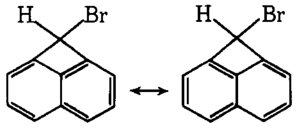
Bromide **1** is, surprisingly, essentially planar (Figure 1a) with the angle between the planes defined by the two six-membered rings being about 1.3° (3) and the bromine atom lying on the "concave" side of the molecule. The buckling of the molecule is only barely significant and it is at this point unclear whether the nonplanarity is actually real or simply a minor artifact due to the remaining absorption errors.[5] The thermal motion (Figure 1) does not indicate any abnormal flexing or disorder in the crystal.

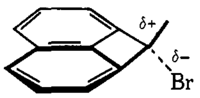
The most striking features of **1** are the changes in the bonding parameters in the naphthalene system on being peri-bridged. The bonds to the bromomethano bridge, which might be expected to be unusually long, are only ca. 0.03 Å longer than a normal carbon-carbon single bond, and their lengths are similar to those in planar cyclobutanes.[7] The strain due to the bridging of the peri-positions is not concentrated solely in the C(1)-C(1a) and C(1)-C(7a) bridge bonds, but rather is expressed by adjustments (particularly in interbond angles), throughout the molecule. This finding accounts for the unexpected thermal stabilities of **1** and **2** and their derivatives.

The net effect of bridging the peri positions has been to compress that portion of the naphthalene nucleus directly connected to the bridge and to cause the opposite side of the molecule to be expanded. In particular, the C(1a)-C(8)-C(7a) angle is compressed to 99°, all of the bonds to C(8) are substantially shorter than in naphthalene, and the C(4)-C(9)-C(5) angle is opened to 138°. The hybridizations of the valence orbitals of C(1), C(8), and C(9) are the most seriously affected of any in **1**. It is tempting to ascribe the variation in the bond distances in the ring to a greater resonance contribution of **1** to the structure than of **5**. From the somewhat greater bond lengths about C(4) and C(5) than about C(2) and C(7) we infer greater p character in the bonds of the former and predict that in **2** electrophilic substitution will occur very selectively at C(4) and C(5).

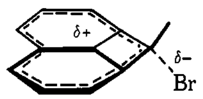


5

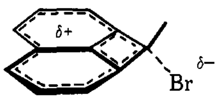
Silver tosylate and silver acetate convert **1** efficiently in hexamethylphosphoramide (75 °C) to **3a** and **3b**, respectively.[8] Of note is that tosylate **3a** solvolyzes slowly in acetic acid at 75 °C (18% in 120 h)[9a] whereas at 25 °C acetic acid converts 9-fluorenyl tosylate rapidly (53% in 5.2 min)[9b] and benzhydryl tosylate (too fast to measure)[9c] to their acetates. Further, sodium azide in hexamethylphosphoramide reacts slower with **1** than with 9-bromofluorene.[10] Displacement of the bromine atom from **1** will be retarded because of the small C(1a)-C(1)-C(7a) bond angle available to its S_N1 (**6a–c**) and S_N2 transition states. What are not yet clear are the extents of the outer ring delocalization (**6b**) in these systems and the complications of the 1,3-cyclobutadiene components (**6c**) therein.



6a



6b



6c

Acknowledgments. We gratefully acknowledge the use of the IBM 370/158 computer at The Ohio State University IRCC and the support of the donors of the Petroleum Research Fund, administered by the American Chemical Society, the National Science Foundation, and the Procter and Gamble Company.

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(2) Cell constants: $a = 7.620$ (1) Å, $b = 8.981$ (2) Å, $c = 12.367$ (2) Å, $\beta = 75.99$ (1)° at $T = -60$ (5) °C; space group $P2_1/c$ (No. 14), $Z = 4$; μ(Mo Kα) = 13.13 cm^{-1}, $e^{-\mu r}{}_{\max} = 0.50$, $e^{-\mu r}{}_{\min} = 0.57$

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(4) All calculations were performed using the CRYM crystallographic computing system. $R = \sum \| |F_o| - |F_c| \| / \sum |F_o|$, the function minimized in the least-squares refinement is $\sum w(F_o^2 - F_c^2)^2$. The goodness of fit is defined by $(\sum w(F_o^2 - F_c^2)^2/(n - p))^{1/2}$ where $w = \sigma^{-2}(F_o^2)$, n = number of observations and p = number of refined parameters.

(5) The full details of the structures of **1** and derivatives will be published by M. Gessner and G. G. Christoph.

