

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

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Figure S-1; Isotropic NICS ($NICS_{iso}$) vs. electron density (ρ) (a), Out-of-plane component of NICS ($NICS_{zz}$) vs. electron density (ρ) (b), (b-1) and (b-2) represent linear parts of (b) plot, Variations of electron density (ρ) vs. distance in Angstrom (c), Variations of Isotropic NICS ($NICS_{iso}$) vs. distance (d) and out-of-plane NICS ($NICS_{zz}$) vs. distance (e) for ionic dimers, p. S-12.

Figure S-2; Isotropic NICS ($NICS_{iso}$) vs. electron density (ρ) (a), (a-1) and (a-2) represent linear parts of (a) plot, Out-of-plane component of NICS ($NICS_{zz}$) vs. electron density (ρ) (b), (b-1) and (b-2) represent linear parts of (b) plot, Variations of electron density (ρ) vs. distance in Angstrom (c), Variations of Isotropic NICS ($NICS_{iso}$) vs. distance (d) and out-of-plane NICS ($NICS_{zz}$) vs. distance (e) for ions, p. S-18.

Figure S-3; Plot of electron density vs. distance for $C_3H_3^+$, $C_3H_3^-$, $C_4H_4^{2+}$ and C_4H_4 (S3-1) and $C_5H_5^-$, $C_5H_5^+$, C_6H_6 , $C_6H_6^{2+}$, $C_7H_7^+$ and $C_7H_7^-$ (S3-2); the rate of decrease of electron density is different for rings with different sizes so molecules with different ring sizes are depicted in two different plots. Although the charge contents of these molecules are very different but always the electron density in the RCP of aromatic species are more than their anti-aromatic counterparts. This is evident for small rings but is difficult to be verified in case of larger rings, specially in case of 5-membered rings in which difference is small; 0.512 au for $C_5H_5^-$ vs. 0.502 au for $C_5H_5^+$, p. S-23.

Figure S-4; The graph of electron density vs. NICS_{zz} for the antiaromatic 3- to 6-member rings hydrocarbons. This plot suggests similar antiaromaticity order for benzene dication and cyclobutadiene as the curves of these molecules have similar slopes at low-electron density region of the plot, p. S-25.

Figure S-5; Plot of electron density vs. NICS_{zz} for $C_3H_3^+$, $C_4H_4^{2+}$, $C_5H_5^-$, C_6H_6 , $C_7H_7^+$, $C_8H_8^{2+}$ and $C_8H_8^{2-}$; the full scale plot S-3-1 and in the low electron density regions S-3-2, p. S-26

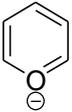
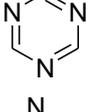
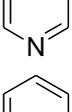
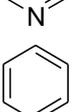
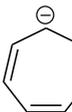
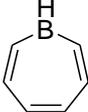
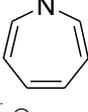
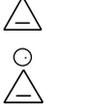
Influence of Basis set size on the magnitude of NICS at the center of cyclopropenyl anion and **Table S-3**, p. S-28.

Figure S-6; Plot of ρ vs. NICS_{zz} at low-electron density limit for aromatic hydrocarbons (as Figure 4 in the manuscript); equation of regression lines and correlation coefficients of linear relationships are presented, p. S-29.

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		C_{2v}	AA	0
2 Alumol		C_{2v}	AA	0
3 Silolyl cation		C_{2v}	AA	0
4 Cyclopentadiene		C_{2v}	NA	0
5 Phosphole		C_s	NA	0
6 Silolyl anion		C_s	A	0
7 Thiophene		C_{2v}	A	0
8 Furan		C_{2v}	A	0
9 Pyrrole		C_{2v}	A	0
10 Cyclopentadienyl anion		D_{5h}	A	0
11 Benzene dication		D_{2d}	AA	0
12 Alumazine		D_{3h}	NA	0
13 S-triphosphatriborin		D_{3h}	A	0
14 Borazine		D_{3h}	NA	0

15	Pyrylium cation		C_{2v}	A	0
16	Borabenzene anion		C_{2v}	A	0
17	S-triazine		D_{3h}	A	0
18	Pyrazine		D_{2h}	A	0
19	Pyridine		C_{2v}	A	0
20	Benzene		D_{6h}	A	0
21	Tropylium cation		D_{7h}	A	0
22	Borepin		C_{2v}	A	0
23	Alepin		C_{2v}	NA	0
24	Oxepin		C_{2v}	AA	1
25	Azepin		C_{2v}	AA	1
26	Cyclopropenyl cation		D_{3h}	A	0
27	Cyclopropenyl anion		C_s	AA	0
28	Borirrene		C_{2v}	A	0
29	Cyclopropenone		C_{2v}	A	0

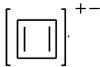
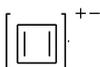
30 1H-azirine		C_s	NA	0
31 Cyclobutadiene		D_{2h}	AA	0
32 Cyclobutadiene dication		D_{4h}	NA	1
33 Cyclobutadiene dication		D_{2d}	A	0

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

C₃H₃⁺	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

C₄H₄²⁺ (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

C₄H₄²⁺ (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

C₅H₅⁻	NICS(X)			
X Å	NICS iso	NICSπ	NICSσ_{zz}	NICSπ_{zz}
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

C₆H₆	NICS(X)			
X Å	NICS iso	NICSπ	NICSσ_{zz}	NICSπ_{zz}
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

C₇H₇⁺	NICS(X)			
X Å	NICS iso	NICSπ	NICSσ_{zz}	NICSπ_{zz}
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

C₈H₈²⁺	NICS(X)			
X Å	NICS iso	NICSπ	NICS$_{zz}$	NICSπ_{zz}
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

C₈H₈²⁻	NICS(X)			
X Å	NICS iso	NICSπ	NICS$_{zz}$	NICSπ_{zz}
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.

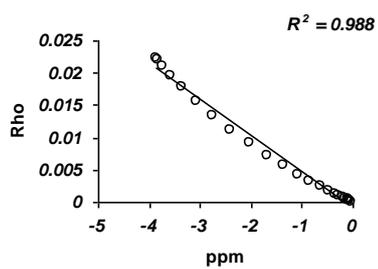
Since rings like ionic dimers (Li_2F_2 , Li_2Cl_2 , Na_2F_2 , Na_2Cl_2 , K_2F_2 and K_2Cl_2 within the D_{2h} point group of symmetry) and their constituent ions do not sustain induced ring currents, they are employed as ideal models for benchmarking the relationship between the one-electron density 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 Biot–Savart rule a relationship between shielding and electron density has been obtained in these species, Figure S-2.*

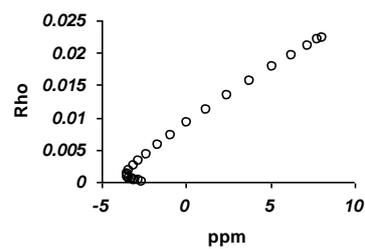
However, in general, the relation between one-electron density and shieldings (particularly non-nuclear shieldings) has not derived theoretically for molecular species. Thus, in current situation, computational case studies are the only methodology to decipher this relationship.

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.

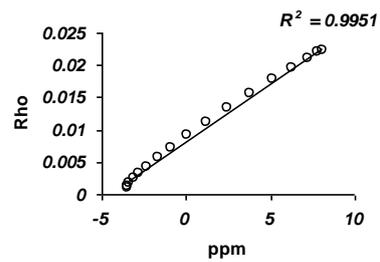
* (a) R. K. Harris, Nuclear Magnetic Resonance Spectroscopy A Physicochemical View, Chap 8, pp 189-190, Longman Scientific and Technical, 1986. (b) W. C. Dickinson, Phys. Rev. 1950, 80, 563. (c) E. Hylleraas, S. Skavlem, Phys. Rev. 1950, 79, 117.



