Schulich Faculty of Chemistry

הטכניון מכון טכנולוגי לישראל | Technion Israel Institute of Technology

Is there a “best” NICS criterion for tropicity?

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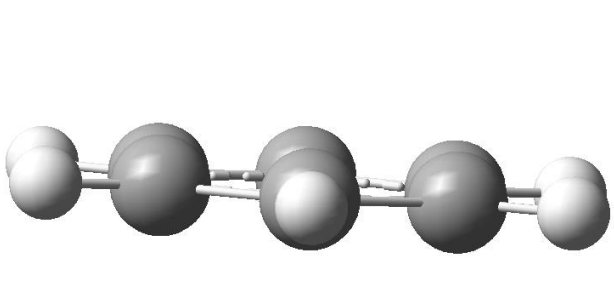
ISNA 20, Toronto, August 2024

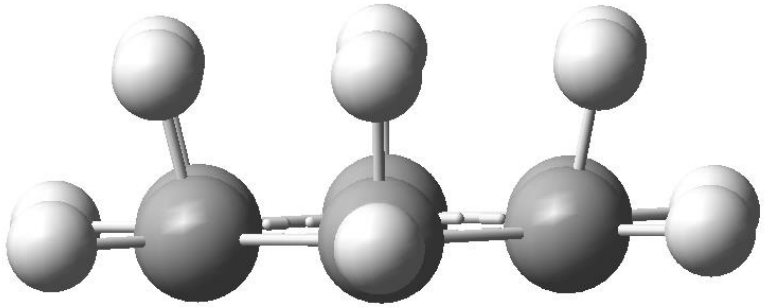
Methods

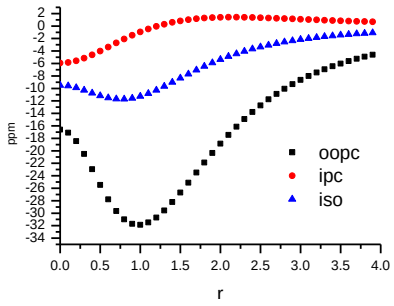
CMO-NICS$_{\pi,zz}$ for planar systems at closed shell S_0 ground state

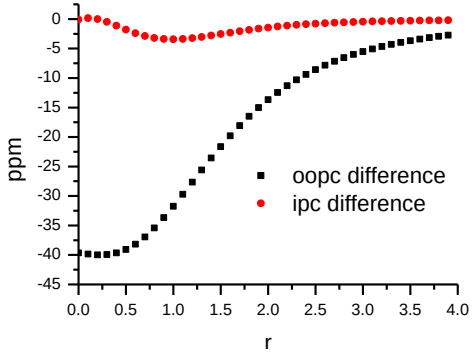
σ-only-NICS$_{\pi,zz}$ for all the rest, i.e.,

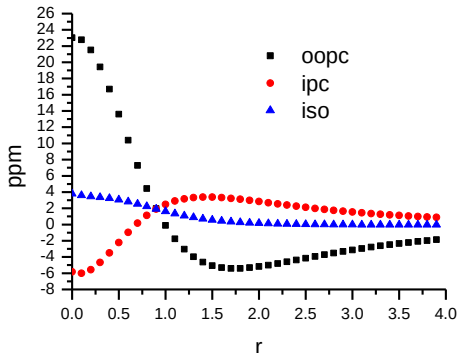
broken symmetry singlet, triplet, non-planar systems.

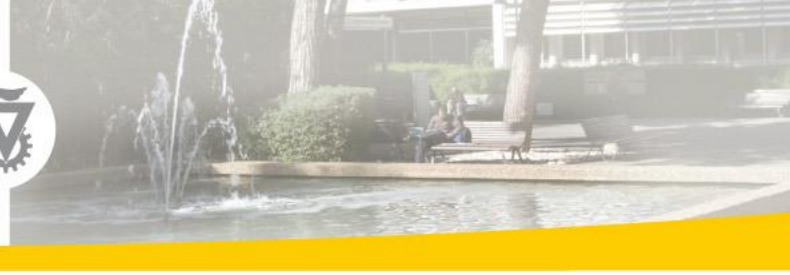












$$Iso(conj)=1/3(\sigma_{xx}+\sigma_{yy}+\sigma_{ZZ})$$

$$=1/3(\sigma_{xx}(\sigma)+\sigma_{yy}(\sigma)+\sigma_{ZZ}(\sigma)+(\sigma_{xx}(\pi)+\sigma_{yy}(\pi)+\sigma_{ZZ}(\pi))$$

For the σ-only model: $Iso(model)=1/3(\sigma_{xx}+\sigma_{yy}+\sigma_{ZZ})$

Assumptions: the π contribution to the ipc is minimal;

