Theor Chem Acc (2000) 105:86–92
DOI 10.1007/s002140000190

Theoretical
Chemistry Accounts

Regular article

Theoretical predictions of the structure, gas-phase acidity and aromaticity of 1,2-diseleno-3,4-dithiosquaric acid

Lixin Zhou

Department of Chemistry, Fuzhou University, Fuzhou, Fujian 350002, P. R. China
e-mail: quant@fzu.edu.cn

Received: 11 April 2000 / Accepted: 7 July 2000 / Published online: 27 September 2000

Abstract. Results of ab initio self-consistent-field (SCF) and density functional theory (DFT) calculations of the gas-phase structure, acidity (free energy of deprotonation, ΔG°), and aromaticity of 1,2-diseleno-3,4-dithiosquaric acid (3,4-dithiohydroxy-3-cyclobutene-1,2-diselenone, $H_2C_4Se_2S_2$) are reported. The global minimum found on the potential energy surface of 1,2-diseleno-3,4-dithiosquaric 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 cyclobutenedithiol. The computed aromatic stabilization energy (ASE) by homodesmotic reaction (Eq 1) is −20.1 kcal/mol (MP2(fu)/6-311 + G** //RHF/6-311 + G**) and −14.9 kcal/mol (B3LYP// 6-311 + G**//B3LYP/6-311 + G**). The aromaticity of 1,2-diseleno-3,4-dithiosquaric acid is indicated by the calculated diamagnetic susceptibility exaltation (Λ) −17.91 (CSGT(IGAIM)-RHF/6-311 + G**//RHF/6-311 + G**) and −31.01 (CSGT(IGAIM)-B3LYP/6-311 + G**// B3LYP/6-311 + G**). Thus, 1,2-diseleno-3,4-dithiosquaric acid fulfils the geometric, energetic and magnetic criteria of aromaticity. The calculated theoretical gas-phase acidity is $\Delta G^{o}_{1(298K)} = 302.7$ kcal/mol and $\Delta G^{o}_{2(298K)} = 388.4$ kcal/mol. Hence, 1,2-diseleno-3,4-dithiosquaric acid is a stronger acid than squaric acid(3,4-dihydroxy-3-cyclobutene-1,2-dione, $H_2C_4O_4$).

Key words: 1,2-Diseleno-3,4-dithiosquaric acid – Ab initio – Density functional theory (DFT) – Gas-phase acidity – Aromaticity

Introduction

In the 40 years since the oxocarbon anions $C_nO_n^{2-}$ have been recognized as members of a new class of stabilized carbocyclic nonbenzenoid aromatic compounds [1], knowledge of their chemical-physical properties has developed rapidly. Their unique electronic structures, high degree of symmetry, and aesthetically beautiful geometry has generated a fresh impetus to study the effect of replacing the oxygens by various other functional groups, such as nitrogen [2], sulfur [3–7], selenium [8] and phosphorus [9]. Our interests have focused on studies pertinent to the aromatic oxocarbons or to squaric acid in which the original carbonyl and hydroxy oxygen atoms in $C_nO_n^{2-}$ or $H_2C_4O_4$ are either partially or completely replaced by sulfur and selenium. By analogy to the oxocarbon dianions, the thioxocarbon or selenoxocarbon can be characterized by the general formula $C_nS_n^{2-}$ or $C_nSe_n^{2-}$, in which n is any positive integer. A considerable amount of information about these fascinating sulfur-substituted or selenium-substituted analogs of the oxocarbon anions has been accumulated [10, 11]. The concept of aromaticity is of central importance to the theory and practice of teaching and research in organic chemistry. Among carbocyclic nonbenzenoid aromatic compounds, the aromatic derivatives form an extremely important class, and stability, reactivity, and physical properties are very strongly influenced by their aromatic character. Similarly, 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. As mentioned above, the aromaticity of oxocarbons and pseudo-oxocarbons has been well studied; however, high level ab initio and density functional theory (DFT) studies of the gas phase structure, acidity, and aromaticity of squaric acid and its derivatives, especially those that containing S and Se have not, to our knowledge, been reported. In order to provide a useful information of physical and chemical properties and a fundamental database for the syntheses of these squaric acids and their anions, we studied the structure, gas-phase acidity and aromaticity of squaric acids containing oxygen, sulfur, and selenium and their anions. This work is part of a wider study of the structure, aromaticity, and gas-phase acidity of these squaric acids. We report optimized molecular geometries of the three planar conformers of 1,2-diseleno-3,4-dithiosquaric acid (3,4-dithiohydroxy-3-cyclobutene-1,2-diselenone, $H_2C_4Se_2S_2$) and corresponding anions at ab initio and DFT levels of theory using 6-311G** and 6-311 + G** basis sets, in addition to the MP2(full) single-point energies. We report 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 studied were optimized at the RHF/6-311G(d,p), RHF/6-311 + G(d,p) ab initio, and the B3LYP/6-311 + G(d,p) density functional levels using the gradient procedure [12] with the Gaussian 94 program package [13]. In view of the fact that X-ray structure of squaric acid ($H_2C_4O_4$ or H_2Sq) is practically planar and that the title compound is similar, C_s symmetry was considered during the optimization of $H_2C_4Se_2S_2$. The nature of each stationary point was characterized by computing the harmonic vibrational frequencies at the various levels of theory. The correlation energies were calculated by means of Moller-Plesset perturbation theory [14, 15]. Single-point energies were also computed at the MP2(fu)/6-311 + G(d,p)//RHF/6-311 + G(d,p) level of theory. The 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 (Λ) was computed using the Continuous Set of Gauge Transformations (CSGT) [16, 17] and IGAIM [17] (a slight variation on CSGT which uses atomic centers as the gauge origin) methods at the RHF/6-311 + G(d,p) and B3LYP/6-311 + G(d,p) levels for the RHF/6-311 + G(d,p) and B3LYP/6-311 + G(d,p) geometries, respectively.

