on carbon-3 at δ 4.17. The two substrates afforded the same results within experimental error, viz., $k_H/k_D = 4.9 \pm 0.1$.

All of these results are consistent with a free radical chain mechanism for reaction 1 in which the propagation sequence is represented in Scheme I.

Scheme I

$$HC(CH_3)_2CH_2HgR + CCl_3 \rightarrow \cdot C(CH_3)_2CH_2HgR + HCCl_3 \quad (4)$$

$$\cdot C(CH_3)_2CH_2HgR \rightarrow (CH_3)_2C{=}CH_2 + \cdot HgR \quad (5)$$

$$\cdot HgR \rightarrow Hg^0 + R\cdot \quad (6)$$

$$R\cdot + CCl_4 \rightarrow R\text{-}Cl + Cl_3C\cdot \quad (7)$$

There are several mechanistic features in Scheme I which merit emphasis. Fragmentation as the exclusive fate of the alkylmercuric radical in eq 6 is consistent with the low bond energy (~6 kcal mol^{-1}) calculated for such species[12] and also with their apparent behavior in other processes, notably demercuration.[2] Chlorine atom transfer from carbon tetrachloride by alkyl radicals in eq 7 is known to be facile.[13] Of particular interest, however, is the selective removal of a hydrogen located β to mercury with such facility as to afford high yields of elimination products in competition with other processes. In order to obtain a quantitative assessment of this activation we carried out competition studies for hydrogen transfer.

The reactivity of I toward hydrogen abstraction by trichloromethyl radical was determined in CCl_4 solutions relative to isooctane and to cyclohexane. Reactions described in Table II were carried out to less than 10% conversions in order to maintain an essentially constant ratio of substrates. Based on the relative yields of neopentyl chloride and 2-chloro-2,4,4-trimethylpentane in the absence of initiator, we find the hydrogen in I to be 580 times more reactive than that in isooctane. Similarly, the β-hydrogen in I is 600 times more reactive than a given hydrogen in cyclohexane. As a cross-check, the relative hydrogen reactivities of cyclohexane and isooctane were determined directly using di-*n*-butyryl peroxide as initiator. The average (per hydrogen) value of $k_{C_6H_{12}}/k_{C_8H_{18}} = 0.94$ is in good agreement with the indirect value of 0.97 obtained from competition with the mercurial.[14] In all cases studied the chloroform was always formed in equimolar amounts relative to alkyl chlorides, and side products arising from the bimolecular reactions of radicals were negligible.

To our knowledge these data represent the first evidence for substantial activation of a β-hydrogen in a metal alkyl to homolytic abstraction.[15] As such they bear an interesting relationship to hyperconjugative effects observed in β-metallocarbonium ions formed by hydride transfers,[17] and it is reasonable that similar effects are applicable to radicals in measure. We hope to extend these studies to the reductive elimination of other organometallic species, particularly those derived from transition metals.[18,19]

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(6) A mixed mercurial RHgR′ allows the separate fates of the two alkyl groups to be differentiated. The choice of an isobutyl group reflects the increasing ease of hydrogen atom abstraction in the series: primary < secondary < tertiary; the neopentyl group was selected for its lack of β-hydrogens.

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(8) Initiation in the absence of promoters may proceed by slow thermolysis of the mercurial or electron transfer with CCl_4. In either case, *i*-BuCl and NpCl should be found rather indiscriminately; the low yields of isobutyl chloride suggest a kinetic chain length of greater than 50.

(9) Alkylmercuric chloride reported in earlier studies[4a] actually consists of a mixture of benzoate derived from benzoyl peroxide as initiator, with the chloride arising from a competing chlorinolysis.[10]

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(15) Hydrogen transfer and elimination in Scheme I may occur stepwise as in eq 4 and 5 or they may be concerted. An alternative pathway involving oxidative addition of $\cdot CCl_3$ to form a Hg(III) species followed by reductive elimination of $CHCl_3$ and alkene is disfavored but cannot be rigorously disproved at present. For other examples of β-hydrogen activation in free radical reactions see ref 16.

