Conformation effects on the molecular orbitals of serine*

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This paper calculates the five most stable conformers of serine with Hartree–Fock theory, density functional theory (B3LYP), Møller–Plesset perturbation theory (MP4(SDQ)) and electron propagation theory with the 6-311++G(2d,2p) basis set. The calculated vertical ionization energies for the valence molecular orbitals of each conformer are in agreement with the experimental data, indicating that a range of molecular conformations would coexist in an equilibrium sample. Information of the five outer valence molecular orbitals for each conformer is explored in coordinate and momentum spaces using dual space analysis to investigate the conformational processes, which are generated from the global minimum conformer Ser1 by rotation of C_2–C_3 (Ser4), C_1–C_2 (Ser5) and C_1–O_2 (Ser2 and Ser3). Orbitals 28a, 27a and 26a are identified as the fingerprint orbitals for all the conformational processes.

Keywords: serine conformers, vertical ionization energies, molecular orbital, momentum distribution

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1. Introduction

The molecular potential energy surfaces of amino acids are very floppy because of the balance of covalent and noncovalent interactions (especially the intramolecular hydrogen bonding), which may lead to a large number of low-lying conformers. This conformational behaviour has triggered many attempts to perform deep experimental and theoretical investigations into amino acids.[1,2] Serine is an α-amino acid with a hydroxyl group in the side chain. It is required for the metabolism of fat, tissue growth and the immune system as it assists in the production of immunoglobulins and antibodies. It is also an important constituent of brain proteins and nerve coverings.

The conformational behaviour of serine has been the subject of many studies.[3−11] Most theoretical studies have focused on the influence of intramolecular hydrogen bonds on the order of stability and structural parameters of serine conformers,[3−5] comparison of experimental and calculated gas-phase infrared (IR) frequencies and rotamerization constants,[6] calculation of proton affinities, intrinsic basicities and vibrational frequencies,[7,8] investigation of optical rotation sensitive to the serine conformers,[9] and simulation of water potential for the electronic structure of serine.[10] An experimental matrix-isolation Fourier transform IR spectroscopy study showed four low-energy conformers present in the gas phase.[6] However, an analysis of the conformation effects on molecular orbitals (MO) of serine has not been reported so far.

Recently, the electron structure of conformations for amino acids, such as glycine,[12] L-Alanine[13,14] and guanine,[15] have been investigated. A unique orbital-based insight into the bonding environment within the conformers in both coordinate and momentum spaces were provided using a technique known as dual space analysis (DSA). In this paper, we focus on information that could differentiate the conformers of serine, such as equilibrium geometries and relative energies, vertical ionization energies (VIEs) and orbital momentum distributions (MDs). In particular, conformational variations in energies and orbitals are discussed in relation to rotations about the C_2–C_3, C_1–C_2 and C_1–O_2 bond rotations of serine in order to provide an orbital-dependent representation of the bonding mechanisms within each conformation.

2. Computational methods

Ab initio calculations were carried out using the Gaussian03 programme.[16] The hybrid density functional B3LYP method[17] was employed to optimise the various rotational isomers. The obtained conformers of serine were confirmed as local minima

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by evaluating the harmonic frequencies. The 6-311++G(2d,2p) basis set was used for all calculations in this article. Over the B3LYP optimised geometries, the relative energies were performed at the B3LYP and the extrapolated MP4(SDQ) (including the fourth-order corrections and using the space of the single, double and quadruple substitutions)[18] levels of theoretical method. Considering that conformers with the relative energies higher than 5 kJ/mol are too rare to be detected,[19−22] we only study the low-lying conformers of serine whose relative energies fall within the scope of this article. The ionization energy (IE) values of each conformer were evaluated in the partial third-order quasiparticle (P3) approximation of the electron propagator theory,[23] which included electron correlation and orbital relaxation effects. Each IE calculated with the electron propagator methods corresponds to a Dyson orbital. The Dyson orbital can further be simplified to be proportional to the canonical Hartree–Fock (HF) orbital in P3 approximations. Pole strength is equal to the integral over all space of the absolute value squared of the Dyson orbital, representing the perturbation to the results of Koopmans' theorem. The approximations are validated only when the pole strengths lie between 0.85 and unity.[23] This method has been proved to be reliable in predicting the IEs of 2-aminoethanol[24] and amino acids.[20−22]

