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The Far-Infrared Spectra of Monomeric and Aggregated Chlorophylls a and b[1]

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Abstract: The mid- and far-infrared spectra of chlorophylls a and b, methyl chlorophyllides a and b, deuteriochlorophylls a and b, pheophytins a and b, and methyl pheophorbides a and b have been examined in the solid state and in solution in the 667–160-cm^{-1} region. The solution spectra of the magnesium-containing chlorophylls and methyl chlorophyllides in the 340–160-cm^{-1} region are found to be solvent dependent, while those of the pheophytins are not. The solvent dependence is attributed to the presence of aggregates of the chlorophylls in nonpolar solvents (cyclohexane or benzene) as well as in the solid state, and to monomeric chlorophyll in basic solvents (cyclohexane–pyridine and cyclohexane–methanol mixtures). The solvent effect is entirely analogous to the previously observed solvent dependence of the carbonyl region infrared spectra. The spectra of chlorophylls a and b and methyl chlorophyllides a and b show an absorption peak at 313–303 cm^{-1} in nonpolar solvents or mulls that can be attributed to intermolecular coordination involving magnesium and oxygen, which leads to chlorophyll aggregation. Strong absorption bands at 292–296 and 195–196 cm^{-1} observed in the spectra of monomeric chlorophylls a and b and methyl chlorophyllides a and b can be attributed to magnesium–nitrogen vibrational modes.

Recent investigations have provided a basis for the supposition that chlorophyll exists *in vivo* in a variety of forms, and that these forms may represent different states of aggregation of chlorophyll. Most of the evidence is based on absorption and fluorescence spectroscopy in the visible.[3] The aggregation behavior of chlorophyll has thus become a subject of keen interest, particularly in the context of the two-light-reactions hypothesis in photosynthesis.[4] That aggregated chlorophyll functions as an auxiliary pigment in photosynthesis and that both monomeric and polymeric (aggregated) chlorophyll are involved in photosynthesis place a premium on knowledge about the aggregation behavior of chlorophyll *in vitro*. Although it cannot be alleged that information derived from chlorophyll studies in defined solution can easily be applied to situations involving the intact photosynthetic apparatus, nevertheless, conclusions on the aggregation behavior of chlorophyll derived from *in vitro* studies must surely be pertinent to the problem of photosynthesis.

Intermolecular aggregation of chlorophylls a and b in solution has been inferred from measurement of the infrared,[5] electronic,[6] and proton magnetic resonance[7] spectra of these materials in nonpolar solvents. Aggregation is envisioned to involve coordination of ketone and aldehyde carbonyl oxygen atoms of one chlorophyll molecule with the central magnesium atom of

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(2) Resident Research Associate.

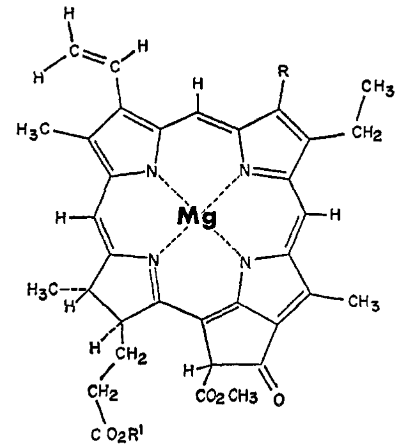
(3) M. B. Allen, C. S. French, and J. S. Brown in "Comparative Biochemistry of Photoreactive Systems," M. B. Allen Ed., Academic Press Inc., New York, N. Y., 1960, Chapter 3, p 33.

(4) G. E. Hoch in "Biochemical Dimensions of Photosynthesis," D. W. Krogman and W. H. Powers, Ed., Wayne State University Press, Detroit, Mich., 1965, p 5.

(5) J. J. Katz, G. L. Closs, F. C. Pennington, M. R. Thomas, and H. H. Strain, *J. Am. Chem. Soc.*, **85**, 3801 (1963).

(6) A. F. H. Anderson and M. Calvin, *Arch. Biochem. Biophys.*, **107**, 251 (1964).

(7) G. L. Gloss, J. J. Katz, F. C. Pennington, M. R. Thomas, and H. H. Strain, *J. Am. Chem. Soc.*, **85**, 3809 (1963).