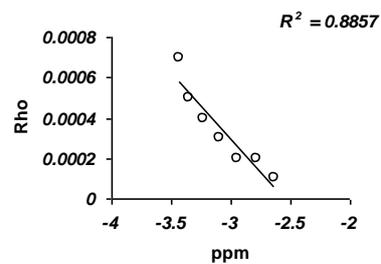
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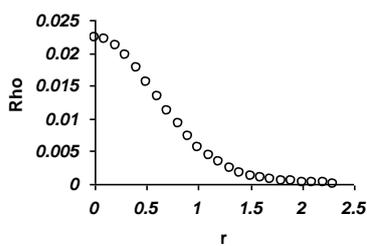
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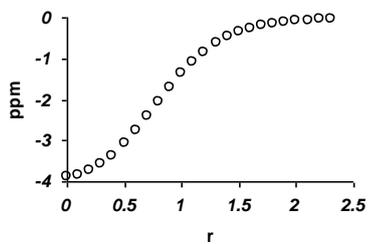
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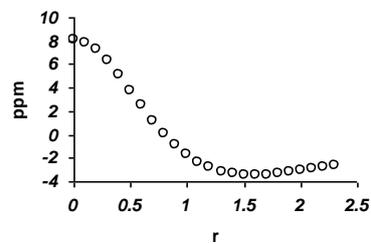
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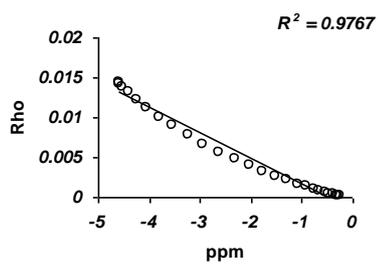


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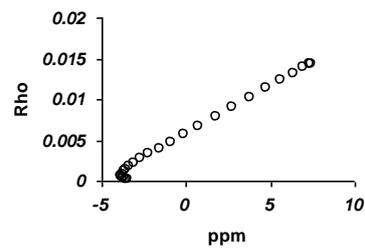


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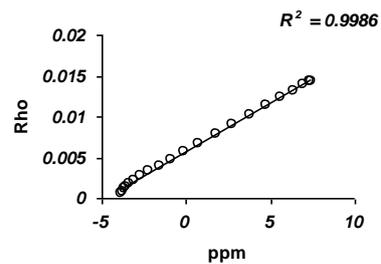
Lithium Fluoride Dimer
Figure S-1-1



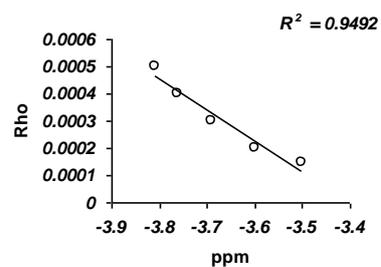
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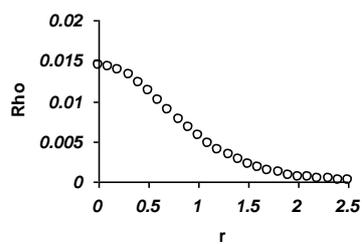
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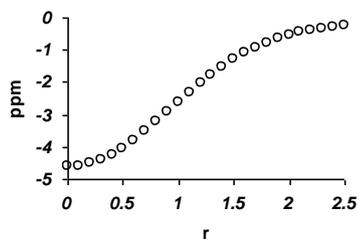
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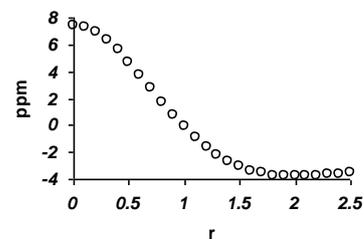
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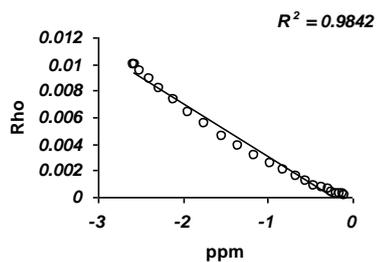


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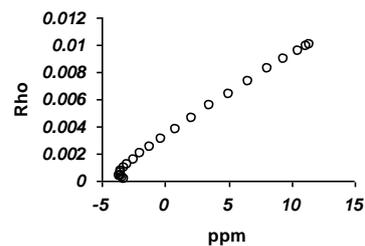


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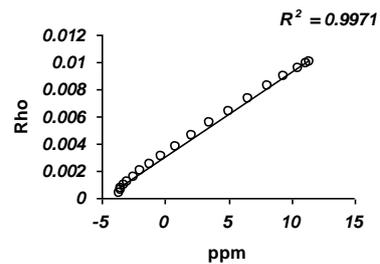
Lithium Chloride Dimer
Figure S-1-2



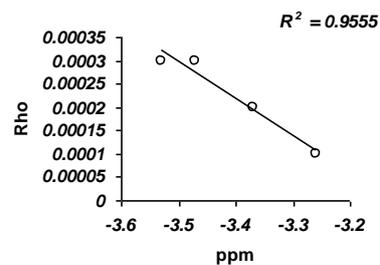
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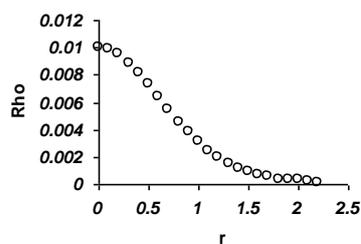
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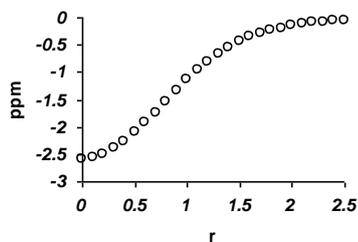
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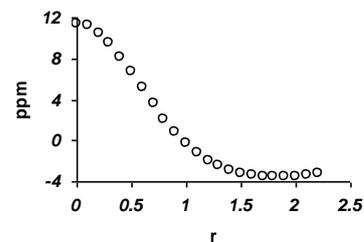
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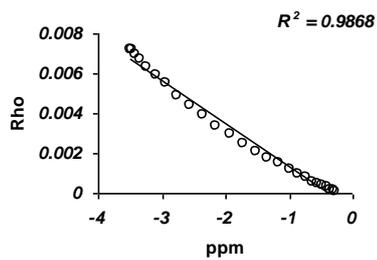


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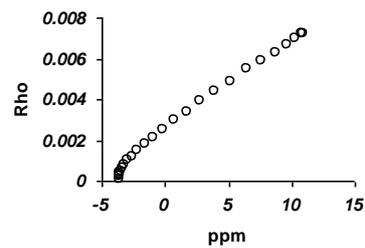


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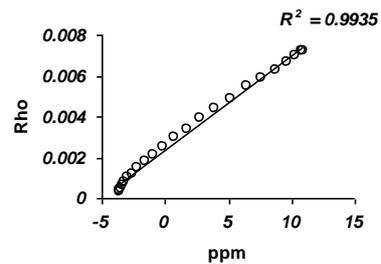
Sodium Fluoride Dimer
Figure S-1-3