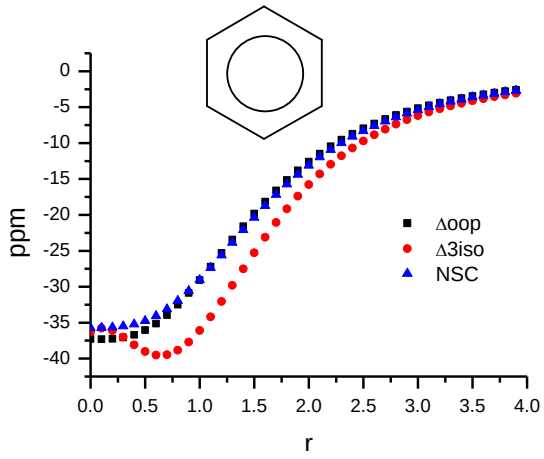
$\sigma_{xx}(\pi)=\sigma_{yy}(\pi)=0$

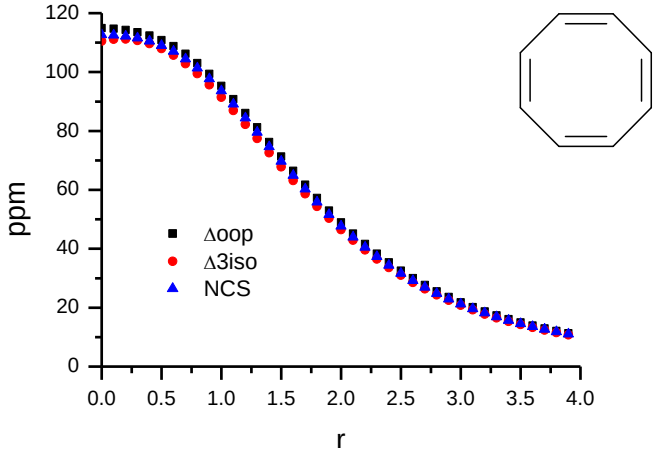
For a perfect σ-only model: $\sigma_{xx}=\sigma_{xx}$ $\sigma_{yy}=\sigma_{yy}$ $\sigma_{ZZ}(\pi)=0$

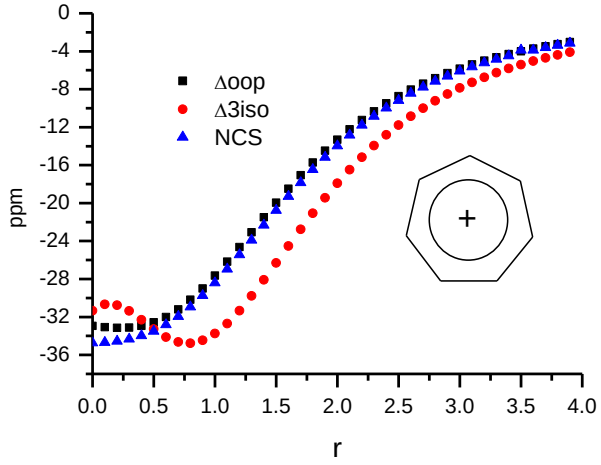
$Iso(conj)-Iso(model)=1/3(\sigma_{ZZ}(\pi))$ $1/3(\Delta\sigma_{ZZ})=\Delta(iso)$

