Full Articles

Electronic structure and reactivity of S—S dications

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The electronic structure and reactivity of some S—S dications were studied at the MP2/6-31G* level of theory. The results obtained indicate a stepwise electrophilic addition of disulfonium dication moiety to the double C=C bond to be the preferable mechanism.

Key words: disulfonium dications, *ab initio* quantum-chemical calculations, electrophilic addition, conformational analysis.

Disulfonium dications, or S—S dications, are a recently discovered class of organic sulfur compounds containing two directly connected sulfonium atoms.[1,2] Mutual influence of adjacent charged centers in such compounds is responsible for unusual physicochemical properties, which are basically different from the properties of monosulfonium salts or disulfonium salts with nonbonded onium atoms. In particular, disulfonium dications exhibit pronounced oxidative properties.[3,4] Another interesting example of their chemical properties is provided by the recently reported addition of the S—S dications to the multiple carbon—carbon bonds to give the corresponding 1,2-disulfonium salts.[5,6] Some other compounds also contain N—N,[7] S—N,[8] Se—N,[9] Se—Se,[10] and Te—Te [11] moieties with two directly connected charged heteroatoms; however, the addition of the disulfonium dications to alkenes or alkynes is at present the only example of addition of the dication moiety to the multiple bonds.

Based on the available experimental data, two possible mechanisms were proposed for this reaction, namely, a concerted mechanism involving a four-membered cyclic transition state and a stepwise addition through formation of carbocationic intermediates (Scheme 1).[5]

The lack of experimental data prevents from choosing between these mechanisms. In this connection it is of considerable interest to investigate the structure and reactivity of S—S dications by modern methods of theoretical chemistry including the *ab initio* quantum-chemical methods. This was the subject of the present work.

Calculation Procedure

The total energies of the optimized structures were calculated by the *ab initio* MP2/6-31G* method using the PC-GAMESS program.[12,13] Assignment of the stationary points on the potential energy surfaces to particular conformers or transition states of corresponding order was checked by calculating the complete Hessian at these points. The potential energy of internal rotation in dication **2a** was calculated using the density functional approach (PBE96 functional)[14] and the TAINA program.[15,16] The

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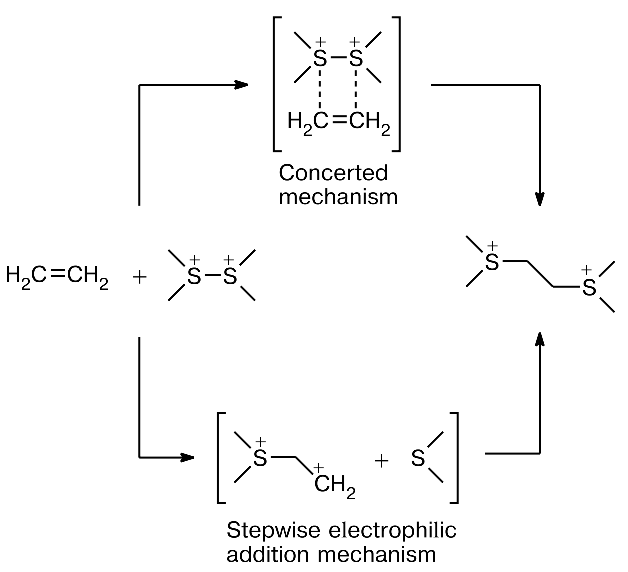
Scheme 1

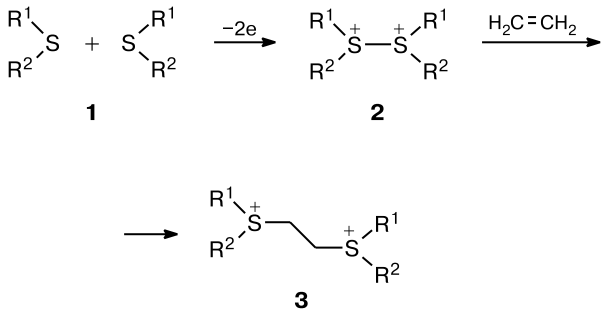


relative energies were calculated without inclusion of zero-point vibrational energy correction.

Results and Discussion

Calculations were carried out for three related series of structures **1**—**3** (Scheme 2). Formally, dications **2** can be formed from nonbonded sulfide moieties (or molecules for **2a**) upon two-electron oxidation. Subsequent addition of an ethylene molecule results in disulfonium salts **3**.

