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Intramolecular Thiiranocyclobutane–Open Chain Isomerization of 3,3'-Dithioxo Sulfide Derivatives: A Quantum-Chemical Study

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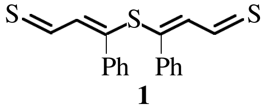
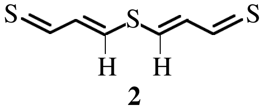
Abstract—The thermodynamic stability and structural and electronic characteristics of thiabicyclic structures, expected products of photochemical isomerization of bis(3-thioxo-1-phenylpropenyl), bis(3-thioxo-1-propenyl), and bis(5,5-dimethyl-3-thioxocyclohex-1-enyl) sulfides, were evaluated by quantum-chemical calculations. The energy in the thiabicyclic structures is accumulated owing to formation of metastable highly strained fused systems. The heats of dark isomerization of thiabicyclic structures into acyclic ones range from 50 to 250 kJ mol^{-1}. The activation energy of thermal transformations into acyclic isomers are 90–310 kJ mol^{-1}. Higher thermal effects and lower activation energies are obtained when the polarity of the medium is taken into account. The calculation results show that this class of compounds is promising for solar energy conversion.

Conformational isomerism of the recently prepared first representatives of 1,7-dithioxo compounds [1, 2] is extremely diverse, and numerous spectroscopically discernible states can be formed [3]. This gives rise to a wide spectrum of intramolecular interfragment interactions, affecting the electronic characteristics of the central fragment and thiocarbonyl atoms. The central moiety can acquire pronounced ylide character, and terminal fragments, thioketene character. Therefore, 1,7-dithioxo compounds are potentially capable of various intramolecular rearrangements [3].

In this study, we examined the highly strained thiabicyclic structures that are expected isomerization products of bis(3-thioxo-1-phenylpropenyl) sulfide (**1**), bis(3-thioxo-1-propenyl) sulfide (**2**), and bis(5,5-dimethyl-3-thioxocyclohex-1-enyl) sulfide (**3**), and also of the hypothetical compound $S[(CH{=}CH)_3CH{=}S]_2$ (**4**). The probability of such photoinitiated rearrangements depends on the initial molecular stereochemistry and seems to be high, taking into account the well-known photochemical rearrangement of a related compound, bis(1-phenylvinyl) sulfide [4]. For the rearrangement to be facile, the steric structure should be favorable for the photochemical ring closure. The principal possibility of formation of thiabicyclic and thiatricyclic structures was demonstrated by semi-empirical calculations in [3].



1



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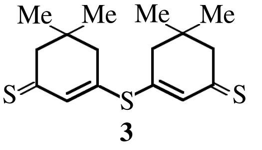

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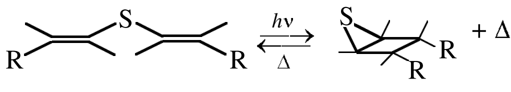
The high strain of the thiiranocyclobutane structure and the C–C bond strengths in the thiirane and cyclobutane rings suggest high thermal effect and high activation barrier of the reverse dark reaction:



By choosing appropriate substituents, it may be possible to increase the probability of photoinitiated valence isomerization. On the other hand, variation of the donor and acceptor properties of substituents at the double bonds may shift the long-wave absorption edge and affect the quantum yield Φ of the direct photoreaction.

Compound **4**, not synthesized yet, and its structural analogs, e.g., bis(1,3-butadien-1-yl) sulfide [5, 6], under sterically favorable conditions can be expected to undergo a sequence of photochemical transformations yielding stable and highly strained thiacyclic structures.

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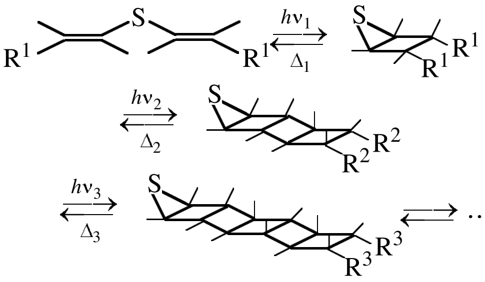
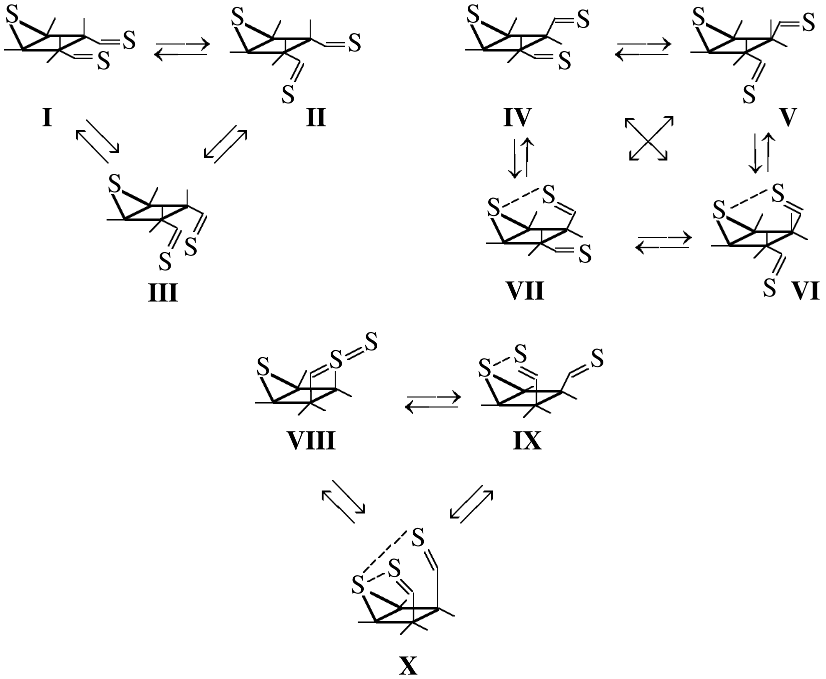


It is not improbable that compounds **1**–**4** or their stereoelectronic analogs will meet requirements to solar energy storage systems [7] or, at least, be starting compounds in a search for effective solar energy converters.

