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Geometrical and Kinetic Isotope Effects on R–H(D)···R Type Intramolecular Hydrogen Bonds (R = CH_2, NH, and O) Using a Multi-Component Molecular Orbital Method

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We theoretically analyzed the geometrical isotope effect and kinetic isotope effect for R–H(D)···R type proton (deuteron) transfer on the intramolecular hydrogen bond of (*Z*)-1,3-pentadiene (R = CH_2), 3-imino-1-propen-1-amine (R = NH), and malonaldehyde (R = O) by using Hartree–Fock (HF) and second-order Møller–Plesset (MP2) levels of a multi-component molecular orbital (MC_MO) method to treat the quantum effects of nuclei. As the protonic and deuteronic basis functions, our proposed exponent values of 24.1725 and 35.6214 for the single protonic and deuteronic Gaussian-type functions were employed, respectively. In the case of R = NH and O, the calculated R^5–D^6 and R^1···D^6 bond lengths are shorter and longer than those of the R^5–H^6 and R^1···H^6 bonds due to the anharmonicity of the potential. The charge densities around the deuteron for all R = CH_2, NH, and O cases are larger than those around the proton because the deuteron is more localized than the proton. The ratio of rate constant (k_a^H/k_a^D) obtained by MP2 level theory of the MC_MO method is estimated as 10.16, which is in reasonable agreement with the experimental result (12.2). For the systematic analysis of the intramolecular proton (deuteron)-transfer reaction, we also estimated the k_a^H/k_a^D of R = NH and O.

Hydrogen (or proton) transfer has been a topic of much interest because of its importance in many chemical and biological processes.[1,2] To explore detailed reaction mechanisms, the kinetic isotope effect (KIE) on the reaction is often analyzed after replacing hydrogen with deuterium.

(*Z*)-1,3-Pentadiene is the simplest model for a molecule representing thermal [1,5]-sigmatropic hydrogen-shift, which is not only one of the most important sigmatropic rearrangements, but also one of the most fundamental hydrogen-transfer reactions.[3–5] The experimental hydrogen/deuterium ratio in the KIE of the homogeneous gas-phase reaction for (*Z*)-1,3-pentadiene was examined by Roth and König.[6,7] The large $k^H/k^D = 12.2$ (k^H and k^D refer to the rate constant of the reaction for H and D compounds, respectively) at 298 K was measured. Recently, Itou et al.[8] studied the KIE with geometrical isotope effect (GIE) for thermal [1,5]-sigmatropic H and D shifts of (*Z*)-1,3-pentadiene by including the direct quantum effect of the migrating H or D nucleus in the multi-component molecular orbital (MC_MO) method,[9–11] which determines both the electronic and protonic (deuteronic) wave functions simultaneously. They have reported that the k^H/k^D of the reaction for the thermal [1,5]-H and -D shifts using the Hartree–Fock (HF) level of the MC_MO method (8.28) is closer to the experimental value than those using either conventional HF (4.10) or second-order Møller–Plesset (MP2) (3.79) methods based on the Born–Oppenheimer approximation. Their results suggested the efficiency of the MC_MO method to estimate the KIE. Also, the electron–electron correlation effect cannot improve the accuracy of the value of k^H/k^D from the comparison with the HF and MP2 calculations of the conventional MO.

On the other hand, 3-imino-1-propen-1-amine and malonaldehyde are known as isoelectronic compounds of (*Z*)-1,3-pentadiene. 3-Imino-1-propen-1-amine and related compounds were studied concerning proton transfer and excited states.[12,13] Malonaldehyde was also studied concerning the intramolecular hydrogen bond, proton transfer, and tunneling dynamics using experimental and theoretical techniques.[14–25] For systematic understanding of isoelectronic compounds of (*Z*)-1,3-pentadiene, the analysis of GIE and KIE is an important approach.

