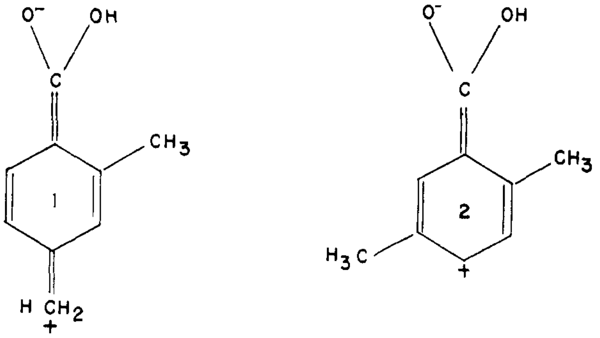


Fig. 2.—Resonance structures for: (1) 2,4-dimethylbenzoic acid and (2) 2,5-dimethylbenzoic acid.

the π-electron density associated with their rings is somewhat greater than that of the conjugated phenyl group. The non-conjugated rings give rise to the band at *ca.* 734 cm.$^{-1}$, whose intensity depends on the number of these groups present.

Intensity Changes Related to the Degree of Rehybridization.—The pronounced intensity change which accompanies the positive shift in frequency of the out-of-plane C–H bending vibration results directly from the decreased π-electron concentration around the ring. Eggers[11] has recently shown, on the basis of orbital following, that π-electrons give a dipole moment perpendicular to the molecular plane which is in addition to that produced by the C–H bonds vibrating normal to that plane. These two moments interact so that the total dipole moment change is manifested in the intensity of the C–H out-of-plane bending vibration bands. A decrease in π-electron concentration therefore gives rise to both a positive shift in frequencies and lower intensity bands.

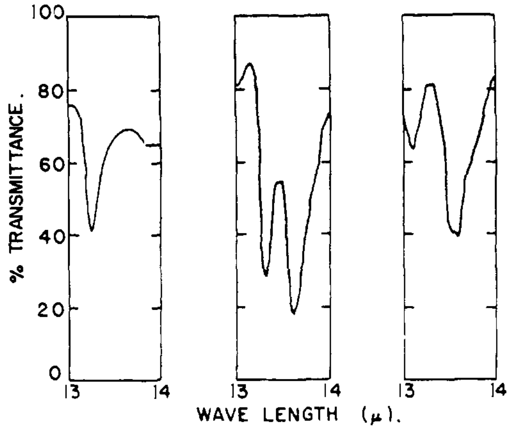


Fig. 3.—Spectra from 13–14 μ of (from left to right) phenylacetic acid, diphenylacetic acid and triphenylacetic acid as mineral oil slurries.

AMES, IOWA

---

[11] D. F. Eggers, Jr., *J. Chem. Phys.*, **23**, 221 (1955).

[CONTRIBUTION OF THE DEPARTMENT OF CHEMISTRY OF CLARK UNIVERSITY]

Tetraphenylporphine and Some *para*-Substituted Derivatives[1,2]

BY DANIEL W. THOMAS AND ARTHUR E. MARTELL

RECEIVED SEPTEMBER 22, 1955

Tetraphenylporphine and its *para* methyl, methoxy, chloro and nitro derivatives have been synthesized by direct reaction of pyrrole with the corresponding aldehyde. Chlorins and other by-products were separated chromatographically and characterized by spectrophotometric analysis. The yields of main product decrease as the acceptor activity of the aldehyde carbonyl increases.

Since the early investigations of the preparation and properties of porphine by Fischer and Gleim[3] and by Rothemund,[4] the recent studies of tetraphenylporphine[5–7] and of other α,β,γ,δ-tetrasubstituted porphyrins[8,9] have provided further information and a greater understanding of the structure and internal bonding in chelate compounds derived from porphine. The purpose of this investigation was to prepare and study a number of derivatives of tetraphenylporphine in which the *para* positions have been substituted with polar groups having well-known inductive and resonance effects. This study is the first part of a more extensive investigation which includes a study of various metal chelates of these substituted tetraphenylporphines.

The synthesis of tetraphenylporphine has been reported previously[10–13] and the isolation of the *p*-methoxy derivative also has been reported by Rothemund.[8] None of the other derivatives of tetraphenylporphine prepared in this Laboratory have appeared in the literature.

