spinodal decomposition. In order to reach a more conclusive interpretation, measurement of the lifetimes of the ordered regions in macroion solutions would be necessary. Furthermore, we have no information at the moment as to how large the ordered clusters are.[84]

(84) An approximate estimate of the dimensions of the ordered region is made as follows: since $2D_{expt}$ is roughly one-half of $2D_0$ under our experimental conditions (see Table I), the total volume of the ordered region must be at most one-eighth of the volume of the solution, provided that all the macroions are in the ordered region. If this condition is not fulfilled, the ordered region must occupy a smaller space.

Further intensive study is certainly necessary in order to clarify the essential characteristics of the structure of ionic solutions.

We wish to express our gratitude to our co-workers, whose names are referred to in the bibliography, for their collaboration. Also we have the pleasure of thanking Professor H. Kawai, Dr. T. Hashimoto, and Mr. M. Fujimura for making their X-ray equipment available to our solution study. We also acknowledge the valuable comments given by the reviewers and by Professors Sei Hachisu and Tsunenobu Yamamoto.

Structure of a Green Bacteriochlorophyll Protein

BRIAN W. MATTHEWS* and ROGER E. FENNA

Institute of Molecular Biology and Department of Physics, University of Oregon, Eugene, Oregon 97403

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The conversion of sunlight into chemical energy is essential for life as we know it, and the ability to effect this interconversion, albeit very inefficiently, must have occurred very early in evolution.

The light-gathering and energy-transducing systems in green plants and other photosynthetic organisms that we see today have evolved to become very efficient, but they are also complex. The remarkable efficiency of photosynthesis is now known to result from the participation of a variety of chemical components. While all the steps involved in the conversion of a quantum of light energy into chemical energy are not understood, the following outline of the process is well established.[1-3]

First, light energy is absorbed by an "antenna" system, consisting primarily of chlorophyll molecules (Figure 1) but also including pigments such as carotenoids and xanthophylls, which help ensure that the full spectrum of light is used. As we shall discuss in more detail below, there is now good evidence that the chlorophyll molecules, and probably the other pigments as well, are closely associated with protein.

The light energy collected by the antenna is rapidly transferred from one antenna chlorophyll to another until it reaches special chlorophyll molecules in a "reaction center" or "energy trap" where the first step in energy transduction, a charge separation, occurs. Typically, 300 antenna chlorophyll molecules might absorb light and feed it to one reaction center. In the purple photosynthetic bacteria it has been established that in the reaction center the initial charge separation consists of the transfer of an electron from a special pair of chlorophylls to an electron acceptor. The primary acceptor has recently been identified as a bacteriopheophytin molecule. Subsequently, the electrons are funneled through the biochemical electron-transport chain in which the potential energy generated by the charge separation is converted into energy-rich chemical bonds. In green plants and algae there are actually two distinct reaction centers and two electron-transport chains which combine to reduce carbon dioxide to carbohydrate and oxidize water to molecular oxygen, producing NADPH and ATP in the process.

By absorbing incident light with an antenna system, rather than with the reaction center chlorophyll itself, it is possible to ensure that the complex electron-transport systems are utilized efficiently. At normal light intensities, a single electron-transport chain can convert the excitation energy collected by several hundred chlorophyll molecules, and for this reason only 1% or less of the total chlorophyll in green plants and photosynthetic bacteria is found in the reaction centers, the remainder being in the antenna system.

Because of the role of chlorophyll in both the collection and trapping of light energy, there has been considerable interest in determining the arrangement of this ubiquitous pigment in photochemical systems. Although the chemical structures of the commonly occurring forms of chlorophyll have long been known, it has proven very difficult to obtain reliable information on the environment and organization of the pigment in vivo.

A major experimental difficulty arises from the fact that most of the light-harvesting and transducing components of all known photosynthetic organisms are incorporated within membranes within the cells and are very difficult to extract and isolate in an active form.

In the higher plants and algae, both the light-absorbing chlorophyll and the reaction centers are in-

Brian Matthews is Professor of Physics and Research Associate in the Institute of Molecular Biology, University of Oregon. Born in Australia in 1938, he received his undergraduate and graduate training at the University of Adelaide. Prior to going to Oregon, he was a member of staff of the MRC Laboratory of Molecular Biology, Cambridge, England, and spent 2 years at the National Institutes of Health, Bethesda, Md. He is the recipient of Sloan and Guggenheim Fellowships, and his research centers on the structure and function of macromolecules.

Roger Fenna, born in England in 1947, took his undergraduate degree at the University of Leeds and his doctorate with David Phillips at the University of Oxford. He joined Matthews' group in 1973 and was responsible for much of the crystallographic work which is the basis of this Account. He spent 2 years as a postdoctoral fellow at UCLA and has recently assumed the position of Assistant Professor of Biochemistry at the University of Miami School of Medicine.

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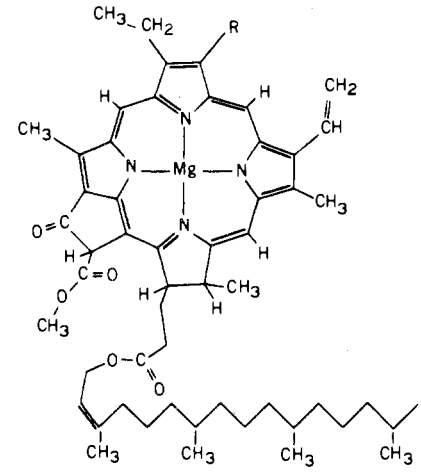
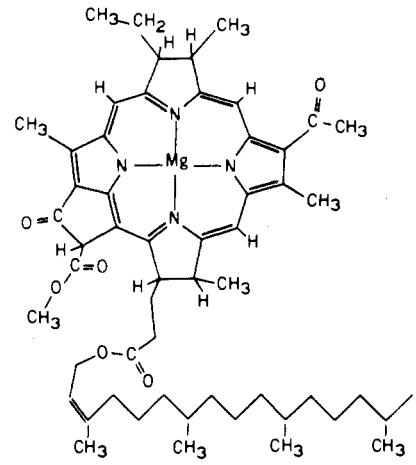
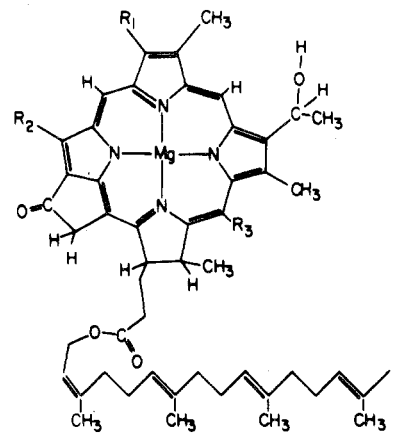


