

MINDO/3 Theoretical Studies on Sigmatropic Hydrogen Rearrangements (II): Systems with Central Nitrogen Atom*

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MINDO/3 theoretical studies were carried out on sigmatropic hydrogen rearrangements in systems with central nitrogen atom; three systems studied being (1) N-methylformaldimine, (2) nitrous acid, and (3) formaldoxime-nitrosomethane systems. It was found that in system (1), 1,3-H shift is preferred whereas in systems (2) and (3), 1,2-H shifts are favored. The relative order of reactivity for the three systems was found to be (2) < (3) < (1), which is exactly the opposite to that found for the corresponding systems with central carbon atom.

1. Introduction

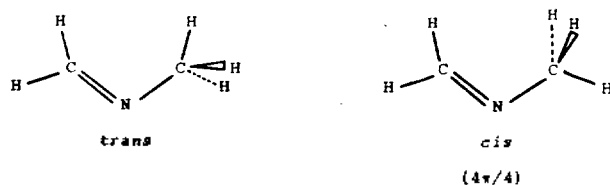
The MINDO/3 theoretical studies on the sigmatropic hydrogen rearrangements in systems with central carbon atom¹ have shown that steric effect, aromaticity, and orbital interactions are important in determining the stability of the transition state (TS), besides the consideration of orbital symmetry. Moreover comparison of the relative barrier heights with those obtained by more sophisticated MO calculations indicated that the MINDO/3 results give correct prediction of the relative order of the activation barriers. The success with the MINDO/3 method² in the study of sigmatropic hydrogen shifts in systems involving central carbon atom prompted us to extend our work to systems with central nitrogen atom; these systems, having lone pair orbitals on the central nitrogen atom, are known to exhibit unusual behavior of preference for 1,2-hydrogen shift over the normally favorable antarafacial 1,3-hydrogen shift due to the lone pair on the central atom inducing considerable protonic character in the moving hydrogen atom.

2. Calculation

Full MINDO/3 geometry optimizations of ground state structures were carried out using a gradient optimization procedure. The geometries of transition states were obtained at the MINDO/3 level by minimization of the gradient norm while ensuring that the Hessian matrix had only one negative eigenvalue.

3. Results and Discussion

N-Methylformaldimine (1). The stable conformer^{1b} has a



trans arrangement since in the *cis* form there is a $(4\pi/4)$ π -nonbonded structure which is strongly end-to-end repulsive.

The *trans* form is calculated to be more stable by 0.6 kcal/mol than the *cis* form. Optimized geometric parameters of the *trans* form is summarized in Table 1.

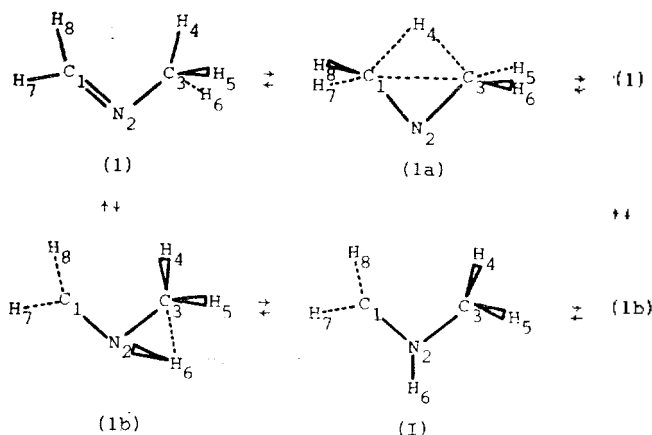
Two pathways are conceivable for 1,3-hydrogen rearrangement: (a) a direct 1,3-sigmatropic hydrogen shift (1,3-(C, N, C)-H shift) via the TS(1a), and (b) two 1,2-hydrogen (1,2-(C, N, C)-H) shifts via TS(1b) involving an intermediate (I) as shown in Scheme 1.

