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Quantum Chemical Study of Valence Isomerization of Bis(5-thioxopenta-1,3-dien-1-yl) Sulfide in the Ground and Excited States

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Abstract—Molecular modeling methods were employed to investigate the potential energy surface in the valence isomerization of bis(5-thioxopenta-1,3-dien-1-yl) sulfide initiated by generation of thiirane and thiophene biradical structures in the lowest triplet state. The channel of the cascade formation of condensed systems containing the thiirane and polycyclobutane fragments was analyzed.

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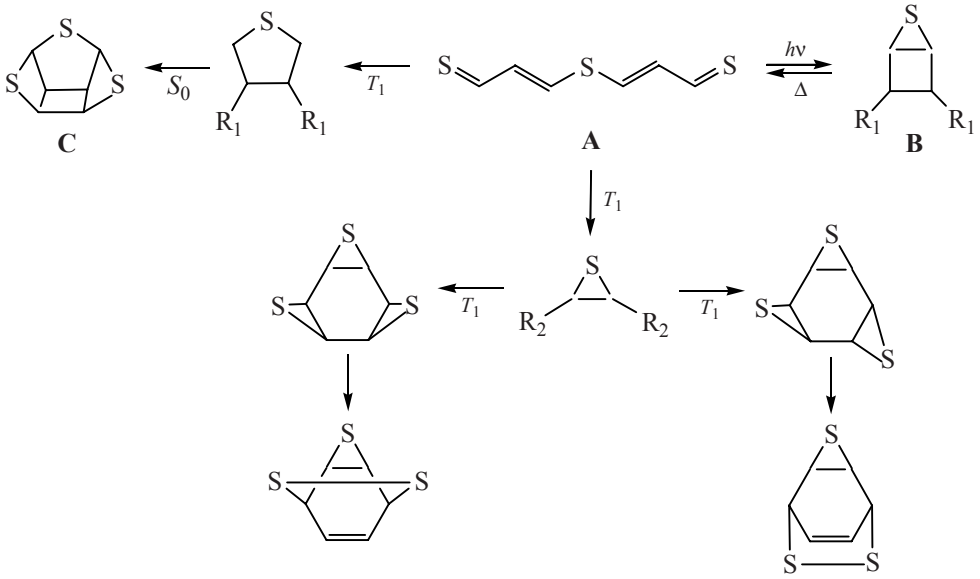
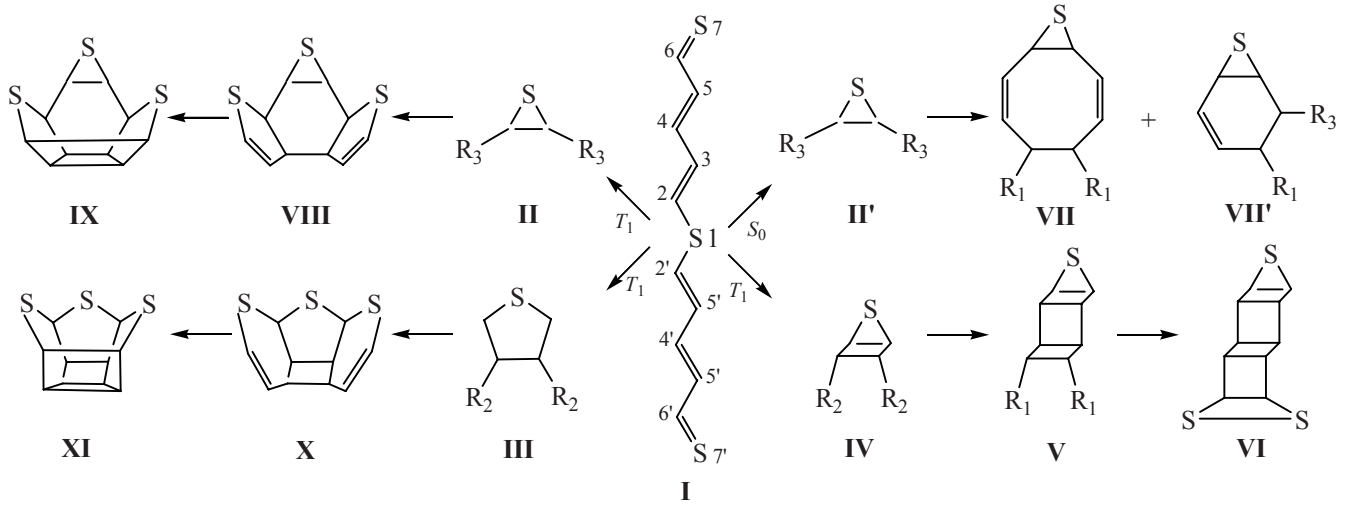
Sulfide systems are very sensitive to thermal or photochemical initiation bringing about various intramolecular rearrangements including the formation of mono- or polycyclic structures [1–6]. In a flexible (bis)thioxopentadienyl) sulfide system **I** the formation is possible of structurally light-sensitive heterocyclic compounds. For the earlier studied [7, 8] bis(thioxopropenyl) sulfide **A** a principal possibility of formation of various thiabicyclic and trithiatetracyclononane structures (with participation of the ground and low-lying excited states) of different stability in the ground and excited states was established.



