Table I. 32.1-MHz ^{11}B NMR Data (Toluene-d_8)

Compd	Rel area	δ^a	J_{B-H_t}, Hz^b
I	2	44.4	145
	2	8.2	146
	1	−53.0	140
II		5.1	145

^{a} Parts per million relative to BF$_3$·O(C$_2$H$_5$)$_2$, with positive sign indicating shift to lower field. ^{b} All signals were observed as doublets in the undecoupled spectra, and as singlets in the ^{1}H-decoupled spectra.

Table II. 100-MHz ^{1}H NMR Data (Toluene-d_8)

Compd	δ^a	Multiplicity (J, Hz)	Rel area	Assignment
I	4.04	Singlet	5	C$_5$H$_5$
	6.96	Quartet (147)	2	H$_t$-B
	3.86	Quartet (153)	2	H$_t$-B
	−0.55	Quartet (141)	1	H$_t$-B
	−1.70	Broad singlet	2	B-H-B
	−2.33	Broad singlet	1	B-H-B
	−15.99	Quartet (70)	2	Fe-H-B
II	4.23	Singlet	1	C$_5$H$_5$
	3.50	Singlet^b	1	H$_t$-B
	−4.52	Broad singlet	1	B-H-B

^{a} Parts per million relative to (CH$_3$)$_4$Si, with positive sign indicating shift to lower field. ^{b} Measured from ^{11}B-decoupled spectrum.

spectrum (calcd for ^{56}Fe^{11}B$_5$^{12}C$_5$^{1}H$_{16}$$^+$ (M + 1 peak), 187.1067; found, 187.1062), the undecoupled and proton-decoupled ^{11}B Fourier transform NMR spectra (Table I), and the undecoupled and ^{11}B-decoupled proton NMR spectra (Table II), which confirm the presence of five B-H$_{terminal}$ units and five bridging hydrogen atoms. The high-field ^{1}H NMR signal of two of the bridging hydrogen atoms is consistent with the presence of two Fe-H-B bridge groups. The assigned nido geometry is in agreement with these data as well as with the presence of 16 skeletal valence electrons (1 from (C$_5$H$_5$)Fe, 1 from each H bridge, and 2 from each BH unit) in a 6-vertex framework, corresponding to a [2n + 4]-electron system.[2]

Since I is isoelectronic with ferrocene, it was of interest to attempt the thermal rearrangement of I to the 1-(η^5-C$_5$H$_5$)-FeB$_5$H$_{10}$ isomer (II) in which iron occupies the apex position in the FeB$_5$ pyramid, corresponding to ferrocene with one C$_5$H$_5$$^-$ ligand replaced by B$_5$H$_{10}$$^-$. Precedent for a metalloborane rearrangement of this kind was given by the thermal conversion[1a,b] of the square pyramidal species 2-(η^5-C$_5$H$_5$)-CoB$_4$H$_8$ to the 1 isomer, in which cobalt moves from a basal to an apical location. In the present system, the isomerization of I to II was conducted by heating a 20-mg sample without solvent in a sealed tube at 175 °C, which in 20.5 h resulted in the isomerization of approximately a third of the sample as measured by NMR. The mixture was placed in toluene-d_8 and heated for 70 h at 175 °C and 5 h at 180 °C with periodic monitoring by ^{1}H NMR, producing essentially complete conversion to isomer II together with small amounts of insoluble decomposition products.