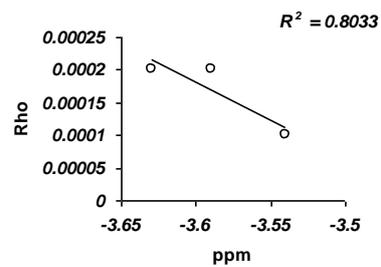
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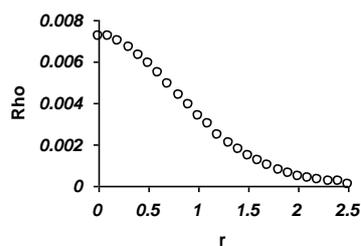
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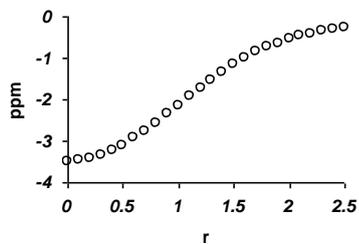
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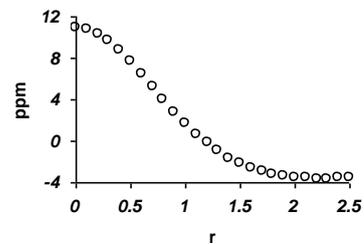
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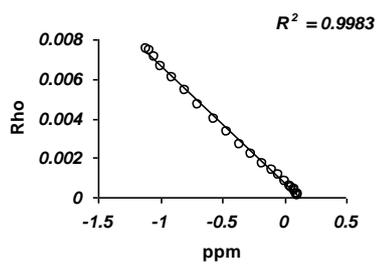


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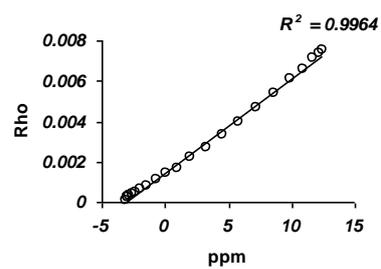


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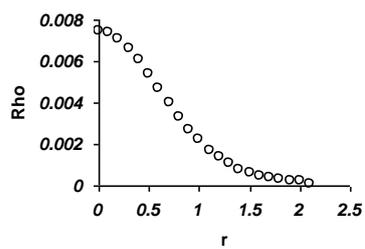
Sodium Chloride Dimer
Figure S-1-4



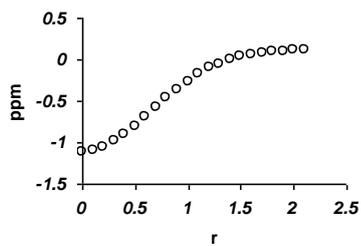
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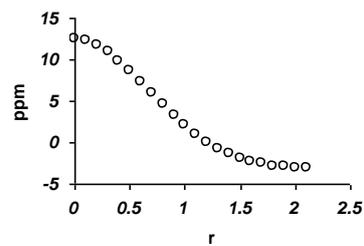
(b)



(c)

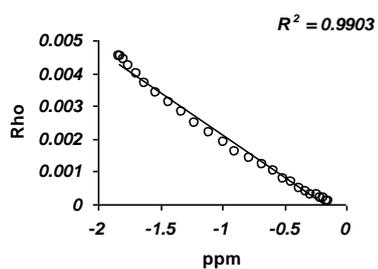


(d)

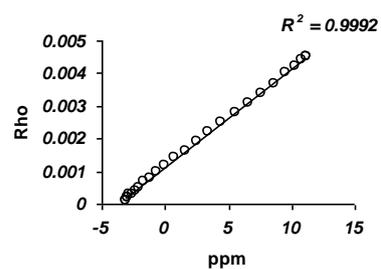


(e)

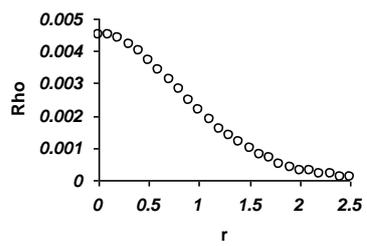
Potassium Fluoride Dimer
Figure S-1-5



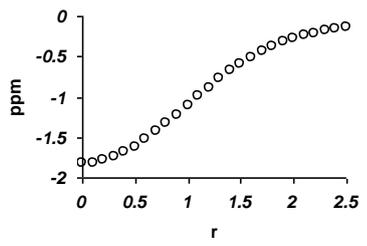
(a)



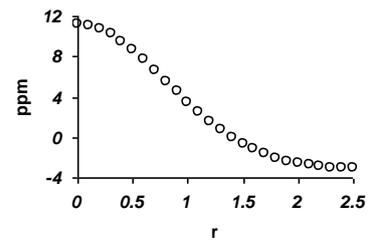
(b)



(c)

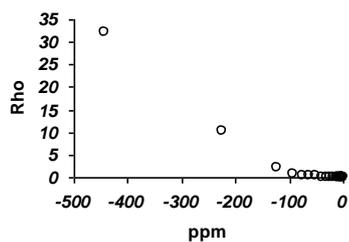


(d)

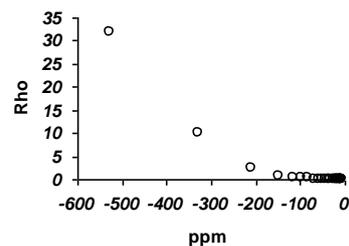


(e)

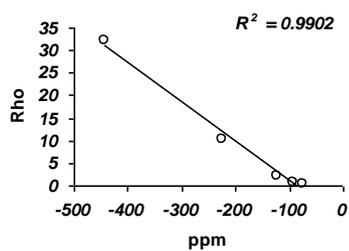
Potassium Chloride Dimer
Figure S-1-6



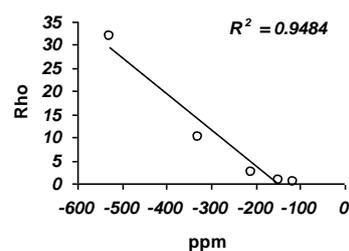
(a)



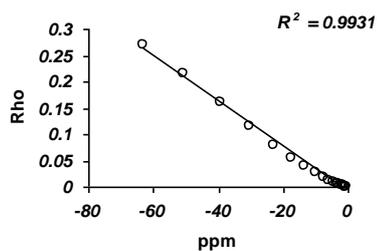
(b)



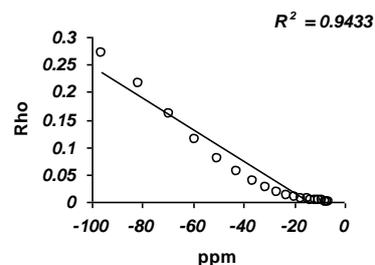
(a-1)



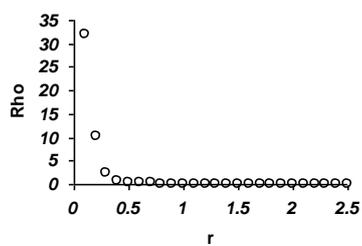
(b-1)



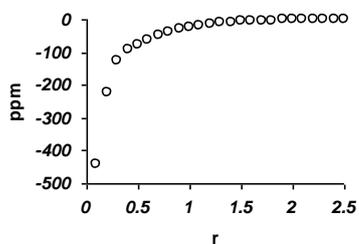
(a-2)



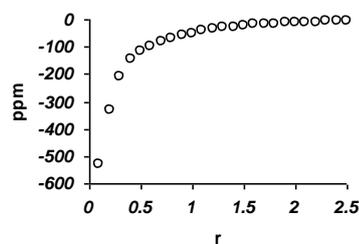
(b-2)



(c)

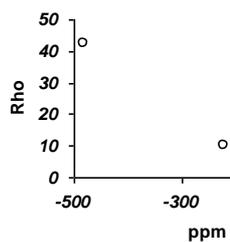


(d)

