

V, the orientation of the anthracene moiety of I is quite similar to that of unsubstituted anthracene²⁶ despite the presence of the butanoic acid substituent.

The axis of the butanoic acid chain, calculated from atoms C1, C104-C101, intersects the anthracene least-squares plane at 37.2°, while glide-plane-related chains cross at an angle of 69.9°. Butanoic acid groups in neighboring bilayers form hydrogen-bonded dimers. The disorder in the oxygen atoms is borne out by two positions for each atom with almost equal weight as represented in Figures 1 and 2. Therefore hydrogen bonding cannot be quantified by only one distance (compare Tables II and III). An examination of the anisotropic temperature factors for the carboxylic acid oxygen atoms reveals a fair amount of thermal motion more or less perpendicular to the plane described by the hydrogen-bonded carboxylic acid dimer unit.

The crisscrossing of the butanoic acid chains represents a departure from the usual crystal packing of most fatty acids, where the chains are parallel to each other in an orthorhombic subcell.^{20,21} This configuration is realized, however, by certain potassium salts of short chain fatty acids.³⁷ In monoclinic potassium caproate, for instance, the alkyl chains within a given *ac* layer are parallel, but chains in neighboring layers are inclined at 57.5° to one another.^{37,38} In I this crossing of the butanoic acid chains apparently permits the crystalline packing of both alkyl and aromatic groups despite their different space-filling requirements.

(37) Lomer, T. R. *Acta Crystallogr.* **1950**, 5, 14.

(38) Kitaigorodskii, A. I. *Organic Chemical Crystallography*; Consultants Bureau: New York, 1955; p 290.

Bilayer-type single crystals with aromatic moieties are interesting systems for the study of various structural and spectroscopic phenomena. Temperature-dependent studies, such as have been carried out with other layered systems,²³ might show interesting phase changes and additional low-temperature structures. Varying the length of the fatty acid chain could indicate the relative contribution of the aromatic, alkyl, and carboxylic acid groups to the energetics of crystal packing.

Electronic excitations involving the anthracene moiety of I might prove interesting.^{1,2} Transport of excitons and charge carriers in two dimensions^{3,4} can also be profitably studied in such bilayer-type crystals.

Bilayer-type single crystals have several obvious advantages over conventional multilayer assembly techniques. Long-range crystallinity, for instance, is not possible in LB assemblies. Materials such as I can also be zone-refined and crystals can be grown by sublimation under inert atmosphere, thus affording extremely high purity. Bilayer-type single crystals can serve as well-ordered reference systems when interpreting local order and island formation in LB films containing related molecules.

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Supplementary Material Available: Tables of fractional coordinates, thermal parameters, bond distances and angles, and the final structural refinement (6 pages); tables of structure factors (56 pages). Ordering information is given on any current masthead page.

Tetra(pentafluorophenyl)porpholactone

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Abstract: Tetra(pentafluorophenyl)porphyrin [$H_2(TFPP)$] in refluxing acetic acid with $AgNO_3$ converts to tetra(pentafluorophenyl)porpholactone, I; i.e. one $exo\ C_2H_2$ unit becomes CO_2 . This change is proven by mass spectrometry and supported by 1H NMR, ^{19}F NMR, and FTIR. I has a porphyrinic absorption spectrum and a strong fluorescence, with a quantum yield of 0.2. Addition of oxalic acid allows reproducible conversion of $H_2(TFPP) \rightarrow I$, and a 15% yield has been obtained. Iterative extended Hückel (IEH) calculations confirm a porphyrinic electronic structure with the π orbitals on both the oxa and oxo oxygen present in three of the porphyrin "four orbitals" responsible for the optical spectra. Under similar conditions another metal-free porphyrinic substance has been made, which is tentatively identified as a porphodilactone. Also Ag, Ni, and Cu derivatives have been made that are presumed to be porpholactones or porphodilactones. IEH calculations predict that in the free bases the central protons are trans, avoiding the azlactone ring in the porpholactone and the opposite porphodilactone; in the adjacent porphodilactone, they are also predicted to be trans rather than cis.

Three years ago a species with an unusual porphyrin spectrum was made serendipitously in our laboratory, as described herein. We propose that this species is tetra(pentafluorophenyl)porpholactone, I; i.e. one of the pyrrole rings has been converted to the azlactone ring¹ as shown in Figure 1. Furthermore, as described below, the same synthetic procedure has yielded a second metal-free porphyrinic substance as well as metal derivatives. Analogy

suggests that the metal-free species may be a porphodilactone (IIA–IIE in Figure 1) and that the metal species are either porpholactones or porphodilactones. As shown in Figure 1, porphodilactone has five isomers.

