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Effect of ring strain on disulfide electron attachment

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ABSTRACT

The possibility of excess electron binding of a series of (bi)cyclic, ring-constrained disulfides, in gas phase was investigated by ab initio MP2/6-31+G** calculations. It is shown that ring strain favors electron attachment, as neutral compounds are very sensitive to angular and dihedral compressions: cyclic disulfides will preferentially undergo a spontaneous electron capture compared to linear analogs, with superior positive values for adiabatic electron affinity. Cyclisation effect is progressively switched off for higher-member rings, but remains important for disulfides grafted on molecular bridges. Its structural consequences are analysed, with different behaviors for neutral and radical anionic moities.

1. Introduction

In proteins, two cysteine residues can associate to form covalent disulfide bonds via thiolate–disulfide exchanges, one of the most rapid reaction known and which occurs in cascade [1,2]. So-formed disulfides bridges are crucial for maintaining a protein fold, by locally increasing residues concentration (i.e. hydrophobicity and entropy), which in turn destabilizes the unfolded form of a given protein [3]. Paradoxically enough, the disulfide bond is intrinsically relatively weak, with an experimental dissociation energy of 272.8 ± 3.8 kJ mol^{-1} for dimethyl disulfide [4]. Sulfur bridges can easily undergo spontaneous and reversible cleavage and it is of tremendous importance to get an understanding of the possible evolution of disulfide bridges in a variety of biological situations (oxidative stress, enzymatic reactions, etc.).

Thiolates are also usual and versatile ligands in organometallic synthesis, with the possible formation of disulfide bonds: three-electron two-centers complexes with charge separation have also been evidenced [5]. Chemistry of sulfur uncontestedly offers a remarkable richness, and one would like to fully explore new exciting possibilities they have to offer. Many recent studies have aimed to propose clever ways to tune the disulfide bond, for instance its spectroscopic properties [6,7]. A major obstacle comes from the recognition that disulfide bonds can hardly be modulated by indirect electronic substituent effects, as the highest occupied molecular orbital (HOMO) is almost exclusively sulfur-centered. Elegant solutions will come from an ultimate understanding of disulfide properties and reactivity, possibly inspired by biological systems [8].

One of the key feature of disulfide bond is a dihedral τ(C–S–S–C) close to 90° in the most favorable conformation: it has been recognized that a modification of this angle, by steric hindrance, ring closure or other structural constraints [9], drastically changes reactivity: first, the disulfide bond is weakened, with a slight lengthening of S–S bond, and is potentially more reactive. Secondly, different mechanisms will be in competition for a nucleophilic addition on disulfide, depending on the angle of attack—SN_2 vs. addition–elimination for disulfide–thiolate exchange [10,11]. Enhanced reactivity [12] or loss of stability [13] due to the strain at the disulfide linkage (angle compression) have also been reported.

Apart from the aforementioned disulfide–thiolate exchange, another chemical act that has recently raised interest is the electron addition on a given protein or polypeptide. This very simple act can be induced either by X-ray irradiation [14] or by oxidant agents [15]. In both biological and organometallic contexts, getting solid experimental evidences for disulfides reduction process—by NMR, UV and Raman spectroscopy [16,17]—still constitutes a real 'tour-de-force': recent evidences for existence of stable disulfide radical anions for both model compounds or macromolecular systems have nevertheless been conjointly obtained (various spectroscopy studies [18,19,14], electrochemistry [20], ab initio calculations [21,22]). During this process, the sulfur–sulfur distance undergoes a significant elongation, roughly equal to 0.7 Å, while other geometrical parameters are conserved. The so-formed radical anion is stable towards heterolytic dissociation, with a barrier close to 100 kJ mol^{-1} for dimethyl disulfide. Such a structural evolution of hemi-bonded [23] systems is rarely observed (a key originality) in daily chemistry: one would like to rationalise the reactivity of disulfide bridges, and for example to predict where the electronic attachment will occur in a given protein. A first step towards this goal is to build up a solid understanding of electron capture by disulfides on small saturated compounds. Disulfide radical anions cannot be formed on unsaturated skeletons, because low-lying π^* LUMOs will preferentially capt the electron. The only exception is when a conjugation prevents this capture, as for