The proposed structure of II (Figure 1) is supported by its NMR spectra as given in Tables I and II. The observation of only one boron environment, and of single B-H$_{terminal}$ and B-H-B resonances, virtually establishes the structure shown. Compound II represents the first known complex containing a cyclic B$_5$ ligand, although the planar C$_2$B$_3$H$_7$$^{2-}$ and C$_2$B$_3$H$_5$$^{4-}$ ligands are found in such species as (η^5-C$_5$H$_5$)-CoC$_2$B$_3$H$_7$,[3] (CO)$_3$FeC$_2$B$_3$H$_7$,[4] and 1,7,2,3- and 1,7,2,4-(η^5-C$_5$H$_5$)$_2$Co$_2$C$_2$B$_3$H$_5$;[3,5] the last three stuctures mentioned have been confirmed by x-ray studies.[5a,6,7] Examples are also known of transition metals pentacoordinated to a B$_5$ ring which is part of a larger borane ligand, as in the (η^5-C$_5$H$_5$)NiB$_{11}$H$_{11}$$^-$

ion.[8] Both I and II may be viewed as analogues of B$_6$H$_{10}$ with a (η^5-C$_5$H$_5$)FeH group replacing a basal or apical BH unit, and are similarly related to the known species (CO)$_3$FeB$_5$H$_0$.[9] At the same time, the metallocene-like sandwich structure of II suggests the trivial name "pentaboraferrocene". These complexes further illustrate the structural and electronic relationship which is currently emerging between the borane and metallocene classes,[2a,5c,10] in much the same manner that the recently reported Co$_3$B$_3$, Co$_3$B$_4$, and Co$_4$B$_4$ metalloboron clusters[1] tend to bridge the gap between the metal clusters and the polyhedral boranes. Systematic studies of their chemistry should help define more clearly the nature and extent of these analogies.

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Green Plant Photosynthesis. Upconversion or Not?

Sir:

Franck[1] suggested an uphill conversion model for photosynthesis to explain the enhancement[2] of O$_2$ evolution in far red (system I wavelength region) light by red light (system II region) (also see ref 3–5). In this model, one light quantum raised the chlorophyll a molecule to a singlet which, by intersystem crossing, formed a triplet state. The second quantum, then, raised it to a higher triplet level, from where photochemistry took place. This hypothesis was soon abandoned because the interaction of two pigment systems required 6,7 chemical intermediates (quinones, cytochrome f and plastocyanin) and, therefore, such a physical cooperation of two light quanta is untenable. Recently, Fong[8-10] has proposed that such an uphill conversion (e.g., "upconversion") to a higher state (which he calls charge transfer, CT, state) operates in both pigment systems I and II. His scheme[11] is as follows.

$$2S_0 + 2h\nu \rightarrow 2S_1 \qquad (1)$$

where S_0 = ground state, S_1 = first singlet excited state, and $h\nu$ = light quantum.
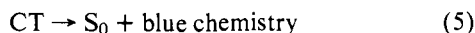
$$S_1 \rightarrow T_0 \qquad (2)$$

where T_0 (first triplet state) is produced by intersystem crossing followed by upconversion to a charge transfer state.

$$S_1 + T_0 \rightarrow S_0 + CT \qquad (3)$$

If plants have already received light, they are present in T_0 state and, if we do not count these photons, then there is a cycling between T_0 and S_1 by a one-photon process.

$$CT \rightarrow S_1 + \text{red chemistry} \qquad (4)$$

or

$$CT \rightarrow S_0 + \text{blue chemistry} \qquad (5)$$
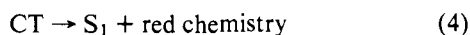
In completely dark-adapted plants, Fong's theory predicts (1) oxidation of reaction center chlorophyll a of pigment system I, P700 to $P700^+$, to require two quanta; and (2) quantum requirement of O_2 evolution in photosynthesis, which requires transfer of 4 electrons from $2H_2O$ and proceeds via two light reactions for the reduction of pyridine nucleotide ($NADP^+$), to have a minimum value of 16 quanta; this is due to upconversion in system II four times (4 electron transfers with 2 quanta each, requiring 8 quanta) plus upconversion in system I (4 electron transfers with two quanta each). Alternatively Fong[11] suggests that, perhaps, only one of the two systems operates by eq 5. This would require a minimum number of 12 quanta for the evolution of one O_2 molecule. We also have to remember that cyclic photophosphorylation (around system I) may also occur in vivo (see, e.g., Bedell and Govindjee[12]) and this places additional quantum requirements. The value of 16 may have to be increased by, say, e.g., 2 quanta, and that of 12 also by 2 quanta.

