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Reactions of Heterocumulenes with Organometallic Reagents: XIII.* Quantum-Chemical Study on the Mechanisms of *syn*-(*Z*)/*anti*-(*E*)-Isomerization of Methyl 2-Methoxy-*N*-methylbuta-2,3-dienimidothioate

V. A. Shagun and N. A. Nedolya

Favorskii Irkutsk Institute of Chemistry, Siberian Division, Russian Academy of Sciences, ul. Favorskogo 1, Irkutsk, 664033 Russia
e-mail: nina@irioch.irk.ru

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Abstract—Mechanisms of *syn*-(*Z*)/*anti*-(*E*) isomerization of methyl 2-methoxy-*N*-methylbuta-2,3-dienimidothioate, including rotational, inversion, promoted by N-protonation, and nucleophile-catalyzed, were studied by quantum-chemical methods, and the corresponding thermodynamic and kinetic parameters were calculated. The most probable mechanisms of isomerization of buta-2,3-dienimidothioates were found to be inversion (E_a = 74.4 kJ/mol) and nucleophile-catalyzed (E_a = 61.6 kJ/mol).

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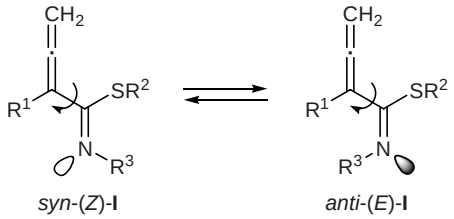
Geometrical isomerism in unsaturated systems containing carbon–carbon or carbon–heteroelement bonds attracts not only theoretical but also strong practical interest, primarily from the viewpoints of biology, medicine, and optoelectronics [2–5]. N-Substituted Schiff bases, i.e., compounds having a C=N−R fragment, give rise to so-called *syn*-(*Z*)/*anti*-(*E*) isomerism arising from relative rigidity of the C=N bond and nonlinear structure of molecules containing that bond [2, 4, 5].

Buta-2,3-dienimidothioates (1-aza-1,3,4-trienes) are key intermediates in a novel strategy of carbo- and heterocyclic syntheses; they have become readily accessible since we have discovered a new reaction of lithiated allenes and alkynes with isothiocyanates [6, 7]. These compounds constitute a new family of polyunsaturated Schiff bases (ketone imines) and exist as mixtures of *syn*-(*Z*) and *anti*-(*E*) isomers with respect to the double C=N bond (Scheme 1), as follows from the ^{1}H and ^{13}C NMR data.

Scheme 1.



syn-(*Z*)-**I** *anti*-(*E*)-**I**

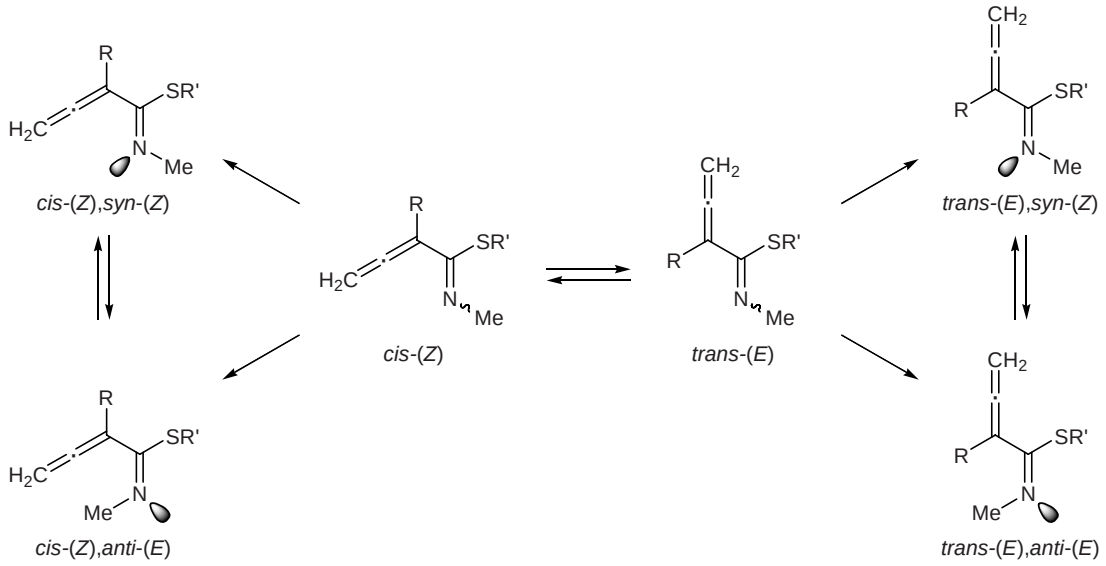
R^1 = OMe, R^2 = R^3 = Me.

We recently proposed a method for distinguishing *syn*-(*Z*) and *anti*-(*E*) isomers of 1-aza-1,3,4-trienes on the basis of their NMR spectra. Using methyl 2-methoxy-*N*-methylbuta-2,3-dienimidothioate (**I**) as an example, we were the first to measure the ^{13}C–^{13}C coupling constants of 1-aza-1,3,4-trienes, determine the ratio of their *syn*-(*Z*) and *anti*-(*E*) isomers (C_6D_6, –10°C, 35:65), and assign signals in the ^{1}H and ^{13}C NMR spectra to particular isomers [8]. The experimental data were reliably confirmed by quantum-chemical calculations. It was also found that the *syn*-(*Z*)/*anti*-(*E*) isomer ratio unusually strongly depends on the solvent nature: for instance, it changes from ~1:2 in C_6D_6 [8] to ~1:1 in $CDCl_3$. In proton-donor solvents (such as CD_3OD), the equilibrium concentration of the *syn*-(*Z*) isomer of **I** even exceeds the concentration of *anti*-(*E*)-**I**.

