

# *Ab initio* and density functional theory studies of the structure, gas-phase acidity and aromaticity of tetraselenosquaric acid

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Results of *ab initio* self-consistent-field (SCF) and density functional theory (DFT) calculations of the gas-phase structure, acidity (free energy of deprotonation,  $\Delta G^\circ$ ) and aromaticity of tetraselenosquaric acid (3, 4-diselenyl-3-cyclobutene-1,2-diselenone,  $H_2C_4Se_4$ ) are reported. The global minimum found on the potential energy surface of tetraselenosquaric acid presents a planar conformation. The ZZ isomer was found to have the lowest energy among the three planar conformers and the ZZ and ZE isomers are very close in energy. The optimized geometric parameters exhibit a bond length equalization relative to reference compounds, cyclobutanediselenone, and cyclobutenediselenol. The computed aromatic stabilization energy (ASE) by homodesmotic reaction is  $-77.4$  (MP2(fu)/6-311+G\*\*//RHF/6-311+G\*\*) and  $-54.8$  kJ/mol (B3LYP/6-311+G\*\*//B3LYP/6-311+G\*\*). The aromaticity of tetraselenosquaric acid is indicated by the calculated diamagnetic susceptibility exaltation ( $\Lambda$ )  $-19.13$  (CSGT(IGAIM)-RHF/6-311+G\*\*//RHF/6-311+G\*\* and  $-32.91(4\pi \cdot 10^{-6} \text{ m}^3/\text{mol})$  (CSGT(IGAIM)-B3LYP/6-311+G\*\*//B3LYP/6-311+G\*\*). Thus, tetraselenosquaric acid fulfils the geometric, energetic and magnetic criteria of aromaticity. The calculated gas-phase acidity is  $\Delta G_{1(298K)}^\circ = 1257.7$  and  $\Delta G_{2(298K)}^\circ = 1617.1$  kJ/mol. Hence, tetraselenosquaric acid is the strongest acid among the three squaric acids (3, 4-dihydroxy-3-cyclobutene-1, 2-dione,  $H_2C_4O_4$ , 3, 4-dithiohydroxy-3-cyclobutene-1, 2-dithione,  $H_2C_4S_4$ , 3, 4-diselenyl-3-cyclobutene-1, 2-diselenone,  $H_2C_4Se_4$ ).

**Keywords** Tetraselenosquaric acid, *ab initio*, density functional theory (DFT), gas-phase acidity, aromaticity

## Introduction

In the 40 years since the oxocarbon anions  $C_nO_n^{2-}$

were recognized as members of a new class of stabilized carbocyclic nonbenzenoid aromatic compounds<sup>1</sup>, knowledge of their chemical-physical properties has been developing rapidly. Their unique electronic structures, high degree of symmetry and aesthetically beautiful geometry generated a fresh impetus to study the effect of replacing oxygens by various other functional groups, such as nitrogen, sulfur, selenium and phosphorus.<sup>2</sup> My interests have been focused on studies pertinent to the aromatic oxocarbons and squaric acid in which the original carbonyl and hydroxy oxygen atoms in  $C_nO_n^{2-}$  and  $H_2C_4O_4$  are either partially or completely replaced by sulfur and selenium. Analogous to the oxocarbon dianions, the selenoxocarbon can be characterized by the general formula  $C_nSe_n^{2-}$ , in which  $n$  is any positive integer. However, to our knowledge, high level *ab initio* and density functional theory (DFT) studies of the gas phase structure, acidity and aromaticity of tetraselenosquaric acid (3, 4-diselenyl-3-cyclobutene-1, 2-diselenone,  $H_2C_4Se_4$ ) have not yet been reported. This study will report optimized molecular geometries of the three planar conformers of the title compound and corresponding anions at the *ab initio* and DFT levels of theory using 6-311G\*\* and 6-311+G\*\* (ZZ isomer) basis sets, the MP2 (full) single-point energies as well as the results of the *ab initio* and DFT predictions of the aromaticity and gas-phase acidity of the title compound.

