

# Studies on structures and electron affinities of the simplest alkyl dithio radicals and their anions with gaussian-3 theory and density functional theory

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**Abstract** The equilibrium geometries and electron affinities of the R-SS/R-SS<sup>-</sup> (R=CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>, *n*-C<sub>3</sub>H<sub>7</sub>, *i*-C<sub>3</sub>H<sub>7</sub>, *n*-C<sub>4</sub>H<sub>9</sub>, *t*-C<sub>4</sub>H<sub>9</sub>, *n*-C<sub>5</sub>H<sub>11</sub>) species have been studied using the higher level of the Gaussian-3(G3) theory and 21 carefully calibrated pure and hybrid density functionals (five generalized gradient approximation (GGA) methods, seven hybrid GGAs, three meta GGA methods, and six hybrid meta GGAs) in conjunction with diffuse function augmented double- $\zeta$  plus polarization (DZP++) basis sets. The geometries are fully optimized with each method and discussed. The reliable adiabatic electron affinity has been presented by means of the high level of G3 technique. With the DZP++ DFT method, three measures of neutral/anion energy differences reported in this work are the adiabatic electron affinity, the vertical electron affinity, and the vertical detachment energy. The adiabatic electron affinities, obtained at the BP86, M05-2X, B3LYP, M06, B98, M06-2X, mPW1PW91, HCTH, B97-1, M05, PBE1PBE, and VSXC methods, are in agreement with the G3 results. These methods perform better for EA prediction and are considered to be reliable.

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## Introduction

The alkyl dithio radicals (RSS) have been studied because of their intrinsic interest from the point of view of chemical structure energies, spectroscopies, and so on [1–12]. Some radicals have generated people's concern because of their potential significance in atmospheric chemistry, combustion chemistry, and environmental chemistry. For example, the methyl dithio radical plays an important role in the formation of the acid rain, photochemical smog, and atmospheric ozonosphere destruction. It is a crucial reactive intermediate which is produced upon thermal and photochemical decomposition of DMDS and gives rise to international scientific wide interests for years. However, it is restricted on both experimentally and theoretically studies on the important radical because of its ultrashort lifetime. In addition, little is known about the other alkyl dithio radicals. The electron affinity (EA) is both a key spectroscopic value and of vital importance for use in the chemical cycle in order to determine bond dissociation energy. However, there has been only one experimental study for EA of above radicals [8]. The thermochemical properties, the ground or electronic states of the neutral and anion species are indispensable tools for understanding chemical reactivity and predicting the reaction mechanism. With this motivation, we have carried out a detailed study of structures, thermochemistry, and electron affinities of the above radicals and their anions using the higher level of the Gaussian-3(G3) techniques [13, 14] and density functional theory (DFT) [15–17]. The combined G3 methods are the higher level of ab initio calculations of molecular energies of compounds containing first-, second-, and third-row atoms. The average absolute

deviation from experiment for the electron affinities are only  $0.99 \text{ kcal mol}^{-1}$  for a set of 63 molecules. Density functional theory (DFT) has become a widely applicable computational tool for calculating molecular properties, requiring much less computational effort than convergent quantum mechanical methods such as coupled cluster theory. The application of gradient-corrected density functional theory has been shown to be effective for many organic species. The theoretical prediction of electron affinities has historically been generally difficult due to the desired result being a small difference between two large energies.

The object of the present study is to systematically apply the higher level of Gaussian-3 theory and 21 contemporary forms of density functional theory to determine the electron affinities and other properties of the R-SS/R-SS $\cdot$  (R=CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>, *n*-C<sub>3</sub>H<sub>7</sub>, *i*-C<sub>3</sub>H<sub>7</sub>, *n*-C<sub>4</sub>H<sub>9</sub>, *t*-C<sub>4</sub>H<sub>9</sub>, *n*-C<sub>5</sub>H<sub>11</sub>) species. Of specific interest is (a) the comparison of the theoretical electron affinities with available experimental results; (b) the relationship between the neutral R-SS (R=CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>, *n*-C<sub>3</sub>H<sub>7</sub>, *i*-C<sub>3</sub>H<sub>7</sub>, *n*-C<sub>4</sub>H<sub>9</sub>, *t*-C<sub>4</sub>H<sub>9</sub>, *n*-C<sub>5</sub>H<sub>11</sub>) species and their anions as reflected by the three types of energy separations, e.g., the adiabatic electron affinity (EA<sub>ad</sub>), the vertical electron affinity (EA<sub>vert</sub>), and the vertical detachment energy of the anion (VDE); and (c) the comparison of the G3 schemes and various DFT methods in order to check the various commonly used density functionals and perhaps even suggest a superior method. In this work, the experimental electron affinities are EA<sub>ad</sub> which are available on the Internet as part of the NIST Chemistry Webbook [18]. We would like to establish reliable theoretical predictions for the R-SS/R-SS $\cdot$  (R=CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>, *n*-C<sub>3</sub>H<sub>7</sub>, *i*-C<sub>3</sub>H<sub>7</sub>, *n*-C<sub>4</sub>H<sub>9</sub>, *t*-C<sub>4</sub>H<sub>9</sub>, *n*-C<sub>5</sub>H<sub>11</sub>) species in the absence of experimental results and in some cases to challenge existing experiments.