Theoretically, the MC_MO method has been successfully used to analyze the isotope effect induced by H/D.[26–28] In this MC_MO method, both protonic (deuteronic) and electronic molecular orbitals are expressed as linear combinations of Gaussian-type functions (GTFs). However, the protonic and deuteronic basis functions have not yet been systematically determined. In a previous study using the MC_MO method, the nuclear GTF variable parameters such as exponent and center in the protonic and deuteronic basis functions were optimized for given molecular systems. However, optimization of GTF variable parameters in protonic and deuteronic GTF in a molecular system is very difficult for larger molecules. Very recently, we have proposed an adequate exponent value in protonic and deuteronic GTF as the protonic and deuteronic basis functions.[29] The proposed nuclear basis function enables

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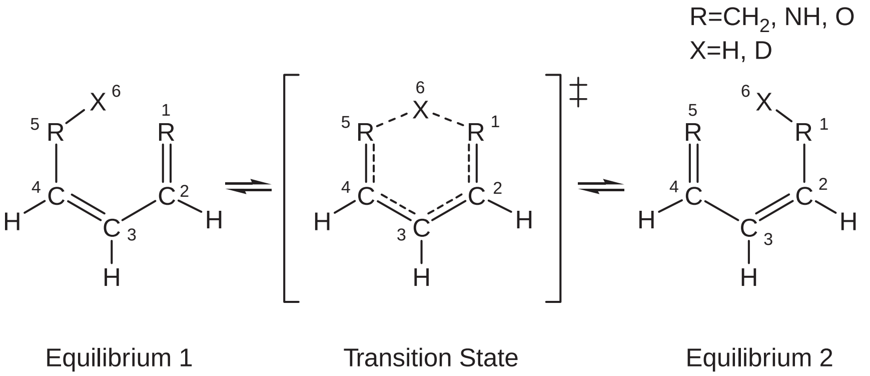


Figure 1. The intramolecular proton-transfer reaction scheme of (*Z*)-1,3-pentadiene ($R = CH_2$) and its isoelectronic compounds: 3-imino-1-propen-1-amine (R = NH) and malonaldehyde (R = O).

the reduction of computational cost considerably and extension of the application ranges of the MC_MO method.[30]

We report an important effect of the quantum mechanical feature of the proton and deuteron on the GIE and KIE by applying the MC_MO method to (*Z*)-1,3-pentadiene, 3-imino-1-propen-1-amine, and malonaldehyde. The geometrical changes and the electronic charge distributions are explained by the difference of the protonic and deuteronic wave functions. In this study, our proposed exponent values for protonic and deuteronic GTFs are used as the protonic and deuteronic basis functions.

Theory of the MC_MO Method

We first describe an outline of the MC_MO method under the HF approximation. In order to obtain both electronic and nuclear wave functions simultaneously and directly, Tachikawa et al. have proposed the MC_MO method. In the MC_MO method, the effective one particle operators for an electron f^e and a proton f^p are given by the variational method as

$$f^e\phi_i = \varepsilon_i\phi_i,\ f^e = h^e + \sum_i^{N_e}(J_i - K_i) - \sum_p^{N_p} J_p \tag{1}$$

$$f^p\phi_p = \varepsilon_p\phi_p,\ f^p = h^p + \sum_p^{N_p}(J_p - K_p) - \sum_i^{N_e} J_i \tag{2}$$

where J and K are Coulomb and exchange operators, respectively. The effective field f^e of the electronic MOs ϕ_i in eq 1 depends on the nuclear MOs ϕ_p and the remaining electronic MOs. The effective field f^p of the nuclear MOs ϕ_p in eq 2 depends on the electronic MOs ϕ_i and the remaining nuclear MOs. The MOs ϕ_i and ϕ_p are obtained by solving eqs 1 and 2, iteratively. The differences between protons and deuterons appear as the masses in the kinetic operator, which have the values 1836.59 and 3664.58 au, respectively. We used the linear combination of GTFs (LCGTFs) for both electronic and nuclear MOs as

$$\phi_i = \sum_r C_{ri}{}^e \chi_r{}^e \tag{3}$$

$$\phi_p = \sum_v C_{vi}{}^p \chi_v{}^p \tag{4}$$

$$\chi_r^e = (x - X_r)^{l_r}(y - Y_r)^{m_r}(z - Z_r)^{n_r}\exp\{-\alpha_r(r - R_r)^2\} \tag{5}$$

$$\chi_v^p = (x - X_v)^{l_v}(y - Y_v)^{m_v}(z - Z_v)^{n_v}\exp\{-\alpha_v(r - R_v)^2\} \tag{6}$$

where, $C_{ri}{}^e$ and $C_{vi}{}^p$ are LCGTF coefficients for electron and proton, respectively. In eqs 5 and 6, there are two kinds of parameters such as GTF exponents (α_r, α_v) and their centers ($R_r = \{X_r, Y_r, Z_r\}$, $R_v = \{X_v, Y_v, Z_v\}$), respectively.