CHLOROPHYLL A (R=CH_3)
B (R=CHO)



BACTERIOCHLOROPHYLL A



CHLOROBIUM CHLOROPHYLL

Figure 1. The structures of chlorophyll *a*, chlorophyll *b*, bacteriochlorophyll *a*, and chlorobium chlorophyll. A number of forms of chlorobium chlorophyll (also called bacteriochlorophyll *c*) have been identified with different alkyl substituents R_1, R_2, and R_3.

corporated within stacked internal membranes (thylakoids) of the chloroplasts. Previous work by Thornber and colleagues[4] suggested that most of the chlorophyll occurs as a chlorophyll *a*/*b* protein consisting of 3 mol of Chl *a* and 3 mol of Chl *b* associated with a single polypeptide of molecular weight 25 000. In higher plants and algae the photochemical reaction centers appeared to be associated with a 110 000 molecular weight protein containing 14 molecules of chlorophyll, most of which were presumed to function as light harvesters.[4] Recently, however, Thornber and coworkers[5] have developed a milder technique for the dissociation of chloroplasts and have found four chlorophyll–protein complexes of molecular weights ranging from 60 000 to 250 000. It remains to be seen if these larger complexes are supramolecular associations of the previously characterized complexes.

In the green photosynthetic bacteria, the arrangement of the light-absorbing pigments is quite different. Here, the reaction centers are incorporated within the cytoplasmic membrane of the bacterium, but the bulk light-harvesting chlorophyll is incorporated within "chlorosomes" (previously called chlorophyll bodies or chlorobium vesicles), about 400 Å in diameter and 1400 Å long, lying inside the cytoplasmic membrane. The chlorosomes contain a number of different types of chlorophyll, collectively termed bacteriochlorophyll *c* or "chlorobium chlorophyll" (Figure 1). In addition to chlorobium chlorophyll, which constitutes about 95% of the total chlorophyll, and a small amount of chlorophyll in the reaction centers (less than 1%), the green bacteria contain a third chlorophyll component, which is, in fact, the principal subject of this report. The arrangement of the pigments within the chlorosome is discussed in the following section.

Bacteriochlorophyll-Protein

In 1962 John Olson showed that about 5% of the chlorophyll in green photosynthetic bacteria occurred in a water-soluble chlorophyll–protein complex which could be purified from aqueous extracts by standard chromatographic procedures.[6] Chemical and spectroscopic analysis confirmed that the complex contained only bacteriochlorophyll *a* and protein.[7,8] Furthermore, Olson was able to crystallize the chlorophyll protein as chunky hexagonal rods. The green bacterium was originally identified as *Chlorobium limicola*, but is now known to be *Prosthecochloris aestuarii*.[9] Fluorescence studies[10-12] suggested that the bacteriochlorophyll protein functions as an intermediary in the transfer of excitation energy from the antenna chlorophyll, which absorbs most strongly at about 750 nm, to the photochemical reaction center, whose absorption is greatest at 840 nm. The bacteriochlorophyll protein itself absorbs at 809 nm and is not photochemically active. These observations, together with conventional and

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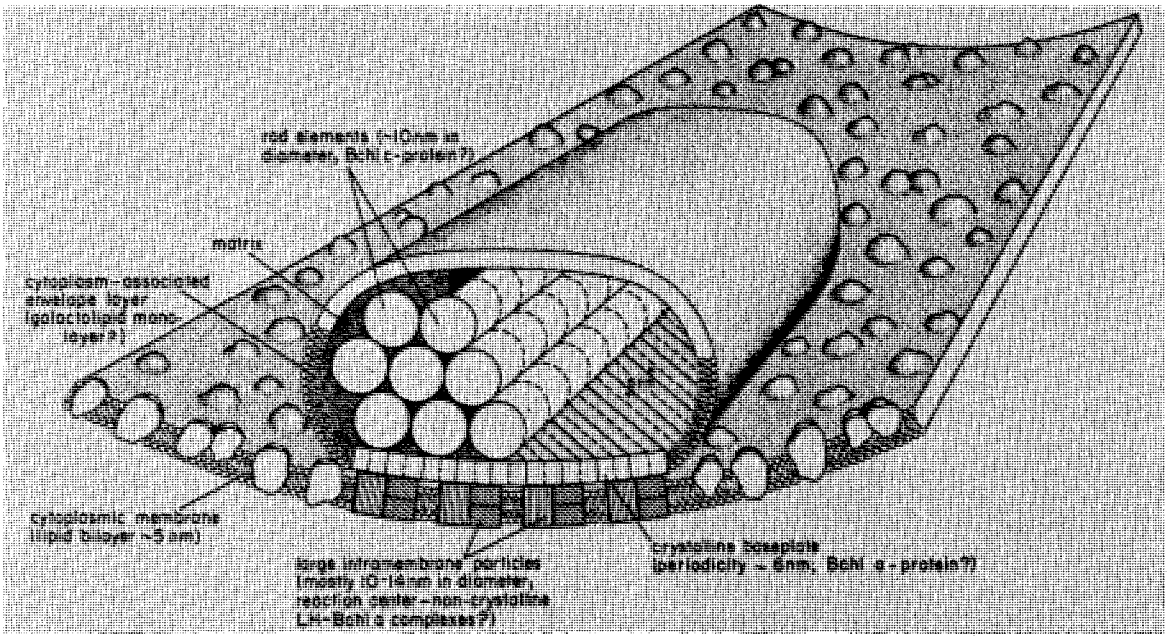

