Double aromaticity arising from σ- and π-rings

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Aromaticity has been a central concept in chemistry since the discovery of benzene in the 19th century and has impacted the science of delocalized π-electron systems. The aromaticity of conventional aromatic compounds usually originates from electron delocalization through a single ring that consists of π-symmetric orbitals. Although double aromaticity, i.e. aromaticity composed of two circularly delocalized orbitals, has been theoretically predicted for over 20 years, the double aromaticity of a bench-stable compound is not well explored by experiment. Here we report the synthesis and isolation of the dication of hexakis (phenylselenyl)benzene, as well as its double aromaticity based on structural, energetic, and magnetic criteria. In this dication, cyclic σ-symmetric and π-symmetric delocalized orbitals are formally occupied by ten and six electrons, respectively, and the aromaticity thus follows the $4n + 2$ ($n = 1, 2,...$) electron Hückel rule, regardless of the σ-orbital or π-orbital symmetry.

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Since the discovery of benzene, aromaticity has become one of the most fundamental principles for the understanding of various phenomena in chemistry. Aromaticity is usually derived from conjugated cyclic orbitals that contain $4n + 2$ ($n = 1, 2,…$) electrons, and aromatic compounds exhibit unusually high stability and unique structural characteristics that cannot be rationalized using chemical formulae based on the formalism of organic chemistry developed prior to the discovery of aromaticity. For a long time, aromaticity has been considered to emerge exclusively from interactions between π-symmetric orbitals; however, this symmetry constraint has meanwhile been expanded to include interactions of σ-type[1–3], δ-type[4–6], and φ-type symmetry[7]. Since double aromaticity arising from σ-orbital and π-orbital interactions has been proposed by Schleyer[8], compounds exhibiting double aromaticity have been predicted theoretically[9–17], and metal clusters and compounds with monocyclic carbon/boron rings that bear double aromaticity, generated in the gas phase, have already been characterized[18–23]. The concept of the σ-double and π-double aromaticity has also been discussed in the synthetic investigation of an anionic C_2B_3 ring compound[24]. However, the structural characterization of the double aromaticity of a bench-stable compound remains to be targeted.

Herein, we report the experimental evaluation of double aromaticity using the bench-stable hexakis(phenylselenyl)benzene dication, which exhibits double aromaticity caused by σ-orbital and π-orbital interactions that are consistent with the structural, energetic, and magnetic criteria based on the established definition of aromaticity. An X-ray diffraction analysis of this dication exhibited that the distances between adjacent selenium atoms converge to average values, and that simultaneously the C−C bond distances in the core benzene ring remain unaffected. We have also examined the ring currents due to the cyclic σ-orbitals and π-orbitals that contain 10 and 6 electrons, respectively: both induced ring currents decrease the external magnetic field. Our results demonstrate that the conventional Hückel rule, i.e., that aromaticity arises from π-electron delocalization, is also applicable to double aromaticity on account of the delocalization of σ-electrons and π-electrons. The experimental results presented herein may afford new arguments for the discussion on "what is aromaticity?"[25–28]. Currently, this issue, which has been ongoing since the nineteenth century, has become a hot topic, and should allow the chemical community to attain a better understanding of electronic structures. Moreover, the delocalization of electrons in orthogonal σ-orbitals and π-orbitals could become a strategy for the formation of multi-dimensional charge-transportation systems in the condensed phase.

Results

Molecular design for exhibiting double σ-aromaticity and π-aromaticity.