The present communication examines the upconversion model and arguments of Fong[11] on the basis of (a) the experimental *minimum* quantum requirement of O_2 evolution; and (b) the recent observations of Warden[13] on the ESR signal due to $P700^+$ in dark-adapted chloroplasts exposed to red light. It is concluded here that there is no experimental evidence which supports the upconversion theory in its present form.

A. Minimum Quantum Requirement. Measurements on minimum quantum requirement (or maximum quantum yield) on young synchronously grown cells of green alga *Chlorella* have given a value of 8 quanta/O_2 (Govindjee et al.[14]). A value of 10 quanta/O_2 is, however, usual in nonsynchronously grown cells (Emerson and Lewis;[15] also see Emerson[4]); cyclic phosphorylation may occur in vivo.[12] *Only a minimum value of quantum requirement, when cyclic photophosphorylation may not be significant, is meaningful.* One can always obtain a higher quantum requirement when inactive cells or chloroplasts are used (see Rabinowitch[16]). Even gentle methods of preparation of chloroplasts lead to some inactivation as compared to their status in vivo. There is never any problem in attaining a higher quantum requirement because of the lability of O_2 evolving "enzyme" (Cheniae[17]), or due to the possible presence of inactive chlorophyll molecules (unconnected to photosynthetic units; see ref 18a and 18b). Thus, Fong, who cites a recent measurement of quantum requirement in the 10–12 range (Arnon[19]) is not justified[29] in believing that this data unequivocally supports his upconversion theory. The 8 quanta requirement (*minimum*) which may also be increased to give a 10 quanta requirement (when cyclic phosphorylation may occur) is *not* consistent with Fong's theory. Rather one would have to consistently obtain minimum values of more than 16 quanta (for upconversion in both systems) and more than 12 quanta (for upconversion in one system only) in active algal cells or in intact chloroplasts prepared from young active leaves of higher plants. This has never been demonstrated; in fact, the most thoroughly made measurements[14] on active algal cells contradict this. Measurements on intact chloroplasts gave quantum yields which were 40% of that in active *Chlorella* cells (see Rabinowitch and Govindjee[20a]). Chloroplast preparations usually have higher quantum requirements due to damage during preparative methods.[20b]

B. ESR Signal from $P700^+$. Intensity and Flash Dependence. ESR measurements on fully dark-adapted chloroplast and subchloroplast samples indicate that the first flash (in a series of nonsaturating, weak 200-ns actinic flashes) is *sufficient* to induce P700 oxidation (Warden[13]). These data are in contrast to the prediction of the upconversion hypothesis that photooxidation of P700 should only be effective on the second flash. Furthermore, in contradiction with the assertion by Fong[11] (cf. Note Added in Proof[11]), "blue chemistry" (e.g., $2S_1 \rightarrow S_0$ (~3.6 eV)) would be extremely unlikely as indicated by recent quantum yield measurements.[21] A range of actinic flash intensities was chosen by Warden[13] to eliminate the possibility of biphotonic processes at the reaction center. The minimum intensity used had $\sim10^{11}$ photons per flash. For a sample having a chlorophyll content of 1 mg mL^{-1} and a chlorophyll:P700 ratio of 100 (e.g., in Triton-subchloroplast fragment 1), and for an ESR sample tube volume of 0.2 mL, a simple calculation indicates that during the flash there are $\sim10^4$ P700 traps for every photon absorbed. Clearly, the possibility of a two-photon process per trap in these experiments was vanishingly small. Thus, Warden's experiments contradict the predictions of the hypothesis.

