The Electron Density vs. NICS Scan: A New Approach to Assess Aromaticity in Molecules with Different Ring Sizes

Cina Foroutan-Nejad[a], Shant Shahbazian[b] and Parviz Rashidi-Ranjbar[a]*

a. School of Chemistry, College of Science, University of Tehran, Tehran, Iran.

b. Department of Chemistry, Faculty of Sciences, Shahid Beheshti University, G.C., Evin, Tehran, Iran.

cina-foroutan@khayam.ut.ac.ir, chemist_shant@yahoo.com, ranjbar@khayam.ut.ac.ir,

Corresponds to Parviz Rashidi-Ranjbar, School of Chemistry, College of Science, University of Tehran, Tehran, Iran.

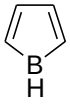
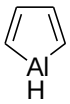
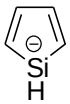
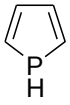
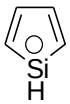
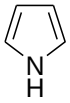
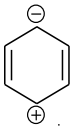
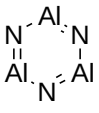
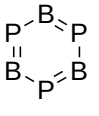
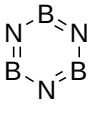
Phone ++98 21 6111 3301

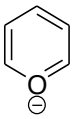
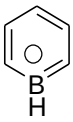
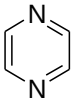
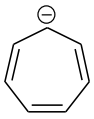
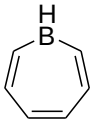
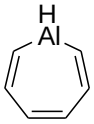
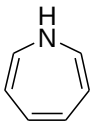
Fax ++98 21 6649 5291

Email; ranjbar@khayam.ut.ac.ir

Figure S-7; Plot of $NICS_{zz}$ vs. distance, at 2.0 to 2.5 Å above the ring plane (as Figure 5 in the manuscript); equation of regression lines and correlation coefficients of linear relationships are presented, p. S-30.

Chart S-1:

Molecule	Structure	Point Group	Aromatic Character	Number of Imaginary Frequencies
1 Borol		***C₂v***	**AA**	**0**
2 Alumol		***C₂v***	**AA**	**0**
3 Silolyl cation		***C₂v***	**AA**	**0**
4 Cyclopentadiene		***C₂v***	**NA**	**0**
5 Phosphole		***Cs***	**NA**	**0**
6 Silolyl anion		***Cs***	**A**	**0**
7 Thiophene		***C₂v***	**A**	**0**
8 Furan		***C₂v***	**A**	**0**
9 Pyrrole		***C₂v***	**A**	**0**
10 Cyclopentadienyl anion		***D₅h***	**A**	**0**
11 Benzene dication		***D₂d***	**AA**	**0**
12 Alumazine		***D₃h***	**NA**	**0**
13 S-triphosphatriborin		***D₃h***	**A**	**0**
14 Borazine		***D₃h***	**NA**	**0**

15 Pyrylium cation		***C₂v***	**A**	**0**
16 Borabenzene anion		***C₂v***	**A**	**0**
17 S-triazine		***D₃h***	**A**	**0**
18 Pyrazine		***D₂h***	**A**	**0**
19 Pyridine		***C₂v***	**A**	**0**
20 Benzene		***D₆h***	**A**	**0**
21 Tropylium cation		***D₇h***	**A**	**0**
22 Borepin		***C₂v***	**A**	**0**
23 Alepin		***C₂v***	**NA**	**0**
24 Oxepin		***C₂v***	**AA**	**1**
25 Azepin		***C₂v***	**AA**	**1**
26 Cyclopropenyl cation		***D₃h***	**A**	**0**
27 Cyclopropenyl anion		***Cs***	**AA**	**0**
28 Borrirene		***C₂v***	**A**	**0**
29 Cyclopropenone		***C₂v***	**A**	**0**

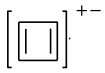
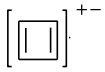
30 1H-azirine		***Cs***	**NA**	**0**
31 Cyclobutadiene		***D_2h***	**AA**	**0**
32 Cyclobutadiene dication		***D_4h***	**NA**	**1**
33 Cyclobutadiene dication		***D_2d***	**A**	**0**

Table S-1:

Molecule	$NICS(Ext)_{zz}$	Molecule	$NICS(Ext)_{zz}$	Molecule	$NICS(Ext)_{zz}$
1	**62.81**	**12**	**11.35**	**23**	**-10.21**
2	**26.37**	**13**	**-8.84**	**24**	**83.45**
3	**53.33**	**14**	**-15.20**	**25**	**122.80**
4	**-14.37**	**15**	**-24.64**	**26**	**-38.27**
5	**-16.03**	**16**	**-26.02**	**27**	**9.92**
6	**-19.16**	**17**	**-26.45**	**28**	**-29.73**
7	**-29.56**	**18**	**-29.20**	**29**	**-12.86**
8	**-28.32**	**19**	**-29.19**	**30**	**-18.16**
9	**-32.25**	**20**	**-29.73**	**31**	**110.91**
10	**-34.56**	**21**	**-26.83**	**32**	**-12.18**
11	**39.43**	**22**	**-20.56**	**33**	**-30.95**

Table S-2

$C_3H_3^+$	NICS(X)			
X Å	NICS iso	NICSπ	NICSzz	NICSπzz
0.0	–21.10	–31.43	–31.52	–14.15
0.5	–27.46	–22.39	–36.43	–16.80
1.0	–14.68	–4.80	–28.42	–11.49
1.5	–5.68	0.89	–16.62	–5.78
2.0	–2.72	1.16	–9.45	–2.71
2.5	–1.57	0.78	–5.67	–1.39
3.0	–1.00	0.50	–3.61	–0.79

$C_4H_4^{2+}$ (D4h)	NICS(X)			
X Å	NICS iso	NICSπ	NICSzz	NICSπzz
0.0	17.74	–25.27	36.32	–13.93
0.5	–1.08	–19.29	9.38	–15.27
1.0	–7.84	–5.97	–10.48	–11.79
1.5	–4.62	–0.26	–10.05	–6.45
2.0	–2.66	0.57	–6.65	–3.30
2.5	–1.66	0.48	–4.27	–1.78
3.0	–1.10	0.34	–2.82	–1.04

$C_4H_4^{2+}$ (D2d)	NICS(X)			
X Å	NICS iso	NICSπ	NICSzz	NICSπzz
0.0	–5.27	–15.52	–8.96	–13.44
0.5	–17.38	–13.75	–25.22	–13.87
1.0	–14.53	–5.07	–27.58	–10.06
1.5	–6.90	–0.63	–17.80	–5.24
2.0	–3.52	0.08	–10.58	–2.62
2.5	–2.04	0.10	–6.50	–1.42
3.0	–1.28	0.06	–4.20	–0.85

$C_5H_5^-$	NICS(X)			
X Å	NICS iso	NICSπ	NICSzz	NICSπzz
0.0	–13.03	–25.78	–17.49	–35.21
0.5	–12.42	–18.30	–28.44	–35.01
1.0	–9.81	–8.03	–33.64	–28.75
1.5	–6.75	–3.19	–26.25	–19.31
2.0	–4.44	–1.43	–17.77	–12.05
2.5	–2.91	–0.73	–11.74	–7.53
3.0	–1.39	–0.39	–7.89	–4.83

C_6H_6	NICS(X)			
X Å	NICS iso	NICSπ	NICSzz	NICSπzz
0.0	–7.55	–23.93	–10.85	–35.52
0.5	–9.30	–19.50	–19.65	–34.41
1.0	–9.81	–11.50	–27.07	–28.64
1.5	–7.58	–5.84	–23.53	–20.10
2.0	–5.02	–2.82	–16.89	–12.94
2.5	–3.17	–1.32	–11.49	–8.21
3.0	–2.03	–0.62	–7.84	–5.32

$C_7H_7^+$	NICS(X)			
X Å	NICS iso	NICSπ	NICSzz	NICSπzz
0.0	–5.76	–22.09	–16.28	–34.93
0.5	–7.63	–19.03	–21.47	–33.71
1.0	–8.90	–12.48	–25.98	–28.44
1.5	–7.45	–6.89	–22.93	–20.63
2.0	–5.31	–3.61	–17.14	–13.80
2.5	–3.61	–1.90	–12.11	–9.06
3.0	–2.46	–1.04	–8.52	–6.04

$C_8H_8^{2+}$	NICS(X)			
X Å	NICS iso	NICSπ	NICSzz	NICSπzz
0.0	–6.43	–19.13	–19.73	–32.98
0.5	–7.65	–17.07	–22.53	–31.67
1.0	–8.64	–12.29	–25.00	–27.16
1.5	–7.63	–7.62	–22.49	–20.57
2.0	–5.79	–4.44	–17.56	–14.44
2.5	–4.15	–2.59	–12.91	–9.88
3.0	–2.94	–1.54	–9.36	–6.79

$C_8H_8^{2-}$	NICS(X)			
X Å	NICS iso	NICSπ	NICSzz	NICSπzz
0.0	–13.46	–17.21	–39.67	–49.78
0.5	–13.13	–19.75	–40.80	–47.91
1.0	–11.61	–14.56	–39.72	–41.63
1.5	–9.02	–9.41	–33.63	–32.41
2.0	–6.46	–5.76	–25.73	–23.50
2.5	–4.55	–3.59	–18.79	–16.58
3.0	–3.25	–2.35	–13.58	–11.69

Electron density and non-atom centred shieldings.

