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## QUANTUM-CHEMICAL STUDY OF PHOTOCHEMICAL *E-Z* ISOMERIZATION OF METHANIMINE AND ITS FLUORO DERIVATIVES

Peter ERTL and Jaroslav LEŠKA

*Department of Organic Chemistry,  
Comenius University, 842 15 Bratislava*

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The CNDO/2 CI method has been used for full optimization of geometry of methanimine and its fluoro derivatives in the first excited singlet state ( $S_1$ ). The reaction paths of the photochemical *E-Z* isomerization of these molecules in the  $S_1$  state by inversion and rotation mechanisms have been studied by the method of reaction coordinate with full optimization of all other coordinates. Each of the two mechanisms mentioned goes through an energy minimum, the rotation minimum being deeper. The non-radiative transition from the rotation minimum in the  $S_1$  state to the corresponding Franck-Condon ground state enables the isomerization of the molecule. The reaction paths obtained are similar to, and the energy differences of the corresponding Franck-Condon states are close to or identical with results of the model *ab initio* calculations published by other authors.

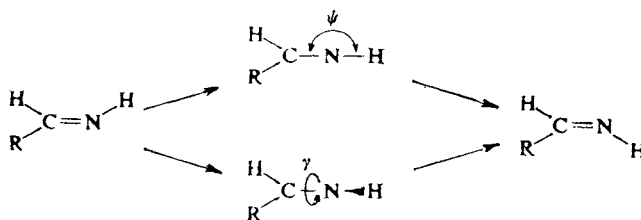
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Recently increasing attention has been paid to photochemistry of compounds containing C=N bond due to their importance in organic synthesis as well as in physiological chemistry, where the imines play the key role in the process of vision, *viz* for transformation of light into electric impulse<sup>1</sup>. The most important photochemical reaction of imines is their *E-Z* isomerization whose mechanism has not been satisfactorily elucidated yet because of extreme instability of imines. Measurements of quantum yields after irradiation showed that various imine derivatives are isomerized by direct irradiation in the singlet state and — if sensitizers are used — in the triplet state<sup>2-5</sup>. The transformation of the *E*-isomer into *Z*-isomer can take place by two different mechanisms, *viz* by inversion (in-plane mechanism) with retention of planarity of the molecule and with variation of the CNH angle or by rotation around the CN bond (lateral shift) (Scheme 1). The thermal isomerization goes by the inversion mechanism<sup>6,7</sup>. Examination of substituent effects on the quantum yields shows that — in the excited state — the reaction goes by a different mechanism<sup>8,9</sup> from that of the thermal isomerization.

Elucidation of mechanism of the photochemical *E-Z* isomerization of methanimine requires information on geometry and electronic structure in the excited states. No experimental data are available, there only exist several quantum-chemical calculations: Sandorfy<sup>10</sup> and Russegger<sup>11</sup> investigated the effect of excitation of methanimine to the lowest triplet state on its geometry change. Nishimoto and coworkers<sup>12</sup> examined the geometry of methanimine in the lowest singlet and triplet excited states, and they also dealt with elucidation of the photoisomerization mechanism<sup>13</sup>. Most recently, a paper by Bonačić-Koutecký<sup>14</sup> presents a detailed study of the changes of electronic structure of imines with the geometry changes in the singlet and triplet states. However, the geometries obtained by different authors are considerably different which is

obviously due to the different methods used and to the fact that only some of the internal coordinates were optimized. So far, no complete optimization of geometry of methanimine in its excited states has been carried out.

In the present communication we have optimized the geometry of methanimine and its C- and N-fluoro derivatives in the first excited singlet state ( $S_1$ ) by the CNDO/2 CI method (with all singly monoexcited configurations in CI) according to ref.<sup>15</sup>. We have studied the isomerization reaction paths by two possible mechanisms (Scheme 1) by the method of reaction coordinate<sup>16,17</sup>. All the geometry parameters



SCHEME 1

except the reaction coordinate were fully optimized at various points of the reaction path. It was also the aim of this paper to investigate suitability of the optimization method<sup>15</sup> for calculation of reaction paths of photochemical reactions.

