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

Rinat R. Aysin,*[a] Andrey V. Lalov[b] and Sergey S. Bukalov[a]

[a] *A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 119991 Moscow, Russian Federation. E-mail: aysin@ineos.ac.ru*

[b] *N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 119991 Moscow, Russian Federation*

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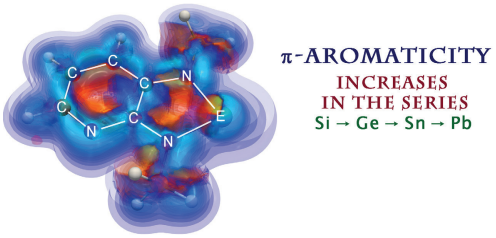
The aromaticity in 2,3-pyrido-annulated 1,3,2λ^2-diazatetroles $C_5H_3N(NR)_2E^{II}$ (E^{II} = C, Si, Ge, Sn, Pb) was studied using a set of experimental and calculated criteria: UV-VIS, Raman, ISE, NICS, GIMIC and EDDB. The data obtained indicate either a slight decrease in aromaticity (NICS, GIMIC, ISE methods) or equal aromaticity (UV-VIS, ISE methods) compared to benzo-annulated analogues $C_6H_4(NR)_2E$. The π-aromaticity increases down the group from Si to Pb.



Keywords: tetrylenes, heavier carbene analogues, aromaticity, Raman spectroscopy, electron density of delocalized bonds, gauge-including magnetically induced currents.

N-Heterocyclic carbenes and their heavier analogues (tetrylenes) are an important class of divalent compounds of the 14th group. The interest in these compounds has not subsided over the past 25 years.[1–9] The Arduengo carbene **1a**[10] and its heavy analogues containing E = Si,[11] Ge[12] or Sn[13,14] were the first synthesized compounds of this kind. Benzo-annulation results in an additional increase in thermal stability[6,15] because tetrylenes **2**[16–21] are known even in the case of E = Pb (**2e**),[21] while kinetic stabilization with bulky substituents is not required for germylene **2c** and stannylene **2d**.[16,22,23] Benzo-annulated unsymmetrical tetrylenes of amidophenolate series **3** required additional steric shielding to ensure kinetic stability.[24–27] Pyrido-annulated derivatives **4**[28,29] and **5**[30,31] were also thermally stable despite the predicted destabilizing effect,[32] while compounds of type **4** (E = Ge, Sn, Pb) exist as tetramers.[30]

The high stability of N-heterocyclic tetrylenes is due not only to the inductive acceptor effect of N or O atoms but also to the existence of the aromaticity effect[12,33–35] since the number of π-electrons satisfies the 4*n*+2 rule. We have previously studied compounds **1–3** for cyclic delocalization using a wide range of experimental and theoretical aromaticity criteria.[33–38] On passage from five-membered Arduengo tetrylenes **1** to benzo-annulated **2** and amidophenolates **3**, a gradual decrease in the degree of π-aromaticity occurred.[38] Therefore, the purpose of this work was to study the degree of cyclic delocalization of 2,3-pyrido-annulated 1,3,2λ^2-diazatetroles **5** in order to estimate their degree of aromaticity and to make a comparison with systems **1–3** in order to understand whether delocalization weakens upon incorporation of an electron-deficient pyridine ring into molecule **5** in comparison to **2**. By analogy with **1–3**, a wide range of modern aromaticity criteria were applied for the series of compounds **4**, such as the theoretical isomerization stabilization energy (ISE),[39] nuclear-independent chemical shift (NICS),[40] electron density of delocalized bonds (EDDB),[41] gauge-including magnetically induced currents (GIMIC),[42] and optical (UV-VIS and Raman) spectroscopy.[33,34] Series **5** was supplemented with calculated data for plumbylene **5e** (see Online Supplementary Materials).