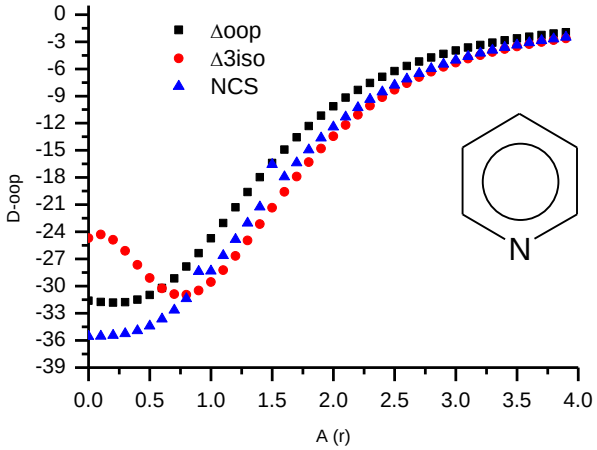
Since oopc= σ_{ZZ}

$\Delta(oopc)=3\Delta(iso)$

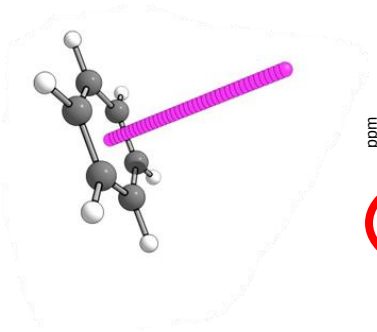

ppm
r
Δoop
Δ3iso
NSC

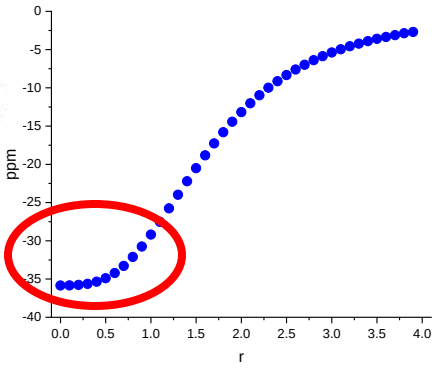

ppm
r
Δoop
Δ3iso
NCS


ppm
r
Δoop
Δ3iso
NCS
+


D-oop
A (r)
Δoop
Δ3iso
NCS
N

For single ring systems



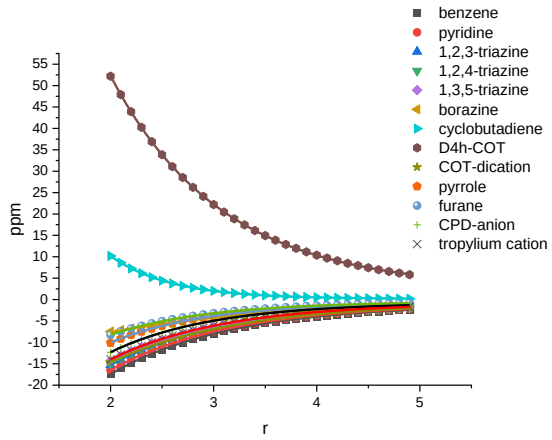


3rd degree polynomial fit (usually between 1-4 Å)

Recalculating $NICS(r)_{\pi,zz}$ From the fit parameters.

$NICS(r)^{S}_{\pi,zz}$

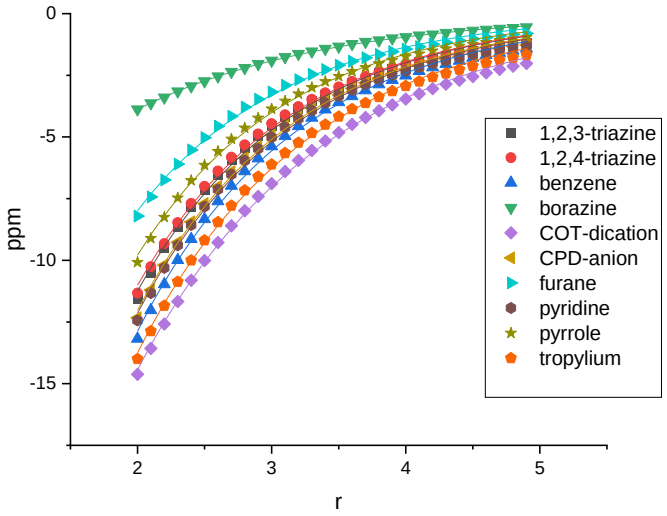
Scan between 2-5 Å



$NICS_{\pi,zz}(r)=A*B^{r} + C$

Extrapolating $NICS(r)_{\pi,zz}$ From the fit parameters.

$NICS(r)^{L}_{\pi,zz}$



$$NICS_{\pi,zz} = A * B^{r}$$

$$\int NICS_{\pi,zz} = -A/lnB$$

$\int NICS_{\pi,zz}$

Diatropicity in compounds containing 2ed and 3rd row elements

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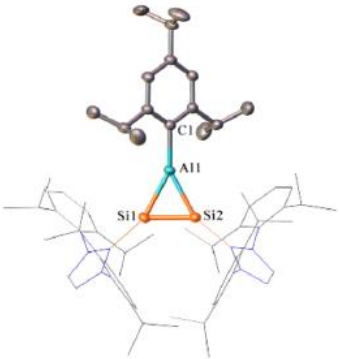
Communication

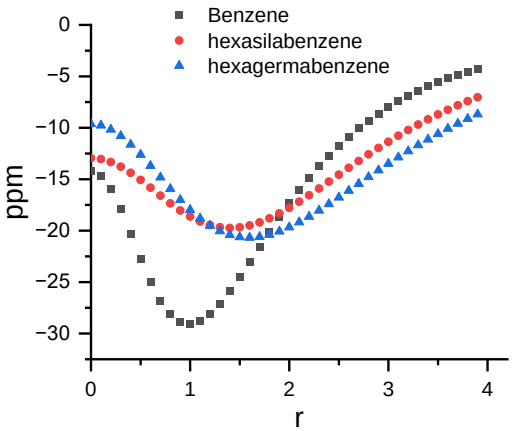
Synthesis and Reactivity of Aluminum Disilacyclopropenes. Cyclic $AlSi_2$ Delocalized 2π Systems