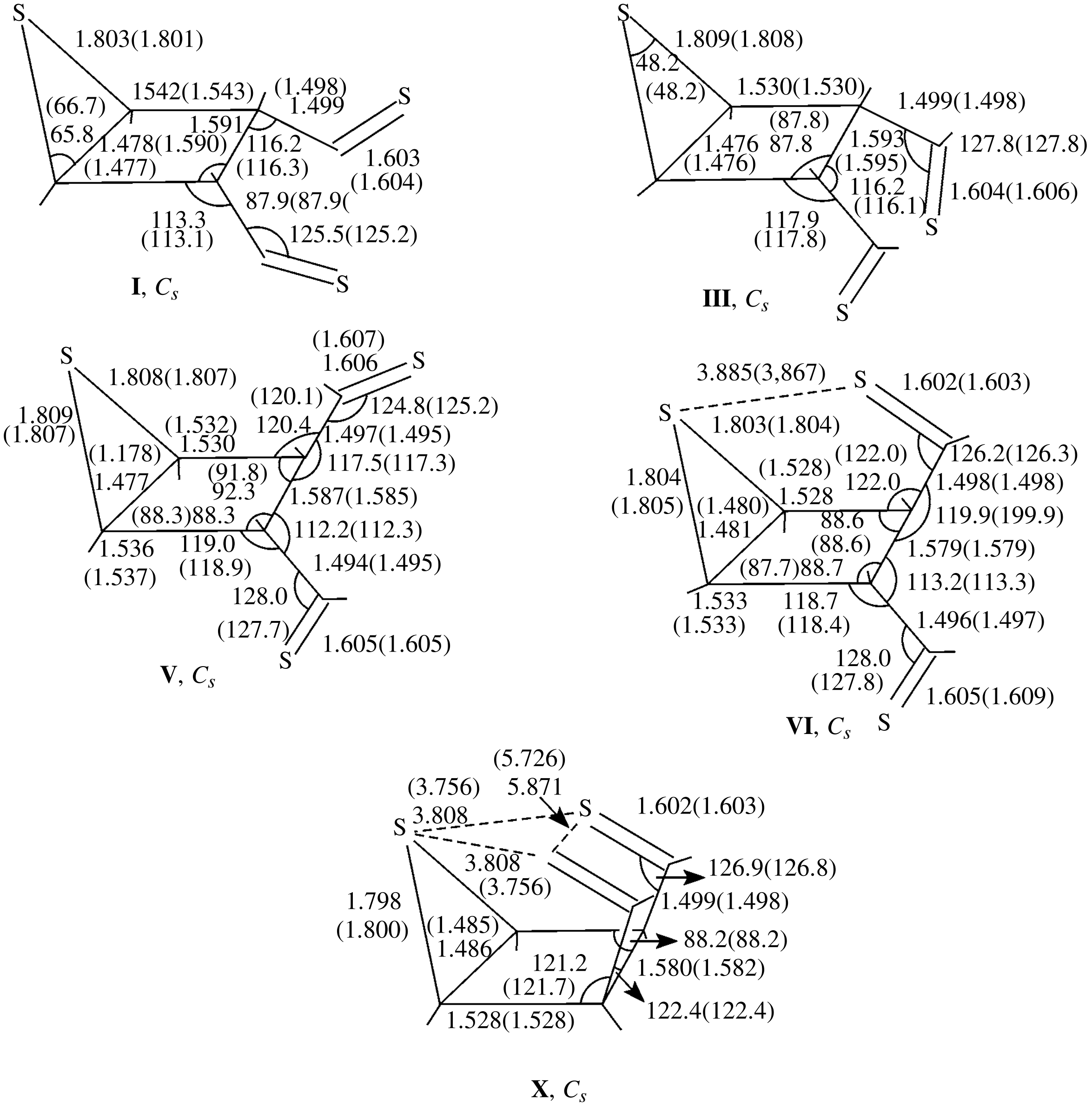
In this work, we performed a quantum-chemical study of the potential energy surfaces of dark intramolecular transformations of thiabicyclic isomers of **1**–**4** into acyclic structures, with the aim to estimate the thermal effects and activation energies of such transformations. *Ab initio* calculations were performed by the restricted Hartree–Fock method [8, 9] in the 6-31G** valence-split basis set using the GAUSSIAN 94 software [10]. The geometry of molecular systems corresponding to the transition states (number of negative eigenvalues of the Hesse matrix in the given stationary point λ 1 [11]) and energy minima (λ 0) were fully optimized to a gradient of 10^{-5} hartree/bohr. The force constant matrix was calculated analytically using appropriate program included in GAUSSIAN. The structures corresponding to the energy minima on the potential energy surface were identified by the steepest descent along the gradient line from the saddle point to the neighboring critical point, with a small initial shift along the transition vector, which allowed the gradient reaction pathway to be found correctly [11]. In the vicinity of stationary states, the structures were optimized by the Newton–Raphson method in the Berny scheme.

The calculations showed that three groups of stationary states (**I**–**III**, **IV**–**VII**, **VIII**–**X**) can exist on the potential energy surface of conformational transformations of thiabicyclic isomers of **2** differing in the orientation (*cis, trans*) of the CH=S substituent relative to the epithio group (Scheme 1, Fig. 1).

Scheme 1.



Within each group, there are several spectroscopically discernible (with the transformation barriers exceeding 25 kJ mol^{-1}) rotational states produced by rotation around the C_{ring}–C_R single bond. The activation energies of the transformations of *cis-cis* conformers to *cis-trans* conformers in structures **VI**, **VII**, **IX**, and **X** exceed those of the other transformations approximately by half (35–40 kJ mol^{-1}). This fact sug-



I, C_s

III, C_s

V, C_s

VI, C_s

X, C_s

Fig. 1. Steric structures and geometric characteristics of some thiabicyclic conformational states of **2**. Figures without parentheses refer to the gas phase (RHF/6-31G**), and those in parentheses, to a condensed medium [ε 80; SCRF (RHF/6-31G**)]. Here and in Figs. 2–7, the bond lengths are given in Å, and bond angles, in degrees.

gests relatively strong donor–acceptor interaction between the thiirane and thiocarbonyl sulfur atoms in structures **VI**, **VII**, **IX**, and **X**. This effect is clearly manifested in variation of the total effective charges and also in structural features (the dihedral angle between the thiirane and cyclobutane ring planes increases, Table 1). This stabilizing interaction is apparently responsible for the presence on the potential energy surface of stationary states corresponding to sterically more strained structures **VI**, **VII**, **IX**, and **X**. The cyclobutane fragment in symmetrical thiabicyclic structures **I**, **III**, **VIII**, and **X** is planar, and in the other structures it is slightly (within 4°–6°) distorted; therefore, when estimating the dihedral angle between the thiirane and cyclobutane ring planes, we averaged the positions of atoms on the side of the cyclobutane ring opposite to the thiirane ring. Thiabicyclic structures **I**–**X** differ in stability insignificantly; the maximal difference is 22 kJ mol^{-1} (Table 1). At the same time, they considerably differ in polarity. The dipole moments of structures **I**–**X** vary from 0.70 to 4.66 D, which may lead to inversion of the series of relative stability in polar solvents. The effect exerted by the transition from the gas phase to a condensed medium on the structure, electronic characteristics, and relative stability of thiabicyclic conformers was estimated