Our serendipitous synthesis occurred when one of the authors (G.E.K.) was attempting to synthesize silver tetra(pentafluorophenyl)porphyrin [$Ag(TFPP)$]. $AgNO_3$ (0.5 g) and the free base,

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(1) *Oxazoles*; Turchi, I. J., Ed.; Chemistry of Heterocyclic Compounds, Vol. 45, John Wiley: New York, 1986.

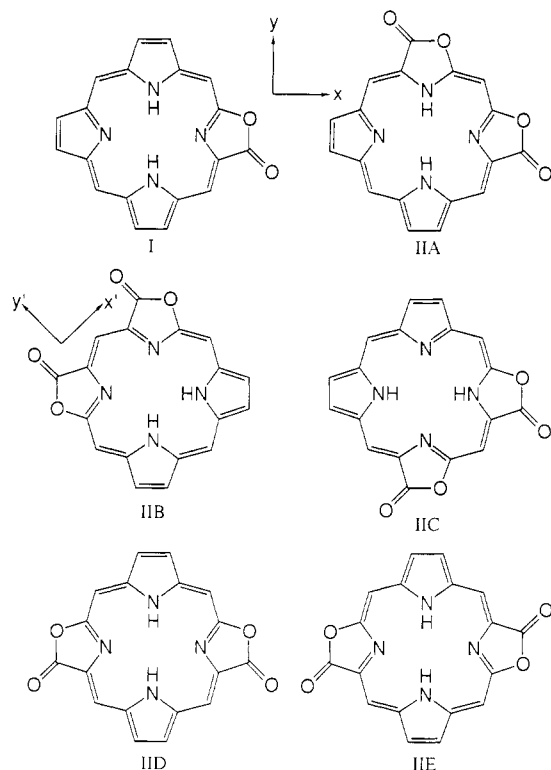
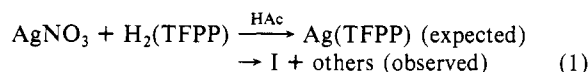


Figure 1. Porpholactone I and porphodilactone II. Although the location of the central protons with respect to the lactone rings is not yet known, we predict that the trans tautomers shown are more stable and that IIB is not stable. See the text.

$\text{H}_2(\text{TFPP})^2$ (25 mg), were heated for 6 h in glacial acetic acid (150 mL) at reflux:



A dramatic spectral change was observed during reaction 1 that was quite different from that expected for $\text{Ag}(\text{TFPP})$. Purification of the reaction mix led to the four banded absorption spectrum (Figure 2A) characteristic of a metal-free porphyrin³ but with the farthest red band unusually intense. The compound has a strong fluorescence (Figure 2C). This fluorescence immediately indicated that the species producing the spectra in Figure 2 was metal free. [This deduction is unambiguous since the only metal present was silver and silver porphyrins show no emission.³] Spectra of the free base, $\text{H}_2(\text{TFPP})$, are also shown in Figure 2.

The new spectra of Figure 2 were quite surprising, unlike that of any known porphyrin, and we began a series of studies designed to determine the nature of the product. In this paper we report on research that shows that the spectra in Figure 2 are from tetra(pentafluorophenyl)porpholactone, I, a rather surprising product from the rather simple reagents used in reaction 1. Subsequent to our identification, we found that tetraphenylporpholactone had been previously prepared by Crossley and King⁴ from the amine and from the keto imine of tetraphenylporphyrin using *m*-chloroperbenzoic acid. They also prepared it from the anhydride using $\text{NaOH-H}_2\text{O}$ -dimethylformamide. Thus we had prepared tetra(pentafluorophenyl)porpholactone directly from the free base using mild reagents.

In this paper we first report on exploratory syntheses that show that not only I but related species are produced by reaction 1. We then report the synthetic procedure that allows synthesis of I

