分子素子に関する理論的研究

Theoretical Study on the Molecular Electronic Device*

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Potential energy surfaces of 1,2-hydrogen migration for pyrazol and 5-methyl pyrazol at the ground state and triplet excited state were calculated by the ab initio molecular orbital methods. All potential energy surfaces along the reaction path have high energy barriers. The occurrence of the structural change indispensable to the switching function is doubtful for pyrazol and 5-methyl pyrazol. The possibility of switching function by 1,2-hydrogen migration was also studied on the basis of a simple model molecule. The possibility of the switching mechanism was found at the $n^2 \rightarrow \pi^2$ excitation with the relaxation of the CNN angle.

1. INTRODUCTION

The concepts of molecular electronic devices were proposed by Carter[1] in 1981. It had been considered that molecular devices are only ideal concept. Such concept, however, is growing realistic one under the recent progress of experimental technique. The molecular level fabrication of various electronic devices such as the molecular switch and molecular memories, recently, has been a very active area for both of experimental[3,4] and theoretical[1,2,5-6] studies. The proposed

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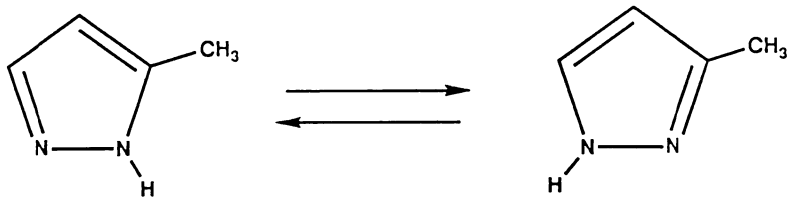
ideas for the switching mechanism are a hydrogen shift, a charge transfer, and so on. Carter[1] has proposed a utilization of the hydrogen transfer-switching function in 5-methyl pyrazol for the architecture of hydrogen switching devices of molecular size.



(1)

The basic idea of this switching lies in the potential surface change of 5-methyl pyrazol upon photon excitation. They stipulated three hypothetical potential energy surfaces for 5-methyl pyrazol as shown in Figure 1. Namely the potential energy surface along the hydrogen transfer path at the ground state has a double well, and two excited state surfaces have a single minimum. The energy barrier between point-0 and point-1 at the ground state is high enough; at the ground state that the hydrogen migration does not occur thermally. The idealized switching scheme from point-0 to point-1 is the excitation from A-surface to B-surface at point-0. The hydrogen moves to the minimum point along B-surface, and the state transfer from B-surface to A-surface occurs at point-1. The switching scheme from point-1 to point-0 occurs through the C-surface the same as the switching from point-0 to point-1.

On the other hand, few theoretical treatments for pyrazol have been carried out. Bofill and co-workers[9] studied, recently, the low-lying electronic states of pyrazol and pyrazol radicals. There are no theoretical calculations for hydrogen

migration in pyrazol and substituted pyrazol.

In this paper, we calculated potential energy potentials for 1,2 hydrogen shift of pyrazol and 5-methyl pyrazol, to assess the possibility of above switching mechanism.

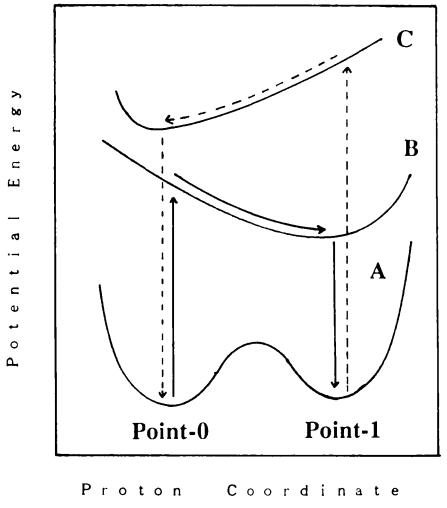


Figure 1 Idealized photochemical switching scheme.