Table 1. Total energies (E_{tot}, au[a]), relative energies (ΔE, kJ mol^{-1}), dipole moments (μ, D), effective Mulliken charges on sulfur atoms, and dihedral angles between the thiirane and cyclobutane ring planes (ϑ, deg) of thiabicyclic structures **I**–**X** (RHF/6-31G** calculations)

Structure no.	$-E_{tot}$	ΔE	μ	Atomic charge[b]			ϑ
				S_t	S_1	S_2	
I	1423.13242	17.9	3.13	0.060	–0.061	–0.061	59.8
II	1423.13527	10.4	0.70	0.046	–0.070	–0.063	60.3
III	1423.13376	14.4	2.85	0.034	–0.068	–0.068	61.0
IV	1423.13777	3.9	3.42	0.048	–0.075	–0.068	60.8
V	1423.13924	0.0	0.89	0.036	–0.076	–0.070	61.4
VI	1423.13562	9.5	2.11	0.068	–0.085	–0.067	63.9
VII	1423.13581	9.0	2.87	0.070	–0.079	–0.073	63.8
VIII	1423.13545	9.9	3.41	0.050	–0.071	–0.071	59.7
IX	1423.13659	7.0	3.77	0.070	–0.078	–0.072	64.0
X	1423.13083	22.1	4.66	0.071	–0.082	–0.082	64.4

[a] 1 au = 2626.4 kJ mol^{-1}. [b] S_t, thiirane sulfur atom; S_1, sulfur atom of the thiocarbonyl group, located at a shorter distance from S_t in the case of an asymmetric structure; S_2, sulfur atom of the other thiocarbonyl group.

Table 2. Total energies (E_{tot}, au), solvation energies (E_s, kJ mol^{-1}), relative energies (ΔE, kJ mol^{-1}), cavity radii (r, Å), dipole moments (μ, D), effective Mulliken charges on sulfur atoms, and dihedral angles between the thiirane and cyclobutane rings (ϑ, deg) of structures **I**–**X** in a solvent (water, ε 80) [SCRF (RHF/6-31G**) data]

Structure no.	$-E_{tot}$	E_s	ΔE	r	μ	Atomic charge			ϑ
						S_t	S_1	S_2	
I	1423.13606	9.5	22.3	4.410	3.53	0.044	–0.087	–0.087	60.4
II	1423.13654	3.3	21.1	4.085	1.02	0.056	–0.097	–0.075	60.6
III	1423.13759	10.1	18.3	4.096	3.61	0.044	–0.091	–0.091	61.3
IV	1423.14304	13.8	4.0	4.311	4.65	0.059	–0.117	–0.094	60.9
V	1423.13962	1.0	13.0	4.277	1.15	0.035	–0.105	–0.076	61.6
VI	1423.13684	3.2	20.3	4.780	2.53	0.055	–0.078	–0.076	64.2
VII	1423.13812	6.1	16.9	4.706	3.41	0.058	–0.084	–0.079	63.9
VIII	1423.13954	10.7	13.2	4.449	4.21	0.034	–0.088	–0.088	59.9
IX	1423.14458	21.0	0.0	4.126	5.42	0.056	–0.116	–0.114	64.4
X	1423.13794	18.6	17.4	4.536	5.70	0.061	–0.083	–0.083	64.7

using the self-consistent reactive field (SCRF) method [12] based on the Kirkwood–Onsager continual model. This method allows evaluation on the *ab initio* level of the contribution of electrostatic effects to solvation. Calculations showed (Table 2) that the reactive electrostatic field of a solvent shifts the electron density to terminal sulfur atoms, increasing the dipole moment of the molecule in all the conformational states. On the structural level, the dihedral angle between the thiirane and cyclobutane ring planes slightly increases. Structure **IX** becomes the most stable. The range of variation of the relative stabilities of conformers **I**–**X** remains virtually the same.

The search for transition states in thiiranocyclobutane–open chain isomerizations was performed as follows. First, the C–C bond in the thiirane ring and the parallel bond in the cyclobutane ring were stretched with a step of 0.15 and 0.30 Å, respectively, with subsequent optimization of the other geometries. After “obtaining” the acyclic structure, the transition states were sought for by moving along the gradient line connecting the two stationary states.

Examination of the potential energy surface of the isomeric transformations shows that intramolecular rearrangements of conformers **II**, **IV**–**VII**, **IX**, and **X** occur in two elementary steps involving poorly stable thiirane form **A** as intermediate (Scheme 2, Fig. 2). Calculations show that the ring opening occurs as follows. Initially, in all the thiabicyclic structures the C–C bond in the cyclobutane ring opposite to the thiirane ring is cleaved, without appreciable deformation of the C–C bond in the thiirane ring. This is followed by rotation of the side bonds of the "opened" four-membered ring (conrotatory in structures **IV**–**VII** and disrotatory in structures **II**, **IX**, and **X**); after that, the C–C bond in the thiirane ring is cleaved. It should be noted that cleavage of the cyclobutane ring unambiguously leads to the thiirane intermediate not in all the initial thiabicyclic states. In structures I, **III**, and **VIII**, transformation into structure **E** with fused thiirane and dithiaoctadiene rings (structure **XIV**, Fig. 3, Table 3), which is less stable thermodynamically than structure **B** or **D**, is more favorable kinetically. These results may give ideas of new routes to compounds of type **E**.

The main representatives of acyclic structures of compound **2**, obtained by intramolecular isomerizations, are shown in Fig. 3. Structures **XI**–**XIII** are among the most stable final states of the transformations **II** → **B**, **IV**–**VII** → **C**, and (**IX**, **X**) → **D**, respectively (Schemes 1, 2). These are rotamers incapable of mutual transformations under normal conditions. The energy effect of the rearrangement **II** → **B** in the gas phase is 54.2 kJ mol^{-1}, and consideration of the reactive electrostatic field of the solvent increases this value to 79.3 kJ mol^{-1}. For the rearrangement **IV**–**VII** → **B**, the solvent effect is less significant; the enegry effect ranges from 49.9 (**VI**) to 53.3 (**V**) kJ mol^{-1} for the gas phase and from 46.3 (**IV**) to 62.5 (**VI**) kJ mol^{-1} for the condensed medium. For the third group of thiabicyclic structures (**IX, X**), in going from the gas phase to solution, the relative stability of acyclic structures grows to a similar extent: from 42.1 to 48.2 kJ mol^{-1} for **IX** and from 57.2 to 65.6 kJ mol^{-1} for **X**. The limiting step of isomerizations of all the

