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Ab initio Study of Hyperconjugative Effect on Electronic Wavefunctions of 2-chloroethanol

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The electronic structure of five conformers of 2-chloroethanol was studied by *ab initio* calculations at B3LYP and MP2 levels of theory with aug-cc-pVTZ basis set. The existing hydrogen bond and hyperconjugation effects on the stability of 2-chloroethanol conformers were discussed on the base of natural bond orbital analyses. The result exhibits that hyperconjugation is the main factor to determine the stability of conformers. Such effects on the electron wavefunctions of the highest-occupied molecular orbital (HOMO) of different conformers are demonstrated with electron momentum spectroscopy, exhibiting the obviously different symmetries of the HOMO wavefunctions in momentum space.

Key words: *Ab initio*, Hydrogen bond, Natural bond orbital, Hyperconjugative effect, Momentum distribution

I. INTRODUCTION

As a relatively simple molecule, 2-chloroethanol is important material of organic impregnant and synthesis. It can be used to synthesize oxirane, rubber, dyestuff, medicine, and insecticide 1059. It has been the subjects of numerous experiment, theoretical, and combined studies for the past 40 years. Infrared [1−5], Raman [4−7], microwave [8], electron diffraction [9], and penning ionization electron spectroscopic [10] studies showed that this molecular exists predominantly in the gas phase as the gauche conformer (with respect to the rotation around the C−C bond), which is stabilized by an OH$\cdots$N intramolecular hydrogen bond (HB). The formation of this bond influences structural and spectroscopic parameters of the molecule. These experimental findings were confirmed by *ab initio* calculations [4, 10−12] at different levels of theory ranging from Hartree-Fock (HF) up to the second-order Møller-Plesset perturbation theory (MP2) and the coupled cluster singles and doubles (CCSD) level of theory. Most theoretical studies have focused on the stability and structural parameters of 2-chloroethanol conformers [4, 10, 11], comparison of experimental and calculated the gas-phase vibrational spectra of 2-chloroethanol [4, 7], calculation of barriers to internal rotation between different conformers [7]. However, the analysis of hyperconjugative effects on the stability and electronic wavefunctions of 2-chloroethanol conformers has not been reported so far.

Hyperconjugation is a basic conception of chemistry. Nearly 70 years ago Mulliken primarily introduced hyperconjugation to describe σ-extended conjugation regarding $\sigma\rightarrow\pi^*$, $\pi\rightarrow\sigma^*$, and $\sigma\rightarrow\sigma^*$ donor-acceptor interactions in alkyl and other saturated substituents [12, 13]. Kirby *et al.* [14], Alabugin *et al.* [15], and Beckwith *et al.* [16] discussed the nature of hyperconjugation by studies of its effects on molecular properties such as anomeric effect and chemical reactivity and selectivity. The routine experiments, such as NMR spin-spin couplings [17, 18], vibrational shifts [19], and other experimental diagnostics [20−22], convey limited information about hyperconjugative effects on structural and energetic domains. On the other hand, the theoretically quantitative descriptions of hyperconjugative interactions can be obtained employing natural bond orbitals (NBO) method [23, 24]. Recently, hyperconjugative effect on the electronic wavefunctions of ethanol [25] and ionization energies of hydroxyalkyl radicals [26] were studied on the basis of the NBO theory analyses combined with electron momentum spectroscopy (EMS) [27−29] and electronic structure calculations.

In the present work, NBO theory was applied to analyze orbital interactions in 2-chloroethanol conformers and exhibited that hyperconjugative effect is the key factor to determine the stability of conformers. Such effects on the electron wavefunctions of the highest-occupied molecular orbitals (HOMO) of five 2-chloroethanol conformers are demonstrated with EMS.

II. THEORETICAL METHODS

Ab initio calculations were carried out using the Gaussian 03 program [30]. Preliminary geometry opti-

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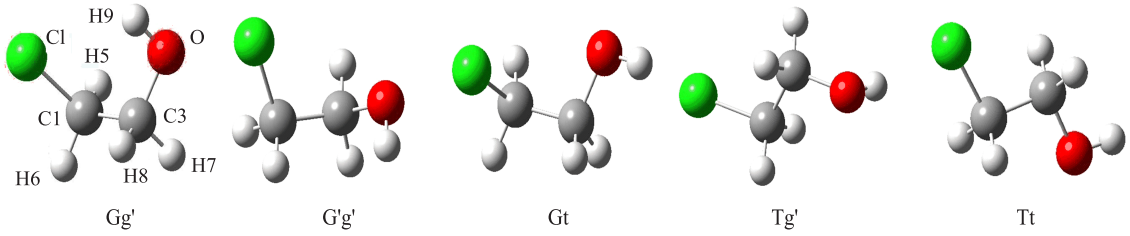

FIG. 1 Five 2-chloroethanol conformers optimized at the MP2/aug-cc-pVTZ.

mizations on various rotational isomers were performed with the B3LYP/aug-cc-pVTZ model. The five conformers were obtained and reoptimized at the MP2 level using the same basis set, and confirmed as local minima by evaluation of harmonic frequencies.

