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Dedicated to Full Member of the Russian Academy of Sciences
B.A. Trofimov on his 70th anniversary

Theoretical Conformational Analysis of Divinyl Selenide

Yu. Yu. Rusakov, L. B. Krivdin, N. V. Istomina, V. A. Potapov, and S. V. Amosova

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

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Abstract—Theoretical conformational analysis of divinyl selenide was performed in terms of the Møller–Plesset second-order perturbation theory (MP2/6-311G**). Angular distribution of the probability density of populations of its rotational conformers was determined by analysis of the rotational potential energy surface. Divinyl sulfide was found to exist as an equilibrium mixture of three conformers having essentially nonplanar structure; the major conformer is *syn-s-cis-s-trans*, and the two others are *syn-* and *anti-s-trans-s-trans* with higher energy.

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Divinyl selenide (**I**) is an important intermediate product in the synthesis of various organoselenium compounds [1]. We previously developed a highly efficient procedure for the preparation of divinyl selenide from accessible initial compounds, elemental selenium and acetylene [2], which favored wide application of divinyl selenide in organoselenium chemistry. The steric structure of divinyl selenide molecule attracts specific interest; it was extensively studied in 1990s with the aid of various physical and quantum-chemical methods, and the main results of these early studies were reviewed in [3].

In the present work we turned back to the steric structure of divinyl selenide and performed theoretical analysis of its conformations at a higher level of theory by considering the relative total energy surface and particular localized conformers and transition states in terms of a new approach implying calculation of continuous angular distribution of the probability density of rotamer populations [4].

Figure 1 shows a three-dimensional potential energy surface for internal rotation in the divinyl selenide molecule about both Se−C bonds, which was calculated at the MP2/6-311G** level of theory with account taken of electron correlation. The angular distribution of rotational states was determined from the two-dimensional Boltzmann distribution at 300 K on the basis of the potential energy surface. Numerical integration of the corresponding areas on the three-dimensional surface allowed us to determine the conformational composition of divinyl sulfide with a high accuracy.

Analysis of the three-dimensional potential energy surface (Fig. 1) and its two-dimensional representation, potential energy map,* showed that divinyl selenide exists as an equilibrium mixture of three rotational conformers: one fourfold degenerate *s-cis-s-trans* and two nonplanar doubly degenerate *s-trans-s-trans*, which are converted into each other through the corresponding transition states. More detailed analysis of the rotational potential energy surface in the above regions revealed three conformers **A**, **B**, and **C**, and five transition states **AA**, **AB**, **AC**, **BC**, and **AA′** whose parameters are given in table. The transition states between the three localized conformers are also degenerate: the transformations **A** ↔ **A** through **AA** and **AA′** are doubly degenerate, and the transitions **A** ↔ **B**, **A** ↔ **C**, and **B** ↔ **C** through **AB**, **AC**, and **BC**, respectively, are fourfold degenerate.

The nature of all localized conformers and transition states of divinyl selenide was determined by analysis of harmonic vibration frequencies for each particular structure. All transition states **AA**, **AB**, **AC**, **BC**,

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* The potential energy surface is available from the authors upon request by e-mail.