It is known [2, 4] that stereoisomers with respect to a double C=N bond are interconvertible. However, general mechanism of interconversion of *syn*/*anti* isomers of Schiff bases is unlikely to exist, for factors determining the isomerization mechanism are very fine

* For communication XII, see [1].

Scheme 2.

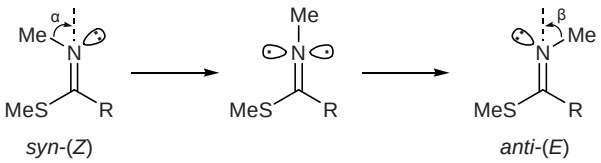


and interrelated. Two main channels for $Z \rightleftarrows E$ isomerization have been postulated. These are (1) out-of-plane rotational process involving a dipolar transition state and (2) planar inversion (lateral shift) mechanism with a linear transition state [4]. The activation parameters for the *sin*-(*Z*) $\rightleftarrows$ *anti*-(*E*) inversion of *N*-alkyl-substituted ketone imines are consistent with the latter mechanism [9].

Buta-2,3-dienimidothioates are very reactive compounds which readily undergo thermal intramolecular transformations leading to important carbo- and heterocyclic structures, such as cyclobutenes, pyrroles, cyclobuta[1,2-*b*]pyrroles, 2,3-dihydropyridines, quinolines, and pyridine-2(1*H*)-thiones [6, 7, 10]. Diversity of cyclization pathways of 1-aza-1,3,4-trienes originates from their high conformational [11, 12] and sigmatropic lability. We showed [6, 11, 13] that the formation of, e.g., dihydropyridine ring is preceded by [1,5]-H shift leading to the corresponding 2-aza-1,3,5-triene (the latter was isolated as individual substance). Sigmatropic rearrangements of 1-aza-1,3,4-trienes, specifically those involving migration of not only hydrogen atoms [6] but also alkylsulfanyl groups [10] were postulated in the reactions yielding cyclobutene [10], cyclobutapyrrole [13–15], and pyridinethione derivatives [15]. Only pyrroles [6, 12, 16, 17] and quinolines [6, 13, 17, 18] are formed via direct intramolecular cyclization of 1-aza-1,3,4-trienes. Obviously, apart from structural and stereoelectronic substituent effects and reaction conditions, the main factor determining the operative reaction path is configuration of the substrate, primarily *cis*-(*Z*) or *trans*-(*E*) orientation of the allene and imine fragments [11, 12] and *syn*-(*Z*) or *anti*-(*E*) orientation of substituents with respect to the C=N bond (Scheme 2).

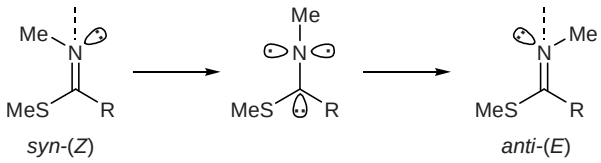
Study on the mechanisms of rotational isomerism of azatrienes with a view to reveal factors responsible for the height of activation barriers to interconversions of geometric isomers should provide recommendations for carrying out simulated reactions. In the present work we used molecular modeling to study some theoretically possible mechanisms of *sin*-(*Z*)/*anti*-(*E*) isomerization of methyl 2-methoxy-*N*-methylbuta-2,3-dienimidothioate (1-aza-1,3,4-triene **I**), whose thermally induced heterocyclization leads to a mixture of structural isomers, 3-methoxy-1-methyl-2-methylsulfanyl-1*H*-pyrrole and 5-methoxy-6-methylsulfanyl-2,3-dihydropyridine at a ratio of ~70:30 [6].

Scheme 3.

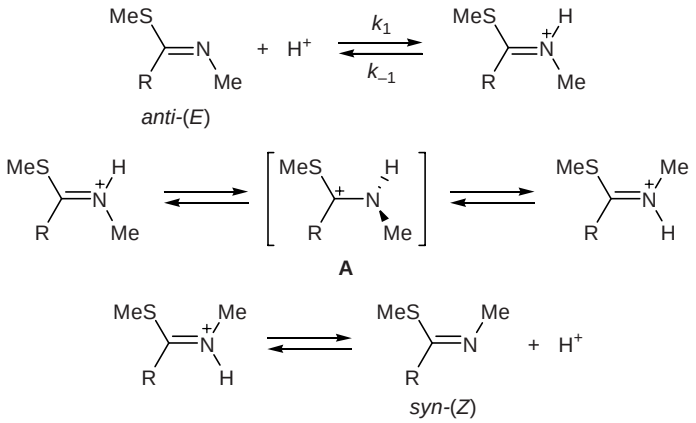


R = H_2C=C=C(OMe).