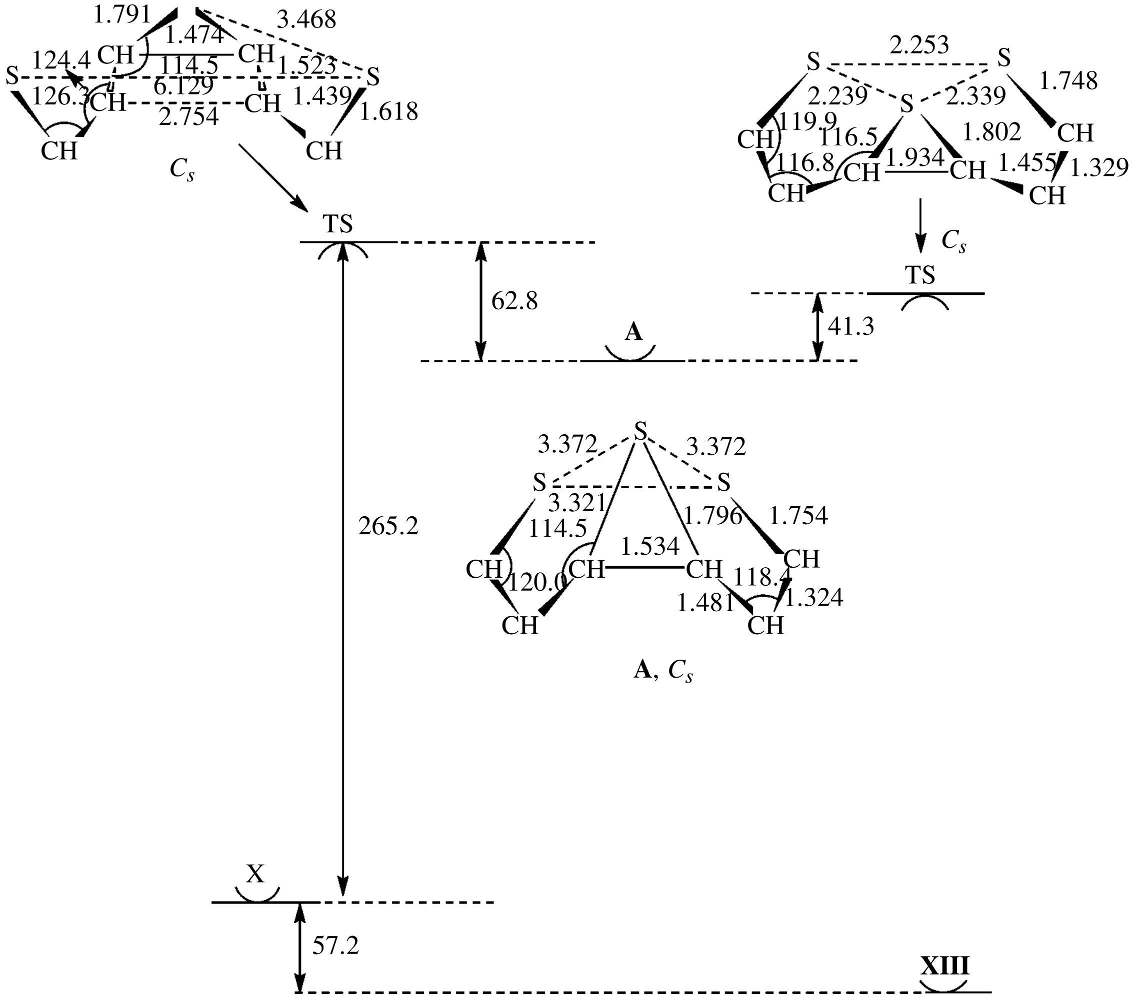
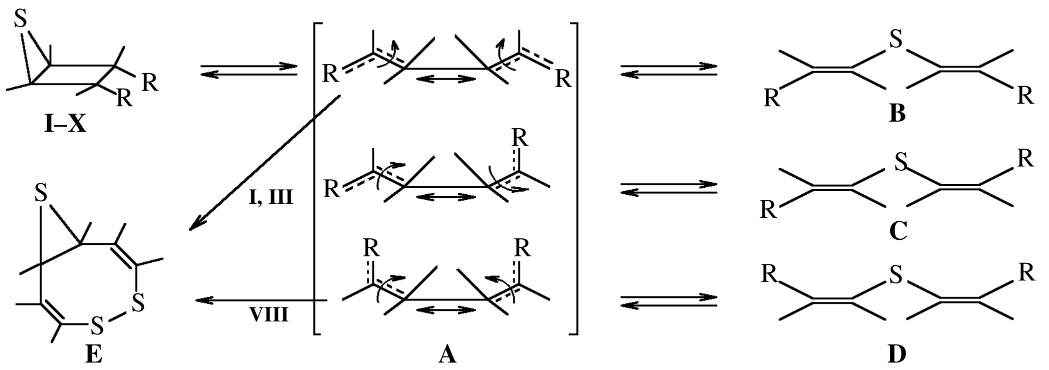


