Available online at www.sciencedirect.com

ScienceDirect

Mendeleev Commun., 2021, **31**, 481–483

Mendeleev Communications

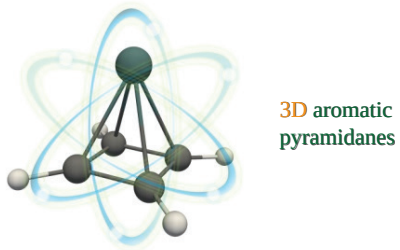
Three dimensional aromaticity in pyramidanes C_4R_4E and Ge_4R_4Ge

Rinat R. Aysin* and Sergey S. Bukalov

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

DOI: 10.1016/j.mencom.2021.07.014

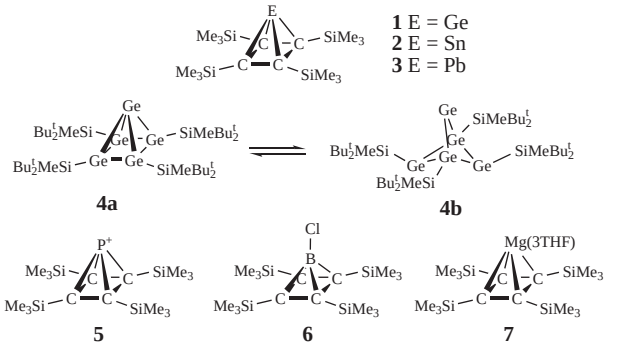
Three dimensional aromaticity in pyramidanes $C_4(SiMe_3)_4E$ (E = Ge, Sn, Pb, P^+, BCl, Mg) and $Ge_4(SiMe_3)_4Ge$ was investigated using gauge-included magnetically induced currents and electron density of delocalized bonds as two criteria. For the $C_4(SiMe_3)_4E$ compounds, different series of the aromaticity degree have been obtained by the two methods, respectively: P > Ge ⩾ Sn ~ Pb > B and Pb ⩾ Sn ⩾ Ge > B > P. Two isomers of $Ge_4(SiMe_3)_4Ge$ possess nearly equal aromaticity.



Keywords: pyramidanes, three dimensional aromaticity, aromaticity degree, 4*n*+2 rule, EDDB, GIMIC.

Pyramidanes are nonclassical cage compounds of the general formula C_4R_4E or Ge_4R_4E containing an apex E atom in tetrahedral inverted valence state, called pyramidal (Scheme 1). Structures **1**–**7** represent pyramidanes investigated in this work by quantum chemistry methods. Compounds **1**–**3** are the first reported examples of this class having the 14 group elements Ge, Sn or Pb as the pyramidal atoms.[1] A stable analogue of pentagermanium pyramidane **4** bearing di-*tert*-butyl(methyl)silyl groups is known to exist in its crystal in two forms, namely pyramidal and slightly distorted ones corresponding to structures **4a** and **4b**, respectively.[2] In the last five years compounds **5** and **6** with boron and phosphorus atoms in the apex position have been reported.[3,4]

The pyramidal valence state cannot be described by classical bonding, therefore its electronic structure has been investigated using various theoretical and experimental methods.[†,1–7] The E–C interaction in structures **1**–**6** has been found to be polar covalent, contrary to the ionic one in magnesium-containing compound **7**.[6] Using the nucleus-independent chemical shift (NICS) scan and Raman data we proposed a three dimensional conjugation in molecules **1**–**3**.[6] Multicentered E–C bonds in pyramidanes **1**–**6** originate from three orbital interactions, namely three *p*-orbitals of the C_4R_4 moiety and three *p*-orbitals of the E atom.[1–4] Therefore, the six interstitial electrons correspond to the known 4*n*+2 rule of aromaticity for pyramidane-like molecules,[8] whereas the lone pair of the apex atom E in compounds **1**–**5** is excluded from the conjugation. The four-membered base in pyramidanes **1**–**7** is trivial π-aromatic.[1,2,5–7] Probing the three dimensional delocalization represents an intricate challenge and requires the corresponding criteria to clarify it. In this work we employed electron density of delocalized bonds (EDDB)[9] and gauge-included magnetically induced currents (GIMIC)[10] as the modern and reliable criteria of aromaticity to explore delocalization in the series of compounds **1**–**7**. For comparison, the computations were also performed for simplified model molecules **1′**–**6′** (C_4H_4E or Ge_4H_4Ge)[†] bearing hydrogen atoms instead of the silyl substituents.



Scheme 1 The known pyramidanes **1**–**7**.