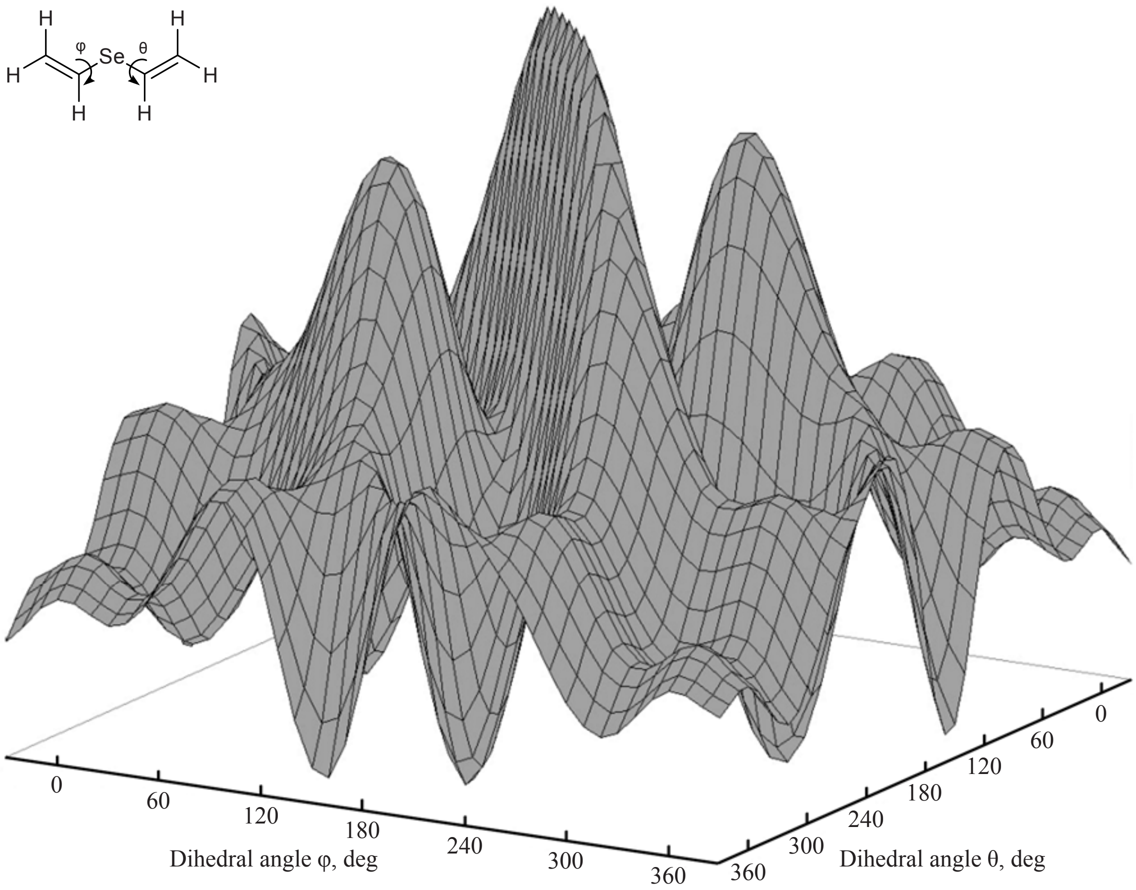


Fig. 1. Rotational potential energy surface of divinyl selenide according to the MP2/6-311G** calculations.

and **AA′** are characterized by one imaginary frequency (see table), while no imaginary frequencies were found for conformers **A**, **B**, and **C**. The equilibrium structures of all conformers and transition states, optimized at the MP2/6-311G** level of theory, are shown in Fig. 2.

According to the calculations, the most energetically favorable conformer is *syn-s-cis-s-trans* (**A**), where the vinyl groups decline from the C–Se–C plane by dihedral angles of ~20 and 45°. The two other conformers having higher energies, *anti-s-cis-s-trans* (**B**)

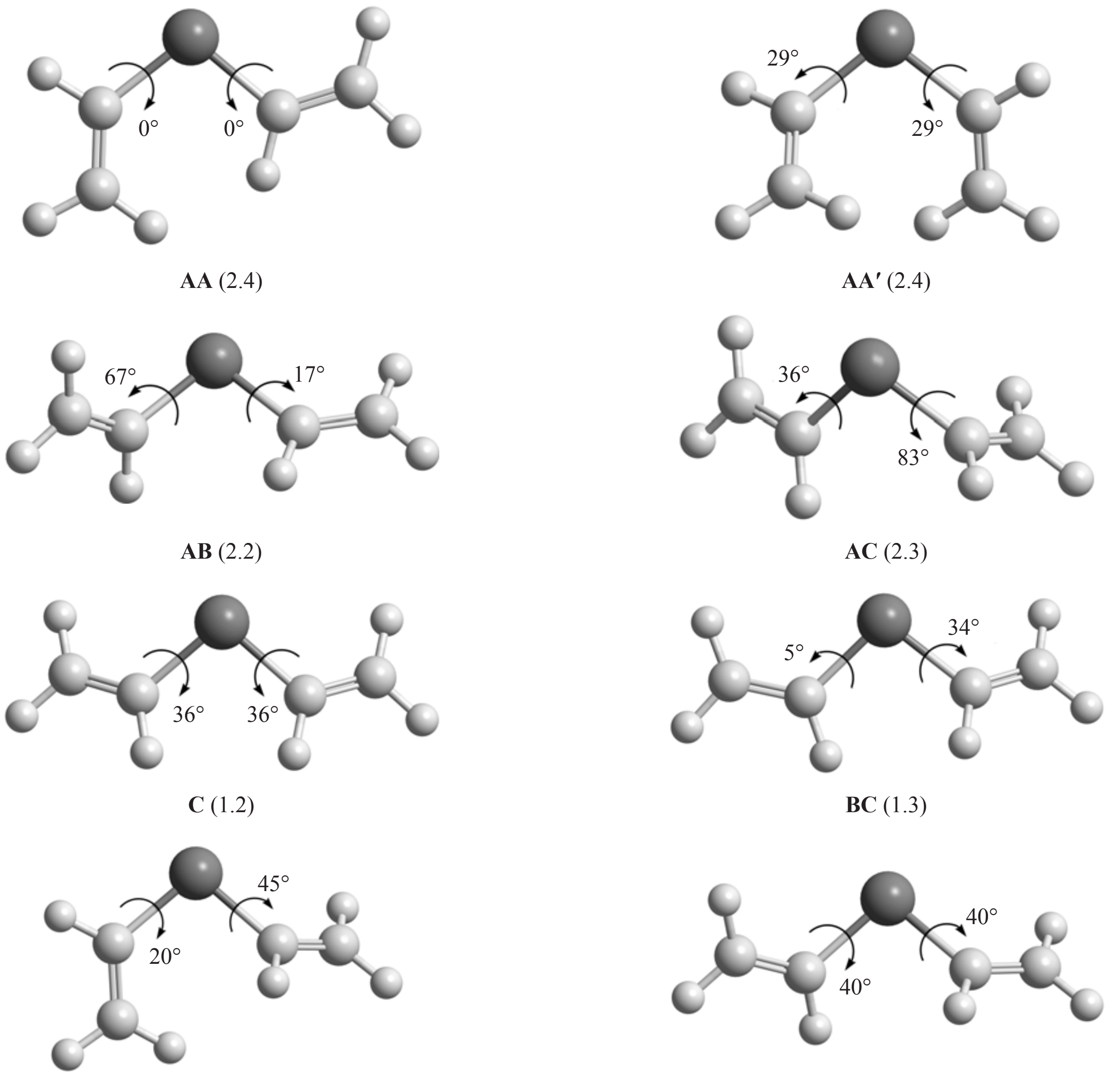
Conformers of divinyl sulfide and the corresponding transition states

