Polyhedron 80 (2014) 69–80

Contents lists available at ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

DFT investigation of the influence of Jahn–Teller distortion on the aromaticity in square-planar arsenic and antimony clusters

Marko Perić [a], Ljubica Andjelković [a], Matija Zlatar [a], Claude Daul [b], Maja Gruden-Pavlović [c,*]

[a] Center for Chemistry, IHTM, University of Belgrade, Studentski Trg 12-16, 11001 Belgrade, Serbia
[b] Department of Chemistry, University of Fribourg, Chemin du Musée 9, CH-1700 Fribourg, Switzerland
[c] Faculty of Chemistry, University of Belgrade, Studentski Trg 12-16, 11001 Belgrade, Serbia

ARTICLE INFO

Article history:
Received 26 December 2013
Accepted 4 February 2014
Available online 13 February 2014

Keywords:
DFT
Metalloid clusters
Aromaticity
Jahn–Teller

ABSTRACT

Density functional theory (DFT) calculations were performed to investigate aromaticity of tetra atomic metalloid clusters, As_4^{2-} and Sb_4^{2-}. The careful analysis of nuclear independent chemical shifts (NICS) revealed strong σ antiaromatic and week π aromatic character of investigated species. This unexpected behavior is explained through the analysis of antagonistic paratropic and diatropic contributions, and with detailed adaptive natural density partitioning (AdNDP) analysis. Furthermore, we investigated aromatic/antiaromatic behavior of Jahn–Teller (JT) active species As_4^- and Sb_4^-. NICS parameters have been scanned along the Intrinsic Distortion Path (IDP) showing strong antiaromaticity which decreases with increasing deviation from D_{4h} to D_{2h} symmetry.

1. Introduction

Language of chemistry is composed of vast number of concepts, like aromaticity, hybridization, electronegativity, covalency, steric hindrance... These concepts became integral part of what is considered to be a chemical intuition, enabling easy understanding of different chemical phenomena and rationalization of both experimental and theoretical results based on such understanding. Usefulness of various chemical concepts goes even further, as their employment is frequently first step towards a prediction of new properties, at least in a qualitative manner. From these reasons, it is evident why computational studies are often focused to seek origin, accurate determination of such concepts, and their precise definitions in quantum mechanical terms. Aromaticity and its antipode, antiaromaticity, are examples of such notions [1–6], vastly used to intuitively describe chemical bonding in organic chemistry. Delocalized electronic structure of aromatic compounds yields enhanced planarity, equalized bond lengths, enhanced stability, favoring of substitution instead of addition that would be typical for isolated double bonds, and the ability to sustain ring currents when exposed to external magnetic fields. Initially aimed to describe properties of planar organic cyclic compounds, with $4n + 2$ π electrons, concept of aromaticity, has been extended to $4n$ triplet aromaticity [7], pericyclic transition states [8], Moebius aromaticity [9], 3D and spherical aromaticity [10], and in particular, entered the field of inorganic chemistry [11–13]. Aromaticity in metal and metalloid clusters is subject of intensive research [13–18] since the discovery of Al_4^{2-} using photoelectron spectroscopy and *ab initio* calculations [19,20]. The aromaticity in these species is unusual and its analysis is challenging task due to the so-called multifold aromaticity and conflicting aromaticity [14,15,18,21], necessitating careful inspection of typical counting rules [22] and application of different aromaticity criteria [17,23–26].

Despite of diverse utilization of aromaticity and antiaromaticity, both in organic and in inorganic chemistry, these two concepts are still mainly confined to molecules with an even number of electrons. Species with $4n + 2$ π electrons are aromatic, whereas structures with $4n$ π electrons are defined as antiaromatic. Molecules with odd number of π electrons are seldom studied, and are supposed to show antiaromaticity [27–30]. Thus, removal of one electron from $4n + 2$ π system should result in a $4n + 1$ π system, and transition from aromaticity to antiaromaticity is expected. Understanding this transition and relation between $4n + 2$ π and $4n + 1$ π systems is connected fundamentally to the understanding of concepts of aromaticity and antiaromaticity. Detachment of electron from typical aromatic molecule, which is closed shell, planar, highly symmetric and with degenerate frontier orbitals, will lead to a $4n + 1$ π molecule in a degenerate electronic state that is subject to the Jahn–Teller (JT) effect [31,32]. Bearing in the mind that JT theorem state that a molecule with a degenerate electronic state

