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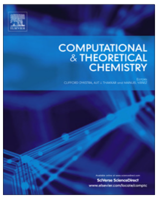

Spherical aromaticity in C-, Si-, and Ge-containing compounds

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ABSTRACT

Various dismutative structures of the form $[E(EX)(EX_2)]_2$ with E being C, Si, and/or Ge and X being some side group (H, CH_3, F, or Cl) were studied with the special purpose of identifying signals for aromaticity in those compounds. Also a dismutative analogue of pyridine was studied. In order to identify signals of aromaticity we focused on the total energy, the HOMO–LUMO energy gap, the variation of the nearest-neighbour bond lengths along the backbone, and NICS and $NICS_{zz}$ as functions of the distance along a normal to a plane of the molecule. In many cases, strong distortions from a nearly-planar structure were observed. Only in few cases, the bond lengths could suggest the existence of aromaticity or anti-aromaticity. On the other hand, in many cases NICS and $NICS_{zz}$ give signals that suggest the existence of aromaticity similar to that of spherical cluster compounds.

1. Introduction

Aromaticity and anti-aromaticity are phenomena that have inspired generations of theoretical and experimental chemists [1,2]. Aromatic compounds are ubiquitous in all areas of organic chemistry from biological species to materials. The definition of as well as the relevant observable criteria for (anti-) aromaticity have changed over the years, and they are still subject to controversy even about 85 years after Hückel's seminal paper on the $4n+2$ rule [3,4]. The presence of one or more cyclically or spherically delocalized electrons, however, is a necessary albeit trivial condition. Conversely, the notion of increased stability often associated with aromaticity heavily depends on a suitable reference system and is thus not free of ambiguity [5]. The same applies to most geometric criteria (e.g. bond-length equalization and planarity), which constitute an oversimplifying idealization based on the optimization of orbital overlap [6]. According to Ampere's law, the application of an external magnetic field induces a closed current loop in the delocalized electrons, which – although not experimentally observable in itself – generates an internal magnetic field that may either increase (diatropic, aromatic compounds) or decrease (paratropic, anti-aromatic compounds) the local magnetic field. As a consequence, atomic nuclei within this induced internal field experience a shift of their magnetic resonance, intricately associated to aromaticity effects [7]. This shift can either be observed experimentally for real nuclei such as ^7Li (see, e.g., the review by Mitchell [8]) or – according to Schleyer – be calculated as a nucleus independent chemical shift (NICS) for ghost atoms arbitrarily positioned in or close to the current loop [9,10].

In the context of the invalidation of the so-called 'double bond' rule [11] through the isolation of stable compounds with double bonds between heavier maingroup elements in the late 1970s and early 1980s [12–17], heavier Hückel aromatic and antiaromatic species were soon considered, in which carbon would be formally substituted by heavier group-14 elements [18,19]. Since then numerous stable examples were isolated including homonuclear silicon analogues of the cyclopropenium cation [20], cyclobutadiene [21], and its dianion [22]. Analogues of the cyclopentadienyl anion [23,24] and benzene [25,26] with partial replacement of the carbon atoms of the cyclic scaffold by silicon are known, but shown to be non-aromatic in the case of the former. In most of these cases, the theoretical characterization of these compounds as being aromatic, anti-aromatic, or non-aromatic was based on using the NICS criterion.

Inorganic chemistry contributed particularly to the development of complementary concepts of aromaticity that were shown to be thermodynamically competitive if not – in some cases – superior to Hückel aromaticity [27–30]. For instance, the surprisingly strong homo-aromaticity of certain boron heterocycles [31] is intricately related to the assumed spherical aromaticity of boron clusters [32]. Some of us have recently disclosed a stable tricyclic

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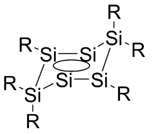
isomer **1** of the hypothetical hexasilabenzene, which based on the computed NICS(0) value was concluded to be aromatic [33]. The term 'dismutational aromaticity' was coined to account for the fact that the substitution pattern was formally the result of a twofold dismutation of the ring silicon atoms. Notably, the six electrons presumably involved consist of pairs of non-bonding, σ-bonding, and π-bonding electrons. The global minimum isomer **2** is obtained by thermal rearrangement of **1** [34]. Unprecedentedly wide chemical-shift distributions were attributed to magnetically induced currents, which are topologically related to those typically observed for clusters such as the P_4 tetrahedron and related species [35]. The description of **1** and **2** as metalloid clusters gained further support by experimental evidence for the absence of through-space bonding between the unsubstituted bridgehead atoms [36]. On the basis of the notion of cluster bonding in silicon-rich compounds with unsubstituted silicon atoms with hemispheroidal coordination environment as well as due to similarities to structural motifs encountered on silicon surfaces and the elemental bulk the term 'siliconoids' was recently coined for these and related species [37].



