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ELECTRONIC STRUCTURE OF SOME IMPORTANT CHLOROPHYLLS *

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The electron energy levels of three important chlorophylls were calculated by the FEMO method with the maximum accuracy on the computer ICL-4-72. The optical transitions between top filled and lowest empty levels were found. These agree well with experimental values.

Recently LE BRECH, LEBLANC and ANTIPPA /1/ applied the FEMO method to the branched network of the chlorophyll molecule and calculated its energy spectrum. In this paper we used the FEMO method analogous to that developed by RUEDENBERG and SCHERR /2/ and calculated the energy spectra of chlorophyll a, chlorophyll b and bacteriochlorophyll molecules. We followed LE BRECH's procedure /1/ and constructed the network of conjugated bonds exactly according to the structural formulae of dyes. As LE BRECH et al./1/ pointed out, the best agreement with the experiment was obtained when all conjugated bonds including the peripheral substituted groups as well as the central Mg atom were considered.

The network of chlorophyll a contains 27 atoms (22 carbon atoms, 4 nitrogen atoms and 1 magnesium atom). If each of the four nitrogen atoms contributes one free electron to the π - electron network there are 26 electrons in the network. When on the other hand two nitrogen atoms bonded to the central Mg atom contribute two free electrons, there are 28 electrons altogether in the network. Similarly we have a network of 29 atoms (28 or 30 π- electrons) and 25 atoms (24 or 26 π- electrons) for chlorophyll b

* Presented at the 14th Symposium on Pigment-Protein Complex, Szeged 1977

and bacteriochlorophyll, respectively. Both networks are very similar to that of chlorophyll a (in bacteriochlorophyll network atoms 13 and 14 are missing and in chlorophyll b network a new two-membered branch at the site 13 is included).

The calculations were carried out on the computer ICL 4-72 using a double precision arithmetic. The system of energy levels was filled with π- electrons using PAULI principle and differences between top filled and lowest empty levels were calculated, wavelength expressed in nanometers and drawn in diagrams (see Figs. 1, 2, 3). The arrows in these diagrams correspond to the transitions in the absorption spectrum (each arrow labelled by the transition wavelength in nm). The levels are drawn in the scale of energy in electron-Volts and levels are numbered. The transitions labelled by asterisk disappear when we consider the lower number of π- electrons.

If we compare the calculated spectrum of chlorophyll a as well as chlorophyll b (see Fig. 1,2) with the experimental values (see Tab. 1), it can be clearly seen that the asterisk-labelled transitions lie far from all observed spectral bands. So we can conclude that in these molecules the picture with lower number of π- electrons is more realistic.

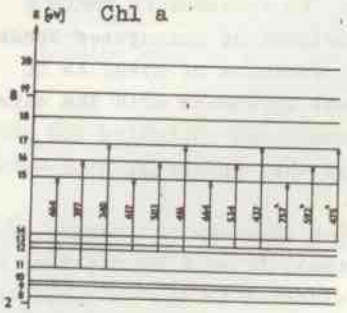

FIG.1. Transition wavelengths of chlorophyll a (in nm). (Transition labelled by asterisk correspond to the higher number of π- electrons).

The agreement is very good for chlorophyll a but worse for chlorophyll b. This method apparently does not correctly reflect the effect of side substituted groups on the main system of conjugated π- bonds and therefore the difference between the calculated chlorophyll a and chlorophyll b spectra is much smaller than

in beality. In bacteriochlorophyll (see Fig. 3, Tab. 1) the long-wave band has not its corresponding transition among non-asterisk--labelled values. It is possible that in this case the system with the 26 π- electrons is more probable.

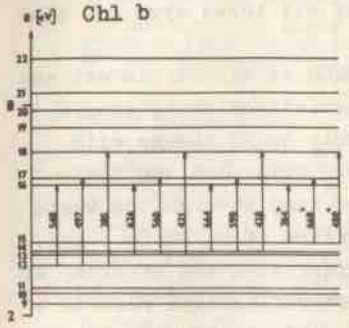

FIG.2 Transition wavelengths of chlorophyll b (in nm).

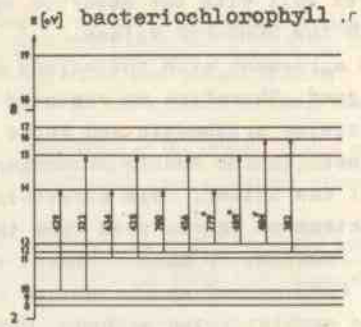

FIG.3 Transition wavelengths of bacteriochlorophyll (in nm).

(Transition labelled by asterisk correspond to the higher number of π- electrons).

TAB. 1 Absorption band maxima

Dye		Band maxima in nm									
		Blue region					Red region				
chl a	exp	325	380	410	430		533	578	615	662	
	calc	340	397	416	437		503	534	617	664	
chl b	exp			430	455			549	595	644	
	calc	385	421	438	497		548	560	590	626	664
bchl	exp	358	391				530	577	697	773	
	calc	323	382	404*	428	456	489*	634	700	779*	

Exp. values taken from /3/ (pigments dissolved in ether).

All spectra contain more transitions than observed because the FEMO method does not include any information about spin and symmetry and therefore we cannot distinguish allowed and forbidden transitions. From the diagrams we see that the six transitions between the two top filled and three lowest empty levels agree well with the observed spectra of all three dyes and also with the SCMO-PPP values.

The agreement with the values of LE BRECH et al. /1/ is not very good. Therefore we repeated our calculations using single precision arithmetic and found relatively large change with respect to the double precision case. In this case the agreement was better. This effect is not the same through the whole spectrum as can be seen from the comparison of LE BRECH's and our results. We cannot expect that by improving the accuracy of the FEMO method we can obtain results competing with results of more sophisticated methods. However the calculation is cheap and simple - it takes only seconds on a computer - and thus it enables us to carry out long series of calculations with varying parameters and calculations of more complicated networks (e.g. networks of complexes or higher aggregates). These calculations are under way in our Department and some resluts are expected in near future.

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/2/ RUEDENBERG, K., SCHERR, C., J. Chem. Phys. 21 (1953) 1565
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Вычисляются уровни энергии электронов трех важных хлорофиллов /хлорофилла а, хлорофилла б, бактериохлорофилла/ методом свободного электрона (FEMO). Вычисления сделаны на компютере ICL-4-72 с наивысшей доступной точностью. Определены оптические переходы между наивысшими заполненными и наинизшими незаполненными уровнями. Результаты сравнены с экспериментальными данными и с результатами вычислений Лебреха. Найдено хорошее согласие с экспериментальными данными, небольшие разницы по сравнению с результатами Лебреха могут быть объяснены меньшей точностью его вычислений.

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