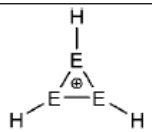
Lulu Guo, Jianying Zhang, and Chunming Cui*

*first $AlSi_2$ three-membered ring
*first isolable strained systems with a donor-free Al atom
*heavy main group 2π systems



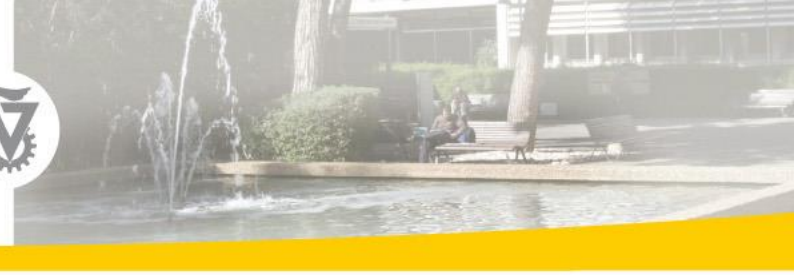
Aromaticity by NICS(1)$_{zz}$

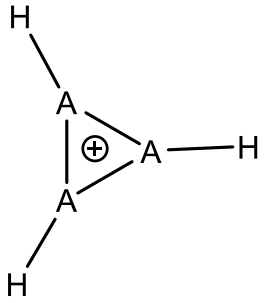




	E = C	E = Si	E = Ge	E = Sn[b]	E = Pb[c]
NICS(0)$_{zz}$[a]	−14.10	−9.03	−9.36	−8.55	−7.75
NICS(1)$_{zz}$[a]	−28.49	−7.12	−6.37	−3.36	−6.28

Fernández, Duvall, Wu, Schleyer, Frenking *Chem. Eur. J.* 2011, *17*, 2215-2244.





A=C

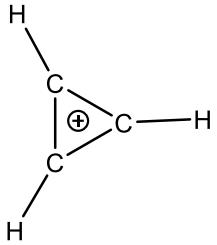
r(Å)	$NICS(r)^{s}_{\pi,zz}$	$NICS(r)^{L}_{\pi,zz}$	$\int NICS_{\pi,zz}$
1	-11.6	-10.6	-23.0
2	-1.8	-2.8	
3	-0.8	-0.8	

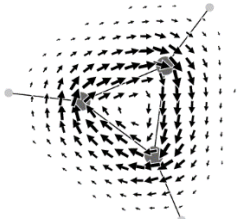
A=Si

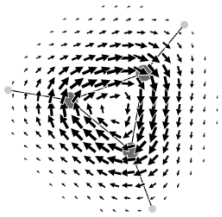
r(Å)	$NICS(r)^{s}_{\pi,zz}$	$NICS(r)^{L}_{\pi,zz}$	$\int NICS_{\pi,zz}$
1	-11.9	-15.8	-37.1
2	-5.1	-5.3	
3	-1.8	-1.9	

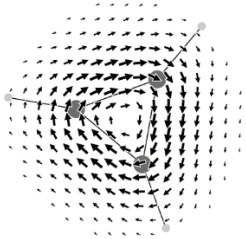
A=Ge

r(Å)	$NICS(r)^{s}_{\pi,zz}$	$NICS(r)^{L}_{\pi,zz}$	$\int NICS_{\pi,zz}$
1	-12.1	-15.3	-37.4
2	-5.6	-5.5	
3	-2.1	-2.1	




r=0.5


r=1.0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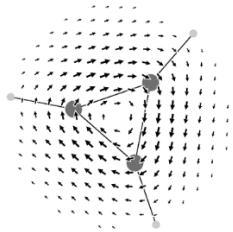
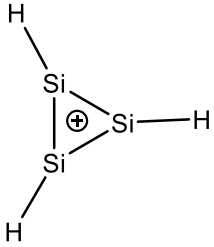
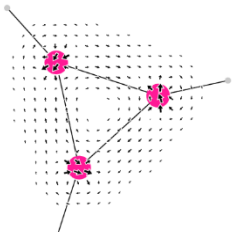
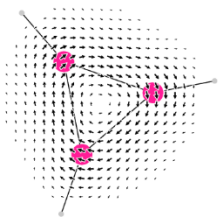
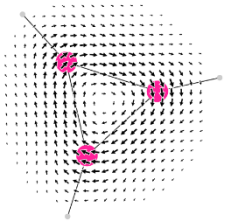
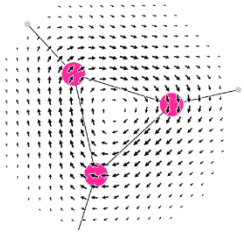