The capability of acyclic compounds **A** to photoreversible and that of compounds **B** to thermoreversible transitions [1, 7] can be employed in the design of energy transformers, while the presence of a potential well formed in the cavities of some trithiatetracyclononane structures in the excited state suggests that they can be used as optical ionic traps. Symmetrical growth of the number of allyl groups in



the sulfide fragments may increase the diversity of channels of photo- and thermoinitiated valence isomerization and decrease the activation barriers of cyclization by lowering deformational constraints in critical points of the potential energy surface (PES) of rearrangements.

In the present work, using the methods of molecular modeling, the channels of valence isomerization of compound **I** initiated by generation of thiirane and thiophene biradical structures in the lowest triplet state are investigated and the channel of the cascade formation of condensed thiirane and polycyclobutane fragments is analyzed.

The calculation of molecular structures and the investigation of the gradient channels connecting them was performed by density functional theory method (DFT) with three-parametric functional B3LYP [9]. Double-exponential basis set of atomic orbitals augmented with polarization functions on all atoms was used (6-31G**). Full geometry optimization of the molecular systems was performed to the accuracy of 10^{-5} au/bohr. For analysis of flat segments of the PES the values of gradients were fixed at the level of 10^{-6} au/bohr. Stationary points were identified by analysis of the Hessian matrix. The search for and localization of transition states (TS) was performed by the method of linear synchronous transit QST2 [10]. This was used for determination of approximate structure of the TS with its subsequent refinement by the method of quadratic synchronous transit QST3. Analysis of vibration frequencies in the saddle point was performed and localization of critical points on the gradient line connecting them was proved by the method of internal reaction coordinate (IRC). Taking into account that wave functions for the $T_1(n,\pi^*)$ state in similar compounds are predominantly of a single configurational character [1–6], the critical points on the T_1-surface were analyzed by the use of UB3LYP procedure. All calculations were performed using the GAUSSIAN 98 program package [11].

Rotational isomerism of acyclic compound **I** is very versatile. Using the data of [7, 12] concerning investigation of the stationary states of rotamers in bis (thioxopropenyl) sulfide systems, we defined for structure **I** five rotational states **Ia–Ie** (Fig. 1).

One of them **Ia** is the lowest, the others, judged from their sterical characteristics, as shown by the calculations, are the most suitable for generation of thiophene and thiirane intermediates as well as for the cascade formation of thiabicyclic structures on T_1-surfaces. Rotamers (**Ia–Ie**) with respect to possible transformations on the S_0 PES lie in relatively deep potential wells. Activation barriers of interconversions of forms **Ia–Ie** exceed 23 kcal mol^{-1} that may be indicative of their stability and possible accumulation in the reaction mixture. The most deeply lying *trans*-structure (**Ia**) in the S_0-state is virtually planar. The dihedral angle C^3–C^2–$C^{2'}$–$C^{3'}$ does not exceed 4° and is due to the repulsive interactions of the 2-H and 2'-H protons. In the other rotamers this angle lies within 17°–53°. The variation of relative stability falls in the range of 17 kcal mol^{-1} (Table 1). Based on the degree of separation of the charges in structures **Ia–Ie** (judged from the values of electric dipole moment, Table 1) it is expectable that the stability of rotamers **Id, Ie** would increase on going to condensed polar media.

