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Melvin Calvin

October 22, 1958

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ABSTRACT

FROM MICROSTRUCTURE TO MACROSTRUCTURE AND FUNCTION IN THE PHOTOCHEMICAL APPARATUS*

Professor Melvin Calvin

Department of Chemistry and Radiation Laboratory, University of California, Berkeley

ABSTRACT

October 22, 1958

A discussion is presented of the macrostructure of the chloroplast insofar as it is known and knowable by means of microscopy (visible, ultraviolet and electron). This leads to a number of principles of structure to be found in the granum universally distributed throughout the plant kingdom. A chemical analysis of the constitution of these lamellar structures leads to a deduction of structural principles for such molecules as are found therein. The application of these structural principles to the visible structure of the lamella leads to a microstructure on a molecular level of these lamellae which, in turn, leads to a theory of their function.

FROM MICROSTRUCTURE TO MACROSTRUCTURE AND FUNCTION IN THE PHOTOCHEMICAL APPARATUS*

Professor Melvin Calvin

Department of Chemistry and Radiation Laboratory

University of California, Berkeley, California

October 22, 1958

When the symposium was described to me some months ago and it was suggested that I might participate in it on any subject that I chose, I selected the ambitious title which you find in your program. I felt that we really should know something about the microstructure and function of the photosynthetic apparatus. In fact, I still think we should (and wish we did) so I could tell you about it !

You have heard in the last two days (and you will hear more again tomorrow) something about both the function and the structure of the photosynthetic apparatus. You heard a whole series of discussions of the elements of structure which were common to all of the photosynthetic apparatus. You also heard a number of descriptions of the things of which the photosynthetic apparatus is capable, or is called upon to do. And I want to review just briefly what these things appear to be.

Clearly we expect the photosynthetic apparatus ultimately to reduce carbon dioxide and evolve oxygen from water to make carbohydrate, or whatever else the plant has to make. The essential feature that we have more or less

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agreed on that the photosynthetic apparatus must accomplish is the production, from water, of a reducing moiety of some sort and an oxidizing moiety of some sort; and that reducing entity, whatever it may be, with the cooperation of additional fragments having their origin in these two, reduces carbon dioxide to the carbohydrate level, primarily. The other entity which is to be produced by the photosynthetic apparatus will lead eventually, in the green plant, to molecular oxygen. In those organisms which do not produce molecular oxygen the oxidizing moiety, whatever it may be, will oxidize the electron donor characteristic of that particular organism.

The structures that we have seen described, both for the green plants and the lower organisms (the bacteria), contain in them the essential feature, the lamellae, which Dr. Sager[1] previously described and to which I will call to your attention again in a moment with another picture which you haven't yet seen. The enzymatic apparatus for the reduction of carbon dioxide seems to be relatively easily parted from what we will henceforth call the photosynthetic apparatus, and which performs the primary energy conversion.

Another function which is closely associated with the photosynthetic apparatus, in both the green plants and the lower organisms, is the phosphorylation function which also in the case of the green plants, as you already know, can be parted from the oxygen-producing function. In the case of the bacteria, so far at least the only test that we have for biological activity(the only test that has been described for biological activity) of a fragment less than the whole organism is the phosphorylation function and this is separable from the carbon dioxide reducing scheme as Dr. Bergeron[2] has described.

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1. R. Sager, Brookhaven National Laboratory Biology Conference No. 11 (1958), page _____.

2. J. Bergeron, Brookhaven National Laboratory Biology Conference No. 11 (1958), page _____.

I would like to eliminate discussion of the enzymatic functions which probably exist, either close to or outside of the discs described by Dr. Sager and the chromatophores, and limit our discussion to how the electromagnetic energy is converted into some sort of chemical potential.

The type of structure that performs this transformation you have seen in many pictures this morning, but I would like to show one more. Figure 1 is a picture, by Vatter, which was missing from the earlier discussions; this shows a nice clean ordered array of these lamellar discs which we have seen and heard described earlier. Now we have had a description of what must be accomplished and we have seen about as much of the structure of the apparatus that does it, as we really know, in this figure. There are many modifications and variations of this structure, but I think this picture represents the extent of what we really do know about the apparatus, at least insofar as it can be made visible.

For many years the problems associated with the conversion of electromagnetic energy into the first kind of chemical potential have been discussed by a variety of workers in the field. Notable among the discussions are Franck[3] and Gaffron[4] who defined the problem in very precise terms and recognized the need for the separation of the primary oxidant from the primary reductant and the problem of the lifetime which the initial excitation in a physical form must have in order for this transformation to take place in an efficient way. There must be a long life for the excitation and/or a large amount of acceptor for the conversion of this electromagnetic energy into chemical energy. A variety of other problems were associated with the fundamental question. We

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3. J. Franck, Daedalus, 86, 17 (1955).

4. H. Gaffron in Rhythmic and Synthetic Processes in Growth, Chapter VII, Ed. by D. Rudnick, Princeton University Press, Princeton, New Jersey (1957), p. 127.

Figure 1. Ultrastructure of chloroplasts

encountered the same problems when we began to think about how this sort of thing might be accomplished, but by the time we got to thinking about it we already had the beautiful ordered pictures of the photosynthetic apparatus which you have seen. We already had some model systems and a background of information about ordered arrays of various kinds for energy transformation, and it seemed to us that the search in statistical photochemistry in solution had not been fruitful in fulfilling the demand that would be required for a process such as this.

We therefore proposed to try to account both for the basic problems involved in this process and the structures that were visible to the electron microscopist almost to the molecular level in terms of a primary photophysical process rather than a photochemical one.[5,6] You have heard the term photophysics before in this conference, and the question was raised as to what was really the distinction between the two terms. It's a rather simple distinction. In a photophysical process the separation of the oxidant and the reductant takes place without the motion of nuclei, without actually having to separate atomic nuclei, one from the other (break or make bonds, in other words), whereas in a photochemical process nuclear separation does take place.

Model systems of such a transformation, namely, the solar converters had been known for many years (i.e., barrier layer cells and the like)[7] and more recently the junction cells in atomic lattices, such as silicon and germanium. We thought it might be possible to devise a similar apparatus using molecular

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5. E. Katz, in Photosynthesis in Plants, Chapter XV, Ed. by W. E. Loomis, and J. Franck, Iowa State College Press, Ames, Iowa (1949), p. 291.

6. D. F. Bradley and M. Calvin, Proc. Nat. Acad. Sci. 41, 563 (1955).

7. D. M. Chapin, C. S. Fuller and G. L. Pearson, Bell. Lab. Record, 33, 241 (1955).

lattices instead of atomic lattices. Fortunately, there had been some work done on the electrical properties of molecular lattices. I think one of the earliest observations of this sort was that of D. D. Eley at the University of Nottingham, who made the first definitive measurements of the semiconducting properties of a molecular substance, in a formal sense rather closely related to chlorophyll, namely, phthalocyanin.[8]

Since that time, research in the area of examination of the electrical properties of molecular crystals, both as semiconductors and as photoconductors, has made considerable progress, and I will try to say a few words about this as we go along.[9] However, the progress is not enough for me to be able to define for us absolutely the structural requirements that one would have to have in order to achieve the kind of photobattery which seems to be operating in the photosynthetic apparatus.[6]

With this background of thought, it seemed wise to us to seek some more direct experimental method of observing such a phenomenon, if it existed, in the photosynthetic apparatus itself. The most direct kind of measurement would be something of the sort which Dr. Arnold[10] described to you yesterday, namely, to pull out one of these lamellae and put electrodes on either side of the lamella and turn on the light to see what kind of potential is generated. Un-

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8. D. D. Eley, Nature, 162, 819 (1948).

9. D. C. Northrup and O. Simpson, Proc. Roy. Soc. A234, 124 (1956); H. Akamatu, H. Inokuchi and Y. Matsumaga, Bull. Chem. Soc. Japan, 29, 213 (1956); D. D. Eley, G. D. Parfitt, M. Perry and D. H. Taysum, Trans. Faraday Soc. 49,79 (1953); D. D. Eley and G. D. Parfitt, Trans. Faraday Soc. 51, 1529 (1955); Felmayer and Way, J. Electrochem. Soc. 105, 141 (1958).

10. W. Arnold and H. Maclay, Brookhaven National Laboratory Biology Conference No. 11 (1958), page ____; W. Arnold and H. K. Sherwood, Proc. Nat. Acad. Sci. 43, 105 (1957).

fortunately, these lamellae are too small for us to do this yet. I think it may be possible to devise ways of making direct measurements of photo-induced conduction, or I should say carriers, in such systems which one cannot trace between two contact electrodes, and Dr. Arnold has already made a step in this direction. We have devised other ways of handling the chloroplasts with a view to doing a similar thing, and perhaps one day we may have something to report on this.

However, there is another property associated with this type of lamellar structure which we thought we might be able to observe. When the light is turned on to a semiconducting system and the electrons are raised from their ground state into some conduction level, they can wander around independently of the positive charge (if they are in the conduction level, that is, by definition, what they are doing). Eventually these electrons find themselves in a position where there will be an acceptor for the electron at a potential slightly below that of the conduction band(for the electron), and similarly for the hole which finds itself at a place where it can be trapped at a somewhat lower energy than the conduction band itself. Thus, we would have separated, without moving nuclei, the reducing agent and the oxidizing agent from each other, provided the traps were themselves separated in space and if they were at a somewhat lower potential than the conduction band itself.[11] One would then have available whatever lifetime the trapped electrons and holes had, to use them for the oxidation of water or the reduction of some suitable hydrogen carrier at leisure; that is, leisure with respect to the lifetime of the original excited electronic molecular state, but this would still be a pretty fast reaction.

