Using crystallographic models to experimentally measure partial atomic charges with comparison to quantum calculations

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Introduction

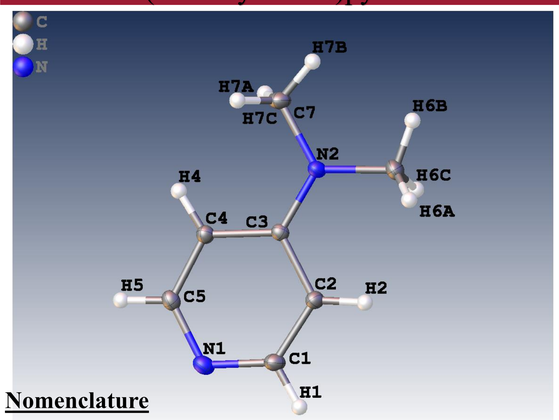
Atoms are typically represented in a neutral state. However bonded atoms exhibit partial charge arising from intramolecular forces. These partial atomic charges are an essential component to understanding molecular electronics and bulk molecular properties. Current spectroscopic methods like IR and Raman lack the detail to focus individual atoms and determine partial charge. X-Ray crystallography allows us to target individual atoms. Current crystallographic refinement techniques treat atoms spherically. By refining individual parameters, we can experimentally model partial atomic charge.

Experimental

Samples were taken on a Bruker KAPPA APEX II DUO with a molybdenum radiation source and equipped with a CCD area detector. COSMO (Bruker AXS) was used for strategy determination. SAINT (Bruker AXS) was used for integration and refinement. SADABS (AXS) was used for scaling and absorption correction. XPREP (Sheldrick) was used to determine the space group. XL (Sheldrick, 2008) was used for computing structure refinement and XS (Sheldrick, 2008) was used for computing the structure solution. XL refinement used least squares minimization with a minimum of 128 cycles. APEX3 and OLEX2 were used as interfaces to run the aforementioned software. Crystals were solved as normal before any analysis took place. Once solved, atom positions were fixed and occupancy values were allowed to float. This allowed for the electron density in the covalent bond to not be perfectly distributed between the atoms, resulting in partial charges on the atoms. Other parameters such as hydrogen distances, thermal parameters, anisotropic/isotropic refinement were considered when doing the analyses.

Results & Discussion

4-(dimethylamino)pyridine



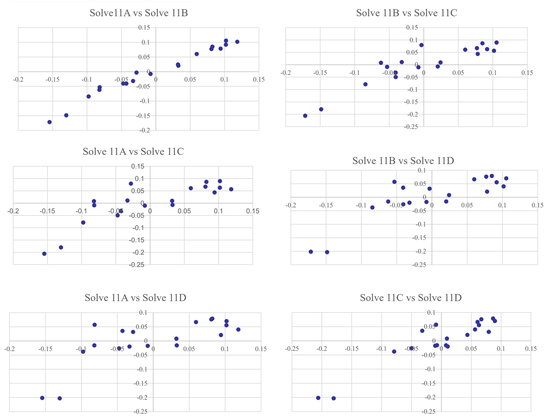
Nomenclature

Numbers refer to which dataset
11- crystal 1, dataset 1
12- crystal 1, dataset 2
21- crystal 2, dataset 1
22- crystal 2, dataset 2

Letters refer to the resolution cutoff.
A- 0.55 Angstroms
B- 0.70 Angstroms
C-0.85 Angstroms
D-1.00 Angstroms

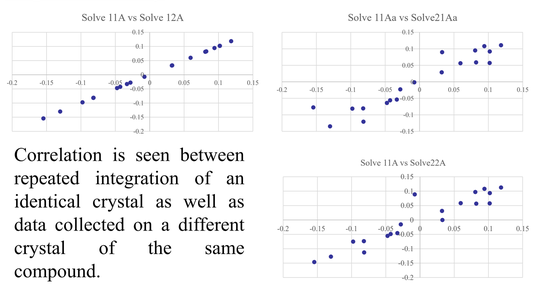
From Left to Right atoms are C1, C2, C3, C4, C5, C6, C7, N1, N2, H1, H2, H3, H4, H5, H6A-c, & H7A-C

Resolution Effects



Correlation is seen at all resolutions analyzed, but is best below 0.85 Angstroms. This indicates the normal 0.76 Angstrom used during a molybdenum collection is sufficient.

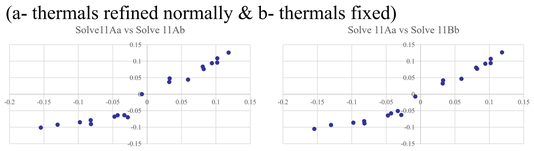
Reproducibility



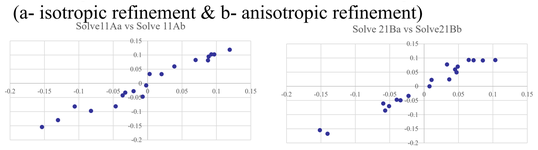
Correlation is seen between repeated integration of an identical crystal as well as data collected on a different crystal of the same compound.

