Paper

Atomic configuration around retinal in squid rhodopsin

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Abstract: Distances among retinal carbons and amino acid residues around a retinal molecule are calculated. We draw an image for chain−A and chain−B contact with squid retinal. Thus the area of each retinal's chain−A and chain−B is decided in an average sense that is not exact. We discuss about distances and determined areas of retinals.

Introduction

We have been studying the retinal in squid rhodopsin, whose configuration is changed between photo-absorbed states and non-absorbed states [1, 2], specifically the eleven cis-trans conformation change in squid retinal [1]. We found a small change of effective charge at the eleventh atom (C_{11}) out of retinal twenty carbons [1]. We analysed four sets of PDB data [3], 2Z73, 2ZIY, 3AYM, and 3AYN [4] for squid rhodopsin. The data included both A−chains and B−chains, except for the 2ZIY that only included the A−chain. Details are presented in reference [2]. We have previously shown contact maps of the rhodopsin A−chain and B−chain of 2Z73 [2]. We also showed contact maps between retinal and rhodopsin atoms [2]. The nearest atoms are tabulated in Table II and III of reference [2]. We only included calculations for the nearest atom to each retinal carbon [2].

In the present paper we give a summary of calculated results from each retinal carbon, namely nearest, second nearest, third nearest, so on. The results are somewhat complicated, so we show near atoms selected from pairs of retinal carbons. The carbon numbering scheme is illustrated in Fig. 1.

The calculated results cover the distance between each retinal carbon and atoms of the amino acids in squid rhodopsin. The next section (§2) is devoted to the results of distances between every retinal carbon and amino acid in squid rhodopsin. The chain−A distances show the ring's contact of retinal with rings of phenyalanine [5] and tryptophan [6], while the linear chain residues contact

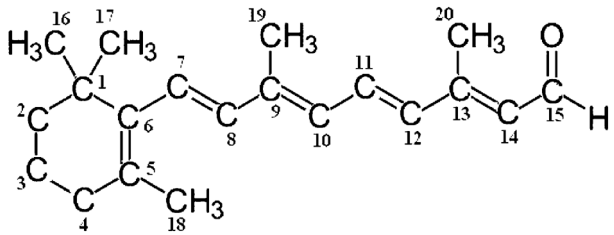

Fig. 1 Carbon numbering scheme of the retinal molecule

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with the retinal carbon ring of the retinal in chain–B. We also show the detailed structure of phenylalanine and tryptphan and present the numbering α, γ, δ, ε, η, ξ for the amino acid residues. Overall the analysis makes it clear that it is important to think about the ring structures of the amino acid residues. In scction 3 (§3), we consider the retinal area of chain–A and chain–B of the squid rhodopsin since the chain–B includes a linear chain form of amino acid residues and the chain–A contacts rings of amino acid residues. Section 4 (§4) is devoted to a discussion of the structure of squid retinal and rhodopsin.

2. Distance between retinal carbons and residue atoms of the rhodopsin molecule

We calculated distances between each retinal carbon and every atom of the rhodopsin molecule. By every atom of rhodopsin we refer to the residue molecules of each amino acid component. The names of organic compounds follow IUPAC rules. IUPAC stands for International Union of Pure and Applied Chemistry. As anyone knows, three kinds of amino acids have rings like six membered Benzene. The three amino acids with such residues are phenylalanine, tyrosine, and tryptophan. Tryptophan has combined six and five membered rings, alternatively the NH molecule can be viewed as bridging carbon $\delta 1$ and carbon $\varepsilon 2$. Looking at residues of amino acids around retinal carbon atoms one finds: phenylalanine (Phe), alanine (Ala), tryptophan (Trp), glycine (Gly), lysine (Lys), serine (Ser), methionine (Met), valine (Val), arginine (Arg), isoleucine (Ile), leucine (Leu), aspartic acid (Asp), asparagine (Asn), and cysteine (Cys). Thus we can see that phenylalanine and tryptophan have ring-form residues near retinal carbons. The other residues found around the retinal carbons have the form of linear chains. The structures of phenylalanine [5] and tryptophan [6] are illustrated in Fig. 2. The atomic numbering order of the linear residues follow IUPAC rules.