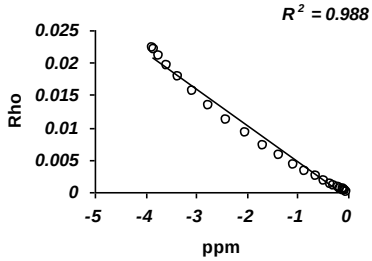
Since rings like ionic dimers (Li_2F_2, Li_2Cl_2, Na_2F_2, Na_2Cl_2, K_2F_2 and K_2Cl_2 within the D_{2h} point group of symmetry) and their constituent ions do not sustain induced ring currents, they are employed as ideal models for benchmarking the relationship between the one-electron density and non-nuclear shieldings.

In the atomic ions with ^1S states (here, alkaline and halide ions), the one-electron density distribution exclusively determines nuclear-centered shielding; through Boit–Savart rule a relationship between shielding and electron density has been obtained in these species, Figure S-2.*

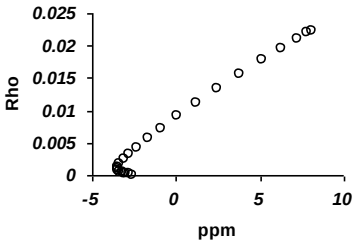
However, in general, the relation between one-electron density and shieldings (particularly non-nuclear shieldings) has not derived theoretically for molecular species. Thus, in current situation, computational case studies are the only methodology to decipher this relationship.

Like aromatic molecules, the plots of $NICS_{zz}$ vs. distance in Li_2F_2, Li_2Cl_2, Na_2F_2 and Na_2Cl_2 reveal a shallow minimum, in which $NICS_{zz}$ decreases and becomes negative at 1 Å above the ring plane of some ionic species, Figure S-1.[13] This pattern suggests that the *local* paratropic currents are operative in the ring planes of these species but above (and below) the ring planes *local* diatropic currents are the major contributor to the magnetic shieldings. The similarity between these patterns and those of aromatic molecules is sometimes misinterpreted as evidence against efficiency of NICS scan method.[15b,15c] However, the NICS scan method is a sensitive tool for probing the diatropic and paratropic currents.

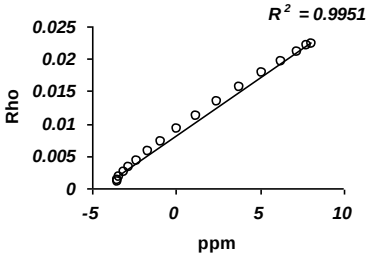
* (a) R. K. Harris, Nuclear Magnetic Resonance Spectroscopy A Physicochemical View, Chap 8, pp 189-190, Longman Scientific and Technical, 1986. (b) W. C. Dickinson, Phys. Rev. 1950, 80, 563. (c) E. Hylleraas, S. Skavlem, Phys. Rev. 1950, 79, 117.



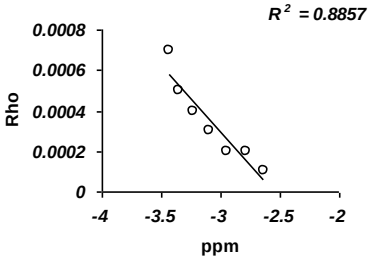
(a)



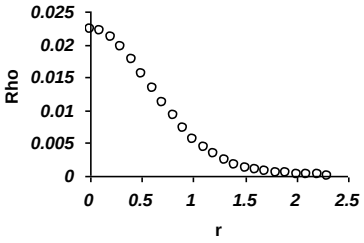
(b)



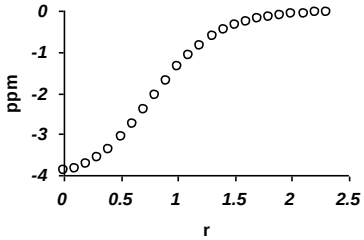
(b-1)



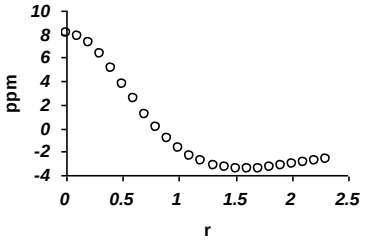
(b-2)



(c)



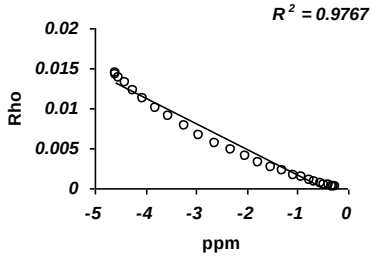
(d)



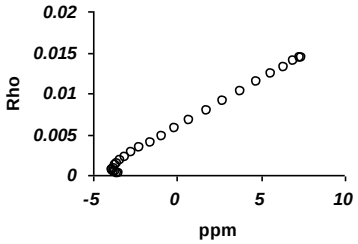
(e)

Lithium Fluoride Dimer

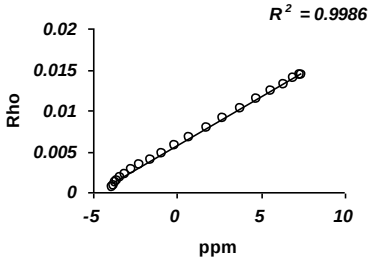
Figure S-1-1



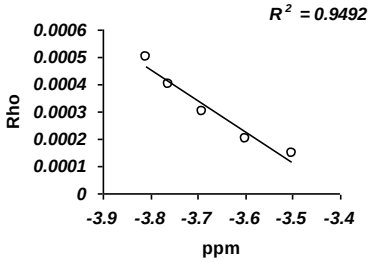
(a)



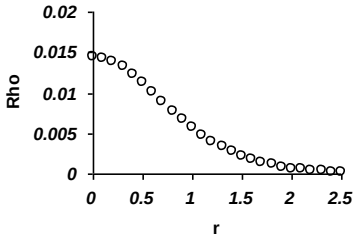
(b)



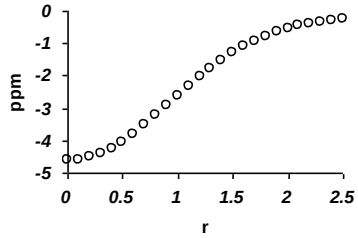
(b-1)



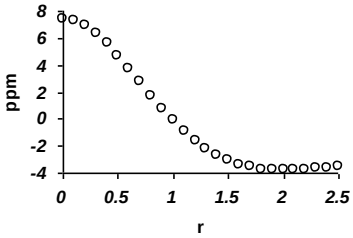
(b-2)



(c)



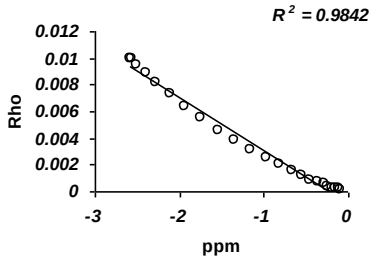
(d)



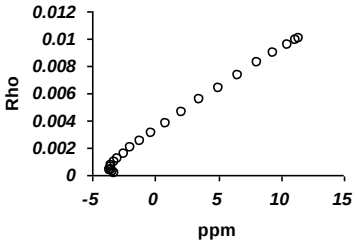
(e)

