

SUPPORTING INFORMATION

Which NICS Aromaticity Index for Planar π Rings is Best?

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Table S1. NICS aromaticity indexes (in ppm) at the ring centers and 1 Å above for (C₄H₄X) five membered monoheterocycles at the PW91/IGLO-III//B3LYP/6-311+G** level.¹

X	NICS (0) _{iso}	NICS (0) _π	NICS (0) _{πzz}	NICS (1) _{iso}	NICS (1) _π	NICS (1) _{πzz}	ASE ²
BeH ⁻	6.5	-5.4	11.2	1.9	2.8	12.5	-8.39
BH	18.2	2.6	40.2	9.6	11.6	37.6	-24.01
AlH	5.7	-4.8	13.6	2.2	3.4	15.1	-10.83
GaH	6.0	-3.8	16.0	2.4	4.0	15.9	-10.84
BH ₂ ⁻	-2.3	-14.0	-11.0	-4.7	-1.7	-8.4	0.29
AlH ₂ ⁻	0.8	-8.6	0.2	-1.7	-0.4	-0.1	-1.65
GaH ₂ ⁻	-0.8	-9.2	-0.8	-2.6	-0.8	-1.2	-0.77
Al ⁻	5.3	-4.8	11.4	0.5	2.8	12.7	-7.04
CH ⁻	-14.0	-22.8	-36.0	-11.5	-7.2	-29.4	20.45
CH ₂	-4.1	-15.8	-13.6	-5.6	-3.3	-10.0	0.0
SiH ₂	-0.7	-9.8	-0.4	-2.7	-0.5	1.0	-4.75
GeH ₂	-1.4	-8.4	1.0	-2.9	-0.2	-0.2	-3.28
C(CH ₂) ₂	-3.9	-15.0	-12.8	-5.0	-2.1	-9.6	3.74
C(CH ₃) ₂	-2.6	-13.8	-8.2	-4.6	-2.0	-6.0	0.85
C(SiH ₃) ₂	-7.9	-19.6	-23.0	-9.1	-6.4	-19.7	9.87
C(GeH ₃) ₂	-7.2	-19.2	-22.6	-8.5	-6.0	-18.5	9.25
C(SnH ₃) ₂	-8.5	-20.5	-27.4	-9.6	-7.1	-22.6	13.76
CF ₂	2.2	-6.6	10.2	-0.2	3.0	9.2	-12.40
CCl ₂	-0.2	-8.9	1.6	-2.7	0.6	3.4	-5.13
C=CH ₂	0.2	-12.5	-2.9	-3.0	0.0	0.9	-5.10
C=S	14.2	-5.3	18.6	4.6	6.0	16.8	-16.30
C=Se	16.5	-4.5	21.2	5.8	6.6	19.2	-17.61
SiH ⁺	13.8	2.4	37.9	9.1	11.0	37.4	-28.72
GeH ⁺	13.4	3.0	38.8	8.8	11.0	37.8	-25.22
NH	-14.5	-22.2	-33.2	-11.1	-6.7	-26.2	18.04
NH ₂ ⁺	-5.9	-15.6	-12.4	-5.7	-2.9	-8.8	-2.54
PH ₂ ⁺	-2.1	-10.2	0.1	-3.2	-0.2	2.2	-9.37
AsH ₂ ⁺	-2.5	-9.2	2.0	-3.0	0.0	0.9	-8.16
N ⁻	-14.1	-22.1	-35.7	-11.8	-6.5	-28.5	18.22
P ⁻	-14.8	-20.8	-32.3	-12.3	-7.6	-27.7	18.97
As ⁻	-14.5	-20.2	-30.0	-11.8	-7.8	-25.1	17.29
O	-13.0	-20.5	-28.6	-10.2	-5.4	-21.8	12.26
S	-14.3	-20.7	-28.8	-11.5	-6.9	-23.7	15.62
Se	-13.5	-19.6	-25.6	-10.7	-6.7	-20.3	13.67

¹ NICS indexes were computed using the IGLO method with the Pipek-Mezey localization procedure as implemented in the deMon-Master NMR program (see (a) Malkin, V. G.; Malkin, O. L.; Eriksson, L. A.; Salahub, D. R. *Modern Density Functional Theory*; Seminario, J. M., Politzer, P., Eds.; Elsevier: Amsterdam, 1995; p 273. (b) Malkin, V. G.; Malkin, O. L.; Eriksson, L. A.; Salahub, D. R. *J. Am. Chem. Soc.* **1994**, *116*, 5898) at the PW91/IGLO-III//B3LYP/6-311+G** level.

² ASE values (in kcal/mol) for all heteroaromatics with planar minima have been taken from ref. 10.

Table S2. NICS aromaticity indexes (in ppm) at the ring centers and 1 Å above for five-membered polyheterocycles at the PW91/IGLO-III//B3LYP/6-311+G** level.¹

Compound	NICS (0) _{iso}	NICS (0) _π	NICS (0) _{πzz}	NICS (1) _{iso}	NICS (1) _π	NICS (1) _{πzz}	ASE ²
2-azafuran	-13.6	-20.6	-28.1	-11.2	-5.3	-20.9	14.32
2-azathiophene	-14.6	-20.2	-28.1	-12.1	-6.7	-22.6	16.24
2-azapyrrole	-14.7	-22.4	-34.1	-12.1	-6.4	-26.0	20.46
3-azafuran	-12.7	-19.9	-28.0	-10.5	-4.7	-20.7	9.81
3-azathiophene	-14.2	-20.3	-28.4	-12.2	-6.4	-22.8	14.46
3-azapyrrole	-14.1	-21.9	-32.9	-11.5	-5.9	-25.0	16.18
2,3-diazafuran	-15.3	-20.2	-27.9	-12.3	-4.8	-20.3	14.07
2,3-diazathiophene	-15.3	-20.6	-29.4	-13.8	-6.6	-23.3	15.71
2,3-diazapyrrole	-15.3	-22.6	-35.2	-13.6	-6.2	-26.3	20.21
2,5-diazafuran	-15.3	-21.0	-28.7	-12.9	-5.3	-21.2	15.37
2,5-diazathiophene	-16.2	-20.3	-30.6	-13.6	-6.4	-24.2	17.07
2,5-diazapyrrole	-15.4	-23.4	-35.5	-13.3	-6.2	-26.6	22.21
2,3,4-triazathiophene	-17.4	-20.4	-27.9	-15.0	-6.0	-21.5	10.02
2,3,4-triazapyrrole	-15.8	-22.3	-33.9	-14.1	-5.6	-24.6	14.13
2,3,5-triazathiophene	-17.7	-20.4	-30.6	-15.4	-6.2	-23.7	15.02
2,3,5-triazapyrrole	-16.1	-22.6	-36.0	-14.4	-5.8	-26.2	21.17
2,4-diazafuran	-13.4	-19.0	-26.7	-11.4	-4.3	-19.4	11.42
2,4-diazathiophene	-15.0	-20.1	-28.3	-13.1	-5.8	-22.4	14.57
2-phosphafuran	-13.1	-18.6	-26.0	-10.8	-5.7	-20.9	11.91
2-phosphathione	-14.7	-19.4	-27.4	-12.5	-7.7	-23.3	14.66
2-phosphapyrrole	-14.3	-20.3	-30.3	-11.7	-7.0	-25.0	18.55
3-phosphafuran	-13.4	-19.2	-26.1	-11.5	-6.2	-21.2	10.34
3-phosphathiophene	-14.1	-19.6	-27.4	-12.5	-7.6	-23.7	13.44
3-phosphapyrrole	-14.6	-20.7	-30.5	-12.1	-7.2	-25.2	16.07
2,5-diphosphafuran	-13.0	-16.9	-24.0	-11.3	-5.8	-20.2	11.90
2,5-diphosphathiophene	-14.8	-18.4	-26.4	-13.4	-8.3	-23.1	13.66
2,5-diphosphapyrrole	-14.1	-18.7	-28.1	-12.5	-7.2	-24.2	17.72
3,4-diazathiophene	-15.5	-20.2	-26.9	-13.4	-5.8	-21.2	10.52
3,4-diazapyrrole	-13.9	-21.6	-31.6	-12.1	-5.3	-23.5	12.19
3,4-diphosphafuran	-14.6	-18.4	-25.0	-12.9	-7.1	-21.1	8.34
3,4-diphosphathiophene	-14.8	-19.0	-26.7	-13.8	-8.6	-24.0	12.26
3,4-diphosphapyrrole	-15.6	-19.6	-28.8	-13.3	-8.1	-24.9	14.16
2,3,4-triphosphafuran	-15.8	-17.3	-22.9	-13.8	-7.4	-19.9	9.70
2,3,4-triphosphathiophene	-16.1	-18.1	-25.1	-14.9	-9.2	-22.9	11.49
2,3,4-triphosphapyrrole	-16.5	-18.6	-26.7	-14.3	-8.6	-23.8	14.44
2,3,5-triphosphafuran	-14.7	-16.5	-22.2	-12.9	-6.7	-19.2	11.70
2,3,5-triphosphathiophene	-15.8	-17.9	-24.9	-14.7	-9.0	-22.5	12.03
2,3,5-triphosphapyrrole	-15.3	-18.1	-26.2	-13.8	-8.1	-23.4	15.70
2,3,4,5-tetraphosphafuran	-17.7	-16.6	-21.0	-15.5	-8.1	-18.8	11.37
2,3,4,5-tetraphosphathiophene	-17.2	-17.0	-23.9	-16.5	-10.4	-22.2	10.50
2,3,4,5-tetraphosphapyrrole	-17.8	-18.1	-24.8	-16.0	-9.5	-22.7	14.02