## Theoretical methods

The Gaussian-3 method [13, 14] and the 21 DFT methods are performed for their ability to accurately calculate seven radicals' properties. Gaussian-3 theory is a composite technique in which a sequence of well-defined ab initio molecular orbital calculations is performed to arrive at a total energy of given molecular species. The DFT methods that we will test include generalized gradient approximation methods (GGA), meta-GGA functionals (M-GGA), hybrid density functional methods (H-GGA), and hybrid-meta-GGA methods (HM-GGA). The GGA methods that we will assess are G96LYP [19, 20], HCTH [21], OPW91 [22, 23], mPWPW91 [24], and BP86 [25, 26]. The hybrid GGA methods that we are using are B97-1 [21], B97-2 [27], B98 [28], O3LYP [19, 22, 29], mPW1PW91 [23, 24],

PBE1PBE [30, 31], and B3LYP [19, 25, 32]. The meta DFT methods that we have tested are BB95 [25, 33], VSXC [34], and M06-L [35]. The hybrid meta GGA methods that we will study in this paper are B1B95 [25, 33], M06 [36], M06-2X [36], TPSSH [37, 38], M05 [39], and M05-2X [40].

The standard double- $\zeta$  plus polarization (DZP) basis sets are constructed from the Huzinaga-Dunning-Hay [41–44] sets of contracted Gaussian functions by adding a set of five pure *d*-type polarization functions for C, S, and a *p*-type polarization functions for H [ $\alpha_p$ (H)=0.75,  $\alpha_d$ (C)=0.75,  $\alpha_d$ (S)=0.70]. Since diffuse functions are important for the anions, the DZP basis was augmented with diffuse functions; each heavy atom received one additional *s*-type and one set of *p*-type functions and H atom received one *s*-diffuse function. The diffuse function orbital exponents were determined in an “even tempered sense” as a mathematical extension of the primitive set, according to the prescription of Lee and Schaefer [45]. [ $\alpha_s$ (C)=0.04302,  $\alpha_p$ (C)=0.03629,  $\alpha_s$ (H)=0.04415,  $\alpha_s$ (S)=0.04267, and  $\alpha_p$ (S)=0.04096]. The final basis sets are thus H (5s1p/3s1p); C (10s6p1d/5s3p1d); and S (13s9p1d/7s5p1d). This extended basis will be denoted as “DZP++”.

All computations were carried out with the GAUSSIAN 09 program package [46]. All species stationary point geometries were interrogated by the evaluation of their harmonic vibrational frequencies at the higher level of Gaussian-3 schemes and various DFT levels of theory. Restricted methods were used for all closed-shell systems, while unrestricted methods were employed for the open-shell species. Zero-point vibrational energies (ZPVEs) are evaluated at the G3 level and the 21 DFT methods (Table S1 and Table S2). These differences may be used as corrections to the adiabatic electron affinities.

The electron affinities are evaluated as the difference of total energies in the following manner: the adiabatic electron affinity is determined as, EA<sub>ad</sub> = E (optimized neutral)—E (optimized anion), the vertical electron affinity by EA<sub>vert</sub> = E (optimized neutral)—E (anion at optimized neutral geometry), and the vertical detachment energy of the anion by VDE = E (neutral at optimized anion geometry)—E (optimized anion).

## Results and discussion

The change trends of the geometrical parameters predicted by the G3 theory and 21 DFT methods are in agreement with each other, and the B3LYP is able to compete in accuracy with the most existing sophisticated density functionals in terms of geometry determination (bond lengths and angles) [47–50], therefore, we only list the optimized geometries for the seven radicals and their corresponding

anions at the B3LYP/DZP++ level of theory, and theoretical results are displayed in Figs. 1 and 2.