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11. G. Tollin, P. B. Sogo and M. Calvin, Ann. N. Y. Acad. Sci. (in press); G. Tollin, P. B. Sogo and M. Calvin, J. Chim. Phys. (France), in press.

With this idea in mind, we thought we could measure the rate at which electrons are produced and how many there were by the method of electron spin resonance. Those of you who are familiar with this type of experiment will have to bear with those who are not, because I want to say just a word about it.

When an upaired electron, which has a spin, is placed between the pole pieces of a magnet, the spinning electron acts like a little magnet and will orient itself with the field or against it; there are two possible orientations. The energy difference (ΔE) between these two orientations corresponds to a frequency (ν) and is dependent upon the strength of the magnetic field (H). All that is required, then, to detect such unpaired electrons is to place the sample

$$\Delta E = h\nu = g\beta H$$

(chloroplasts, chromatophores, bacteria, etc.) between the pole pieces of a magnet and pass radiation of a suitable wavelength through it. If the wavelength corresponds to the energy of the transition between the two orientations, then that energy will be absorbed; an ordinary absorption measurement is all that it is. Instead of varying the wavelength what we usually do is vary the strength of the magnetic field because the energy spread between the two orientations is dependent upon the strength of the magnetic field. We keep the wavelength constant, usually at about 3 cm; for this transition the field is of the order of about 3000 gauss. The energy involved is extremely little and one can detect very small numbers of the electrons by measuring the resonance absorption, that is, the proper field at which they absorb this set frequency. The machine we use can measure, under the best conditions, as few as 10^{11} electrons, but normally it isn't running under those conditions; it usually runs under somewhat poorer conditions.

We made these electron spin resonance measurements on a variety of organisms and fragments of organisms and we indeed saw an electron spin resonance when we

turned the photosynthetic light on. Figure 2 will show what the resonance looks like at room temperature for whole spinach chloroplasts. This resembles the resonance of an ordinary free radical which you can get from a wide variety of organic substances upon mild oxidation. The question was: was this also an ordinary organic free radical, obtained as a semiquinone either by reduction or oxidation of some component in the cell (or in the chloroplasts).[12] If this radical were the result of some ordinary chemical or enzymatic reactions which took place relatively rapidly at room temperature, one might expect that as one cools the sample down to -150° the reaction would not take place. However, when one does cool it down to -150°, one still gets a photo-induced signal in the chloroplasts; its behavior is somewhat different from what it is at 25°, but a signal is there, nevertheless. This speaks for the nonenzymatic character of the formation of this odd electron (this unpaired electron spin).[13]

One would like to know how efficient the light is in producing these unpaired electron spins. One of the questions that was raised, and with which we were concerned right from the beginning, was a possible rate-limiting step for photosynthesis in these regions of the process. We had reason to suppose, from such experiments as the early ones of Emerson and Arnold[14] that there might be some limiting process with a lifetime of the order of a few hundredths of a second, and we have seen this time limitation in a variety of other cases. We were interested to see how fast the spin resonance signal would rise, and we set the machine on a peak of the signal (first finding it with the light on, then turning the light off to allow the signal to disappear) and then we see how fast it comes in upon illumination. Figure 3 shows for

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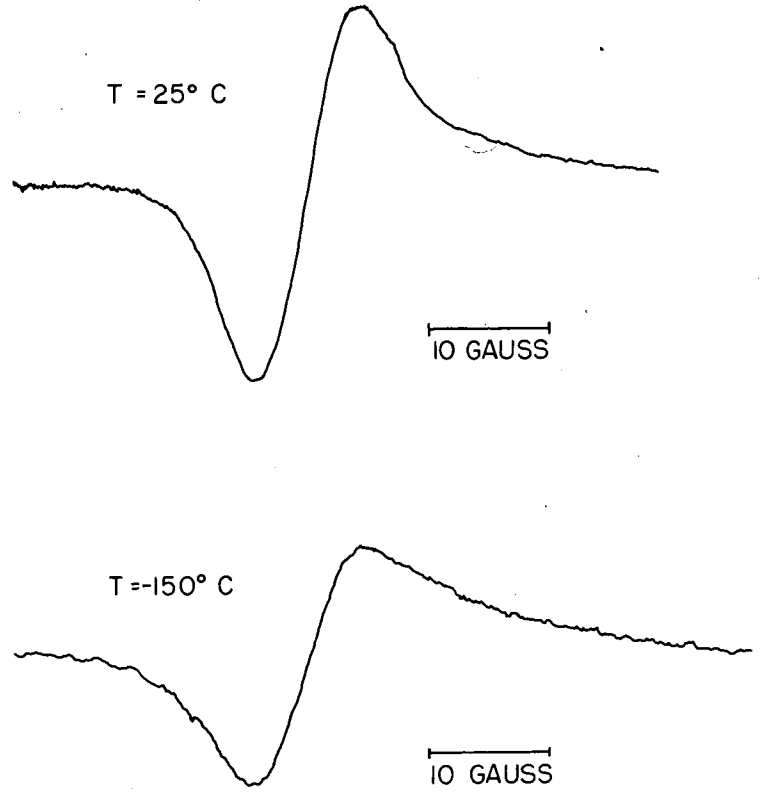
12. P. B. Sogo, M. R. Jost and M. Calvin, Radiation Res. (in press).

13. P. B. Sogo, N. G. Pon and M. Calvin, Proc. Nat. Acad. Sci. 43, 387 (1957).

14. R. Emerson and W. Arnold, J. Gen. Physiol. 15, 391 (1932); 16, 190 (1932).



LIGHT SIGNALS FROM WHOLE SPINACH CHLOROPLASTS

MU-14534

Figure 2. Spin resonance of whole spinach chloroplasts

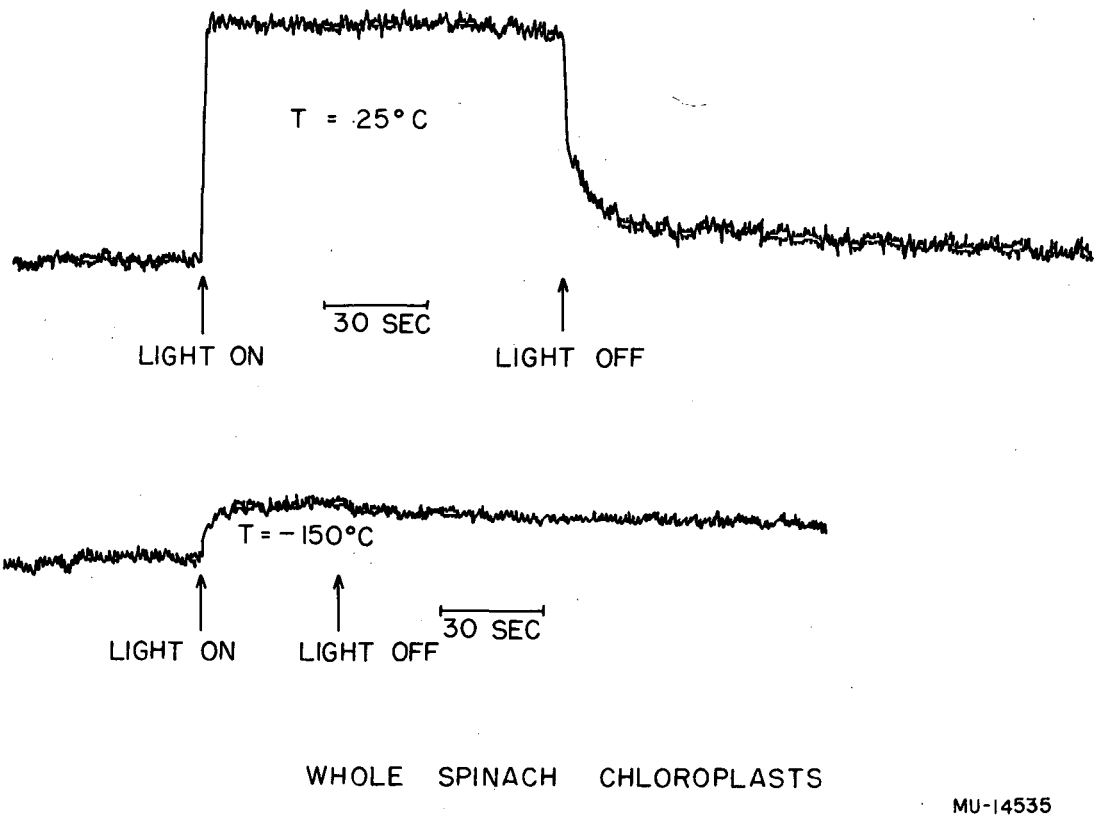


Figure 3. Growth and decay curves of whole spinach chloroplasts at T = 25°C

spinach chloroplasts that the signal rises at room temperature as fast as the machine can go. We have no way of measuring under present circumstances the limitation on the intrinsic rate of formation of these radicals at room temperature. The same thing is true at -150°. The height of the signal seems a bit smaller here (and indeed it is), although part of the change may be due to broadening. In both cases, however, the rate of rise was instrument-limited, not limited by the material. When we did measure the rate of rise under conditions when it was limited by the rate at which we put in quanta, we found that the rate of rise corresponded to a quantum yield of the order of unity for these unpaired spins at the low temperature. The number of unpaired spins with respect to the number of chlorophyll molecules was on the order of one in a hundred, or one in five hundred, depending upon the material used.[15]