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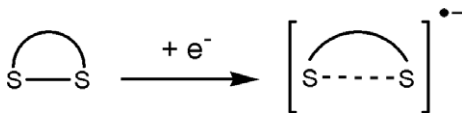

Fig. 1. Generic reaction considered: the one-electron addition on cyclic disulfides. The sulfur–sulfur hemi-bond in the radical anion is represented with a dashed line.

aromatic disulfide. In spite of their apparent simplicity, only a few model systems have been characterized up to now [24–27]. We are still far from a satisfactory knowledge of the factors influencing the ease with which a disulfide bond can fix an electron: any subtle modifications of the substrate, leading to non-electronic substituent effects (charged groups [28], steric contributions or geometrical effects) can potentially modulate the disulfide reactivity. Solvent effects are also crucial, with a dramatic stabilisation of the anionic form.

Such a reference benchmark of isolated simple compounds appears to be well suited before considering macromolecular systems, with a subtle interplay between several not-so-well identified components. It may also be useful for other applications, as engineering of disulfide bonds to increase protein stability [29].

Due to the considerable lengthening of disulfide bond upon electron capture, ring constraint are likely to strongly influence disulfide reducible properties, in a direction which is not *a priori* easily predictable. In this work, we propose a model study of electron capture for a series of cyclic disulfides, as displayed in Fig. 1. To the best of our knowledge, no experimental results for such compounds have been published yet, and pionnering theoretical investigations are desirable. Calculations on disulfide radical anions require the use of sophisticated ab initio methods: a description of the methodology employed is given in Section 2. To describe a variety of arcs (cf. Fig. 1), ten compounds were chosen, as detailled in Section 3.1. A simple model situation, the torsion of dimethyl disulfide (DMDS), is analysed in Section 3.2. The two following subsections are respectively devoted to structural properties and reactivity towards electron attachment for real cyclic disulfides. A special emphasis is given to the dihedral angle, which was found to play a key role.

2. Methodology

The reasons for choosing the second-order Møller-Plesser perturbation theory (MP2 [30]) method to describe electron attachment of cyclic disulfides are twofold. Three-electron two-centers bonds are, from an energetic point of view, intermediate between covalent and Van der Waals interactions. Their intrinsic stability comes from the charge fluctuation (charge-shift bond) between two resonant Lewis structures, as initially proposed by Pauling within the framework of valence bond theory. Such bonds can alternatively be described in term of molecular orbital theory, the resulting bond order being close to 0.5. We refer the reader to the recent review by Fourré and Silvi for a general discussion concerning topological characterization (ELF analysis) of three-electrons two-centers bonds [31]. Odd-electrons bonds are intrinsically rather delicate to treat by ab initio methods, because electron correlation has to be included accurately enough to allow a proper description [21,32–35]. This requirement almost precludes DFT functionals, for which the self-interaction dramatically underestimates the strength of the sulfur–sulfur hemi-bond [34]. The physical origin of inadequacy for Hartree–Fock method has also been analyzed [35]. Conversely, the validity of the MP2 method to describe properly symmetric three-electrons two-centers bonds, is well established, while failures for unsymmetric situations have been reported [36]. All compounds considered in this study belong to this category. (It should be mentionned that neutral disulfides are also well described by MP2 method [37].)

Secondly, deficiencies of most of the DFT functionals to properly describe small-ring compounds have been pointed out [38], and, here again, accurate description of electron correlation has proved to play a crucial role: this is a necessary condition to properly reproduce major geometrical changes (disulfide elongation).

