Ab Initio Calculations on Bismuth Cluster Polycations

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Abstract: Ab initio calculations on bismuth polycationic species of the types $\mathrm{Bi}_n^{(n-2)+}$, $\mathrm{Bi}_n^{(n-4)+}$, and $\mathrm{Bi}_n^{(n-6)+}$ ($n = 3-12$) were performed at the Hartree–Fock and density functional theory levels in order to investigate their general properties and the applicability of Wade's rules on bismuth polycations. Some exceptions to Wade's rules were encountered, and, moreover, several predicted and calculated minima show only meta-stable behavior. The bonding in bismuth polycations is characterized by a high degree of electron delocalization and "three-dimensional aromaticity".

Keywords: ab initio calculations · bismuth · cluster compounds · ELF (Electron Localization Function)

Introduction

The diversity of bismuth subvalent compounds is a fascination within cluster chemistry of the main group elements. Among the variety of subvalent species, homonuclear polycations of bismuth are of particular interest; this interest arises from the beauty and complexity of their structures, and also from the difficulty to properly explain their structures in terms of classic concepts of chemical bonding.

In general, the structures of the homonuclear polyatomic ions of main group elements are subject for the rationalization based on the number of their skeletal electrons.[1] The peculiarity of bismuth polycations is their electron-deficiency, that is, the number of their skeletal electrons (also known as electron count (EC) for the main group elements) is not sufficient to form localized two-center two-electron (2c–2e) bonds along the relevant edges of the polyhedra. Hence, a degree of electron delocalization is necessary to account for the bonding in such species. Fortunately, a concept exists that deals with systems characterized by electron delocalization. This concept is known as Wade's rules and is based on the work on polyboranes by Lipscomb,[2] Williams,[3, 4] and Wade,[5–7] later amended by Rudolph[8, 9] and Mingos.[1, 10, 11] Wade's rules divide all the electron-deficient polyhedra $\mathrm{M}_n^{\,l}$ into three classes depending on their EC: *closo*-polyhedra ($\mathrm{EC} = 4n + 2$), *nido*-polyhedra ($\mathrm{EC} = 4n + 4$), and *arachno*-polyhedra ($\mathrm{EC} = 4n + 6$). *closo*-Polyhedra are described in terms of deltahedra (i.e., polyhedra with only triangular faces), and removal of one or two vertices leads to *nido*- and *arachno*-polyhedra, respectively.

Wade's rules have proven to be a very convenient tool for qualitative estimation of the geometries of many main group clusters. However, applied to the bismuth polycations, they have produced somewhat controversial results. Of the three "well-known" polycations—Bi_5^{3+},[12, 13] Bi_8^{2+},[14, 15] and Bi_9^{5+}[15–20]—only the first two obey Wade's rules, since their geometries are in agreement with the prescribed EC. However, the Bi_9^{5+} should, according to Wade's rules, adopt a *nido*-configuration, that is, a mono-capped square antiprism (C_{4v}), while in all crystal structures it is found to be rather close to the tri-capped trigonal prism (D_{3h}), that is, a *closo*-polyhedron (see Figure 1). This deviation from the geometry given by Wade's rules has been the subject for several theoretical investigations that make use of different methods, but no conclusive answer has been given to the question of relations of stability between the two different configurations.[21–23] The

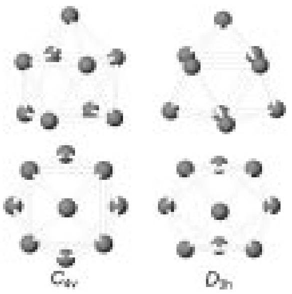

Figure 1. The two configurations of the Bi_9^{5+} polycation, C_{4v} and D_{3h}.

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0947-6539/01/0713-2821 $ 17.50+.50/0

latest contribution to this discussion comes from Ichikawa and co-workers[24] who showed that at the MP2 level of calculation (by using the Los Alamos basis sets) the D_{3h} configuration represents a true minimum on the potential energy surface. This fact makes it possible to assume the D_{3h} symmetry to be the more stable one at this level of computation. Structural determinations and calculations have also been made for other nine-atom naked main group clusters analogous to Bi_9^{5+}, such as Si_9^{4-},[25] Pb_9^{4-},[26] and Sn_9^{4-}.[23, 27, 28] These structures all adopt the C_{4v} configuration both experimentally and theoretically.

Moreover, two new bismuth polycations—Bi_5^+ and Bi_6^{2+}—were recently discovered within the structure of the $Bi_{34}Ir_3Br_{37}$ compound,[29] of which only the former cluster obeys Wade's rules. Thus, the question of the applicability of Wade's rules to the bismuth polycations has not received a definite answer. In this work, we present the results of ab initio calculations on a number of bismuth polycationic clusters, experimentally observed as well as hypothetical.