Compound	Mg Present	R	R'
Chlorophyll a	+	CH3	Phytyl
Chlorophyll b	+	CHO	Phytyl
Methyl Chlorophyllide a	+	CH3	CH3
Methyl Chlorophyllide b	+	CHO	CH3
Deuteriochlorophyll a[a]	+	CD3	Phytyl
Deuteriochlorophyll b[a]	+	CDO	Phytyl
Pheophytin a	-	CH3	Phytyl
Pheophytin b	-	CHO	Phytyl
Methyl Pheophorbide a	-	CH3	CH3
Methyl Pheophorbide b	-	CHO	CH3

[a] Deuterium atoms substituted for all hydrogens.

Figure 1. Structure and nomenclature of chlorophylls.

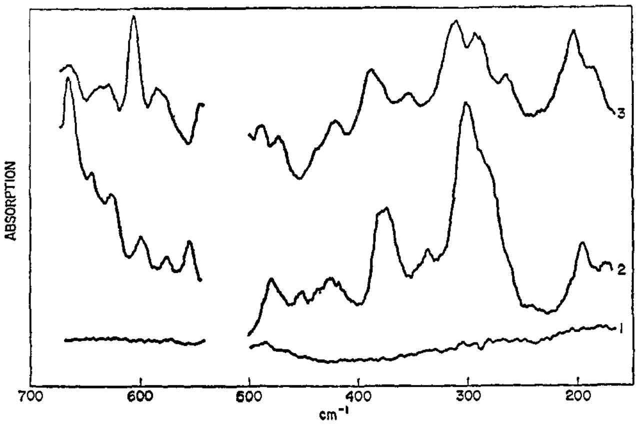


Figure 2. Far-infrared spectra of (1) cyclohexane blank; (2) deuteriochlorophyll a in cyclohexane solution; (3) chlorophyll a in cyclohexane solution.

another. In basic or coordinating solvents, chlorophyll exists in the monomeric form, with solvent molecules loosely filling the axial coordination positions of the magnesium atom.

Previous studies of the infrared spectra of the chlorophylls have been limited to the sodium chloride region of the spectrum and have dealt primarily with the 1550-1750-cm^{-1} region.[3,4] The far-infrared spectra (below 700 cm^{-1}) of the chlorophylls have not yet been reported. However, Weigl and Livingston[8] did examine chlorophyll a in the 667-370-cm^{-1} region and reported that no bands could be attributed to the "magnesium-nitrogen oscillation." Nevertheless, the far-infrared (<370 cm^{-1}) spectra of the chlorophylls should show absorption bands associated with the magnesium-nitrogen vibrational modes. More importantly, the metal-carbonyl oxygen interactions, postulated to arise from the self-aggregation of the chlorophylls in nonpolar solvents, should give rise to absorption in the far-infrared.

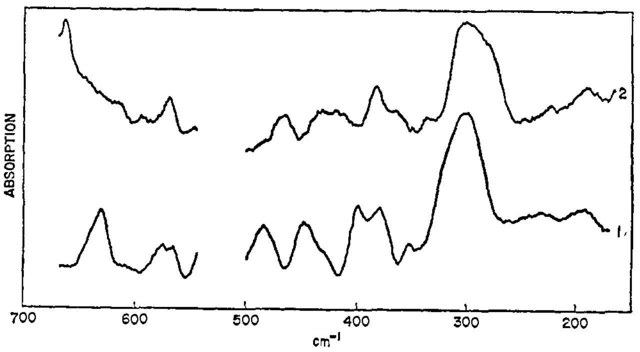


Figure 3. Far-infrared spectra of (2) deuteriochlorophyll b, suspension in cyclohexane; (1) chlorophyll b, suspension in cyclohexane.

This paper describes work done on the far-infrared spectra of chlorophylls a and b and their related compounds, in both the solid state and in solution. The substances studied are shown in Figure 1.