Lithium Chloride Dimer

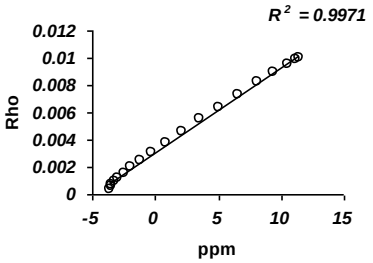
Figure S-1-2



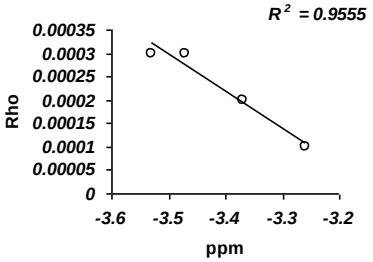
(a)



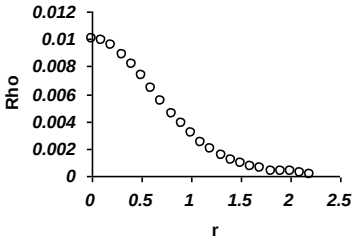
(b)



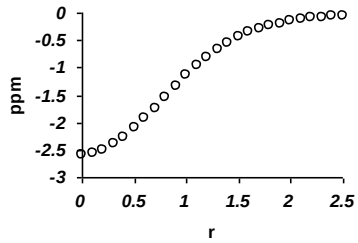
(b-1)



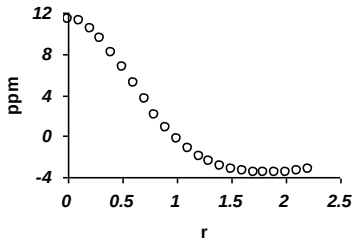
(b-2)



(c)



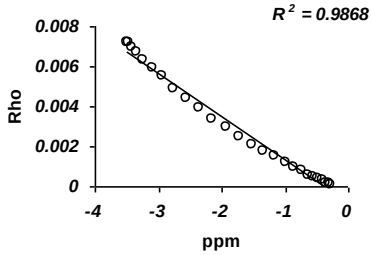
(d)



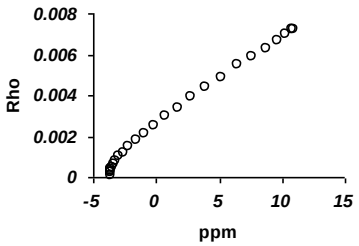
(e)

Sodium Fluoride Dimer

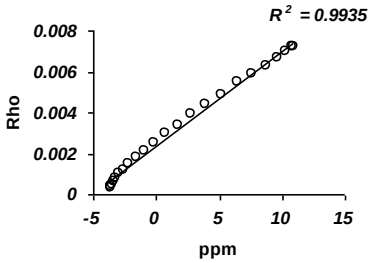
Figure S-1-3



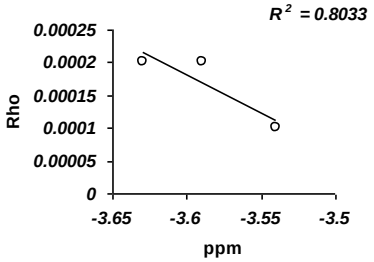
(a)



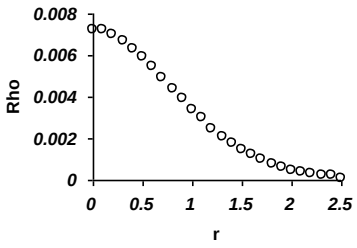
(b)



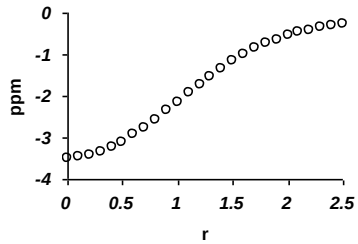
(b-1)



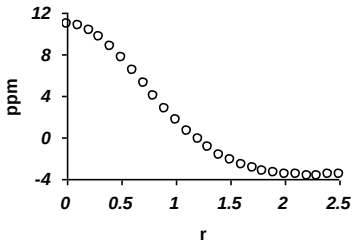
(b-2)



(c)

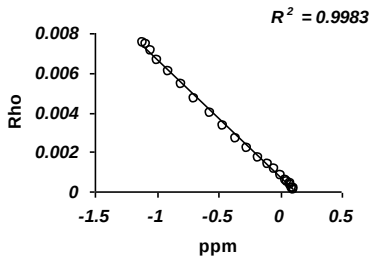


(d)

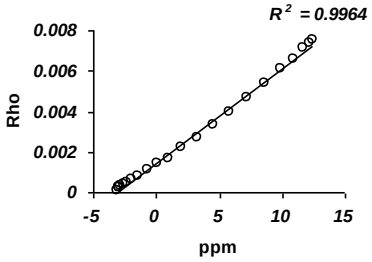


(e)

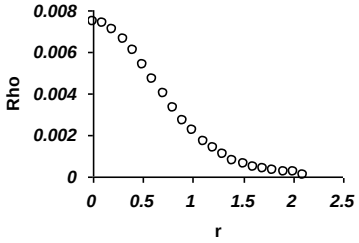
Sodium Chloride Dimer
Figure S-1-4



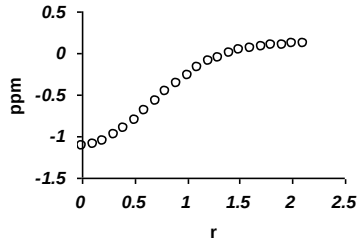
(a)



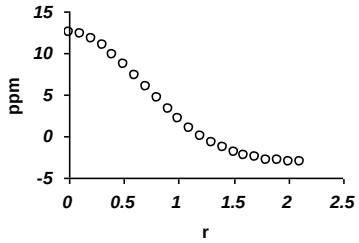
(b)



(c)

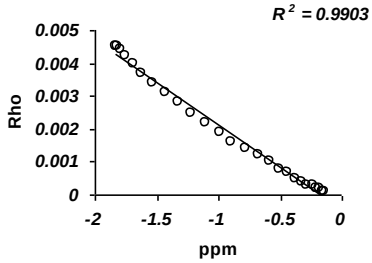


(d)

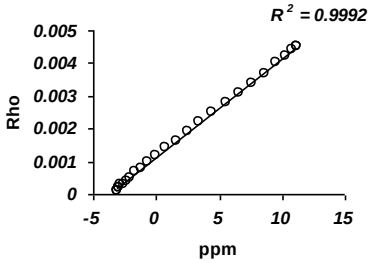


(e)

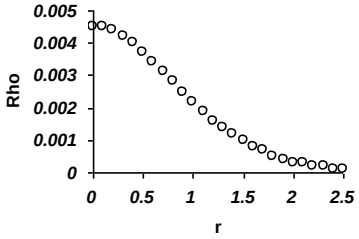
Potassium Fluoride Dimer
Figure S-1-5



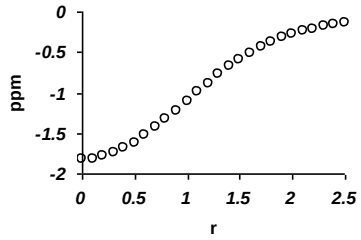
(a)



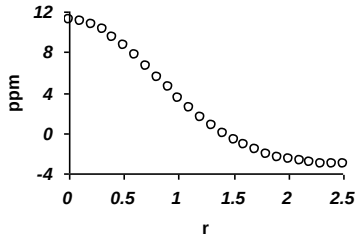
(b)



(c)



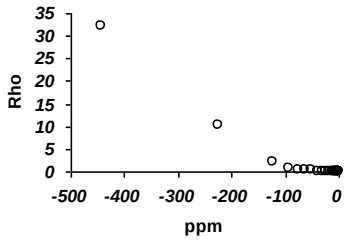
(d)



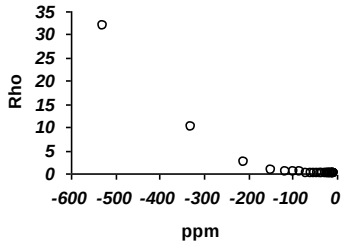
(e)