Results and Discussion

The geometry optimization and energy calculations were performed for the species of the types $Bi_n^{(n-2)+}$, $Bi_n^{(n-4)+}$ and $Bi_n^{(n-6)+}$, $n = 3-12$ (only cationic species were considered). The second-derivative matrix (Hessian) was used in order to evaluate the nature of the stationary points. As a starting point, a geometry prescribed by Wade's rules was used in each case (excluding $n = 3$, since, strictly speaking, a planar geometry is not a polyhedron and, hence, not handled by Wade's rules). In order to make the study more complete, the full matrix of the structures was investigated, that is, for each n both *closo*-, *nido*- and *arachno*-configurations with all three possible charges were studied. The matrix was additionally supplemented with species of other symmetries, mostly subgroups to the *closo*-cluster symmetries. This process was repeated with different methods (HF/DFT) and effective core potentials (ECPs) (large core, 78 electrons in core/small core, 60 electrons in core). This was made in an effort to exclude possible errors in the choices regarding basis sets, ECPs, and level of computation. When applying the smaller ECP, only structures with $n = 3-9$ were investigated owing to the heavy computational effort. The results are presented in Table 1 and the geometries of the minima are displayed in Figure 2.

We have not been able to identify any true local minima (i.e., without negative eigenvalues in the second-derivative matrix) for *closo*-Bi_{11}^{9+} and *closo*-Bi_{12}^{10+}, nor for *closo*-Bi_9^{7+} using the small-core ECP (SC-ECP).

Wade's rules and the topologies of bismuth polycations: As can be seen in Table 1, following the scheme for geometry selection described above, the majority of the minima adopt a geometry in agreement with Wade's rules, and the symmetries of the energy minima calculated by using the HF and DFT methods are consistent. With the large-core ECP (LC-ECP), only one direct discrepancy is found for the *closo*- and *nido*-clusters—the Bi_8^{4+} cluster, for which the true minimum structure is a dodecahedron (D_{2d}) rather than the bicapped trigonal prism (C_{2v}) predicted by Wade's rules. The latter is found to be the transition state, which has one negative eigenvalue in the Hessian, with an energy difference between D_{2d} and C_{2v} of approximately 10 and 15 kJ mol^{-1} for HF and B3LYP calculations, respectively. Moreover, the *nido*-Bi_6^{2+} entity violates the suggestion by Williams[3] and Rudolph[8] that the formation of a *nido*-structure proceeds through the removal of one of the vertices with the highest connectivity. If that would be the case, the *nido*-structure for Bi_6^{2+} should be a pentagonal pyramid (C_{5v}), but our calculations show that this geometry to corresponds to a local energy minimum, while the true minimum structure is formed by the removal of one of the ring atoms (C_{2v} symmetry), with the difference in energy (HF level) between these two geometries being only approximately 17 kJ mol^{-1} in HF and 16 kJ mol^{-1} in B3LYP. However, this case does not represent a violation of Wade's rules, since, as pointed out by Mingos,[1] the missing vertex in a *nido*-structure is usually but not necessarily the one of highest connectivity. Among the *arachno*-structures, there are deviations from the symmetry suggested by Williams, but they all adopt alternative symmetries proposed by Wade.[30]

Table 1. Symmetries of energy minima for calculated bismuth polycation structures.[a]

n	Method	*closo*-Structures	*nido*-Structures	*arachno*-Structures
4	HF/LC		T_d	
	HF/SC		T_d	
	B3LYP		T_d	
	Wade		T_d	
5	HF/LC	D_{3h}	C_{4v}	
	HF/SC	D_{3h}	C_{4v}	
	B3LYP	D_{3h}	C_{4v}	
	Wade	D_{3h}	C_{4v}	
6	HF/LC	O_h	C_{2v}	
	HF/SC	D_{2d}	C_{2v}	
	B3LYP	O_h	C_{2v}	
	Wade	O_h	C_{5v}/C_{2v}	
7	HF/LC	D_{5h}	C_s	C_{3v}
	HF/SC	D_{5h}	C_s	C_{3v}
	B3LYP	D_{5h}	C_s	C_{3v}
	Wade	D_{5h}	C_s	C_1
8	HF/LC	D_{2d}	D_{2d}	D_{4d}
	HF/SC	D_{2d}	D_{2d}	D_{4d}
	B3LYP	D_{2d}	D_{2d}	D_{4d}
	Wade	D_{2d}	C_{2v}	D_{4d}
9	HF/LC	D_{3h}	C_{4v}	C_s
	HF/SC	(D_{3h})	C_{4v}	C_s
	B3LYP	D_{3h}	C_{4v}	C_s
	Wade	D_{3h}	C_{4v}	C_1
10	HF/LC	D_{4d}	C_{2v}	D_{5d}
	B3LYP	D_{4d}	(C_{2v})	D_{5d}
	Wade	D_{4d}	C_{2v}	D_{5d}/C_{2v}
11	HF/LC	–	C_{5v}	
	B3LYP	–	C_{5v}	
	Wade	C_{2v}	C_{5v}	
12	HF/LC	(I_h)		
	B3LYP	(I_h)		
	Wade	I_h		

[a] The charges of the polycations are $(n-2)+$, $(n-4)+$ and $(n-6)+$ for *closo*-, *nido*-, and *arachno*-structures, respectively.