* Corresponding author. Tel.: +381 11 3336754.
E-mail address: gmaja@chem.bg.ac.rs (M. Gruden-Pavlović).

http://dx.doi.org/10.1016/j.poly.2014.02.005
0277-5387/

distorts along non-totally symmetric vibrational coordinates by removing the degeneracy and lowering the energy, it is obvious that JT effect is in sharp contrast to the aromaticity. In other words, JT effect induces unequalization of bond lengths, leading to the stabilization of the system upon distortion. It is worthwile mentioning that, differently to the concept of aromaticity, JT effect is deply rooted in quantum mechanics [32], and there is no ambiguity in its deffinition. Ramifications of the JT effect are far reaching, it influences the high-T_C superconductivity [33], large magnetoresistance in manganites [34], superconductivity in fullerides [35–37] and many other properties. Connection between aromatic $4n + 2$ π molecule, and related $4n + 1$ π JT active molecule has been studied in the case of benzene and its cation [29]. Based on the analysis of nuclear independent chemical shifts (NICS) [38,39] benzene cation showed unusually high antiaromaticity in the high symmetry nuclear configuration (D_{6h}) which decreases upon the distortion [29]. In this work, we will expand this type of analysis to investigate the aromaticity of four-atomic metalloid clusters based on arsenic and antimony. More specifically, detailed density functional theory (DFT) analysis of the JT active $4n + 1$ π As_4^- and Sb_4^- and their parent, square-planar, $4n + 2$ π As_4^{2-} and Sb_4^{2-} species has been performed. JT effect in mono-anionic clusters, the simplest $E\otimes(a_1 + b_1 + b_2)$ multimode JT problem [32,40], has been analyzed by the means of multideterminantal DFT approach [41,42], and their full NICS profile along the Intrinsic Distortion Path (IDP) [41,43] has been scanned in order to understand their aromatic behavior [29,44]. IDP gives direct insight to the microscopic origin, mechanism and consequences of distortion [43,45]. Square-planar, As_4^{2-} and Sb_4^{2-} are well-known building blocks of solid materials, for example in $(2,2,2\text{-crypt-}K^+)_2Sb_4$ crystal [46], $(K@18\text{-crown-}6)_2As_4$ [47], $[Na(NH_3)_5]_2As_4{\cdot}2NH_3$ [48], $[Nb(\eta^5\text{-}Cp^*)(CO)_2(\eta^4\text{-}As_4)]$ [49]. These clusters are valent isoelectronic to the classical aromatic $C_4H_4^{2-}$ di-anion, and often considered to be examples of inorganic aromatic compounds. Aromatic character of $2Na^+As_4^{2-}$ and $2Na^+Sb_4^{2-}$, and antiaromatic character of $Na^+As_4^-$ and $Na^+Sb_4^-$, was confirmed from molecular orbital (MO) analyses and verified by experimental photodetachment spectra [30]. Contrary to these findings, NICS profile of As_4^{2-} and Sb_4^{2-} show anti-aromoaticity [50], or non-aromaticity [51] and electron localization function for As_4^{2-} exhibit delocalization trough the lone pairs [47]. It seems that, in spite of relatively simple composition, the structure and aromatic properties of four-member metalloid rings, though studied experimentally [30,47,52,53] and computationally [30,47,51,54–57] have not been fully rationalized so far. Thus, in this work, in addition to answering the important issue of the JT influence on the aromatic behavior of As_4^- and Sb_4^-, we try to rationalize above mentioned discrepancies in determination of aromaticity in As_4^{2-} and Sb_4^{2-}. The standard NICS analysis is supplemented by determination of the most significant $T_{x,y}$ (translationaly)- and R_z (rotationaly)-allowed occupied → unoccupied MO transitions [58] and with adaptive natural density partitioning (AdNDP) analysis [26] and compared to the well-known aromatic Al_4^{2-}.