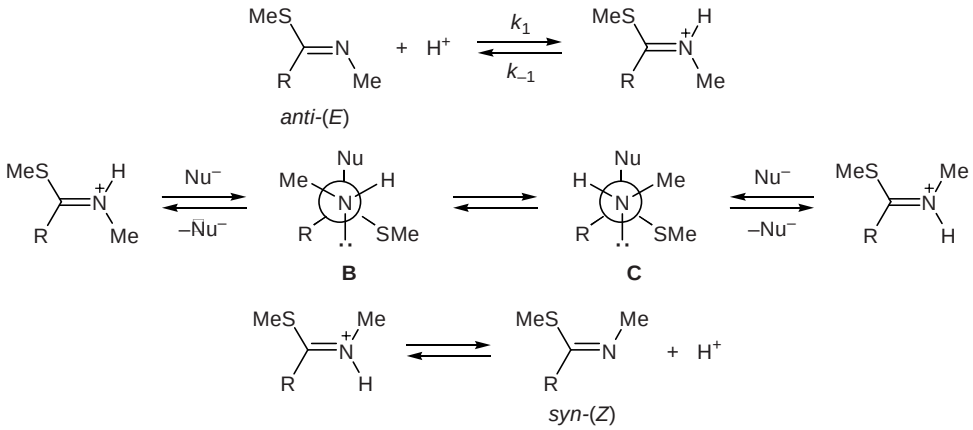
Scheme 4.



Scheme 5.



Scheme 6.



We considered two concurrent channels on the potential energy surface (PES) for the transformation of 1-aza-1,3,4-triene **I**. One of these involves the Me–N=C bond angle (Scheme 3, Fig. 1) as the major component of the reaction coordinate, while the other is related to variation of the torsion angle C^3C^4NMe (Scheme 4, Fig. 1). We also analyzed catalytic *syn*-(*Z*)/*anti*-(*E*) isomerization processes illustrated by Schemes 5 and 6. The mechanism of well known acid-catalyzed isomerization of compounds containing a double carbon–nitrogen bond is treated in the literature in different ways. However, in most cases it is reduced to two boundary reaction channels [19–26], one of which involves the corresponding counterion (Nu^-), and the other does not. In the latter case, rotation occurs in iminium ion like **A** (Scheme 5) [21, 22, 26], while in the former, in tetrahedral intermediate like **B** (Scheme 6) [24–26]. Presumably, the contribution of counterion Nu^- to the catalytic process depends on stereoelectronic properties of the substrate.

All calculations were performed using Gaussian-98 software package [27] with 6-311+G** basis set. The molecular structures and gradient paths connecting them were calculated on the DFT (density functional theory) level using B3LYP/6-311+G** three-parameter functional [28]. Geometric parameters of molecular systems were optimized up to a value of 10^{-5} a.u./bohr. In the analysis of flat PES areas, gradient values were set at 10^{-6} a.u./bohr. Stationary points were localized by analysis of Hessian eigenvalues. Transition states were identified by the linear synchronous transit-guided quasi-Newton method (QST2) [29]. Approximate transition state structure thus determined was then refined using the quadratic synchronous transit protocol (QST3) [29]. Analysis of vibration frequencies at saddle points was performed, and conformity of critical points to the gradient line connecting them was proved by the internal reaction coordinate (IRC) technique. The energies of zero-point harmonic vibrations (*ZPE*) were calculated with the use of a calibration factor of 0.9806 [29].

The structure of 1-aza-1,3,4-triene **I** is conformationally nonrigid; it is characterized by high rotational lability and therefore can be stabilized in different