¹ NICS indexes were computed using the IGLO method with the Pipek-Mezey localization procedure as implemented in the deMon-Master NMR program at the PW91/IGLO-III//B3LYP/6-311+G** level.

² ASE values (in kcal/mol) for all heteroaromatics with planar minima have been taken from ref. 10.

Table S3. NICS aromaticity indexes (in ppm) at the ring centers and 1 Å above for (C₄H₄X) five membered monoheterocycles at the PW91/IGLO-III//B3LYP/6-311+G** level.

X	NICS (0) _{4 πzz}	NICS (1) _{4 πzz}	NICS (0) _{zz}	NICS (1) _{zz}	ASE
BeH ⁻	11.2	12.5	24.7	9.7	-8.39
BH	40.2	37.6	58.7	33.9	-24.01
AlH	13.6	15.1	26.4	12.1	-10.83
GaH	16.0	15.9	32.3	12.8	-10.84
BH ₂ ⁻	-6.6	-4.4	6.2	-12.0	0.29
AlH ₂ ⁻	1.4	0.6	13.3	-1.3	-1.65
GaH ₂ ⁻	0.2	-0.8	14.9	0.0	-0.77
Al ⁻	11.4	12.7	21.8	8.9	-7.04
CH ⁻	-24.0	-19.6	-18.3	-34.4	20.45
CH ₂	-8.6	-7.8	7.4	-2.3	0.0
SiH ₂	1.2	2.2	15.0	-2.5	-4.75
GeH ₂	1.0	-0.2	17.8	0.7	-3.28
C(CH ₂) ₂	-9.0	-5.8	7.3	-13.6	3.74
C(CH ₃) ₂	-5.6	-3.2	12.1	-9.4	0.85
C(SiH ₃) ₂	-16.8	-13.4	-3.1	-23.2	9.87
C(GeH ₃) ₂	-15.0	-11.8	-1.7	-21.4	9.25
C(SnH ₃) ₂	-18.0	-14.8	-7.8	-25.6	13.76
CF ₂	8.2	8.5	25.6	5.2	-12.4
CCl ₂	1.8	2.6	19.0	-1.8	-5.13
C=CH ₂	1.4	2.8	17.3	-5.2	-5.10
C=S	21.6	19.8	37.7	14.1	-16.30
C=Se	24.6	22.3	41.3	16.5	-17.61
SiH ⁺	37.9	37.4	51.2	33.4	-28.72
GeH ⁺	38.8	37.8	55.1	33.0	-25.22
NH	-22.8	-18.2	-14.9	-32.0	18.04
NH ₂ ⁺	-8.2	-5.2	7.4	-13.6	-2.54
PH ₂ ⁺	1.7	4.4	16.6	-3.4	-9.37
AsH ₂ ⁺	2.4	0.6	19.9	1.7	-8.16
N ⁻	-23.4	-19.0	-20.5	-35.2	18.22
P ⁻	-22.2	-18.2	-18.6	-33.6	18.97
As ⁻	-20.2	-15.6	-14.1	-31.8	17.29
O	-20.0	-15.5	-12.1	-28.6	12.26
S	-20.0	-15.8	-13.0	-30.4	15.62
Se	-17.4	-12.4	-7.5	-27.8	13.67

Table S4. NICS aromaticity indexes (in ppm) at the ring centers and 1 Å above for five-membered poly- heterocycles at the PW91/IGLO-III//B3LYP/6-311+G** level.

Compound	NICS (0) _{4πzz}	NICS (1) _{4πzz}	NICS (0) _{zz}	NICS (1) _{zz}	ASE
2-azafuran	-19.4	-14.6	-15.9	-30.0	14.32
2-azathiophene	-19.2	-14.8	-16.9	-31.5	16.24
2-azapyrrole	-22.4	-17.3	-18.2	-33.8	20.46
3-azafuran	-19.8	-14.7	-14.3	-29.4	9.81
3-azathiophene	-20.0	-15.3	-16.5	-31.7	14.46
3-azapyrrole	-23.0	-17.5	-16.9	-32.8	16.18
2,3-diazafuran	-19.6	-14.3	-24.0	-32.4	14.07
2,3-diazathiophene	-20.4	-15.5	-23.7	-35.3	15.71
2,3-diazapyrrole	-24.2	-18.1	-23.4	-36.7	20.21
2,5-diazafuran	-19.2	-14.4	-24.1	-33.4	15.37
2,5-diazathiophene	-20.3	-15.6	-26.9	-36.3	17.07
2,5-diazapyrrole	-23.0	-17.6	-24.1	-36.7	22.21
2,3,4-triazathiophene	-19.2	-14.1	-30.8	-37.5	10.02
2,3,4-triazapyrrole	-23.4	-16.9	-27.2	-37.9	14.13
2,3,5-triazathiophene	-20.9	-15.7	-35.7	-39.9	15.02
2,3,5-triazapyrrole	-24.4	-18.0	-29.9	-39.1	21.17
2,4-diazafuran	-18.7	-13.6	-18.2	-30.4	11.42
2,4-diazathiophene	-19.6	-14.9	-22.9	-34.2	14.57
2-phosphafuran	-19.0	-15.4	-15.1	-28.5	11.91
2-phosphathiophene	-19.6	-16.0	-15.8	-31.1	14.66
2-phosphapyrrole	-21.7	-18.0	-16.7	-31.6	18.55
3-phosphafuran	-19.7	-15.0	-14.1	-29.1	10.34
3-phosphathiophene	-18.3	-15.7	-15.5	-30.9	13.44
3-phosphapyrrole	-20.1	-17.2	-16.1	-32.0	16.07
2,5-diphosphafuran	-17.9	-15.1	-19.2	-29.0	11.90
2,5-diphosphathiophene	-19.2	-16.2	-19.3	-32.1	13.66
2,5-diphosphapyrrole	-20.6	-17.8	-19.7	-32.0	17.72
3,4-diazathiophene	-18.8	-14.0	-21.9	-33.4	10.52
3,4-diazapyrrole	-22.2	-16.4	-18.7	-33.5	12.19
3,4-diphosphafuran	-16.6	-14.8	-17.5	-30.9	8.34
3,4-diphosphathiophene	-17.4	-15.8	-19.4	-32.6	12.26
3,4-diphosphapyrrole	-18.4	-16.8	-18.7	-33.1	14.16
2,3,4-triphosphafuran	-16.1	-14.6	-22.7	-31.8	9.70
2,3,4-triphosphathiophene	-17.0	-15.6	-22.9	-33.7	11.49
2,3,4-triphosphapyrrole	-18.1	-16.8	-22.5	-33.9	14.44
2,3,5-triphosphafuran	-16.2	-14.3	-23.7	-30.8	11.70
2,3,5-triphosphathiophene	-17.6	-15.6	-23.4	-33.6	12.03
2,3,5-triphosphapyrrole	-18.7	-17.0	-23.2	-33.3	15.70
2,3,4,5-tetraphosphafuran	-15.2	-14.0	-29.6	-34.1	11.37
2,3,4,5-tetraphosphathiophene	-16.6	-15.4	-26.0	-34.6	10.50
2,3,4,5-tetraphosphapyrrole	-17.4	-16.4	-27.6	-35.5	14.02