The gas-phase acidity of Brünsted acids is defined as the free energy of deprotonation and designated ΔG^0 acid [18]. The gas-phase acidity (ΔG°_1 and ΔG°_2) of the $H_2C_4Se_2S_2$ have been calculated at the MP2(fu)/6-311 + G(d,p)//HF/6-311 + G(d,p) and B3LYP/6-311 + G(d,p) levels of theory for the first time.

Results and discussion

Aromaticity

The optimized geometric parameters for the three planar conformers of the $H_2C_4Se_2S_2$ molecule and the $HC_4Se_2S_2^-$ and $C_4Se_2S_2^{2-}$ 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 Tables 1 and 2. The structures and atom numbering are displayed in Fig. 1.

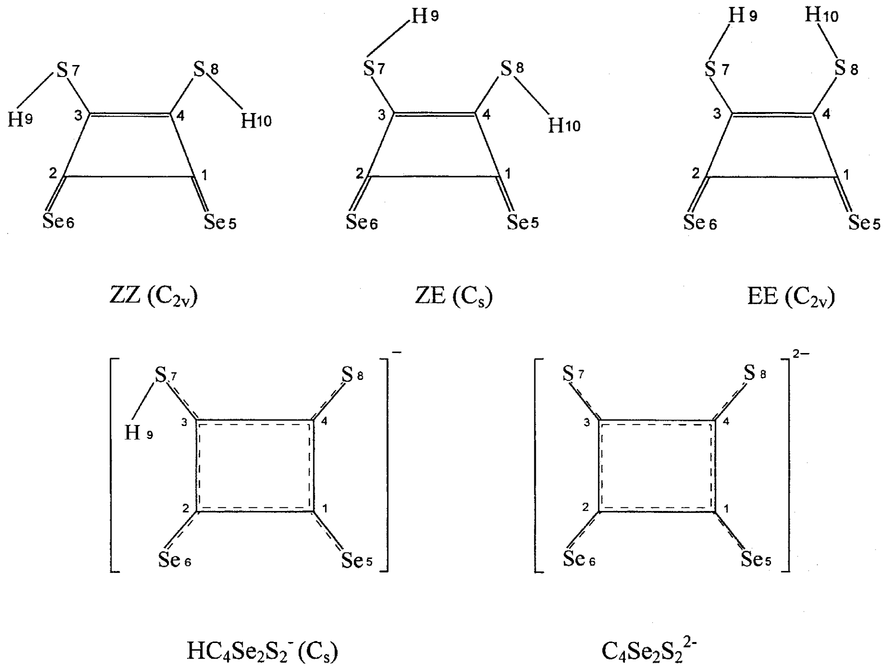
As shown in Tables 1 and 2, the difference between the computed parameters is negligible for the RHF/6-311G(d,p) and RHF/6-311 + G(d,p) basis sets, but the difference is not negligible when using the former two basis sets and the B3LYP/6-311 + G(d,p) method. Most of the bond lengths except C—S single bond are longer at B3LYP than at SCF, by about 0.03 Å. As can be seen in Tables 1 and 2, the computed bond lengths of the three planar isomers are very similar. The calculated results reveal larger differences 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 0.05 Å and 0.01 Å, and the C—C and C—S single bonds are shortened by 0.06 Å and 0.05 Å, relative to the reference