Experimental Section

Infrared Measurements. A Perkin-Elmer No. 301 double-beam grating spectrometer with a dry nitrogen purge was used to study the 667-160-cm^{-1} region. Solid-state spectra were obtained at 25° with mineral oil mulls of the material (*ca.* 25 mg) placed between thin disks of polyethylene. Two disks of polyethylene were also placed in the reference beam. Solution spectra, 25°, were measured in 5-mm path length high-density polyethylene cavity cells ($\sim$2 ml) mounted in metal frames, with an equivalent cell filled with solvent in the reference beam. Solutions were prepared by dissolving 15 mg of chlorophyll in 2 ml of the appropriate solvent. All solvents were spectroscopic grade (where available) and were used without further purification. The frequencies reported are reproducible to $\pm$2 cm^{-1}.

Materials. Chlorophylls a and b were prepared from spinach by the procedure of Strain, *et al.*[9] Fully deuterated chlorophylls a and b were obtained as previously described.[10] The methyl chlorophyllides were prepared from cockleburr by the *in situ* reaction with methanol.[11] Pheophytins a and b and methyl pheophorbide a were prepared from the corresponding chlorophylls by standard procedures.[12] Methyl pheophorbide b was also obtained from Fluka AG Chemische Fabrik Buchs/S. G., Switzerland.

Results and Discussion

General Features of the Spectra. The frequencies of the absorption peaks in the region 667-160 cm^{-1} for chlorophylls a and b, deuteriochlorophylls a and b, pheophytins a and b, and methyl pheophorbides a and b, in mineral oil mulls, are presented in Table I. More highly resolved spectra were obtained in cyclohexane solution. This solvent is transparent, except for the region 540-500 cm^{-1}, in the 667-160-cm^{-1} region (Figure 2). Unfortunately, the utility of cyclohexane

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[8] J. W. Weigl and R. Livingston, *J. Am. Chem. Soc.*, 75, 2173 (1953).

[9] H. H. Strain, M. R. Thomas, H. L. Crespi, M. I. Blake, and J. J. Katz, *Ann. N. Y. Acad. Sci.*, 84, 617 (1960).

[10] H. H. Strain, M. R. Thomas, and J. J. Katz, *Biochim. Biophys. Acta*, 75, 306 (1963).

[11] F. C. Pennington, H. H. Strain, W. A. Svec, and J. J. Katz, *J. Am. Chem. Soc.*, 86, 1418 (1964).

[12] H. Fischer and H. Orth, "Die Chemie des Pyrrols," Vol. II, Akademische Verlagsgesellschaft, Leipzig, 1940.

Table I. Infrared Absorption Bands of Chlorophylls and Related Compounds in the 667–160-Cm^{-1} Region[a]

Chlorophylls				Methyl chlorophyllides		Pheophytins		Methyl pheophorbides	
Ordinary		Deuterio							
a	b	a	b	a	b	a	b	a	b
		661 s	661 s						
654 m		640 w							
629 m	623 m	622 m	624 m	630 m	622 m	615 s	616 s	613 s	616 s
604 s		597 m		606 m					
579 m		572 w		583 m		586 m		586 w	
	568 m		563 m		568 m		569 m		563 m
545 m		552 m	542 w	545 w					
522 w		508 w	519 w						
504 w			498 w	506 w	509 w				508 w
488 w	480 m	478 m		489 w	480 w	482 w	484 w	480 w	477 w
469 w			460 m	476 w		462 w	464 w	460 w	
					438 w	422 w	433 w	433 w	434 w
418 m	449 m	424 m	409 m	422 m	404 m				
393 m	395 m	369 m	380 m	387 w		393 m	393 m	391 m	394 m
	378 m		359 w			372 m	376 m	372 m	376 m
350 w	346 w	334 w		352 w		341 w	339 w		336 w
						307 w	307 w	308 w	308 w
		294 s	289 m	318 m	313 s				
308 s		284 s		303 m					
290 s	295 s	275 s	267 s	287 s	296 s				
259 w									241 w
197 s	189 w	190 s	183 m	197 s	193 s		181 w		

[a] For mineral oil mulls. s = strong, m = medium, w = weak.

as a solvent is limited by the low solubility of the chlorophylls. Typical far-infrared spectra of saturated solutions of chlorophyll a and deuteriochlorophyll a in cyclohexane solution are shown in Figure 2. The spectra of colloidal suspensions of ordinary and deuteriochlorophyll b in cyclohexane are shown in Figure 3. The solution spectra of pheophytins a and b in cyclohexane were also recorded, but the sparing solubility of the methyl pheophorbides and methyl chlorophyllides in cyclohexane precluded the measurement of solution spectra.

