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Probing the aromaticity in 2,3-pyrido-annulated N-heterocyclic carbene and its heavier analogues

Rinat. R. Aysin, Andrey V. Lalov and Sergey S. Bukalov

Table of content

Experimental

Compounds **5** were provided by Professor Alexander V. Zabula (University of Pennsylvania)[S1].

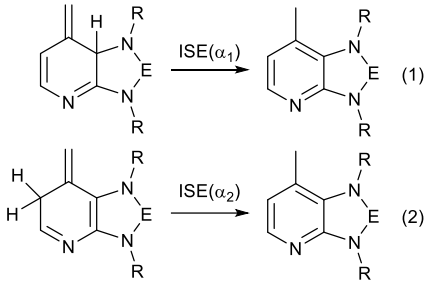
The Raman spectra in the range of 100–3500 cm^{-1} for the samples sealed in thin-walled capillaries were recorded on a Jobin-Yvon LABRAM 300 spectrometer equipped with a microscope and a laser CCD detector. The exciting line was a He–Ne laser line with a wavelength of 632.8 nm and a power of no more than 2 mW. UV-vis absorption spectra were registered with using a Agilent 8453 spectrophotometer for a heptane solution ($1.2 \div 3.5 \cdot 10^{-4}$ M) prepared in Ar-glove box

Computations

Geometry optimization, normal coordinate analysis (NCA) for **5** (R = CH_2Bu^t) and model molecules **5'** (R= Me) were carried out in the Gaussian09 program[S2] at the DFT level with PBE0[S3] and TPSS[S4] functionals, the latter is used only for NCA. The extended Def2-TZVP[S5] basis set was chosen for all atoms. The EDDB and GIMIC analyses were performed at PBE0/Def2-ZTVPP level using RunEDDB[S6] и GIMIC 2.0[S6,S8] programs, correspondingly. The molecular and NOBD orbitals were plotted with using the Avogadro pogram.[S9] The isosurface of the EDDB(**r**) function, IC modulus and IC streamlines were sketched using the Paraview 5.7 program.[S10]

ISE evaluation

For the bicyclic molecule **5**, the isomerisation reaction for the ISE estimation can be constructed by different ways, but only two of them (reactions (1) and (2)) are significant like as for **2** earlier.[S11] It should be noted that the energy of reaction (1) evaluate the conjugation of whole moleclued, whereas reaction (2) measuse only piridin ring. The ISE(a1) and ISE (a2) values obtained for **5** and model **5'** at the PBE0/Def2-ZTVPP level of theory are presented in Table S1 and S2. As can be seen the ISE values for **5** with Np-substituents (Table S1) are admixed with the steric substituent effect. The ISE values for model **5'** with methyl substituents seems to be more accurate (Table S2).



Scheme S1. The isodesmic reactions for the ISE evaluation of **5**.

Table S1. The estimated ISE (ΔE_{tot} with ZPVE correction/kcal·mol^{-1}) values for **5** (R = Np) at the PBE0/Def2-TZVP level

R= Np	C(**a**)	Si(**b**)	Ge(**c**)	Sn(**d**)	Pb(**e**)
ISE(α_1)	-40.8	-33.8	-34.1	-35.9	-35.6
ISE(α_2)	-32.3	-30.7	-29.8	-31.8	-31.1
ΔISE_{1-2}	-8.5	-3.1	-4.4	-4.0	-4.5

Table S2. The estimated ISE (ΔE_{tot} with ZPVE correction/kcal·mol^{-1}) values for **5'** (R = Me) at the PBE0/Def2-TZVP level

R= Me	C(**a**)	Si(**b**)	Ge(**c**)	Sn(**d**)	Pb(**e**)
ISE(α_1)	-40.6	-38.4	-39.0	-38.2	-38.0
ISE(α_2)	-32.3	-33.9	-33.0	-32.0	-31.2
ΔISE_{1-2}	-8.3	-4.5	-6.0	-6.1	-6.8

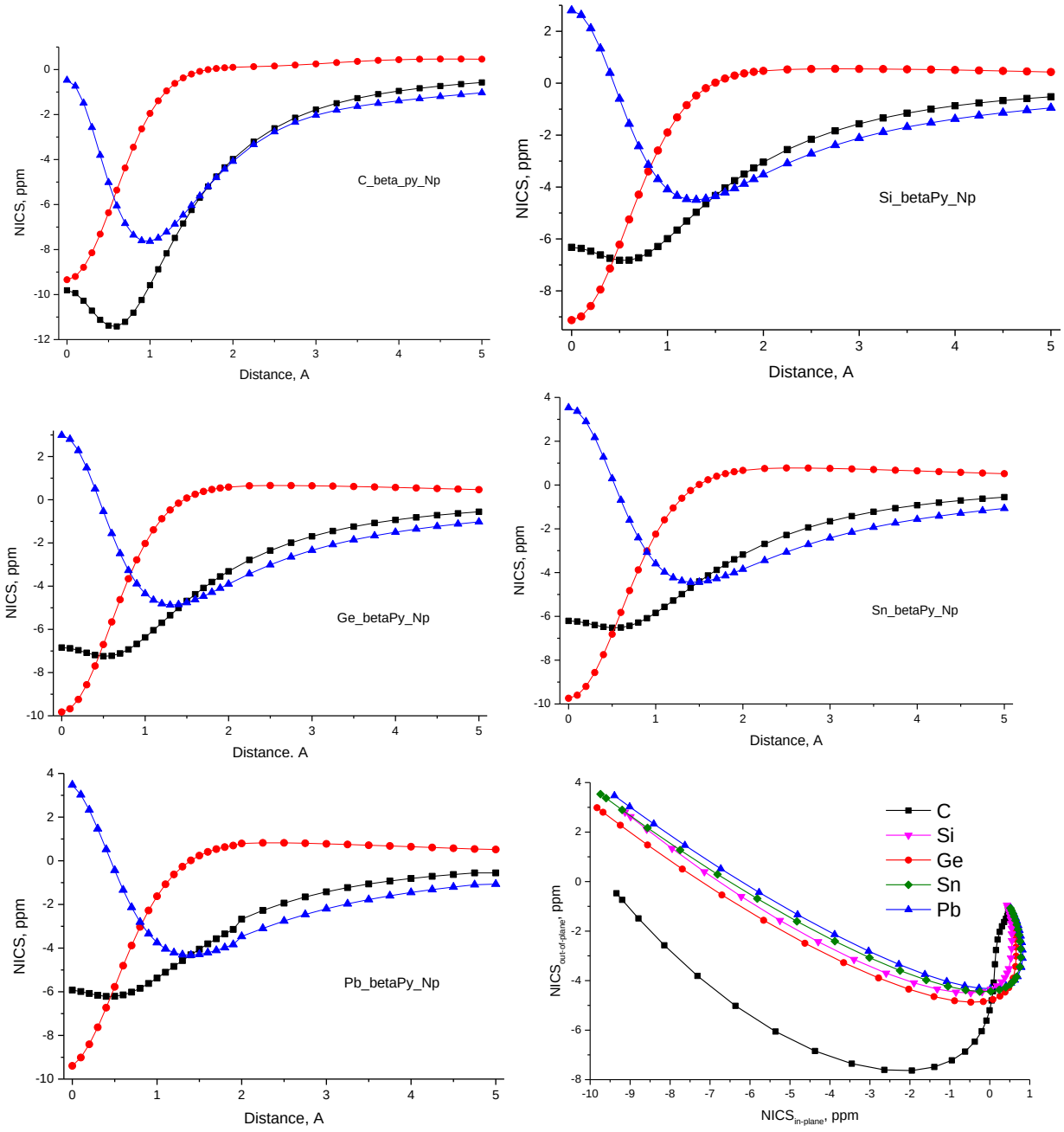


Figure S1. NICS-scan curves for **5**.

