**Table I.** Observed Proton Chemical Shifts (δ) and Observed and Calculated Complexation Shifts ($\Delta\delta$) for Methyl Bacteriochlorophyllide *d* [Et,Et] (**1**)

| | | | | complexation shifts[c] | | | |
| | | | | calcd (Figure 3A) | | calcd (Figure 3B) | |
proton	monomer[a]	aggregate[b]	obsd	mol. 1	mol. 2	mol. 1	mol. 2
meso							
β	9.59	9.68	0.1	0.2	0.2	0.1	0.1
α	9.43	7.47, 6.75	-2.0, -2.7	-2.6	-2.1	-2.5	-2.0
δ	8.25	8.36, 7.91	0.1, -0.3	-0.1	-0.3	-0.1	-0.4
2b-Me	2.07	0.73, 0.41	-1.3, -1.7	-1.8	-1.9	-1.3	-1.7

[a] +25 μL of methanol-d_4. [b] 4.7 mM in $CDCl_3$. [c] $\delta_{aggregate} - \delta_{monomer}$.
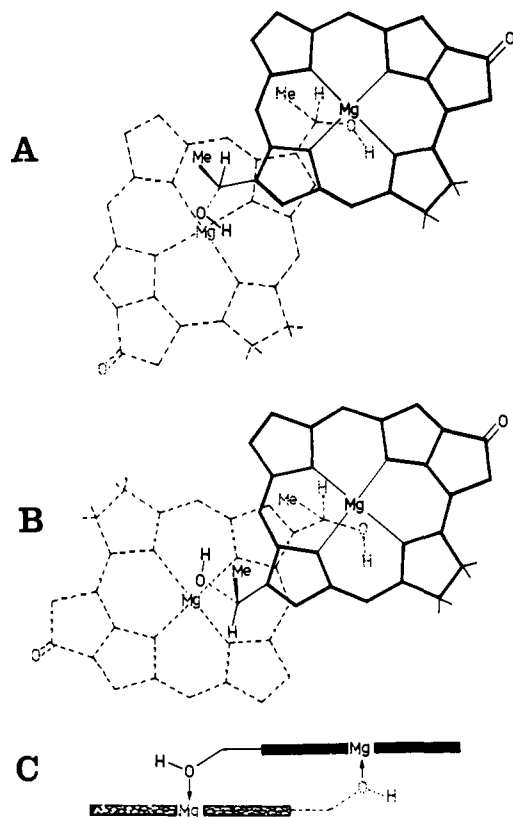
Figure 3. Proposed dimer structure of Bchlide *d* [Et,Et] (**1**). (A) Face-to-face, (B) "piggy-back",[12] (C) end-on projection.

presumably with methanol coordinated to the magnesium atom.

The monomer spectrum may be completely interpreted and assigned by using previous chemical shift data. Using a combination of regioselective deuterium labeling, integration, nuclear Overhauser enhancement (NOE), and saturation transfer experiments between the components, the dimer/aggregate spectrum

(11) We note that in a layered aggregate, ring current effects are such that a molecule inside the sandwich will have very different chemical shifts from an end molecule (see ref 12 for a full discussion). Thus, simple symmetry arguments alone show that there are only three aggregates that will reproduce the observed spectrum. These are the dimer (AB), a tetramer (ABBA), and a polymer [(AB)$_n$] in which *n* is so large that end units are not observed (i.e. *n* > 10). Of these, the dimer (which we favor) has a simple chemical interpretation, the tetramer requires two different types of chlorophyll/chlorophyll interaction, and the polymer would give broad unresolved peaks (see ref 13, Figure 9C) *and* is excluded on the basis of the optical spectra.[14]

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(14) The long-wavelength band of the BChlide *d* in $CDCl_3$ absorbs at 672 nm, shifting to 656 nm ($\Delta\lambda$ = 16 nm) upon addition of pyridine; the 672-nm absorption appeared to be independent of concentration, at least over the range from 4.0 mM to about 40 μM. In contrast, the long-wavelength band of BChl *d* in hexane[17] (for the proposed oligomer) appears at 728 nm and suffers a hypsochromic shift to 656 nm ($\Delta\lambda$ = 72 nm) upon disaggregation with methanol.