### CH<sub>3</sub>SS and CH<sub>3</sub>SS<sup>-</sup>

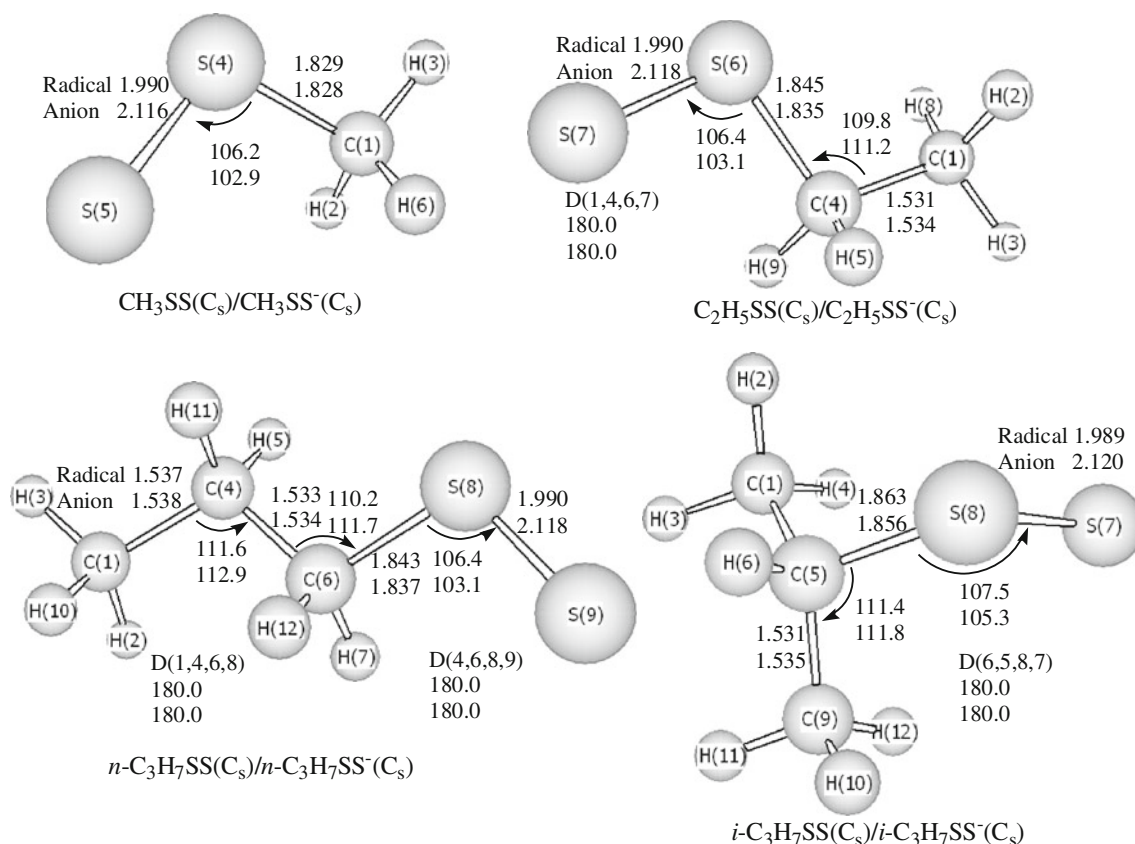
Methyldithio radical, CH<sub>3</sub>SS is one interesting and important reactive intermediate in chemistry. There have been several experimental and theoretical studies [1–7, 10–12] of the methyldithio radical about structures, energies and spectroscopies. On the theoretical aspect, in 2009, Shu [11] theoretically investigated the electronic spectra, structures, vertical ionization energy, adiabatic ionization energy and vibrational frequencies of the methyldithio radical using CASPT2//CASSCF level of theory. In 2012, Pei and Gao [12] reported the electron affinities of the alkyldithio radicals at the first-generation density functionals (B3LYP, BLYP, BPW91 and BP86) with DZP++ basis set, and predicted that the BP86 method is a reliable method for predicting the electron affinities for these species. In the present paper, we test the performance of the second-generation and third-generation DFT methods and the higher level of the G3 theory.

Our optimized geometries for both CH<sub>3</sub>SS and CH<sub>3</sub>SS<sup>-</sup> are shown in Fig. 1. The equilibrium geometry of the