Figure 2. Model of the photosynthetic apparatus of the green photosynthetic bacterium, *Chlorobium limicola f. thiosulfatophilum*, showing one chlorosome and the abutting cytoplasmic membrane. Light energy is collected by the chlorobium chlorophylls (Bchl *c*) and funneled via the Bchl *a*-protein in the baseplate to the reaction centers in the cytoplasmic membrane. Cytochrome *c* and other electron-transfer components are not shown. Reprinted with permission from ref 14. Copyright 1980, Springer Verlag.

freeze–fracture electron microscopy, have recently led to the model shown in Figure 2 for the arrangement of the light-collecting chlorophyll pigments of *Chlorobium limicola f. thiosulfatophilum*.[13,14] The bacteriochlorophyll protein is thought to constitute a crystalline baseplate, periodically about 60 Å, interposed between rod elements of a presumed Bchl *c*-protein inside the chlorosome, and reaction centers embedded in the cytoplasmic membrane.

Because so little was known about the geometrical arrangement of chlorophyll in vivo and also because Olson's bacteriochlorophyll protein provided the only known example of a chlorophyll–protein available in crystalline form, it seemed worthwhile undertaking a detailed structure analysis of the protein, even though, being water soluble, its properties were somewhat atypical. Following an initial suggestion from Dr. Benno Schoenborn, we seriously began such an analysis in 1973, using protein generously provided by Dr. Olson.

The Molecule Is a Trimer

An unexpected result to emerge from the preliminary X-ray characterization of the bacteriochlorophyll–protein crystals was that the molecule is a trimer of three identical subunits arranged about a threefold symmetry axis.[15] The molecule had previously been assumed to be tetrameric. It is well-known that oligomeric proteins almost always contain an even number of subunits, presumably because of the propensity of subunits to associate about twofold axes.[16] Well-documented examples of oligomers with an odd number of equivalent subunits are rare.[17] To date, five examples of trimeric symmetry have been confirmed crystallographically, one being the Bchl–protein, the second an aldolase,[18] two others are C-phycocyanins,[19-21] and the fifth is a B-phycocrythrin.[21,22] It is remarkable that of these five cases, four are pigment-containing proteins which transfer light energy in different photosynthetic systems. It seems likely that threefold symmetry is advantageous for such accessory pigments, possibly because the pigments are then arranged at three different azimuthal angles and can accept energy over a wider range of angles than would be the case for a monomer or a dimer. Threefold symmetry is the minimum necessary for isotropic absorption of light incident normal to the symmetry plane.

There is good evidence that the threefold symmetry of the Bchl–protein is not an artifact of crystallization: (1) We were able to show that in a second crystal form, the protein also packs as trimers.[15] (2) The protein cannot be dissociated into monomers without separating the bacteriochlorophyll from the protein. (3) In the three-dimensional structure of the protein, as it is now known, the intersubunit contacts about the threefold axis are very extensive. Therefore there is every reason to believe that the Bchl–protein functions in vivo as a trimer. The molecular weight of this timer is estimated to be 150000, and, in agreement with the early chemical studies,[23] it is now known to contain 21 bacterio-

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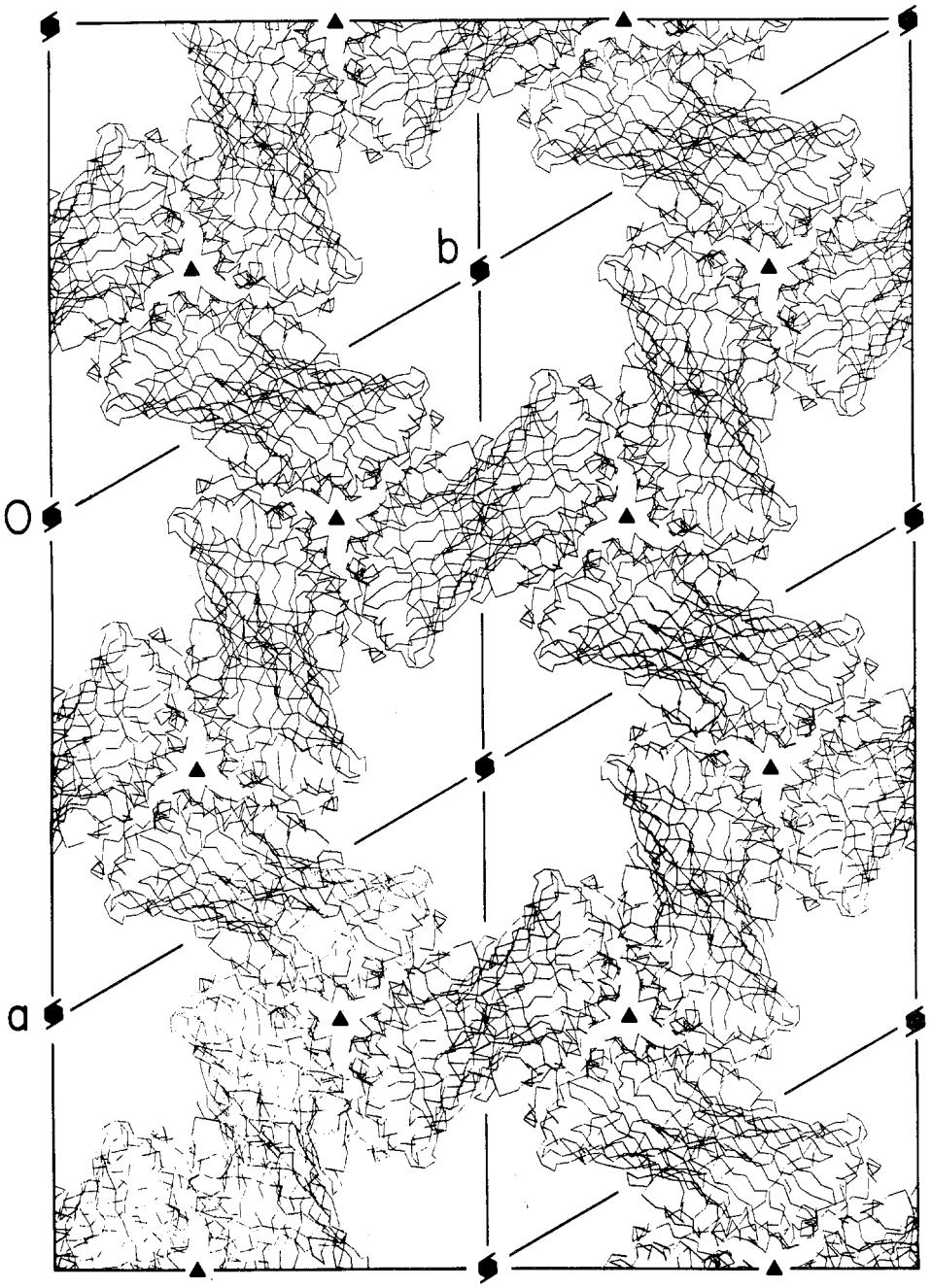

