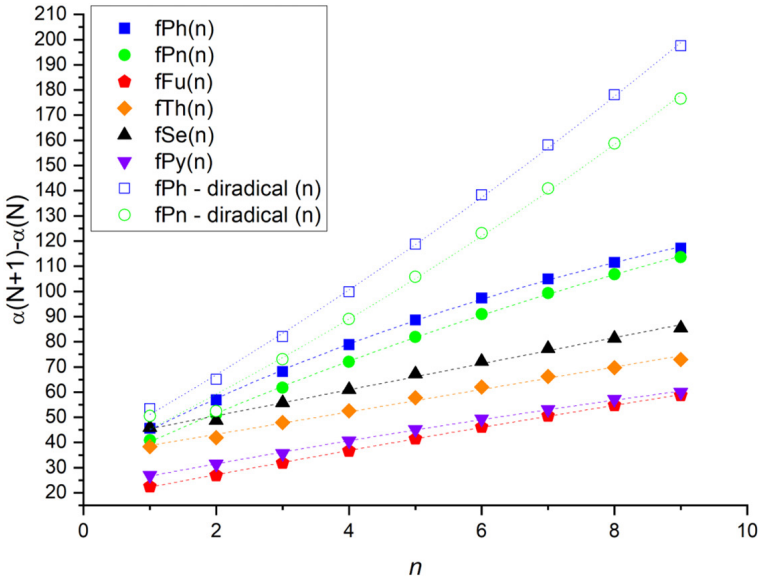
A comparison of six-membered ring-fused series and their oligomeric analogues (**fPh/oPh**, **fP/oP**) shows smaller differences between molecules with the same number of rings. As an example, slight increase can be noticed going from fused **fPh1**0 (826 Bohr^3) to oligomeric **oPh1**0 (852 Bohr^3). Heteroaromatic structures are much more affected in this manner, especially longer molecules. Relatively small difference, e.g., 105 and 134 Bohr^3 for **fSe**2 and **oSe2**, respectively, develops into significant change as the number of rings increases. The highest polarizability of 1437 Bohr^3 was theoretically calculated for **oSe10**, which is twice as high as that of **fSe1**0 (707 Bohr^3).

Identifying the relation between optical properties and molecular structure is the key tool for a rational design of new electronic fabrics. Experimental data for linear and non-linear optical properties also reveal the initial strong increase with the chain length. The mean value of polarizability (α_{av}) measured by Zhao et al. (1988) (in tetrahydrofuran solutions

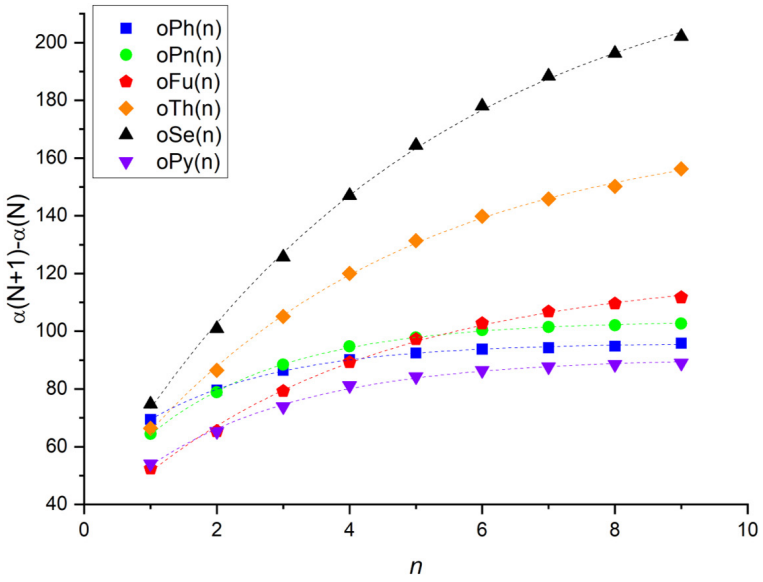
at 589 nm) and extrapolated to the static limits by Champagne et al. (1992) is: 124.2 Bohr^3 for bithiophene, 195.8 Bohr^3 for terthiophene, 377.7 Bohr^3 for tetratiophene, 652.1 Bohr^3 for pentothiophene, and 1418.0 Bohr^3 for hexothiophene. The corresponding B3LYP/6-31G(2d,p) values are slightly lower than the experimental ones. Similar trends are observed in data obtained with the semiempirical AM1 method (Champagne et al. 1992).

A comparison of static polarizabilities for acenes and fused pyridines as singlets and diradical electronic states indicate significant differences. Hollow symbols in Fig. 3a show a significant increase of values for larger oligomers. Polymer limits for diradicals are not indicated for the studied size of oligomers. This observation can be connected to the unique electric properties of diradicals (Dressler et al., 2020).