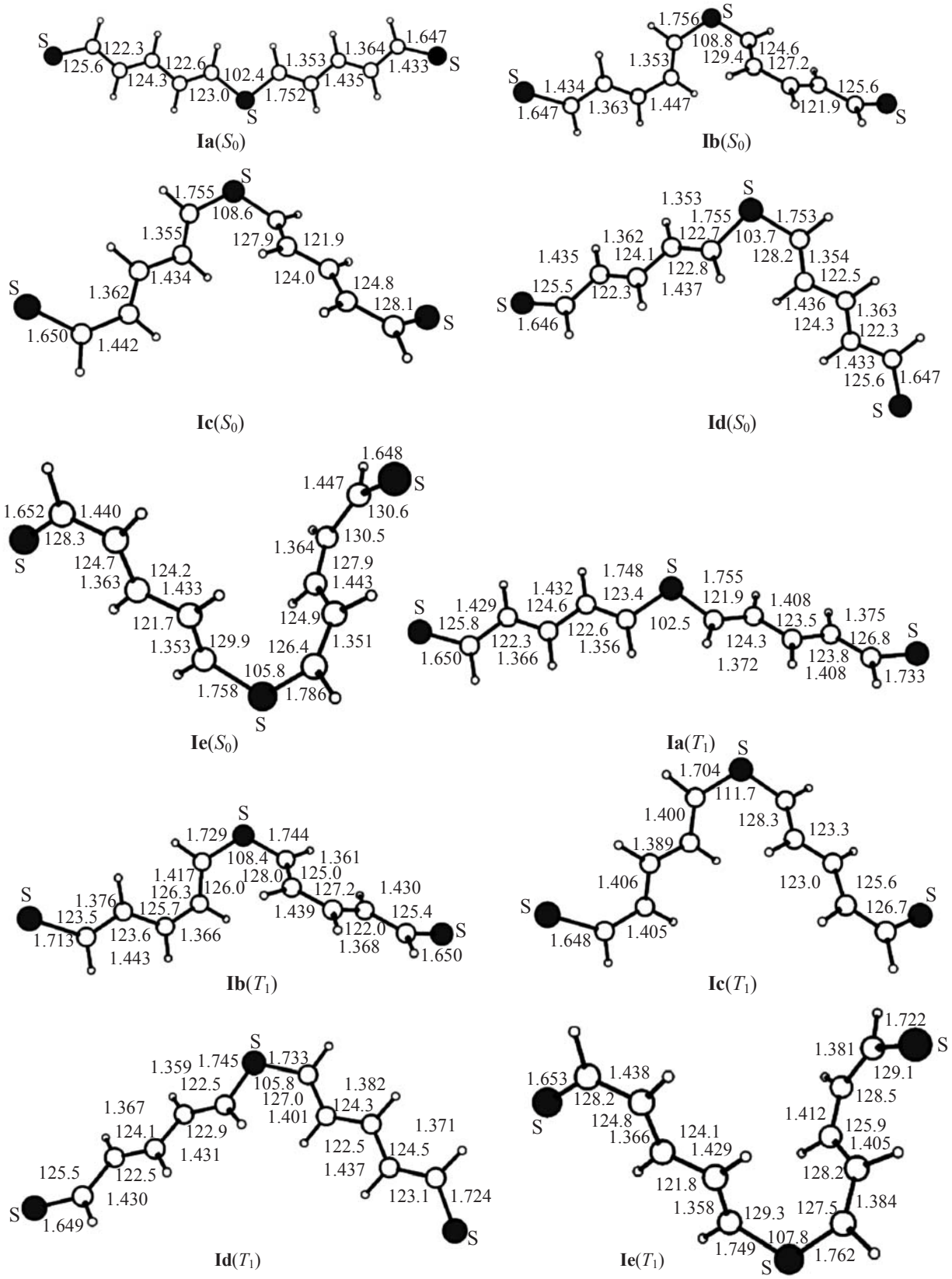


Fig. 1. Molecular structures and principal geometric characteristics of the optimized states of rotational forms **Ia–Ie** in the S_0 and T_1 states. Bond lengths are given in Å, angles in degrees.