Table 1. Optimized geometrical parameters (Å deg)

Parameters	ZZ			ZE	EE
	RHF		B3LYP	RHF	RHF
	6-311G**	6-311 + G**	6-311 + G**	6-311G**	6-311G**
C_1—C_2	1.499	1.499	1.498	1.501	1.501
C_2—C_3	1.459	1.459	1.466	1.461	1.461
C_1—C_4	1.459	1.459	1.466	1.458	1.461
C_3=C_4	1.368	1.369	1.397	1.366	1.366
C_1=Se_5	1.745	1.746	1.771	1.745	1.742
C_2=Se_6	1.745	1.746	1.771	1.742	1.742
C_3—S_7	1.722	1.722	1.714	1.725	1.728
C_4—S_8	1.722	1.722	1.714	1.725	1.728
S_7—H_9	1.333	1.334	1.362	1.331	1.331
S_8—H_{10}	1.333	1.334	1.362	1.333	1.331
C_1—C_2—C_3	87.4	87.4	88.0	87.3	87.3
C_2—C_1—C_4	87.4	87.4	88.0	87.5	87.3
C_2—C_3—C_4	92.6	92.6	92.0	92.6	92.7
C_1—C_4—C_3	92.6	92.6	92.0	92.6	92.7
C_2—C_1=Se_5	137.4	137.4	139.1	137.5	136.9
C_4—C_1=Se_5	135.1	135.1	132.9	135.1	135.8
C_1—C_2=Se_6	137.4	137.4	139.1	136.8	136.9
C_3—C_2=Se_6	135.1	135.1	132.9	135.9	135.8
C_2—C_3—S_7	132.6	132.6	130.9	129.8	128.9
C_4—C_3—S_7	134.8	134.8	137.2	137.6	138.5
C_1—C_4—S_8	132.6	132.6	130.9	132.7	128.9
C_3—C_4—S_8	134.8	134.8	137.2	134.7	138.5
C_3—S_7—H_9	95.1	95.1	92.3	96.6	97.0
C_4—S_8—H_{10}	95.1	95.1	92.3	95.3	97.0

Table 2. Further examples of optimized geometrical parameters (Å deg)

Parameters	$HC_4Se_2S_2^-$			$C_4Se_2S_2^{2-}$		
	HF		B3LYP	HF		B3LYP
	6-311G**	6-311 + G**	6-311 + G**	6-311G**	6-311 + G**	6-311 + G**
C_1-C_2	1.483	1.482	1.494	1.437	1.434	1.456
C_2-C_3	1.404	1.404	1.425	1.449	1.450	1.466
C_1-C_4	1.486	1.486	1.491	1.449	1.450	1.466
C_3-C_4	1.416	1.418	1.434	1.459	1.463	1.476
C_1-Se_5	1.759	1.761	1.784	1.827	1.831	1.832
C_2-Se_6	1.803	1.806	1.808	1.827	1.831	1.832
C_3-S_7	1.730	1.729	1.727	1.663	1.659	1.671
C_4-S_8	1.648	1.647	1.658	1.663	1.659	1.671
S_7-H_9	1.332	1.333	1.360			
$C_1-C_2-C_3$	88.5	88.5	88.0	90.4	90.5	90.4
$C_2-C_1-C_4$	88.8	88.8	89.5	90.4	90.5	90.4
$C_2-C_3-C_4$	94.9	94.8	94.6	89.5	89.3	89.6
$C_1-C_4-C_3$	87.9	87.9	87.8	89.5	89.3	89.6
$C_2-C_1-Se_5$	136.0	136.0	135.2	135.5	135.6	135.3
$C_4-C_1-Se_5$	135.2	135.2	135.3	134.1	134.0	134.3
$C_1-C_2-Se_6$	136.5	136.4	136.8	135.5	135.6	135.3
$C_3-C_2-Se_6$	135.1	135.1	135.2	134.1	134.0	134.3
$C_2-C_3-S_7$	132.7	132.9	134.8	135.9	136.1	135.7
$C_4-C_3-S_7$	132.4	132.3	130.5	134.6	134.6	134.7
$C_1-C_4-S_8$	136.9	137.1	138.8	135.9	136.1	135.7
$C_3-C_4-S_8$	135.2	135.1	133.4	134.6	134.6	134.7
$C_3-S_7-H_9$	94.8	94.7	92.0			
$H_9-S_7-C_3-C_2$	180.0	180.0	180.0			
$C_3-C_2-C_1-C_4$	0.0	0.0	0.0	−4.2	−5.3	0.1



