Methyl orbital signatures in 2-amino-1-propanol*

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Electron density distributions of 2-aminoethanol (2AE) and 2-amino-1-propanol (2AP) are calculated in both the coordinate and the momentum spaces using the B3LYP/TZVP method. Using the dual space analysis, molecular orbital signatures of the methyl substituent in 2AP are identified with respect to 2AE. Relaxations of the geometry and the valence orbital in 2AP are found to be due to the insertion of the methyl group. Five orbitals, not four orbitals, are identified as the methyl signatures. They are orbital 5a in the core shell, orbitals 9a and 10a in the inner valence shell, and orbitals 15a and 16a in the outer valence. In the inner valence shell, the attachment of methyl to 2AE causes a splitting of its orbital 8a into orbitals 9a and 10a of 2AP, whereas in the outer valence shell, the methyl group results in the insertion of an additional orbital pair of 15a and 16a. The frontier molecular orbitals 21a, 20a, and 19a are found to have no significant role in the methylation of 2AE.

Keywords: electron density distribution, orbital signature of methyl, molecular orbital

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1. Introduction

Structures and spectra of molecules have aroused the interest of many people.[1,2] Chiral amino alcohol derivatives are important constituents of molecules, which play a role in life-related processes, such as transmission of nerve impulse and building of cell membranes. For this reason, understanding the dynamics of amino alcohol through the analysis of their structural and chemical properties is of great importance.

The smallest chiral amino alcohol is 2-amino-1-propanol (2AP). It is an important intermediate of organic synthesis, which is used to synthesize ofloxacin. The analyses through microwave spectroscopy,[3] matrix-isolation infrared spectroscopy,[4] synchrotron radiation photoelectron spectroscopy,[5] and photoelectron circular dichroism experimental studies of 2AP[6] indicated that there exist two conformers for the isolated 2AP. *Ab initio* calculations[4] at different levels of theory ranging from Hartree-Fock (HF) up to the second-order Møller–Plesset perturbation theory (MP2) predicted 25 different stable conformations of 2AP. The relative stabilities and the behaviors of these conformers depend on the interplay of the intramolecular hydrogen bonds, which have been demonstrated in 2-aminoethanol (2AE),[7] N, N-dimethylaminoethanol,[8] 3-Amino-1-propanol,[9] and N,N-dimethylaminopropanol.[10] The intramolecular hydrogen bond OH–N increases the stability of the most stable conformer of 2AP. With respect to 2AE, the attachment of methyl complicates the conformational landscape of 2AP, and gives rise to the increased number of plausible conformations. However, this methyl substituent effect has scarcely been revealed before.

Recently, the molecular orbital signatures of the methyl substituent in L-alanine were identified with respect to those of glycine using the dual space analysis.[11] In the present work, we report a comprehensive study of the most stable conformations of 2AP using the DFT B3LYP method by comparison with 2AE. Their anisotropic properties, such as dipole moments, rotational constants, Dyson orbitals, and momentum distributions (MDs), are studied. The effects of the substitution of methyl in 2AE on the bonding environment in both position and momentum spaces are investigated.

2. Theoretical methods

Ab initio calculations are carried out using the Gaussian03 program.[12] The DFT B3LYP

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method[13,14] is employed to optimize the ground-state geometries of 2AP and 2AE. The triple-ζ valene polarized (TZVP) basis set[15] is used for all the calculations in this article. The B3LYP/TZVP model has proved to be reliable in the prediction of the properties and the orbital momentum distributions for molecular systems.[11,16]

Next, the molecular wave functions are obtained from the single-point calculations at the B3LYP/TZVP//B3LYP/ TZVP level of theory, and then Fourier transformed into the momentum space as orbital MDs using the HEMS program developed at UBC.[17] Under the Born–Oppenheimer approximation, the independent particle description, and the plane wave impulse approximation (PWIA), the MD σ is given by[18,19]