Computational Details

We calculated the optimized structures and the total energies in each equilibrium and transition state of three molecules forming R–H(D)···R type intramolecular hydrogen bonds of (*Z*)-1,3-pentadiene ($R = CH_2$), 3-imino-1-propen-1-amine (R = NH), and malonaldehyde (R = O), as shown in Figure 1. The MC_MO method was used under the HF and MP2 level of theory for all calculations. We used the 6-31G(d,p) basis function[31–34] for each electron. The single s-type ([1s]) GTFs, $\exp\{-\alpha(r - R)^2\}$, as a basis function are employed for the transferring proton and deuteron, and the GTF variable parameter of center (R) was optimized. Our proposed orbital exponent (α) values, 24.1825 and 35.6214, were used in the protonic and deuteronic GTF, respectively.[30] The positions (geometries) of the point charges were determined by ordinary optimization procedures using analytical gradient.[35] To analyze the GIE, the position of the proton and deuteron treated as a quantum wave is regarded as the GTF center of the [1s] GTF for proton and deuteron. The centers of the electronic GTFs for C, N, and O atoms were fixed at the center of each nucleus. The center of the electronic GTF for the hydrogen (deuterium) is also fixed on the center of [1s] GTF of the proton (deuteron). Accuracy for the discussion of the geometrical difference induced by H/D is less than 0.001 Å in this calculation. In order to compare the calculated results, conventional MO method calculations were carried out. All calculations are performed by using the Gaussian03 package program,[36] in which the MC_MO method is embedded.

The MC_MO method cannot obtain the conventional transition-state structure because the proton and deuteron are treated quantum-mechanically as well as electrons. We define the transition state under the MC_MO method beyond the classical framework. The geometry of the transition state concerning the motion of the proton (deuteron) is determined so that the position of the nucleus is regarded as the [1s] GTF in proton and deuteron as well as the geometry of the equilibrium structure. Correction for the transition state, such as zero-point energy (ZPE), is not necessary since the transition state obtained by

Table 1. Bond Lengths (Å) in Equilibrium and Transition-State Structures of (*Z*)-1,3-Pentadiene ($R = CH_2$), 3-Imino-1-propen-1-amine ($R = NH$), and Malonaldehyde ($R = O$) Obtained by the Conventional MO and MC_MO Calculations under the HF Level of Theory[a)]

		Equilibrium structure			Transition-state structure		
		CH_2	NH	O	CH_2	NH	O
R^5–X^6	MC_MO (H)	1.104	1.020	0.983	1.461	1.275	1.201
	MC_MO (D)	1.097	1.013	0.974	1.455	1.271	1.197
	Conventional MO	1.082	0.996	0.956	1.440	1.262	1.188
$R^1 \cdots X^6$	MC_MO (H)	2.780	2.053	1.807	1.461	1.275	1.201
	MC_MO (D)	2.782	2.070	1.830	1.455	1.271	1.197
	Conventional MO	2.786	2.110	1.880	1.440	1.262	1.118

a) R^1 and R^5 denote C^1, N^1, and O^1, in R^1 group and C^5, N^5, and O^5 in R^5 group, respectively.

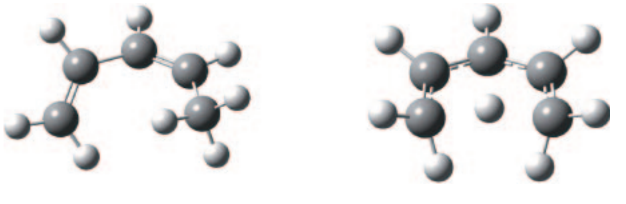
the MC_MO calculation includes the ZPE and the effect of anharmonicity of the potential.

