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Molecular structure and thermal stability of α-halogen-*gem*-dithiols

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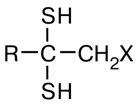
The electronic structure of α-halogen-*gem*-dithiols $RC(SH)_2CH_2X$ (R = Me, Ph; X = F, Cl, Br, I) was studied by quantum chemistry methods. Four most stable rotamers were located, differing in the mutual orientation of the thiol groups and the halogen atom. The thermodynamic and kinetic characteristics of the thermolysis of α-halogen-*gem*-dithiols were obtained. Thermolysis of chlorine- and bromine-substituted *gem*-dithiols depends on the properties of the medium, namely, in aprotic media aromatic dithiols form trithianorbornane derivatives while aliphatic dithiols form thiirane derivatives. In an aqueous medium (R = Me, Ph), water promoted elimination of hydrogen sulfide with the formation of corresponding thiones is more preferable. Thermolysis of aliphatic iodine-substituted *gem*-dithiols proceeds as bimolecular deiodination resulting in the formation of a new C—C bond.

Key words: quantum-chemical calculations, α-halogen-*gem*-dithiols, rotational isomerism, thermolysis, potential energy surface, mechanism.

Geminal dithiols[1] containing the $>C(SH)_2$ fragment are still a poorly studied class of compounds.[2] At the same time they are of considerable inrterest for fundamental synthetic and applied studies. Unlike their oxygen-containing analogs, *gem*-diols,[3] the title compounds are sufficiently stable, which permits their use as promising synthons (for, *e.g.*, the synthesis of organic semiconductors[4]).

In this work we report a quantum-chemical study of the stereoelectronic properties and potential energy surfaces (PES) of thermolysis of α-halogen-*gem*-dithiols we have synthesized recently.[5]



$$R-C(SH)_2-CH_2X$$

1, **2**

R = Me (**1**), Ph (**2**); X = F (**a**), Cl (**b**), Br (**c**), I (**d**)

Computational Procedure

Calculations were carried out by the HF/6-31G** and B3LYP/LANL2DZ methods using the GAUSSIAN-98 suite of programs.[6] Full geometry optimization of the molecular systems corresponding to the transient structures (λ[*] = 1) and energy minima ($\lambda = 0$) on the PES was conducted to a value of 10^{-5} hartree Bohr^{-1}. When analyzing flattened areas of the PES in the studies of conformationally nonrigid states, the convergence criterion was set to 10^{-6} hartree Bohr^{-1}. The structures corresponding to the energy minima were identified by moving along the gradient line from a saddle point to the neighboring critical point starting with a small displacement along the transient vector. This allowed the gradient reaction pathway to be determined correctly.

Results and Discussion

The main energy characteristics and geometric parameters of the most stable conformers of isolated molecules **1a—d** and **2a—d** are listed in Table 1 (see also Fig. 1). Four energy minima corresponding to rotamers with different mutual position of the thiol protons and the X atom were located on the PES of all systems studied. (In the text below we consider the *cis*- and *trans*-arrangement of the halogen atoms and the thiol protons relative to the substituent R.) The most stable rotamers of molecules **1a—d** are (i) rotamer **A** with *trans*-arrangement of the thiol protons and the X atom (molecules **1a—c**) and (ii) rotamer **D** with one *cis*-oriented thiol proton (molecule **1d**). Their thermal stabilities calculated without inclusion of zero-point vibrational energy correction (ZPVE) differ by at most 2 kJ mol^{-1}. When calculated with inclusion of ZPVE, the relative stability difference between the rotamers insignificantly increases (by at most 0.2 kJ mol^{-1}) for **1a—c** and nearly vanishes for **1d**. The calculated values of the dipole moments show that

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[*] λ is the number of negative eigenvalues of the Hessian matrix at a given stationary point.[7]

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Table 1. Total energies (E_{tot}/a.u.),[a] relative energies (ΔE/kJ mol^{-1}), electric dipole moments (μ/D), zero-point vibrational energies (ZPVE/a.u), and lowest harmonic frequencies (ω_i/cm^{-1}) of the rotamers **A**—**H** of molecules **1a**—**d** and **2a**—**d**

Compound	Rotamer	$-E_{tot}$	ΔE	μ	ZPVE	ω_i
1a[b]	**A**	1012.13676	0	1.75	0.10241	141
	B	1012.13426	6.6	1.66	0.10231	135
	C	1012.13250	11.2	4.05	0.10239	121
	D	1012.13600	2.0	2.36	0.10250	116
1b[b]	**A**	1372.18582	0	1.58	0.10066	124
	B	1372.18361	5.8	1.76	0.10040	111
	C	1372.18176	11.1	4.16	0.10066	106
	D	1372.18529	1.4	2.56	0.10075	107
1c[b]	**A**	3482.59514	0	1.68	0.09982	111
	B	3482.59318	5.1	1.71	0.09972	108
	C	3482.59119	10.4	4.06	0.09989	97
	D	3482.59464	1.3	2.53	0.09996	98
1d[c]	**A**	150.07910	0.4	1.57	0.09142	93
	B	150.07835	2.4	1.54	0.09134	88
	C	150.07483	11.6	3.93	0.09136	78
	D	150.07926	0	2.19	0.09167	83
2a[b]	**E**	1202.64318	0	1.91	0.15959	51
	F	1202.64121	5.2	1.33	0.15950	53
	G	1202.63782	14.1	4.53	0.15937	43
	H	1202.64176	3.7	2.88	0.15948	46
2b[b]	**E**	1562.69090	0	1.94	0.15778	53
	F	1562.68805	7.5	1.53	0.15746	46
	G	1562.68580	13.4	4.66	0.15746	44
	H	1562.68840	6.6	3.13	0.15756	20
2c[b]	**E**	3673.10028	0	1.92	0.15688	52
	F	3673.09825	5.3	1.43	0.15673	44
	G	3673.09549	12.6	4.54	0.15671	42
	H	3673.09894	3.5	3.12	0.15680	32
2d[c]	**E**	341.77672	0.1	1.52	0.14476	47
	F	341.77549	3.4	1.27	0.14473	37
	G	341.77330	9.1	4.31	0.14481	44
	H	341.77677	0	3.13	0.14472	26

[a] 1 a.u. = 2622.9897 kJ mol^{-1}.

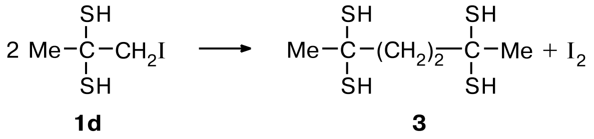
[b] Obtained from HF/6-31G** calculations.