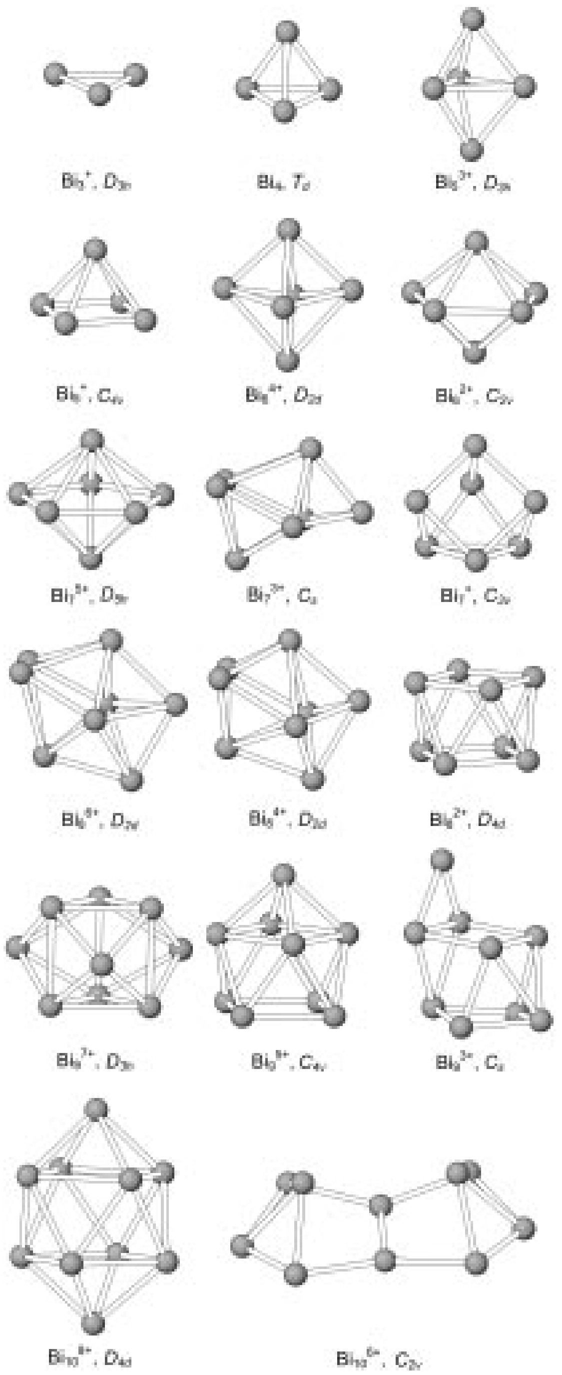

Figure 2. The geometries of the minima found in the calculations.

As mentioned above, no local minima have been found for *closo*-Bi_{11}^{9+} and *closo*-Bi_{12}^{10+}. In the case of the icosahedron, the global minimum symmetry of *closo*-Bi_{12}^{10+} according to Wade's rules, the optimized structure is found to have five negative eigenvalues in the Hessian, while *closo*-Bi_{11}^{9+} (C_{2v}) shows no convergence in reference to either geometry or energy.

When using the SC-ECP, the two deviations reported for the LC-ECP calculations, Bi_8^{4+} (D_{2d}/C_{2v}) and Bi_6^{2+} (C_{2v}/C_{5v}), are again observed, with energy differences of approximately 29 kJ mol^{-1} and 9 kJ mol^{-1}, respectively. In addition, two new discrepancies are encountered, the first one being that the energy minimum of Bi_6^{4+} is found to be a slightly distorted octahedron in D_{2d} symmetry; the true octahedron has three degenerate negative eigenvalues in the Hessian, while the imaginary vibrational modes lead to a D_{2d} geometry, and the total energy difference is very small, 3 kJ mol^{-1}. Further, the Bi_9^{7+} ion with D_{3h} symmetry, by using the SC-ECP, has two negative eigenvalues in the Hessian, much in the same manner as for the icosahedron (Bi_{12}^{10+}) with the LC-ECP.

Except for these two differences there is full agreement regarding the symmetry between the calculations with the two different ECPs. Moreover, the difference in total energy between structures that have the same charge and number of cluster atoms is in good agreement for the two calculation series. However, there are discrepancies in the calculated bond lengths, the shortest bond length being 0.12–0.15 Å shorter (there are occasional variations for low-symmetry species) when the SC-ECP is used. In an effort to make the study complete and to form an opinion about the stability of the structures suggested by Wade's rules, calculations without any symmetry constraints were performed, with special interest directed towards the icosahedral Bi_{12}^{10+} and Bi_9^{7+}, which both are found to have negative eigenvalues in the Hessian; this indicates that the structures are transition states. For the icosahedron only small movements away from the ideal structure are needed to make the structure completely resolve and the atoms split up into six independent and separate atom pairs. Other species show better stability, but still it is possible to make all *closo*- and *nido*-clusters that contain 8–12 atoms start diverging in both energy and geometry. The clusters split up into smaller parts, mostly fragments of two or three atoms, forming nearly equilateral triangles, but occasionally in larger fractions. Species that, up to date, do not show any tendencies to fall apart include the smaller *closo*-clusters and also *arachno*-Bi_8^{2+}. One can conclude that at least some, if not all, small bismuth clusters following Wade's rules only experience meta-stable behavior in the absence of a stabilizing environment (such as the reaction media in ligand state or anions in solid compounds), with enhanced stability for the smaller clusters. This fact, together with the two "direct" exceptions reported (Bi_6^{4+} and Bi_8^{4+}) to Wade's rules, provide arguments for taking these rules not as a strict law, but only as a first guess in the search for possible structures of small bismuth clusters. From a synthetic point of view, however, the present results encourage attempts in isolation and stabilization of new bismuth clusters.