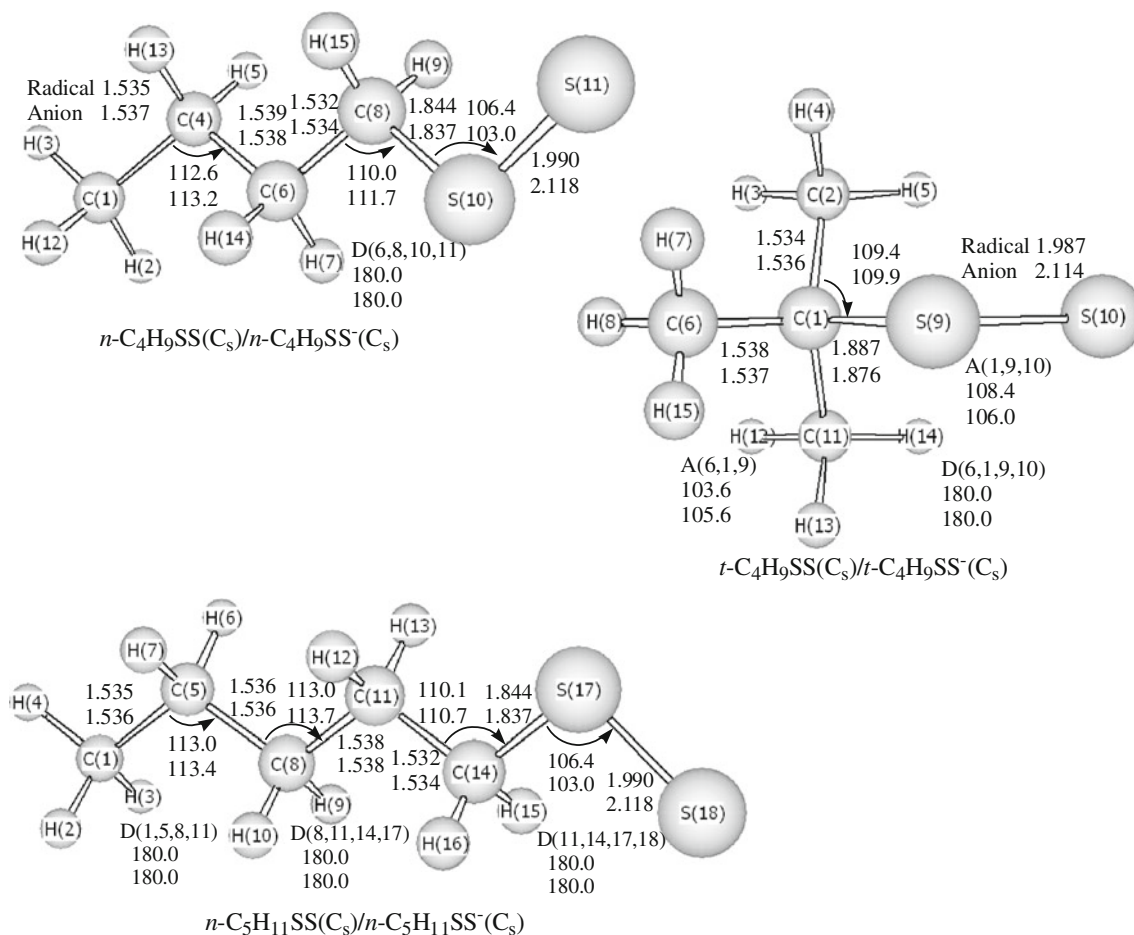
methyldithio radical in its <sup>2</sup>A'' ground state has C<sub>s</sub> symmetry. The corresponding anion has a <sup>1</sup>A' ground state with C<sub>s</sub> symmetry. The methyldithio radical has all real harmonic vibrational frequencies at the higher level of G3 theory and the 21 DFT functionals.

For the CH<sub>3</sub>SS radical structure, there are no experimental geometries for comparison, but there is one theoretical value. Theoretical C-S and S-S bond lengths of 1.856 Å and 1.982 Å with the ANO-S basis sets at the CASPT2//CASSCF level of theory were reported by Shu in 2009 [11]. Theoretical C-S-S bond angle of 105.4° was predicted. Compared with the above bond lengths and bond angle results, our present theoretical predicted the bond lengths of C-S and S-S are 1.829 Å and 1.990 Å for the neutral CH<sub>3</sub>SS radical, while 1.828 Å and 2.116 Å for corresponding anion. The value of A(C-S-S) is 106.2° for radical and 102.9° for anion, respectively (Fig. 1).

The radical and anion geometries (C-S bond length) are quite similar (see Fig. 1), with them decreasing slightly by about 0.001 Å from the radical to the anion. However, it is noticeable that both bond length (S-S) and bond angle (C-S-S) between the neutral radical and anion have some changes. The bond distance of S-S increases by about 0.126 Å. The value of A(C-S-S) decreases by about 3.3° from radical to anion.



