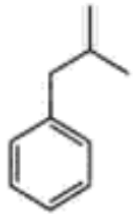
Modernizing and Accelerating the Development of Benson Group Values for Reliable Thermodynamic Characterizations

Benson Groups:

• The idea is to decompose molecular properties (ΔH_f, ΔS_f, ΔC_p) as the sum of "group" contributions.

• Group contributions are calculated based on trusted experimental or computational data, and transferability is assumed.

From Anslyn and Dougherty



$5\ C_B-(H) = 5(3.30) =$	16.50
$1\ C_B-(C) = 1(5.51) =$	5.51
$1\ C-(C_B)(C)(H)_2 = 1(-4.86) =$	−4.86
$1\ C-(H)(C)_3 = 1(-1.90) =$	−1.90
$2\ C-(H)_3(C) = 2(-10.20) =$	−20.40
	−5.15 kcal/mol

Experimental: −5.15 ± 0.34 kcal/mol

Problems we want to address:

• **Provenance:** inconsistent thermodynamic data is available/used to determine group contributions.

• **Specificity:** the definition of a "group" has never been formalized and inconsistent granularity is applied. Limited information on group interactions.

• **Extensibility:** because of the provenance and specificity problems, it isn't possible to develop new groups in a consistent way.

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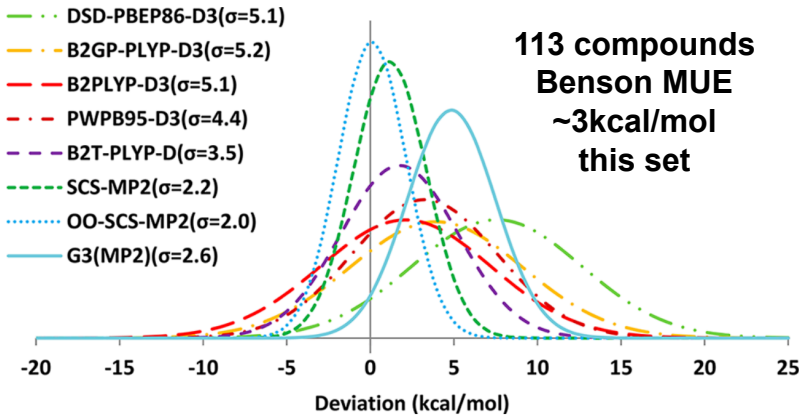
ΔH_f from modern quantum chemistry



Minenkov, Y.; Wang, H.; Wang, Z.; Sarathy, S. M.; Cavallo, L. *J. Chem. Theory Comput.* **2017**, *13* (8), 3537–3560.

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TAFFI-based Atom Increments

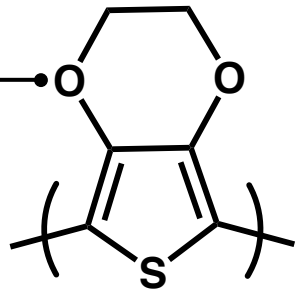
The fundamental idea:

- Systematize group-definitions and model compound selection with rigorous graph-based atom-typing.

TAFFI syntax for machine-readable atom types

[8[6[6][1][1]][6[6][6]]]

Depth 2



graph/structure equivalence

S	0	1	0	0	1	0	0	0	0	0	0	0
C	1	0	1	0	0	0	0	0	0	0	0	0
C	0	1	0	1	0	1	0	0	0	0	0	0
C	0	0	1	0	1	0	0	0	0	0	1	0	0
C	1	0	0	1	0	0	0	0	0	0	0	0	0
O	0	0	1	0	0	0	1	0	0	0	0	0	0
C	0	0	0	0	0	1	0	1	1	1	0	0	0
C	0	0	0	0	0	0	1	0	0	0	1	1	1
H	0	0	0	0	0	0	1	0	0	0	0	0	0
H	0	0	0	0	0	0	1	0	0	0	0	0	0
O	0	0	0	1	0	0	0	1	0	0	0	0	0
H	0	0	0	0	0	0	0	1	0	0	0	0	0
H	0	0	0	0	0	0	0	1	0	0	0	0	0

Adjacency matrix for pedot monomer

Davis, V. K.; et al. Room-Temperature Cycling of Metal Fluoride Electrodes: Liquid Electrolytes for High-Energy Fluoride Ion Cells. *Science* **2018**, *362* (6419), 1144–1148.

Savoie, B. M.; Webb, M. A.; Miller, T. F., III. Enhancing Cation Diffusion and Suppressing Anion Diffusion via Lewis-Acidic Polymer Electrolytes. *J. Phys. Chem. Lett.* **2017**, *8* (3), 641–646.