## Computational details

The geometries of the compounds under study were optimized at the RHF/6-311G(d,p), RHF/6-311+G

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(d,p)(*ZZ* isomer) *ab initio*, and the B3LYP/6-311 + G(d,p)(*ZZ* isomer) density functional levels by the gradient procedure<sup>3</sup> with the Gaussian 94 program package.<sup>4</sup> In view of the fact that the X-ray structure of squaric acid ( $\text{H}_2\text{C}_4\text{O}_4$  or  $\text{H}_2\text{Sq}$ ) is practically planar and that the title compound is similar with it,  $C_s$  symmetry was considered during the optimization of the  $\text{H}_2\text{C}_4\text{Se}_4$ . The nature of each stationary point was characterized by computing the harmonic vibrational frequencies at the various levels. The correlation energies were calculated by means of Moller-Plesset perturbation theory.<sup>5,6</sup> Single-point energies were also computed at MP2(fu)/6-311 + G(d,p) with the correlated geometries. Energies have been corrected for zero-point vibrational energy (ZPVE).

The homodesmotic reaction (Eq. (1)) was used to evaluate the aromatic stabilization energy (ASE). Because all the reference compounds were computed in their most stable conformations, strain effects should be cancelled to a large extent. The magnetic susceptibility exaltation ( $\Delta$ ) was computed with the Continuous Set of Gauge Transformations (CSGT)<sup>7,8</sup> and IGAIM<sup>8</sup> (a slight variation on CSGT which uses atomic centers as the

gauge origin) methods at the RHF/6-311 + G(d,p) and the B3LYP/6-311 + G(d,p) levels with the RHF/6-311 + G(d,p) and B3LYP/6-311 + G(d,p) geometries, respectively.

Gas-phase acidity of Brønsted acids is defined as the free energy of deprotonation and designated  $\Delta G_{\text{acid}}^\circ$ .<sup>9</sup> The gas-phase acidity ( $\Delta G_1^\circ$  and  $\Delta G_2^\circ$ ) of the  $\text{H}_2\text{C}_4\text{Se}_4$  were calculated at the MP2(fu)/6-311 + G(d,p)//HF/6-311 + G(d,p) and the B3LYP/6-311 + G(d,p) levels for the first time.

## Results and discussion

### Aromaticity

The optimized geometric parameters for the three planar conformers of the  $\text{H}_2\text{C}_4\text{Se}_4$  molecule and the  $\text{HC}_4\text{Se}_4^-$  and  $\text{C}_4\text{Se}_4^{2-}$  anions calculated at the RHF/6-311G(d,p), RHF/6-311 + G(d,p) and the B3LYP/6-311 + G(d,p) levels of theory are presented in Table 1. The structures and atom numbering of them are displayed in Fig. 1.

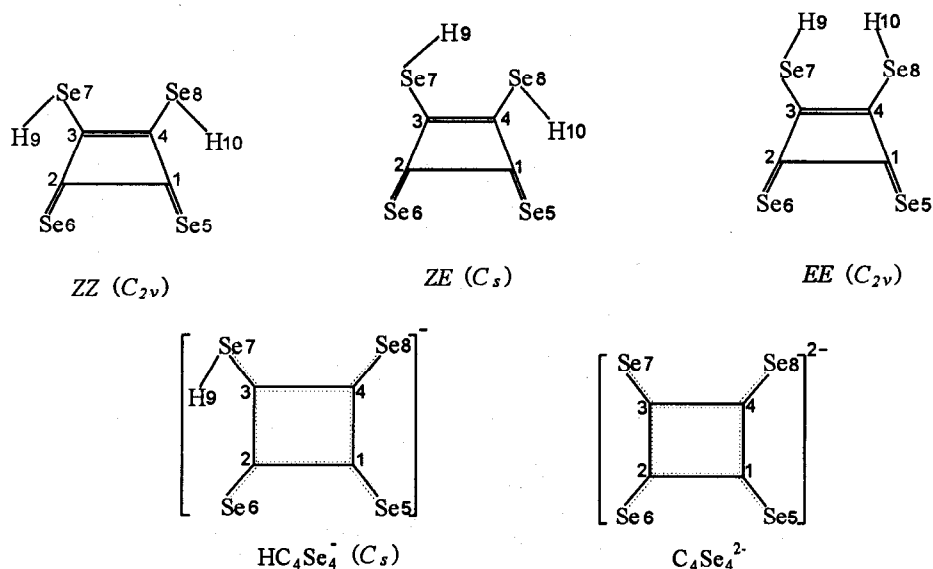


Fig. 1 Structures and atom numbering for the three planar isomers of  $\text{H}_2\text{C}_4\text{Se}_4$  and anions.