Discussion of Results

Synthesis.—The method of synthesis which proved most satisfactory for the purposes of this investigation is the direct one-step procedure simi-

---

[1] This research was supported by the National Institute of Health of the U. S. Public Health Service under Grant No. G-3819(c).

[2] Abstracted from a dissertation submitted by Daniel W. Thomas to the Faculty of Clark University in partial fulfillment of the requirements for the degree of Master of Arts.

[3] H. Fischer and W. Gleim, *Ann.*, **521**, 157 (1935).

[4] P. Rothemund, THIS JOURNAL, **57**, 2010 (1935).

[5] V. M. Albers and H. V. Knorr, *J. Chem. Phys.*, **9**, No. 7, 497 (1941).

[6] G. D. Dorough and K. T. Shen, THIS JOURNAL, **72**, 3939 (1950).

[7] G. D. Dorough, J. R. Miller and F. M. Huennekens, *ibid.*, **73**, 4315 (1951).

[8] P. Rothemund, *ibid.*, **61**, 2912 (1939).

[9] V. M. Albers and H. V. Knorr, *J. Chem. Phys.*, **9**, No. 3, 197 (1941).

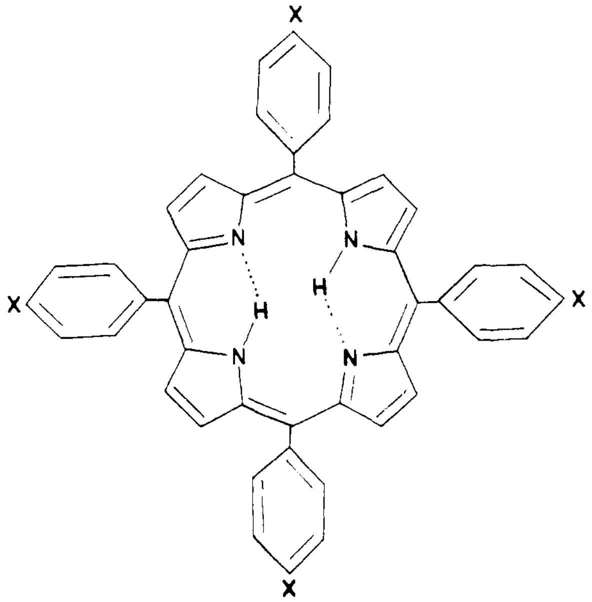
[10] P. Rothemund and A. R. Menotti, THIS JOURNAL, **63**, 267 (1941).

[11] S. Aronoff and M. Calvin, *J. Org. Chem.*, **8**, 205 (1943).

[12] R. H. Ball, G. D. Dorough and M. Calvin, THIS JOURNAL, **68**, 2278 (1946).

[13] J. H. Priesthoff and C. V. Banks, *ibid.*, **76**, 937 (1954).

lar to the one outlined by Rothemund and Menotti[10] and by Ball, Dorough and Calvin.[12] Although the amounts of starting materials were increased twenty-fold over that described by Rothemund and Menotti, the same ratio of reagents was maintained. In this way, tetraphenylporphine and its *para chloro, methoxy* and *methyl* derivatives were prepared. In the synthesis of the *p*-nitro compound, milder conditions were found to be necessary. The structures of the porphines which were synthesized are indicated by formula I.



Formula I, X = H, CH_3, OCH_3, Cl, NO_2

The yields of tetraphenylporphine obtained in the present investigation compare favorably with those reported by other investigators for this type of reaction. The conditions described in the Experimental part seem to be the optimum values. In agreement with the observations of Ball, *et al.*,[12] the addition of zinc acetate to the reaction mixture considerably increased the yield of porphine in certain cases. Thus, the 7.5 and 2.6% yields of tetraphenylporphine and its *p*-chloro derivative were increased to 10 and 15%, respectively, in the presence of Zn(II) ions. On the other hand, from the few reactions attempted, no crystalline zinc porphine could be isolated when a zinc salt was added in the preparation of the *p*-methyl and *p*-nitro derivatives of tetraphenylporphine. The smaller proportion of chlorin formed as a by-product in the present investigation is due to the use of somewhat milder reaction conditions than those in cases where appreciable amounts of chlorins were reported as an impurity.