Scheme 2



a: $R^1 = R^2 = Me$
b: $R^1 + R^1 = R^2 + R^2 = —(CH_2)_2—$
c: $R^1 + R^1 = —(CH_2)_2—; R^2 + R^2 = —(CH_2)_3—$
d: $R^1 + R^1 = R^2 + R^2 = —(CH_2)_3—$

We started with the conformational analysis of dications **2a**—**d**. Both internal rotation about the S—S bond and planar inversion of tricoordinated sulfur atom are possible for tetramethyldisulfonium dication **2a**. We calculated the potential curve for internal rotation about the S—S bond (Fig. 1) using the density functional approach.

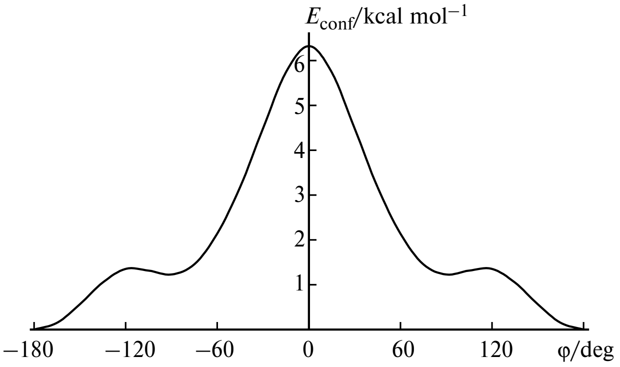
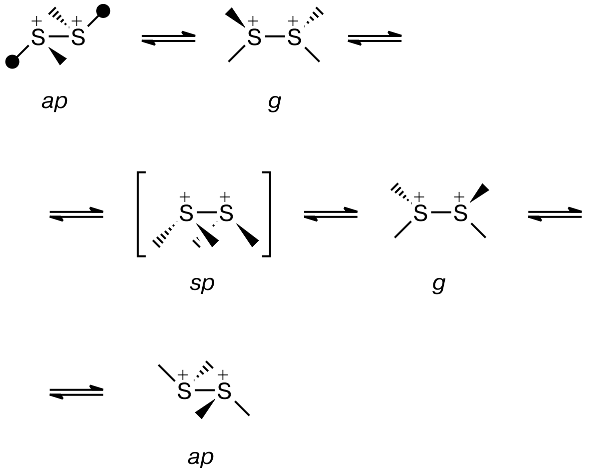
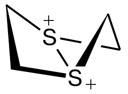


Fig. 1. The potential curve for internal rotation about the S—S bond in dication **2a** (φ is the C—S—S—C torsion angle).

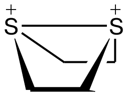


The C—S—S—C torsion angle is zero in the synperiplanar (*sp*) and ±180° in the antiperiplanar (*ap*) conformation of the dication moiety. A number of structures including the planar conformation, *p*, of molecule **2a** were optimized at the MP2/6-31G* level of theory; hereafter the corresponding energies are listed in parentheses. In addition to the energy minimum corresponding to the most stable conformer, *ap*, local potential energy minima corresponding to the *gauche*-conformer, *g*, with an energy of 1.2 (1.4) kcal mol^{-1} were found at torsion angles of 90° and −90°. According to calculations, the energy of the *sp* conformation is 6.3 (8.0) kcal mol^{-1}. The planar structure is a second-order transition state. Its energy is 64 kcal mol^{-1} higher than that of the *ap* conformer. Therefore the barrier to inversion can be estimated at 32 kcal mol^{-1} per sulfonium center, which is much higher than the barrier to internal rotation. Thus, internal rotation about the S—S bond should be considered as a preferred conformational process in the tetramethyldisulfonium dication **2a**.