**Fig. 1** Optimized geometries for the methyl dithio, ethyl dithio and propyl dithio radicals and anions. All bond distances are in Å, all bond angles are in ° and all results were obtained at the B3LYP/DZP++ level of theory



**Fig. 2** Optimized geometries for the butyl dithio and pentyl dithio radical and anion. All bond distances are in Å, all bond angles are in ° and all results were obtained at the B3LYP/DZP++ level of theory

The theoretical  $EA_{\text{ad}}$ ,  $EA_{\text{vert}}$ , and VDE (DFT functionals), as well as the experimental electron affinity data, are listed in Table S3. The adiabatic electron affinity predicted at the G3 theory is shown in Table 1. The range of  $EA_{\text{ad}}$  corrected is predicted from 1.533 to 1.860 eV with the G3 level and the various DFT methods. In 1988, Moran and Ellison [8]

reported the experimental adiabatic electron affinity of the methyl dithio radical to be  $1.757 \pm 0.022$  eV via the technique of negative-ion photoelectron spectroscopy. Compared with the more reliable experimental result [8], at the higher level of the Gaussian-3 techniques, the absolute errors of the adiabatic electron affinity and ZPVE-corrected electron affinity for the methyl dithio radical are 0.018, and 0.034 eV, respectively. The G3 theory is regarded as a method benchmark and is convincing. The B3LYP, BP86, M05-2X, B98, HCTH, mPW1PW91, M06, M05, B97-1, PBE1PBE, M06-2X, mPWPW91, and TPSSH results are in agreement with the G3 value, with the deviation being 0.001, 0.003, 0.007, 0.009, 0.028, 0.034, 0.042, 0.045, 0.051, 0.062, 0.069, 0.077, and 0.089 eV, respectively. Our predicted EA results are considered to be reasonable and these methods are reliable. In addition, the G96LYP method predicts the smallest  $EA_{\text{ad}}$  (1.533 eV) which give the most deviation (0.258 eV lower) from the G3 value, and M06-2X method predicts the largest  $EA_{\text{ad}}$  (1.860 eV). The B1B95, O3LYP, OPW91, and BB95 methods also give more deviation (0.154, 0.158, 0.191, and 0.216 eV) from the G3 result.

**Table 1** Adiabatic electron affinities for the alkyl dithio radicals

Radicals	$EA_{\text{ad}}$	Corrected $EA_{\text{ad}}$	Expt.
$\text{CH}_3\text{SS}$	1.775	1.791	$1.757 \pm 0.022^a$
$\text{C}_2\text{H}_5\text{SS}$	1.774	1.795	
$n\text{-C}_3\text{H}_7\text{SS}$	1.777	1.798	
$i\text{-C}_3\text{H}_7\text{SS}$	1.799	1.818	
$n\text{-C}_4\text{H}_9\text{SS}$	1.781	1.803	
$t\text{-C}_4\text{H}_9\text{SS}$	1.826	1.847	
$n\text{-C}_5\text{H}_{11}\text{SS}$	1.784	1.807	

Presented in eV with the G3 schemes

<sup>a</sup> Ref. 8

The theoretical vertical electron affinity  $EA_{\text{vert}}(\text{CH}_3\text{SS})$  predicted by 21 DFT methods is from 1.393 to 1.697 eV, and the vertical detachment energy VDE ( $\text{CH}_3\text{SS}^-$ ) is 1.636–1.986 eV.

### $\text{C}_2\text{H}_5\text{SS}$ and $\text{C}_2\text{H}_5\text{SS}^-$

The optimized geometries of the  $^2\text{A}''$  ground states of the ethyldithio radical and  $^1\text{A}'$  ground state of its anion with  $\text{C}_s$  symmetry are given in Fig. 1.

For the radical, our results predict the C-S and S-S bond distances to be 1.845 Å and 1.990 Å, respectively. The bond angle value of C-S-S is 106.4°. The differences between the radical and corresponding anion are somewhat evident. For instance, the S-S and C-C bond lengths increase by about 0.128 and 0.003 Å for the anion (with respect to the radical), respectively, while the C-S bond length decreases by about 0.010 Å. Like  $\text{CH}_3\text{SS}$  and  $\text{CH}_3\text{SS}^-$ , the bond angle value of C-S-S decreases by about 3.3° when an electron is attached to the radical. In addition, the dihedral angle D(1,4,6,7) stays at 180.0° for both the radical and the corresponding anion. There are no experimental data available for comparison.