Next, the molecular wave functions were obtained from single point calculations at the B3LYP/6-311++(2d,2p)//B3LYP/6-311++(2d,2p) level of theory, and then Fourier transformed into momentum space as an orbital MD using the HEMS programme developed at the University of British Columbia.[25] Under the Born–Oppenheimer approximation, the independent particle description and the plane wave impulse approximation (PWIA), the MD (σ) is given by[26,27]

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

which is proportional to the momentum space one-electron Dyson orbital $\psi_j(\boldsymbol{k})$. The Dyson orbitals are approximated by Kohn–Sham orbitals, $\psi_j(\boldsymbol{k})$ and correspond to each IE in the density functional theory (DFT) calculation.

3. Results and discussion

3.1. Geometric correlation of the serine conformers

The twelve most stable conformers of serine in Ref. [4] were used as a starting point for the geometrical optimisations at the B3LYP/6-311++(2d,2p) level in this work and five low-lying ones were obtained and are shown in Fig. 1. The B3LYP-optimised geometrical parameters were given in Table 1, where R is the bond length, A is the bond angle and D is the dihedral angle. With regard to Ser1, the rotation of the C_2–C_3 bond generates Ser4 and has a minor effect on the bond length and angles, except in the orientation of the amine N. To our surprise, this rotation does not destroy the O_3H_2 ... N HB in Ser1, and each has the similar hydrogen bond (HB) length: 2.267 Å (1 Å = 0.1 nm) in Ser1 and 2.296 Å in Ser4. The rotations of the C_2–C_3 and C_1–C_2 bonds generate Ser5. During the course, rotation about the C_2–C_3 bonds breaks the O_3H_2 ... N HB and then rotation about the C_1–C_2 bonds produces the new type OH ... O(C) HB. During such a rotation, the dihedral angles $O_1C_1C_2N$ and $C_2C_3O_3H_2$ change to 88.4° and 21.4°, respectively, but the bond lengths remain almost invariable. The combining rotations about the C_2–C_3, C_1–C_2 and the C_1–O_2 bonds generate Ser2 and Ser3. Both of them have similar structural parameters except for the different $C_1C_2C_3O_3$ dihedral angle: –66.39° in Ser2 and 63.44° in Ser3, respectively. The H_2 ... N distance of these two conformers are predicted to be 1.928 Å and 1.940 Å, respectively, which is obviously shorter (0.327–0.368 Å) than the H_2 ... N distances predicted for Ser1 and Ser2, indicating a stronger HB in Ser2 and Ser3.

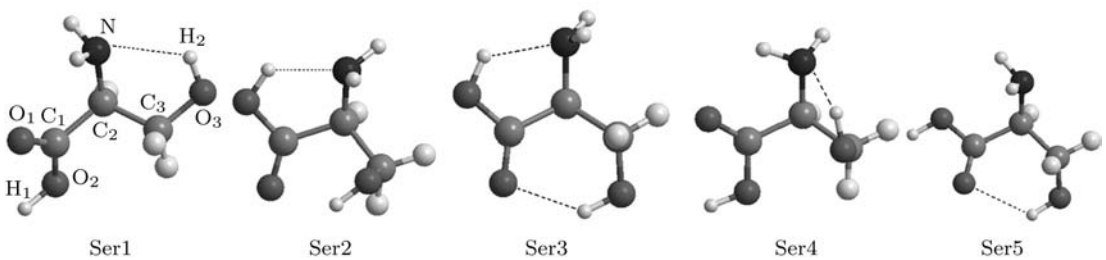


Fig. 1. Five low-lying conformers of serine.

Table 1. Optimised geometrical parameters (bond length in Å; angle in degree).