In studying the conformational behavior of bicyclic dications we used the characteristics of the corresponding conformations of the initial neutral dithiaheterocycles 1,4-dithiane (**1b**), 1,4-dithiepane (**1c**), and 1,4-dithiocane (**1d**) (more detailed consideration goes beyond the scope of this work). Based on the X-ray diffraction data[17] for the salt of dication **2d** with trifluoromethanesulfonate anions and on the results of a theoretical study,[18] which revealed the preference of *cis*-fusion of the five-membered rings in the structure of 1,5-dithioniabicyclo[3.3.0]octane **2d**, we restricted ourselves to the investigation of the structures of bicyclic dications **2b—d** with *cis*-fused rings in which the dication moiety adopts a nearly synperiplanar conformation. For dication **2b** the energy minimum corresponds to the structure **T** with C_2 symmetry, while the more symmetrical structure **B** (C_{2v}) is a transition state. The energy difference between these structures is small (less than 1 kcal mol^{-1})



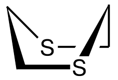
T



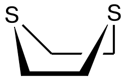
B

Confor-mation	Symmetry	$-E_{\text{tot}}$ /hartree	E /kcal mol^{-1}
T	C_2	951.1455004	0
B	C_{2v}	951.1439459	0.96

The **T** and **B** conformers of dication **2b** respectively correspond to the **B[C]** (C_2 symmetry) and **B[S]** (C_{2v} symmetry) conformers of 1,4-dithiane **1b** in which the six-membered ring adopts a boat conformation. Both structures, **B[C]** and **B[S]**, are transition states, which is typical of saturated six-membered rings. The conformational stability of the neutral molecule follows the same pattern as the relative conformational stability of the dication. However, the energy difference between the conformers increases.



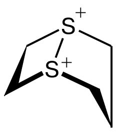
B[C]



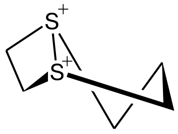
B[S]

Confor-mation	Symmetry	$-E_{\text{tot}}$ /hartree	E /kcal mol^{-1}
B[C]	C_2	951.9110340	0
B[S]	C_{2v}	951.9041516	4.32

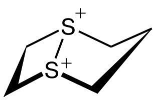
In the case of 1,4-dithioniabicyclo[3.2.0]heptane **2c** conversion of the most stable conformer **B** with C_s symmetry and *endo*-orientation of methylene group in the C—CH$_2$—C fragment of the bicyclic system into asymmetric conformer **T** occurs through transition state **C** with C_s symmetry and *exo*-position of the methylene group.



B



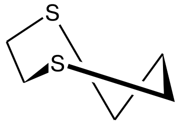
T



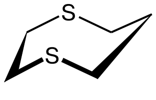
C

Confor-mation	Symmetry	$-E_{\text{tot}}$ /hartree	EE /kcal mol^{-1}
B	C_s	990.3635552	0
T	C_1	990.3593036	2.67
C	C_s	990.3583880	3.24

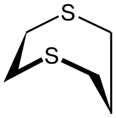
Analogous results were also obtained for the corresponding conformers of neutral 1,4-dithiepane (**TC**, **B**, and transition state **C**), the first structure, **TC**, being the most stable.



TC



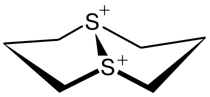
C



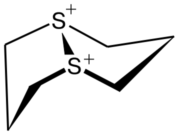
B

Confor-mation	Symmetry	$-E_{\text{tot}}$ /hartree	E /kcal mol^{-1}
TC	C_1	991.0778662	0
C	C_s	991.0746597	2.01
B	C_s	991.0694321	5.29

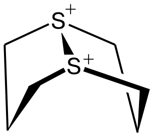
Our calculations of conformers of dications **2b**,**c** predict some puckering of the four-membered sulfur-containing rings, which causes a distortion of the synperiplanar conformation of disulfonium moiety. The bicyclic system of dication **2d** comprises five-membered rings only; the structures of all conformers of this dication retain the *sp*-conformation of the S$^+$—S$^+$ moiety. The stabilities of different conformers estimated from their total energies change as follows: **CB** > **BB** > **CC**, which is in agreement with the known computational results.[18]



CC



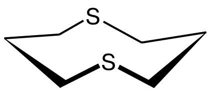
CB



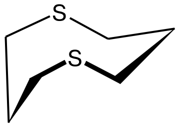
BB

Confor-mation	Symmetry	$-E_{\text{tot}}$ /hartree	E /kcal mol^{-1}
CB	C_s	1029.5744936	0
BB	C_{2v}	1029.5721862	1.45
CC	C_{2v}	1029.5706471	2.41

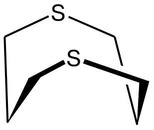
An X-ray diffraction study[17] of a salt of dication **2d** with trifluoromethanesulfonate anions showed that the eight-membered ring of the dication in the crystal adopts a distorted chair—chair conformation, **CC**, the *cis*-fused five-membered rings being in envelope conformation and the disulfonium moiety having the *sp* conformation. According to calculations of conformers of a neutral 1,5-dithiocane molecule, corresponding to the minimum-energy conformers of the dication, their stabilities change in the order **CC** > **CB** > **BB**.[19]