The two types of ISE values for **5** (R = CH_2Bu^t) and **5′** (R = Me) were estimated by analogy with **2**[35] at the PBE0/Def2-TZVPP level (see Online Supplementary Materials, Tables S1, S2). The obtained ISE(α1) values that estimate the π-effect in both rings vary in a narrow range (–38.0 to –40.6 kcal mol^{-1}) and are slightly smaller than those for **2** (by up to 2–4 kcal mol^{-1}).[35] The values of ISE(α2) (–31.2 to –33.9 kcal mol^{-1}) that estimate the aromaticity in the pyridine ring of **4** vary slightly, too. In this case, the difference in the values of ISE(α1) and ISE(α2) (ΔISE = 4.5–8.3 kcal mol^{-1}) corresponding to the effect of the participation of the E^{II} atom in delocalization is approximately two times smaller than that for **2**.[35] It is interesting that silylenes **2b** and **5b** have the lowest stabilization energy.

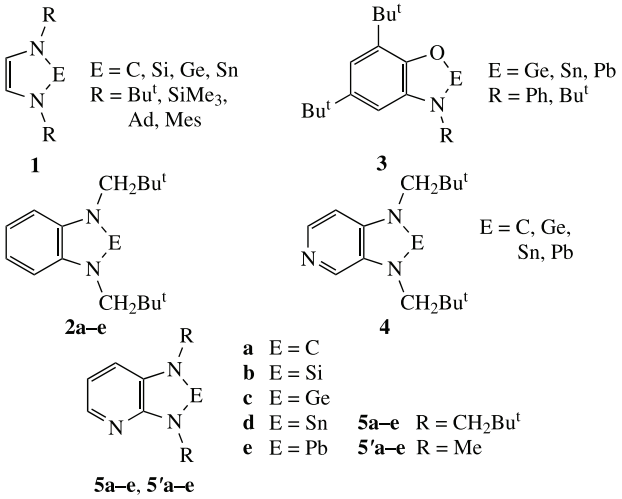


Table 1 Parameters of the calculated aromaticity criteria for **5**.

Compound (E)	ΔISE/ kcal mol^{-1}	IRCS/ nA T^{-1}	π-EDDB/ ē	$EDDB_F$ C_2N_2E/ē	Min $NICS_{zz}$	FiPC-$NICS^{40(b)}$
5a (C)	–8.3	9.6	7.28	2.50	–7.5	–4.7
5b (Si)	–4.5	7.0	7.25	2.35	–4.4	–4.2
5c (Ge)	–6.0	7.6	7.49	2.54	–4.8	–4.7
5d (Sn)	–6.1	7.4	7.68	2.54	–4.4	–4.4
5e (Pb)	–6.8	7.5	7.67	2.54	–4.3	–4.3

NICS, the most popular aromaticity criterion, was used as a combination of NICS-scan[40(*a*)] and $NICS_{in-out}$,[40(*b*)] tested previously for **1–3**.[33–36] Since the systems in question are bicyclic, the NICS values of the carbene 5-membered ring are most interesting. The graphical results for NICS (see Online Supplementary Materials) indicate that π-aromaticity exists. In fact, the NICS-scan curves completely repeat those of **2** and **3**.[33,35] To estimate π-aromaticity quantitatively, it is expedient to use the $NICS_{zz}$ and FiPC-$NICS^{40(b)}$ minima that are close in the case of heavy **5b–e** (~ –4.5 ppm) (Table 1). The absolute values of these parameters are slightly smaller than those in series **2** (by no more than 1 ppm in the case of E = Si to Pb).[35] Based on these values and from a visual comparison of the $NICS_{in-out}$ curves (see Online Supplementary Materials), the following series of decreasing aromaticity in **5** was obtained:

C > Ge ⩾ Si ~ Sn ~ Pb.