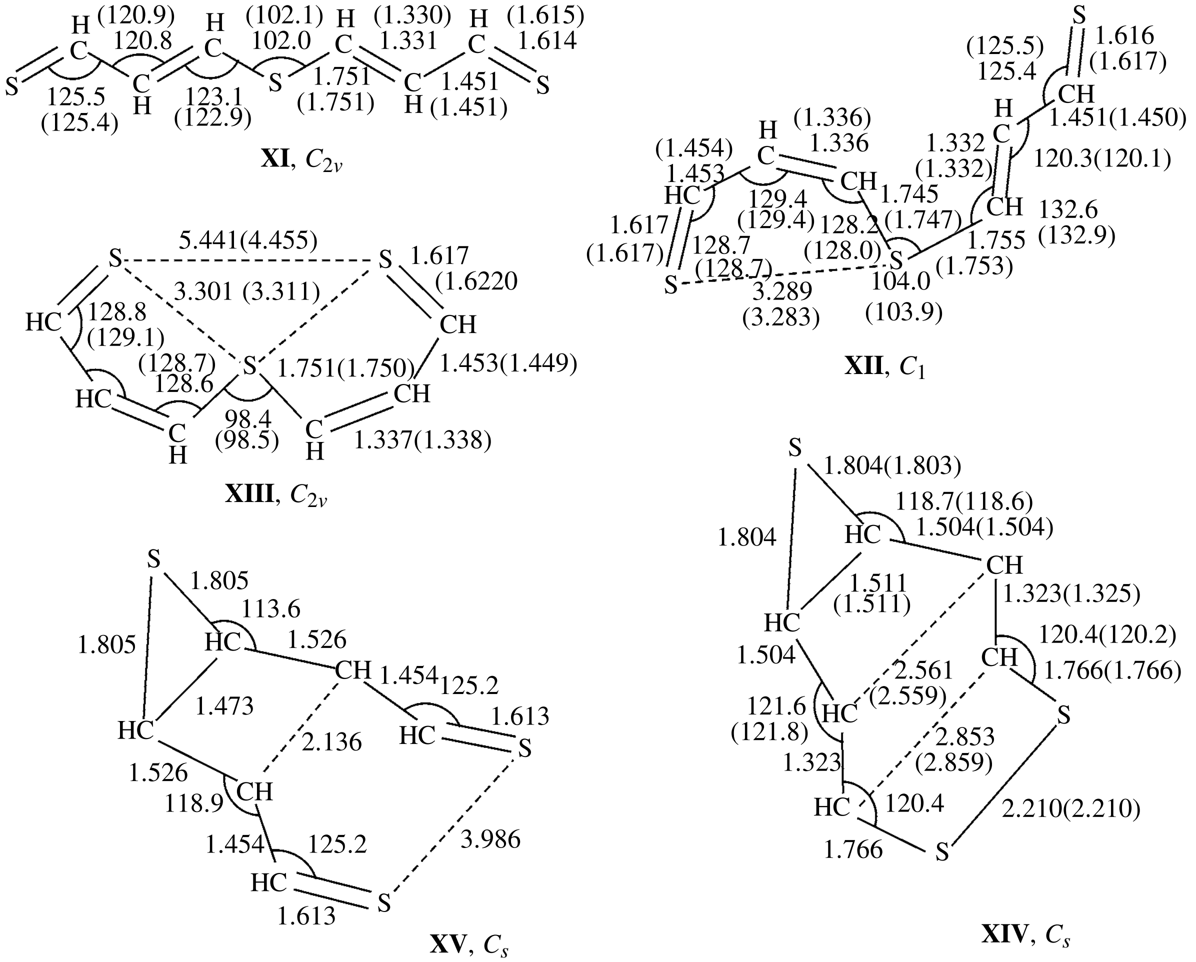
Fig. 2. Scheme of the energy balance and transformation of thiabicyclic structure **X** of compound **2** along the pathway of intramolecular rearrangement into acyclic compound **XIII** (the figures at arrows are energies in kJ mol^{-1}). The geometries of **X** are given in Fig. 1, and those of **XIII**, in Fig. 3. Here and in Fig. 7, TS denotes the transition state.

Scheme 2.



thiabicyclic structures of **2** into acyclic structures, as suggested by analysis of the potential energy surface, is the elementary transformation (**II**, **IV**–**VII**, **IX**, **X**) → **A**.

A specific feature of structures **VI**, **VII**, **IX**, and **X**, manifested on the structural level in the course of the rearrangement, is preservation of the stabilizing donor–acceptor interaction between the thiirane and *cis*-*cis*-terminal thione sulfur atoms (the upper limit of the interatomic distance S_t–S_{thione} does not exceed 3.8 Å). Such a structural feature is manifested in the isomerization kinetics. The activation energies of the rearrangements involving **VI**, **VII**, **IX**, and **X** are lower



XI, C_{2v}

XII, C_1

XIII, C_{2v}

XV, C_s

XIV, C_s

Fig. 3. Molecular structures and principal geometries of certain acyclic (**XI**–**XIII**) and thiabicyclic (**XIV**) conformations of compound **2** and those of the transition state of the rearrangement **I** → **XIV** (structure **XV**). Figures without parentheses refer to the gas phase, and those in parentheses, to a condensed medium.

Table 3. Total energies (E_{tot}, au), relative energies (ΔE, kJ mol^{-1}), gas-phase dipole moments (μ, D, RHF/6-31G** calculations), solvation energies (E_s, kJ mol^{-1}), cavity radii (r, Å), relative stabilities taking into account solvation energies (ΔE_s), and dipole moments in a condensed medium [μ_s, D, ε 80, SCRF (RHF/6-31G**) calculations] of structures **XI–XV**

Structure no.	Gas phase			Condensed medium			
	$-E_{tot}$	ΔE	μ	$-E_s$	r	$\Delta\partial_s$	μ_s
XI	1423.15595	6.0	1.59	28.4	6.245	0.0	1.74
XII	1423.15824	0.0	1.44	6.4	5.311	16.0	1.80
XIII	1423.15262	14.8	6.60	27.1	5.016	10.1	7.96
XIV	1423.11516	113.1	3.09	5.5	4.994	129.9	3.53
XV	1423.06023	257.4	4.10	38.9[a]	5.067	239.9	4.81

[a] The solvent effect for transition state **XV** (**I** → **XIV**) was taken into account at a fixed gas-phase geometry.

Table 4. Total energies (E_{tot}, au), relative energies (ΔE, kJ mol^{-1}), dipole moments (μ, D), and numbers of negative eigenvalues of the Hessian (λ) of structures **XVI–XXX** (*ab initio* RHF/6-31G** calculations)