CC



CB



BB

Conformation	Symmetry	$-E_{tot}$ /hartree	E /kcal mol^{-1}
CC	C_{2v}	1030.2381761	0
CB	C_s	1030.2360209	1.35
BB	C_{2v}	1030.2251373	8.18

Such a pattern of stability changes is probably due to a change in the character of transannular interaction between the sulfur atoms from repulsion between the lone electron pairs (LEP) in neutral molecules to the formation of a rather strong chemical bond in dications. The bond lengths and the carbon—sulfur and sulfur—sulfur interatomic distances in the structures optimized are listed in Table 1. The results obtained in this work for **2d** are in good agreement with the data of X-ray diffraction study.[17]

The interaction diagram between the LEP orbitals of two sulfide sulfur atoms is shown in Fig. 2. Three cases (**A**, **B**, and **C**) corresponding to successive increase in the orbital perturbation were considered. The case of weak interaction was analyzed earlier taking a neutral compound **1d** and its radical cation as examples.[20] In all cases the p$^-$ orbital has the highest energy. In the case **A** the next is the p$^+$ orbital. As the perturbation strength grows, the energy of the n$^-$ orbital becomes higher than that of the p$^+$-orbital. If we deal with two-electron oxidation, six electrons occupy three out of the four perturbed orbitals, thus providing chemical bonding between two S atoms. The p$^-$ orbital becomes the LUMO, the p$^+$ orbital being responsible for the bonding between sulfur atoms in the structure of the newly formed dication.

Table 1. Bond lengths and interatomic distances (d/Å) calculated by the MP2/6-31G* method

Structure	d(S—S)	d(C—S)		d(C—C)	
		I[a]	II[b]	I[a]	II[b]
1a	—	1.807	—	—	—
1b	3.122	1.811	—	1.552	—
1c	3.319	1.807	1.816	1.551	1.525
1d	3.677	—	1.819	—	1.525
2a (*ap*)	2.164	1.813	—	—	—
2a (*g*)	2.153	1.808	—	—	—
2a (*sp*)	2.207	1.810	—	—	—
2a (*p*)	2.095	1.844	—	—	—
2b	2.184	1.859	—	1.540	—
2c	2.169	1.862	1.842	1.540	1.529
2d	2.171	—	1.841	—	1.528
3b	3.137	1.816	—	1.543	—
3c	3.312	1.815 1.812	1.830	1.545 1.540	1.520
3d	3.557	—	1.834	—	1.520

[a] For four-membered rings.

[b] For five-membered rings.

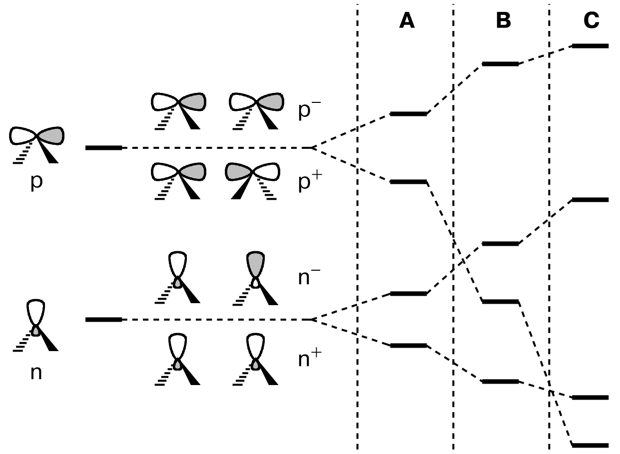


Fig. 2. Interaction diagram between the LEP orbitals of sulfur atoms.

We analyzed the MOs of the lowest-energy conformers of bicyclic S—S dications **2b—d** and of the corresponding conformations of both neutral rings **1b—d** and cations **3b—d** with nonbonded cationic centers.

