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Ab initio SCF Calculations of Potential Energy Surfaces for the Proton Transfer in a Formamide Dimer

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Potential energy surfaces for the proton transfer in a formamide dimer have been obtained by *ab initio* SCF calculations with STO-3G, 3-21G, and 4-31G basis sets and several features have been discussed. Energy minima for a formamide dimer and its tautomer are varied with basis sets. But the general features of the potential energy surfaces are similar among them.

Introduction

The hydrogen bond and the proton transfer are very important to understand various phenomena in many chemical and biological systems. Due to those importances, there are many studies on the single or multiple and the inter or intramolecular hydrogen bonds and the proton transfers[1-13]. Löwdin suggested that the proton transfer in a DNA base pair might be an origin of the mutation[3] and Clementi *et al.* performed an *ab initio* study for the hydrogen bond in the guanine-cytosine base pair[4]. Del Bene *et al.* and other groups also performed an *ab initio* calculations for the proton transfers in a formic acid dimer and other systems[5]. The study on the potential energy surface of the proton transfer is very important as a starting point for the theoretical study of the proton transfer rate. In this study, the potential energy surfaces for the proton transfer in a formamide dimer have been obtained by *ab initio* SCF calculations with three kinds of basis sets, such as STO-3G, 3-21G, and 4-31G. The proton transfer in formamide dimer can be considered as a simple model for the asymmetric intermolecular double proton transfer whereas the proton transfer in a formic acid dimer can be considered as a simple model for the symmetric intermolecular double proton transfer. As mentioned above, there are some studies on the proton transfer in a formic acid dimer. But in the case of the proton transfer in a formamide dimer, it is not so. That is the direct motive of this study. Therefore, the results obtained in this study have been compaired with other's results.

Methods of Calculations

All *ab initio* calculations in this study have been performed on a Cray-2 computer using the program of Gaussian-86 version. Three kinds of basis sets, such as STO-3G, 3-21G, and 4-31G, have been used. The initial geometry for a formamide dimer is taken from Ottersen *et al.*[14] The schematic structures of a formamide dimer (A) and its tautomer (B), which

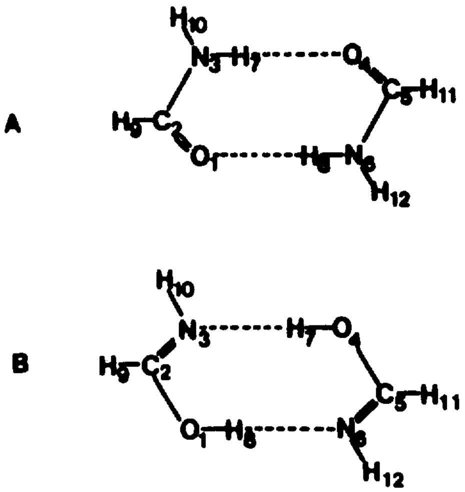

Figure 1. The schematic structures of a formamide dimer (A) and its tautomer (B).

have C_{2h} symmetry, are shown in Figure 1. The structure of B has been made by the double proton transfer in a formamide dimer. In order to obtain the potential energy surface for the proton transfer in a formamide dimer, two structural parameters have been chosen. One is the distance between a proton-donor (N_3) and a proton-acceptor (O_4), d(N_3-O_4), and the other is the distance between a proton-donor (N_3) and a transferred proton (H_7), d(N_3-H_7). (See Figure 1 for the numbering system). For the reliable potential energy surface, all structural parameters, except above two parameters, have been optimized and C_{2h} symmetry has been maintained. Full-optimized structures and energies for a formamide dimer and its tautomer have been also obtained. In this case, above two selected structural parameters, such as d(N_3-O_4) and d(N_3-H_7) have been also optimized, and C_{2h} symmetry has been also maintained. The obtained results have been discussed in the next section.