ZZ (C_{2v}) ZE (C_s) EE (C_{2v})

$HC_4Se_2S_2^-$ (C_s) $C_4Se_2S_2^{2-}$

Fig. 1. The structures and atom numbering for the three planar isomers of $H_2C_4Se_2S_2$ and anions

compounds, cyclobutenedithiol (the optimized C=C double bond and =C—S single bond are 1.324 Å and 1.347 Å, respectively) and cyclobutanediselenone (the optimized =C—C single bond and C=Se double bond are 1.521 Å and 1.738 Å, respectively), suggesting that the titled compound displays an equalization of bond length. Hence, the title compound exhibits a character of aromaticity [19, 20].

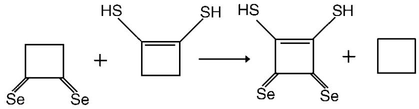
It can be seen from the computed geometric parameters of the $HC_4Se_2S_2^-$ and $C_4Se_2S_2^{2-}$ anions, given in Tables 1 and 2, that the C—C and C—Se bonds do not have a clear single or double bond character, indicating that π electron delocalization is quite strong in these anions.

It must be pointed out that the dianion has an imaginary frequency in the optimization with C_s symmetry.

However, it does not has an imaginary frequency when optimized without using any symmetry, and the lowest energy corresponds to C_1 symmetry. However, the all atoms are almost in the same plane and the dihedral angle deviate from the molecule plane about 5° (RHF) and 0.1° (B3LYP), and other optimized geometric parameters and the total energy are almost same exactly. The molecule (ZZ) does not have any imaginary frequency in optimization with C_s and C_1 symmetry, and optimized geometric parameters and total energy are exactly the same. However, it is easier to find the stationary point when optimized without using any symmetry.

The calculated total and relative energies for the three planar conformers of the $H_2C_4Se_2S_2$ at the various computational levels are listed in Table 3. It can be seen that the ZZ conformer is the most stable among the three planar isomers. In fact, the ZZ and ZE conformers are very close in energy. This is consistent with the computational results for squaric acid [21] and its isomer, 1,2-dithio-3,4-diselenosquaric acid [22].

The computed aromatic stabilization energies (ASEs) using the homodesmotic reaction (Eq. 1) are given in Table 4. As all compounds in Eq. (1) were calculated in their most stable conformations, strain effects should to a large extent be cancelled. Equation (1) gives 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 $H_2C_4Se_2S_2$ at the various levels are all negative values, suggesting that the $H_2C_4Se_2S_2$ is possibly aromatic.



(1)

$H_2C_4Se_2S_2$ is aromatic according to the geometric and energetic criteria for aromaticity. $H_2C_4Se_2S_2$ also fulfils the magnetic criterion for aromaticity. The magnetic susceptibility exaltation (Λ) 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.

That aromatic compounds exhibit enhanced diamagnetic susceptibility was noted by Pascal [23] in his pioneering investigation. Pauling [24] ascribed these effects to ring currents in 1936. Flygare et al. [25, 26] used the magnetic susceptibility anisotropies and Dauben et al. [27] used the magnetic susceptibility exaltation to characterize the aromatic compounds comprehensively. Recently, Cremer et al. [28–30] established that homo- and bishomo-cations were aromatic by means of their computed magnetic susceptibilities. However, for many interesting systems, including $H_2C_4Se_2S_2$ compound, there is no experimental magnetic data for some of the molecules. In a new development and application, Kutzelnigg et al. [31, 32] and Schleyer et al. [33–41] have shown that magnetic susceptibilities can now be calculated to a reasonable accuracy for molecules of interest to organic and inorganic chemists.

