MNDO STUDY OF THE *E-Z* ISOMERIZATION MECHANISM OF $H_2C=NR$ MOLECULES (R = H, CH_3, NH_2, OH, F)

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The geometry and *E-Z* isomerization mechanism were studied by the MNDO method for $H_2C=NR$ molecules with R = H, CH_3, NH_2, OH and F. All the molecules save $H_2C=NNH_2$ possess a plane of symmetry and isomerize by the inversion mechanism, whereas $H_2C=NNH_2$ has a nonsymmetrical geometry and the inversion-rotation mechanism is more favourable for its isomerization. Dependent considerably on the substituent at the nitrogen atom, the isomerization barrier height increases in order R = CH_3, H, NH_2, OH, F.

Compounds containing C=N double bonds play an important role in organic chemistry and biochemistry[1]. Their electronic structure and reactivity are affected particularly by the substituent at the nitrogen atom. With respect to this substituent, the compounds are classed as azomethines, or Schiff bases, oximes, hydrazones and other groups. A feature they have in common is the presence of the polar double bond between the carbon and nitrogen atoms and a lone electron pair at the nitrogen atom. Due to the absence of free rotation about the C=N bond, they can exist as two stereoisomers, *E* and *Z*. The isomerization barrier height depends primarily on the substituent at the nitrogen atom, electron acceptor substituents causing the barrier to increase[2].

Conversion of the *E*-isomer to the *Z*-isomer can occur by two mechanisms[2-4], viz. by inversion, during which atom X bonded at the nitrogen atom remains in the molecular plane while the CNX angle changes, and by rotation, during which the NX bond tilts out of the molecular plane (similarly as in the twisting of olefins). A mixed mechanism representing a linear combination of the two basic types is also feasible (Scheme 1).

Experimental data indicate that in the ground state, isomerization proceeds largely by the inversion mechanism[2], whereas in the excited $n \rightarrow \pi^*$ state, where the double bond nature of the C=N bond is disturbed by the presence of an electron in the antibonding π^* orbital, the rotation mechanism is more favourable[2,3].

These conclusions are also confirmed by *ab initio* calculations. The theoreticians, efforts have centered particularly on the basic compounds from the class of imines

and oximes, viz. methanimine[5-7] and formaldoxime[8,9]. Theoretical information on the isomerization mechanism of other types of compounds with C=N bonds, particularly C-alkylimines or hydrazones, however, is as yet rather incomplete. To our knowledge, no comprehensive *ab initio* study exists (except for ref.[8], confined to the inversion mechanism) where the mechanism of the *E–Z* isomerization of different types of compounds with C=N bonds is studied in a complex manner using a common theoretical approach to all of them.
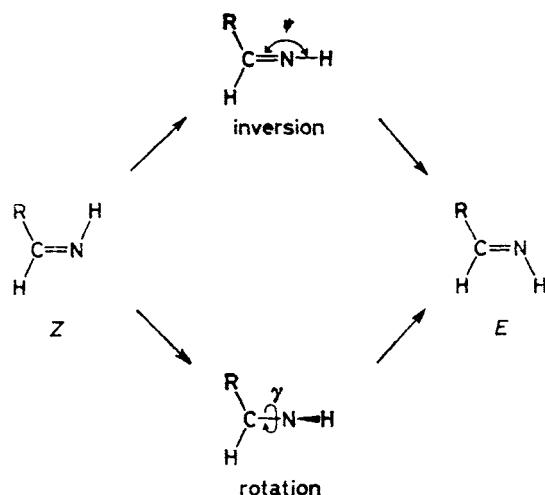
SCHEME 1

The aim of the present work was to contribute to the understanding of this mechanism based on a study of a set of H$_2$C=NR compounds using the MNDO semiempirical approach[10]. Widely and successfully employed for the investigation of reaction mechanisms[11], the MNDO method makes a reasonable compromise between precision demands and computer time consumption.

CALCULATIONS

The semiempirical MNDO method[10] was used for the calculations. The geometries of the molecules studied were optimized by employing the Davidon–Fletcher–Powell procedure. The isomerization mechanism was examined and the geometries of the transition states approximately determined by the reaction coordinate method[12], i.e., all internal coordinates were optimized completely for fixed inversion or rotation angles. The transition structures so obtained were characterized by analysis of eigenvalues of the force constant (Hess) matrix[13] so that just one of them be negative.

