References and Notes

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Photoreduction of Tetraphenylporphyrins by Amines in the Visible. Photochemical Syntheses of Reduced Tetraphenylporphyrins and the Mechanism of Photoreduction

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Abstract: Irradiation of meso tetraphenylporphyrins with visible light in the presence of aliphatic amines leads to their photoreduction and chlorins and isobacteriochlorins are formed. 7-H,8-Amino substituted tetraphenylchlorins are obtained on photoreduction by tertiary amine, and the nonsubstituted tetraphenylchlorin and tetraphenylisobacteriochlorin are obtained on photoreduction by pyrrolidine. A hydroxy substituted chlorin, 7-hydro-8-hydroxytetraphenylchlorin, is obtained on chromatography of the amino-substituted chlorins. The photochemical syntheses of the compounds and some of their physical properties are described. ^{1}H NMR data indicate a gradual decrease in ring current in the order H$_2$TPP > H$_2$TPC > H$_2$TPB > H$_2$TP-*i*-B. The mechanism of the photoreduction is elucidated by the use of EPR and photochemical techniques. Porphyrin free radicals are formed in the primary photochemical reaction with all the amines used. The different stable reaction end products are formed in subsequent dark reactions.

Introduction

Synthetic porphyrin macrocycles and their metallo complexes are useful model compounds in physical–chemical studies vital to the understanding of the biological function of the natural porphyrins. Over a decade meso tetraphenylporphyrins (TPP) and octaethylporphyrins (OEP) have been popular model compounds in such studies owing to their relatively easy synthesis.[1]

Synthetically reduced porphyrins, i.e., chlorins and bacteriochlorins, more related to the chlorophylls and bacteriochlorophylls received less attention because of the difficulties encountered in their synthesis. The only synthetic procedure described in the literature for the preparation of the reduced derivatives of the porphyrin ring system is based on chemical reduction by the diimide precursor *p*-toluenesulfonylhydrazine.[2] This procedure has its own limitations: (a) in the synthesis of tetraphenylchlorin the final mixture contains a relative large amount (~38%) of tetraphenylbacteriochlorin and additional dehydrogenation with *o*-chloranil and selective extraction with phosphoric acid are required in order to improve the yield and purity of the product. (b) Free base isobacteriochlorin cannot be made directly by this method and has to be synthesized by way of the zinc complex.

An alternative and attractive route, the photoreduction of parent porphyrins, has been the subject of many studies, few of which proved to be of synthetic value. Photoreduction of water-soluble free base porphyrins with EDTA as reducing agent results in the production of the isomeric, less stable, phlorins[3] whereas photoreduction of ZnTPP by benzoin proceeds only with light absorbed by the benzoin, to a mixture of products.[4] Similar results have been reported on the photoreduction of Zn porphine,[5] and of protochlorophyll and some of its derivatives with ascorbic acid.[6] In these studies it was indicated that addition of amines to the reaction mixture causes a catalytic effect on the reaction rate.

Some success was obtained in the photoreduction of Sn(IV) and Ge(IV) OEP to the corresponding isobacteriochlorins with EDTA in acetic acid[7] and with SnCl$_2$·H$_2$O in pyridine.[8]

In recent years it has been found that many aromatic carbonyl compounds with low-lying π,π^* and charge-transfer triplet states which are not photoreduced by alcohols or hydrocarbons are photoreduced efficiently by amines which contain α hydrogen.[9,10] The proposed mechanism involves a rapid charge transfer interaction between the carbonyl compound excited state and the ground-state amine. More recently it was found that aromatic macrocycles having π-π^* configurations—unreactive in photoreduction processes via radi-

cal-like hydrogen abstraction from hydrocarbons and alcohols—also interact in their excited states with the amines through a mechanism similar to that of aromatic carbonyl compounds, leading to photoreduction products.[11-14]

In a previous paper[15] we have reported preliminary results on the direct photoreduction of free base tetraphenylporphyrins to chlorins by tertiary amines. We proposed a mechanism involving a charge-transfer interaction between the photoexcited porphyrin singlet and the amine which leads to the formation of the porphyrin free radicals detected by ESR.

In the present paper we report the photochemical synthesis of several reduced porphyrins in high yield and purity. Furthermore, the mechanism of the photochemical reaction and some physical properties of the products will be discussed.

Stable Products of Photoreduction. Figure 1 shows the structural formulas of the products which are obtained under different experimental conditions: (a) compound B-1, free base tetraphenylchlorin, H_2TPC, and compound D, free base tetraphenylisobacteriochlorin, $H_2TP-i-B$, by photoreduction of free base tetraphenylporphyrin, H_2TPP, with pyrrolidine; (b) compound B-2, 7-H,8-C(H)(CH_3)N(CH_2CH_3)_2 amino substituted tetraphenylchlorin by photoreduction of H_2TPP with triethylamine (Et_3N), and compound B-3, 7-H,8-C(H)(CH_2)_3NCH_3, by photoreduction with N-methylpyrrolidine (NMP); (c) compound B-4, 7-hydro-8-hydroxytetraphenylchlorin, obtained by chromatography of B-2 and B-3 on silica.