The new electronic criterion EDDB[41] proved to be a convenient quantitative criterion for estimating the degree of aromaticity in systems **1–3**.[38] In this method, delocalization is estimated by separating the electron density components [EDDB(**r**) related to delocalized bonds] matching the natural orbitals of delocalized bonds (NODB).[41] The results of the analysis of the NODB orbitals in **5** (see Online Supplementary Materials) repeat those for **2**,[38] namely, there are five highly occupied NODB1–5 orbitals, *i.e.*, ten π-electrons participate in conjugation (Figure 1 demonstrates π-type delocalization for **5c** as an example). NODB1 and NODB2 (~1.8 ē) consist of the π-AO of the pyridine, while the least populated NODB4 and NODB5 (~1.1 ē) consist of the carbene ring's AO. Atoms of the entire ring contribute to NODB3. The total population of NODB1–5 gives the π-EDDB value, which is by ~0.3 ē larger for the entire series of **5** than for the series of **2** and little changes in the following series:

Pb ~ Sn ⩾ Ge⩾ Si ~ C.

Analysis of magnetically induced currents (IC) by the GIMIC approach enables a reliable comparison of the degree of the aromaticity in systems with similar structures. In fact, at a qualitative level, the distribution of IC in **2**[36] and **5** is quite similar (see Online Supplementary Materials) and obviously indicates that the entire system is aromatic (Figure 2). It should be noted that the repetitive shape of the isosurface of IC modulus near the E atom on passage from **1** to **2**, **3** and **5** is due to the individual local current characteristics in the vicinity of the E atom.

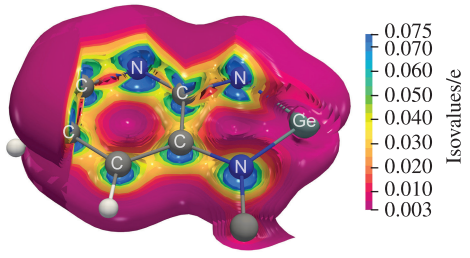


Figure 1 Multi-isosurface of the EDDB(**r**) for **5c** (Ge).

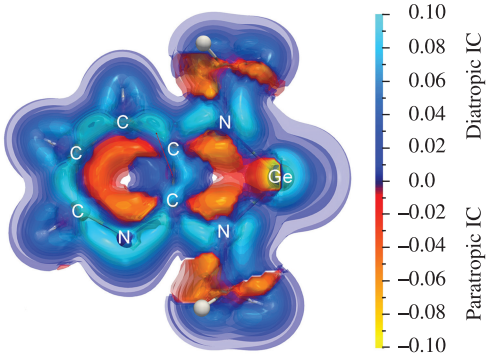


Figure 2 Isosurface of IC modulus for **5c** (Ge), isovalue scale (atomic units).

Moreover, its increase on passage to the heavy Sn and Pb can be noted (see Online Supplementary Materials). In a quantitative assessment of the induced ring current strength (IRCS values in Table 1), it turns out that in the case of pyrido 1,3,2λ^2-diazaylidene **5a**, the IRCS value is even higher by ~1.5 nA T^{-1} compared to **2a**, but it is slightly smaller in heavier **5b–e** (no more than 0.5 nA T^{-1}). Also, in the series from Si to Pb, the IRCS value changes even less than in **2**: C > Pb ~ Sn ~ Ge ⩾ Si. It should be noted that, according to the GIMIC criterion, silylenes **1** (E = Si, R = Bu^t), **2b** and **5b** are the least aromatic.

To compare the intensities of the Raman spectra of different compounds, an internal standard has to be used. In this case, the Raman spectra of **5** [Figure 3(*a*)] are normalized by the νCH stretching vibration lines of aliphatic CH_2 and CH_3 groups in the region of 2800–3000 cm^{-1}. These bands are the same in all the spectra of compounds **5**. Their intensities are not subject to the resonance effect since these groups are not involved in the π-conjugation. To assign the Raman spectra, normal coordinate analysis was performed at the TPSS/Def2-TZVP level (see Online Supplementary Materials). All the vibrations except the νCH stretching vibrations have a complex shape. These are slightly more complex than those of **2** due to a decrease in symmetry, but a general similarity exists. According to normal coordinate analysis (see Online Supplementary Materials) for **5**, the ν^1 and ν^2 vibrations of the *ortho*-substituted pyridine ring are 'pure', *i.e.* the E atom does not participate (the shapes are presented in Online Supplementary Materials), so their changes reflect the electronic structure changes. The ν^1 vibration frequency of ~1550 cm^{-1} decreases in the series from **5a** to **5e**, while its Raman intensity increases [see Figure 3(*a*)], which indicates an increase in the degree of aromaticity in this series.