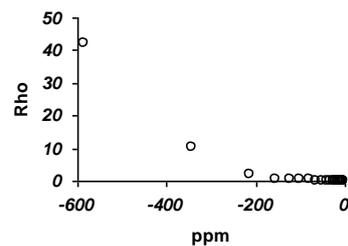


(e)

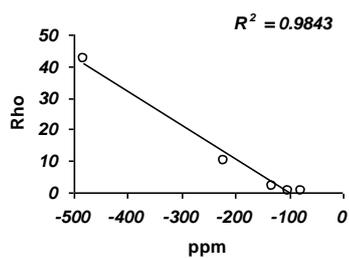
Chloride Anion
Figure S-2-1



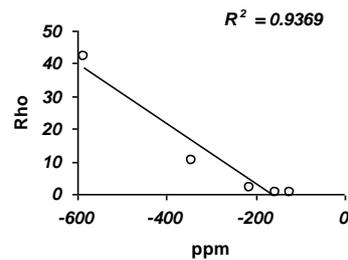
(a)



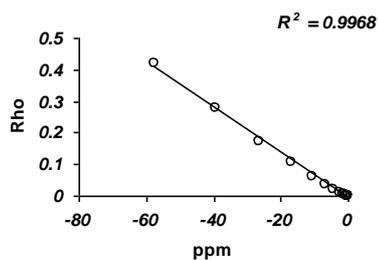
(b)



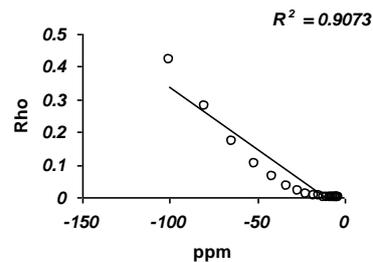
(a-1)



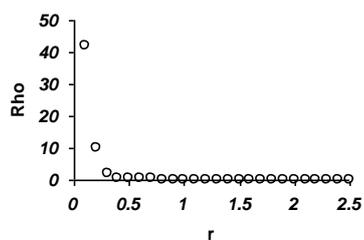
(b-1)



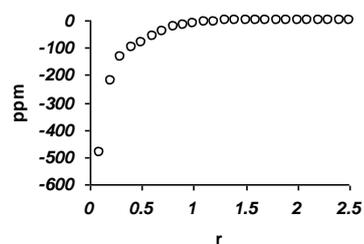
(a-2)



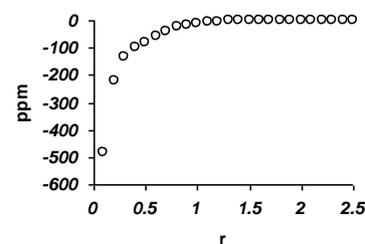
(b-2)



(c)

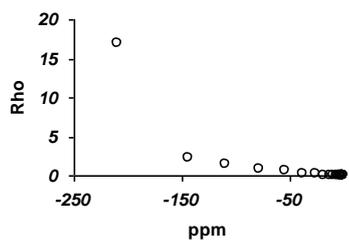


(d)

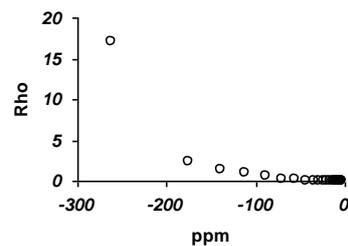


(e)

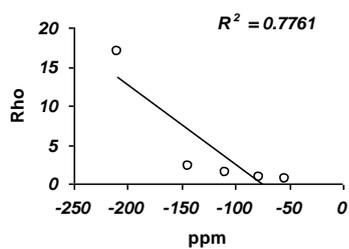
Potassium Cation
Figure S-2-2



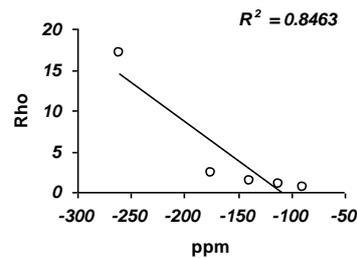
(a)



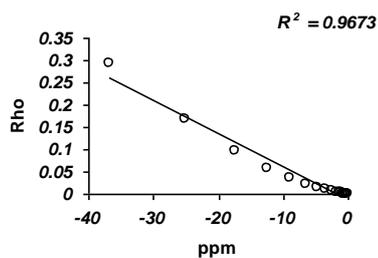
(b)



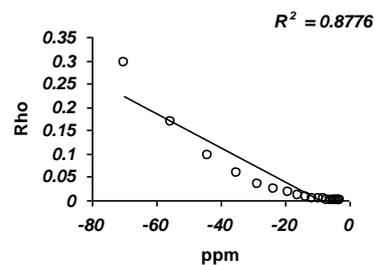
(a-1)



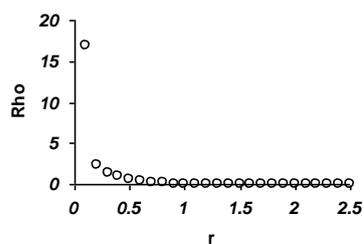
(b-1)



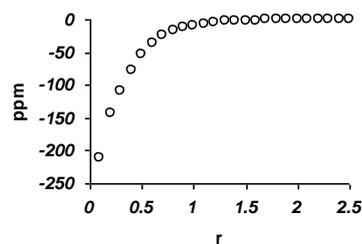
(a-2)



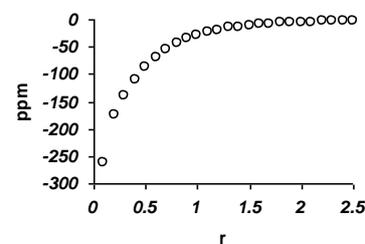
(b-2)



(c)

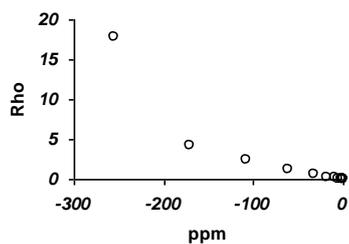


(d)

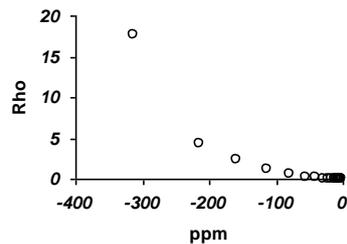


(e)

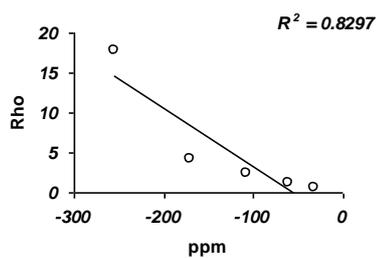
Fluoride Anion
Figure S-2-3



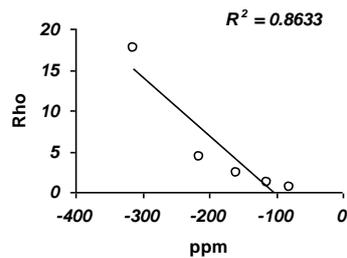
(a)



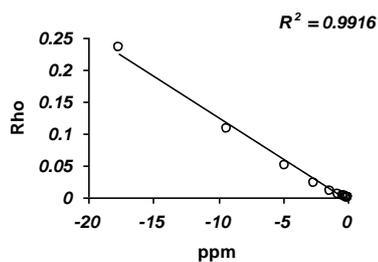
(b)