2. CALCULATIONS

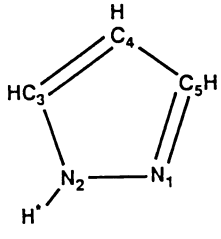
The basis sets used were the split-valence 3-21G set[10] and the split-valence plus polarization 6-31G** set.[11,12] All stationary point geometries were determined using analytical energy gradients[13] at the Hartree-Fock (HF) level with the 3-21G set. In this paper, we calculated the triplet states for pyrazol and 5-methyl pyrazol. The triplet state for open shell systems was calculated by the Unrestricted HF method. Electron correlation was included using second, third, and fourth order many body perturbation theory[14-18] (referred to as the MP2, MP3, and MP4(SDTQ) approximations by Pople and co-workers) with the

6-31G** set. The calculations were performed using the GAUSSIAN86 and GAUSSIAN88[19] programs.

3. RESULTS and DISCUSSION

a. PYRAZOL

The calculated stationary point geometries for 1,2-hydrogen migration of pyrazol obtained at the HF/3-21G calculation level are listed in Table I. Experimental geometric parameters[20] for pyrazol at the ground state are: N_1-C_5=1.359 A, C_4-C_5=1.372 A, C_3-C_4=1.419 A, C_3-N_2=1.331 A, and N_1-N_2=1.349 A. The largest absolute deviation from experiment of the 3-21G optimized geometrical parameters is 0.03 A in the N_1-N_2 bond length. Therefore, we used the HF/3-21G method for optimizing the geometrical parameters below discussion.



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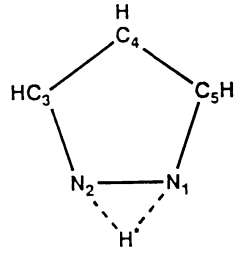
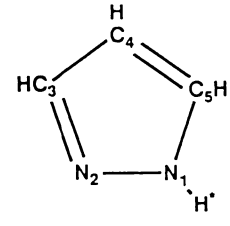


TS



(I)

The structure of pyrazol (I,II) in its ground state has C_s symmetry with all atoms located on the same plane. Assuming C_s symmetry, the geometries of the n--> π^* and π --> π^*, one-

Table I Geometrical parameters of Pyrazol and methyl pyrazol for the reactants and the transition state at the ground state and the triplet state.

	Distance (angstrom)					
	N_1-C_5	C_4-C_5	C_3-C_4	C_3-N_2	N_1-N_2	ϕ *(HNNC)
Pyrazol						
Ground State						
I	1.356	1.363	1.420	1.313	1.378	180.0
TS	1.342	1.385	1.385	1.342	1.503	116.3
Triplet State						
I	1.444	1.403	1.371	1.539	1.447	144.2
TS	1.530	1.345	1.345	1.530	1.498	108.1
Methyl Pyrazol						
Ground State						
I	1.356	1.365	1.419	1.312	1.383	180.0
II	1.312	1.424	1.361	1.354	1.382	180.0
TS	1.342	1.390	1.382	1.342	1.507	116.3
Triplet State						
I	1.448	1.400	1.373	1.539	1.444	143.8
II	1.541	1.369	1.405	1.446	1.443	143.9
TS	1.531	1.383	1.386	1.530	1.497	108.2

* ϕ means dihedral angle of HNNC, where H denote the active hydrogen atom.

Table II Activation Energy[a)] and Heat of Reaction[a)] of substituted pyrazol with HF/3-21G optimized geometries.

