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σ-Aromaticity in Hexa-Group 16 Atom-Substituted Benzene Dications: A Theoretical Study

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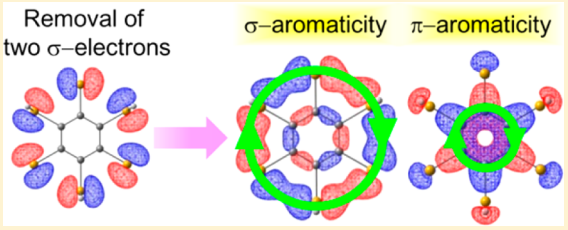
Supporting Information

ABSTRACT: $C_6I_6^{2+}$ has been reported to have a σ-aromatic character since removal of two σ anti-bonding electrons localized on iodines results in fulfilling Hückel (4n+2) rules for I_6^{2+} as well as C_6 parts. To search for molecules possessing similar character, hexa-group 16 atom-substituted benzene dications $C_6(ChH)_6^{2+}$ (Ch = S, Se, Te) and their derivatives are examined for aromatic character by using nucleus-independent chemical shift (NICS). For these dications, in which iodines in $C_6I_6^{2+}$ are replaced by group 16 atoms, negative NICS values larger in magnitude than for benzene are found when a σ anti-bonding orbital localized on group 16 atoms is unoccupied. To clarify the origin of large negative NICS values, they are decomposed into individual molecular orbitals. It has been shown that both π bonding orbitals on C_6 and σ bonding orbitals on Se_6 or Te_6 contribute to the negative NICS values, indicating that the aromaticity of these dications have a substantial σ character as well as π characters. Aromaticity of group 14 and 15 atom-substituted benzene dications is also discussed.

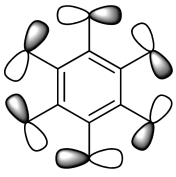


1. INTRODUCTION

Aromaticity is a fundamental concept in chemistry. Though the typical aromaticity is shown in π-electron delocalized systems, many systems that show aromaticity caused by σ, δ,[1−3] and φ[4] electrons have been reported. The concept of σ-aromaticity or double aromaticity caused by σ and π orbitals was first suggested for cyclic hydrocarbons by theoretical studies.[5−14] Nowadays, not only cyclic hydrocarbons but also hydrogen clusters[15−17] and metal clusters[18−24] are suggested to have σ-aromatic characters both from theoretical and experimental viewpoints.

One of the candidates that show σ-aromaticity is hexa-iodobenzene dication, $C_6I_6^{2+}$.[25−28] As shown in Scheme 1, the HOMO of neutral C_6I_6, derived from 5p orbitals of iodines lying on the molecular plane, has a σ anti-bonding character. When two electrons are removed from the HOMO, the +2 charges should be localized on the I_6 part, which results in fulfilling the Hückel (4n+2) electron rule both for C_6 and I_6^{2+} parts. Therefore, $C_6I_6^{2+}$ is considered to have π-aromatic character on C_6 and σ-aromatic character on I_6^{2+}. However, such σ-aromatic character is not found in $C_6Br_6^{2+}$ and $C_6Cl_6^{2+}$, because smaller overlaps of in-plane valence p orbitals of halogens cause smaller destabilization of σ anti-bonding orbitals and result in removal of two electrons not from the anti-bonding σ orbital but from a delocalized π orbital.[27] (The detailed electronic states will be discussed in Figure 2.) Although this idea has been discussed since the 1980s, a recent experimental study unfortunately has demonstrated that the oxidation of C_6I_6 yields $C_6I_6^{+}$ radical, not $C_6I_6^{2+}$.[29]

Scheme 1. σ Anti-bonding HOMO of Neutral C_6I_6, Which Is the LUMO of Its Dication



On the other hand, dicationic hexa-group 16 atom-substituted benzenes can also be candidates for σ-aromatic compounds, because of the similarity of electronic states between halogens and group 16 atoms capped by hydrogens or substituents.[30] One of the merits of hexa-group 16 atom-substituted benzenes is that geometries and electronic structures can be controlled by modifying substituents on the group 16 atoms. In the case of hexa-halobenzene dications, σ-aromaticity is shown only when overlap of in-plane valence p orbitals of halogens is large enough, as in $C_6I_6^{2+}$. If the magnitude of overlap of valence p orbitals can be controlled by changing geometry and electronic structures with different substituents, hexa-group 16 atom-substituted benzene derivatives that show σ-aromaticity may be found.

In this study, we examine theoretically the aromaticity of hexa-group 16 atom-substituted benzene dications, such as $C_6(ChH)_6^{2+}$ (Ch = S, Se, Te) and their derivatives (Scheme 2). To evaluate the aromaticity, we calculate the isotropic nucleus-independent chemical shift ($NICS_{iso}$) and its zz component

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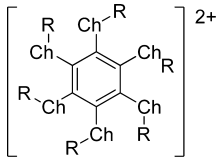
Scheme 2. Hexa-Group 16 Atom-Substituted Benzene Dications (Ch = S, Se, Te)



(NICS$_{zz}$), magnetic indices of aromaticity introduced by Schleyer and co-workers.[31−34] NICS(0) is defined as the negative of the magnetic shielding computed at the ring center, and NICS(1) is that at 1.0 Å above the ring center. NICS(1) is considered to be a better indicator of the magnitude of the ring current, as the paramagnetic effect of nearby σ bonds is minimized at this point.[32,36] Negative NICS values indicate a diatropic ring current and aromaticity, while positive values represent a paratropic ring current and anti-aromaticity. Although several different methods have been proposed for evaluating aromaticity of complex systems,[17,37,38] NICS is still considered to be a reasonable index for benzene derivatives. The results for hexa-group 16 atom-substituted benzene dications are compared to those of hexahalobenzene dications. We also discuss the aromaticity of hexa-groups 14 and 15 atom-substituted benzene dications by comparing their geometries and NICS values.