Intermediates **II** and **III** formed on the T_1-surface upon diabatic transition into the S_0-state are incapable of concerted cycloaddition reactions with the formation of heterocycles **VIII** and **X**. The thiophene intermediate **III**, in spite of its relatively high stability in the groumd state (the depth of the potential well from the side of transition to the acyclic form is 17.03 kcal mol^{-1}), in an attempt to localize the gradient channel of transition into structure **X** falls down either to the acyclic **I** or thiabicyclic **IV** state {in bis-(thioxopropenyl) sulfide **A**; as shown in [8], asynchronous interaction of the thioxo groups with the carboradical centers can result in the formation of trithiatetracyclononane structures of the type **C**}. While the thiophene intermediate **III** in the ground state is not of interest because of more probable return into the initial acyclic state, the thiirane intermediates generated by rotamers **Id** (T_1) and **Ie** (T_1) in their ground states are capable of transition into the initial or the bicyclic states **VII, VII'** with practically equal probability (Fig. 2).

The depth of the potential well in which the thiirane intermediate is located (TS1 and TS2), from the side of its transition into the acyclic state **Id** (**Ie**) is 3.96 (3.53) kcal mol^{-1}, and into the state **VII** (**VII'**), 4.84 (3.84) kcal mol^{-1}. Structure **VII** is thermodinamically less stable than rotamer **Id** by 24.73 kcal mol^{-1}, and

Table 1. Total energies (-E_{tot}, au)[a], zero point harmonic vibrations energies (*ZPVE*, au), relative energies (ΔE, kcal mol^{-1}), lowest harmonic frequencies (ω_1, cm^{-1}), and values of electric dipole moment (μ, D) for stationary states of compound **I** on the PES S_0 and T_1

Structure	$-E_{tot}$	*ZPVE*	ΔE	ω_1	μ
Ia (S_0)	1581.58940	0.16853	0.00	19	0.49
Ib (S_0)	1581.56605	0.16922	15.08	18	0.50
Ic (S_0)	1581.57008	0.16924	12.57	22	1.56
Id (S_0)	1581.58015	0.16918	6.21	18	4.83
Ie (S_0)	1581.56267	0.16930	17.26	8	4.41
Ia (T_1)	1581.52678	0.16653	1.10	19	7.03
Ib (T_1)	1581.51939	0.16739	6.28	18	0.98
Ic (T_1)	1581.51843	0.17032	8.72	19	3.06
Id (T_1)	1581.52844	0.16643	0.00	17	4.80
Ie (T_1)	1581.51758	0.16704	7.20	18	3.99

[a] 1 au = 627.506 kcal mol^{-1}.