Table 4. Calculated ASE (in kcal/mol)[a]

Method	ASE
RHF/6-311G**//RHF/6-311G**	−10.4
RHF/6-311 + G**//RHF/6-311 + G**	−11.6
MP2/6-311 + G**//RHF/6-311 + G**[b]	−20.1
B3LYP/6-311 + G**//B3LYP/6-311 + G**	−14.9

[a] Scaled by ZPVE
[b] Scaled by RHF/6-311 + G** ZPVE

The magnetic susceptibility exaltation (Λ, Eq. 2) is defined as the difference between the computed magnetic susceptibility (x_M) for the observed compound ($H_2C_4Se_2S_2$) and the value estimated for the hypothetical system without cyclic electron delocalization (x'_M). The latter is based on the bond increments that we have determined by computations on appropriate model compounds (Eq. 1). The exaltations, Λ, are negative (diamagnetic) for the aromatic compounds, but positive (paramagnetic) for the antiaromatic cases:

$$\Lambda = x_M - x'_M \tag{2}$$

The computed Λ are collected in Table 5. The magnetic susceptibility data presented in Table 5 include all of the molecules needed for the steps involved in calculating Λ. In Table 5, we list the eigenvalues of the magnetic susceptibility tensor as well as the isotropic part x_{av}, and the anisotropic, Δx, parts. The computed Λ in Table 5 are large negative values, corresponding to an aromatic compound.

To sum up, tests of the geometric, energetic, and magnetic criteria for aromaticity of the title compound have been carried out. Comparing the computed ASEs and Λs of the title compound with our earlier calculated results for squaric acid [21] (ASE = −16.3 kcal/mol (MP2), −12.9 kcal/mol (B3LYP), and Λ = −2.07 ppm cgs (CSGT-RHF), −2.16 ppm cgs (CSGT-B3LYP)),

Table 3. Calculated total and relative energies of the three isomers (total energies in hartrees, relative energies in kcal/mol)[a]

Method	Total energy			Relative energy		
	ZZ	ZE	EE	ZZ	ZE	EE
HF/6-311G(d,p)	−5747.19443	−5747.19132	−5747.18659	0	2.0	4.9
MP2/6-311G(d,p)[b]	−5748.25459	−5748.25077	−5748.24596	0	2.4	5.4
HF/6-311 + G(d,p)	−5747.19938					
MP2/6-311 + G(d,p)[b]	−5748.26558					
B3LYP/6-311 + G(d,p)	−5753.08504					

[a] Scaled by ZPVE
[b] Using the HF/6-311G(d,p) and HF/6-311 + G(d,p) geometries and scaled by HF/6-311G(d,p) and HF/6-311 + G(d,p) ZPVE respectively

tetrathiosquaric acid [42] (ASE = −18.4 kcal/mol (MP2), −15.1 kcal/mol (B3LYP), and $\Lambda = -11.77$ ppm cgs (CSGT-RHF), −18.08 ppm cgs (CSGT-B3LYP)), and 1,2-dithio-3,4-diselenosquaric acid [22] (ASE = −17.3 kcal/mol (MP2), −13.3 kcal/mol (B3LYP), and $\Lambda = -12.88$ ppm cgs (CSGT-RHF), −20.36 ppm cgs (CSGT-B3LYP)), indicating that the title compound seems to be more aromatic than squaric acid, tetrathiosquaric acid and its isomer, 1,2-dithio-3,4-diselenosquaric acid because it has a more negative value of Λ. These results also suggest that squaric acids whose carbonyl oxygen atoms are replaced by larger atomic number elements seem to be more aromatic than those whose hydroxy oxygen atoms are replaced.

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 [43–45]. 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 the gas-phase acidities of carbon-containing acids have recently been reported using both ab initio and density functional theory methods [46–55]. Of these investigations, excellent agreement with experiment were obtained by the G2(MP2, SVP), G2(MP2), and G2 procedures. Various G2 methods, however, are sufficiently time consuming to be impractical for anything 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 Brünsted acids is defined as the free energy of deprotonation and designated ΔG^{o}_{acid} [54]. Both the $H_2C_4Se_2S_2$ and $HC_4Se_2S_2^-$ lose a proton when acting as acid and the different components of the energy of dissociation are shown in Tables 6 and 7. All the energies of dissociation are calculated for the most stable conformer (ZZ) in the gas phase. As can be seen in Tables 6 and 7, the computed $\Delta G^{o}_{1(298\ K)}$ and $\Delta G^{o}_{2(298\ K)}$ at the MP2 (full)/6-311 + G(d,p)//HF/6-311 + G(d,p), and B3LYP/6-311 + G(d,p) levels are very close, being $\Delta G^{o}_{1(298\ K)} = 304.1$ (MP2) kcal/mol, and 302.7 (B3LYP) kcal/mol and $\Delta G^{o}_{2(298\ K)} = 389.7$ (MP_2) kcal/mol, and 388.4 (B3LYP) kcal/mol, respectively. The