Another important point is to compare the results of the calculations with experimental data (where available). Such data are presented in Table 2.

As seen in Table 2, for the three bismuth polycations Bi_5^{3+}, Bi_5^+, and Bi_8^{2+} the calculated and experimental symmetries and bond lengths are in good agreement. A slight systematic overestimation in the LC-ECP calculations and underestimation in the SC-ECP calculations, respectively, of the bond lengths is observed (less than 0.1 Å as compared with the experimental values). These differences are most likely caused by calculational approximations relating to the valence space size. Test calculations extending both the valence basis sets of LC- and SC-ECPs show that increasing basis sets

Table 2. Calculated bond lengths of the minimum structures of bismuth polycations.

	Symmetry		Bond lengths [Å]			
	exptl	calcd	exptl[a]	calcd/HF, LC	calcd/HF, SC	calcd/B3LYP, LC
Bi^{3+}		D_{3h}		2.92	2.79	2.94
Bi$_5^{3+}$	D_{3h}	D_{3h}	3.02(1)–3.32(1)[13]	3.10–3.43	2.96–3.25	3.12–3.41
Bi^{5+}	C_{4v}	C_{4v}	3.15(13)–3.17(14)[29]	3.01–3.17	2.89–3.03	3.03–3.18
Bi$_6^{4+}$		O_h/D_{2d}		3.28	3.03–3.34	3.31
Bi$_6^{2+}$	O_h	C_{2v}	3.17(15)[29]	2.98–3.31	2.85–3.17	2.99–3.35
Bi$_7^{5+}$		D_{5h}		3.18–3.47	3.08–3.35	3.22–3.49
Bi$_7^{3+}$		C_s		3.01–3.54	2.83–3.27	3.07–3.46
Bi$_7^{+}$		C_{3v}		3.07–3.34	2.92–3.23	3.07–3.33
Bi$_8^{6+}$		D_{2d}		3.27–3.58	3.09–3.43	3.24–3.62
Bi$_8^{4+}$		D_{2d}		3.17–3.29	3.03–3.19	3.19–3.30
Bi$_8^{2+}$	D_{4d}	D_{4d}	3.09(1)–3.11(2)[15]	3.12–3.24	2.99–3.11	3.14–3.23
Bi$_9^{7+}$		D_{3h}		3.43–3.62	3.35–3.46	3.48–3.70
Bi$_9^{5+}$	D_{3h}	C_{4v}	3.10(2)–3.21(5)[16]	3.24–3.53	3.10–3.25	3.27–3.57
Bi$_9^{3+}$		C_s		3.03–3.46	2.90–3.39	3.04–3.45
Bi$_{10}^{8+}$		D_{4d}		3.47–3.74		3.54–3.76
Bi$_{10}^{6+}$		C_{2v}		3.09–3.49		3.03–3.43
Bi$_{10}^{4+}$		D_{5d}		3.18–3.25		3.22–3.24
Bi$_{11}^{7+}$		C_{5v}		3.35–3.58		3.33–3.55
Bi$_{12}^{10+}$		I_h		3.75		3.88

[a] The experimentally found clusters are distorted from the ideal symmetries. The numbers given are average distances with standard deviations (deviations with respect to the ideal symmetry; not crystal structure determination standard deviations).