The solid-state spectra of the chlorophylls and pheophytins closely agree in band position and intensity to the corresponding cyclohexane solution spectra. This indicates that the solid state absorptions do not arise only from molecular lattice vibrations. The general appearance of the solution spectra of the ordinary and deuteriochlorophylls are similar, except for the slight (<20 cm^{-1}) downward shift of some of the absorption peaks, for the deuterated materials, presumably from the mass isotope effect. In addition to a large number of weak absorptions, the spectra of the chlorophylls, methyl chlorophyllides, pheophytins, and methyl pheophorbides all show medium-strong intensity absorption peaks in the 610–630- and 370–420-cm^{-1} regions. These bands can be attributed to the chlorin ligand vibrational modes. The band at 622–630 cm^{-1} for the chlorophylls is not sensitive to deuterium substitution and appears at 615–616 cm^{-1} for the magnesium-free derivatives. This absorption band may be assigned to an ester bending mode.[13] An absorption peak in the second region, 550–600 cm^{-1}, is most likely due to an in-plane cyclopentanone ring bending mode.[14] The spectra of the corresponding a and b series of compounds are similar. No new bands that can be related to the –CHO bending modes[15] are observed in the b series. The aldehyde carbonyl absorption bands cannot be strong, and are most likely masked by the ester and ring absorptions. The two medium intensity bands at 420–370 cm^{-1} are sensitive to deuterium substitution but not to the presence of the phytyl group. Substituted pyrroles,[16] as well as porphyrins and metalloporphyrins,[17] also show absorption peaks in the 360–400-cm^{-1} region, which can be assigned to pyrrole ring deformation modes. The assignment of the absorption bands reported here to chlorin ring modes thus seems reasonable. The remaining weak absorption peaks common to all the materials in Table I can be attributed to other chlorin ring deformations, to the in- and out-of-plane bending modes[18] of the alkyl group ring substituents, or of the vinyl,[15] or of the ester[13] substituents, among other possibilities. Further, examination of a phytol film, or a phytol–cyclohexane solution, reveals only very weak broad bands centered at 560 and 490 cm^{-1}. This and the near identity of the spectra of the chlorophylls and methyl chlorophyllides make it unlikely that any of the absorption peaks in Table I arise from phytyl vibrations. Finally, the spectra of the chlorophylls contain strong absorption peaks in the 320–270- and 190-180-cm^{-1} regions. These magnesium-sensitive bands are absent from the spectra of the magnesium-free derivatives.

Spectra in Basic Solvents. When chlorophylls a and b, methyl chlorophyllides a and b, and deuteriochlorophylls a and b are dissolved in pyridine–cyclohexane mixtures, the spectra show a marked decrease in absorption in the 320–270-cm^{-1} region and an increase in the 200–180-cm^{-1} absorption, in addition to a general sharpening of the other bands. Absorption in the 320–270-cm^{-1} region decreases as the concentration of pyridine in the cyclohexane increases, and

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(13) J. J. Lucier and F. F. Bentley, *Spectrochim. Acta*, **20**, 1 (1964).
(14) J. E. Katon and F. F. Bentley, *ibid.*, **19**, 639 (1963).
(15) R. K. Harris and R. E. Witkowski, *ibid.*, **20**, 1651 (1964).
(16) "Catalog of Infrared Spectral Data," American Petroleum Institute Research Project 44, Carnegie Institute of Technology, Pittsburgh, Pa., 1961, No. 1762, 1764.
(17) L. J. Boucher and J. J. Katz, to be published.
(18) R. J. Jakobsen and F. F. Bentley, *Appl. Spectry.*, **18**, 88 (1964).