The introduction of six lone-pair-bearing heteroatom functionalities onto the benzene ring carbon atoms is of crucial importance for the creation of compounds that exhibit double σ-aromaticity and π-aromaticity. The central benzene ring provides π-orbitals that are circularly delocalized over the benzene platform, while the lone-pair electrons in the p-orbitals of the heteroatoms create σ-orbitals that are delocalized in the periphery of the benzene core (Fig. 1a). Martin has reported the synthesis of hexaiodobenzene dication **2** from the two-electron oxidation of hexaiodobenzene **1**[29], which contains 12 electrons in the σ-orbitals of six lone pairs on the six iodine atoms (Fig. 1b)[30]. Dication **2** satisfies the Hückel rule as it contains 10 ($4n + 2$; $n = 2$) electrons in circularly delocalized σ-orbitals. However, on account of the prohibitively low solubility of **2**, an X-ray diffraction analysis, which is one of the most informative experimental analysis techniques for the determination of the molecular structure, remains elusive. Alternative prospective precursors for
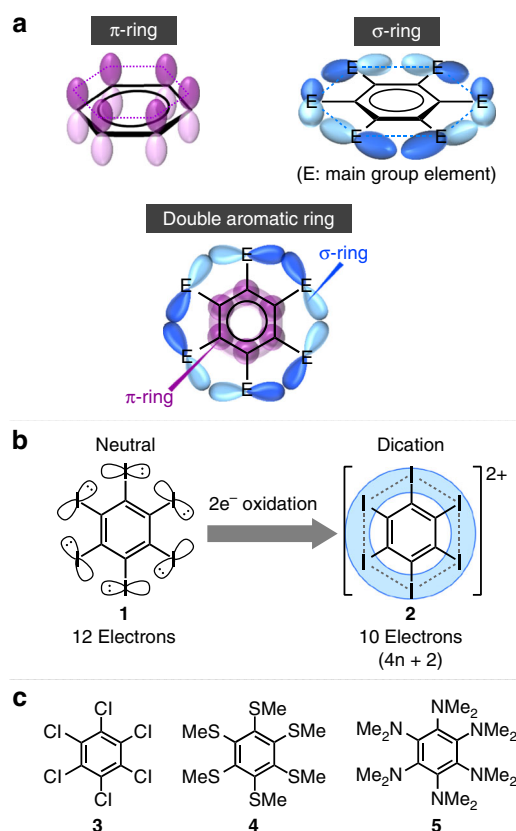

Fig. 1 Double aromaticity arising from σ-orbital and π-orbital interactions in hexaheteroatom-substituted benzenes. **a** Schematic illustration of a double aromatic ring and its π-aromatic and σ-aromatic rings, which consist of six vertically or perpendicularly arranged p-orbitals on a central benzene framework, respectively. **b** Synthesis of hexaiodobenzene dication **2** from the two-electron oxidation of the neutral precursor **1**. **c** Chemical structures of **3**, **4**, and **5** as potential precursors for double σ-aromatic and π-aromatic compounds

double σ-aromatic and π-aromatic compounds are the dications of hexachlorobenzene (**3**) and hexakis(methylsulfanyl)benzene (**4**). However, triplet ground states have been predicted for these dications, and accordingly, their isolation as stable entities in the condensed phase should be relatively difficult (Fig. 1c)[31–33]. The two-electron oxidation of hexakis(dimethylamino)benzene (**5**) afforded the corresponding dication, which revealed a alternation of the C−C bonds in the central benzene ring[34], indicative of a considerable contribution from a quinoidal resonance structure, which indicates the absence of double aromaticity.

A central design feature for the development of bench-stable double σ-aromatic and π-aromatic compounds that can be characterized by single-crystal X-ray diffraction analysis is the introduction of six arylselenyl groups on the benzene ring. Given the relatively large atomic radius of selenium, each selenium atom can interact with its adjacent selenium atoms to produce a circular array of σ-orbitals on the benzene periphery. The substituents on the selenium atoms should suppress molecular aggregation, and thus increase solubility, which would facilitate the generation of single crystals by recrystallization. Furthermore, electron-donating phenylselenyl groups should raise the energy of the highest occupied molecular orbital (HOMO), and thus facilitate the two-electron oxidation of the resulting molecule. The oxidation of hexakis(phenylselenyl)benzene (**6**) was independently investigated by Martin[35]. However, an experimental
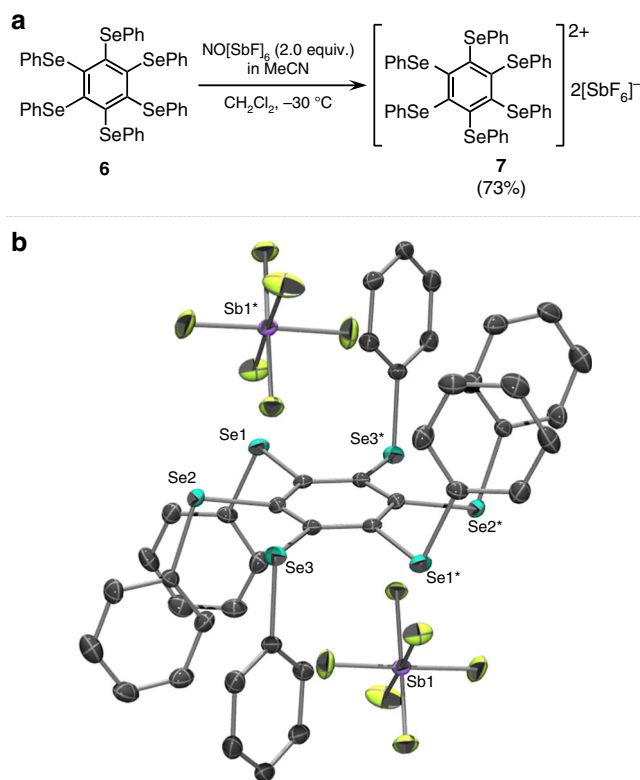
Fig. 2 The isolation of hexakis(phenylselenyl)benzene dication (7). **a** Synthesis of dication **7**. **b** Molecular structure of **7** obtained from a single-crystal X-ray diffraction analysis; thermal ellipsoids set at 50% probability, and all hydrogen atoms and solvent molecules are omitted for clarity