The GIMIC criterion for pyramidanes **1**–**7** was applied at the recommended level of theory B3LYP/Def2-TZVP.[11] Induced currents (ICs) distribution depends on the magnetic field direction, thus for these structures two orthogonal directions should be considered,[†] namely the *Z*-direction normal to the C_4 or Ge_4 base, which clearly characterizes this base, as well as the *X*-direction, which reveals delocalization in the C_2E or Ge_2Ge face and the whole cage. The plotted J_{mod} isosurfaces and streamline maps allow one to divide molecules **1**–**7** into three types.

Pyramidanes **1**–**3**, **4a** with pyramidal non-distorted geometry as well as compounds **5** and **6** all belong to type I, an example is given in Figure 1 for the simplified structure **1′**. For this type of substances, both field orientations provide a J_{mod} isosurface with diamagnetic ICs flow along the polyhedron edges and also between them, thus covering the whole polyhedron (see Figure 1),[†] while the paramagnetic ICs are weak. The IC streamline maps[†] confirm that the J_{mod} isosurfaces are formed mainly by net diamagnetic current. It is the net current that spins outside of the polyhedra around the E–C and C–C bonds.[†] Thus, the GIMIC visualization clearly demonstrates the three dimensional aromaticity in structures **1**–**3**, **4a**, **5** and **6**.

For ionic pyramidane **7**, which belongs to type II, the J_{mod} isosurface is concentrated in the region of the C_4 cycle (Figure 2). In the *Z*-field direction, the IC density distribution is typical of

† See details in Online Supplementary Materials.

© 2021 Mendeleev Communications. Published by ELSEVIER B.V. on behalf of the N. D. Zelinsky Institute of Organic Chemistry of the Russian Academy of Sciences.

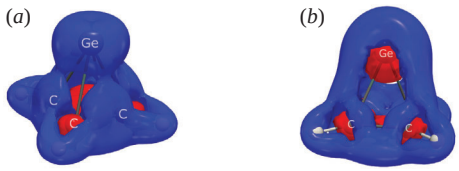


Figure 1 J_{mod} isosurfaces at 0.04 a.u. isovalue for structure **1′** (C_4H_4Ge) in the magnetic field directions (*a*) *Z* and (*b*) *X*. Diamagnetic ICs are in blue and the paramagnetic ones are in red.

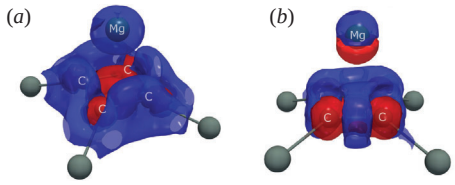


Figure 2 J_{mod} isosurfaces at 0.03 a.u. isovalue for structure **7** in the magnetic field directions (*a*) *Z* and (*b*) *X*. C, H and O atoms are omitted for clarity. Diamagnetic ICs are in blue and the paramagnetic ones are in red.

classical π aromatic ring [Figure 2(*a*)].[10] In the *X*-field direction, the density in the region of Mg–C interaction is negligible [Figure 2(*b*)]. Thus, ionic magnesium pyramidane **7** demonstrates only π-aromatic ICs in the C_4 base, as expected.

Pentagermanium cage structure **4b** with slightly distorted geometry exhibits the J_{mod} isosurface of type III (Figure 3). In both field directions, the diamagnetic ICs flow along the shortest Ge···Ge distances, *i.e.*, the Ge–Ge bond paths.[2] In the area of the longest Ge···Ge spacings, the IC density is the lowest. The streamline maps† determine the presence of net diamagnetic current, which flows along the Ge–Ge bonds (see Figure 3 and Online Supplementary Materials). Thus, the IC distribution confirms that the pseudo-pyramidane structure **4b** exhibits three dimensional aromaticity as well, but its topology differs from the one for compound **4a**.

The induced ring current strength values† for the *Z*-direction ($IRCS_Z$) characterize only aromaticity in a four-membered base, whereas the $IRCS_X$ values reflect the degree of three dimensional delocalization (Table 1). The $IRCS_Z$ values are significantly smaller than the $IRCS_X$ ones, as expected. Among the molecules explored, the $IRCS_Z$ value is the smallest for ionic structure **7**. For covalent pyramidanes **1**–**6**, the $IRCS_X$ values are 12.6–18.0 nA T^{-1}, in contrast to that for compound **7** (1.3 nA T^{-1}), for which no three dimensional delocalization has been observed. Note that the introduction of $SiMe_3$ substituents slightly decreases the IRCS values up to ~1 nA T^{-1}, as expected. The degrees of aromaticity for structures **2** and **3**, namely 14.9 and 15.2 nA T^{-1}, can be considered as nearly equal. Thus, the quantitative GIMIC data of Table 1 demonstrates that the degree of aromaticity for C_4E pyramidanes diminishes in the series P (compound **5**) > Ge (compound **1**) ⩾ Sn (compound **2**) ~ Pb (compound **3**) > B (compound **6**).