Table 5. Computed Λ (ppm cgs)

Method	Compound	ε_1^{b}	ε_2	ε_2	x_{av}^{c}	Δx^{d}	Λ
CSGT(IGAIM)[a]-RHF//RHF	Cyclobutanediselenone	−95.96	−54.41	−35.64	−62.00	39.54	
	Cyclobutenedithiol	−73.78	−64.92	−64.14	−67.61	5.21	
	Cyclobutane	−44.57	−44.55	−32.59	−40.57	11.98	
	$H_2C_4Se_2S_2$ (ZZ)	−140.44	−96.27	−84.14	−106.95	34.21	−17.91
CSGT(IGAIM)-B3LYP//B3LYP	Cyclobutanediselenone	−93.27	−32.45	−8.89	−44.87	53.97	
	Cyclobutenedithiol	−70.83	−63.71	−63.23	−65.92	4.04	
	Cyclobutane	−43.52	−43.51	−30.60	−39.21	12.91	
	$H_2C_4Se_2S_2$ (ZZ)	−141.98	−85.86	−79.92	−102.59	34.00	−31.01

[a] Both methods give the same results
[b] ε_1, ε_2, ε_3: eigenvalues of the magnetic susceptibility tensor as reported in the Gaussian 94 output file (where arbitrarily, $\varepsilon_1 < \varepsilon_2 < \varepsilon_3$)
[c] x_{av} is the isotropic part ($x_{av} = 1/3(\varepsilon_1 + \varepsilon_2 + \varepsilon_3)$) or defined in terms of in-plane ($x_{xx} + x_{yy}$) and out-of-plane (x_{zz}) components ($x_{av} = 1/3(x_{xx} + x_{yy} + x_{zz})$)
[d] Δx is the anisotropic part ($\Delta x = \varepsilon_3 – (\varepsilon_1 + \varepsilon_2)/2$)

Table 6. Energy contribution to the Dissociation Free Energy of the reaction $H_2C_4Se_2S_2 \xrightarrow{\Delta G^{o}_{1}} HC_4Se_2S_2^- + H^+$ (in kcal/mol)

Method	ΔE_1	$\Delta(ZPVE)_1$	$\Delta(thermal)_1$	ΔH_1	$-T\Delta S^{o}_{1}$	$\Delta G^{o}_{1(298K)}$
HF/6-311G(d,p)	309.0	−6.0	−6.4	302.6	0.5	303.1
HF/6-311 + G(d,p)	308.2	−6.0	−6.4	301.8	0.4	302.2
MP2(full)/6-311 + G(d,p)[a]	310.1	−6.0	−6.4	303.7	0.4	304.1
B3LYP/6-311 + G(d,p)	308.2	−5.6	−5.8	302.4	0.3	302.7

[a] Using the HF/6-311 + G(d,p) geometry, ZPVE, thermal (including the ZPVE) and entropy

Table 7. Energy contribution to the Dissociation Free Energy of the reaction $HC_4Se_2S_2^- \xrightarrow{\Delta G^{o}_{2}} C_4Se_2S_2^- + H^+$ (in kcal/mol)

Method	ΔE_2	$\Delta(ZPVE)_2$	$\Delta(thermal)_2$	ΔH_2	$-T\Delta S^{o}_{2}$	$\Delta G^{o}_{2(298K)}$
HF/6-311G(d,p)	394.8	−6.1	−6.4	388.4	0.1	388.5
HF/6-311 + G(d,p)	392.4	−6.0	−6.3	386.1	0.7	386.8
MP2/6-311 + G(d,p)[a]	395.3	−6.0	−6.3	389.0	0.7	389.7
B3LYP/6-311 + G(d,p)	393.6	−5.5	−5.8	387.8	0.6	388.4