As shown in Table 1, the difference of the parameters computed is negligible by the RHF/6-311G(d,p) and RHF/6-311 + G(d,p) basis sets, but the difference is not negligible using the former two basis sets and the

B3LYP/6-311 + G(d,p) method. Most bond lengths excluding C—C and C—Se single bond B3LYP are longer than those at SCF, and their differences are about 0.003 nm. As can be seen in Table 1, the computed

Table 1 Optimized geometrical parameters (nm, deg.)

parameters	ZZ			ZE		EE
	RHF	B3LYP	RHF	RHF	RHF	
	6-311G**	6-311+G**	6-311+G**	6-311G**	6-311G**	
C1—C2	0.1501	0.1501	0.1501	0.1530	0.1502	
C2—C3	0.1462	0.1462	0.1467	0.1498	0.1462	
C1—C4	0.1462	0.1462	0.1467	0.1498	0.1462	
C3 = C4	0.1366	0.1366	0.1395	0.1356	0.1365	
C1 = Se5	0.1743	0.1744	0.1770	0.1697	0.1742	
C2 = Se6	0.1743	0.1744	0.1770	0.1695	0.1742	
C3—Se7	0.1866	0.1866	0.1859	0.1868	0.1869	
C4—Se8	0.1866	0.1866	0.1859	0.1867	0.1869	
Se7—H9	0.1454	0.1454	0.1485	0.1454	0.1453	
Se8—H10	0.1454	0.1454	0.1485	0.1453	0.1453	
C1-C2-C3	87.3	87.4	87.9	87.3	87.3	
C2-C1-C4	87.3	87.4	87.9	87.3	87.3	
C2-C3-C4	92.7	92.6	92.1	92.7	92.7	
C1-C4-C3	92.7	92.6	92.1	92.7	92.7	
C2-C1=Se5	136.9	136.9	138.4	137.0	137.0	
C4-C1=Se5	135.7	135.7	133.6	135.7	135.7	
C1-C2=Se6	136.9	136.9	138.4	137.0	137.0	
C3-C2=Se6	135.7	135.7	133.6	135.7	135.7	
C2-C3-Se7	132.5	132.5	130.5	129.4	128.4	
C4-C3-Se7	134.9	134.9	137.5	137.9	138.9	
C1-C4-Se8	132.5	132.5	130.5	132.4	128.4	
C3-C4-Se8	134.9	134.9	137.5	135.0	138.9	
C3-Se7-H9	93.5	93.5	90.0	95.0	95.4	
C4-Se8-H10	93.5	93.5	90.0	93.6	95.4	
parameters	HC <sub>4</sub> Se <sub>4</sub> <sup>-</sup>			C <sub>4</sub> Se <sub>4</sub> <sup>2-</sup>		
	RHF	B3LYP	RHF	RHF	RHF	
	6-311G**	6-311+G**	6-311+G**	6-311G**	6-311+G**	
C1—C2	0.1486	0.1486	0.1496	0.1446	0.1464	
C2—C3	0.1409	0.1409	0.1427	0.1446	0.1464	
C1—C4	0.1484	0.1484	0.1488	0.1446	0.1464	
C3—C4	0.1409	0.1409	0.1428	0.1446	0.1464	
C1—Se5	0.1757	0.1758	0.1782	0.1818	0.1825	
C2—Se6	0.1796P	0.1797	0.1806	0.1818	0.1825	
C3—Se7	0.1870	0.1869	0.1870	0.1818	0.1825	
C4—Se8	0.1800	0.1801	0.1809	0.1818	0.1825	
Se7—H9	0.1455	0.1455	0.1487			
C1-C2-C3	88.2	88.2	87.8	89.7	90.0	
C2-C1-C4	88.7	88.7	89.4	89.7	90.0	
C2-C3-C4	94.9	94.9	94.7	89.7	90.0	
C1-C4-C3	88.2	88.3	88.1	89.7	90.0	
C2-C1-Se5	135.6	135.6	135.2	135.2	135.0	
C4-C1-Se5	135.7	135.7	135.4	135.2	135.0	
C1-C2-Se6	136.7	136.7	137.1	135.2	135.0	
C3-C2-Se6	135.2	135.1	135.1	135.2	135.0	
C2-C3-Se7	131.9	131.9	134.3	135.2	135.0	
C4-C3-Se7	133.2	133.2	131.0	135.2	135.0	
C1-C4-Se8	136.6	136.6	138.4	135.2	135.0	
C3-C4-Se8	135.1	135.1	133.5	135.2	135.0	
C3-Se7-H9	93.3	93.4	89.6			
C4-C1-C2-C3	0.0	0.0	0.0	8.9	0.0	
H9-Se7-C3-C2	180.0	180.0	180.0	10.2		