Photoreduction of H_2TPP by Tertiary Amines. In the photoreduction of H_2TPP by tertiary amines the major product is an amino-substituted chlorin. For photoreduction with Et_3N the ^{1}H NMR spectrum of the crude shows compound B-2 as the major product (~85%) and the nonsubstituted chlorin, compound B-1, as the minor product (~15%). This can be deduced from the ratio of the methylene protons of the reduced pyrroline ring which appears as a doublet (2 H) at 4.19 and 4.25 ppm whereas the corresponding protons of the nonsubstituted chlorin appear as a singlet (4 H) at 4.14 ppm. Separation of the products is achieved by column chromatography. The amino-substituted chlorins react with silica and tend to decompose, but 2-propanol reduces the retention time and prevents the decomposition partially.

The mass spectra of compounds B-2 and B-3 do not show molecular ion peaks as is encountered usually in mass spectra of tertiary amine compounds.[16] They show a pattern similar to that of 7,8-substituted chlorins, where the whole substituent is usually lost from the reduced ring and readily observed in the spectra.[17] The most significant peaks are at m/e 615 and 616, chlorin fragments, assigned to (M − 100) and (M − 99) for compound B-2 and to (M − 84) and (M − 85) for compound B-3, and the corresponding m/e 99, 100 and 84, 85 peaks of the amino chain fragments. Compounds B-2 and B-3 react with silica on the column to compound B-4. Compound B-3 decomposes more rapidly than compound B-2. Compound B-4 has a chlorin type optical spectrum with auxochromic shifts compared to spectra of other chlorins. Mass spectra of compound B-4 show a molecular peak at m/e 632. Other significant fragments are present at m/e 316 (M/2e), 555 (M − phenyl), and 614 (M+ of H_2TPP) formed by loss of an water molecule. These fragments are characteristic of electron-impact spectra of meso tetraphenylchlorins.[18] The assigned structures are confirmed by ^{1}H NMR spectra. For compound B-4 the hydroxyl proton, appearing as a doublet at 2.24 and 2.24 ppm (J_{CH-OH} = 1.5 Hz), disappears on addition of D_2O, owing to fast deuteration.

Photoreduction of H_2TPP by Pyrrolidine. Primary and secondary amines were found to be less effective in the photoreduction of H_2TPP. The secondary cyclic aliphatic pyrrolidine was found efficient enough to be used for synthetic purposes. Moreover, the photoreduction of H_2TPP by pyr-
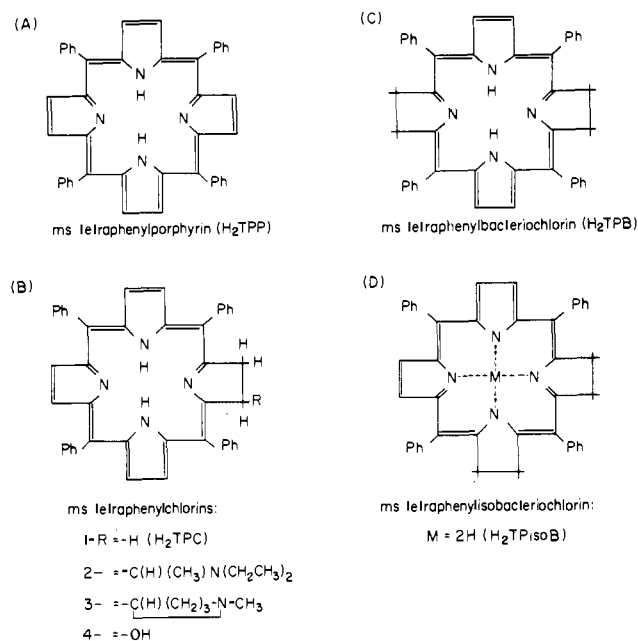

Figure 1. Structures of reduced meso tetraphenylporphyrins discussed in the paper.

rolidine is different from that by tertiary amines. It leads to the nonsubstituted free base tetraphenylchlorin, compound B-1 only, and adduct products are not formed. Continuation of the irradiation leads to further photoreduction of H_2TPC to compound D, free base tetraphenylisobacteriochlorin, $H_2TP-i-B$.

The ^{1}H NMR spectrum of the crude product of chlorin synthesis shows the typical ^{1}H NMR spectrum of H_2TPC characterized by the singlet at 4.14 ppm, assigned to the four methylene protons of the reduced pyrroline ring. Absence of a signal at 8.75 ppm, characteristic of β-pyrrole protons of H_2TPP, indicated that the photoreduction was complete.

The ^{1}H NMR spectrum of the product in the isobacteriochlorin synthesis shows a singlet for eight protons of reduced rings at 3.25 ppm. The ^{1}H NMR spectrum of $H_2TP-i-B$ has not been published previously. An AX system for the β-pyrrole protons, δA 7.36, δX 6.86 ppm, is strong evidence in favor of the assigned structure. Free base bacteriochlorin, H_2TPB, is not formed in the photoreduction, not even in traces. This is proved by complete absence of its characteristic absorption band, at 742 nm, in the optical spectrum.

Kinetics and Quantum Yields. Argon-saturated solutions of H_2TPP in benzene containing amine were irradiated with visible light $\lambda > 500$ nm and the absorption spectra before and after the irradiation were recorded.