With the exception of the methoxy derivative, the yields of the *para*-substituted tetraphenylporphine were in general much lower than that of the parent compound. The poorest yield was obtained with the nitro compound, probably as the result of greater activity of the aldehyde group. In this case the use of much milder reaction conditions was necessary. The yield of product seems to vary approximately inversely as the activity of the aldehyde group, the poorest results being obtained with a strongly electron-attracting substituent. Poor yields were associated with the formation of larger amounts of liquid or solid "tars" which probably contained polymeric condensation products of the aldehyde and pyrrole. In the case of *p*-chlorobenzaldehyde, the isolation of considerable amounts of *p*-chlorobenzoic acid in a nitrogen atmosphere indicates that the Cannizzaro reaction may be an important side reaction.

Various conditions, other than those described in the Experimental part, were investigated for the preparation of the nitro compound. Reactions in a pressure vessel at 165° and at lower temperatures for 48 hours gave only a solid tar from which the desired product could not be obtained readily. The nitroporphine was prepared at room temperature in a very small yield by allowing the reactants to stand in a closed flask for three weeks. The use of a solvent such as methanol was found to be useful in cutting down side reactions and increasing the yield of the nitro derivative in a number of small-scale refluxing reactions.

The by-products obtained in the chromatographic purification of the porphine derivatives, listed in Table I, were obtained as acetone solutions, which were measured directly in the visible and near-ultraviolet regions with a Beckman DU spectrophotometer. Since the amounts of these substances were insufficient to allow isolation and purification, only optical densities of the solutions were obtained. Separation of the impurities on talc columns was accomplished through the use of relatively polar samples of trichloroethylene. The resolution obtained with a highly purified solvent was incomplete in most cases.

The melting point of tetraphenylporphine was reported as 450° by Rothemund.[10] In the present investigation, the order of melting points was determined by observing the melting point of each derivative with respect to tetraphenylporphine when all the compounds were placed on a uniformly heated metal surface. The nitro derivative did not melt but sublimed near the melting point of the *p*-chloro compound. The decreasing order of melting points was found to be *p*-nitro > *p*-chloro > *p*-methoxy > phenyl > *p*-methyl.

The approximate solubilities of the porphines in various solvents are listed in Table II, from which it is possible to observe the influence of the polar groups on solubility. The most pronounced effect may be observed in the nitro compound, which is much less soluble than the other porphines in the usual solvents of low polarity and will only dissolve in those of somewhat higher polarity. This behavior is the result of the four strongly polar nitro groups located at the periphery of the molecule (see formula I) where intermolecular interactions would be greatest. The solubility also correlates with the melting points in accordance with well-established principles.

In certain cases the elementary analyses gave somewhat lower than theoretical values. In view of the careful purification and spectral characterization of all of these compounds, they are believed to be quite pure, and the low analyses, therefore, seem

TABLE I

ABSORPTION CHARACTERISTICS OF BY-PRODUCTS

Characteristics of chromatographic separation	Absorption maxima, mμ					Spectral type	Characterization
Tetraphenylporphine	645	590	545	512	480	.....	.....
2-mm. brown band	645	590	545	510	475	Phyllo	Porphine
1-mm. brown-yellow band	645	590	545	512	480	Etio	Porphine + trace chlorin
Blue-green-brown bands (mixture)	640	610	537	510		Etio[a]	Porphine
1-mm. faint maroon band	645	590	545	512	480	Etio[a]	Porphine + trace chlorin
Tetra-*p*-tolylporphine	647	590	547	513	480	.....	.....
2-mm. brown-green band	645	585	545	510		Etio	Porphine
3-mm. brown band	650	590	545	514		Etio	Porphine + chlorin
2-mm. blue-green band	645	590	540	510	475	Etio[a]	Porphine
1-mm. maroon band	645	588	545	513	478	Etio[a]	Porphine
Tetra-(*p*-methoxyphenyl)-porphine	650	593	553	517	483	.....	.....
2-mm. brown-green band	650	595	555	517		Etio	Porphine + chlorin
Red-green-brown bands (mixture)	645		553	524	485	Rhodo[a]	Porphine
Tetra-(*p*-chlorophenyl)-porphine	645	589	546	513	480	.....	.....
12-mm. dark green band	652	592	545	513	481	Chlorin	Chlorin + trace porphine
25-mm. pale green section	653	594	545	513		Chlorin	Chlorin
40-mm. pale-brown green band	647	589	545	513	480	Etio	Porphine + trace chlorin
40-mm. grass green layer	645	589	546	513	480	Etio	Porphine
Tetra-(*p*-nitrophenyl)-porphine	645	590	552	515	480	.....	.....
12-mm. green-brown layer	648	590	552	515		Etio	Porphine
12-mm. tan-brown-green band	647	590	552	515	480	Etio	Porphine

