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Pericyclic Transition-State-Like Aromaticity in the Inorganic Ions $Se_2I_4^{2+}$ and $S_2O_4^{2-}$

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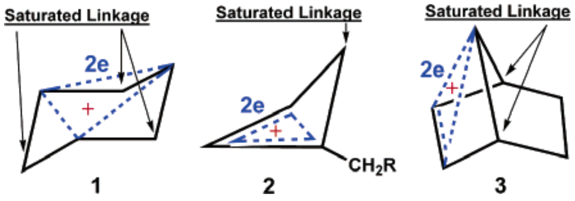
We show, by means of quantum chemical calculations, that the inorganic ions $Se_2I_4^{2+}$ and $S_2O_4^{2-}$, whose structures have been long-known and well-characterized, have aromaticity resulting from through-space conjugation, analogous to the aromaticity in the transition states of some pericyclic reactions, such as Cope rearrangements and Diels–Alder reactions.

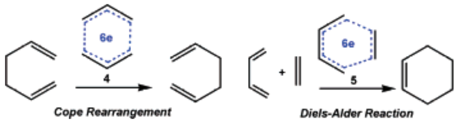
Introduction

The concept of homoaromaticity was first introduced by Winstein to describe compounds that have one or more saturated linkages interrupting the formal cyclic conjugation, yet they display aromaticity (e.g., tris-homocyclopropenyl cation **1**).[1] So far, homoaromaticity has been well-established in a large number of organic cationic and anionic systems, in which the homoconjugative interaction completes the otherwise cyclic delocalization of $4n + 2$ electrons.[2,3] An exclusive feature of these homoaromatic systems is the presence of one or more saturated linkages interrupting the conjugated bond between adjacent centers (e.g., cyclobutenyl cation **2**, 3,5-bridged bishomocyclopropenyl cation **3**; Scheme 1).[3] Hence, for most of the homoaromatic systems, their homoconjugatively interacting subunits are geometrically far apart from each other, but they are united by *through-space conjugation*.[3] Similar aromatic through-space conjugation has been recognized within the transition states of some pericyclic organic reactions such as Cope rearrangements and Diels–Alder reactions (Scheme 2).[4,5] For example, both pericyclic transition states (PTSs) of the prototype Cope rearrangement and Diels–Alder reaction, **4** and **5** (Scheme 2), have six *mobile electrons*[6] to attain the aromatic through-space conjugation. These aromatic PTSs, which differ from the aforementioned homoaromatic systems, have no saturated linkages to connect the conjugative subunits. Herein, we show, by means of quantum chemical calculations, that the inorganic ions $Se_2I_4^{2+}$ (**6**) and $S_2O_4^{2-}$ (**7**), whose structures have been long-known and are well-characterized,[7,8] have PTS-like aromaticity resulting from 10-electron through-space conjugation between their spaced conjugative subunits.

Scheme 1. Selected Homoaromatic Systems



Scheme 2. Representative Pericyclic Reactions with Aromatic Transition States



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(5) For a recent review on the applications of nucleas-independent chemical shift, see: Chen, Z.; Wannere, C. S.; Corminboeuf, C.; Puchta, R.; Schleyer, P. v. R. *Chem. Rev*. **2005**, *105*, 3842. The aromaticity in pericyclic-reaction transition states has also been reviewed.

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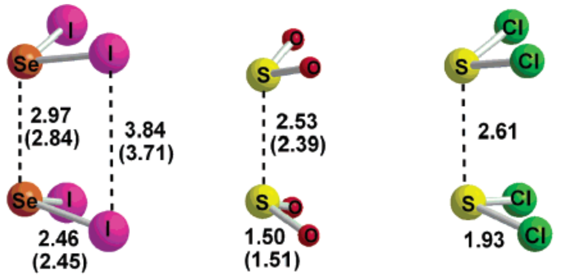
Computational Details

All calculations were performed using the hybrid density functional MPW1PW91 method, which is a combination of the modified PW exchange functional by Barone et al.[9] and the 1991 PW correlation functional,[10] implemented in Gaussian 98.[11] The basis sets employed are the relativistic effective core potential (RECP),[12a] the valence triple-ζ basis set (denoted SDB-cc-pVTZ)[12b] for $Se_2I_4^{2+}$, and the standard 6-311+G(3df)[13] for other ions. Such a combination of theoretical methods and basis sets has been shown to be reasonable at predicting the geometries of S- and Se-containing ions such as S_8^{2+} and Se_8^{2+}.[17b]