RESULTS AND DISCUSSION

The conformation and E–Z isomerization mechanism were studied for $H_2C{=}NR$ molecules where R was H, CH_3, NH_2, OH and F. The basic geometry parameters of these molecules obtained by MNDO calculations are given in Table I. The calculated dependence of their energy on the inversion angle ψ for the planar arrangement of the $H_2C{=}N$ grouping (rotation angle $\gamma = 0°$) is plotted in Fig. 1, whereas Fig. 2 shows the dependence of the molecular energy on the out-of-plane angle α, which characterizes the tilting of the substituent R from the molecular plane at the rotation angle $\gamma = 90°$.

TABLE I

Structure and energy parameters of $H_2C{=}NR$ molecules

Molecule	$r_{C=N}$ pm	CNX angle deg	Heat of formation kJ mol^{-1}	Inversion energy, kJ mol^{-1}	
				MNDO	*ab initio*[8]
$H_2C{=}NCH_3$	128·2	123·6	68·6	79·2	109·6
$H_2C{=}NH$	128·2	114·5	82·6	111·7	108·8
$H_2C{=}NNH_2$	129·6	119·4	129·9	131·4[a]	137·7
$H_2C{=}NOH$	130·4	117·1	− 30·4	187·8	246·0
$H_2C{=}NF$	131·0	118·1	38·9	213·8	321·7

[a] Inversion-rotation energy.

TABLE II

Electronic parameters of $H_2C{=}NR$ molecules

Molecule	Net atomic charge		Orbital energy, eV[a]			Dipole moment D[b]
	C	N	π	n	π^*	
$H_2C{=}NCH_3$	0·102	−0·299	− 11·4	− 10·7	1·1	1·70
$H_2C{=}NH$	0·070	−0·241	− 12·1	− 11·2	1·2	1·93
$H_2C{=}NNH_2$	0·052	−0·190	− 11·4[c]	− 10·0[c]	1·0	1·70
$H_2C{=}NOH$	0·021	−0·128	− 10·5	− 11·4	1·0	0·45
$H_2C{=}NF$	0·028	−0·043	− 11·8	− 12·2	0·2	2·71

[a] $1 \text{ eV} = 96·4868 \text{ kJ mol}^{-1}$; [b] $1 \text{ D} = 3·33564 . 10^{-30} \text{ C m}$; [c] n and π orbitals are mixed.

Table I also gives the calculated total energies of the molecules and their iso-merization barrier heights along with the *ab initio* data from ref.[8]; the relevant electronic characteristics are given in Table II.

Methanimine $H_2C=NH$

Methanimine is the simplest compound containing a $C=N$ bond. The hydrogen atoms have neither electron donor nor electron acceptor properties, and so the compound can serve as a model for examining the electronic structure of the $C=N$ bond virtually unaffected by substituents. For this reason, methanimine has been subject to both semiempirical and *ab initio* studies[5-7,14].
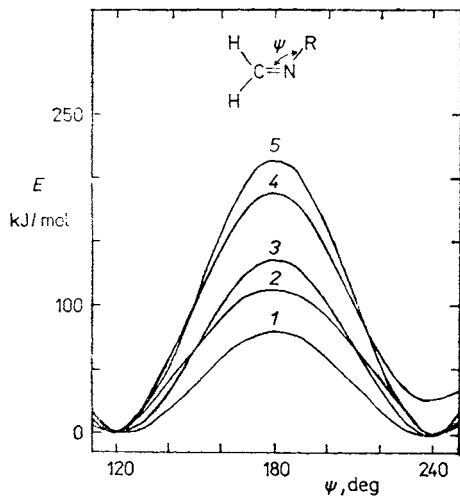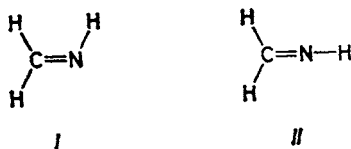
FIG. 1

Dependence of molecular energy on the inversion angle ψ for *1* $H_2C=NCH_3$, *2* $H_2C=NH$, *3* $H_2C=NNH_2$, *4* $H_2C=NOH$, *5* $H_2C=NF$
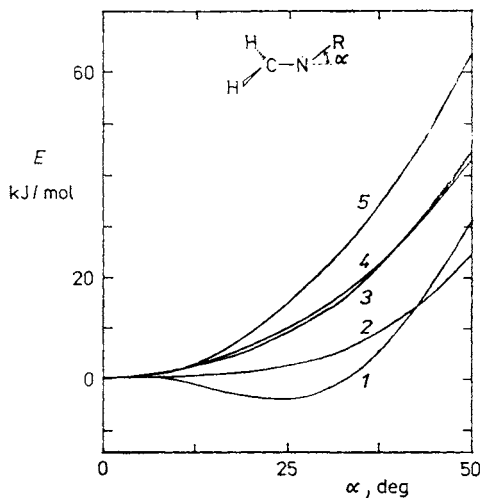
FIG. 2

Dependence of molecular energy on the out-of-plane angle α for *1* $H_2C=NNH_2$, *2* $H_2C=NF$, *3* $H_2C=NOH$, *4* $H_2C=NH$, *5* $H_2C=NCH_3$

The MNDO optimized geometry *I* is in a good agreement with experimental data[15]. The transition state of isomerization *II* is 111·7 kJ mol⁻¹ higher than for *I*. The loss of planarity in *II* due to the tilting of the hydrogen at the nitrogen atom out of the molecular plane brings about an energy increase (Fig. 2); so, the pure inversion mechanism can be assumed to operate in methanimine.