Table S3. NICS-values (ppm) for 5m ring in **5**

	C(**a**)	Si(**b**)	Ge(**c**)	Sn(**d**)	Pb(**e**)
NICS(0)	-9.4	-6.0	-6.5	-5.9	-5.7
$NICS(0)_{zz}$	-0.5	2.8	3.0	3.5	3.6
NICS(1)	-9.5	-5.9	-6.3	-5.8	-5.6
$NICS(1)_{zz}$	-7.5	-4.0	-4.2	-3.5	-3.3
Min $NICS_{zz}$	-7.5	-4.4	-4.8	-4.4	-4.3
FIPC-NICS	-4.7	-4.2	-4.7	-4.4	-4.3

Table S4. The views of the NODB1–5 for **5**

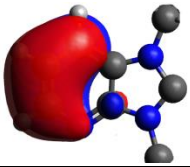
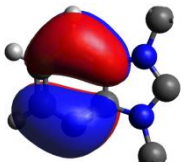
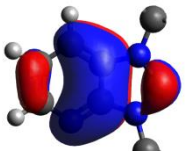
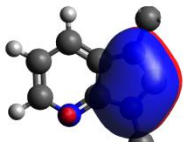
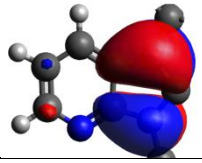
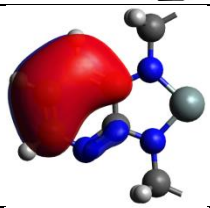
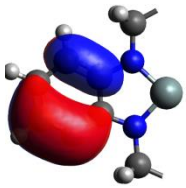
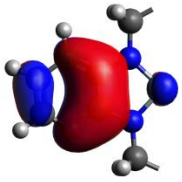
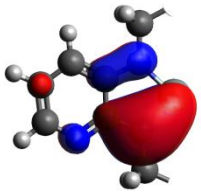
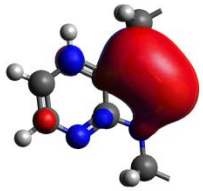
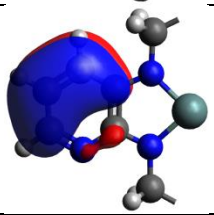
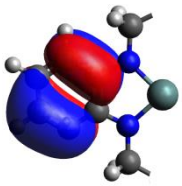
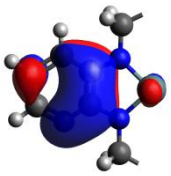
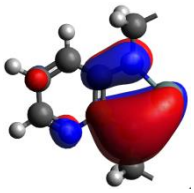
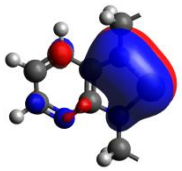
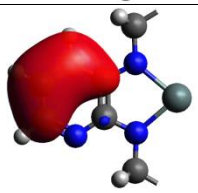
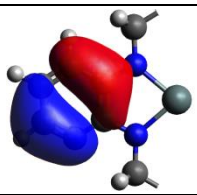
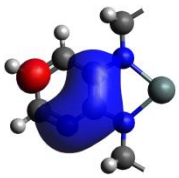
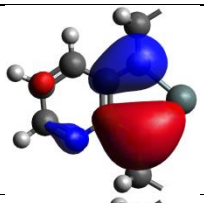
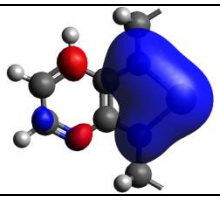
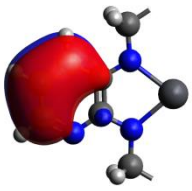
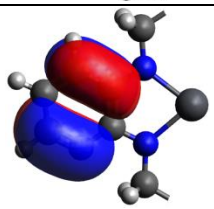
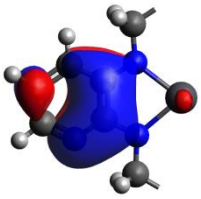
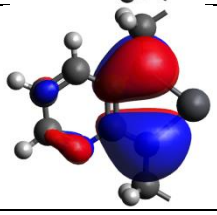
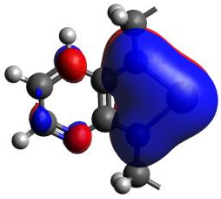
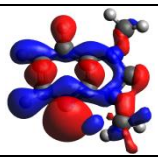
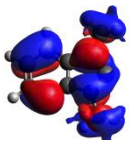
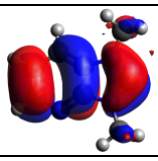
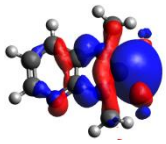
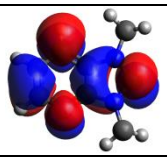
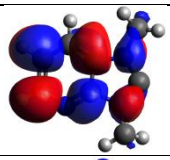
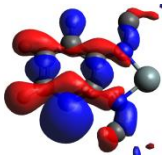
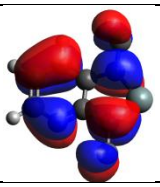
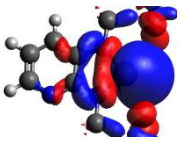
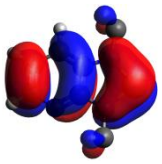
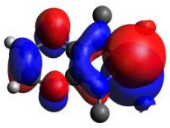
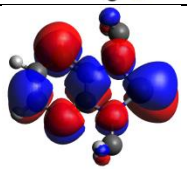
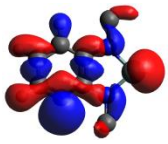
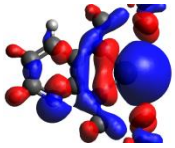
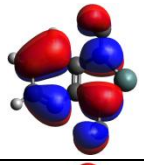
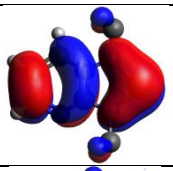
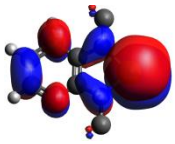
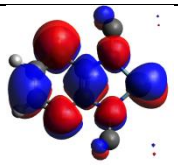
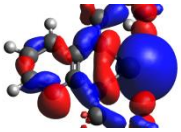
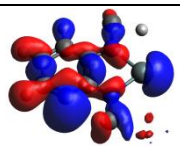
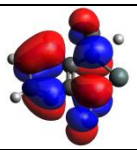
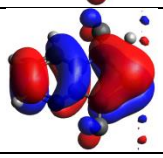
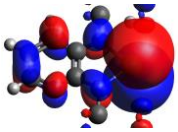
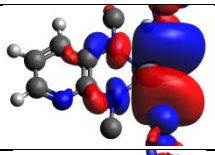
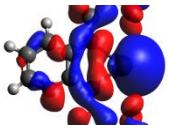
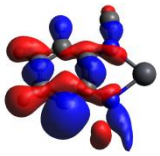
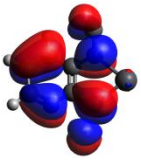
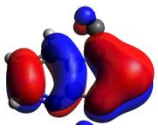
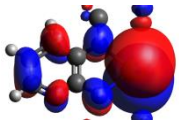
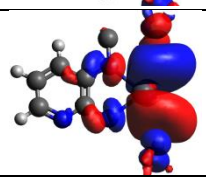
E =	NOBD1	NOBD2	NOBD3	NOBD4	NOBD5
5a (C)					
5b (Si)					
54c (Ge)					
5e (Sn)					
5d (Pb)					