To characterize the aromaticity of the inorganic ions concerned, the nucleas-independent chemical shifts (NICS)[5,14] at their geometric centers were computed using the gauge-independent atomic orbital (GIAO) method[15] at the MPW1PW91 level of theory. A negative NICS value is associated with aromaticity, and a positive NICS value is associated with antiaromaticity.[5] For an up-to-date review on the definition and applications of NICS, please see to ref 5.

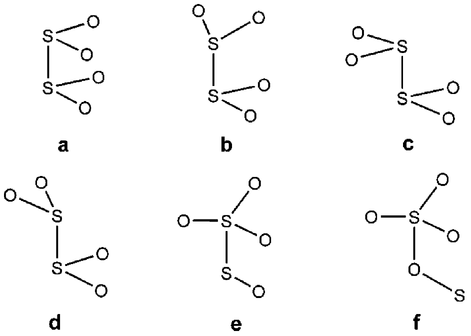
Results and Discussion



6 $Se_2I_4^{2+}(C_{2v})$ NICS = −17.4 **7** $S_2O_4^{2-}(C_2)$ NICS = −6.1 **8** $S_2Cl_4^{2+}(C_{2v})$ NICS = −13.5

Figure 1. Geometries (bond lengths in Å) and GIAO−NICS values (in ppm) of $Se_2I_4^{2+}$ (**6**), $S_2O_4^{2-}$ (**7**), and $S_2Cl_4^{2+}$ (**8**) predicted at the MPW1PW91 level, along with the available experimental data given in parentheses. The $S_2O_4^{2-}$ ion is nearly C_{2v} symmetric, but it is of C_2 symmetry.

Scheme 3. Possible Isomers of $S_2O_4^{2-}$



Previous X-ray diffraction experiments[7] showed that the $Se_2I_4^{2+}$ ion, **6**, in $Se_2I_4(AsF_6)_2{\cdot}SO_2$ and $Se_2I_4(Sb_2F_{11})_2$ crystals adopts a trigonal prism structure consisting of two eclipsed V-shaped units (VSUs), SeI_2^+ (Figure 1). The $S_2O_4^{2-}$ ion, **7**, also adopts this form (Scheme 3a), in which it is nearly eclipsed in some Na^+, Zn^{2+} and Sn^{2+} salts.[8] A nearly staggered structure (Scheme 3b) with an O−S−S−O torsional angle of ~56° was also found in the $Na_2S_2O_4{\cdot}2H_2O$ crystal.[8d] In addition, a C_{2h} symmetric staggered structure (Scheme 3c), a C_2 symmetric gauge structure (Scheme 3d), and two other isomers (Scheme 3e and f) were predicted, using quantum chemical calculations, to be candidates for the ground-state structure of $S_2O_4^{2-}$.[16] Yet, an accurate theoretical prediction on the ground-state structure of $S_2O_4^{2-}$ remains unavailable. Nevertheless, we consider only the well-characterized eclipsed structure (Scheme 3a).

Some structural features are noticeable for the eclipsed structures of $Se_2I_4^{2+}$, **6**, and $S_2O_4^{2-}$, **7** (Figure 1).[17] First, the bond length of Se−I (2.45 Å) or S−O (1.51 Å) within each VSU is shorter than that of an ordinary single bond (~2.51 Å for Se−I and ~1.69 Å for S−O), implying π-bonding within the VSU. Second, between two eclipsed VSUs, the distance of two opposite atoms, Se···Se (2.84 Å)/I···I (3.71 Å) in **6** or S···S (2.39 Å) in **7**, is much shorter than the sum of the van de Waals radii (~4.0 Å for Se···Se, 4.3 Å for I···I, and 3.7 Å for S···S), but it is considerably longer than the corresponding single bond (~2.34 Å for Se−Se and ~2.05 Å for S−S), indicating an unusual VSU−VSU interaction. By taking a hypothetical dication, $S_2Cl_4^{2+}$ (**8**), as a model for $Se_2I_4^{2+}$, Nandana et al.[7b] performed ab initio SCF single-point calculation on $S_2Cl_4^{2+}$. Since each VSU has 3-center 5-electron (3c5e) π-bonding, they concluded that the unusual inter-VSU interaction in these dications could be attributed to the 6-center 10-electron (6c10e) $\pi-\pi$ interaction, which can be further simplified as "a 6-center, 2-electron $\pi^*-\pi^*$ bond involving the interaction of π^* SOMO's" of each VSU (Scheme 4 and Figure S1).[7b] In this