The absorption spectra of irradiated solutions were found to be of the chlorin type for the amines: N-methylpyrrolidine, tri-n-butylamine, tri-n-octylamine, N,N-diethylcyclohexylamine, and triethylamine.

Initial rates of chlorin formation are summarized in Table I. The rates show dependence on the amine used in photoreduction, the cyclic aliphatic NMP being the most reactive and the straight-chain aliphatic Et_3N the least reactive. NMP and Et_3N were used in further studies as typical representatives.

Quantum yields and initial rates of chlorin formation in the photoreduction with Et_3N and NMP were measured using monochromatic light of 520 nm. Chlorin absorption bands were monitored at 656 nm for the photoreduction with Et_3N and at 654 nm for the photoreduction with NMP. The rates (Figure 2) increase linearly with amine concentration. A linear
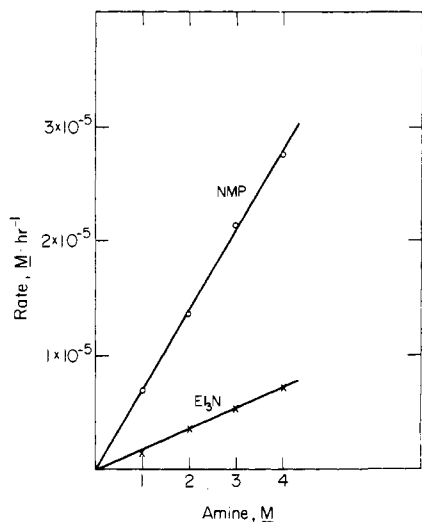
Figure 2. Dependence of rate of products formation on amine concentration (2×10^{-4} M H_2TPP in benzene at room temperature, irradiation wavelength 520 nm).
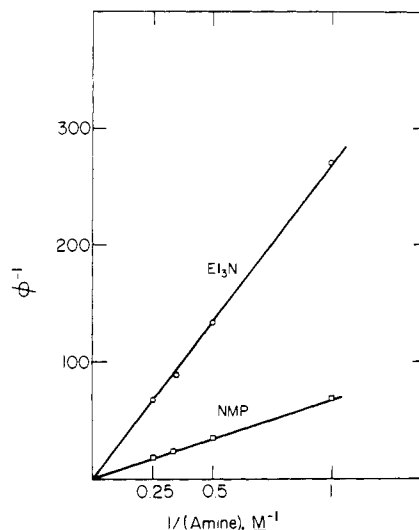

Figure 3. Plot of the reciprocal of the quantum yields vs. the reciprocal of amine concentration (2×10^{-4} M H_2TPP in benzene at room temperature, irradiation wavelength 520 nm).

Table I. First-Order Rates[a] of Chlorin Formation for 5×10^{-5} M H_2TPP and 1 M Tertiary Amine

amine	solvent	rate $\Delta OD^b/ \Delta t$, min^{-1}
N-methylpyrrolidine (NMP)	benzene	0.65
tri-n-octylamine	benzene	0.40
tri-n-butylamine	benzene	0.35
N,N-diethylcyclohexylamine	benzene	0.20
triethylamine (Et$_3$N)	benzene	0.15
NMP	benzene, O$_2$ satd	0.30
NMP	benzene–2-propanol (1:1)	0.20

[a] From initial slopes. [b] At λ 652 nm.

Table II. Quantum Yields of Chlorin Formation as a Function of Amine Concentration and Solvent for 2×10^{-4} M H_2TPP in Benzene at Room Temperature

amine, M	solvent	quantum yields $\times 10^3$
Et$_3$N, 1	benzene	3.5
2	benzene	7.5
3	benzene	11.3
4	benzene	14.8
2	benzene–2-propanol (1:1)	3.5
NMP, 1	benzene	15
2	benzene	29
3	benzene	45
4	benzene	56
2	benzene–2-propanol (1:1)	15

Figure 4. Dependence of rate of product formation on amine concentration for the photoreduction of H_2TPP by pyrrolidine (2×10^{-4} M H_2TPP in benzene at room temperature, irradiation at λ >500 nm).

plot (Figure 3) is obtained for the reciprocal of the quantum yield vs. the reciprocal of amine concentration.

Quantum yields and rates of chlorin formation with pyrrolidine are about one order of magnitude lower than those for the formation of the amino-substituted chlorins with tertiary amines. The rate of chlorin formation shows similar linear dependence on amine concentration as for the tertiary amines (Figure 4). A plot of H_2TPC formed vs. time of irradiation is
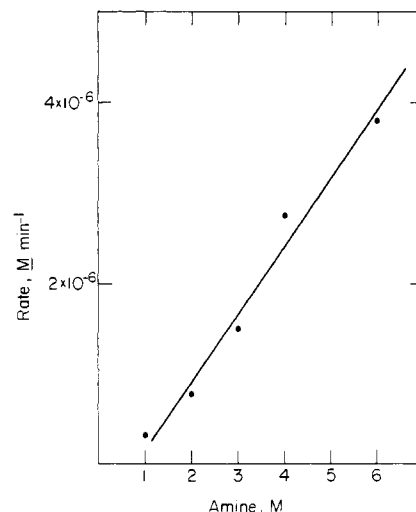
shown in Figure 5. A second product with a broad absorption band (λ_{max} ~695 nm) is formed here during irradiation and its characteristic kinetic behavior is shown in Figure 5. Its formation dependence on irradiation time indicates that this product is probably a light-sensitive intermediate. The broad absorption band in the near-IR region is characteristic of absorption spectra of porphyrin radical π-π dimers.[19]