Table 1. Energies Calculated with STO-36 basis set for the Double Proton Transfer in a Formatide Dimer

d(N_2-H_7)/d(N_3-O_4)	E(Hartree)							
	2.35	2.45	2.55	2.65	2.75	2.85	2.95	3.05
0.92	−333.3476857	−333.3596397	−333.3658843	−333.3684990	−333.3689122	−333.3680910	−333.3666670	−333.3650311
1.02	−333.3823851	−333.3928690	−333.3976527	−333.3989580	−333.3982238	−333.3964061	−333.3941272	−333.3917699
1.12	−333.3871882	−333.3933903	−333.3938611	−333.3915151	−333.3878831	−333.3838151	−333.3798001	−333.3761058
1.22	−333.3856015	−333.3870851	−333.3801214	−333.3704246	−333.3606513	−333.3518387	−333.3442899	−333.3380065
1.32	−333.3822593	−333.3877100	−333.3749997	−333.3553074	−333.3350295	−333.3171870	−333.3026660	−333.2912987
1.42	−333.3595966	−333.3896569	−333.3833696	−333.3587640	−333.3272571	−333.2960428	−333.2691681	−333.2480301
1.52	−	−333.3699033	−333.3915677	−333.3765981	−333.3427133	−333.3011490	−333.2593441	−333.2224264
1.62	−	−	−333.3746571	−333.3904711	−333.3693464	−333.3287193	−333.2794833	−333.2287242
1.72	−	−	−	−333.3759605	−333.3877950	−333.3624649	−333.3172127	−333.2626558
1.82	−	−	−	−	−333.3751890	−333.3843881	−333.3562811	−333.3079945
1.92	−	−	−	−	−	−333.3732577	−333.3807663	−333.3508883
2.02	−	−	−	−	−	−	−333.3707717	−333.3772382
2.12	−	−	−	−	−	−	−	−333.3681194

Bond lengths in Å

Table 2. Energies Calculated with 3-21G Basis Set for The Double Proton Transfer in a Formamide Dimer

d(N_3-H_7)/d(N_3-O_4)	E(Hartree)					
	2.45	2.55	2.65	2.75	2.85	2.95
0.95	−335.9669531	−335.9772492	−335.9831705	−335.9861628	−335.9872210	−335.9870158
1.02	−335.9853120	−335.9955955	−336.0012959	−336.0039581	−336.0046337	−336.0040276
1.12	−335.9787792	−335.9872701	−335.9912326	−335.9923485	−335.9916974	−335.9899720
1.22	−335.9671364	−335.9720615	−335.9723054	−335.9700340	−335.9665006	−335.9624095
1.32	−335.9599353	−335.9616482	−335.9568930	−335.9492960	−335.9408397	−335.9325362
1.42	−335.9553894	−335.9595625	−335.9515490	−335.9381787	−335.9231865	−335.9085929
1.52	−335.9390159	−335.9597738	−335.9556195	−335.9396130	−335.9187306	−335.8968766
1.62	−	−335.9460393	−335.9604540	−335.9498869	−335.9274407	−335.9001718
1.72	−	−	−335.9491679	−335.9588950	−335.9434448	−335.9159082
1.82	−	−	−	−335.9497779	−335.9560582	−335.9369215
1.92	−	−	−	−	−335.9488128	−335.9525634
2.02	−	−	−	−	−	−335.9469100

Bond lengths in Å

Table 3. Energies Calculated with 4-31G Basis Set for The Double Proton Transfer in a Formamide Dimer

$d(N_3\text{-}H_7)/d(N_3\text{-}O_4)$	E(Hartree)					
	2.45	2.55	2.65	2.75	2.85	2.95
0.92	–337.3494089	–337.3607397	–337.3676659	–337.3715808	–337.3734715	–337.3740321
1.02	–337.3648205	–337.3761398	–337.3829726	–337.3867106	–337.3883528	–337.3886144
1.12	–337.3556820	–337.3648748	–337.3699795	–337.3723319	–337.3728439	–337.3721631
1.22	–337.3424885	–337.3472081	–337.3482437	–337.3472473	–337.3450981	–337.3423168
1.32	–337.3356715	–337.3357373	–337.3308128	–337.3241248	–337.3171277	–337.3104242
1.42	–337.3337813	–337.3347489	–337.3250942	–337.3116263	–337.2977114	–337.2848303
1.52	–337.3220876	–337.3382218	–337.3308874	–337.3132924	–337.2924369	–337.2718913
1.62	–	–337.3295172	–337.3393559	–337.3256636	–337.3017244	–337.2746558
1.72	–	–	–337.3332590	–337.3384532	–337.3199434	–337.2910371
1.82	–	–	–	–337.3345667	–337.3363347	–337.3142061
1.92	–	–	–	–	–337.3343013	–337.3335424
2.02	–	–	–	–	–	–337.3330573

Bond lengths in Å.

