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Electronic spectra, excited-state geometries and molecular electrostatic potentials of aromatic amino acids

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Abstract

Lowest singlet excitation and emission energies of the three aromatic amino acids (phenylalanine, tyrosine and tryptophan) that are known to absorb ultraviolet radiation strongly were obtained using gas phase ab initio calculations. The 3-21G basis set was used and the excited states were generated using configuration interaction involving singly excited configurations (CIS). The calculated excitation and emission energies reproduce the observed trends satisfactorily. The changes in geometry consequent to excitation take place in the molecules mainly in the corresponding six-membered rings. The rings of phenylalanine and tyrosine get somewhat expanded consequent to excitation. This is in qualitative agreement with experimental results on substituted benzenes obtained from high resolution spectroscopy. The changes in the geometry of tryptophan following excitation are somewhat different from those of phenylalanine and tyrosine. Ground and excited state molecular electrostatic potentials suggest that hydrogen bonding patterns of the three amino acids would not change appreciably following electronic excitation of the molecules which explains why structures and activities of proteins and enzymes are not seriously modified on ultraviolet irradiation.

Keywords: Proteins; Amino acids; Excited states; Photochemistry; Photobiology

1. Introduction

It is known that enzyme activity is not seriously affected by ultraviolet irradiation although it is appreciably sensitive to heat treatment [1]. It is somewhat surprising in view of the fact that three of the naturally occurring amino acids, namely, phenylalanine, tyrosine and tryptophan (Fig. 1) absorb ultraviolet radiation strongly like the nucleic acid bases which undergo photochemical changes modifying the properties of nucleic acids appreciably. Activities of enzymes are dependent on their ability to form hydrogen bonds [2] and, therefore, an important question arises whether hydrogen bonding abilities of the above mentioned three amino acids are appreciably altered consequent to electronic excitation or not. It has been amply demonstrated earlier that molecular electrostatic potentials (MEP) and molecular electric fields (MEF) can serve as reliable descriptors of hydrogen bond forming ability of molecules [3–7]. Therefore, information about the possible effects of ultraviolet irradiation on the structures and properties or activities of proteins and enzymes can be obtained though a study of excited state MEP maps of the three aromatic amino acids. It may be noted that ground state MEP maps of a large number of molecules have been studied with regard to different properties and activities [3–9], e.g. those relevant to drug design, but studies of excited state MEP maps are scarce [10,11].

From the structural point of view, phenylalanine, tyrosine and tryptophan are monosubstiuted benzene, phenol and indole, respectively, the substituent in all the cases being the $CH_2CHNH_2COOH(R)$ group. Electronic spectra and photophysics of indole, tryptophan and other related molecules have been studied extensively earlier [12–17]. These aspects of phenylalanine and tyrosine have also been studied [18,19] but they do not seem to have evoked as keen interest as those of tryptophan. However, electronic spectra, excited state geometries and properties of several substituted benzenes have been studied in detail earlier using both experimental and theoretical methods [20–23] and a qualitative similarity can be expected between the properties of those molecules and two of the amino acids, i.e. phenylalanine and tyrosine. It has been conjectured that migration of energy absorbed by the aromatic amino acids would occur through some mechanism consequent to ultraviolet irradiation of proteins [1]. Useful information in this context can be obtained by studying excited state geometries of the molecules. Thus, if the geometry of the substituent group R and the portion of the ring where this group R is attached to the molecule

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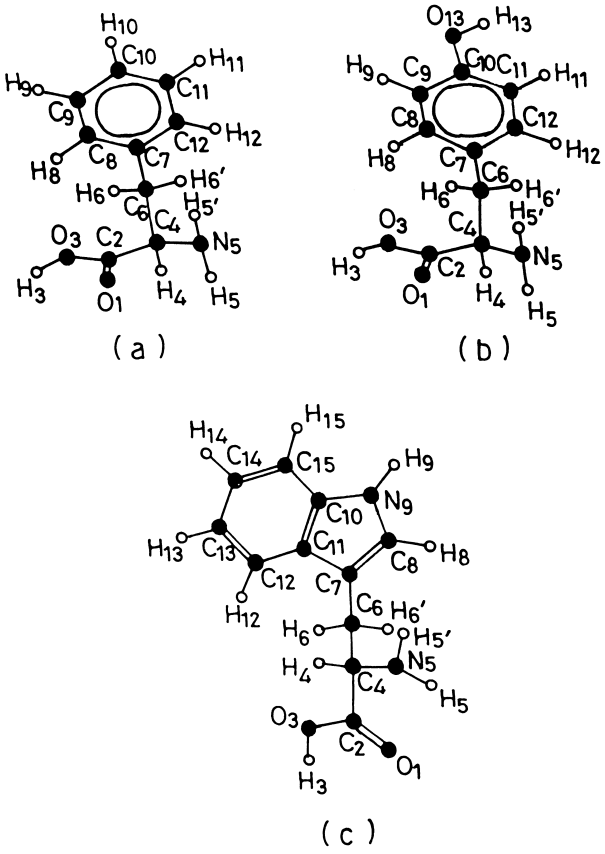

Fig. 1. Structures of the aromatic amino acids: (a) phenylalanine; (b) tyrosine and (c) tryptophan. The adopted atomic numbering scheme is also shown in each case.

are appreciably modified following excitation, it would be indicative of possibility of partial migration of excitation energy through it. Further, in the process of energy transfer, those normal modes of vibration may be effectively involved that would be composed of internal coordinates that would be particularly modified on excitation.