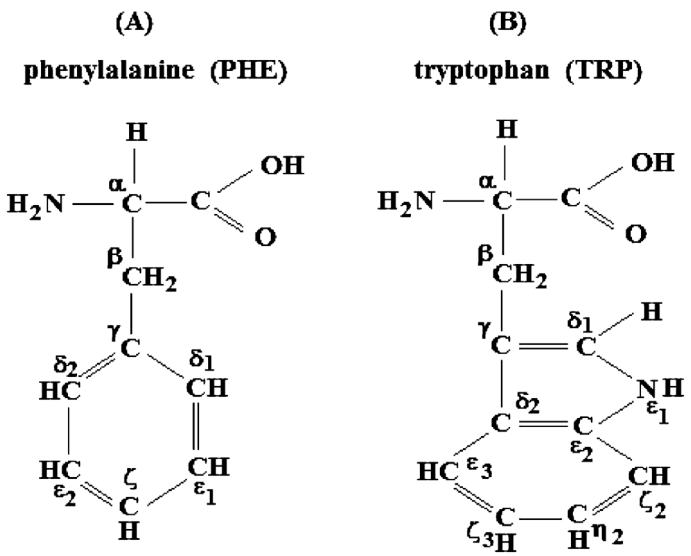

Fig. 2 Numbering order of phenylalanine and tryptophan

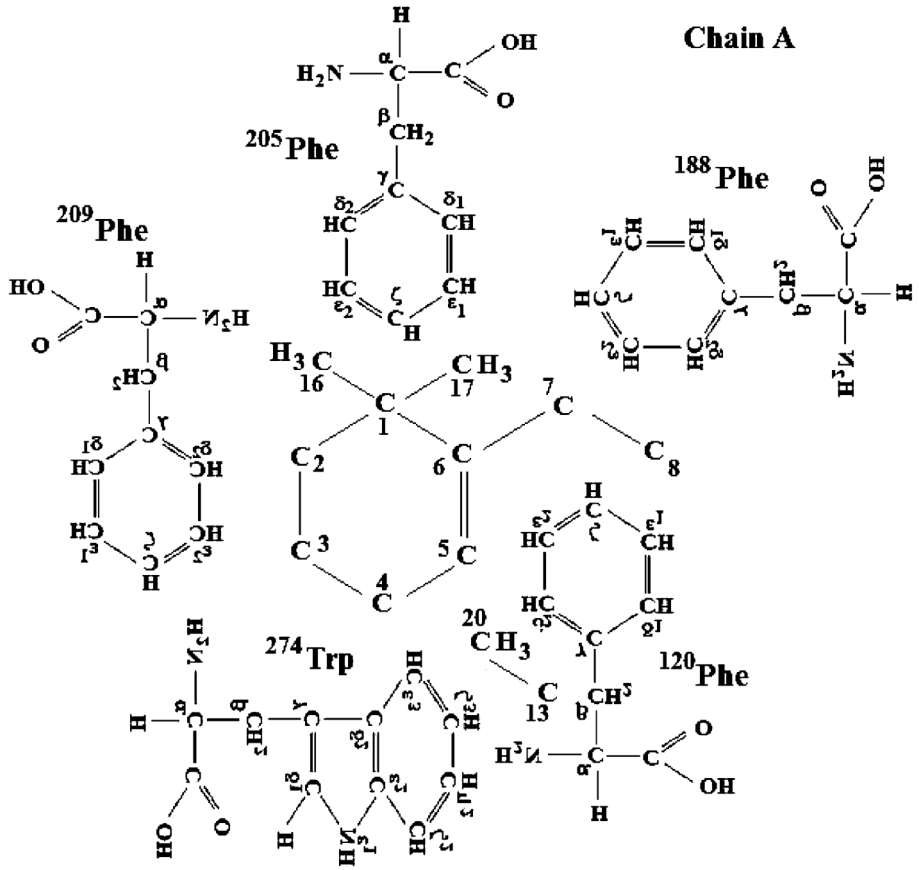

Fig. 3 Chain–A amino acid residues around retinal carbons (1–8, 16–17, 13–20)