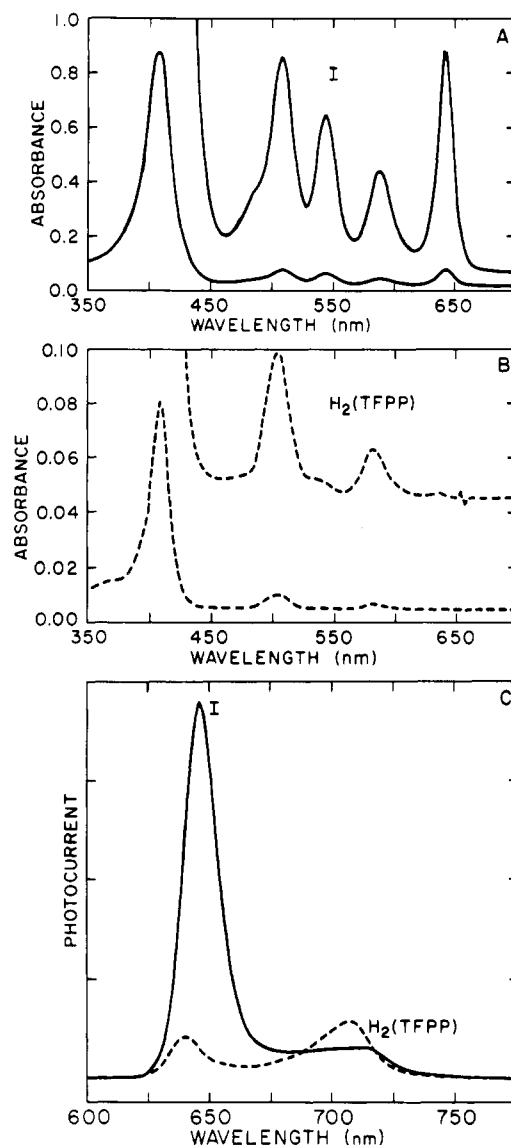


Figure 2. (A) Absorption spectrum of tetra(pentafluorophenyl)porpholactone, I; (B) absorption spectrum of tetra(pentafluorophenyl)porphyrin, $\text{H}_2(\text{TFPP})$; and (C) emission spectra of I (solid line) and $\text{H}_2(\text{TFPP})$ (dashed line). The solvent is CH_2Cl_2 . The emission spectra are uncorrected for the wavelength sensitivity of the detector.

reproducibly in moderate yield and the spectroscopic and mass spectroscopic evidence that supports our identification. We conclude with some iterative extended Hückel calculations on these types of rings. While Crossley and King⁴ gave the name "18-oxo-17-oxachlorin" to tetraphenylporpholactone, we believe that the optical spectra and the calculations show rather clearly that these compounds are closer to porphyrins than chlorins, since the π orbitals of the lactone are thoroughly conjugated into the HOMO and LUMO orbitals known to characterize a porphyrin.³

Exploratory Syntheses

Subsequent to our initial preparation of I and obtaining the spectra of Figure 2, we repeated reaction 1 to obtain more material. As is not surprising with a serendipitous synthesis, in the hands of a second worker (P.C.M.) the product I was not produced in large yield. Instead, several products were obtained on purifying the reaction mixture by chromatography: One product was I, obtained in low yield. Obtained in much higher yield was a second product, which also fluoresced and showed a Soret band but only two visible bands. We shall call this substance X(2). This product had also been obtained, but in low yield, with our initial synthesis. As with I, the fluorescence shows that this too is a metal-free porphyrinic species. A third porphyrinic product, which did not fluoresce, was also obtained. The lack of fluorescence from the

(2) Spellane, P. J.; Gouterman, M.; Antipas, A.; Kim, S.; Liu, Y. C. *Inorg. Chem.* **1980**, *19*, 386-391.

(3) Gouterman, M. In *The Porphyrins*; Dolphin, D., Ed.; Academic Press: New York, 1978; Vol. 3, pp 1-165.

(4) Crossley, M. J.; King, L. G. *J. Chem. Soc., Chem. Commun.* **1984**, 920-922.

Table I. Absorption Peaks (nm)

| compound | solvent | Soret | visible |
|-----------------------|---------------------------------|-------|--------------------|
| H ₂ (TFPP) | CH ₂ Cl ₂ | 410 | 505, 535, 582, 635 |
| Ag(TFPP) | CH ₂ Cl ₂ | 416 | 536, 570 |
| Ni(TFPP) | CH ₂ Cl ₂ | 402 | 524, 559 |
| I | CH ₂ Cl ₂ | 406 | 508, 542, 590, 644 |
| X(2) | toluene | 424 | 560, 608 |
| Ag(2) | ethyl acetate | 422 | 554, 600 |
| Cu(2) | CH ₂ Cl ₂ | 416 | 544, 590 |
| Ni(2) | toluene | 432 | 548, 596 |
| Ni(2) | pyridine | 444 | 570, 608 |

third substance suggests that it is a silver derivative, and we shall refer to it as Ag(2).