In view of the above mentioned reasons, we have studied ground and lowest singlet excited state geometries and MEP maps of the three aromatic amino acids here using ab initio calculations. Study of electronic transitions of the molecules would be limited to the extent of examining if the broad spectral features corresponding to the lowest singlet transition in the different cases, e.g. shifts of peaks or (0,0) bands in going from one case to another are reproduced satisfactorily. A study of this aspect is desirable as it would reveal if the computational method used would be expected to yield molecular properties qualitatively satisfactorily and consistently in the different cases or not.

2. Computational details

Ground state molecular geometries were optimized in gas phase using the ab initio restricted Hartree–Fock procedure. Excited states were generated using configuration interaction among singly excited configurations (CIS) involving n_1 occupied and n_2 unoccupied molecular orbitals where $n_1, n_2 =$ 10, 46 for phenylalanine, 10, 50 for tyrosine and 12, 56 for tryptophan, respectively. Excited state geometries were also optimized using the CIS wavefunctions. The CIS approach is an approximate procedure to compute excited state molecular properties but it has been shown to be quite reliable [24–27]. Better procedures than CIS, e.g. that based on complete active space (CAS) [28] would be too difficult for the molecules studied here. A moderate basis set, i.e. 3-21G was used in all the calculations due to large size of the molecules studied. Earlier studies [10] have shown that fairly reliable information can be obtained using this basis set along with the CIS procedure. Vertical CIS calculations performed at the geometry of the ground state yield excitation energies that can be compared with observed absorption peaks. Similarly, the calculated vertical excitation energies from the optimized excited states would correspond to observed fluorescence peaks. The total energy difference between the ground and excited states would correspond to the (0,0) transition energy observed in absorption or fluorescence spectra under the assumption that the zero point energies of the two states are nearly equal. Vibrational frequency analysis was performed in order to ensure that the stationary points located on the potential energy surfaces by geometry optimization were minima. The calculations were performed using the Windows version of Gaussian 94 (Revision E.3) program [29]. MEP values on the van der Waals surfaces of molecules were obtained using the potential-derived ChelpG charges [30].

3. Results and discussion

3.1. Transition energies

The calculated lowest three singlet transition energies and the corresponding oscillator strengths for each of phenylalanine, tyrosine and tryptophan are presented in Table 1 and Fig. 2. As Fig. 2 shows, when the lowest singlet excited state which is of π–π^* type is optimized, the ground state total energy is raised up by $\sim$0.14 to $\sim$0.17 eV in the different cases. The experimentally observed transition energies in absorption and fluorescence spectra [12,18,19] are also presented in Table 1. The experimental studies were carried out usually in aqueous media [12,18,19]. The molecules under study, particularly phenylalanine and tyrosine, are appreciably hydrophobic in nature. Therefore, the solvation of these two molecules in water would not affect their spectral properties much. Due to this reason, solvation calculations were not performed. As the photochemical and photobiological effects of excitation of the molecules would mainly originate in the lowest singlet excited states, we would discuss only the nature of these excited states and the corresponding transitions. We find that there is a qualitative

Table 1
Calculated excitation and emission energies of phenylalanine, tyrosine and tryptophan in gas phase and experimentally observed absorption and fluorescence energies (in eV)[a]

Molecule	Calculated excitation energy (eV)		Experimented absorption[b] energy (eV)	Calculated emission energy (eV)	Experimented fluorescence[a] energy (eV)
	Vertical	Total energy difference			
Phenylalanine	6.59 (0.001) 6.91 (0.015) 7.26 (0.014)	6.45	4.81	6.31 (0.001)	4.40
Tyrosine	6.48 (0.038) 6.85 (0.014) 7.25 (0.058)	6.32	4.51	6.16 (0.049)	4.08
Tryptophan	6.29 (0.053) 6.54 (0.156) 6.95 (0.008)	6.11	4.43	5.94 (0.082)	3.49

[a] Oscillator strengths are given in parentheses.
[b] From [12,18,19].

agreement between the calculated and observed transition energies [31] in the sense that the observed trend in going from one case to another is satisfactorily reproduced (Table 1). Thus, the observed absorption and fluorescence energies of the three molecules lie in the order [12,18,19] phenylalanine > tyrosine > tryptophan and the present calculated corresponding energies also follow the same order. The vertical excitation energies that would correspond to absorption peaks are greater than those obtained as total energy differences of the ground and excited states of the molecules that would correspond to (0,0) bands. According to the calculated results (Table 1), the (0,0) bands would be shifted appreciably on the longer wavelength side of the absorption peaks and this is actually observed in benzene and its derivatives [31]. If the calculated excitation energies are scaled down by the constant factor 1.43, the different observed transition energies presented in Table 1 would be reproduced within the RMS error of 0.27 eV. However, if