In spite of the different topology of IC density for the two geometric isomers of the pentagermanium pyramidane **4**, namely **4a** of the type I and **4b** of the type III, their IRCS values are close

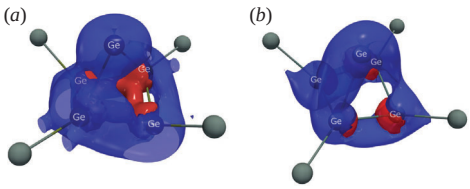


Figure 3 J_{mod} isosurfaces at 0.025 a.u. isovalue for structure **4b** in the magnetic field directions (*a*) *Z* and (*b*) *X*. C and H atoms are omitted for clarity. Diamagnetic ICs are in blue and the paramagnetic ones are in red.

with the difference 0.4–0.9 nA T^{-1} and change their sign for the hydrogen-substituted simplified model compounds. This fact suggests the nearly equal degree of aromaticity and corresponds to a small energy gap between the di-*tert*-butyl(methyl)silyl counterparts of isomers **4a** and **4b** coexisting in the crystal.[2]

The results of EDDB population analysis† demonstrate that only three natural orbitals of delocalized bonds (NODBs) are characterized by high populations with nearly equal values, which proves the conjugation of six delocalized interstitial electrons. Compounds **1**–**3** exhibit the highest NODB population of ~1.2 ē, pyramidanes **5** and **6** have the medium population of ~0.9 ē, while structures **4a** and **4b** reveal the lowest one of ~0.6 ē. The forms of the three NODBs† resemble canonical molecular orbitals responsible for pyramidane bonding.[1–4] The similarity of orbitals for isomeric structures **4a** and **4b** is notable.† The forms of NODBs with significant participation of the E atom point to delocalization over the cage, thus the EDDB(*r*) isosurfaces for compounds **1**–**6** are mainly created by delocalized pyramidane bonds (Figure 4).

According to Figure 4, a cavity around the apex atom is present, which originates from the exclusion of the inner shell of heavy E atom from the EDDB(*r*) function. The reduced density in the region of E atoms, *i.e.*, the E–C bonds, is observed, though this effect is smaller compared with the one reported for E–N bonds in tetrylenes.[12] The EDDB(*r*) isosurface data allows one to divide the pyramidane series into the following three types. Structures **1**–**3**, **4a**, **5** and **6** all belong to type I [Figure 4(*a*)–(*d*),(*f*),(*g*)], ionic compound **7** is of type II as a π-cloud [Figure 4(*h*)] and finally distorted structure **4b** is of type III [Figure 4(*e*)]. This classification coincides exactly with the GIMIC visualization results. It is notable that the isovalue for compounds **5** and **6** is greater than that for structures **1**–**4**, which indicates a high density of the EDDB(*r*) function due to the smaller cage size [see Figure 4(*f*),(*g*)].

The integrated EDDB values were estimated considering (i) all atoms in the molecule ($EDDB_H$) as well as (ii) the C_4E-polyhedron and C_4 base moieties ($EDDB_F$) (Table 2). The $EDDB_H$ values are greater than their counterparts dissected by the three NODBs and the $EDDB_F$ values for the C_4E cage, which points out the significant participation of conjugated $SiMe_3$ groups. The amount of efficient delocalized electrons in the C_4E cage ($EDDB_F$) for structures **1**–**7** is 2.28–4.05 ē. For the covalent pyramidanes **1**–**6** these values are doubled compared with those for the C_4 base, and this observation additionally proves the three dimensional effect. For ionic compound **7**, the $EDDB_F$ values for the C_4 base and C_4Mg moieties are nearly equal, namely 3.44 and 3.54 ē. Therefore, the delocalization with a degree of 57% in structure **7** is only of a π-type for the C_4-ring, in contrast to the three dimensional

Table 1 IRCS values obtained for the magnetic field directions *Z* and *X*.