evaluation of the double aromaticity of **6** was not carried out due to a lack of structural information. The clarification of the double aromaticity of the dication of **6** (**7**) thus remains challenging and fundamentally important.

Preparation of dication 7 and its characterization. We synthesized **7** via a two-electron oxidation of precursor **6**[36]. Treatment of **6** with two equivalents of nitrosonium hexafluoroantimonate afforded the targeted dication **7** in 73% yield as a blue-green solid (Fig. 2a). The product is sufficiently stable to be stored in a vial under ambient conditions. Single crystals of **7** were obtained from the slow diffusion of hexane into a concentrated dichloromethane solution of **7**. An X-ray diffraction analysis of these single crystals revealed that the molecular structure contains two hexafluoroantimonate counter anions, indicating a dicationic nature for the hexasubstituted benzene unit (Fig. 2b and Supplementary Data 1).

Based on structural criteria, we concluded that dication **7** exhibits double aromaticity. To elucidate the electronic structure of dication **7**, four possible resonance forms were considered (Fig. 3a). The anticipated structural characteristics for dication **7** with double aromaticity should be: (i) the distances between adjacent selenium atoms should be comparable, and (ii) the benzene core should exhibit comparable C–C bonds (structure I). The open-shell structure with a triplet state (structure II) should possess two cationic selenium atoms that should be coordinated to their adjacent selenium atoms, resulting in alternating Se–Se distances. The quinoidal structure (structure III) should be characterized by a significant alternation of the C–C bonds in the benzene ring, resulting from enhanced double-bond character of the Se–C (benzene core) bonds. In the

structure of the diselenide dication (structure IV), one of the pairs of two adjacent selenium atoms should form a single bond, leading to alternation of the distances between two adjacent selenium atoms. In the following section, the experimentally determined X-ray structure of **7** is compared to these four potential structures.

Both neutral **6** and dicationic **7** contain two structurally independent molecules per unit cell (red: unit A; blue: unit B), which are slightly different from each other (Fig. 3b, c). The distances between adjacent selenium atoms fall into a relatively narrow range [3.240(1)–3.338(1) Å] (Table 1), and are much longer than standard Se–Se single bonds (2.29 Å)[37]. These structural features clearly refute a potential contribution from resonance structure IV to the electronic state of dication **7**. The C–C bond distances [1.382(7)–1.399(7) Å] in the benzene core of **7** exhibit negligible alternation, even though they are slightly shorter than those of **6** [1.398(4)–1.405(5) Å]. The distances between the Se and C atoms on the central benzene ring of **7** [1.906(5)–1.912(5) Å] are also slightly shorter than those in **6** [1.916(3)–1.924(3) Å] but much longer than standard Se–C double bonds (1.82–1.86 Å)[38]. These structural features rule out a potential contribution from quinoidal resonance structure III. As electron paramagnetic resonance (EPR) signals were not observed in a dichloromethane solution of **7** at room temperature, **7** should not adopt a triplet state (structure II). This experimental result is consistent with our previous theoretical prediction that a singlet state of $C_6(SeH)_6^{2+}$ is more stable than that of a triplet state by 3 kcal mol^{-1}[33], and is a sharp contrast with the triplet state in benzene dication ($C_6H_6^{2+}$) having four π-electrons, known as Baird-aromaticity[39–41]. Based on the entirety of the structural characteristics encountered, it is feasible to conclude that **7** exhibits double aromaticity with averaged C–C and Se–Se distances in and around the benzene core, respectively. Another characteristic structural feature that sets apart **6** and **7** are the dihedral angles C1–C2–Se2–C_{Ph} (Fig. 3d, e): in **6**, angles of 48.4(3)° and 59.3(3)° avoid electronic repulsion between the phenyl groups and the lone pairs on the Se atoms, whereas those in **7** are almost perpendicular [83.1(5)°/96.6(5)°], maximizing the interactions between σ-symmetric *p*-orbitals on the Se atoms (Fig. 1a).