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

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

3. Results and discussion

3.1. Properties of 2AP

The most stable conformers of 2AP and 2AE have been identified in the previous experiments and theoretical calculations,[3−7,20−24] and are shown in Fig. 1. The optimized geometrical parameters are listed in Table 1. The present calculations are in good agreement with the previous theoretical predictions and experimental results. The calculated bond distances for characteristic single bonds (N_1C_2, C_2C_3, C_3O_4, and N_1H) by using the B3LYP/TZVP method exhibit minor differences (less than 0.01 Å) between those two conformations, which is similar to the experiments. For 2AE, the differences in bond angle $\angle C_3O_4H$ and dihedral angles $\angle C_2C_3O_4H$ between the predicted and the measured values are 3.0° and 13.5°, respectively, which show large deviations. The results indicate that it is difficult to use quantum mechanics to accurately predict the bond angles, because they are not sensitive to the energy. Compared to 2AE, 2AP associated with the methyl group is found to have remarkable structural relaxations, which are also shown in Table 1. When one of the hydrogen in the $-CH_2$ is replaced by methyl, the dihedral angle of the backbone (nonhydrogen) atoms changes in order to accommodate the methyl group. According to the values based on the B3LYP/TZVP model, these dihedral angles vary from 1° to 2°.

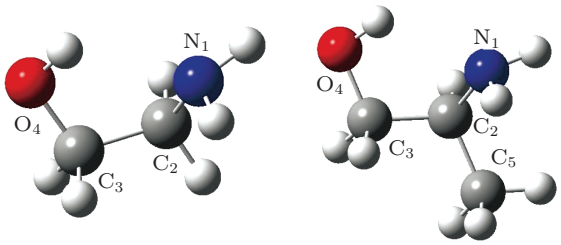


Fig. 1. (colour online) Structures of (a) 2AE and (b) 2AP.

The dipole moments are analysed as a reference for monitoring the influence of the methyl group on the polarity of 2AP. According to the present results based on the B3LYP/TZVP method, the total moment slightly increases from 3.25 D in 2AE to 3.29 D in 2AP upon the methylation. These values accord satisfactorily with the experimental results of 3.05 D[22,23] and 3.13 D[24] and the MP2 predicted results of 3.30 D[22,23] and 3.58 D.[4] It is evident that the redistribution of charge causes the changes of the dipole moment components upon the insertion of the methyl. The μ_x component in 2AE is -2.99 D and changes significantly to 3.19 D in 2AP, whereas μ_y and μ_z vary slightly. Rotational constants A, B, and C are also given in Table 1. The calculated rotational constants of 2AE are in good agreement with the experimental values, indicating that the B3LYP/TZVP method is good to predict the rotational constants. The rotational constants of 2AP calculated at the B3LYP/TZVP level are also expected to be accurate. The rotational constants of 2AP have not been measured before. The calculated rotational constants may be helpful for explaining the future measurements of the microwave spectra of gaseous 2AP. That the rotational constants of 2AP is much larger than those of 2AE is due to the methyl substituent in 2AE increasing the three moments of inertia.

Table 1. Optimized geometrical parameters of the most stable conformations of 2AE and 2AP.

Parameter	2-aminoethanol				2-amino-1-propanol		
	B3LYP/TZVP	B3LYP[a)]	MP2[b)]	Exp[c)]	B3LYP/TZVP	MP2[d)]	Exp[e)]
N_1C_2/Å	1.469	1.471	1.470	1.475	1.473	1.473	
C_2C_3/Å	1.525	1.524	1.518	1.526	1.532	1.526	
C_3O_4/Å	1.417	1.419	1.421	1.396	1.415	1.417	
N_1H/Å	1.012	1.011	1.009	1.017		1.021	
C_2H/Å	1.092				1.094	1.096	
O_4H/Å	0.970	0.966	0.965	1.000	0.971	0.976	
$\angle N_1C_2C_3$/(°)	108.9	109.0	108.0	108.1	107.2	106.2	
$\angle C_2C_3O_4$/(°)	111.1	111.4	110.7	112.1	111.4	110.6	
$\angle C_3O_4H$/(°)	105.1	105.8	104.8	108.0	104.8	103.2	
$\angle C_3C_2R$/(°)	109.7				111.9	112.4	112.4
$\angle N_1C_2C_3O_4$/(°)	55.2	56.3	57.1	55.4	53.3	53.9	–54.0
$\angle C_2C_3O_4H$/(°)	–40.5	–41.3	–41.8	–27.0	–39.3	–39.5	
$\angle HN_1C_2C_3$/(°)	–160.3	–161.4	–163.6	–159.5	–160.8	194.9	
$\angle HN_1C_2C_3$/(°)	78.8	78.7	77.6		79.1	78.3	
$\angle O_4C_3C_2H$/(°)	–61.8				–60.3	–59.4	
$\angle O_4C_3C_2R$/(°)	–179.5				179.9	179.9	180.0
μ/D	3.25	3.10	3.30	3.05	3.29	3.58	3.13
μ_x/D	–2.99				3.19		
μ_y/D	1.13				0.71		
μ_z/D	0.58				0.38		
A/GHz	14.46			14.51	7.95		
B/GHz	5.57			5.55	3.63		
C/GHz	4.57			4.57	2.74		

[a)]BLYP/6-311++G(2d,2p) from Ref. [19], [b)]MP2/6-311++G(2d,2p) and [c)]microwave spectroscopy from Refs. [20] and [21], [d)]MP2/6-31G* from Ref. [2], [e)]from Ref. [22].