bond lengths of the three planar isomers are very similar. The calculated results reveal larger difference between the double bonds C = C and C = Se and between the corresponding single bonds C—C and C—Se, indicating that the resonance effect should be small. However, the optimized C = C and C = Se double bonds are lengthened by 0.005 nm and 0.001 nm, C—C and C—Se single bonds are shortened by 0.006 nm and 0.004 nm relative to those reference compounds, cyclobutenediselenol and cyclobutandiselenone, suggesting that the title compound has equalization bond length. Hence, the title compound is aromatic according to the geometric criteria of aromaticity.<sup>10,11</sup>

It can be seen from the computed geometric parameters of the  $\text{HC}_4\text{Se}_4^-$  and  $\text{C}_4\text{Se}_4^{2-}$  anions in Table 1 that C—C and C—Se bonds do not have a clear single or double bond character, indicating that  $\pi$  electron delocalization is quite strong in these anions. It must be

pointed out that the dianion has an imaginary frequency when it is optimized with  $C_s$  symmetry, indicating that the optimized geometry at the level and symmetry is not a stationary molecular configuration. However, the dianion exhibits a non-planar equilibrium geometry when optimized without using any symmetry. This is not consistent with the dianion of squaric acid<sup>12</sup> and tetrathiosquaric acid.<sup>13</sup> However, the difference of planar configuration with non-planar in energy is about 0.4 kJ/mol.

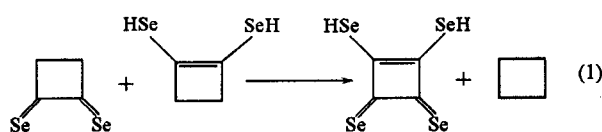
The calculated total and relative energies for the three planar conformers of the  $\text{H}_2\text{C}_4\text{Se}_4$  at the various computational levels are listed in Table 2. It can be seen that the ZZ conformer is the most stable among the three planar isomers. In fact, the ZZ and ZE isomers are very close in energy. This is consistent with the computational results of squaric acid<sup>12</sup> and tetrathiosquaric acid.<sup>13</sup>

Table 2 Calculated total and relative energies of the three isomers (kJ/mol)<sup>a</sup>

Method	Total energy			Relative energy		
	ZZ	ZE	EE	ZZ	ZE	EE
RHF/6-311G**	-25603119.8	-25603115.0	-25603107.8	0	4.8	12.0
RHF/6-311 + G**	-25603127.4					
MP2/6-311G** <sup>b</sup>	-25605857.7	-25605850.9	-25605843.1	0	6.8	14.6
MP2/6-311 + G** <sup>c</sup>	-25605880.0					
B3LYP/6-311 + G**	-25624313.3					

<sup>a</sup> Scaled by ZPVE. <sup>b</sup> Using the RHF/6-311G\*\* geometry and scaled by the RHF/6-311G\*\* ZPVE. <sup>c</sup> Using the RHF/6-311 + G\*\* geometry and scaled by the RHF/6-311 + G\*\* ZPVE.

The computed aromatic stabilization energies (ASEs) using the homodesmotic reaction (Eq. (1)) are given in Table 3. Because all the compounds in Eq. (1) were calculated in their most stable conformations, strain effects should be cancelled to a large extent. Eq. (1) gave the ASEs associated with cyclic delocalization (negative energies denote the stabilization for aromatic molecules) or with cyclic localization (positive energies denote destabilization of antiaromatic compounds). The computed ASEs of  $\text{H}_2\text{C}_4\text{Se}_4$  at the various levels are all negative values, suggesting that the  $\text{H}_2\text{C}_4\text{Se}_4$  is aromatic according to the energetic criteria of aromaticity.