Proton Magnetic Resonance Spectra. Valuable information concerning the structure and aromaticity of the reduced porphyrin compounds can be deduced from 90- and 270-MHz ^{1}H NMR spectra of these compounds. Chemical shifts of β-pyrrole protons and reduced ring protons are summarized in Table III.

Whereas in H_2TPP the β-pyrrole protons appear at 8.75 ppm, pyrrole protons in tetraphenylchlorins, in H_2TPB, and H_2TP-i-B are gradually shifted to higher field owing to a reduced ring current. For H_2TP-i-B these shifts are largest, indicating that the ring current is lower than in H_2TPB whereas the degree of the reduction is the same. The same effect is expressed in the chemical shifts of the reduced ring protons. In

Table III. Chemical Shifts[a] of β-Pyrrole Protons in H₂TPP and of β-Pyrrole Protons and Reduced Ring Protons in Reduced Tetraphenylporphyrins

compd, no.	β-pyrrole protons	reduced ring protons
H₂TPP,[b] A	8.75 s (8 H)	
H₂TPC,B-1	8.40 s (2 H); 8.56; 8.16 AX (4 H)	4.14 s (4 H)
H₂TPCC(H)(CH₃)-N(CH₂CH₃)₂, B-2	8.39 s (2 H); 8.56, 8.19 AX (4 H)	4.22 d (2 H), 5.10 m (1 H)
H₂TPC-C(H)(CH₂)₃N-CH₃, B-3	8.38 s (2 H); 8.56, 8.24 AX (4 H)	4.20 m (2 H), 5.06 m (1 H)
H₂TPCOH, B-4	8.46 s (2 H); 8.61, 8.32, 8.29 AX (4 H)	4.30 m (2 H), 6.37 (1 H)
H₂TPB, C	7.85 d (4 H)	3.92 s (8 H)
H₂TP-*i*-B, D	7.36, 6.86 AX (4 H)	3.25 s (8 H)

[a] In parts per million downfield from Me₄Si; s, singlet; d, doublet; AX, AX system; m, multiplet. [b] From ref 17. [c] From ref 2.

H₂TPC they appear at 4.14 ppm, in H₂TPB at 3.92 ppm, and in H₂TP-*i*-B at 3.25 ppm. Thus again in H₂TP-*i*-B the ring current is lowest indicating a low degree of aromaticity in this compound, relative to other reduced porphyrins. These observations are consistent with general aspects of the ring current model as applied to porphyrins and agree with similar observations on the reduced octaethylporphyrin derivatives.[20]

Chemical shifts of phenyl protons are summarized in Table IV.

The effect of reduced ring current is pronounced here also. In the H₂TPP ¹H NMR spectrum *o*-phenyl protons, closer to the ring, appear at 8.30 ppm, downfield from the meta and para protons which appear at 7.80 ppm. As a result of a decrease in the ring current, the *o*-phenyl protons appear gradually at higher field from H₂TPC to H₂TP-*i*-B, and in H₂TPB and H₂TP-*i*-B they are practically indistinguishable from the meta and para protons. An interesting experimental fact is observed in the H₂TPC ¹H NMR spectrum. Here it is possible to distinguish between two distinct groups of *o*-phenyl protons at 7.86 and 8.10 ppm. The first value can be assigned to the ortho portons of the phenyls at meso positions adjacent to the pyrroline reduced ring and the second value can be assigned to the *o*-phenyl protons at meso positions adjacent to the unreduced pyrrole rings.

The substituted tetraphenylchlorins show typical chlorin ¹H NMR spectra where the β-pyrrole protons of the ring opposite to the reduced pyrroline appear as a singlet of two protons and the β-pyrrole protons of adjacent rings show AX system pattern with doublets positions at both sides of the singlet. In ¹H NMR 270-MHz spectra of these compounds the nonequivalency of β-pyrrole protons adjacent to the reduced ring can be seen, and the four protons form two distinguishable AX systems, where the effect is more pronounced in the spectrum of compound B-4.