r=2.0

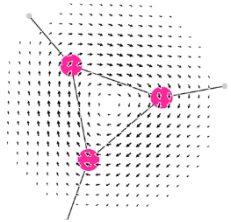



r=0.5


r=1.0


r=1.5


r=2.0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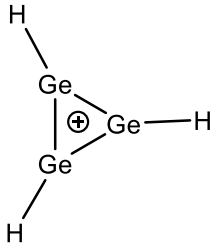
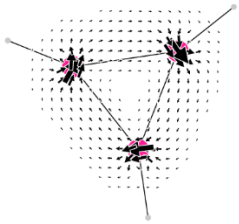
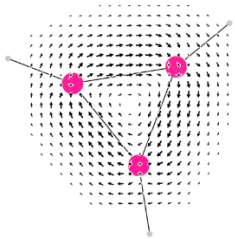
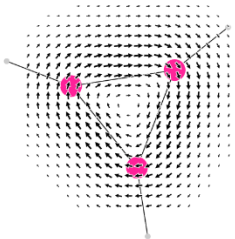
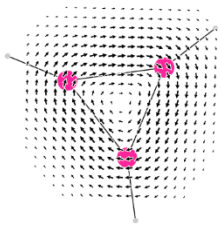
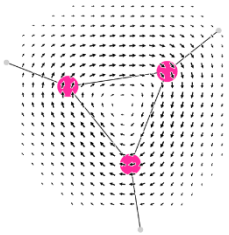


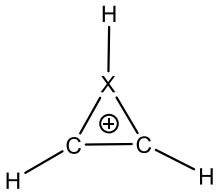












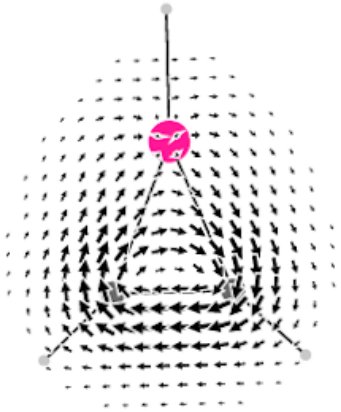
X=Si

r(Å)	$NICS(r)^{s}_{\pi,zz}$	$NICS(r)^{L}_{\pi,zz}$	$\int NICS_{\pi,zz}$
1	-6.2	-6.3	-13.2
2	-1.9	-1.9	
3	-0.6	-0.6	

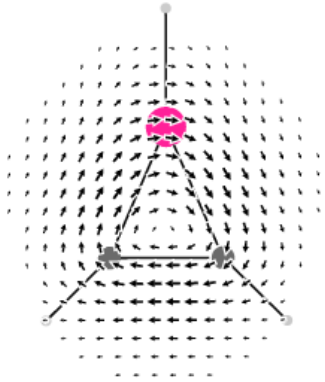
X=Ge

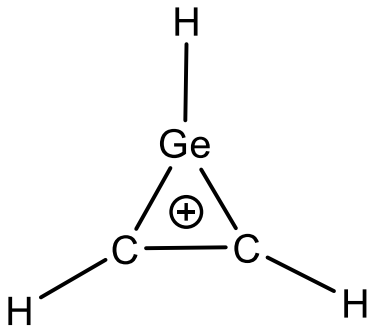
r(Å)	$NICS(r)^{s}_{\pi,zz}$	$NICS(r)^{L}_{\pi,zz}$	$\int NICS_{\pi,zz}$
1	-14.8	-11.6	-25.9
2	-5.2	-3.3	
3	-1.3	-1.0	

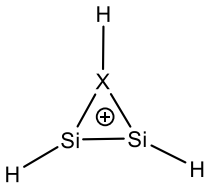
1 a.u.



2 a.u.