We went to another type of organism. About the time we were doing this experiment I heard from Dr. R. C. Fuller about his chromatophores from the Chromatium. So we asked him for a sample of his chromatophores from the Chromatium (which he kindly sent us (it must have been a year ago). We stored the sample in the deepfreeze for six months. (We didn't do this on purpose, but for reasons which I am sure all of you who ever had to work in the laboratory are fully aware of: the machine wasn't working and we had to get it going again). We finally got the machine going again (a new one was built, in fact) and we put Dr. Fuller's chromatophores into the machine. Sure enough, they gave very nice signals, better than the green material, in fact. Then we put in whole Rhodospirillum rubrum cells, without breaking them up. We put the whole cells in because they are easier to handle than the chromatophores and we got pretty much the same kind of results, although with the refined equipment I expect that we will be able to see the difference between chromatophores and

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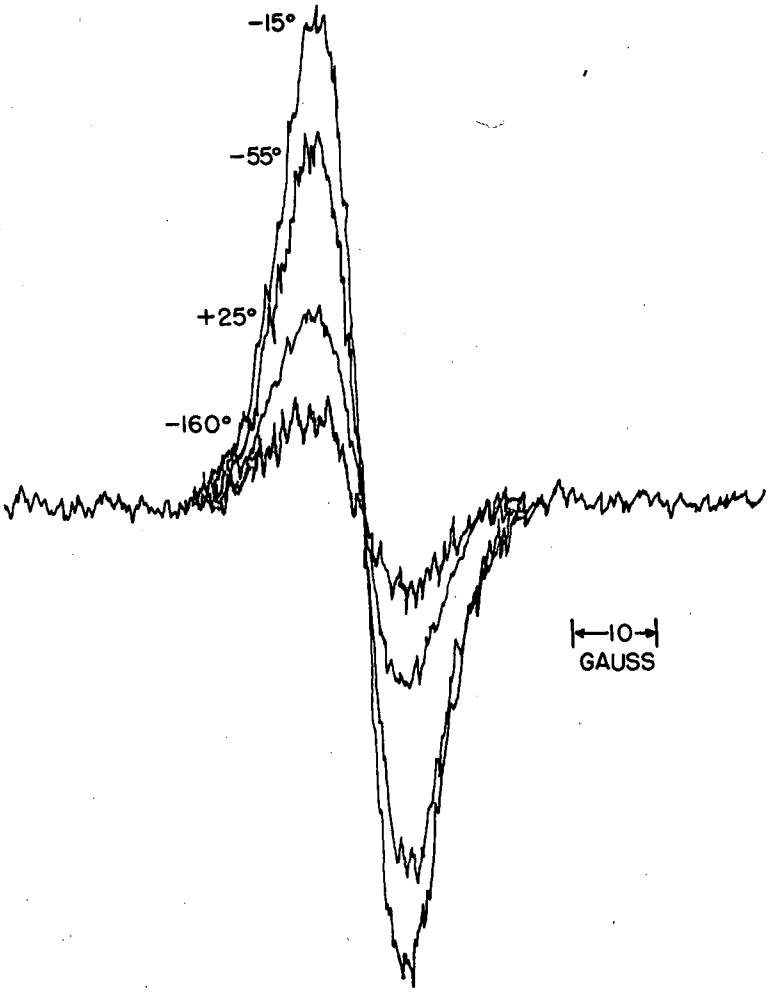
15. P. B. Sogo and M. Calvin, unpublished results from this laboratory.

whole cells when the proper experiments were done.

At the moment, I want to report to you only that the general pattern of behavior of the chromatophores and of the Rhodospirillum rubrum (which I am going to describe to you now) is about the same, to the degree of resolution that I can discuss today. Figure 4 will show the signals that one gets from Rhodospirillum. Notice that at room temperature (the third signal down) the signal was actually smaller than it is at -15° or -55°. At -160° it is smaller than it is at any of the other three temperatures. One can take the distance between the top and bottom of this peak as a measure of the number of unpaired electrons in steady-state equilibrium with the light on (the light is on all the time here). The next experiment was again a growth and decay experiment with the Rhodospirillum and the results are shown in Figure 5. Notice that both the rise time and the decay time at -160° are as fast as the machine can follow. As we warm the material up to -55°, you see a somewhat different type of curve. There is a very fast rise time, followed by a slower one; then (after 30 seconds) we turn the light off and there is a fast fall, followed by a slower one. As we warm the material up a little more (to -15°) there is a still bigger fast rise (pretty near saturation) and when we turn it off, there is only a very small, rapid fall. When we get up to 25°, we get a curve which looks very much like the very low temperature one (-160°); it both goes up and drops very rapidly and there seems to be no long-life signal.

The way this information was interpreted was as follows. At the very lowest temperature we were making and seeing conduction electrons which had extremely short lifetimes. As we warmed the sample up, there was a possibility for these conduction electrons to find their way into traps. In this case (the Rhodospirillum) there appears to be a small temperature coefficient for the conversion of the conduction electrons into the trap electrons. The



ESR SIGNALS FROM *RHODOSPIRILLUM RUBRUM*
5 MINUTES CONTINUOUS ILLUMINATION

MU-15137

Figure 4. ESR signals from Rhodospirillum rubrum five minutes continuous illumination.

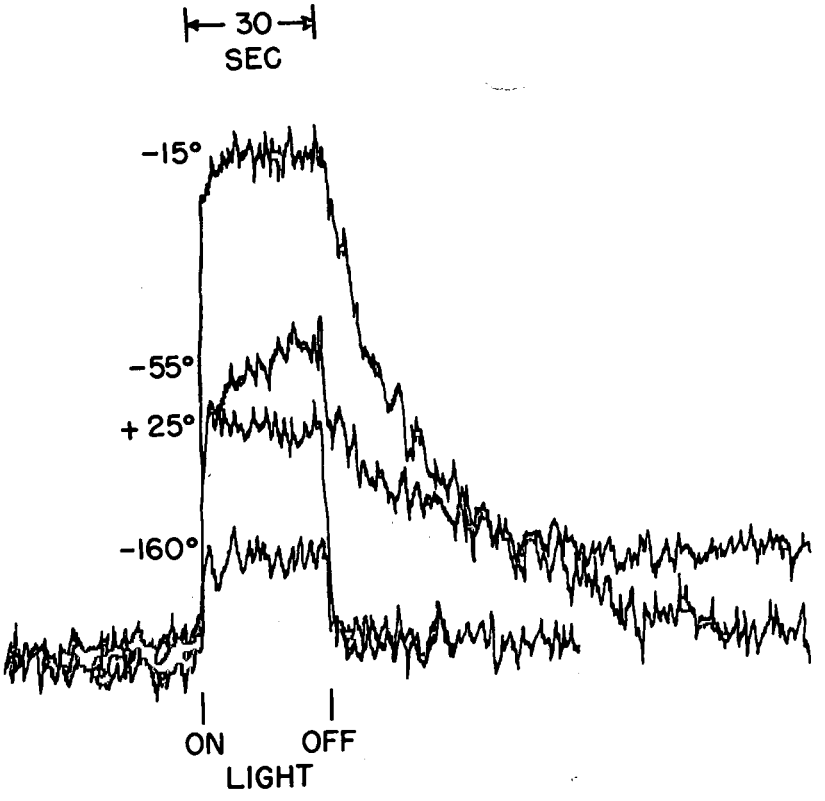


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Figure 5. Rise and Decay of ESR Signals from Rhodospirillum rubrum.

conduction electrons disappear easily and the trapped electrons more slowly, at -55°. At -15° we go even further into the traps and no conduction electrons were visible then; they were going on beyond the conduction band into the next stage (into the trap) and beyond that into enzymatic reactions, possibly of free radical nature. And, finally, at +25°, no slow reactions remain; all the reactions are fast reactions and these almost certainly are enzymatic reactions.

This is described diagrammatically in Figure 6. The chlorophyll goes first to its excited state; the excited state wanders around as an exciton until it finds a point of ionization leading to the electron and hole, which can move separately. The electron and holes find their way into the traps, where they can survive for relatively long periods of time. The trapped holes (positive charges or oxidants) can take an electron away from water (or some equivalent molecule) to form chemical radicals which lead eventually to oxygen, while the trapped electrons(reductant) are handed on to suitable acceptors leading through chemical radicals to the more stable reducing agents used for the ultimate reduction of carbon dioxide.

All we had to do, you see, in order to account for this sequence is to recognize that as we go from left to right (in Figure 6) there is an increasing temperature coefficient for each of the steps, and as we warm the material up we go further along in this sequence in a given period of time. We could diagram this in other ways, and Figure 7[11] indicates one of the alternatives, similar to that of Dr. Arnold. The ground state of chlorophyll is broadened out because of interaction and the excited state is broadened still more. The triplet state band is relatively narrow; the electrons, after ionization, go into the conduction band where they are separated into traps (they drop into electron and hole traps). These electrons can then be picked up by suitable carriers and handed down to pyridine nucleotides, etc. for quinone re-