Figure 3. Packing of bacteriochlorophyll protein molecules in the hexagonal crystals used for the X-ray structure determination. The backbone of each subunit is projected down the hexagonal axis to show the characteristic solvent-filled channels which extend through the crystals.

chlorophyll molecules and no carbohydrate.

The overall packing of the Bchl–protein molecules in the crystals used for the X-ray structure determination, as viewed down the hexagonal axis, is shown in Figure 3. The figure shows only the projected polypeptide backbone of each subunit. The clustering of the subunits about the respective threefold axes results in a very open arrangement with about 30% of the crystal volume occupied by protein. There are large open channels, about 62 Å in diameter, extending through the crystal. These solvent-filled channels are a characteristic feature of the crystals and were clearly seen in previous electron micrographs of stained, sectioned crystals.[24-27]

Structure of the Protein

The three-dimensional structure of the Bchl–protein was determined by standard X-ray crystallographic procedures[28] using the isomorphous replacement method of phase determination. By using four heavy-atom substitutions, it was possible to obtain a reasonably accurate electron density map,[29-31] although the detail

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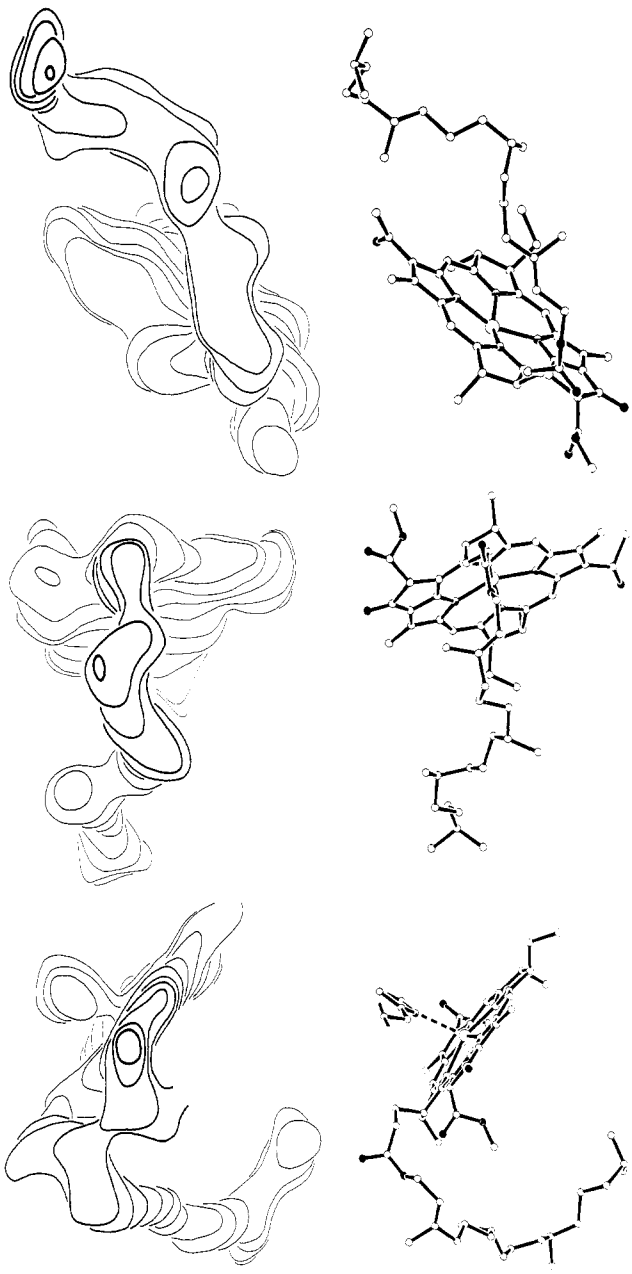

Figure 4. Electron density corresponding to three of the seven bacteriochlorophylls in the Bchl–protein. The contours (left) show a constant level of electron density enclosing one Bchl molecule, as seen on a series of sections, 0.73 Å apart, perpendicular to the crystallographic *z* axis. The corresponding molecular shape is shown on the right. Carbon atoms are drawn open, oxygen are solid, and nitrogen half-solid. The larger circle represents magnesium. Note the different arrangement of the phytyl tail relative to the chlorin head group in each of the three cases. (a) Bacteriochlorophyll 2; (b) bacteriochlorophyll 5; (c) bacteriochlorophyll 7 with a presumed imidazole acting as a ligand to the magnesium.

is limited by the resolution limit of 2.8 Å. At this resolution, individual atoms are not resolved, but the size and shape of the electron density of the different amino acid side chains give a clue to their chemical identity.