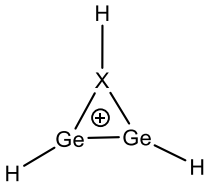


X=C

r(Å)	$NICS(r)^{s}_{\pi zz}$	$NICS(r)^{L}_{\pi zz}$	$\int NICS_{\pi zz}$
1	-8.1	-8.9	-20.2
2	-3.0	-3.0	
3	-1.0	-1.1	

X=Ge

r(Å)	$NICS(r)^{s}_{\pi zz}$	$NICS(r)^{L}_{\pi zz}$	$\int NICS_{\pi zz}$
1	-12.0	-15.0	-36.2
2	-5.3	-5.3	
3	-1.9	-1.9	

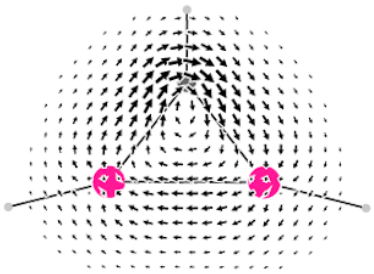


X=C

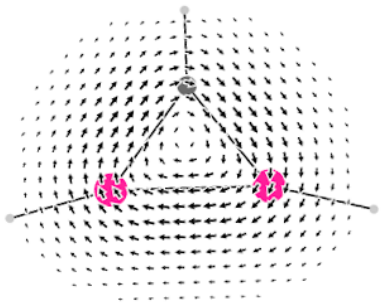
r(Å)	$NICS(r)^{s}_{\pi zz}$	$NICS(r)^{L}_{\pi zz}$	$\int NICS_{\pi zz}$
1	-11.3	-13.7	-32.0
2	-4.5	-4.4	
3	-1.5	-1.5	

X=Si

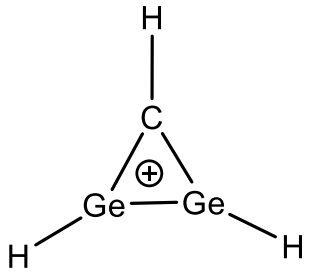
r(Å)	$NICS(r)^{s}_{\pi zz}$	$NICS(r)^{L}_{\pi zz}$	$\int NICS_{\pi zz}$
1	-12.1	-15.2	-36.8
2	-5.4	-5.4	
3	-2.0	-2.0	

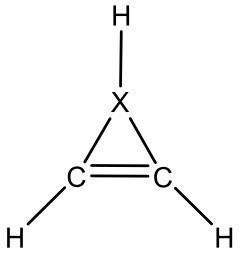


1 a.u.



2 a.u.



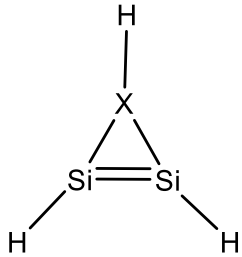


X=B

r(Å)	$NICS(r)^{s}_{\pi,zz}$	$NICS(r)^{L}_{\pi,zz}$	$\int NICS_{\pi,zz}$
1	-11.1	-11.3	-25.0
2	-3.2	-3.1	
3	-0.9	-0.9	

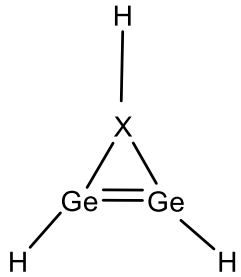
X=Al

r(Å)	$NICS(r)^{s}_{\pi,zz}$	$NICS(r)^{L}_{\pi,zz}$	$\int NICS_{\pi,zz}$
1	-9.0	-10.4	-23.8
2	-3.2	-3.1	
3	-1.0	-1.0	



r(Å)	$NICS(r)^{s}_{\pi,zz}$	$NICS(r)^{L}_{\pi,zz}$	$\int NICS_{\pi,zz}$
1	-11.7	-14.4	-35.0
2	-5.1	-5.0	
3	-1.8	-1.8	

r(Å)	$NICS(r)^{s}_{\pi,zz}$	$NICS(r)^{L}_{\pi,zz}$	$\int NICS_{\pi,zz}$
1	-10.6	-13.4	-34.0
2	-5.2	-5.2	
3	-2.1	-2.1	

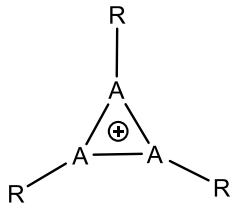


r(Å)	$NICS(r)^{s}_{\pi,zz}$	$NICS(r)^{L}_{\pi,zz}$	$\int NICS_{\pi,zz}$
1	-12.3	-14.9	-36.4
2	-5.4	-5.3	
3	-2.0	-2.0	

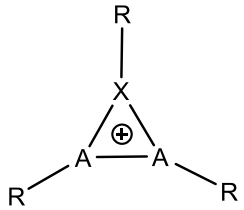
r(Å)	$NICS(r)^{s}_{\pi,zz}$	$NICS(r)^{L}_{\pi,zz}$	$\int NICS_{\pi,zz}$
1	-11.2	-14.0	-35.7
2	-5.5	-5.5	
3	-2.2	-2.2	

What happens when (tri)methyl substituted?

