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(17) Abbreviations used are TPP = *ms*-tetraphenylporphin, T(*p*-CN)PP = *ms*-tetra(*p*-cyano)phenylporphin, etc., $T(CH_3)P$ = *ms*-tetramethylporphin, etc., $TPPH_2^{2+}$ = acid dication of TPP, etc., ϵ = the absorption coefficient.

(18) For identification of the spectral bands I–IV see Table I. The dipole strength ratios were calculated as $(f_I/f_{II})(\nu_{II}/\nu_I)$, where the oscillator strength is $f = 4.32 \times 10^{-9} \int \epsilon_{\bar{\nu}} d\bar{\nu}$ and $\bar{\nu}$ is the wave number.

(19) For the present purposes we used the classical approach[14] $\sigma_R = \sigma_p - \sigma_m$, $\sigma_I = \sigma_m$ (σ_m and σ_p from ref 13). The use of σ' (obtained for substituted bicyclo compounds by J. D. Roberts and W. T. Moreland, *J. Am. Chem. Soc.*, **75**, 2167 (1953)) for σ_I, an approach preferred by several authors, does not significantly change the results when applied to our data, since σ_m and σ' are similar[14] for most of the substituents used in our work. In fact with any of the commonly used sets of σ_I and σ_R our results yield better linearity when predominantly resonance-type combination σ coefficients are used.

Luminescence Studies on Several Tetraarylporphins and Their Zinc Derivatives

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Abstract: The fluorescence spectra and quantum yields were determined for a series of free base tetraarylporphins and their Zn derivatives in benzene. These porphins were substituted on positions 2, 3, and 4 of the phenyl rings. The heavy atom halogen substituents were found to quench fluorescence, especially when substituted at the 2-phenyl position. The quenching of the fluorescence was interpreted in terms of a heavy atom induced increase in intersystem crossing from S_1 to T_n. The absorption and fluorescence (0–0) band intensities of the Zn derivatives were found to be reduced by the presence of an ortho substituent. A similar ortho substituent effect has previously been observed for free base tetraphenylporphins. We have identified a weak emission from the Zn tetraarylporphins at 560 nm as a fluorescence hot band. The phosphorescence spectra and relative quantum yields of phosphorescence were also determined for a number of the Zn derivatives in methylcyclohexane–isopentane glass at 77°K. Phosphorescent emission could not be detected from the free base tetraarylporphins.

The tetraarylporphins are an interesting class of synthetic porphyrins. Derivatives with symmetrical substitution on the phenyl rings are readily prepared by the Rothmund reaction using the appropriately substituted benzaldehyde.[1] Para substituted tetraarylporphins have been most extensively studied.[1-3] Para substituents have been found, in general, to have only a slight effect on the absorbance spectra of free base and metalloporphyrins. This lack of interaction between "para phenyl" substituents and the porphin π system is attributed to the large dihedral angle between the planes of the phenyl and porphin π systems.[4]

Kim, Leonard, and Longo[1] recently synthesized and studied a number of tetraarylporphins prepared from ortho-substituted benzaldehydes. They found that certain ortho substituents produced a marked reduction in the Q(0–0) band intensities of the free base. Ortho-substituted halogens were most effective while the ortho-methyl substituent produced little effect.

One part of the work reported in this paper is an extension of the investigation of ortho substituent effects to the metallotetraarylporphins, specifically the Zn derivatives.

Excited state processes in porphyrins are extremely important, especially those in biologically important porphyrins such as the chlorophylls.[5,6] The fluorescence yield of most porphyrins is less than 0.2.[7,8] Thus the excited state S_1 is primarily deactivated by radiationless decay. It appears fairly certain that the spin forbidden process $S_1 \rightsquigarrow T_n$ is the predominant route for radiationless deactivation of S_1 in porphyrins.[9]

In this paper we report a study of the halogen heavy atom effect on spin forbidden processes in free base and zinc tetraphenylporphin. The heavy atom effect on spin forbidden processes in porphyrins has been studied, for the most part, by substitution of various closed shell heavy metals into the porphyrin nucleus.[10,11] Gouterman et al.[12] have recently reported a study of the luminescence of group 4 metalloporphyrins. Both the effects of central metal and of axial ligands such as Cl, Br, and I were studied. They found that the extent of spin-orbit coupling depended much more on the nature of the ligand than on that of the metal. Solov'ev et al.[13] studied the effect of para-phenyl substituents Cl, Br, and I on the luminescence of free base, magnesium, and zinc tetraphenylporphin. They obtained fluorescence quantum yields as well as other luminescence data including relative increases in triplet-triplet absorption due to the various para substituents. Using the methods developed by Medinger and Wilkinson[14] they were able to calculate a quantum yield for triplet formation of 0.87 for free base tetraphenylporphin.

Experimental Section

Compounds and Solvents. The free base tetraphenylporphin used in this study was prepared by Dr. E. Brown following the procedure of Adler et al.[15] All the substituted tetraphenylporphins were

Table I. Visible Band Oscillator Strengths of Free Base Tetraarylporphins[a]

Compd	$Q_x(0-0)$	$Q_x(1-0)$
TPP	0.0079	0.0180
OMeTPP	0.0064	0.0186
OFTPP	0.0032	0.0186
OClTPP	0.0018	0.0192
OBrTPP	0.0017	0.0194
OITPP	0.0015	0.0193
MClTPP	0.0060	0.0187
PClTPP	0.0074	0.0197
PBrTPP	0.0082	0.0201

[a] Calculated by integration of $f = 4.32 \times 10^{-9} \int \epsilon(\nu)d\nu$. ν is the absorption frequency in wave numbers.