Optimized geometric parameters for all the key struc-

TABLE 1: Optimized Geometric Parameters for N-Methylformaldimine (1), Transition States(1a,b), and Intermediate (I) for 1,3- and 1,2-Hydrogen Shifts

Parameter ^a	1	1a	1b	I
C ₁ -N ₂	1.241	1.398	1.278	1.311
N ₂ -C ₃	1.392	—	1.343	1.311
C ₁ -C ₃	—	1.640	—	—
C ₃ -H ₄	1.125	1.318	1.114	1.108
C ₃ -H ₅	1.120	1.124	1.117	1.108
C ₃ -H ₆	1.120	1.124	1.367	—
N ₂ -H ₇	—	—	—	1.046
C ₁ -H ₇	1.113	1.124	1.111	1.108
C ₁ -H ₈	1.122	1.124	1.115	1.108
<C ₁ N ₂ C ₃	136.8	71.8	148.2	137.3
<N ₂ C ₃ H ₄	119.3	105.7	122.6	118.7
<N ₂ C ₃ H ₅	110.5	123.5	117.2	119.3
<N ₂ C ₃ H ₆	110.5	123.5	52.0	—
<C ₁ N ₂ H ₇	—	—	—	111.3
<N ₂ C ₁ H ₇	119.8	123.5	119.3	119.3
<N ₂ C ₁ H ₈	131.8	123.5	123.3	118.7
<C ₁ N ₂ C ₃ H ₄	—	—	-8.2	-16.0
<C ₁ N ₂ C ₃ H ₅	-121.5	108.3	219.2	204.8
<C ₁ N ₂ C ₃ H ₆	121.5	-108.3	143.5	—
<C ₃ N ₂ C ₁ H ₇	—	-108.3	201.1	204.8
<C ₃ N ₂ C ₁ H ₈	—	108.3	-13.7	-16.0

^a Throughout this paper, bond lengths are in angstroms and bond angles are in degrees.



tures are presented in Table 1.

Pathway (a) may seem similar to the 1,3-(C, C)-H shift of propene system,^{1b} but in fact the two processes are quite different. In the TS (1a) the contribution of $C_1 \cdots C_2$ overlap is also important in addition to the $C_1 \cdots H_4 \cdots C_2$ interaction. The geometric parameters for TS (1a) in Table 1 reveals that $C_1 \cdots C_2$ distance is relatively short (1.64 Å) and C-N bond length increases only by 0.01 Å in the TS formation. The two types of bonding interactions in (1a) lower the energy barrier by about 29 kcal/mol in comparison with the 1,3-(C, C)-H shift.

In general, 1,2-hydrogen shift involves a proton type hydrogen and a lone pair orbital. However in the pathway the energy barrier is dictated by the hydrogen affinity of the central N atom. Here electronegativities of the end carbon atoms are relatively small and hence the hydrogen affinity of the central N atom becomes large so that the barrier tends to be depressed. However due to the relatively small proton character of the moving hydrogen, there is little change in the barrier height; overall, 1,3-H shift (pathway a) is favored over 1,2-H shift (pathway b) due to the more favorable orbital interactions in the former.

Nitrous Acid (2). In this compound,^{1,3} a weak hydrogen bond, $O-H \cdots O$, favors the *cis* conformer, whereas lone pair-lone pair repulsion disfavors the *trans* form; the *cis* form is calculated to be more stable by 11.3 kcal/mol.

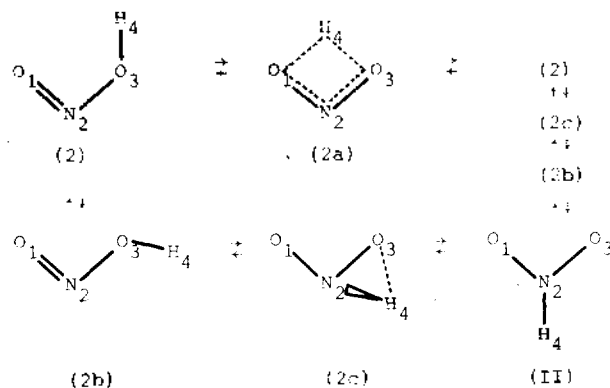


The MINDO/3 optimized geometric parameters for the *cis* form are summarized in Table 2 together with those for the TSs for the two pathways, (2a) and (2c), and for the intermediate (II) shown in scheme 2.