In the region of electron density corresponding to a single subunit of the Bchl–protein, density for seven bacteriochlorophylls can be clearly seen. Three of these are illustrated in Figure 4. The figure serves to indicate both the quality and the limitations of the present electron density map. There is no question that the respective portions of the electron density map shown in Figure 4, a–c, correspond to three bacteriochlorophyll molecules. Also the approximate orientation of each chromophore is clearly defined within about 5°. On the other hand, the detailed conformation of the individual ring substituents is often uncertain, and, in the absence of the amino acid sequence, the identity of most of the protein side chains, including those that interact with the chlorophylls, cannot be determined with certainty. From the electron density map it was possible to follow the apparent course of the protein backbone from one end to the other. This tracing seems reasonably unambiguous, but necessitates traversing several regions of very weak density on the surface of the molecule and must remain tentative pending determination of the amino acid sequence.

The overall arrangement of the protein backbone in the Bchl–protein trimer is shown in Figure 5. The most striking feature of the structure is the large wall of β sheet which consists of 15 polypeptide strands and extends from the front (as seen in Figure 5), around the side, and across the back of each subunit, curving in such a way that the front and back strands are approximately perpendicular to each other. In the region of subunit–subunit contact, the folding of the polypeptide chain is more complicated and includes several short α helices.

Enclosed within the protein shell of each subunit are seven bacteriochlorophyll *a* molecules, as illustrated in Figure 6. This figure provides a different view of the protein backbone. As can be seen, the overall structure is dominated by a large β sheet, the left and right extremities of which have been folded toward the front to enclose the seven chlorophylls, not unlike a taco or a Cornish pastie. As can be seen in Figure 6, the polypeptide chain extends from the left and right in large open loops to enclose the chlorophylls beneath. There is an apparent opening at the bottom of Figure 6 where bacteriochlorophylls 1 and 2 are not covered by protein, but in the trimer this opening is occluded by an adjacent subunit, so that none of the Bchls is exposed to the surrounding solvent.

Clearly, the role of the extended β sheet is to provide an efficient amphipathic layer shielding the hydrophobic Bchls from the aqueous environment. Although the amino acid sequence of the Bchl–protein is not known, it can be expected that in the extended β sheet there will be hydrophilic side chains on the outside alternating with hydrophobic ones on the inside.

Additional views of the Bchl–protein are shown in Figure 7a,b. These computer-drawn figures were generated by R. J. Feldmann using a novel interactive surface display system.[32] In these figures each amino acid residue is represented by a single sphere. The single subunit in Figure 7a is viewed from the "back" of Figure 6, i.e., from the outside of the Bchl *a*–protein. The extensive β-sheet layer covering the underlying bacteriochlorophyll core (shown in red) is clearly seen. Figure 7b shows the Bchl *a*–protein trimer, seen down the threefold axis (cf. Figure 5). The view shows the

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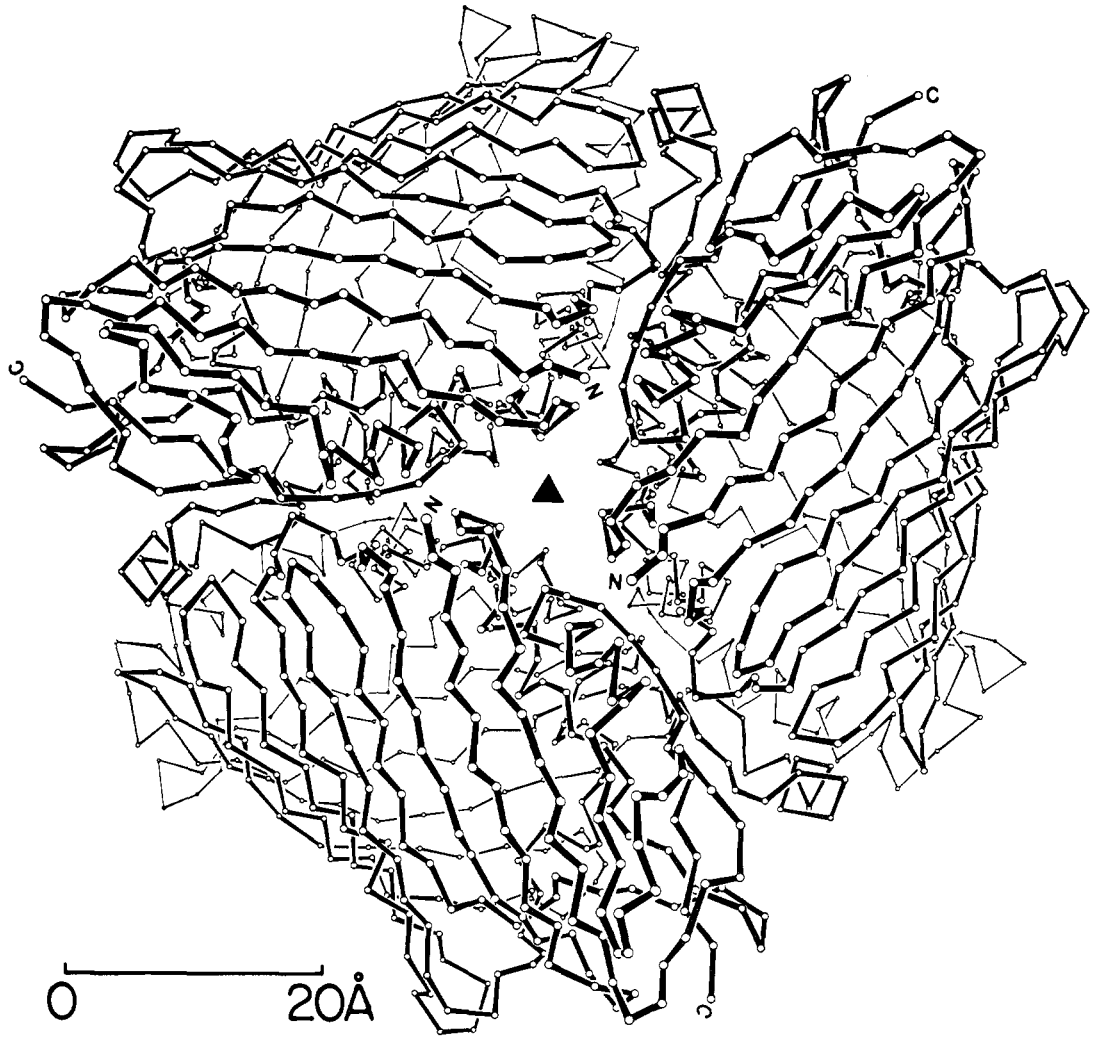

Figure 5. The bacteriochlorophyll protein viewed down the threefold symmetry axis. Only the backbone of the protein portion of the molecule is shown, with each α-carbon atom indicated by a circle; the chlorophylls have been omitted.

intimate contact between the three subunits and also shows how the β-sheet layer comprises much of the exterior of the Bchl–protein.