2. RESULTS AND DISCUSSION

2.1. Geometry, Electronic State, and Aromaticity of $C_6(SR)_6^{2+}$. First, several conformers of $C_6(SH)_6^{2+}$ are examined. Table 1 shows the relative electronic energies and NICS values

Table 1. Relative Electronic Energies ΔE (kcal/mol) and NICS Values (ppm) of Two Conformers of $C_6(SH)_6^{2+}$ with NICS Values of Benzene and $C_6I_6^{2+}$ for Comparison

molecule	conf	2S + 1	ΔE	NICS(0)$_{iso}$	NICS(1)$_{iso}$	NICS(1)$_{zz}$
$C_6(SH)_6^{2+}$	A	1	17.2	−15.4	−15.6	−38.6
		3	16.2	−4.3	−5.6	−9.8
	B	1	0.0	8.8	3.2	19.7
		3	6.0	−3.9	−6.8	−10.9
C_6H_6		1		−8.0	−10.1	−28.7
$C_6I_6^{2+}$		1		−13.7	−11.9	−39.7

of two typical conformers. (Other conformers that have similar structures are shown in Supporting Information.) The most stable is the closed shell singlet conformer B where four H atoms are located on the plane formed by C_6S_6 and two H atoms extend to the opposite vertical directions to each other, as shown Figure 1. The corresponding triplet is 6 kcal/mol higher in energy. The other conformer A where all of the H's extend to the directions vertical to the C_6S_6 plane is more than 16 kcal/mol unstable both for singlet and triplet states. The S−S distances are 3.22 Å for singlet conformer A (D_{3d} symmetry) and 3.30 and 3.08 Å for singlet conformer B (C_{2h} symmetry), which are shorter than twice the van der Waals radius of a S atom (1.80 Å × 2) and short enough to provide in-plane σ-overlap between sulfur 3p orbitals. Note that they are longer (except for 3.08 Å) than the Cl−Cl distance 3.14 Å, but shorter than the I−I distance 3.53 Å in singlet $C_6X_6^{2+}$. Focusing on NICS values, those of the singlet states have positive values for the conformer B and negative values for the conformer A, although those for triplet states are independent of the

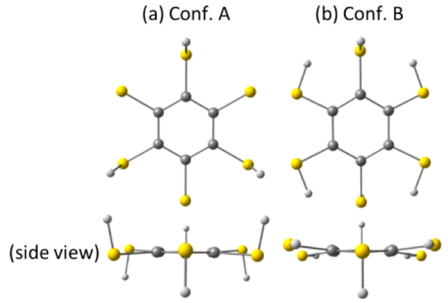


Figure 1. Geometries of two conformers A and B of $C_6(SH)_6^{2+}$.

geometry. Although the difference in geometry between conformers A and B is only the direction of H atoms, their singlet states have opposite characters, aromaticity and anti-aromaticity, respectively.

Why do they have the opposite aromatic characters? To clarify the reason for the difference in aromaticity between singlet conformers A and B, their relevant molecular orbitals are shown in Figure 2. It is found that their electronic structures are

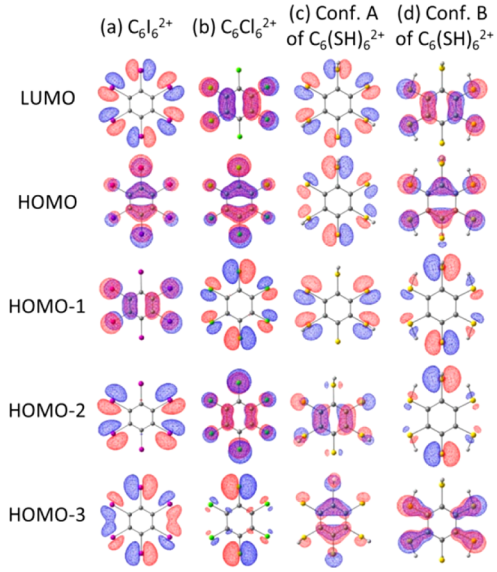


Figure 2. Molecular orbitals of singlet dications (a) $C_6I_6^{2+}$, (b) $C_6Cl_6^{2+}$, and (c, d) conformers A and B of $C_6(SH)_6^{2+}$.

