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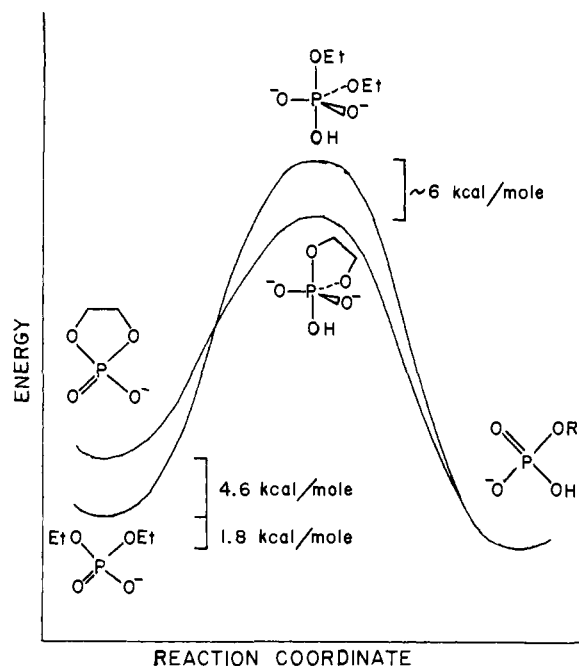*Riverside, California 92521*
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Figure 1. Reaction profiles for $^-$OH-catalyzed hydrolysis of diethyl phosphate, **1**, and ethylene phosphate, **2**. Figure taken from ref 4.

Stereoelectronic Effects in the Hydrolysis of Cyclic Five-Membered-Ring Phosphate Esters. Ab Initio and CNDO Molecular Orbital Calculations on Alkyloxyphosphoranes

Sir:

Strained cyclic five-membered-ring phosphate esters react 10^6- to 10^8-fold faster than their acyclic counterparts.[2,3] Westheimer and coworkers[2] proposed that this rate acceleration was due to relief of ring strain in the five-membered rings. However, as pointed out by Gerlt et al.,[4] the energy released in a strained cyclic ester in going to a "strain-free" cyclic phosphorane transition state is insufficient to explain the total activation energy lowering. As shown[4] in Figure 1 for hydrolysis of ethylene phosphate, **1**, and diethyl phosphate, **2**, the strain energy only accounts for 4–5 kcal/mol of the 10-kcal/mol difference in activation energies between the cyclic and acyclic reactions. Nearly 6 kcal/mol *extra* stabilization of the cyclic vs. the acyclic transition states is unaccounted for by strain theory arguments alone. We wish to propose in this communication that a significant fraction of this 6-kcal/mol difference comes from orbital stereoelectronic effects in the trigonal bipyramid transition states.

Molecular orbital calculations were performed on various conformational isomers of the trigonal bipyramidal, neutral, and dianionic dimethoxyphosphoranes **3** and **4** (Figure 2). Semiempirical CNDO/2 calculations[5] on **3** used idealized geometries based upon x-ray crystallographic structures of appropriate molecules while partial geometry optimization was performed on **4** using the ab initio programs Gaussian 70[6] and a minimal STO-3G basis set.[7] The overlap populations[8] for the axial $P-OCH_3$ bond obtained in these calculations are shown in Figure 2. As has been previously pointed out for tetracoordinated carbon and phosphorus species the dependence of the overlap populations on conformation about ester bonds derives from an "anomeric"-type effect: an interaction of a trans-antiperiplanar (app) oxygen lone pair with the antibonding orbital on the adjacent bond.[9-12] This anomeric effect strengthens the bond with the oxygen atom bearing the app lone pair and in turn weakens the bond adjacent to the bond

Table I. Summary of Overlap Population Changes in Structures **3a–e**.

A. app Interactions Leading to Bond Weakening

	$3a^a$	$3b^a$	$3c^a$
Conformation about $P-O_eR$	spp	g	t
No. of lone pairs app to $P-O_aR$	$(2)^b$	1	0
Net overlap population change	-0.031	-0.020	0

B. app Interactions Leading to Bond Strengthening

	$3e^c$	$3d^c$	$3c^c$
Conformation about $P-O_aR$	g	spp	t
No. of lone pairs app to $P-O_eR$	1	$(2)^a$	0
Net overlap population change	0	-0.007	-0.01

^{a} Trans apical ester bond. ^{b} Partial app lone pairs. See footnote 14. ^{c} Trans equatorial ester bond.

containing the lone pair (we assume overlap population changes reflect relative bond strengths[9]).