Because the initial reaction 1 generally gave only small amounts of I, several variant synthetic procedures were tried. We prepared some authentic Ag(TFPP) by using silver acetate rather than silver nitrate in reaction 1. On heating of Ag(TFPP) in 15 mL of acetic acid with 3 drops of nitric acid at reflux, we obtained small amounts of I but good yields X(2) and Ag(2) defined above. The X(2) material gave a complex proton NMR spectrum in the range $\delta = 8.55$ –8.95 ppm, whereas the Ag(2) material showed no NMR, as expected for a Ag porphyrin compound.

In another variant approach we prepared Ni(TFPP) by refluxing nickel acetate and H₂(TFPP) in acetic acid. As with other nickel porphyrins,³ it showed no fluorescence. The proton NMR was shifted to $\delta = 53.5$ ppm in C₅D₅N. This shift is expected for nickel porphyrins due to the formation of the triplet state in pyridine.⁵ When Ni(TFPP) is heated at reflux for 6 h in 15 mL of acetic acid with 3 drops of nitric acid, a spectral change is observed, leading to a compound we shall refer to as Ni(2). Like Ni(TFPP), it does not fluoresce. The NMR in C₅D₅N shows three broad peaks at $\delta = 66.5$, 65, and 63 ppm.

In a third variant we tried a synthesis in which Cu(NO₃)₂ was substituted for AgNO₃ in reaction 1. The result was a non-fluorescing porphyrinic species that we call Cu(2) that is quite distinct from Cu(TFPP) reported earlier.²

These exploratory studies did not succeed in providing a better synthesis of I. However, we obtained several other species: X(2), Ag(2), Ni(2), and Cu(2). The peak maxima of the species mentioned herein are listed in Table I. We hope to more fully characterize these species in the future. In addition, we found that reaction 1 produces only Ag(TFPP) when formic acid is used in place of acetic acid or when silver acetate is substituted for silver nitrate. Furthermore, none of the unusual porphyrinic species is produced when similar reactions are carried out on tetraphenylporphyrin.

While these exploratory studies produced some interesting metal-free and metal-substituted porphyrinic substances, we still could not reproducibly synthesize I in moderate yield. Analysis of the exploratory reactions suggested that acetic acid was one of the reagents and that perhaps a variant molecule containing CCO might do better. Several were tried. With oxalic acid, (COOH)₂, we were able to reproducibly make I in modest yields, as described in the next section.

Experimental Section

Synthesis and Purification. Tetra(pentafluorophenyl)porphyrin, H₂(TFPP), from which the porpholactone is made, is not easy to purify due to the difficulty in removing the chlorin impurity. Spellane et al.² accomplished this by a metalation–demetalation procedure. We here give more synthetic details since the original paper was not clear.

H₂(TFPP) is made according to Longo et al.⁶ by heating at reflux the pyrrole and pentafluorobenzaldehyde in propionic acid for 6 h. The product is a black tar, which is first cleaned with a wet-packed neutral alumina column with a mixture of petroleum ether and hexane (5 mL:8 mL) as an eluent. Both green and red bands are collected, with a black band remaining at the top. A second purification is accomplished through metalating the porphyrin/chlorin mix in a refluxing chloroform

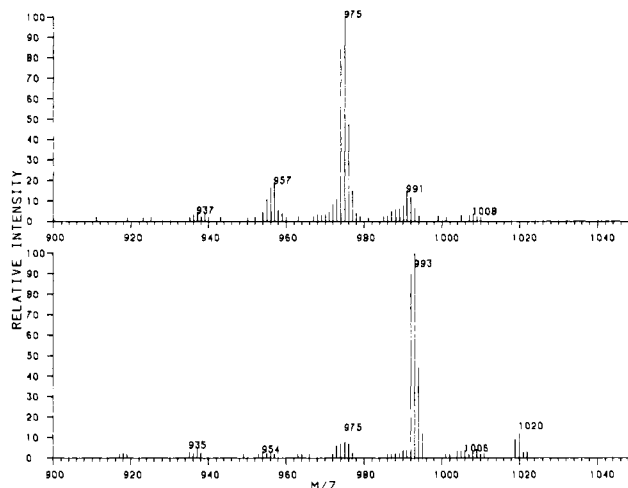


Figure 3. The FAB mass spectrum of tetra(pentafluorophenyl)porphyrin, H₂(TFPP) (top), and of tetra(pentafluorophenyl)porpholactone, I (bottom).

solution with saturated zinc acetate in methanol. The metalated mix is then stripped of solvent and eluted on a wet-packed basic alumina column with a 1:1 mix of hexane and methylene chloride. The red Zn(TFPP) band is left at the top of the column and the green chlorin band is eluted until the column is clear. The Zn(TFPP) is brought down with methylene chloride.