N-*Methylmethanimine* $H_2C{=}NCH_3$

The optimum geometry of N-methylmethanimine *III* is 0·85 kJ mol⁻¹ more stable than the geometry of conformer *IV*, from which it only differs by the methyl group rotation angle. Due to the electron donor properties of the methyl substituent, a considerable charge separation between the carbon and nitrogen atoms exists in this compound.


III

IV

V

VI
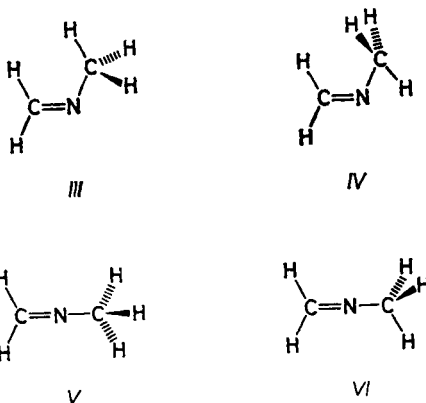
The isomerization transition states *V* and *VI* possess identical energies; the isomerization barrier height is 79·2 kJ mol⁻¹, which is the lowest of the molecules studied. Fig. 2 demonstrates that with N-methylmethanimine, also, isomerization proceeds by the inversion mechanism.

Formaldehyde Hydrazone $H_2C{=}NNH_2$

Establishing the optimum geometry of hydrazones is an interesting, and so far not completely solved, conformation problem[16]. According to our MNDO calculations, $H_2C{=}NNH_2$ exists in the nonsymmetric structure *VII* where the CH_2 group is about 5° out of the CNN plane and the amine group nitrogen is sp^3 hybridized. This geometry possesses a lower energy than as obtained by the earlier MNDO calculation[16] where complete optimization apparently was not performed. Our results agree with experimental data[16] as well as with the recent *ab initio* calcula-

tions[8]. The symmetric structure *VIII* is only 0·95 kJ mol^{-1} above *VII*, and structures *IX* and *X* are 34·0 and 30·7 kJ mol^{-1}, respectively, higher. These calculations indicate the possibility of a basically free conformation change at the amine group nitrogen.
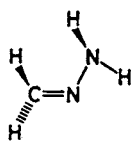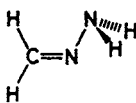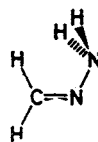
     VII   *VIII*   *IX*
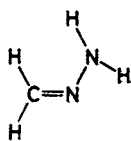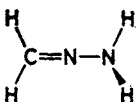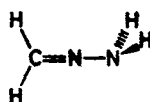
     X   *XI*   *XII*
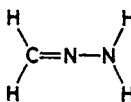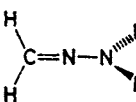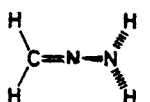
     XIII   *XIV*   *XV*

     For establishing the geometry of the *E–Z* isomerization transition state, structures *XI – XIV* were optimized assuming the linear arrangement of the CNN grouping. These structures lie 135·5, 158·7, 185·5 and 533·5 kJ mol^{-1}, respectively, above *VII*. The most stable, however, is structure *XV* with the amine group slightly out of the molecular plane and with the CNN angle 164·5°; this structure lies 131·4 kJ mol^{-1} above *VII* (see also Fig. 2). By analysis of the force constant matrix eigenvalues, structure *XV* was characterized as a true transition state, with a single negative value corresponding to the rotary motion about the C=N bond. It is not possible to compare our results directly with the *ab initio* data[8] because the combined mechanism has not been treated in the latter, although experimental studies have indicated the occurrence of this mechanism for some heterosubstituted imines[17]. The possibility of occurrence of the combined mechanism is also confirmed by the fact that the experimental height of the *E–Z* isomerization barrier, 90 – 100 kJ mol^{-1}, is considerably lower than as would be expected based on empirical dependences on the N-substituent electronegativities[2].