Table II. Absorption Data for Zinc Tetraarylporphins in Benzene

Compd	Q(0-0)[a]	Q(1-0)[a]	B(0-0)[b]
ZnTPP	586	548	423
	0.368	2.28	54.4
	0.0105	0.100	
ZnOMeTPP	584	547	422
	0.203	2.42	57.7
	0.0058	0.106	
ZnOFTPP	584	547	422
	0.164	2.36	52.5
	0.0047	0.101	
ZnOClTPP	584	550	422
	0.172	2.37	52.9
	0.0045	0.110	
ZnOBrTPP	585	551	425
	0.179	2.44	53.3
	0.0049	0.110	
ZnMClTPP	588	549	423
	0.276	2.38	53.9
	0.0092	0.107	
ZnPClTPP	589	550	424
	0.391	2.41	55.5
	0.0122	0.112	
ZnPBrTPP	589	550	424
	0.407	2.41	55.6
	0.0117	0.110	

[a] The three numbers listed for each band are, in descending order, the wavelength of maximum absorption in nm, the molar extinction coefficient at the maximum $\times 10^{-4}$, and the oscillator strength of the band. [b] The oscillator strength was not calculated for this band.

prepared by Drs. Kim and Leonard.[1] The Zn derivatives were prepared by the method of Adler et al.[16] using the free base porphyrin and a fourfold molar excess of $ZnCl_2$ (Baker reagent) in boiling dimethylformamide (MCB reagent). All the free base and zinc tetraarylporphins used in this study were recrystallized from toluene-methanol and dried, under vacuum, at 70-80° for 16-24 hr.

The benzene used was Fisher Scientific spectral quality. The glass-forming solvent was a mixture of two parts methylcyclohexane and one part isopentane; both were MCB spectroquality grade. All solvents were free of emission at excitation wavelengths of 420 and 550 nm.

Apparatus. All absorption spectra were recorded on a Cary 14 recording spectrophotometer. Emission spectra were recorded on an Aminco-Bowman spectrophotofluorometer. Room temperature fluoroescence was detected with a Hammamatsu R446UR photomultiplier tube. Emission from glass solutions at 77°K was detected with an RCA 7102 photomultiplier tube cooled with solid CO_2. Luminescence spectra were corrected for variation in detector response. Correction factors were determined using the emission data of Lippert et al.[17] for 4-dimethylamino-4′-nitrostilbene (Eastman Chemical Co.).

Fluorescence Spectra and Quantum Yields. Fluorescence spectra and quantum yields were obtained from benzene solutions of the porphyrins contained in 1.00 cm^2 pyrex fluorescence cells. Dissolved O_2 in air-saturated benzene was found to reduce the fluorescence yield of free base porphyrins by approximately 15%. Therefore, solutions were purged with N_2 before quantum yields were determined. Relative yields were determined as suggested by Parker and Rees.[18] Solutions of low optical density (0.04/cm or less) were used. The relative number of absorbed photons was taken as the integral of the product of the optical density and relative photon intensity of the source, integrated over the bandpass of the excitation monochromator slit. The relative fluorescence yield of a porphyrin was determined by comparing its integrated fluorescence spectrum per absorbed photon to that of free base tetraphenylporphin. Absolute quantum yields were calculated assuming a value of 0.11 for free base tetraphenylporphin in air-saturated benzene.[8]

Luminescence at 77°K. Solutions of the zinc tetraarylporphins in methylcyclohexane-isopentane (4×10^{-6} to 2×10^{-5} M) were contained in a 0.5 cm diameter Pyrex tube, degassed by freeze-pump-thaw and sealed off under vacuum. The tube was cooled with liquid N_2 in a small dewar whose bottom was tapered to a small diameter and unsilvered (Aminco part No. B28-62140). Luminescence was excited and viewed through the unsilvered portion of the dewar. Purely phosphorescent emissions were recorded using a rotating can phosphoroscope with two optical ports (Aminco part No. 4-8237).

Results

It would be awkward to use systematic nomenclature for the various tetraarylporphins. To facilitate discussion the names of the compounds will be abbreviated: free base tetraphenylporphin as TPP, free base tetra(*o*-chlorophenyl)porphin as OClTPP, zinc tetra(*p*-chlorophenyl)porphin as ZnPClTPP, etc.

Absorption Spectra. The absorption spectra of the free base tetraarylporphins, except OITPP, have been previously reported.[1] We have calculated the oscillator strengths of the Q_x visible bands by direct integration of $\int \epsilon(\nu)d\nu$. These are given in Table I. Several interesting trends are evident. As has been previously noted para substituents produce little effect on band position or intensity. Ortho-halogen substituents, on the other hand, significantly reduce (0-0) band intensity and clearly the trend is that I is the most effective and F the least effective of the halogens. The ortho-methyl group and meta-chloro group induce small reductions in (0-0) band intensity, but meta-chloro substitution is much less effective than ortho chloro.

The zinc tetraarylporphins have typical metalloporphyrin absorption spectra. Band positions, molar extinction coefficients, and oscillator strengths are given in Table II. As with the free base derivatives the intensity of the Q(0-0) band is sensitive to the position of the substituent on the phenyl rings. The ortho halogen Zn derivatives all have reduced (0-0) band intensity, but there is little difference in the effectiveness of the various halogens. The ortho-methyl group is almost as effective as the ortho halogens in reducing Q(0-0) band intensity whereas it has only a rather marginal effect in the free base derivative.