The molecular wave functions were obtained from single point calculations at the B3LYP/aug-cc-pVTZ//MP2/aug-cc-pVTZ level of theory, and then Fourier transformed into momentum space as orbital momentum distribution (MD) using the HEMS program developed at UBC [27]. Under the Born-Oppenheimer approximation, independent particle approximation and the plane wave impulse approximation (PWIA), the MD (σ) is given by [28, 29]

$$\sigma \propto \int \mathrm{d}\Omega \, |\psi_j(\mathbf{k})|^2 \tag{1}$$

which is proportional to the momentum space one-electron Dyson orbital $\psi_j(\mathbf{k})$. Corresponding to each ionization energy in the DFT calculation, Dyson orbitals are approximated by Kohn-Sham orbitals, $\psi_j(\mathbf{k})$.

NBO theory [23, 24] has been successfully used to analyze orbital interactions such as HB [31] and hyperconjugative interactions [25]. The NBO analysis transfers the delocalized MOs into the localized ones that are closely tied to chemical bond concepts. The interaction between filled (*e.g.*, the lone-pair) and anti-bonding orbitals represents the deviation of the molecule from the Lewis structure and can be used as a measure of the delocalization due to the intramolecular HBs and hyperconjugative interactions studied in this work. The energy lowering due to the delocalization caused by the intramolecular HB and hyperconjugative interactions can be treated by the second-order perturbation energy $E(2)$ in the NBO theory,

$$E(2) = -\frac{n_\sigma F_{ij}^2}{\Delta\varepsilon} \tag{2}$$

where n_σ is the population of the lone-pair (n) orbital, F_{ij} is the Fock matrix (or Kohn-Sham matrix in DFT) element between the NBOs $i(n)$ and $j(\sigma^*)$, and $\Delta\varepsilon$ is the energy level differences between these two orbitals.

III. RESULTS AND DISCUSSION

A. Structures

According to restricted rotations around the C−C and C−O bonds of 2-chloroethanol, there are nine possible conformers. All of these but the Tt conformer has antimers (mirror images), and these pairs are energetically and spectroscopically equivalent, leaving five distinctly different conformers: Gg′, G′g′, Gt, Tg′, and Tt, where G and T denote gauche and trans positions, respectively, with reference to the C−C bond, and g and t denote gauche and trans conformations relative to the C−O bond. The B3LYP/aug-cc-pVTZ and MP2/aug-cc-pVTZ optimized geometrical parameters together with the experimental data [8, 9] are listed in Table I. MP2 optimized bond length of C−Cl, C−C and C−O are somewhat shorter than that of B3LYP results. Comparing with the experimental data indicates that B3LYP/aug-cc-pVTZ is a better method to predict the geometry. Then the five 2-chloroethanol conformers optimized at the MP2/aug-cc-pVTZ are shown in Fig.1. Among of them, Tt conformer has C_s point group and the other ones have the C_1 point group. The calculated OH$\cdots$N distance is 2.624 Å for Gg′ conformer and slightly smaller than the sum of their van der Waals radii. This result points to the existence of weak OH$\cdots$N HB in Gg′ conformer.

B. Energies

The total energies of 2-chloroethanol conformers are displayed in Table II. The B3LYP relative energies are within 1.67 kJ/mol of their MP2 counterparts. Zero-point corrections have little effect on these results. The global minimum predicted by both methods, Gg′ conformer, is less than 8.36 kJ/mol more stable than conformers Tg′ and Tt. Our results are in agreement with previous experimental and theoretical studies [1−11] which conclude that Gg′ conformer is the most stable one. Combined with Boltzmann equation, conformational distributions at normal temperature T=298 K are computed according to the MP2 and B3LYP calculated relative energies, and are also shown in Table II.

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TABLE I B3LYP and MP2 optimized geometries parameters. Bond length R in Å, bond angle A and dihedral angle D in (°).