completely different. In conformer A, the LUMO, which is the HOMO of neutral $C_6(SH)_6$, has a σ anti-bonding character derived from the in-plane 3p orbitals on sulfur atoms. On the other hand, the LUMO of conformer B is a π orbital delocalized both on carbon and sulfur atoms. LUMOs of conformers A and B are quite similar to those of singlet $C_6I_6^{2+}$ and $C_6Cl_6^{2+}$, respectively. In other words, both C_6 and S_6 parts of conformer A fulfill the Hückel 4n+2 electron rule, which results in the double aromaticity, π-aromaticity on C_6 and σ-aromaticity on S_6, as shown for $C_6I_6^{2+}$ in previous theoretical studies.[27,28] Those of conformer B do not fulfill the Hückel 4n +2 electron rule, resulting in anti-aromaticity like $C_6Cl_6^{2+}$. Focusing on triplet states, HOMO and LUMO in Figure 2 are singly occupied orbitals, and +2 charges localize on S_6 for conformer A and delocalize both on C_6 and S_6 for conformer B. Therefore, both C_6 and S_6 parts satisfy the 4n+2 electron rule for conformer A, while both parts dissatisfy 4n and 4n+2 electron rule for conformer B. It confirms Baird's rule[39−43] that

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triplet states in the π-annulenes with 4n electrons show aromaticity and those with 4n+2 electrons show anti-aromaticity. As shown above, the electronic states of $C_6(SH)_6^{2+}$ can be controlled by directions of hydrogen atoms or substituents on sulfur atoms. Therefore, to find a molecule that shows σ-aromaticity, we should explore a molecule whose most stable conformer has the geometry where all of the substituents are directed perpendicular to the C_6S_6 plane.

Toward such a goal, derivatives of $C_6(SR)_6^{2+}$ are examined as shown in Table 2. With fluorine as the substituent (R = F), the most stable singlet conformer is B, as in $C_6(SH)_6^{2+}$, with a large anti-aromaticity. On the other hand, for dications with larger halogens, such as chlorine and bromine (R = Cl and Br), only stable conformers A are found but no B, presumably because the bulkier (than hydrogens) halogens cannot be accommodated in-plane with C_6S_6. In these cases, singlet conformers A have large negative NICS values as expected. However, the triplet states are the ground states, for which the σ-aromaticity cannot be seen because of Baird's rule.[39−43] From comparison between $C_6(SR)_6^{2+}$ (R = F, Cl, Br) molecules, we can say that the conformer A can be made to be the most stable by bulky substituents (R) on sulfur atoms. Therefore, the dications with bulkier substituents such as alkyl, silyl, and phenyl groups are examined as shown in Table 2. By adding such bulky substituents, conformers A are the most stable for all of the molecules. However, their singlet states never became more stable than triplet states showing substantially smaller aromaticity for all of the substituents in Table 2. It should be noted that hexakis(methylthio)benzene (R = Me) was synthesized and examined in a previous study,[30] but no σ-aromaticity has been demonstrated.

Table 2. Relative Electronic Energies ΔE (kcal/mol) and NICS Values (ppm) of Singlet and Triplet States $C_6(SR)_6^{2+}$

R	conf	2S+1	ΔE	NICS(0)$_{iso}$	NICS(1)$_{iso}$	NICS(1)$_{zz}$
H[a]	A	1	17.2	−15.4	−15.6	−38.6
F	A	1	20.1	−13.1	−13.5	−35.3
		3	16.4	−6.5	−6.9	−15.3
	B	1	5.7	19.4	16.2	55.3
		3	0.0	−4.0	−4.9	−7.6
Cl	A	1	1.9	−12.0	−13.1	−31.2
		3	0.0	−5.3	−6.9	−12.7
Br	A	1	2.8	−11.8	−13.0	−30.2
		3	0.0	−6.9	−8.4	−16.0
Me	A	1	3.2	−14.3	−14.5	−36.7
		3	0.0	−7.8	−8.5	−18.1
*t*Bu	A	1	3.1	−11.8	−12.4	−34.8
		3	0.0	−2.4	−3.9	−8.0
$SiMe_3$	A	1	3.7	−12.8	−13.0	−35.6
		3	0.0	−3.4	−4.7	−9.8
Ph	A	1	7.6	−9.1	−9.2	−27.4
		3	0.0	−6.1	−6.3	−17.7

[a]Data in Table 1 is shown for comparison.

2.2. Geometries and Aromaticity of $C_6(SeR)_6^{2+}$ and $C_6(TeR)_6^{2+}$. Considering that heavier halogens are more favored for σ-aromaticity, the effects of heavier group 16 atoms were examined for $C_6(SeH)_6^{2+}$ and $C_6(TeH)_6^{2+}$. As shown in Table 3, singlet conformers A (D_{3d} symmetry) are the most stable both for $C_6(SeH)_6^{2+}$ and $C_6(TeH)_6^{2+}$. (Other less stable conformers are shown in Supporting Information.) Unlike $C_6(SH)_6^{2+}$, it appears that hydrogen atoms cannot be accommodated in-plane, and thus no conformation B is found. The Se−Se and Te−Te distances in singlet conformation A are 3.36 and 3.56 Å, respectively, which are shorter than twice the van der Waals radius of a Se atom (1.90 Å × 2) and a Te atom (2.06 Å × 2) and are short enough to provide in-plane σ-overlap of the valence p orbitals, as in $C_6(SH)_6^{2+}$. The NICS values of these singlet states have larger negative values than those of neutral benzene, −8.0 ppm for NICS(0), −10.1 ppm for NICS(1), and −28.7 ppm for NICS(1)$_{zz}$, calculated with the same level of theory. The LUMOs of $C_6(SeH)_6^{2+}$ and $C_6(TeH)_6^{2+}$ (see Supplementary Figure S4) have the expected σ anti-bonding character, as in $C_6(SH)_6^{2+}$, and +2 charges are localized on selenium and tellurium atoms, which results in fulfilling the Hückel (4n+2) rules.