	Ser1	Ser2	Ser3	Ser4	Ser5
$R(C_1O_1)$/Å	1.205	1.204	1.208	1.205	1.210
$R(C_1O_2)$/Å	1.352	1.337	1.334	1.349	1.353
$R(C_1C_2)$/Å	1.522	1.543	1.538	1.521	1.528
$R(O_2H_1)$/Å	0.9690	0.9817	0.9811	0.9678	0.9687
$R(C_2N)$/Å	1.458	1.469	1.469	1.462	1.464
$R(C_2C_3)$/Å	1.545	1.530	1.539	1.540	1.529
$R(C_3O_3)$/Å	1.411	1.425	1.409	1.413	1.420
$R(O_3H_2)$/Å	0.9673	0.9630	0.9685	0.9674	0.9650
$R(O_3H_2\ldots N)$/Å	2.267			2.296	
$R(O_2H_1\ldots N)$/Å		1.928	1.940		
$R(O_3H_2\ldots O_1)$/Å		2.792	2.031		2.177
$A(C_1C_2N)$/(°)	113.4	109.3	109.5	109.1	111.8
$A(C_1C_2O_1)$/(°)	125.0	123.0	123.0	125.0	126.1
$A(C_2C_3O_3)$/(°)	110.2	111.2	113.0	110.9	112.5
$A(C_3O_3H_2)$/(°)	105.9	108.2	106.8	105.9	106.8
$A(O_1C_1O_2)$/(°)	122.9	122.9	122.3	123.0	122.0
$D(C_1C_2C_3O_3)$/(°)	–179.8	–66.39	63.44	–65.83	–64.66
$D(C_2C_3O_3H_2)$/(°)	44.98	81.24	–53.23	–46.52	66.39
$D(C_2C_1O_2H_1)$/(°)	177.5	–5.294	–3.854	–178.0	–176.5
$D(O_1C_1C_2N)$/(°)	–16.31	–161.9	–163.9	6.999	–104.7
$D(O_1C_1C_2H_1)$/(°)	–0.7866	175.53	177.0	–1.666	1.393

3.2. Relative stabilities of conformers

Over the B3LYP/6-311++G(2d,2p) optimised geometries of serine, the relative energies computed with different methods together with the previous calculations[6,9] are listed in Table 2. The MP4(SDQ) calculation predicts the relative energies of the five conformers to be within 5 kJ/mol of each other. These five conformers are studied here. The Ser1 and Ser2 are isoenergetic and have the lowest energy. The B3LYP method with different basis sets predicts the same stability order: Ser1 > Ser2 > Ser3 > Ser4 > Ser5, indicating that the basis set is not that important. The stability orders strongly depend on the intramolecular HBs, which has been discussed by Miao *et al.*[5] and Lambie *et al.*[6] It is noted that conformer Ser1, which exhibits the weaker HB, is the most stable, but without explanations. This may be influenced by gauch arrangements of carboxylic acid (OH) within this conformer. Considering that the equilibrium constant (K_T) can be simply estimated by the equation $\ln K_T = -\Delta G/(RT)$, where ΔG is the relative energy, R is the gas constant and T is the solid-sample vapourizing temperature in the experiment (here $T \sim 360$ K[28]), one can derive the equilibrium abundances of serine: Ser1:Ser2:Ser3:Ser4:Ser5 = 38%:30%:15%:12%:5% at the B3LYP level; or Ser1:Ser2:Ser3:Ser4:Ser5 = 32%:32%:10%:17%:9% at the MP4(SDQ) level. This was also listed in Table 2.

Table 2. Relative energies (in kJ/mol) and conformer abundance percentages.

conformers	B3LYP[a)]	MP4(SDQ)	Ref. [6][b)]	Ref. [9][c)]	abundance[d)]/%
Ser1	0	0	0	0	32(38)
Ser2	0.67	0.06	0.75	0.74	32(30)
Ser3	2.73	3.62	2.25	1.88	10(15)
Ser4	3.37	1.93	3.97	3.43	17(12)
Ser5	5.93	3.79	6.79	5.88	9(5)

[a)] Including the zero-point energy correction. [b)] At the B3LYP/6-31++G** level. [c)] At the B3LYP/aug-cc-pVDZ level. [d)] The values obtained using the MP4(SDQ) and B3LYP (in the parentheses)

3.3. Conformer-dependent vertical ionization energies

The first six VIE values for the valence molecular orbitals of each conformer are shown in Table 3 and compared with the experimental data in the photoelectron spectra (PES).[11] The pole strengths for P3 IEs are ∼0.9, which validates the perturbative approximations used by the P3 method. In addition to the P3 results, the values based on Koopmans' theorem (KT) (HF/6-311++G(2d,2p)) are also presented. Discrepancies between the Koopman and P3 results indicate that the relaxation and correlation corrections vary from 1.2 to 1.7 eV.