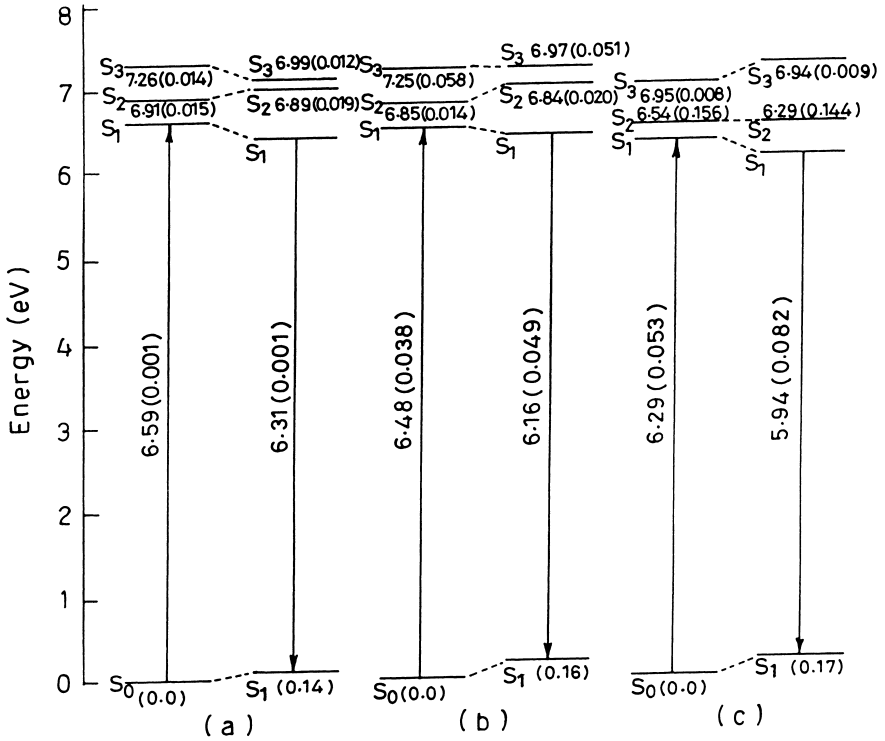

Fig. 2. Energy level diagrams for the aromatic amino acids in gas phase: (a) phenylalanine; (b) tyrosine and (c) tryptophan. The upward arrows indicate absorption while the downward arrows indicate emission. Transition energies (in eV) corresponding to the different excited states and the corresponding oscillator strengths (in parentheses) are given. The ground state energy differences (eV) obtained by separate ground and lowest singlet excited state (S_1) geometry optimization are also given.

this type of scaling is adopted, it should be noted that the optimized geometries, transition energies and vibrational frequencies would be consistent only with total energies of the ground and excited states and with the differences between these energies, but not with the scaled values of these energy differences. In an earlier study on substituted benzenes also [10], the observed lowest singlet transition energies were reproduced qualitatively satisfactorily.

3.2. Ground and excited state geometries

The optimized ground (S_0) and lowest singlet excited (S_1) state geometries of phenylalanine, tyrosine and tryptophan are presented in Tables 2–4, respectively, where the experimentally observed ground state crystallographic geometries [32–35] are also given. The average magnitudes of error in the calculated bond lengths of phenylalanine, tyrosine and tryptophan with respect to the crystallographic values are 0.016, 0.016 and 0.042 Å, respectively, while the corresponding errors in the calculated bond angles of the three molecules are 1.4°, 1.7° and 3.7°, respectively. The differences between the calculated and crystallographic bond angles of the side chain (R) are quite appreciable while the corresponding differences for the rings are comparatively much smaller in all the three cases. This is because the calculated geometries correspond to the gas phase while the observed ones correspond to the crystal environment. It is expected that the packing forces in crystals would modify the side chain geometries of the molecules much more than those of the rings since the former are quite flexible while the latter are rigid. This is clearly indicated by the fact that the differences between the calculated gas phase and crystallographic dihedral angles of the side chain atoms in all the three molecules are also usually quite appreciable (Tables 2–4). The orientation of the amino group of tryptophan in the crystal environment is appreciably different from that in gas phase as shown by the crystallographic [34,35] and theoretical values of the $H_4C_4N_5H_5$ dihedral angle (Table 4).

The computed excited state geometries of the three aromatic amino acids differ from the corresponding ground state geometries as follows (Tables 2–4):

1. No appreciable changes in shapes of the molecules take place following excitation, as shown by the dihedral angles.
2. The changes in bond angles of the molecules following excitation are usually quite small, the largest bond angle change not exceeding 2°.
3. As regards changes in bond lengths of the molecules following excitation, the behaviors of phenylalanine and tyrosine are similar but both these molecules behave somewhat differently from tryptophan as follows: (a) The C_6C_7 (six-membered ring-R) bond length decreases by 0.013 and 0.012 Å in phenylalanine and tyrosine, respectively, while the corresponding (five-membered ring-R) bond length decreases by a much smaller amount, i.e.

Table 2
Optimized bond lengths (Å), bond angles (°) and dihedral angles (°) in the ground state (S_0) and lowest singlet excited state (S_1) of phenylalanine