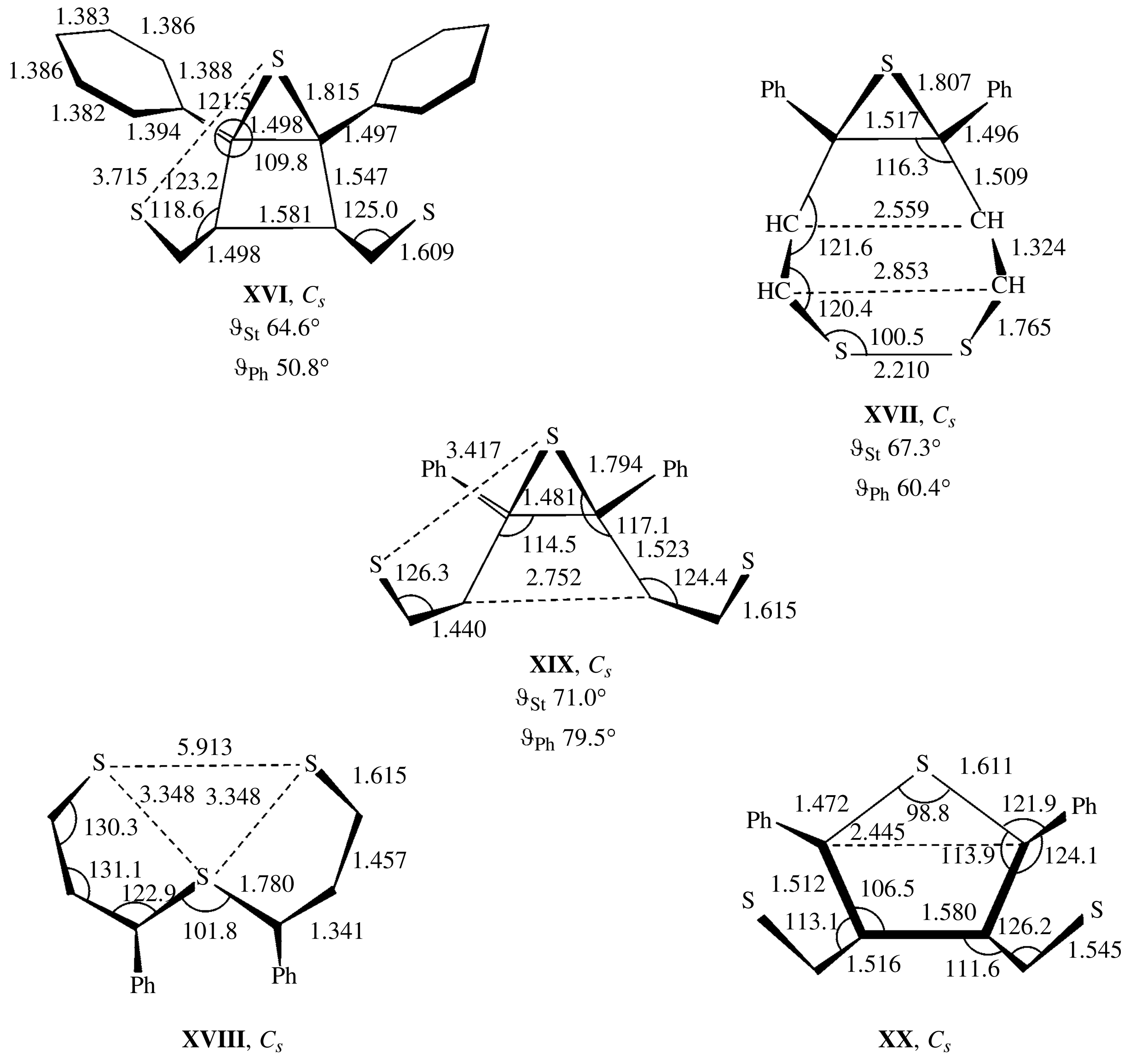
Structure no.	$-E_{tot}$	ΔE	μ	λ	Structure no.	$-E_{tot}$	ΔE	μ	λ
XVI	1822.24738	51.8[a]	5.12	0	**XXIV**	1730.64647	239.1[c]	0.83	0
XVII	1822.22306	115.7[a]	3.29	0	**XXV**	1730.73751	0.0	3.16	0
XVIII	1882.26711	0.0	7.19	0	**XXVI**	1730.61512	321.4[c]	3.89	1
XIX	1882.16084	279.1[a]	6.61	1	**XXVII**	1730.67790	156.6[c]	2.63	0
XX	1822.19616	186.3[a]	4.57	0	**XXVIII**	1730.64488	243.3[c]	4.08	1
XXI	1811.14575	251.1[b]	3.07	0	**XXIX**	1730.70854	76.1[c]	3.01	0
XXII	1811.24135	0.0	5.33	0	**XXX**	1730.67441	165.7[c]	3.38	1
XXIII	1811.10113	368.3[b]	4.97	1					

[a] Relative to structure **XVIII**. [b] Relative to structure **XXII**. [c] Relative to structure **XXV**.

as compared to the other thiabicyclic structures of **2**. For example, the activation energies of the transformations **VI** → **XII**, **VII** → **XII**, **IX** → **XIII**, and **X** → **XIII** are 281.4, 288.1, 310.1, and 265.2 kJ mol^{-1}, and those of the transformations **II** → **XI**, **IV** → **XII**, and **V** → **XII**, 337.2, 316.8, and 308.1 kJ mol^{-1}, respectively. Furthermore, donor–acceptor binding of the thiirane and thiocarbonyl sulfur atoms "protects" the reaction system to a certain extent from various external scavengers and from the tendency to spontaneous trimerization [1, 3]. The extent of charge separation in the transition state of the thiiranocyclobutane → **A** transformation of compound **2** grows: The increase in the dipole moment ranges from 0.25 D for the transition state of the transformation **II** → **A** to 1.22 D for that of **X** → **A** (Tables 1, 2). As a result, the activation energy of the rearrangements decreases in going from the gas phase to a polar solvent. When the reactive field of the solvent (ε 80) is taken into account, even with a fixed gas-phase geometry, calculations of the transition states give decreased E_{act} values; the decrease ranges from 12.6 kJ mol^{-1} for **V** → **A** to 26.1 kJ mol^{-1} for **IX** → **A**. Thus, in going from the gas phase to condensed medium, the relative stability of the acyclic structures increases, and the activation parameters of thiiranocyclobutane–open chain isomerizations in **2** decrease.

The stable conformers of **1** are analogs of rotamers **VIII**–**X** of **2**. The other potential rotamers of types **I**–**VII** either have no stationary states (such as **II**, **III**, **V**, **VI**) or are poorly stable (**I, IV, VII**; the depth of the potential well does not exceed 30.0 kJ mol^{-1}), because of strong nonvalent interactions between the phenyl fragments and *trans*-oriented substituents.

The mechanism of the rearrangement of the thiabicyclic form of **1** into the acyclic form is illustrated by the example of structure **XVI** (for the other conformers, the isomerization mechanisms are similar), which is an analog of structure **X** of compound **2** (Fig. 4, Table 4). For **1** and **2**, the isomerization pathways are different. In the case of **1**, the potential