Emission Spectra. Room temperature fluorescence spectra of free base PClTPP and OFTPP are shown in Figures 1 and 2. They are mirror symmetric to the absorption spectra in the Q_x region.[1] Emission data for these compounds are given in Table III. The natural radiative lifetimes τ_f^0, were calculated from absorption and fluorescence spectra using the Birks-Dyson[19] modification of the Strickler-Berg equation.[20] For Cl and Br substituted tetraphenylporphin the fluorescence yield is strongly dependent on the proximity of the halogen atom to the porphin π system. The ortho-Cl and -Br derivatives are much less fluorescent than the corresponding para derivatives. The natural radiative lifetimes of the ortho-halogenated tetraarylporphins are about 30% longer than those of the para derivatives of unsubstituted TPP. This reflects the decrease in the probability of the $Q_x(0-0)$ transition. The slight reduction in the fluorescence yield with ortho-F substitution is apparently due solely to

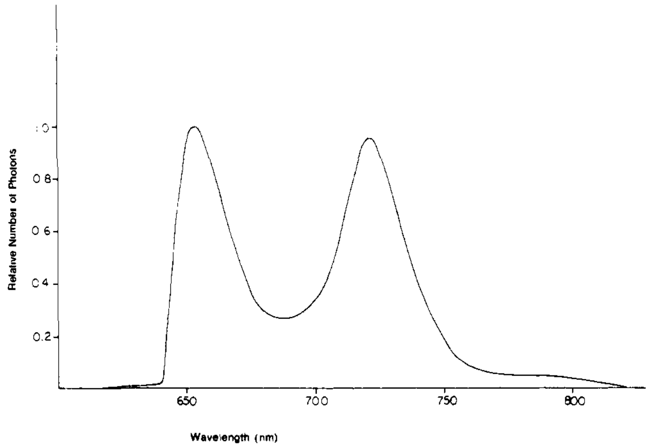

Figure 1. Fluorescence spectrum of free base PClTPP in benzene (room temperature).

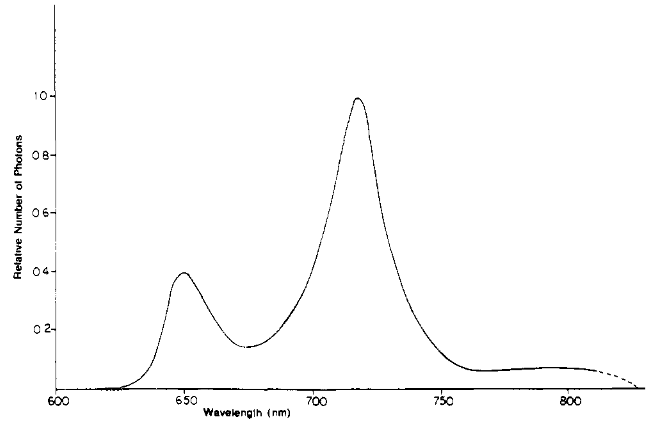

Figure 2. Fluorescence spectrum of free base OFTPP in benzene (room temperature).

Table III. Fluorescence Data for Free Base Tetraarylporphins[a]

Compd	Q(0-0)[b]	Q(0-1)[b]	ϕ_f[c]	τ_f^0[d]
TPP	652 1.11	718 1.00	0.13	142
OMeTPP	652 1.00	718 1.00	0.12	146
OFTPP	648 0.42	716 1.00	0.10	180
OClTPP	652 0.30	717 1.00	0.020	191
OBrTPP	651 0.25	718 1.00	0.0013	188
MClTPP	652 0.85	718 1.00	0.080	152
PClTPP	653 1.11	720 1.00	0.090	136
PBrTPP	655 1.02	720 1.00	0.017	132

[a] In benzene solution at room temperature. [b] Wavelength in nm/relative number of photons. [c] Fluorescence quantum yield. [d] Natural fluorescence lifetime in nanoseconds.

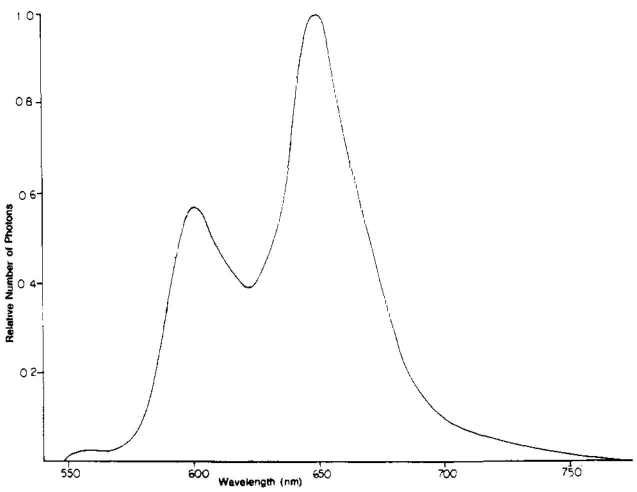

Figure 3. Fluorescence spectrum of ZnPClTPP in benzene (room temperature).

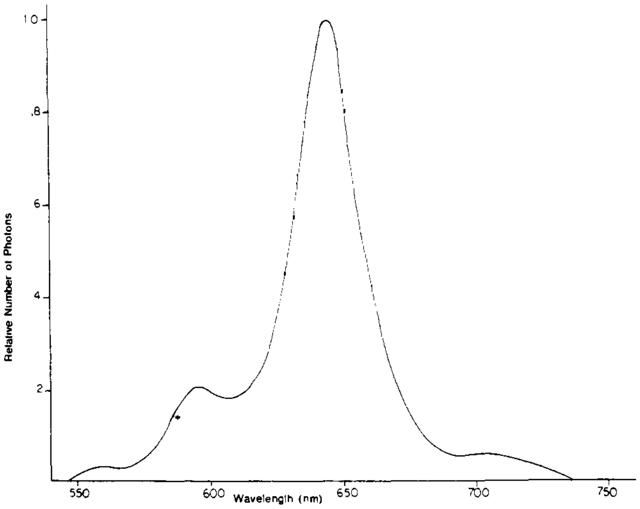

Figure 4. Fluorescence spectrum of ZnOFTPP in benzene (room temperature).

the increased lifetime of OFTPP, since the product $(\phi_f)(\tau_f^0)$ is constant, to within ±3%, for TPP, OMeTPP, and OFTPP. Similarly the slight difference in the quantum yields of MClTPP and PClTPP is due to the difference in their radiative lifetimes rather than any difference in the effect of meta-Cl vs. para-Cl substitution on the rates of nonradiative quenching of S_1.