Evaluation of double σ-aromaticity and π-aromaticity. Theoretical calculations using a dispersion-corrected density functional theory (DFT) method on model dication **7Me**, which contains six methyl instead of six phenyl groups, revealed that the double aromaticity in the dication is caused by five pairs of circularly arranged σ-type orbitals in the periphery of the benzene core and three pairs of π-type orbitals on the benzene core. The most stable π-type orbital (HOMO-8) does not exhibit any nodes and is delocalized over the entire benzene core, while the degenerate HOMO-4 and HOMO-5 contain one node, and thus represent the second most stable π-type orbitals (Fig. 4a). The arrangement of the molecular orbitals (MOs) clearly indicates π-aromaticity for the benzene core, similar to that in benzene. More interestingly, the σ-type orbitals are delocalized in a similar fashion on the periphery of the benzene core. The most stable σ-type orbital, derived from the 4*p* orbitals of the Se atoms (HOMO-6), corresponds to the π-orbital with no nodes in the π-aromatic compound. The second and third most stable MOs are nearly degenerate with one and two nodes, respectively. Based on the MO description of the π-aromaticity established by Hückel, it can be concluded that these σ-type orbitals produce σ-aromaticity with 10 (4*n* + 2; *n* = 2) electrons. It should be noted that the two types of aromaticity evolve independently, as the σ-type and the π-type orbitals described here are orthogonal with respect to each other.
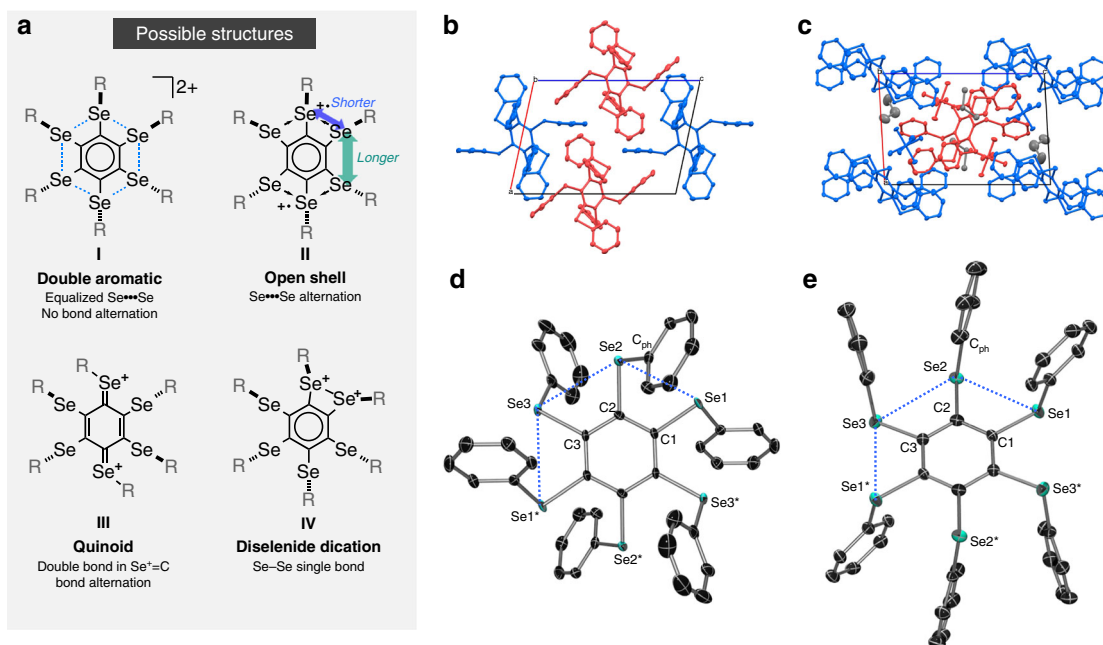
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Fig. 3 A structural perspective on the double aromaticity in dication **7**. **a** Four conceivable resonance structures for **7**: equalized double aromatic, open shell, and bond-alternating quinoidal structures, as well as a diselenide dication with a Se–Se single bond. **b, c** Crystal packing structures of **6** and **7**; crystals of **6** and **7** contain two structurally independent molecules per unit cell (red: unit A; blue: unit B). **d, e** Molecular structures of neutral **6** and dication **7** with thermal ellipsoids set at 50% probability; all hydrogen atoms, solvent molecules, and counter anions ([SbF$_6$]$^-$) are omitted