The operation of a two-photon pump (eq 5) in photosystem 1 of green plants or in photosynthetic bacteria, as proposed by Fong,[11] necessitates efficient singlet–triplet annihilation at the reaction center.[22,23] Thus, via this formalism the rate-limiting step in photochemistry of the reaction center is implicitly the intersystem crossing process ($S_1 \rightarrow T_0$). Hence, to permit photooxidation to proceed efficiently in the picosecond time domain, as is observed in bacterial reaction centers ($\tau \leq 6$ ps),[24] an intersystem crossing rate of the order of 10^{12}–10^{13} s^{-1} is required. However, the intersystem crossing rates observed for chlorophyll a in vitro are on the order of 1.3×10^6 s^{-1},[25] a factor of 10^6 smaller than required for in vivo S–T mediated photoconversion. Furthermore the existence of such rapid (10^{12} s^{-1}) spin-forbidden processes is without precedence. From these observations one can conclude that photooxidation of the reaction-center, chlorophyll dimer via S–T fusion is most unlikely.

All experiments with green plants are consistent with the general belief that photochemistry takes place from the singlet state,[26-28] and to our knowledge no experimental evidence supports the view that the triplet state of chlorophyll a is on the main path of photosynthesis in either photosynthetic bacteria or green plants.

In conclusion, the experimentally determined minimum quantum yields for photosynthesis not only do not support Fong's version[11] of upconversion, but contradict it. Fong's requirement for long-lived chlorophyll triplet-state participation is also incompatible with the experimental data. Unless new experimental evidence that supports it can be advanced, the upconversion hypothesis, in its present form, will remain speculative.

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(29) NOTE ADDED IN PROOF. The quantum requirement of 12, as measured by Arnon and coworkers,[19] is for *both* NADP$^+$ reduction (2NADPH) and ATP production (3ATP). We *do not* dispute these results. In fact NADP$^+$ can be reduced *without* ATP production with full operation of primary photochemistry, simply by uncoupling phosphorylation, and the minimum quantum requirement for the reduction of 2 molecules of NADP$^+$ (just noncyclic electron flow) is indeed much less than 12, and closer to 8.

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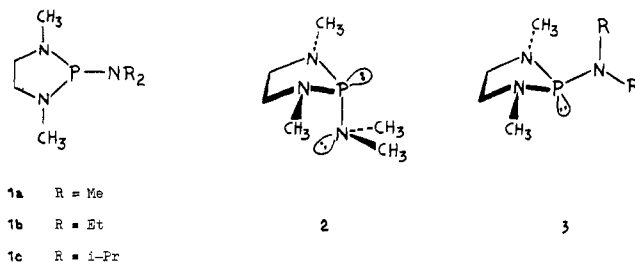*Rensselaer Polytechnic Institute, Troy, New York 12181*

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1a R = Me
1b R = Et
1c R = i-Pr

Conformations of Aminophosphines. 2-Dialkylamino-1,3-dimethyl-1,3,2-diazaphospholanes

Sir:

In a recent report[1] of ^{15}N NMR studies, Gray and Albright have on the basis of FPT calculations within the CNDO/2 approximation on ^{15}N–^{31}P coupling constants concluded that 2-dimethylamino-1,3-dimethyl-1,3,2-diazaphospholane (1a) should exist predominantly in a conformation (2) in which the exocyclic nitrogen is pyramidal and the lone-pair electrons are antiperiplanar to those of the adjacent tervalent phosphorus atom. This prompts us to communicate the results of low-temperature ^{13}C NMR studies on a series of 2-dialkylamino-1,3-dimethyl-1,3,2-diazaphospholanes (1a–c)[2] which conflict with the above interpretation.