Table S5. The EDDB results for **5** and **2** (values/ē)

E =	C(**a**)	Si(**b**)	Ge(**c**)	Sn(**d**)	Pb(**e**)
$C_5H_3N(N\text{-}Me)_2E$ (**5**)					
π-EDDB	7.28	7.25	7.49	7.68	7.67
NOBD1	1.815	1.800	1.825	1.839	1.852
NOBD2	1.727	1.750	1.764	1.873	1.794
NOBD3	1.585	1.698	1.73	1.750	1.753
NOBD4	1.119	1.030	1.119	1.138	1.165
NOBD5	1.036	0.969	1.051	1.077	1.102
$C_6H_4(N\text{-}Me)_2E$ (**2**)					
EDDB-π all	6.91	6.98	7.17	7.34	7.51

For the diamine $C_5H_3N(NHMe)_2$ π-EDDB values is 5.79 e.

Table S6. The views of canonical molecular orbital (CMO) for **5**

	HOMO-3	HOMO-2	HOMO-1	HOMO	LUMO	LUMO+1
5a (C)						
5b (Si)						
5c (Ge)						
5e (Sn)						
5d (Pb)						

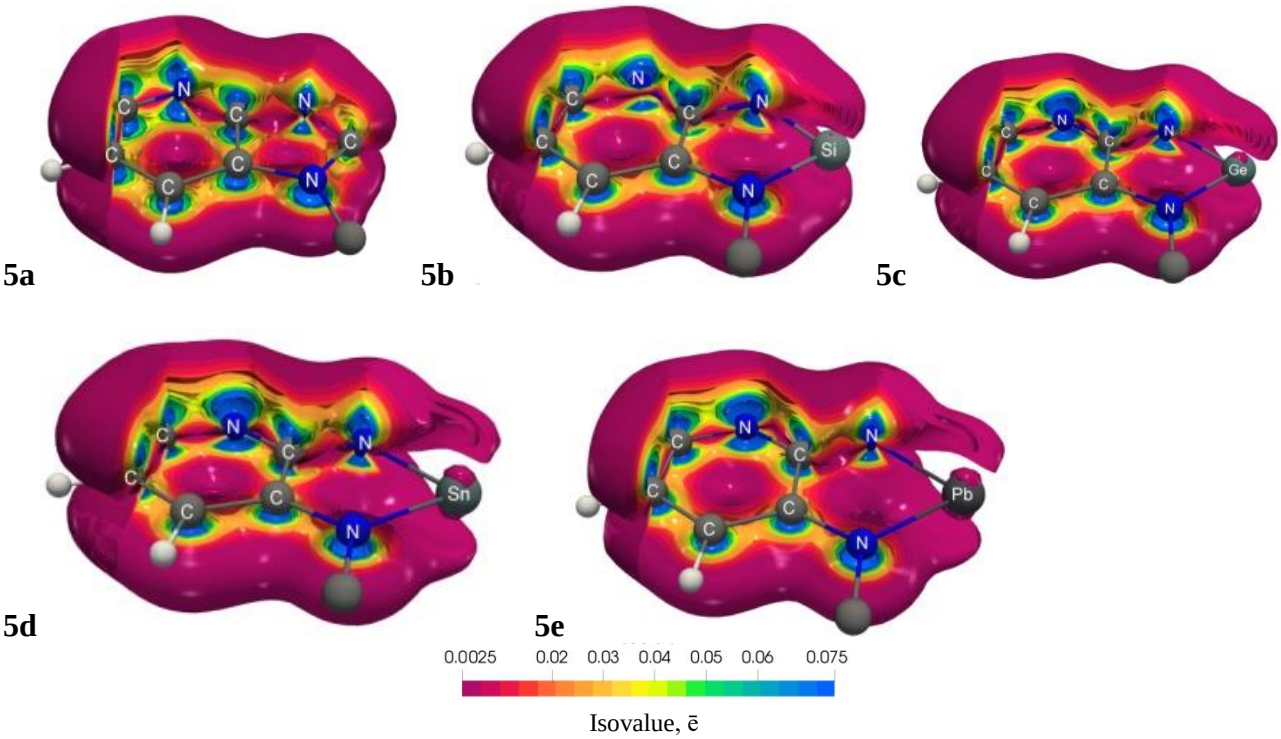


Figure S2. The multi-isosurface of the π-component of the EDDB(**r**) for **5**

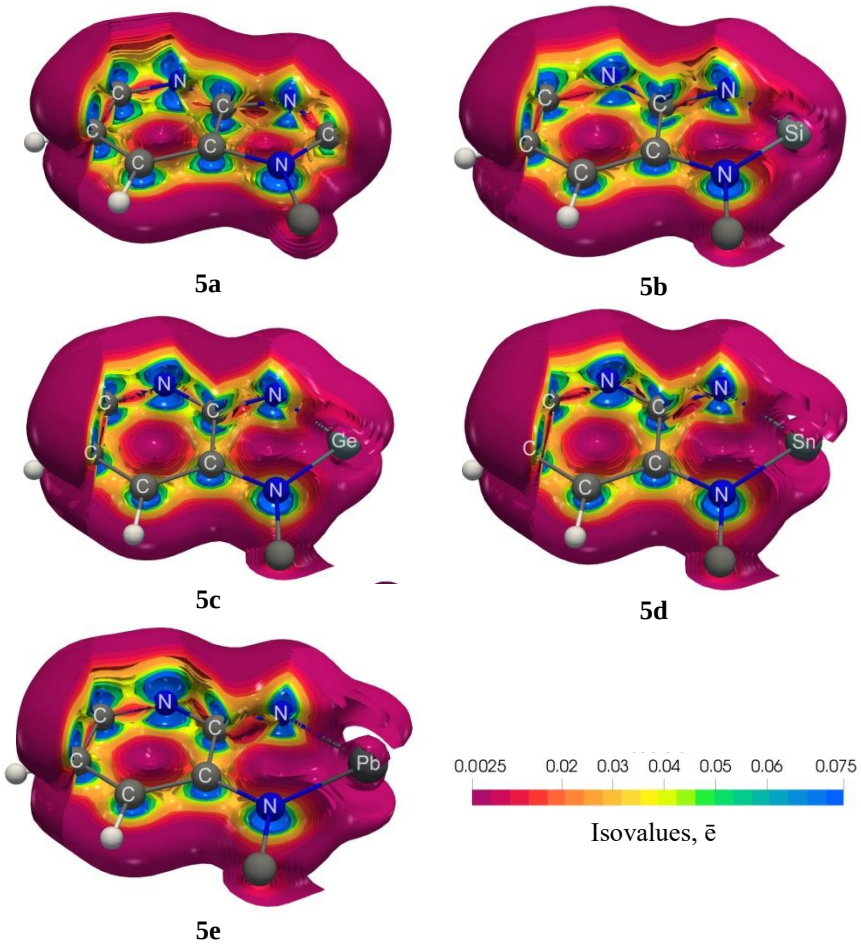


Figure S3. The multi-isosurface of full EDDB(**r**) for **5**.