It should be noted here that Solov'ev et al.[13] have reported fluorescence yields for free base, Zn, and Mg derivatives of unsubstituted TPP and of the para-Cl, -Br, and -I derivatives. Our results for the para-Cl and para-Br derivatives are in very good relative agreement with theirs. They based the absolute yield of the derivatives on the unsubstituted porphyrins. Our fluorescence yield for ZnTPP is in agreement with theirs. However, for free base TPP in degassed benzene, they report a fluorescence yield of 0.09, about 30% lower than ours.

Room temperature fluorescence spectra of ZnPClTPP and ZnOFTPP are shown in Figures 3 and 4. These spectra are approximately mirror symmetric to the absorption spectra and in particular show the same Q(0-0) sensitivity to phenyl substituent position. Emission data for the Zn derivatives are given in Table IV. The shoulder which appears in these spectra near 560 nm has an excitation spectrum in the Soret region which is identical with that of the other two main fluorescence bands. This shoulder is absent in the low temperature (77°K) fluorescence spectra (see Figures 6 and 7). To further elucidate the nature of this shoulder a study was made of its intensity as a function of temperature for ZnOFTPP and ZnTPP. The results of ZnOFTPP are shown in Figure 5. I(0-1) and I(0-0) represent the intensities of fluorescence bands Q(0-1) and Q(0-0), respectively. A straight line results when ln $[I(0\text{-}1)/I(0\text{-}0)]$ is plotted vs. T^{-1}. The slope of the line in Figure 5 corresponds to an

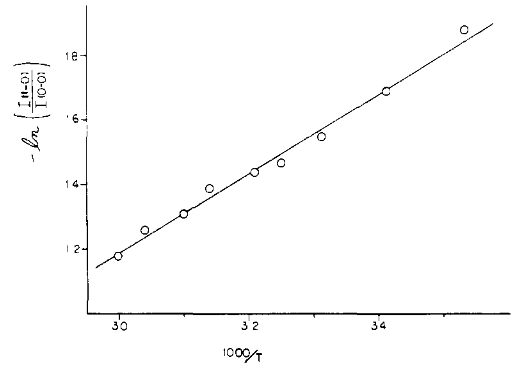

Figure 5. Plot of ln [I(0-1)/I(0-0)] vs. the reciprocal of the absolute temperature. I(0-1) and I(0-0) are the intensities of fluorescence bands Q(0-1) and Q(0-0) of ZnOFTPP in benzene.

energy of 860 cm^{-1}. A similar plot for ZnTPP was also linear with slope 1030 cm^{-1}.

The fluorescence yield we obtained for ZnOClTPP is anomolously high; in fact, it was higher than that of unsubstituted ZnTPP; see Table IV. This is difficult to understand, especially in light of the fact that free base OClTPP is much less fluorescent than free base TPP; see Table III. We have prepared a number of samples of ZnOClTPP and obtained the same results from each. We have no explanation, at this time, for the high fluorescence yield of ZnOClTPP but we are continuing to study this compound.

Table IV. Fluorescence Data for Zinc Tetraarylporphins[a]

Compd	Q(1-0)[b]	Q(0-0)[b]	Q(0-1)[b]	ϕ_f[c]	τ_f^0[d]
ZnTPP	560	598	647	0.033	57
	0.026	0.54	1.00		
ZnOMeTPP	560	595	645	0.027	57
	0.026	0.26	1.00		
ZnOFTPP	560	595	643	0.033	63
	0.030	0.20	1.00		
ZnOClTPP	560	594	646	0.038	59
	0.027	0.16	1.00		
ZnOBrTPP	560	594	646	0.0004	58
	0.059	0.18	1.00		
ZnMClTPP	560	600	648	0.017	55
	0.027	0.43	1.00		
ZnPClTPP	560	600	648	0.020	52
	0.028	0.58	1.00		
ZnPBrTPP	560	600	646	0.0052	52
	0.028	0.60	1.00		

[a] In benzene solution at room temperature. [b] Wavelength in nm/relative number of photons. [c] Fluorescence quantum yield. [d] Natural fluorescence lifetime in nanoseconds.

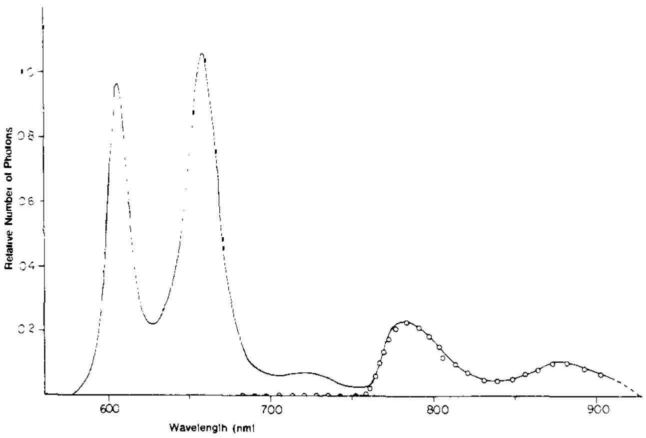

Figure 6. Emission spectrum of ZnTPP in methylcyclohexane-isopentane glass at 77°K. Circles indicate phosphorescence.

