Electron Delocalization in Linearly $\pi$-Conjugated Compounds: Discovering Acceptor-Acceptor Conjugation

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Manipulating $\pi$-conjugation – Modulating Properties

Donor/acceptor functionalized linearly $\pi$-conjugated oligomers with various electron delocalization patterns induced by the type of substituents and other factors

Source: J.L. Brédas
Basic Facts

- D/A-functionalized $\pi$-conjugated compounds are compounds with potential application in a number of areas (opto-electronics, nanomaterials, and also biology).

- For the rational design compounds with tailored properties it is important to understand how electron delocalization extends along the different paths and how it responds to donor/acceptor substitution and the environment.
Tuning Properties: Degrees of Freedom

Substituents:
- Type (Strength) of Substituent
- Number of Substituents
- Site of Substitution (lateral, end-capped)

Backbone:
- Type of backbone
- Type of conjugation (*through*, *cross*)
- Length of backbone

Environment
The Basic Approach

Force Lewis-structure using NBO [1]

\[ E_{\text{tot}} = E_{\text{Lewis}} + E_{\text{non-Lewis}} \]

The Cyano-Ehynylethenes (CEEs)

**TEE**

*gem, trans, cis*

...
... and Their Donor-Substituted Derivatives

“geminal” isomer
2 donors in gem
2 acceptors in gem

“trans” isomer
2 donors in trans
2 acceptors in trans
CON2F Path Energies

![Graph showing E(del) (kcal/mol) for geminal, trans, and cis configurations with different symbols for EE, EX, gem, tra, cis, and XX.]
2CN2D: Path-Energies

E(del) (kcal/mol)

geminal     trans

cis        trans

gem
Conjugation: Rules and Facts

Rules:
- D/A conjugation is favoured by *through*-pathways
- A/A conjugation is favoured if *cross*-pathways
- D/D conjugation is somewhat insensitive

This set of rules gives you the *relative stabilities* of (many) structural Donor/Acceptor isomers on the back-of-the-envelope.
THE LARGER SCALE

Automation:

Statistical Analysis of Quantum Chemical Data Using Generalized XML/CML Archives
The “Larger Scale”: Incentives

- Finding rules often means analysing very large amounts of data. These data should be available in an intelligent format such that they can be viewed in many different ways.

- Rather than to analyze the data “by hand” we wish to apply various methods of analysis to find more – and also unexpected – dependencies between delocalization and the molecular properties.
Large Amounts of Data: Example

Example: “Learning” how to modulate the properties of D/A functionalized trans-DEEs based on a set of compounds with chain length up to hexamer and with three substituents (types H; OH, NH$_2$; CN, NO$_2$; end capped plus one lateral) we will be dealing with 1434 structural isomers
The Larger Scale: Issues

- **Automation:**
  Generation of a workflow with minimal manual operations

- **Data format and storage**
  - Archiving
  - Extraction

- **Data Analysis** (→ *Knowledge Generation*)
Data

Why XML/CML:
- Standardized Archiving (or nearly so)
- Data transformation: XSLT
- Extensibility (“open”)
Knowledge Generation

- **Statistical Analysis:**
  So far Linear Models only

- **Question (longer term):**
  Is the delocalization energy a potential descriptor for the analysis of $\pi$-conjugated D/A functionalized materials?
The Workflow

Steps:
- Generation and Archiving of data
- Extraction XPath queries
- Statistical Analysis

Diagram:
- QC Application
- Parser
- XPath Query
- XSLT
- Statistical Analysis
- QC Input
- QC Output
- XML
- Input
- Output
Step I: Generation/Archiving of Data

Geometry Optimization

Mol. Properties NBO Analysis

Delocalization Energy

XSLT

DB

XML

Parser: JumboMarker

Note: automated input generation
Step II: Data Extraction

XPath Query

XSLT

DB

Input for Statistical Analysis

Database: XINDICE

"/molecule[@name='all-trans-1-mer']/results/properties/energy/e_delocalization[@units='a.u.']/"
Step III: Statistical Analysis

- Limited to Validation of Concept
  The quality of the data (B3LYP/3-21G) does not permit a chemically very meaningful analysis yet
Preliminary Results
Dependencies between components
Electron delocalization energy as a predictor for other properties
Conclusions

- Workflow has **successfully been tested** on approximately 1’100 D/A substituted small chain (n<=6) DEEs
- High level of Automation; error recovery
- Statistical Analysis shows expected and unexpected (?) correlations
- Archiving Data in XML DB is key to “better life”

  Application code owners should agree on an XML grammar and generate output accordingly
Discussion

- We are still interested in …
  - Similar investigations on a more sophisticated set of compounds
  - More accurate quantum chemical data

- This will take …
  - a more elaborate XML/CML schema
  - a more flexible and more robust workflow
  - a more powerful computing infrastructure (Grid)
Thank you for your attention!