3.2. Molecular orbital information in coordinate space

The 2AP and 2AE have 21 and 17 doubly occupied molecular orbitals (MOs), respectively. The methyl group brings additional eight electrons, which ought to form four doubly occupied MOs in 2AP, one in the core and three in the valence regions. The orbital energies of the core, the inner, and the outer valence shells of 2AP and 2AE are listed in Table 2. The methylation of 2AE in the core shell is identified as MO 5a (C_5), as the core orbitals are localized on the individual atom sites. However, the methylation causes only small variations in the core orbital energy. It is noted that the core orbital energies of all atom sites shift up (less negative) except for the C_2 site, which shifts down in energy. The same phenomenon has been found in L-alanine, but without any explanation.[11]

Table 2. Calculated orbital energies and symmetry labels of 2AP with respect to 2AE.

2-amino-1-propanol				2-aminoethanol			
MO	$-\varepsilon_i$/eV	symmetry	site	MO	$-\varepsilon_i$/eV	symmetry	site
core							
1	519.934	1a	O_4	1	519.975	1a	O_4
2	389.448	2a	N_1	2	389.481	2a	N_1
3	277.843	3a	C_3	3	277.890	3a	C_3
4	277.796	4a	C_2	4	277.635	4a	C_2
5	276.788	5a	C_5				
Inner valence							
6	27.528	6a		5	27.550	5a	
7	24.461	7a		6	24.346	6a	
8	20.638	8a		7	19.754	7a	
9	18.465	9a					
10	16.334	10a		8	16.744	8a	
Outer valence							
11	14.399	11a		9	14.253	9a	
12	12.954	12a		10	13.057	10a	
13	12.638	13a		11	12.830	11a	
14	12.043	14a		12	12.190	12a	
15	11.421	15a					
16	10.951	16a					
17	10.659	17a		13	10.919	13a	
18	9.682	18a		14	10.186	14a	
19	8.778	19a		15	8.939	15a	
20	7.367	20a		16	7.448	16a	
21	7.027	21a		17	7.009	17a	

3.3. Orbital MDs of 2AP in valence space

The valence orbitals of 2AP are divided into three kinds: methyl-dominated orbitals, methyl-associated orbitals, and methyl-perturbated orbitals, which are shown in Fig. 2. The methyl-dominated orbitals of 9a, 10a, 15a, and 16a are direct contributions from methyl, which are signature orbitals of methyl. The adjacent signature orbitals of methyl are the methyl-associated ones. They are orbital 8a in the inner valence shell, orbitals 11a, 12a, 13a, 14a, 17a, and 18a in the outer valence shell. These orbitals have apparent energy shifts, as shown in Fig. 2. In the inner valence shell, orbitals 6a and 7a are far away from the signature orbitals of methyl (9a, 10a). Then the influences of methyl on these orbitals are negligible. In the same way, orbitals 19a, 20a, and 21a in the outer valence shell also receive small energy perturbations from the methyl signature orbitals 15a and 16a. These four orbitals belong to the methyl-perturbated orbitals. The further determination of the methyl signature and the influence of methylation on its surrounding environment requires more orbital-based information. The information from the momentum space will be discussed in the following.