[c] Obtained from B3LYP/LANL2DZ calculations.

rotamer **D** is more polar than rotamer **A** (see Table 1); this must lead to an increase in the fraction of the **D** conformation in polar solvents. With any X, rotamer **C** with *cis*-oriented thiol protons and the largest dipole moment is the least stable. Rotamer **B** is intermediate in the relative stability; structurally, it differs from other rotamers in that the halogen atom deviates from the plane formed by the atoms of the carbon skeleton of the molecule (see Fig. 1) by 55°—65° (the angle of deviation increases with an increase in the atomic number of halogen). Replacement of the substituent, Me→Ph, leads to some changes in the structural parameters and energy characteristics of the rotamers of molecules **2a**—**c** compared to the corresponding rotamers of molecules **1a**—**c**. The most stable are rotamers **E**. Their thermal stabilities calculated relative to the nearest rotamer **H** increase to 3.5—6.5 kJ mol^{-1} (see Table 1). The **E** and **H** rotamers of molecule **2d** are characterized by nearly identical relative stabilities. The main structural difference between the molecules **1a**—**d** and **2a**—**d** is a shorter (by 0.01 Å on the average) C—S bond in the first group of molecules. This can be a reason for different thermal stabilities of these molecules (see below). The activation energy for interconversions of the rotamers **A**—**D** and **E**—**H** lies between 19.5 and 28.3 kJ mol^{-1}, which suggests that the rotamers in question can be spectroscopically discernible.

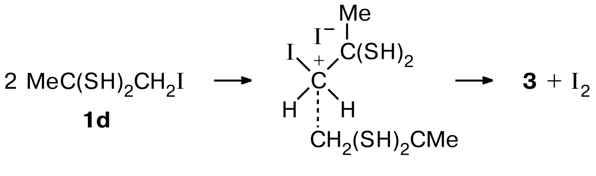
Unlike other compounds under study, 1-iodo-2,2-propanedithiol (**1d**) is unstable and undergoes a nearly instantaneous dimerization to give hexane-2,2,5,5-tetrathiol (**3**) and elemental iodine (Scheme 1).

Scheme 1

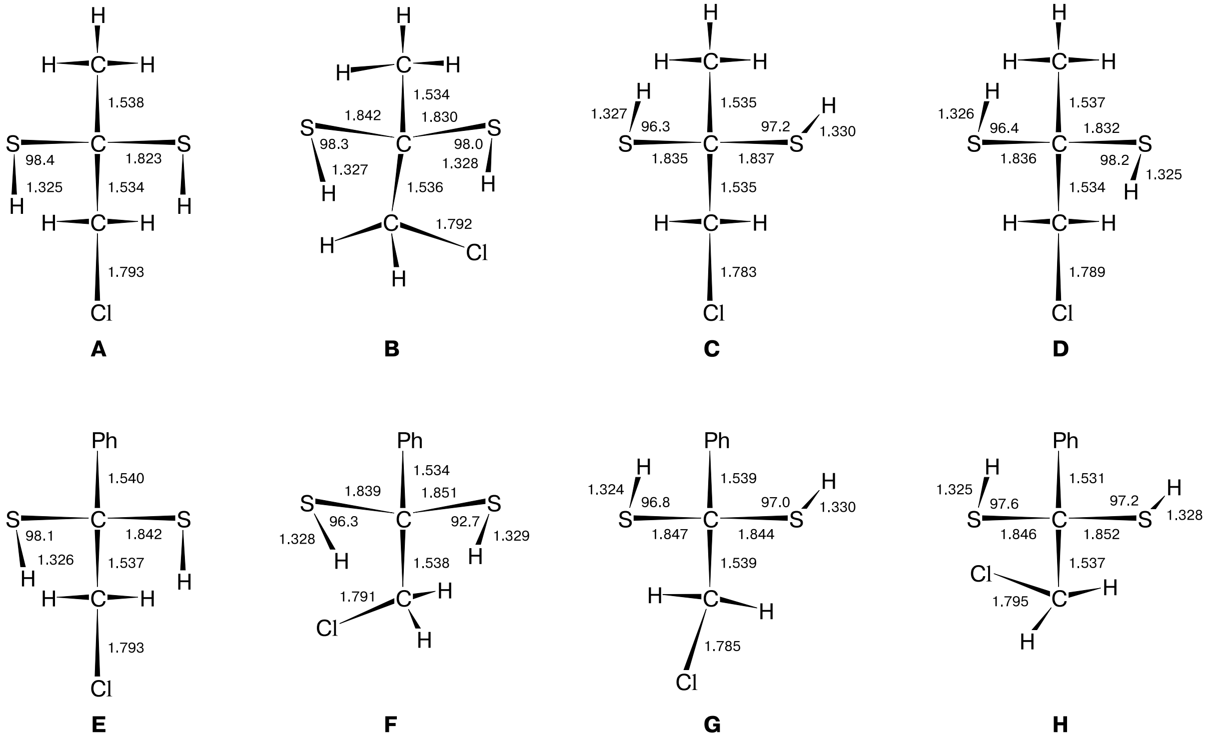


To establish the thermodynamic and kinetic reasons that favor a bimolecular reaction of deiodination of *gem*-dithiol **1d** (see Scheme 1) and preclude analogous reactions of compounds **1a**—**c**, we studied the PES of the dimerization reaction of compound **1d** and considered the mechanisms of formation of dimer **3**. The pre-reaction bimolecular complex **1d** + **1d** (Fig. 2) is 6.4 kJ mol^{-1} more stable than the noninteracting reagents. The enthalpy of the reaction (1) estimated as the total energy difference between the initial reagents and reaction products is 14.1 kJ mol^{-1}. Deiodination can proceed by two mechanisms. The first mechanism (Scheme 2) involves dissociation of a C—I bond and formation of an ion pair followed by its S_N2-transformation in which the anion I$^-$ acts as nucleophile.

Scheme 2



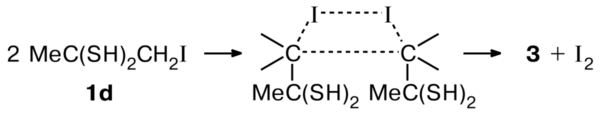
The second mechanism (Scheme 3) implies a tighter interaction of neutral fragments of the associate with the formation of a four-center transition state (TS) followed by elimination of elemental iodine and formation of a new C—C bond.



Angle	ω/deg							
	A	**B**	**C**	**D**	**E**	**F**	**G**	**H**
C—C—C—Cl	179.0	59.5	176.8	179.3	179.0	65.9	178.8	63.9
Ph—C—C	—	—	—	—	0.0	175.5	169.6	167.4

Fig. 1. Main structural parameters of the most stable rotamers of α-halogen-*gem*-dithiols predicted by the HF/6-31G** method. Listed are the data for $MeC(SH)_2CH_2Cl$ (**1b**) and $PhC(SH)_2CH_2Cl$ (**2b**). Here and in Figs. 2—7 the bond lengths are given in Å and the bond angles are given in degrees.