Table 3. Ionization energies (in eV) of serine conformers.

Ser1		Ser2		Ser3		Ser4		Ser5		Exp[a)]
KT	P3	KT	P3	KT	P3	KT	P3	KT	P3	
11.52	10.22	11.53	10.21	11.57	10.22	11.31	10.05	11.05	9.74	10.0
12.40	10.88	12.60	11.05	12.34	10.87	12.18	10.68	12.37	10.85	11.0–11.25
12.86	11.25	12.97	11.78	13.18	11.94	12.98	11.29	13.16	11.68	12.0
13.44	12.25	13.39	11.74	13.40	11.81	13.38	12.18	13.75	12.40	12.4–12.6
14.07	12.74	14.08	12.77	14.45	12.94	13.88	12.57	13.92	12.54	
15.04	13.65	15.11	13.64	15.24	13.83	15.16	13.83	15.30	14.01	13.8

[a)] From Ref. [11]

The photoelectron spectra (PE) of serine reported by Cannington and Ham[11] using a He I radiation source is shown in Fig. 2(a), in which four diffuse bands were observed. The P3 values of the IEs for five low-lying conformers are presented with short vertical bars. As shown in Fig. 2(a), the P3 predicts an apparent energy gap between the fifth and sixth outermost orbitals, which, in turn, contributes to the separation of the 9–13 and 13–20 eV regions. In the outermost region (9–13 eV), it seems that the IEs of the Ser1 conformer match the PES better than the other ones. However, some differences exist. The first difference is the disagreement between the predicted lowest IE (10.2 eV) of Ser1 and the position of the first peak in the experimental PES (10.0 eV).[11] Another significant discrepancy is the lack of the three predicted peaks matching the experimental shoulders at 11.6, 12.0 and 12.9 eV. Both conformers Ser2 and Ser3 seem to provide a worse match to the experimental spectra. They predict a band in a place where there is a clear valley in the PES at 13.2 eV. The first five IEs of Ser2 overlap with that of Ser1 and Ser3. As a result, whether there is Ser2 existing in the gas phase PES is unknown despite the fact that it has the isoenergetic energy with the most stable conformer. Unlike the Ser1, Ser2 and Ser3 conformers, Ser4 predicts the lowest IE at 10.0 eV. Given the small relative energies of conformers Ser2, Ser3 and Ser4, it is impossible to ignore the possibility that they also contribute to the observed peaks. The broad band in the region above 13 eV in the PES will not be discussed here because the corresponding final-state energies seriously overlap.

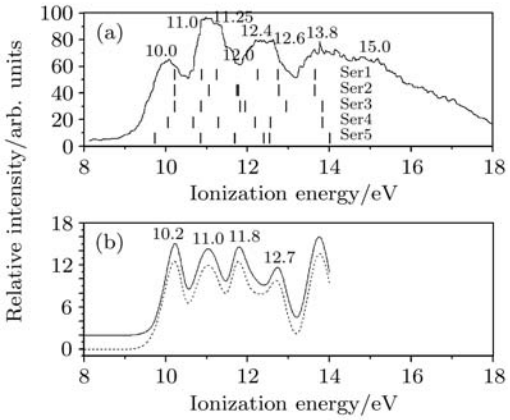


Fig. 2. Comparison between (a) the experimental spectra adopted from Ref. [11] and (b) the simulated spectra of serine at $T = 360$ K (solid line). The short vertical bars represent the P3/-311++G(2d,2p) of the IEs for the five low-lying conformers. The solid and dash lines in (b) represent the theoretical spectra with the abundance ratios predicted at the B3LYP and MP4(SDQ) levels, respectively.