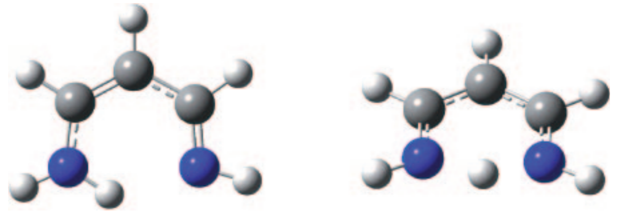
Results and Discussion

Geometrical Change Induced by H/D. We first discuss the equilibrium structures of (*Z*)-1,3-pentadiene ($R = CH_2$), 3-imino-1-propen-1-amine ($R = NH$), and malonaldehyde ($R = O$). The geometrical parameters of the covalent bond (R^5–X^6) and hydrogen bond ($R^1 \cdots X^6$) of (*Z*)-1,3-pentadiene, 3-imino-1-propen-1-amine, and malonaldehyde are shown in Table 1. In Table 1, the results of conventional MO calculations are shown for comparison with the MC_MO calculations. Optimized equilibrium structures are also shown in Figure 2. The equilibrium structures of $R = CH_2$ have torsional C_1 symmetry and those of $R = NH$ and O planer C_s symmetries, respectively. The transferring proton (deuteron) is located out of the molecular plane, indicating torsional structure with a C^3–C^4–R^5–C^6 torsion angle of about 30 degrees in the case of $R = CH_2$. On the other hand, the transferring proton (deuteron) is located on a cyclic molecular plane in the case of $R = NH$ and O.

In the case of $R = NH$, comparing the conventional MO method with the MC_MO method under the HF level of theory, the N^5–X^6 and $N^1 \cdots X^6$ obtained by the MC_MO method are longer and shorter than those of the conventional MO method in both cases of $X = H$ and D respectively, due to the quantum treatment of proton and deuteron. The covalent bond length of N^5–H^6 is 1.020 Å. The calculated N^5–D^6 bond length is shorter by 0.007 Å than that of the N^5–H^6 bond due to the anharmonicity of the potential. Reflecting this geometrical change in the covalent bond, the $N^1 \cdots D^6$ hydrogen bond is longer than the $N^1 \cdots H^6$ bond.

By replacing the NH with O, the covalent bond O^5–X^6 length is shorter than covalent N^5–H^6 in the conventional MO and MC_MO calculations. The $O^5 \cdots X^6$ hydrogen bond is also shorter than $N^5 \cdots X^6$. This contraction of bond distance by replacing NH with O is caused by the strength of the hydrogen bond. The geometrical change in $R = O$ induced by the H/D isotope effect shows the same tendency as well as the case of $R = NH$. The geometrical parameters of malonaldehyde are different between the experimental[22] and present results. The detailed discussion about the deviation of geometrical parameters abbreviates, because the evaluation of quantum behavior induced by H/D isotope effect is important in this study. Also, it is expected that the implementation of wave functions and basis functions enables satisfaction of the geometrical parameters obtained by experiment. Similar geometries of $R = O$ are theoretically obtained in comparison with present and previous[16] studies by using the conventional MO method.


Equilibrium ($R = CH_2$) Transition State ($R = CH_2$)


Equilibrium ($R = NH$) Transition State ($R = NH$)

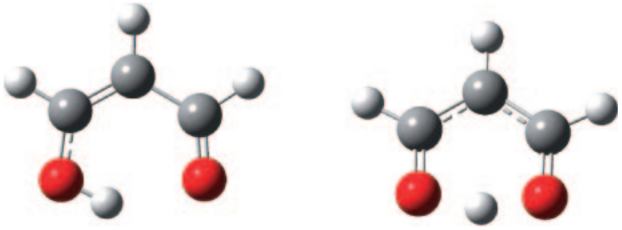

Equilibrium ($R = O$) Transition State ($R = O$)

Figure 2. Optimized structures of equilibrium and transition-state structures of (*Z*)-1,3-pentadiene ($R = CH_2$) and its isoelectronic compounds: 3-imino-1-propen-1-amine ($R = NH$) and malonaldehyde ($R = O$).

In the case of $R = CH_2$, similar results are obtained concerning the geometrical change induced by the H/D isotope effect in comparison with previous work.[8] These result confirm the efficiency of the proposed exponent values for protonic and deuteronic GTFs in Ref. 28 to analyze the H/D isotope effect not only for $R = CH_2$ but also for $R = NH$ and O in the equilibrium structures.

Table 2. Mulliken Charges in Equilibrium and Transition-State Structures of (*Z*)-1,3-Pentadiene (R = CH_2), 3-Imino-1-propen-1-amine (R = NH), and Malonaldehyde (R = O) Obtained by the Conventional MO and MC_MO Calculations under the HF Level of Theory[a)]

		Equilibrium structure			Transition-state structure		
		CH_2	NH	O	CH_2	NH	O
X^6	MC_MO (H)	0.167	0.417	0.467	0.155	0.535	0.567
	MC_MO (D)	0.158	0.402	0.450	0.150	0.527	0.558
	Conventional MO	0.134	0.362	0.404	0.136	0.503	0.525
R^1	MC_MO (H)	−0.279	−0.669	−0.611	−0.419	−0.824	−0.705
	MC_MO (D)	−0.278	−0.664	−0.607	−0.413	−0.818	−0.699
	Conventional MO	−0.278	−0.667	−0.588	−0.396	−0.801	−0.664
R^5	MC_MO (H)	−0.411	−0.798	−0.675	−0.419	−0.824	−0.705
	MC_MO- (D)	−0.398	−0.782	−0.659	−0.413	−0.818	−0.699
	Conventional MO	−0.364	−0.737	−0.598	−0.396	−0.801	−0.664

a) R^1 and R^5 denote C^1, N^1, and O^1, in R^1 group and C^5, N^5, and O^5 in R^5 group, respectively.