	S_0	S_1	Experimental (S_0)
Bond lengths			
O_1C_2	1.201	1.201	1.164
C_2O_3	1.362	1.363	1.344
O_3H_3	0.969	0.969	0.940
C_2C_4	1.512	1.511	1.497
C_4H_5	1.084	1.084	1.080
C_4N_5	1.455	1.454	1.475
N_5H_5	1.005	1.005	1.079
$N_5H_{5'}$	1.005	1.005	1.079
C_4C_6	1.545	1.552	1.548
C_6H_6	1.080	1.081	1.079
$C_6H_{6'}$	1.081	1.082	1.080
C_6H_7	1.516	1.503	1.567
C_7C_8	1.389	1.419	1.385
C_8C_9	1.384	1.413	1.385
C_9C_{10}	1.384	1.413	1.385
$C_{10}C_{11}$	1.384	1.412	1.384
$C_{11}C_{12}$	1.384	1.413	1.384
$C_{12}C_7$	1.389	1.419	1.384
C_8H_8	1.072	1.070	1.080
C_9H_9	1.072	1.070	1.080
$C_{10}H_{10}$	1.072	1.070	1.080
$C_{11}H_{11}$	1.072	1.070	1.080
$C_{12}H_{12}$	1.072	1.071	1.080
Bond angles			
$O_1C_2O_3$	122.0	122.0	123.8
$O_1C_2C_4$	126.6	126.6	127.2
$H_3O_3C_2$	111.7	111.7	105.9
$C_2C_4H_4$	106.7	106.8	110.6
$C_2C_4N_5$	111.8	112.1	105.6
$H_4C_4N_5$	108.9	109.2	110.6
$C_4N_5H_5$	112.2	112.3	109.5
$C_4N_5H_{5'}$	113.1	113.1	109.5
$H_5N_5H_{5'}$	110.4	110.6	109.4
$C_2C_4C_6$	110.8	110.6	115.8
$C_4C_6H_6$	108.6	108.2	108.6
$C_4C_6H_{6'}$	106.8	106.4	108.6
$C_4C_6C_7$	112.4	112.8	113.4
$C_6C_7C_8$	120.5	120.2	120.6
$C_7C_8C_9$	120.6	120.4	120.0
$C_8C_9C_{10}$	120.2	120.0	120.0
$C_9C_{10}C_{11}$	119.6	120.0	120.0
$C_{10}C_{11}C_{12}$	120.2	120.0	120.0
$C_{11}C_{12}C_7$	120.6	120.4	120.0
$C_{12}C_7C_8$	118.9	119.2	120.0
$H_8C_8C_7$	119.2	119.1	120.0
$H_8C_8C_9$	120.2	120.5	120.0
$H_9C_9C_8$	119.8	119.9	120.0
$H_9C_9C_{10}$	120.0	120.0	120.0
$H_{10}C_{10}C_9$	120.2	120.0	120.0
$H_{10}C_{10}C_{11}$	120.2	120.0	120.0
$H_{11}C_{11}C_{10}$	120.0	120.1	120.0
$H_{11}C_{11}C_{12}$	119.8	119.9	120.0
$H_{12}C_{12}C_{11}$	120.1	120.4	120.0
$H_{12}C_{12}C_7$	119.3	119.2	120.0
$C_7C_6H_6$	110.2	110.1	108.6
$C_7C_6H_{6'}$	109.9	110.0	108.6
$O_3C_2C_4$	111.4	111.3	109.0
Dihedral angles			
$O_1C_2C_4H_4$	−114.0	−114.7	121.5
$O_2C_2O_3H_3$	0.5	0.0	0.0

Table 2 (*Continued*)

	S_0	S_1	Experimental (S_0)
$C_2C_4C_6C_7$	−63.5	−62.7	−59.4
$C_2C_4N_5H_5$	60.2	63.2	60.0
$C_2C_4N_5H_{5'}$	−65.5	−62.9	−60.0
$H_5N_5C_4H_4$	177.8	181.3	179.6
$H_{5'}N_5C_4H_4$	52.1	55.2	59.6
$H_4C_4C_6H_6$	−57.4	−56.8	−58.7
$N_5C_4C_6H_{6'}$	−59.2	−58.6	−58.6
$H_6C_6C_4N_5$	183.6	184.2	182.9
$H_6C_6C_4H_4$	59.8	60.4	59.8
$C_4C_6C_7C_8$	89.4	88.0	83.6
$C_4C_6C_7C_{12}$	−89.9	−91.1	−96.4
$C_6C_7C_8C_9$	180.8	181.2	180.0
$C_6C_7C_{12}C_{11}$	−180.8	−180.9	−180.0
$C_7C_8C_9C_{10}$	0.0	0.0	0.0
$C_8C_9C_{10}C_{11}$	0.0	0.0	0.0
$C_9C_{10}C_{11}C_{12}$	0.0	−0.4	0.0
$C_{10}C_{11}C_{12}C_7$	0.0	−0.4	0.0
$C_6C_7C_8H_8$	0.7	1.3	0.0
$H_8C_8C_9H_9$	0.0	−0.4	0.0
$H_9C_9C_{10}H_{10}$	0.0	0.0	0.0
$H_{10}C_{10}C_{11}H_{11}$	0.0	0.4	0.0
$H_{11}C_{11}C_{12}C_{13}$	0.0	0.0	0.0
$H_{10}C_{10}C_9H_9$	0.0	0.0	0.0
$H_{11}C_{11}C_{10}C_9$	180.2	180.3	180.1
$H_{12}C_{12}C_7C_8$	−180.0	−180.2	−180.1
$H_{12}C_{12}C_{11}C_{10}$	−180.0	−180.3	−180.0

0.002 Å in tryptophan; (b) all the six-membered ring (CC) bond lengths increase by 0.02–0.03 Å in phenylalanine and tyrosine while in tryptophan, the different bond lengths of the five- and six-membered rings change quite differently. Thus, three of the CC bond lengths of the six-membered ring of tryptophan increase by large amounts (∼0.03–0.06 Å) while the other three alternate ones of the same ring increase by much smaller amounts (∼0.004–0.01 Å). The C_7C_{11} and N_9C_{10} bond lengths of the five-membered ring of tryptophan decrease by 0.015 and 0.023 Å while the C_7C_8 and C_8N_9 bond lengths of the same ring increase by 0.011–0.026 Å, respectively; and (c) the changes in CH bond lengths following excitation are negligibly small. The lengths of CH bonds attached to the six-membered ring decrease following excitation of the molecules by different amounts lying between 0.001 and 0.004 Å.