Potassium Chloride Dimer

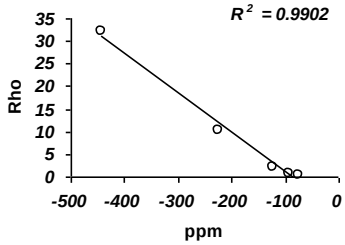
Figure S-1-6



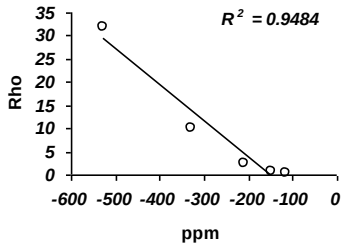
(a)



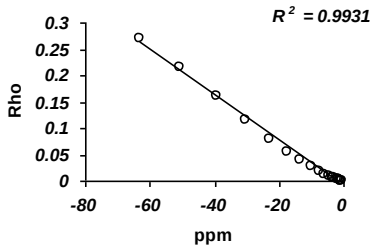
(b)



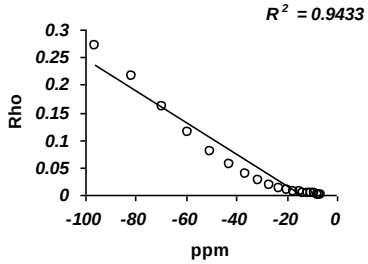
(a-1)



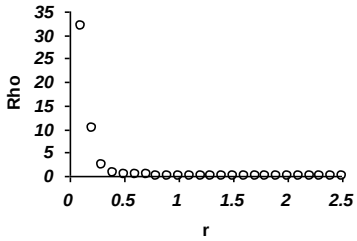
(b-1)



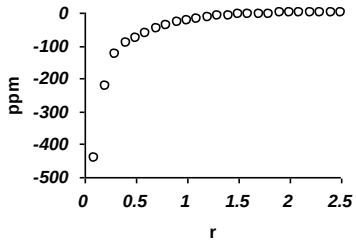
(a-2)



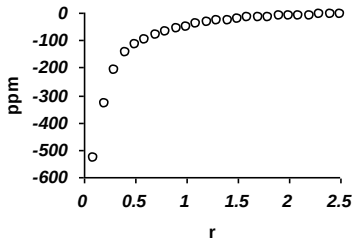
(b-2)



(c)



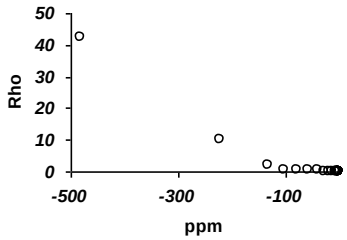
(d)



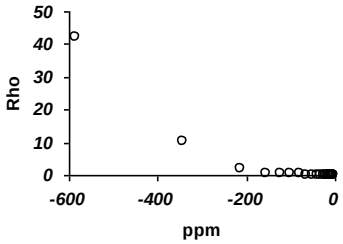
(e)

Chloride Anion

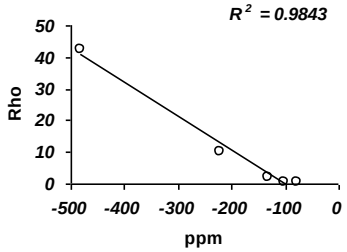
Figure S-2-1



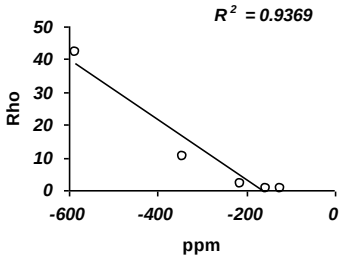
(a)



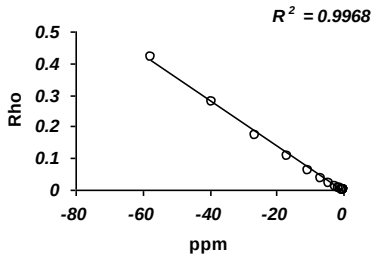
(b)



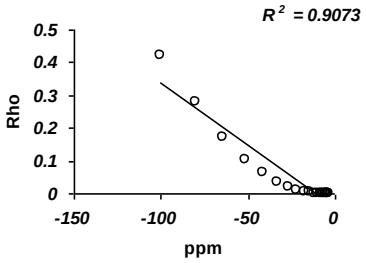
(a-1)



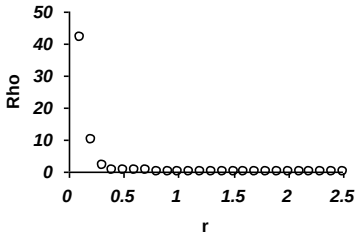
(b-1)



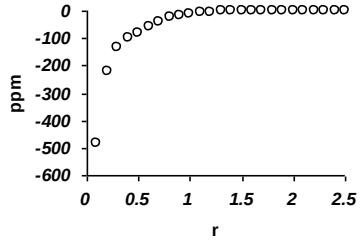
(a-2)



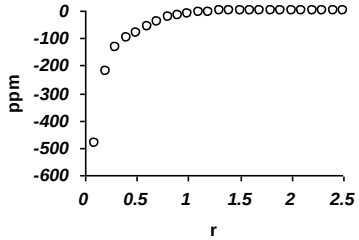
(b-2)



(c)



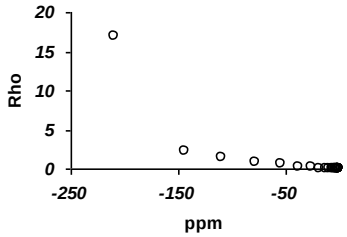
(d)



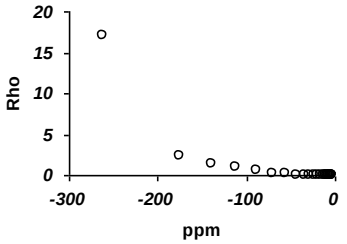
(e)

Potassium Cation

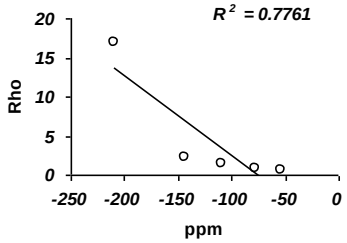
Figure S-2-2



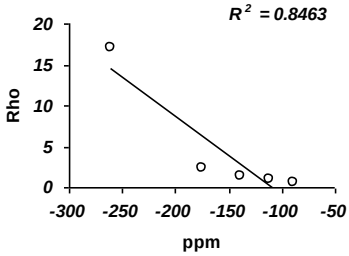
(a)



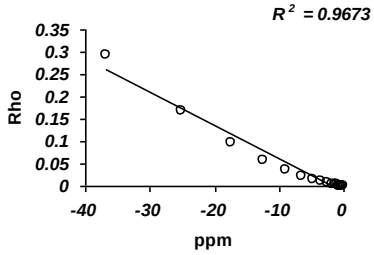
(b)



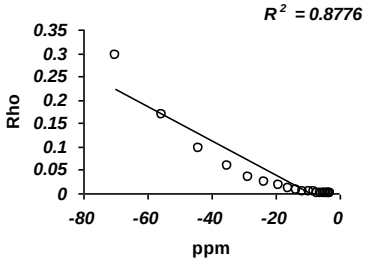
(a-1)



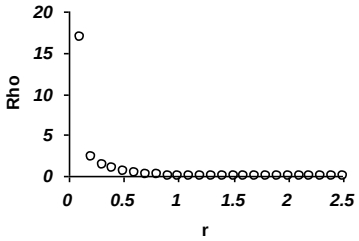
(b-1)



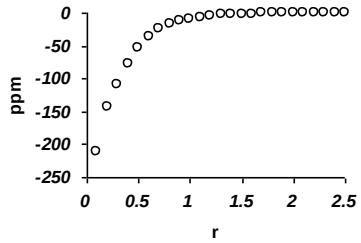
(a-2)



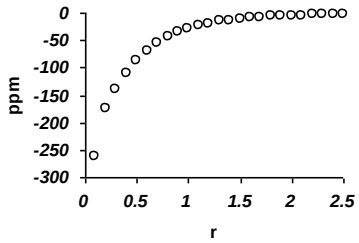
(b-2)



(c)



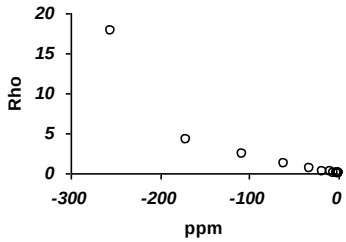
(d)