[a] The last two chromatographic separations listed for tetraphenylporphine and tetra-*p*-tolylporphine, and the red-green-brown bands isolated from the methoxy derivative were obtained from a rechromatograph of the porphyrin eluate.

TABLE II

Solvent	Dielectric constant	A[a]	B	C	D	E
Dioxane	2.209	3	3	2	3	1
Benzene	2.282	3	3	2	3	1
Carbon disulfide	2.647	4	4	4	3	0
Trichloroethylene	3.42	4	4	1	3	0
Ether	4.335	1	1	1	1	0
Chloroform	5.05	4	4	3	3	2
Pyrrole	7.48	4	4	4	3	2
Pyridine	12.5	4	4	4	3	3
Acetone	21.4	1	1	1	2	1
Methanol	33.1	0	0	0	0	0
Water	80.37	0	0	0	0	0
Concd. sulfuric acid		4	4	4	3	4
Concd. hydrochloric acid		2	1	1	1	1
Dil. hydrochloric acid		0	0	1	0	0
Glacial acetic acid		3	3	4	2	0

[a] Numbers represent relative solubilities: 0, insoluble; 1, slightly; 2, sparingly; 3, moderately; and 4, very soluble. A, tetraphenylporphine; B, tetra-*p*-tolylporphine; C, tetra-(*p*-methoxyphenyl)-porphine; D, tetra-(*p*-chlorophenyl)-porphine, E, tetra-(*p*-nitrophenyl)-porphine.

to be the result of incomplete combustion of the highly stable porphine ring.

Experimental

Tetraphenylporphine.—Two hundred ml. of distilled benzaldehyde, 200 ml. of distilled pyridine and 100 ml. of distilled pyrrole (Eastman Organic Chemicals) reacted according to the general procedure of Ball, *et al.*,[12] for 48 hours at 170°. The product which was obtained by dilution of the tar with a 10:1 ether–acetone mixture was 18.8 g. or 7.5% of the theoretical value. A 0.2-g. sample of this product was dissolved in trichloroethylene and chromatographed with additional solvent on a 5.5-inch, 3-inch diameter talc column. The deep maroon porphyrin eluate was evaporated to dryness and the residue was recrystallized from a chloroform–methanol solvent mixture. Over 150 mg. of crystalline tetraphenylporphine was thus obtained for spectrophotometric study.

Anal. Calcd. for $C_{44}H_{30}N_4$: C, 85.99; H, 4.89; N, 9.12. Found: C, 85.73; H, 5.00; N, 9.15.

In addition to a thin layer of tar on the top of the column, impurities were isolated as a number of bands, which are listed in Table I in the order of descending position on the column.

Tetra-*p*-tolylporphine.—The same general procedure as the one described above was employed with the following modifications. The reaction mixture, consisting of 100 ml. of *p*-tolualdehyde (obtained from City Chemical Co., N. Y.), 50 ml. of pyrrole and 81 ml. of pyridine, was heated to 176–181° for 48 hours. An immiscible yellow-brown liquid was separated from the tar, which was then diluted with a 10:1 ether–acetone mixture. Since no solid material was isolated, the solution was further diluted with ether alone until precipitation occurred. The resulting mixture was then allowed to stand for two days to ensure complete crystallization. Filtration yielded 3.7 g. of porphyrin, relatively free of chlorin, and an additional 0.5-g. batch was recovered by the addition of more ether to the mother liquor and allowing the mixture to stand at room temperature overnight. The combined products were dissolved in chloroform in a Soxhlet apparatus, and the resulting maroon solution was evaporated to 30 ml. and diluted to 500 ml. with methanol. The crystalline product thus obtained weighed 3.7 g., and an additional 0.1 g. was obtained by evaporation of the mother liquor. The total yield was 3% of the theoretical amount. A 0.2-g. sample was chromatographed and recrystallized as described above. Needle-like crystals weighing 120 mg. were isolated.