Table 1 Selected interatomic distances, bond distances, and bond angles for neutral 6 and dicationic 7

	6		7	
	Unit A	Unit B	Unit A	Unit B
Atomic distance (Å)				
Se1···Se2	3.3899 (5)	3.2554 (6)	3.265 (1)	3.3105 (9)
Se2···Se3	3.3789 (5)	3.3662 (6)	3.3329 (9)	3.240 (1)
Se3···Se1*	3.3136 (6)	3.4040 (6)	3.288 (1)	3.338 (1)
Bond length (Å)				
C1-C2	1.398 (4)	1.403 (4)	1.388 (7)	1.390 (6)
C2-C3	1.403 (4)	1.402 (4)	1.399 (7)	1.392 (8)
C3-C1*	1.402 (5)	1.405 (5)	1.382 (7)	1.391 (8)
C1-Se1	1.922 (3)	1.916 (3)	1.911 (5)	1.906 (6)
C2-Se2	1.922 (4)	1.921 (3)	1.908 (5)	1.912 (5)
C3-Se3	1.924 (3)	1.924 (3)	1.907 (5)	1.906 (5)
Dihedral angle (°)				
C1-C2-Se2-C$_{ph}$	48.4 (3)	59.3 (3)	83.1 (5)	96.6 (5)

We estimated the resonance energy that arises from the σ-aromaticity in dication **7** based on the energy difference between the conformational isomers of the same molecule. To estimate the resonance energy derived from the σ-symmetric orbitals, a conformer that contains one *p*-orbital orthogonal to the original σ-symmetric conjugated *p*-orbitals should be an appropriate reference, as the σ-aromaticity should then collapse (Fig. 4b). Accordingly, we used DFT methods to calculate the electronic energies with zero-point corrections for three conformations. In conformer **7'-[3u,3d]**, three adjacent peripheral phenyl groups are located on the upper side of the central benzene ring, while the other three adjacent phenyl groups are located on the opposite side. A structural optimization of the cationic part (**7'**) encountered in the crystal structure of **7** suggested that this conformer is the

most stable. Conformer **7'-[4u,2d]** is obtained from **7'-[3u,3d]** by bringing a fourth phenyl group to either side of the central benzene. These two conformers are separated by a small energy difference of 1.9 kcal mol^{-1}. In their optimized structures, the phenyl rings are arranged almost perpendicular to the central benzene ring (**7'-[3u,3d]**: 80.38°; **7'-[4u,2d]**: 102.11°), and their molecular orbitals are circularly delocalized through the σ-symmetric orbitals (Figure S1a,c). The third conformation is the transition state **7'-TS** for the conformational transition from **7'-[3u,3d]** to **7'-[4u,2d]**. In the obtained TS structure, the C^2–C^1–Se^1–C$_{ph}$ dihedral angle (171.22°) induces an almost coplanar arrangement with the central benzene ring, which results in partial delocalization due to the orthogonal p-orbitals on the Se atoms (Supplementary Figure 9b). The energy difference between **7'-[3u,3d]** and **7'-TS** (8.3 kcal mol^{-1}) should thus correspond to the aromatic stabilization by the σ-symmetric orbitals. A similar energy was obtained from calculations on model compound **7$_{Me}$** and its corresponding conformers (Supplementary Figure 10). In contrast to the σ-system, it is very difficult to estimate the resonance stabilization in ten-electron delocalized π-systems such as [10]annulene derivatives, due to the presence of severe levels of strain in the carbon framework[42]. In dication **7**, the σ-cyclic orbitals are, however, not located on such a covalently bound C–C framework, i.e., the resonance stabilization by σ-delocalization of ten electrons proceeds without increasing the intrinsic levels of strain. An atoms in molecule (AIM) analysis of **7'-[3u,3d]** showed six bond critical points (BCPs) between all neighboring Se atoms (Supplementary Figure 11). The Wiberg bond indices (WBIs) of the neighboring Se atoms (Se1···Se2: 0.075; Se2···Se3: 0.075; Se3···Se1*: 0.073) indicate the presence of weak bonding interactions between them. In neutral **6**, BCPs were not observed between neighboring Se atoms, and their WBIs (0.011–0.017) are smaller than those of **7'**.