EPR Studies. Nitrogen-purged solutions of H₂TPP in benzene containing either a tertiary amine or pyrrolidine were irradiated in situ in the EPR cavity with visible light (λ >450 nm). On continuous excitation a single EPR line centered at g = 2.0024 ± 0.0002 was observed. The line width between the inflection points was ΔH = 5.2 ± 0.2 G (5.2 × 10⁻⁴ T). These values are very close to those found for other free base porphyrins radicals[21] (ΔH = 5.0 G, g = 2.0020) and slightly different from those reported for the anion radical of H₂TPP which was prepared electrochemically[22] (ΔH = 3.8 G, g = 2.0027).
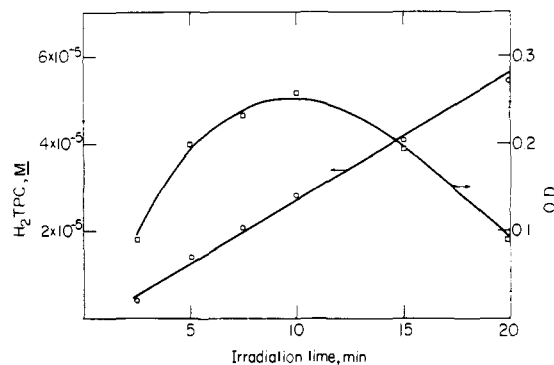
Figure 5. ○, dependence of H₂TPC formation on irradiation time; □, dependence of intermediate formation on irradiation time, for the photoreduction of H₂TPP (10⁻⁴ M) by pyrrolidine (4 M) in benzene at room temperature (irradiation at λ >500 nm).

Table IV. Chemical Shifts[a] of Phenyl Protons in H₂TPP and Reduced Tetraphenylporphyrins

compd, no.	*o*-phenyl H	*m*-, *p*-phenyl H
H₂TPP, A	8.30	7.80
H₂TPC, B-1	7.86, 8.10	7.70
H₂TPCC(H) (CH₃)N(CH₂CH₃)₂, B-2	7.90, 8.10	7.60
H₂TPCC(H) (CH₂)₃NCH₃,B-3	7.90, 8.10	7.60
H₂TPCOH, B-4	8.20, 8.30	7.70
H₂TPB,[b] C	7.52	7.52
H₂TP-*i*-B, D	7.50	7.50

[a] In parts per million downfield from Me₄Si. [b] From ref 2.

The same single EPR line with the same g and ΔH values was observed for the amines: TEA, NMP, *N*-ethyl-*N*,*N*-diisopropylamine, and pyrrolidine. The amino radicals formed in the initial reaction between the photoexcited porphyrin and the amine escape detection owing to their very short lifetimes.[21,23] Therefore the EPR signal was assigned to the porphyrin free radical. Since the stable products of photoreduction are different for pyrrolidine and for tertiary amines the EPR studies were extended in order to gain more information on the mechanism of the photoreduction.

The variation of the EPR line intensity with dark time period was recorded by monitoring the derivative of the EPR line (Figure 6).

When H₂TPP solutions containing a tertiary amine were irradiated a slow rise of the EPR signal is observed (Figure 6a). When the shutter was reopened immediately a fast rise followed by a slow rise of the EPR signal was observed. The relative amplitudes of the fast and slow components of the signal intensity depended strongly on the length of the dark period. Thus, when the sample solution was subjected to light after a long dark period, the EPR signal intensity was built up slowly, having a rise time identical with that observed in a fresh solution. On the other hand, when H₂TPP solutions containing pyrrolidine were irradiated, the EPR signal arose immediately and decreased to its steady-state value. When the shutter was reopened after short dark periods, the signal arose immediately. After a long dark period the signal has the same characteristics as the signal observed in a fresh solution.

The decay of the EPR signal, upon termination of the light pulse, was identical for all the tertiary amines and different for pyrrolidine. In solutions containing tertiary amines the porphyrin free radical has a half-lifetime of ∼50 ms and decays in a second-order reaction, whereas in solutions containing
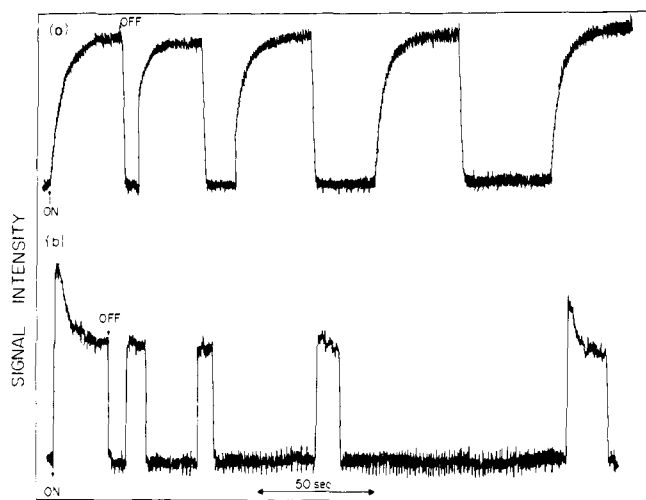
Figure 6. Rise and decay of the EPR signal intensity as a function of the dark period: (a) recorded for H_2TPP (5×10^{-4} M), Et_3N (0.1 M) in benzene at room temperature, (b) recorded for H_2TPP (5×10^{-4} M), pyrrolidine (0.5 M) in benzene at room temperature.

pyrrolidine the half-lifetime is ~5 ms and the decay is a first-order reaction. For both pyrrolidine and tertiary amine the signal intensity shows a linear dependence on $[H_2TPP]^{1/2}$ and on $I^{1/2}$ where $[H_2TPP]$ stands for initial H_2TPP concentration and I for light intensity, provided that no total absorption by the ground singlet occurs.