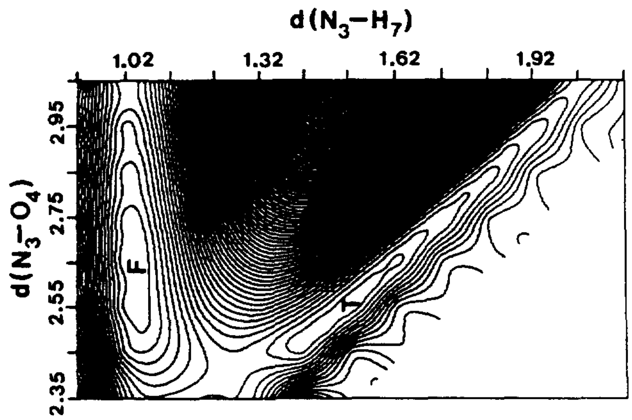

Figure 2. The contour map of the potential energy surface for the proton transfer in a formamide dimer obtained with STO-3G basis set. The interval between the lines is 0.002 Hartree. F and T are potential energy minima for a formamide dimer and its tautomer, respectively.

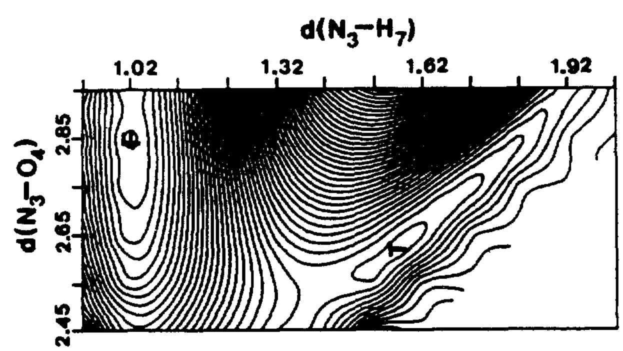

Figure 3. The contour map of the potential energy surface for the proton transfer in a formamide dimer obtained with 3-21G basis set. The interval between the lines is 0.002 Hartree. F and T are potential energy minima for a formamide dimer and its tautomer, respectiviely.

Results and Discussion

The optimized potential energies calculated with STO-3G,

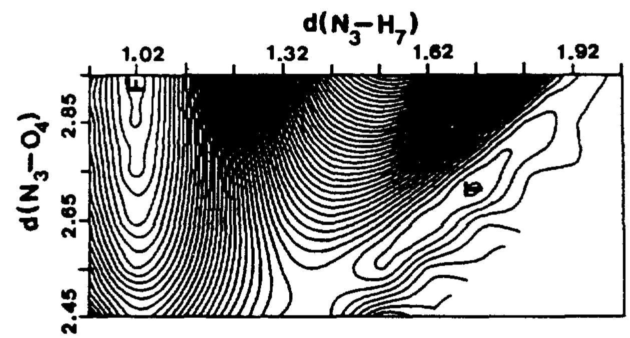

Figure 4. The contour map of the potential energy surface for the proton transfer in a formamide dimer obtained with 4-31G basis set. The interval between the lines is 0.002 Hartree. F and T are potential energy minima for a formamide dimer and its tautomer, respectively.

3-21G, and 4-31G for the proton transfer in a formamide dimer as a function of two structural parameters, d $(N_3\text{-}O_4)$ and $(N_3\text{-}H_7)$, are listed in Tables 1, 2, and 3, respectively. And potential energy surfaces for the proton transfer in a formamide dimer obtained with STO-3G, 3-21G, and 4-31G are also shown in Figures 2, 3, and 4, respectively. Energy minima for a formamide dimer (F) and its tautomer (T) are varied with basis sets. But the general features of potential energy surfaces are similar among them. The proton transfer mechanism for a formamide dimer may be predicted by the lowest potential energy trajectory in the potential energy surface. At first, the distance between a proton-donor and a proton-acceptor, d $(N_3\text{-}O_4)$, is shortened relatively faster than the distance between a proton-donor and a transferred proton, d $(N_3\text{-}H_7)$, is elongated. But after passing a transition state, $d(N_3\text{-}O_4)$ and $d(N_3\text{-}H_7)$ are elongated with a similar rate. The shape of a potential energy profile at a fixed $d(N_3\text{-}O_4)$ can be known from the potential energy surfaces. When the fixed $d(N_3\text{-}O_4)$ becomes smaller, the shape of potential energy profile is changed from the double-well to the single-well. The shapes of potential energy profiles obtained with several fixed distances between a proton-donor and a proton-acceptor have been already reported by us[15]. Energies and geometries obtained with diffe-