Molecule	$IRCS_Z$/nA T^{-1}	$IRCS_X$/nA T^{-1}
1 [$C_4(SiMe_3)_4Ge$]	8.1	16.1
2 [$C_4(SiMe_3)_4Sn$]	7.6	14.9
3 [$C_4(SiMe_3)_4Pb$]	7.6	15.2
4a [$Ge_4(SiMe_3)_4Ge$]	9.0	18.0
4b [$Ge_4(SiMe_3)_4Ge$]	8.7	17.1
5 [$C_4(SiMe_3)_4P^+$]	9.1	18.2
6 [$C_4(SiMe_3)_4BCl$]	6.3	12.6
7 [$C_4(SiMe_3)_4Mg$-3THF]	4.2	1.3
1′ (C_4H_4Ge)	8.4	16.8
2′ (C_4H_4Sn)	8.3	16.2
3′ (C_4H_4Pb)	8.1	15.3
4′a (Ge_4H_4Ge)	8.9	16.7
4′b (Ge_4H_4Ge)	8.6	17.3
5′ ($C_4H_4P^+$)	9.3	18.5
6′ (C_4H_4BCl)	6.4	13.1

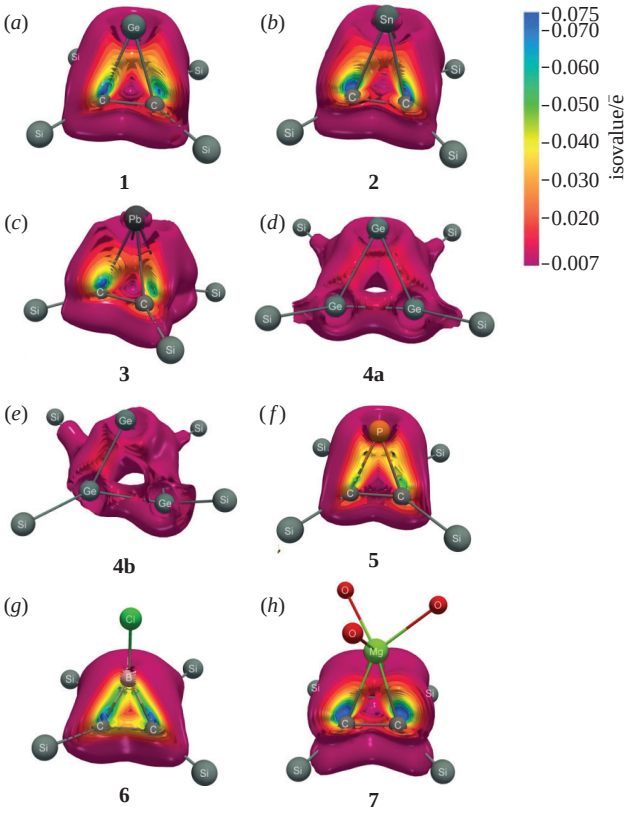


Figure 4 EDDB(*r*) isosurface for structures **1**–**7** at isovalue range of 0.007–0.075 ē. C and H atoms are omitted for clarity.

aromatic molecules **1**–**6**. The quantitative EDDB results demonstrate that the aromaticity degree for C_4E pyramidanes decreases in the series Pb (compound **3**) ⩾ Sn (compound **2**) ⩾ Ge (compound **1**) > B (compound **6**) > P (compound **5**).

In this series the strongest aromaticity with ~60% delocalization degree is obtained for pyramidanes **1**–**3** of the group 14 elements, which disagrees with the GIMIC results. Note that the EDDB values for isomeric structures **4a** and **4b** are practically the same with less than 2% difference and indicate the smallest aromaticity degree for compound **4** among the pyramidanes investigated, which corresponds to the GIMIC data.

In conclusion, the results from the two methods applied agree qualitatively with each other and demonstrate the three dimensional aromaticity for compounds **1**–**6**. According to the quantitative data for C_4E-pyramidanes **1**–**3**, **5** and **6**, two different series of the aromaticity degree are obtained, namely P > Ge ⩾ Sn ~ Pb > B using GIMIC and Pb ⩾ Sn ⩾ Ge > B > P with EDDB. The GIMIC results for compounds **1**–**3** correspond to NICS scan data, whereas the EDDB ones agree well with Raman spectra.[6] Analogous series aromaticity degree have been demonstrated for aromatic tetrylenes.[13,15] According to both methods employed, the aromaticity degrees for isomeric pentagermanium compounds **4a** and **4b** are nearly equal and represent the smallest ones in the series explored. The little difference between structures **4a** and **4b** is not surprising due to their similar molecular orbital patterns.

The phenomenon of aromaticity represents a multidimensional property and cannot be measured directly, thus an incongruity of qualitative descriptors frequently occurs for various hydrocarbons as well.[9,16,17] Probably, the discrepancies for the pyramidane series are associated with characteristics of the methods employed† as well as σ-conjugation, because the EDDB approach in some instances cannot provide an accurate estimation for the σ-aromaticity,[18] contrary to the GIMIC method.[11,19]

Table 2 Amount of delocalized electron in molecules **1**–**7** ($EDDB_H$) as well as their C_4 and C_4E moieties ($EDDB_F$).