Bacteriochlorophyll Core

Each subunit of the Bchl–protein contains a core of seven bacteriochlorophyll *a* molecules enclosed within an envelope of protein. The electron density for three representative Bchls was shown in Figure 4a–c. As can be seen, the orientation of each Bchl, including both the planar head group and the hydrocarbon phytyl chain, is well defined. The electron density map shows clearly that each of the seven Bchls occupies a well-defined position, analogous to the side chains within a typical globular protein, and should not be compared with the disordered arrangement of lipids in bilayer.

The overall arrangement of the Bchls is shown in Figures 6 and 8. There are a number of "sideways" contacts between the ring substituents of adjacent rings, but in no case does any pair of rings overlap. There are extensive contacts between the Bchls and the surrounding protein and between the head groups and phytyl chains of the different Bchls. The seven phytyl chains make extensive van der Waals interactions with each other and tend to cluster together to form an inner hydrophobic core in the center of the subunit, which may well be a nucleus important in the folding of the molecule. There is no indication that one or more Bchls can be reversibly removed from the protein, and inspection of the molecules suggests that the folding process must be a cooperative one involving both the protein and the Bchls.

As can be seen in Figure 8, the phytyl chains are arranged in such a way that a hydrocarbon chain always extends across one face of each chlorin ring. Therefore, the central magnesium ion of each ring is screened from contact with solvent and/or protein on one side, but is free to accept a ligand on the other side. In fact, all seven magnesiums appear to be five-coordinated with the metal ion about 0.4 Å out of plane toward liganding group, as in the crystal structure of ethyl chlorophyllide *a*.[33] For Bchls 1, 3, 4, 6, and 7 the magnesium ligand appears to be a histidine side chain; for Bchl 5 the ligand seems to be a peptide oxygen of the protein backbone; and for Bchl 2 the ligand appears to be a water molecule. Such identifications must remain tentative until confirmed by the amino acid sequence.

The observed absorption and circular dichroism spectra of the bacteriochlorophyll protein provided early evidence that there were five or more bacteriochlorophylls clustered together with center-to-center distances of about 12–15 Å, as is observed.[34-36] On the

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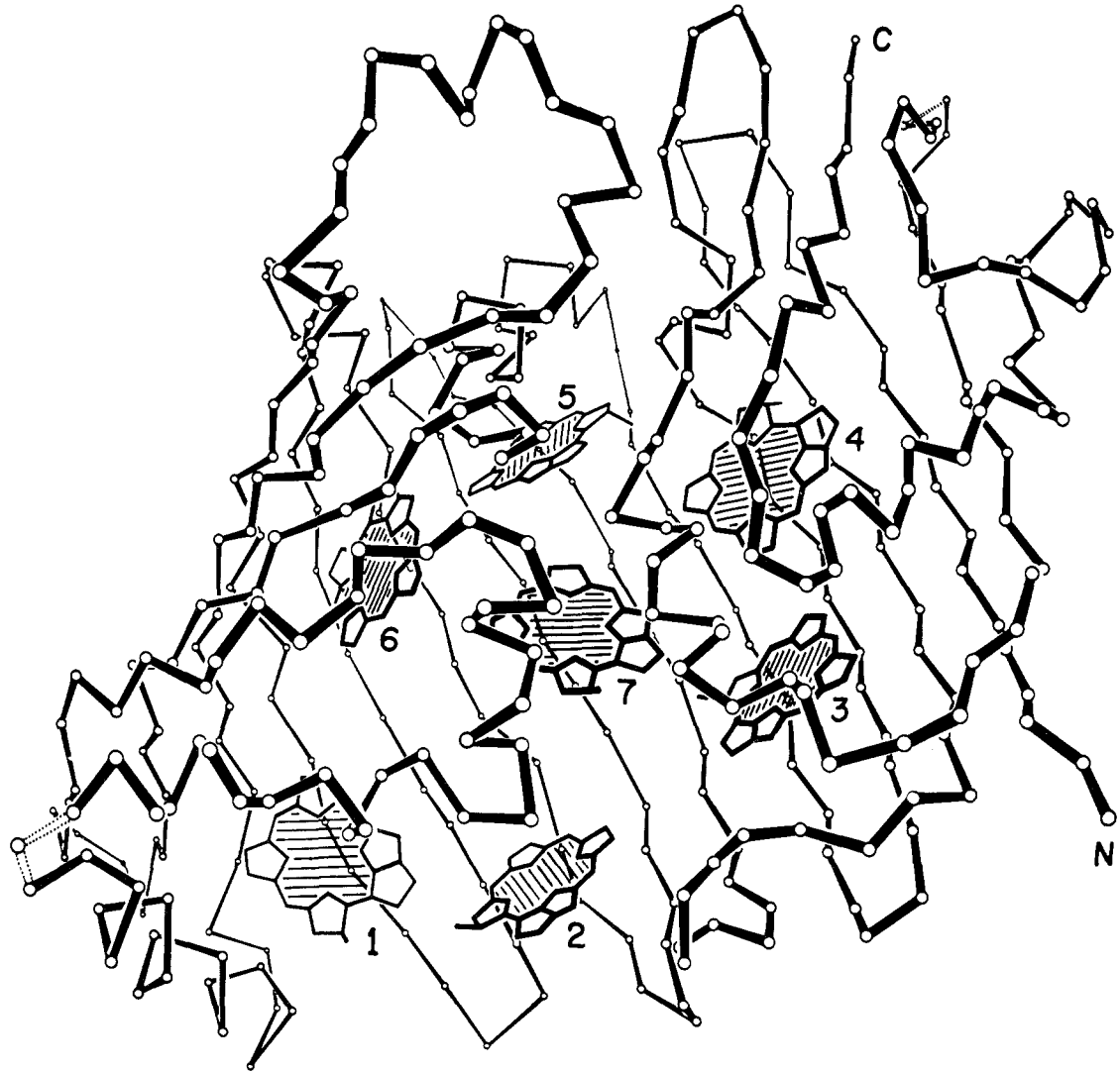