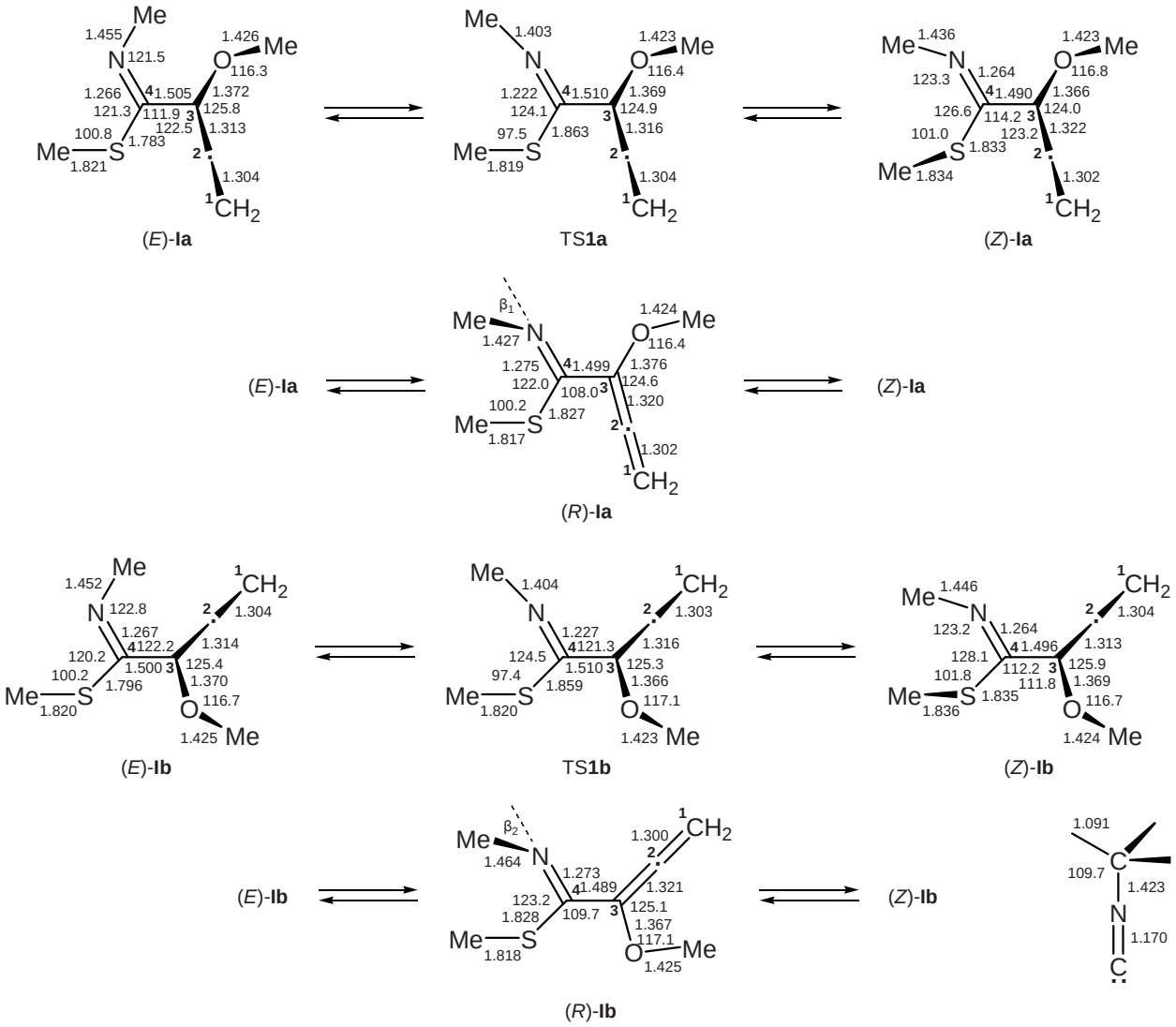


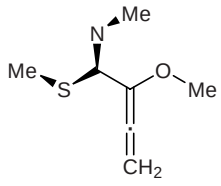
Fig. 1. Structures and principal geometric parameters of stationary and transition states along the gradient path for the inversion and rotational *syn*-(Z)/*anti*-(*E*) isomerizations of conformers **Ia** and **Ib**.

conformations. The main structural parameters determining the rotational state of molecule **I** are the dihedral angle between the methoxyallene and imidothioate fragments and torsion angles for the methyl groups. In the previous study [12] we examined by the B3LYP/6-311G** method the potential energy surface for rotational isomerism of azatriene **I**. Among the stationary states localized therein we selected four most stable structures which were used as initial ones in the study on its *syn*-(*Z*)/*anti*-(*E*) isomerization.

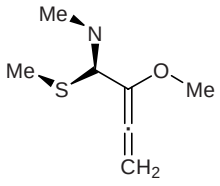
The *syn*-(*Z*)/*anti*-(*E*) inversion in structures *cis*-(*Z*)-**Ib** and *trans*-(*E*)-**Ia** is related to variation of the bond angle C^4NMe (φ, Scheme 3); it is characterized by an activation barrier of 74.4 and 75.9 kJ/mol, respectively (Table 1). The presence of an allene fragment and flattening of the molecular skeleton in the course of inversion isomerization enhances conjugation in the molecule; therefore, the activation barrier decreases as compared to methylenimine derivatives [30, 31]. The barrier to inversion in unsubstituted methanimine ($H_2C{=}NH$) [30] was estimated at 128 kJ/mol [MP2(fc)/6-311+G**]. A lower value, 98 kJ/mol, was obtained for the conjugated system of iminodiazomethane ($^-N{=}^+N{=}CH{-}CH{=}NH$) in terms of the B3LYP/6-311+G** + 0.98 *ZPE* (B3LYP/6-311+G**) calculation scheme [31].

The formation of transition states TS**1a** and TS**1b** involves considerable structural reorganization of the imidothioate fragment, which is related to rehybridization of the nitrogen atom (Fig. 1). The order of the

trans-(*E*) Conformations (**Ia**)

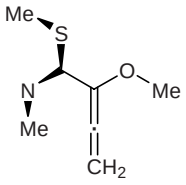


anti-(*E*)-**Ia**

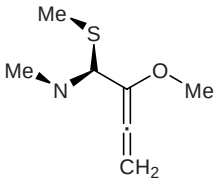


syn-(*Z*)-**Ia**

cis-(*Z*) Conformations (**Ib**)



anti-(*E*)-**Ib**



syn-(*Z*)-**Ib**

C^4–S and C^3–C^4 bonds decreases, while the C^4–N and N–Me bonds acquire enhanced double-bond character. As a result, the imidothioate fragment becomes carbene-like, its reactivity increases, and intramolecular sigmatropic rearrangements (primarily those involving migration of the methylsulfanyl group) become more probable [10]. According to the B3LYP/6-311+G** calculations, the optimal structure of isolated carbene in the lowest singlet state is linear with respect to heavy atoms (Fig. 1; the triplet state $^1B_3$ has a higher energy than $^1A_3$ by 0.17002 a.u. and is nonlinear; the C=N–Me bond angle is 122.6°). The PES area covering critical point TS**1a** may be crucial for thermally initiated gradient channel leading to cyclobutene structures; such structures were formed from azatrienes having a phenyl substituent instead of the methoxy group [10]. The inversion process involving variation of the C^4NMe bond angle occurs smoothly with almost monotonous change of the total energy of the system and structural parameters of the imidothioate fragment. No appreciable response of the torsion angle C^3C^4NMe (ψ) was observed (~ 4°, Fig. 2) upon variation of φ.