	B3LYP/ aug-cc-pVTZ					MP2/aug-cc-pVTZ					Exp.	Exp.
	G′g′	Gg′	Gt	Tg′	Tt	Gg′	G′g′	Gt	Tg′	Tt	[8]	[9]
R(C1Cl2)	1.809	1.820	1.812	1.811	1.808	1.792	1.782	1.784	1.7848	1.783	1.789	1.801
R(C1C3)	1.516	1.514	1.509	1.521	1.515	1.512	1.513	1.506	1.5163	1.511	1.519	1.519
R(C3O4)	1.416	1.415	1.420	1.424	1.426	1.415	1.416	1.419	1.4219	1.425	1.411	1.413
R(C1H5)	1.088	1.086	1.087	1.088	1.086	1.086	1.088	1.807	1.0876	1.086		1.093
R(C1H6)	1.089	1.087	1.086	1.086	1.086	1.087	1.089	1.807	1.0859	1.086		1.093
R(C3H7)	1.089	1.092	1.098	1.089	1.094	1.090	1.088	1.096	1.0878	1.092		1.093
R(C3H8)	1.099	1.095	1.093	1.093	1.094	1.094	1.096	1.092	1.092	1.092		1.093
R(O4H9)	0.9622	0.9640	0.9605	0.9617	0.9611	0.9655	0.963	0.9618	0.9625	0.9623	1.008	1.033
A(C3O4H9)	109.6	108.3	109.5	109.4	109.2	107.0	108.4	108.6	108.36	108.4	105.8	125.0
A(C1C3O4)	114.6	113.2	109.1	110.6	106.2	112.4	113.7	108.0	110.566	105.8	112.8	113.8
A(Cl2C1C3)	112.8	110.8	112.5	110.3	110.1	109.77	111.7	111.5	109.52	109.4	110.1	110.7
D(Cl2C1C3O4)	64.24	−64.55	−71.50	178.1	−180.0	−63.38	62.81	−69.69	178.10	−180.0		
D(C1C3O4H9)	62.30	60.50	165.5	76.40	−180.0	58.61	62.56	167.0	75.98	−180.0		

TABLE II Total and relative energy of 2-chloroethanol conformers.

Conformers	MP2/aug-cc-pVTZ				B3LYP/aug-cc-pVTZ			
	$E_{\rm total}$/a.u.	$\Delta E^{\rm a}$	$\Delta E_{\rm ZPE}{}^{\rm b}$	Weight$^{\rm c}$/%	$E_{\rm total}$/a.u.	$\Delta E^{\rm a}$	$\Delta E_{\rm ZPE}{}^{\rm b}$	Weight$^{\rm c}$/%
Gg′	−613.88174	0	0	87.2	−614.67195	0	0	83.6
Tg′	−613.87895	7.302	6.663	5.90	−614.66973	6.161	5.810	7.98
Tt	−613.87894	7.319	6.216	3.53	−614.66963	6.943	6.065	3.60
Gt	−613.87784	10.224	8.979	2.31	−614.66889	9.158	8.013	3.28
G′g′	−613.87716	11.997	10.972	1.03	−614.66819	10.651	9.852	1.56

[a] Total energy differences without zero-point energy correction in kJ/mol.
[b] Total energy differences with zero-point energy correction in kJ/mol.
[c] Calculation according to the Boltzman equation.

TABLE III Intramolecular HB lengths and NBO analyses for HBs of Gg′ conformer.

Hydrogen bond	OH···N
Bond length/Å	2.624
$\Delta\varepsilon$/a.u.	1.16
F_{ij}/a.u.	0.025
$E(2)$/(kJ/mol)	2.88