Anal. Calcd. for $C_{48}H_{38}N_4$: C, 85.97; H, 5.67; N, 8.36. Found: C, 85.71; H, 5.74; N, 8.20.

A number of colored bands which appeared on the column were separated and analyzed spectrophotometrically. The results, listed in Table I, indicate that all contained porphines except for one band which contained a small amount of chlorin.

Tetra-(*p*-methoxyphenyl)-porphine.—A reaction mixture consisting of 100 g. of anisaldehyde, 50 ml. of pyrrole and 90 ml. of pyridine was heated at 168–175° for 48 hours. The crystalline porphine was recovered by direct filtration after diluting the tarry reaction mixture with a 2:1 mixture of ether and acetone. The crystals were then washed with 100 ml. of the mixed solvent. The yield was 9.3 g. or 7.1% of the theoretical amount. The compound was extracted with 250 ml. of chloroform in a Soxhlet apparatus and, after concentrating this solution, it was diluted with two times its volume of hot methanol. The lustrous silver-blue-violet crystalline product weighed 8.4 g., and 0.5 g. of fine violet-black crystals were recovered by evaporation of the mother liquor. A 180-mg. sample of the recrystallized product was chromatographed and crystallized as described above to give 51 mg. for spectrophotometric study.

Anal. Calcd. for $C_{48}H_{38}N_4O_4$: C, 78.47; H, 5.18; N, 7.63. Found: C, 77.41; H, 4.77; N, 7.95.

Spectrophotometric analysis given in Table I of the various colored impurity bands separated from the chromatographic column gave, in addition to the usual etio-type spectra, a rhodo-type spectrum, which indicated that perhaps a phenyl ring is missing or that a pyrrole ring may be substituted in one of the fractions.

Tetra-(*p*-chlorophenyl)-porphine.—A reaction mixture consisting of 47.7 g. of pyrrole, 100 g. of *p*-chlorobenzaldehyde (m.p. 47.8°) and 98 ml. of pyridine was treated as outlined above for 48 hours at 176°. Direct filtration of the reaction mixture resulted in the isolation of 3.2 g. of purple crystals. Dilution of the mother liquor with ether–acetone resulted in the crystallization of 0.5 g. of additional porphyrin. Further dilution with ether resulted in the isolation of a quantity of *p*-chlorobenzoic acid. The porphyrin was extracted with chloroform; the chloroform solution evaporated to a small volume, and diluted with four times its volume of methanol. The crystalline material thus formed weighed 3.5 g., which represents 2.6% of the theoretical amount. A 174-mg. sample of this material dissolved in a less polar trichloroethylene solvent than previously used was chromatographed as described above and recrystallized from chloroform–methanol to yield 67 mg. of purified porphine.

Anal. Calcd. for $C_{44}H_{26}N_4Cl_4$: C, 70.21; H, 3.46; N, 7.45; Cl, 18.88. Found: C, 70.34; H, 3.38; N, 7.30; Cl, 18.65.

Separation and analysis of the isolated bands gave, in addition to some relatively pure porphine which had been adsorbed on the lower region of the talc, three fractions containing appreciable to large quantities of chlorin. It can be observed in Table I that the presence of a greater amount of chlorin impurity is indicated by an increase of wave length of the first absorption peak near 650 mμ.

Tetra-(*p*-nitrophenyl)-porphine.—A number of small-scale refluxing reactions were run at temperatures between 100 and 130° for lengths of time which varied from 24 to 48 hours. A number of successful reactions are summarized below:

p-Nitrobenzaldehyde, g.	Pyrrole, ml.	Pyridine, ml.	Methanol, ml.	*t*, °C.	Time, hr.	Yield, mg.
2.5	2.0	1.0	3.1	105	24	7
2.5	2.0	1.0	3.0	112	24	30
2.5	2.0	1.0	2.6	120	40	13
5.0	4.0	1.5	4.0	130	40	33
5.0	4.0	2.0	3.3	130	44	50
2.5	1.1	1.0	2.8	120	24	84

The last of the runs listed above represents about 2.6% of the theoretical yield. The combined yields obtained above (~0.20 g.) was extracted with 200 ml. of chloroform in a Soxhlet apparatus. Eight days were necessary to dissolve most of the porphine, which began to crystallize out of the solution before the extraction was complete. The product was recrystallized by the addition of methanol to a chloroform solution. The amount of purified material thus obtained weighed 138 mg.