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(8) Products **3a–b** are of proper analyses, exact masses, and NMR spectra: **3a**, mp 115.5–117.5 °C; **3b**, bp 86 °C (0.15 mm); picrate, mp 113–115 °C.

(9) (a) Reaction is only 87.5% complete after 650 h at 75 °C. (b) G. W. Corwell, T. D. George, A. Ledwith, and D. G. Morris, *J. Chem. Soc. B*, (1169 (1966). (c) G. W. Corwell, A. Ledwith, and D. G. Morris, *Ibid.*, 700 (1967). (d) Additions of 9-bromofluorene and benzhydryl bromide, respectively, to ethanolic silver nitrate give total silver bromide precipitates instantaneously; under these conditions, **2** gives a *trace* silver bromide test in 5 min.

(10) Bromide **1** is 49% converted to the azide by sodium azide in hexamethylphosphoramide at 25 °C in 20 min; in a comparable experiment, reaction of 9-bromofluorene is 100% complete in <4 min.

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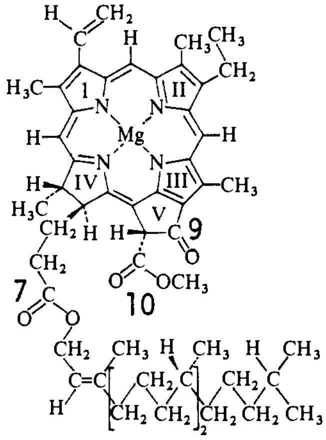
Endo and Exo Carbomethoxy Carbonyl Bonding in Hydrated Chlorophyll a Dimers. Experimental Criteria for the Determination of the P700 Structure in Photosynthesis[1]

Sir:

There exists the belief that the photosystem I reaction center dimer P700 is a C_2 symmetrical dimer of chlorophyll a monohydrate $(\text{Chl a}\cdot\text{H}_2\text{O})_2$.[2-4] However, two slightly different models have been proposed. Both have been established on experimental grounds.[3,4] The difference lies in the choice of the C9 keto carbonyl[4] or the C10 carbomethoxy group[2,3] as being responsible for the reciprocal C=O···H(H)O···Mg interactions that interlink the monomeric Chl a units in P700. In this communication, we describe the various physical conditions under which both models can exist as stable equilibrium structures and delineate the experimental criteria for identifying the configuration of the in vivo P700 adduct.



The presence of the C9 keto and C10 carbomethoxy carbonyls in ring V and the C7 propionic ester carbonyl in ring IV of the chlorophyll a molecule gives rise to several possible self-aggregating interactions between monomeric units of

Table I. Comparison of the Q_y Band of the P700 Difference Spectrum with the Corresponding Q_y Bands of A and B[a]

	No. of Gaussian components	$\sigma = D_\alpha/D_\beta$	θ, deg	$\Delta\nu_{1/2}$ (cm^{-1})	$\eta = \Delta\nu_{1/2}(\beta)/\Delta\nu_{1/2}(\alpha)$	ξ (cm^{-1})
P700	2	3	60	299 (α) 440 (β)	1.47	112
A	2	3	60	469 (α) 703 (β)	1.50	140
B	1	0	180	722	—	—

[a] σ is the ratio of the transition intensities (D) of the α (red) and β (far red) exciton components (see ref 3). The angle θ, subtended by the transition moments of the two Chl a molecules, has been calculated from σ according to eq 4 of ref 3. $\Delta\nu_{1/2}$ and ξ are the half-width and the exciton interaction parameter given by eq 1 of ref 3, respectively.

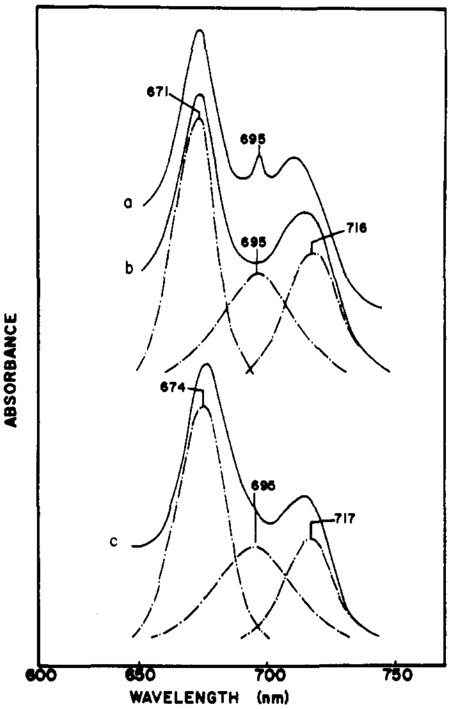
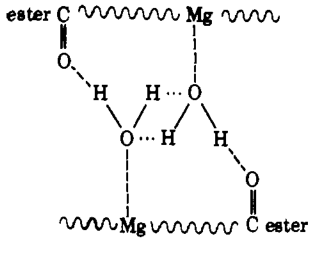