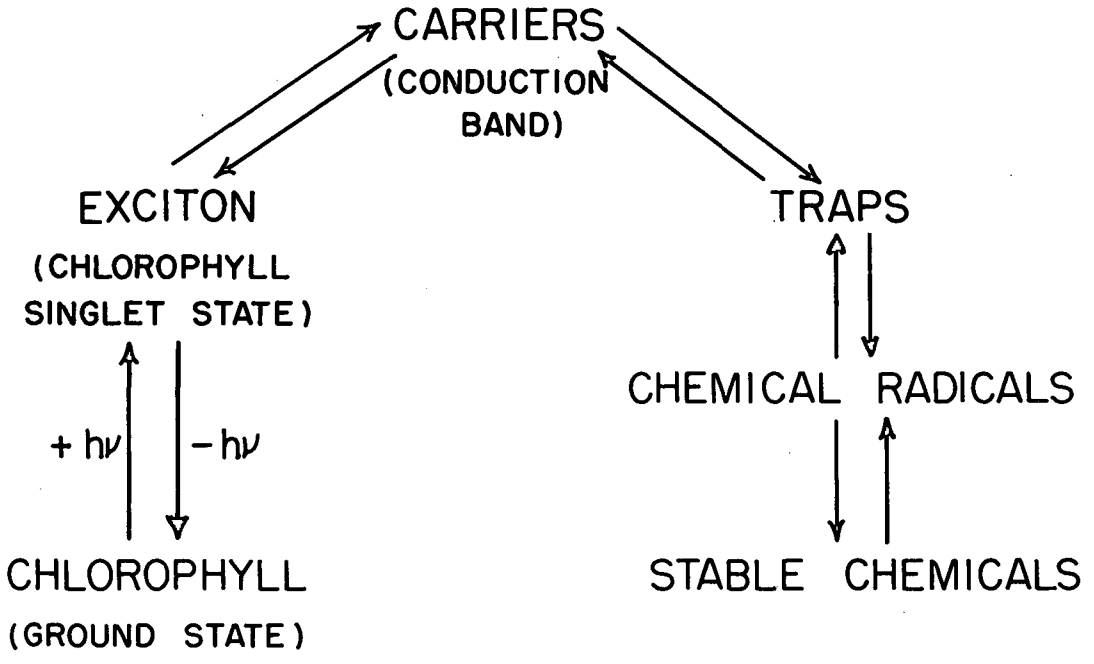
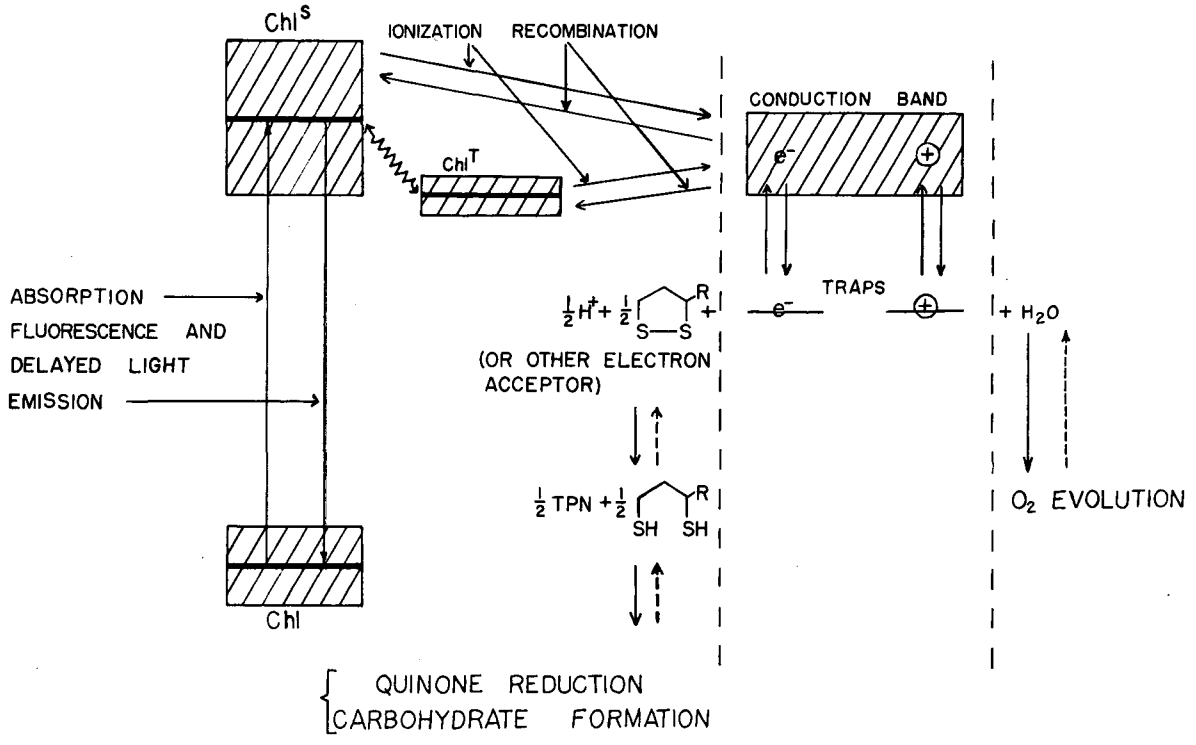


Figure 6. Hypothetical Scheme for light-energy Utilization on Chloroplasts.



PROPOSED SCHEME FOR VARIOUS PHOTOCHEMICAL PROCESSES IN PHOTOSYNTHESIS

MU-14256-C

Figure 7. Proposed scheme for various photochemical processes in photosynthesis.

duction and carbohydrate formation, and the hole on the other side we don't know very much about. Presumably the cytochromes are involved in this process as well as perhaps also the carotenoids, but we really don't know.

It should be mentioned at this point that the possibility of direct photodissociation to produce chemical radicals as the first photochemical act has been considered.[16,17] It was considered unlikely in the case of the green material (which was observed first) because the spin signals appeared just as rapidly at -170° as they did at 25°C. But it may be argued that there is precedent in chemistry for the direct photoformation of radicals even at this low temperature because of the high energies localized in the absorption of even a red quantum, which should lead to the separation of radicals so that they might be observed.[18] But if this were the case, then they should be stable, once formed, and separated at the low temperature, a situation for which there is also ample chemical precedent. While the signal induced in the green material is stable at low temperatures, that induced in purple bacteria is not. It decays as fast as the instrument can follow it at -160°. Furthermore, the photo-induced signals in both the red and green structured elements are insensitive to the presence of oxygen at both room temperature and low temperatures in contrast to the photo-induced signals in the alcohol extracts of these particles (chlorophyll-carotenoid-lipid structures) which are due primarily

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16. H. Linschitz and S. A. Weissman, Arch. Biochem. and Biophys. 67, 491 (1957).

17. A. A. Krasnovskii, J. Chim. Phys. (France), in press.

18. J. A. Baltrop, P. M. Hayes and M. Calvin, J. Am. Chem. Soc. 76, 4348 (1954).

to chemical radicals of various types and which are not even formed at the low temperatures. It seems reasonable to suppose that the initial processes in both organisms are similar, the difference being that the illumination of the green preparations leads to relatively more deeply trapped electrons and holes.[11]

Returning to the basic plan shown in Figure 7, the next stage in our exploration is to see if there is any possible way of accounting for such a system as this and account for it within the framework of the electron microscope structures which we saw this morning. Here I want to introduce a basic notion. It seems to me that it isn't necessary to assume that the whole form of the lamellar structure is built on templates; it may be so, but we have no evidence for this. I would rather seek to find ways of building this structure out of the molecules of which we know it must be composed (we are on the edge, now, of seeing the molecules as a result of the molecular properties themselves). In order to do this we would like to examine some of the basic principles of molecular int eraction(aside from electrostatic ones introduced by the presence of charges) as they have been developed in recent years (and, for that matter, a long time ago for some of the simpler types).

When molecules find themselves in solution, they will (as you heard earlier yesterday) take up configurations of the lowest energy. This leads to crystallization when the number of molecules in the solution exceeds a certain minimum value characteristic of those particular molecules. Such molecular interaction described in terms of crystallization can be extended to the kinds of molecule we find must be present in these lamellar systems. There are really three basic kinds of molecules present that we can describe unequivocally. There may be others that we can't describe as yet. These basic kinds of molecules are the proteins, the lipids, the chlorophyll and, presumably, the carotenoid when it is there; these are the basic kinds of molecules with which we

are going to try and build the lamellar structure.

Let us have a look at the specificity of molecular interaction, both on the micro level and on the macromolecular level, and, finally, discuss the kind of structures to which these interactions may lead. In seeking examples of such specific molecular interactions I was impressed by some work which really has not much to do with lamellar structure but which does have something to do with molecular interaction and specificity, and I would like to take a moment to describe it to you. As you know, it is possible to make polyadenylic acid from the mononucleotide and a suitable enzyme. This material, when dissolved, in a medium of proper pH and ion strength, and examined by the usual methods of macromolecular chemistry, shows itself to be a random coil. Similarly, one can make polyuridylic acid in the same way; put it in a corresponding solution of the same ion strength and the same pH and it will also be a random coil[19].

If we mix these two solutions(the solution of polyadenylic acid and the solution of polyuridylic acid) a very interesting thing happens. A rather specific interaction between these two solutions takes place and instead of being random coils we find that they become a stiff double helix, in which the adenine and uridine rings form hydrogen bonds with each other between each of the coils to give rigid, rod-like structure(Figure 8). Here is a very specific and powerful interaction leading to a marked change in the behavior of the solution and, in fact, it may lead (and I think under certain suitable circumstances could be made to lead) to visible structures in solution, because this kind of helix under the right conditions can form crystals.

This leads us to the next example. In fact, such a thing has been done with the protein components. For example, we can make a synthetic polypetide of molecular weight of about 100,000 which is called polybenzylglutamate.

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19. G. Felsenfeld, and A. Rich, Biochim. et Biophys. Acta, 26, 457 (1957).