decrease the differences in calculated Bi–Bi bond lengths. Also, as the calculated distances are slightly shorter than the experimentally observed ones, a systematic error of 0.1 Å only represents a relative error in bond lengths of about 3 % and, thus, is acceptable for the present analysis. The most interesting outcome of the calculations was observed for the Bi$_9^{5+}$ cluster. As mentioned earlier, Wade's rules predict the C_{4v} symmetry for this cation, while in crystal structures it adopts the D_{3h} configuration, although with some distortions. Our calculations suggest that the true (local, disregarding symmetry break-ups) minimum structure for Bi$_9^{5+}$ is the C_{4v} one, that is, a monocapped square antiprism (see Tables 1 and 2). The tricapped trigonal prism (D_{3h}) only corresponds to the second-order saddle point on the potential energy surface, with one doubly degenerate eigenvalue in the Hessian. The imaginary frequencies are of E′ symmetry, which is the vibrational mode that converts the D_{3h} structure to the C_{4v} one.[28] The reason for such a stability of the D_{3h} symmetry of the cation relative to the true minimum C_{4v} configuration is most likely is hidden in the uniqueness of the C_{4v}/D_{3h} geometries for nine-vertex polyhedra; this allows an easy transfer between them. A monocapped square antiprism can be derived from tricapped trigonal prism by relatively small shifts of two atoms only. This is confirmed by the energy calculations, which show that the difference in total energy between these two configurations is less than 9 kJ mol^{-1} (DFT; 4 kJ mol^{-1}, SC-ECP; 3 kJ mol^{-1}). This small difference in total energy is also found in calculations on other nine-atom clusters, for example, Si$_9^{4-}$.[25] Such a small difference can be easily compensated for in the solid state by packing effects (which can be larger by at least one order of magnitude[31]), since from the point of packing with counterions the D_{3h} cation is more "spherical" than C_{4v} and, hence, more energetically favorable. All this means that the deviation of the Bi$_9^{5+}$ geometry from the one predicted by Wade's rules could be accounted for by the crystal field effects rather than an intrinsic property of its electronic structure. The multi-configuration HF calculations also confirm that singlet ground-state calculations represent a good approximation. Attention should also be payed to the results presented by Ichikawa and co-workers[24] who assign only positive frequencies to the D_{3h} form of Bi$_9^{5+}$ at the MP2 level indicating this to be the favorable configuration. The conclusion is that the two configurations are very close to each other in both energy and geometry and that results of any calculation will be highly influenced by the choice of level and method of calculation. The last of the experimentally observed bismuth polycations, Bi$_6^{2+}$, also does not follow Wade's rules. Unfortunately, the amount of information on this cation is not sufficient for a definitive conclusion. The cation has been characterized within one compound only, Bi$_{34}$Ir$_3$Br$_{37}$,[29] and is described by the author as a distorted octahedron. However, with one vertex more than 0.3 Å closer to the equatorial plane than the other, it is possible to interpret Bi$_6^{2+}$ not as a unit, but rather as an associate of two other species—the Bi$_5^{+}$ and Bi^{+} cations. If this is taken into consideration, although it cannot be directly supported or ruled out from the available data, it would account for the violation of the Wade's rules in case of the six-atom entity. Another explanation of the anomalous behavior of this cation is the fact that the distances between bismuth atoms and closest bromine atoms from the anions are less than 3.1 Å and thus comparable to the inter-atomic distances within the polycation. This is by far the shortest Bi–X distance observed in the structures containing polycations. From this point of view, it is questionable if Bi$_6^{2+}$ should be regarded as a truly "naked" cluster, since such short distances between the structural units indicates a significant degree of covalent interaction between them.

On the bonding in bismuth polycations: Several molecular orbital (MO) calculations have previously been performed on *closo*-boranes.[8, 9, 30] All of them agree in terms of the degeneracy of the LUMO in the *closo*-boranes, B$_n$H$_n^{2-}$, for $n = 5-7,10,12$. The orbital symmetries of the corresponding optimized *closo*-bismuth structures behave accordingly, although the symmetries differ in some cases (see Table 3). The degeneracy of the LUMO explains the change in the structure of a *closo*-cluster when two electrons are added; according to the Jahn–Teller effect a nonlinear molecule with a partially filled, degenerate HOMO is distorted in such a way that the degeneracy is eliminated.[32] For the two *closo*-clusters with nondegenerate LUMOs, Bi$_8^{6+}$ and Bi$_9^{7+}$, the lack of Jahn–

Table 3. Symmetries of molecular orbitals in bismuth clusters and *closo*-boranes.

	Bismuth polycations		*closo*-Boranes[a]	
N	HOMO	LUMO	HOMO	LUMO
5	e'	e'	e''	e'
6	t_{1u}	t_{2u}	t_{2g}	t_{2u}
7	a_2''	e_2''	e_2'	e_2''
8	e	a_2	b_2	a_2
9	a_2''	a_2''	a_2''	a_2'
10	e_1	e_3	e_1	e_3
12	t_{1u}	g_g	g_u	g_g

[a] Taken from reference [30].

Teller effect is evident as "*closo*"-Bi_8^{4+} (i.e., D_{2d}) is found to be the minimum configuration, altough the electron count suggest a *nido*-geometry and "*closo*"-Bi_9^{5+} (D_{3h}) is, if not the minimum, very close in energy to the minimum. The Mulliken overlap population analysis was used for depicting chemical bonds between bismuth atoms within polycations, as it provides a reasonable guess on whether the overlap electron density is sufficient for bonding or not. The highest values of the overlap populations (ca. 0.35) were observed in the case of the Bi_3^+ ion. A direct correlation between the bond lengthening in the polycations and the decreasing overlap population was also observed; this may serve as an indication of the increasing degree of the delocalization of electrons participating in bonding. However, no direct information on the number of electrons or contributing bismuth atoms involved in the formation of particular bonds is available from Mulliken overlap population data. We have made an attempt to perform a localized bond analysis in the bismuth clusters by applying the natural bond orbital (NBO)[33, 34] program included in the Gaussian package to the Hartree–Fock results based on the two different ECP's. However, the choice of ECP caused only minor differences in the results of the NBO calculations, in the following we will refer to the small-core results.