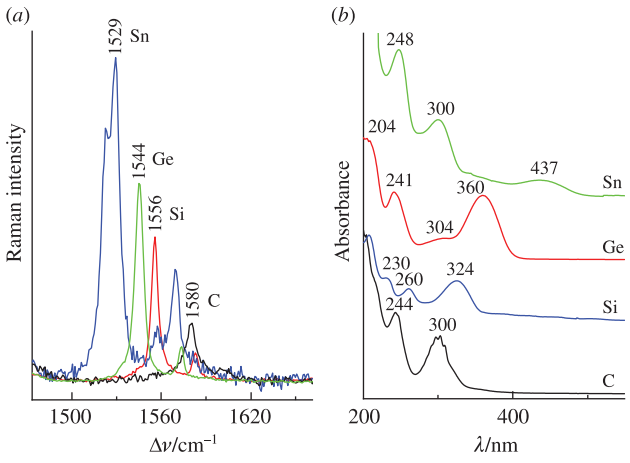


Figure 3 Fragments of (*a*) Raman spectra and (*b*) UV-VIS absorption spectra of compounds **5a–d**.

The Raman intensity increasing is connected with absorption band by pre-resonance effect.[43] The λ_{max} positions of silylene **5b** and germylene **5c** absorption, as reported previously,[28] are nearly the same as those of **2b**,**c**, respectively. The missing data on the UV-VIS spectra of **5a**,**d** were obtained for solutions in heptane and analyzed for the entire series of **5**. The results of TD-DFT calculations (see Online Supplementary Materials) show that the general appearance and changes in the UV-VIS spectra of **5a–d** should be completely analogous to those of **2a–d**. In fact, the wavelength of the π–π* transition in the absorption spectra in the series of **5** as well as in the series of **2** increases from carbene down the group [Figure 3(*b*)]. It should be noted that the band with λ_{max} = 244 nm has to be considered for carbene **5a** because exactly this line corresponds to the π–π transition (see Online Supplementary Materials). In general, the band of the π–π* transition in **5** is shifted very little with respect to that in **2**.[35] This observation indicates that the electronic structures of **2** and **5** are quite similar.

The degree of aromaticity in 2,3-pyrido-annulated tetrylenes **5** was estimated using a wide range of aromaticity criteria. The following series of aromaticity decrease were obtained:

ISE:	C ~ Pb ~ Sn ~ Ge ~ Si
Raman (ν^1), EDDB, λ_{max}(π–π*):	(Pb) > Sn > Ge > Si > C
NICS, GIMIC:	C > Ge ~ Sn ~ Pb ~ Si

These series generally differ in the position of carbene **4** (E = C), like previously for tetrylenes **1** and **2**, while the variation in the degree of aromaticity in the series of heavy **5** Si–Ge–Sn–Pb is less pronounced in comparison with **1** and **2**. The difference between the series obtained is due to the fact that IRCS value depends on the ring size. The IRCS values are greater for small ring all other things being equal. Thus, the magnetic (NICS and GIMIC) series is misrepresented. The aromaticity degree increasing in the series down the group is common for the tetrylenes **1**, **2** and also **5**, which can be rationalized by increasing the Lewis acidity (see Online Supplementary Materials) and polarizability. In general, 2,3-pyrido annulation does not result in a significant decrease in the degree of aromaticity.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2021.11.009.