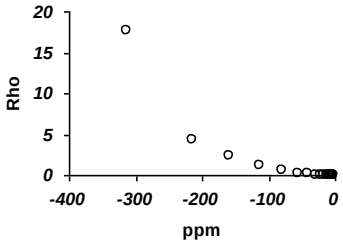
(e)

Fluoride Anion

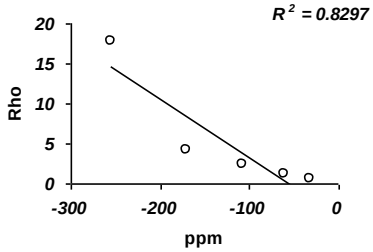
Figure S-2-3



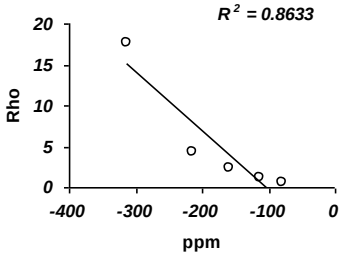
(a)



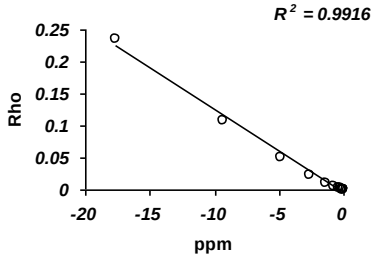
(b)



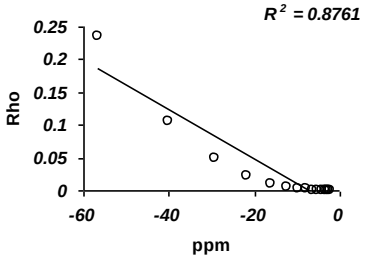
(a-1)



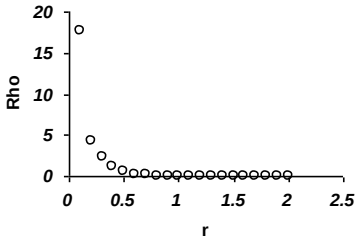
(b-1)



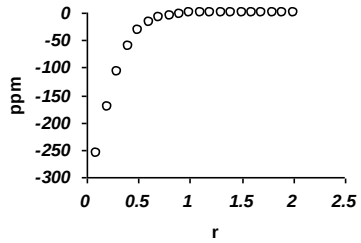
(a-2)



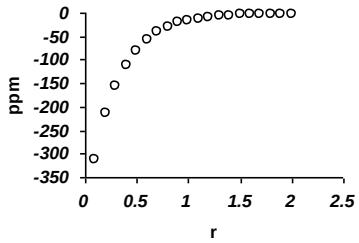
(b-2)



(c)



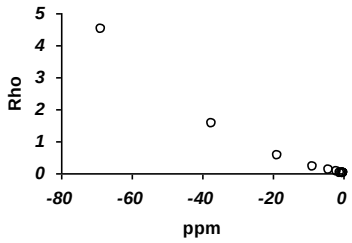
(d)



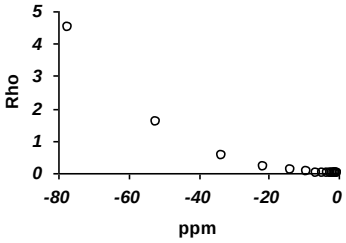
(e)

Sodium Cation

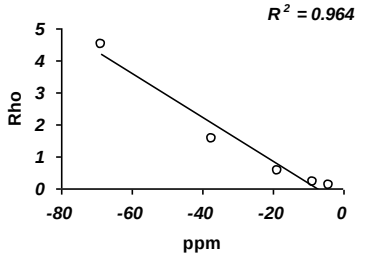
Figure S-2-4



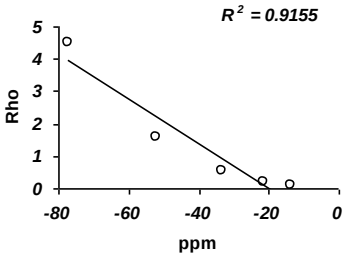
(a)



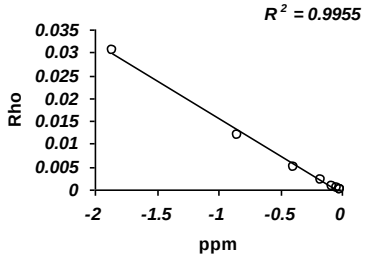
(b)



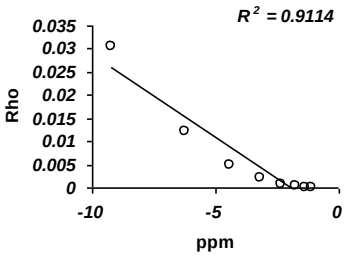
(a-1)



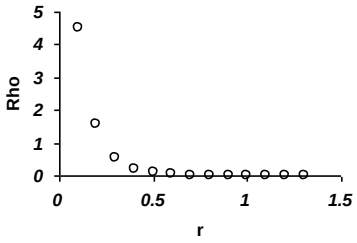
(b-1)



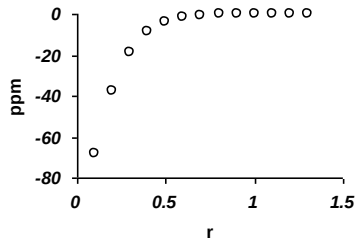
(a-2)



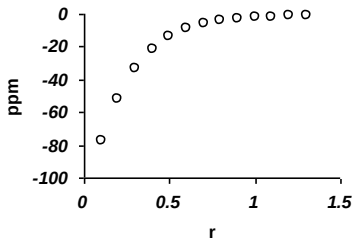
(b-2)



(c)



(d)



(e)