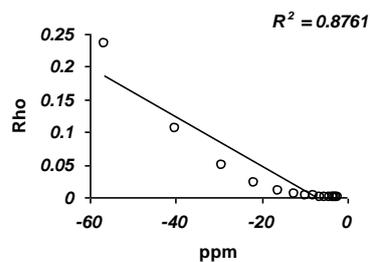
(a-1)



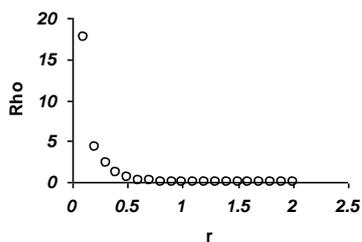
(b-1)



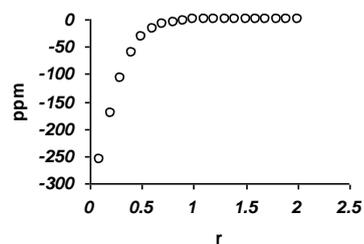
(a-2)



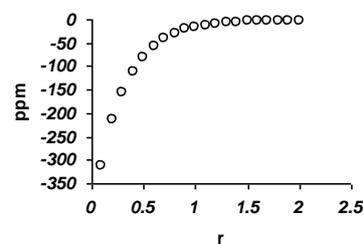
(b-2)



(c)

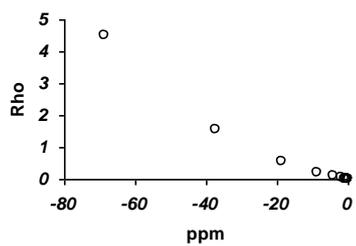


(d)

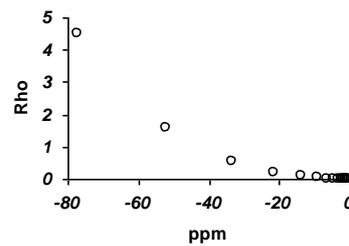


(e)

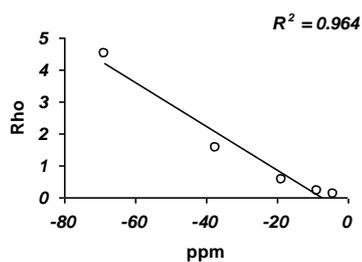
Sodium Cation
Figure S-2-4



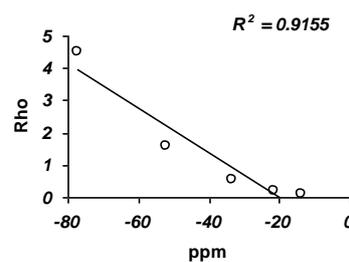
(a)



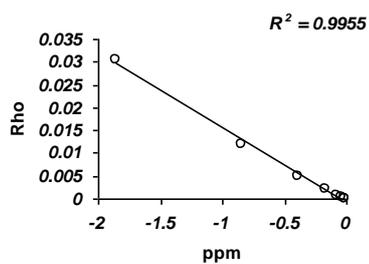
(b)



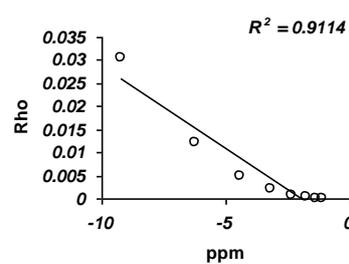
(a-1)



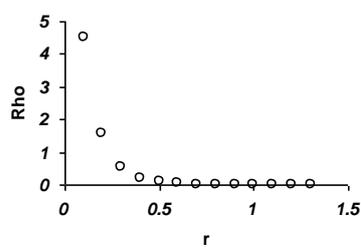
(b-1)



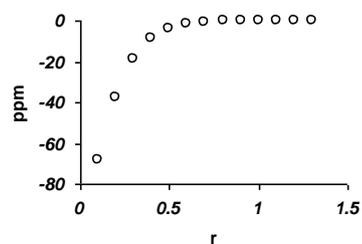
(a-2)



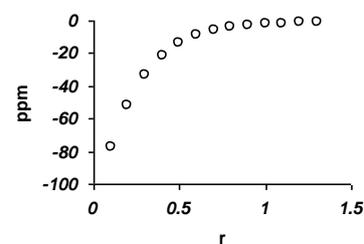
(b-2)



(c)



(d)



(e)