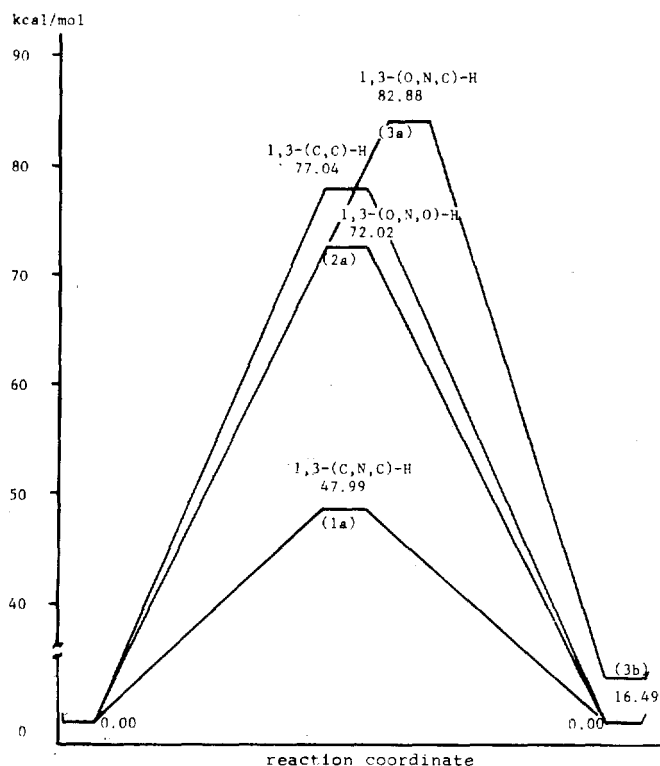
The TS(2a) (1,3-(O, N, O)-H shift) in Scheme 2 is similar to the TS in 1,3-(O, O)-H shift involved in formic acid,^{1b} but in the former the antibonding interaction between the rearranging hydrogen and P_y lone pair of N atom increases substantially as the TS is being formed along the reaction coordinate, and hence becomes unfavorable compared with the 1,3-(O, O)-H shift. In the TS(2a), the $N \cdots H$ distance is short relative to the $O \cdots O$ distance.

TABLE 2: Optimized Geometric Parameters for Nitrous Acid (2,2b), Transition States (2a,c), and Intermediate (II) for 1,3- and 1,2-Hydrogen Shifts

Parameter	2	2a	2b	2c	II
O_1-N_2	1.197	1.282	1.197	1.199	1.210
N_2-O_3	1.315	1.282	1.373	1.305	1.210
O_3-H_4	0.962	1.280	0.954	1.201	—
N_2-H_4	—	—	—	—	1.074
$\angle O_1N_2O_3$	133.5	105.2	122.3	137.8	136.8
$\angle N_2O_3H_4$	130.6	74.7	112.1	54.6	—
$\angle O_1N_2H_4$	—	—	—	—	111.6
$\angle O_1N_2O_3H_4$	—	—	—	176.4	—

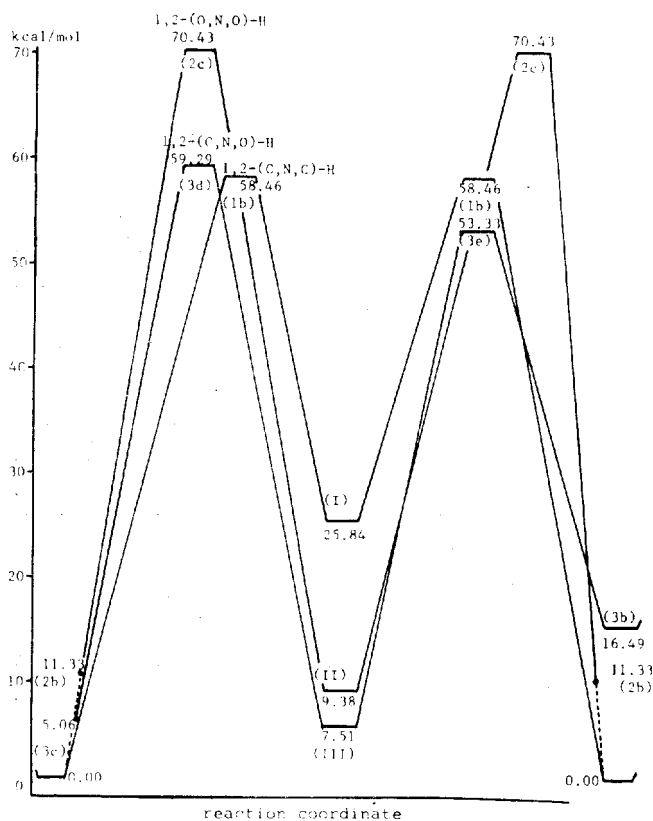


In the TS(2c) (1,2-(O, N, O)-H shift) the energy barrier is expected to be relatively high since the proton affinity of N is smaller than that for O atom. However the 1,2-H shift is favored over the 1,3-H shift, since in the latter there are two types of repulsions; between two O atoms and between s orbital of hydrogen and P_y lone pair of N atom. In this process, energy levels of the around state (2a) and the



(In this profile, all energies are relative ones.)