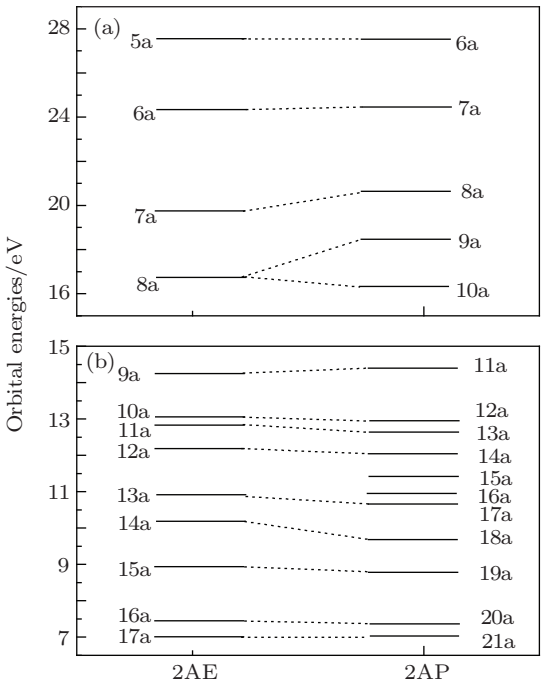


Fig. 2. B3LYP/TZVP calculated (a) inner and (b) outer valence molecular orbital energies of 2-amino-1-propanol with respect to 2-aminoethanol.

In the present study, orbital momentum distributions (MDs) in the complete valence space of 2AP are simulated. Although both 2AE and 2AP lack symmetry, the symmetry-correlated orbitals are identified through comparing the orbital energies, the orbital electron densities, and the Dyson orbital MDs. In order to identify the methylation in 2AP, the orbital MDs of 2AE are also simulated and employed as references.

The methyl signature orbital MDs of 9a and 10a in the inner valence shell and 15a and 16a in the outer valence shell are presented in Fig. 3 with respect to 2AE. The corresponding Dyson orbital plots are also shown in Fig. 3. In Fig. 3(a), orbitals 9a and 10a in 2AP are uniquely correlated with orbital 8a in 2AE. The differences among these orbital MDs indicate the redistribution of electron density, which is due to the methyl group. As a result, ortibal 9a weakens the bondings of C_2–N_1 and $C_3(H)$–O_4, but strengthens the bonding of the methyl group. At the same time, orbital 10a enhances the bondings of C_2–C_3 and the methyl group. The insertion of the methyl group in the outer valence region forms the signature orbitals of 15a and 16a, as shown in Fig. 3(b). These two orbitals of 2AP have no recognizable 2AE orbital analogy. It is seen from the Dyson orbitals that their electron densities concentrate mainly on $C_3(H)$–$O_4(H)$ and the methyl group. Orbital 15a indicates a strong p-type in nature, which is clearly visible in the Dyson orbitals. In orbital 16a, the Dyson orbital is more localized than that in orbital 15a, so the contributions from the 1s hydrogen atom orbitals in orbital 16a show stronger s-type MDs than that in orbital 15a.

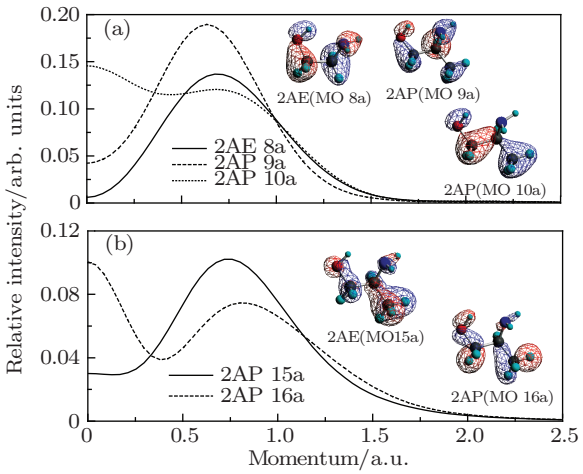


Fig. 3. (colour online) Signature orbitals (a) 9a and 10a in the inner valence shell and (b) 15a and 16a in the outer valence shell. The insets show the orbital electron densities using Chem3D.

The highest occupied molecular orbital (HOMO) 21a, the next HOMO (NHOMO) 20a, and the third

HOMO (THOMO) 19a in the outer valence shell of 2AP, which experience small perturbation by the methylation, are presented in Fig. 4. These frontier MOs are closely related to chemical reactions involving the structural manipulation. It is obvious that they are not much different from those of 2AE. The MDs for HOMOs of both 2AE and 2AP exhibit a mixture of sp-type character with a dominant p-type component, which stems from the contribution of the lone pair on the N atom of the amine group and the O atom of the –OH group. Upon the methylation, the C_2–H σ bond is replaced by the C_2–C_3 σ bond, and the s contribution to the HOMO of 2AP reduces, which causes the MD to lower down in the low momentum region. This demonstrates that the orbital MD is more sensitive for identifying electron redistribution than the orbital contours, which have been used to identify the conformational behavior of serine.[25] It is seen from the Dyson orbital contours in Fig. 4(b) that the NHOMOs for both 2AE and 2AP are also associated with predominant O and N lone-pair orbitals. The methyl group evidently has no active role in the outermost valence region of 2AP. A similar trend is also observed in the THOMO.