Lithium Cation
Figure S-2-5

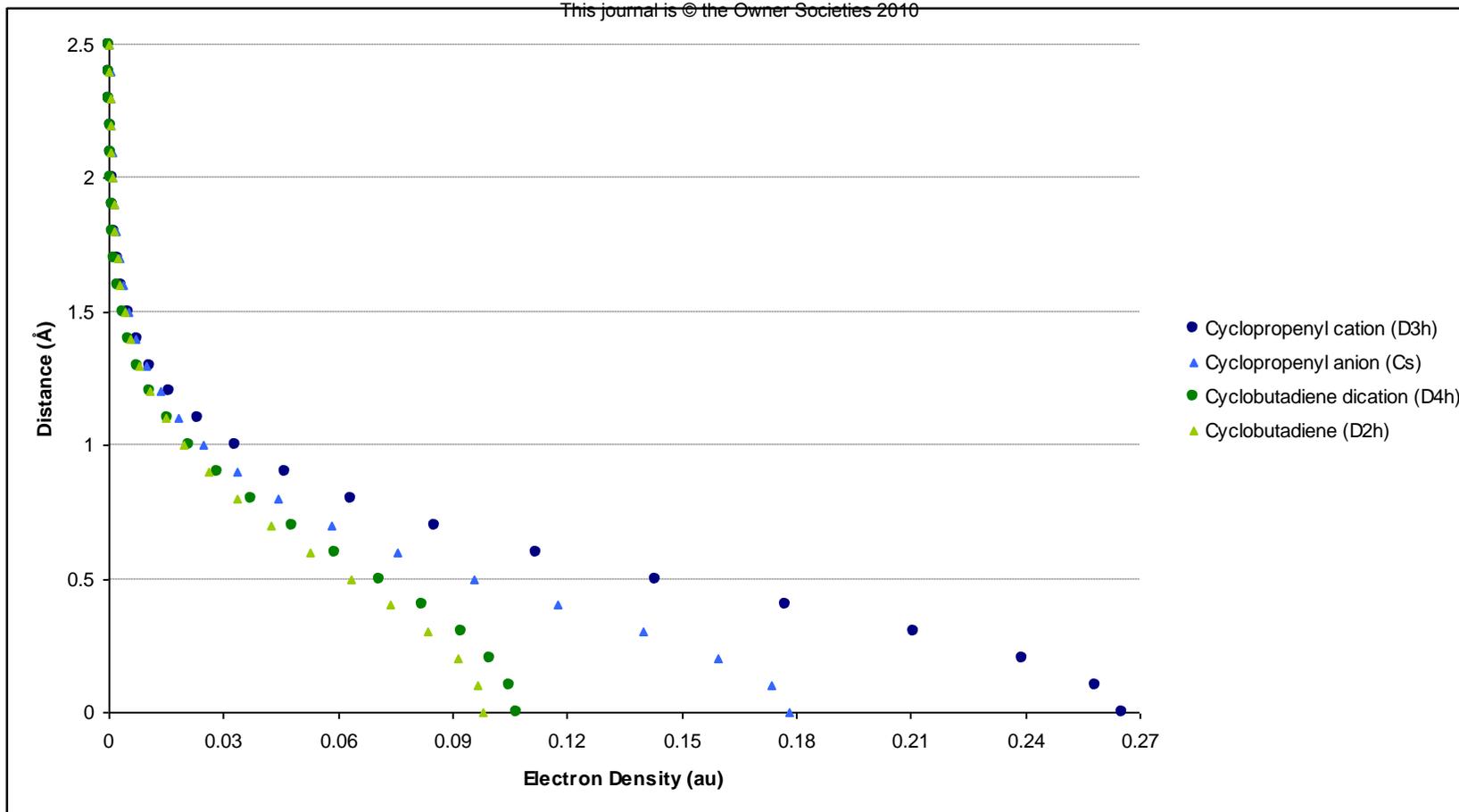


Figure S-3-1

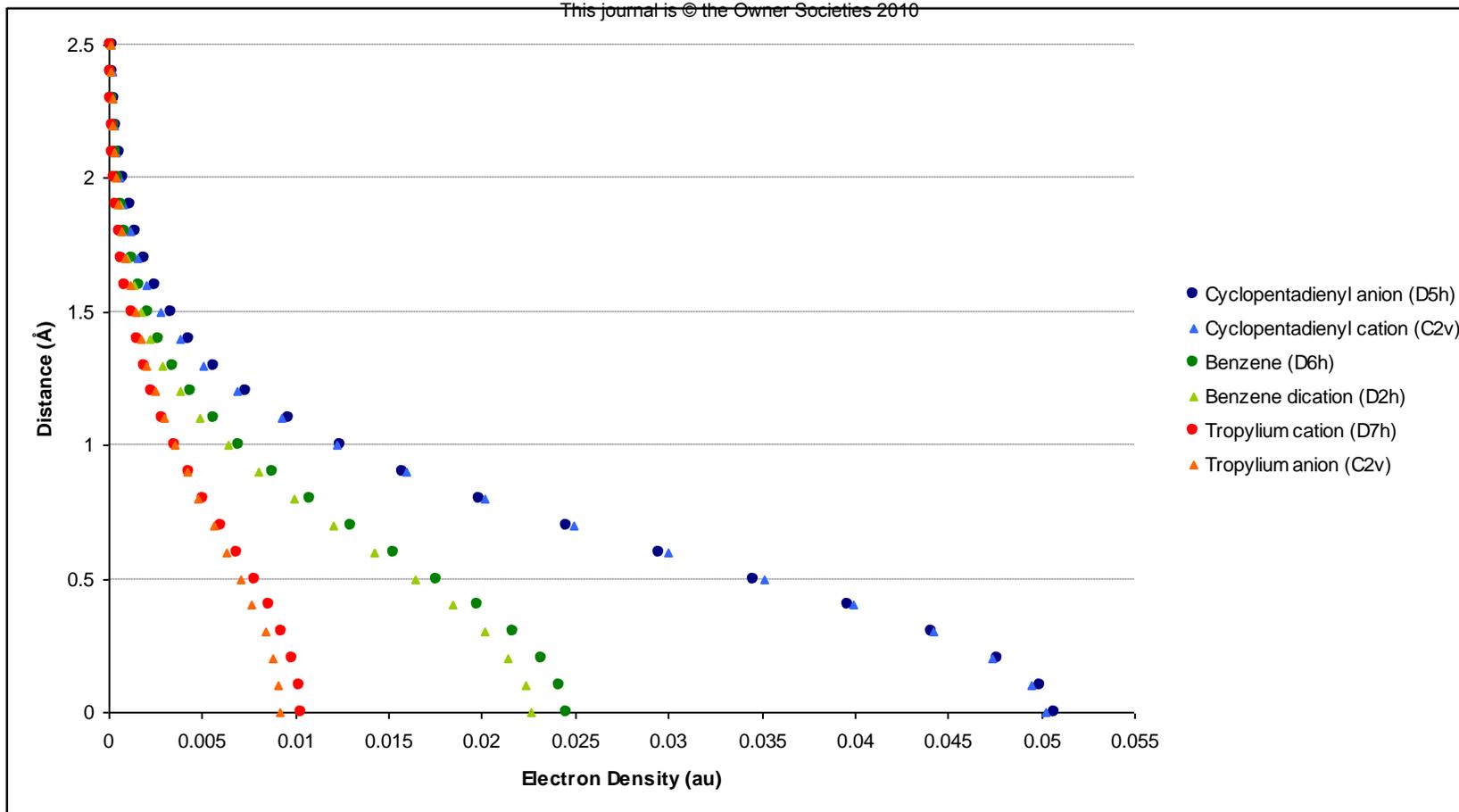


Figure S-3-2

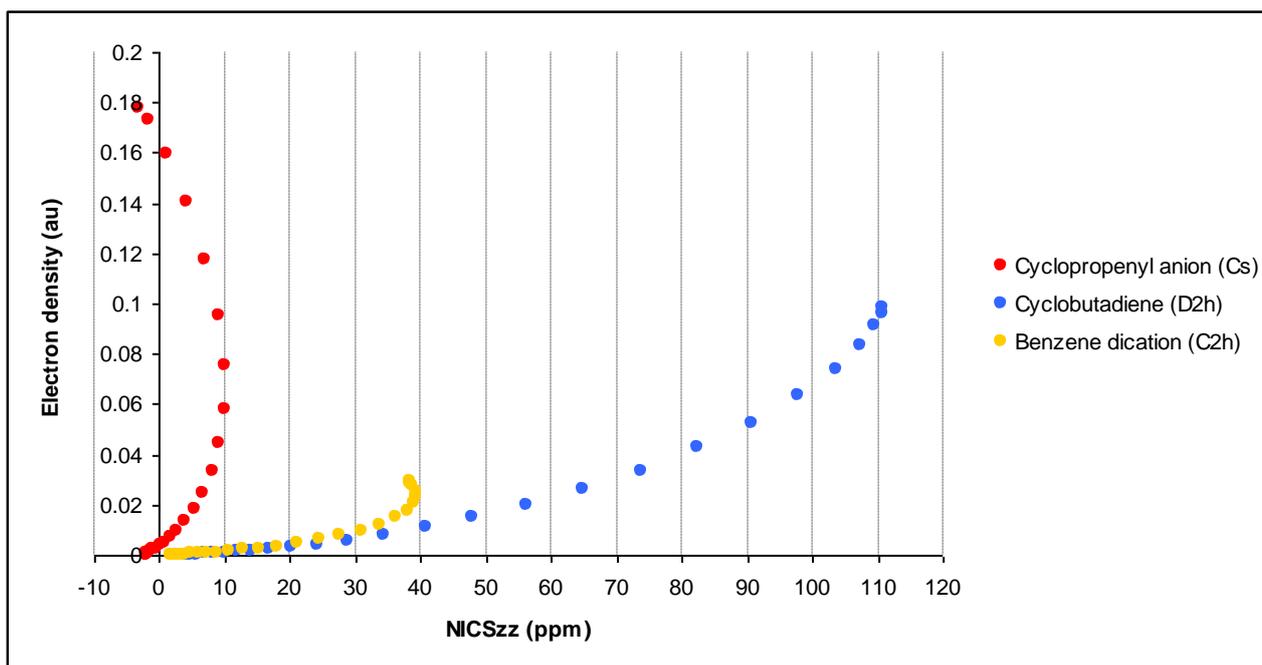


Figure S-4

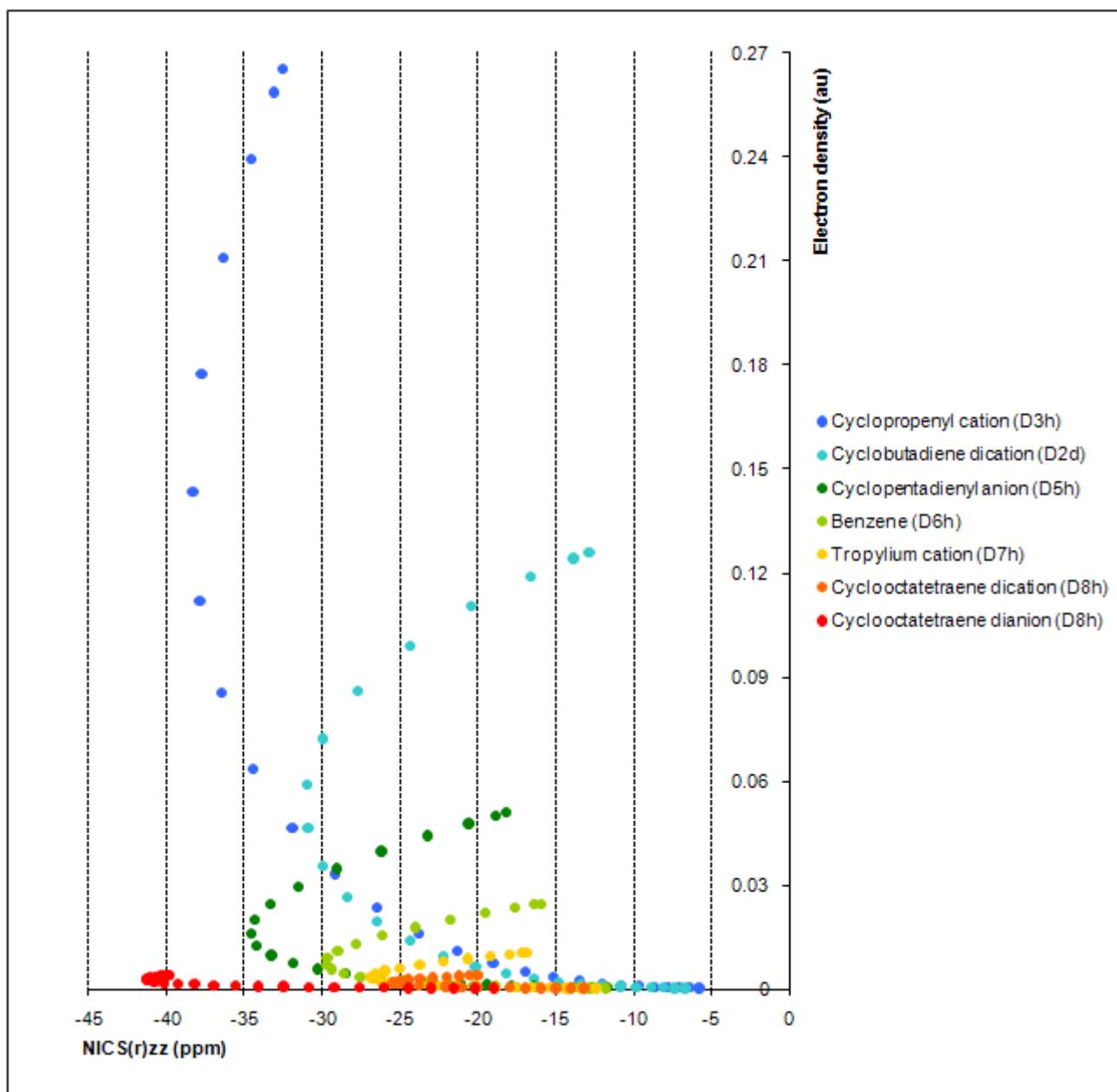


Figure S-5-1