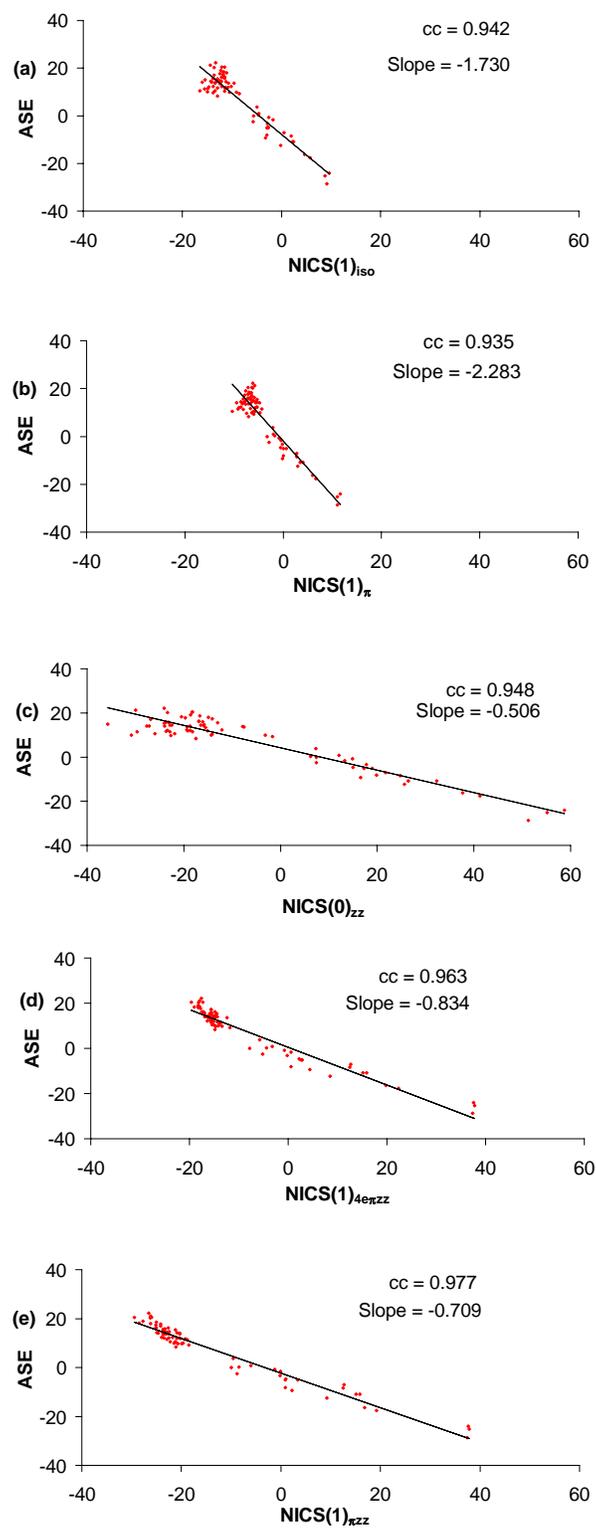


Figure S2. Comparison plots of ASE versus five NICS indexes, at the distance where each performs best statistically: 1 Å above for $\text{NICS}(1)_{\text{iso}}$, $\text{NICS}(1)_{\pi}$, $\text{NICS}(0)_{4e\pi zz}$, and $\text{NICS}(1)_{\pi zz}$, but at the ring center for $\text{NICS}(0)_{zz}$.

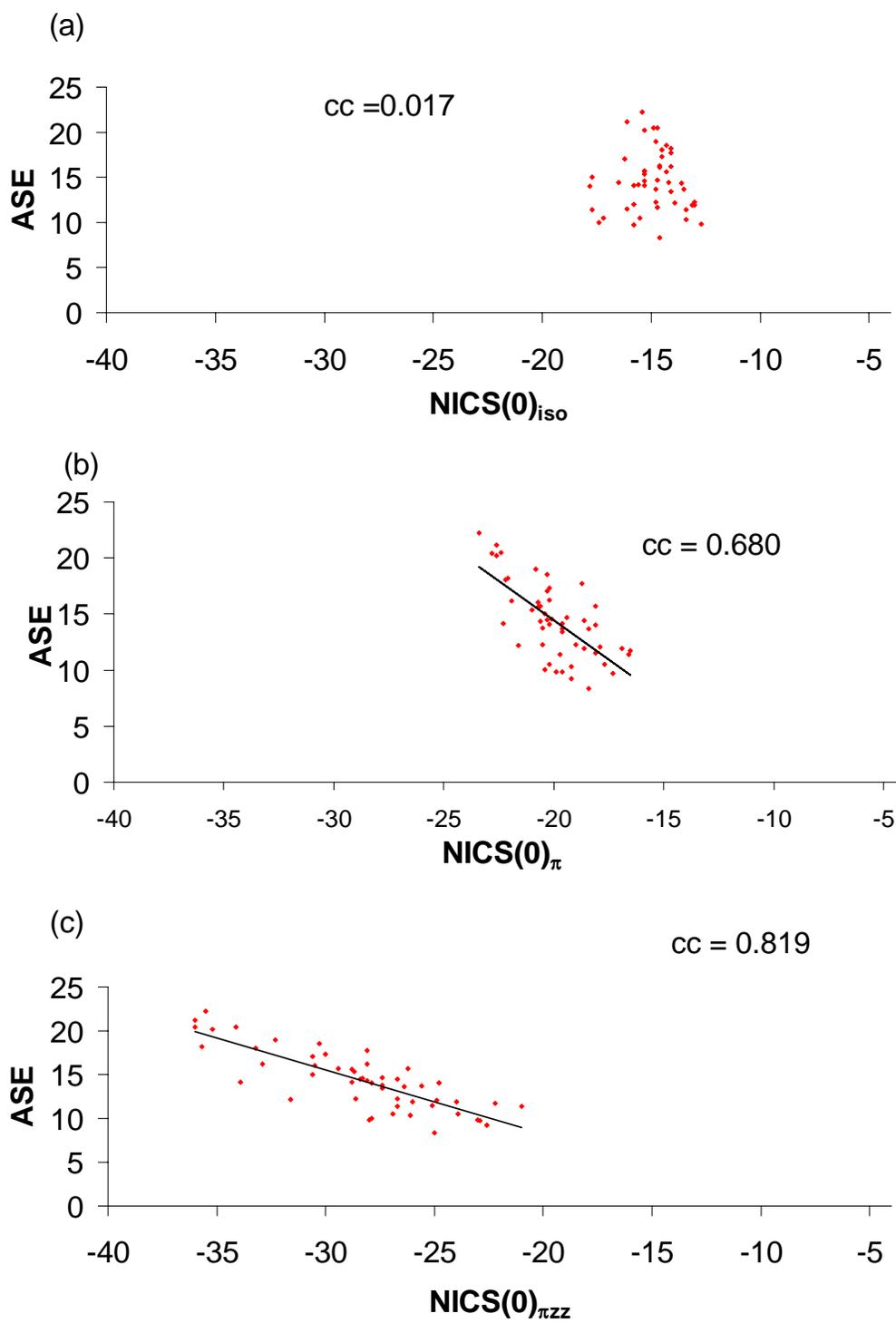


Figure S3. Comparison plots of $\text{NICS}(0)_{\text{iso}}$, $\text{NICS}(0)_{\pi}$ and $\text{NICS}(0)_{\pi\text{zz}}$ versus ASE for the same subset of the most aromatic five-membered rings.