Our theoretical neutral-anion energy separations at the various DFT methods for the  $\text{C}_2\text{H}_5\text{SS}$  and  $\text{C}_2\text{H}_5\text{SS}^-$  are shown in Table S3. We predicted the adiabatic electron affinity  $EA_{\text{ad}}$  with ZPVE for the ethyldithio radical ranges from 1.512 to 1.847 eV. At the higher level of the G3 calculation (Table 1), the  $EA_{\text{ad}}$  is predicted to be 1.795 eV. The results that the BP86, B3LYP, M06, M05-2X, B98, HCTH, M06-2X, mPW1PW91, B97-1, M05, and PBE1PBE methods assessed are in agreement with the G3 value. The absolute deviation from the G3 result is 0.018, 0.021, 0.024, 0.025, 0.028, 0.050, 0.052, 0.054, 0.070, 0.072, and 0.080, respectively. These methods are recognized as reliable and acceptable at predicting EA aspect. Large deviation occur for the G96LYP (0.283 eV), BB95 (0.237 eV), OPW91 (0.220 eV), O3LYP (0.283185 eV), and B1B95 (0.172 eV) methods compared with the G3 value. The  $EA_{\text{vert}}$  value is predicted to range from 1.361 to 1.682 eV, and the VDE value varies from 1.661 to 1.981 eV. The values for  $EA_{\text{ad}}$ ,  $EA_{\text{vert}}$ , and VDE are fairly close to each other, due to the small differences in geometry between neutral and anion.

### $\text{C}_3\text{H}_7\text{SS}$ and $\text{C}_3\text{H}_7\text{SS}^-$

There are two isomers for the propyldithio radical:  $n\text{-C}_3\text{H}_7\text{SS}$  ( $n$ -propyldithio radical) and  $i\text{-C}_3\text{H}_7\text{SS}$  (isopropyldithio radical). The  $\text{C}_s$  symmetry structure of the  $^2\text{A}''$  ground state for the neutral  $n\text{-C}_3\text{H}_7\text{SS}$  and  $i\text{-C}_3\text{H}_7\text{SS}$  radical and the  $\text{C}_s$  symmetry structure of the  $^1\text{A}'$  ground state for the anionic  $n\text{-C}_3\text{H}_7\text{SS}^-$  and  $i\text{-C}_3\text{H}_7\text{SS}^-$  are shown in Fig. 1. The  $i\text{-C}_3\text{H}_7\text{SS}$

radical is predicted to lie 0.156 eV lower in energy than the  $n\text{-C}_3\text{H}_7\text{SS}$  radical with the Gaussian-3 method. The G3 energy for  $i\text{-C}_3\text{H}_7\text{SS}^-$  is 0.176 eV lower than that for  $n\text{-C}_3\text{H}_7\text{SS}^-$ .

From the  $n\text{-C}_3\text{H}_7\text{SS}$  radical to corresponding anion, with the B3LYP functional, the C-S bond distance decreases by about 0.006 Å, while the S-S bond distance increases by about 0.128 Å, respectively. At the bond angle aspect, A(6,8,9) angle decreases by about 3.3°, while A(4,6,8) angle increases by about 1.5°. The dihedral angles have no change: D(4,6,8,9) stays at 180.0° for the radical and anion. As for  $i\text{-C}_3\text{H}_7\text{SS}$  radical and anion, the S-S bond distance changes by about 0.131 Å. A(5,8,7) angle decreases by about 2.2°. Others are in a manner analogous to the case for  $n\text{-C}_3\text{H}_7\text{SS}$  radical. There are still no experimental or theoretical bond angle and bond length data available for comparison.

The theoretical  $EA_{\text{ad}}$ ,  $EA_{\text{vert}}$ , and VDE for the  $\text{C}_3\text{H}_7\text{SS}$  radical are given in Table S3. At the G3 level of theory, the ZPVE corrected adiabatic electron affinities are predicted to be 1.798 eV for the  $n\text{-C}_3\text{H}_7\text{SS}$  radical and 1.818 eV for the  $i\text{-C}_3\text{H}_7\text{SS}$  radical. The B3LYP, BP86, mPW1PW91, HCTH, B98, M05-2X, M06, M06-2X, B97-1, M05, and PBE1PBE methods are in accord with the G3 results and are considered to be more reliable. The G96LYP, BB95, OPW91, O3LYP, and B1B95 methods give more deviation from the G3 results. No experimental or theoretical EA data are available for comparison.

### $\text{C}_4\text{H}_9\text{SS}$ and $\text{C}_4\text{H}_9\text{SS}^-$

We have obtained two isomers ( $n\text{-C}_4\text{H}_9\text{SS}$  and  $t\text{-C}_4\text{H}_9\text{SS}$ ) for the butyldithio radical. The equilibrium geometries of the  $^2\text{A}''$  ground state of the  $\text{C}_4\text{H}_9\text{SS}$  radical and the  $^1\text{A}'$  ground state of  $\text{C}_4\text{H}_9\text{SS}^-$  are displayed in Fig. 2. All methods predict the  $n\text{-C}_4\text{H}_9\text{SS}$  radical and corresponding anion to be  $\text{C}_s$  symmetry zigzag structure.