Scheme 3



According to calculations, the second reaction mechanism is kinetically more preferable than the first one. The activation energy for mechanism 2 (131.4 kJ mol^{-1}) is much lower than the experimental C—I bond dissociation energy (192.3 kJ mol^{-1}).[8] In this case the main component of the reaction coordinate (see Scheme 3) is the I—I contact. At r(I—I) ≈ 3.0 Å, dissociation of the C—I bonds and the interaction between the "releasing" carbon p-orbitals begin, resulting in the formation of a new C—C bond (see Fig. 2). The calculated dipole moment values point to substantial increase in the degree of charge separation in the transition state, from 2.29 to 7.14 D (Table 2). This indicates a possible decrease of the activation barrier in polar solvents. The first reaction mechanism (see Scheme 2) is characterized by a much higher activation barrier of 217.6 kJ mol^{-1}; probably, that is why it cannot be realized. Analogous reactions of compounds **1a—c** are impossible for thermodynamic reasons. Associates of molecules **1a—c** are more stable than products of the reaction **3** + X_2 (X = Br, Cl, F) by 4.33, 9.56, and 17.8 kJ mol^{-1}, respectively.

Thermal transformation of *gem*-dithiols **1b,c** and **2b,c** (these compounds are stable at low temperatures) begin as the temperature increases to room temperature. The composition of thermolysis products is determined by the presence or the absence of trace amounts of water. In the presence of water dithiols **1b,c** and **2b,c** eliminate hydrogen sulfide and undergo a transformation into thiones[5] (Scheme 4).

Scheme 4

$$R—C(SH_2)CH_2X + H_2O \longrightarrow$$

$$\longrightarrow R—C(=S)CH_2X + H_2O + H_2S$$

R = Me, Ph; X = Cl, Br

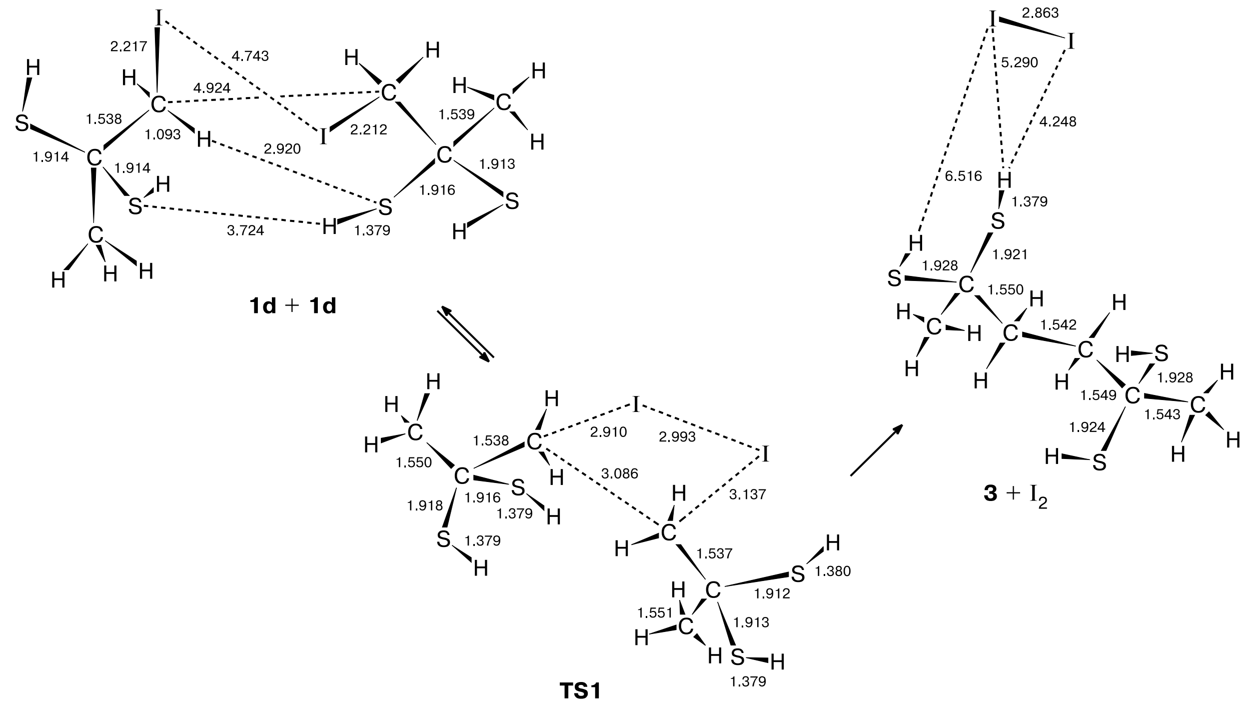
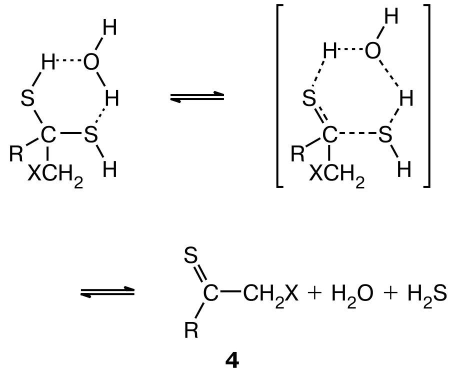


Fig. 2. B3LYP/LANL2DZ calculated structures and geometric parameters of the pre-reaction bimolecular complex **1d** + **1d**, reaction products **3** + I_2, and the corresponding transition state **TS1**.

Experimental data suggest that water molecules are involved in the reaction as mediators only. The reaction requires a concerted intermolecular proton transfer (Scheme 5).