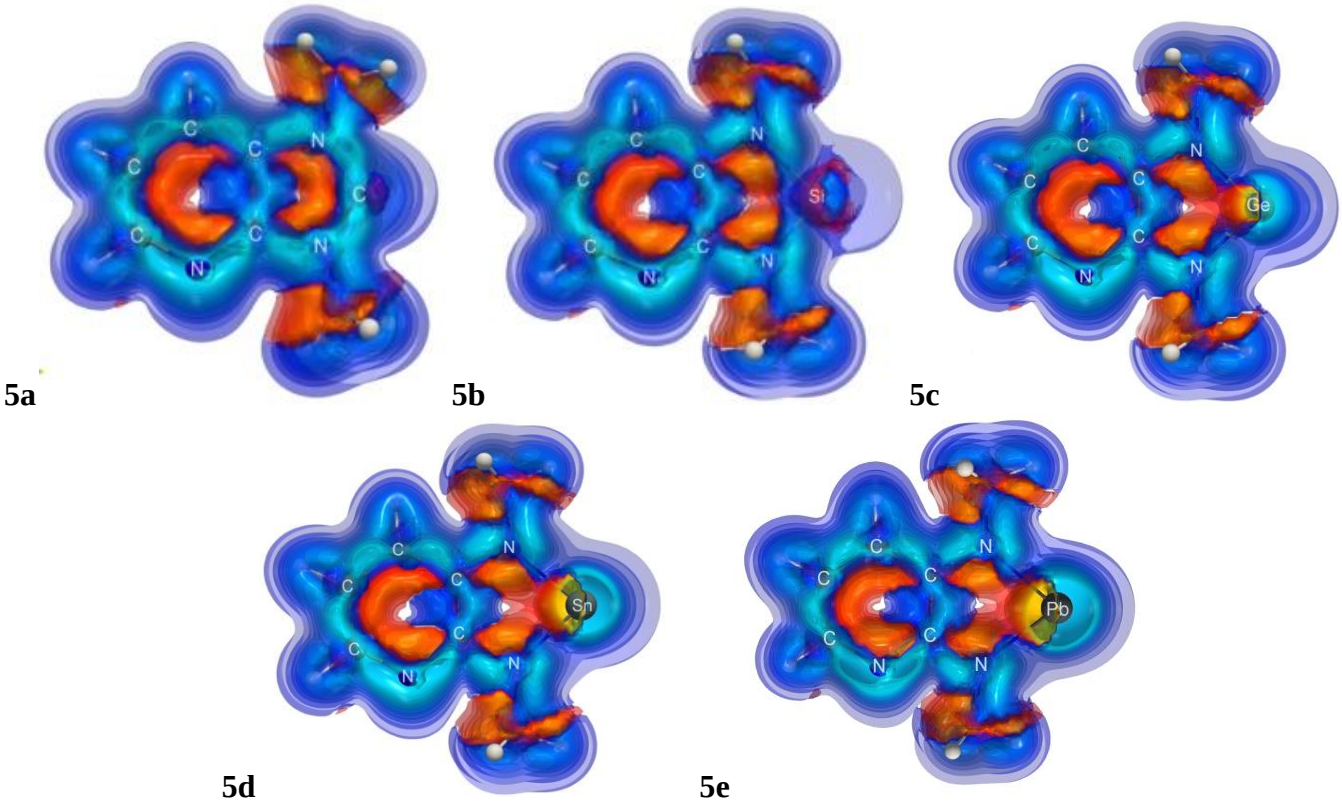
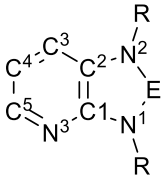


Figure S4. Isosurface of IC modulus for **4'** (*blue* – diatropic ICs, *orange* – paratropic ICs).

Table S7. IRCS values (nA/T) for **5'**

R= Me	C(**a**)	Si(**b**)	Ge(**c**)	Sn(**d**)	Pb(**e**)
E-N^1	9.6	7.0	7.6	7.4	7.5
E-N^2	9.5	7.0	7.6	7.4	7.5
C^2-N^1	5.0	8.6	7.0	6.8	5.7
C^1-N^1	3.5	6.4	7.0	6.7	6.9
C^1-C^2	2.93	4.8	4.7	4.8	4.6
C^2-C^3	11.4	6.5	7.6	6.5	6.0
C^3-C^4	13.0	12.1	12.3	12.1	12.0
C^4-C^5	12.9	12.2	12.4	12.2	12.1
C^5-N^3	12.9	12.2	12.4	12.2	12.1
C^1-N^3	0.3	4.8	6.3	4.8	4.7