The  $t\text{-C}_4\text{H}_9\text{SS}$  radical is predicted to lie about 0.325 eV lower in energy than the  $n\text{-C}_4\text{H}_9\text{SS}$  radical (at the G3 level) and are more stable. For the two corresponding anionic isomers, the G3 energy for  $t\text{-C}_4\text{H}_9\text{SS}^-$  is 0.368 eV lower than that for  $n\text{-C}_4\text{H}_9\text{SS}^-$ . A vibrational analysis was carried out for each radical and anion, and all are found to be genuine minima.

In the present study, the C-S and S-S bond distances of the neutral  $n\text{-C}_4\text{H}_9\text{SS}$  radical are predicted to be 1.844 Å and 1.990 Å, respectively. They are very close to their counterparts in  $\text{C}_2\text{H}_5\text{SS}$  and  $a\text{-C}_3\text{H}_7\text{SS}$  radicals. For the anion  $n\text{-C}_4\text{H}_9\text{SS}^-$ , the C-S bond length is 1.837 Å, and the S-S bond length is 2.118 Å. Compared with the corresponding values in a neutral species, we find that the C-S bond shortens by 0.007 Å and the S-S bond lengthens by 0.128 Å. A(8,10,11) angle is 106.4° for the radical and 103.0° for

anion, that is, the bond angle changes by about  $3.4^\circ$ . There are no experimental geometry data for comparison.

The theoretical predictions support a  $C_s$  symmetry structure for the *tert*-butyldithio radical and the corresponding anion. The geometries between radical and anion have some changes. For example,  $A(1,9,10)$  decreases by about  $2.4^\circ$  for structure of the anion (with respect to the radical). The S-S bond length increases by about  $0.127 \text{ \AA}$ , while C-S bond distance decreases by about  $0.011 \text{ \AA}$ . There are no experimental and theoretical geometries of the *t*- $C_4H_9SS$  available for comparison. For two butyl dithio radicals and corresponding anions, the changes of the dihedral angles are still very small (in Fig. 2).

The reliable predicted adiabatic electron affinities (with the higher G3 schemes) are  $1.803 \text{ eV}$  (*n*- $C_4H_9SS$ ) and  $1.847 \text{ eV}$  (*t*- $C_4H_9SS$ ). The M06, BP86, B3LYP, M05-2X, B98, M06-2X, HCTH, mPW1PW91, VSXC, B97-1, and PBE1PBE methods (Table S3) are in agreement with the G3 values (Table 1). The G96LYP method predicts the smallest corrected  $EA_{ad}$ , which deviates  $0.288$  and  $0.304 \text{ eV}$  lower for two isomers, respectively, while the M06-2X method gives the largest ones. No experimental values are available for comparison. The values for  $EA_{ad}$ ,  $EA_{vert}$ , and VDE are fairly close to each other, due to the small differences in geometry between neutral and anion.

#### $C_5H_{11}SS$ and $C_5H_{11}SS^-$

The optimized geometries of the ground state of the *n*- $C_5H_{11}SS$  pentyldithio radical and *n*- $C_5H_{11}SS^-$  are given in Fig. 2. The radical displays  $C_s$  symmetry in the  $^2A''$  ground state and its anionic counterpart has  $^1A'$  ground state. All structures are predicted to have a real vibrational frequency.

In the neutral *n*- $C_5H_{11}SS$  radical, the bond distances of the three C-C bonds nonadjacent to the C-S bond are very close to each other, the adjacent one is shorter by about  $0.005 \text{ \AA}$ . This trend also occurs in *n*- $C_3H_7SS$  and *n*- $C_4H_9SS$  radical. The bond length value of C-S calculated with the B3LYP method is  $1.844 \text{ \AA}$ , whereas the S-S bond length is  $1.990 \text{ \AA}$ . For the anion *n*- $C_5H_{11}SS^-$ , three distant C-C bonds are very similar to each other, as well as those in the neutral species. The theoretical C-S and S-S bond distances are  $1.837 \text{ \AA}$  (shortening by about  $0.007 \text{ \AA}$ ) and  $2.118 \text{ \AA}$  (lengthening by about  $0.128 \text{ \AA}$ ). They are in the same way very close to those in *n*- $C_3H_7SS^-$  and *n*- $C_4H_9SS^-$ . The C-S-S bond angle is about  $106.4^\circ$  in the neutral species, whereas it is  $103.0^\circ$  in the anion (decreased about  $3.4^\circ$ ). For the *n*- $C_5H_{11}SS$  radical and corresponding anion, the dihedral angles basically have no changes. For instance, the dihedral angle C-C-S-S stays at  $180.0^\circ$  at various different methods. To our knowledge, there are still no experimental and theoretical geometries available for comparison.