The rotational channel of *syn*-(*Z*)/*anti*-(*E*) isomerization was examined in two ways. According to the first of these, the torsion angle θ was scanned with full optimization of all other structural parameters, and the second procedure implied "fixed scan" assuming a constant value of φ (β_1 in **Ia** and β_2 in **Ib**; Fig. 1); the angles β were determined as described in [30]. The first channel resulted in a collapsed state. Initial variation of ψ to 35° did not produce an appreciable structural reorganization of azatriene **I**. Only monotonous increase of φ to 126° was observed. The above change of the torsion angle corresponds to increase in the total energy of the molecule by 27 kJ/mol. Such "energy pumping" level is sufficient to initiate structural reorganization of the imidothioate fragment and flattening

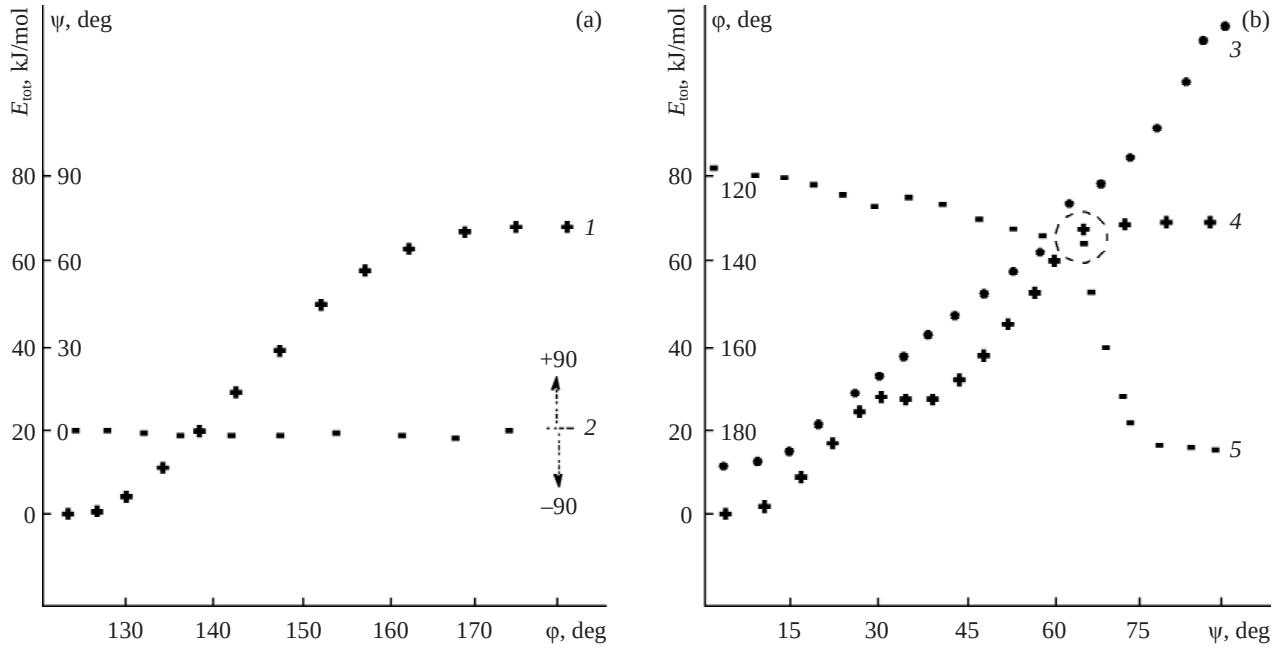


Fig. 2. (a) Change of (*1*) the total energy of the system and (*2*) torsion angle ψ upon variation of the bond angle φ. (b) Change of the total energy of the system upon variation of the torsion angle ψ (*3*) in the fixed scan mode and (*4*) with complete optimization; plot *5* corresponds to variation of φ in *4*. Area of transition to the collapsed state is marked with a circle. Given are the data for rotamer **Ia**.

Table 1. Total energies (E_{tot}, a.u.),[a] energies of zero-point harmonic vibrations (*ZPE*, a.u.),[b] relative energies (ΔE, kJ/mol), imaginary or least harmonic frequencies (iw/w_1, cm^{-1}), electrical dipole moments (μ, D), and dihedral angles between the imidothioate and methoxyallene fragments ($NC^4C^3C^2$, deg) of structures **Ia** and **Ib** and transition states TS**1a** and TS**1b**, calculated by the B3LYP/6-311G** method (Schemes 1, 2)

Structure	$-E_{tot}$	*ZPE*	ΔE	iw/w_1	μ	$NC^4C^3C^2$
(*E*)-**Ia**	801.57842	0.16352	0.0	30	2.00	124.2
TS**1a**	801.54824	0.16170	74.4	*i*294	1.29	174.0
(*Z*)-**Ia**	801.57160	0.16338	17.5	24	1.79	169.1
(*E*)-**Ib**	801.57748	0.16365	2.8	36	2.37	45.0
TS**1b**	801.54776	0.16180	75.9	*i*302	2.36	0.5
(*Z*)-**Ib**	801.57029	0.16365	21.7	35	1.54	39.4
(*R*)-**Ia**	801.52790	0.16515	128.4	*i*214	2.24	176.6
(*R*)-**Ib**	801.53238	0.16519	116.7	*i*234	2.05	5.6

[a] 1 a.u. = 2622.9897 kJ/mol.
[b] With correction by a factor of 0.9806.

of the molecular skeleton of azatriene **I**. In the ψ range from 74 to 76° (ΔE = 72 kJ/mol, Fig. 2), the structure approaches collapsed state with linear configuration of the C^4−N−Me fragment. This state resides in the vicinity of transition state TS**1** (TS**2**).