Therefore EPR observations indicate that the mechanism of H_2TPP photoreduction is similar in the initial steps for pyrrolidine and tertiary amine, leading to the formation of porphyrin free radicals. At steady state the porphyrin radicals are in equilibrium with a light-sensitive dimer as previously proposed by us.[15]

However, the formation of the porphyrin free radicals, the lifetime, the decay kinetics in the dark, and the variation of the signal intensity as a function of the dark period are different for pyrrolidine and tertiary amines. These observations suggest that the reactions which lead to the formation of the stable products from the porphyrin free radicals are different for tertiary amines and for pyrrolidine.

Mechanism of the Photoreduction. Our experimental data indicate that the photoreduction of porphyrins by tertiary amines and by pyrrolidine is consistent in the initial steps with the main features of the charge-transfer mechanism proposed for the photoreduction of aromatic ketones by amines[9] and more recently for the photoreduction of anthracene by dimethylaniline.[14] The initial step in such a mechanism is accepted to proceed via rapid formation of an exciplex followed by electron transfer from the amine and decay to the corresponding radicals. Whereas in the case of aromatic ketones experimental evidence indicates that the excited triplet state is involved in the exciplex formation, for aromatic macrocycles such as naphthalene and anthracene the experimental evidence indicated a singlet excited state.[14,24,25]

Laser photolysis studies performed on oxygen-free benzene solutions containing porphyrin and amine gave an apparent triplet lifetime of ~40 μs, which was independent of the amine concentration (up to 4 M in amine). In the presence of air the porphyrin triplet lifetime was reduced to ~3 μs. The photoreduction of porphyrin by NMP in benzene is depressed by a factor of 2 only, when saturated with oxygen (Table I), and the reaction proceeds nicely in the presence of air. Flash photolysis experiments on H_2TPP-NMP solutions reveal the presence of an intermediate with a lifetime of ~50 ms having a broad absorption band centered at 445 nm. When the same solutions

are photolyzed in the presence of air the intermediate still shows up, although the yield is decreased. This intermediate may be identified with the free porphyrin radical detected in EPR measurements.[15] Therefore the independence of the porphyrin triplet lifetime on amine concentration on the one hand and the fact that the photochemical reaction is relatively insensitive to oxygen on the other rule out the porphyrin triplet as the excited state involved. A small decrease in the triplet yield was observed at high NMP concentration, but not with Et_3N.

Fluorescence studies on porphyrin solutions in benzene in the presence of high concentrations of amine (up to 6 M) failed to show any quenching by NMP as well as by Et_3N. As a quantum yield of 0.056 was found for chlorin formation in benzene solutions at the maximum possible concentration of 4 M in NMP (Table II), quenching of fluorescence should have been found, when the singlet in question would have been the intermediate. Therefore this seems to rule out also the singlet as the excited state in this reaction (it is interesting in this respect that with $Sn^{IV}TPPCl_2$, where much higher quantum yields are found on photoreduction with amine, fluorescence quenching is observed, which increases with increasing amine concentration).

As no signs could be found for charge transfer complex formation between the amines and porphyrin in the ground state, the nature of the excited state in this reaction must be considered an unsolved problem for the time being.[31]

Whatever the nature of the excited state, the linearity of the plots in Figures 2 and 3 indicates the importance of deactivation and quenching processes in this reaction. This is in agreement with the EPR results, where an increase in signal was found with increasing amine concentration up to 4 M, which indicates a relative small cross section for the radical formation reaction.

The photoreduction reaction shows the characteristics of hydrogen transfer by a charge transfer mechanism and not by hydrogen abstraction[9,26] because:

(a) Classical hydrogen donors like 2-propanol are inactive in this reaction, whereas most amines are active. (b) Rates are depressed by the addition of protonic solvents like 2-propanol. 2-Propanol does not influence the product distribution, however, which suggests that rates are governed by polar processes, but product distribution by radicals. Therefore EPR as well as photochemical measurements suggest a common photochemical path for the formation of the porphyrin free radicals and different dark reactions leading to stable products from radicals, for tertiary amines and pyrrolidine.

On photoreduction of porphyrin by pyrrolidine the chlorin is photoreduced further to isobacteriochlorin. The formation of isobacteriochlorin instead of bacteriochlorin is in agreement with Fukui's frontier orbitals theory as applied to the reactivity of the porphyrin periphery.[32] The reactivity parameters of the chlorin macrocycle indicate that peripheral double bonds of pyrrole units adjacent to the reduced pyrroline ring should be more reactive than those in the opposite pyrrole unit. Therefore the free radicals formed from chlorin can be expected to have a hydrogen atom on one of the pyrrole units adjacent to the reduced pyrroline, and isobacteriochlorin is formed instead of bacteriochlorin.

Experimental Section

were irradiated in a constant temperature cylindrical cell (Light Path Optical Co., England). The temperature in the cell was kept constant with the aid of a Haake FK2 thermostat system.