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(19) We wish to thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation for financial support, and the Lubrizol Corporation for a fellowship to W. A. Nugent.

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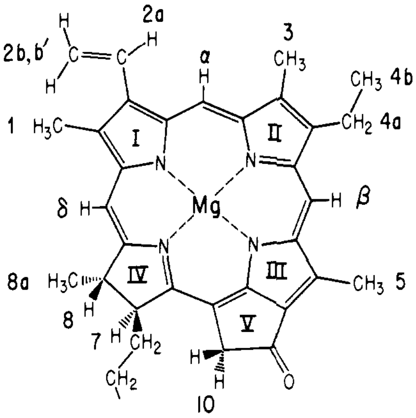
A Covalently Bound Dimeric Derivative of Pyrochlorophyllide *a*. A Possible Model for Reaction Center Chlorophyll[1]

Sir:

Molecular aggregation of chlorophyll has been the subject of intense study in several laboratories.[2-6] While there is good evidence for keto carbonyl-Mg interactions in nonbasic solvents, there is much less structural information on a different form of association postulated to contain a Mg-H_2O-carbonyl link. Reaction center chlorophyll (P-700) has been associated with such a "special pair"[3] structure where exciton interactions presumably give rise to the observed red shift in the absorption maximum. Attempts to produce a well-defined molecular assembly in vitro which mimic these properties have only been marginally successful.[4]

It occurred to us that it might be possible to construct a model for P-700 by linking two chlorophyll chromophores covalently, thus reducing the entropy of dissociation. We



= MgPChl

1, $H_2PChl\text{-}CO_2CH_3$
2, $H_2PChl\text{-}CO_2CH_2CH_2OH$
3, $(H_2PChl\text{-}CO_2CH_2\text{-})_2$
4, $(MgPChl\text{-}CO_2CH_2\text{-})_2$
5, $MgPChl\text{-}CO_2CH_3$

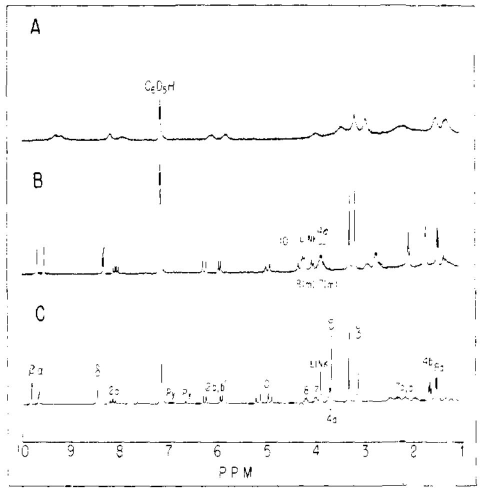


Figure 1. Solvent dependence of the ^{1}H NMR spectrum of **4** (270-MHz FT-^{1}H NMR): (A) dry benzene-d_6; (B) benzene-d_6 saturated with D_2O; (C) benzene-d_6 containing 5% pyridine-d_5 (Py).

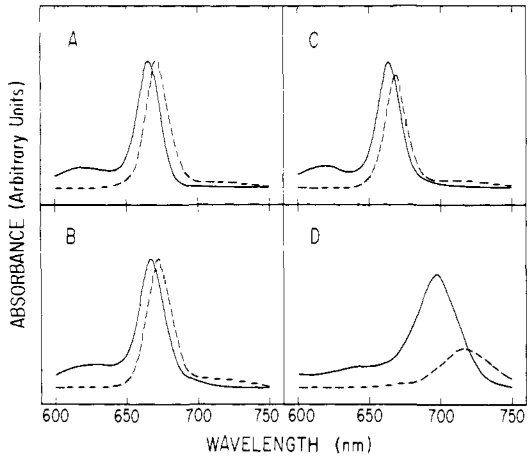


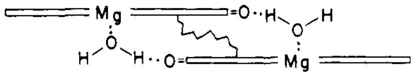
Figure 2. Solvent dependence of the absorption (solid line) and fluorescence (dashed line, excitation at 430 nm) spectra of monomer **5** and diester **4**. A and B are **5** and **4**, respectively, in benzene containing pyridine. C and D are **5** and **4**, respectively, in benzene saturated with water.