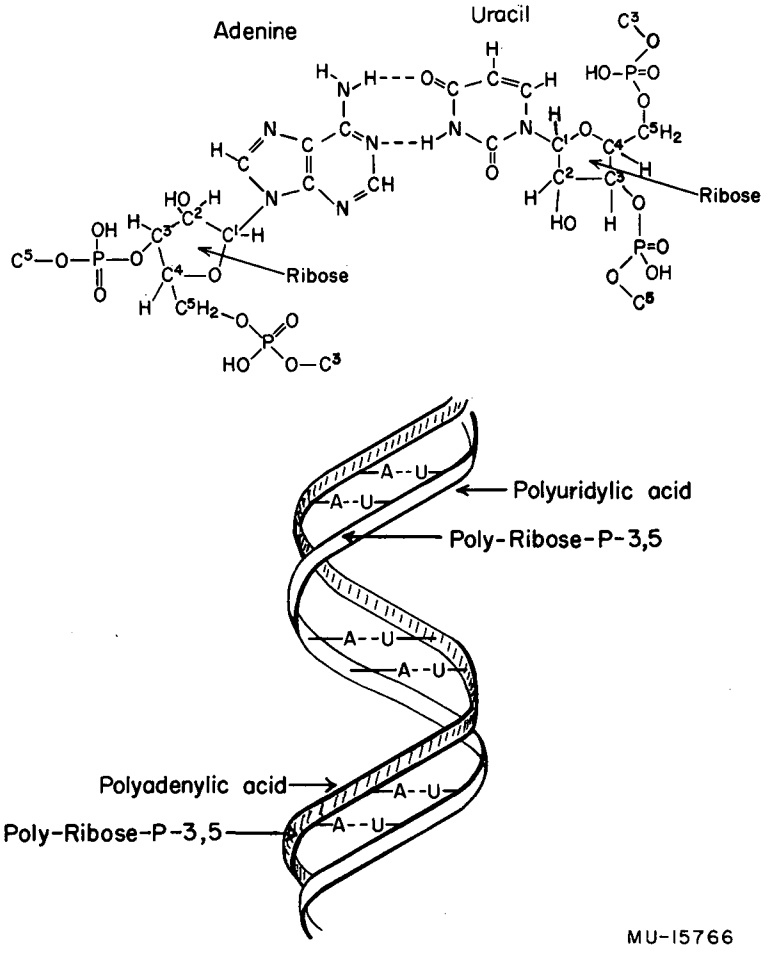

Figure 8. Polyadenylic acid-polyuridylic acid coupled helices

This material, in solution by itself, forms a nice alpha-helix because of the possibility of internal hydrogen bonds which it has (Figure 9). If one makes a concentrated solution of this alpha-helix, polybenzylglutamate (equimolar D and L), in a suitable solvent under the right conditions, at first it looks isotropic (no structure visible). If you let the solution stand in a small capillary tube or between two plates, it takes on a banded structure, showing gradients of refractivity (Figure 10). This effect has been interpreted in terms of the interaction between the alpha-helices.[20]

It became immediately evident that when such regular helices pack they first tend to line up with their long axes parallel and adjacent, thus giving the greatest energy lowering because of the greater van der Waals interaction between the molecules;[21] but because the spirals are regular (all the amino acids in each molecule have the same configuration) they will pack somewhat better if the axes of neighboring molecules are inclined to each other at an angle related to the pitch of the molecular helix. This leads to the formation of a macrohelix made of large numbers of individual alpha-helices. These macrohelices will aggregate in an ordered fashion, giving rise to the visible regular fluctuations in refractive index seen in Figure 10. Thus you can see that such visible structures can readily be produced out of materials resembling, in some measure at least, natural materials and whose molecular structure we know, i. e., we know exactly what the structures are of poly-

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20. C. Robinson and J. C. Ward, Nature, 180, 1183 (1957).

21. W. T. Simpson and D. L. Peterson, J. Chem. Phys. 26, 588 (1957).

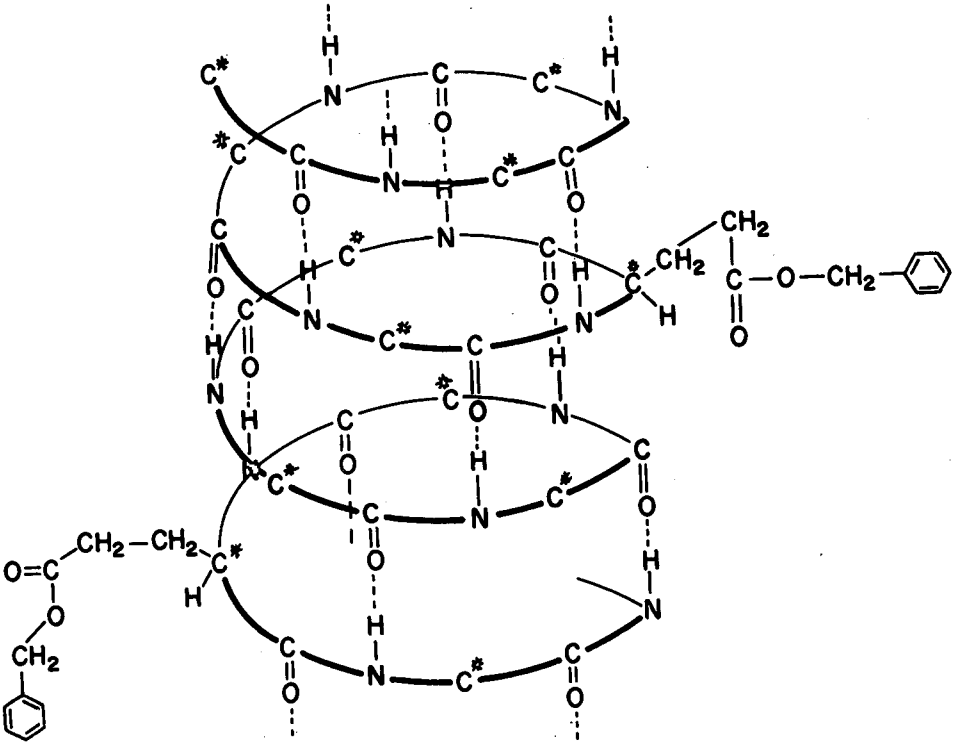

Figure 9. Polybenzylglutamate --alpha-helix

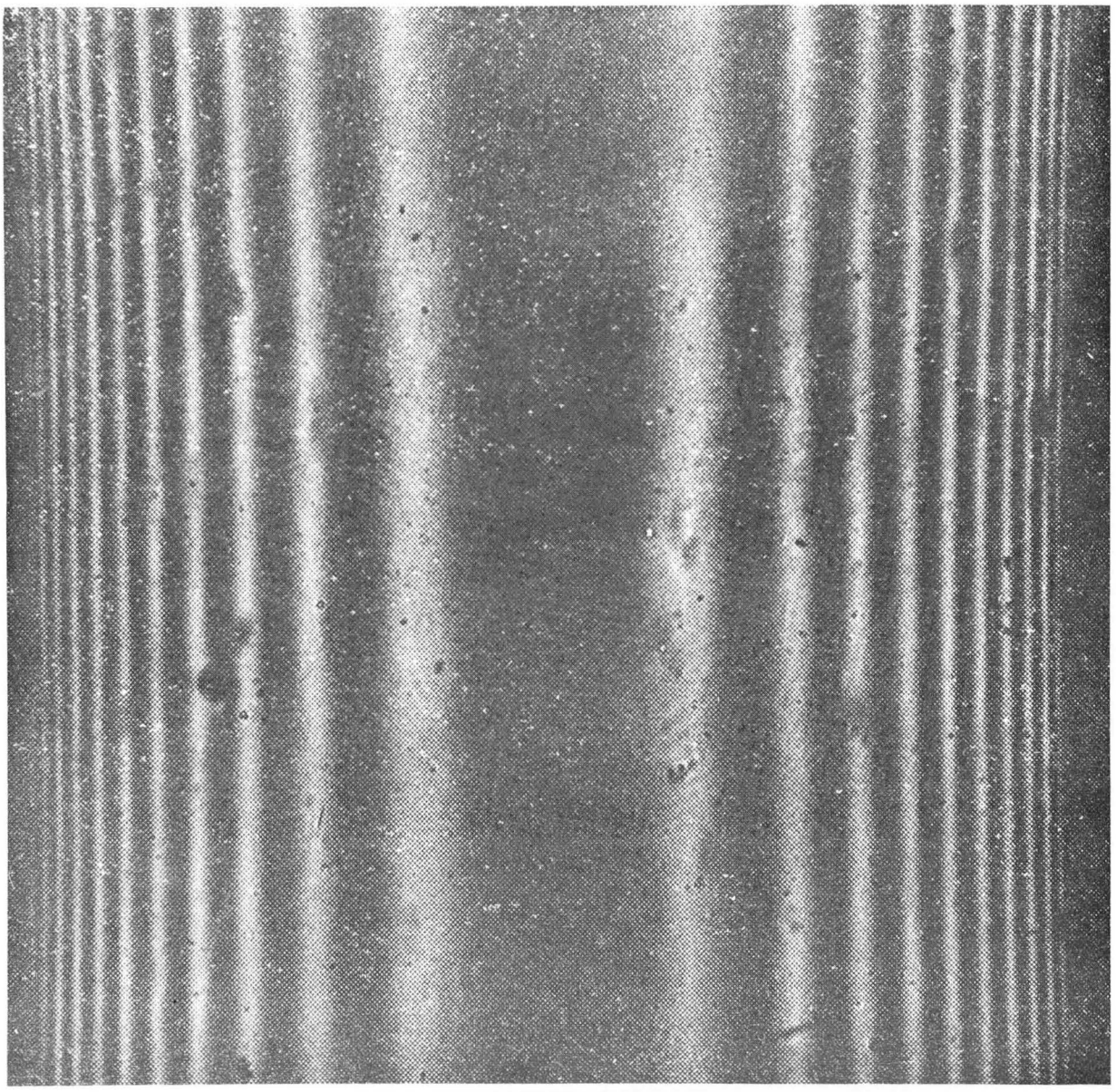

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Figure 10. Banded structure of polybenzylglutamate

The single liquid crystal of the racemic mixture of D and L polymers seen between crossed polarizers (diameter of capillary, 1.05 mm)[20]

adenylic acid and we know the structure of polybenzylglutamate.