[a] Using the HF/6-311 + G(d,p) geometry, ZPVE, thermal (including the ZPVE) and entropy

differences between the results obtained using these methods is very small. These results are consistent with those of other authors [56], B3LYP is as effective as MP2; however B3LYP is generally computationally more economical. Comparisons of the computed $\Delta G^{o}_{1(298K)}$ and $\Delta G^{o}_{2(298K)}$ with experimental values in the gas phase has not been carried out because the determination of gas phase acidity of the title compound has not, to our knowledge, been reported. As mentioned above, we believe that a reliable theoretical gas-phase acidity is $\Delta G^{o}_{1(298K)} = 302.7$ kcal/mol and $\Delta G^{o}_{2(298K)} = 388.4$ kcal/mol, because the B3LYP method ordinarily provides the most reliable thermochemical predictions [57] and the differences of results obtained using B3LYP and MP2 is very small. Comparisons of the calculated $\Delta G^{o}_{1(298K)}$ and $\Delta G^{o}_{2(298K)}$ of $H_2C_4Se_2S_2$ with $\Delta G^{o}_{1(298K)} = 311.4$ (B3LYP) kcal/mol and $\Delta G^{o}_{2(298K)} = 421.0$ kcal/mol (B3LYP) of the $H_2C_4O_4$ (H_2Sq) [21], indicating that the $H_2C_4Se_2S_2$ is a stronger organic acid than the $H_2C_4O_4$.

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 $H_2C_4Se_2S_2$ exhibit an equalization of the bond lengths relative to reference compounds, cyclobutanediselenone, and cyclobutenedithiol. The computed ASEs and those obtained by homodesmotic reaction in the most stable conformation of $H_2C_4Se_2S_2$ and the reference compounds in Eq. (1) are negative values, suggesting that $H_2C_4Se_2S_2$ is aromatic. The calculated theoretical gas-phase acidity is $\Delta G^{o}_{1(298K)} = 302.7$ kcal/mol and $\Delta G^{o}_{2(298K)} = 388.4$ kcal/mol. Comparisons of the calculated $\Delta G^{o}_{1(298K)}$ and $\Delta G^{o}_{2(298K)}$ of the $H_2C_4Se_2S_2$ with that for $H_2C_4O_4$ indicate that $H_2C_4Se_2S_2$ is a stronger organic acid than $H_2C_4O_4$.

Acknowledgements. We gratefully acknowledge the Natural Science Foundation of Fujian Province for their grants in support of this work. We thank the editor and referees for their detailed and helpful instructions to update the paper.