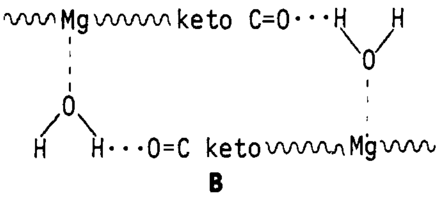
Figure 1. Absorption spectra of a 1:1 methylcyclohexane:*n*-pentane solution of Chl a (2.0×10^{-5} M) and H_2O (10^{-2} M): (a) 77 K, sample plunged into liquid N_2; (b) 121 K, sample slowly cooled from room temperatures at the rate 1 K/min; (c) absorption spectrum of a 1:1 methylcyclohexane:*n*-pentane solution of pyroChl (2.0×10^{-5} M) and H_2O (10^{-2} M) at 77 K. See text for a discussion of the three-component deconvolutions of (b) and (c).

hydrated Chl a molecules. The Chl a molecule is epimeric[5] about the asymmetrical carbon at C10.[6] Aggregating interactions may occur either on the same side of the carbomethoxy group (endo interactions) or on the opposite side of the carbomethoxy group (exo interactions). It is clear from stereochemical properties that C_2 symmetric interactions between two Chl a molecules involving either the C10 or C7 carbonyls must necessarily be exo interactions.

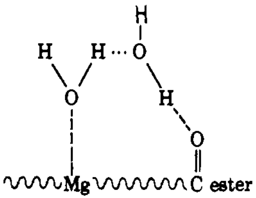
On cooling, rigorously dried hydrocarbon solutions of chlorophyll a monohydrate[7] yield the P700 dimer (Chl a·$H_2O)_2$ that has been characterized in terms of C10 carbomethoxy C=O···H(H)O···Mg interactions[3,8] (A). On the other hand, the observation of a 700-nm absorbing dimer formed from two hydrated pyrochlorophyll chromophores (in which the C10 carbomethoxy groups have been replaced by hydrogen atoms) has been interpreted in terms of C9 keto C=O···H(H)O···Mg linkages[4] (B). The optical spectra of A and B are distinctly different[3,4] (see Table I). It occurred to us that it should be possible to obtain hydrated Chl a dimers derived from C_2 symmetrical interactions involving either the C10 keto or the C7 propionic ester functions, if the C10 carbomethoxy interactions were blocked. A possible means of blocking the C10 ester interactions would be to introduce into our sample preparations an excess of water such that the monomeric Chl a complexes exist predominantly in the dihydrate form[8,9] (C). Polymeric addition of C leads to the formation[8,10] of the 743-nm absorbing (Chl a·$2H_2O)_n$. In dilute hydrocarbon solutions of Chl a (~2×10^{-5} M) containing 500-fold excess water, the precipitation of (Chl a·$2H_2O)_n$ occurs over a period of 2 weeks.[8] We have reasons to expect that on cooling (over a duration of seconds to minutes) of these solutions there is a good chance that dimeric adducts of C, held together by exo C7 or C9 C=O···H(H)O···Mg interactions, may be obtained instead of (Chl a·$2H_2O)_n$. We further expect that, because the C10 carbomethoxy groups have been blocked from participation in dimeric interactions, these exo dimers may give overall appearances very closely similar to corresponding dimers of pyrochlorophyll.



A



B



C

Chlorophyll a and pyrochlorophyll have been prepared and purified using standard procedures.[11,12] The effect of the rate of cooling on the absorption spectrum of Chl a (2.0×10^{-5} M):H_2O (1.0×10^{-2} M) in 1:1 methylcyclohexane and *n*-pentane is shown in Figure 1a and b. In Figure 1b, the absorption spectrum has been measured at 121 K on slow sample cooling (1.0 K/min) from room temperatures. The spectrum shown in Figure 1a has been obtained at 77 K without prior control over the rate of sample cooling, the sample having been plunged into liquid nitrogen. The 77 K optical absorption spectrum of an identically prepared solution of pyroChl is given