The double aromaticity of dication **7** is also corroborated by its magnetic behavior. The ring currents induced under an external magnetic field can be used as a diagnostic magnetic criterion for aromaticity. Assuming that dication **7** exhibits a double aromatic
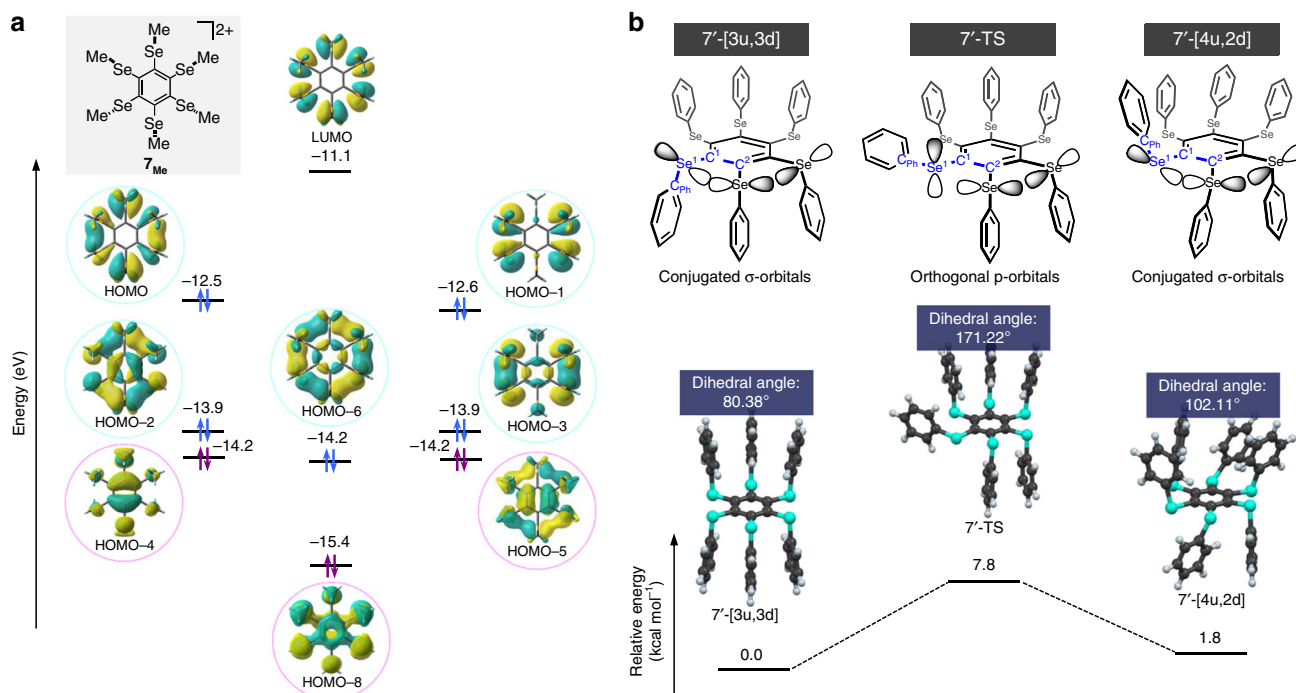
Fig. 4 Calculated molecular orbitals and resonance energies for the σ-aromaticity of dication 7. **a** Chemical structure of model compound **7$_{Me}$** and its calculated molecular orbitals. Blue and purple circles represent σ-symmetric and π-symmetric occupied orbitals, respectively. **b** Schematic drawings of the two conformers **7′-[3u,3d]** and **7′-[4u,2d]**, as well as the transition state **7′-TS**, together with the p-orbitals on their selenium atoms (top). Calculated structures for **7′-[3u,3d]**, **7′-[4u,2d]**, and **7′-TS**, as well as relative electronic energies with zero-point corrections (bottom)

