tion of **8**. Radical intermediates were evidently not involved in this reaction, since radicals are known to add to the terminal olefinic carbon of **7**.[17]

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J. K. Stille,* J. L. Eichelberger, Jerry Higgins, M. E. Freeburger
Department of Chemistry, University of Iowa
Iowa City, Iowa 52240

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Interpretation of Linear Hammett Constant Correlations in Substituted *ms*-Tetraphenylporphins

Sir:

The biological significance of porphyrins is well known, but their usefulness as model compounds in empirically discovering or exploring structure–reactivity or structure–property relationships has only been recently emphasized.[1] Below we give a preliminary report showing one of each of these types of relationships in terms of the well-known Hammett constants.[2,3]

Pseudo-first-order reaction rate constants for the reaction[4]

$$\mathrm{T}(p\text{-X})\mathrm{PP} + \mathrm{CuCl_2} \longrightarrow \mathrm{CuT}(p\text{-X})\mathrm{PP} + 2\mathrm{HCl}$$

in dimethylformamide at various controlled temperatures, with a copper chloride concentration of 1.6×10^{-3} *M* and initial porphyrin concentration of 3.2×10^{-5} *M*, were obtained by spectrophotometric monitoring with time of the free base porphyrin peaks at about 510 nm and their copper derivatives at about 540 nm. ΔG^* was obtained by conventional methods.[5] Plots of ΔG^* *vs.* Hammett's σ and σ^+ parameters[2] exhibit reasonable linearity with σ^+, while considerable deviation from linearity is seen for the σ plot, especially for the T(p-OH)PP and T(p-OCH$_3$) derivative (*cf.* Figure 1). In substituted benzenoid compounds such behavior is characteristic of reactions proceeding through electron-deficient intermediates and is usually ascribed to resonant electron donation from these substituents to the reactive center by some conjugated path.[6,7]

Visible absorption spectra of the dications, T(p-X)PPH$_2$$^{2+}$, prepared by saturating 10^{-5} *M* solutions of these bases in dimethylformamide with dry gaseous HCl at 298°K, were obtained on a Coleman-Hitachi 124 double-beam spectrophotometer. Spectroscopic energy shifts of the Q band, π–π transitions,[8] relative to TPPH$_2$$^{2+}$ at 7511 cm^{-1}, are plotted *vs.* the Hammett σ, σ^+ and ($\sigma^+ - \sigma$) constants of the respective p-X substituents (*cf.* Figure 2). No linear correlations with σ and σ^+ themselves are observed, while the observed frequency shift yields a good linear correlation with ($\sigma^+ - \sigma$). Similar spectral shifts, though of much smaller magnitude, and similar correlations were also observed in the free base spectra.

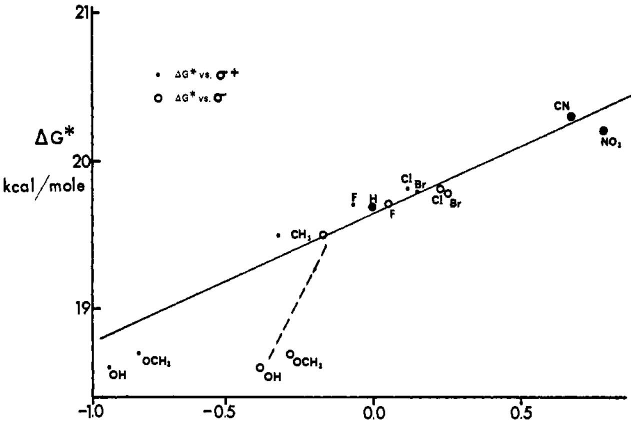

Figure 1. Free energy of activation for binding of Cu^{2+} in *N*,*N*-dimethylformamide by various para-substituted *ms*-tetraphenylporphyrins correlated to Hammett's σ and σ^+ constants. Note superimposed points for CN, NO$_2$, and H.

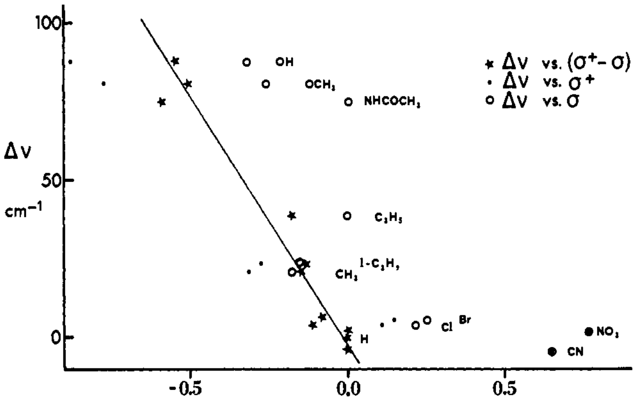

Figure 2. Frequency difference between the acid forms of *ms*-tetraphenylporphin as reference and various of its para-substituted derivatives in the 600–700-nm region correlated to Hammett's σ, σ^+, and ($\sigma^{+} - \sigma$) constants. Note superimposed points for H, CN, NO$_2$, C$_6$H$_5$, and NHCOCH$_3$.

Such energy shifts by substituents are usually ascribed to inductive σ and π effects and to resonant π effects.[3,6,7] The differences from σ to σ^+ are conventionally explained[3] by an additional conjugation between filled substituent p orbitals and an electron-deficient center *via* some aromatic π system.