Table 3. Relative Electronic Energies ΔE (kcal/mol) and NICS Values (ppm) of singlet and Triplet States of $C_6(ChH)_6^{2+}$ (Ch = Se and Te)

Ch	conf	2S+1	ΔE	NICS(0)$_{iso}$	NICS(1)$_{iso}$	NICS(1)$_{zz}$
S[a]	A	1		−15.4	−15.6	−38.6
Se	A	1	0.0	−16.6	−16.6	−42.7
		3	3.0	−1.9	−3.6	−3.3
Te	A	1	0.0	−18.9	−18.9	−50.3
		3	11.2	4.7	2.5	13.6

[a]Data in Table 1 is shown for comparison.

Can we show how important the contribution of σ-aromaticity is to these large negative NICS values of $C_6(SeH)_6^{2+}$ and $C_6(TeH)_6^{2+}$? There should be also contributions of π orbitals of Se_6^{2+} and Te_6^{2+} as well as C−Se and C−Te bonds. To clarify the origin of large negative NICS values, NICS(1)$_{iso}$ values of singlet dications are divided into contributions of canonical molecular orbitals (CMO)[44] and localized natural bond orbitals (NBOs).[45] It should be noted that individual orbital contributions to NICS are not gauge-invariant, although the total sums are independent of the gauge origin.[46,47] We just note that different dissection schemes may sometimes provide different interpretations.[46,47] Therefore, two dissection schemes[44,45] are applied and compared for NICS(1)$_{iso}$ of $C_6I_6^{2+}$ (D_{6h}), in which σ and π orbitals are separated by symmetry. Figure 3 shows the contributions of Kohn-Sham CMOs to the NICS(1)$_{iso}$ value. The π orbitals, some localized and some delocalized, have 55% contribution. Of 45% contributions from σ orbitals, in-plane σ orbitals derived almost exclusively from 5p orbitals of iodine atoms have 32% contribution, and all other σ orbitals contribute only 13%; although there are large minus contribution (−88%) from HOMO-13 and 14, they are canceled out by contributions from other σ orbitals. Focusing on each CMO, bonding and anti-bonding orbitals tend to contribute to aromaticity and anti-aromaticity, respectively. The relationship between bonding character and aromatic character here is similar to the well-accepted picture of aromaticity of benzene; neutral benzene is very stable since only bonding π orbitals are occupied, and anions are unstable because of occupancy of anti-bonding π orbitals. We next dissect the NICS(1)$_{iso}$ values of $C_6I_6^{2+}$ (D_{6h}) into contributions of NBOs using natural chemical shielding (NCS) analysis,[45] as shown in Table 4. As expected, the total σ NBO as well as π NBO contributions are same as in the CMO analysis, 55% and 45%, respectively. The π contributions can be divided into 105% from π NBOs mainly localized on C_6, which is canceled nearly halfway by −50% from π NBOs mainly localized on I_6^{2+}. The σ NBO contribution can be divided into

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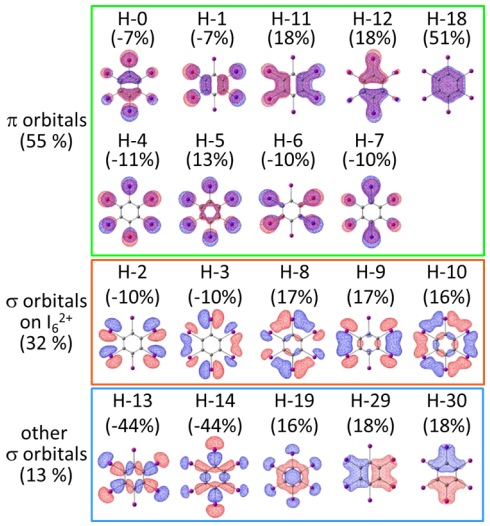

Figure 3. Contribution of Kohn-Sham CMOs to NICS(1)$_{iso}$ of singlet $C_6I_6^{2+}$. "H-" means "HOMO-" and the number in parentheses is the contribution in % from each CMO. Only CMOs having large contributions are shown.

52% from NBOs localized on I $p_{x,y}$ orbitals, −43% from C−I orbitals, and 36% from others. Although a qualitative picture is similar, these values are somewhat different from the contributions from σ CMOs. Concluding, $C_6I_6^{2+}$ has a σ and π mixed aromatic characters, with nearly half and half contributions from σ and π orbitals.