$\text{H}_2\text{C}_4\text{Se}_4$  is aromatic according to the geometric and energetic criteria of aromaticity. The magnetic property of  $\text{H}_2\text{C}_4\text{Se}_4$  fulfils the magnetic criterion of aromaticity as well. The magnetic susceptibility exaltation ( $\Lambda$ ) was calculated using the CSGT and IGAIM methods at the RHF/6-311 + G(d, p) and B3LYP/6-311 + G(d, p) levels of theory.

Table 3 Calculated ASE (kJ/mol)<sup>a</sup>

Method	ASE
RHF/6-311G**//RHF/6-311G**	-35.6
RHF/6-311 + G**//RHF/6-311 + G**	-40.6
MP2/6-311 + G**//RHF/6-311 + G** <sup>b</sup>	-77.4
B3LYP/6-311 + G**//B3LYP/6-311 + G**	-54.8

<sup>a</sup> Scaled by ZPVE. <sup>b</sup> Scaled by RHF/6-311 + G\*\* ZPVE.

That aromatic compounds exhibit enhanced diamag-

netic susceptibility was noted by Pascal in his pioneering investigation.<sup>14</sup> Pauling ascribed these effects to ring currents in 1936.<sup>15</sup> Flygare and colleague<sup>16,17</sup> used the magnetic susceptibility anisotropies and Dauben *et al.*<sup>18</sup> used the magnetic susceptibility exaltation to characterize the aromatic compounds comprehensively. Recently, Cremer *et al.*<sup>19-21</sup> established that homo- and bishomocyclic systems were aromatic by means of their computed magnetic susceptibilities. However, for many interesting systems, including  $\text{H}_2\text{C}_4\text{Se}_4$  compound, there are no experimental magnetic data on some of the molecules which one wants for the group increments. In a new development and application, Kutzelnigg<sup>22,23</sup> and Schleyer *et al.*<sup>24-28</sup> have shown that magnetic susceptibilities can be now calculated to reasonable accuracy for molecules of interest to organic and inorganic chemists.

The magnetic susceptibility exaltation ( $\Lambda$ , Eq. (2)) is defined as the difference between the computed magnetic susceptibility ( $\chi_M$ ) for the observed compound

( $\text{H}_2\text{C}_4\text{Se}_4$ ) and the value estimated for the hypothetical system without cyclic electron delocalization ( $\chi'_M$ ). The latter is based on the bond increments that we have determined by computations on appropriate model compounds (Eq. (1)). The exaltation  $\Lambda$  are negative (diamagnetic) for the aromatic compounds, but positive (paramagnetic) for the antiaromatic cases.

$$\Lambda = \chi_M - \chi'_M \quad (2)$$

The computed  $\Lambda$  are collected in Table 4. The magnetic susceptibility data presented in Table 4 include all of the molecules needed for the increments involved in calculating  $\Lambda$ . In Table 4 the eigenvalues of the magnetic susceptibility tensor as well as the isotropic part  $\chi_{av}$  and the anisotropic  $\Delta\chi$  are listed. The computed  $\Lambda$  here are negative and large numbers do correspond to an aromatic compound.

Table 4 Computed  $\Lambda$  ( $4\pi \cdot 10^{-6} \text{ m}^3/\text{mol}$ ) (with 6-311+G\*\* basis set)

Method	Compound	$\epsilon_1^b$	$\epsilon_2$	$\epsilon_3$	$\chi_{av}^c$	$\Delta\chi^d$	$\Lambda$
CSGT(IGAIM) <sup>a</sup> -RHF//RHF	cyclobutanediselenone	-95.96	-54.41	-35.64	-62.00	39.54(11.40)	
	cyclobutenediselenol	-92.18	-82.14	-81.29	-85.20	5.87(5.87)	
	cyclobutane	-44.57	-44.55	-32.59	-40.57	11.98(-5.50)	
	$\text{H}_2\text{C}_4\text{Se}_4$ (ZZ)	-158.78	-116.90	-101.61	-125.76	36.23(-49.53)	-19.1
CSGT(IGAIM)-B3LYP//B3LYP	cyclobutanediselenone	-93.27	-32.45	-8.89	-44.87	53.97(-72.60)	
	cyclobutenediselenol	-88.94	-80.55	-79.65	-83.05	5.10(5.10)	
	cyclobutane	-44.57	-44.55	-32.59	-40.57	11.98(12.91)	
	$\text{H}_2\text{C}_4\text{Se}_4$ (ZZ)	-161.41	-106.43	-97.01	-121.62	36.91(-59.70)	-32.9