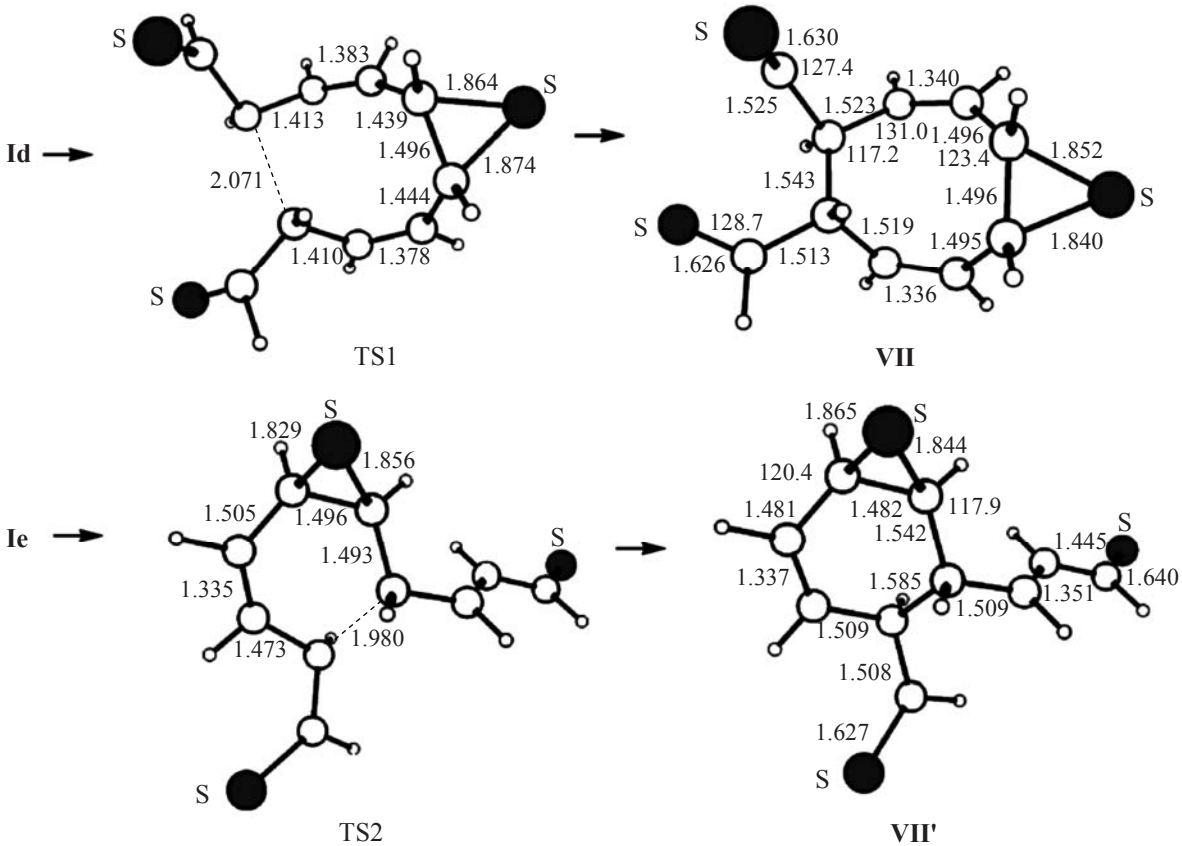


Fig. 2. Structural characteristics of compounds **VII, VII'** and transition states TS1 and TS2 connecting them with the thiirane intermediates on the S_0-surface. Bond lengths are given in Å, angles in degrees.

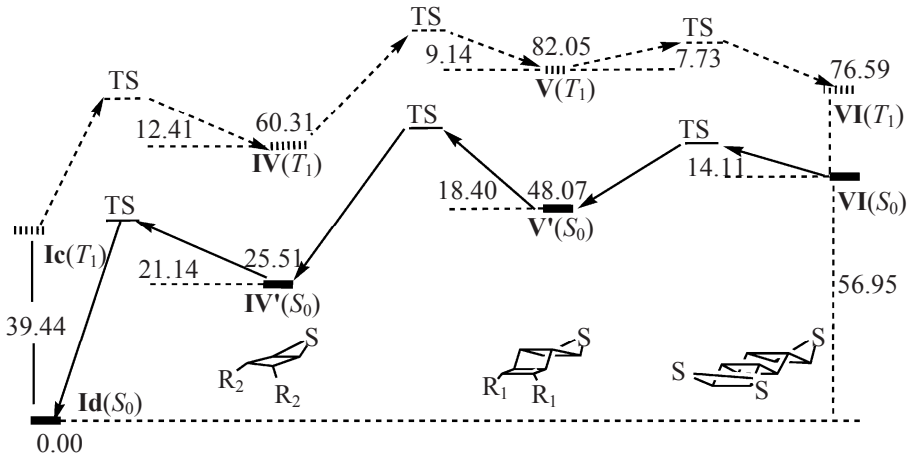


Fig. 3. Schematic representation of the reaction channels of photochemical cyclization and thermochemical ring opening in isomers **I**, **IV** (**IV'**), **V** (**V'**), **VI** (values in kcal mol^{-1}).

structure **VII'** has practically the same energy as **Ie** (the energy difference is as low as 0.40 kcal mol^{-1}). The depth of the potential well for compounds **VII** and **VII'** with respect to the thiirane intermediates of 24.00 and 37.43 kcal mol^{-1}, respectively, suggests their possible accumulation in photoinitiated reactions.