(Figure 1), consisting of two slightly broadened and overlapping BChlide *d* spectra, has been assigned.[15]

The chemical shifts of the meso and 8-methyl peaks in the aggregate are recorded in Table I, together with the corresponding values for the monomer and the resulting complexation shifts ($\delta_{aggregate} - \delta_{monomer}$). These shifts, along with further refinement using other peaks in the remainder of the spectrum, were then used to deduce the dimer geometry, using the ring current model of the Chl ring described[16] and applied[12] previously. Following an earlier optical study of these systems in which aggregates of Bchl *c* and *d* were shown to form in hexane solution,[14,17] two possible aggregates were considered; one was a dimer, while the other was a larger oligomer. The spectrophotometric studies in hexane indicated[17] that the higher oligomer was more likely. In the present work, both models of the aggregate were again considered. Unlike the aggregate seen in hexane,[17] the head-to-head (oligomeric) model is clearly incompatible with the observed shifts (cf. the Chl *b* complexation shifts[12]), but the head-to-tail model proposed for the dimer gave sufficiently good agreement for the positional coordinates of the dimer to be refined on the basis of the observed shifts. Two different head-to-tail models were compatible with the observed shifts for the dimer, a face-to-face model (Figure 3A) and a "piggy-back"[12] model (Figure 3B); the calculated shifts for each are given in Table I. In the dimer both magnesium atoms are coordinated to the C-2 hydroxyl of the adjacent molecule, and the separation between the parallel macrocyclic planes is ca. 3.5 Å, with Mg–O distances of ca. 2.6 Å. In both models (Figure 3A,B) the observed nonequivalence in the proton spectra is accurately reproduced in the calculated complexation shifts (e.g., Table I).

(15) Full details of these extensive experiments will be described elsewhere.

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Photoreactivities of *o*-Alkoxy- and *o*-*tert*-Butylphenyl Ketones: A Dramatic Example of Conformational Inversion of Selectivity

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Alkoxy radicals abstract hydrogen atoms from ethers far more rapidly than from alkanes because the resulting α-alkoxy radicals

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are stabilized by conjugation with a lone pair on oxygen.[1,2] Comparable selectivity is expected for n,π* triplet ketones[3] and indeed is evident in some intramolecular hydrogen-abstraction reactions.[4] We now report that both *o-tert*-butylbenzophenone (*o-t*-BuBP) and *o*-methoxybenzophenone (*o*-MeOBP) undergo efficient photoinduced δ-hydrogen abstraction to produce benzocyclopentenols, as would have been anticipated from reports on more heavily substituted analogues.[5,6] What could not have been anticipated is that the *tert*-butyl ketone triplet reacts over 1000 times more rapidly than the methoxy ketone triplet at room temperature. This situation represents an unprecedented reversal of selectivity due to conformational factors: the methoxy ketone is less reactive and the *tert*-butyl ketone far more reactive than expected from the acyclic examples.[4]

We have studied both compounds by a combination of laser-flash and steady-state techniques. Irradiation of *o-t*-BuBP over a wide range of temperatures and in several solvents furnishes 3,3-dimethyl-1-phenyl-1-indanol (2) quantitatively. The quantum
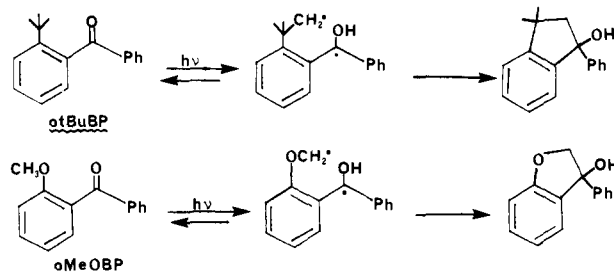

efficiency varies from 0.08 in hexane to 1 in methanol. The reaction is quenched inefficiently by conjugated dienes, $k_q\tau = 2.3$ M^{-1} in hexane and 11 M^{-1} in methanol. Laser-flash excitation[7] of alcohol solutions held at temperatures from –100 to 25 °C reveals a transient with a temperature-independent lifetime of 43 ± 3 ns and an absorption profile consistent with an alkyl ketyl biradical (λ_{max} at 470, 320 nm).[8] No triplet transient could be observed at room temperature. However, a triplet was clearly observable (λ_{max} at 325, 510, ~700 nm) in an ethanol–methanol mixture between –90 and –130 °C, with lifetimes ranging from 8 to 60 ns. Extrapolation of the measured Arrhenius parameters ($\log A = 11$, $E_a = 2.34$ kcal/mol) indicates a rate constant for δ-hydrogen abstraction of 2×10^9 s^{-1} at 25 °C. The quenching results suggest an even greater value in hydrocarbon solvents.