Figure 1. Reaction profiles for the intramolecular rearrangements by 1,3-hydrogen shifts.

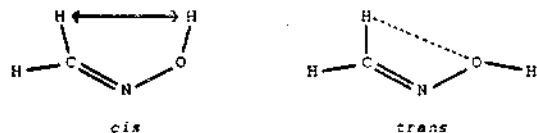


In this profile, all energies are relative ones. 1

Figure 2. Reaction profiles for the intramolecular rearrangements by 1,2-hydrogen shifts.

intermediate (II) are nearly the same so that the level of the TS (2c) is also located in the middle part. However in the 1,2-(C, N, C)-H shift, the intermediate (I) is relatively unstable and hence the TS (1b) is located near (I) in agreement with the Hammond postulate.⁵ (Figures 1 and 2)

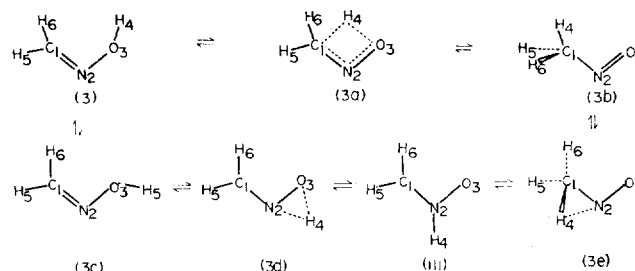
Formaldoxime (3, 3c) and Nitrosomethane (3b). Formaldoxime^{1,3} has two conformers, *cis* and *trans*; in the former repulsive interaction between hydrogen atoms is expected while in the latter weak hydrogen bond, C-H...O, is expected.



However our MINDO/3 results showed the former to be more stable by 5.1 kcal/mol, whereas various *ad initio* calculations⁴ gave the latter to be the preferred one. The results of calculations with 6-31G basis set, in which both split-valence and polarization functions are used, gave the *trans* to be more stable by 5.9 kcal/mol. The cause of this discrepancy is a well known failure of the MINDO/3 method in properly accounting for the hydrogen bond energy.⁶ For nitrosomethane (3b),^{1,3} *syn* form is more stable than the *anti* form on two accounts: a weak H bond favoring the *syn* form and a (4π/4) repulsive π nonbonded interaction disfavoring the *anti* form; the MINDO/3 results show that the latter is more stable by 1.0 kcal/mol.



The 1,3- and 1,2-hydrogen rearrangements involved in this system are summarized in Scheme 3.



The MINDO/3 optimized ground state and TSs geometries are summarized in Tables 3 and 4.

TABLE 3: Optimized Geometric Parameters for Formaldoxime (3), Transition State (3a), and Nitrosomethane (3b) for 1,3-Hydrogen Shift

parameter	3	3a	3b
C ₁ -N ₂	1.257	1.281	1.422
N ₂ -O ₃	1.325	1.312	1.200
O ₃ -H ₄	0.963	1.379	—
C ₁ -H ₅	1.109	1.116	1.117
C ₁ -H ₆	1.114	1.179	1.117
C ₁ -H ₄	—	—	1.120
<C ₁ N ₂ O ₃	128.5	102.7	124.8
<N ₂ O ₃ H ₄	119.2	80.7	—
<N ₂ C ₁ H ₅	115.4	126.7	108.6
<N ₂ C ₁ H ₆	134.1	129.9	108.6
<N ₂ C ₁ H ₄	—	—	122.2
<O ₃ N ₂ C ₁ H ₅	—	—	122.9

TABLE 4: Optimized Geometric Parameters for Formaldoxime (3c), Transition States(3d, e), and Intermediate (III) for 1,2-Hydrogen Shift