Table 3. Activation Energies (kJ mol^{-1}) of (*Z*)-1,3-Pentadiene (R = CH_2), 3-Imino-1-propen-1-amine (R = NH), and Malonaldehyde (R = O) Compounds Obtained by Conventional MO and MC_MO Calculations under the HF and MP2 Level of Theory

	R	E_a	E_a^H	E_a^D	E_a^H	E_a^D
		MO	MO with ZPEC[a)]		MC_MO	
HF	CH_2	230.29	220.79	224.26	213.05	218.07
	NH	69.37	58.91	62.63	49.50	54.98
	O	42.97	30.59	34.52	26.44	31.00
MP2	CH_2	142.30	133.39	136.69	66.86	72.59
	NH	33.22	23.05	26.61	9.83	14.14
	O	15.19	4.69	8.16	8.08	10.50

a) Zero-point energy correction.

We show in Table 2 the charge densities calculated by using Mulliken population analysis of R^1, R^5, and X^6 in the intramolecular hydrogen bond. The charge densities around the deuteron for all R = CH_2, NH, and O cases are larger than those around the proton. This tendency is caused by the difference of the distribution of proton and deuteron because the exponent value in deuteronic GTF is larger than that in the proton. In other words, the distribution of deuteron is more localized than that of proton. In addition, the difference of charge densities induced by the difference of quantum effect of proton and deuteron reflects the difference of charge densities surrounding C, N, and O atoms.

We next show the results of transition-state structures of R = CH_2, NH, and O. The geometrical parameters of R^5–X^6 and R^1–X^6 bonds in the transition states are also shown in Table 1. The R^5–X^6 and R^1–X^6 bond lengths are the same as each other because of the symmetry plane. In the case of R = NH, calculated N^5–H^1 bond length is 1.275 Å in the MC_MO calculation. The calculated N^5–D^1 bond length is shorter by 0.004 Å than that of N^5–H^1. By replacing the NH with O, the geometrical difference between O^5–H^1 and O^5–D^1 is 0.004 Å in the MC_MO calculation as well as the case of R = NH. Contrary to the equilibrium structure in the case of R = CH_2, the C^5–H^6 and C^5–D^6 bond distances obtained by the present calculation are about 0.006 Å shorter than those of a previous study. However, we reproduce the geometrical difference induced by the H/D isotope effect because the C^5–D^6 bond length is shorter by 0.006 Å than the C^5–H^6 because the difference of bond distance between C^5–H^6 and C^5–D^6 obtained by the previous study was 0.007 Å.

We show in Table 2 the charge densities calculated by using Mulliken population analysis of R^1, R^5, and X^6 in the hydrogen bond part of transition-state structure. The charge densities around the deuteron are larger than those of the proton as well as in the equilibrium structure.

Energy Change Induced by H/D. We analyzed the energy difference between the equilibrium and transition-state structures. The activation energies of R = CH_2, NH, and O are listed in Table 3. The activation energies become large in the order R = O, NH, and CH_2. The activation energies obtained by the MC_MO method are smaller than those obtained by conventional MO method under the HF level of theory with the ZPE corrections. Conversely, the energy difference between the activation energy of H and D compounds obtained by the MC_MO method is larger than that obtained by conventional MO. The change of nuclear quantum effect by replacing a proton with a deuteron, as treated directly by the MC_MO method, enables evaluation of activation energy difference with geometrical difference although the conventional MO calculation cannot estimate the GIE directly.

Furthermore, we performed the MC_MO calculation under the MP2 level of theory in order to analyze the importance of electron correlation energy for the activation energy induced by the H/D isotope effect. The activation energies of

Table 4. Ratio of Rate Constant (k_a^H/k_a^D) of (*Z*)-1,3-Pentadiene (R = CH_2), 3-Imino-1-propen-1-amine (R = NH), and Malonaldehyde (R = O) Compounds Obtained by Conventional MO and MC_MO Calculations under the HF and MP2 Level of Theory

	R	MO	MC_MO	Obs.
HF	CH_2	4.03	7.53	12.2[a)]
	NH	4.50	9.18	
	O	4.92	6.24	
MP2	CH_2	3.79	10.16	
	NH	4.22	5.66	
	O	4.03	2.66	

a) See Ref. 6.