## RESULTS AND DISCUSSION

### *Equilibrium Geometries, Electronic Structures, and Excitation Energies*

Figure 1 gives the geometry parameters of the optimized geometries of methanimine and its fluoro derivatives in the  $S_1$  states. For comparison, the figure also gives the geometries of the ground states ( $S_0$ ) of the same molecules optimized by us with the use of the same method.

Methanimine in the  $S_0$  state exhibits the  $C_s$  symmetry which agrees with the microwave measurements<sup>18</sup> as well as with the *ab initio* calculations<sup>19,20</sup>. The wave function of this state belongs to the  $A'$  representation. The excitation to the  $S_1$  state is accompanied by considerable structural changes. The molecule loses its planar shape and assumes a bent geometry, which also has the  $C_s$  symmetry, with the NH bond and the  $CH_2$  group at *trans* position (Fig. 1), with electronic configuration  $(1a')^2 (2a')^2 (1a'')^2 (3a')^2 (4a')^2 (2a'')^1 (5a')^1$ . The wave function of the excited molecule belongs to the  $A''$  representation, the corresponding transition being practically pure  $6 \rightarrow 7$  (weight 0.983). The *ab initio* calculations by Nishimoto and coworkers<sup>12</sup> gave the geometry of the same symmetry in the  $S_1$  state. It is, however, impossible to compare the geometry parameters, because not all of them were optimized.

Fluoromethanimine in  $S_0$  state exists as *E*- and *Z*-isomer, the latter being (against expectation) more stable than the former by 0.02 eV (1 eV = 96.4868 kJ/mol). This stabilization, which is also confirmed by the *ab initio* calculations<sup>19</sup>, is obviously due to interaction between the fluorine and N-hydrogen atom. The two stereoisomers in the  $S_1$  state lead to the same geometry (Fig. 1) of two different chiral forms. The wave function is without symmetry, having the character of a 9→10 transition (weight 0.977).

N-Fluoromethanimine in  $S_0$  state is planar, and in the  $S_1$  state it assumes the bent geometry of  $C_s$  symmetry (Fig. 1) and electronic configuration  $(1a')^2 (2a')^2 (3a')^2 \cdot (1a'')^2 (4a')^2 (5a')^2 (2a'')^2 (6a'')^2 (3a'')^1 (7a')^1$ . The wave function belongs to the  $A''$  representation, the transition 9→10 having the highest representation (weight 0.981). It is noteworthy that the NF bond in the  $S_1$  state is shortened as compared with the  $S_0$  state. This fact is probably due to the lowered electron density at the nitrogen

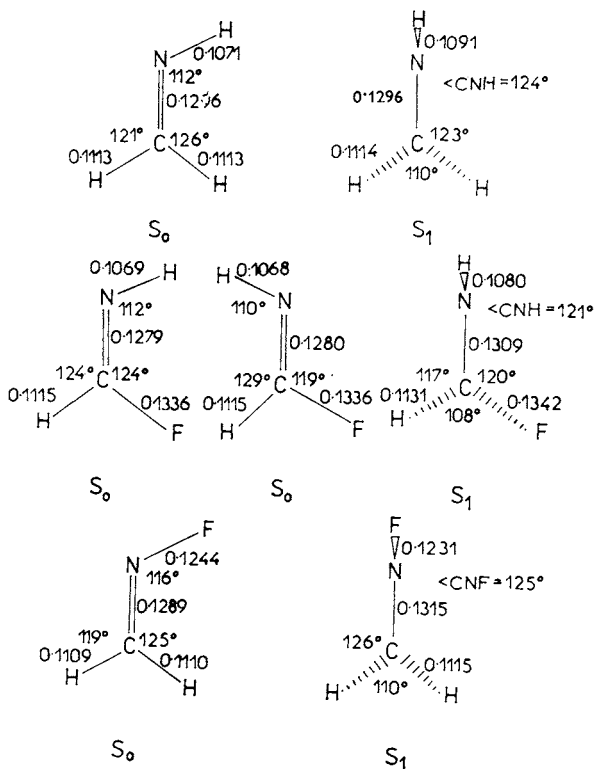


FIG. 1

The optimized geometries of methanimine and its fluoro derivatives in the  $S_0$  and  $S_1$  states. The lengths in nm.

atom caused by transition of one electron from  $n$ -orbital of the nitrogen atom to the antibonding  $\pi^*$  orbital.