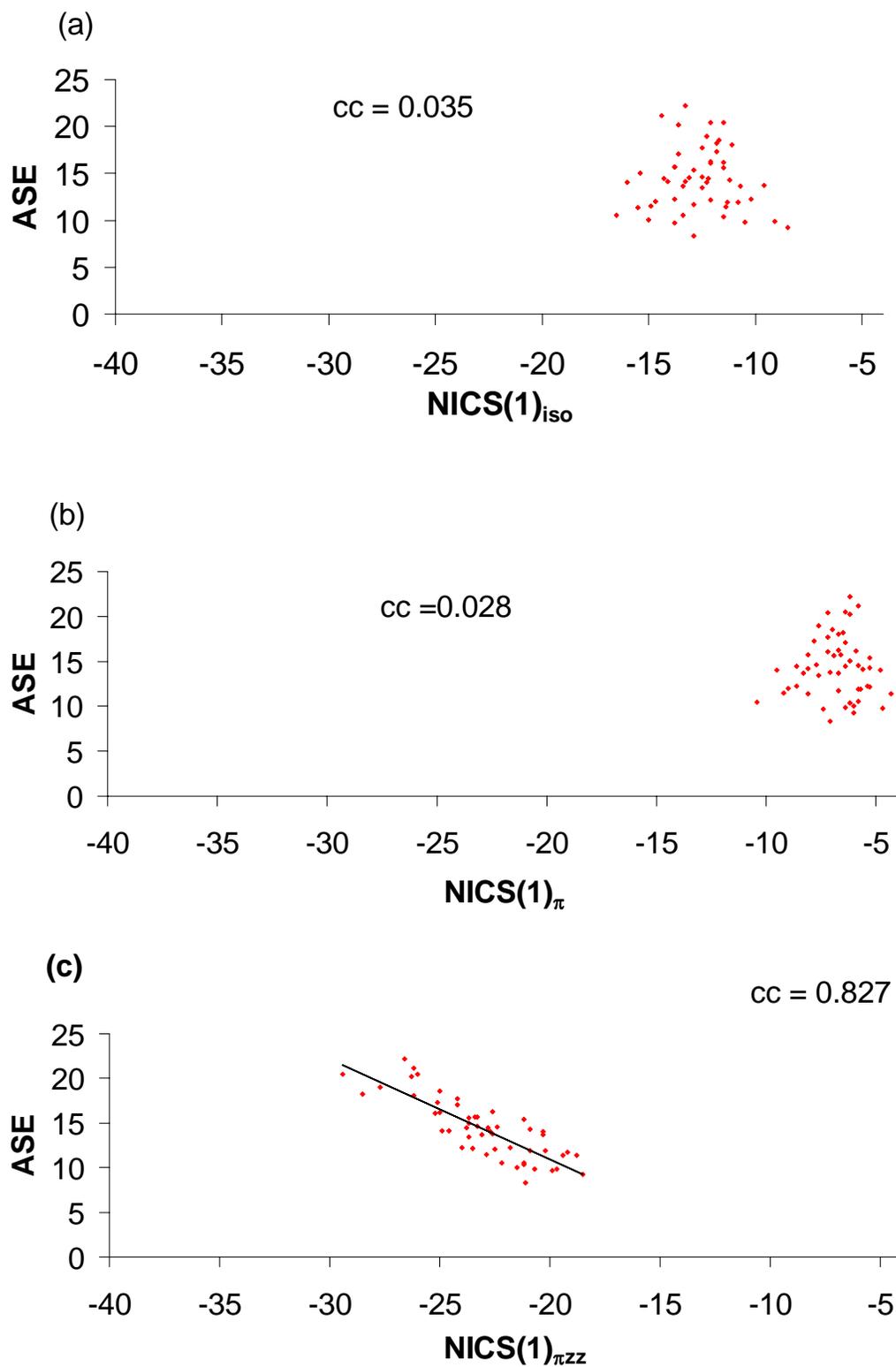


Figure S4. Comparison plots of $\text{NICS}(1)_{\text{iso}}$, $\text{NICS}(1)_{\pi}$ and $\text{NICS}(1)_{\pi\text{zz}}$ versus ASE for the same subset of the most aromatic five-membered rings .