Conformation[a]	Denotation[b]	Type	Relative energy, kcal/mol	Deviation from planar structure,[c] deg		Imaginary frequency, cm^{-1}
syn-s-cis-s-trans	**A**	Conformer	0.0	20	45	None
anti-s-trans-s-trans	**B**	Conformer	0.8	40	40	None
syn-s-trans-s-trans	**C**	Conformer	1.2	36	36	None
syn-s-trans-s-trans	**BC**	Transition state **B** ↔ **C**	1.3	5	34	64.81
anti-s-cis-s-trans	**AB**	Transition state **A** ↔ **B**	2.2	67	17	76.49
syn-s-trans-s-cis	**AC**	Transition state **A** ↔ **C**	2.3	36	83	81.85
s-cis-s-trans	**AA**	Transition state **A** ↔ **A**	2.4	0	0	160.80
anti-s-cis-s-cis	**AA′**	Transition state **A** ↔ **A**	2.4	29	29	67.08

[a] Denotations *syn* and *anti* refer to mutual orientation of the two vinyl groups with respect to the C–Se–C plane, and *s-cis* and *s-trans* refer to orientation of each vinyl group with respect to the nearest Se–C bond.

[b] See Fig. 2.

[c] Dihedral angles between the vinyl group and the C–Se–C plane are given (Fig. 2).



AA (2.4) **AA′** (2.4)

AB (2.2) **AC** (2.3)

C (1.2) **BC** (1.3)

A (0.0) **B** (0.8)

Fig. 2. Equilibrium conformers and conformational transition states of divinyl selenide, optimized at the MP2/6-311G** level of theory. The relative total energies (kcal/mol) are given in parentheses. Arrows show angular deviations of the vinyl groups from the C–Se–C plane.

and *syn*-*s*-*trans*-*s*-*trans* (**C**), are also essentially nonplanar: deviations of both vinyl groups from the C–Se–C plane reach 35–40°.

Among five localized transition states, that corresponding to the **B** ↔ **C** transition, *syn*-*s*-*trans*-*s*-*trans* (**BC**), has the lowest energy; its relative total energy is as low as 1.3 kcal/mol. The relative total energies of *anti*-*s*-*cis*-*s*-*trans* (**B**) and *syn*-*s*-*trans*-*s*-*trans* (**C**) are 0.8, and 1.2 kcal/mol, respectively. Thus the conformational transition **B** ↔ **C** is characterized by a very low activation barrier. On the other hand, the relative total energies of four other transition states **AB**, **AC**, **AA**, and **AA′** are considerably larger; they range from 2.2 to 2.4 kcal/mol. It is interesting that conformational transition between two degenerate conformers **A** can take two paths through transition states **AA** and **AA′** with an activation barrier of 2.4 kcal/mol in each case (Fig. 2).

By numerical integration of the three-dimensional probability density surface we estimated the percentage of each conformer in the gas phase with account taken of degeneracy of the conformers: 82% of *syn*-*s*-*cis*-*s*-*trans*, 11% of *anti*-*s*-*trans*-*s*-*trans*, and 7% of *syn*-*s*-*trans*-*s*-*trans*. Our results are more accurate than those obtained previously [5] at the HF SCF level (with no account taken of electron correlation), according to which the mole fraction of the *s-cis-s-trans* conformer in the gas phase at 300 K was only 40%, i.e., this conformer could not be regarded as predominant.

Optimization of the geometric parameters of divinyl selenide conformers and calculation of their total energies were performed in terms of the Møller–Plesset second-order perturbation theory (MP2/6-311G**) using GAMESS software [6].

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