R = CH_2, NH, and O obtained by MP2 calculation are also listed in Table 3. The activation energies obtained by the MP2 calculation are smaller than those obtained by HF as well as the previous study[16] of R = O.

We have already reported the efficiency to estimate the KIE using the activation energy obtained by the MC_MO calculation.[8,27] Based on the activation energies obtained by our MC_MO calculation, we evaluate the ratio of rate constant (k_a^H/k_a^D) using the following equation,

$$k_a^H/k_a^D = \exp\{-(E_a^H - E_a^D)/RT\} \quad (7)$$

where R and T are the gas constant and temperature (298 K), respectively. The k_a^H/k_a^D of R = CH_2, NH, and O obtained by conventional MO and MC_MO methods under the HF and MP2 level of theory are shown in Table 4. In the conventional MO calculations, large differences between HF and MP2 results of k_a^H/k_a^D do not appear in all compounds. This result indicates that the electron correlation energy is not important for improvement of k_a^H/k_a^D because the geometrical difference induced by the H/D isotope effect cannot be directly expressed in the framework of conventional MO. On the other hand, the k_a^H/k_a^D of R = CH_2, obtained by the MC_MO calculation (7.53) is larger than that obtained by the conventional MO, even though this value is obtained by HF level of theory. By applying the single point MC_MO calculation under the MP2 level of theory using the optimized structure by the MC_MO under the HF, the k_a^H/k_a^D of R = CH_2 is estimated as 10.16, which is in reasonable agreement with the experimental result of 12.2. This result confirms that the electron correlation energy based on the different structure of H- and D-compounds plays an important role to improve the k_a^H/k_a^D. The result of k_a^H/k_a^D obtained by the present calculation enables qualitative analysis of the difference of quantum effect between proton and deuteron. Therefore, we have clearly demonstrated that representation of k_a^H/k_a^D is possible due to expression of the activation energy difference using the MC_MO method which takes into account the quantum effect of the proton and deuteron.

Contrary to the case of R = CH_2, the k_a^H/k_a^D of R = NH and O obtained by MP2 are smaller than those obtained by the HF level of the MC_MO calculation. The k_a^H/k_a^D obtained by MC_MO method under the MP2 level of theory becomes small in the order of CH_2, NH, and O. We theoretically predicted that the k_a^H/k_a^D of R = NH and O would be estimated as 5.66 and 2.66, respectively. The reliability of these values are not estimated directly since there are no experimental results for k_a^H/k_a^D of R = NH and O. In the case of R = NH and O obtained by present calculations, the activation energies are quite small compared with R = CH_2. This result suggests that treatment of proton tunneling is necessary.

Concluding Remarks

We theoretically analyzed the GIE and KIE for R–H(D)···R type proton/deuteron transfer on the intramolecular hydrogen bond of (*Z*)-1,3-pentadiene (R = CH_2), 3-imino-1-propen-1-amine (R = NH), and malonaldehyde (R = O) by using HF and MP2 levels of the MC_MO method to treat the quantum effects of nuclei. In the case of R = NH and O, the R^5–X^6 covalent bond and $R^1\cdots X^6$ hydrogen bond obtained by the MC_MO method are longer and shorter than those of the conventional MO method under the HF level of theory in both cased of X = H and D. The calculated R^5–D^6 and $R^1\cdots D^6$ bond lengths are shorter and longer than those of the R^5–H^6 and $R^1\cdots H^6$ bonds due to the anharmonicity of the potential. We have confirmed the applicability of the protonic and deuteronic GTFs, which have been developed as protonic and deuteronic basis functions, to analyze the geometrical difference induced by H/D. The charge densities around the deuteron for all R = CH_2, NH, and O cases are larger than those around the proton because the deuteron is more localized than the proton. The k_a^H/k_a^D obtained by the MP2 level of the MC_MO method is estimated as 10.16 (experimental result: 12.2), which is largely improved in comparison with the conventional MO method (4.03). For the systematic analysis of the intramolecular proton-transfer reaction, we also estimated the k_a^H/k_a^D of R = NH and O.

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