The lowest singlet electronic transitions of several substituted benzenes have been studied experimentally under high resolution and the spectra analyzed rotationally [20–23]. Further, using these rotational constants, approximate estimates of changes in the bond lengths of the benzene ring in these molecules were obtained [20]. Thus, it has been shown that the different CX (X = substituent F, Cl, NH_2) bond lengths decrease by 0.009–0.086 Å while the CC bond lengths increase by ∼0.03 Å in the different cases [20]. A theoretical analysis of the problem was carried out in our laboratory using the CIS/6-31 + G* approach, and the following results obtained [10]. The theoretical calculations

Table 3
Optimized bond lengths (Å), bond angles (°) and dihedral angles (°) in the ground state (S_0) and lowest singlet excited state (S_1) of tyrosine[a]

	S_0	S_1	Experimental (S_0)
Bond lengths			
C_2O_1	1.201	1.201	1.241
C_2O_3	1.362	1.363	1.311
O_3H_3	0.969	0.969	0.950
C_2C_4	1.512	1.511	1.529
C_4H_4	1.084	1.084	1.094
C_4N_5	1.456	1.454	1.488
N_5H_5	1.005	1.005	1.014
N_5H_5	1.005	1.004	1.036
C_4C_6	1.545	1.552	1.538
$C_6H_{6'}$	1.080	1.081	1.088
C_6H_6	1.082	1.082	1.094
C_6C_7	1.515	1.503	1.511
C_7C_8	1.392	1.417	1.394
C_8C_9	1.378	1.410	1.391
C_9C_{10}	1.384	1.407	1.388
$C_{10}C_{11}$	1.381	1.414	1.393
$C_{11}C_{12}$	1.385	1.408	1.392
$C_{12}C_7$	1.385	1.418	1.398
$C_{12}H_{12}$	1.072	1.070	1.085
$C_{11}H_{11}$	1.073	1.071	1.083
$C_{10}O_{13}$	1.376	1.359	1.366
$O_{13}H_{13}$	0.964	0.965	0.981
C_9H_9	1.070	1.068	1.086
C_8H_8	1.072	1.068	1.088
Bond angles			
$O_1C_2O_3$	122.0	122.1	126.4
$C_2O_3H_3$	111.7	111.6	107.8
$O_1C_2C_4$	126.6	126.6	116.9
$O_3C_2C_4$	111.4	111.2	116.6
$C_2C_4H_4$	106.8	106.7	109.2
$C_2C_4N_5$	111.7	112.1	109.7
$C_4N_5H_5$	112.0	112.3	111.9
$C_4N_5H_{5'}$	113.1	113.1	110.9
$H_5N_5H_{5'}$	110.3	110.7	107.0
$C_4C_6H_6$	108.7	108.2	107.3
$C_4C_6H_{6'}$	106.8	106.7	108.5
$C_2C_4C_6$	110.7	110.7	111.1
$C_4C_6C_7$	112.5	112.6	114.5
$C_6C_7C_8$	120.8	119.8	120.5
$C_7C_8C_9$	121.2	119.9	121.4
$C_8C_9C_{10}$	120.1	119.2	119.6
$C_9C_{10}C_{11}$	119.5	121.7	120.3
$C_{10}C_{11}C_{12}$	120.1	118.9	119.5
$C_{11}C_{12}C_7$	121.0	120.1	121.3
$C_7C_8H_8$	119.1	119.3	119.5
$H_8C_8C_9$	119.7	120.7	119.1
$C_8C_9H_9$	121.5	122.3	120.9
$H_9C_9C_{10}$	118.4	118.5	119.6
$H_{13}O_{13}C_{10}$	112.9	113.7	111.1
$O_{13}C_{10}C_{11}$	123.2	121.7	121.8
$O_{13}C_{10}C_9$	117.2	116.6	117.9
$C_{10}C_{11}H_{11}$	120.2	120.3	120.4
$H_{11}C_{11}C_{12}$	119.7	120.8	120.2
$H_{12}C_{12}C_7$	119.4	119.3	119.8
$N_5C_4H_4$	108.9	109.1	107.2
Dihedral angles			
$O_1C_2C_4H_4$	−113.8	−114.8	31.4
$O_1C_2O_3H_3$	0.6	−0.5	000.0
$O_1C_2C_4N_5$	5.2	4.7	14.2
$C_2C_4N_5H_5$	58.8	63.4	57.0

Table 3 (*Continued*)