For $C_6(ChH)_6^{2+}$ (Ch = S, Se, and Te) with nonplanar hydrogen atoms, σ orbitals cannot be separated from π orbitals and CMO analysis is not very useful (see Supplementary Figure S5). NBOs of $C_6(SeH)_6^{2+}$ show a reasonable separability between σ and π NBOs. The dissected NICS(1)$_{iso}$ are shown in Table 4. According to this analysis, the net contributions of π vs σ contributions are 80% vs 20% for Ch = S and Se and 84% vs 16% for Ch = Te. Although the ratios of σ-aromaticity derived from in-plane Ch p orbitals are smaller than that of $C_6I_6^{2+}$, the absolute dissected values are comparable. Focusing on the dissected values, only the contributions from π orbitals derived from p_z of I or Ch (row 3 of Table 4) are different, while others are quite comparable. The reason may be understood by the amount of delocalization (or charge transfer) of π electrons between C_6 and I_6^{2+} or Ch_6^{2+}. For $C_6I_6^{2+}$, π charge transfer takes place from I_6^{2+} to C_6 that results in reduced the π-aromaticity. On the other hand, the π_z orbitals on Ch form the Ch-H σ orbitals, have smaller overlap with π orbitals of the C_6 part, and thus make only small contributions to NICS. Thus we can conclude that all $C_6(ChH)_6^{2+}$ (Ch = S, Se, and Te) have mixed σ and π mixed aromatic characters, with more than half of contributions from π orbitals.

Next, in hope of finding molecules that may have larger negative NICS values, derivatives of $C_6(ChH)_6^{2+}$ (Ch = Se and Te) were examined as shown in Table 5. All of them have the singlet ground states and show large negative NICS values. However, contrary to our expectation NICS values are almost independent of the substituents R. The independency may be explained by the small contributions of p_z orbitals of Ch, as discussed with Table 4.

2.3. Hexa-Group 14 and 15 Atom-Substituted Benzene Dications. Finally, we examined groups 15 and 14 atoms instead of group 16 atoms for possible σ-aromatic molecules. As shown in Figure 4, hexa-group 15 atom-substituted benzene dications, such as $C_6(PH_2)_6^{2+}$, $C_6(AsH_2)_6^{2+}$, and $C_6(SbH_2)_6^{2+}$, keep the planar structures (except for H atoms), while hexa-group 14 atom-substituted benzene dications, such as $C_6(SiH_3)_6^{2+}$, $C_6(GeH_3)_6^{2+}$, and $C_6(SnH_3)_6^{2+}$, cannot keep the planar structure because of the steric repulsion between hydrogen atoms, which results in small negative NICS values (Table 6). The nonplanar structures of hexa-group 14 atom-substituted benzenes are observed in the X-ray structures of $C_6(SiMe_3)_6$ and its dianion.[48,49] Among three group 15 atoms, P, As, and Sb, all of these singlet states have large negative NICS values, although only $C_6(SbH_2)_6^{2+}$ has a singlet ground state. To compare the origin of large negative NICS values, CMOs of singlet $C_6(SbH_2)_6^{2+}$ are shown in Supplementary Figure S8. The shape of LUMO of $C_6(SbH_2)_6^{2+}$ is quite similar to those of $C_6I_6^{2+}$ and $C_6(ChH)_6^{2+}$(Ch = Se and Te), although the in-plane σ orbitals on antimony atoms contain the s component of H atoms. We expected that we could control the electronic states and density on antimony by changing hydrogens to other substituents. However, even though the smallest substituent of fluorine is used, the molecule cannot keep the planar structure because of the steric repulsion. Therefore, though $C_6(SbH_2)_6^{2+}$ itself can be a candidate of an σ-aromatic molecule, its derivatives $C_6(SbR_2)_6^{2+}$ should be difficult to keep in planar structures, resulting in less aromaticity.

3. CONCLUSIONS

In this study, we examined the aromatic character of $C_6(ChR)_6^{2+}$ (Ch = S, Se, Te) molecules since they are expected to have an electronic structure similar to that of $C_6I_6^{2+}$ having mixed aromaticity caused by π orbitals on the C_6 ring and σ orbitals on the iodine atoms. The key to the σ-aromaticity is the in-plane σ anti-bonding LUMO derived from 5p orbitals of iodine atoms, which results in localized charges

Table 4. Contribution of NBOs to NICS(1)$_{iso}$ (ppm) for Singlet $C_6I_6^{2+}$ and $C_6(ChH)_6^{2+}$ (Ch = S, Se, and Te)[a]

	contributions from			
	I	S[b]	Se	Te
π orbitals on C_6	−12.5 (105)	−12.2 (78)	−12.5 (75)	−14.6 (77)
π orbitals derived from p_z of I or Ch and 1s of H	6.0 (−50)	−0.3 (2)	−0.8 (5)	−1.3 (7)
σ orbitals localized on I or Ch and derived from $p_{x,y}$	−6.2 (52)	−5.0 (32)	−6.1 (37)	−6.6 (35)
C-I or -Ch delocalized σ orbitals	5.1 (−43)	2.7 (−17)	4.3 (−26)	5.9 (−31)
other σ orbitals[c]	−4.3 (36)	−0.8 (5)	−1.5 (9)	−2.3 (12)
total	−11.9 (100)	−15.6 (100)	−16.6 (100)	−18.9 (100)

[a]Numbers in parentheses are in %. [b]For conformer A. [c]Containing σ and core orbitals on C_6, and σ orbitals localized on Ch derived from valence s orbitals.