Thus the calculations show that all the imines studied have – in their lowest excited singlet states – non-planar geometries with the NR bond and CHR group at *trans* position. The deviation of the CR<sub>2</sub> group from the CN bond is a consequence of the hybridization change  $sp^2 \rightarrow sp^3$  at the carbon atom caused by the charge increase.

Electronic structure of the molecules studied is evident from Table I for their ground and first excited singlet states as it follows from the calculated net charges at the atoms in these states.

The excitation causes considerable charge redistribution especially from nitrogen to carbon atom, which is due to the  $n \rightarrow \pi^*$  transition. The bond orders of the C=N  $\pi$  bonds (also given in the Table) indicate the C=N bond lengthening.

The calculated vertical absorption, emission, and adiabatic transition energies of methanimine and its fluoro derivatives (Table II) cannot be compared with experimental data, because the latter have not been measured yet. It is, however, known<sup>21,22</sup> that the  $n \rightarrow \pi^*$  transition of simple N-alkylimines lies in the interval from 5.0 to 5.4 eV. Even though the drawbacks of the CNDO/2 approximation used for description of the excitation energies are well known<sup>23,24</sup>, the value 6.40 eV calculated by us for methanimine agrees remarkably with the result 6.20 eV obtained<sup>25</sup> by the *ab initio* method with application of a 3 461-dimensional configuration interaction. The substitution of hydrogen atom at carbon by fluorine atom leads to an increase in the excitation energy. According to experience with the method<sup>15</sup>, the calculated vertical emission energies are (in spite of their different physical mean-

TABLE I

Net charges at the atoms<sup>a</sup> and bond orders of C=N  $\pi$  bonds in the ground state and in the first excited singlet state

Molecule	State	C	N	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	$\pi$
H <sub>2</sub> C=NH	S <sub>0</sub>	+·097	-·149	+·068	-·015	-·001	·997
	S <sub>1</sub>	-·303	+·177	+·002	+·062	+·062	·581
(E)-FHC=NH	S <sub>0</sub>	+·318	-·205	+·086	-·188	-·012	·961
	S <sub>1</sub>	-·124	+·187	+·044	-·163	+·056	·499
(Z)-FHC=NH	S <sub>0</sub>	+·315	-·216	+·097	-·198	+·002	·961
	S <sub>1</sub>	-·124	+·187	+·044	-·163	+·056	·499
H <sub>2</sub> C=NF	S <sub>0</sub>	+·018	+·056	-·125	+·026	+·025	·975
	S <sub>1</sub>	-·348	+·296	-·072	+·062	+·062	·491

<sup>a</sup> R<sub>2</sub>R<sub>3</sub>C—NR<sub>1</sub>.

ing) very close to the experimental adiabatic transition energies (deviations 2–10%). Therefore, also in this case they can represent a good approximation to the yet unknown adiabatic transition energies.

### *The Reaction Paths of Photochemical Isomerization*

We examined the mechanism of the photochemical isomerization by investigating the dependence of total energy of the molecule on the inversion ( $\psi$ ) or rotation ( $\gamma$ ) angles which represented the reaction coordinate. The other coordinates were fully optimized.