Table II. Infrared Absorption Bands[a] of Monomeric[b] Chlorophylls and Pheophytins in the 400–160-Cm^{-1} Region

Chlorophyll				Methyl chlorophyllides		Pheophytins	
Ordinary		Deuterio					
a	b	a	b	a	b	a	b
400 m	397 m	383 m	380 m	. . .[c]	. . .	391 w	391 s
380 m	380 m	363 m	359 m	. . .	. . .	372 m	370 s
	348 w			. . .	. . .	343 w	341 w
		295 w	292 w	314 m	318 m	305 w	307 w
292 s	294 s	271 s	275 s	296 s	295 s		
							282 w
						214 w	
195 s	196 s	188 s	188 s	195 s	196 s		
						188 w	180 w

[a] Intensity of symbols as in Table I. [b] Spectra taken in 1% (v/v) methanol–cyclohexane (400–350 cm^{-1}) and 10% (v/v) pyridine–cyclohexane. [c] Materials not soluble in 1% methanol–cyclohexane.

then remains constant for all pyridine concentrations greater than ~10% (v/v). The same effect is noted when methanol–cyclohexane mixtures are used as solvents, except that a lower concentration, around 1% (v/v), seems to be adequate. The spectra of pheophytins a and b, in the 320–260-cm^{-1} region, are not solvent dependent; *i.e.*, the spectra are the same in pyridine–cyclohexane as in cyclohexane solution.

The chlorophylls form stable monosolvates with Lewis bases such as water, alcohols, amines, ketones, and ethers.[19] Further, magnesium porphyrins have been reported to form dipyridinates and pyrrole adducts, with the base molecules coordinated to the magnesium atom above and below the plane of the porphyrin.[20] Finally, the chlorophylls are known to be disaggregated by the addition of methanol to a chloroform solution[7] and pyridine to a carbon tetrachloride solution.[6] The dissociation of the aggregate is brought about by the axial coordination of the methanol or pyridine to the magnesium atom. On the basis of the above observations, it is reasonable to conclude that the chlorophylls exist in pyridine–cyclohexane and methanol–cyclohexane solution as monomers, and the spectra of these solutions are typical of the disaggregated forms. The solvent effects on the mid- and far-infrared spectra are entirely consistent with solvent effects on the carbonyl region infrared spectra previously reported.[5]

The absorption frequencies (400–160 cm^{-1}) of the monomeric chlorophylls, deuteriochlorophylls, methyl chlorophyllides, and pheophytins are shown in Table II. The strong absorptions, present in the spectra of the chlorophylls and methyl chlorophyllides, at 291–296 and 195–196 cm^{-1} are absent from the spectra of the metal-free pheophytins and pheophorbides. These bands may be assigned mainly to magnesium–pyrrole nitrogen vibrational modes. Data from model systems lend support to this conclusion. From comparisons of the spectra of phthalocyanine and other metallophthalocyanines[21] with magnesium phthalocyanin, intense bands at 270 and 165 cm^{-1} in the spectrum of the latter can be assigned to magnesium–nitrogen modes. The spectra of magnesium dimethyl protoporphyrin IX, dimethyl haematoporphyrin IX, and their dipyridinate derivatives show strong absorptions at 343–337 and 196–193 cm^{-1} which can also be assigned to magnesium–nitrogen vibrations. Finally, the metal-sensitive absorptions of the chlorophylls are shifted to lower frequencies in the fully deuterated materials and appear at 271–275 and 188 cm^{-1}. From this it can be concluded that the vibrations that give rise to these absorption peaks are not isolated stretching or bending motions, but are coupled with some of the hydrogenic and chlorin ring vibrations. This is perhaps to be expected for molecular systems as complicated as the chlorophylls.