Additional Conclusions

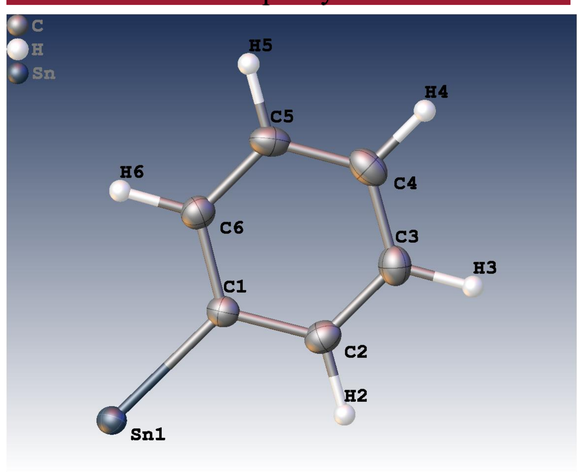
There was a slight change in correlation when the thermal parameters were fixed as noted by the bend. However, results were inconclusive as to why for this molecule.
(a- thermals refined normally & b- thermals fixed)



Anisotropic refinement correlated well with isotropic refinement.
(a- isotropic refinement & b- anisotropic refinement)



Tetraphenyltin



Atom	Charge
Sn1	1.441333409
C1	-0.244736994
C2	-0.069043229
H2	0.052578296
C3	-0.105621711
H3	0.060937698
C4	-0.057221063
H4	0.039692916
C5	-0.116507467
H5	0.02159876
C6	-0.008878941
H6	0.06686829

Atom	Charge
Sn1	-0.50038182
C1	-0.207159677
C2	-0.113519671
H2	0.24825689
C3	-0.207706569
H3	0.252196536
C4	-0.17744523
H4	0.226502755
C5	-0.180422751
H5	0.188676081
C6	-0.114431157
H6	0.210146643

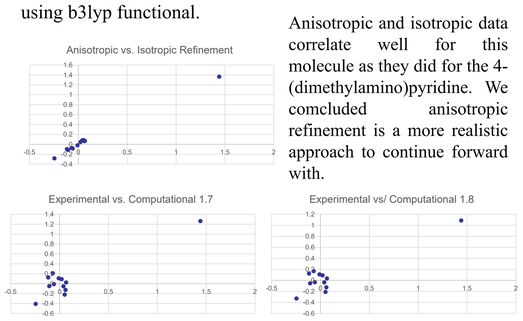
Left: Anisotropically refined data with elongated realistic hydrogen distances and floating thermal parameters. **Right:** Anisotropically refined data with elongated realistic hydrogen distances and fixed thermal parameters.

Unlike the 4-(dimethylamino)pyridine, fixing the thermal parameters completely changed the charge on tin. We concluded floating the thermals allows for the maximum amount of electron density to be accounted for.

Atom	Charge
Sn1	1.363822115
C1	-0.284604655
C2	-0.074378551
H2	0.084922869
C3	-0.115743163
H3	0.064113438
C4	-0.085409114
H4	0.079153337
C5	-0.098727932
H5	0.044252557
C6	-0.021220625
H6	0.066665723

MP2/ECP(Sn)+6-31+G*	
r(Sn) = 1.7	1.8
1.261736	1.087364
-0.408836	-0.330187
0.210764	0.166374
-0.221417	-0.211096
-0.050401	-0.054076
-0.127769	-0.127314
-0.010199	-0.035299
-0.053032	-0.036336
0.124587	0.123219
0.090138	0.091113
0.107094	0.107949
0.023638	0.033814

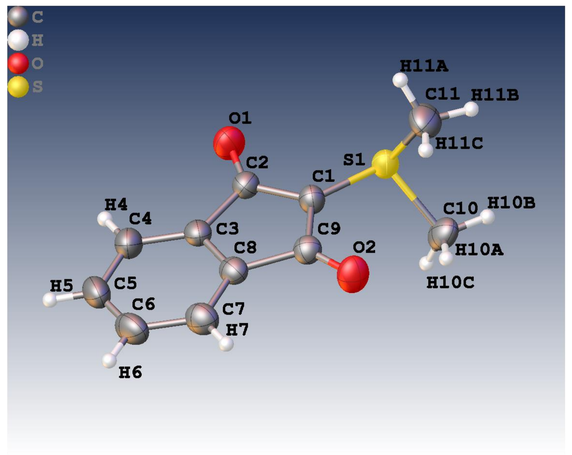
Left: Isotropically refined data with elongated realistic hydrogen distances and floating thermal parameters. **Right:** Computational Data with optimized geometry using b3lyp functional.



Anisotropic and isotropic data correlate well for this molecule as they did for the 4-(dimethylamino)pyridine. We comcluded anisotropic refinement is a more realistic approach to continue forward with.

Computational data agrees well with experimental data.