An analysis of the overlap population changes for the axial ester bonds in the neutral phosphoranes, **3**, is presented in Table I. The equatorial ester oxygen in the g_e,t_a conformation, **3b** (see Figure 1 for definition of symbols), has one lone pair app to the axial $P-OCH_3$ bond, leading to a reduction (relative to the t_e,t_a conformation, **3c**) of 0.020 e in the axial $P-OCH_3$ overlap population. By contrast, the apical ester oxygen atom in the t_e,g_a conformation, **3e**, has one lone pair app to the equatorial ester bond, resulting in an increase (relative to the t_e,t_a conformation, **3c**) of 0.01 e in the *axial* $P-OCH_3$ overlap population. The ab initio calculations on **4a–c** demonstrate similar sensitivity of the bond overlap populations to the ester torsional conformations.[13]

To a first approximation these differential effects are only sensitive to the torsional conformation of the bond app to the lone pair. Thus, the additional app lone pair on the equatorial ester oxygen in **3b** (g_e,t_a) vs. **3c** (t_e,t_a) leads to a decrease of
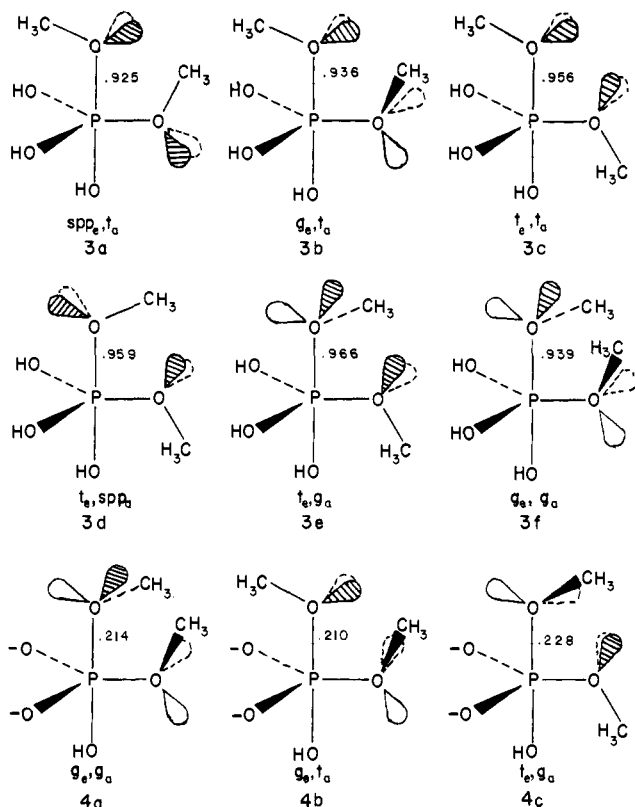
Figure 2. Structures and overlap populations for phosphoranes **3** and **4**. Structures are identified by the torsional conformations about the equatorial (e) ester bond and the apical (a) ester bond. Torsional conformations about the bonds are defined by the MeOPOMe structural fragment and are either trans (t), gauche (g), or synperiplanar (spp). Details of the structures and energies will be published in a full paper and are available upon request.

0.020 e in the axial trans bond overlap population. The additional app lone pair on the equatorial ester oxygen in **3f** (g_c,g_a) vs. **3e** (t_e,g_a) leads to a decrease of 0.027 e in the overlap population of the gauche axial bond. Assuming then that the apical and equatorial bond app lone pair interactions operate independently, we can use the data in Table I to calculate the overlap population changes for structures not previously calculated. Specifically, the synperiplanar$_e$, synperiplanar$_a$ (spp$_e$,spp$_a$) conformation should show an overlap population reduction in the axial ester bond of ~0.038 e (−0.031–0.007). This bond would be weaker than that in any other conformation except for the spp$_e$,t$_a$ (apical overlap population difference, −0.041 e).

While for acyclic dialkoxyphosphoranes the spp$_c$,spp$_a$ conformation, of course, is sterically inaccessable, it should be the lowest energy conformation of the transition state in the hydrolysis of the five-membered cyclic phosphates (Figure 1, ethylene phosphate transition state). One might not have anticipated this stereoelectronic, apical bond weakening in the cyclic transition state since the two lone pairs on the apical ester oxygen are partially[14] app to the equatorial ester bond (and hence *strengthen* the apical bond) while the two lone pairs on the equatorial ester oxygen are partially app to the axial ester bond (and hence weaken the apical bond). That a substantial *net* bond weakening results for the apical bond is presumably due to the longer apical bond and the simple fact that these bond-weakening effects are larger than the bond-strengthening effects.[15a]