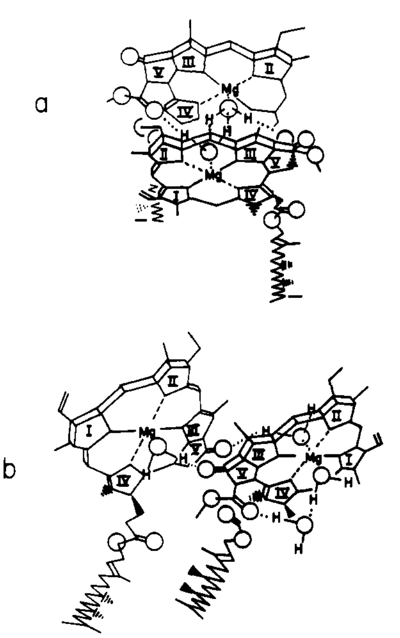


Figure 2. Two C_2 symmetrical dimers of hydrated Chl a: (a) model representation of the monohydrate dimer (Chl a·H_2O)$_2$ displaying reciprocal endo C10 carbomethoxy C=O···H(H)O···Mg interactions; (b) model representation of the polyhydrate dimer featuring reciprocal exo C9 keto C=O···H(H)O···Mg interactions.

in Figure 1c. The spectra in Figure 1a and b are similar except for the sharp peak at 695 nm in Figure 1a. The disappearance of the 695-nm peak in Figure 1b suggests that it has originated from a metastable aggregate, possibly a dimeric segment of the dihydrate polymer (Chl a·$2H_2O$)$_n$. This assignment has been based on the fact that, under experimental conditions similar to those described above, the 695-nm peak has not been observed in a rigorously dried solution in which the chlorophyll exists as the monohydrate.[7] This assignment also appears to be consistent with the fact that the 695-nm peak is not obtained in Figure 1c, because there is no pyroChl analogue of C.

We note the remarkable similarity between the optical absorption spectra in Figures 1b and c. Each of these spectra has been deconvoluted into three Gaussian components of approximately the same peak positions and spectral distributions. A rather unambiguous assignment of these three components can be made in view of the work by Boxer and Closs,[4] who reported the preparation of a dimeric adduct of hydrated pyrochlorophyll chromophores covalently linked at the C7 propionic ester function. We observe that the 674- and 695-nm components in Figure 1c correspond respectively to the monomeric and dimeric complexes of the Boxer–Closs preparations (see Figures 2C and D of ref 4, respectively). We attribute the 717-nm component in Figure 1c to an exo dimeric complex intermolecularly linked via C7 ester C=O···H(H)O···Mg interactions. Such interactions are sterically forbidden in the Boxer–Closs preparation due to the C7 diesterification in their work, and were accordingly not observed by them.[4]

The three components at 671, 695, and 716 nm in Figure 1b are correspondingly attributed to the monomer and exo dimers of C formed from C9 and C7 C=O···H(H)O···Mg interactions, respectively. In confirmation of these assignments, we have distilled off the solvent of the Chl a solution employed in the present study and prepared from the residual material a rigorously dry solution after the standard procedure for the preparation of monohydrate Chl a solutions.[8] On cooling of the dry solution, we have reproduced the observation of A which has been fully characterized in an earlier investigation.[3] (See also Figure 9.19 of ref 2.)

The conclusions we have thus arrived at are summarized in Figure 2. Under an anhydrous environment, (Chl a·H_2O)$_2$ exists in the endo configuration A given in Figure 2a. The blocking of the endo interactions by an excess of water molecules that cluster around the C10 carbomethoxy group as in C results in the formation of two exo dimers, one (Figure 2b) of which corresponding to the Boxer–Closs dimer B. The question of interest is whether the in vivo PSI reaction center provides an environment conducive to the participation of the endo interactions found in A or the balance of competing endogenous and exogamous interactions is tipped in favor of having the C10 carbomethoxy groups bound to polar groups in such a way that the otherwise weaker[13] exo interactions depicted in Figure 2b become the dominant factor in stabilizing the P700 dimer.[14]

In A and B the angles θ subtended by the $S_0 \rightarrow S_1$ Q_y transition moments (along the N1–N3 axes) in the two Chl a molecules are 60°[3] and 180°,[3,4] respectively. On the basis of standard exciton theory, it can be shown[15] that the $\theta = 60°$ value for A accounts for the observed 3:1 intensity ratio for the α and β components[3] of the 700-nm band of A. It has also been pointed out that the $\theta = 180°$ value for B is responsible for the single Gaussian component observed for the Q_y transition in B.[3] The observed features of the spectral analysis of A and B are listed in Table I. Also listed in Table I are corresponding properties derived from published[16] light-minus-dark absorption change spectra of the in vivo P700 reaction center.[17]