Figure 6. One subunit of the bacteriochlorophyll protein showing the seven bacteriochlorophylls enclosed within an envelope of protein. For clarity, the phytyl tails of each bacteriochlorophyll have been omitted. In this figure, the threefold symmetry axis extends from left to right across the front of the molecule.

other hand, attempts to calculate the spectra from the known X-ray coordinates have resulted, in general, in poor agreement between the observed and calculated spectra.[31,37] Further analysis of this problem is required, and, in the meantime, models of chromophore arrangements based on exciton calculations should be regarded with caution.

Organization of Chlorophyll in Vivo

Although it was once believed that chlorophyll in green plants and other photosynthetic organisms is arranged in extended sheetlike aggregates associated in some way or another with the lipid bilayers of the photosynthetic membrane, there is increasing evidence that this is not the case. Rather, it is now thought that chlorophyll is usually, if not always, intimately associated with protein.[4,5,29]

Several lines of evidence support this idea. For example, many components of photosynthetic membranes have been shown to have complex absorption and fluorescence spectra which revert to the simplified spectra of Chl *a*, Chl *b*, Bchl *a*, etc., on extraction with organic solvents. In many instances the wavelength maxima are appreciably red-shifted from those of the isolated pigments, although generally not so much as for crystals of the pigments. Also a number of protein–chlorophyll complexes have been isolated. These include not only the reaction center particles and components of the antenna system of photosynthetic bacteria[38-40] but also the major light-collecting component of green algae and higher plants.[4,5] Sauer[41,42] has incorporated the idea of chlorophyll–proteins in his "pebble-mosaic" model of photosynthetic membranes, an extension of the fluid-mosaic membrane model formulated by Singer and Nicolson.[43]

The determination of the structure of the Bchl–protein showed, for the first time, the details of chlo-

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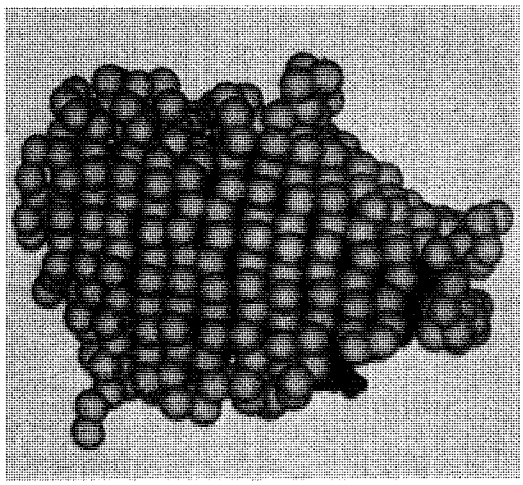
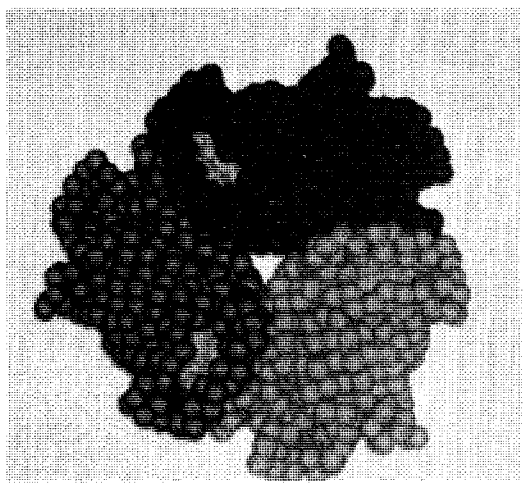


(a)



(b).

Figure 7. (a) Computer graphic representation of the structure of one subunit of the bacteriochlorophyll protein. Each amino acid residue is represented by a single yellow sphere, centered on the α-carbon position. The atoms of the chlorophyll core are shown in red. (b) View down the threefold symmetry axis of the chlorophyll protein, showing the three subunits in red, yellow, and blue. The chlorophyll core is shown in turquoise (figures provided by R. J. Feldmann).

rophyll arrangement as it can occur in nature and led us to suggest that the state of chlorophyll in vivo is universally determined by its association with protein.[29]

The Bchl–protein is membrane bound in vivo, but is atypical in being water soluble in vitro, whereas virtually all chlorophyll-containing components of photosynthetic systems are insoluble in aqueous solvents. Nevertheless, the Bchl–protein shields the chlorophyll molecules from the solvent by enclosing them within an envelope of protein. It is therefore reasonable to expect that other membrane-bound chlorophyll–proteins will also have their chlorophyll largely buried, with the enclosing protein shell protecting the chromophores from nonspecific interactions with the surrounding lipids in the membrane. In this way the specific orientation and environment of the chlorophylls will be preserved, notwithstanding structural changes and fluctuations of the lipids and other components of the photosynthetic membrane.

In order for photosynthesis to take place efficiently, light energy absorbed by the antenna chlorophyll must be rapidly transferred to the photochemical reaction center where the primary charge separation occurs. In the case of the bacteriochlorophyll protein, the threefold symmetry of the molecule may facilitate the formation of close-packed planar arrays of the molecules on the surface of the cytoplasmic membrane, with all molecules facing the same way.[27,31] In the trimer, the three disklike groups of seven bacteriochlorophylls form a funnel-shaped array not unlike the dish of a radio telescope. Possibly this geometrical shape facilitates the collection of energy from a wide range of azimuthal angles and its transfer to the reaction center.