Scheme 5

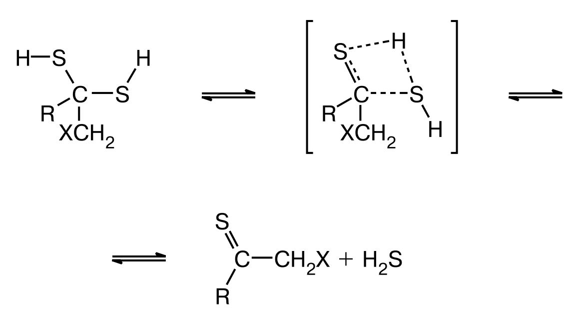


4

R = Me, Ph; X = Cl, Br

Experimental data[2] showed that direct elimination reaction promoted by intramolecular autoprotonation (Scheme 6) does not occur likely due to a higher activation barrier, which is related to symmetry forbiddenness on superficial 1,3-prototropic shifts.[9]

Scheme 6



4

R = Me, Ph; X = Cl, Br

Analysis of the PES of these two reactions (see Schemes 5 and 6) was carried out taking *gem*-dithiol **1b** as an example. Formation of the pre-reaction bimolecular complex **1b** + H_2O (see Table 2, Fig. 3) is energetically favorable. The thermal balance of the complexation reaction is 19.3 kJ mol^{-1}. The heat of the elimination reaction estimated as the total energy difference between the pre-reaction complex and the reaction product (see Table 2) is 18.1 kJ mol^{-1}. The activation energy for intermolecular prototropic shift and H_2S elimination is 241.7 kJ mol^{-1}. The calculated value of the dipole moment (4.54 D, see Table 2) indicates an appreciable increase in the degree of charge separation in the transition state. Autoprotonation of **1b** and elimination of H_2S are characterized by a much higher activation barrier of 376.1 kJ mol^{-1}. Our study of the PES regions of similar reactions of *gem*-dithiols **1a**

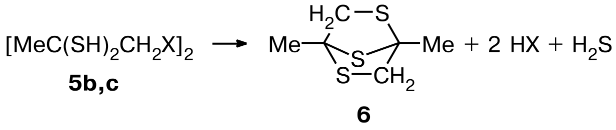
Table 2. Total energies (E_{tot}/a.e.), relative energies (ΔE/kJ mol^{-1}), electric dipole moments (μ/D), zero-point vibrational energies (ZPVE/a.u.), and the lowest harmonic frequencies (ω_i/cm^{-1}) of the critical points on the PES of deiodination reaction (see Scheme 1), obtained from B3LYP/LANL2DZ calculations and of the reactions shown in Schemes 4—11 according to HF/6-31G** calculations

Structure	$-E_{\text{tot}}$	ΔE	μ	ZPVE	ω_i
1d + **1d**	300.16096	14.1	2.29	0.18307	5
TS1	300.11088	145.5	7.14	0.18186	i276
3 + I_2	300.16634	0	0.12	0.18280	17
1b + H_2O	1448.21626	18.1	2.78	0.12647	53
TS2	1448.12410	259.8	4.54	0.12531	i744
4 + H_2O + + H_2S	1448.22317	0	1.36	0.12493	184
H_2O	76.02361	—	2.15	0.02320	1769
H_2S	398.67503	—	1.39	0.01627	1341
trans-**5b**	2744.37508	52.5	0.07	0.20146	11
cis-**5b**	2744.37543	51.6	1.39	0.20175	9
TS3	2744.25923	356.4	2.87	0.20218	i476
cis-**7b** + + 2 HCl	2744.38429	28.4	6.70	0.19852	10
trans-**7b** + + 2 HCl	2744.38957	14.5	0.58	0.19893	9
TS4	2744.28173	297.4	4.23	0.20431	i1342
8 + HCl	2744.37690	47.8	3.42	0.20097	11
TS5	2744.28987	276.0	3.87	0.20384	i846
TS6	2744.30580	234.3	11.38	0.20464	i1637
6 + 2 HCl + + H_2S	2744.39511	0	2.00	0.19840	13
4b	973.49697	—	2.02	0.07887	53
1b + **4b**	2345.68591	83.0	3.10	0.17920	16
TS7	2345.59487	321.8	4.97	0.17864	i978
9	2345.68987	72.6	2.65	0.17935	14
11	2345.70928	21.7	3.85	0.18100	15
6 + 2HCl	2345.71757	0	1.57	0.17949	12
2b + HCl	2022.75917	0	2.58	0.16563	2
TS8	2022.67553	219.4	15.61	0.16218	i820
12 + 2 HCl	2022.75357	14.7	2.89	0.16258	10
TS9	2022.68452	195.8	3.92	0.16193	i201
13 + 2 HCl + + H_2S	2022.69892	158.0	4.04	0.15531	12

and **1c** showed that elimination of hydrogen sulfide (see Scheme 5) is virtually independent of the halogen atom and has an activation barrier similar to that of **1b**, namely, 371.9 kJ mol^{-1} for **1a** and 378.4 kJ mol^{-1} for **1c**. In the reaction shown in Scheme 4 the effect of the halogen atom is more pronounced, *viz.*, the activation barriers are 197.5 (**1c**) and 263.4 kJ mol^{-1} (**1a**). A study of the same reactions involving *gem*-dithiols **2a—c** showed that replacement of the Me substituent by Ph has no effect on both the heats of formation of the pre-reaction complexes and the enthalpies of reactions (with an accuracy of 4 kJ mol^{-1}). The barriers to the reactions differ appreciably, being equal to 251.1 (**2a**), 226.3 (**2b**), and 180.2 kJ mol^{-1} (**2c**). They are 12—18 kJ mol^{-1} lower than the barriers to the reactions involving molecules **1a—c**, which is probably due to weaker C—S bonds in dithiols **2a—c** compared to **1a—c** (see Fig. 1). Thus, our calculations showed that the probability for thionic forms of *gem*-dithiols to be formed in the presence of water increases as follows: **1a** < **2a** < **1b** < **2b** < **1c** < **2c**.

In aprotic media, an increase in temperature "switches on" other reaction channels, the corresponding reaction mechanisms being fundamentally dependent on the character of the substituent R. For instance, thermolysis of compounds **1b** and **1c** probably involves the formation of dimers **5b** or **5c** followed by elimination of two hydrogen halide molecules and one hydrogen sulfide molecule and results in 1,4-dimethyl-2,5,7-trithianorbornane (**6**) (Scheme 7), which is not observed in the case of *gem*-dithiols **2b,c**.

Scheme 7



X = Cl (**b**), Br (**c**)

The bimolecular pre-reaction complex **5** is mainly stabilized through intermolecular interaction between the thiol protons and the halogen atoms (Fig. 4). According to calculations, two most stable types of coordination are possible in the complex, with the *cis*- and *trans*-arrangement of the nonbonded SH fragments. Elimination of two hydrogen halide molecules from the complexes *cis*-**5b,c** and *trans*-**5b,c** results in the *cis*-SH-substituted (*cis*-**7**) and *trans*-SH-substituted (*trans*-**7**) six-membered heterocycles, respectively (Scheme 8).