Lithium Cation

Figure S-2-5

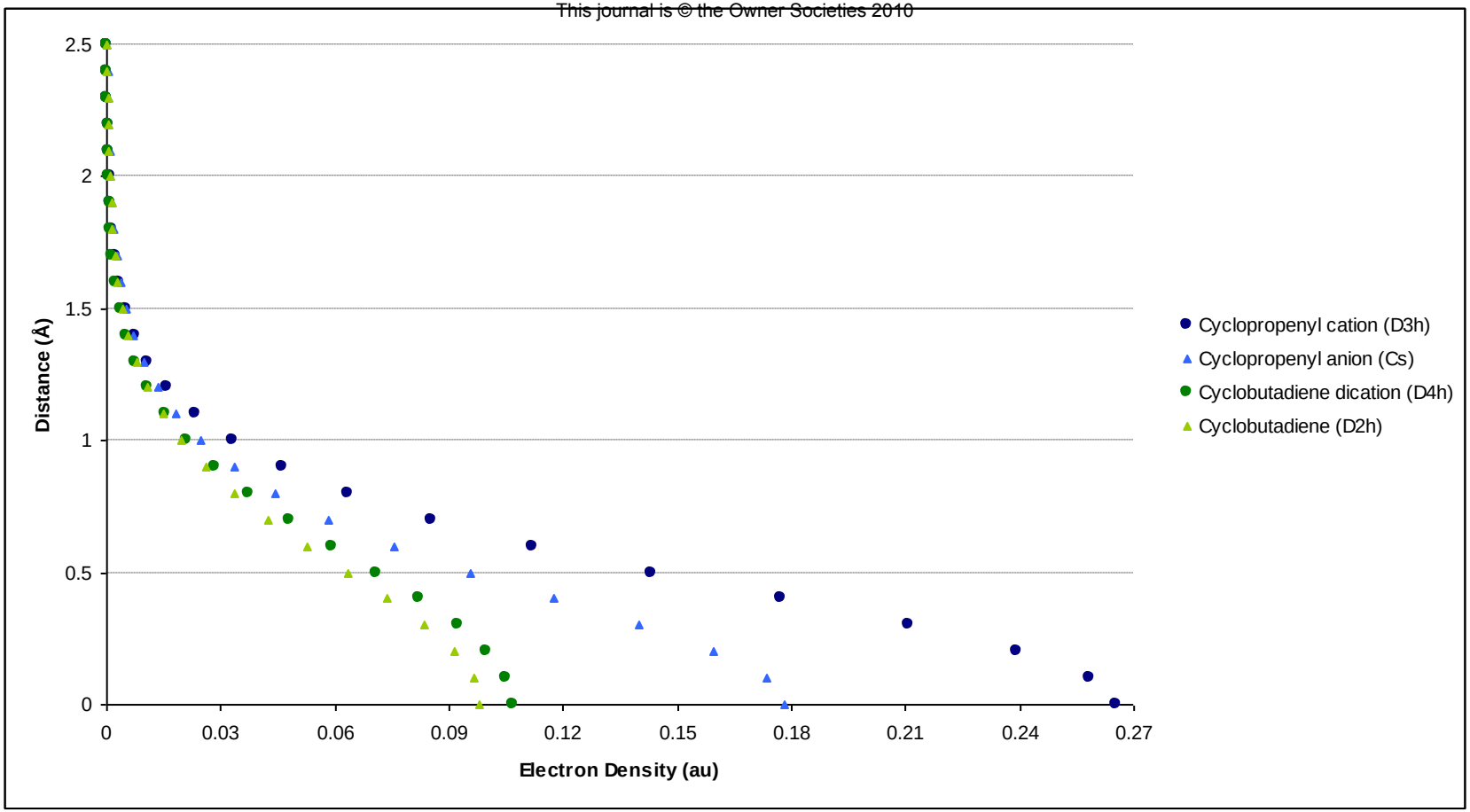


Figure S-3-1

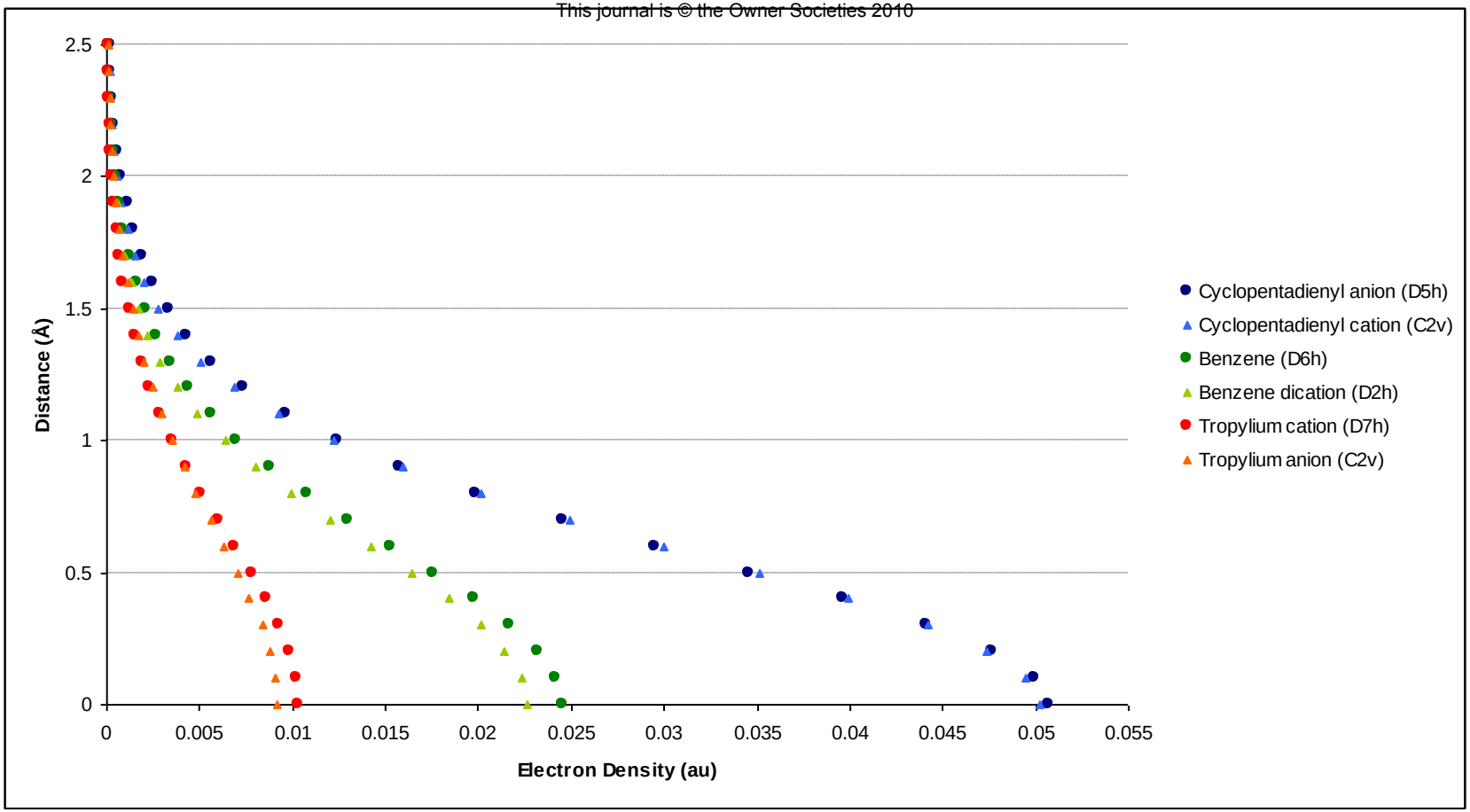


Figure S-3-2

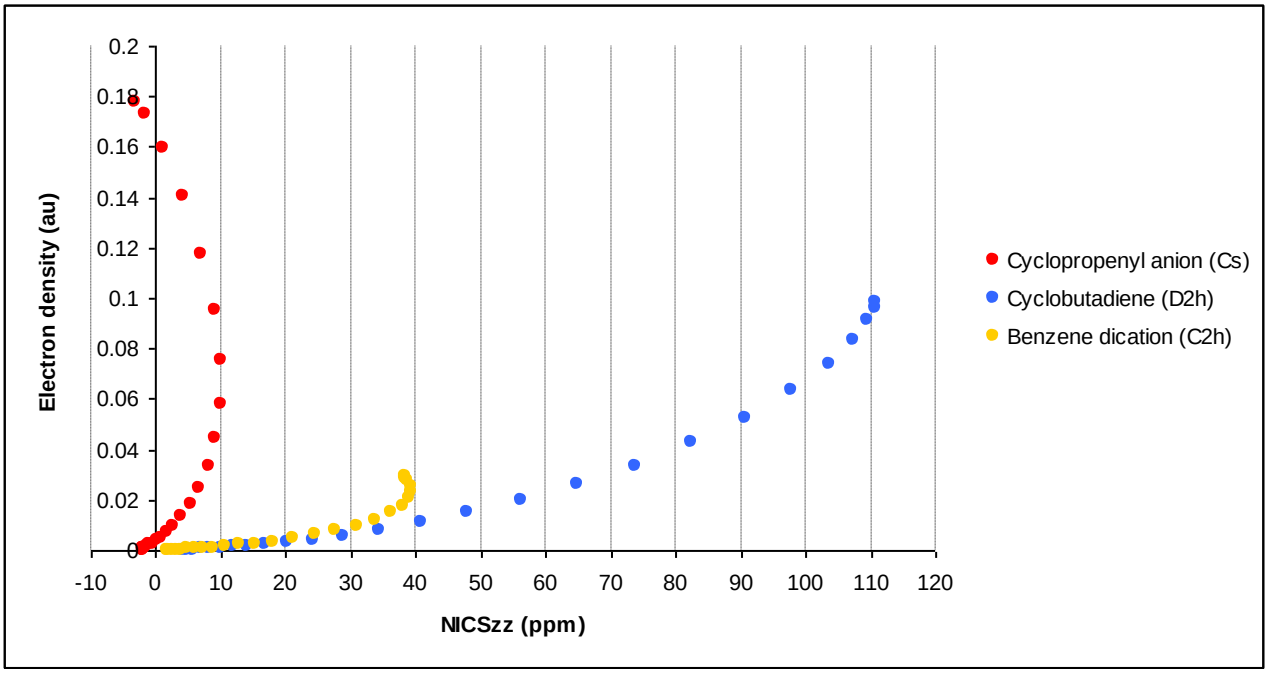


Figure S-4

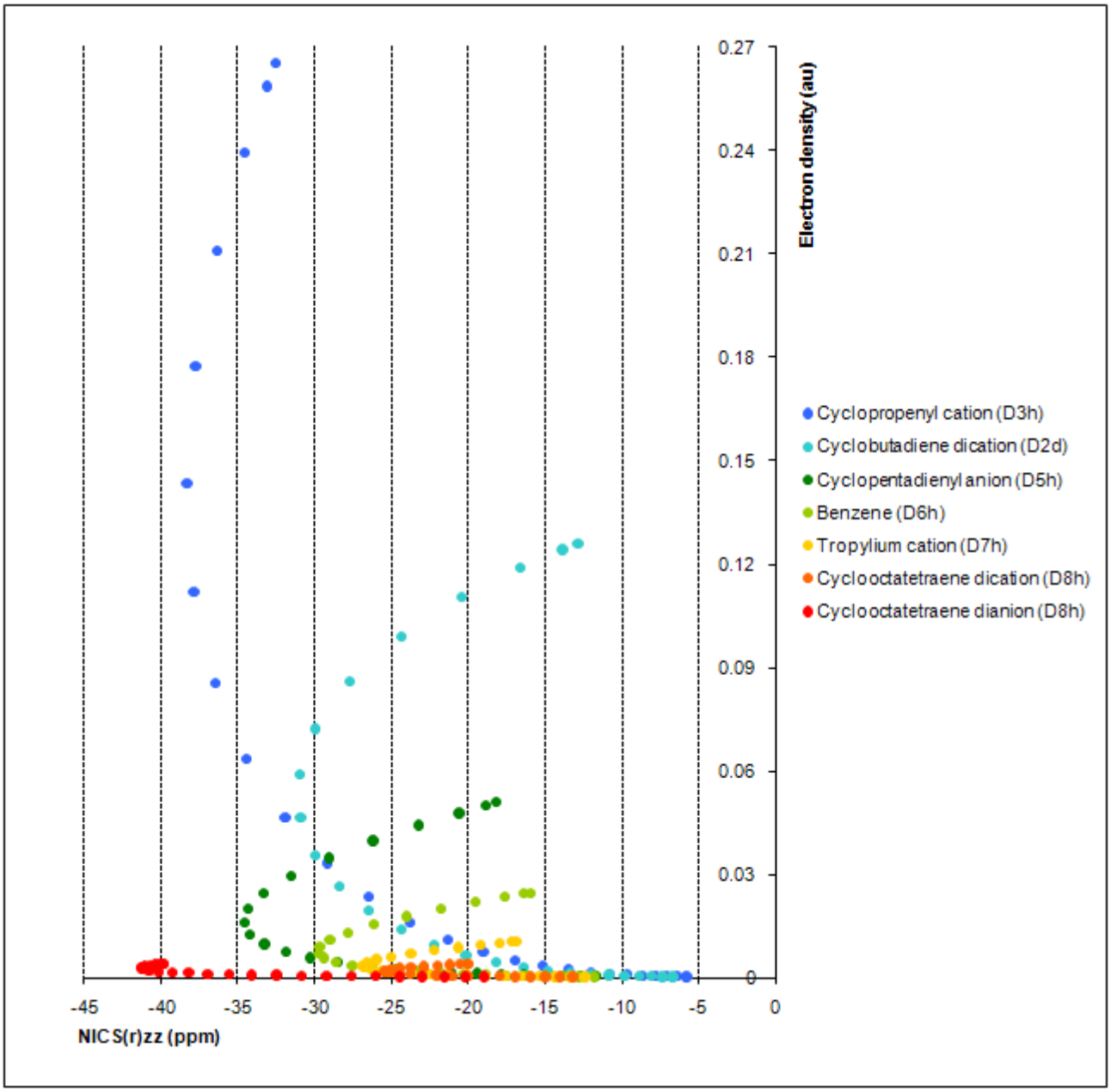


Figure S-5-1

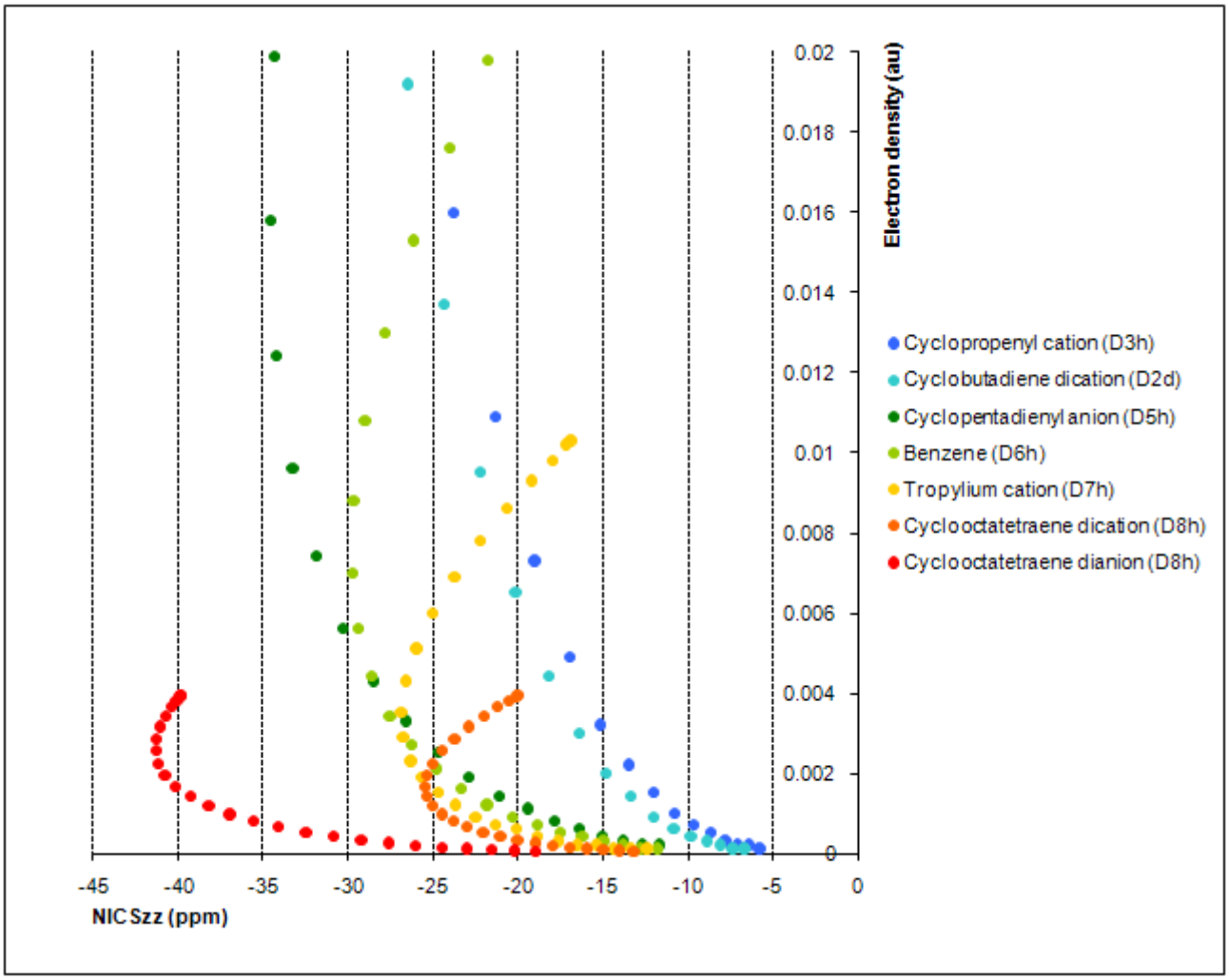


Figure S-5-2

The positive isotropic NICS value of cyclopropanyl anion, a text book example of antiaromatic species, provoked some controversies and criticisms about NICS.[36] As Lazzeretti describes[9] considering the isotropic NICS can cause the loss of information about the electronic ring currents. Accordingly, if one considers the out-of-plane component of shielding can gain more reliable information about the nature of electronic ring currents. In addition, it is well-known that augmented basis sets are more successful in description of negatively charged molecules. The Table S-3, clearly shows that using augmented basis sets can partly solve the problem in case of this molecule. Compared with the other antiaromatic molecules, small positive single point NICS values of the cyclopropenyl anion suggest this molecule to be non-aromatic or weakly antiaromatic. However, electron density vs. $NICS_{zz}$ scans clearly shows that this species has paratropic currents.

Table S-3. NICS values are calculated at the framework of DFT by B3LYP hybrid functional.