References

1 N. Tokitoh and R. Okazaki, *Coord. Chem. Rev.*, 2000, **210**, 251.
2 O. Kühl, *Coord. Chem. Rev.*, 2004, **248**, 411.
3 N. J. Hill and R. West, *J. Organomet. Chem.*, 2004, **689**, 4165.
4 S. S. Karlov, G. S. Zaitseva and M. P. Egorov, *Russ. Chem. Bull., Int. Ed.*, 2019, **68**, 1129 (*Izv. Akad. Nauk, Ser. Khim.*, 2019, 1129).
5 N. Sen and S. Khan, *Chem. – Asian J.*, 2021, **16**, 705.
6 A. V. Zabula and F. E. Hahn, *Eur. J. Inorg. Chem.*, 2008, 5165.
7 V. Ya. Lee and A. Sekiguchi, *Organometallic Compounds of Low-Coordinate Si, Ge, Sn and Pb: From Phantom Species to Stable Compounds*, Wiley, Hoboken, NJ, 2010.
8 M. Asay, C. Jones and M. Driess, *Chem. Rev.*, 2011, **111**, 354.
9 Y. Mizuhata, T. Sasamori and N. Tokitoh, *Chem. Rev.*, 2009, **109**, 3479.
10 A. J. Arduengo, III, R. L. Harlow and M. Kline, *J. Am. Chem. Soc.*, 1991, **113**, 361.
11 M. Denk, R. Lennon, R. Hayashi, R. West, A. V. Belyakov, H. P. Verne, A. Haaland, M. Wagner and N. Metzler, *J. Am. Chem. Soc.*, 1994, **116**, 2691.
12 W. A. Herrmann, M. Denk, J. Behm, W. Scherer, F.-R. Klingan, H. Bock, B. Solouki and M. Wagner, *Angew. Chem., Int. Ed.*, 1992, **31**, 1485.
13 (*a*) T. Gans-Eichler, D. Gudat and M. Nieger, *Angew. Chem., Int. Ed.*, 2002, **41**, 1888; (*b*) T. Gans-Eichler, D. Gudat, K. Nättingen and M. Nieger, *Chem. – Eur. J.*, 2006, **12**, 1162.
14 A. V. Piskunov, I. A. Aivaz'yan, V. K. Cherkasov and G. A. Abakumov, *J. Organomet. Chem.*, 2006, **691**, 1531.
15 (*a*) J. Heinicke and A. Oprea, *Heteroat. Chem.*, 1998, **9**, 439; (*b*) J. Heinicke, A. Oprea, M. K. Kindermann, T. Karpati, L. Nyulászi and T. Veszprémi, *Chem. – Eur. J.*, 1998, **4**, 541.
16 (*a*) J. Pfeiffer, W. Maringgele, M. Noltemeyer and A. Meller, *Chem. Ber.*, 1989, **122**, 245; (*b*) J. Pfeiffer, M. Noltemeyer and A. Meller, *Z. Anorg. Allg. Chem.*, 1989, **572**, 145.
17 O. Kühl, P. Lönnecke and J. Heinicke, *Polyhedron*, 2001, **20**, 2215.
18 F. E. Hahn, L. Wittenbecher, R. Boese and D. Bläser, *Chem. – Eur. J.*, 1999, **5**, 1931.
19 B. Gehrhus, M. F. Lappert, J. Heinicke, R. Boese and D. Bläser, *J. Chem. Soc., Chem. Commun.*, 1995, 1931.
20 H. Braunschweig, B. Gehrhus, P. B. Hitchcock and M. F. Lappert, *Z. Anorg. Allg. Chem.*, 1995, **621**, 1922.
21 F. E. Hahn, D. Heitmann and T. Pape, *Eur. J. Inorg. Chem.*, 2008, 1039.
22 F. E. Hahn, L. Wittenbecher, D. Le Van and A. V. Zabula, *Inorg. Chem.*, 2007, **46**, 7662.
23 R. R. Aysin, L. A. Leites, S. S. Bukalov, A. V. Zabula and R. West, *Inorg. Chem.*, 2016, **55**, 4698.