The compound was chromatographed on an 8-cm. by 3-cm. talc column. A 25-mg. sample was dissolved in 400 ml. of hot chloroform to give a deep orange-red solution which appeared green on the talc. Development of the chromatogram with more chloroform resulted in the recovery of the compound in solution and the formation of a 12-mm. green-brown layer at the top of the column, which was coated with tar impurities. Below this was found a 12-mm. tan-brown-green band. Spectrophotometric analysis of both bands in acetone solution gave spectra very similar to that of tetra-(*p*-nitrophenyl)-porphine itself.

Anal. Calcd. for $C_{44}H_{26}N_4O_8$: C, 71.55; H, 3.52; N, 15.15. Found: C, 67.12; H, 3.63; N, 12.60.

Acknowledgment.—The authors are indebted to Dr. Richard B. Martin for assistance with, and supervision over, the initial phases of this work.

WORCESTER, MASS.

[CONTRIBUTION OF THE DEPARTMENT OF CHEMISTRY OF CLARK UNIVERSITY]

Absorption Spectra of *para*-Substituted Tetraphenylporphines[1,2]

BY DANIEL W. THOMAS AND ARTHUR E. MARTELL

RECEIVED SEPTEMBER 29, 1955

Absorption spectra of tetraphenylporphine, tetra-(*p*-methoxyphenyl)-porphine, tetra-*p*-tolylporphine, tetra-(*p*-chlorophenyl)-porphine and tetra-(*p*-nitrophenyl)-porphine in the ultraviolet, visible and infrared regions are reported. The visible and ultraviolet spectra indicate that the *para*-substituents exert only a small effect on the electronic transitions of the porphine ring system. Assignments of infrared frequencies are made where possible.

The syntheses of tetraphenylporphine and its *p*-methyl, methoxy, chloro and nitro derivatives have been described in a recent publication.[3] In the present paper are described the ultraviolet, visible and infrared spectra of these compounds, with a view to determining the influence, if any, of the *p*-phenyl substituents on the porphine ring and on the electron-donor properties of the central nitrogen atoms.

A small amount of work has been reported on the infrared spectra of the porphines, but nothing has yet appeared on the tetraphenylporphines. Of the infrared studies made on pyrrole-substituted prophyrins, assignments have been suggested chiefly for the substituent groups,[4,5] and few for the porphine structure itself. However, a number of investigations of N–H bonding have been reported by Falk and Willis[4] and Vestling and Downing.[6] Visible and ultraviolet spectra have been reported for tetraphenylporphine.[7–10] No spectra have

---

(1) This research was supported by the National Institutes of Health of the U. S. Public Health Service under Grant No. G-3819(c).

(2) Abstracted from a dissertation submitted by Daniel W. Thomas to the Faculty of Clark University in partial fulfillment of the requirements for the degree of Master of Arts.

(3) D. W. Thomas and A. E. Martell, THIS JOURNAL, **78**, 1335 (1956).

(4) J. B. Falk and J. B. Willis, *Aust. J. Scient. Research*, **4**, No. 4, 579 (1951).

(5) C. W. Craven, K. R. Reissmann and H. I. Chinn, *J. Anal. Chem.*, **24**, No. 7, 1214 (1952).

(6) C. S. Vestling and J. R. Downing, THIS JOURNAL, **61**, 3511 (1939).

(7) V. M. Albers and H. V. Knorr, *J. Chem. Phys.*, **9**, No. 7, 497 (1941).

(8) R. H. Ball, G. D. Dorough and M. Calvin, THIS JOURNAL, **68**^{2}, 2278 (1936).

(9) G. D. Dorough and K. T. Shen, *ibid.*, **72**, 3939 (1950).

(10) G. D. Dorough, J. R. Miller and F. M. Huennekens, *ibid.*, **73**, 4315 (1951).