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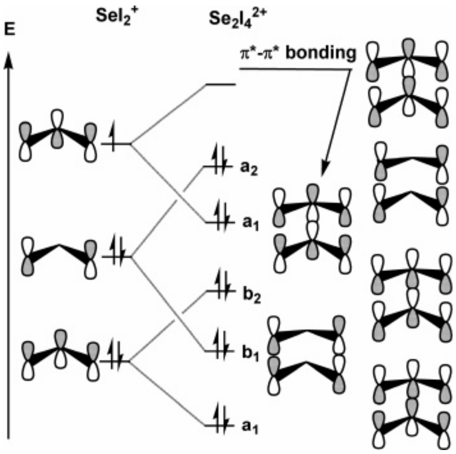
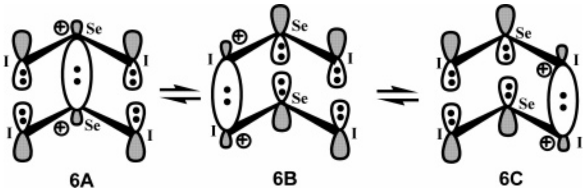
Scheme 4. Selected Molecular Orbitals of $Se_2I_4^{2+}$ Originating from the π-Orbitals of Two SeI_2^+ Radicals (ref 7b)



Scheme 5. Resonance of Three Valence-Bond (VB) Structures which Account for the 6c10e Through-Space π-Conjugation within $Se_2I_4^{2+}$ (ref 7b)



regard, **6** and **7** can be simply regarded as inorganic analogues of two allyl dianion radicals ($C_3H_5^{2-}$) linked by a bond involving the two unpaired electrons in the antibonding π^*-orbitals. Similar $\pi^*-\pi^*$ interactions were found in the π-dimers of some organic π-radicals, such as the tetracyanoethylene anion radical and octamethydiphenylene cation radical.[18] Nandana et al.[7b] also proposed that the bonding in **6** could be described with three valence-bond (VB) structures, each containing an inter-VSU σ-bond (Scheme 5): the VB structure, **6A**, contributes dominantly to the inter-VSU bonding with a minor contribution from the **6B** and **6C** structures. Following their suggestion, we noticed that the resonance of these VB structures results in *6c10e through-space π-conjugation*, which satisfies the ($4n + 2$)-electron Hückel rule for aromaticity (or homoaromaticity). Hence, we infer that the unusual inter-VSU interaction within **6** or **7** could be described as a *6c10e through-space conjugation*, and consequently, it is aromatic in nature.

The MPW1PW91-optimized geometries of $Se_2I_4^{2+}$ **6** and $S_2O_4^{2-}$ **7** are shown in Figure 1. Both ions are predicted to have a singlet ground state, in accordance with the experimental observation[7b,8b] that they are diamagnetic. For both ions, the agreement between the experimental and theoretical geometries is fairly good. The $Se_2I_4^{2+}$ ion, **6**, is C_{2v} symmetric (Figure 1). $S_2O_4^{2-}$, **7**, is not ideally C_{2v} symmetric, but it is C_2 symmetric with an O−S−S−O torsional angle of 7.7° (Figure 1). Its ideally eclipsed structure (C_{2v}) corresponds to a rotational transition state that connects two equivalent C_2 structures. The predicted NICS values are −17.4 ppm for $Se_2I_4^{2+}$, **6**, and −6.1 ppm for $S_2O_4^{2-}$, **7**, showing that both ions are aromatic.