	Activation Energy		Heat of Reaction	
	Ground State	Excited State	Ground State	Excited State
Pyrazol				
HF/6-31G**	58.2	61.9	0.0	0.0
MP4/6-31G**	44.2	46.9	0.0	0.0
Methyl Pyrazol				
HF/6-31G**	57.6	61.1	0.1	-0.6
MP4/6-31G**	49.0	51.1	0.1	-0.6

a) included zero point energy by HF/3-21G calculation level. unit is kcal/mol.

electron excited states, were calculated(not shown here). The $\pi \rightarrow \pi^*$ state is 39 kcal/mol more stable in energy than the $n \rightarrow \pi^*$ state at the MP4/6-31G** level. The force constant matrix of pyrazol at the ground state has no imaginary frequencies, but the force constant matrixes of the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ states of pyrazol (I or II) have one imaginary frequency A" (out-of-plane) mode. Therefore; we optimized the geometry of the triplet state of pyrazol (I) in C_1 symmetry. The resulting optimized geometry is similar to that of the $\pi \rightarrow \pi^*$ state with $C_s$symmetry, except for the location of hydrogen atom bonding to nitrogen; this hydrogen atom is located out of the ring plane of pyrazol. At the MP4/6-31G** level this triplet state with C_1 symmetry is 5 kcal/mol more stable in energy than the $\pi \rightarrow \pi^*$ state assuming C_s symmetry. In the transition state of hydrogen migration, the geometry at the ground state has C_s symmetry; the active hydrogen is located out of the ring plane of pyrazol. The C_3-C_4 bond length in structure (I) at the ground state is longer than that at the triplet state, and the other bond lengths are shorter than those at the triplet state. The geometrical difference between the ground state and the triplet excited state can be explained from the phase of the lowest unoccupied molecular orbital (LUMO: π^*; not shown here). Namely the C_3-C_4 is the bonding phase, and the others are the antibonding phases. This result shows that the ring structure closed to (II) is not produced with an electron promotion to the π^* (LUMO) orbital. From similar orbital phase analysis, the ring structure closed to (II) is not to be expected for the other excited states at the structure (I).

The activation energy and the heat of reaction for the hydrogen migration are listed in Table II. First of all both potential energy surfaces for the ground state and the triplet state have double minima. The activation energy at the ground

state is lower than that at the triplet state. The activation energy at the n--> π^* state, assuming a plana geometry, is about 85 kcal/mol at the MP4/6-31G** level; the activation barrier of the second triplet excited state is possibly higher than that of the first one.

The energy barrier at the ground state is high enough for the switching function, while that at the excited state is too high in the quest for the excited state surface of the switching function.

b. METHYL PYRAZOL

5-methyl pyrazol is a switching model molecule proposed by Carter. The methyl group is expected to change the potential energy surfaces at the excited state; a substituted group raises (or lowers) the potential energy at one side (I or II). If the potential energy at one side rises higher than that at the transition state, the potential surface of reaction resembles the B- or C-surface in Figure 1.

Calculated geometrical parameters of 5-methyl pyrazol are summarized in Table I. For the ground state, the largest absolute deviation of the geometrical parameters between pyrazol and 5-methyl pyrazol is 0.005 A in the N_1-N_2 bond length (I) and 0.005 A in the C_4-C_5 bond length (TS), while, for the triplet state, the largest absolute deviation is 0.042 A in the C_3-C_4 bond length.

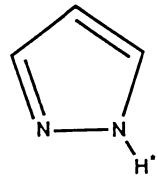
Calculated energy barriers and the heats of reaction are listed in Table II. In the ground state, the activation energy for 5-methyl pyrazol is higher by 5 kcal/mol than that for pyrazol; in the triplet state, the activation energy for 5-methyl

pyrazol is higher by 4 kcal/mol than that for pyrazol. The substitutional effects for the heat of reaction are negligible at the ground state or the triplet state.

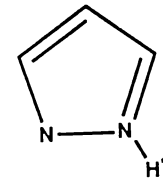
From above results, one can conclude that the effect of methyl substitution on the reaction are negligible. The bond elongation and bond shrinkage for the N_1-C_5 and the N_2-C_3 bonds by the excitation may be important for the mechanism of reaction (1). However, the behavior of the bonds by the excitation is not expected from the orbital phase concepts. Thus, we conclude that both of pyrazol and 5-methyl pyrazol are not useful as switching molecules.

c. SWITCHING POSSIBILITY by N,N-hydrogen shift

To distinguish π and σ effects for the potential energy surface of the hydrogen shift, two approaches were studied. For the π effects (the bond alternation of the ring), we calculated the following models (III and IV). III is just pyrazol. The ring structure in IV was kept that in the structure (II), and the location of the active hydrogen atom was optimized.