Parameter	3c	3d	3e	III
C ₁ -N ₂	1.258	1.246	1.361	1.272
N ₂ -O ₃	1.364	1.337	1.232	1.234
O ₃ -H ₄	0.958	1.239	—	—
C ₁ -H ₅	1.110	1.109	1.113	1.103
C ₁ -H ₆	1.114	1.110	1.120	1.102
N ₂ -H ₄	—	—	—	1.059
C ₁ -H ₄	—	—	1.324	—
<C ₁ N ₂ O ₃	117.2	135.7	128.1	133.2
<N ₂ O ₃ H ₄	106.9	50.6	—	—
<N ₂ C ₁ H ₅	114.1	119.5	118.9	122.8
<N ₂ C ₁ H ₆	135.8	128.2	131.9	123.5
<C ₁ N ₂ H ₄	—	—	—	110.5
<N ₂ C ₁ H ₄	—	—	55.2	—
<O ₃ N ₂ C ₁ H ₄	—	—	110.0	—
<O ₃ N ₂ C ₁ H ₅	—	—	195.6	—
<O ₃ N ₂ C ₁ H ₆	—	—	-1.6	—

The TS(3a) (1,3-(C, N, O)-H shift) is similar to the TS in the 1, 3-(O, C)-H shift of vinyl alcohol,^{1b} but here again large antibonding interaction between the rearranging H atom and p_y lone pair of the central N atom tends to increase barrier height. On the other hand, the position of the TS is consistent with the Hammond postulate as it was found for the 1, 3-(C, O)-H shift.^{1b} In the TS(3a) the OH bond length is considerably long since the enol form is more stable than the keto form.

The relative energy barriers for various 1,3-H shifts studied in this work are presented in Figure 1.

In this system, the reaction pathway via two 1,2-H shifts involving an intermediate, (III), is more favorable than the corresponding 1,3-H shift as it was found to be the case for nitrous acid. The energy profiles for various 1,2-H shifts are presented in Figure 2.

In conclusion, our MINDO/3 results predict the relative reactivity of the three systems studied to be 1,2-(O, N, O)-H < 1,2-(C, N, O)-H < 1,3-(C, N, C)-H, which is exactly the opposite to that found for corresponding systems with central carbon atom.

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Association of Methyl Viologen and Its Cationic Radical with Sodium Dodecyl Sulfate

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The polarographic and conductometric studies of methyl viologen (MV²⁺) solutions with varying concentration of sodium dodecyl sulfate (SDS) showed strong association of MV²⁺ and its cationic radical, MV^{•+}, with SDS below the critical micelle concentration. The stoichiometries of these associations were found to be their electric charge ratios. Both electrostatic and hydrophobic interactions were found to contribute to the associations. The formation constant of MV^{•+}.DS⁻ in 0.1M NaCl was 7×10^8 M. The MV²⁺-SDS association was observed to be cooperative leading to formation of large aggregates. In the presence of MV²⁺, the micellization of SDS was formation of SDS homo-micelle without direct involvement of MV²⁺.

Introduction

The chemistry of N,N'-dimethyl-4,4'-bipyridinium (methyl viologen: MV²⁺) has been subjects of intense studies because of the intrinsic interest of the chemistry and the promise in use of the viologen and related compounds in solar energy conversion and electrochromic displays, and as a herbicide and a probe for various biological systems.^{1,2} Most of interesting properties of methyl viologen arise from strong electron affinity of MV²⁺, and stability of violet-colored cationic radical, MV^{•+}. The radical can be formed via chemical, electrochemical or photosensitized reduction of MV²⁺. Chemical properties of MV^{•+}, as well as MV²⁺ play critical roles in many applications of MV²⁺, and the prop-

erties strongly depend on the nature of the system employed.

To enhance desirable characteristics of MV²⁺ and to provide biologically mimetic environment for MV²⁺, microheterogeneous systems were extensively utilized: these include the use of amphiphilic viologens³⁻⁶, amphiphilic electron donors^{3,7-9}, surfactant vesicles¹⁰⁻¹³, and micelles^{3,7,8,14-20}. The effects of these systems on the reduction potentials of viologens¹⁴, the stability of charge transfer complexes between viologens and electron donors^{15,16}, and the efficiency of the electron transfer process from excited photosensitizers to viologens leading to the formation of viologen radical ions^{4,9,19,20} have been well recognized. These effects were mainly attributed to the interaction of viologens and electron donors with charged micelles or vesicles. However, the