In Fig. 3, we draw above residue rings of the rhodopsin A–chain that contact with the retinal ring (C^1 to C^6), and two methyl groups ($C^{16}H_3$ and $C^{17}H_3$). We also find linear chains of amino acid residues of the rhodopsin B–chain there. The results for rhodopsin B–chain are shown in Fig. 5. We show the second nearest atoms of amino acids from every retinal carbons in Fig. 4 (chain–A) and in Fig. 6 (chain–B). The retinal carbon-ring is formed by six carbons (C^1 to C^6). The carbon rings of the amino acid residues are variously turned in a 90 degree rotation, reversed up-to-down, and reversed left-to-right as seen from Fig. 3 (chain–A of squid rhodopsin). Fig. 4 is the figure form of the table of distances for the chain–A. The first column of Fig. 4 denotes retinal carbons C^1 to C^{20}. The carbon C^{20} has contacts the ξ–carbon of ^{274}Trp. This implies retinal is in its cis-conformation in chain–A.

The fourth column of Fig. 4 represents the distances, and the fifth column indicates the atoms contacting with the atom of every retinal carbon. The sixth column is the name of the amino acid, and the seventh column is the number of the amino acid. The last three decimals denote the coordinate (x, y, z) of each atom belonging to the amino acid. The nearest contact atoms are described in reference [2]. We therefore avoided the repetition and only show contact data for the second nearest atoms in Fig. 4 and Fig. 6. We can now understand the contact between amino acid

2Z73 Chain-A

Second nearest atoms of amino acid residure

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"C1 ",4.38449,4.39935,4.39935,"CE1","PHE",205,23.445,44.825,59.086
"C2 ",3.71352,3.89323,3.89323,"CG ","PHE",209,22.13,45.72,64.773
"C3 ",3.74743,3.82857,3.82857,"CD2","PHE",209,23.09,44.987,64.082
"C4 ",3.86994,4.01023,4.01023,"CB ","TRP",274,19.148,39.919,64.24
"C5 ",3.90139,3.93561,3.93561,"CE2","PHE",120,16.761,48.249,62.516
"C6 ",3.82844,4.37431,4.37431,"CE3","TRP",274,16.651,40.715,62.215
"C7 ",3.55551,3.72255,3.72255,"CZ ","PHE",120,16.152,48.904,61.426
"C8 ",3.85368,3.98794,3.98794,"CZ3","TRP",274,15.43,40.999,61.591
"C9 ",3.68237,3.68358,3.68358,"CE2","PHE",188,16.855,44.589,56.264
"C10",3.82936,3.9561,3.9561,"CD2","PHE",188,15.758,45.21,55.664
"C11",3.47337,3.52733,3.52733,"N  ","GLY",116,10.617,45.485,60.654
"C12",3.64904,3.92383,3.92383,"CA ","SER",187,11.873,42.945,53.991
"C13",3.74402,3.82694,3.82694,"OG ","SER",187,13.988,42.417,55.062
"C14",2.50797,3.27735,3.27735,"O  ","CYS",186,10.081,40.927,54.692
"C15",1.33932,2.43408,2.43408,"CE ","LYS",305,10.33,36.63,57.807
"C16",3.76403,3.86239,3.86239,"CG ","PHE",205,23.324,47.235,59.109
"C17",3.88743,3.95946,3.95946,"CZ ","PHE",188,18.153,44.929,55.871
"C18",3.83742,3.83814,3.83814,"CD2","PHE",120,16.164,48.3,63.783
"C19",3.48863,3.60473,3.60473,"CD2","PHE",188,15.758,45.21,55.664
"C20",3.66736,3.80268,3.80268,"CH2","TRP",274,14.222,40.928,62.305
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Fig. 4 Figure form of a table of distances of the chain–A of squid retinal.