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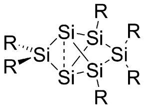

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Also many theoretical studies have been carried through with the purpose of identifying aromatic molecules. As in experiment, the precise definition of 'aromaticity' is not clear and several different criteria can be and have been applied. By comparing with the prototype of the aromatic molecules, benzene, many studies have focused on identifying molecules for which the most stable structure is planar and cyclic, which indeed is the case for benzene [38] and which provides criteria that also can be applied experimentally. In a fairly recent study with direct relevance for the present work, Boldyrev et al. studied the systems obtained by replacing n of the silicon atoms of Si_6H_6 scaffold with n carbon atoms and investigated the potential energy landscapes of the resulting $Si_{6-n}C_nH_6$ manifolds [39]. Three silicon atoms turned out to be sufficient to favor a cluster-like arrangement analogous to the global minimum isomer **2** in comparison to a planar benzene-like structure. Experimentally, the formal substitution of the bridgehead positions of Si_6R_6 (R = 2,4,6-triisopropylphenyl) was recently realized [40]. In passing we add that the global minimum motif of Si_6H_6 has also served as inspiration in the computational prediction of silicon nanosheet structures [41].

However, many other criteria for aromaticity have been proposed of which most are accessible with theoretical methods only. Such criteria have been applied first of all to carbon-based systems [42–44] whereby benzene can act as a useful reference system. But also quite different types of systems have been studied under the rubric aromaticity including metal clusters [45,46] although these appear to be those most distant from the traditional area of aromatic systems. It is clear that in this case it is no longer possible to compare directly with benzene and adjusted criteria have to be applied.

Also in the present work we shall consider carbon-free systems as well as carbon-based structures. We shall study planar and non-planar structures of the form E_6R_6, whereby E equals C, Si, and/or Ge, and R equals H, CH_3, F, and/or Cl. Special emphasis will be put on the question how different molecules can be and still possess properties that can be related to aromaticity.

Related planar systems of the form $E_2E'H_3^+$ with E and E′ being C, Si, Ge, Sn, and/or Pb have been treated by Fernández et al. [47], whereas Rouf et al. [48] studied various cyclic $C_xSi_yN_{6-x-y}H_z$ molecules with a largely planar backbone. In our analysis of aromaticity we shall use a criterion recently applied by Velian and Cummins [49] on $P_2N_3^-$, i.e., a NICS-derived quantity whereby the NICS is calculated as a function of distance along a given direction above a predefined plane. This, we believe, will allow to take into account effects due to the different sizes of the C, Si, and Ge atoms and of having structures that are far from planar.

In its original formulation [9], NICS is the isotropic magnetic shielding of a dummy atom placed at the center of the ring system whose aromaticity shall be determined. A negative value implies aromaticity and a positive value anti-aromaticity. As a criterion of aromaticity, NICS has several advantages. It is computationally easy to calculate and can be applied to also larger molecules. In addition, NICS is not restricted to planar compounds but can also be used for three-dimensional clusters and cage molecules. Being a local property calculated relatively distant from the nuclei, NICS is fairly insensitive to the level of theory employed (i.e., basis set and method). Moreover, NICS is an absolute measure of aromaticity in the sense that its evaluation does not rely upon information for any reference compounds. Finally, NICS often correlates very well with other quantitative or qualitative aromaticity indexes, which may be much more difficult to obtain or to define reliably.

However, even for planar systems NICS does not depend purely on the existence of a π-electron system but also on other magnetic shielding contributions due to, e.g., σ orbitals, lone pairs and core electrons. NICS can be an absolute measure of cyclic electron delocalization only when the radii of the systems are relatively large and hence local shielding effects are negligible. In this case, the contribution from the σ orbitals to NICS is much smaller than that of the π orbitals. However, when the contribution from delocalized σ electrons to the magnetic shielding is dominating, one may classify the systems as being σ aromatic.

Often, it is useful to separate NICS into contribution from the different types of orbitals, i.e., for planar systems, NICS will be separated into NICS_π and NICS_σ contributions [10]. Then, when shifting the position of the dummy atom along the normal to the ring system (which we will define as the z axis with $z = 0$ in the plane of the system), NICS_σ falls off faster than NICS_π. For this reason, a NICS(1) value has been introduced, which is the value of NICS for z being 1 Å above the ring center [50]. Furthermore, for σ-aromatic compounds NICS as a function of z will have a minimum at $z = 0$ but for π-atomatic compounds a minimum will occur for $z > 0$.

In order to characterize the π systems better, NICS_{zz} was introduced [51], which quantifies the z component of the shielding field for an applied magnetic field along the z direction. NICS_{zz} was found to be more useful in quantifying aromaticity than the isotropic NICS, as it corresponds more directly to the induced current densities in a molecular ring system. When comparing various NICS indexes, the $\text{NICS}_{\pi,zz}(0)$ was found to perform best for planar ring systems containing π electrons with the easily calculatable $\text{NICS}_{zz}(1)$ index being a useful alternative [52].

For non-planar ring systems and for systems containing other types of atoms than carbon, it is less obvious how to identify aromaticity. One reason is that the z direction then is not unique. Second, different sizes of the atoms and spatial extend of π-like orbitals compared to the case for planar, carbon-based systems make it unclear whether a distance of 1 Å above a ring is an optimal distance for identifying a π-electron dominating contribution. Third, lacking reference results, it becomes difficult to correlate a single number with aromaticity or anti-aromaticity. Therefore, following an earlier proposal by Stanger [53], Velian and Cummins [49] decided to plot some NICS-derived quantity as a function of the position along the pre-chosen z axis. A local minimum for a