Table 4. Energies Calculated with Three Different Basis Sets for a Formamide Dimer and Its Tautomer

Basis set	E(Hartree)		ΔE(kcal/mol)[a]
	Formamide dimer	Its tautomer	
STO-3G	−333.3996599	−333.3915783	5.07
3-21G	−336.0046736	−335.9605572	27.68
4-31G	−337.3889763	−337.3403000	30.54

[a]ΔE = E(tautomer) − E(formamide dimer).

rent basis sets for a formamide dimer and its tautomer are summarized in Tables 4 and 5, respectively, In these calculations, all geometric parameters are optimized. The relative energy differences between a formamide dimer and its tautomer are changed according to basis sets. The energy difference obtained with STO-3G (5.07 kcal/mol) is smaller than those obtained with 3-21G and 4-31G (27.68 and 30.54 kcal/mol, respectively). That is, STO-3G basis set lowers the energy of the tautomer relatively more than 3-21G and 4-31G. Optimized geometries are also affected by basis sets. $d(N_3\text{-}O_4)$ obtained with STO-3G (2.631 Å) is shorter than those obtained with 3-21G and 4-31G (2.848 and 2.934 Å, respectively). The result obtained with STO-3G is underestimated by about 10%, compaired with the experimental result (2.94 Å), although the experimental result is the measurement in a crystal[16]. Similar results for a formic acid dimer were reported by Del Bene *et al.*. The distinguished changes between a formamide dimer and its tautomer in a geometry are the distances ($d(O_1\text{-}C_2)$ and $d(C_2\text{-}N_3)$). $d(O_1\text{-}C_2)$ is changed from double-bond character to a single-bond character as the result of a proton transfer, while $d(C_2\text{-}N_3)$ is changed from single-bond character to double-bond character. Therefore, the geometry optimization of the neighboring fragments must be done in the study on the proton transfer in order to obtain the reliable data. Another feature is that $d(N_3\text{-}O_4)$ of the tautomer is shorter than that of the formamide dimer. Total atomic charges for a formamide dimer and its tautomer are listed in Table 6. The characteristic change is the negative charge transfer from a proton-donor (N_3) to a proton-acceptor (O_4) as the result of a proton transfer.

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Table 5. Geometries Obtained with Different Basis Sets for a Formamide Dimer and Its Tautomer

	Formamide dimer			Its tautomer		
	STO-3G	3-21G	4-31G	STO-3G	3-21G	4-31G
$d(O_1\text{-}C_2)$	1.234	1.232	1.232	1.337	1.317	1.320
$d(C_2\text{-}N_3)$	1.377	1.331	1.329	1.293	1.268	1.264
$d(N_3\text{-}O_4)$	2.631	2.848	2.934	2.559	2.615	2.702
$d(N_3\text{-}H_7)$	1.042	1.015	1.006	1.533	1.579	1.707
$d(C_2\text{-}H_9)$	1.106	1.082	1.080	1.100	1.076	1.073
$d(N_3\text{-}H_{10})$	1.014	0.995	0.990	1.034	1.005	0.999
$a(O_1\text{-}C_2\text{-}H_9)$	122.0	120.4	120.2	113.3	112.6	112.2
$a(O_1\text{-}C_2\text{-}H_3)$	124.5	125.1	124.3	123.9	124.0	123.3
$a(C_2\text{-}N_3\text{-}O_4)$	121.0	119.4	119.3	128.3	122.2	121.5
$a(H_7\text{-}N_3\text{-}H_{10})$	119.9	119.0	118.9	121.2	121.1	121.6
$a(N_3\text{-}O_4\text{-}C_5)$	114.5	115.5	116.4	107.8	113.8	115.2

Bond lengths in Å, Angles in degrees.