Figure 3 presents the correlation diagram of the frontier MO energy levels obtained for the conformations of neutral cyclic sulfides **1b—d** corresponding to the dication structures. The diagram pattern corresponds to the case of weak interaction (case **A**). The orbital perturbation is primarily due to the transannular interaction between sulfur

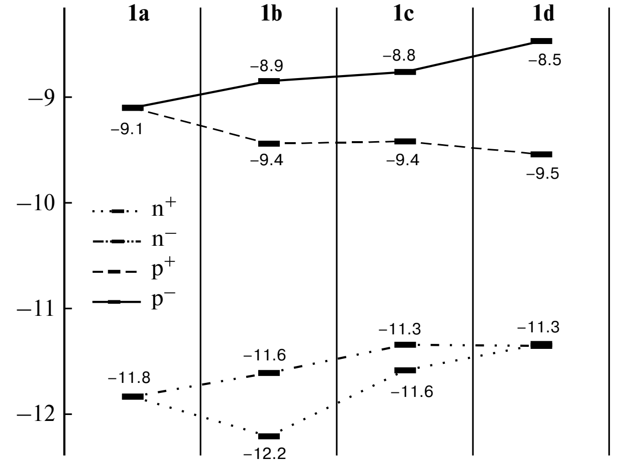


Fig. 3. Correlation diagram of the frontier MO energy levels of sulfides **1a—d**.

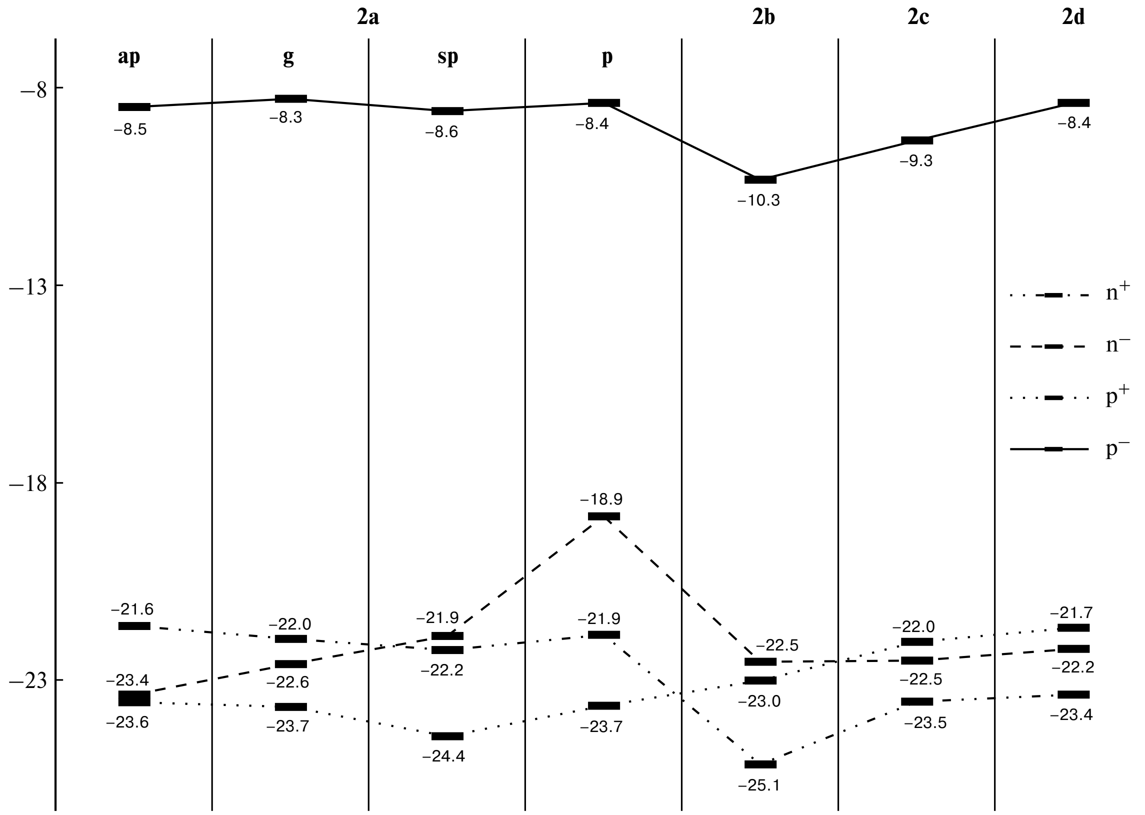


Fig. 4. Correlation diagram of the frontier MO energy levels of S—S dications.

atoms, which is maximum for the n orbitals in the "boat" conformation of 1,4-dithiane (**1a**) and for the p-orbitals in the boat—boat conformation of **1d**. In the latter case the high HOMO energy level (−8.5 eV) of the stable conformation of the neutral compound provides an explanation for a ready oxidizability of **1d**.