2. Computational details

All investigated molecules were optimized by DFT calculations using the Amsterdam Density Functional program package, ADF2010.01 [59–61]. The local density approximation (LDA) characterized by the Vosko–Willk–Nusair (VWN) [62] parameterization was used for the symmetry-constrained geometry optimizations. In addition, BP86 [63,64], B3LYP [65,66] and M06-L [67,68] exchange–correlation functional were employed. An all electron Triple-zeta Slater-type orbitals (STO) plus one polarization function (TZP) basis set was used for all atoms. Analytical harmonic frequencies [69,70] were calculated, and in all cases the character of stationary points was determined.

Calculations of NICS values [38,39] were performed at the B3LYP level of theory using the GAUSSIAN 09W program package [71]. NICS indices were calculated with 6-311+G* basis set for Al_4^{2-}, As_4^{2-} and As_4^-, while LANL2DZ was used for antimony clusters, since the 6-311+G* basis set is not available for Sb. NICS parameters were calculated for ghost atoms located at the center of Al_4^{2-}, As_4^{2-}, Sb_4^{2-}, As_4^- and Sb_4^-. In order to obtain the full profile of aromatic behavior, calculations of NICS parameters were performed from 0 to 5 Å from the center of the rings, in steps of 0.5 Å. Moreover, NICS parameters for JT active molecules were scanned along the IDP [41,43].

Diatropic (aromatic) and paratropic (antiaromatic) contributions to the induced ring current are described with following equation:

$$\sigma = \frac{1}{2c^2}\sum_i^{occ}\left\langle \Psi_i\left|\frac{rr_N I - r_N\otimes \mathrm{r}}{|r-R_N|^3}\right|\Psi_i\right\rangle - \frac{2}{c}\sum_i^{occ}\sum_a^{unocc}\frac{1}{\varepsilon_i-\varepsilon_a}\left\langle \Psi_i\left|\frac{L_N}{|r-R_N|^3}\right|\Psi_a\right\rangle \otimes \langle\Psi_a|L_N|\Psi_i\rangle \quad (1)$$

The symbol r refers to the electronic position and R_N to the vector position where the shielding is calculated. L_N is the angular momentum operator, ε_i and ε_a are the eigenvalues of the occupied and unoccupied molecular orbital, respectively.

The detailed adaptive natural density partitioning (AdNDP) analysis [26] were performed with MULTIWFN3.2 program package [72].

2.1. Relevant theory of JT effect in square-planar molecules

The theory of the JT effect in square-planar systems is documented in detail [32,40,73] and is based on a perturbation expression of the potential energy surface at and near the point of electronic degeneracy. The Hamiltonian for the system is to the second order in the normal coordinates, Q_i:

$$\hat{H} = \hat{H}_0 + \sum_i \frac{\partial \hat{H}}{\partial Q_i}Q_i + \frac{1}{2}\sum_{i,j}\frac{\partial^2\hat{H}}{\partial Q_i\partial Q_j}Q_iQ_j = \hat{H}_0 + \hat{W} \quad (2)$$

where the $\hat{H}_0$ is the Hamiltonian for the reference nuclear configuration, here D_{4h} structure, the summation runs over all the normal coordinates and $\hat{W}$ is the vibronic, or JT opertor. Adiabatic potential energy surface, for f-fold degenerate electronic state, takes the form:

$$E_k(Q) = \frac{1}{2}\sum_i K_iQ_i^2 + \varepsilon_k(Q) \quad (3)$$

where $k = 1,2,\ldots f$, and K_i is the force constant for the vibration Q_i and $\varepsilon_{k(Q)}$ are the roots of the secular equation:

$$|W_{gg'} - \varepsilon I| = 0 \quad (4)$$

Here, W is an fxf vibronic matrix, and I is a unit matrix of the same dimensions. Matrix elements of the vibronic operator, within the basis function of the degenerate term, $\langle\Psi_g|\partial H/\partial Q|\Psi_{g'}\rangle$ are termed linear vibronic coupling constants and they measure the strength of the coupling between the electronic structure and nuclear displacements. JT active vibrations are found by group theory, demanding that vibronic coupling constants are different from zero. Herein studied, As_4^- and Sb_4^- have ^2E_g ground state in D_{4h} point group, and six normal modes that are classified into A_{1g}, B_{1g}, B_{2g}, B_{2u} and E_u irreducible representations (irreps). The symmetric product of the E_g electronic state transforms as $A_{1g} + B_{1g} + B_{2g}$. These