By considering the relative abundances of the conformers at 360 K, as shown in Table 2, we simply simulate the theoretical PES with an energy resolution of about 50 meV (see Ref. [11]) by using the P3 values of the IEs. The intensity is the product of the electron density and pole strength for the relevant molecular orbital.[24] The solid and dashed lines in Fig. 2(b) are based on the abundance ratios predicted with the B3LYP and MP4(SDQ) calculations, respectively. The dashed line seems to match the experimental spectra better than the solid one. A peak

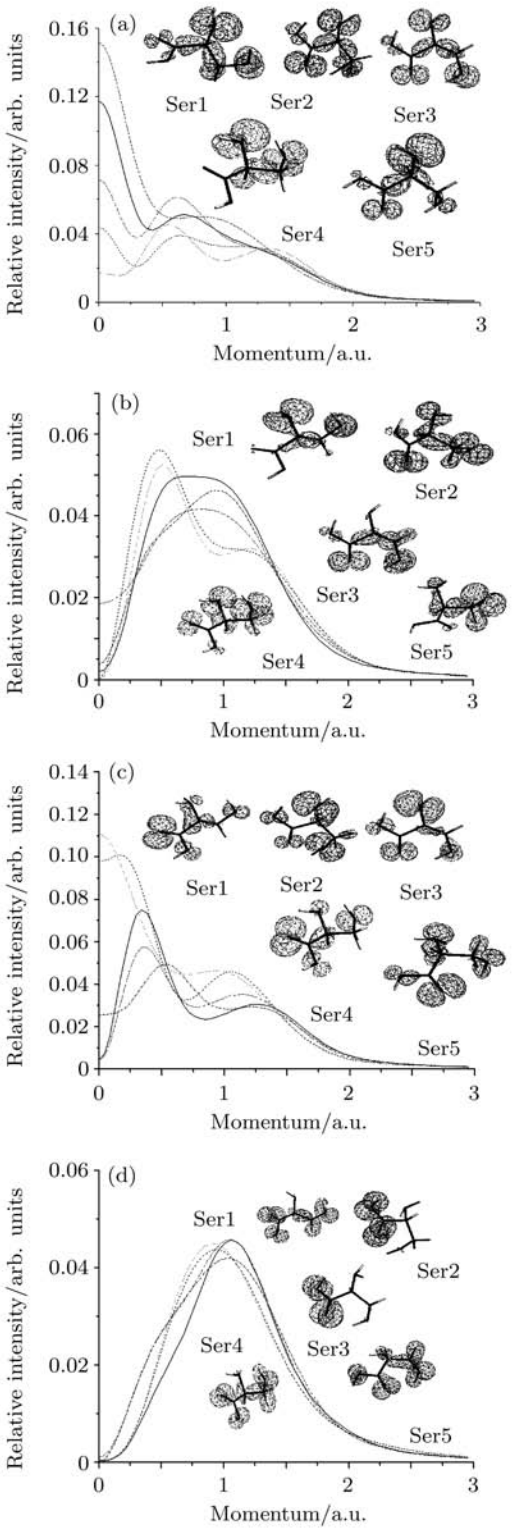
at 11.8 eV in the simulated PES does not emerge in the experimental spectra. More peaks appearing in the theoretical spectra and the calculated IEs will be helpful to make assignments of high-energy resolution spectra measured in the future. Despite the lack of information on the Franck-Condon width for each ionic state, the peak positions in the simulated PES generally match the observed ones and the existence possibilities of Ser1, Ser2, Ser3 and Ser4 (even together with Ser5) in the experiment are indicated.

3.4. Outer valence orbital momentum distributions and the Dyson orbitals of the conformers

Properties obtained from the coordinate space convey limited information about the variations of electronic structure associated with each conformational process.[29] Energy and wave function are the heart and soul of quantum mechanics. Unlike energy, the quality of wave functions is usually indirectly assessed through other measurable molecular properties and qualitatively measured using electron density contours. Until recently, electron momentum spectroscopy (EMS) had been the most direct method to measure molecular wave functions.[26,27] However, further application of EMS has been largely limited by its low coincidence count rate and poor energy resolution (currently 0.5–1.0 eV).[30,31] Moreover, using the theory of EMS[26,27] in momentum space for quantum chemical applications, we find that the dual space analysis[12] is particularly useful in the study of biomolecule conformations and tautomerism.[12−15]

In the present study, the Dyson orbitals of each conformer have been calculated in coordinate space as orbital electron charge densities (CDs) and in momentum space as orbital MDs. Here we combine information obtained from both spaces (dual space analysis)[12] to provide an insight into the electronic structure of each conformation as a result of the various conformational changes.