Increasing of the inversion angle CNH in methanimine is connected with energy decrease (Fig. 2), the minimum being reached at the value  $180^\circ$  (symmetry of the molecule  $C_{2v}$ ); this minimum is, however, indistinct, and the energy does not practically change within the interval  $\psi = 150^\circ - 210^\circ$ . The rotational mechanism is more favourable energetically. The energy decreases markedly with increasing value of the  $\gamma$  angle (Fig. 2), and the energy minimum is deeper by about 0.6 eV than that in the inversion. Comparison of our results with the reaction paths suggested by Nishimoto and coworkers<sup>13</sup> shows practically qualitative identity, the only difference being in that the Nishimoto's path for the inversion has a flat maximum at  $\psi = 180^\circ$  and shallow minima at  $\psi = 145^\circ$  and  $235^\circ$ . This interval corresponds roughly to the above-mentioned region of indistinct minimum in our case. The model calculations carried out by Bonačić-Koutecký<sup>14</sup> give a similar energy course for the torsion.

The energy difference between the torsional minimum and the energy of the corresponding Franck-Condon ground state corresponds to the vertical emission energy of the optimum energy in the  $S_1$  state. The value is 2.16 eV for methanimine (Table II), whereas Nishimoto<sup>13</sup> gives the value about 1.3 eV. The calculations by Bonačić-Koutecký in the basis of closed shell MO in CI gave a value identical

TABLE II  
The excitation energies

Molecule	Transition energy, eV <sup>a</sup>		
	vertical absorption	adiabatic	vertical emission
H <sub>2</sub> C=NH	6.40	4.84	2.16
( <i>E</i> )-HFC=NH	7.11	5.48	2.82
( <i>Z</i> )-HFC=NH	7.43	5.50	2.82
H <sub>2</sub> C=NF	6.36	4.75	0.76

<sup>a</sup> 1 eV = 96.4868 kJ/mol.

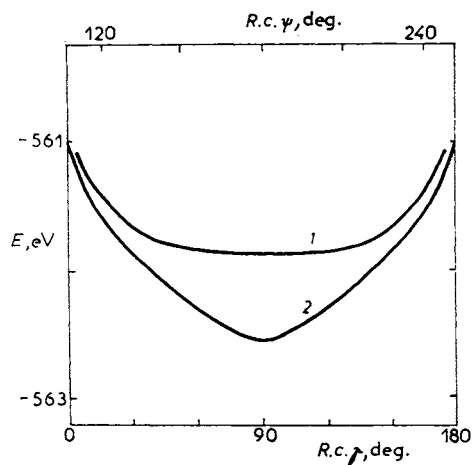


FIG. 2  
Dependence of energy of methanimine in the  $S_1$  state on the reaction coordinate (R.c.) 1 inversion, (R.c.  $\psi$ ), 2 rotation, (R.c.  $\gamma$ )

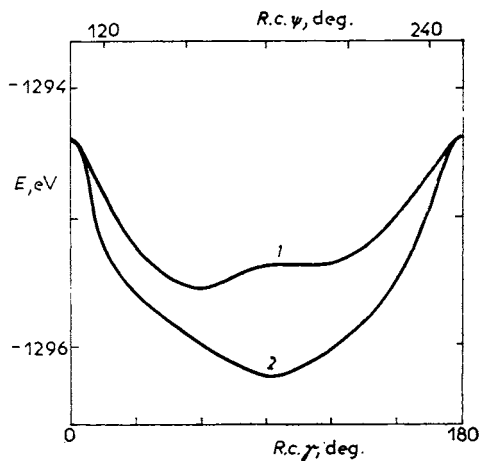


FIG. 3  
Dependence of energy of fluoromethanimine in the  $S_1$  state on the reaction coordinate 1 inversion (R.c.  $\psi$ ) and 2 rotation (R.c.  $\gamma$ )

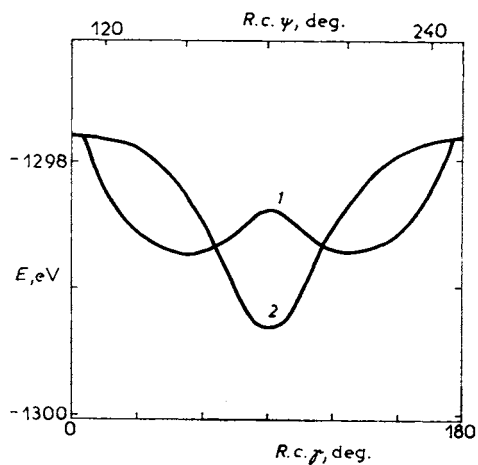


FIG. 4  
Dependence of energy of N-fluoromethanimine in the  $S_1$  state on the reaction coordinate 1 inversion (R.c.  $\psi$ ) and 2 rotation (R.c.  $\gamma$ )