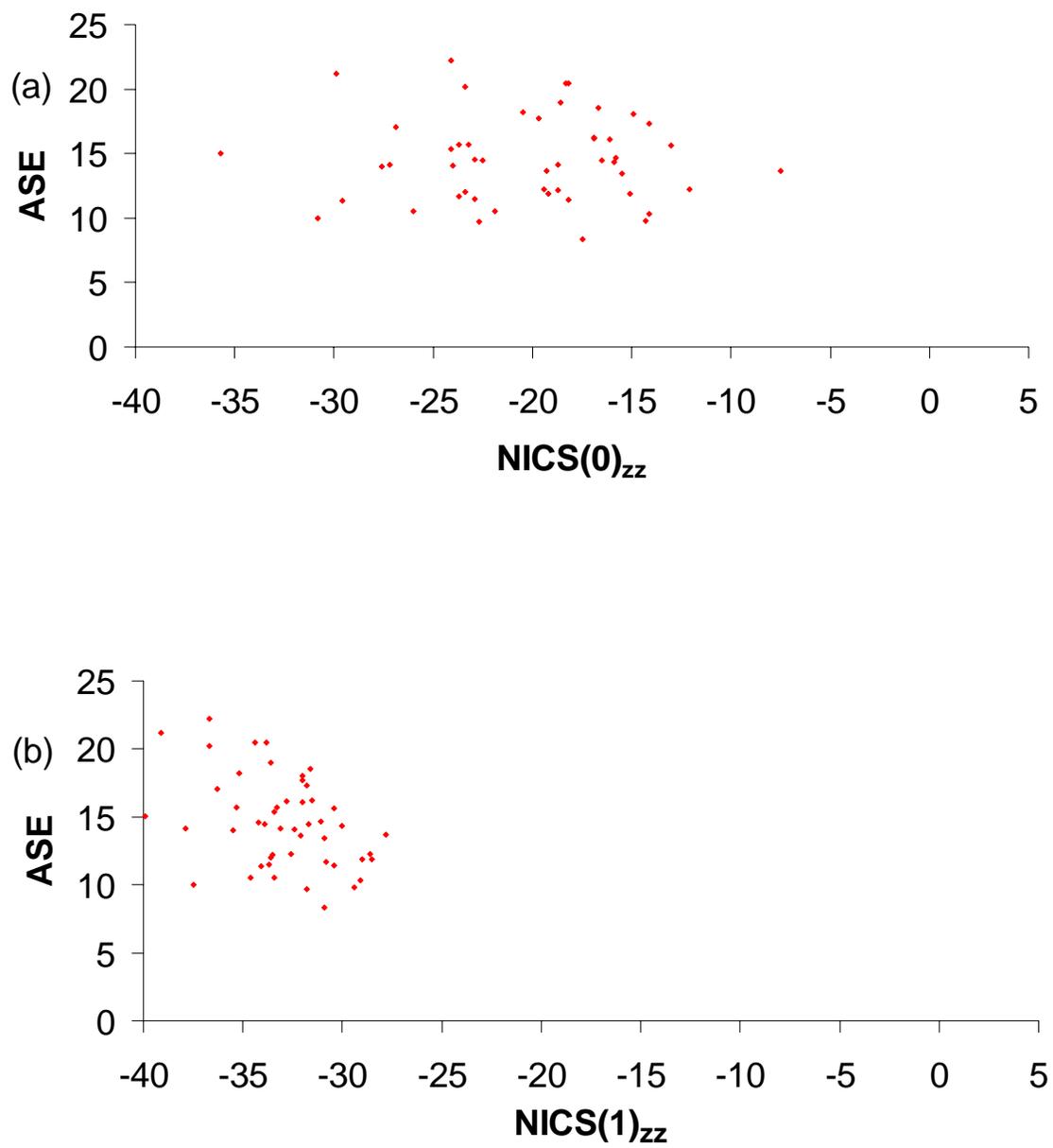


Figure S5. Comparison plots of $\text{NICS}(0)_{zz}$ and $\text{NICS}(1)_{zz}$ versus ASE for the same subset of the most aromatic five-membered rings .

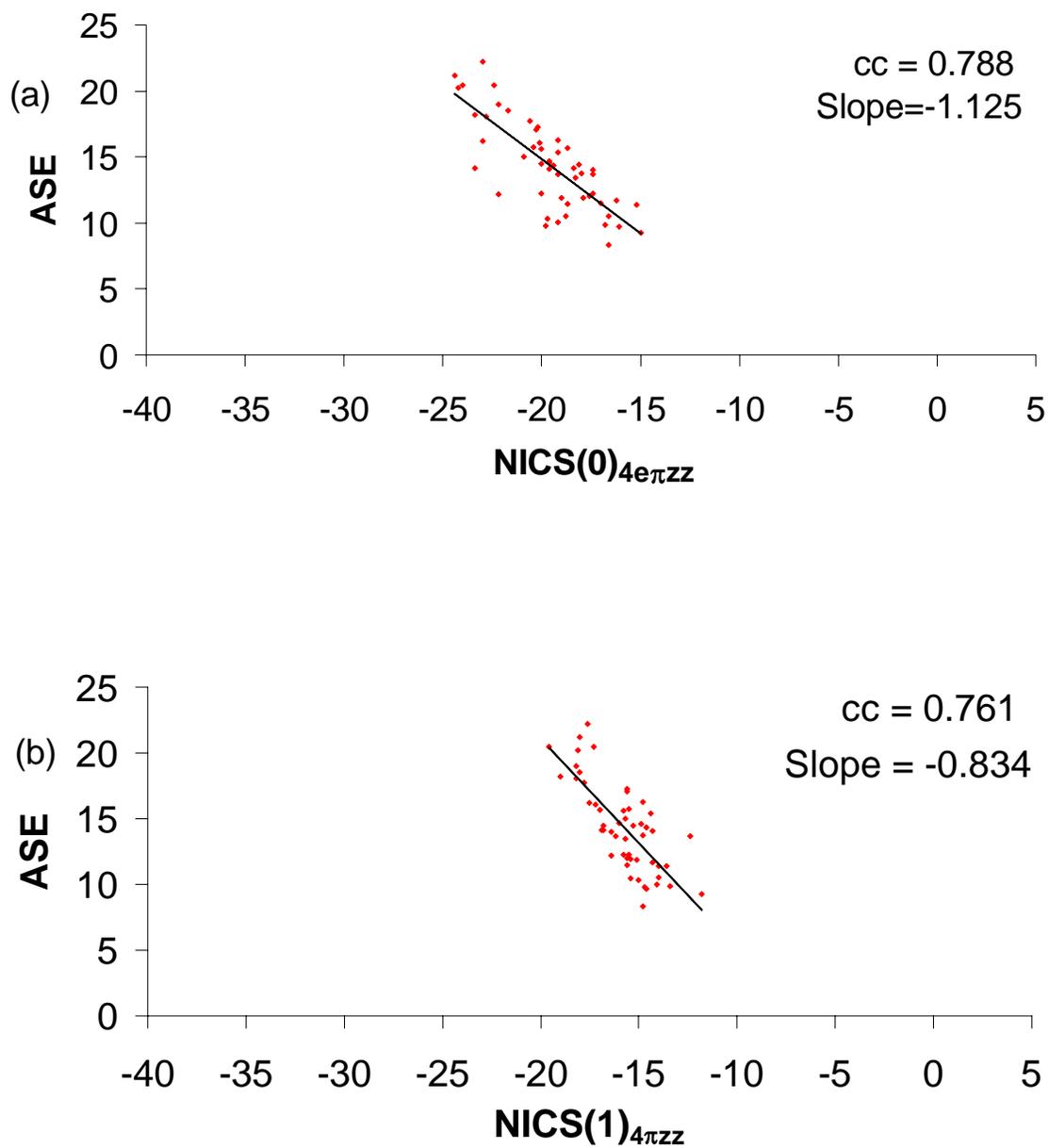


Figure S6. Comparison plots of $\text{NICS}(0)_{4e\pi zz}$ and $\text{NICS}(1)_{4\pi zz}$ versus ASE for the same subset of the most aromatic five-membered rings.