The $T_1 \leftarrow S_0$ excitation of rotational states **Ia–Ie**, as follows from calculations, is accompanied with substantial reorganization of the geometry (Fig. 1). An increase in the internuclear distance d(C=S) and decrease in the C–C–S bond angle is observed, typical of the $n \rightarrow \pi^*$-excitation of thiocarbonyl compounds. Decrease in the degree of conjugation in the sulfide chains leads to an increase in the dihedral angle C^3–C^2–$C^{2'}$–$C^{3'}$ by 4°–9°. Transition into the T_1-state reduces practically twice the range of variation in the relative stability of the rotational forms (S_0 = 17.26 kcal mol^{-1}, T_1 = 8.72 kcal mol^{-1}) with the inversion of their relative order. Rotamer **Id** becomes the most stable, and the least stable is structure **Ic**. Rotamer **Ia**, taking into account the high polarity of its triplet state (Table 1), can compete with state **Id**. Activation barriers of the interconversion of the rotamers decrease by 4–7 kcal mol^{-1}. Structural reorganization of the $T_1 \leftarrow S_0$ transition is indicative of delocalization of excitation in rotamer **Ic** on both sulfide fragments and in the other rotamers, on one fragment.

The investigation of the photo- and thermoinitiated valence isomerization has shown that successive disrotatory cyclization of rotamer **Ic** in the T_1-state leads to building up of the condensed cycles in pairs with lowering the activation barriers of each subsequent step of cyclization by 3–4 kcal mol^{-1} (Fig. 3).

At first, the thermodynamic stability of the intermediate polycyclic structures drops but in the last step of cyclization their stability increases (Table 2). The diabatic transition of structure **VI** into the S_0-state and its subsequent thermolysis with cascade opening of the cycles leads, as showed the analysis of the PES, to acyclic rotamer **Id**. Similarly, in an inverted manner, proceed both the photocyclization and thermodecyclization in the **Id**(T_1) → **Ic**(S_0) processes.

In the reaction channels **Ic** → **II** → **VIII** → **IX** and **Ib** → **III** → **X** → **XI** on the T_1-surface the rate-determining steps are the formation of the thiirane (TS3) and thiophene (TS6) intermediates (Fig. 4). Molecular structures of compounds **VIII–XI** are given in Fig. 5.

Ring closure in transitions **II** → **VIII** (TS4), as in bis(thioxopropenyl) sulfide [8], occurs in an asynchronous manner, which is by 17.31 kcal mol^{-1} more favorable than the synchronous channel localized by the use of the "fixed scan" method. A similar channel **III** → **X** (TS7) requires less energy and is close by the value to the activation parameter of the synchronous process. In the first sequence of intramolecular transformations the accumulation of product **IX** is also possible, whereas in the second sequence, apparently, only accumulation of product **X** will occur. The stability of structures **VIII–X** in the ground state (Fig. 4, Table 2) is comparable with the thermodynamic stability of the lowest acyclic rotamer **Ia**. Structure **VIII** is by 2.50 kcal mol^{-1} more stable than **Ia**, whereas structures **IX** and **X** are less stable by 1.80 and 2.55 kcal, respectively. The results obtained suggest the possibility of realization of photochemical

Table 2. Total energies (-E_{tot}, au), zero point harmonic vibrations energies (*ZPVE*, au), relative energies (ΔE, κcal mol^{-1}), imaginary or lowest harmonic frequencies (ω_1, cm^{-1}), values of electric dipole moment (μ, D) for critical points of the channels of valence isomerization on the S_0 and T_1 surfaces