The next example which may be considered as representative of the lipid group also shows a remarkable and specific interaction with itself and with similar molecules. If propylene is polymerized with a suitable catalyst, one can get what has been called an isotactic polymer, that is, a polymer in which consecutive configurations of the alternate potentially asymmetric carbon atoms (when the two ends are not the same) are identical (Figure 11). This isotactic polymer crystallizes very easily to form very high melting crystallites because these methyl groups are all arranged in a helix, all pointing in the same direction, and they can pack very well with each other. If one makes a random polymer out of propylene(a random one without this isotactic character, i. e., atactic) one does not get this kind of high, melting, dense, very closely packed polymer (Figure 11). This is a very specific kind of interaction, the degree depending upon the nature of this side chain.[22] The reason I picked polypropylene as an example is that it bears a slight resemblance to phytol.

Now let us come to the last of the group of molecules which we know is required for the formation of the lamella, even the very slightest one. This molecule is chlorophyll; this is our favorite subject for obvious reasons. Unfortunately, the crystal structure of chlorophyll itself is not yet completely worked out, although a suggestion for the structure of crystals of methyl chlorophyllides has been made.[23] So I am going to call your attention to two aspects of the structure of chlorophyll and then go on to see what we can make of it, using principles of structure which we might be able to devise.

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22. G. Natta, Stereospecific Catalysis and Stereoisomeric Polymers. Speech at opening conference, XVI Congress of Pure and Applied Chemistry, Paris, France, July 1957.

23. E. A. Hanson, Rec. trav. bot. Neerl. 36, 183 (1939).

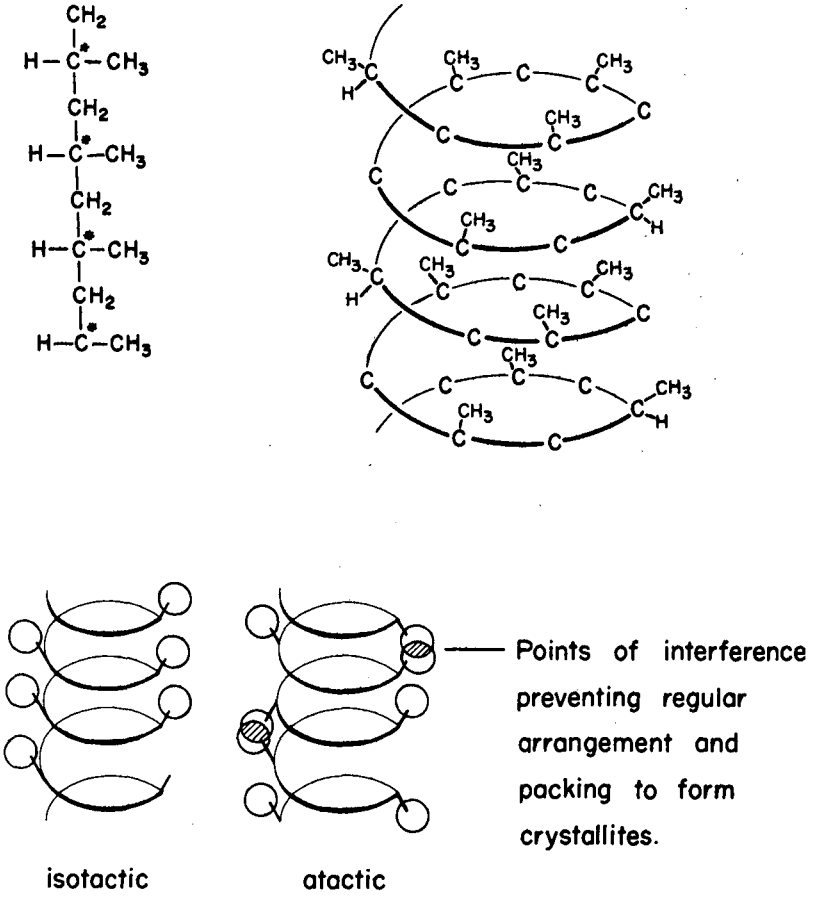

Figure 11. Isotactic polymer (polypropylene)

You all know that chlorophyll is made up of an aromatic plane, about 3.5 to 4.0 Å thick, to which is attached the phytol chain with four methyl groups sticking out. First of all, I want to focus your attention on the fact that chlorophyll is a big aromatic plane (Figure 12). You have heard this described many times I am sure, but what do we know about the way big (or even small) aromatic planes interact with each other when they get close. There is an obvious place to look and that is in the crystal structure of whatever aromatic molecules have been worked out. Although I expected to find something characteristic, I was surprised to find one charaacteristic as universal as I found it. This particular aspect of the structure of aromatic molecules that I did find is that aromatic molecules do not tend to crystallize as stacks of cards. There is something wrong with the arrangement in which the aromatic planes are normal to the stacking axis; aromatic molecules do not tend to crystallize in that way. They are always tipped, at an angle to each other. Figures 13, 14[24] and 15 will give you examples of this characteristic. Figure 13 shows the crystal structure of anthracene. The two outside pairs are tilted to the right so that we see their "under faces" and the pair in the middle is tilted to the left and we see their "upper faces". The angle of the tilt is about 45°; so that successive planes are roughly about 90° to each other. I picked anthracene for another reason. It is one of the few aromatic molecules whose semiconductivity (electrical conductivity) has been examined in single crystals along all of the crystal axes. I was very interested to note what orientation was required between molecules of this kind to give the best transfer of electrons between them. It turns out that the conduct-

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24. R.W.G. Wyckoff, Crystal Structure, Vol. V, Interscience Publishers, Inc., New York, New York.

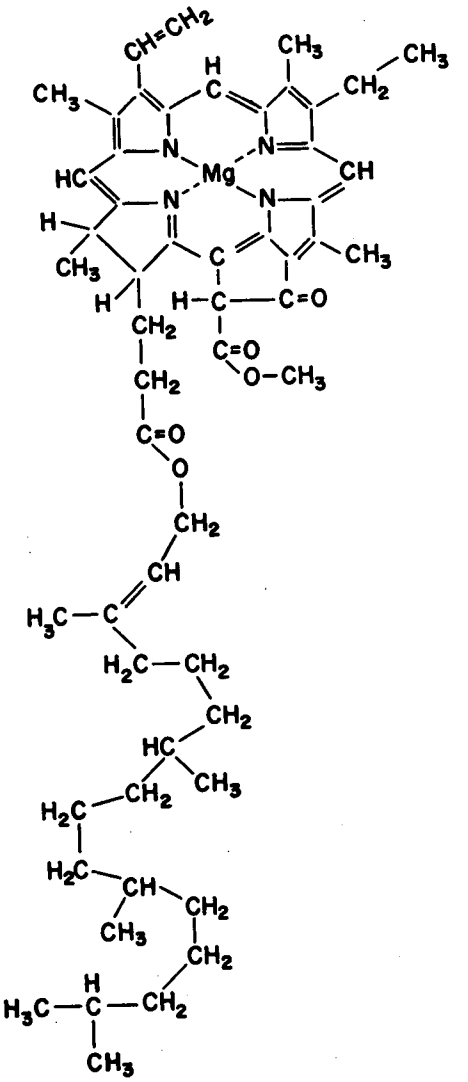


Figure 12a. Structure of Chlorophyll

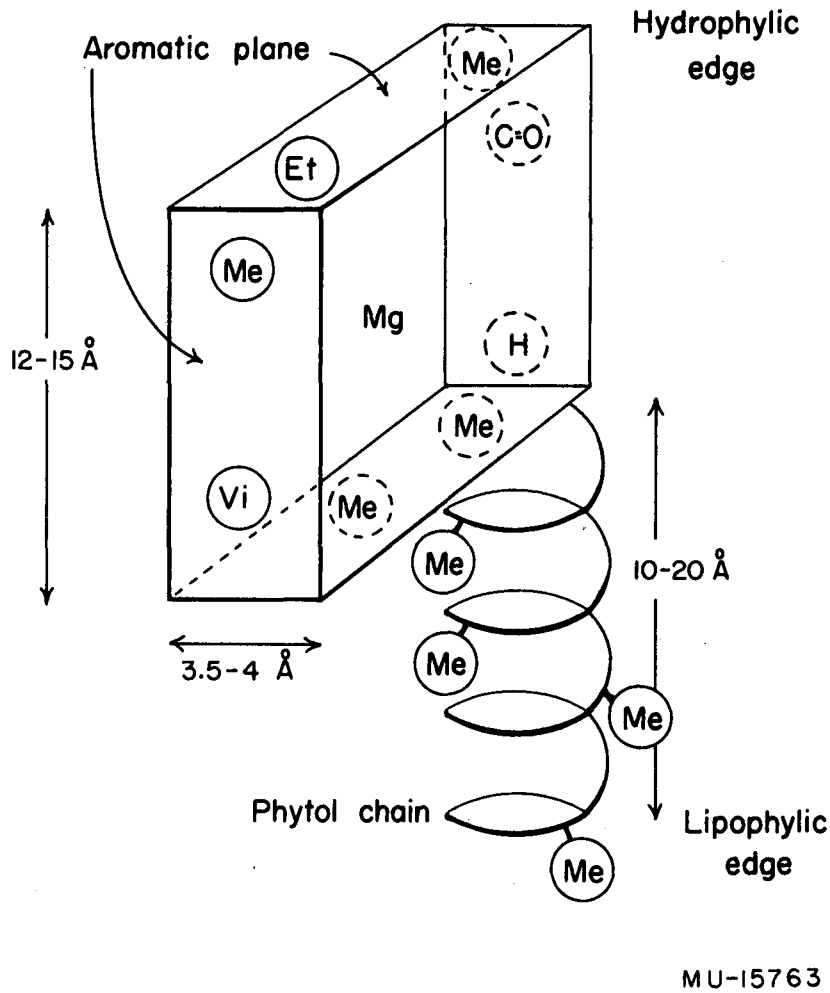
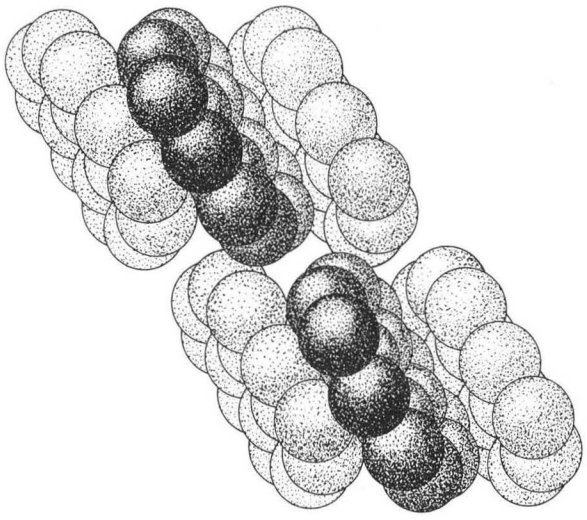


Figure 12b. Space occupied by the chlorophyll molecule



A packing drawing of the anthracene structure projected on its b face.