Quantum yields of chlorin formation were determined with the Reinecke salt actinometer,[27] ϕ = 0.286 at λ 520 nm. Aliquots (3 mL) of 2 $\times$ 10^{-4} M H_2TPP solutions in benzene at different amine concentrations were argon saturated and irradiated in a cylindrical cell of 2 cm light path for periods of time providing a 10% conversion of porphyrin to chlorin. The spectra of irradiated solutions were recorded on a Cary 15 spectrophotometer. The number of moles of chlorin formed was calculated from the optical density of the chlorin absorption bands at 652, 654, and 655 nm. At these wavelengths the molar extinction coefficients of the chlorins exceed that of the porphyrin by about one order of magnitude. Initial rates for chlorin formation were determined in the same way or with continuous light, λ >500 nm, instead of monochromatic light.

Flash and pulsed laser photolysis experiments were performed for benzene solutions of porphyrins containing amines. A description of the technique and apparatus used in these experiments has been given previously.[28]

Photochemical Syntheses. For the photochemical syntheses a simple photochemical reactor was built. A 500-W lamp (Edmund Co.) in a water cooling jacket was inserted in a 3-L round flask equipped with a second cooling jacket, a magnetic stirrer, and a glass tube for argon gas stream. The photochemical syntheses were carried out in benzene, 2-4 M in amine (NMP or Et_3N) or 6 M in amine (pyrrolidine). The low boiling points of these amines simplify the final workup of the products being evaporated together with the solvent at the end of the photochemical synthesis. Progress of the reaction was followed spectrophotometrically by monitoring the chlorin formation at the characteristic absorption bands. For the synthesis of the chlorins the irradiation was stopped when the ratio of the optical densities at Q bands I and IV approached the molar extinction coefficients ratios of pure chlorin. For the synthesis of the isobacteriochlorin free base the irradiation was continued until the optical density of the 652-nm band, nonexisting in isobacteriochlorin spectrum and characteristic of chlorin, was very small relative to the optical density of isobacteriochlorin at 594 nm.

NMR Spectra. ^1H NMR spectra were recorded on a Bruker HFX-10 spectrometer operating at 90 MHz with FFT (internal deuterium lock) or on a WH 270-MHz Bruker spectrometer. The solvents were deuterated chloroform or deuterated methylene chloride and tetramethylsilane was used as internal standard.

Optical Spectra. Ultraviolet and visible absorption spectra were recorded on a Cary 15 spectrophotometer in benzene solutions.

Mass Spectra. Mass spectra were obtained by direct insertion into the ion source of a CH-4 instrument.

Fluorescence Studies. Fluorescence spectra were obtained from benzene solutions of the porphyrins on a Perkin-Elmer MPF 44A spectrofluorimeter. Argon-saturated solutions of H_2TPP of optical densities 0.02-0.04 containing Et_3N or NMP (concentration range 1-6 M) were excited at 460 and 520-nm velengths and fluorescence spectra were recorded.

EPR studies were performed on a E-12 Varian spectrometer. The porphyrin solution was pumped from a light-protected glass container to a standard aquo solution EPR cell fixed in the EPR cavity using a peristaltic pump. The porphyrin solution was irradiated in situ in the EPR cavity by either a 500-W high-pressure mercury lamp or a 150-W tungsten lamp using cutoff filters (λ_{excit} >450 nm). For the kinetic measurements a mechanical shutter was used in front of the light source when possible. Other kinetic measurements were performed by light modulation techniques.

Materials. H_2TPP was synthesized by the method of Adler et al.,[29] and purified by chromatography on basic alumina.

meso-Tetraphenylchlorin. H_2TPP (1.55 g) dissolved in 1.8 L of benzene and 600 mL of pyrrolidine was irradiated in the photochemical reactor for 3 days. The irradiation was stopped when the ratio of the optical density of 652 nm chlorin absorption band to the optical density of 517 nm was close to the extinction coefficients ratio of pure chlorin. Extended periods of irradiation increase the content of the isobacteriochlorin and this can be checked by the ratio of optical densities of the 598- and 652-nm absorption bands. The solvent was evaporated and the residue crystallized from benzene to afford 1.4 g of H_2TPC (>90% yield). This was contaminated with ~5% isobacteriochlorin. Chlorin of high purity can be obtained by repeated crystallizations from concentrated chloroform solutions in a desiccator

containing *n*-pentane. Its absorption and NMR spectra are in agreement with those reported in the literature.[2]

meso-Tetraphenylisobacteriochlorin. The same solution as for the synthesis of tetraphenylchlorin was irradiated in the photochemical reactor for 9 days. The absorption spectrum of the irradiated solution showed contamination with ~5% chlorin. The solvent was evaporated and the residue crystallized from a concentrated chloroform solution in a desiccator containing *n*-pentane. The yield is 1.2 g (~80%). The period of irradiation could be shortened to 6 days by cooling the solution to 15-20 °C.

The absorption spectrum agrees with that published in the literature.[2] ^1H NMR (CDCl$_3$) δ -1.3 (broad, 2 H, NH), 3.25 (singlet, 8 H, -CH$_2$CH$_2$-); δ_A 6.86, δ_X 7.36 (AX system, 4 H, -CH=CH, J_{AX} = 4.4 Hz), 7.46-7.80 (multiplet, PhH, 20 H).