We propose, therefore, that these stereoelectronic effects[15b] are responsible for a significant fraction of the 6-kcal/mol extra stabilization of the cyclic ester vs. acyclic ester transition states shown in Figure 1. It is extremely significant and supportive

of our hypothesis that much of the kinetic acceleration in the hydrolysis of five-membered cyclic ester is entropically derived. Thus, the five-membered cyclic esters show entropies of activation often nearly 18 eu more positive than their acyclic counterparts.[3,16] Note that only a few of the many possible conformations possess the proper app lone pair interactions, and it is quite reasonable that the lowest energy reaction path for the acyclic esters should have a transition state resembling the spp$_e$,t$_a$ structure **3a**. This, of course, essentially requires "freezing" two rotational degrees of freedom about the acyclic ester bonds. The cyclic ester is already "frozen" in the proper lowest-energy conformation, and the 18-eu (or 5.4-kcal/mol) extra stabilization of the cyclic ester must reflect this difference. If the very negative entropy of activation (−34 to −38 eu) for these acyclic esters (values similar to those found in highly rigid transition states such as concerted Diels–Alder reactions[17]), arises from immobilization of freely rotating ester bonds;[18] then, to balance this entropic disadvantage, the enthalpic, stereoelectronic advantages to these reactions must be quite substantial indeed.[19,20]

References and Notes

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(13) These smaller overlap populations in the ab initio calculation are due in part to the minimal basis set used (sp on phosphorus), in contrast to the spd functions used in the CNDO calculations. CNDO calculations using an sp basis set show overlap populations in between those derived from the spd–CNDO and ab initio calculations.
(14) Actually both are anticlinal (120°) to the adjacent ester bond. From Table I it appears that two "partial" app lone pair interactions perturb the overlap populations slightly more than a single "pure" app interaction.
(15) (a) The overlap population changes for the basal bonds in **3c**, **3d**, and **3e** are 1.279, 1.262, and 1.268, respectively. Note that we ignore the substantial lone pair app interactions with the phosphoryl bonds (see ref 7a). (b) The validity of the application of quantum mechanical calculations for isolated molecules in the gas phase to reactions in aqueous solution has been properly raised by a referee. We must agree that solvation forces and certainly the inexact level of these calculations could make any comparison with experiment a fruitless exercise. However, the recent history of molecular orbital, particularly ab initio, calculations suggests meaningful comparisons may often be properly made between "paper" and "wet" chemistry. Note that the ab initio calculations discussed by Lehn for tetrahedral carbon species[9b] are substantiated by the experimental work of Deslongchamps.[19] Apparently solvation effects do not obscure Lehn's results (and hopefully ours as well).
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(19) See P. Deslongchamps, *Tetrahedron*, **31**, 2463 (1975), for remarkable experimental evidence for stereoelectronic control in the reactions of tetrahedral carbon species.
(20) We have recently tested our predictions by studying the kinetics of the hydroxide-catalyzed hydrolysis of the two epimeric phosphate triesters. In agreement with the app long pair stereoelectronic theory, isomer **6** with
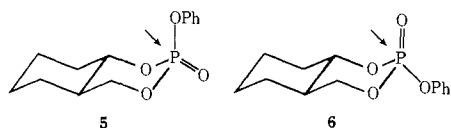
the equatorial phenoxide leaving group, hydrolyzes considerably faster than isomer **5**. Since addition of −OH is rate limiting, the two app long pairs on the endocyclic ester oxygens require hydroxide attack from the top side of both isomers. This will force an O⁻ into an apical position of the trigonal bipyramid intermediate in **5**. Since this is unfavorable according to pseudorotation theory, isomer **6** is the more reactive although sterically isomer **5** should be the more reactive for attack from the bottom side in an "in-line" mechanism (Unpublished work, D. G. Gorenstein and J. B. Findlay).

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Figure 1. The proton chemical shifts for a 10^{-3} M solution of diester **2** in 10% pyridine-d_5 in benzene-d_6 solution, δ (ppm), and in D_2O saturated benzene-d_6 solution, (δ (ppm)).

A Synthetic Biomimetic Model of Special Pair Bacteriochlorophyll a

Sir:

Evidence relating to the molecular organization of chlorophyll in the photoreaction centers of both green plants and photosynthetic bacteria strongly suggests that special pairs of chlorophyll molecules are oxidized in the primary light conversion event in photosynthesis.[1-4] Satisfactory models for green plant photoreaction center special pair chlorophylls have been successfully prepared by the synthesis of covalently bound, dimeric derivatives of pyrochlorophyll a[5] and chlorophyll a (Chl a).[6] These linked dimers, when dissolved at room temperature in nonnucleophilic solvents containing an excess of water or alcohol, assume a folded conformation which has optical properties very similar to photoreaction center P700 chlorophyll in plants. Moreover, the oxidized linked dimeric derivative of chlorophyll a in its folded conformation gives an ESR signal closely resembling that of P700⁺·.[6-9]