character, a double ring current should be induced by the delocalization of the 6 π-electrons and 10 σ-electrons (Fig. 5a). Based on the optimized geometry of the cationic part **7′**, the zz component of the nucleus-independent chemical shift (NICS) was calculated at the center of the central benzene ring [NICS $(0)_{zz}$][43] (Fig. 5b). The calculated NICS$(0)_{zz}$ value of **7′-[3u,3d]** (−25.4 ppm) (Fig. 4b) is more negative than those of **6-[3u,3d]** (−7.8 ppm) and benzene (−13.2 ppm). These results indicate that the levels of aromaticity in **7′** should be higher than those of compounds that exhibit only π-aromaticity. The NICS$(0)_{zz}$ value for the neutral transition state **6-TS** (−8.6 ppm) was not remarkably different from that of **6-[3u,3d]**, whereas that of **7′-TS** (−9.0 ppm) was significantly less negative than that of **7′-[3u,3d]** and comparable to that of **6-TS**. The conformational change in **7′** renders one of the σ-symmetric 4p orbitals orthogonal, resulting in a collapse of the σ-aromaticity. Upon further rotation, the σ-aromaticity recovers in **7′-[4u,2d]** [NICS $(0)_{zz}$: −24.0 ppm], which is comparable to that of the **7′-[3u,3d]** conformer. To evaluate the contribution of the σ-symmetric MOs to NICS values clearly, we decomposed the NICS$(0)_{zz}$ of the dication **7$_{Me}$** (−31.1 ppm) into the contributions from each MO (CMO-NICS)[44]. The contribution from five σ-orbitals (HOMO, HOMO−1, HOMO−2, HOMO−3, and HOMO−6 shown in Fig. 4a), π-orbitals, and other σ-orbitals were −12.1 ppm (39%), −25.0 ppm (80%), and 6.1 ppm (−21%), respectively. Therefore, both π and σ aromaticities have comparable contributions to NICS$(0)_{zz}$ values. The ring currents of **6** and **7′** were also analyzed by the anisotropy of the current (induced) density (ACID) method (Fig. 5c, Supplementary Figure 12)[45], wherein the applied external magnetic field was oriented perpendicular to the molecular plane defined by the carbon framework of the central benzene ring. Despite the fact that clockwise current density vectors were plotted at the central benzene ring of neutral **6**, which usually indicates (diamagnetic) ring currents in aromatic

systems, clockwise vectors through the six selenium atoms were not obtained. On the other hand, dication **7′-[3u,3d]** showed clockwise vectors through the six Se atoms in addition to the central benzene ring, reflecting the double aromatic nature. These results are consistent with theoretical investigations of the analog $C_6(SeH)_6^{2+}$, which have been reported by Liégeois et al.[46].

A ^{13}C solid-state nuclear magnetic resonance (NMR) measurements using cross-polarization (CP) and magic-angle spinning (MAS) methods corroborated the double aromaticity of dication **7**. In neutral **6**, six signals (151.40, 150.02, 149.41, 148.78, 147.89, 145.53 ppm) were observed for the carbon nuclei on the central benzene ring. The signals for the ^{13}C nuclei of the central benzene rings in **6** and **7** were assigned based on the signals of the independently synthesized ^{13}C-enriched compounds **6-[13]C** and **7-[13]C** (Supplementary Figures 7 and 8). In contrast, dication **7** showed only three signals at higher magnetic field (145.84, 141.02, 139.93 ppm). Such an upfield shift would not be expected if the positive charges were delocalized over the π-system of the central C_6Se_6 skeleton. The decrease of the electron density on the C atoms should cause a downfield resonance of the C nuclei[30]. Removal of two electrons from the substrate induced a delocalization of the positive charges over the six Se atoms, resulting in the induction of the σ-ring current.

Methods
General considerations for synthesis, characterization and computations. See Supplementary Methods and Supplementary Figures 1–8.

Theoretical calculations on geometric optimization of the cationic part (7′). See Supplementary Figure 9 and Supplementary Tables 1-3.