The Zn(TFPP) is demetalated as follows: After removal of the solvent by rotary evaporation, the Zn(TFPP) is dissolved in 40 mL of ethyl acetate. This is stirred with 10 mL of concentrated HCl for 30 min. The two-layer solution is then transferred to a separatory funnel and diluted with 200 mL of water. The organic layer is washed repeatedly with water until the pH is near neutral.

Tetra(pentafluorophenyl)porpholactone, I, was synthesized as follows: To 75 mL of refluxing glacial acetic acid containing 500 mg of silver nitrate and 1 g of oxalic acid dihydrate was added 100 mg of tetra(pentafluorophenyl)porphyrin. The solution is heated at reflux (118 °C) for 2 h. Absorption spectra of samples of the reaction mix were taken every half hour to optimize the reaction conditions, in particular the reaction time and the amount of oxalic acid. From the ratio of the absorbance at 644 nm to that at 508 nm in the reaction mix we estimate that roughly 40% of the H₂(TFPP) was converted to I.

The crude product is first purified on a wet-packed silica gel column using a hexane/methylene chloride mix (14 mL:5 mL). The methylene chloride is previously deacidified on a basic alumina column. The column first yields a pink band, which is a combination of Ag(TFPP) and H₂(TFPP). The next band is dark red, which is I contaminated with some H₂(TFPP). A second purification was achieved with a wet-packed neutral alumina column, using a 4:1 mix of hexane or pentane to deacidified methylene chloride. The dark fraction collected was checked by UV–vis spectroscopy as before. The solvent was removed first by a rotary evaporator and then pumping on a vacuum line. The yield of the purified product was roughly 15%.

Mass Spectrometry. The mass spectra were obtained with a Kratos MS-50 triple analyzer at the Midwest Center for Mass Spectrometry. Fast atom bombardment (FAB) by 7 keV argon atoms was used to desorb the ions from a matrix of 5:1 3-nitrobenzyl alcohol/glycerol.

Upon FAB, the starting material H₂(TFPP) produces an M + H ion of m/z 975 (observed 975.0623, theory for C₄₄H₁₁N₄F₂₀ 975.0664, error 4.5 ppm). An (M + H)⁺ ion of m/z 993 is desorbed by FAB for compound I. While the nominal mass difference suggests H₂O addition, exact mass measurements indicate a change of an *exo*-ethynyl unit, C₂H₂, to CO₂, i.e. the change of a porphyrin to a porpholactone (observed 993.0408, theory for C₄₃H₉N₄O₂F₂₀ 993.0406, error 0.2 ppm). This change is compatible with the NMR and IR data discussed in the next sections. The two spectra are shown in Figure 3.

In addition to I, a second component with an (M + H)⁺ of m/z 1020 was observed in the FAB mass spectrum of the reaction product, which was not present in the FAB spectrum of H₂(TFPP). The presence of a small amount of nitro-substituted H₂(TFPP) was confirmed by exact mass determination (observed 1020.0510, theory for C₄₄H₁₀N₅O₂F₂₀ 1020.0515, error 0.7 ppm). Possibly this is an intermediate in the transformation of H₂(TFPP) to I.

¹H NMR spectra were run on a Varian VXR 300- and 500-MHz machines. Samples were made from 10–15 mg of compound dissolved in 0.3 mL of deuterated chloroform. The spectrum of H₂(TFPP), shown

(5) La Mar, G. N.; Walker, F. A. In ref 3; Vol. 4, pp 61–157.

(6) Longo, F. R.; Finarelli, M. G.; Kim, J. B. *J. Heterocycl. Chem.* **1969**, 6, 927–931.

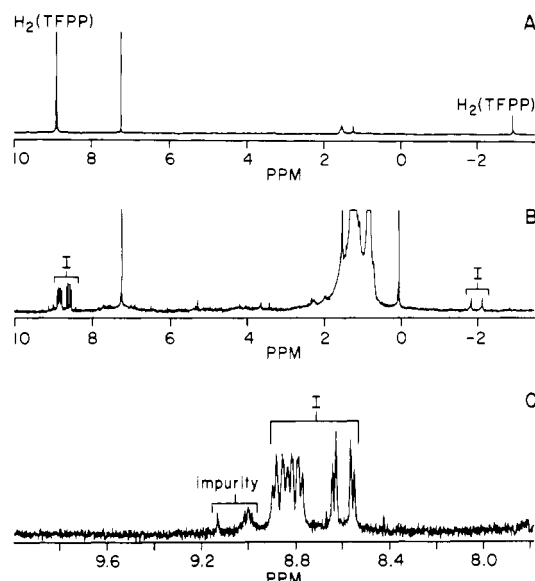


Figure 4. Proton NMR spectra taken at 300 MHz in CDCl_3 : (A) tetra(pentafluorophenyl)porphyrin and (B) and (C) tetra(pentafluorophenyl)porpholactone, I.