References

1. West R, Niu J (1970) In: Zabicky J (ed) The chemistry of the carbonyl group, vol 2. Wiley, New York, p 241
2. (a) Hönig S, Putter H (1977) Chem Ber 110: 2532; (b) Hönig S, Putter H (1972) Angew Chem Int Ed Engl 11,431; (1973) Angew Chem Int Ed Engl 12: 49
3. Coucouvanis D, Hollander FJ, West R, Eggerding D (1974) J Am Chem Soc 96: 3006
4. Eggerding D, West R (1976) J Org Chem 41: 3904
5. Allmann R, Debaerdemaeker T, Mann K, Matusch R, Schmiedel R, Seitz G (1976) Chem Ber 109: 2208
6. Seitz G, Mann K, Schmiedel R, Matusch R (1979) Chem Ber 112: 990
7. Matusch R, Schmiedel R, Seitz G (1979) Justus Liebigs Ann Chem 595
8. Schmidt AH, Ried W, Pustoslemsek P (1977) Chem-Ztg 101: 154
9. Becher HJ, Fenske D, Langer E (1973) Chem Ber 106: 177
10. West R (ed) (1980) Oxocarbons. Academic Press, New York, chap 2
11. Seitz G, Imming P (1992) Chem Rev 92: 1227
12. Schlegel HB (1982) J Comput Chem 3: 314
13. Frisch MJ, Trucks GW, Schlegel HB, Gill PMW, Johnson BG, Robb MA, Cheeseman JR, Keith T, Petersson GA, Montgomery JA, Raghavachari K, Al-Laham MA, Zakrzewski VG, Ortiz JV, Foresman JB, Cioslowski J, Stefanov BB, Nanayakkara A, Challacombe M, Peng CY, Ayala PY, Chen W, Wong MW, Andres JL, Replogle ES, Gomperts R, Martin RL, Fox DJ, Binkley JS, Defrees DJ, Baker J, Stewart JP, Head-Gordon M, Gonzalez C, Pople JA (1995) Gaussian 94, Revision D2. Gaussian, Pittsburgh PA
14. Müller C, Plesset MS (1934) Phys Rev 46: 618
15. Frisch MJ, Head-Gordon M, People JA (1990) Chem Phys Lett 166: 281
16. Keith TA, Bader RFW (1993) Chem Phys Lett 210: 223
17. Keith TA, Bader RFW (1992) Chem Phys Lett 194: 1
18. Bartmess JE, Mciver RT Jr (1979) In: Bowers MT (ed) Gas phase ion chemistry. Academic, New York, vol 2, pp 87–121
19. Minkin VI, Glukhovtsev MN, Simkin BY (1994) Aromaticity and antiaromaticity. Wiley, New York
20. Garratt PJ (1986) Aromaticity. Wiley, New York
21. Zhou L, Zhang Y, Wu L, Li J (2000) J Mol Struct (Theochem) 497: 137
22. Zhou L (2000) Chem Phys Lett 317: 330
23. Pascal P (1910) Ann Chim Phys 19: 5
24. Pauling L (1936) J Chem Phys 4: 673
25. Benson RC, Flygare WH (1970) J Am Chem Soc 92: 7523
26. Davidson JR, Burnham AK, Siegel B, Peak B, Flygare WH (1974) J Am Chem Soc 96: 7394
27. Dauben HJ Jr, Wilson JD, Laity JL (1971) Nonbenzenoid aromaticity. Academic Press, New York, vol II, p 167
28. Cremer D, Reichel F, Kraka E, Ahlberg P (1991) J Am Chem Soc 113: 9459
29. Cremer D, Svensson P, Kraka E, Ahlberg P (1993) J Am Chem Soc 115: 7445
30. Cremer D, Svensson P, Kraka E, Konkol E, Ahlberg P (1993) J Am Chem Soc 115: 7457
31. Fleischer U, Kutzelnigg W, Lazzeretti P, Mulenkamp V (1994) J Am Chem Soc 116: 5298
32. Kutzelnigg W (1989) J Mol Struct (Theochem) 202: 11
33. Jiao H, Schleyer PvR (1993) Angew Chem Int Ed Engl 32: 1763
34. Jiao H, Schleyer PvR (1994) J Chem Soc Faraday Trans 90: 1559
35. Herges R, Jiao H, Schleyer PvR (1994) Angew Chem Int Ed Engl 33: 1376
36. Jiao H, Schleyer PvR (1995) Angew Chem Int Ed Engl 34: 334
37. Schleyer PvR, Freeman PK, Jiao H, Goldfuss B (1995) Angew Chem Int Ed Engl 34: 337
38. Schleyer PvR, Jiao H (1996) Pure Appl Chem 68: 209
39. Zywietz TK, Jiao H, Schleyer PvR, de Meijere A (1998) J Org Chem 63: 3417
40. Gogonea V, Schleyer PvR, Schreiner PR (1998) Angew Chem Int Ed Engl 37: 1945
41. Schleyer PvR, Najafian K (1998) Inorg Chem 37: 3454
42. Zhou L, Mang C, Zhang Y, Xiang S, Huang Z (2000) Int J Quantum Chem 78: 443
43. Gram DJ (1965) Fundamentals of carbanion chemistry. Academic Press, New York
44. Bordwell FG (1988) Acc Chem Res 21: 456
45. Lory TH, Richardson KS (1987) Mechanism and theory in organic chemistry, 3rd edn. Harper & Row, New York, chap 3
46. Ritchie JP, Bachrach SM (1990) J Am Chem Soc 112: 6514
47. Smith BJ, Radom L (1991) J Phys Chem 95: 10,549
48. Koppel IA, Taft RW, Anvia F, Zhu S-Z, Hu L-Q, Sung K-S, DesMaryeau DD, Yagupolskii LM, Yagupolskii YL, Ignat'ev NV, Kondratenko NV, Volkonskii AY, Vlasov VM, Notario R, Maria P-C (1994) J Am Chem Soc 116: 3047

49. Ventura ON, Rama JB, Turi L, Dannenberg JJ (1995) J Phys Chem 99: 31
50. Saunders WH Jr (1994) J Phys Org Chem 7: 268
51. Burk P, Koppel IA, Tapfer J, Anvia F, Taft RW (1994) J Mol Struct (Theochem) 315: 191
52. Notario R, Castano O, Abboud JLM (1996) Chem Phys Lett 263: 367
53. Smith BJ, Radom L (1995) Chem Phys Lett 245: 123
54. Morris RA, Knighton WB, Viggiano AA, Hoffman BC, Schaefer HF III (1997) J Chem Phys 106: 3545
55. Curtiss LA, Raghavachari K, Trucks GW, Pople JA (1991) J Chem Phys 94: 7221
56. Wiberg KB, Ochterski JW (1997) J Comput Chem 18: 108
57. Becke AD (1993) J Chem Phys 98: 1372