The choice of the basis set offers a somewhat dangerous flexibility, and turns out to be not so straightforward. Preliminary calculations on dimethyl disulfide were performed to investigate the basis set convergence for electron binding energy (EA_{ad}). While geometrical parameters are correctly reproduced as soon as the basis set is large enough and includes diffuse functions, electron affinities are much slower to converge. Benchmark calculations show unbalanced basis set may poorly describe the radical anionic species, or even favor a carbon attachment. The reader is referred to the following review for a general discussion [39], as well as this paper by Braida et al. which deals more specifically with disulfide radical anions [40]. We found that a solid compromise consists in using the Pople basis set 6-31+G**, which gives the same value as the one obtained with a much more expensive aug-cc-pVTZ basis set. The value for diethyl disulfide (DEDS) we obtained is slightly negative (−0.02 eV), although the exact value is close to +0.10 eV [40]. As we are interested in *relative* electron affinities (linear vs. cyclic), rather than in absolute values, we decided to perform calculations at this level of theory, in agreement with previous related studies [41].

(U)MP2(fc) calculations were performed with the Gaussian 03 series of programs [42]. Harmonic frequencies were computed to confirm the nature of optimized structures. $\langle S^2 \rangle$ values were never greater than 0.77 (the exact value is 0.75), such that no contamination spin effect will affect our results. Solvent effects were taken into account using the polarizable continuum model (IEF–PCM) with UA0 atomic radii [43].

3. Results and discussion

3.1. Description of the panel

To investigate ring strain effects on both geometries and electron affinities, we have considered a set of model aliphatic disulfides, as listed in Table 1. The first subset corresponds to saturated cyclic disulfides, where the generic arc of Fig. 1 corresponds to n CH_2 groups: n is comprised between 1 and 6—namely 1,2-dithia-cyclopropane, 1,2-dithia-cyclobutane, 1,2-dithia-cyclopentane (respectively, $n = 1, 2, 3$) and higher-member rings $n = 4, 5, 6$). Neutral forms of these compounds have been synthesized and characterized [44]. For the sake of comparison, a ring-free reference has to be chosen: by definition, it would correspond to the two infinite $(CH_2)_x$ chains linked by a disulfide bond $(x \to \infty)$. Fortunately, convergence of linear aliphatic disulfides towards electron attachment was proved to converge very rapidly, with almost identical behaviors of diethyl vs. dipropryl disulfide. Then, diethyl disulfide (DEDS) was added to our panel, and one can verify that convergence of geometrical parameters has been reached for $n = 6$. Consequently, higher values of n were not considered: synthesis strategies for such compounds have been reported [45], and they can be expected almost identical behavior than ring-free DEDS.

Two other bicyclic compounds, bicyclo-[2.2.2]-2,3-dithia-octane (**1**) and bicyclo-[3.2.1]-6,7-dithia-octane (2), were considered. They are similar to well-known molecular bridges, proposed by Swain and Lupton for separating substituent effects [46], and will be studied here for their ring strain (Fig. 2). Bicyclo L-cystine (**3**) was also considered for its biological relevance: this molecule is

Table 1
Geometrical and energetical characterization of a series of aliphatic disulfides – neutral and associated radical anions – represented on Fig. 2