Vibrational polarizabilities describe the polarization of a molecule due to the displacement of nuclei from their equilibrium positions under an electric field. They are calculated from normal vibration frequencies and the corresponding normal absorption intensities (Rinaldi et al., 1986) and are presented in Fig. 4. Calculations were performed on systems where second derivatives of energy and first derivatives of dipole moment are available.

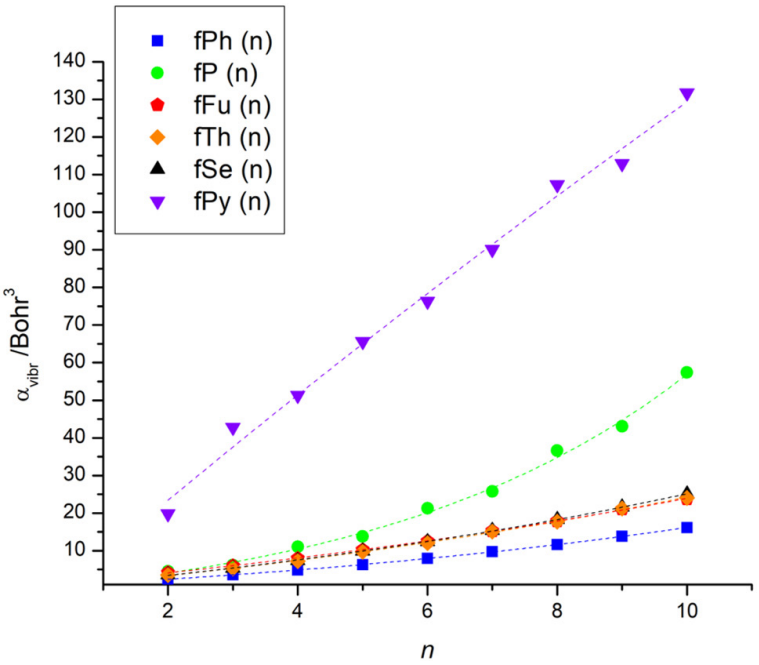


a)

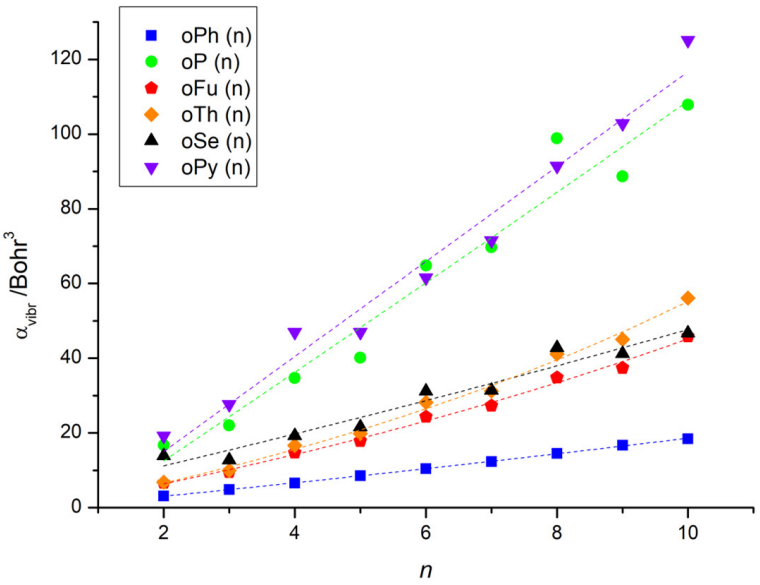


b)

Fig. 3. Dependence of the polarizabilities difference $\alpha_{n+1} - \alpha_n$ on the number of aromatic rings of a) fused and b) oligomeric series.



a)



b)

Fig. 4. Dependence of vibrational polarizabilities on the increasing number *n* of aromatic rings in a) fused molecules and b) oligomers.

Additionally, percentual difference between presented results and results from calculations using a larger base, 6-311++G**, for the studied molecules is 9.36 % on average. For example, percentual difference for **fFu**2 is 15.6 % but for **fFu1**0 it is only 5.0 %. The range of percentual difference is narrower in case of **fPh**, where the percentual difference is 13.5 % and 6.8 % for **fPh**2 and **fPh10**, respectively. Yet, this difference in values has no impact on the trends in general.

Conclusions

Optimal geometries for six model oligomers and acenes have been calculated. Their structural motif is used in many commercially used organic materials applied in optoelectronics. Quantum chemical calculations indicated energetic preference of diradicals for large six-membered acenes. For the obtained equilibrium geometries, static isotropic polarizabilities were calculated and com-

pared. Diradical systems show high values of static polarizability. It was shown that the presence of an open-shell system increases the polarizability of individual molecules compared to closed-shell setting. The predicted polarizabilities can be used for the setting of dispersion and induction corrections which are necessary in the molecular dynamics simulations based on molecular mechanics of studied compounds in model crystals.

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