Molecule		$EDDB_H$	$EDDB_F$		Dissected $EDDB_H$[a]
			C_4	C_4E	
1	$[C_4(SiMe_3)_4Ge]$	6.05	1.70	3.50	3.45
2	$[C_4(SiMe_3)_4Sn]$	6.29	1.72	3.60	3.70
3	$[C_4(SiMe_3)_4Pb]$	7.70	1.46	3.70	3.86
4a	$[Ge_4(SiMe_3)_4Ge]$	5.69	1.03	2.78	2.00
4b	$[Ge_4(SiMe_3)_4Ge]$	5.56	1.04	2.65	1.74
5	$[C_4(SiMe_3)_4P^+]$	4.78	0.89	2.38	2.27
6	$[C_4(SiMe_3)_4BCl]$	5.96	1.27	2.91	2.43
7	$[C_4(SiMe_3)_4Mg\text{-}3THF]$	8.06	3.44	3.54	4.05

[a] Dissected $EDDB_H$ represents a sum of NODB1, NODB2 and NODB3 populations. For comparison, the $EDDB_H$ value for π-aromatic cyclobutadiene dianion is 4.71 ē.

The article is dedicated to the cherished memory of Larissa A. Leites. This work was supported by the Ministry of Science and Higher Education of the Russian Federation.

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2021.07.014.

References

1 V. Y. Lee, Y. Ito, A. Sekiguchi, H. Gornitzka, O. A. Gapurenko, V. I. Minkin and R. M. Minyaev, *J. Am. Chem. Soc.*, 2013, **135**, 8794.
2 V. Y. Lee, Y. Ito, O. A. Gapurenko, A. Sekiguchi, V. I. Minkin and R. M. Minyaev, *Angew. Chem., Int. Ed.*, 2015, **54**, 5654.
3 V. Y. Lee, H. Sugasawa, O. A. Gapurenko, R. M. Minyaev, V. I. Minkin, H. Gornitzka and A. Sekiguchi, *Chem. – Eur. J.*, 2016, **22**, 17585.
4 V. Y. Lee, H. Sugasawa, O. A. Gapurenko, R. M. Minyaev, V. I. Minkin, H. Gornitzka and A. Sekiguchi, *J. Am. Chem. Soc.*, 2018, **140**, 6053.
5 V. Y. Lee, O. A. Gapurenko, Y. Ito, T. Meguro, H. Sugasawa, A. Sekiguchi, R. M. Minyaev, V. I. Minkin, R. H. Herber and H. Gornitzka, *Organometallics*, 2016, **35**, 346.
6 L. A. Leites, R. R. Aysin, S. S. Bukalov, V. Y. Lee, H. Sugasawa and A. Sekiguchi, *J. Mol. Struct.*, 2017, **1130**, 775.
7 O. A. Gapurenko, V. Y. Lee, R. M. Minyaev and V. I. Minkin, *Heteroat. Chem.*, 2019, 3659287.
8 E. D. Jemmis and P. v. R. Schleyer, *J. Am. Chem. Soc.*, 1982, **104**, 4781.
9 D. W. Szczepanik, E. Żak, K. Dyduch and J. Mrozek, *Chem. Phys. Lett.*, 2014, **593**, 154.
10 D. Sundholm, H. Fliegl and R. J. F. Berger, *WIREs Comput. Mol. Sci.*, 2016, **6**, 639.
11 H. Fliegl, S. Taubert, O. Lehtonen and D. Sundholm, *Phys. Chem. Chem. Phys.*, 2011, **13**, 20500.
12 R. R. Aysin and S. S. Bukalov, *Russ. Chem. Bull., Int. Ed.*, 2021, **70**, 706 (*Izv. Akad. Nauk, Ser. Khim.*, 2021, 706).
13 R. R. Aysin, L. A. Leites and S. S. Bukalov, *Int. J. Quantum Chem.*, 2018, **118**, e25759.
14 D. W. Szczepanik and M. Solà, *ChemistryOpen*, 2019, **8**, 219.
15 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.
16 P. v. R. Schleyer, *Chem. Rev.*, 2005, **105**, 3433.
17 M. K. Cyrański, *Chem. Rev.*, 2005, **105**, 3773.
18 D. Chen, D. W. Szczepanik, J. Zhu and M. Solà, *Chem. Commun.*, 2020, **56**, 12522.
19 R. R. Aysin, L. A. Leites and S. S. Bukalov, *Organometallics*, 2020, **39**, 2749.

Received: 24th February 2021; Com. 21/6460