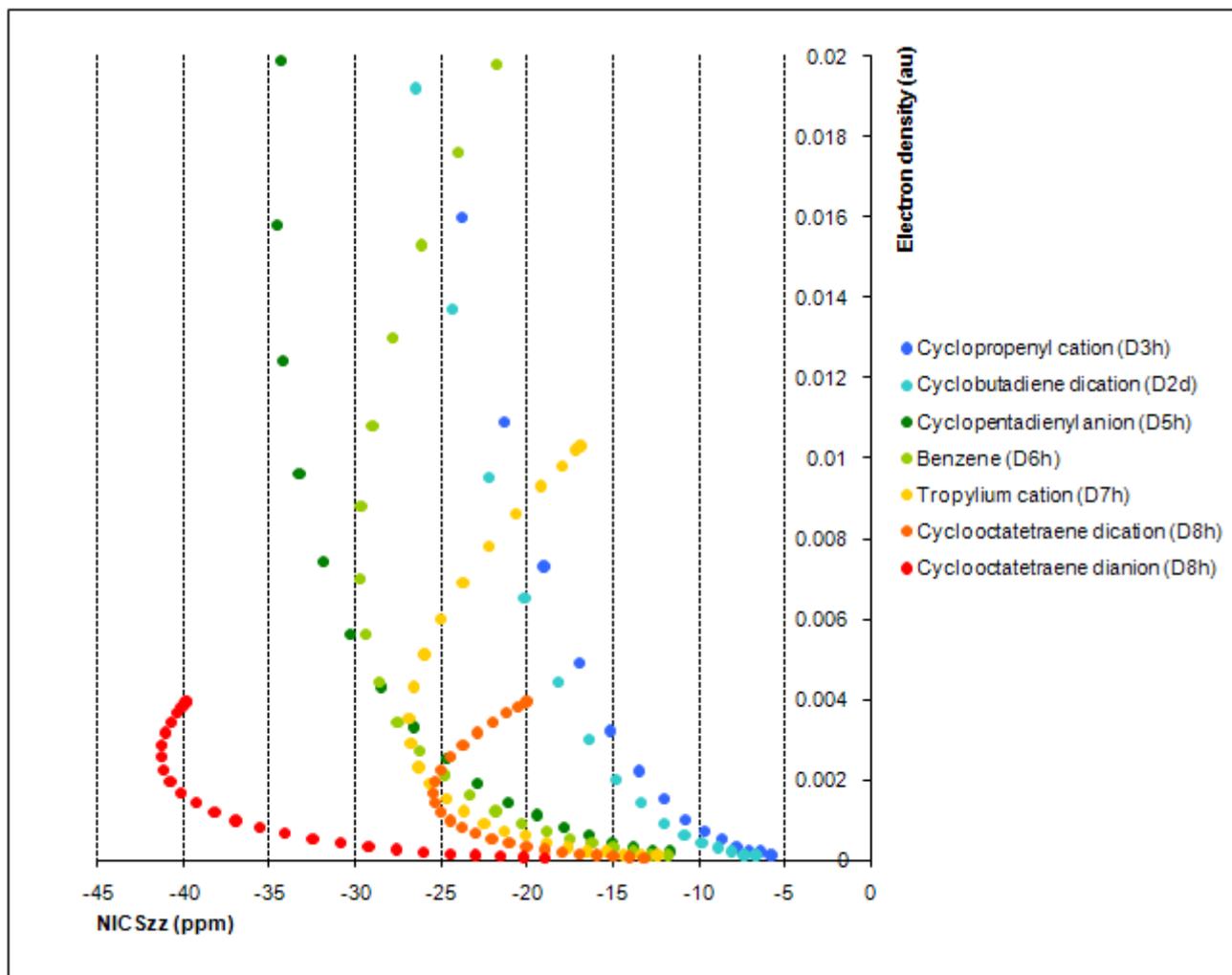


Figure S-5-2

The positive isotropic NICS value of cyclopropenyl anion, a text book example of antiaromatic species, provoked some controversies and criticisms about NICS.³⁶ As Lazzarotti describes⁹ 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.