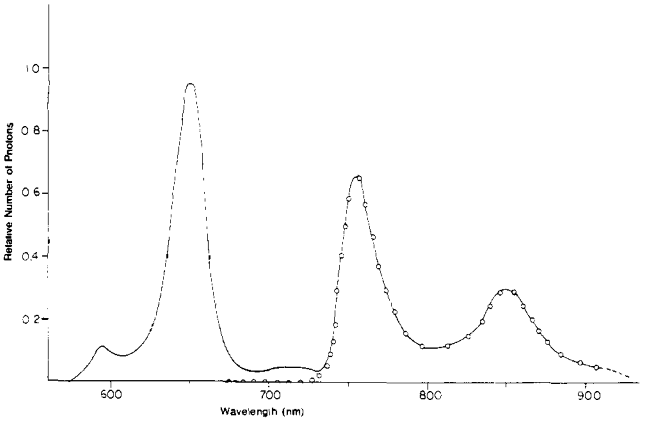

Figure 7. Emission spectrum of ZnOClTPP in methylcyclohexane-isopentane glass at 77°K. Circles indicate phosphorescence.

Low-Temperature Emission Spectra. Low-temperature (77°K) emission spectra of ZnTPP and ZnOClTPP are shown in Figures 6 and 7. The total luminescence spectra of all the Zn derivatives are similar. Band positions, relative intensities, and ratios of phosphorescent to fluorescent yield are given in Table V. The emission spectrum of each Zn derivative consists of five bands, all of which have identical excitation spectra. The first three bands are fluorescence emission. The band near 710 nm is assigned as Q(0-2) and actually appears in the room temperature spectra as an extended tail on the Q(0-1) band. Two phosphorescent bands are observed. In all cases, the T(0-0) band is more intense than the T(0-1). Ortho substituents do not strongly affect

Table V. Emission Data for Zinc Tetraarylporphins[a]

Compd	Q(0-0)[b]	Q(0-1)[b]	Q(0-2)[b]	T(0-0)[b]	T(0-1)[b]	ϕ_p/ϕ_f[c]
ZnTPP	605	660	715	781	875	
	0.91	1.00	0.061	0.18	0.073	0.32
ZnOMeTPP	596	651	710	764	858	
	0.34	1.00	0.053	0.29	0.16	0.55
ZnOFTPP	597	648	710	757	848	
	0.24	1.00	0.059	0.27	0.19	0.60
ZnOClTPP	596	651	710	755	847	
	0.12	1.00	0.053	0.67	0.31	1.32
ZnOBrTPP	600	652		768	865	
	0.01	0.04		1.00	0.80	52
ZnMClTPP	599	653	710	768	860	
	1.00	1.00	0.065	0.87	0.63	1.02
ZnPClTPP	600	652	710	768	860	
	1.00	1.00	0.072	0.80	0.45	1.00

[a] In methylcyclohexane-isopentane glass at 77°K. [b] Wavelength in nm/relative number of photons. [c] Phosphorescent/fluorescent yield ratio calculated from the integrated spectra.

the T(0–0) band intensity. This is not unexpected since extensive configuration interaction, which in the singlet manifold leads to reduced Q(0–0) intensity, does not occur in the triplet manifold.[21] The phosphorescence spectra of the zinc tetraarylporphins are quite similar in band contour to those of PdTPP and PtTPP but are shifted to longer wavelength by about 100 nm.[22]

We searched for phosphorescence from free base TPP and free base ortho-Cl, -Br, and -I derivatives in methylcyclohexane–isopentane glass at 77°K. The monochromator was scanned out to 1000 nm. No phosphorescent emission could be unambiguously detected. Based on the sensitivity of our instrument we estimate the phosphorescent yields of these free base tetraarylporphins to be less than $1/_{100}$ that of ZnTPP.

Discussion

Absorption Spectra. According to the four-orbital model[23] the intensities of porphyrin visible bands are determined by the relative energies of transitions between the top filled and lowest empty porphyrin π orbitals. When these transition energies are exactly equal the Q(0–0) bands have zero intensity. As the equality of the transition energies breaks down the Q(0–0) bands gain intensity. The relative energies of the top filled orbitals $b_1(a_{2u})$ and $b_2(a_{1u})$ depend upon the porphyrin skeleton. For TPP, orbital $b_1(a_{2u})$ is of higher energy than $b_2(a_{1u})$.[24] Reduction of the b orbital energy gap brings the transition energies of TPP nearer equality. Thus ortho-halo substituents must raise the energy of $b_2(a_{1u})$ or lower the energy of $b_1(a_{2u})$. One's first guess would be that phenyl substituents would interact with the porphin π system via the phenyl π system or the phenyl σ bond framework. The nodal properties of $b_1(a_{2u})$ and $b_2(a_{1u})$ are such that the phenyl rings and phenyl substituents can interact conjugatively and inductively only with orbital $b_1(a_{2u})$.[23] (The interaction of the phenyl rings with the lowest empty orbitals $c_1(e_g)$ and $c_2(e_g)$ is symmetric and does not affect the c orbital splitting.) Conjugative interaction of a phenyl halogen substituent with $b_1(a_{2u})$ would tend to raise its energy and thus lead to an increase in (0–0) band intensity. Inductive interaction of an ortho-halo substituent with $b_1(a_{2u})$, however, would tend to lower its energy and lead to reduced (0–0) band intensity. But based on electronegativities one would expect OFTPP to have the lowest (0–0) intensity and OITPP the highest. This is just the reverse of the observed trend for free base tetraarylporphins. An explanation which accounts for both the reduced (0–0) intensity and the trend for the halogens is that the ortho-halogen substituents may be sterically interacting with the porphin π system. Rotation of the phenyl group toward coplanarity with the porphin nucleus would bring the ortho substituent into steric interaction with the β positions of the pyrrole rings and thus with orbital $b_2(a_{1u})$. Interaction with the electron rich halogens would tend to raise the energy of $b_2(a_{1u})$ and thus reduce the b orbital energy gap and (0–0) band intensity. Increased size of the ortho substituent would allow more effective interaction and the expected trend in Q(0–0) intensity would be I < Br < Cl < F < H, which is the experimentally observed trend for free base tetraphenylporphin. Longo et al.[25] offered a similar suggestion to explain the lowering of the C–H rocking frequencies in the ir spectra of tetra(pentahalophenyl)porphins.