Compound		Geometrical parameters					
		d(S–S)	∠(S–S–C)	τ(C–S–S–C)	ν	ρ	EA_{ad}
–S–S–$(CH_2)_n$	$n = 1$	2.10	54.1	–	500.7		
		2.74	40.8	–	261.6	0.533	0.92
	$n = 2$	2.13	78.0	21.8	490.2		
		2.84	65.5	25.7	195.9	0.510	0.83
	$n = 3$	2.08	90.4	46.7	518.3		
		2.80	76.8	54.7	190.4	0.538	0.16
	$n = 4$	2.07	95.6	51.7	505.6		
		2.84	97.4	42.1	207.8	0.482	0.06
	$n = 5$	2.05	100.2	84.5	531.3		
		2.78	89.7	83.2	188.1	0.503	−0.06
	$n = 6$	2.06	103.3	96.8	527.9		
		2.82	94.8	99.7	222.6	0.515	−0.03
DEDS	$n \to \infty$	2.06	101.3	83.6	526.2		
		2.79	88.6	85.3	217.2	0.532	−0.02
(**1**)		2.08	96.9	21.9	485.9		
		2.83	88.2	20.7	196.6	0.506	0.25
(**2**)		2.13	94.8	0.0	478.6		
		2.84	85.0	0.0	206.4	0.521	0.42
(**3**)		2.06	102.8	94.2	517.8		
		2.75	92.4	99.6	233.9	0.521	0.02
(**4**)		2.05	119.6	81.3	523.3		
		2.77	92.6	79.1	213.3	0.548	−0.06

Calculations were performed at the MP2/6-31+G** level of theory. All distances d(S–S) are given in Å, and angles ∠ and τ in degrees. Harmonic frequencies ν corresponding to the S–S stretching mode were not scaled, and are given in cm^{-1}. Mulliken atomic spin densities ρ are reported. Adiabatic electron attachment energies EA_{ad} are given in eV.

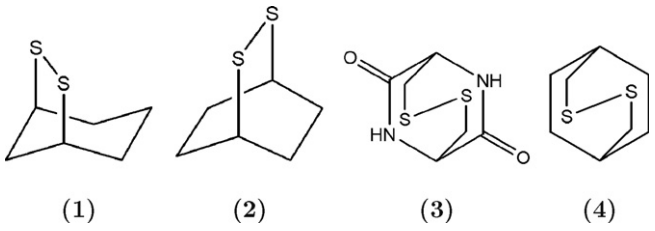

Fig. 2. Chemical structures of neutral cyclic disulfides considered (second subset).

obtained by dimerisation of two cysteine residues, with the formation of two intramolecular *cis* peptidic bonds. Even if this structure is defavorated by a strong ring strain compared to the linear form (L,L-cystine), it has the merit of reducing the number of conformations. A comparison with this linear analog would be of interest: its electron capture was investigated by Simons and coworkers [41]. However, even for this smallest peptide, a family of close-lying conformers for both neutral and anionic forms were found and prevents a straightforward and meaningful comparison. Finally, a fourth compound in this subset, (**4**), structurally similar to (**3**), was added to evalute possible effects of heteroatoms.

3.2. A model system: constrained torsion of DMDS

A key mechanism by which ring strain will affect disulfide – for both neutral and anionic forms – is, among others, a compression or an opening of the dihedral angle τ. The latter certainly is the most flexible geometrical variable (as verified from the computed harmonic frequencies), and hence the first one to be altered by ring closure. As we will see, apart from small-member rings ($n = 1, 2$), a neutral disulfide in cyclic skeleton is affected mostly by its dihedral angle in the first subset of molecules. As additional—electronic, and possibly competitive—effects may coexist, it might be useful to discuss beforehand an 'artificial' chemical situation. Dihedral angle τ of dimethyl disulfide (DMDS) was assigned to take arbitrary values—identical for neutral and radical anions forms, all other parameters being re-optimized during the process. Torsion profile for both neutral and radical anionic forms of DMDS and DEDS are given as supporting informations. Dihedral conservation during the electron attachment process has been reported in earlier communications [18], such that we are confident in the validity of this test. This simple situation will help us hereafter to evaluate the purely geometrical effect of ring closure.