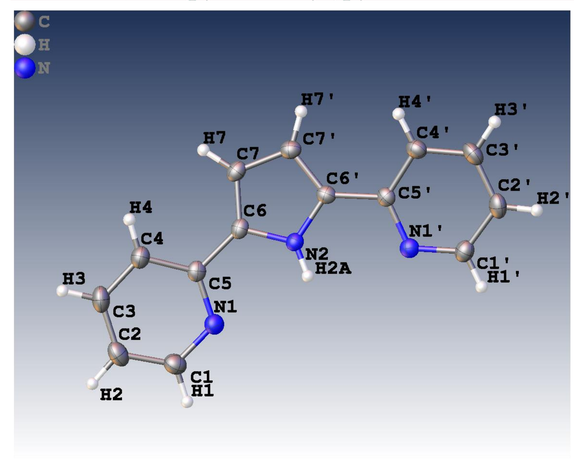
2-dimethylsufuranylidene-1,3-indanedione (YLID)



Atom	Experimental Charge	Computational NBO Charge
C1	**-0.109404375**	**-0.59851**
C2	0.04222339	0.49869
C3	-0.106329241	-0.09822
C4	-0.105146497	-0.20521
C5	0.013187028	-0.23293
C6	-0.048682304	-0.23293
C7	-0.105737869	-0.20521
C8	-0.04754687	-0.09822
C9	0.008870013	0.49869
C10	-0.204437846	-0.83039
C11	-0.249086427	-0.83039
H4	0.01992914	0.25761
H5	0.003232739	0.24395
H6	0.077065526	0.24395
H7	0.080909443	0.25761
H10a	0.065218374	0.26144
H10b	0.120620069	0.31058
H10c	0.087020287	0.26622
H11a	0.018155024	0.31058
H11b	-0.040134537	0.26144
H11c	-0.069101906	0.26622
S1	**0.569607943**	**0.91015**
O1	0.012378631	-0.63208
O2	-0.032802185	-0.63208

The Bruker test crystal is a perfectly spherical crystal that exhibits a formal positively charged sulfur and a formal negatively charged carbon atom. Those atoms are bolded and their charges are as expected. In this dataset, the experimental hydrogens were elongated to realistic bond lengths and all thermals except for the hydrogens were floated. Current analyses are being directed toward the effects of floating the hydrogen thermal parameters and understanding how the occupancies values change with those values.

2,5-di(pyridin-2-yl)pyrrolidine



Experimental Partial Charge	Atom	Computational Charge
0.072863636	C1	0.35
-0.033101795	C2	-0.34
-0.022679953	C3	0.158
-0.038342837	C4	-0.437
-0.027619786	C5	0.596
-0.080572381	C6	-0.199
-0.123826036	C7	-0.122
0.018525479	C1'	0.326
-0.081957944	C2'	-0.324
-0.0086436	C3'	0.152
-0.036234372	C4'	-0.423
0.039489646	C5'	0.577
-0.12846466	C6'	-0.183
-0.125211599	C7'	-0.146
0.0261814	N1	-0.599
0.037918522	N1'	-0.588
-0.03144998	N2	0.07
0.006089632	H1	0.021
0.047084218	H2	0.132
0.042184547	H3	0.06
0.026220454	H4	0.173
0.07596015	H7	0.107
0.032736615	H1'	0.029
-0.021360575	H2'	0.129
0.065066413	H3'	0.059
0.056180739	H4'	0.17
0.050266996	H7'	0.115
0.16277871	H2A	0.132

Experimental and theoretical data disagree when it comes to the aromatic Nitrogen atoms. This could be due to the very covalent nonpolar nature of those bond

Conclusions & Future Direction

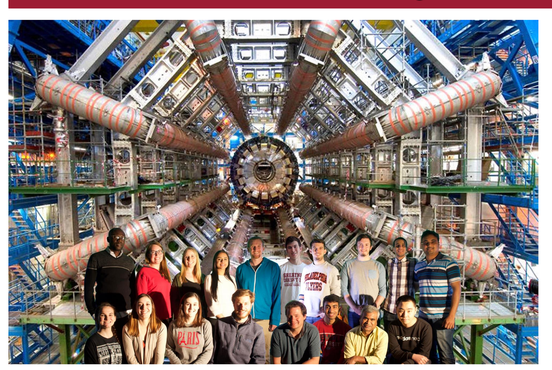
Our methods work for small organic based molecules, zwitter ions, and compounds with metals. We would like to look into the effects of heavy atoms and their scattering. Not included in this data are samples where the calculated charges of heavy atoms were positive when hypothesized to be negative. We would also like to understand the effects the hydrogen thermal parameters have on the datasets. Preliminary analysis has been started.

References

1. Sheldrick, G. M. A short history of SHELX. *Acta Crystallogr. Sect. A Found. Crystallogr.* **64**, 112–122 (2008).

2. Breneman, C. M. & Wiberg, K. B. Determining atom centered monopoles from molecular electrostatic potentials. The need for high sampling density in formamide conformational analysis. *J. Comput. Chem.* **11**, 361–373 (1990).

Acknowledgements



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