Protein molecules appear to be of prime importance in specifying the orientations of the chlorophyll molecules and also in providing the desired environment for these chromophores. By having the individual chlorophylls associated with protein, it is easy to imagine how a requisite arrangement of these molecules for efficient energy transfer could be effected. Appropriate protein–chlorophyll and protein–protein interactions could be used to define the arrangement of the chromophores. Also, modification of the transition moments of individual chlorophyll molecules, which might be essential to the energy-transfer process, could be achieved either by generalized environmental effects or by specific chlorophyll–protein interactions. The special properties of the reaction center chlorophylls which enable charge separation to occur are most likely conferred by the combination of a unique protein environment and a spatial orientation directed by specific chlorophyll–protein and chlorophyll–chlorophyll actions.

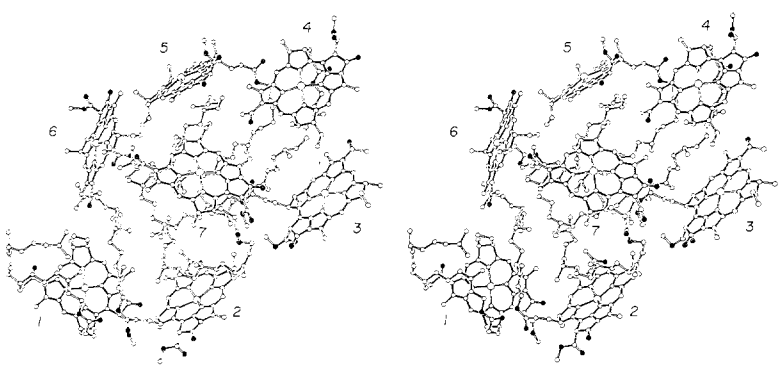


Figure 8. Stereoscopic drawing showing the seven bacteriochlorophylls which constitute the core of one subunit of the bacteriochlorophyll protein. The direction of view is the same as in Figure 6. Bonds between atoms in the chlorin head groups are drawn solid, while bonds to ring substituents, including the phytyl chains, are drawn open. Oxygen atoms are drawn solid and carbon atoms as open circles.

Concluding Remark

Thus, the bacteriochlorophyll–protein structure determination has permitted the first visualization of chlorophyll in a component of a photosynthetic unit. To some extent, the bacteriophyll–protein is atypical, but it is reasonable to expect that the general principles of chlorophyll arrangement and chlorophyll–protein association seen for this protein also apply to the organization of chlorophyll in general.

We are most grateful to Dr. John Olson for providing the bacteriochlorophyll protein for the X-ray structure analysis. Also, we thank Dr. Richard Feldmann for his help in providing Figure 7 and Dr. Andrew Staehelin for providing a copy of his manuscript in advance of publication. This work was supported in part by a grant from the National Science Foundation (PCM 77-19310).

Free-Radical Clocks[1]

DAVID GRILLER and KEITH U. INGOLD*

Division of Chemistry, National Research Council of Canada, Ottawa, Ontario, Canada K1A 0R6

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> "*Most of the methods for measuring the lapse of time have, I believe, been the contrivance of monks and religious recluses who, finding time hang heavy on their hands, were at some pains to see how they got rid of it.*"
>
> William Hazlitt, *Sketches and Essays* (1839)

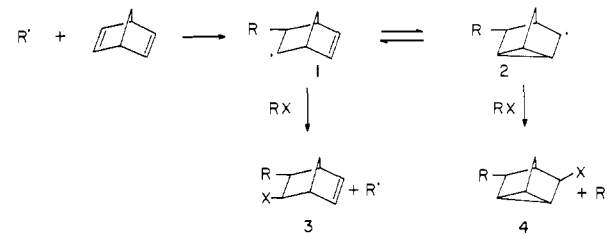
There is no completely general method for measuring the absolute rate constants of radical–molecule reactions.[2] The well-known "rotating sector" method[2,3] is restricted to radical-chain processes which can be initiated photochemically and which are terminated by radical–radical reactions. The chain must be fairly long (not less than five links), and this means that the radical–molecule propagation step(s) must be fairly rapid. Although this technique has proved valuable in kinetic studies of vinyl polymerization[2,4] and of autoxidation,[2,5] there are a great many interesting and important radical–molecule reactions which would be difficult or impossible to make the rate-controlling propagation step in a chain process. Of course, some of these reactions can be studied by flash photolysis, pulse radiolysis, and other special techniques,[2] but many cannot.

All these techniques of physical chemistry are unattractive to the organic chemist who would merely like to know the approximate rate of some new radical–molecule reaction because to use any one would require an inordinate investment of both his time and money. Organic chemists have, therefore, for many years used competing unimolecular radical reactions as qualitative timing devices to investigate the rates of radical–molecule reactions. The relevant information is obtained simply by product analysis.

The norbornenyl–nortricyclyl rearrangement provides a well-known illustration of this approach and has been the subject of numerous investigations.[6,7] The free-radical addition of RX to norbornadiene can be described by Scheme I. The composition of the products, i.e., the [3]/[4] ratio, depends upon whether the equilibrium between norbornenyl (**1**) and nortricyclyl (**2**) has been established. If RX is efficient in chain transfer

Brief biographical sketches of the authors appear on page 193 of this volume.

Scheme I



and/or is present in high concentrations, product **3** will be favored, whereas product **4** is normally predominant when **1** and **2** can reach equilibrium. Thus, the radical rearrangement acts as a timing device or *free-radical clock* and provides a method for examining the radical–molecule reaction. Indeed, any unimolecular radical reaction[8] can be used in this way.

The β scission of *tert*-butoxyl provides an even more simple *clock* which has been in use for over 30 years to measure the relative rates of its hydrogen atom abstractions from organic compounds in solution.[9] In the presence of a hydrogen donor, AH, the following competition will occur.

$$Me_3CO\cdot \xrightarrow{k_\beta} Me\cdot + Me_2CO$$
$$\xrightarrow[AH]{k^{AH}} A\cdot + Me_3COH$$

At low conversions, i.e., when the concentration of AH has not changed significantly, the ratio of the rate

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