Theoretical calculations on 7$_{Me}$ and its conformers. See Supplementary Figure 10 and Supplementary Tables 4-6.
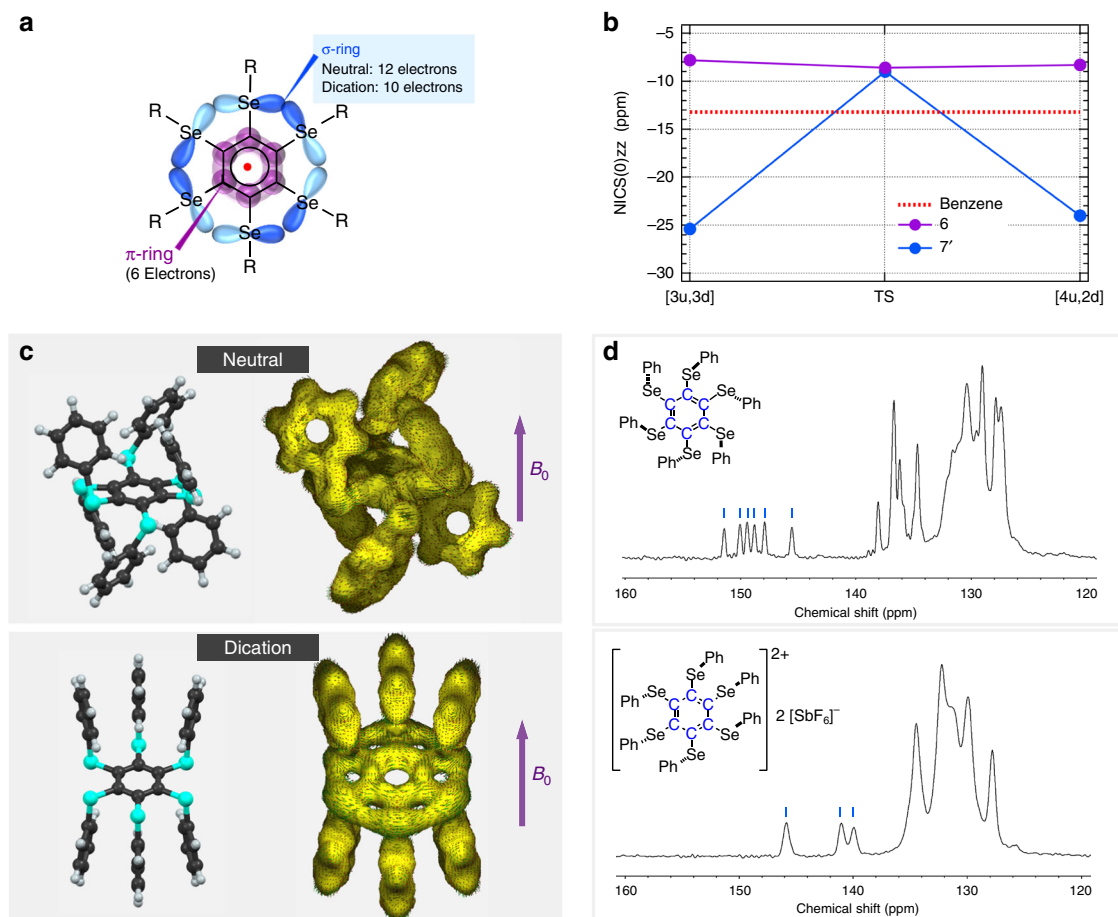
Fig. 5 A magnetic perspective on the double aromaticity in dication **7**. **a** A schematic illustration of the σ- and π-rings in **7**. The π-ring on the central benzene ring contains six electrons, while the σ-ring hosts formally twelve (**6**) or ten electrons (**7**) on the Se atoms. **b** Calculated NICS(0)$_{zz}$ values for **6** and **7′** for the **[3u,3d]**, **TS**, and **[4u,2d]** conformations. The NICS(0)$_{zz}$ values of benzene (red dotted line) are shown for comparison. **c** Molecular structures of **6** and **7′** used for the ACID calculations, and their current density vectors plotted onto the ACID isosurfaces (isosurface value: 0.025). Magnified images are shown in Supplementary Figure 12. **d** ^{13}C CP/MAS solid-state NMR spectra of **6** (top) and **7** (bottom)

AIM analysis of neutral 6 and dicationic 7. See Supplementary Figure 11.

ACID calculations of 6 and 7′. See Supplementary Figure 12.

Comparison of the geometrical parameters of C$_6$(SePh)$_6$$^{2+}$ obtained using different DFT functionals. See Supplementary Note 1 and Supplementary Table 7.

Data availability

The crystallographic information for this paper has been deposited at The Cambridge Crystallographic Data Center (http://www.ccdc.cam.ac.uk) under reference number CCDC1564760 for compound **7**. All other data generated and analyzed during the current study are included in Supplementary Data 1, or are available from the corresponding authors upon reasonable request.

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Author contributions

S.F., M.F., and Y.K. conducted the synthetic experiments and analyzed the data. M.H., K.I., and K.M. performed the computational investigations. M.M. carried out the X-ray diffraction analyses. S.F. and M.S. prepared the manuscript. M.S. conceived the project, which was directed by S.F. and M.S.

Additional information

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