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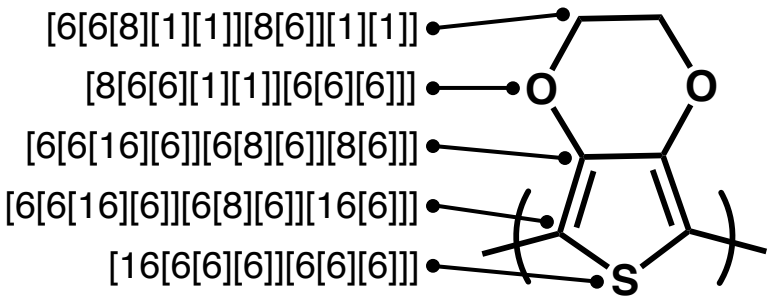

graph/structure equivalence

[16[6[6]][6[6][6]]]	S	0	1	0	0	1	0	0	0	0	0	0	0
[6[6[16[6]][6[8][6]][16[6]]]	C	1	0	1	0	0	0	0	0	0	0	0	0
[6[6[16][6]][6[8][6]]][8[6]]]	C	0	1	0	1	0	1	0	0	0	0	0	0
[6[6[16][6]][6[8][6]]][8[6]]]	C	0	0	1	0	1	0	0	0	0	0	1	0	0
[6[6[16[6]][6[8][6]][16[6]]]	C	1	0	0	1	0	0	0	0	0	0	0	0	0
[8[6[6][1][1]][6[6][6]]]	O	0	0	1	0	0	0	1	0	0	0	0	0	0
[6[6[8][1][1]][8[6]][1][1]]	C	0	0	0	0	0	1	0	1	1	1	0	0	0
[6[6[8][1][1]][8[6]][1][1]]	C	0	0	0	0	0	0	1	0	0	0	1	1	1
[1[6[8][6][1]]]	H	0	0	0	0	0	0	1	0	0	0	0	0	0
[1[6[8][6][1]]]	H	0	0	0	0	0	0	1	0	0	0	0	0	0
[8[6[6][1][1]][6[6][6]]]	O	0	0	0	1	0	0	0	1	0	0	0	0	0
[1[6[8][6][1]]]	H	0	0	0	0	0	0	0	1	0	0	0	0	0
[1[6[8][6][1]]]	H	0	0	0	0	0	0	0	1	0	0	0	0	0

Adjacency matrix for pedot monomer

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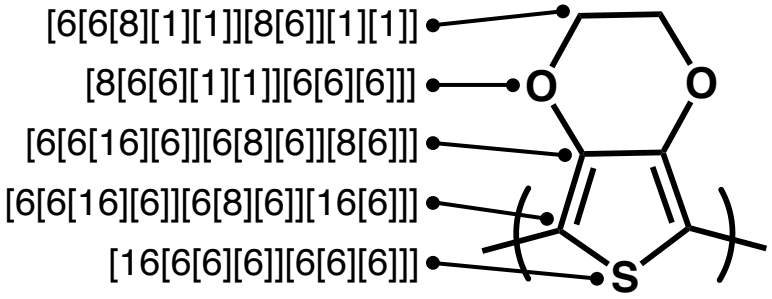
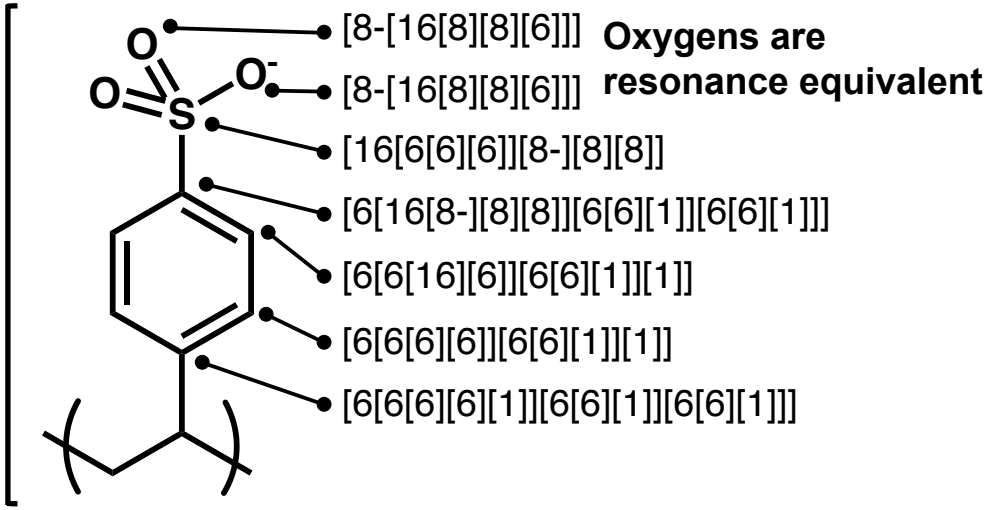


Extending the methodology to charged species requires a local definition of charge identify and resonance equivalent atoms



We utilize formal charges and resonance structures to identify charged atoms for type assignment