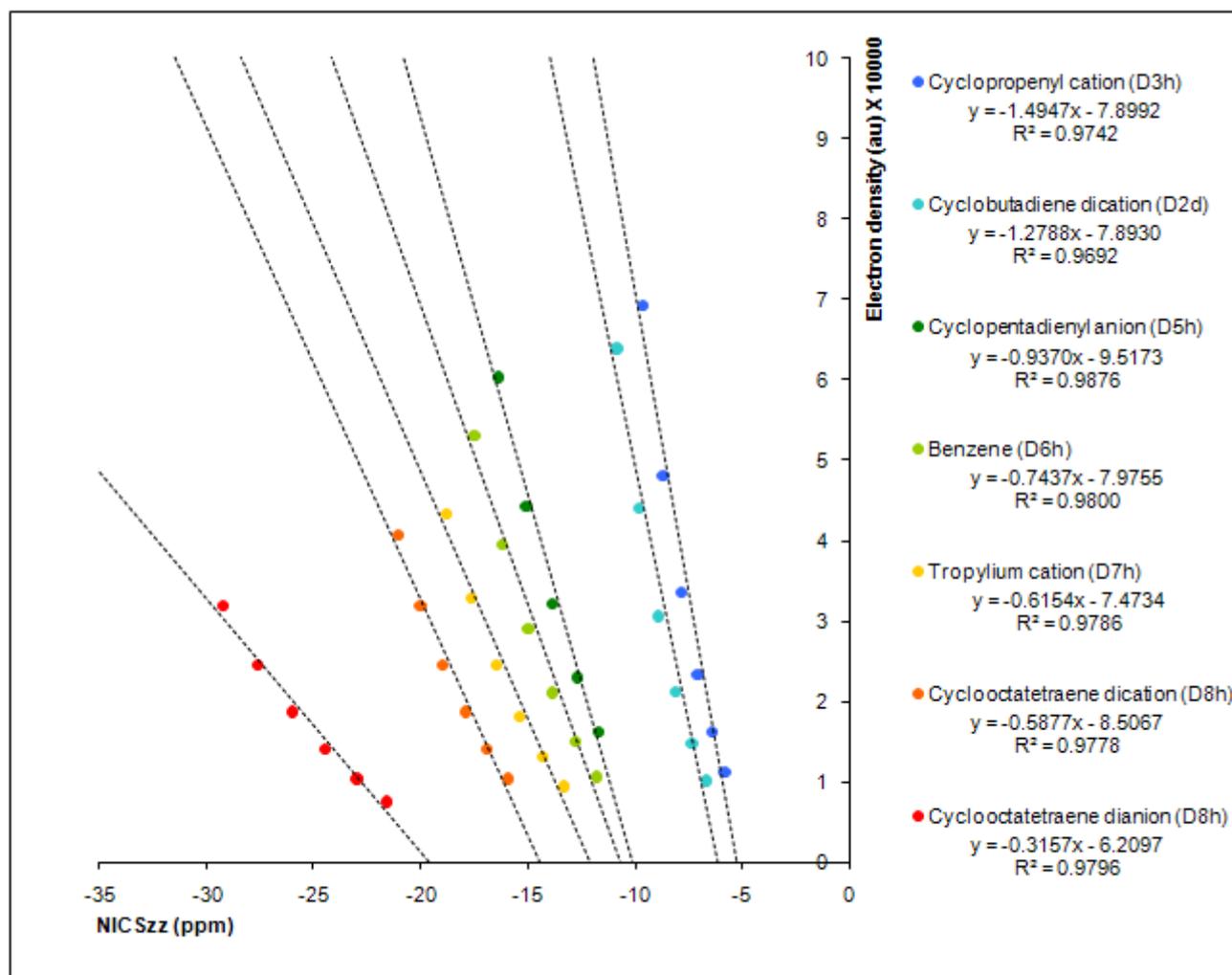


Figure S-6

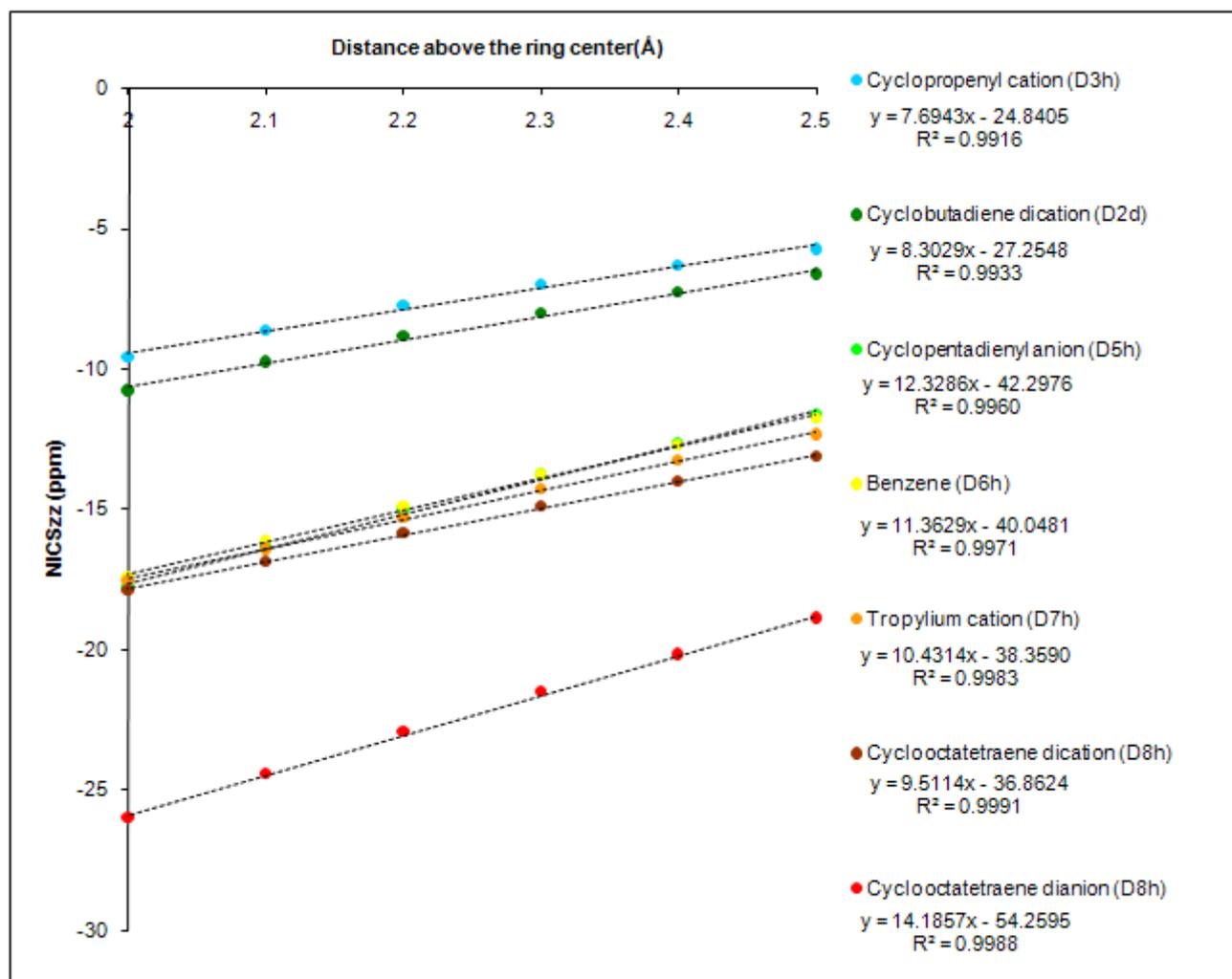


Figure S-7