Table II. Proton NMR Parameters for Tetra(pentafluorophenyl)porpholactone

| | δ , ppm | $\Delta\delta$, ppm | J_{AB} , Hz |
|-----|----------------|----------------------|-----------------|
| I | 8.598 | 0.076 ± 0.001 | 4.65 ± 0.15 |
| II | 8.806 | 0.043 ± 0.001 | 5.6 ± 0.6 |
| III | 8.871 | 0.040 ± 0.001 | 5.5 ± 0.6 |

in Figure 4A, is particularly simple with one peak at $\delta = 8.929$ ppm due to the eight exo protons and a second peak due to the central protons at $\delta = -2.916$ ppm. Figure 4, parts B and C, shows the proton NMR of I. In the region of the exo protons, a complex pattern can be interpreted as one isolated AB pattern in the region $\delta = 8.57$ –8.66 ppm and two overlapped AB patterns in the region $\delta = 8.79$ –8.90 ppm. Additionally, there are two peaks corresponding to the central protons at $\delta = -1.82$ and -2.10 ppm. The integral ratios conform to this identification.

The three AB patterns can be analyzed in terms of an average δ value for each pair, a splitting $\Delta\delta$ for each pair, and a coupling constant, J_{AB} . These are listed in Table II. With these values the 300-MHz and 500-MHz spectra were fit within 1.6 Hz.

^{19}F NMR. Fluorine NMR were taken on a Varian VXR 300-MHz machine. The parent, $\text{H}_2(\text{TFPP})$, shows a doublet of doublets at $\delta = 24.75$ –24.86 ppm identified as ortho fluorine (with respect to the porphyrin ring), a triplet at $\delta = 10.04$ –10.19 ppm identified as para fluorine, and a triplet of doublets at $\delta = (-0.09)$ –(+0.10) ppm identified as meta fluorine. These appear in Figure 5A. Figure 5B shows the same spectrum of the porpholactone I. Each of the simple multiplets of the parent are split into two groups of multiplets. The intensity ratios stand as 6:2:3:1:6:2. Thus four pentafluorophenyl groups remain, but one is distinctly different from the others, as might be expected for the phenyl group next to the carbonyl oxygen in I.

Infrared Spectra. IR spectra were taken on a Nicolet 5DXC FTIR spectrophotometer. In the region 1700 – 1800 cm^{-1} , where $\text{H}_2(\text{TFPP})$ shows no vibrational absorption, I has a strong band with peaks at 1745 , 1760 , and 1790 cm^{-1} . This band compares nicely to bands at 1700 and 1800 cm^{-1} that appear in 4-(ethoxymethylene)-2-phenyl-2-oxazolin-5-one, an unsaturated azlactone compound.⁷ Crossley and King⁴ report a band at 1760 cm^{-1} in tetraphenylporpholactone. That I is not a nitro substituted porphyrin is shown by the absence of characteristic IR absorptions at ~ 1350 and $\sim 1550\text{ cm}^{-1}$.

Optical Absorption. Spectra were run on a Hewlett-Packard 8450 UV/vis spectrophotometer. The main bands appear at the following at λ_{max} (log ϵ) (CH_2Cl_2): 406 (5.05), 508 (4), 542 (3.87), 590 (3.72), 644 nm (4.07). These compare to 423 (5.43), 525 (4.07), 562 (4.09), 592 (3.87), 643 nm (3.49) reported by Crossley and King⁴ for the tetraphenylporpholactone. Our ϵ values have been raised 15% to make log $\epsilon = 4$ for the 508-nm band, since we suspect that our weighed sample had tightly adsorbed hexane.