A correlation diagram of the frontier MO energy levels of the dications studied is shown in Fig. 4. Angular strain in the *sp*-conformation of tetramethyldisulfonium dication **2a** and in 1,4-dithioniabicyclo[2.2.0]hexane **2b** manifests itself as a substantial increase in the energy difference between the n^- and n^+ orbitals. The pattern of the orbital energy levels corresponds to the case **B** in Fig. 2. The orbital patterns for the less strained systems correspond to the case **C** (**3b**) or A (**2a**, *ap*). The energy gain due to addition of these dications to alkenes is small due to the increase in the energy difference between the interacting orbitals; this is responsible for weakening of the orbital perturbation in the formation of new S—C bonds.[21]

The calculated LUMO energy levels of the dications correlate with their electrophilic reactivities. Among the bicyclic dications studied, only 1,4-dithioniabicyclo[2.2.0]hexane (**2b**) (E_{LUMO} = −10.3 eV) reacts with alkenes, whereas 1,4-dithioniabicyclo[3.2.0]heptane (**2c**) and 1,5-dithioniabicyclo[3.3.0]octane (**2d**), which have higher LUMO energies (E_{LUMO} = −9.3 and −8.4 eV, respectively), do not react with these compounds.[22] The E_{LUMO} levels of all the conformations of acyclic dication **2a** studied in this work lie between −8.6 and −8.3 eV. Probably, the high reactivity of **2a** is due to weakening of the S—S bond as a result of noncompensated van der Waals repulsion between Me groups, which can be illustrated by an increased S—S bond length as compared to the cyclic dications.

Figure 5 presents a correlation diagram of the frontier MO energy levels for the reaction between S—S dication and ethylene. The reaction products **3b**—**d** of bicyclic S—S dications with ethylene contain no covalent bond between sulfur atoms. The corresponding correlation diagram is given in Fig. 6. The diagram pattern shows that mutual influence of the nonbonded sulfonium centers in these compounds remains rather strong.

The HOMOs of the cations **3b**—**d** are the in-phase combinations of the n^+ orbitals, corresponding to the (HOMO – 1) orbital of the initial dication, while the LUMO of 1,4-dithioniabicyclo[2.2.2]octane corresponds to the next in energy occupied orbital of the dication. This is due to the "through-bond" interaction between the n^+ and σ(C—C) orbitals in the *cis*-conformation of the $S^+—CH_2—CH_2—S^+$ moiety, which is similar to the interaction in 1,4-diazabicyclo[2.2.2]octane (Fig. 7).[23]

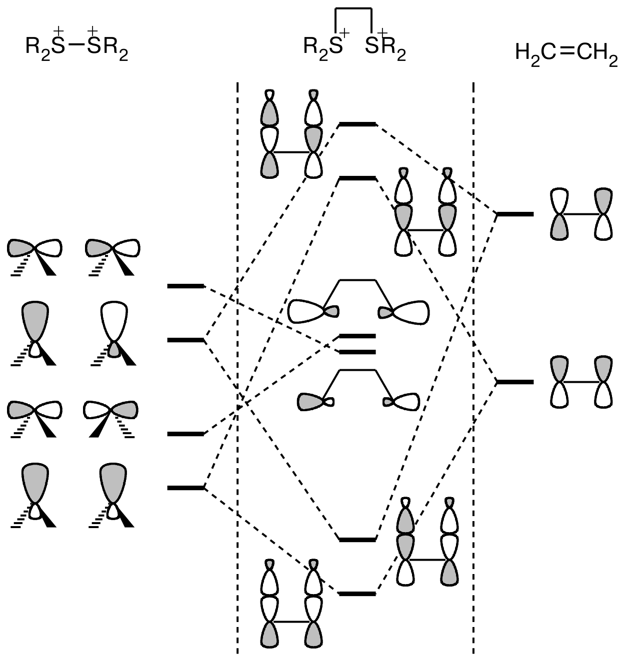


Fig. 5. Correlation diagram of the frontier MO energy levels for the interaction between S—S dication and ethylene.