Structure	$-E_{tot}$	*ZPVE*	ΔE	$i\omega/\omega_1$	μ
II(T_1)	1581.52025	0.16712	42.51	21	5.02
TS4(**II–VIII**)T_1	1581.49218	0.17145	62.84	i255	1.60
VIII(T_1)	1581.49907	0.17259	59.23	52	1.58
IX(T_1)	1581.51877	0.17573	48.84	67	2.73
VIII(S_0)	1581.60057	0.17571	–2.50	35	5.18
IX(S_0)	1581.59844	0.17945	1.18	143	4.95
III(T_1)	1581.48287	0.16688	65.81	27	6.17
TS7(**III–X**)T_1	1581.47948	0.17101	70.53	i496	3.49
X(T_1)	1581.49587	0.17380	62.00	57	3.54
XI(T_1)	1581.47872	0.17213	71.71	69	4.55
X(S_0)	1581.59597	0.17917	2.55	141	3.19
XI(S_0)	1581.56474	0.17804	21.44	130	4.03
IV(S_0)	1581.54261	0.17229	31.72	18	4.16
V(S_0)	1581.50723	0.17286	54.28	36	2.49
VI(S_0)	1581.49614	0.17593	63.16	35	2.21
IV'(T_1)	1581.48368	0.16883	66.53	17	3.57
V'(T_1)	1581.44917	0.16897	88.27	35	1.89
VI(T_1)	1581.45881	0.16990	82.81	34	1.72

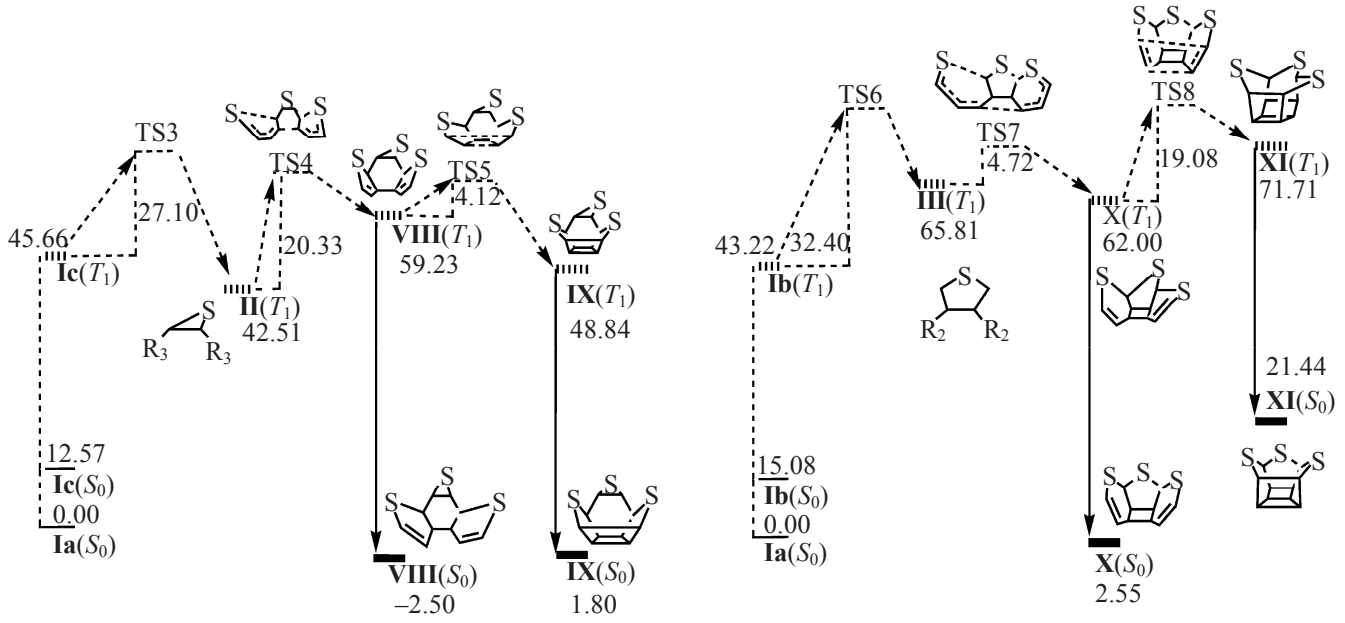


Fig. 4. Schematic representation of the reaction channels of formation of heterocyclic structures **VIII–XI** (values in kcal mol^{-1}).