	S_0	S_1	Experimental (S_0)
$C_2C_4N_5H_{5'}$	−66.6	−62.8	62.4
$N_5C_4C_6H_{6'}$	−59.2	−58.4	54.7
$N_5C_4C_6H_6$	−176.2	−175.9	−169.6
$C_4C_6C_7C_8$	89.9	87.4	95.8
$C_6C_7C_8H_8$	0.5	2.1	−0.9
$C_7C_8C_9H_9$	181.1	181.1	181.6
$C_8C_9C_{10}O_{13}$	181.1	180.2	182.3
$C_8C_9C_{10}C_{11}$	0.0	0.4	1.5
$C_9C_{10}O_{13}H_{13}$	181.1	180.4	182.2
$H_{13}O_{13}C_{10}C_{11}$	0.0	0.0	−1.4
$C_{10}C_{11}C_{12}C_7$	0.0	−0.6	1.1
$O_{13}C_{10}C_{11}H_{11}$	0.0	0.4	−1.4
$H_{11}C_{11}C_{12}H_{12}$	0.0	−0.5	1.7
$H_{12}C_{12}C_7C_6$	−179.9	−1.1	0.0
$C_6C_4N_5H_5$	−65.3	−60.8	−65.9
$C_6C_4N_5H_{5'}$	169.3	173.0	174.7
$C_2C_4C_6C_7$	−63.1	−62.6	−53.1

[a] Experimental data are from [33].

yielded the values of rotational constants and changes in the same following excitation within the error limit of ∼3.5%. Further, these calculations described shortening of the different CX bonds and elongation of the CC bonds following excitation satisfactorily in a qualitative sense but shortening of the CH bond lengths was highly underestimated (experimental ∼0.014 Å, theoretical ∼0.003 Å). It is expected that absolute values of the optimized geometrical parameters would depend on the basis set used in such calculations but changes in these quantities following excitation would not be very sensitive to the same. Therefore, we hope that changes in the geometries of the three amino acids following excitation obtained from the present calculations would have a similar accuracy as that in the earlier theoretical work on substituted benzenes [10]. Thus, changes in geometries of the three amino acids obtained here are expected to be reliable in a qualitative sense.

The above results show that excitation of the three aromatic amino acids is localized in the corresponding rings and migration of excitation energy is not likely to occur to an appreciable extent through the substituent group (R) from the rings to the neighboring amino acids in a protein. This is in agreement with the views expressed earlier [1].

3.3. Ground and excited state MEP values

It has previously been shown that strongly linear relationships exist between hydrogen bond forming abilities of atoms in molecules and MEP values near the same [3–7]. Therefore, a study of MEP patterns around the three amino acid molecules in their ground and excited states would reveal information as to the possible effects of excitation of the molecules on the hydrogen bonds involving them in proteins, enzymes and hydrogen bonded complexes, e.g. enzyme–substrate complexes. The lowest negative MEP values in the ground (S_0) and lowest singlet excited (S_1) states

Table 4
Optimized bond lengths (Å), bond angles (°) and dihedral angles (°) in the ground state (S_0) and lowest singlet excited state (S_1) of tryptophan[a]

	S_0	S_1	Experimental (S_0)
Bond lengths			
O_1C_2	1.202	1.202	1.266
C_2O_3	1.358	1.358	1.312
O_3H_3	0.968	0.968	0.950
C_2C_4	1.503	1.504	1.582
C_4H_4	1.080	1.081	1.036
C_4N_5	1.449	1.448	1.440
N_5H_5	1.000	1.000	1.079
$N_5H_{5'}$	1.002	1.001	1.080
C_6H_6	1.082	1.082	1.009
$C_6H_{6'}$	1.086	1.085	1.068
C_6C_7	1.498	1.496	1.574
C_7C_8	1.351	1.362	1.340
C_8N_9	1.389	1.415	1.451
N_9C_{10}	1.376	1.353	1.275
$C_{10}C_{11}$	1.403	1.461	1.424
$C_{11}C_{12}$	1.394	1.398	1.376
$C_{12}C_{13}$	1.375	1.416	1.410
$C_{13}C_{14}$	1.401	1.412	1.387
$C_{14}C_{15}$	1.374	1.408	1.362
$C_{15}C_{10}$	1.390	1.402	1.397
$C_{15}H_{15}$	1.072	1.070	1.107
$C_{14}H_{14}$	1.072	1.070	1.040
$C_{13}H_{13}$	1.072	1.071	1.023
$C_{12}H_{12}$	1.072	1.070	1.040
C_8H_8	1.067	1.065	1.033
N_9H_9	0.994	0.996	0.964
C_4C_6	1.562	1.563	1.528
$C_{11}C_7$	1.451	1.436	1.398
Bond angles			
$O_1C_2O_3$	122.4	122.4	119.4
$C_2O_3H_3$	111.9	112.0	107.8
$O_1C_2C_4$	127.1	127.1	121.0
$O_3C_2C_4$	110.5	110.5	118.9
$C_2C_4H_4$	107.7	107.7	110.2
$C_2C_4N_5$	107.9	108.1	112.8
$C_4N_5H_5$	114.5	114.7	109.5
$C_4N_5H_{5'}$	114.1	114.2	109.5
$H_5N_5H_{5'}$	114.6	114.7	109.5
$N_5C_4H_4$	110.3	110.5	99.8
$C_4C_6H_6$	108.8	108.8	103.5
$C_4C_6H_{6'}$	108.1	108.2	104.8
$C_4C_6C_7$	111.2	110.7	116.6
$C_6C_7C_8$	127.5	126.9	129.2
$C_7C_8C_9$	110.1	108.5	109.7
$C_8N_9C_{10}$	108.8	110.5	107.7
$N_9C_{10}C_{11}$	107.5	106.4	108.7
$C_{10}C_{11}C_{12}$	119.6	119.2	119.2
$C_{11}C_{12}C_{13}$	118.9	117.9	115.1
$C_{12}C_{13}C_{14}$	120.8	122.4	124.4
$C_{13}C_{14}C_{15}$	121.3	121.0	121.9
$C_{14}C_{15}C_{10}$	117.9	117.1	114.1
$C_{15}C_{10}C_{11}$	121.6	122.5	125.2
$C_7C_8H_8$	129.2	130.7	132.9
$H_8C_8N_9$	120.7	120.8	116.4
$C_8N_9H_9$	125.4	124.4	121.9
$H_9N_9C_{10}$	125.8	125.0	130.1
$H_{12}C_{12}C_{13}$	120.6	120.6	124.9
$H_{13}C_{13}C_{14}$	119.3	118.8	114.0
$H_{14}C_{14}C_{15}$	119.5	119.7	114.0
$H_{15}C_{15}C_{10}$	121.1	121.4	122.6
$H_{12}C_{12}C_{11}$	120.5	121.5	120.1