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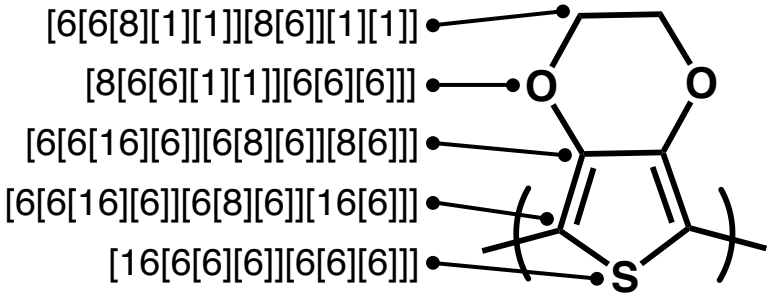
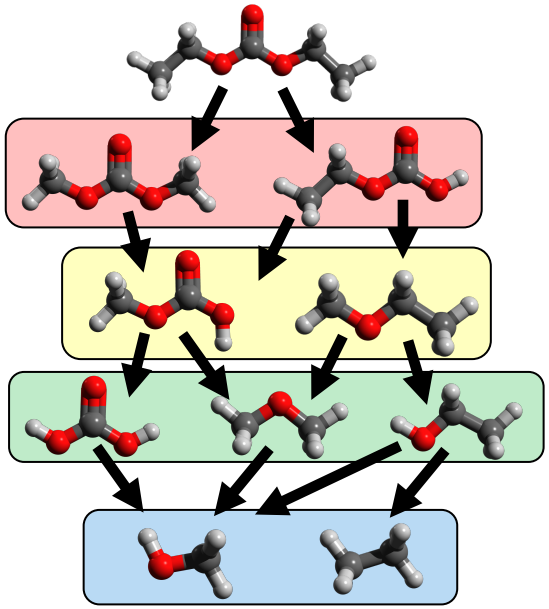
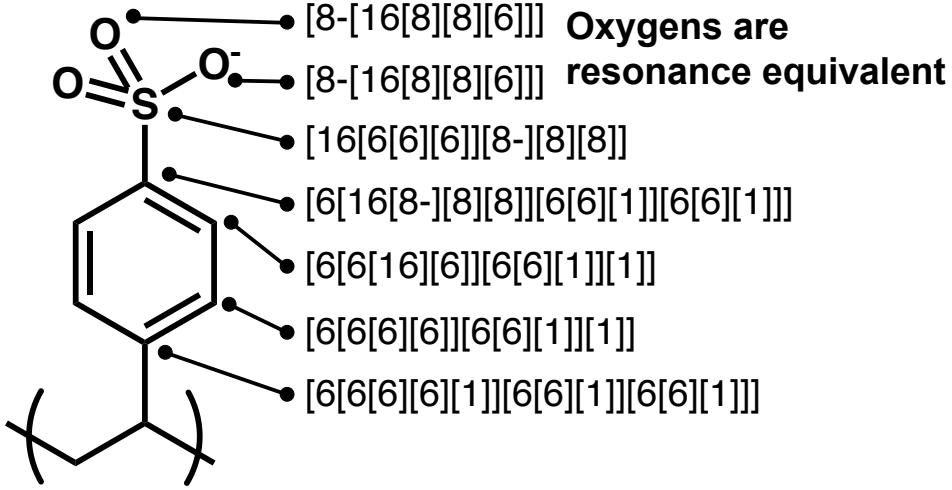


Compounds in the dependency tree for diethyl carbonate:





Oxygens are resonance equivalent

We utilize formal charges and resonance structures to identify charged atoms for type assignment

TAFFI-based Atom Increments

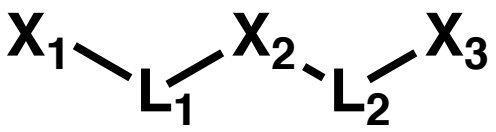
Proposed activities:

- Perform G4 and B97x-D3 level ΔH_f calculations on ~1 million molecules, curated to have combinations of common organic functional groups.

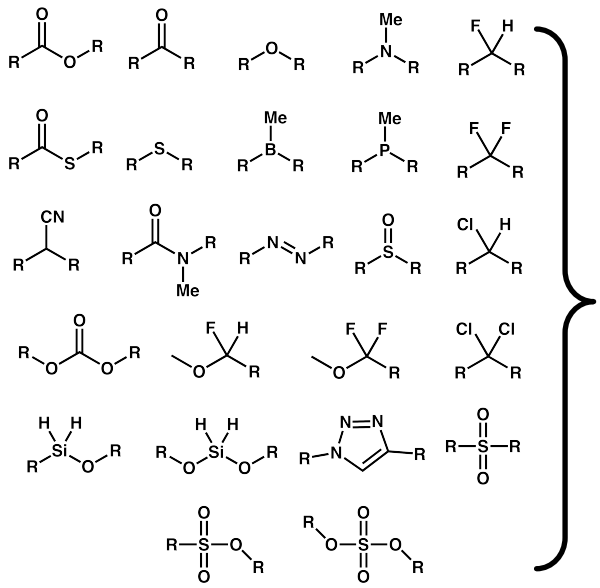
- Build a database infrastructure for data reuse and parameter fitting.

- Guarantee internal consistency by performing group and atom increment parameterizations to *the whole dataset*. This will be periodically redone as the dataset grows.

- Prioritize new chemistries based on important reference calibrations and industrial input.



L = { CH_2 — = }

X = {  }