C. Intramolecular hydrogen bonding and hyperconjugative effects

NBO theory [23, 24] has been successfully used to analyze HB interactions. Here it is also used to analyze the intramolecular OH···N HB of the most stable Gg′ conformer, as show in Table III. The energy lowering by the $n_{\rm N}\rightarrow\sigma^*_{\rm OH}$ delocalization interaction of Gg′ conformer is $E(2)$=2.88 kJ/mol. This results indicate that this HB is very weak and has little contribution to the energy of Gg′ conformer. In order to determine the conformational stability of 2-chloroethanol, NBO analyses for the predominant hyperconjugative interactions for 2-chloroethanol conformers are shown and results are in Table IV. As seen from Table IV, the main interactions between orbitals are $n_{\rm O}\rightarrow\sigma^*_{\rm C-C}$ or $n_{\rm O}\rightarrow\sigma^*_{\rm C-H}$ and $n_{\rm Cl}\rightarrow\sigma^*_{\rm C-C}$ or $n_{\rm Cl}\rightarrow\sigma^*_{\rm C-C}$ interactions. Among of them, the strongest interactions for Gg′, Tg′, and G′g′ conformers are $n_{\rm O}\rightarrow\sigma^*_{\rm C-C}$, and for Tt and Gt are $n_{\rm O}\rightarrow\sigma^*_{\rm C-H}$. As shown in Table IV, the present B3LYP/aug-cc-pVTZ calculation including all the hyperconjugation predicts the stability order: Gg′>Tt>Tg′>Gt>G′g′. When $n_{\rm Cl}\rightarrow\sigma^*_{\rm C-C}$ or $\sigma^*_{\rm C-H}$ interactions are removed, Gt and Gg′ are isoenergetic and have the lowest energy, and the stability order changes completely. When $n_{\rm Cl}\rightarrow\sigma^*_{\rm C-C}$ or $\sigma^*_{\rm C-H}$ removed, the same phenomenon takes place. After all hyperconjugative interactions removed, the B3LYP result shows the dramatically different stability order: Gt>Gg′>Tt>Tg′>G′g′. Therefore we draw a conclusion that it is the hyperconjugative interactions not the intramolecular HB interactions determine the stability order of 2-chloroethanol.

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TABLE IV NBO analyses for hyperconjugative energies of 2-chloroethanol conformers.

	Hyperconjugative energy/(kJ/mol)									
	$n_O \rightarrow \sigma^*_{C1-C3}$	$n_O \rightarrow \sigma^*_{C3-H7}$	$n_O \rightarrow \sigma^*_{C3-H8}$	$n_{Cl} \rightarrow \sigma^*_{C1-C3}$	$n_{Cl} \rightarrow \sigma^*_{C1-H5}$	$n_{Cl} \rightarrow \sigma^*_{C1-H6}$	Total[a]	Del_{n_O}[b]	$Del_{n_{Cl}}$[c]	$Del_{n_{All}}$[d]
Gg′	30.92	14.73	38.33	18.54	24.14	13.93	0	0.29	0	4.60
Tg′	37.11	12.55	20.67	20.63	20.71	19.75	4.39	12.47	15.82	9.92
Tt	5.77	35.44	35.44	20.29	20.21	20.25	3.30	2.09	16.00	6.19
Gt	5.48	45.19	24.35	23.56	20.46	19.54	7.91	0	16.02	0
G′g′	35.90	14.77	33.35	23.93	20.21	20.80	10.17	11.05	19.29	12.13

[a] Single point energy at B3LYP/aug-cc-pVTZ level.
[b] Relative Energy without hyperconjugative interaction of $n_O \rightarrow \sigma^*_{C-C}$ or σ^*_{C-H}.
[c] Relative Energy without hyperconjugative interaction of $n_{Cl} \rightarrow \sigma^*_{C-C}$ or σ^*_{C-H}.
[d] Relative Energy without all hyperconjugative interactions.