<sup>a</sup> Both methods give the same results. <sup>b</sup>  $\epsilon_1, \epsilon_2, \epsilon_3$ : eigenvalues of the magnetic susceptibility tensor as reported in the Gaussian 94 output file (where arbitrarily,  $\epsilon_1 < \epsilon_2 < \epsilon_3$ ). <sup>c</sup>  $\chi_{av}$  is the isotropic part [ $\chi_{av} = 1/3(\epsilon_1 + \epsilon_2 + \epsilon_3)$ ] or defined in terms of in-plane ( $\chi_{xx} + \chi_{yy}$ ) and out-of-plane ( $\chi_{zz}$ ) components ( $\chi_{av} = 1/3(\chi_{xx} + \chi_{yy} + \chi_{zz})$ ). <sup>d</sup>  $\Delta\chi$  is the anisotropic part ( $\Delta\chi = \epsilon_3 - (\epsilon_1 + \epsilon_2)/2$ ), values in parentheses are usually reported as [ $\Delta\chi = \chi_{zz} - (\chi_{xx} + \chi_{yy})/2$ ].

### Gas-phase acidity

Investigations of the acidity of organic compounds have played a central role in the development of physical organic chemistry and the conceptual understanding of organic reactivity.<sup>29</sup> Organic acids, especially those that yield resonance-stabilized anions, are of major importance in synthetic organic chemistry and have also been the subject of many mechanistic investigations. Numerous calculations of gas-phase acidities of carbon acids have been reported in the recent literature by both *ab initio* and density functional theory methods.<sup>30,31</sup> Of

these investigations, excellent agreement with experiments were obtained by the G2(MP2, SVP), G2(MP2) and G2 procedures. Various G2 methods, however, are sufficiently time consuming that it would be impractical for other than very simple acids and for nearly all of the projected reaction profile studies. In the study, we calculated the gas-phase acidity of the title compound at *ab initio* and B3LYP levels of theory with the 6-311G(d, p) and 6-311+G(d, p) basis sets.

Gas-phase acidity of Brønsted acids is defined as the free energy of deprotonation and designated  $\Delta G_{\text{acid}}^{\circ}$ .<sup>32</sup> Both the  $\text{H}_2\text{C}_4\text{Se}_4$  and  $\text{HC}_4\text{Se}_4^-$  lose a proton

when acting as acid. The different components of the energy of dissociation are shown in Table 5 and Table 6. All the energies of dissociation are calculated by the most stable conformer (*ZZ*) in the gas phase. As can be seen in Table 5 and Table 6, the computed free energy of deprotonation are  $\Delta G_{1(298\text{K})}^{\circ} = 1314.2$  (MP2), and 1257.7 (B3LYP) kJ/mol and  $\Delta G_{2(298\text{K})}^{\circ} = 1568.2$  (MP2), and 1617.1 (B3LYP) kJ/mol, respectively. The differences of results obtained using these methods are 50–54 kJ/mol. This is not consistent with those of squaric acid<sup>12</sup> and tetrathiosquaric acid.<sup>13</sup> However, B3LYP is generally computationally more economical. Comparisons of the computed  $\Delta G_{1(298\text{K})}^{\circ}$  and  $\Delta G_{2(298\text{K})}^{\circ}$  with those of experimental in the gas phase have not