The results show that it is almost exclusively p electrons that participate in the skeletal bonding, while s electrons are localized as free electron pairs on each bismuth atom. However, only a fraction of the structures can be fully rationalized in terms of localized bonds; this gives rise to some problems in the use of the NBO method on bismuth polycations. Due to the fact that the NBO calculations give static descriptions of the bonding situation, molecules usually described by several resonance forms may be mistreated by the method. The treatment of bismuth polycations with the NBO routine, which at the present time is limited to three-center two-electron (3c–2e) bonds as the only degree of electron delocalization, results sometimes in schemes that are not quite rational, with some atoms having extra free electrons and others not having a complete nobel gas configuration. This implies that the real bonding schemes are more complex and may involve so-called "three-dimensional aromaticity"; often better referred to as "ring-delocalization".

In order to extend the understanding of the situation electron localization functions (ELF) were calculated, again by using large- and small-core Hartree–Fock results.[35–38] ELF make use of the Pauli exclusion principle, which in short states that if two electrons occupy the same spatial point they must have opposite spin. The ELF value, $\eta(\mathbf{r})$, is a measure of the probability, on condition that there is one electron with given spin in point $\mathbf{r}$, of finding another electron with the same spin in the vicinity of this point. Becke and Edgecombe showed that if the probability of finding another electron with the same spin near $\mathbf{r}$ is low, the reference electron is highly localized to that region.[35] The scale of ELF is normalized and runs between 0 and 1; high values of η correspond to low probability of finding another electron with the same spin in the region, that is, high degree of localization, as free electron pairs or bonds, while $\eta = 0.5$ corresponds to the perfectly delocalized homogeneous electron gas, which is used as a reference state.

A common way of illustrating the ELF results is to plot isosurfaces for certain values of η, as in Figures 3–5 (see below). In general, the ELF values for which interesting effects occur in the bismuth polycations are lower, as expected due to the more diffuse valence orbitals on bismuth, than what previously has been found in studies of lighter elements, for example see references [36] and [39]. Figures 3–5 show, from the results with the SC-ECP, that the electrons of the inner shell are found as spheres around the atom cores, and in all calculations these represent the global maxima of ELF, $\eta \approx 0.80$.

Another way of discussing ELF results is the use of attractors, that is, local maxima in the localization function to which surronding points are assigned, and in that way forming separate basins or "pair regions".[36, 37]

The results from our ELF calculations are in good agreement with the rational results of NBO and they also facilitate the comprehension of the less rational NBO results. By combining the results of two methods the bonding in the majority of the bismuth clusters can be explained. Graphical presentations, in the form of η^{iso} plots, of the ELF calculations on the experimentally found bismuth polycations Bi_5^{3+}, Bi_5^+, Bi_8^{2+}, and Bi_9^{5+} (both possible symmetries) are shown in Figure 3. Starting the analysis with Bi_5^{3+} (D_{3h}) the NBO results assign 3c–2e bonds to four of the triangular surfaces, two up and two down, and partially filled extra lone pairs on three of the atoms. This description of the bonding breaks the symmetry and leaves the apical atoms electron deficient. In ELF results at high values, $\eta^{\text{iso}} > 0.75$, only the core electrons of the inner shell is visible indicating the atom positions. Lowering the value of the η^{iso} the free electron pairs start to show, and at $\eta^{\text{iso}} < 0.55$ a third type of regions can be found in the center of all the triangular surfaces. The low values at which these suggested regions for 3c–2e bonds appear, point to these being delocalized, which makes sense considering the electron count; there are only five electron pairs available for bonding but six 3c–2e bond regions. Together the NBO and ELF results imply a high degree of delocalization in this polycation. The situation is somewhat different in Bi_5^+ (C_{4v}) in which the NBO results indicate four localized bonds in the base, three electron deficient bonds between the apical atom and base atoms, leaving the last base atom with a partially filled extra electron pair. Clearly, this suggests some kind of

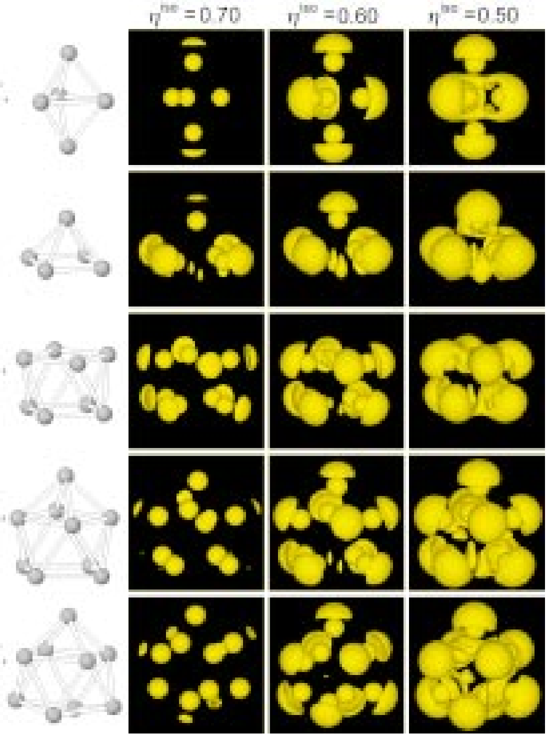

Figure 3. ELF surfaces of Bi_5^{3+}, Bi_5^{+}, Bi_8^{2+} and Bi_9^{5+}, C_{4v} and D_{3h} symmetry, with $\eta^{iso} = 0.70$, $\eta^{iso} = 0.60$ and $\eta^{iso} = 0.50$.