Spectra in Nonpolar Solvents and the Solid State. The cyclohexane solution and the solid-state spectra are taken to be typical of aggregated chlorophyll, since chlorophyll clearly exists as aggregates in nonpolar solvents[5–7] and in the semicrystalline solid.[22] The spectra of chlorophylls a and b, from 340 to 260 cm^{-1}, in various media are displayed in Figures 4 and 5. The aggregated materials, in cyclohexane solution, and in Nujol mulls for chlorophyll a, show two prominent, strong bands at 312–306 and 290–287 cm^{-1}. On the other hand, monomeric chlorophylls a and b, in pyridine–cyclohexane and methanol–cyclohexane solutions, show only one prominent band at 294–291 cm^{-1}. The extra, solvent-dependent peak at 312–306 cm^{-1} for the aggregated material is designated the far-infrared aggregation peak. Spectra in benzene solution also show this aggregation peak, but the 295-cm^{-1} peak then appears only as a weak shoulder. The spectra of the aggregaged methyl chlorophyllides and deuteriochlorophylls, in cyclohexane solution and the solid state, show an aggregation peak at 303 and 285 cm^{-1}, respectively. Unfortunately, the monomeric methyl chlorophyllides and deuteriochlorophylls show, in addition to the strong first magnesium–nitrogen absorption, a weaker band at 314–318 and 295 cm^{-1}, respectively. The overlap of this absorption with the aggregation peak makes detection of the latter difficult. In any event, there is a substantial decrease in absorption in the 300–310- and 280–290-cm^{-1} region for the monomer as compared with the aggregate for the methyl chlorophyllides and deuteriochlorophylls. Finally, the aggregation peak is completely absent from the spectra of the magnesium-free pheophytins and methyl pheophorbides.

The aggregation peak is thought to arise as a result of the magnesium–carbonyl or –aldehyde oxygen interaction in the aggregates. This interaction can be viewed as giving rise to a magnesium–oxygen stretch-

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(19) R. Livingston, *Quart. Rev.* (London), 14, 174 (1960).

(20) P. E. Wei, A. H. Corwin, and R. Arellano, *J. Org. Chem.*, 27, 3349 (1962); C. B. Storm and A. H. Corwin, *ibid.*, 29, 3700 (1964).

(21) J. E. Bloor, J. Schlabitz, C. C. Walden, and A. Demerdache, *Can. J. Chem.*, 24, 2201 (1964).

(22) A. F. H. Anderson and M. Calvin, *Nature*, 194, 285 (1962); *ibid.*, 199, 241 (1963).

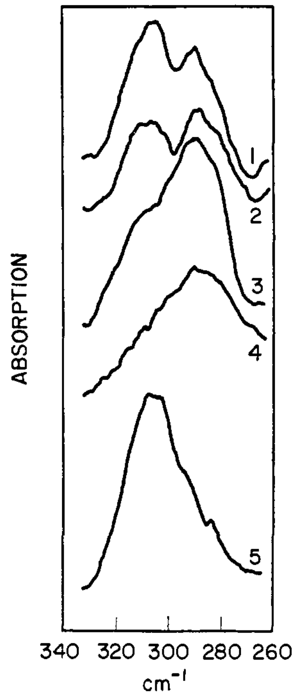

Figure 4. Far-infrared spectra of chlorophyll a in (1) cyclohexane; (2) Nujol mull; (3) 10% (v/v) pyridine–cyclohexane; (4) 1% (v/v) methanol–cyclohexane; (5) benzene.

ing vibration, with the resulting absorption at 312–305 cm^{-1}.[23] It seems, however, unreasonable to expect that the relatively weak magnesium–oxygen interaction in the aggregate should by itself give rise to a strong absorption band. Nevertheless, the aggregation peak is always as intense or more intense than the magnesium–nitrogen absorption at 290 cm^{-1}. The aggregation peak should therefore be assigned to a general metal–ligand (chlorin) vibration in the aggregate. The vibration undoubtedly involves a coupling of the magnesium–nitrogen and magnesium–oxygen vibrational modes. The observation that the aggregation peak is shifted to lower frequency by deuterium substitution is indicative of the coupling of this magnesium–chlorin vibrational with the chlorin modes, and it is probably more correct to consider the aggregation vibration to be composite.