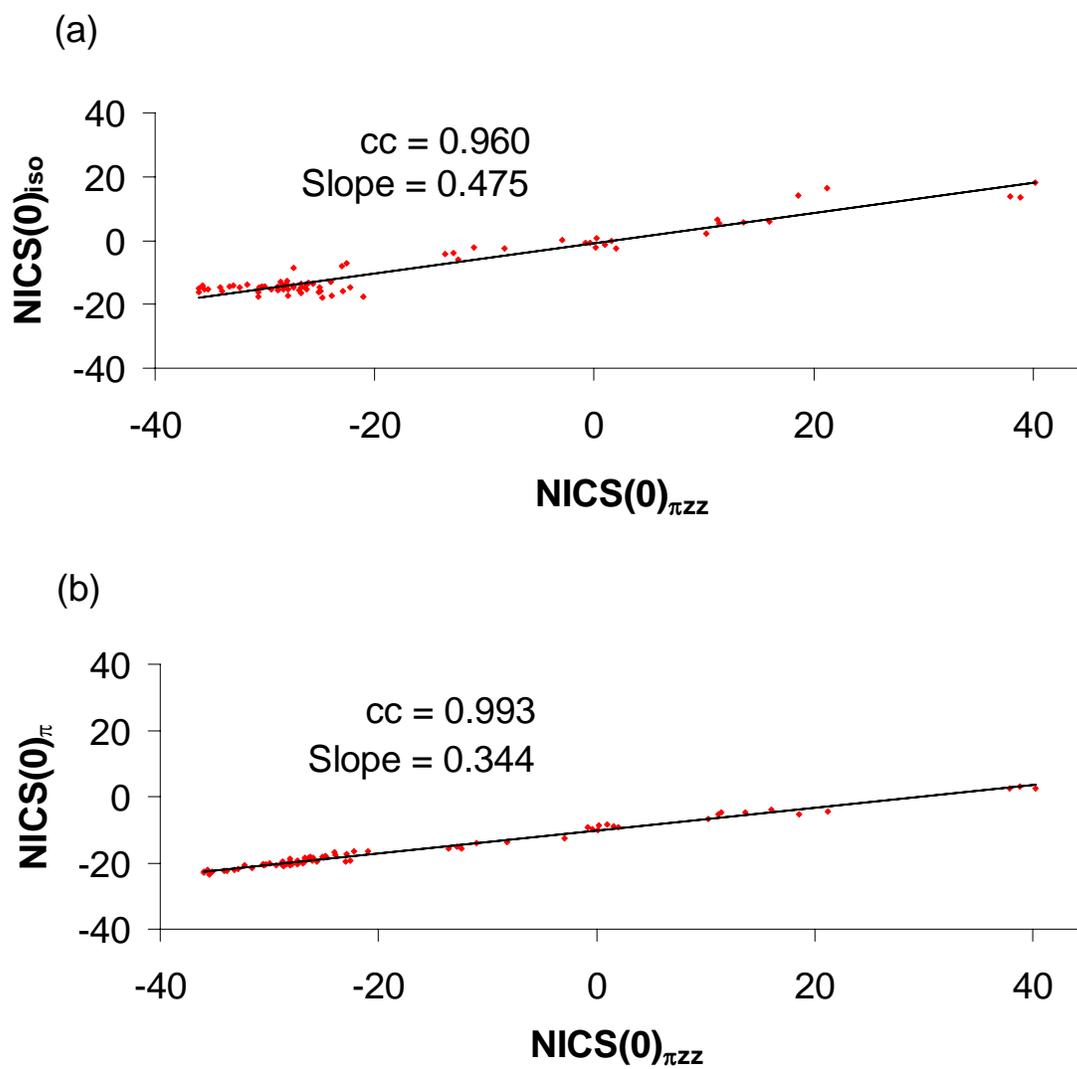


Figure S7. Comparison plots of $\text{NICS}(0)_{\text{iso}}$ and $\text{NICS}(0)_{\pi}$ versus $\text{NICS}(0)_{\pi\text{ZZ}}$ for the entire series of five-membered rings.

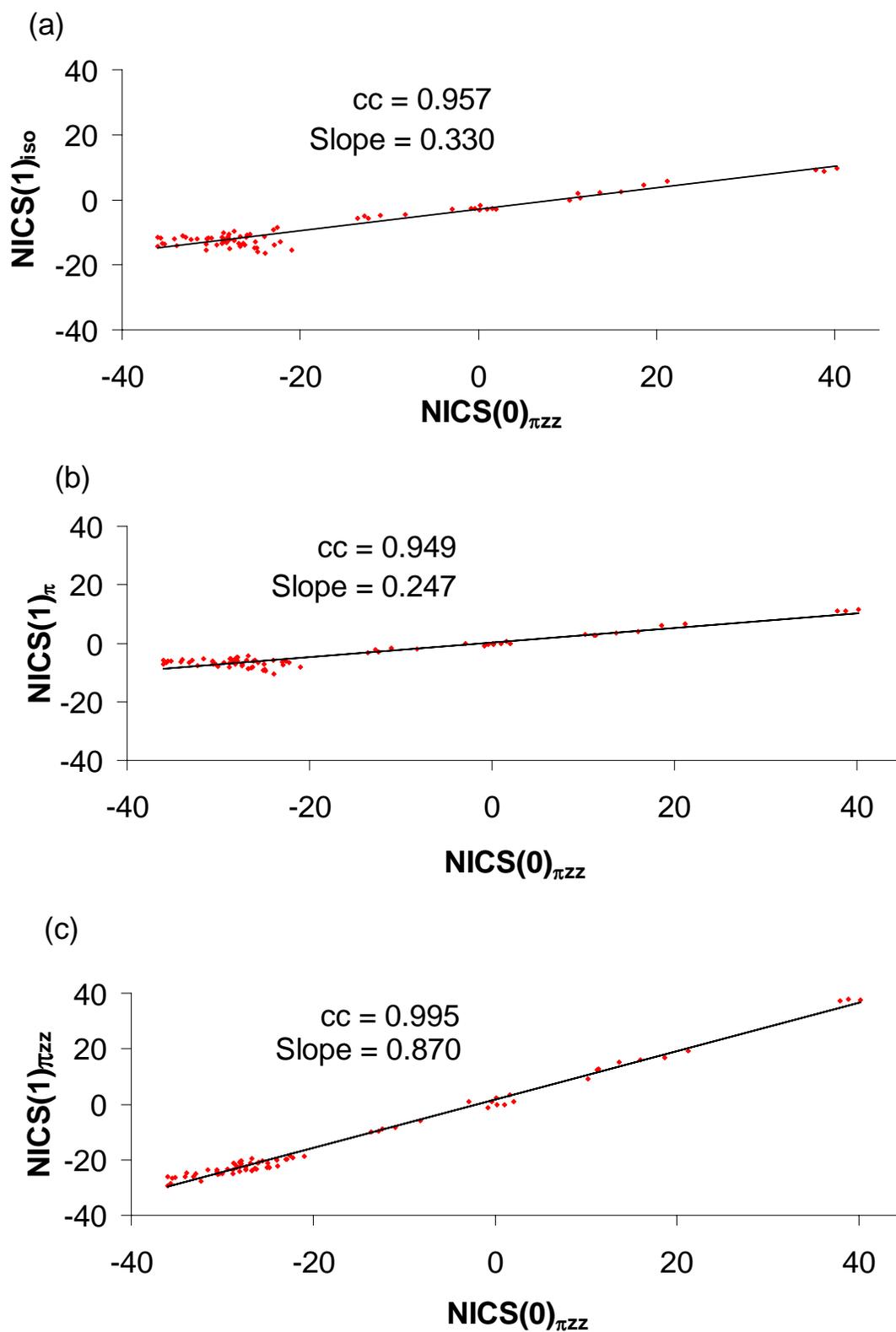


Figure S8. Comparison plots of $\text{NICS}(1)_{\text{iso}}$, $\text{NICS}(1)_{\pi}$ and $\text{NICS}(1)_{\pi\text{ZZ}}$ versus $\text{NICS}(0)_{\pi\text{ZZ}}$ for the entire series of five-membered rings.