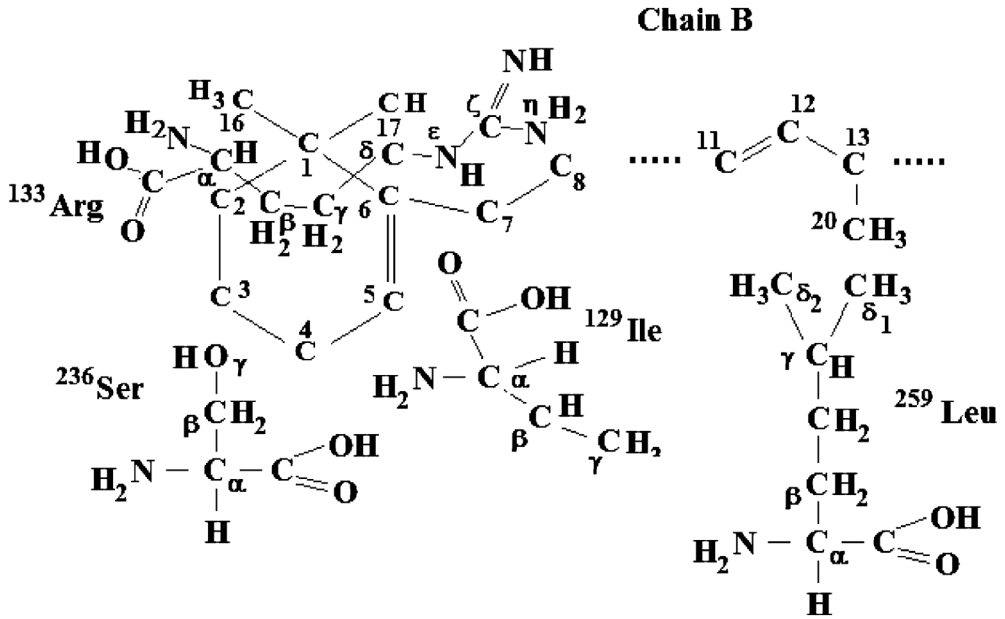

Fig. 5 Chain–B amino acid residues around retinal carbons (1–8, 11–13–20)

residues and retinal carbons. The illustration of contacts in Fig. 3 is somewhat simplified compared to Fig. 5, since the contact of the ring residues with the retinal carbon ring is given by comparison to each other. The residues in chain–B have the linear chain as shown in Fig. 5. We show the standard manner of numbering of the amino acid residues as shown in Fig. 5. This means the contact

2Z73 Chain-B

Second nearest atoms of amino acid residure

"C1 ",1.62435,1.76776,1.76776,"CG ","ARG",133,19,42.888,12.44
"C2 ",1.87465,2.05226,2.05226,"CG ","ARG",133,19,42.888,12.44
"C3 ",2.78134,3.06778,3.06778,"CG ","ARG",133,19,42.888,12.44
"C4 ",3.27346,3.46313,3.46313,"O ","ILE",129,22.599,43.883,10.167
"C5 ",2.67577,3.58565,3.58565,"CD ","ARG",133,20.04,41.816,12.775
"C6 ",2.19377,2.51471,2.51471,"CD ","ARG",133,20.04,41.816,12.775
"C7 ",2.61396,2.88428,2.88428,"CD ","ARG",133,20.04,41.816,12.775
"C8 ",3.00565,3.21444,3.21444,"OD1","ASP",132,24.645,42.324,14.041
"C9 ",2.7627,2.79238,2.79238,"OD1","ASP",132,24.645,42.324,14.041
"C10",3.09865,3.88444,3.88444,"ND2","ASN",70,25.371,35.061,13.721
"C11",2.6447,2.89291,2.89291,"CB ","ALA",69,26.584,39.81,13.789
"C12",1.59221,2.78671,2.78671,"CG ","ASN",70,26.417,34.32,14.049
"C13",2.24055,3.40409,3.40409,"CG ","ASN",70,26.417,34.32,14.049
"C14",2.39014,2.49375,2.49375,"NZ ","LYS",305,22.059,31.918,14.432
"C15",1.33191,1.39564,1.39564,"NE2","HIS",319,21.003,32.349,14.12
"C16",1.22544,1.44845,1.44845,"CA ","ARG",133,20.581,44.799,13.181
"C17",.672662,.944338,.944338,"CG ","ARG",133,19,42.888,12.44
"C18",3.49384,3.69029,3.69029,"CD2","PHE",120,25.133,43.022,7.996
"C19",1.76071,1.93222,1.93222,"OD1","ASP",132,24.645,42.324,14.041
"C20",2.87409,3.10508,3.10508,"CG ","LEU",259,19.432,36.799,15.456