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Figure 13. Crystal Structure of anthracene

XIV. DERIVATIVES OF BENZENE

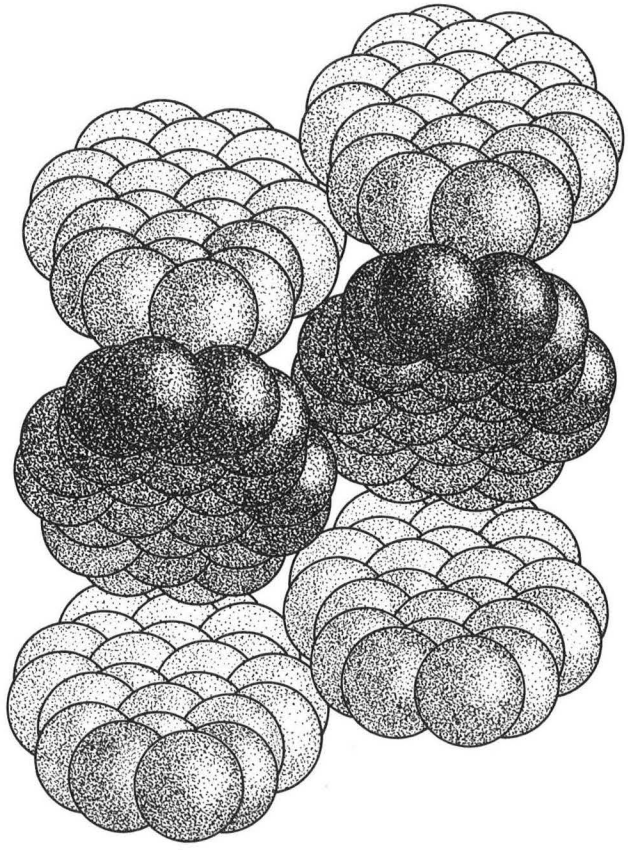

Figure XIVA,6b. A packing drawing of the coronene structure.

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Figure 14. Crystal structure of coronene

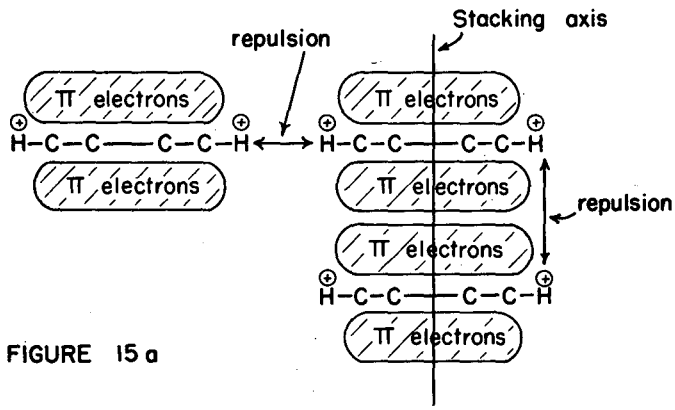

FIGURE 15 a

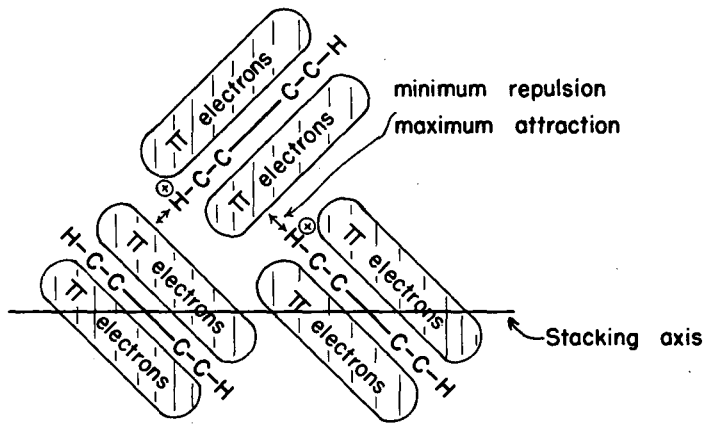

FIGURE 15 b

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Figure 15. Idealized aromatic crystal

ivity in the horizontal plane is isotropic in all directions. The conductivity in the vertical direction is very small. The reason for that is important for us to recognize. But before describing what I believe to be the reason for this behavior of conductivity in anthracene I want to show a few more examples of aromatic molecules in which the crystal structure has been well established.

Figure 14 is a molecule of even bigger aromatic structure, coronene. Here again you will notice that the two bottom molecules and the two top ones are tilted downwards (looking down on the top face of the molecule), the center ones are forward and are tilted up (we are looking at the bottom face of the molecule). Again, the angle of tilt is about 45°. The reason that they are packed at angles like this seems to be that the hydrogen atoms on the carbon atom around the edge of the anthracene, or other aromatics, constitute regions of exposed positive charge and as such would seek to avoid each other.

Thus a crystal in which the aromatic planes were normal to the stacking axis (Figure 15a) would require the exposed hydrogen atoms to lie adjacent to one another in all three directions giving a maximum of repulsion and leading to an unstable form. If the planes are tilted at approximately 45° the exposed hydrogen atom would tend to be buried in the pi-electron clouds of neighboring molecules (Figure 15b), thus leading to a more stable form. This apparently, is the reason why the aromatic rings always tilt to give the best kind of interaction energy.

Let us return to the conductivity question now. It is clear that charge (electrons) will move most easily in the aromatic planes, i.e., conductivity in the aromatic plane will be high compared to conductivity normal to it. The conductivity of graphite in the cleavage plane is

$\sim 10^6$ times the conductivity across it. Furthermore, in an aromatic hydrocarbon for which the aromatic plane is of limited extent (in contrast to graphic) it may be expected that the transfer of charge between the limited aromatic planes will be easier in a direction normal to the aromatic plane than in it across the nonoverlapping areas occupied by the hydrogen atoms (Figure 16). Thus, by tilting the molecules as represented in anthracene the best combination of in-plane motion and transfer of charge between planes in the direction normal to them where the pi-overlap is greatest achieves the best arrangement, or conductivity, in a molecular crystal (Figure 16b).

The last crystal structure which I would like to show you is that of nickel phthalocyanine (Figure 17) which is perhaps the most complex of them all because the tilt is in all three directions. In other words, these molecules are tilted not only with respect to the x and y plane but also with respect to the y and z plane as well, so that if we were to draw the three axes, the molecule would be lying somewhere on a plane tilted to all three axes (Figure 18). The conductivity of the phthalocyanine is very nearly isotropic; there isn't any favored direction.

This kind of layer is the type which I think might best account for the ordering ability of chlorophyll (and of protochlorophyll) in producing the lamellae. This tendency to form layers like those of the aromatic molecules described above (anthracene, coronene, phthalocyanine) in which the molecules are laid out in this alternating pattern would dominate the structure. Looking down on a chlorophyll layer we would then have a situation where one molecule would be tilted one way and the next one would be tilted the other way. They are tilted on all three axes like phthalocyanine,

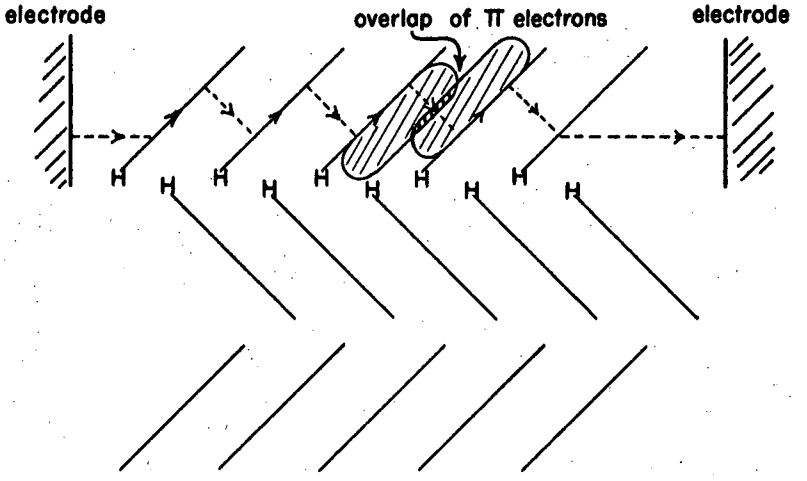

FIGURE 16b

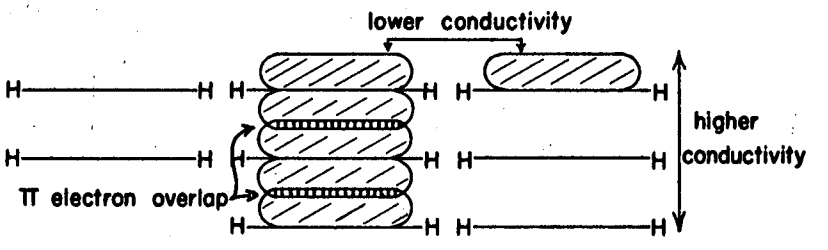

FIGURE 16a

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Figure 16. Semiconduction properties of idealized aromatic structures.