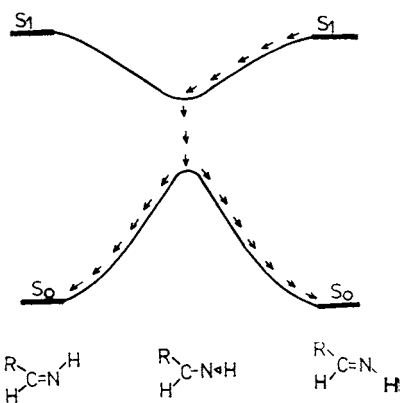


FIG. 5  
Scheme of the isomerization mechanism

with our value, but those with the open shell triplet MO basis (which the author considers to be better) gave a value by one half smaller.

With regard to the existence of two isomers, fluoromethanimine exhibits two different minima at the inversion potential curve (Fig. 3). The more distinct one lies at  $\psi = 150^\circ$ , the other is shallower at about  $210^\circ$ . Here also, the rotation is accompanied by gradual energy decrease (Fig. 3), the minimum value is reached at the angle  $\gamma = 90^\circ$ , whereupon again the energy increases.

The potential curve of the N-fluoromethanimine inversion (Fig. 4) exhibits two equal minima at  $\psi = 145^\circ$  and  $215^\circ$ . The rotation is accompanied by an energy decrease which is slow at first and then steep until the minimum at  $\gamma = 90^\circ$  is reached. Comparison of the potential curves of the rotational mechanism of methanimine and its fluoroderivatives in the  $S_1$  state shows that the rotational mechanism is more favourable in all the cases, the energy minimum being by about 2 eV lower than the energy of the Franck-Condon  $S_1$  state corresponding to the ground state. This value for methanimine also agrees with those obtained by Nishimoto<sup>13</sup> and Bonačić-Koutecký<sup>14</sup>. From these results it can be concluded that the molecule assumes the optimum geometry very rapidly after irradiation. Therefrom it goes by a non-radiative transition to the ground state, because no fluorescence has been observed with imines<sup>7</sup>. As the geometry at the energy minimum of the lowest excited singlet state corresponds to that at the maximum of the potential curve of the ground state, the both stereoisomers can be formed, as it follows from Fig. 5. Introduction of fluorine atom instead of methylene hydrogen atom has practically no effect on the mechanism. This fact agrees with the findings by Nishimoto<sup>13</sup> and Bonačić-Koutecký<sup>14</sup>, viz. that substitution of the methylene group with phenyl or vinyl group does not affect the mechanism. The substitution with fluorine at nitrogen atom makes the inversion more favourable in the first phase and the rotation in subsequent phases.

From comparison it follows that the potential curves of methanimine for the two mechanisms have practically the same course with those obtained by the model *ab initio* calculations by Nishimoto<sup>13</sup> and Bonačić-Koutecký<sup>14</sup>. Also close or identical are the energy differences of the respective Franck-Condon states. This fact justifies the statement that the optimization method<sup>15</sup> is suitable for investigation of photochemical isomerizations of similar type. Therefore, also the results obtained in this work for the isomerization of fluoromethanimines – whose reaction paths have not been studied theoretically yet – can be considered to be probable.

As far as the gradient method<sup>15</sup> is concerned, here we observed several very close local minima, too. So *e.g.* between the optimum structure of methanimine in the  $S_1$  state (Fig. 1) and that having the  $H_2CN$  atoms in one plane in the same state, there exists an energy difference of as little as 0.02 eV. In some cases certain convergence difficulties of the variable metric procedure were observed in close vicinity of energy minima. Therefore, the bond lengths given for the excited states are stabilized at three valid decimals only.

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