As above, a complete analysis of the PESs of the reactions (1) and (2) (see Scheme 8) was carried out taking compound **1b** as an example. The pre-reaction bimolecular complexes *cis*-**5b** and *trans*-**5b** are respectively 9.9 and 9.0 kJ mol^{-1} more stable than the noninteracting fragments (see Tables 1 and 2 and Fig. 4), which points to somewhat more preferred formation of the complex *cis*-**5b**. We considered two mechanisms of closure of the six-membered heterocycle, namely, a concerted elimination of two HCl molecules and a stepwise elimination of HCl. In the former case the major contribution to the reaction coordinate comes from the H—Cl atom—atom contacts. The transition state **TS3** formed at r(H—Cl) ≈ 1.7 Å includes two four-center molecular fragments (see Fig. 4). The activation energy for this process involving *cis*-**5b** (*trans*-**5b**) is 304.8 (297.7) kJ mol^{-1}. The heats of reactions (see Scheme 8) are 23.2 for reaction (1) and 38.0 kJ mol^{-1} for reaction (2) and point to a more probable formation of the six-membered heterocycle *trans*-**7b**.

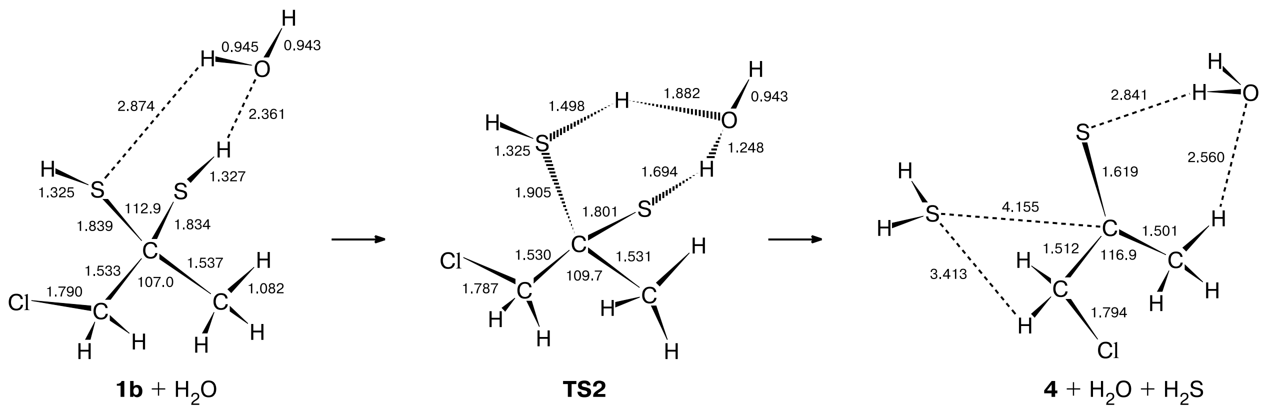
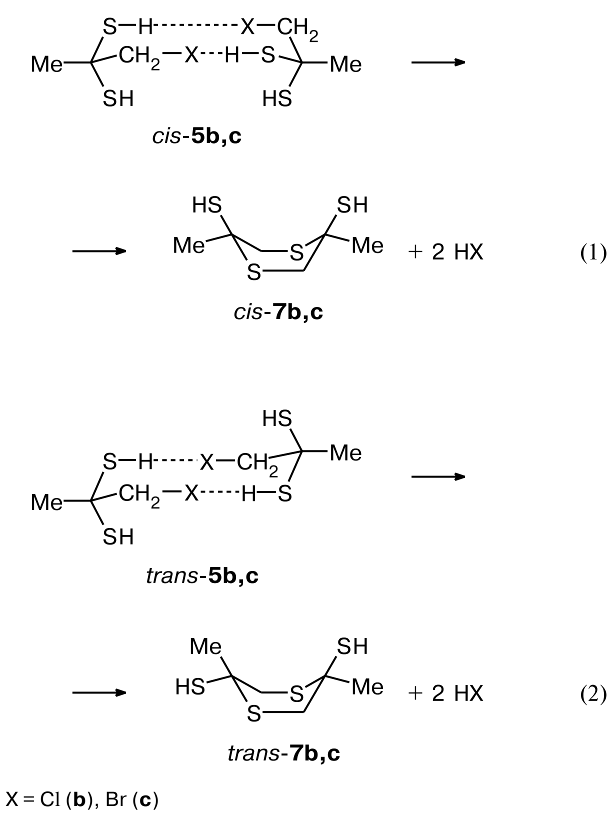


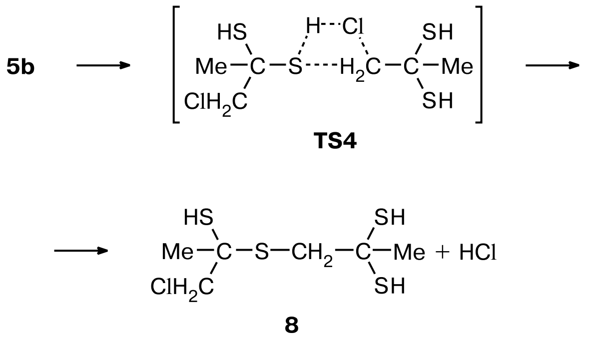
Fig. 3. HF/6-31G** calculated main structural parameters of associate **1b** + H_2O, transition state **TS2**, and products **4** + H_2O + H_2S of the reaction of H_2S elimination.

Scheme 8



Elimination of hydrogen sulfide and the formation of trithianorbornane structure in this case is hardly probable. Experimental results[10] suggest the possibility of formation of not only the norbornane structures but also small amounts of compounds of the type *trans*-**7b** (see Scheme 8, reaction (2)). This probably indicates that concerted HCl elimination is not the main reaction channel. Stepwise elimination results in an intermediate **8** (see Fig. 4), which was not experimentally detected so far, probably, owing to its high reactivity. The activation barrier to the elimination of hydrogen halide by the mechanism shown in Scheme 9 (244.9 for *trans*-**5b** and 245.8 kJ mol^{-1} for *cis*-**5b**) is appreciably lower than the barriers to the reactions shown in Scheme 8.

Scheme 9



Noteworthy is that intermediate **8** is stabilized as the exclusive rotamer irrespective of the *cis*- or *trans*-configuration of the starting complex **5b**. Then, the associate **8** + HCl goes along the gradient line and passes through a saddle point corresponding to the transition state **TS5** (see Fig. 4) with an activation energy of 228.2 kJ mol^{-1} to *cis*-**7b** + 2 HCl. The ratios of the kinetic characteristics of the concerted and stepwise reactions seem to provide an explanation for the absence of a high yield of *trans*-substituted six-membered heterocycles and for difficulties in the experimental stabilization and identification of compounds of the type **8** in the thermolysis reactions (see Scheme 7).

Analysis of the PES of thermolysis of the associate *cis*-**7b** + 2 HCl (see Fig. 5) revealed the possibility of formation of a trithianorbornane structure involving the transition state **TS6** owing to the presence of the mediator molecule (eliminated hydrogen halide).