Atom numbering

Raman results

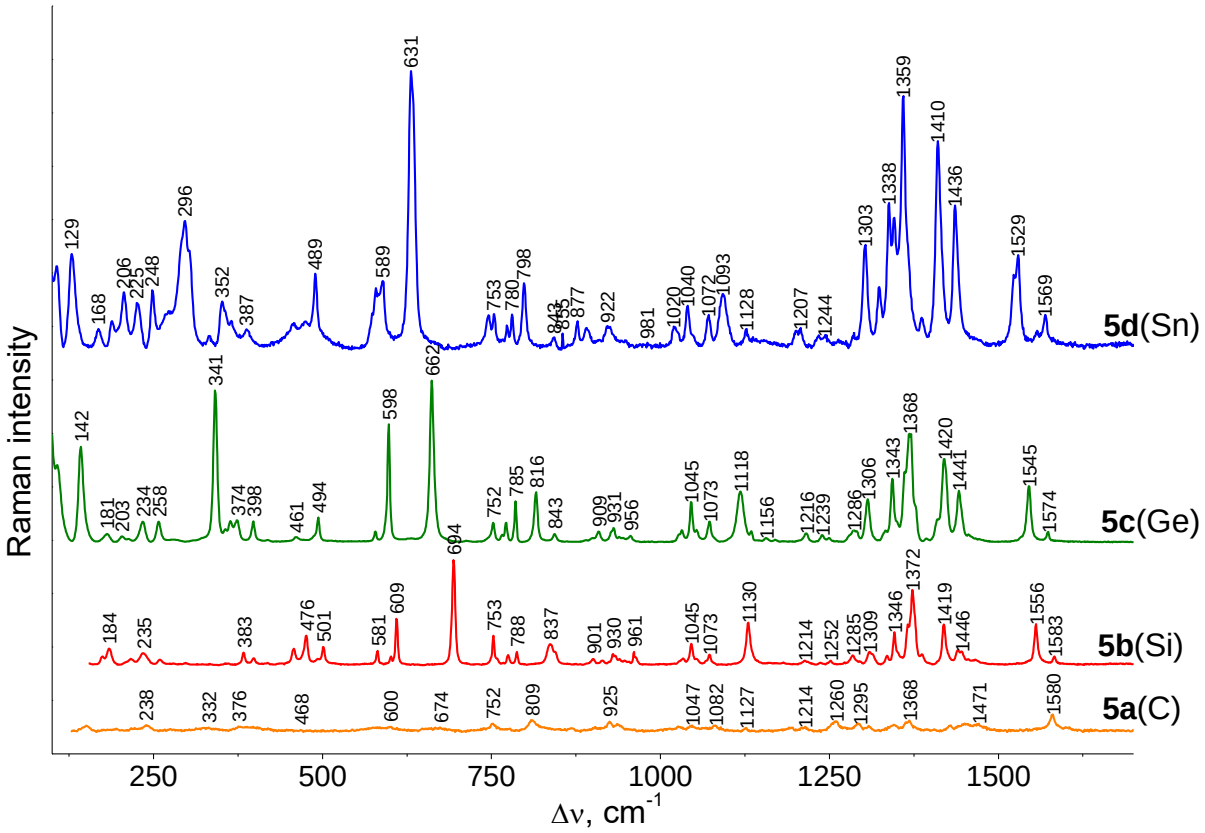


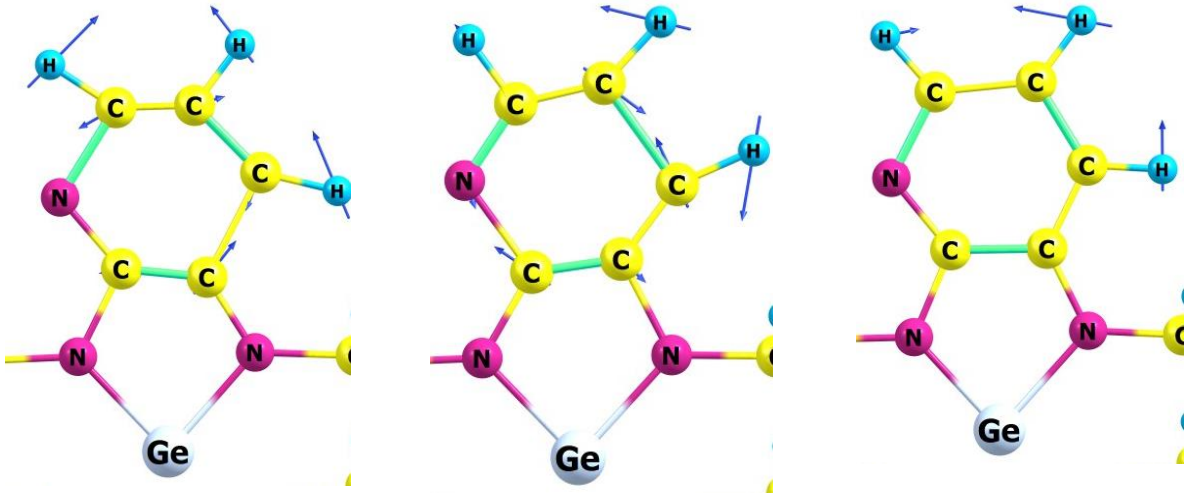
Figure S5. Raman spectra in full range for **5**.

The most intense Raman lines in the 630–770 cm^{-1} region (Fig S5) are related to the "breathing" mode of both rings, i.e., simultaneous stretching of all the bonds in a ring, and thus include the stretching of the N–E^{II} bonds. A decrease in the frequency of this vibration from C to Sn is caused by an increase in the mass of the E atom; at the same time, its intensity increases due to an increase in the polarizability of E. The same changes are observed in all the vibrations where the coordinates of the E atom are involved (Table S8).

Table S8. Experimental frequencies (cm^{-1}) of prominent Raman lines

5a (C)	**5b** (Si)	**5c** (Ge**)**	**5d** (Sn)	Assignment
749 vs 755 vs 765 vs	694 vs	658 vs	631 vs	breathing mode
1038 m	1045 m	1043 m	1040 m	ν3 (Fig. S6)
1185 m	1130 m	1117 m	1093 m	
1398 vs	1372 vs	1369 vs	1359 vs	complex mode ν CC)$_{ar}$+δCH + ν CN
1425 s 1443 s 1466 m 1510 s	1346 s 1419 s 1441 m	1304 s 1341 s 1417 s 1439 s	1338/1346 s 1410 s 1436 s	complex mode ν CC)$_{ar}$
1584 m	1556 m	1543 m	1529 m	ν1 (Fig. S6)
1616w	1583w	1571w	1569w/1557 vw	ν2, (Fig. S6)

s - strong, vs - very strong, m -medium, w - weak



ν1 ν2 ν3

Figure S6. Eigenvectors of ν^1, ν^2 and ν^3 normal modes for **5c**(Ge).

Table S9. Spectral data for **5** and **2**

E =	C(**a**)	Si(**b**)	Ge(**c**)	Sn(**d**)	Pb(**e**)
νC=C (Raman), cm^{-1}	1580	1556	1544	1529	
νC=C (Calc), cm^{-1}	1590	1574	1568	1560	1555
λ_{max}, nm (UV)	300	**324**	**360**	**437**	
in heptane	**244**	260	304	300	
		230	241	248	
λ_{max}, nm (UV)[28]		302	360		
		249	307		
λ_{max}, nm	299	300	331	402	447
TD-DFT	251	272	280	314	334
λ_{max}, nm (UV)	277	**326**	**362**	**448**	**500**
for **2**[35]	**248**	256	250	296	340
				250	

Table S10. TD-DFT results for **5** (R= Np) at PBE0/Def2-TZVPP level

#	Energy, eV	λ_{max}, nm	f	#MO→#MO	
5a(C)					
1	4.14	299	0.0060	71 → 72	HOMO-LUMO
2	4.95	251	0.1402	70 → 72	HOMO[-1]-LUMO
3	5.11	2425	0.0171	69 → 72	HOMO[-2]-LUMO
4	5.21	234	0.0062	68 → 72	HOMO[-3]-LUMO
5b (Si)	4.13	300	0.2536	75 → 76	HOMO-LUMO
1	4.56	272	0.0383	74 → 76	HOMO[-1]-LUMO
2	4.74	261	0.0108	73 → 76	HOMO[-2]-LUMO
3	4.91	252	0.0010	72 → 76	HOMO[-3]-LUMO
4	5.20	238	0.0162	75 → 77	HOMO-LUMO[+1]
5c (Ge)					
1	3.74	331	0.2382	84 → 85	HOMO-LUMO
2	4.42	280	0.0190	83 → 85	HOMO[-1]-LUMO
3	4.63	268	0.0150	82 → 85	HOMO[-2]-LUMO
4	4.74	262	0.0202	81 → 85	HOMO[-3]-LUMO
5	5.03	357	0.0403	84 → 86	HOMO-LUMO[+1]
5d (Sn)					
1	3.08	403	0.1986	79 → 80	HOMO-LUMO
2	3.95	314	0.0218	78 → 80	HOMO[-1]-LUMO
3	4.19	296	0.0067	77 → 80	HOMO[-2]-LUMO
4	4.40	282	0.0002	79 → 81	HOMO-LUMO[+1]
5	4.45	279	0.0343	76 → 80	HOMO[-3]-LUMO
6	4.80	258	0.0853	79 → 82	HOMO-LUMO[+2]
5e (Pb)					
1	2.78	447	0.1850	79 → 80	HOMO-LUMO
2	3.72	334	0.0252	78 → 80	HOMO[-1]-LUMO
3	3.97	312	0.0014	77 → 80	HOMO[-2]-LUMO
4	3.98	311	0.0006	79 → 81	HOMO-LUMO[+1]
5	4.51	275	0.0001	79 → 82	HOMO-LUMO[+2]

Lewis acidity estimation

The Lewis acidity for tetrylenes **1'**, **2'** and **5'** was estimated as general eletrophilicity index (GEI)[S12], which is calculated based on HOMO and LUMO energy values:

$$GEI = \mu^2 / 2\eta,$$

where is chemical potential $\mu = 1/2 (E_{HOMO} + E_{LUMO})$, and the chemical hardness $\eta = E_{LUMO} - E_{HOMO}$. The GEI values (Tables S11) obtained at PBE0/Def2-TZVP level of theory show that Lewis acidity increases in the series **1'**, **2'** and **5'** and also increases in the series from C to Pb.