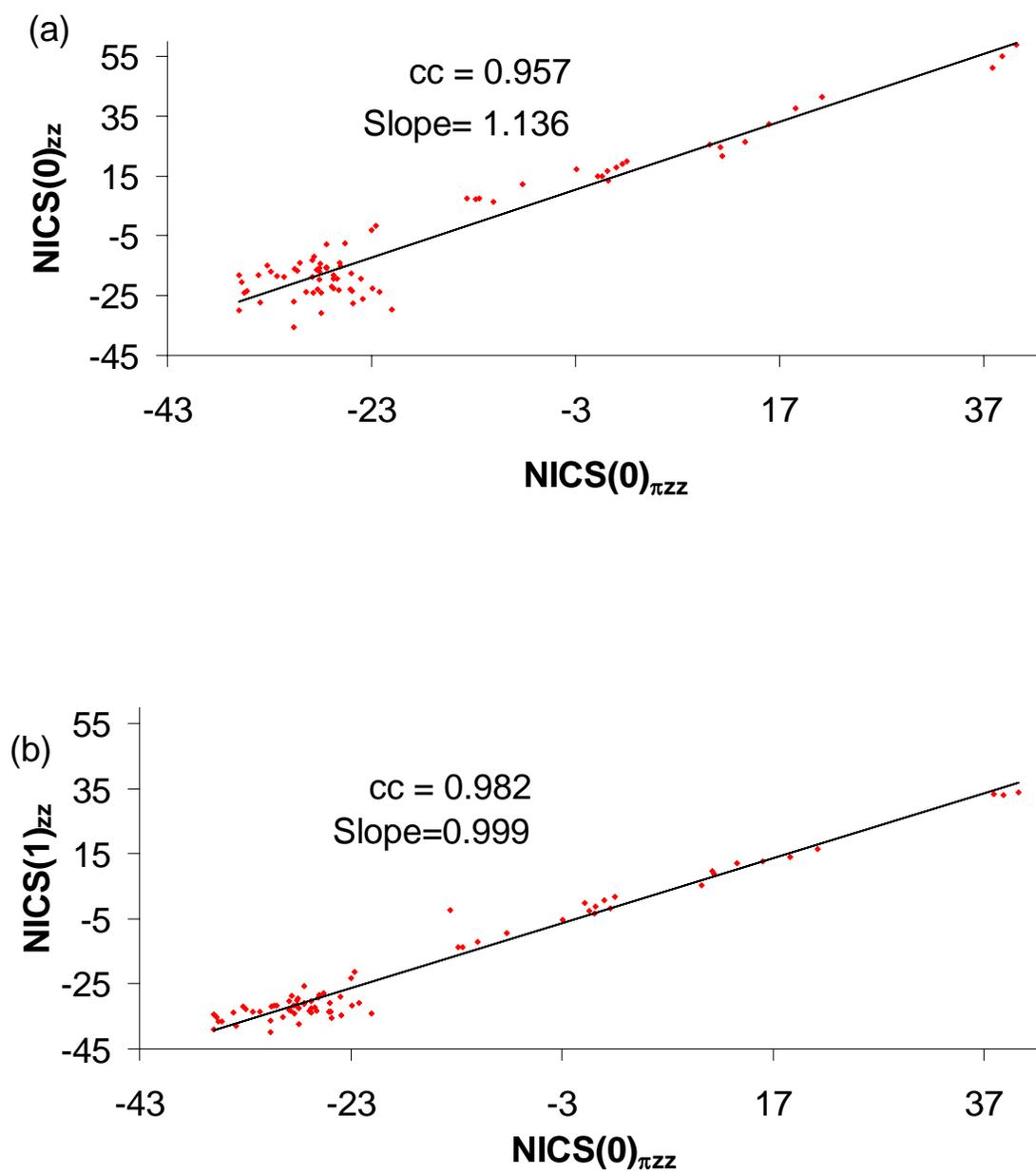


Figure S9. Comparison plots of $\text{NICS}(0)_{zz}$ and $\text{NICS}(1)_{zz}$ versus $\text{NICS}(0)_{\pi zz}$ for the entire series of five-membered rings.

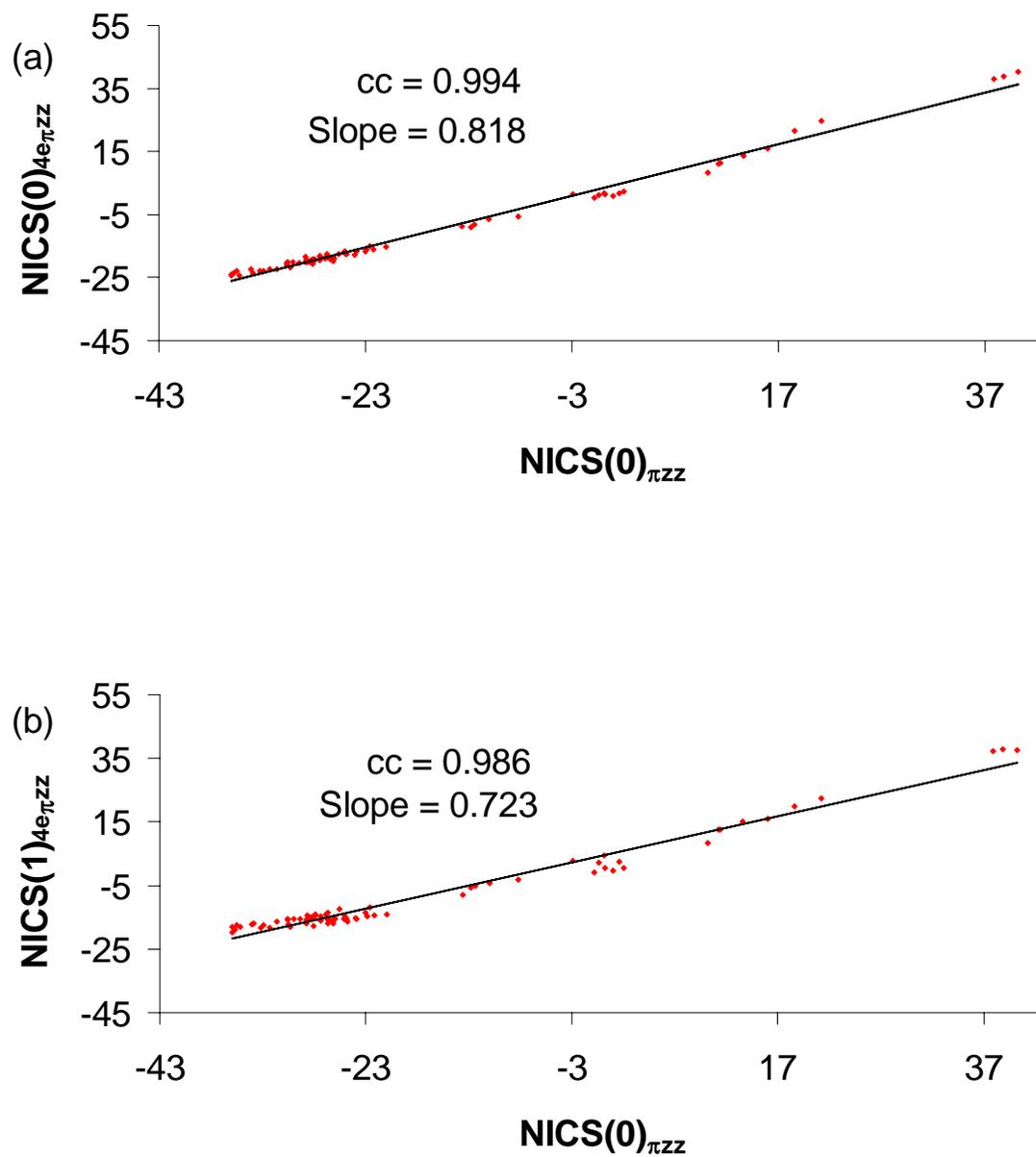


Figure S10. Comparison plots of $\text{NICS}(0)_{4e\pi zz}$ and $\text{NICS}(1)_{4e\pi zz}$ versus $\text{NICS}(0)_{\pi zz}$ for the entire series of five-membered rings .

Glossary of Pertinent NICS and Related Terminology

LMO-NICS	Dissection of total NICS into localized MO contributions
CMO-NICS	Dissection of total NICS into canonical MO contributions
Scalar quantities	Tensors of rank zero. Non-directional quantities, e.g. energies, specified by a single number unrelated to any axis of reference.
Vector quantities	Tensors of rank one. Directional quantities specified by three components (e.g., x, y, and z) each associated with an axis of reference. Dipole moments are an example.
Magnetic shielding tensors	Tensors of rank two. Directional quantities specified by nine components (e.g., xx, xy, xz, yx, yy, yz, zx, zy, and zz), each associated with two axes. A tensor of rank two is fully described by the three diagonal matrix elements (e.g., xx, yy, and zz) in its principal axis system.
Isotropic	Invariant with respect to direction (average of the principal NICS tensor components, xx, yy and zz).
Orientation	By convention, rings are oriented in the xy plane; the z direction is out-of-plane.
Anisotropic	Having different values when measured in different direction. (e.g., the individual NICS tensor components)
Anisotropy	Given by the difference between the zz tensor component and the (xx + yy) average.