Basis set	NICS(0)zz-RCP[1]	NICS(0)zz-GC[2]
6-31g(d,p)	-3.45	+2.29
6-31+g(d,p)	+5.20	+11.11
6-31++g(d,p)	+4.98	+10.96
6-311g (d,p)	-3.59	+3.01
6-311g+(d,p)	+2.44	+9.07
6-311++g(d,p)	+2.32	+8.99
cc-pVDZ	-3.50	+3.60
aug-cc-pVDZ	+1.82	+9.32
cc-pVTZ	-3.25	+2.98
aug-cc-pVTZ	+1.54	+7.56

1- NICS calculated at the Ring Critical Point of QTAIM.

2- NICS calculated at the non-weighted geometric center.

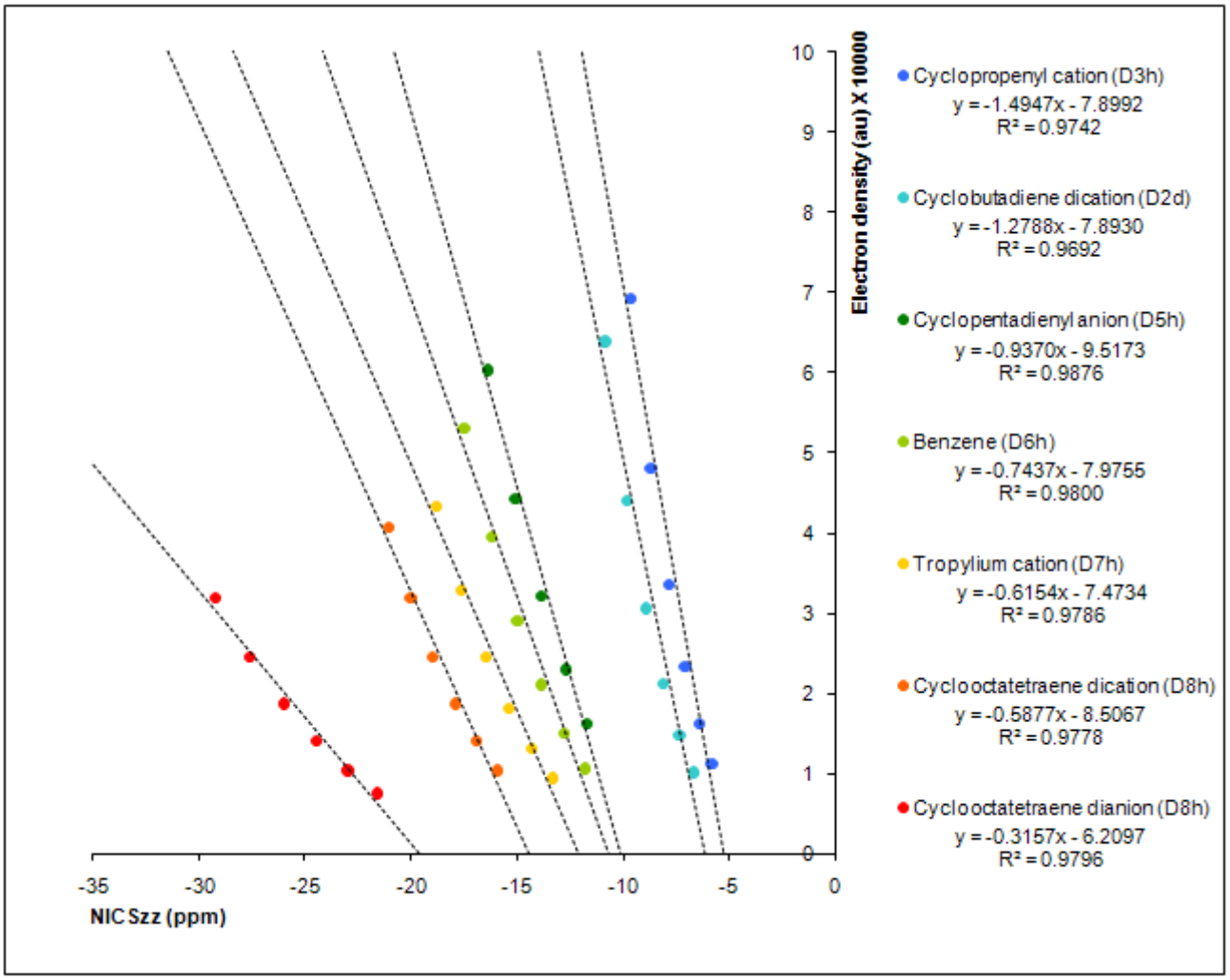


Figure S-6

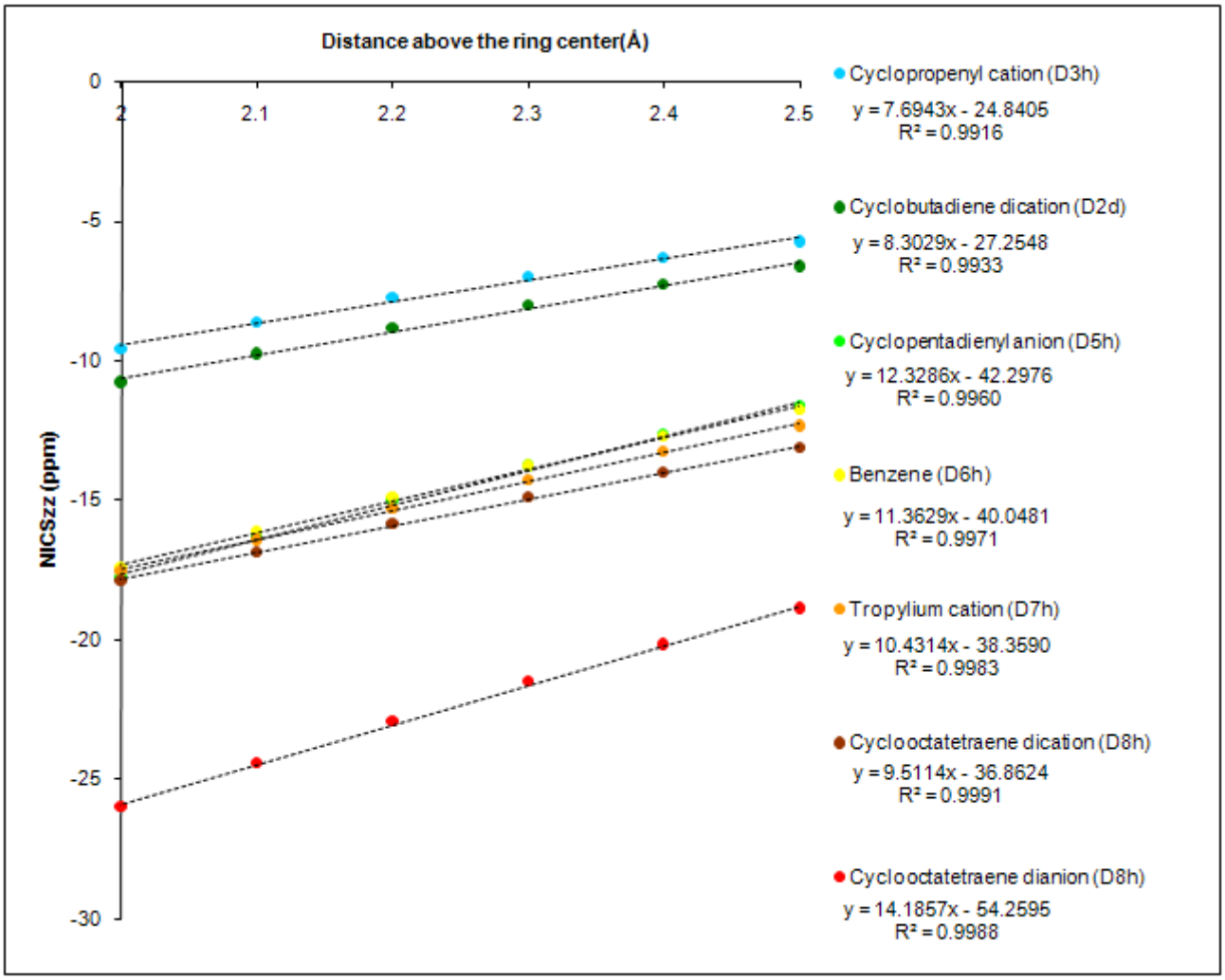


Figure S-7