Trends in the Q(0–0) band intensities of the ortho-substituted zinc tetraarylporphins cannot be accounted for solely in terms of steric interaction of ortho substituents with $b_2(a_{1u})$. Although ortho-substituted halogens reduce Q(0–0) intensity, F, Cl, and Br seem to be about equally effective. We can account for this if we assume that in addition to the steric interaction of ortho substituents with $b_2(a_{1u})$, the phenyl rings of the zinc tetraarylporphins are more extensively conjugated to the porphin π system than those of the free base tetraarylporphins. This would lead to a more extensive conjugative interaction between the halogen and orbital $b_1(a_2)$ leading to an increase in the energy of $b_1(a_{2u})$. Thus, a given halogen substituent would simultaneously increase the energy of $b_1(a_{2u})$ and $b_2(a_{1u})$ but not to an equal extent. Of the halogens, I would be the most effective in increasing the energy of $b_1(a_{2u})$ just as it was with $b_2(a_{1u})$. F would be the least effective. On balance each halogen might produce about the same overall reduction in b orbital splitting leading to results such as observed for the Q(0–0) intensities of the ortho-substituted zinc tetraarylporphins. More extensive conjugative interaction between phenyl rings and porphin rings would lead to para-halogen substituents increasing the b orbital energy gap and Q(0–0) intensity by increasing the energy of orbital $b_1(a_2)$. The para-halogenated zinc tetraarylporphins do in fact show a small increase in Q(0–0) intensity (see Table II). The substantial decrease in Q(0–0) intensity produced by the ortho-methyl substituent is difficult to understand. One would expect little effect due to steric interaction as shown by the free results (see Table I). Electron-donating methyl groups interacting with $b_1(a_{2u})$ should increase the b orbital splitting and increase Q(0–0) intensity.

Fluorescence Spectra. A small but interesting band appears in the room-temperature emission spectra of the zinc tetraarylporphins near 560 nm. Bands similar to this (that is, on the high energy side of the (0–0) band) have been found in the emission spectra of other aromatic molecules in liquid and solid solutions. When seen they are usually assumed to represent emission from a higher electronic state such as $S_2 \rightarrow S_0$. Often this is the case but it need not always be so. The emission may be from higher vibronic levels of S_1. A few examples of this latter type of emission have been reported and those that have can be divided into two types. The first type is emission from vibrational levels of S_1 which are not in thermal equilibrium with each other or with the zero level of S_1. Rieckhoff, Menzel, and Voigt have reported emission of this type from magnesium phthalocyanine.[26] The emitting vibronic levels of S_1 were not thermally equilibrated and, in fact, the emission was more intense at 77°K than at 300°K. The second type is emission from vibronic levels of S_1 which are in thermal equilibrium, at least over some temperature range. Van Den Bogaardt et al. have reported emission of this type from 3,4-benzpyrene at temperatures above 150°K.[27] Emission bands of this second type can properly be called fluorescence hot bands. We believe the 560 nm band in the zinc tetraarylporphin spectra is a fluorescence hot band produced by emission from the group of vibronic levels of S_1 associated with the Q(1–0) absorption band. There are several reasons for this belief. First, it lies mirror image to the Q(1–0) absorption band and its excitation spectrum is identical with that of the other two main fluorescence bands. Second, its relative intensity with respect to the Q(0–1) fluorescence band is the same for all the Zn derivatives, with the unexplained exception of ZnOBrTPP. Third, its intensity varies with temperature in the manner expected for a hot band, Figure 5. The slope of the plot for ZnOFTPP is 860 cm^{-1} which is somewhat lower than the spectroscopic separation of Q(0–0) and Q(1–0) of about 1200 cm^{-1}. A similar study on ZnTPP gave a linear plot whose slope was 1030 cm^{-1} in much better agreement with the spectroscopic separation.

Fluorescence Yields. The fluorescent yield of a molecule depends on the relative rates of the radiative process $S_1 \rightarrow S_0$ and the two radiationless processes $S_1 \rightsquigarrow S_0$ and $S_1 \rightsquigarrow T_n$. The rate constants are k_f, k_{ic}, and k_{isc}, respective-

Table VI. Fluorescence and Intersystem Crossing Rate Constants for Tetraarylporphins

Tetraarylporphin	Free base $k_f{}^a$	Free base $k_{\text{Isc}}{}^a$	Zn derivative $k_f{}^b$	Zn derivative $k_{\text{Isc}}{}^b$
TPP	7.0	47	1.8	51
OMeTPP	6.8	50	1.8	63
OFTPP	5.6	50	1.6	47
OClTPP	5.2	255		
OBrTPP	5.3	4080	1.7	4300
MClTPP	6.6	76	1.8	105
PClTPP	7.4	75	1.9	94
PBrTPP	7.6	440	1.9	370

[a] $k \times 10^{-6}$ sec^{-1}. [b] $k \times 10^{-7}$ sec^{-1}.