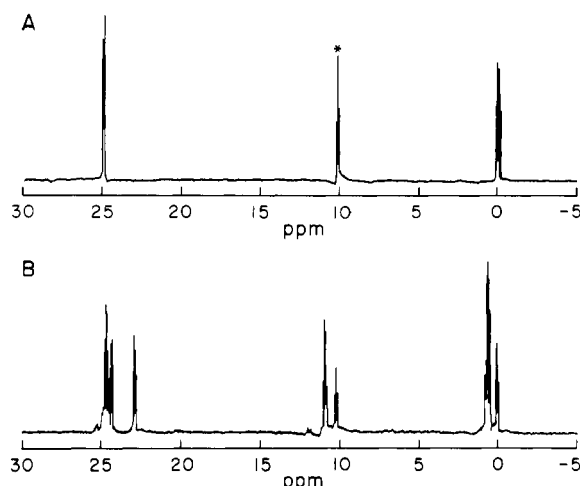


Figure 5. ^{19}F NMR spectra (unreferenced) taken in CDCl_3 : (A) tetra(pentafluorophenyl)porphyrin and (B) tetra(pentafluorophenyl)porpholactone, I. When referenced externally with CCl_3F at 0, the peak with a * is at $\delta = 0.048$.

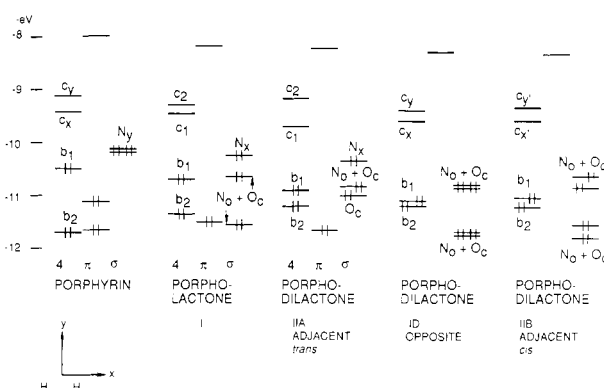


Figure 6. HOMO (high occupied) and LUMO (lowest unoccupied molecular orbital) energy levels by iterative extended Hückel calculations for porphyrin; porpholactone I; adjacent *trans*-porphodilactone IIA; opposite porphodilactone IID; and adjacent *cis*-porphodilactone IIB. See Figure 1 for the structures.

Fluorescence Spectra. The fluorescence spectrum shown in Figure 2C for I was taken on a Perkin-Elmer 650-10S fluorescence spectrophotometer. An excitation spectrum showed that this emission was due to the species whose absorption spectra is shown in Figure 2A. A rough fluorescence quantum yield for I was determined by comparison with $\text{H}_2(\text{TFPP})$. Both species were excited at $\lambda = 510\text{ nm}$ and the integrals of the fluorescence and the absorbances of each sample were measured. Using these numbers and assuming that $\text{H}_2(\text{TFPP})$ has a fluorescence yield of 0.07,² we obtain a fluorescence quantum yield of 0.2.

Iterative Extended Hückel (IEH) Calculations

We have carried out iterative extended Hückel calculations on some of the porpholactone species shown in Figure 1. The parameters used are those of Zerner et al.^{8,9} The geometry for the ring is that used in these papers, except for that of the azlactone ring. For this ring we used the porphyrin pyrrole geometry with the following minimal changes: one H is removed and its ring C is replaced with O; the other H in the azlactone ring is changed to O and the length of the CO bond is made 1.19 \AA compared to 1.08 \AA used for the CH bond it replaced. While this is not expected to be the exact geometry of the azlactone ring, it should be adequate for comparison calculations, whose goal is a qualitative exploration of the electronic structure of porpholactone and porphodilactone.

Figure 1 shows a structure for porpholactone I. In particular it shows the central protons *trans*, avoiding the azlactone ring.

(8) Zerner, M.; Gouterman, M. *Theoret. Chim. Acta* **1966**, *4*, 44–63.

(9) Zerner, M.; Gouterman, M.; Kobayashi, H. *Theoret. Chim. Acta* **1966**, *6*, 363–400.

(7) *The Aldrich Library of FT-IR Spectra*, Pouchert, C. J., Ed.; Aldrich Chemical Co.: Milwaukee, 1985, p 400.

Technische Hochschule in Darmstadt, Prof. David Dolphin of the University of British Columbia, and Prof. C. K. Chang of Michigan State. Prof. Clifford Leznoff of York University suggested the collaboration with Dr. Cerny. In our own Department, discussion with Prof. Norman Rose led to the addition of oxalic acid as a reagent. Dr. Niels Andersen analyzed the AB patterns in the proton NMR providing the data for Table II. J. Wan provided spectral data on Ag(2). Dr. Edmond Green gave

additional help. The research was partly supported by a grant from Abbott Research, inc., of Bothell, WA. The mass spectrometer experiments were conducted at the Midwest Center for Mass Spectrometry, a National Science Foundation Regional Instrumentation Facility (Grant CHE-8620177).