Fig. 6 Figure form of a table for distances relative to the chain–B of squid retinal

distances of Fig. 5 are somewhat shorter than those in Fig. 3. The size of area of retinal is considered in section 3.

The figure form of a table is shown in Fig. 6. The order of columns is the same rule as Fig. 3. The first column refers to the retinal carbon numbering. The distances are depicted in the fourth column. The second column denotes previous distances, in other words the distance between each retinal carbon and nearest atom of the amino acids. The fourth column is greater than the first column. Almost all distances were considered to draw Fig. 3 and Fig. 5 even though we show data for only the second nearest atoms of A–chain and B–chain.

We also considered other distances among retinal carbons and amino acids, namely 2ZIY chain–A, 2AYM chain–A and chain–B, and 2AYN chain–A and chain–B. Using the sense of those distances we drew the Fig. 3 and Fig. 5.

3. Retinal areas of chain–A and chain–B

In this section, we consider the areas of retinal in chain–A and chain–B based on the distances among every retinal carbon and the atoms of the amino acids. We can find carbon C, oxygen O in the distance tables at the farther distance lengths between retinal carbon and residue atom. Given those results the area of retinal relative to chain–A or chain–B was reduced to Fig. 7 for chain–A, and to Fig. 8 for chain–B.

As seen from Fig. 7, the retinal area is large compared with the retinal area given by Fig. 8. The reason is carbon C^{20} contacts ^{274}Trp in chain–A, whereas C^{20} has no contact with ^{274}Trp in chain–B. The retinal takes the cis-conformation in Fig. 7. The contacts of Fig. 7 are the rings of phenylalanine or tryptophan. This fact yields more far contact between retinal carbons to the ring residues of the amino acids. The area of retinal shown in Fig. 8 is smaller because every residue of