The ambient-temperature, proton-decoupled ^{13}C NMR spectrum of 1c consists of a doublet from the ring methylene carbons (δ 57.22, $^2J_{PNC} = 8.8$ Hz), a doublet from the ring N-methyls (δ 34.54, $^2J_{PNC} = 23.6$ Hz), a doublet from the methine carbons attached to the exocyclic nitrogen (δ 45.02, $^2J_{PNC} = 9.3$ Hz), and a doublet from the isopropyl methyl carbons (δ 24.94, $^3J_{PNCC} = 8.0$ Hz). Unambiguous assignments were made on the basis of gated decoupled spectra in which $^1J_{CH}$ couplings of appropriate multiplicity for each of the various signals were observed. On lowering the probe temperature, a broadening of the two isopropyl signals was observed, and at -116 °C each had resolved into two components of equal intensity. The signals of the ring methylene carbons and N-methyl carbons remained essentially unchanged. The new isopropyl-methyl signals occurred at δ 21.75 ($^3J_{PNCC} \approx 0$Hz) at δ 27.75 ($^3J_{PNCC} = 12.6$ Hz), while the methine carbon signals occurred at δ 42.47 ($^2J_{PNC} = 26.0$ Hz) and at δ 46.83 ($^2J_{PNC} = -8.8$ Hz). We interpret these data to indicate that 1c has frozen into conformation 3 (R = i-Pr) in which the two isopropyl groups are contained in a mean plane perpendicular to the pseudoplane of the ring. Since the ring methyls remain equivalent, the exocyclic nitrogen is either planar or rapidly inverting throughout the temperature range studied. Apparently N–C rotation is still rapid. At -116 °C the rotation about the P–N bond must be slow with respect to the NMR time scale. Computer assisted analyses of the line shapes of the exchange-broadened isopropyl methine and methyl signals both gave $\Delta G^{\ddagger} = 10.1$ kcal/mol at -46 °C for the barrier to P–N rotation.

The very different $^2J_{PNC}$ (26.0 vs. -8.8) and $^3J_{PNCC}$ (12.6 vs. 0) for the two nonequivalent isopropyls further confirm the frozen ground-state conformation being 3 (R = i-Pr), since both ^2J and ^3J ^{31}P–^{13}C coupling constants have been shown to be markedly conformation dependent.[3-5] For the former, when the dihedral angle (ϕ) between the phosphorus lone pair and the carbon is $\sim$0 °C, a large positive coupling is expected (hence the methine carbon syn to the phosphorus lone pair has $^2J_{PNC} = 26.0$ Hz in 1c at -116 °C), but when $\phi \approx 180°$ a small (negative) coupling should be observed ($^2J_{PNC} = -8.8$ Hz for the *anti*-methine carbon in 1c).[4] The opposite sign of these couplings is required since the averaged coupling observed at ambient temperature (9.3 Hz) is equal within experimental error to $(26.0-8.8)/2$. A similar situation obtains for the isopropyl methyls, where the methyls approximately syn to the phosphorus lone pair exhibit a $^3J_{PNCC}$ of 12.6 Hz, while those anti to the phosphorus lone pair have $^3J_{PNCC}$ of approximately 0.[5]

We have also succeeded in freezing out P–N rotation in 1b where the signals from the ethyl carbons (at -50 °C, N-CH$_2$CH$_3$, δ 38.92, $^2J_{PNC} = 18.9$ Hz; N-CH$_2$CH$_3$, δ 15.31, $^3J_{PNCC} = 1.8$ Hz) are coalesced at -109 °C in CHCl$_2$F solution and separate into four sets of signals (syn-N-CH$_2$CH$_3$, δ 39.59, $^2J_{PNC} = 47.6$ Hz; $anti$-N-CH$_2$CH$_3$, δ 37.03, $^2J_{PNC} = -6.1$ Hz; N-CH$_2$CH$_3$ at δ 13.97 and at 15.96 with no coupling observed for $^3J_{PNCC}$ in either case) at -128 °C. In compound 1a the doublet for the dimethylamino methyls (δ 37.52, $^2J_{PNC} = 15.6$ Hz) observed under fast exchange conditions at -20 °C (CHClF$_2$ solution) collapsed at -120 °C, and at -138 °C a new doublet was apparent at δ 39.51 ($^2J_{PNC} \approx 43$ Hz). Unfortunately the second methyl signal was superimposed on the lower field component of the ring N-CH$_3$ doublet giving rise to a broad peak at δ 36.04 from which the coupling or exact chemical shift could not be determined. The above observations contradict the conformational proposals of Gray and Albright[1] for 1a, since the observation of non-