Table 4 (*Continued*)

	S_0	S_1	Experimental (S_0)
$H_{13}C_{13}C_{12}$	119.9	118.8	121.5
$H_{14}C_{14}C_{13}$	119.3	119.4	124.1
$H_{15}C_{15}C_{14}$	121.0	121.5	123.2
Dihedral angles			
$O_1C_2C_4H_4$	134.1	133.8	144.9
$O_1C_2O_3H_3$	−0.7	−0.8	0.0
$O_1C_2C_4N_5$	15.0	14.4	34.4
$H_3O_3C_2C_4$	182.1	181.9	189.7
$C_2C_4C_6C_7$	182.2	183.3	189.6
$C_2C_4C_6H_6$	−55.9	−55.4	−48.0
$C_2C_4C_6H_{6'}$	61.2	62.1	70.2
$H_4C_4N_5H_5$	70.2	70.6	−62.8
$H_4C_4N_5H_{5'}$	−154.8	−153.9	−182.8
$H_5N_5C_4C_6$	−52.3	−51.7	−180.0
$H_5N_5C_4C_6$	82.7	83.6	60.0
$C_4C_6C_7C_8$	−100.4	−98.9	−60.9
$C_6C_7C_8C_9$	−181.5	−181.9	−180.8
$C_7C_8N_9C_{10}$	0.0	0.0	4.3
$C_8N_9C_{10}C_{11}$	0.0	0.0	−3.2
$N_9C_{10}C_{11}C_{12}$	−180.4	−179.3	−178.6
$C_{10}C_{11}C_{12}C_{13}$	0.0	0.0	0.4
$C_{11}C_{12}C_{13}C_{14}$	0.0	0.0	−2.6
$C_{12}C_{13}C_{14}C_{15}$	0.0	0.0	4.2
$C_{13}C_{14}C_{15}C_{10}$	0.0	0.0	−3.1
$C_6C_7C_8H_8$	−2.3	−3.7	11.4
$H_8C_8N_9H_9$	0.0	0.7	−11.6
$C_7C_{11}C_{12}H_{12}$	0.0	0.0	0.0
$C_{11}C_{12}C_{13}H_{13}$	−180.0	−180.1	−179.4
$C_{12}C_{13}C_{14}H_{14}$	−180.1	−179.9	−176.0
$C_{13}C_{14}C_{15}H_{15}$	−179.9	−180.1	−179

[a] Experimental data are from [34,35].

on the van der Waals surfaces of phenylalanine, tyrosine and tryptophan near the different atomic sites obtained using CHelpG charges are presented in Table 5. The MEP values presented in Table 5 reveal that the effect of excitation of the molecules on the MEP values is quite small. Therefore, electronic excitation of the corresponding moieties in proteins and enzymes would not cause any significant change on the hydrogen bonds that would involve them. In other words, according to the MEP values (Table 5), structures and activities of proteins and enzymes would not be affected appreciably consequent to ultraviolet irradiation. This is actually observed [1].

Table 5
Lowest MEP values (kcal/mol) in the ground (S_0) and lowest singlet excited (S_1) states near the different atomic sites of phenylalanine, tyrosine and tryptophan on the van der Waals surfaces obtained using CHelpG charges

Molecule/state	Atomic sites[a]				
	O_1	$O_3(O_2)$	N_5 (N)	O_{13} (OE)	N_9 (NE)
Phenylalanine					
S_0	−52.3	−32.6	−49.7		
S_1	−52.4	−32.5	−50.0		
Tyrosine					
S_0	−52.4	−32.9	−49.0	−47.9	
S_1	−53.4	−33.7	−50.1	−43.1	
Tryptophan					
S_0	−53.2	−34.3	−60.4		−31.0
S_1	−52.7	−33.4	−59.4		−28.9

[a] For atomic numbering scheme, see Fig. 1.

4. Conclusion

We arrive at the following conclusions from the present study:

1. The changes in molecular geometries and overall shapes of the three amino acids consequent to excitation are quite small. The changes in ring bond lengths of phenylalanine and tyrosine occurring due to excitation to the lowest singlet excited state are similar to those of substituted benzenes while the corresponding changes in tryptophan follow a somewhat different pattern. This study explains why migration of absorbed electronic energy does not occur to an appreciable extent through the substituent group (R) to the other amino acids in proteins and enzymes.
2. MEP values near the different atomic sites in the aromatic amino acids change to only small extents consequent to excitation of the molecules to the lowest singlet excited state. It suggests that structures, properties and activities of proteins and enzymes would not be modified appreciably consequent to ultraviolet irradiation.