7-Hydro-8-(N,N-diethylmethylamino)tetraphenylchlorin and 7-Hydro-8-hydroxytetraphenylchlorin. H_2TPP (1.55 g) dissolved in 1.8 L of benzene and 600 mL of triethylamine was irradiated in the photochemical reactor for 2 days. The solvent was evaporated and the residue dissolved in chloroform and chromatographed on a silica gel column with chloroform-5% 2-propanol. The first brown band contained tetraphenylchlorin and traces of tetraphenylporphyrin. The second brown band contained 7-hydro-8-hydroxytetraphenylchlorin (λ_{max} 645 nm). A dark green band followed which contained minor quantities of decomposition products with porphyrin-type absorption spectrum. The deep brown band which followed contained the amino substituted tetraphenylchlorin (λ_{max} 655 nm). The two chlorin products were recrystallized from methylene chloride-methanol. The yield was 300 mg of 7-hydro-8-hydroxytetraphenylchlorin (~19% yield) and 900 mg of 7-H,8-(N,N-diethylmethylamino)tetraphenylchlorin (~50% yield).

7-H,8-(N,N-Diethylmethylamino)tetraphenylchlorin absorption spectrum: λ_{max} (C_6H_6) 421 nm (ϵ 196 000), 519 (17 000), 547 (12 000), 600 (6500), 655 (39 600); ^1H NMR (CDCl$_3$) δ -1.44 (singlet, 2 H, NH), 0.07, 0.10 (doublet, 3 H), -C(CH$_3$)N), 0.66, 0.74, 0.82 (triplet, 6 H, -N(CH$_2$CH$_3$)$_2$), 2.21-2.48 (multiplet, 4 H, -N(CH$_2$CH$_3$)$_2$), 3.00 (broad, multiplet, 1 H, -C(H)(CH$_3$)-), 4.19, 4.25 (doublet, 2 H, -CH$_2$CH-), 5.10 (broad, multiplet, 1 H, -CH$_2$-CH-), 7.54-7.69 (multiplet, 12 H, *m*-, *p*-PhH), 7.80-8.20 (broad, multiplet, 10 H, *o*-PhH, 8 H, and -CH=CH-, 2 H), 8.39 (singlet, 2 H, -CH=CH), 8.51, 8.56 (doublet, 2 H, -CH=CH). Anal. Calcd for $C_{50}H_{45}N_5$: C, 83.88; H, 6.34; N, 9.79. Found: C, 83.75; H, 6.39; N, 9.63.

7-Hydro-8-hydroxytetraphenylchlorin absorption spectrum: λ_{max} (C_6H_6) 419 nm (ϵ 216 000), 517 (18 000), 542 (16 500), 592 (7800), 645 (39 000); ^1H NMR (CDCl$_3$) δ -1.76 (singlet, 2 H, NH), 2.24, 2.25 (doublet, 1 H, -OH), 4.18, 4.21 (doublet, 1 H, -CH$_2$CH(OH)-), 4.30, 4.38 (doublet, 1 H, -CH$_2$CH(OH)-), 6.38 (multiplet, 1 H, -CH$_2$CH(OH)-), 7.65-7.76 (multiplet, 12 H, *m*-, *p*-PhH), 7.90-8.30 (multiplet, 10 H, *o*-PhH, 8 H, and -CH=CH, 2 H), 8.46 (singlet, 2 H, -CH=CH-), 8.64, 8.52 (doublet, 2 H, -CH=CH-) Anal. Calcd for $C_{44}H_{32}N_4O$: C, 83.52; H, 5.10; N, 8.85. Found: C, 83.45; H, 5.20; N, 8.81.

7-Hydro-8-pyrrolinomethyltetraphenylchlorin. The synthetic and purification procedure were the same as for 7-H,8-(N,N-diethyl-methylamino)tetraphenylchlorin. On chromatography here also the 7-hydro-8-hydroxytetraphenylchlorin was formed.

Absorption spectrum: λ_{max} (C_6H_6) 421 nm (ϵ 202 000), 519 (16 700), 546 (12 200), 600 (6300), 654 (40 800). ^1H NMR (CDCl$_3$) δ -1.45 (singlet, 2 H, 14 H), 0.50 (multiplet, 1 H), 0.92 (multiplet, 1 H), 1.28 (multiplet, 1 H), 1.51 (multiplet, 1 H), 1.84 (multiplet, 1H), 2.48 (multiplet, 1 H), 2.89 (triplet, 1 H), all protons of -C(H)(CH$_2$)$_3$NCH$_3$ ring, 1.90 (singlet, 3 H, NCH$_3$), 4.16-4.29 (multiplet, 2 H, -CH$_2$CH-), 5.02 (broad, multiplet, 1 H, -CH$_2$CH-), 7.51-7.69 (multiplet, 12 H, *m*-, *p*-PhH), 7.93-8.23 (multiplet, 10 H, *o*-PhH, 8 H, and -CH=CH, 2 H), 8.40 (singlet, 2 H, CH=CH), 8.52, 8.58 (doublet, 2 H, -CH=CH-). Anal. Calcd for $C_{49}H_{41}N_5$: C, 84.09; H, 5.91; N, 10.16. Found: C, 84.18; H, 6.07; N, 9.84.

References and Notes

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