Analysis of the torsion mechanism of *syn*-(*Z*)/*anti*-(*E*) isomerization in the fixed scan mode with β_1 values of 115.5 and 118.3° for rotamers **Ia** and **Ib**, respectively, gave the following activation parameters relative to the *E* state: 128.4 kJ/mol for (*R*)-**Ia** and 113.9 kJ/mol for (*R*)-**Ib**. The obtained values are considerably lower than the activation barrier to *syn*-(*Z*)/*anti*-(*E*) isomerization in methanimine [196.6 kJ/mol, MP2(fc)/6-311+G**] [30]. The principal structural and energetic parameters of states (*R*)-**Ia** and (*R*)-**Ib** are given in Fig. 1 and Table 1. The molecular skeleton in (*R*)-states with rehybridized C^4 and N atoms is almost planar, and variations of the bond lengths in the imidothioate fragment are considerably smaller than in TS**1a** and TS**1b**. In the examined inversion and isomerization processes, the degree of charge separation changes only slightly (judging by the dipole moments; Table 1); presumably, we should expect no appreciable variations in the ratios of thermodynamic and kinetic parameters in going to phase states with different polarities.

Apart from the nitrogen atom, molecule **I** is capable of taking up a proton at the C=N carbon atom and C_α, C_β, and C_γ of the allene fragment, as well as at the O and S atoms in the substituents, with different prob-

Table 2. Total energies (E_{tot}, a.u.), energies of zero-point harmonic vibrations (*ZPE*, a.u.), proton affinities (*PA*), relative energies (ΔE, kJ/mol), imaginary or least harmonic frequencies (iw/w_1, cm^{-1}), electrical dipole moments (μ, D), and dihedral angles between the imidothioate and methoxyallene fragments ($NC^4C^3C^2$, deg) of structures **Ia** and **Ib** and transition states TS**2a** and TS**2b**, calculated by the B3LYP/6-311G** method

Structure	$-E_{tot}$	*ZPE*	*PA*	ΔE	iw/w_1	μ	$NC^4C^3C^2$
(*E*)-**Ia**H^+	801.96541	0.17740	234.1	5.3	40	2.70	146.9
TS**2a**H^+	801.92624	0.17470	–	100.9	*i*352	1.26	160.9
(*Z*)-**Ia**H^+	801.96749	0.17747	239.6	0.0	50	1.77	171.8
(*E*)-**Ib**H^+	801.96411	0.17743	233.9	8.8	41	3.97	30.0
TS**2b**H^+	801.92964	0.17491	–	92.6	*i*326	2.51	9.9
(*Z*)-**Ib**H^+	801.96030	0.17744	236.0	18.8	35	3.91	14.3
I($C_\alpha H^+$)	801.91292	0.17218	204.5	129.3	16	5.50	92.4
I($C_\beta H^+$)	801.95140	0.17165	229.0	26.9	49	2.69	98.5
I($C_\gamma H^+$)	801.88475	0.17234	186.7	203.6	44	2.29	110.2
I($C_N H^+$)	801.91578	0.17304	–	124.0	35	1.48	24.6