Besides the change in the magnesium–chlorin absorptions, aggregation introduces other effects into the spectra of the chlorophylls. For example, a major band in the spectra of aggregated chlorophyll a, methyl chlorophyllide a, and deuteriochlorophyll a at 597–608 cm^{-1} is greatly reduced in intensity for the corresponding aggregated b series of compounds and is absent for the pheophytins or methyl pheophorbides. This absorption peak may be correlated with a cyclopentanone bending mode that is shifted and intensified by aggregation interaction of the ketone oxygen. That the spectra of aggregated chlorophyll b, methyl chlorophyllide b, and deuteriochlorophyll b do not show this strong absorption furnishes support for the view that aggregation interaction in the b series in addition to the ketone oxygen also involves the aldehyde oxygen atom. Since the aldehyde bending mode is too weak for detection, aggregation involving the aldehyde group may not result in readily observable differences between the spectra of aggregated chlorophyll b and pheophytin b or methyl pheophorbide b. Another example of spectral change brought about by aggregation is the upward shift of the pyrrole bending modes from ~397 in the monomer to 400–420 cm^{-1} in the aggregate. This change in the position of the chlorin absorption indicates that the ligand vibrational modes are coupled with metal–chlorin modes by both intra- and intermolecular interactions. The absorptions observed are thus typical of the whole aggregate.

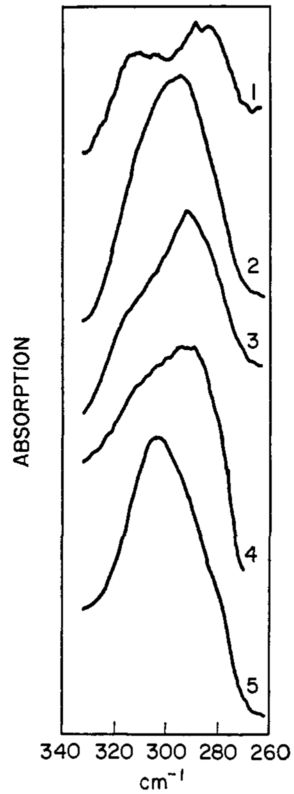

Figure 5. Far-infrared spectra of chlorophyll b in (1) cyclohexane; (2) Nujol mull; (3) 10% (v/v) pyridine–cyclohexane; (4) 1% (v/v) methanol–cyclohexane; (5) benzene.

The far-infrared spectrum of chlorophyll a in cyclohexane is very similar to that of the solid in mulls. Since there is every reason to suppose that chlorophyll is more highly aggregated in the solid state than in solution, it must be concluded that the far-infrared spectra are not particularly sensitive to the exact degree of aggregation. Nevertheless, the solid-state spectra of chlorophyll b are appreciably different from chlorophyll a. In chlorophyll b, the aggregation peak and the first magnesium–nitrogen band merge into a strong broad band, and the second magnesium–nitrogen band is almost totally absent. The solid-state spectra of chlorophyll b are also different from the dilute cyclohexane solution spectra. These differences may reflect differences in the aggregate structures of chlorophylls a and b. It is known from other evidence that,

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[23] Literature data indicate that magnesium–oxygen vibrations should lead to absorption in this region. Studies of the vibration spectra of $Mg(H_2O)_6^{2+}$ led to the assignment of absorptions at 360 and 310 cm^{-1} to symmetric and antisymmetric magnesium–oxygen stretching modes: R. E. Hester and R. A. Plane, *Inorg. Chem.*, 3, 738 (1964); I. Nokagawa and T. Shimanouchi, *Spectrochim. Acta*, 20, 429 (1964). Further, the infrared spectrum of bisacetylacetonatomagnesium(II) contains a very strong bond at 362 cm^{-1} which is attributed to a metal carbonyl–oxygen vibration: K. E. Lawson, *ibid.*, 17, 248 (1961).

in chlorophyll b, both carbonyl and aldehyde oxygen are implicated in aggregate formation.[5,7] Such aggregates should have a geometry different from chlorophyll a, where only ketone oxygen is available for aggregation.

The interpretation of solid-state spectra, however, is not as straightforward as for solution spectra. For example, particle size effects may cause serious discrepancies in solid-state spectra.[24] Furthermore, spectral variation arising from the interaction of lattice modes with molecular vibrations are particularly relevant in the far-infrared. The difference between the solid-state spectra of chlorophylls a and b may then arise because of differences in aggregate structure, lattice structure, or from differences in particle size.