Table 6. Total Atomic Charges for a Formamide Dimer and Its Tautomer

	Formamide dimer			Its tautomer		
	STO-3G	3-21G	4-31G	STO-3G	3-21G	4-31G
O_1, O_4	−0.308	−0.650	−0.676	−0.334	−0.755	−0.785
C_2, C_5	0.262	0.628	0.597	0.225	0.557	0.518
N_3, N_6	−0.463	−0.959	−0.937	−0.414	−0.840	−0.796
H_7, H_8	0.262	0.421	0.467	0.295	0.488	0.531
H_9, H_{11}	0.058	0.206	0.179	0.072	0.232	0.204
H_{10}, H_{12}	0.188	0.354	0.371	0.156	0.318	0.328

Due to C_{2h} symmetry, atomic charges of O_4, C_5, N_6, H_8, H_{11}, and H_{12} are same with those of O_1, C_2, N_3, H_7, H_9, and H_{10}, respectively.

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Synthetic Studies on Jasmonoids (I): Jasmone, Dihydrojasmone, and Tetrahydrojasmone

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Facile and efficient syntheses of terpenic perfumeries *cis*-jasmone, dihydrojasmone, and tetrahydrojasmone have been investigated. *Cis*-jasmone was synthesized by successive metallation followed by alkylation of acetone N,N-dimethylhydrazone with (Z)-2-penten-1-yl tosylate (or 2-pentyn-1-yl tosylate) and propylene oxide in one flask to give a ketonic alcohol, which was oxidized to the corresponding diketone, followed by base-catalyzed intramolecular aldol condensation to give a regioselective cyclization product.

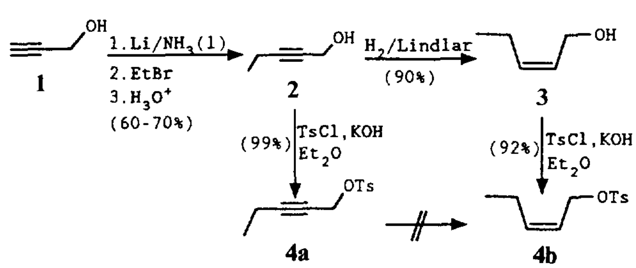
Dihydrojasmone and tetrahydrojasmone could be conveniently obtained from 2-octanone. The dimethylhydrazone of the ketone was lithiated with butyllithium and reacted with propylene oxide to give a ketonic alcohol, which was oxidized to a diketone, followed by base-catalyzed intramolecular cyclization to afford dihydrojasmone. Tetrahydrojasmone was prepared by converting the ketonic alcohol into corresponding iodoketone, followed by base-catalyzed intramolecular cycloalkylation to furnish an odoriferous product.

Introduction

Jasmine and rose oils have long been the core of the finest perfumes, and constant efforts have been made to better understand the composition of these oils. Chemical research on jasmine oil, obtained from the flowers of *Jasminium grandiflorum L.*, was started in 1899 by Verley,[1] followed by Hesse and Müller[2,3] who identified half a dozen compounds. *Cis*-jasmone(**9b**), a naturally occurring derivative of cyclopentenone, is one of the essential components of jasmine oil. Because of the difficulty of its manufacture, the price is still relatively high, and studies have been continuing to find more economical procedures for the synthesis of jasmone and structurally related compounds such as dihydro- and tetrahydro- analogs that are useful in perfumery. We now wish to describe a new and efficient synthesis of *cis*-jasmone (**9b**), dihydrojasmone(**14**), and tetrahydrojasmone(**16**) using chemicals of reasonable price.

Results and Discussion

Several syntheses of *cis*-jasmone(**9b**)[4-9] have been published. In this investigation, we developed a new synthesis of **9b** by means of successive dialkylation technic of acetone N,N-dimethylhydrazone. The starting materials **4a** and **4b**



Scheme 1.

were prepared from propargyl alcohol(**1**) by the procedure as shown in Scheme 1. The propynol **1** was ethylated without protection of hydroxy group, but by treating it with lithium amide followed by reacting the resulted dianion[10] with ethyl bromide to give 2-pentyn-1-ol(**2**). The propargylic alcohol **2** was hydrogenated in the presence of Lindlar catalyst to (Z)-2-penten-1-ol(**3**), which was then tosylated to **4b**. The tosylate **4a** was obtained by treating **2** with tosyl chloride, but it could not be converted efficiently to **4b** by hydrogenation even in the presence of Lindlar catalyst, probably because the hydrogenation was accompanied by reductive cleavage of the tosyl ester moiety.

An effective synthesis of *cis*-jasmone(**9b**) was carried out by the procedure as shown in Scheme 2. Acetone N,N-dime-