One striking feature of the comparison provided in Table I is the significantly narrower widths of the exciton components of P700. This feature suggests that the highly specific interactions in the reaction center aggregate, of which the P700 is a part, allow site inhomogeneity (and hence the Gaussian widths of the exciton components) to a much lesser extent than the random environment of (Chl a·H_2O)$_2$ in a homogeneous hydrocarbon solution. If the foregoing analysis is correct, we conclude that the exogenous Chl a–protein interactions extant in the reaction center are organized in such a manner as not to disturb the integrity of the assembly of endo interactions in A. It is of interest to note that there exists a well-established case in which exogamous Chl a–protein interactions do prevail over the endogenous Chl a–H_2O interactions, resulting in Chl a–protein complexes that are photochemically inactive. Such complexes function as a unit of antenna apparatus as described by Fenna and Mathews.[18] The evidence presented for A as the P700 dimer provides the basis for the two quanta/electron requirement in bacterial and plant photosynthesis.[19,20]

Acknowledgment. We are thankful to Professor Gerhard L. Closs for sending us a preprint of ref 4. This research was supported through the National Science Foundation Grant No. PCM74-11919.

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(13) Due to the deprivation of the two additional hydrogen bonds in A, the exo interactions in B appear to be energetically less favorable than the endo interactions given in A. We note that under identical cooling conditions, the dimerization equilibrium constant is about two orders of magnitude more favorable for A than B (compare Figure 1b of this paper with Figure 9.19 of ref 2).

(14) The question of exagomous Chl a–protein binding in the reaction center aggregate has been discussed in F. K. Fong, translated into Japanese by Y. Inoue, *Protein, Nucleic Acid Enzyme*, **21** (9), 701 (1976).

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Molecular Origin of Long-Wavelength Forms of Hydrated Chlorophyll a

Sir:

There has been a longstanding interest in the aggregation of hydrated Chl a.[1,2] Recent work has established that Chl a exists in three states of hydration.[2-9] Each of these three states gives rise to aggregate species that probably correspond to frequently encountered long-wavelength forms of in vivo and in vitro Chl a.[9b] It is believed[2-4,6-13] that the photoactive aggregate P700[14] (an in vivo Chl a complex that absorbs at 700 nm) in photosystem I is probably a C_2 symmetrical dimer of the monohydrate, (Chl a$\cdot$H$_2$O)$_2$. On aggregation, the dihydrate yields the polymeric species (Chl a$\cdot$2H$_2$O)$_n$ that has a red absorption maximum at 743 nm.[3,4,15] Much of the current work has been concerned with the in vitro preparation and characterization of 700 nm-absorbing Chl a aggregates.[3,9,10-13] Special attention has been focused on the specific roles of the C-9 keto[9,10-13] and C-10 carbomethoxy carbonyl[4,7-9] groups in bonding interactions in (Chl a$\cdot$H$_2$O)$_2$ and on the photoactivity[16,17] of dimeric and polymeric hydrated Chl a.

One of the major unresolved problems is the question of the origin of absorption red shifts observed in Chl a aggregates. This question has been a subject of considerable speculation for some time[18] and has defied analysis on the basis of simple exciton theory.[19] The red shift in the A743 polymer (Chl a$\cdot$2H$_2$O)$_n$ has been attributed[15] to transition dipole–transition dipole interactions according to the McRae and Kasha model.[20] However, the recently determined exciton splitting ($\sim 10^2$ cm^{-1}) in the lowest excited singlet[9] of (Chl a$\cdot$H$_2$O)$_2$ suggests that wavelength shifts due to transition dipole interactions are probably far too small to account for the sizable shift (~ 1500 cm^{-1}) found in A743. The attribution[12] of "environmental" red shifts to "π–π stacking" of neighboring chlorin planes in (Chl a$\cdot$HOC$_2$H$_5$)$_2$ and (Chl a$\cdot$2H$_2$O)$_n$ appears to be inconsistent with the appreciably smaller red shift (~ 288 cm^{-1}) observed in the anhydrous dimer Chl a$_2$[4,7] (with a red absorption maximum at 678 nm) in which π–π stacking occurs to a much larger extent than in the proposed structures for (Chl a$\cdot$HOC$_2$H$_5$)$_2$ and (Chl a$\cdot$2H$_2$O)$_n$. (Compare Figure 1 of ref 4 with Figure 3 of ref 12 and Figure 6 of ref 15.) The purpose of this communication is to present a systematic interpretation of exciton interactions in molecular aggregates in standard perturbation theory.[21] We delineate possible sources for the observed optical frequency shifts in Chl a aggregates, and identify the molecular interaction responsible for the optical frequency shifts characteristic of the various hydrated Chl a aggregates.