wish to report the synthesis of such a compound and some of its remarkable properties. Methyl pyropheophorbide *a* (**1**) was transesterified with ethylene glycol to yield the glycol monoester **2**. Pyropheophorbide *a* was activated with 1,1′-carbonyldiimidazole in dry THF, followed by treatment with 1 equiv of **2** at 70 °C. Conversion of the purified diester **3** (MS *m/e*: 1094) to the desired compound **4** is accomplished either by the method of Eschenmoser[7] or Baum[8] in nearly quantitative yield.

The properties of the magnesium-free diester (**3**) are unexceptional. The visible absorption and fluorescence spectra are indistinguishable from **1**. The ^{1}H NMR spectrum shows all the appropriate resonances of **1** (less the ester CH_3), shifted to somewhat higher field, plus the single resonance of the glycol linkage at 4.14 ppm. From this, there appears to be no specific interaction between the two chromophores.

The properties of the magnesium containing compound **4** contrast sharply with those of its monomeric counterpart, methyl pyrochlorophyllide (**5**). The ^{1}H NMR spectrum shows a remarkable solvent dependence. In dry benzene (Figure 1A) the resonances are extremely broad, while in water-saturated benzene the spectrum becomes well defined with narrow lines (Figure 1B). On addition of pyridine-d_5 (Figure 1C) further major chemical shift differences become apparent. The visible absorption and emission spectra also exhibit significant changes as a function of the solvent (Figure 2). In benzene containing pyridine, **4** and **5** have indistinguishable absorption and emission spectra, but in wet benzene **4**, but not **5**, undergoes a red shift from 666 to 696 nm, in absorption, and to 717 nm in emission.

It is clear from the equivalence of the ^{1}H NMR and electronic spectra of **4** and **5** in solvents containing pyridine that pyridine coordinates strongly with the central magnesium atom, preventing any specific association between the chromophores. This contrasts with the water containing solvent where exciton interaction is observed for **4** only, indicating some preferred proximity of the two chromophores. We would like to propose a structure with C_2 symmetry for this species, schematically represented by **6**. Two water molecules provide the structural "cement" by coordination to the Mg of one chromophore and hydrogen bonding to the keto-carbonyl group in the other. This unique structure is deduced from the following evidence: (1) the ^{1}H NMR spectrum of the "locked" form (Figure 1B) gives one set of resonances for each type of proton,[9] implying that the rings are equivalent on the ^{1}H NMR time scale. (2) The five methyl and one of the ten protons experience dramatic upfield shifts ($\Delta\delta$ = 1.81 and 0.56 ppm, respectively), identifying rings III and V as the region of maximum overlap of the two ring systems.[10] (3) The 4b methyl protons are shifted downfield ($\Delta\delta$ = 0.50 ppm), which requires that the two chlorin planes be approximately parallel to bring this methyl group into the deshielding region of the other ring. (4) Other methyl and methine protons are shifted only slightly excluding them from the region of ring overlap. (5) The two 4a protons have become measurably diastereotopic (ABX_3: $\Delta\delta_{AB}$ = 0.13 ppm; J_{AB} = 14.9; $J_{AX} \sim J_{BX}$ = 7.46 Hz) as have the CH_2 groups of the glycol link ($\Delta\delta$ = 0.16 ppm). This increased chirality is also reflected in the much increased amplitude of the CD spectrum.[11,12] (6) Methanol or ethanol can be substituted for water giving an ^{1}H NMR spectrum equivalent to Figure 1B. Protons α to the hydroxyl group experience large upfield shifts, as do the β protons in ethanol though to a lesser extent. At the point where the ^{1}H NMR spectrum indicates that the folded structure dominates in solution, the integral of the methanol signal corresponds to two methanol molecules per molecule of dimer.[13]