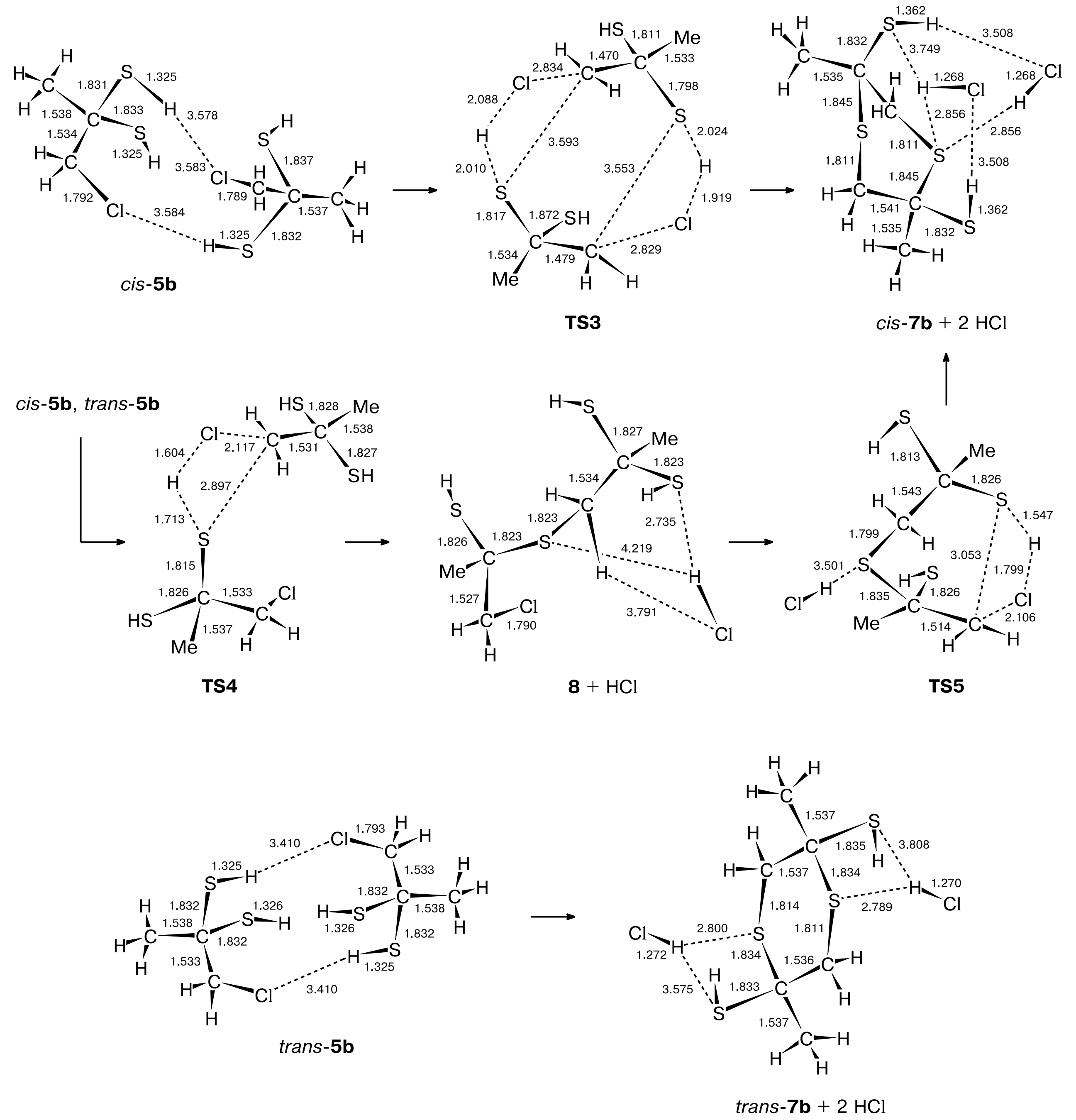


Fig. 4. Molecular structures corresponding to the critical points on the potential energy surface of bimolecular reaction of molecules **5b** and formation of a six-membered heterocycle obtained from HF/6-31G** calculations.

The activation energy for this reaction (205.9 kJ mol^{-1}) is much lower than the barrier to the limiting stage of the stepwise reaction (see Scheme 8). This is also an indirect reason for the low yield of product **8**.

A comparative analysis of the activation parameters of the limiting stages of the reactions in which compounds **6** and **4** are formed (see Table 2) provides an explanation for the absence of the former compound in aqueous solutions of *gem*-dithiols on heating.

Similar trithianorbornane structures were also obtained in the reactions of *gem*-dithiols **1b,c** with alkylthiones **4b,c**.[2] Analysis of the PES of these reactions suggests the following reaction mechanism (Scheme 10).

The reactions shown in Schemes 9 and 10 begin with analogous stages. In the latter case these are the formation of the pre-reaction bimolecular complex **1b** + **4b** (Fig. 6) followed by elimination of hydrogen halide. The heat of formation of the complex, calculated relative to

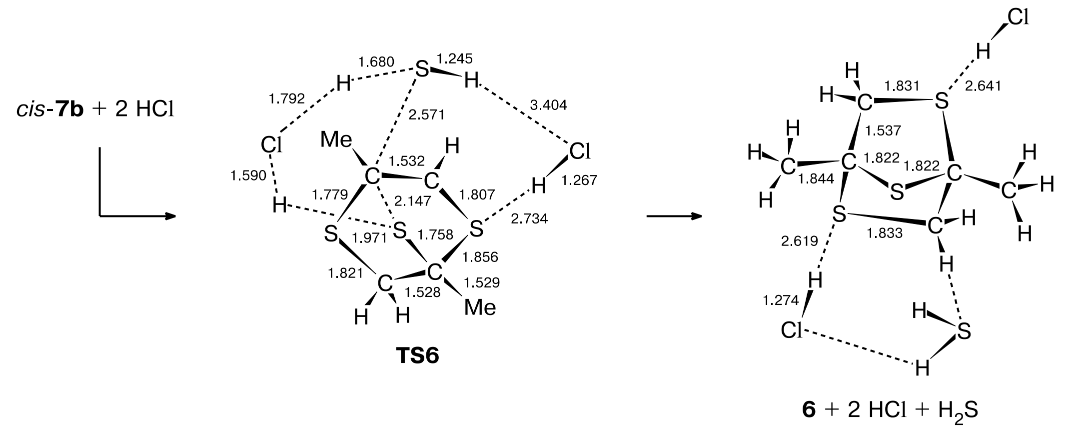
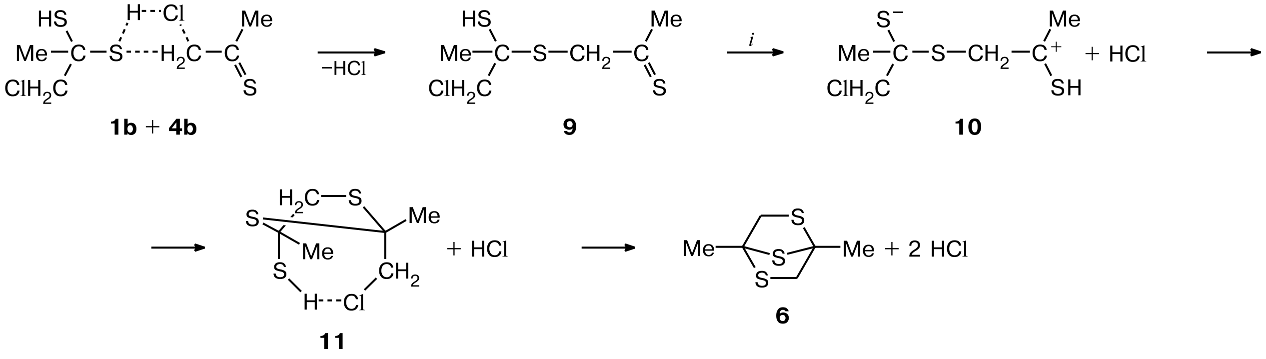