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Table 5. Relative Electronic Energies ΔE (kcal/mol, Relative to Triplet) and NICS(1) Values (ppm) of the Singlet State of $C_6(ChR)_6^{2+}$ (Ch = Se and Te)

	Se			Te		
R	ΔE	$NICS(1)_{iso}$	$NICS(1)_{zz}$	ΔE	$NICS(1)_{iso}$	$NICS(1)_{zz}$
H	−3.0	−16.6	−42.7	−11.2	−18.9	−50.3
Cl	−0.9	−14.3	−35.7	−2.1	−17.4	−45.1
Br	−0.4	−13.6	−32.5	−8.5	−17.2	−44.4
Me	−1.3	−16.1	−41.2	−9.7	−18.9	−50.2
*t*Bu	−2.2	−14.4	−39.3	−9.8	−18.2	−50.6
$SiMe_3$	−3.1	−15.5	−43.9	−11.7	−17.3	−43.9
Ph	−0.4	−11.9	−35.3	−6.8	−15.3	−46.3

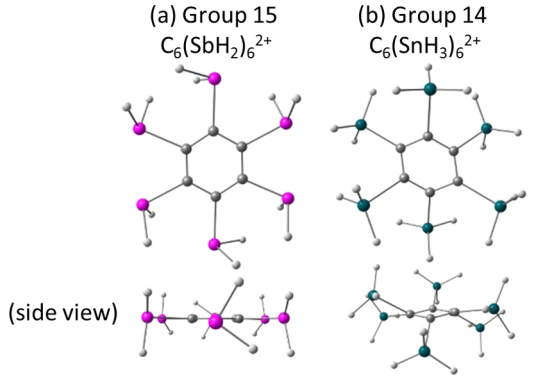

Figure 4. Geometries of hexa-group 15 and 14 atom-substituted benzene dications.

Table 6. Relative Electronic Energies ΔE (kcal/mol, Relative to Triplet) and NICS(1) Values (ppm) of the Singlet State of Hexa-Groups 15 and 14 Atom-Substituted Benzene Dications[a]

molecule	ΔE	$NICS(1)_{iso}$	$NICS(1)_{zz}$
$C_6(PH_2)_6^{2+}$	5.5	−13.2	−32.6
$C_6(AsH_2)_6^{2+}$	1.9	−14.8	−37.2
$C_6(SbH_2)_6^{2+}$	−1.4	−15.0	−41.8
$C_6(SiH_3)_6^{2+}$	−6.1	−2.7	3.1
$C_6(GeH_3)_6^{2+}$	−7.4	−4.8	−4.3
$C_6(SnH_3)_6^{2+}$	−9.3	−8.1	−15.3

[a]Geometries are in Supporting Information.

for C_6 and I_6^{2+}, doubly fulfilling the Hückel (4n+2) electron rule.

For the lightest group 16 atom, sulfur, substituted benzene dications $C_6(SH)_6^{2+}$, two confirmations are found to exist, with totally different electronic structures. When all of the hydrogen atoms are directed perpendicular to the C_6S_6 plane, the LUMO has in-plane σ anti-bonding character as in $C_6I_6^{2+}$, resulting in a large negative NICS value. In order to find molecules that have a singlet ground state with such a geometry, a number of derivatives were examined and several candidates were found, such as $C_6(SeH)_6^{2+}$, $C_6(TeH)_6^{2+}$ and their derivatives, which have more negative NICS and therefore larger aromatic characters than neutral benzene. To clarify the origin of larger aromatic characters, the NICS values were dissected into contributions from canonical molecular orbitals (CMOs) and from localized natural bonding orbitals (NBOs). Both analyses showed the existence of contributions to aromaticity from π orbitals of C_6 ring and in-plane σ orbitals of Se_6 and Te_6 originating from valence p orbitals. Although Se and Te atoms are capped by hydrogens or substituents, when a proper orientation of hydrogens or substituents is retained, the magnitude of aromaticity did not change much from halogen analogues, because the charge transfer between group 16 atoms and substituents takes place only through p_z orbitals that are orthogonal to the in-plane σ orbitals.

Additionally, the aromatic characters of hexa-groups 14 and 15 atom-substituted benzene dications were also examined to seek for other σ-aromatic molecules. Hexa-group 14 atom-substituted benzene dications have nonplanar C_6 ring structures, which results in weak aromaticity. Among hexa-group 15 atom-substituted benzene dications, only $C_6(SbH_2)_6^{2+}$ has the singlet ground state with the planar structure and shows a large negative NICS value.