Figure 3 shows the outer valence orbital MDs of serine. All the conformations belong to the C_1 point group symmetry and their Dyson orbitals are therefore correlated. Five representative orbitals were selected to demonstrate the interesting structure of serine in Fig. 3. Compared to other conformers with Ser1, their orbitals are considered to be the fingerprints of rotation around a particular bond. All of the outer valence orbitals of the five conformers have, to some degree, distortion in their wave functions as a result of rotation. The MO 28a, 27a and 26a are the orbitals significantly affected by the conformational process. The other two orbitals related to the π bonding, 25a and 24a, are slightly affected.



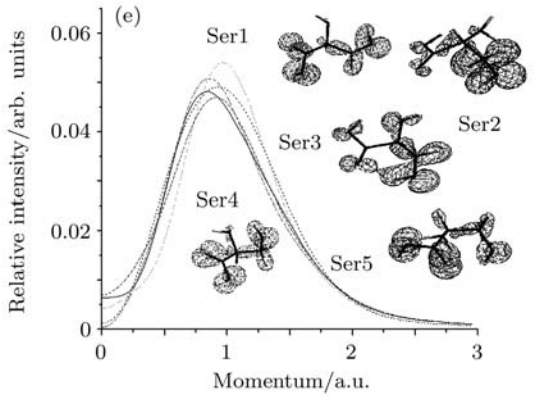


Fig. 3. Simulated orbital MDs for five outer valence orbitals of serine conformers Ser1 (the solid line), Ser2 (the dashed line), Ser3 (the dotted line), Ser4 (the dash-dot line) and Ser5 (the dash-dot-dot line), together with their orbital electron charge densities. (a) 28a, (b) 27a, (c) 26a, (d) 25a, (e) 24a.

The rotation about the C_2–C_3 bond of Ser1 generates Ser4. The orbitals significantly affected by this conformational process are observed in the MOs 28a, 27a and 26a. The corresponding Dyson orbitals in momentum space and coordinate space are given in Fig. 3 to demonstrate the changes between the conformers. In both conformers, MOs 28a are mainly attributed to the lone-pairs on the N and O atoms. Although rotation of the C_2–C_3 bond does not change the charge density on the N and O_2 (in Ser4), the new C_2H σ bond forms instead of a C_2C_3 σ bond, which causes the MD to increase in the low momentum region. In Ser1, MOs 27a are also mainly attributed to the lone-pairs on the N and O atoms, and both have a comparative amplitude of MD. Hence a broad peak forms in the momentum region 0.5 a.u. $< p <$ 1.4 a.u., as shown in Fig. 3(b). By comparison, the C_2–C_3 rotation enhances electron concentration on the O=C region (MO 27a, Ser4), which results in a brae in its orbital MD. In both conformers, the O=C–O group makes the predominant contribution to MO 26a. Rotation of C_2–C_3 slightly changes electron density in the C–C–N region and corresponding changes occur in their MD.

Rotations of the C_1–C_2 and C_2–C_3 bonds of Ser1 generate Ser5. In this case, significant orbital variations occur in 28a, 27a and 26a. In contrast with their MDs, the main differences are not in their shapes, but in their amplitude, except the MO 27a. The stronger MD in the low momentum region of MO 27a of Ser5 is shown in Fig. 3, which is attributed to the s function of C_2–C_3 σ bond. The combined rotations of the C_1–C_2, C_2–C_3 and C_1–O_1 bonds generate the Ser2 and Ser3. Those rotations cause significant orbital variations in 28a, 27a and 26a. The largest variation occurs in the MO 26a. This is reasonable because the dominating components of this orbital are a O lone-pair in Ser1 and a N lone pair in Ser2 and Ser3, respectively.

4. Summary

Five low-lying conformers of serine has been studied by the B3LYP/6-311++G(2d,2p) method. Energetic extrapolation calculations were made at MP4(SDQ) levels of theory. The VIEs calculated with the P3 method agree with the experimental PES, and reassignment to the experimental PES demonstrates that there are at least four conformers, Ser1, Ser2, Ser3 and Ser4 in gas-phase experiments.

Using dual space analysis and information obtained from coordinate and momentum spaces, we investigated the conformational processes generated from the global minimum conformer Ser1 by the rotation of C_2–C_3 (Ser4), C_1–C_2 (Ser5) and C_1–O_2 (Ser2 and Ser3). Orbitals 28a, 27a and 26a are identified as the fingerprint orbitals for all of these conformational processes.

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