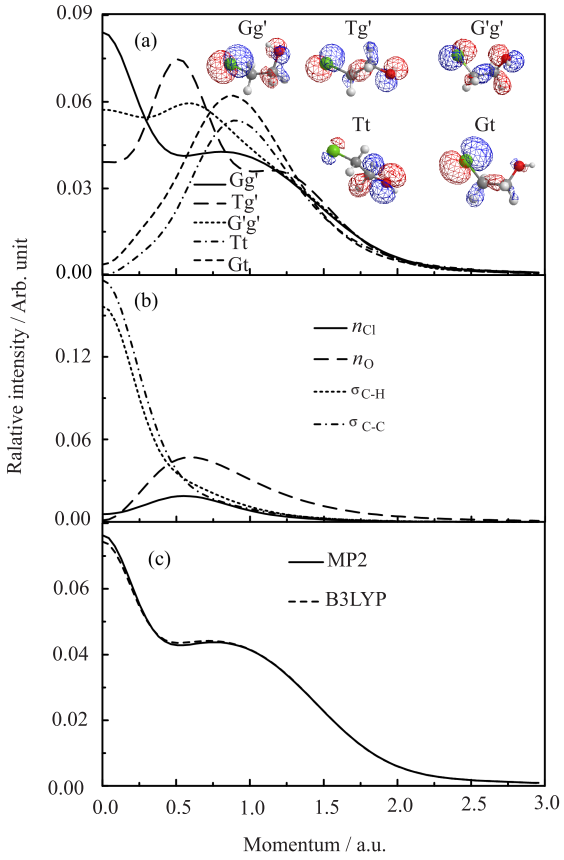

FIG. 2 (a) Theoretical electron momentum profiles and Dyson orbitals plots for HOMOs. (b) Theoretical electron momentum profiles for the localized n_{Cl}, n_O, σ_{C-H}, and σ_{C-C} components of HOMOs. (c) Theoretical electron momentum profiles for HOMO of 2-chloroethanol based on abundance of five conformers calculated at MP2 and B3LYP levels shown in Table II.

D. Hyperconjugative effects on the wavefunctions

Although such hyperconjugative effects in energy domain are discussed above, it could not be observed directly. The delocalization characteristics of the electron density distribution of molecule orbital provide a way. Until recently, EMS has been the most direct method to obtained molecular electron densities [25, 27−29, 32]. In the present study, Dyson orbital of HOMO of each conformer has been calculated in coordinate space as orbital electron charge densities (CDs) and in momentum space as orbital momentum distributions (MDs). Figure 2(a) details Dyson orbitals and MD of HOMO of each 2-chloroethanol conformer. The momentum profiles of HOMOs of Tg′, G′g′, and Gg′ are the hybrid "sp-type" which have the highest intensities at p≈0 a.u. and the second maximum at p≈0.5, 0.6, and 0.8 a.u., respectively. On contrary to this, the momentum profiles of both Tt and Gt obviously exhibit a "p-type" character having the maximum at almost the same momentum at p≈0.9 a.u.. From the Dyson orbitals plots of HOMO of 2-chloroethanol conformers, it is seen that they have different components. Both Tg′ and G′g′ are composed of n_{Cl}+n_O+σ_{C-C}+σ_{C-H}, Gg′ is composed of n_{Cl}+n_O+σ_{C-H} and Gt is composed of n_{Cl}+σ_{C-C}+σ_{C-H}. For Tt conformer, the localized n_O+σ_{C-H} forms a remarkable "pseudo-π" orbital.

To reveal the nature of such remarkable difference of the MD among these conformers, each component of spatial φ_s: Cl, O, C−H, and C−C, are Fourier-transformed to the momentum space and the spherically averaged momentum density profiles are plotted in Fig.2(b). As shown in Fig.2(b), the components of n_{Cl} and n_O orbitals clearly show "p-type" momentum profile and the maximum p≈0.5 and 0.6 a.u., respectively. The other two components of σ_{C-C} and σ_{C-H} orbitals show "s-type" momentum profile. As mentioned above, the different delocalized components of HOMO of 2-chloroethanol conformers are totally induced by the different hyperconjugative interactions as shown in Table III. If there are not these hyperconjugative interactions, the HOMO of 2-chloroethanol conformers should be the localized lone-pair of n_{Cl} and n_O, and the corresponding MP should be the "p-type" character. So the "sp-type" momentum profile of Tg′, G′g′, and Gg′ exhibits the hyperconjugative effects on the electron wavefunctions in momentum space. This approach is

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also successfully used to interpret the distinctly different HOMO wavefunctions of the two ethanol conformers which was caused by hyperconjugative effects [26]. According to Boltzmann-weighted abundances based on MP2 and B3LYP calculated relative energies, the theoretical MP of HOMO of 2-chloroethanol are calculated and shown in Fig.2(c). Since there has been no EMS experiment study on gaseous 2-chloroethanol, the theoretical MP presented in Fig.2(c) may be helpful for the experiments in the future.

IV. CONCLUSION

Five 2-chloroethanol conformers corresponding to minima in potential energy surfaces are calculated with the B3LYP and MP2 models. Employing EMS together with the NBO analyses, we demonstrate the remarkable differences of hyperconjugative interactions between five 2-chloroethanol conformers. The "sp-type" MPs for the HOMOs of Tg′, G′g′, and Gg′ conformers stems from the delocalized electron-distributions on the σ bonds induced by the hyperconjugative effect $n_{\rm O}\rightarrow\sigma^*_{\rm C-C}$ or $\sigma^*_{\rm C-H}$ and $n_{\rm Cl}\rightarrow\sigma^*_{\rm C-C}$ or $\sigma^*_{\rm C-H}$.

V. ACKNOWLEDGMENTS

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