Table VII. Values of the Ratio $\Delta k_{\text{Isc}}/\rho_x{}^2$ [a]

Tetraarylporphin	Free base	Zn derivative
OClTPP	600	
OBrTPP	670	
PClTPP	83	1300
PBrTPP	65	530

[a] See text and eq 11.

Table VIII. Values of the Constants A and C [a]

Derivative	A	C
Free base	59.2	1.3×10^4
Zn	303	5.6×10^5

[a] Constants in eq 11. Calculated for the para-Cl and -Br derivatives.

Table IX. Δk_{Isc} Values for Para-Substituted Tetraarylporphins

Tetraarylporphin	Δk_{Isc}(exptl)[a]	Δk_{Isc}(calcd)[a, b]
PClTPP	0.28	
PBrTPP	3.9	
PITPP	16.2[c]	15.8
ZnPClTPP	4.3	
ZnPBrTPP	32	
ZnPITPP	104[c]	106

[a] $\Delta k \times 10^{-8}$. [b] Calculated from eq 11. [c] Based on fluorescence quantum yields reported by Solov'ev et al.[13]

ly. For many aromatic molecules the sum of the quantum yields of fluorescence and triplet formation is close to 1.0.[14] This implies the $k_{\text{Isc}} \gg k_{\text{Ic}}$ for those molecules. Solov'ev et al.[9,13] have determined the triplet quantum yield of free base TPP to be about 0.85. Since the fluorescence yield is 0.13 we will assume $k_{\text{Isc}} \gg k_{\text{Ic}}$ for free base TPP and also for the Zn derivative. Using the data in Tables III and IV k_{Isc} and k_f have been calculated as

$$k_{\text{Isc}} = k_f[(1 - \phi_f)/\phi_f] \qquad (1)$$

$$k_f = 1/\tau_f{}^0 \qquad (2)$$

The values are given in Table VI. Ortho-methyl and -F substitution produce little change in k_{Isc}. Ortho-Cl and -Br substitution greatly increases k_{Isc} (ZnOClTPP being anomolous as mentioned before). The quantity $\Delta k_{\text{Isc}}/\rho_x{}^2$ was calculated for the Cl- and Br-substituted tetraarylporphins and is given in Table VII. Δk_{Isc} is $(k_{\text{Isc}}{}^{x\text{-TPP}} - k_{\text{Isc}}{}^{\text{TPP}})$ and ρ_x is the atomic spin-orbit coupling constant of the halogen: 587 cm^{-1} for Cl and 2460 cm^{-1} for Br.[28] The values of $\Delta k_{\text{Isc}}/\rho_x{}^2$ are approximately equal for OClTPP and OBrTPP indicating that these substituents interact with the porphin π system to about the same extent. This is as expected since they decrease Q(0–0) intensity by almost the same amount (see Tables I and II). The values of $\Delta k_{\text{Isc}}/\rho_x{}^2$ for the two free base para derivatives differ somewhat more than those of the ortho derivatives and the values of $\Delta k_{\text{Isc}}/\rho_x{}^2$ for ZnPClTPP and ZnPBrTPP are not even approximately equal. We shall attempt to account for the effects of heavy atom halogens on k_{Isc} as follows. Present theory[29] sets

$$k_{\text{Isc}} = \left(\frac{4\pi\rho_{\text{E}}}{h}\right) B^2 \langle \text{S}_1 | H_{\text{so}} | \text{T}_n \rangle^2 \qquad (3)$$

ρ_{E} is the density of final states and B^2 is a sum of Franck-Condon factors representing squares of overlap factors of vibrational wave functions. ρ_{E} and B^2 are considered to be constant for a series of similar molecules such as the ortho or para halotetraarylporphins. H_{so} is the hamiltonian for the transition and contains the spin-orbit coupling operator. McGlynn et al.[28] have shown that in the LCAO-MO format, expansion of the MO's in S$_1$ and T$_n$ over AO's and of H_{so} over atomic centers with restriction to one center terms gives

$$\langle \text{S}_1 | H_{\text{so}} | \text{T}_n \rangle = \sum_k \sum_u \sum_v C^*_{uk} C_{vk} \langle \chi_{uk} | H'_{lk} | \chi_{vk} \rangle \qquad (4)$$

Atomic orbitals χ_u and χ_v are located on atomic center k and H'_{lk} consists of components of H_{so} on center k. For aromatic systems eq 4 can be further reduced to

$$\langle \text{S}_1 | H_{\text{so}} | \text{T}_n \rangle = \sum_k \sum_u \sum_v C^*_{uk} C_{vk} (\rho_{(u,v)k}/Z) \qquad (5)$$

where $\rho_{(u,v)k}$ is the atomic spin-orbit coupling factor for atomic orbitals v or u on center k.[30] For the para-substituted tetraarylporphins the halogens are coupled to the porphin π system through the meso carbon atoms. Some of the terms in eq 5 will involve ρ_x of the halogen and others will not. We will set

$$\langle \text{S}_1 | H_{\text{so}} | \text{T}_n \rangle = a\rho_x + b \qquad (6)$$

a and b will be assumed constant for a particular position of substitution on TPP. The first term in eq 6 represents the contribution of the halogen perturbation and the second term the contribution of the rest of the molecule to the spin-orbit coupling matrix

$$\langle \text{S}_1 | H_{\text{so}} | \text{T}_n \rangle^2 = a^2\rho_x{}^2 + 2ab\rho_x + b^2 \qquad (7)$$

and

$$k_{\text{Isc}}{}^{x\text{-TPP}} = \frac{(4\pi\rho_{\text{E}})}{h} B^2(a^2\rho_x{}^2 + 2ab\rho_x + b^2) \qquad (8)$$

$$= A\rho_x{}^2 + C\rho_x + D \qquad (9)$$

Since the para halogens are weakly coupled to the porphin π system the term b in eq 6 may be nearly equal to $\langle \text{S}_1 | H_{\text{so}} | \text{T}_n \rangle$ in unsubstituted TPP. Then

$$k_{\text{Isc}}{}^{\text{TPP}} = \left(\frac{4\pi\rho_{\text{E}}}{h}\right) B^2(b)^2 = D \qquad (10)$$

and

$$\Delta k_{\text{Isc}} = k_{\text{Isc}}{}^{x\text{-TPP}} - k_{\text{Isc}}{}^{\text{TPP}} = A\rho_x{}^2 + C\rho_x \qquad (11)$$