Let us first comment on the weakening of the covalent sulfur–sulfur bond (neutral form), induced by the forced rotation. Starting from the equilibrium value (2.06 Å and $\tau = 83.6°$), the sulfur–sulfur distance rises up to 2.13 and 2.10 Å, respectively, for $\tau = 0°$ and 180°, in a near-linear regime. This corresponds to the increasing gap between the occupied π and π^* orbitals as the dihedral angle is either compressed or opened with respect to the 90° value: according to Walsh rule, this results in an energetic four electrons destabilisation, further amplified by an additional 1,4 steric repulsion in the *cis* ($\tau = 0$) case. One can note that disulfide and peroxide dihedral angles differ noticeably: at the same level of calculation, a value of 121.3° is obtained for H_2O_2. This probably corresponds to weaker hybridization of the sulfur atom orbital in neutral disulfides [49].

The sulfur–sulfur distance in the radical anion behaves similarly with respect to this dihedral compression (from 2.79 to 2.89 Å for τ varying from 85.2° to 0.0°), but remains constant when an angular opening is imposed: this shows that, at this longer S–S bond length, only the steric hindrance remains, and the four electron repulsion is greatly reduced. We are interested in predicting the evolution of electron affinity: as the latter is close to zero for the equilibrium geometry, it is important to determine whether torsion favors or conversely precludes electron attachment. A similar shape for energetic destabilization as a function of τ is found, in agreement with the previous orbital argument. This geometrical effect is less enhanced for the hemi-bonded radical anion, with a sensitivity roughly divided by three. It follows that electron affinity of neutral disulfides is strongly reinforced by torsion: its evolution as a function of τ is displayed in Fig. 3. It is worth asking if solvatation modulates effects of this dihedral compression. Accordingly, solvent effects were considered: *N*,*N*-dimethylformamide (DMF, $\varepsilon = 37$) was chosen as an aprotic, usual solvent for studying aliphatic radical anions [24]. A consequent but uniform shift

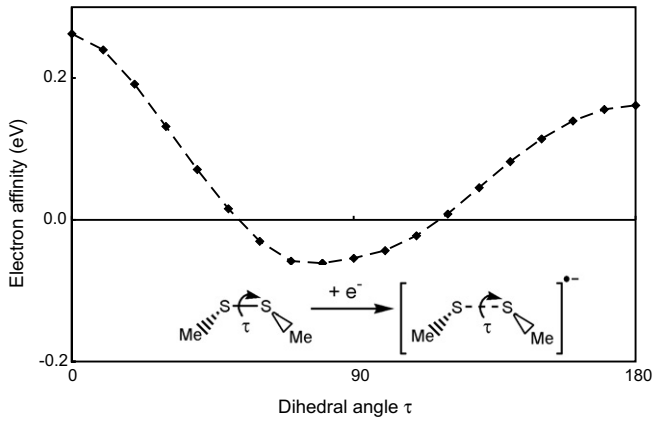

Fig. 3. Evolution of electron affinity for torsional constrained dimethyl disulfide. Level of calculation MP2/6-31+G**, in gas phase.

towards higher electron affinities is observed, due to the preferential stabilisation of radical anionic species (close to 2.3 eV). While charged species is relatively stabilized, distribution charges is symmetric and almost exclusively sulfur-centered, such that no difference is observed for different dihedrals τ; a similar explanation for peroxide was recently reported [47].

Yet simple, this model suggests that dihedral compression or opening may constitute an elegant way to differentiate disulfides in terms of reducible potential, for instance in proteins – values up to $\tau = 126$ degrees for disulfide linkage has been reported for chymotrypsin [48]. It also provides an order of magnitude for this purely geometrical effect: in Section 3.4, it will serve as an useful measure to check whether ring closure in real systems can either be understood only in terms of geometrical constraints, or if electronic contributions also need to be considered.

3.3. Geometries of small cyclic disulfides – neutral and radical anionic forms

Before investigating ring strain effects on electron attachment, it is of interest to first discuss structural evolution of cyclic disulfides, that is the evolution of distance d(S–S), angle $\angle$(C–S–S) and dihedral τ(C–S–S–C). As they exhibit different behaviors, neutral and radical anions will be discussed separately for the sake of clarity.