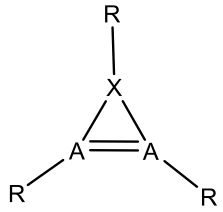
Comparisons of NICS(1)$^{L}_{\pi,zz}$



A	R=H	R=Me
C	-10.6	-4.9
Si	-15.8	-14.7
Ge	-15.3	-15.3



A,X	R=H	R=Me
C,Si	-6.3	-8.9
C,Ge	-11.6	-9.3
Si,C	-8.9	-12.8
Si,Ge	-15.0	-15.0
Ge,C	-13.7	-13.1
Ge,Si	-15.2	-15.1



A,X	R=H	R=Me
C,B	-11.3	-9.8
C,Al	-10.4	-9.9
Si,B	-14.4	-14.1
Si,Al	-13.4	-13.6
Ge,B	-14.9	-14.5
Ge,Al	-13.9	-14.1

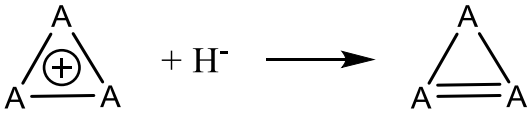
A note about aromaticity

G4 energies

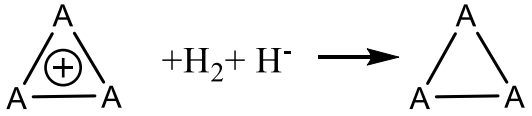
Which of the relevant numbers are known?

Bond energies (kcal mol^{-1}): C-H 98.7; Si-H 76.0; Ge-H 68.8

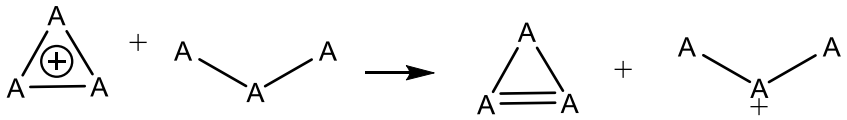
Strain energies (kcal mol^{-1}): cyclopropane – 27; cyclopropene – 54.1



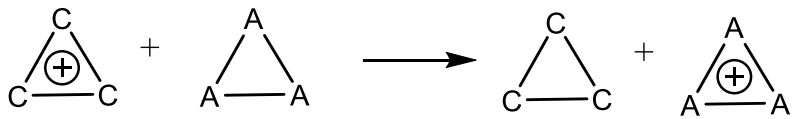
A=C	A=Si	A=Ge	A=C	A=Si	A=Ge
-232.4	-220.0	-212.2	0.0	-10.3	-9.7



A=C	A=Si	A=Ge	A=C	A=Si	A=Ge
-287.8	-260.4	-247.5	0.0	-40.7	-49.4



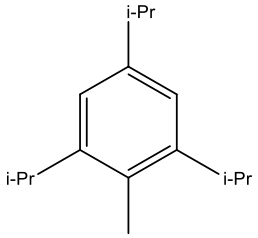
A=C	A=Si	A=Ge
28.8	29.4	27.7

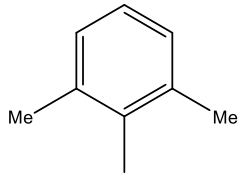


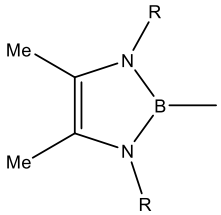
A=C	A=Si	A=Ge
0	-27.4	-40.2
0	**-4.7**	**-10.3**