Isotropic NICS π aromaticity indexes

NICS	Nucleus-Independent Chemical Shifts based on the total (isotropic) absolute shieldings computed at chosen points. The sign of shielding value given by the program is reversed to conform to the "chemical shift" convention.
NICS(0)	NICS computed in the center of unweighted ring or cage atoms. Designated simply as "NICS" initially.
NICS(1)	NICS computed 1 Å away from the center, typically above rings
NICS(n)	NICS computed n Å away from the center
NICS(n) $_{\pi}$	Sum of π orbital contributions obtained from CMO or LMO dissections of the total NICS

Aromaticity indexes based on the NICS tensor-components

NICS(n) $_{zz}$	(NICS(n) $_{out-of-plane}$) Total MO contribution to the zz component of the NICS tensor.
NICS(n) $_{\pi zz}$	(NICS(n) $_{\pi, out-of-plane}$) Only the π MO contribution to NICS $_{zz}$
NICS(n) $_{4e\pi zz}$	NICS contribution from the two localized π MO's in five-membered ring heterocycles

Manual for evaluating dissected NICS

Because of political and commercial restrictions, all the NICS data in this manuscript were computed using the deMon-Master NMR program, which employs the individual gauge for localized orbitals (IGLO) method and two choices of localization procedures (Pipek-Mezey or Boys). Pipek-Mezey was employed here to give localized molecular orbital (LMO) data. This also can be obtained using the commercially available NBO 5.0g program installed in Gaussian03. This employs the GIAO technique and gives both natural molecular orbital (LMO) as well as CMO (canonical molecular orbital) analyses of the shielding data. The results evaluated using the different programs and dissection procedures usually differ insignificantly, provided the same theoretical levels are employed. The NBO5.0g LMO- and CMO-derived NICS values (including π_{zz}) usually are identical to the first decimal.

Input. The input for computing NICS(0) and NICS(1) for benzene given below includes the commands for the preliminary NBO5.X program with Gaussian 98. (A different IOP is necessary for the currently available NBO 5.0g in Gaussian 03.) Note that the molecule is oriented in the XY plane so that the NICS points (given by “Bq”) are along the Z axis. This orientation is not required, but is recommended so that the p- π orbitals are perpendicular to the ring and parallel to the conventional Z direction of the applied magnetic field.

```
$RunGauss
# B3LYP/6-31+G* NMR pop=nboread IOP(10/46=1)

C6H6 benzene D6h //B3LYP/6-31+G*

0 1
C -0.69729405 1.20774583 0.00000000
C 0.69729107 1.20774832 0.00000000
C 1.39458646 0.00000000 0.00000000
C 0.69729377 -1.20774678 0.00000000
C -0.69729174 -1.20774707 0.00000000
C -1.39458675 -0.00000096 0.00000000
H -1.23949525 2.14686504 0.00000000
H 1.23949176 2.14686622 0.00000000
H 2.47898701 0.00000118 0.00000000
H 1.23949525 -2.14686504 0.00000000
H -1.23949176 -2.14686622 0.00000000
H -2.47898701 -0.00000118 0.00000000
Bq 0.00000000 0.00000000 0.00000000
Bq 0.00000000 0.00000000 1.00000000

$NBO NPA NBO NBOSUM BNDIDX E2PERT NLMO DIPOLE CMO NRT NCS <XYZ MO> $END
```

Output. In the standard convention, the principal components of the chemical shielding tensor (σ_{11} , σ_{22} , σ_{33}) are labelled according to the high frequency-positive order. Thus, σ_{11} corresponds to the direction of least shielding, while σ_{33} corresponds to the direction of highest shielding. We are interested in the out-of-plane (z) direction of the shielding tensor, which corresponds to the label “3” in the first table below. The Gaussian NBO 5.X output for the NICS(0) point, designated gh(13), is:

Cartesian XYZ to principal shielding axes for atom gh (13):

	1	2	3
X	0.302683	0.953091	0.000014
Y	0.953091	-0.302683	-0.000004
Z	0.000000	-0.000014	1.000000

Full Cartesian NMR shielding tensor (ppm) for atom gh(13):

Canonical MO contributions									
MO	XX	YZ	ZX	XY	YY	ZY	XZ	YZ	ZZ
2	0.11	0.00	0.00	0.00	-0.26	0.00	0.00	0.00	0.95
3	-0.26	0.00	0.00	0.00	0.11	0.00	0.00	0.00	0.95
4	0.06	0.00	0.00	0.00	-0.09	0.00	0.00	0.00	2.46
5	-0.09	0.00	0.00	0.00	0.07	0.00	0.00	0.00	2.46
6	0.05	0.00	0.00	0.00	0.05	0.00	0.00	0.00	3.86
7	5.29	0.00	0.00	0.00	5.29	0.00	0.00	0.00	14.41
8	2.04	-2.05	0.00	-2.05	2.29	0.00	0.00	0.00	10.77
9	2.29	2.05	0.00	2.05	2.04	0.00	0.00	0.00	10.77
10	2.25	0.62	0.00	0.62	2.71	0.00	0.00	0.00	6.30
11	2.71	-0.62	0.00	-0.62	2.25	0.00	0.00	0.00	6.30
12	4.75	0.00	0.00	0.00	4.75	0.00	0.00	0.00	11.82
13	-1.04	0.00	0.00	0.00	-1.04	0.00	0.00	0.00	-1.17
14	-11.00	0.00	0.00	0.00	-11.00	0.00	0.00	0.00	1.40
15	-3.94	-7.64	0.00	-7.64	-7.07	0.00	0.00	0.00	-12.04
16	-7.07	7.64	0.00	7.64	-3.94	0.00	0.00	0.00	-12.04
17	15.14	0.00	0.00	0.00	15.15	0.00	0.00	0.00	12.83
18	-6.38	3.02	0.00	3.02	-3.37	0.00	0.00	0.00	-35.05
19	-3.37	-3.02	0.00	-3.02	-6.38	0.00	0.00	0.00	-35.05
20	9.02	-1.00	0.00	-1.00	-5.18	0.00	0.00	0.00	11.66
21	-5.18	1.00	0.00	1.00	9.03	0.00	0.00	0.00	11.66
Total	5.38	0.00	0.00	0.00	5.39	0.00	0.00	0.00	13.15

Principal components of the tensor (ppm) for atom gh(13):
 Canonical MO contributions

MO	11	22	33	CSA	ISO
2	0.11	-0.26	0.95	1.02	0.27
3	-0.26	0.11	0.95	1.02	0.27
4	0.06	-0.09	2.46	2.47	0.81
5	-0.09	0.07	2.46	2.47	0.81
6	0.05	0.05	3.86	3.82	1.32
7	5.29	5.29	14.41	9.11	8.33
8	2.04	2.29	10.77	8.60	5.03
9	2.29	2.04	10.77	8.60	5.03
10	2.25	2.71	6.30	3.82	3.75
11	2.71	2.25	6.30	3.82	3.75
12	4.75	4.75	11.82	7.07	7.11
13	-1.04	-1.04	-1.17	-0.14	-1.08
14	-11.00	-11.00	1.40	12.41	-6.87
15	-3.94	-7.07	-12.04	-6.53	-7.68
16	-7.07	-3.94	-12.04	-6.53	-7.68
17	15.14	15.15	12.83	-2.32	14.37
18	-6.38	-3.37	-35.05	-30.17	-14.93
19	-3.37	-6.38	-35.05	-30.18	-14.93
20	9.02	-5.18	11.66	9.73	5.17
21	-5.18	9.03	11.66	9.73	5.17
Total	5.38	5.39	13.15	7.76	7.97

MO's 17, 20, and 21 can be identified as the π -orbitals by examining the molecular orbital coefficients or by using a standard visualization program (like Molekel or Molden). For clarity, the π -orbital shielding components are shown above in **bold font** and color-coding is applied for prominence. The [3x3] matrix of the "Cartesian XYZ to principal shielding axes for atom gh (13)" (first table at the top of the output) shows that the shielding component contributions along the Z-axis (which is perpendicular to the XY ring plane) are given by the 33 tensor.

The signs of the NICS values are reversed from those of the shielding data in the output. Thus, the NICS $_{\pi zz}$ value is the negative of the sum of the shielding contributions of MOs 17, 20, and 21 to the 33-tensor components: $-(12.83 + 11.66 + 11.66) = -36.15$
 The NICS $_{zz}$ value is **-13.15** ppm.
 The isotropic NICS value is **-7.97** ppm.
 The isotropic NICS(π) value is evaluated as $-(14.37 + 5.17 + 5.17) = -24.71$ ppm..