We now report the synthesis of a model for special pair bacteriochlorophyll a (Bchl a) in photosynthetic bacteria, the dimeric ethylene glycol diester of bacteriochlorophyllide a, **2**. The well-known reactivity of the Bchl a ring system required the development of a synthetic scheme differing substantially from that previously employed in the synthesis of Chl a linked dimers.[10] Bchl a, obtained from *R. spheroides*, was treated with trifluoroacetic acid to obtain bacteriopheophorbide a (Bphide a), which was esterified at 25 °C with ethylene glycol using benzotriazole *N*-methanesulfonate and Et₃N in dry THF.[11] The glycol monoester was coupled with an equivalent of Bphide a using the same esterification method, but substituting 4-dimethylaminopyridine as the base and CH_2Cl_2 as the solvent. The diester **1**, obtained in 30% overall yield based on Bchl a, exhibited a mass spectrum (*m/e* 1246, M⁺), ¹H NMR, and electronic spectrum consistent with **1**. The reinsertion of the magnesium atoms was accomplished by a modification of the method of Eschenmoser to yield diester **2** (Figure 1).[12,13]

The electronic transition spectrum of **2** in nucleophilic solvents is indistinguishable from that of monomeric Bchl a recorded under identical conditions (Figure 2). Similarly, the ¹H NMR spectrum of **2** is consistent with the assigned spectrum of Bchl a,[14] except that the phytyl resonances are replaced by a sharp singlet at δ 4.00 assigned to the glycol protons (Figure 1). The electronic transition spectrum of 10^{-5} M covalent dimer in dry benzene (Figure 2) displays an intense absorption at 780 nm and a shoulder at 812 nm, which are very similar to those observed for self-aggregated Bchl a.[15] The ¹H
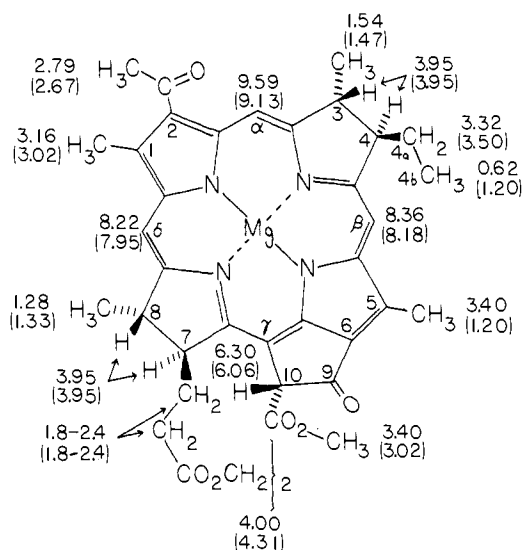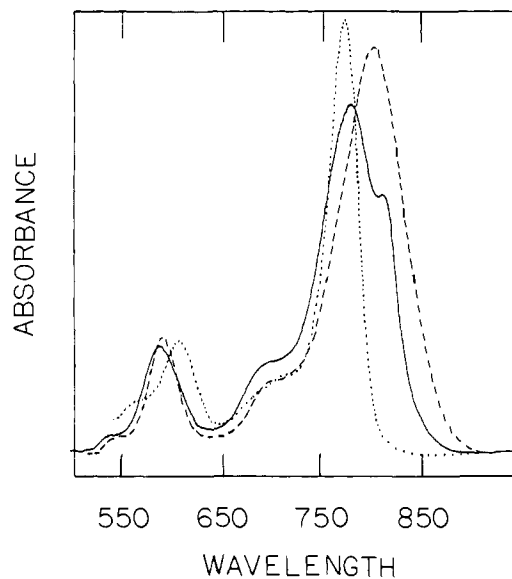
Figure 2. The electronic transition spectrum of a 10^{-5} M solution of diester **2** in 10% pyridine in benzene (·····), in dry benzene (—), and in water-saturated benzene (- - - -).

NMR spectrum of a 10^{-3} M solution of **2** in dry benzene displays severely broadened resonances, as is typical of anhydrous aggregated chlorophylls.[16]

When the benzene solution of **2** is saturated with water, the absorption maximum at 780 nm is replaced by a broad band centered at 803 nm (Figure 2).[17] This change is accompanied by a sharpening of the ¹H NMR lines, yielding a spectrum indicative of a single macrocyclic species in the solution. A comparison between the two sets of chemical shifts given in schematic form in Figure 1 reveals that several resonances of **2** in the water-saturated solution are substantially shifted from their respective positions in the fully disaggregated species. These chemical shift changes closely parallel those observed by Boxer and Closs in the pyrochlorophyll linked dimer.[5] Since **2** displays only one set of resonances in the wet benzene solution, the two rings of the dimer must be equivalent on the ¹H NMR time scale. The 5-methyl group and the 10 proton experience substantial upfield shifts, 2.20 and 0.24 ppm, respectively, while the 4b methyl group shifts downfield 0.58 ppm. The methyl resonance of the acetyl groups shifts very