delocalization. In the ELF η^{iso} plots the inner electron spheres and free electron pairs are evident, and also the much more localized character of the bonds in the base, in contrast to the 3c–2e bonds of Bi_5^{3+}. The attractor analysis state the maximum ELF value in these bond regions to be 0.74, to be compared with 0.80 for the free electron pairs and 0.56 in the 3c–2e bonds of Bi_5^{3+}. In Bi_5^{+} there are also four attractors found for the apical-to-base connections, but the maximum value of ELF along these paths is only 0.53, that is, the three electron pairs available for these bonds are almost fully delocalized. In Bi_8^{2+} (D_{4d}), the NBO calculations suggest ordinary, but somewhat electron-deficient, 2c–2e bonds between the atoms in the individual squares, and additionally three 3c–2e bonds connecting the two squares. The ELF results show that the bonds in the squares are evident for $\eta^{iso} = 0.60$, (maximum of the attractors at $\eta = 0.63$, thus at a somewhat lower value than was found in Bi_5^{+} in accordance with the electron-deficient bonds of the NBO results), while no attractors can be found between the squares. There should be eleven electron pairs participating in cluster bonding and the NBO and ELF results appear to agree with respect to the fact that eight of these are fairly, but not completely, localized to the individual squares, and the remaining three are delocalized between the squares. This situation, including localized bonds within the squares and only some three electron pairs delocalized in eight possible connections between the squares, may imply that some additional disorder could appear in X-ray analysis due to rotational flexibility of the individual squares around the fourfold axis. The related Bi_9^{5+} (C_{4v}) structure also displays a bonding structure that is similar to the one in Bi_8^{2+}. Taking into account both the NBO and ELF results, there are essentially localized bonds in the lower square, four 3c–2e bonds between the two squares, and the remaining three electron pairs are split over the four expected connections to the apical atom. The, by now, well-known, extra free electron pairs appear on atoms in the middle square and on the apical atom in the NBO analysis, and an evident conclusion is that whenever NBO allocates electrons to these extra, partially filled, lone pairs it is a sign of delocalization. In ELF, the attractor analysis gives the maximum values to be 0.62 for the bonds in the base, 0.58 for the 3c–2e bonds between the squares, and 0.51 for four 3c–2e bonds between the apical atom and the middle square. The first two bond types are surely not fully localized, and in the case of the last type, the value is so close to the perfect delocalization that it is hardly meningful to speak of any localized bonds.

In the Bi_9^{5+} (D_{3h}) entity, the two 3c–2e bonds in each of the two peripherical triangles become very distinct in ELF at $\eta^{iso} < 0.6$, as illustrated in Figure 4 ($\eta^{iso} = 0.55$) looking down the threefold axis; these are also found within the NBO results. As to the rest of the cluster, NBO results are difficult to interpret in terms of the distribution of free electrons. As mentioned earlier this is an indication of delocalization, also displayed by ELF results for which no localized regions, except the two 3c–2e bonds of the peripherical triangles can be seen until the η^{iso} value is very close to 0.50. Six 3c–2e bonds start to show at $\eta = 0.53$.

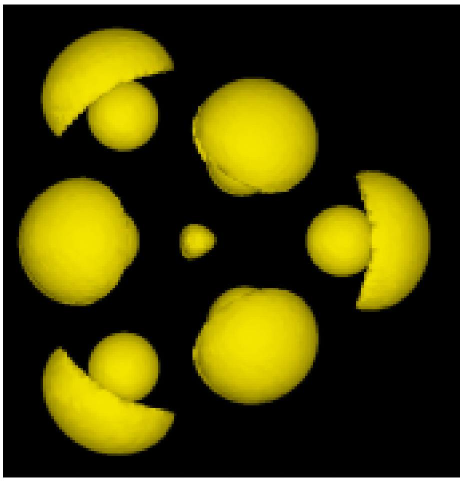

Figure 4. ELF surface ($\eta^{iso} = 0.55$) in Bi_9^{5+} (D_{3h}) looking down the threefold axis. The 3c–2e bond in the upper triangle is clearly displayed.

Some general observations considering the ELF results for the bismuth clusters include firstly that the highly symmetrical clusters (symmetries O_h and I_h) are extensively delocalized. Secondly, once symmetry is lower, typically four-membered and five-membered ring systems tend to display a localized bonding, whereas the bonding between rings and between rings and capping atoms is highly delocalized. For instance, in Bi_8^{2+} localized electron pairs are found in the two squares, but the two squares are tied together by highly delocalized electrons. The same is observed for Bi_{10}^{4+}, derived from the Bi_{12}^{10+} icosahedron, in which localized bonding is observed in the two five-membered rings and the bonding between the rings is delocalized. The situation in clusters with two rings and a capping atom is somewhat more complicated. In Bi_9^{5+} (C_{4v}) the base square exhibits localized bonding, wheras the square closest to the capping atom is expanded to the extent that no intra-ring bonding exists. The rings and capping atom are connected through delocalized electrons. The situation is analogous for the icosahedral derivative Bi_{11}^{7+}, which consists of two five-membered rings and a capping atom.