6

Models show that the ten atom linking chain is long enough to allow conformations different from the one discussed here. We believe it serves primarily to reduce the $T\Delta S$ term, rather than forcing any specific folded geometry. To test this hypothesis another diester linked by four carbon atoms was synthesized. The same chemical shift trends are observed though the magnitudes are somewhat smaller. This behavior is expected if only the entropy term is involved, and one predicts that as the link is made longer the chromophores will behave more like independent molecules.

We would like to emphasize that **6** is different from the unsymmetrical model of Katz[3] and another structure with C_2 symmetry proposed by Fong[4] in which the H bonding is postulated to involve the naturally occurring carbomethoxy group at position 10 and the planes are much further separated (6 Å vs. ~3.6 Å in **6**).[14] Experiments directed at further characterization of the structure, excited states, and photochemistry of **4** are in progress, along with construction of a dimer containing the 10-carbomethoxy group, to further test the validity of **6** as a model for reaction center chlorophyll.[15]

Note Added in Proof. We note that Katz and co-workers (*Proc. Natl. Acad. Sci., U.S.A.*, **73,** 1791 (1976)), having had full access to our data and interpretation, consider a structure equivalent to ours as a viable alternative to their previous model of P-700.

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(9) The term "locked" is not meant to imply a static or rigid structure (all NMR evidence pertains at most to averages), rather it is used to convey the remarkably good fit which can exist between two molecules of water and the diester in 6.
(10) The ^{1}H NMR spectrum of the "locked" form is assigned by the well-established method of titrating with a solvent (pyridine) capable of strongly coordinating Mg and following each signal as it returns to its assigned "open" position.
(11) Three different ways of folding can be visualized depending on the sidedness of the rings in the locked form. The propionic acid side chains might both project toward the center of the structure (in-in), both outside (out-out), or one inside and one outside (in-out). The "in-out" form can be excluded because chemical shift changes vastly different from what is observed are predicted. Though the ten atom chain is long enough to accommodate the "out-out" structure, a model shows that the 8a methyl protons will fall within the deshielding region of the other ring; no shift is observed. One is then left with the "in-in" form (**6**) as the only one consistent with the ^{1}H NMR data. This is important because it predicts that the chlorophyllides containing the carbomethoxy group at position 10 and located trans to the propionic side chain,[2,6] will be able to fold the same way without encountering any steric crowding.
(12) The CD spectrum (associated with the low energy transitions) in benzene containing water shows strong maxima at 698 and 603 nm both of negative sign.
(13) In addition to chemical shift differences, line broadening is observed in the alcohol indicating that an exchange process is occurring. It has not been possible to freeze out two populations at temperatures to −80 °C, indicating, as expected, a low activation barrier to exchange.
(14) We have constructed an accurate three-dimensional model of **6** using bond lengths and angles from the crystal structure.[6] The *y* axes of the two chromophores are nearly antiparallel, the interplanar separation is about 3.4–3.6 Å and the inter-Mg distance is 9 Å. A possible structure in which the *y* axes subtend an angle of 120° is believed to be less favorable.
(15) Small scale preparations of the dimer containing the 10-carbomethoxy group have been accomplished. Preliminary experiments indicate optical properties equivalent to **4**.
(16) ANL-ERDA Laboratory Graduate participant.