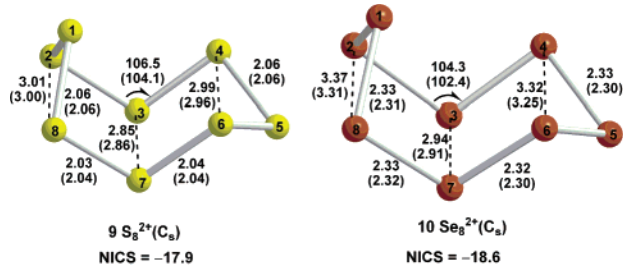


Figure 2. Geometries (bond lengths in Å and angles in degree) and GIAO−NICS values (in ppm) of S_8^{2+} and Se_8^{2+} predicted at the MPW1PW91/6-311+G(3df) level of theory. The available experimental data are given in parentheses.

We then considered the hypothetical ion, $S_2Cl_4^{2+}$ (**8**), that was previously proposed by Nandana et al.[7b] $S_2Cl_4^{2+}$ (Figure 1) shows structural features similar to those of $Se_2I_4^{2+}$; the optimal S−S distance of 2.61 Å in **8** is much longer than a normal S−S single bond, but it is much shorter than the sum of the van der Waals radii. Ion **8** is also aromatic with a predicted NICS value of −13.5 ppm.

The order of the predicted NICS values of **6**, **7**, and **8** implies that the aromaticity of these ions follows the order **6** > **8** > **7**. This is in agreement with the general trend that larger electronegativity (EN) differences between constituent atoms result in more-polarized chemical bonds. The Pauling EN[19] difference is 0.11 for Se−I, 0.58 for S−Cl, and 0.86 for S−O, suggesting that the π-bonds would be more polarized in **7** than in **6** and **8**. Consequently, the through-space conjugation (in-plane π-electron delocalization) is stronger in **6** and **8** than in **7**. The much smaller NICS value of **7** implies that the cyclic through-space conjugation between its two subunits should be much weaker than that within **6** and **8**. This may be the reason rotational acyclic isomers of $S_2O_4^{2-}$ can be readily observed experimentally.[20]

In addition to the ions described above, we have considered other inorganic ions, S_8^{2+} (**9**) and Se_8^{2+} **(10)**, which display peculiar structural features. The MPW1PW91/6-311+G(3df)-optimized geometries of **9** and **10** are shown in Figure 2, along with key bond lengths determined by X-ray diffraction.[17,21,22] Both eight-membered ring cyclic ions X_8^{2+} (X = S, Se) have unusually short transannular X−X distances (ranging from 2.9 to 3.3 Å for Se3−Se7, Se4−Se6, and Se2−Se8 in **10** and around 2.9 Å for S2−S8, S3−S7, and S4−S6 in **9**), which is longer than a normal X−X single bond but much shorter than the sum of van der Waals radii. It should be noted that a comprehensive density functional study was previously conducted by Cameron et

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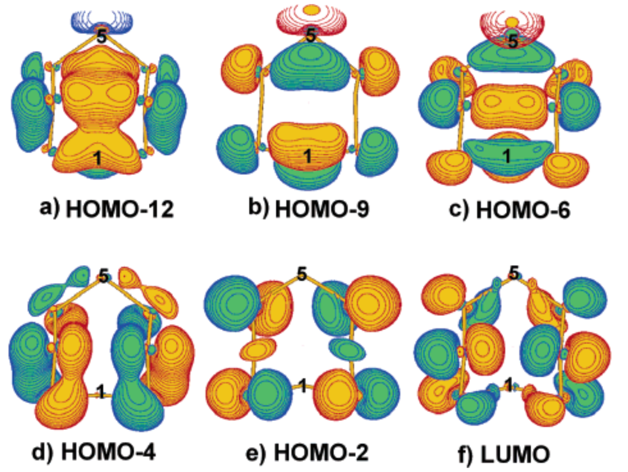

Figure 3. Selected molecular orbitals[23] of S_8^{2+} showing the 10πe conjugation. The lone-pair electrons of the S1 and S5 atoms contribute to HOMO−6, HOMO−9, and HOMO−12, showing the involvement of these electrons in the through-space conjugation of the two S_3^+ subunits.