Fig. 5. HF/6-31G** calculated transition-state geometry of **TS6** obtained in the course of formation of 1,4-dimethyl-2,5,7-trithianorbornane (**6**).

Scheme 10



i. 1,6-Proton shift.

the noninteracting reagents is 8.2 kJ mol^{-1} (see Tables 1 and 2), the activation energy for the formation of molecule **9** *via* the transition state **TS7** is 238.8 kJ mol^{-1} (see Table 2), and the enthalpy of reaction **1b** + **4b** → **9** is 10.3 kJ mol^{-1}. Thermolysis of intermediate **9** can lead to elimination of hydrogen halide and formation of a heterocycle. An analysis of the corresponding PES showed that the optimum reaction mechanism involves a 1,6-prototropic shift promoted by the hydrogen halide molecule (analogously to Scheme 9) and the formation of a bipolar intermediate **10**, which undergoes an almost barrierless (E_a = 1.1 kJ mol^{-1}) transformation into associate **11**. The activation energy for the prototropic rearrangement is 185.2 kJ mol^{-1}. Hydrogen halide also plays a key role in the next reaction stage, **10** → **11** (see Fig. 6). The activation energy for this stage is 219.8 kJ mol^{-1} and the enthalpy of reaction is 21.7 kJ mol^{-1}. The total thermal balance of the reaction (see Scheme 10) is 83.0 kJ mol^{-1}.

A study of regions of the PES containing the critical points of the reactions of α-halogen-*gem*-dithiols (see Schemes 7—10) using molecule **1c** as an example suggests an appreciable decrease in the activation barriers to elimination of hydrogen bromide ($\Delta E_a \approx$ 15—25 kJ mol^{-1}). This is due to the lower energy of the C—Br bond compared to the energy of the C—Cl bond.[7] Thermolysis of fluorinated *gem*-dithiols (see Schemes 8—10) does not proceed probably due to a much higher C—F bond dissociation energy.

Analysis of the reaction (see Scheme 6) of phenyl-substituted analogs (**2b**) shows that from the thermodynamic point of view the formation of the *cis*- and *trans*-dimers similar to **5b** stabilizes the system ($\Delta H \approx$ 10 kJ mol^{-1}). However, transition **5b** → **8** causes an appreciable increase in the tansition-state energy (E_a(**TS4**) = 463.4 kJ mol^{-1}). This provides an explanation for the impossibility of formation of trithianorbornanes or heterocycles similar to compound **7** during thermolysis of phenyl-substituted *gem*-dithiols. In the absence of water, thermolysis of compound **2b** results in 2-phenyl-2-mercaptothiirane. As time passes, this compound can eliminate hydrogen sulfide and undergo a rearrangement

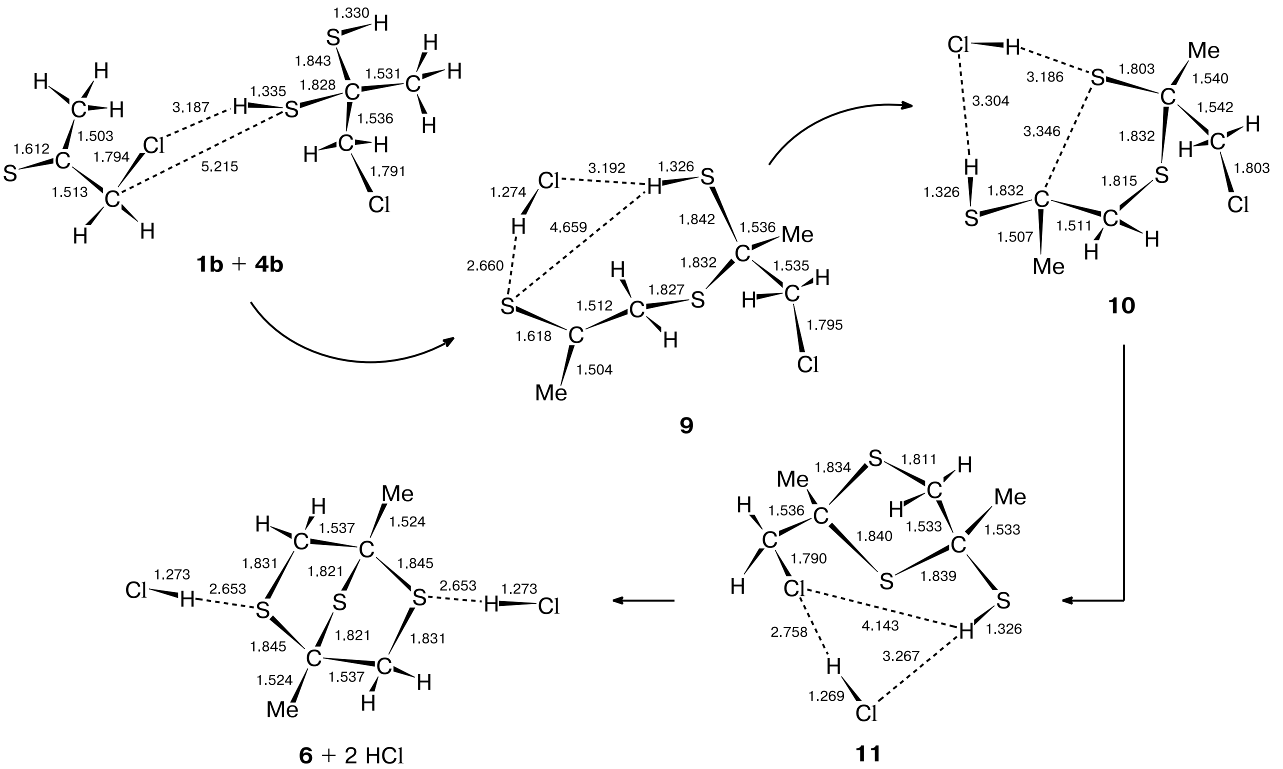
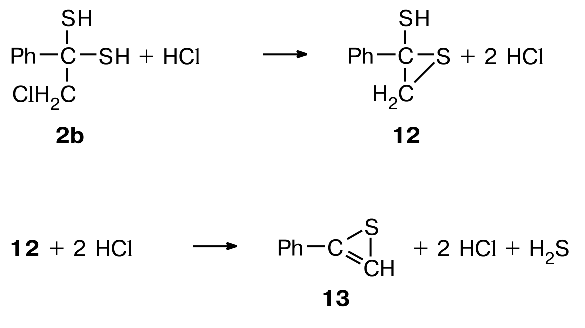