Covalent disulfide bonds in neutral compounds are expected to be strongly modulated by ring strain, due to their relative flexibility (softness) compared to more rigid aliphatic skeleton: this intuitive picture is confirmed by our calculations. The perusal of Table 1 shows that cyclisation tends to weaken the disulfide bond with respect to ring-free DEDS reference: vibrational frequencies ν are lower (hence force constants), with a noticeable lengthening (up to 0.08 Å for an initial value of 2.06 Å). As carbon and sulfur atoms have very different geometrical characteristics, one has to pay a certain price to insert a disulfide bond in an aliphatic cycle. Their variations are linearly related to the dihedral angle τ. The latter ranges from 0.0° to 96.8°, for a reference DEDS-value of 83.6°, with a quite regular spacing. In the first subset, one can note that convergence of ν and d(S–S) with respect to ring size n is not perfectly monotonous: the disulfide bond is found to be weaker in 1,2-dithia-cyclobutane (four-member ring compound, $n = 2$) than in the smaller, more highly constrained 1,2-dithia-cyclopropane (three-member ring compound, $n = 1$). This singularity probably reflects an additional angular $\angle$(C–S–S) compression for these smallest cycles ($n = 1, 2$): its consequence on electron affinity will be commented further. By progressively adding CH_2 groups, the overall flexibility of this system increases, leading to a rapid convergence to DEDS-values.

We now move on the discussion to radical anionic species: the drastic lengthening of disulfide bond constitutes the chemical specificity of the one-electron addition (compared to other reactions as thiolate–disulfide exchange) and one of our goals is to investigate the geometrical rearrangement of the cyclic disulfide with respect to an electron capture. For linear reference compounds, this effect is static with respect to other parameters: this may not be true for cyclic compounds, where geometrical variations are intrinsically correlated. Thus, one may expect very different ring effects, and it is not a priori clear if hemi-bonds will be reinforced or weakened by ring strain. First of all, it is remarkable that, in spite of ring strain, all radical anions were found to be stable, and we never observe disulfide cleavage (distance superior to 3 Å). In sharp contrast with neutral moities, our results show that the sulfur–sulfur hemi-bond can be either shorter or longer in cyclic compounds with respect to the reference DEDS-value (2.79 Å). S–S stretching frequencies vary accordingly, yet the linear dependence with τ is not verified anymore (see value for $n = 3$). It is remarkable that evolution in the first subset is not regular anymore, but presents oscillations that suggest the existence of a second effect in close competition with the aforementioned dihedral compression. Oppositely, a slight but significant shortening of the sulfur–sulfur hemi-bond (up to 0.05 Å) is observed for three compounds: 1,2-dithia-cyclopropane ($n = 1$), (**3**) and (**4**). We note in passing that introducing two additional CH_2 groups, as in (**3**) and (**4**) is sufficient to almost restore the original preference for a dihedral angle close to 90°. We noticed that such systems act as molecular 'pincers': for 1,2-dithia-cyclopropane, the single CH_2 entity is not flexible enough to completely follow the important opening of $\angle$(S–C–S) (+24.6°), concomitant to the disulfide elongation. In that case, it becomes energetically more favorable to slightly compress the hemi-bond. An order of magnitude for the relative softness of hemi-bonded vs. covalent disulfides was quickly derived from a potential energy curve $E = f(d)$, where d stands for the sulfur–sulfur distance. We found that force constant k for DMDS is divided by roughly three from neutral to radical anionic form. Complete ring opening is also hindered for highly rigid compounds (**3**) and (**4**), with a six-member base and two CH_2 groups setting the disulfide bond: the latter is found to be slightly shorter than in ring-free DEDS compound, with a dihedral geometrically constrained to a value close to 90°.