XV. ALICYCLIC AND HETEROCYCLIC COMPOUNDS

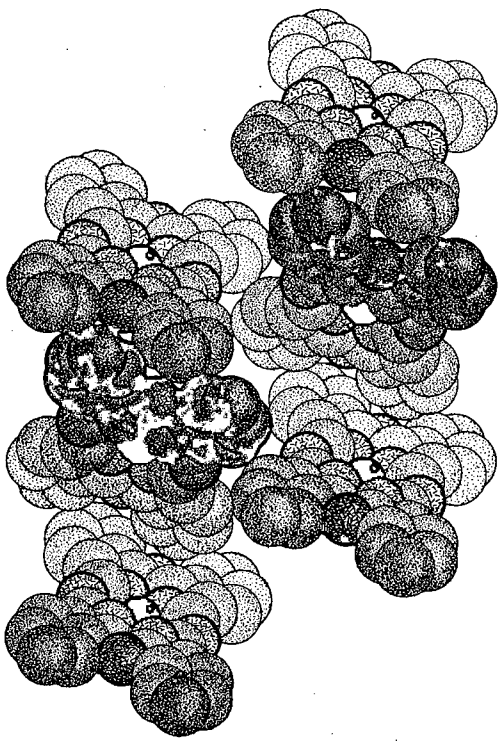

Figure XV,C,1b. A packing drawing of the nickel phthalocyanine structure viewed along the b_o-axis. The metallic atom is black, the nitrogen atoms are line-shaded.

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Figure 17. Crystal structure of nickel phthalocyanine

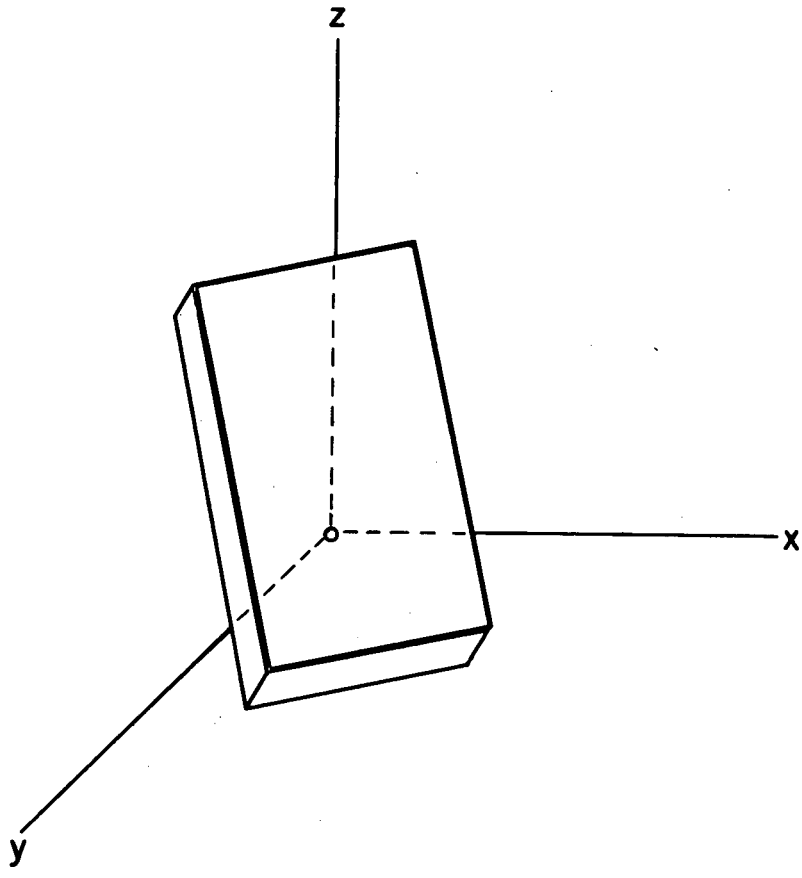

Figure 18. Porphyrin plane inclined to all three axes

and this would account for Goedheer's ability to see only a small dichroism in the lamellae in the layered chloroplasts of one of these algae (Mougatea)[25], in which all the lamellae are parallel to one of the axes of the algae.

Using these rather elementary, but basic and far-reaching principles of molecular interaction which we have just described, we can suggest an arrangement of the three principal types of molecules which we know to be present in and essential to the functioning of the photochemical apparatus in the lamellar form. Such a proposal is shown in two sections in Figure 19. Figure 19a depicts the arrangement of aromatic chlorophyll plates, shown in more detail in Figure 12b, as they would presumably arrange themselves in determining not only the lamellar structure itself but also its asymmetry, and in its two-sidedness. These tilted aromatic plates will provide the uniform horizontal conductivity in the lamellae on either side of which will lie the sites for trapping of electrons and holes. A vertical section through a lamellae is shown in Figure 19b, and the relationship is depicted on the porphyrin plate to the carbon-reducing enzymes on the aqueous side of the layer and of the phytol and the carotenoid and oxygen-evolving systems on the other side. As presently viewed you can see that the dominating influence in the formation of these layer-like structures appears to be the aromaticity of the porphyrin head (see also the crystal structure suggested by Hanson for methyl chlorophyllide), and the principles of the interaction of such aromatic molecules, together with the lipid character of the phytol tail,

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25. J. C. Goodheer, Biochim. et Biophys. Acta, 16, 471 (1955).

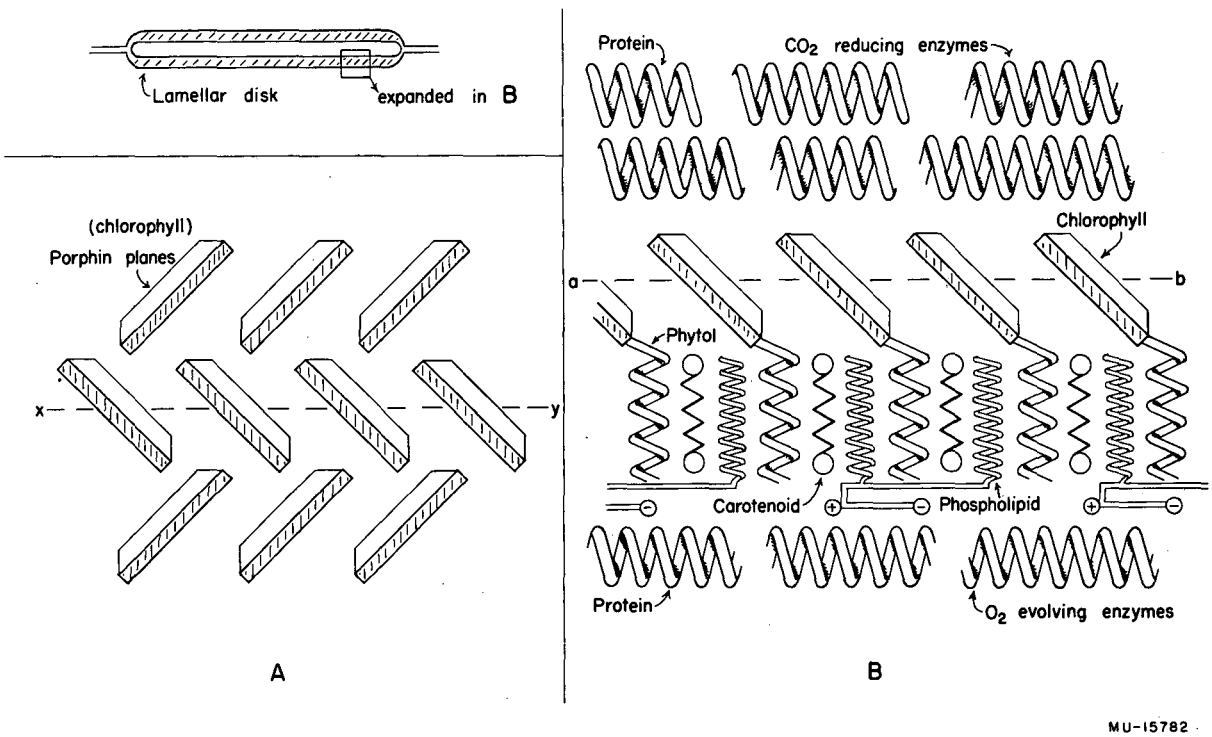

Figure 19. Schematic representation of possible molecular structure for a lamella

and the principles of the interaction of such lipid molecules as suggested by the crystallization of polypropylene.

The determination of the nature of the electron traps, on the one hand, and of the hole traps, on the other, would appear to be one of the fruitful areas of future investigation. One can imagine that the site of electron trapping might very well be such things as iron porphyrins or iron chlorphyll, occasionally interleaved with the magnesium compound, or perhaps imbedded, as heme, in the protein adjacent to the chlorophyll layer. On the other side, the sites of the hole capture might also be another type of metal complex, for example, copper or perhaps even the carotenoid itself, or something related to it, which could provide the electrons for neutralizing, or trapping, the holes.

It will be of considerable interest to see how this concept of the separation of oxidizing and reducing power will eventually merge with ordinary solution chemistry in which such possibilities as cytochrome and copper enzymes play corresponding roles.