Values of A and C for free base TPP and ZnTPP were calculated using Δk_{Isc} values for the para-Cl and -Br derivatives. These are given in Table VIII. Fitting two pieces of experimental data with two parameters demonstrates little. To test eq 11 we calculated k_{Isc} for free base and ZnPITPP. We have not studied these compounds but Solov'ev et al.[13] have. Using their relative fluorescence yields and assuming k_f equal to 7.5×10^6 for the free base and 19.2×10^6 for the Zn derivative, values for k_{Isc} were calculated by eq 1 and the Δk_{Isc} values obtained from these are given in Table IX as Δk_{Isc}(exptl). Taking ρ_{I} as 5060 cm^{-1} and using values of A and C from Table VIII, Δk_{Isc} values were calculated using eq 10 and are listed in Table IX as Δk_{isc} (calcd). As can be seen the agreement is quite good. In fact if the experimental values of k_{isc} for the Cl, Br, and I derivatives of free base or ZnTPP were used to calculate D directly from eq 9 the value obtained would have been close to k_{isc} of the unsubstituted derivative supporting the assumption of eq 10. Equation 11 indicates that it is the cross term $C\rho_x$ involving the product (ab) and the first power of ρ_x which accounts for the variation in $\Delta k_{\mathrm{isc}}/\rho_x^2$ for the para derivatives. For the ortho derivatives the constant a in eq 6 would be much larger than that of the para derivatives because the ortho substituent interacts more strongly with the porphin π system. Thus the first term in eq 9 would dominate the others even for the Cl derivative.

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(30) One of our referees, Dr. Martin Gouterman, has pointed out to us that the seemingly anomolously high fluorescence quantum yield of ZnOClTPP may be due to the fact that the terms involving the ortho halogen heavy effect and those involving the Zn heavy atom effect might enter into eq 5 with different sign. Since ortho-Cl substituents and Zn have spin-orbit effects of similar magnitude, as shown in Table IV, the ortho-Cl substituents might act to weaken the Zn effect. If this interpretation is correct it is probably the first observed case of counteracting heavy atom effect.

Kinetic and Equilibrium Studies on the Formation of Zinc(II)–Salicylaldehyde Schiff Bases Derived from Ethylenediamine and 1,3-Diaminopropane

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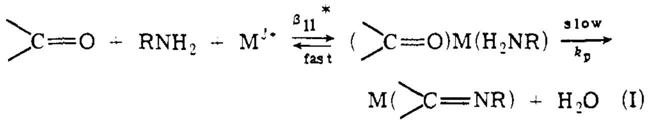
Abstract: The kinetic and equilibrium properties of Schiff bases derived from salicylaldehyde and either ethylenediamine or 1,3-diaminopropane in both the absence and presence of zinc(II) were studied over the pH range of 4.6 to 12.5 at 25.0°, 0.5 *M* ionic strength. Unprotonated, mono-, di-, and triprotonated sal$^-$-diamine adducts were found and their stabilities were established. The Zn(II)–Schiff base complexes have stabilities consistent with tridentate coordination of two nitrogen atoms and one oxygen atom. The rate law for diamine Schiff base formation was found to be similar to those found earlier for the reactions of amino acids with sal$^-$. Both unprotonated and monoprotonated diamines were found to be kinetically active. Coulombic effects account to a large extent for the reactivity differences exhibited by various amines toward sal$^-$; the cationic monoammonium ions show the largest rate constants and aminoacidate ions the smallest. Zn(II) promoted paths for Schiff base formation were found. The magnitudes of the rate constants are consistent with a mechanism which involves the preequilibrium formation of a mixed complex, (sal)Zn(diamine)$^+$.

The equilibrium and kinetic properties of Schiff bases and their metal ion complexes have received considerable attention owing to their relationship to vitamin B$_6$ chemistry. A quantitative study of the kinetic activity associated with metal ions in Schiff base formation was first reported from our laboratories in 1966 and 1967[2,3] but it was not until a few years later that the nature of the metal ion promoted step was more clearly recognized.[4] Metal ions were postulated to function by forming a mixed ligand complex with the amine donor and carbonyl compound in a preequilibrium step, followed by Schiff base formation in the primary, or secondary, coordination sphere of the metal ion,



$$\mathrm{>C{=}O} + \mathrm{RNH_2} + \mathrm{M^{2+}} \underset{\text{fast}}{\overset{\beta_{11}^*}{\rightleftharpoons}} (\mathrm{>C{=}O})\mathrm{M(H_2NR)} \xrightarrow[k_p]{\text{slow}} \mathrm{M(>C{=}NR)} + \mathrm{H_2O} \quad (\mathrm{I})$$

The observed third-order rate constant is the product, $\beta_{11}{}^*k_p$.

The metal ion is considered to function by effectively reducing the condensation reaction from a second-order to a first-order process. The term *promnastic* (matchmaker) was applied to this effect.[4] A systematic variation in divalent metal ions revealed that Pb^{II}, Cd^{II}, Mn^{II}, Mg^{II}, and