XVI, C_s
ϑ_{St} 64.6°
ϑ_{Ph} 50.8°

XVII, C_s
ϑ_{St} 67.3°
ϑ_{Ph} 60.4°

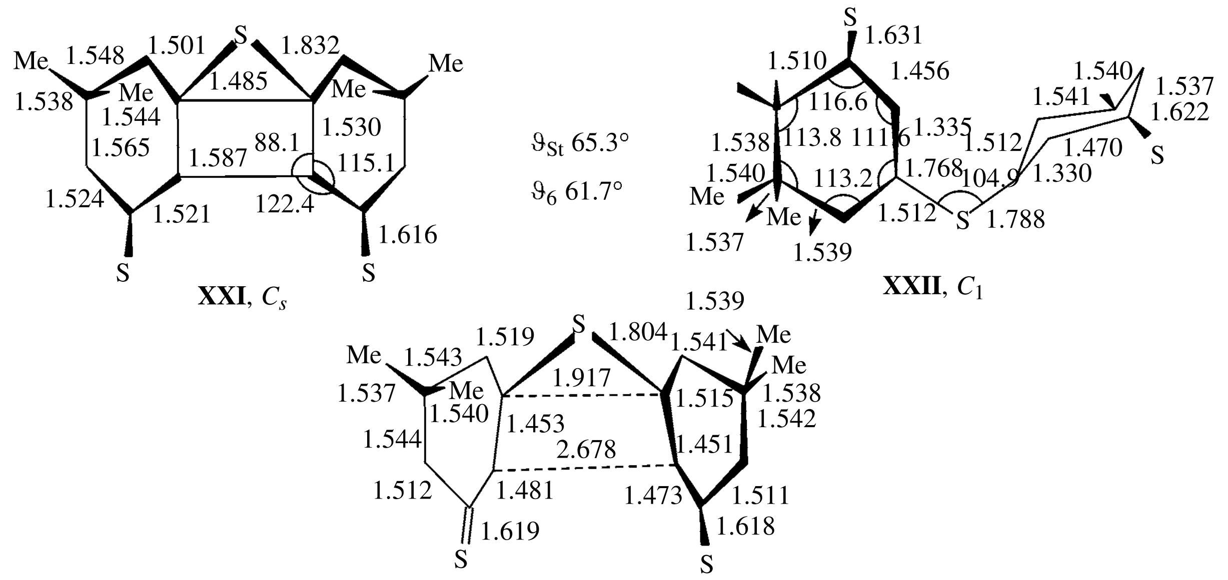
XIX, C_s
ϑ_{St} 71.0°
ϑ_{Ph} 79.5°

XVIII, C_s

XX, C_s

Fig. 4. Molecular structures and geometries of stationary states **XVI–XVIII** and **XX** of compound **1** and those of the transition state of the rearrangement **XVI** → **XVIII** (structure **XIX**) (*ab initio* RHF/6-31G** calculations; ϑ_{S_t} and ϑ_{Ph} denote, respectively, the dihedral angles between the thiirane and cyclobutane rings planes and between the phenyl and cyclobutane ring planes, respectively).

energy surface of the transition exhibits no local stationary states corresponding to thiirane structures of type **A**. At the same time, the calculations do not rule out the existence on the potential energy surface of structures of type **E** in the rotamers of **1** with *cis-trans*-oriented substituents (structure **XVII**, Fig. 4), although the stability of such a structure is low: The activation energy of the transformation **XVII** → thiiranocyclobutane is ~42.0 kJ mol^{-1}. According to the calculations, the cyclobutane ring in **XVI** can open by two reaction pathways. The first pathway is similar to that considered for **2** and involves asynchronous disrotatory rotation of the S_t–C bonds, so that the phenyl rings "slip" relative to each other, and thiabicyclic structure **XVI** transforms into "skewed" acyclic form **XVIII** via transition state **XIX**. The energy effect of this rearrangement is comparable with that for **1**, and the activation energy is somewhat lower (Fig. 2, Table 4). Reorganization of structure **XVI** by the second pathway involves "flattening" of the thiirane moiety, with the phenyl rings tending to occupy the position coplanar with the plane of the rings. As a result, the C–C bond in the thiirane ring is cleaved, and structure **XVI** transforms into intermediate **XX**

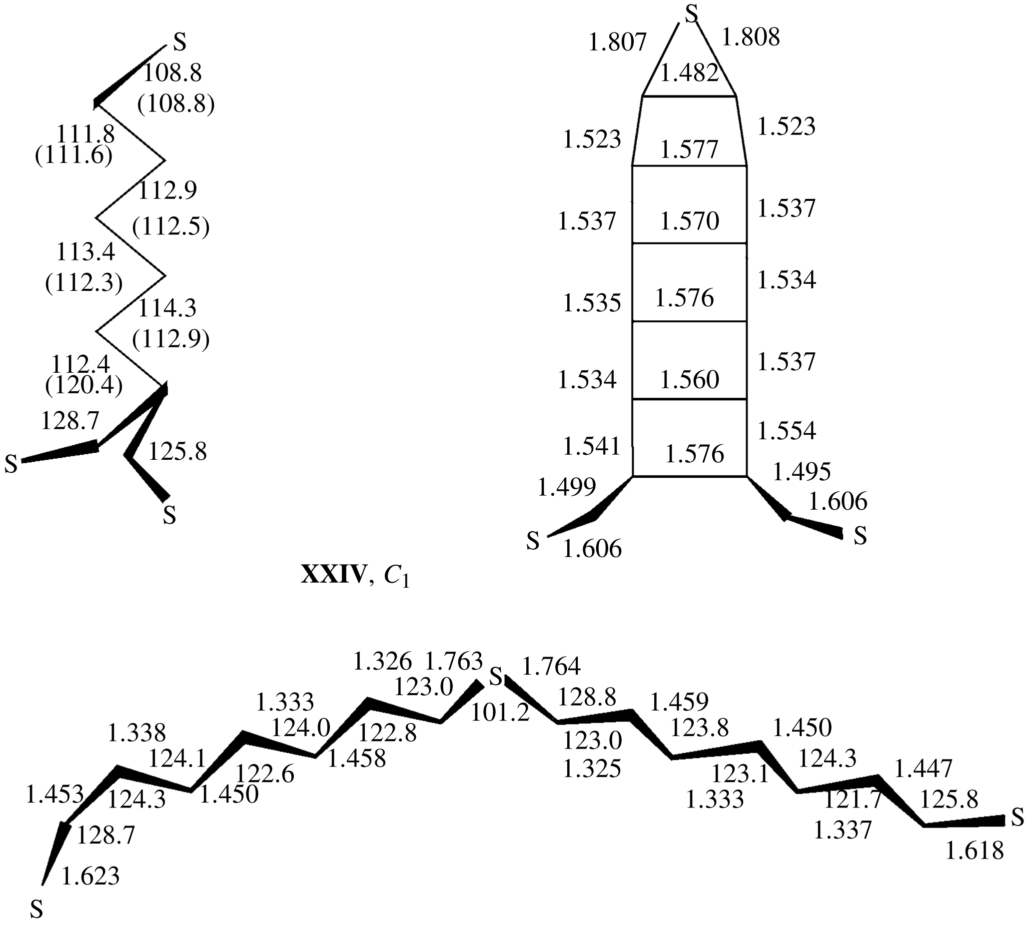


XXI, C_s

XXII, C_1

XXIII, C_1

Fig. 5. Molecular structures and geometries of stationary states **XXI** and **XXII** of compound **3** and of the transition state of the rearrangement **XXI** → **XXII** (structure **XXIII**) (*ab initio* RHF/6-31G** calculations). $(\vartheta_{S_t}, \vartheta_6)$ Dihedral angles between the thiirane and cyclobutane ring planes and between the six-membered and cyclobutane ring planes, respectively.



XXIV, C_1

XXV, C_1

Fig. 6. Principal geometries of the stationary states of "fully connected" (**XXIV**, in two projections) and acyclic (**XXV**) forms of compound **4** (the figures in parentheses are bond angles in the eclipsed chain).

whose central fragment is biradical thiophene (Fig. 4). Structure **XX** is poorly stable and readily transforms into the acyclic state. The relationships between the dipole moments of cyclic and acyclic structures of **1** and **2**, on the one hand, and the activation parameters, on the other hand, suggest that, in going from the gas phase to a polar solvent, the thermodynamic and kinetic parameters of isomerization of **1** will vary similarly to those of **2**.