Aggregated Chlorophyll in Wet and Dry Benzene. Chlorophylls a and b, methyl chlorophyllides a and b, and deuteriochlorophylls a and b in benzene solution show only a strong broad absorption peak at the typical aggregation peak position, with a vestigial shoulder at the first magnesium–nitrogen absorption position; the second magnesium–nitrogen band is also greatly reduced in intensity. The band shape is not concentration dependent over a fourfold variation in pigment concentration. The differences between cyclohexane and benzene solution spectra may be due to a solvent effect,[25] or may reflect a real difference in the structure of the aggregates in the two solvents.

The effect of water on the state of aggregation of chlorophyll in benzene solution also appears to have some anomalous aspects. The far-infrared spectra of chlorophyll are the same in dry benzene as in benzene saturated with water.[26] Although the bases methanol and pyridine dissociate chlorophyll aggregates in benzene, water does not appear to do so. This is rather surprising, since water is reported to coordinate strongly to chlorophyll.[27,28] It appears that the extent to which water acts as a disaggregating base depends on the nonpolar solvent to which it is added. While a water–chloroform mixture is disaggregating, a water–carbon tetrachloride mixture is not.[5,7] The rate at which disaggregation occurs may be an important factor here. Both methanol and pyridine disaggregate chlorophyll in benzene very rapidly. Either water reacts very much more slowly, or the solvation properties of the bulk solvent are a decisive factor. It will be important to establish whether these differences are a consequence of differences in rate processes, or whether the chlorophyll aggregates have considerably different structures in different solvents.

Acknowledgment. We are deeply indebted to Dr. A. J. Perkins of the University of Illinois (College of Pharmacy) for his advice and instruction in the experimental procedures of far-infrared spectroscopy.

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[24] C. N. R. Rao, "Chemical Applications of Infrared Spectroscopy," Academic Press Inc., New York, N. Y., 1963, p 587 ff.

[25] C. N. R. Rao, ref 24, p 577 ff.

[26] Infrared measurements in the carbonyl region indicate that the chlorophylls are aggregated in both wet and dry benzene.

[27] E. Rabinowitch, "Photosynthesis," Vol. I, Interscience Publishers, Inc., New York, N. Y., 1945, p 450.

[28] E. E. Jacobs and A. S. Holt, *J. Chem. Phys.*, 20, 1326 (1952).

Bromine Atom Catalyzed Isomerization of Terminal Olefins

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Contribution from the Department of Chemistry, University of Rhode Island, Kingston, Rhode Island. Received August 23, 1965

Abstract: The mechanism of isomerization of terminal olefins to the corresponding olefins with nonterminal double bonds, catalyzed by photolyzed hydrogen bromide in the gas phase, has been shown to proceed by abstraction of an allylic hydrogen from the olefin by a bromine atom, with subsequent replacement of a hydrogen on the terminal carbon. Propene, 1-butene, and 1-pentene have been examined and shown to behave in the same way. The *cis–trans* ratios of the 2-butenes and 2-pentenes resulting from this isomerization have been measured, and ΔH, ΔG, and ΔS values for these geometrical isomerizations are reported.

Two recent papers have been concerned with equilibration of 1-butene with *cis*- and *trans*-2-butene. Benson and co-workers[1,2] report that iodine is a fairly efficient equilibrating agent, while Maccoll and Ross[3] show that hydrogen bromide plus heat is an effective way of accomplishing the same thing. It had already been shown[4] that 1-butene was very rapidly converted to *cis*- and *trans*-2-butene while attempting to add gaseous hydrogen bromide, using ultraviolet light to dissociate the HBr. We had already started a further examination of the mechanism of this isomerization when the papers by Benson and Maccoll appeared. We now wish to report the results, which supplement and reinforce the work of those investigators.

Our concern was largely mechanistic rather than for thermodynamic information. It appeared likely that the course of the isomerization was *via* hydrogen abstraction, with replacement of the hydrogen largely at the terminal carbon

$$CH_3CH_2CH{=}CH_2 + Br\cdot \longrightarrow CH_3\dot{C}HCH{=}CH_2 + HBr \tag{1}$$

$$CH_3\dot{C}HCH{=}CH_2 \rightleftarrows CH_3CH{=}CH\dot{C}H_2 \tag{2}$$

$$CH_3CH{=}CH\dot{C}H_2 + HBr \longrightarrow CH_3CH{=}CHCH_3 + Br\cdot \tag{3}$$

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