4. COMPUTATIONAL DETAILS

Geometries were fully optimized at the dispersion-corrected B3LYP-D3 level[50−52] with basis set 6-31G* for C and H, and SDD with the Stuttgart-Dresden large-core relativistic effective core potential (RECP) for other atoms other than C and H was used throughout.[53] After geometry optimization, single point calculations were performed at the B3LYP-D3 level with 6-31+G* for C and H and SDD for others (BS2). The isotropic NICS values ($NICS_{iso}$) and their zz components ($NICS_{zz}$) were computed employing the GIAO method[54] with the BS2 basis set. Though $NICS_{zz}$ values are considered to be better indexes for aromaticity of plane molecules than $NICS_{iso}$ values[23,24] and show positive linear correlation as shown in Supporting Information. To examine the dependence of calculation methods, we compared other basis sets and functionals, such as M062X[55] and BLYP-D3.[50−52] (see Supporting Information) The optimized structures, singlet−triplet energy differences, and NICS values did not depend much on the computational methods. All calculations were performed by the Gaussian09 program.[56] The partitioning of NICS into the contributions from CMOs and NBOs was carried out by the NBO 6.0 program.[57]

■ ASSOCIATED CONTENT

Supporting Information

Relative electronic energies, NICS values, and geometries of all conformers of $C_6(ChH)_6^{2+}$ (Ch = S, Se, Te). Kohn-Sham orbitals and their contributions to NICS(1) of singlet $C_6(ChH)_6^{2+}$ (Ch = Se, Te). Geometries and Kohn-Sham orbitals of singlet $C_6(XH_2)_6^{2+}$ (X = P, As, Sb) and $C_6(XH_3)_6^{2+}$ (X = Si, Ge, Sn). Comparison of $NICS_{iso}$ and $NICS_{zz}$. Dependency on calculation methods. Cartesian coordinates and electronic energies for all species. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Huang, X.; Zhai, H. J.; Kiran, B.; Wang, L. S. *Angew. Chem., Int. Ed.* **2005**, *44*, 7251−7254.
(2) Wannere, C. S.; Corminboeuf, C.; Wang, Z. X.; Wodrich, M. D.; King, R. B.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **2005**, *127*, 5701−5705.
(3) Zhai, H.-J.; Averkiev, B. B.; Zubarev, D. Y.; Wang, L.-S.; Boldyrev, A. I. *Angew. Chem., Int. Ed.* **2007**, *46*, 4277−4280.
(4) Tsipis, A. C.; Kefalidis, C. E.; Tsipis, C. A. *J. Am. Chem. Soc.* **2008**, *130*, 9144−9155.
(5) Dewar, M. J. S. *Bull. Soc. Chim. Belg.* **1979**, *88*, 957−967.
(6) Chandrasekhar, J.; Jemmis, E. D.; Schleyer, P. v. R. *Tetrahedron Lett.* **1979**, *39*, 3707−3710.
(7) Dewar, M. J. S.; McKee, M. L. *Pure Appl. Chem.* **1980**, *52*, 1431−1441.
(8) Dewar, M. J. S. *J. Am. Chem. Soc.* **1984**, *106*, 669−682.
(9) Cremer, D.; Kraka, E. *J. Am. Chem. Soc.* **1985**, *107*, 3800−3810.
(10) Cremer, D.; Kraka, E. *J. Am. Chem. Soc.* **1985**, *107*, 3811−3819.
(11) Cremer, D.; Gauss, J. *J. Am. Chem. Soc.* **1986**, *108*, 7467−7477.
(12) Cremer, D. *Tetrahedron* **1988**, *44*, 7427−7454.
(13) Schleyer, P. v. R.; Jiao, H.; Glukhovtsev, M. N.; Chandrasekhar, J.; Karaka, E. *J. Am. Chem. Soc.* **1994**, *116*, 10129−10134.
(14) Feixas, F.; Matito, E.; Poater, J.; Sola, M. *Wiley Interdiscip. Rev.: Comput. Mol. Sci.* **2013**, *3*, 105−122.
(15) Jiao, H.; Schleyer, P.v.R.; Glukhovstev, M. N. *J. Phys. Chem.* **1996**, *100*, 12299−12304.
(16) Jursic, B. S. *Int. J. Quantum Chem.* **1999**, *73*, 451−458.
(17) Havenith, R. W. A.; Proft, F. D.; Fowler, P. W.; Geerlings, P. *Chem. Phys. Lett.* **2005**, *407*, 391−396.
(18) Li, X.; Kuznetsov, A. E.; Zhang, H.-F.; Boldyrev, A. I.; Wang, L. S. *Science* **2001**, *291*, 859−861.
(19) Kuznetsov, A. E.; Boldyrev, A. I.; Li, X.; Wang, L. S. *J. Am. Chem. Soc.* **2001**, *123*, 8825−8831.
(20) Kuznetsov, A. E.; Corbett, J. D.; Wang, L. S.; Boldyrev, A. I. *Angew. Chem., Int. Ed.* **2001**, *40*, 3369−3372.
(21) Boldyrev, A. I.; Kuznetsov, A. E. *Inorg. Chem.* **2002**, *41*, 532−537.