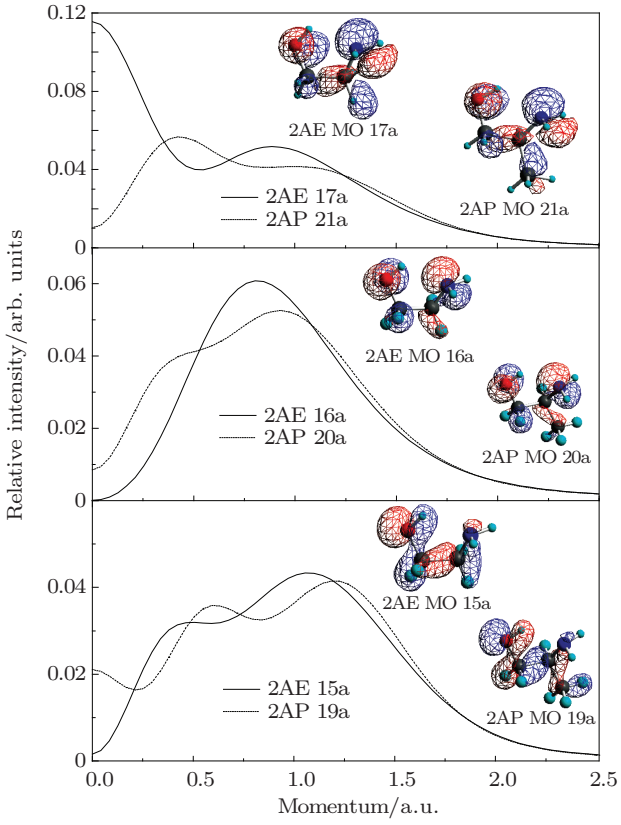


Fig. 4. (colour online) Orbitals (a) 21a, (b) 20a, and (c) 19a of 2AP least affected by the methyl in the outer valence shell. The insets show the orbital electron densities using Chem3D.

The methyl-affected orbitals in the outer valence shell of 2AP provide an insight into the localized changes with respect to 2AE. Orbital 13a is regarded as a representative for this group and given in Fig. 5. In 2AE, this orbital is contributed from the fragments of H–O_4–C_3–H_2 and C_2–N_1–H_2. Upon methylation, C_3–H_2 and C_2–N_1–H_2 contributions remain, while a new O–C_4(H)–C_3(H)–C_5 fragment forms. As a result, the orbital MDs of 13a in 2AP exhibit a p-type character.

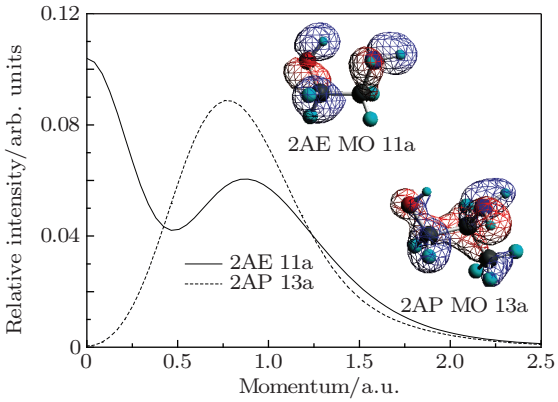


Fig. 5. (colour online) Selected orbital 13a of 2AP as a representative of the methyl-affected orbitals in the valence shell. The insets show the orbital electron densities using Chem3D.

4. Conclusion

Using the information obtained in the coordinate and the momentum spaces, the molecular orbital signatures of the methyl substituent in 2AP are identified with respect to those of 2AE. Five orbitals are identified as the methyl signature ones. Although the methylation gives negligible variations to the other core orbitals, it causes the energies of all atom sites to shift up (less negative) with respect to the 2AE counterparts, except for the C_2 site, which shifts down in energy. In the inner valence shell, the methyl causes orbital 8a of 2AE to split into orbitals 9a and 10a of 2AP, whereas in the outer valence shell, the methyl group brings an insertion of an additional orbital pair of 15a and 16a in 2AP. The methyl group obviously has no active role in the bondings of the least affected orbitals, including HOMO, NHOMO, and THOMO of 2AP.

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