The adiabatic electron affinity  $EA_{ad}$  (with ZPVE correction) is predicted to be  $1.516$ – $1.844 \text{ eV}$  by the various DFT functionals (Table S3). The G3 method predicts the ZPVE corrected adiabatic electron affinity for the *n*- $C_5H_{11}SS$  radical to be  $1.807 \text{ eV}$ . Similarly to the methylthio and ethyldithio radical, The M06, BP86, B3LYP, M05-2X, B98, M06-2X, HCTH, mPW1PW91, M05, B97-1, and PBE1PBE results are in accord with the G3 value. The M06-2X method predicts the largest corrected  $EA_{ad}$  ( $1.844 \text{ eV}$ ), and the G96LYP method predicts the smallest ( $1.516 \text{ eV}$ ). The G96LYP, BB95, OPW91, O3LYP, and B1B95 methods give more deviation ( $0.291$ ,  $0.242$ ,  $0.233$ ,  $0.198$ , and  $0.179 \text{ eV}$ ) from the G3 value. The range of  $EA_{vert}$  is from  $1.360$  to  $1.681 \text{ eV}$ , and the range of VDE is from  $1.614$  to  $1.986 \text{ eV}$  for the *n*- $C_5H_{11}SS$  radical. The values of  $EA_{ad}$ ,  $EA_{vert}$ , and VDE are fairly close to each other due to the small differences in geometry between the radical and the anion. No experimental and theoretical electron affinities are available for comparison.

## Conclusions

In this work, we systematically study the structures and electron affinities of seven alkyl dithio radicals  $R-SS/R-SS^-$  ( $R=CH_3$ ,  $C_2H_5$ , *n*- $C_3H_7$ , *i*- $C_3H_7$ , *n*- $C_4H_9$ , *t*- $C_4H_9$ , *n*- $C_5H_{11}$ ) by means of the higher level of Gaussian-3 schemes and 21 carefully selected DFT methods. All the results show some consistent trends listed below: (a) All the bond lengths of S-S in the radicals are a little shorter than those in the corresponding anions (ranging from  $0.126$  to  $0.131 \text{ \AA}$ ), whereas the C-S bond lengths in radicals are a little longer than those in the corresponding anions (ranging from  $0.001$  to  $0.011 \text{ \AA}$ ). This is because when an electron attaches to the radicals, it will enter the antibonding orbital, and it decreases the bonding interaction of the S-S bond. The C-C bond length near the C-S bond increases while the other C-C bonds are almost unchanged when an extra electron is attached to the radical. (b) The bond angle C-S-S in the radical is larger than that in the anion by about  $2.2$ – $3.4^\circ$ , whereas the C-C-S bond angle is a little smaller.

The reliable ZPVE-corrected adiabatic EAs, predicted at the higher level of the Gaussian-3 theory, are  $1.791 \text{ eV}$  (for  $CH_3SS$ ),  $1.795 \text{ eV}$  (for  $C_2H_5SS$ ),  $1.798 \text{ eV}$  (for *n*- $C_3H_7SS$ ) and  $1.818 \text{ eV}$  (for *i*- $C_3H_7SS$ ),  $1.803 \text{ eV}$  (for *n*- $C_4H_9SS$ ), and  $1.847 \text{ eV}$  (for *t*- $C_4H_9SS$ ), and  $1.807 \text{ eV}$  (for *n*- $C_5H_{11}SS$ ), respectively. The BP86, M05-2X, B3LYP, M06, B98, M06-2X, mPW1PW91, HCTH, B97-1, M05, PBE1PBE, and VSXC results are in agreement with the G3 values, and the average absolute deviations from the G3 values for the simplest alkyl dithio radicals are  $0.017$ ,  $0.022$ ,  $0.024$ ,  $0.028$ ,  $0.030$ ,  $0.054$ ,  $0.055$ ,  $0.057$ ,  $0.071$ ,  $0.076$ ,  $0.081$ , and  $0.085 \text{ eV}$ , respectively. These methods are regarded as

reasonable. Our theoretical alkyl dithio radicals' results are convincing and may provide a reference for further studies. No experimental values are available for comparison.

We hope that our theoretical predictions will provide strong motivation for further experimental investigation of these important alkyl dithio radical species and their anions.

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