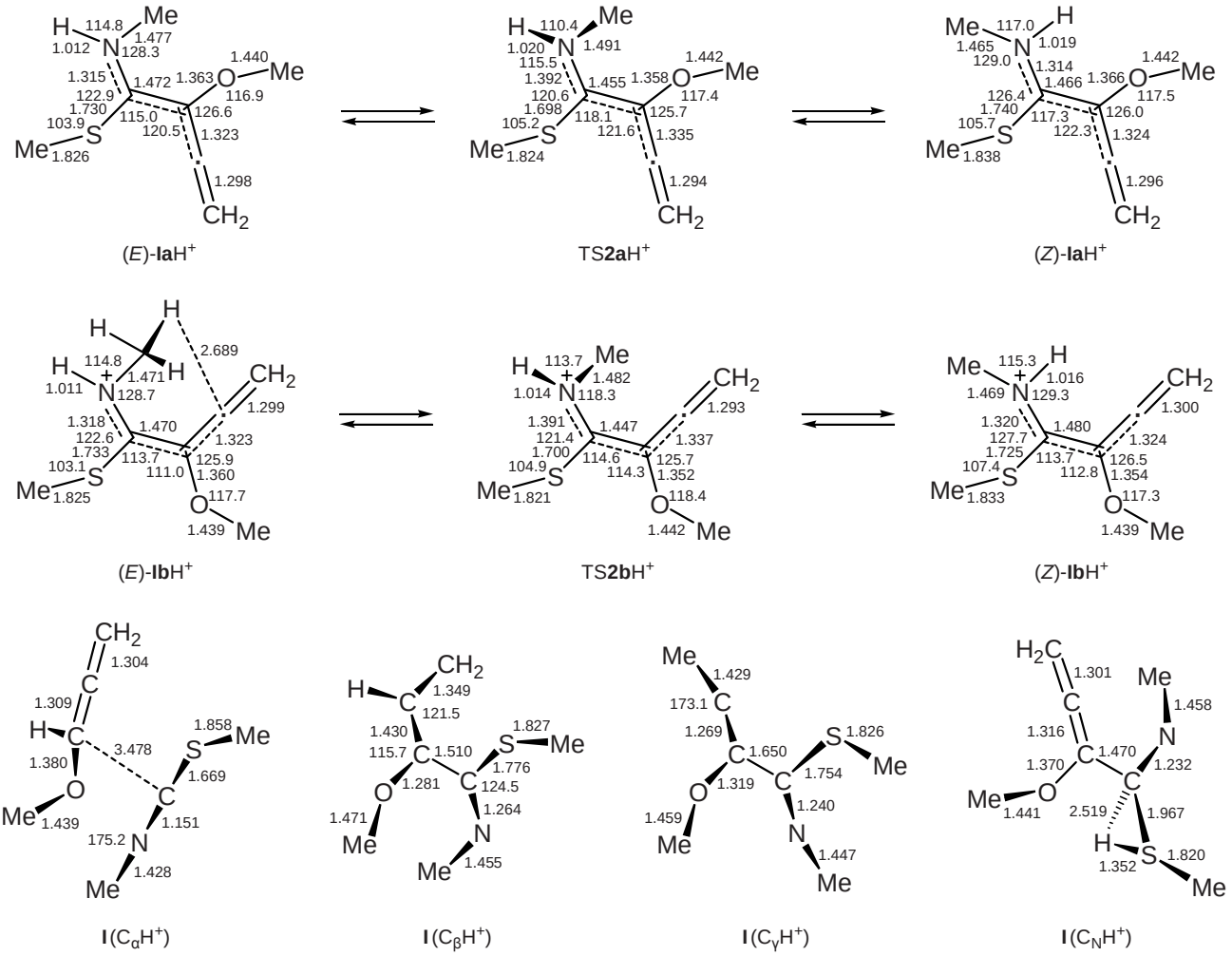


Fig. 3. Structures and principal geometric parameters of protonated forms of azatriene **I** and the corresponding transition states.

abilities. In addition, the C_β atom is a potential center for spatially oriented attack by a proton on the π-system of the C_α=C_β or C_β=C_γ bond. In order to estimate the relative probabilities for protonation of azatriene **I** at different centers, we calculated the thermodynamic stabilities of the corresponding protonated structures: NH^+: (*E*)-**Ia**H^+, (*Z*)-**Ia**H^+, (*E*)-**Ib**H^+, (*Z*)-**Ib**H^+; C_N: **I**(C_NH^+); C_α: **I**($C_\alpha H^+$); C_β: **I**($C_\beta H^+$); C_γ: **I**($C_\gamma H^+$); also, their proton affinities were estimated. The principal structural parameters of the most stable protonated species are given in Fig. 3.

The proton affinities were calculated using the standard formula: $PA(B) = \Delta E_{tot} - \Delta ZPE$, where $\Delta E_{tot} = E(B) - E(BH^+)$ and $\Delta ZPE = \Delta ZPE(B) - \Delta ZPE(BH^+)$]. The results showed (Table 2) that the most stable structures are (*E*)-**Ia**H^+, (*Z*)-**Ia**H^+, (*E*)-**Ib**H^+, (*Z*)-**Ib**H^+, and **I**($C_\beta H^+$). Their stability interval is confined to 27 kJ/mol, and the proton affinities range from 230 to 240 kcal/mol. N-Protonated structures are flattened, whereas protonation of alternative centers (except for C_N) leads to orthogonalization of the imidothioate and methoxyallene fragments (Tables 1, 2). Proton addition at the α-carbon atom of the allene fragment (fixed scan) gives rise to no-barrier elimination of the imidothioate fragment with formation of bimolecular complex **I**($C_\alpha H^+$) (Fig. 3) which was not detected experimentally. An analogous procedure for the C_N center, followed by complete optimization, gave stable S-protonated structure **I**(C_NH^+) via [1,2]-prototropic rearrangement with $E_a \approx 4$ kJ/mol (Fig. 3).

We failed to localize stationary state for the structure protonated at the C_β=C_γ π-bond system: barrierless proton migration yields the orthogonal state. Thus, only the C_β atom of the allene fragment can compete (to insignificant extent) with the nitrogen atom for proton. N-Protonation leads to inversion of the relative