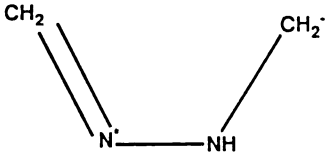
(III)



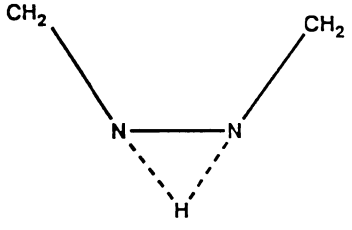
(IV)

Model IV indicates the ideal geometry by the excitation. This structure IV, of course, is not realistic system due to the orbital phase. The energy difference of structures III and IV is 13.6 kcal/mol at the MP3/6-31G** calculation level. This energy is quite different from the energy barrier for the hydrogen shift.

For the σ effects, we studied the following model molecules (V and VI).



(V)



(VI)

These models are an anion; the structure at the ground state is $H_2C=N-NH-CH_2^-$. It was assumed for the geometry optimization that all atoms are located co-planar. The optimized geometry parameters of V and VI (transition state) at the ground state, the $n \rightarrow \pi^*$ state, and the $n^2 \rightarrow \pi^{*2}$ state were listed in Table III. These three states differ in the occupation number (two, one, and zero) of the lone pair orbital in the nitrogen atom in the model V. Table III shows that the largest geometrical variation among three states is the C-N*(with a lone pair) bond

Table III Geometry Parameters of Models V and VI at the ground State, the n--> π^* State, and the n^2--> π^{*2} State.

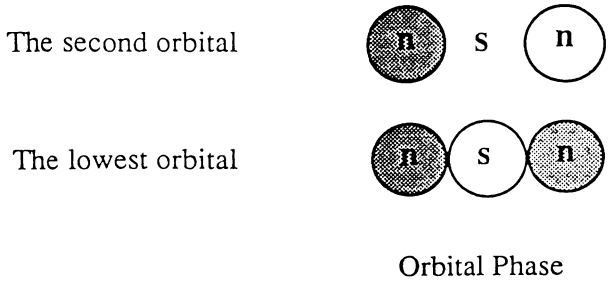
	Bond Length (A)			Angle (degree)	
	C-N*	N*-N	N-C	CN*N	N*NC
Ground State					
(V)	1.309	1.306	1.452	121.4	129.5
(VI)	1.367	1.339	1.367	128.5	128.5
n--> π^* State					
(V)	1.389	1.375	1.537	142.5	122.4
(VI)	1.484	1.336	1.484	145.8	145.8
n^2--> π^{*2} State					
(V)	1.700	1.464	1.600	177.0	113.5
(VI)	1.775	1.396	1.775	179.5	179.5

Table IV Total energies and relative energies of the model molecules (V and VI) with MP3/6-31G**//3-21G.

	Total Energy (a.u.)	Relative Energy (kcal/mol)
Ground State		
(V)	-187.99839	0.0
(VI)	-187.89569	64.5
n--> π^* State		
(V)	-187.78786	0.0
(VI)	-187.68829	62.5
n^2--> π^{*2} State		
(V)	-187.53267	0.0
(VI)	-187.49374	24.4

length and the C-N*-N angle. The geometry variation between the n-->π^* state and the n^2-->π^{*2} state is larger than that between the ground state and the n-->π^* state.