3.4. Impact of ring strain on disulfide electron affinity

We are now focussing on electron attachment: adiabatic electron binding energies are reported in the last column of Table 1. Evolution turns out to be mostly governed by neutral compound, and consequently more regular: for compounds of the first subset, electron affinities EA_{ad} vary monotonously with ring size n. As established on torsion of DMDS, the one-electron addition introduces more flexibility in the system, and neutral species are consequently more affected by ring closure due to their higher rigidity. Ring strain almost systematically enhances electron affinities compared to DEDS ring-free value (−0.02 eV): +0.83 eV for 1,2-dithia-cyclopropane, +0.25 eV for (**1**), etc.

It is legitimate to ask whether or not the evolution is governed purely by geometrical constraints: clearly, other electronic contributions (inductive, resonance...) and electrostatic effects (dipoles [41]) may also impact the electron affinity. A valuable test to estimate their participation consists in simply reporting EA_{ad} values on the torsion curve for ring-free DEDS, and to check if there is or not close agreement. The corresponding plot is displayed on Fig. 4. For most of the compounds we have considered, electron affinities can indeed be interpolated. A systematic underestimation is observed for compounds with an important dihedral compression, such as 1,2-dithia-cyclopropane ($n = 1$), (**2**) and also 1,2-dithia-cyclobu-

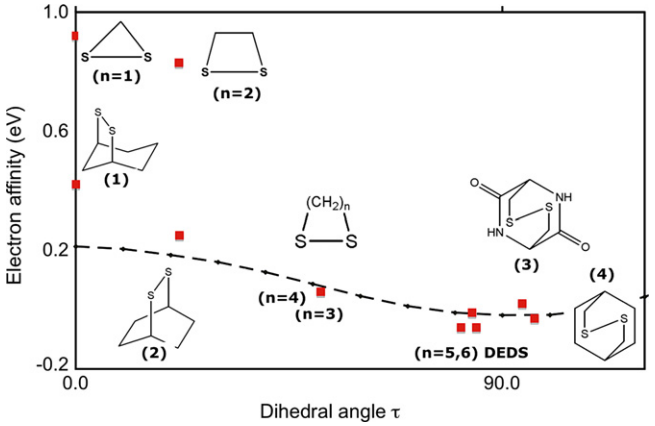

Fig. 4. Evolution of EA_{ad} as a function of the dihedral angle τ for DEDS – gas phase, level of theory MP2/6-31+G**. Values for the ten compounds of Table 1 are reported to identify possible electronic contributions. Dihedral angle for 1,2-dithia-cyclopropane was conveniently taken as 0°.

tane ($n = 2$): this exaltation of electron affinity can be traced back to an angular decompression of aliphatic carbons ($\angle$(S—C—S)), concomitant to the elongation of the disulfide bond upon electron capture. This energetically favors radical anions, although a proper quantification of this effect cannot be easily proposed. Bond dissociations energies cannot be computed for these two compounds. Another possibility is to evaluate ring strain energies according to the group equivalent method of Bachrach [11]. This more quantitative estimation does not apply for bicyclic compounds, but for 1,2-dithia-cycloalkanes, for which a linear correlation with electron affinities is found ($N = 7, R^2 = 0.971$). The corresponding figure is given as supporting informations. The ring strain energy accounts for both dihedral and angular compressions, the latter being probably at the origin of the exaltation of electron affinity for low-member rings. Interestingly enough, the slope is close to unity (0.892), which may suggest that others contributions than ring stain are negligeable for this model compound.

4. Concluding remarks

In this study, ring strain effects on electron affinities of simple cyclic disulfides was investigated by ab initio calculations: our results show a systematic trend to increase disulfide reducible properties, which was traced back to a higher flexibility of the sulfur–sulfur bond in the radical anionic form. The dihedral angle was found to play a key role, and could be an useful index to predict reducible properties.

We hope that this study could be helpful to synthesize and characterize new disulfide radical anions, which are expected to be very stable—with respect to experimental difficulties encountered for such strained systems, let alone hemi-bonded—with traditional strategies.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.cplett.2008.05.010.

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