been carried out because the determination of gas phase acidity of the title compound has not, to our knowledge, yet been reported. As mentioned above, it is believed that the reliable theoretical gas-phase acidity is  $\Delta G_{1(298\text{K})}^{\circ} = 1257.7$  kJ/mol and  $\Delta G_{2(298\text{K})}^{\circ} = 1617.1$  kJ/mol, because the B3LYP method ordinarily provides the most reliable thermochemical predictions.<sup>33</sup> Comparisons of the calculated  $\Delta G_{1(298\text{K})}^{\circ}$  and  $\Delta G_{2(298\text{K})}^{\circ}$  of the  $\text{H}_2\text{C}_4\text{Se}_4$  with  $\Delta G_{1(298\text{K})}^{\circ} = 1302.9$  (B3LYP) and  $\Delta G_{2(298\text{K})}^{\circ} = 1761.5$  kJ/mol (B3LYP) of the  $\text{H}_2\text{C}_4\text{O}_4$  ( $\text{H}_2\text{Sq}$ ) and  $\Delta G_{1(298\text{K})}^{\circ} = 1270.7$  (B3LYP) and  $\Delta G_{2(298\text{K})}^{\circ} = 1648.9$  kJ/mol (B3LYP) of the  $\text{H}_2\text{C}_4\text{S}_4$  indicate that the  $\text{H}_2\text{C}_4\text{Se}_4$  is the strongest organic acid among the three squaric acids.

**Table 5** Energy contribution to the dissociation free energy of the reaction  $\text{H}_2\text{C}_4\text{Se}_4 \xrightarrow{\Delta G_1^{\circ}} \text{HC}_4\text{Se}_4^- + \text{H}^+$  (in kJ/mol)

Method	$\Delta E_1$	$\Delta(\text{ZPVE})_1$	$\Delta(\text{thermal})_1$	$\Delta H_1$	$-T\Delta S_1^{\circ}$	$\Delta G_{1(298\text{K})}^{\circ}$
RHF/6-311G**	1284.1	-22.6	-24.3	1259.8	2.5	1262.3
RHF/6-311+G**	1277.4	26.8	18.0	1295.4	20.5	1315.9
MP2(full)/6-311+G** <sup>a</sup>	1275.7	26.8	18.0	1293.7	20.5	1314.2
B3LYP/6-311+G**	1279.5	-21.8	-22.6	1256.9	0.8	1257.7

<sup>a</sup> Using the RHF/6-311+G\*\* geometry, ZPVE, thermal (including ZPVE) and entropy.

**Table 6** Energy contribution to the dissociation free energy of the reaction  $\text{HC}_4\text{Se}_4 \xrightarrow{\Delta G_2^{\circ}} \text{C}_4\text{Se}_4^{2-} + \text{H}^+$  (in kJ/mol)

Method	$\Delta E_2$	$\Delta(\text{ZPVE})_2$	$\Delta(\text{thermal})_2$	$\Delta H_2$	$-T\Delta S_2^{\circ}$	$\Delta G_{2(298\text{K})}^{\circ}$
RHF/6-311G**	1640.1	-23.0	-24.3	1615.9	5.0	1620.9
RHF/6-311+G**	1623.0	-72.0	-66.5	1556.0	-15.5	1540.5
MP2/6-311+G** <sup>a</sup>	1636.8	-72.0	-66.5	1570.3	-15.5	1554.8
B3LYP/6-311+G**	1631.8	-20.5	-19.7	1609.6	7.5	1617.1

<sup>a</sup> Using the RHF/6-311+G\*\* geometry, ZPVE, thermal (including ZPVE) and entropy.

## Conclusion

The calculated total energies indicate that the *ZZ* isomer is the lowest energy conformation among the three planar conformers. The optimized geometrical parameters of  $\text{H}_2\text{C}_4\text{Se}_4$  exhibit a bond length equalization relative to reference compounds cyclobutanediselenone, and cyclobutanediselenol. The computed ASEs and  $\Lambda$  by homodesmotic reaction in the most stable conformation of  $\text{H}_2\text{C}_4\text{Se}_4$  and reference compounds in Eq. (1) are negative values, suggesting that  $\text{H}_2\text{C}_4\text{Se}_4$  be aromatic. The reliable theoretical gas-phase acidity is  $\Delta G_{1(298\text{K})}^{\circ} = 1257.7$  kJ/mol and  $\Delta G_{2(298\text{K})}^{\circ} = 1617.1$  kJ/mol. Comparisons of the calculated  $\Delta G_{1(298\text{K})}^{\circ}$  and  $\Delta G_{2(298\text{K})}^{\circ}$  of

the  $\text{H}_2\text{C}_4\text{Se}_4$  with those of the  $\text{H}_2\text{C}_4\text{O}_4$  and the  $\text{H}_2\text{C}_4\text{S}_4$  indicate that the  $\text{H}_2\text{C}_4\text{Se}_4$  is the strongest organic acid among the three squaric acids.

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