24 K. V. Tsys, M. G. Chegerev, G. K. Fukin, A. G. Starikov and A. V. Piskunov, *Mendeleev Commun.*, 2020, **30**, 205.
25 M. G. Chegerev, A. V. Piskunov, K. V. Tsys, A. G. Starikov, K. Jurkschat, E. V. Baranov, A. I. Stash and G. K. Fukin, *Eur. J. Inorg. Chem.*, 2019, 875.
26 K. V. Tsys, M. G. Chegerev, G. K. Fukin and A. V. Piskunov, *Mendeleev Commun.*, 2018, **28**, 527.
27 K. V. Arsenyeva, I. V. Ershova, M. G. Chegerev, A. V. Cherkasov, R. R. Aysin, A. V. Lalov, G. K. Fukin and A. V. Piskunov, *J. Organomet. Chem.*, 2020, **927**, 121524.
28 S. Saravanakumar, A. I. Oprea, M. K. Kindermann, P. G. Jones and J. Heinicke, *Chem. – Eur. J.*, 2006, **12**, 3143.
29 A. V. Zabula, I. A. Guzei, R. West, J. Li and A. Yu. Rogachev, *Angew. Chem., Int. Ed.*, 2016, **55**, 13465.
30 F. Ullah, G. Bajor, T. Veszprémi, P. G. Jones and J. W. Heinicke, *Angew. Chem., Int. Ed.*, 2007, **46**, 2697.
31 A. V. Zabula, A. Yu. Rogachev and R. West, *Chem. – Eur. J.*, 2014, **20**, 16652.
32 J. Heinicke, A. Oprea, M. K. Kindermann, T. Karpati, L. Nyulaszi and T. Veszprémi, *Chem. – Eur. J.*, 1998, **4**, 541.
33 L. A. Leites, S. S. Bukalov, R. R. Aysin, A. V. Piskunov, M. G. Chegerev, V. K. Cherkasov, A.V. Zabula and R. West, *Organometallics*, 2015, **34**, 2278 and references herein.
34 R. R. Aysin, L. A. Leites, S. S. Bukalov, A. V. Zabula and R. West, *Inorg. Chem.*, 2016, **55**, 4698.
35 R. R. Aysin, S. S. Bukalov, L. A. Leites and A. V. Zabula, *Dalton Trans.*, 2017, **46**, 8774.
36 R. R. Aysin, L. A. Leites and S. S. Bukalov, *Int. J. Quantum Chem.*, 2018, e25759.
37 R. R. Aysin, S. S. Bukalov, L. A. Leites, A. V. Lalov, K. V. Tsys and A. V. Piskunov, *Organometallics*, 2019, **38**, 3174.
38 R. R. Aysin and S. S. Bukalov, *Russ. Chem. Bull., Int. Ed.*, 2021, **70**, 706 (*Izv. Akad. Nauk, Ser. Khim.*, 2021, 706).
39 P. v. R. Schleyer and F. Pühlhofer, *Org. Lett.*, 2002, **4**, 2873.
40 (*a*) A. Stanger, *J. Org. Chem.*, 2006, **71**, 883; (*b*) J. J. Torres-Vega, A. Vásquez-Espinal, J. Caballero, M. L. Valenzuela, L. Alvarez-Thon, E. Osorio and W. Tiznado, *Inorg. Chem.*, 2014, **53**, 3579.
41 D. W. Szczepanik, E. Żak, K. Dyduch and J. Mrozek, *Chem. Phys. Lett.*, 2014, **593**, 154.
42 D. Sundholm, H. Fliegl and R. J. F. Berger, *Wiley Interdiscip. Rev.: Comput. Mol. Sci.*, 2016, **6**, 639.
43 P. P. Shorygin, *Russ. Chem. Rev.*, 1978, **47**, 907 (*Usp. Khim.*, 1978, **47**, 1697).

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