On the potential energy surface of intramolecular transformations of the least conformationally flexible compound **3**, according to the calculations, there can exist only a single thiabicyclic structure **XXI** (without taking into account degenerate states and states produced by rotation of methyl groups) (Fig. 5). Among the above-considered structures, structure **XXI** is the most strained, although its gas-phase stability is relatively high (Table 4). The energy effect of the transformation of structure **XXI** into acyclic structure **XXII** via transition state **XXIII** is 251.1 kJ mol^{-1}. The steric strain of structure **XXI** is responsible for the decreased activation energy of the transformation **XXI** → **XXII** (117.2 kJ mol^{-1}) as compared to the already considered thiabicyclic structures. Calculations show that the rearrangement occurs in one step. One of the main structural parameters determining the coordinate of the reaction **XXI** → **XXII** is "flattening" of one of the six-membered rings relative to the cyclobutane fragment, with the subsequent in-plane deformation of the four-membered ring. As a result, in optimized acyclic structure **XXII**, the fragments are turned relative to each other by the angle ϑ 71.9°.

The energies of the fully "connected" conformational state of compound **4** (structure **XXIV**, Fig. 6) and its acyclic form **XXV** is 239.1 kJ mol^{-1} (Fig. 7). The activation energy of cyclobutane ring opening

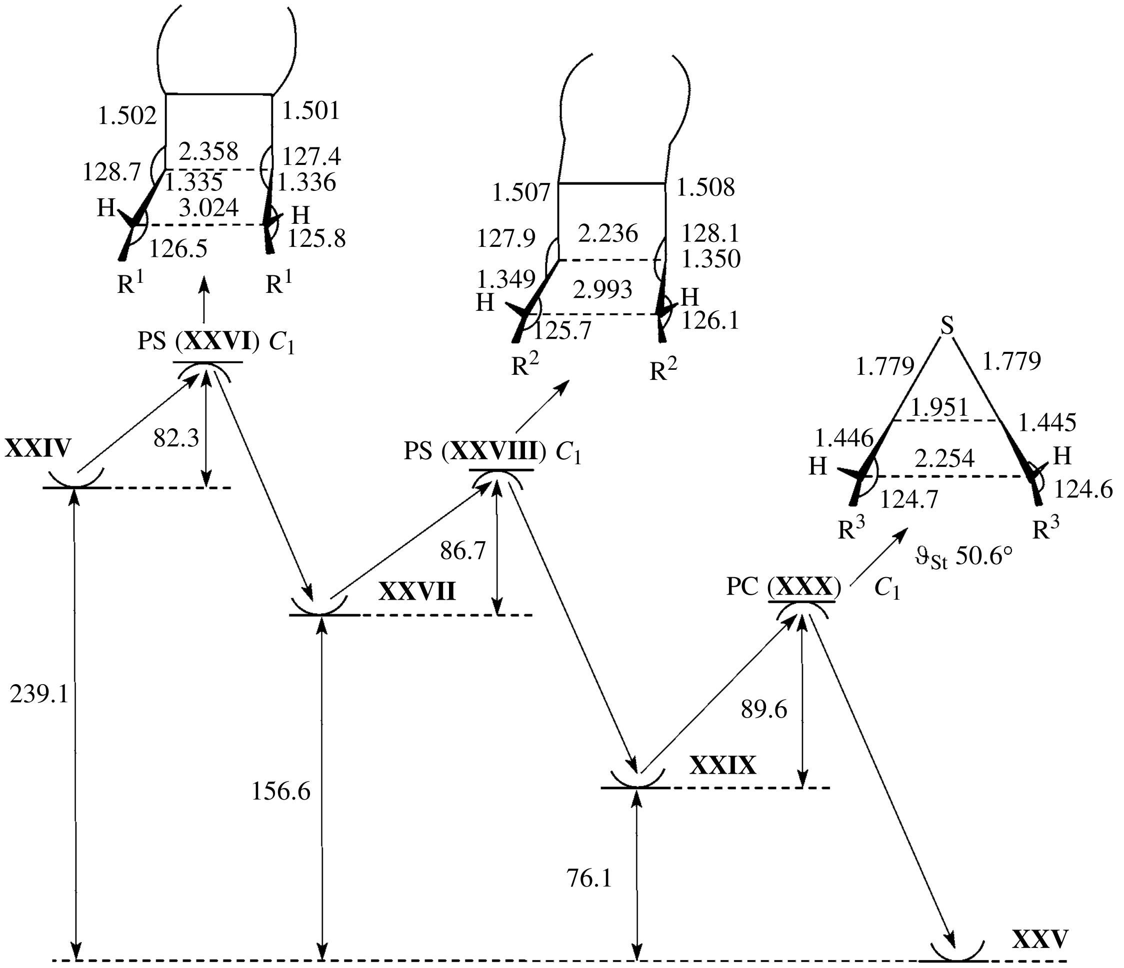


Fig. 7. Schematic representation of the energy balance (ΔE, kJ mol^{-1}) and transformation of "fully connected" structure **XXIV** of **4** along the pathway of intramolecular rearrangement via intermediate stationary states **XXVII** and **XXIX** and transition states **XXVI, XXVIII**, and **XXX** into acyclic state **XXV**. The geometries of molecular fragments are given for the transition states.

increases with the progress of transformation of **XXIV** into the acyclic form, and the thermal balance decreases. Each transition **XXIV** → **XXVII**, **XXVII** → **XXIX**, and **XXIX** → **XXV** occurs in one stage. The calculations do not suggest the existence of intermediates of type **A** or of competitive reaction pathways resulting in accumulation of isomeric states of type **E** (Scheme 2). From the topological viewpoint, the cyclobutane ring opening in **4** starts with "flattening" of the corresponding chair form and disrotatory rotation of the C–C (S_t–C) bonds. The trends in variation of the dipole moment in the critical points (Table 4) are similar to those observed in **1**–**3**. The larger the number of rings in the stationary state, the higher its dipole moment; the extent of charge separation in the transition state of each event of the cyclobutane ring opening is greater than that in the initial and final states. This fact suggests that, in polar solvents, the energy effect of the rearrangements, at least, should not decrease, and the activation energies of elementary transformations should not increase.

It should be noted in conclusion that, in initial semiempirical express analysis of the potential energy surfaces of rearrangements, the AM1 method [13, 14] gives the best results relative to the results of *ab initio* calculations; therefore, the AM1 method can be recommended as the starting method for studying large potential energy surfaces of related compounds.

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