Table S11. The values for E_{HOMO}, E_{LUMO} and GEI index

	Values, eV	C(**a**)	Si(**b**)	Ge(**c**)	Sn(**d**)	Pb(**e**)
$(HCNR)_2E$ **1'**, R=Me	E_{HOMO}	-5.829	-5.344	-5.043	-4.716	
	E_{LUMO}	1.060	-0.411	-0.649	-1.136	
	GEI	**0.41**	**0.84**	**0.92**	**1.20**	
$C_6H_4(NR)_2E$ **2'**, R=Me	E_{HOMO}	-5.913	-5.859	-5.609	-5.288	-5.016
	E_{LUMO}	-0.419	-1.108	-1.313	-1.702	-1.773
	GEI	**0.91**	**1.28**	**1.39**	**1.70**	**1.78**
b-$C_5NH_3(N\text{-}R)_2E$ **5'**, R=Me	E_{HOMO}	-6.302	-5.99	-5.729	-5.351	-5.077
	E_{LUMO}	-1.023	-1.222	-1.424	-1.759	-1.827
	GEI	**1.27**	**1.36**	**1.49**	**1.76**	**1.83**

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xyz-Optimized Cartesian coordinates at the PBE0/Def2-TZVPP level

5a E_{tot}= -788.337831777 a.u.

C	-0.641261000000	1.111927000000	-0.260784000000
C	0.653344000000	1.112601000000	0.273985000000
C	1.255384000000	2.325508000000	0.548454000000
C	0.510196000000	3.459835000000	0.248989000000
C	0.005642000000	-1.051295000000	-0.007191000000
H	2.251766000000	2.400288000000	0.966445000000
H	0.916761000000	4.445902000000	0.436008000000
C	2.259015000000	-0.704621000000	0.935239000000
H	2.621814000000	0.028606000000	1.662767000000
H	2.030696000000	-1.623646000000	1.478191000000
C	-2.261092000000	-0.662506000000	-0.944579000000
H	-2.637501000000	0.149350000000	-1.571518000000
H	-2.057381000000	-1.526067000000	-1.580645000000
C	3.369117000000	-0.994220000000	-0.089654000000
C	3.712485000000	0.252581000000	-0.899043000000
H	4.517205000000	0.032893000000	-1.605566000000
H	2.855413000000	0.608632000000	-1.475038000000
H	4.053643000000	1.068089000000	-0.254386000000
C	4.594921000000	-1.432516000000	0.709516000000
H	4.381141000000	-2.323464000000	1.306753000000
H	5.422886000000	-1.673074000000	0.038110000000
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C	2.949694000000	-2.119222000000	-1.030679000000
H	2.726296000000	-3.034356000000	-0.476719000000
H	2.053425000000	-1.857986000000	-1.595704000000
H	3.754527000000	-2.335305000000	-1.738891000000
C	-3.333745000000	-1.036789000000	0.092171000000
N	1.003592000000	-0.216660000000	0.402027000000
N	-0.990104000000	-0.216645000000	-0.407439000000
C	-2.933349000000	-2.296526000000	0.853833000000
H	-1.982429000000	-2.165450000000	1.373420000000
H	-3.700586000000	-2.551390000000	1.590570000000
H	-2.817255000000	-3.146493000000	0.175758000000
C	-4.617569000000	-1.304612000000	-0.691107000000
H	-5.418571000000	-1.617431000000	-0.016539000000
H	-4.954992000000	-0.408747000000	-1.220264000000
H	-4.474119000000	-2.100293000000	-1.428219000000
C	-3.566594000000	0.109612000000	1.071693000000
H	-2.677815000000	0.303564000000	1.677170000000
H	-3.824755000000	1.034555000000	0.550671000000
H	-4.382812000000	-0.140613000000	1.754835000000
H	-1.335360000000	4.230066000000	-0.541731000000
N	-1.357638000000	2.175122000000	-0.559771000000
C	-0.763976000000	3.339120000000	-0.300364000000

5b E_{tot}= -1039.71051085 a.u.

C	-0.541970000000	3.897897000000	-0.000236000000
C	-1.336242000000	2.754517000000	-0.000160000000
C	-0.701586000000	1.524574000000	-0.000083000000
C	0.710852000000	1.510375000000	-0.000087000000
H	-0.994457000000	4.881874000000	-0.000297000000
H	-2.416085000000	2.833907000000	-0.000161000000
N	-1.249973000000	0.257994000000	0.000002000000
N	1.232491000000	0.232967000000	-0.000005000000
C	-2.704820000000	0.191110000000	0.000011000000
H	-3.067913000000	0.741028000000	-0.878689000000
H	-3.067908000000	0.741128000000	0.878651000000
C	2.691555000000	0.148387000000	-0.000001000000
H	3.054508000000	0.704596000000	-0.870920000000
H	3.054511000000	0.704652000000	0.870882000000
Si	-0.017601000000	-1.003971000000	0.000083000000
C	-3.392847000000	-1.178771000000	0.000091000000
C	-4.894187000000	-0.880831000000	0.000091000000
H	-5.465159000000	-1.812234000000	0.000150000000
H	-5.187162000000	-0.309118000000	0.885395000000
H	-5.187181000000	-0.309218000000	-0.885272000000
C	-3.061807000000	-1.983600000000	1.255431000000
H	-2.011856000000	-2.283481000000	1.289146000000
H	-3.279916000000	-1.408362000000	2.159759000000
H	-3.663249000000	-2.896379000000	1.285152000000
C	-3.061833000000	-1.983734000000	-1.255169000000
H	-3.279964000000	-1.408594000000	-2.159554000000
H	-2.011881000000	-2.283615000000	-1.288875000000
H	-3.663272000000	-2.896519000000	-1.284778000000
C	3.349821000000	-1.234286000000	0.000043000000
C	3.004822000000	-2.034285000000	-1.254802000000
H	1.949253000000	-2.315156000000	-1.290110000000
H	3.233979000000	-1.462924000000	-2.158773000000
H	3.588236000000	-2.958896000000	-1.284590000000
C	3.004882000000	-2.034181000000	1.254970000000
H	3.234084000000	-1.462745000000	2.158882000000
H	1.949316000000	-2.315048000000	1.290353000000
H	3.588298000000	-2.958790000000	1.284807000000
C	4.856762000000	-0.965731000000	-0.000004000000
H	5.410710000000	-1.907676000000	0.000027000000
H	5.158880000000	-0.398059000000	-0.884544000000
H	5.158920000000	-0.397978000000	0.884471000000
H	1.470749000000	4.649201000000	-0.000290000000
C	0.835627000000	3.768377000000	-0.000232000000
N	1.465594000000	2.592623000000	-0.000158000000

5c E_{tot}= -2827.07643335 a.u.