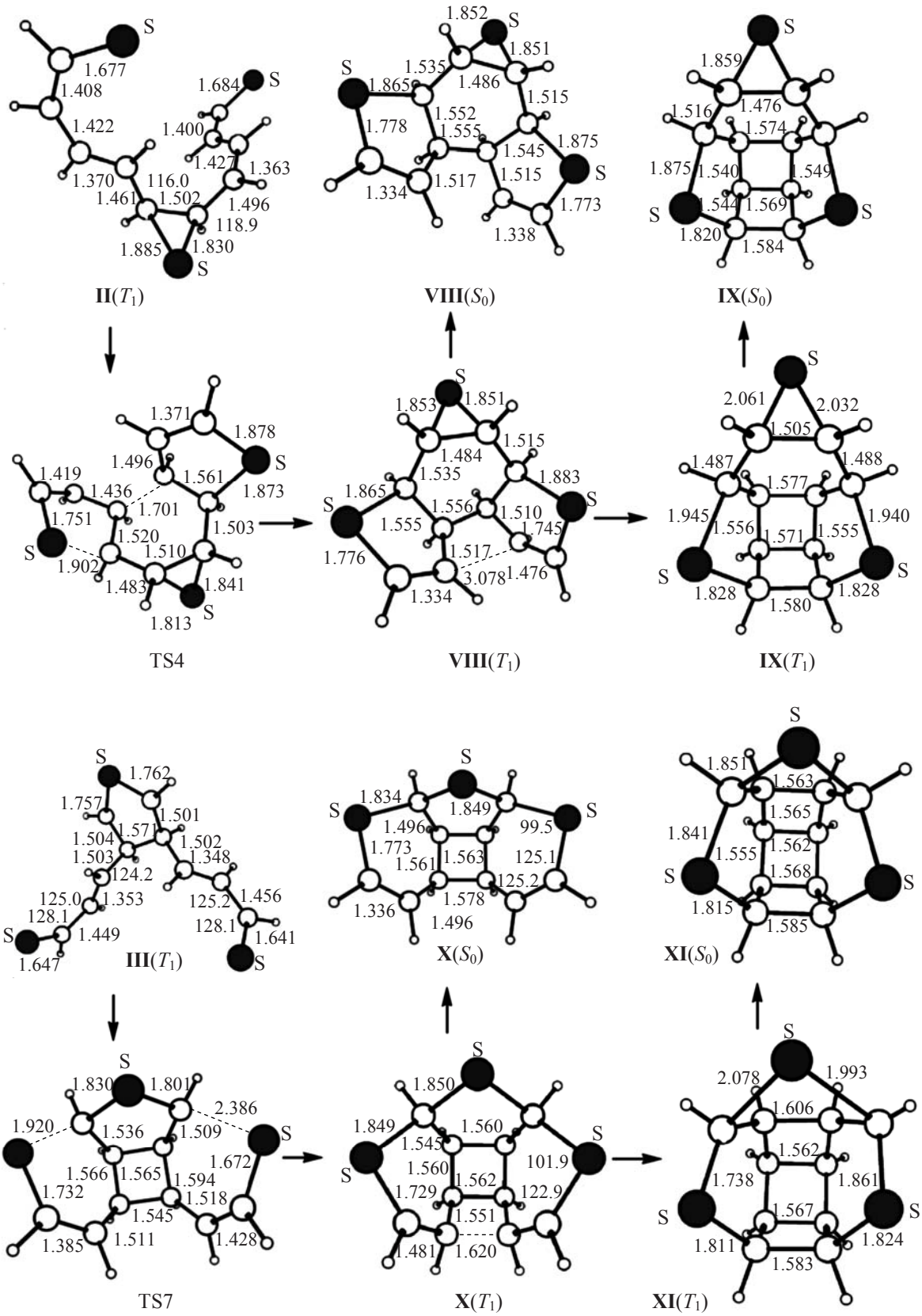


Fig. 5. Molecular structures and principal geometric characteristics of heterocyclic compounds **VIII–XI** in the S_0- and T_1-states. Bond lengths are given in Å, angles in degrees.

channel of formation of heterocyclic structures **VIII–XI**.

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