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References

[1] K.C. Smith, P.C. Hanawalt, Molecular Photobiology Inactivation and Recovery, Academic Press, New York, 1969, p. 85.
[2] A.L. Lehninger, Principles of Biochemistry, CBS Publishers & Distributors, Delhi, 1987, p. 95.
[3] P.C. Mishra, A. Kumar, in: K.D. Sen (Ed.), Molecular Similarity II, Vol. 174, Springer, Heidelberg, 1995, p. 27.
[4] P.C. Mishra, A. Kumar, in: J.S. Murray, K.D. Sen (Eds.), Molecular Electrostatic Potentials: Concepts and Application, Elsevier, Amsterdam, 1996, p. 257.
[5] A. Kumar, C.G. Mohan, P.C. Mishra, Int. J. Quant. Chem. 55 (1995) 53.
[6] A. Kumar, C.G. Mohan, P.C. Mishra, J. Mol. Struct. (Theochem.) 361 (1996) 135.
[7] P.S. Kushwaha, P.C. Mishra, Int. J. Quant. Chem. 76 (2000) 700.
[8] C. Santhosh, P.C. Mishra, J. Mol. Model. 3 (1997) 172.
[9] C. Santhosh, M.K. Shukla, P.C. Mishra, J. Mol. Model. 4 (1998) 250.
[10] D.M. Upadhyay, M.K. Shukla, P.C. Mishra, J. Mol. Struct. (Theochem.), in press.
[11] S.K. Mishra, M.K. Shukla, P.C. Mishra, Spectrochim. Acta A56 (2000) 1355.

[12] J.W. Longworth, in: R.B. Cundall, R.E. Dale (Eds.), Time-Resolved Fluorescence Spectroscopy in Biochemistry and Biology, Plenum Press, New York, 1983, p. 651.
[13] E.F. Gudgin-Templeton, W.R. Ware, J. Phys. Chem. 88 (1984) 4626.
[14] G.B. Strambini, M. Gonnelli, J. Am. Chem. Soc. 117 (1995) 7646.
[15] A.G. Szabo, D.M. Rayner, J. Am. Chem. Soc. 102 (1980) 554.
[16] Y. Chen, F. Gai, J.W. Petrich, J. Phys. Chem. 98 (1994) 2203.
[17] M.K. Shukla, P.C. Mishra, J. Chem. Phys. 230 (1998) 187.
[18] L. Miclo, E. Perrin, A. Driou, M. Mellet, G. Linden, Int. J. Peptide Protein Res. 46 (1995) 186.
[19] K.S. Pandey, P.C. Mishra, Indian J. Biochem. Biophys. 27 (1990) 245.
[20] T. Cvitaš, J.M. Hollas, G.H. Kirby, Mol. Phys. 19 (1970) 305.
[21] W.E. Sinclair, D.W. Pratt, J. Chem. Phys. 105 (1996) 7942.
[22] T. Cvitaš, J.M. Hollas, Mol. Phys. 18 (1970) 101, 261, 793, 801.
[23] G.H. Kirby, Mol. Phys. 19 (1970) 289.
[24] D. Maurice, M. Head-Gordon, Mol. Phys. 96 (1999) 1533.
[25] J.F. Stanton, J. Gauss, N. Ishikawa, M. Head-Gordon, J. Chem. Phys. 103 (1995) 4160.
[26] C.M. Gittins, E.A. Rohlfing, C.M. Rohlfing, J. Chem. Phys. 105 (1996) 7323.
[27] J.B. Foresman, M. Head-Gordon, J.A. Pople, J. Phys. Chem. 96 (1992) 135.
[28] F. Bernardi, A. Bottini, J.J.W. Mc Dougall, M.A. Robb, H.B. Schlegel, Far-Symp. Chem. Soc. 19 (1984) 137.
[29] M.J. Frisch, G.W. Trucks, H.B. Schlegel, P.M. W. Gill, B.G. Johnson, M.A. Robb, J.R. Cheeseman, T. Keith, G.A. Petersson, J.A. Montgomery, K. Raghavachari, M.A. Al-Laham, V.G. Zakrzewski, J.V. Ortiz, J.B. Foresman, J. Cioslowski, B.B. Stefanov, A. Nanayakkara, M. Challacombe, C.Y. Peng, P.Y. Ayala, W. Chen, M.W. Wong, J.L. Andres, E.S. Replogle, R. Gomperts, R.L. Martin, D.J. Fox, J.S. Binkley, D.J. Defrees, J. Baker, J.P. Stewart, M. Head-Gordon, C. Gonzalez, J.A. Pople, Gaussian 94W (Revision E.3), Gaussian, Inc., Pittsburgh, PA, 1995.
[30] C.M. Breneman, K.B. Wiberg, J. Comp. Chem. 11 (1990) 361.
[31] J. Petruska, J. Chem. Phys. 34 (1961) 1120.
[32] G. Bolis, E. Clementi, J. Am. Chem. Soc. 99 (1977) 5550.
[33] E. Clementi, F. Cavallone, R. Scordamaglia, J. Am. Chem. Soc. 99 (1977) 5531.
[34] W.A. Sokalski, K. Maruszewski, P.C. Hariharan, J.J. Kaufman, Int. J. Quant. Chem. 16 (1989) 119.
[35] R.A. Pasternak, Acta Cryst. 9 (1956) 341.