Total energies and the relative energies of the model molecules are listed in Table IV. The energy barrier at the ground state is about 10 kcal/mol higher than that of pyrazol at the same level of theory. The energy barrier at the ground state is about 2 kcal/mol lower than that at the n-->π^* state. In pyrazol, the energy barrier at the ground state is about 2 kcal/mol higher than that at the triplet state. We consider that this difference of the energy barrier between the model and pyrazol arises from the relaxation of the CN*C angle. This becomes clearer for the n^2-->π^{*2} state. The energy barrier reduces for the decrease of the occupation number in the lone pair orbital. This reason can be explained easily from orbital overlaps. We consider in-plane bonding closely related to the transition state (VI). The 1s orbital of the active hydrogen atom and two n orbitals of nitrogen are important for the transition state. The overlap between n and 1s (or n) orbitals increases with an increase in the CN*N angle. Consequently, the lowest occupied orbital becomes stable for the increase in the CN*N angle. The second orbital becomes unstable because of is antisymmetric character.



The differences between the vertical and adiabatic excitation energies from the ground state to the $n \rightarrow \pi^*$ or the $n^2 \rightarrow \pi^{*2}$ states in (V) are 12.8 kcal/mol and 61.5 kcal/mol at the MP3/6-31G** level, respectively. This energy difference at the $n^2 \rightarrow \pi^{*2}$ state is drastic, and the reason arises from the deformation of the CN*N angle. Though the transition state at the $n \rightarrow \pi^*$ state is about 49.7 kcal/mol higher in energy than the vertical excited state of the structure (V), the transition state at the $n^2 \rightarrow \pi^{*2}$ state is about 37.0 kcal/mol lower than the vertical excited state. Therefore, the $n^2 \rightarrow \pi^{*2}$ state is a good candidate for the switching mechanism. If the excitation of the $n^2 \rightarrow \pi^{*2}$ state and the N-N-H bending mode occurs, there is a possibility of the switching by the hydrogen shift as shown in Figure 2.

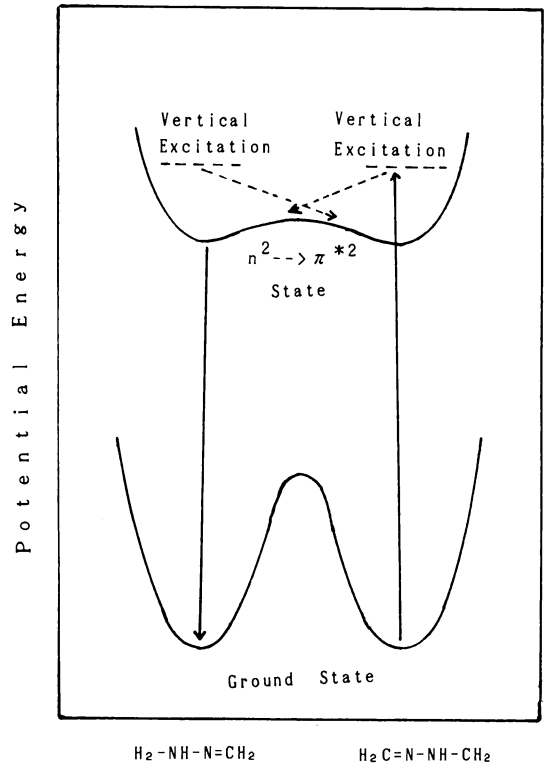


Figure 2 Switching scheme for $H_2CNNHCH_2$ model.

4. CONCLUSIONS

The potential energies of pyrazol and 5-methyl pyrazol at the ground state and the triplet excited state were calculated by the ab initio molecular orbital methods. These potential energies have high energy barriers for 1,2 hydrogen migration and are not ideal potential surfaces for the switching mechanism by the hydrogen shift. From the molecular orbital phase concept, it is also considered that the ideal switching does not occur at the other excitations.

To search for the possibility of switching molecule, we studied the π effects and the σ effects; the bond alternation of ring and the occupation number of the lone pair in nitrogen atom. The energy of π effects was small compared with the energy barrier of the hydrogen migration. The simple model molecule was used to study the σ effects. In the simple model, the possibility of the switching mechanism was found at the $n^2 \rightarrow \pi^{*2}$ excitation with the relaxation of the CNN angle. Namely the mechanism is the hydrogen anion shift, and the relaxation of the CNN angle is the important.

ACKNOWLEDGMENT

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