The difference $\sigma^+ - \sigma$ is thus expected to be mainly indicative of the presence in such resonance effects of electron-deficient intermediates.[6]

However, to get such resonance forms with strong conjugation in these macrocyclic ring systems would require either considerable coplanarity of the phenyl and porphin π systems or a breakup of the conjugative bonding in the porphin system itself. The present X-

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(4) The materials were prepared and characterized by previously reported methods. See A. D. Adler, F. R. Longo, F. Kampas, and J. Kim, *J. Inorg. Nucl. Chem.*, **32**, 2443 (1970), for references. Abbreviations: TPP = *ms*-tetraphenylporphin; T(p-X)PP = *ms*-tetra(p-X)phenylporphin, where X = Cl, Br, etc.; TPPH$_2$$^{2+}$ = the acid dication of TPP.

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ray structural[9] and combustion data[10] make such possibilities, except in a dynamic sense or in an excited state, both structurally and energetically unlikely. A similar instance of this same difficulty has been seen in the empirical application of the usual Hückel ($4n + 2$) aromatic rules to the end products of the metallotetraphenylporphin type monocations under electron impact in mass spectroscopy,[11] where the phenyl π electrons must be added to those of the porphin ring to make simple sense of the observed data.

These empirical correlations therefore all suggest some interesting problems either with the behavior of porphyrin structures or, perhaps, with the conventional interpretation of resonance phenomena and parameters. In particular, they suggest that the usual inferences drawn from Hammett parameter correlations may still be susceptible to alternative explanations. If so, a continued study of such phenomena could considerably deepen our understanding of electronic effects in molecular structures.

They also demonstrate the utility of porphyrins in discovering and exploring structural relationships. Thus the above data can be combined to demonstrate a relationship between a relative spectral shift (a molecular property parameter) and a relative specific reaction rate (a reactivity parameter).

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M. Meot-Ner, Alan D. Adler*
New England Institute
Ridgefield, Connecticut 06877

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Radiation Chemistry of Nucleic Acids. Isolation and Characterization of Thymine Glycols[1]

Sir:

Since the discovery by Muller[2] in the late twenties that X-rays cause mutagenic effects, the radiation chemistry of nucleic acids has received considerable attention.[3] Radiation effects on thymine have been in the forefront, and 5,6-dihydroxy-5,6-dihydrothymines of trans (I) and cis (II) configurations have been indicated as products.[4] However, the actual isolation and identification of I has not been previously accomplished. We now wish to report the successful characterization of I and the chemistry of I and II.

Thymine, dissolved in triply distilled water, was saturated with oxygen. The solution (375 ml/run, 3×10^{-2} *M*, pH ~6) was irradiated with ^{137}Cs-Gammator[5] at a dose rate of 2 krads/min[6] for a total of 10 hr, and resaturated with oxygen at 2-hr intervals. The irradiated solution was evaporated (35°) until dry and the residue was extracted with methanol. The combined methanolic extract was concentrated, applied on Whatman No. 3 paper, and eluted with *n*-butyl alcohol saturated with water. Materials with R_f values of 0.47 and 0.40 were cut out and rechromatographed twice. The purified material was recrystallized from methanol.

The R_f 0.40 material was found to have identical ir, uv, and nmr spectra as the *cis*-thymine glycol (II)[4b,7] prepared by permanganate oxidation of thymine[8] at pH 6.8.

The trans isomer (I), R_f 0.47, has mp 145–147° dec, shows only end absorption in the uv region, has peaks for CH$_3$ (s, δ 1.60), C(6)H (d, δ 4.70, $J = 2.0$ Hz), C(5)OH (s, δ 6.15), C(6)OH (m, δ 6.60) N(1)H (d, δ 8.32, $J = 2.0$ Hz), and N(3)H (s, δ 9.65) in the nmr spectrum (in (CD$_3$)$_2$SO at 100 MHz with internal standard (CH$_3$)$_4$Si), and displays bands at 3430 (sh) and 3370 cm^{-1} for OH groups in its ir spectrum (KBr pellet). A mass spectrum of I gives no parent ion, but an M − 18 peak. However, after silylation with Regisil No. 27002 in pyridine, a molecular ion peak at *m/e* 448 corresponding to a tetratrimethylsilyl derivative of I was evident. Compound I slowly decomposes when stored in a vacuum desiccator at ambient temperature. When paper chromatography with *n*-propyl alcohol–water (10:3) was carried out with this material, another compound (R_f 0.38) was detected in addition to the unchanged I. This new compound was shown to be 2,3,4,5-tetrahydro-2,4-dioxy-5-hydroxy-5-methylpyrimidine (III). It shows only end absorption in the uv region, has peaks for CH$_3$ (s, δ 1.60), C(6)H (s, δ 7.57), C(5)OH (br, δ 7.18), and N(3)H (br, δ 9.60) in the nmr spectrum in (CD$_3$)$_2$SO (addition of D$_2$O eliminates the signals for OH and NH protons), and it displays an ir band at 3360 cm^{-1} for the OH group. A mass spectrum of III gives the parent ion at *m/e* 142.

With the purified I on hand, the interrelation of I and II could then be examined. When a solution of II (20 mg/ml of H$_2$O) was heated at 90° for 4 hr, four products with R_f 0.27, 0.32, 0.39, and 0.57 (I) were detected together with II (0.47) by Fink's reagent on tlc (Eastman 6065, cellulose, with fluorescent indicator *n*-PrOH–HOH). The formation of I was also followed chromatographically by examining samples withdrawn at 30-min intervals. Although a very weak spot of I appeared for the 30-min sample, it never exceeded 2% at the end of 4 hr. When the solution of II was allowed to stand at 37° for 10 hr, only I and II could be detected. A time study revealed that I began to appear

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