Registry No. I, TFPP derivative, 119998-79-7; IIA, 119998-81-1; IIB, 119998-82-2; IID, 119998-80-0; TFPD, 25440-14-6.

Novel Rearrangement of 5,6-Disubstituted Bicyclo[4.2.0]octan-2-ones with AlCl_3 . Application to Total Synthesis of (\pm) -5-Oxosilphiperfol-6-ene and (\pm) -Silphiperfol-6-ene

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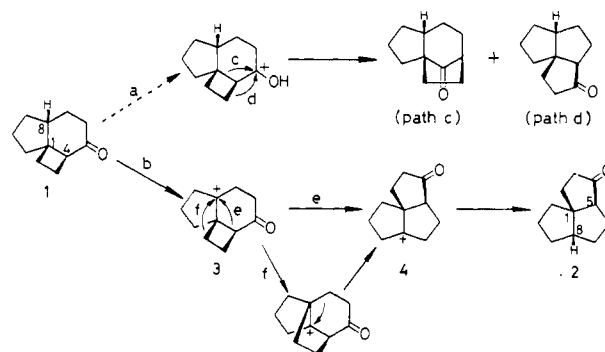
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Abstract: The acid-catalyzed rearrangement of bi- and tricyclic cyclobutyl ketones **8–20** having a bicyclo[4.2.0]octan-2-one moiety with AlCl_3 was studied to elucidate the scope and limitations of the novel rearrangement by which the tricyclic ketone **1** gave the angularly fused triquinane ketone **2**. 5- or 6-methylbicyclo[4.2.0]octan-2-ones (**8** and **9**) did not rearrange. 5,6-Disubstituted bicyclo[4.2.0]octanones **10–18** without methyl substituent at C(1) rearranged smoothly via the new-type pathways to give diquinane derivatives **23–32**. Ketones **19** and **20** having a C(1) methyl group of the bicyclo[4.2.0] unit rearranged through the Cargill-type pathway to give bicyclo[3.2.1]octan-8-one derivatives **33** and **35** and the diquinane ketone **34**. Tetracyclic ketone **21** and bicyclo[5.2.0]nonan-2-one derivative **22** also rearranged via the new-type pathway to give the tetraquinane ketone **36** and homotriquinane **37**. A plausible reaction mechanism for the novel rearrangement is proposed which involves the fission of the central cyclobutane bond to generate the homoallylcarbiny cation **43** (path g) as the primary process followed by the 1,2-hydride shift (path h) and the subsequent transannular cyclization (path i) of the cation **44** to the product. With this rearrangement as the key step, the facile total syntheses of the angularly fused triquinane natural products (\pm) -5-oxosilphiperfol-6-ene (**5**) and (\pm) -silphiperfol-6-ene (**6**) were performed.

The acid-catalyzed rearrangement of cyclobutyl ketones involved in polycyclic ring systems such as $[m.n.2]$ propellanes is well-known as the Cargill reaction¹ and has been used in natural product syntheses.² Recently we have found that $(1S^*,4S^*,8R^*)$ -tricyclo[6.3.0.0^{1,4}]undecan-5-one (**1**) rearranges under action of Lewis acid through a new pathway (path b) to give angularly fused triquinane **2** with high selectivity and proposed the mechanism via the cations **3** and **4** which is entirely different from the Cargill pathway (path a) (Scheme I).³ This novel rearrangement is noteworthy not only from the viewpoint of the novelty in the reaction path, but also in view of the product whose skeleton is in common with angularly fused triquinane-type natural products.⁴ In this connection, we wish to describe here the scope and limitations of the new-type rearrangement for various types of bicyclo[4.2.0]octan-2-one and bicyclo[5.2.0]nonan-2-one derivatives **8–22** catalyzed by Lewis acid (AlCl_3), a new proposal for the reaction mechanism which involves the homoallylcarbiny cation **43**, and its application to the total syntheses of the angularly fused triquinane natural products (\pm) -5-oxosilphiperfol-6-ene (**5**)^{5,6} and (\pm) -silphiperfol-6-ene (**6**)^{7,8} in order to exemplify the utility of the rearrangement.

Scheme I



Previously, we tentatively assigned the stereochemistry of **1** to be $1S^*,4S^*,8S^*$ based on the well-known Wiesner's empirical

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