We consider a polymeric system consisting of N_0 identical monomeric units. The position vector $\mathbf{R}_n$ of unit n is given by integral multiples of the unit vector $\mathbf{a}$, i.e., $\mathbf{R}_n = n\mathbf{a}$. The total Hamiltonian may be written

$$\mathbf{H}_\mathrm{M} = \sum_{n=1}^{N_0} \mathbf{H}(n) + \frac{1}{2}\sum_{n,m}{}' \mathbf{V}(n.m) \tag{1}$$

where $\mathbf{H}(n)$ is the Hamiltonian operator for the nth molecular unit, and $\mathbf{V}(n.m)$ is the pairwise interaction between the nth and mth units. In Chl a$_2$, (Chl a$\cdot$H$_2$O)$_2$ and (Chl a$\cdot$2H$_2$O)$_n$, the monomeric units are Chl a, Chl a$\cdot$H$_2$O, and Chl a$\cdot$2H$_2$O, respectively. In the following discussion monomeric units are referred to as "molecules", whereas the aggregate is designated as the "system". The molecular eigenstates and the eigenvalues of $\mathbf{H}(n)$ are given by $|\Phi_\lambda(n)\rangle$ and ϵ_λ, respectively. The eigenstates $|\Psi_\mathrm{k}\rangle$ and eigenvalues E_k of the system are determined by the Schrödinger equation

$$\mathbf{H}_\mathrm{M}|\Psi_\mathrm{k}\rangle = E_\mathrm{k}|\Psi_\mathrm{k}\rangle \tag{2}$$

In zeroth-order approximation, the ground state of the system is given as the product state

$$|\Psi_0\rangle = \prod_n |\Phi_0(n)\rangle \tag{3}$$

The ground state energy of the system is accordingly written

$$E_0 = N_0\epsilon_0 + \delta_0 \tag{4}$$

where the energy of aggregation

$$\delta_0 = \frac{1}{2}\sum_{n,m}{}' \langle \Phi_0(n)\Phi_0(m)|V(n.m)|\Phi_0(n)\Phi_0(m)\rangle \tag{5}$$

is the total of attractive interactions that stabilize the system in its ground state. A zeroth order excited state of the system may likewise be written

$$|X_\beta(n)\rangle = |\Phi_\beta(n)\rangle \prod_{m\neq n} |\Phi_0(m)\rangle \tag{6}$$

in which the nth unit is prepared in the βth molecular state. Each excited eigenlevel of the aggregate is composed of N_0 components

$$|\Psi_{\beta\mathbf{k}_\nu}\rangle = N_0{}^{-1}\sum_{n=0}^{N_0-1} \exp[i\mathbf{k}_\nu\cdot\mathbf{R}_n]|X_\beta(n)\rangle \tag{7}$$

where the wave vector is given by

$$\mathbf{k}_\nu = 2\pi\nu/N_0\hat{a} \tag{8}$$

with

$$\nu = -(N_0-1)/2, -(N_0-1)/2+1, \ldots, (N_0-1)/2 \tag{9}$$

and

$$\nu = -N_0/2+1, -N_0/2+2, \ldots, N_0/2 \tag{10}$$

for systems with an odd and even number of molecules, respectively. On substitution of eq 7 in eq 2, we obtain the eigenvalues

$$E_{\beta\mathbf{k}_\nu} = \epsilon_\beta + (N_0-1)\epsilon_0 + \delta_\beta + M_\beta\cos(k_\nu a) \tag{11}$$

where the aggregation energy of the excited-state system

$$\delta_\beta = \sum_m{}' \langle \Phi_0(m)\Phi_\beta(n)|\mathbf{V}(n.m)|\Phi_\beta(n)\Phi_0(m)\rangle$$
$$+ \frac{1}{2}\sum_{m,s\neq n}{}' \langle \Phi_0(m)\Phi_0(s)|\mathbf{V}(m.s)|\Phi_0(s)\Phi_0(m)\rangle \tag{12}$$

differs from δ_0 in eq 5 in that the intermolecular interactions are of two types—those occurring between (N_0-1) ground state molecules and those between these ground state molecules and the remaining excited molecule, and