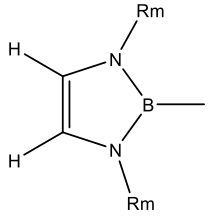
experimental

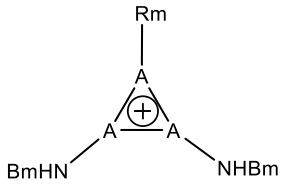
Computational model

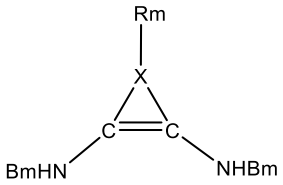
R= 

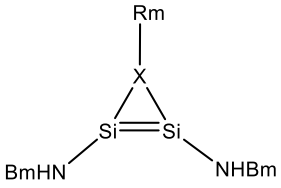
R_m= 

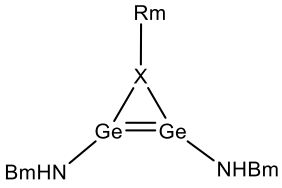
NHB= 

NHB_m= 









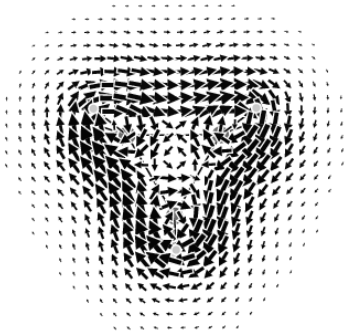
A=C, Si, Ge

X=B, Al

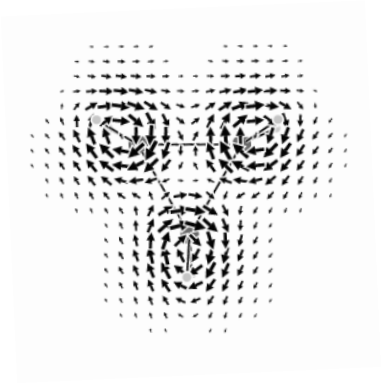
Non-planar

Use the σ-only model for $NICS_{\pi,zz}$

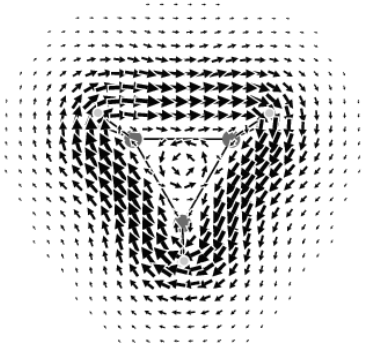
The σ-only model cyclopropenium and cyclopropene is cyclopropane



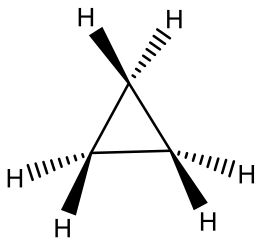
All e

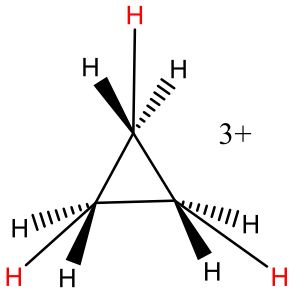


π-only e

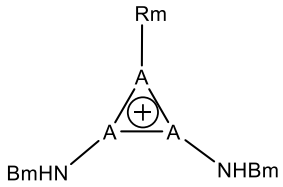


σ-only e

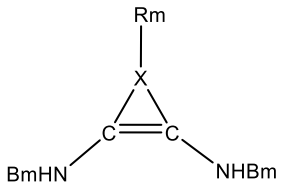




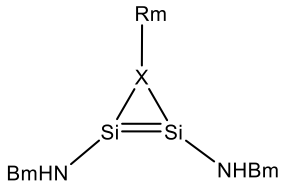
	$NICS(1)^{s}_{\pi,zz}$	$NICS(1)^{L}_{\pi,zz}$	$\int NICS_{\pi,zz}$
Cyclopropane	-11.2	-9.2	-21.3
Trisilacyclopropane	-9.3	-10.7	-30.4
trigermacyclopropane	-5.4	-6.6	-22.5



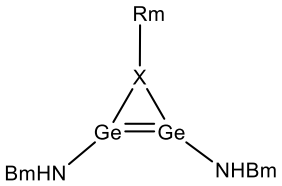
	Parent, $NICS^s$	Subst. $NICS^s$	Parent, $NICS^L$	Subst. $NICL^s$
A=C	-8.0	-2.7	-0.1	-0.1
A=Si	-21.5	-16.5	-28.6	-22.6
A=Ge	-22.7	-16.8	-29.6	-22.0



	Parent, $NICS^s$	Subst. $NICS^s$	Parent, $NICS^L$	Subst. $NICL^s$
X=B	-9.8	-8.2	-1.0	-1.1
X=Al	-13.1	-9.4	-17.6	-11.6



	Parent, $NICS^s$	Subst. $NICS^s$	Parent, $NICS^L$	Subst. $NICL^s$
X=B	-19.9	-8.4	-26.2	-11.8
X=Al	-20.9	-16.6	-27.3	-23.1



	Parent, $NICS^s$	Subst. $NICS^s$	Parent, $NICS^L$	Subst. $NICL^s$
X=B	-19.9	-14.8	-25.3	-19.0
X=Al	-22.1	-16.6	-26.9	-22.4

Summary and conclusions

NICS methods, **when correctly used**, can provide valuable information and understanding.

$NICS(1)^{S}_{\pi,zz}$, $NICS(1)^{L}_{\pi,zz}$ and $\int NICS_{\pi,zz}$, give better understanding of the tropicity in systems containing elements beyond the first row.

The experimental systems are diatropic – in contrast to the paper's conclusion.

Is there a “best” NICS criterion for tropicity?

NO

Acknowledgements

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Thank you

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