al. on the electronic structures, chemical bonding, heats of formation, and Raman spectra of these dications.[17b] They showed that the aforementioned structural feature of **9** and **10** can be related to the 6c10e $\pi-\pi$ interaction (or the simplified 6c2e $\pi^*-\pi^*$ bond) between the X2−X3−X4 and X6−X7−X8 subunits (X = S, or Se, see Figure 2 for the numbering of the atoms), which is analogous to the inter-VSU bonding within dications $Se_2I_4^{2+}$ (**6**), $S_2O_4^{2-}$ (**7**), and $S_2Cl_4^{2+}$ (**8**).[17b] The selected Kohn−Sham orbitals of S_8^{2+} shown in Figure 3 support this conclusion. Similarly, we infer here that the transannular interaction in **9** and **10** also can be understood with use of the aforementioned 10-electron aromaticity resulting from the through-space homoconjugative interaction between the X2−X3−X4 and X6−X7−X8 subunits with each subunit contributing 5 π-electrons. The computed NICS values of S_8^{2+} (**9**) and Se_8^{2+} (**10**) are −17.9 and −18.6 ppm, respectively, showing that *they are indeed homoaromatic*. Furthermore, Cameron et al. found that the electron delocalization in the cyclic ions X_8^{2+} (X = S, Se) is more complex than that within $Se_2I_4^{2+}$ (**6**), $S_2O_4^{2-}$ (**7**), and $S_2Cl_4^{2+}$ (**8**).[17b] In the X_8^{2+} (X = S, Se) ions, the lone-pair electrons of the X1 and X5 atoms (i.e., the atoms connecting the two conjugated X_3^+ subunits) also contribute to the through-space electron delocalization (Figure 3). Such effects account for the shortening of the X−X bonds around X1 and X5.[17b]

Concluding Remarks

In summary, we have shown the existence of 10e aromaticity in a series of inorganic ions, $Se_2I_4^{2+}$, $S_2O_4^{2-}$, S_8^{2+}, and Se_8^{2+}, which accounts for the unusual through-space X···X (X = S, Se) interaction within these ions. In particular, the aromatic ions $Se_2I_4^{2+}$ and $S_2O_4^{2-}$ have no saturated linkage to connect the spaced conjugative subunits and are geometrically analogous to the aromatic transition states of some pericyclic reactions. Such PTS-like aromaticity should be prevalent in some other diamagnetic inorganic ions and molecules (e.g., $(I_2)_2^{2+}$ and $(NO)_2$)[24,25], consisting of two weakly interacting radical subunits linked by a bond involving the two unpaired electrons in the antibonding π^*-orbitals.[26,27] A systematic theoretical investigation to disclose the presence of PTS-like aromatic through-space conjugation in analogous inorganic systems is currently underway in our laboratory.

Acknowledgment. We are indebted to the reviewers for their insightful comments. This work was sponsored by NSFC (Grants 20021002, 20425312, 20203013, and 20423002), MOE of China (Grant 20010384005), Fok Ying-Tung Education Foundation, NSF of Fujian Province (Grants E0210001 and 2002F010), and MOST of China (Grant 2002CCA01600).

Supporting Information Available: Figure S1, Cartesian coordinates, total energies, and electronic states for the molecules predicted at the MPW1PW91 level of theory. This material is available free of charge via the Internet at http://pubs.acs.org.

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(25) For the diamagnetic ion $(I_2)_2^{2+}$, preliminary MPW1PW91/SDB-cc-pVTZ calculations predicted a NICS value of −20.7 ppm, showing that the through-space conjugation between its two I_2^+ subunits is remarkably aromatic.

(26) Many homopolyatomic cations of Groups 16 and 17 were disclosed to have $\pi^*-\pi^*$ bond(s), see: Brownridge, S.; Krossing, I.; Passmore, J.; Jenkins, H. D. B.; Roobottom, H. K. *Coord. Chem. Rev.* **2000**, *197*, 397 and references therein.

(27) $S_2I_4^{2+}$ was recently disclosed to have two sets of $\pi^*(S_2)-\pi^*(I_2^+)$ bonds, see: Brownridge, S.; Cameron, T. S.; Du, H.; Knapp, C.; Köppe, R.; Passmore, J.; Rautiainen, J. M.; Schnöckel, H. *Inorg. Chem.* **2005**, *44*, 1660 and references therein.