Steady-state irradiation of *o*-MeOBP in nonphotoreducing solvents at room temperature produces 3-phenyl-3-hydroxy-2,3-dihydrobenzofuran quantitatively, with a quantum yield of 0.35 in benzene. Stern–Volmer quenching with dienes yielded a $k_q\tau$ value of 2600 M^{-1}. Laser excitation did not produce a detectable biradical transient;[9] but the long-lived triplet indicated by product quenching is readily discernible (λ_{max} at 525 nm) from –84 to 70 °C. At room temperature, $1/\tau = 9 \times 10^5$ s^{-1} in benzene ($\log A = 9.9$, $E_a = 5.63$ kcal/mol) and 6×10^6 s^{-1} in methanol ($\log A = 8.5$, $E_a = 2.40$ kcal/mol).

Triplet *o-t*-BuBP undergoes δ-hydrogen abstraction some 1000 times faster than does *o*-MeOBP. This finding explains O'Connell's brief report that 2-methoxy-4,6-di-*tert*-butylbenzophenone

Scheme I
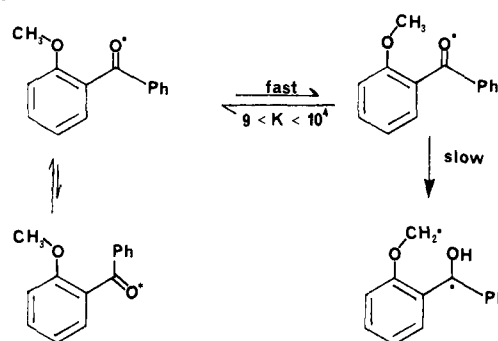
(4) photocyclizes to 2-methoxy-4-*tert*-butyl-2.[6] His finding did not show that internal hydrogen abstraction from an *o-tert*-butyl is intrinsically faster than from an *o*-methoxy, since the ring rotation caused by the *tert*-butyl group keeps the methoxy group in 4 farther than bonding distance from the carbonyl.[6]

Noting the 6/1 selectivity reported for alkoxy radicals toward anisole/*tert*-butylbenzene[1] and the close parallel between alkoxy radicals and n,π* ketone triplets,[10,11] we conclude that these two intramolecular triplet-state δ-hydrogen-abstraction reactions show a 10 000-fold inversion of C–H bond selectivity relative to the intrinsic values for conformationally unrestricted systems. Cyclic systems such as these normally display *enhanced* intramolecular reactivities because high populations of reactive conformers are possible in molecules with few freely rotating bonds.[12] Such obviously is the case for *o-t*-BuBP, which has a C–H bond close to the carbonyl in all reasonable conformations, unlike the unreactive acrylic analogue γ,γ-dimethylvalerophenone ($k_H < 10^6$ s^{-1}).[4] *o*-MeOBP, on the other hand, is *less* reactive than a comparable acyclic compound, β-ethoxypropiophenone ($k_H = 3 \times 10^7$ s^{-1}).[4]

The Arrhenius parameters for δ-hydrogen abstraction are intriguing. *o-t*-BuBP has a higher A factor than *o*-MeOBP, but much of its enhanced reactivity comes from a low E_a value. We believe that the relatively low reactivity of triplet *o*-MeOBP is caused primarily by an equilibrium constant for rotation about the phenyl–methoxy C–O bond which greatly favors an unreactive conformation. Inasmuch as the ether lone pair is conjugated with the benzene ring, the methyl group apparently is held predominantly anti to the *o*-acyl group. The greater reactivity in methanol relative to benzene probably reflects how solvation of the methoxy group changes the rotational equilibrium. We have confirmed that this particular bond rotation is involved by a series of structural modifications. In particular, 2,6-dibenzoylanisole also undergoes photocyclization in high quantum yield (0.77 in benzene) and with a triplet reactivity 9 times greater than that of *o*-MeOBP. This diketone cannot exist in any conformation with the methyl hydrogens farther than bonding distance from a carbonyl oxygen. Scheme I displays the conformational equilibrium believed to control triplet-state reactivity.

The tremendous difference in triplet reactivities of *o-t*-BuBP and *o*-MeOBP, in a direction opposite to expectations, is important not only because it is unprecedented. It means that the presence of an *o*-alkoxy group probably will not interfere with other potentially useful photochemical reactions. Thus *o*-(benzyloxy)-valerophenone undergoes type II cleavage and cyclization quantitatively.

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