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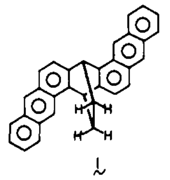
The Absolute Stereochemistries of 6,15-Dihydro-6,15-ethanonaphtho[2,3-*c*]pentaphene and Related Homologues as Determined by Both Exciton Chirality and X-Ray Bijvoet Methods

Sir:

It is well known that in addition to the x-ray Bijvoet method, the circular dichroic Cotton effects due to a chiral exciton coupling between two or more chromophores enable one to determine the absolute stereochemistry in a nonempirical manner.[1-6] In this optical method it is important to choose the proper electronic transition of proper chromophores which satisfy the following requirements of chiral exciton coupling:[7] (i) large extinction coefficient values in uv spectra; (ii) isolation of the band in question from other strong absorptions; (iii) established direction of the electric transition moment in the geometry of the chromophore; (iv) unambiguous determination of the exciton chirality in space, inclusive of the configuration and conformation; and (v) negligible molecular orbital overlapping between the chromophores.

This communication reports the very strong chiral exciton coupling of the $^{1}B_{b}$ transition of polyacene chromophores in (6*R*,15*R*)-(+)-6,15-dihydro-6,15-ethanonaphtho[2,3-*c*]-pentaphene (**1**) and the related homologues, **2a** and **2b**, which rigidly meet the above requirements of the exciton chirality method. Namely, the allowed $^{1}B_{b}$ transition of the component chromophore of **1**, i.e., anthracene, exhibits a very strong ϵ value of the order of 10^5; ϵ_{max} = 134 300 for **1**. The location of the present band around 260 nm is sufficiently separated from weak $^{1}L_{a}$ and $^{1}L_{b}$ transitions around 400-320 nm and also from the $^{1}C_{b}$ transition around 200 nm so that the minor contribution from the weak absorption bands can be neglected (see Figure 1). Next, the polarization of the $^{1}B_{b}$ transition in polyacenes is well established to be along the long axis of the chromophore. Furthermore, because of the rigidity of the present hydrocarbon **1**, one can unambiguously determine the positive exciton chirality in space (see Figure 1). Finally there is no direct conjugation between the two component chromophores, and the contribution of homoconjugation is also negligible, if any, because of the large exciton dipole-dipole coupling term.[8] Thus compound **1** ideally meets the above-mentioned criteria.



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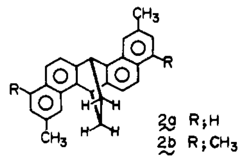

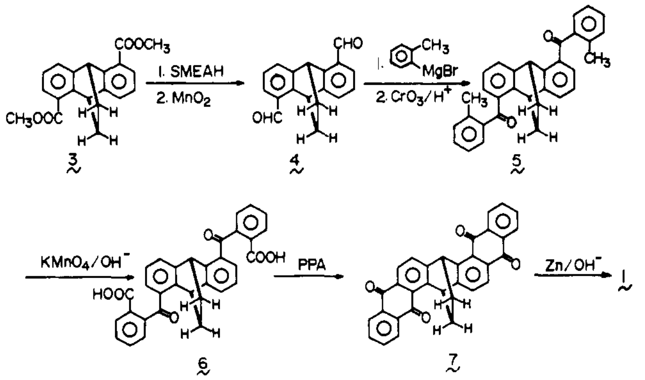

The hydrocarbon **1** was synthesized[9] from (9*R*,10*R*)-(+)-1,5-dimethoxycarbonyl-9,10-dihydro-9,10-ethanoanthracene (**3**), the absolute configuration of which has been established by the x-ray Bijvoet method[10] and by chemical correlations.[11] Reduction of **3** with $NaAlH_2(OC_2H_4OCH_3)_2$ (SMEAH) in benzene and successive oxidation with activated MnO_2 in acetone gave dialdehyde **4**, mp 128-129.5 °C, which was then treated with *o*-toluyl magnesium bromide in ether, followed by oxidation with Jones reagent to afford diketone **5**, mp 151-152.5 °C. Selective oxidation of the methyl groups of **5** was achieved by refluxing with $KMnO_4$ in aqueous NaOH-pyridine to give dicarboxylic acid **6**. Cyclization of **6** in polyphosphoric acid afforded quinone **7**, mp 268-268.5 °C, as the sole product; the yield of **7** from **5** was 64%. Reduction