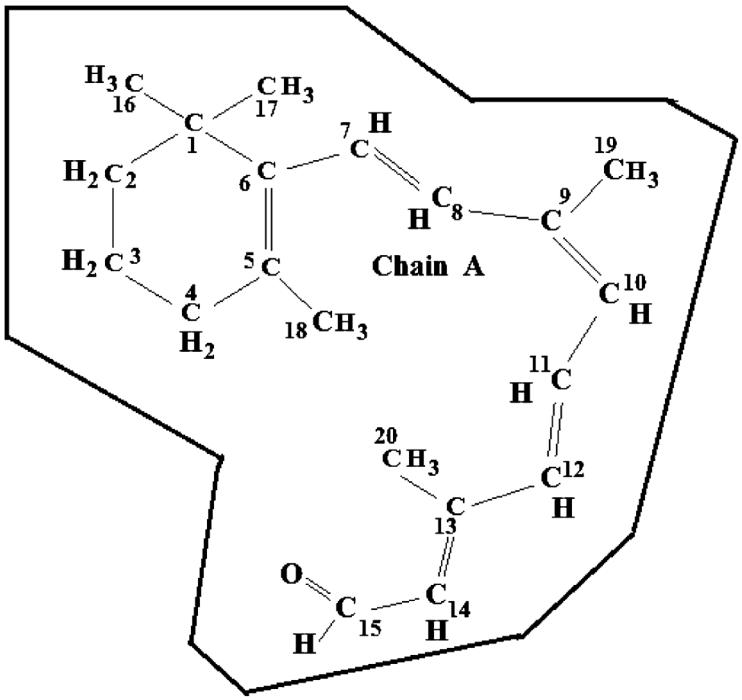

Fig. 7 The retinal area for chain–A

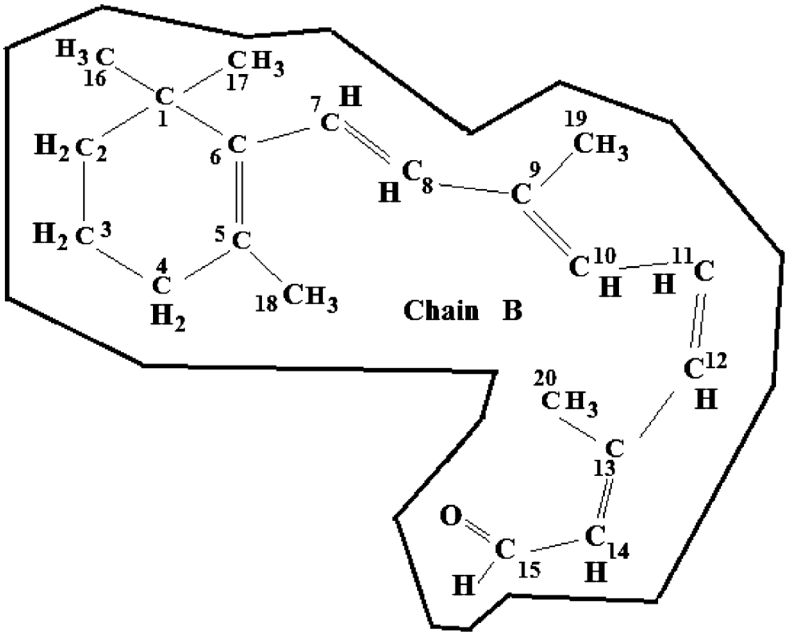

Fig. 8 The retinal area for chain–B

the amino acids contacts the chain. The retinal carbon C^{20} contacts with ^{259}Lue for 2Z73 and 3AYN of chain–B, and ^{187}Ser for 3AYM of chain–B [2]. These residues are linear chains.

The retinal conformations are similar for chain–A and chain–B in 2Z73. But the two sets of contacts are different to each other as indicated by Fig. 7 and Fig. 8. The conformations are the different to each other at the other PDB identification codes. The observed difference depends on the distance between retinal carbon C^{20} and atoms of the amino acid residues. The length is shorter than 0.1 nm between C^{17} and ^{133}Arg C_δ of amino acid residue in chain–B, whereas the length of the same distance is 0.387 nm for the C_ξ carbon of ^{205}Phe in chain–A: a four times larger distance between retinal carbon C^{17} and the atom of amino acid residue. As the results we now understand that the retinal area of the chain–B can become small compared with the chain–A depending upon whether tryptophan ring contact occurs or not.

4. Discussion

The retinal area in a rhodopsin is an important concept for understanding energy transfer from retinal conformation change to rhodopsin conformation change. We knew the conformation change occurred between the cis-conformation and trans-conformation. This conformation corresponds to the absorption of light energy, in other words, the electromagnetic field absorption is held in retinal carbon bonds. As seen in section3, we came to understand that retinal area size is changed because the contacting atoms form the ring or linear chain at the residue of amino acids.

The main reason for the observed differences is that either ring contact or linear chain contact was found. Conventional wisdom says that the conformation change occurs on the energy absorption of incoming electromagnetic waves from outside of retinal. This conformation change may give energy transfer at the interaction between retinal and rhodopsin as stated in previous communications [1,2]. We also showed the evidence for retinal carbon in section 3.

The next stage in considering energy transfer is to find what conformation change takes place in the rhodopsin molecule. We knew that retinal conformation change can be seen by comparing chain–A and chain–B of the squid retinal molecule, namely, the change of cis-conformation and trans-conformation. This change means that the energy transfer corresponds to a change of the contact amino acid residues with the rhodopsin molecule. Our progress on rhodopsin investigations is based on where the conformation change of molecules is happen.

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