Fig. 6. Molecular structures obtained in the course of formation of 1,4-dimethyl-2,5,7-trithianorbornane in the bimolecular reaction **1b** + **4b**. Obtained from HF/6-31G** calculations.

into extremely unstable thiirene. The reaction probably proceeds as a monomolecular process, but the prototropic shift responsible for the optimum gradient reaction pathway is promoted by external molecules similarly to the eliminations of hydrogen halide or hydrogen sulfide considered above. This can cause an appreciable decrease in the barrier to the elimination reactions (see above). We studied the PESs of the reactions of thiirane and thiirene formation (Scheme 11).

Scheme 11



The energy of stabilization of complex **2b** + HCl is 5.4 kJ mol^{-1}, which is much lower than the energy of the interaction of compounds **1b** or **2b** with water. The activation energy for the reaction **2b** → **12** involving the formation of transition state **TS8** (Fig. 7, see Table 2) is 219.4 kJ mol^{-1}, being comparable with the activation energy for water-promoted H_2S elimination (see above). Probably, it is the higher strength of the pre-reaction complex in the thermolysis in aqueous solution that makes the H_2S elimination and thione formation more preferable. The reaction **2b** → **12** is endothermic (ΔH = 14.7 kJ mol^{-1}).

According to calculations, the optimum mechanism of the reaction **12** → **13** (see Scheme 11) involves two hydrogen halide molecules (ΔE_a = 181.1 kJ mol^{-1}) (see Fig. 7, Table 2). This mechanism is 54.7 kJ mol^{-1} more preferable than the channel promoted by one HCl molecule. The endothermicity of reaction **12** → **13** (143.3 kJ mol^{-1}) is much higher than that of the reaction **2b** → **12**. Analysis of the PES regions including the critical points of the reactions (see Scheme 11) taking bromine-substituted *gem*-dithiol **2c** as an example showed that if the activation barrier to the first reaction is expected to decrease by ~16 kJ mol^{-1}, the use of one or another halogen has almost no effect on the formation of thiirene.

Thus, in contrast to non-halogenated *gem*-dithiols[2,11] (here, thermolysis in aqueous solutions and in aprotic media leads to formation and subsequent oligomerization

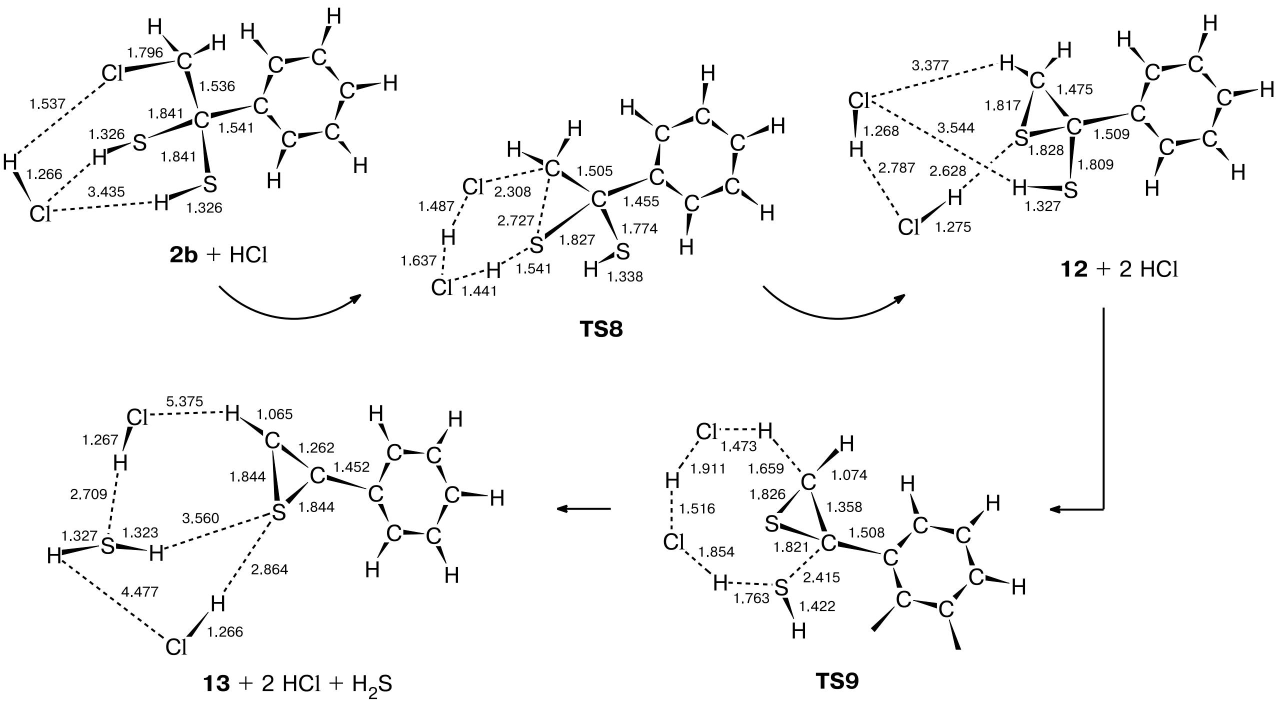


Fig. 7. Molecular structures and geometric parameters of the stationary and transition states of the reactions of thiirane and thiirene formation obtained from HF/6-31G** calculations.

of thiones), thermolysis of halogenated analogs results in rather stable monomeric products.

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