(22) Zhan, C. G.; Zheng, F.; Dixon, D. A. *J. Am. Chem. Soc.* **2002**, *124*, 14795−14803.
(23) Tsipis, A. C.; Stalikas, A. V. *J. Comput. Chem.* **2012**, *32*, 620−638.
(24) Cervantes, E. D.; Poater, J.; Robles, J.; Swart, M.; Solà, M. *J. Phys. Chem. A* **2013**, *117*, 10462−10469.
(25) Sagl, D. J.; Martin, J. C. *J. Am. Chem. Soc.* **1988**, *110*, 5827−5833.
(26) Martin, J. C.; Schaad, L. J. *Pure Appl. Chem.* **1990**, *62*, 547−550.
(27) Ciofini, I.; Lainé, P. P.; Adamo, C. *Chem. Phys. Lett.* **2007**, *435*, 171−175.
(28) Havenith, R. W. A.; Fowler, P. W.; Fias, S.; Bultinck, P. *Tetrahedron Lett.* **2008**, *49*, 1421−1424.
(29) Molski, M. J.; Mollenhauer, D.; Gohr, S.; Paulus, B.; Khanfar, M. A.; Shorafa, H.; Strauss, S. H.; Seppelt, K. *Chem. Eur. J.* **2012**, *18*, 6644−6654.
(30) Kobayashi, K.; Takahashi, O.; Namatame, K.; Kikuchi, O.; Furukawa, N. *Chem. Lett.* **1998**, *27*, 515−516.
(31) Schleyer, P. v. R.; Maerker, C.; Dransfeld, A.; Jiao, H.; Hommes, N. J. R. v. E. *J. Am. Chem. Soc.* **1996**, *118*, 6317−6318.
(32) Schleyer, P. v. R.; Manoharan, M.; Wang, Z.-X.; Kiran, B.; Jiao, H.; Puchta, R.; Eikema Hommes, N. J. R. *Org. Lett.* **2001**, *3*, 2465−2468.
(33) Corminboeuf, C.; Heine, T.; Seifert, G.; Schleyer, P. v. R.; Weber, J. *Phys. Chem. Chem. Phys.* **2004**, *6*, 273−276.
(34) Chen, Z.; Wannere, C. S.; Corminboeuf, C.; Puchta, R.; Schleyer, P. v. R. *Chem. Rev.* **2005**, *105*, 3842−3888.
(35) Fallah-Bagher-Shaidaei, H.; Wannere, C. S.; Corminboeuf, C.; Puchta, R.; Schleyer, P. v. R. *Org. Lett.* **2006**, *8*, 863−866.
(36) Schleyer, P. v. R.; Jiao, H.; Hommes, N. J. R. v. E.; Malkin, V. G.; Malkina, O. L. *J. Am. Chem. Soc.* **1997**, *119*, 12669−12670.
(37) Poater, J.; Cruz, I. G.; Illas, F.; Solà, M. *Phys. Chem. Chem. Phys.* **2004**, *6*, 314−318.
(38) Kaipio, M.; Patzschke, M.; Fliegl, H.; Pichierri, F.; Sundholm, D. *J. Phys. Chem. A* **2012**, *116*, 10257−10268.
(39) Baird, N. C. *J. Am. Chem. Soc.* **1972**, *94*, 4941−4948.
(40) Baird, N. C.; West, R. M. *J. Am. Chem. Soc.* **1971**, *93*, 4427−4432.
(41) Feixas, F.; Vandenbussche, J.; Bultinck, P.; Matito, E.; Solà, M. *Phys. Chem. Chem. Phys.* **2011**, *13*, 20690−20703.
(42) Karadakov, P. B. *J. Phys. Chem. A* **2008**, *112*, 7303−7309.
(43) Karadakov, P. B. *J. Phys. Chem. A* **2008**, *112*, 12707−12713.
(44) Heine, T.; Schleyer, P. v. R.; Corminboeuf, C.; Seifert, G.; Reviakine, R.; Weber, J. *J. Phys. Chem. A* **2003**, *107*, 6470−6475.
(45) Bohmann, J. A.; Weinhold, F.; Farrar, T. C. *J. Chem. Phys.* **1997**, *107*, 1173−1184.
(46) Kaupp, M. In *Calculation of NMR and EPR Parameters: Theory and Applications*; Kaupp, M., Bühl, M., Malkin, X. G., Eds.; Wiley-VCH: Weinheim, 2004; pp 293−306.
(47) Auer, D.; Kaupp, M.; Strohmann, C. *Orgamonetallics* **2004**, *23*, 3647−3655.
(48) Sakurai, H.; Ebata, K.; Kabuto, C.; Sekiguchi, A. *J. Am. Chem. Soc.* **1990**, *112*, 1799−1803.
(49) Sekiguchi, A.; Ebata, K.; Kabuto, C.; Sakurai, H. *J. Am. Chem. Soc.* **1991**, *113*, 1464−1465.
(50) Lee, C. T.; Yang, W. T.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785−789.
(51) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648−5652.
(52) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. *J. Chem. Phys.* **2010**, *132*, 154104−154119.
(53) Dolg, M.; Stoll, H.; Savin, A.; Preuss, H. *Theor. Chim. Acta* **1989**, *75*, 173−194.
(54) Wolinski, K.; Hilton, J. F.; Pulay, P. *J. Am. Chem. Soc.* **1990**, *112*, 8251−8260.
(55) Zhao, Y.; Truhlar, D. G. *Theor. Chem. Acc.* **2008**, *120*, 215−241.
(56) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09, Revision D.01*; Gaussian, Inc.: Wallingford, CT, 2009.

(57) Glendening, E. D.; Badenhoop, J. K.; Reed, A. E.; Carpenter, J. E.; Bohmann, J. A.; Morales, C. M.; Landis, C. R.; Weinhold, F. *NBO 6.0*; Theoretical Chemistry Institute, University of Wisconsin: Madison, 2013.