C	-0.543005000000	3.992168000000	-0.000235000000
C	-1.331162000000	2.847085000000	-0.000153000000
C	-0.703083000000	1.609575000000	-0.000082000000

C	0.715632000000	1.595867000000	-0.000100000000
H	-0.998572000000	4.974802000000	-0.000291000000
H	-2.410795000000	2.926802000000	-0.000145000000
N	-1.286749000000	0.365778000000	0.000004000000
N	1.272281000000	0.340573000000	-0.000029000000
C	-2.739428000000	0.335599000000	0.000023000000
H	-3.093632000000	0.892772000000	-0.878643000000
H	-3.093611000000	0.892880000000	0.878628000000
C	2.729884000000	0.294086000000	-0.000042000000
H	3.082584000000	0.858473000000	-0.870561000000
H	3.082605000000	0.858536000000	0.870428000000
Ge	-0.015814000000	-1.016003000000	0.000075000000
C	-3.458294000000	-1.018872000000	0.000114000000
C	-4.953019000000	-0.689174000000	0.000111000000
H	-5.544831000000	-1.607568000000	0.000175000000
H	-5.232853000000	-0.110723000000	0.885182000000
H	-5.232874000000	-0.110832000000	-0.885024000000
C	-3.147876000000	-1.831017000000	1.256036000000
H	-2.107096000000	-2.160059000000	1.294656000000
H	-3.351146000000	-1.249235000000	2.159446000000
H	-3.772101000000	-2.728294000000	1.287170000000
C	-3.147906000000	-1.831170000000	-1.255718000000
H	-3.351194000000	-1.249497000000	-2.159193000000
H	-2.107128000000	-2.160219000000	-1.294321000000
H	-3.772133000000	-2.728450000000	-1.286728000000
C	3.420597000000	-1.073160000000	-0.000001000000
C	3.097205000000	-1.881364000000	-1.255384000000
H	2.050666000000	-2.193051000000	-1.295461000000
H	3.310696000000	-1.302901000000	-2.158489000000
H	3.704994000000	-2.790067000000	-1.286602000000
C	3.097261000000	-1.881262000000	1.255463000000
H	3.310793000000	-1.302726000000	2.158511000000
H	2.050723000000	-2.192944000000	1.295613000000
H	3.705050000000	-2.789964000000	1.286727000000
C	4.921178000000	-0.770793000000	-0.000046000000
H	5.497457000000	-1.699338000000	-0.000017000000
H	5.209445000000	-0.195756000000	-0.884351000000
H	5.209482000000	-0.195678000000	0.884197000000
C	0.834865000000	3.863317000000	-0.000243000000
H	1.470828000000	4.743848000000	-0.000306000000
N	1.461838000000	2.688786000000	-0.000177000000

5d E_{tot}= -964.642075555 a.u.

C	0.721575000000	1.668040000000	-0.000127000000
C	-0.707468000000	1.680726000000	-0.000121000000
C	-1.323895000000	2.928866000000	-0.000201000000
C	-0.545645000000	4.078839000000	-0.000284000000
H	-2.402688000000	3.011484000000	-0.000200000000
H	-1.007542000000	5.058660000000	-0.000348000000

N	1.335191000000	0.441436000000	-0.000044000000
N	-1.347636000000	0.465345000000	-0.000038000000
C	2.791296000000	0.481784000000	-0.000055000000
H	3.116923000000	1.065210000000	0.869178000000
H	3.116918000000	1.065046000000	-0.869400000000
C	-2.797335000000	0.518657000000	-0.000025000000
H	-3.126596000000	1.093432000000	0.878213000000
H	-3.126622000000	1.093337000000	-0.878316000000
Sn	-0.013995000000	-1.123741000000	0.000069000000
C	3.560639000000	-0.843796000000	0.000068000000
C	5.041710000000	-0.456558000000	0.000059000000
H	5.671937000000	-1.349570000000	0.000147000000
H	5.295100000000	0.134961000000	-0.883922000000
H	5.295071000000	0.135115000000	0.883946000000
C	3.289275000000	-1.670072000000	-1.255531000000
H	2.264610000000	-2.048974000000	-1.302106000000
H	3.465648000000	-1.078553000000	-2.157955000000
H	3.950328000000	-2.540822000000	-1.288015000000
C	3.289234000000	-1.669858000000	1.255799000000
H	3.465592000000	-1.078191000000	2.158128000000
H	2.264561000000	-2.048737000000	1.302412000000
H	3.950275000000	-2.540611000000	1.288445000000
C	-3.592621000000	-0.793394000000	0.000059000000
C	-3.333135000000	-1.622284000000	1.256239000000
H	-2.314762000000	-2.016303000000	1.301429000000
H	-3.500341000000	-1.028404000000	2.158939000000
H	-4.008574000000	-2.481691000000	1.288491000000
C	-3.333368000000	-1.622312000000	-1.256151000000
H	-3.500725000000	-1.028448000000	-2.158833000000
H	-2.315011000000	-2.016350000000	-1.301514000000
H	-4.008827000000	-2.481709000000	-1.288266000000
C	-5.066845000000	-0.381164000000	0.000189000000
H	-5.710667000000	-1.264050000000	0.000265000000
H	-5.312483000000	0.212818000000	0.884993000000
H	-5.312648000000	0.212787000000	-0.884589000000
N	1.451947000000	2.776466000000	-0.000208000000
C	0.830656000000	3.951435000000	-0.000284000000
H	1.469341000000	4.830420000000	-0.000349000000

5e E_{tot}= -943.195855141 a.u.

C	0.727699000000	1.844705000000	-0.000117000000
C	-0.707395000000	1.858384000000	-0.000111000000
C	-1.317050000000	3.113181000000	-0.000192000000
C	-0.542022000000	4.263941000000	-0.000265000000
H	-2.395473000000	3.198109000000	-0.000198000000
H	-1.005309000000	5.243228000000	-0.000328000000
N	1.362745000000	0.633782000000	-0.000050000000
N	-1.371207000000	0.660054000000	-0.000032000000
C	2.815469000000	0.700531000000	-0.000062000000

H	3.135248000000	1.288537000000	0.868964000000
H	3.135238000000	1.288430000000	-0.869164000000
C	-2.817022000000	0.740460000000	-0.000031000000
H	-3.140914000000	1.319725000000	0.878218000000
H	-3.140926000000	1.319576000000	-0.878375000000
Pb	-0.012666000000	-1.040105000000	0.000051000000
C	3.605028000000	-0.613851000000	0.000014000000
C	5.080836000000	-0.206836000000	-0.000016000000
H	5.724377000000	-1.090457000000	0.000033000000
H	5.325166000000	0.388716000000	-0.883751000000
H	5.325173000000	0.388820000000	0.883646000000
C	3.348077000000	-1.443859000000	-1.256054000000
H	2.328786000000	-1.835853000000	-1.308974000000
H	3.518474000000	-0.849336000000	-2.157508000000
H	4.020190000000	-2.306169000000	-1.287990000000
C	3.348086000000	-1.443709000000	1.256183000000
H	3.518494000000	-0.849079000000	2.157564000000
H	2.328795000000	-1.835693000000	1.309159000000
H	4.020197000000	-2.306017000000	1.288215000000
C	-3.632885000000	-0.559651000000	0.000085000000
C	-3.388050000000	-1.391952000000	1.256828000000
H	-2.375190000000	-1.798664000000	1.308754000000
H	-3.549735000000	-0.795169000000	2.158473000000
H	-4.074177000000	-2.242919000000	1.288315000000
C	-3.388050000000	-1.392178000000	-1.256507000000
H	-3.549720000000	-0.795555000000	-2.158260000000
H	-2.375195000000	-1.798913000000	-1.308353000000
H	-4.074185000000	-2.243144000000	-1.287848000000
C	-5.101395000000	-0.127461000000	0.000045000000
H	-5.758521000000	-1.000642000000	0.000117000000
H	-5.337940000000	0.470508000000	0.884545000000
H	-5.337936000000	0.470357000000	-0.884559000000
N	1.452227000000	2.960734000000	-0.000188000000
H	1.474415000000	5.013853000000	-0.000314000000
C	0.834161000000	4.135692000000	-0.000259000000

5a' E_{tot}= -474.105060887 a.u.