These general observations can be used in an attempt to understand the somewhat surprising results regarding Bi_6^{2+}; the minimum structure is obtained by removing one of the equatorial atoms from the pentagonal bipyramid (ELF results for C_{5v} and C_{2v} Bi_6^{2+}, $\eta^{iso} = 0.55$, are presented in Figure 5).

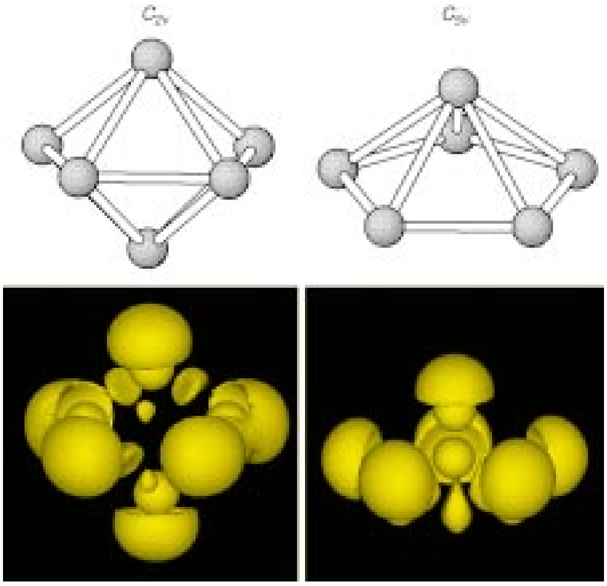

Figure 5. ELF surface ($\eta^{iso} = 0.55$) of Bi_6^{2+}, C_{5v} and C_{2v} symmetry.

Despite the low ELF value no signs of bonding to the apical atom can be found in the pentagonal pyramid (C_{5v}), leaving this only loosely linked to the other five atoms, while in the C_{2v} structure all atoms are connected. This "free" apical atom of the pyramid may be the important factor of the higher energy in this structure. The general rule seems to be that when two alternative structures are available, and the one having the more homogenous bonding situation is favored, for example C_{2v}-Bi_6^{2+} and D_{5d}-Bi_{10}^{4+}. This principle could be called the "rejection of the black sheep"; the black sheep being the most weakly bonded atom. This is another argument for the D_{3h}-Bi_9^{5+} being highly stable, since the capping atom in the C_{4v} structure is a typical "black sheep".

Conclusion

Starting from geometries suggested in discussions about Wade's rules, calculations on small bismuth polycations with different number of atoms, charge, and configuration by using different calculational methods have been made. These confirm that Wade's rules generally are applicable to bismuth polycations with certain exceptions. By working in parallell with NBO and ELF data, a good description of the bonding in bismuth clusters can be achieved. In conclusion, our calculations show that the electrons involved in bonding in the polycations are found both as localized in bonds and delocalized over larger regions. The localized bonds are predominantly found in the rings within the cations and these are in turn kept together by delocalized electrons.

Computational Methods

The calculations were performed by using the Gaussian 98[40] and Turbomole 4.4[41] program packages. All calculations included geometry optimization and evaluation of the nature of the critical points (eigenvalues of the Hessian). Both Hartree–Fock (HF) and hybrid density functional theory (DFT) calculations were performed. In the HF calculations, two different quasi-relativistic effective core potentials (ECP) by substituting the inner 78 and 60 (Table 4) core electrons;[42, 43] the small-core ECP was obtained by the energy adjustment method also used for the large-core ECP, and optimized valence basis sets corresponding to the two ECPs were used, (6s6p2d)/[321/321/2] and (9s9p6d2f)/[42111/42111/3111/11], respectively. The hybrid DFT calculations were done by using the B3LYP[44] functional in Gaussian 98 together with the large-core ECP and corresponding basis set. CASSCF(6,6) calculations were also performed for the bigger clusters in order to verify that the singlet ground-state calculations were good approximations. For the analysis of the bonding in bismuth polycations, the natural bond orbital (NBO) facility included in Gaussian package,[33, 34] was applied to the results from Hartree–Fock calculations from both ECPs. The electron localization function (ELF)[35] was also calculated from the Hartree-Fock results by utilizing the ToPMoD package[45, 46] and visualized with the Vis5d (v5.2) program.[47]

Table 4. Quasi-relativistic ECP for Bi, 60 core electrons.

	Exptl	Coefficient
s	13.0430902	283.26422704
	8.2216825	62.47195881
p	10.4677774	72.00149911
	9.1189007	144.00227689
	6.7547910	5.00794478
	6.2525918	9.99155031
d	8.0814741	36.39625901
	7.8905947	54.59766450
	4.9555557	9.98429401
	4.7045590	14.98148549
f	4.2145458	13.71338341
	4.1334006	18.19430752
g	– 10.2474433	6.20570896
	– 12.9557100	6.22778157

Acknowledgement

This research is supported by the Swedish Natural Science Research Council and by INTAS (No. 1999-01672).

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Received: October 23, 2000 [F2820]