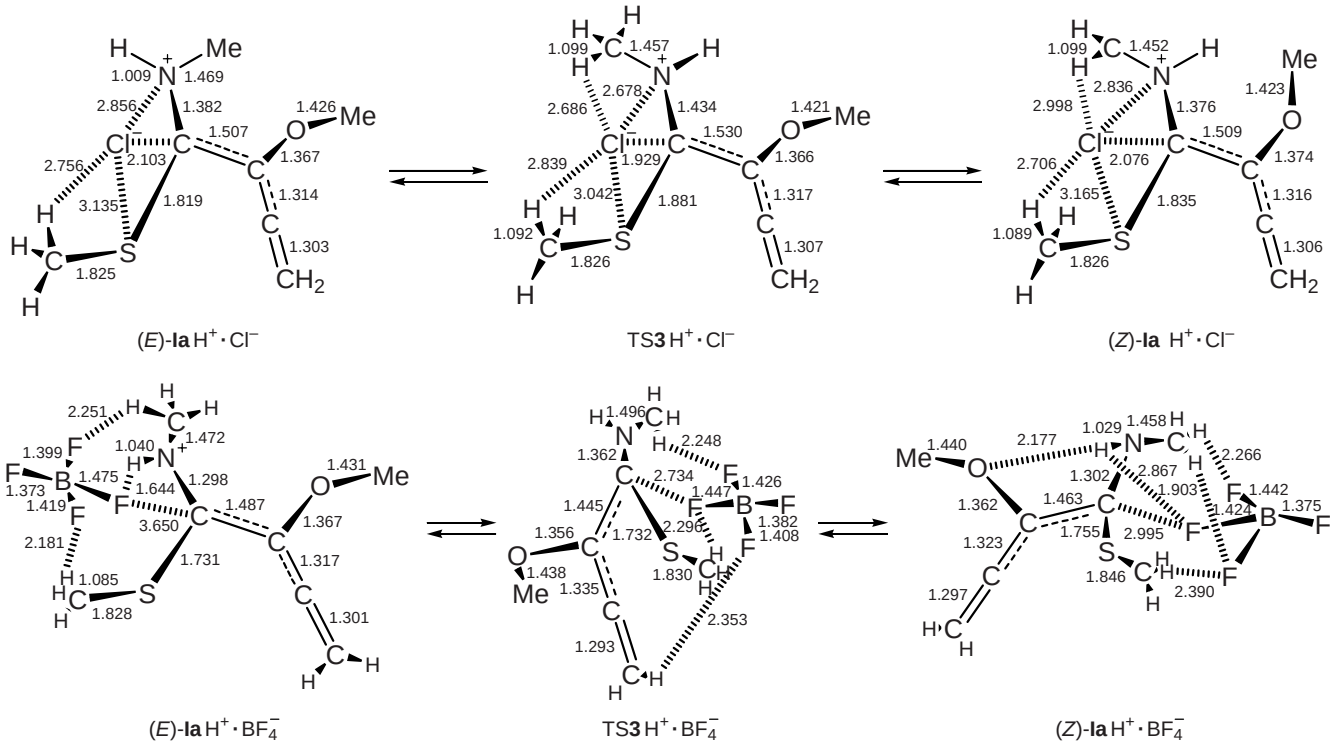


Fig. 4. Structures and principal geometric parameters of species involved in nucleophile-catalyzed *syn*-(Z)/*anti*-(*E*)-isomerization of azatriene **I**.

stabilities of rotamers **Ia** and **Ib**, so that the least polar structure (*Z*)-**Ia**H^+ possessing the maximal proton affinity becomes the most stable (Tables 1, 2). The energies of activation for *syn*-(*Z*)/*anti*-(*E*) isomerization in protonated rotamers (*Z*)-**Ia**H^+ and (*Z*)-**Ib**H^+ are 95.6 and 83.8 kJ/mol, respectively. The structures and geometric parameters of transition states TS**2a**H^+ and TS**2b**H^+ are given in Fig. 3. The obtained values occupy intermediate place between those found for the inversion and torsion mechanisms of isomerization.

Table 3. Total energies (E_{tot}, a.u.), energies of zero-point harmonic vibrations (*ZPE*, a.u.), relative energies (ΔE, kJ/mol), imaginary or least harmonic frequencies (iw/w_1, cm^{-1}), and electrical dipole moments (μ, D) of structures (*E*)-**Ia**H^+ and (*Z*)-**Ia**H^+ and transition states TS**3**H^+, calculated by the B3LYP/6-311G** method (Scheme 6)

Structure	$-E_{tot}$	*ZPE*	ΔE	iw/w_1	μ
(*E*)-**Ia**$H^+\cdot Cl^-$	1262.41084	0.17872	12.6	22	2.71
TS**3**$H^+\cdot Cl^-$	1262.38856	0.17511	61.6	*i*958	1.98
(*Z*)-**Ia**$H^+\cdot Cl^-$	1262.41491	0.17799	0.0	27	2.44
(*E*)-**Ia**$H^+\cdot BF_4^-$	1226.78372	0.19225	8.4	24	13.99
TS**3**$H^+\cdot BF_4^-$	1262.74910	0.19112	96.2	*i*1128	9.78
(*Z*)-**Ia**$H^+\cdot BF_4^-$	1262.78655	0.19188	0.0	29	9.35

With a view to estimate the activation parameters for nucleophile-catalyzed *syn*-(*Z*)/*anti*-(*E*) isomerization we used Cl^- and BF_4^- as counterions. As initial structure we selected the most stable (*Z*)-**Ia**H^+ rotamer. Figure 4 shows the optimal structures of bimolecular ionic complexes.

The optimal biionic state of complex (*Z*)-**Ia**$H^+\cdot Cl^-$ is invariant to the position of the chloride ion. The minimal depth of the potential well is 26 kJ/mol with respect to interaction with the C^4 center. Complex (*Z*)-**Ia**$H^+\cdot BF_4^-$ turned out to be even more stable toward variation of the position of the counterion. The potential energy surface for *syn*-(*Z*)/*anti*-(*E*) isomerization catalyzed by nucleophile was analyzed as follows. Initially, the torsion angle C^3C^4NMe was varied through a step of 10 deg, the other geometric parameters being optimized completely. As a result, we defined an area containing transition state which was then localized by the procedure described above. This approach allowed us to avoid fitting into the gradient channel leading to a product with a covalent C^4–Cl bond. While moving to the C^4 atom in transition state TS**3**$H^+\cdot Cl^-$ (Fig. 4), the chloride ion partially blocks excess positive charge accumulated during the rotation process (from the π system with quaternized nitrogen

atom). Due to high mobility of the counterion, the *syn*-(*Z*)/*anti*-(*E*) isomerization is characterized by a fairly low barrier. It was estimated at 61.6 kJ/mol (Table 3); this value is comparable with the barrier to inversion isomerization (Table 1).

The BF_4^- counterion in (*Z*)-**Ia**$H^+ \cdot BF_4^-$ ion pair forms stronger dative bonds with protons of the methyl and NH groups, and it cannot effectively block the C^4 center. Therefore, the activation barrier to *syn*-(*Z*)/*anti*-(*E*) isomerization increases by 34.6 kJ/mol relative to that found for (*Z*)-**Ia**$H^+ \cdot Cl^-$. Presumably, the activation parameters for nucleophile-catalyzed reactions should increase when nearest solvate environment is taken into account, and phase barriers are likely to be intermediate between those for isomerization of protonated forms with and without participation of the counterion.

Thus, the results of our study show that the most probable mechanisms for *syn*-(*Z*)/*anti*-(*E*) isomerization in methyl 2-methoxy-*N*-methylbuta-2,3-dienimidothioate (**I**) are inversion and nucleophile-catalyzed with a single-atom counterion.

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