Computational Chemistry **457**

Statistical Analysis of Quantum Chemical Data Using Generalized XML/CML Archives for the Derivation of Molecular Design Rules

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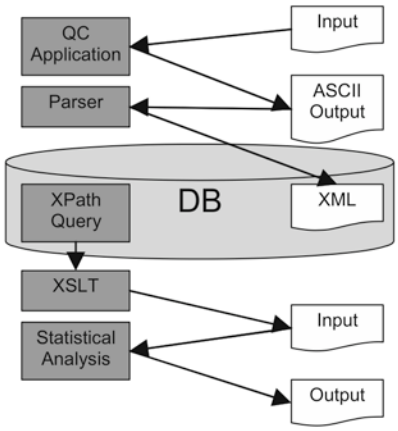
The rational design of novel compounds with tailored properties requires rules ("knowledge") describing the relationship between the molecular and electronic structure and the properties. Today, this information can be generated by means of computations at very high throughput. The main challenge remaining is the transformation of this information to knowledge.

In this work we describe a highly automated procedure ("workflow") for the analysis of data obtained from quantum chemical computations on a training set of over 1'500 donor / acceptor functionalized ethynylethenes.



The data generated as part of this workflow are archived in an XML/CML database and processed by means of statistical analysis methods. This production and analysis "machinery" is applied towards the interference of dependencies between the electron delocalization energy and the properties of the training set.

Computational Chemistry **458**

On the Research Avenue Towards the Rational Design of π-Conjugated Oligomers with Enhanced Optoelectronic Properties

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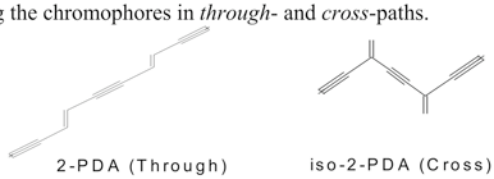
The linear, non-linear optical response, electronic spectral and thermal properties of polydiacetylene (PDA) oligomers are studied as functions of the number N of chromophoric units and the electron delocalization effects due to grafting the chromophores in *through*- and *cross*-paths.



2-PDA (Through) iso-2-PDA (Cross)

PDAs and iso-PDAs exhibit vastly different behavior in properties as a function of N: (1) Static dipole polarizability grows linearly and quadratically for the *cross*- and *through*-paths, respectively (2) Second hyperpolarizability grows weakly cubic (*cross*) and strongly cubic (*through*) (3) For iso-PDA the first two allowed $\pi \rightarrow \pi^*$ transitions as well as the hardness converge very rapidly, whereas the associated transition dipole moments steadily grow. These observations support recent experimental work [1].

The PDA isomers are relatively more stable, but softer and more polarizable than their cross-counterparts, thus deposing the validity of the maximum hardness and minimum polarizability principles (MHP, MPP). On the other hand, the scaling of the response properties as well as hardness are well ascribed by the delocalization energies computed.

[1] R.R. Tykwinski *et al*., *Chem. Eur. J.*, **2005**, *11*, 321

Computational Chemistry **459**

π-Electron Delocalization in Cyanoethynylethenes and Donor-Substituted Cyanoethynylethenes

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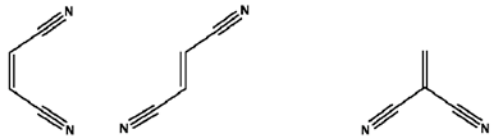
Donor functionalized cyanoethynylethenes were shown to have enhanced charge-transfer behaviour and excellent NLO properties [1]. Since the efficiency of donor-acceptor conjugation is key for the properties of these compounds, the thorough understanding of the origins of the efficiency of the different conjugation pathways is highly desirable.



In this computational study an extension of the natural bond orbital (NBO) analysis is applied to investigate conjugation in these compounds [2]. The study confirms that donor-acceptor conjugation is most efficient in a *through* (*cis/trans*) configuration. The analysis also reveals the important role of acceptor-acceptor conjugation which greatly enhances the efficiency of *cross* (*geminal)* conjugation.

The rules for conjugation efficiency derived here will be useful to design functionalized ethynylethenes (and possibly other) with optimal properties.

[1] N.N.P. Moonen, PhD Thesis (ETH Zürich), **2004.**
[2] M. Bruschi, PhD Thesis (ETH Zürich), **2005**.