AB INITIO STUDY OF THE CONFORMATIONAL AND
GEOMETRICAL ISOMERISM IN HETEROALLYL
AND HETEROPROPENYL SYSTEMS

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Conformational isomerism has been studied by ab initio methods (RHF/6-31+G*, MP2/6-31+G*) for
CH₂=CHCH₂X heteroallyl and CH₃CH=CHX heteropropenyl systems (X = H, Me, NMe₂, OMe, PMe₂,
SMe, ONCH₂). In 3-heteroprop-1-enes, substituents preferably occupy the AC position relative to the C=C
double bond. The E isomers of 1-methylthio- and 1-methoxyprop-1-enes, which are thermodynamically
more stable, have two stable forms, SP and AC; for 1-dimethylamino- and 1-imethylphosphinoprop-1-enes,
the stable forms are AP and SC. The molecule of the E isomer of formoxime propenyl ether exists in two
stable rotamer forms, SC and AP, the latter being predominant. The Z isomers preferably exist in the form
of AC (X = CH₂O, CH₃S) and AP (X = (CH₃)₂N, (CH₃)₂P, CH₂=NO) conformations. Migration of the
double bond toward an heteroatom in formoxime allyl ether, forming the E and Z isomers, is energetically
favorable, the Z isomer being thermodynamically preferable.

Key words: heteroallyl compounds, heteropropenyl compounds, isomerism, conformation, ab initio
calculation.

Previously, we have considered a number of propenes (CH₂=CHCH₂X, CH₃CH=CHX, X = H, CH₃, OCH₃,
SCH₃, N(CH₃)₂, P(CH₃)₂) [1-3] in an effort to study the substituent effect on isomerization of the double bond position in heteroallyl
systems. We discussed only thermodynamic aspects of isomerization. At the same time, the conformational structure of
heteroallyl and heteropropenyl systems deserves special consideration.

Heteroallyl and heteropropenyl molecules are often characterized by structural nonrigidity. A study of their
conformational isomerism involves a number of difficulties because the conformers have internal nuclear motions with large
amplitudes. The results of experimental studies are directly related to the characteristic time of the methods used and lifetime
of the corresponding conformer. When the lifetime of a molecular conformation exceeds characteristic time of the method
(and hence transitions between conformers are impossible), the resulting structures correspond to minima on the potential
energy surface (PES). If, however, the system has enough time to pass from one form to another during the measurements,
then the experiment yields an average picture. In these cases the potential energy surface of the molecule obtained by
quantum-chemical calculations serves as an additional reliable source of information about the number of stable conformers,
their relative stability, and paths of mutual transformations [4].

The present account aims at an ab initio quantum-chemical investigation of conformational isomerism in the series
of CH₂=CHCH₂X heteroallyl and CH₃CH=CHX heteropropenyl compounds (X = CH₃, OCH₃, SCH₃, N(CH₃)₂, P(CH₃)₂,
ON=CH₂).
CALCULATION PROCEDURE

Internal rotation curves of all molecules are obtained in the 6-31+G* basis within the framework of the restricted Hartree–Fock method. Potential functions of internal rotation are plotted by stepwise variation of a corresponding torsion angle by 30°. The geometry of local minima and transition states is refined using standard techniques of the GAMESS program. For all transition states, the Hesse matrix has one negative eigenvalue at a critical point. Relative energies of stable conformers are refined with inclusion of correlation effects in the MP2 approximation using GAMESS [5] software on a Pentium III computer (LINUX).

CONFORMATIONAL ISOMERISM OF HETEROALLYL COMPOUNDS

As is known, rotation around a single bond in organic compounds has energy barriers resulting from long-range interactions between valence-nonbonded atoms. This leads to the formation of a number of stable conformers. Molecules from the propene series, X–C(3)H2–C(2)H=C(1)H2, can exist as four structural conformations depending on the position of the X substituent (Scheme 1): synplanar (SP), antiplanar (AP), synclinal (SC), and anticlinal (AC) [6].

For unsubstituted propene 1 (X=H), the characteristic conformation is SP with a torsion angle \( \angle \text{HC}(3)\text{C}(2)\text{C}(1) \) equal to 0 [7]. This structure corresponds to a minimum on the potential curve of internal rotation in the propene molecule, since it has minimal repulsion between the electrons of the C–H \( \sigma \)-bonds and those of the C(2)=C(1) \( \pi \)-bond. In an SC conformation, this repulsion is maximal, and the structure corresponds to a transition state (Table 1), which is responsible for the internal rotation barrier of 9.20 kJ/mole. Further rotation of the methyl group leads to an AC structure, where the \( \angle \text{HC}(3)\text{C}(2)\text{C}(1) \) torsion angle is 120°. For the propene molecule, this structure is identical to the SP structure.

Based on the structure of the unsubstituted propene, we can predict either the SP or AC position of substituents in 3-heteroprop-1-enes. Indeed, the curve of internal rotation around the C(3)–C(2) bond in but-1-ene CH3C(3)H2C(2)H=C(1)H2 (2) shows that this structure exists in the form of SP and AC conformers. For a stable AC conformer, the value of a \( \angle \text{MeC}(3)\text{C}(2)\text{C}(1) \) torsion angle is close to that of \( \angle \text{HC}(3)\text{C}(2)\text{C}(1) \) in the AC form of unsubstituted propene (Table 1). As in 1, the AP and SC rotamers are transition states. The activation barrier of a transition between the two AC structures is 9.20 kJ/mole.

<table>
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<tr>
<th>X substituent</th>
<th>SP</th>
<th>SC</th>
<th>AC</th>
<th>AP</th>
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<tr>
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<td>8.79</td>
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<td>120.0</td>
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<td>–10.75</td>
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</table>

TABLE 1. Relative Energies of the Conformers (\( \Delta E \), kJ/mole) and Values of the \( \angle \text{XC}(3)\text{C}(2)\text{C}(1) \) Torsion Angles (\( \varphi \), deg) in Heteroallyl Systems