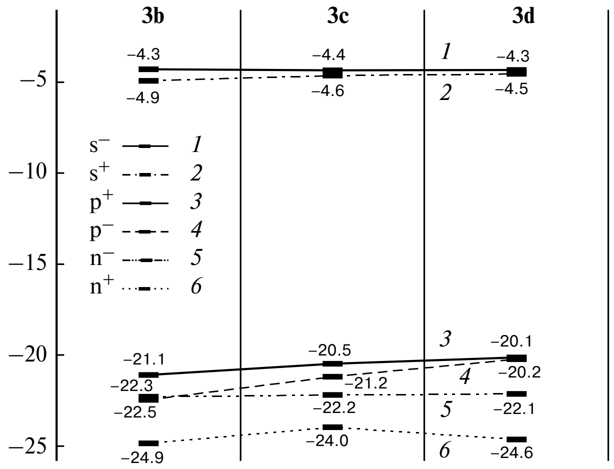


Fig. 6. Correlation diagram of the frontier orbital energy levels of reaction products **3b—d**.

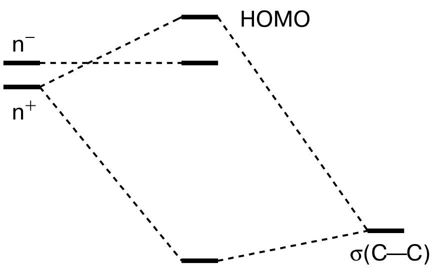
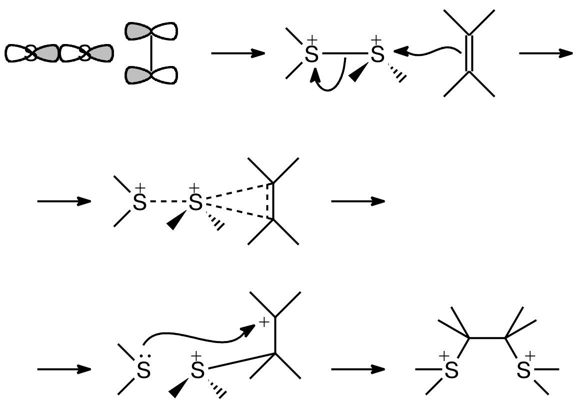


Fig. 7. "Through C—S bond" interaction in structures of dications **3b—d**.

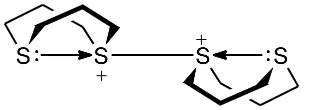
In the concerted addition reaction the S—S dications act as the six-electron components, while the alkene acts as the two-electron component (see Fig. 5). According to the Woodward—Hoffmann rules, such an addition is thermally forbidden since the number of the (4*n* + 2)-electron and (4*n*)-electron components (2 and 0, respectively) is even.[20] Therefore, we focussed on the stepwise addition mechanism.

In the case of sidewise addition of reagents (Scheme 3) both the orbital and steric factors favor nucleophilic attack of the alkene π-system on one of the sulfur atoms of disulfonium dication. The process can be described as nucleophilic substitution at the sulfur atom, $S_{\rm N}2$(S), or as electrophilic addition to the double bond, Ad_E. We optimized the structure of the intermediate π-complex at this geometry of reagents. Calculations of the π-complex of dication **2b** with ethylene were carried out assuming retention of the symmetry plane passing through both sulfur atoms and the ethylene carbon atoms. The distances between the reaction centers in the complex (the ethylene carbon atoms and the nearest S atom of the dication) are 2.74 and 2.96 Å, while the S—S bond length in the dication increases to 2.25 Å. The reaction mechanism of S—S dication with alkene is shown in Scheme 3.

Scheme 3



It is in agreement with the results of a theoretical study of the structure of yet another S—S dication, namely, a dimer of 1,5-dithiocane radical cation (**4**).[24] The optimum structure is characterized by collinear geometry of the tetraatomic sulfur moiety bound by the four-center six-electron bond, which permits **4** to be considered as an intramolecular complex of dication and neutral sulfide.



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Thus, in this work we studied the geometry, electronic structure, and reactivity of some S—S dications and related structures by *ab initio* computational methods. According to calculations of various conformations of tetramethyldisulfonium dication, the preferred conformational process is internal rotation about the S—S bond with an activation energy of 8.0 kcal mol^{-1} rather than inversion of the sulfonium S atom with a potential barrier estimated at 32 kcal mol^{-1}. The concerted addition mechanism of disulfonium dications to alkenes involves a thermally forbidden transition state. The reaction most likely proceeds by the mechanism of electrophilic addition to the C=C double bond, Ad_E.

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