C	0.700350000000	0.002161000000	0.000000000000
C	-0.700350000000	-0.002161000000	0.000000000000
C	-1.358413000000	-1.216904000000	0.016770000000
C	-0.552389000000	-2.349161000000	0.017885000000
C	0.000000000000	2.163603000000	0.000000000000
H	-2.438704000000	-1.294531000000	0.022262000000
H	-0.996989000000	-3.336476000000	0.029778000000
C	-2.441577000000	1.810512000000	0.008727000000
H	-3.052733000000	1.072595000000	0.538358000000
H	-2.440227000000	2.726100000000	0.603059000000
C	2.453916000000	1.781217000000	-0.003247000000
H	3.043273000000	0.973443000000	-0.443709000000

H	2.506215000000	2.648777000000	-0.663867000000
N	-1.076412000000	1.326192000000	-0.007637000000
N	1.075298000000	1.331706000000	0.005370000000
H	1.457252000000	-3.113996000000	-0.012822000000
N	1.479378000000	-1.058974000000	-0.009028000000
C	0.834681000000	-2.224711000000	-0.002696000000
H	-2.823769000000	1.978696000000	-0.999820000000
H	2.815826000000	2.034753000000	0.994884000000

5b' E_{tot}= -725.487491587 a.u.

C	-0.567572000000	-2.375509000000	-0.000006000000
C	-1.351731000000	-1.225170000000	-0.000003000000
C	-0.706254000000	-0.000872000000	0.000000000000
C	0.706254000000	0.000872000000	0.000000000000
H	-1.028718000000	-3.355458000000	-0.000009000000
H	-2.432232000000	-1.295035000000	-0.000003000000
N	-1.243452000000	1.270494000000	0.000001000000
N	1.239137000000	1.273631000000	0.000001000000
C	-2.697652000000	1.350204000000	0.000002000000
H	-3.065578000000	0.803451000000	0.878666000000
H	-3.065578000000	0.803468000000	-0.878674000000
C	2.698889000000	1.345342000000	-0.000002000000
H	3.056927000000	0.785897000000	0.870878000000
H	3.056924000000	0.785957000000	-0.870924000000
Si	0.000000000000	2.521544000000	0.000000000000
H	1.438444000000	-3.144533000000	-0.000009000000
C	0.811114000000	-2.258142000000	-0.000006000000
N	1.451424000000	-1.087989000000	-0.000004000000
H	-3.025544000000	2.398459000000	0.000012000000
H	3.035779000000	2.390739000000	0.000031000000

5c' E_{tot}= -2512.85311297 a.u.

C	-2.384028000000	0.572340000000	0.000000000000
C	-1.231385000000	1.349397000000	0.000001000000
C	0.000000000000	0.709391000000	0.000000000000
C	0.000000000000	-0.709391000000	0.000000000000
H	-3.362215000000	1.037379000000	0.000000000000
H	-1.300666000000	2.429750000000	0.000002000000
N	1.249377000000	1.281013000000	0.000000000000
N	1.249857000000	-1.278142000000	0.000001000000
C	1.293591000000	2.733332000000	0.000003000000
H	0.739810000000	3.092891000000	0.878638000000
H	0.739814000000	3.092894000000	-0.878633000000
C	1.282259000000	-2.736126000000	-0.000002000000
H	0.714435000000	-3.083368000000	0.870476000000
H	0.714483000000	-3.083366000000	-0.870513000000
Ge	2.618815000000	-0.003214000000	0.000000000000
C	-2.268496000000	-0.806711000000	-0.000002000000
H	-3.155130000000	-1.434136000000	-0.000003000000

N	-1.100078000000	-1.445003000000	-0.000002000000
H	2.336505000000	3.080153000000	0.000005000000
H	2.321001000000	-3.095249000000	0.000024000000

5d' E_{tot}= -650.419039 a.u.

C	-0.000000000008	0.714549335809	0.000000000000
C	0.000000000008	-0.714549335809	0.000000000000
C	1.242619059161	-1.342032450910	0.000003079652
C	2.399455342946	-0.574021300737	0.000003101043
H	1.315657812310	-2.421516430242	0.000004585602
H	3.375137421270	-1.044597725771	0.000004426524
N	-1.221108411456	1.339030428376	0.000001391518
N	-1.221015360928	-1.343903981503	-0.000003866231
C	-1.167836243634	2.794719833414	0.000000177797
H	-0.581602802016	3.115150643839	0.869275027135
H	-0.581646914231	3.115154490957	-0.869303105280
C	-1.180574783584	-2.794019012233	0.000005835067
H	-0.608805417798	-3.128372994672	0.878281936128
H	-0.608779498696	-3.128390722110	-0.878247190350
Sn	-2.798200417393	0.003790787888	0.000000000000
N	1.114866336566	1.435053217445	-0.000001073094
C	2.284273389946	0.803356438539	0.000000938806
H	3.168893938165	1.434213963495	-0.000000392693
H	-2.206410821039	-3.191194790381	-0.000008976865
H	-2.188630904690	3.204678893449	0.000024930598

5e' E_{tot}= -628.972448317 a.u.

C	0.000000000000	0.717579000000	0.000000000000
C	0.000000000000	-0.717579000000	0.000000000000
C	-1.248929000000	-1.339167000000	-0.000012000000
C	-2.407024000000	-0.575142000000	-0.000016000000
H	-1.323575000000	-2.418351000000	-0.000019000000
H	-3.381851000000	-1.047742000000	-0.000025000000
N	1.204815000000	1.364139000000	0.000001000000
N	1.204603000000	-1.369940000000	0.000008000000
C	1.124223000000	2.816161000000	0.000000000000
H	0.533245000000	3.130317000000	0.869061000000
H	0.533253000000	3.130315000000	-0.869067000000
C	1.137981000000	-2.816455000000	0.000006000000
H	0.561880000000	-3.145857000000	0.878287000000
H	0.561929000000	-3.145861000000	-0.878306000000
Pb	2.891735000000	0.004745000000	0.000000000000
N	-1.122884000000	1.431437000000	-0.000004000000
H	-3.176122000000	1.434056000000	-0.000013000000
C	-2.291898000000	0.802200000000	-0.000011000000
H	2.121220000000	3.231368000000	0.000004000000
H	2.156362000000	-3.224021000000	0.000034000000