Formaldoxime $H_2C=NOH$

Formaldoxime can exist in two conformations, *XVI* and *XVII*; the former, with the OH bond in the *trans* position with respect to the $C=N$ bond, is $26.7\ kJ\ mol^{-1}$ more stable than the latter, which is consistent with microwave measurements[18] and *ab initio* calculations[8,9]. The two conformers can transform into one another via the transition state *XVIII* with a barrier of $29.6\ kJ\ mol^{-1}$ above *XVI* The transition state *XIX* is considerably less favourable, lying $224.1\ kJ\ mol^{-1}$ above *XVI*.
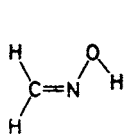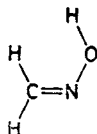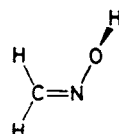

XVI   XVII   XVIII
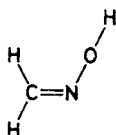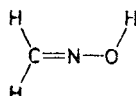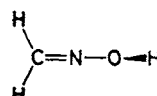
XIX   XX   XXI
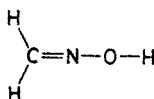
XXII

The *E–Z* isomerization at the $C=N$ bond proceeds by inversion via *XX* with a barrier of $187.8\ kJ\ mol^{-1}$. The transition structures *XXI* and *XXII* lie 221.2 and $614.0\ kJ\ mol^{-1}$, respectively, above *XVI*. The dependence of the energy of *XX* on the OH out-of-plane angle again demonstrates that the inversion mechanism is preferred over the rotation mechanism for this compound.

N-*Fluoromethanimine* $H_2C=NF$

In its ground state, N-fluoromethanimine assumes the planar geometry *XXIII*, similarly as methanimine. The inversion barrier is rather high, $213.8\ kJ\ mol^{-1}$ — the highest barrier of those studied. This is a consequence of the unfavourable electronic interaction between the lone electron pairs at the nitrogen and fluorine atoms in

XXIV. For simple haloimines, high isomerization barriers have also been observed experimentally[2]. Fig. 2 again demonstrates preference of the inversion mechanism over the rotation mechanism.

XXIII   XXIV
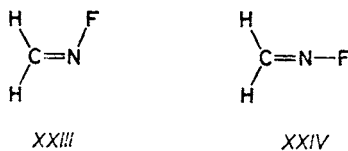
The optimum geometries of the H$_2$C=NR molecules studied have some features in common. The imine group nitrogen is sp^2 hybridized and the CNX angle lies within the region of 114—124°, in contrast to similar compounds with strongly electropositive substituents such as H$_2$C=NBeH or H$_2$C=NBH$_2$ where the CNX angle is 180° (ref.[7]). Except for H$_2$C=NNH$_2$, the molecules studied possess a plane of symmetry. The substituent at the nitrogen atom also affects appreciably the charges at the carbon and nitrogen atoms as well as the C=N bond length, which increases with increasing electron acceptor nature of the substituent (from 128·2 pm in H$_2$C=NH to 131·0 pm in H$_2$C=NF). These results are consistent with experimental data[1] as well as with *ab initio* calculations[8].

The *E-Z* isomerization barrier height also depends appreciably on the substituent at the nitrogen atom (Table I). Whereas the electron donor methyl substituent lowers this barrier in comparison to the unsubstituted methanimine, electron acceptor substituents increase it in order NH$_2$, OH, F. The experimental isomerization barrier heights lie within the region of 40—160 kJ mol^{-1} for various C=N compounds and also depend on substituents, particularly those at the nitrogen atom[1,2]: the barrier height increases with increasing electronegativity of this substituent. Our MNDO results are in a fairly good agreement with the *ab initio* calculations[8] (Table I), frequently, however, the MNDO data are lower than the *ab initio* data, particularly for H$_2$C=NF.

The isomerization mechanism is inversion in all cases except for H$_2$C=NNH$_2$, although the slight tilting of the nitrogen substituent out of the molecular plane is only little less energetically favourable (Fig. 2). Formaldehyde hydrazone isomerizes by the inversion-rotation mechanism, which is apparently due to the asymmetry of its molecule and, thereby, the possibility of interaction of the electron pair at the amine group nitrogen with the π-electrons of the C=N bond, owing to which the rotational barrier is lowered.

The fact that compounds possessing a C=N bond isomerize largely by the inversion mechanism has been known. A new finding is the occurrence of the combined inversion-rotation isomerization mechanism for hydrazones. The feasibility of this combined mechanism for heterosubstituted imines is borne out by experimental

observations[2,17]. It would be of interest to investigate the *E–Z* isomerization mechanism of hydrazones at a higher *ab initio* level.

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Translated by P. Adámek.