

Schmeisser and Schröter¹⁰ report that CCl_2 is a major product from the pyrolysis of CCl_4 in a graphite tube at temperatures around 1300° . No evidence for this product was obtained in the present work. Extrapolation of our data to temperatures of 1300° suggests $\text{C}_2\text{Cl}_2(\text{g})$ and $\text{Cl}_2(\text{g})$ to be the only major products. The only explanation that we can offer for the results of Schmeisser and Schröter is that the condensed product they obtained was a 1:1 mixture of C_2Cl_2 and Cl_2 . On the basis of the limited knowledge of the explosive nature of C_2Cl_2 , it would be surprising if a stable mixture could be prepared.

The hexachlorobenzene and hexachloroethane reported in the earlier literature as products from the pyrolysis of CCl_4 are not formed under the conditions of this present work. It would thus seem that the formation of these two materials is due to subsequent recombination of the primary pyrolysis products outside of the pyrolysis zone. No evidence was obtained for the formation of compounds containing three or more carbon atoms.

Our observations that the pyrolysis of CCl_4 goes through C_2Cl_4 and C_2Cl_2 is consistent with the early suggestion of Lüb.⁷

Although we have evidence that the removal of chlorine atoms from adjacent carbon atoms involves a surface reaction with graphite, we are not in a position to discuss in detail the nature of the chlorine absorbed on the surface. There is some general concern as to which type of lattice site the chlorine is bound. It is known that halogen atoms combine with graphite to give compounds with approximate formulas C_4F , C_8Cl and C_8Br . Ubbelohde¹¹ recently has discussed the bonding properties in this type of system.

For reactions of the form

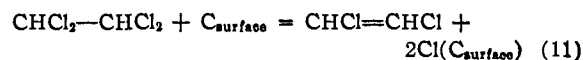


the available thermochemical data indicate values of ΔH_0 between +40 and +50 kcal. for the cases where R is H or Cl. This is also the range in ΔH

(10) M. Schmeisser and H. Schröter, *Z. angew. Chem.*, **72**, 349 (1960).

(11) A. R. Ubbelohde, *J. chim. phys.*, **58**, 107 (1961).

to be expected from simple bond additivity considerations.¹² For the reaction

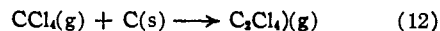


we have determined $\Delta H = +14.2 \pm 3.0$ kcal. This implies that an additional 25 to 35 kcal. are required to remove 2 Cl atoms from the surface as Cl_2 molecules. The reported value¹⁸ of -31.9 kcal. for the heat of absorption of $\text{Cl}_2(\text{g})$ on charcoal is in qualitative agreement with these considerations. This is consistent with the supposition that chlorine atoms from the chloroethanes are chemisorbed on graphite and/or are intercalated between graphite planes as Cl atoms. The ultimate fate of an absorbed chlorine atom is apparently determined to some degree by the presence of hydrogen or other surface contaminants which react to form $\text{HCl}(\text{g})$.

The mechanism of the removal of an H and a Cl atom from adjacent carbon atoms is apparently a more complicated process as indicated by the pressure data for CH_3-CCl_3 (Fig. 10). On the basis of the high HCl pressure, it appears that HCl is not strongly absorbed on the graphite surface. When $\text{H}_2(\text{g})$ was passed in at 600 to 1000° after the completion of a C_2Cl_4 pyrolysis, a 75% conversion of the $\text{H}_2(\text{g})$ to $\text{HCl}(\text{g})$ was observed.

When $\text{H}_2(\text{g})$ and $\text{C}_2\text{Cl}_4(\text{g})$ were run together through the hot oven, the $\text{C}_2\text{Cl}_2/\text{C}_2\text{Cl}_4$ ratio was the same as that observed in the absence of $\text{H}_2(\text{g})$. The presence of $\text{H}_2(\text{g})$ in the crucible does not therefore enter into the surface dechlorination of C_2Cl_4 directly.

Examination of the crucibles after pyrolysis of CCl_4 gave no evidence for the uptake of carbon by CCl_4 . We can therefore eliminate the reaction



This is also supported by the fact that Cl_2 is evolved and that the pyrolysis of C_2Cl_4 did not give the reverse reaction.

(12) T. L. Cottrell, "Strengths of Chemical Bonds," 2nd Ed., Butterworths, London, 1958.

(13) F. G. Keyes and M. J. Marshall, *J. Am. Chem. Soc.*, **49**, 156 (1927).

[CONTRIBUTION FROM THE NATIONAL INSTITUTES OF HEALTH, BETHESDA, MARYLAND, AND THE MEDICAL SCHOOL, UNIVERSITY OF MINNESOTA, MINNEAPOLIS, MINNESOTA]

Proton Magnetic Resonance Studies of Porphyrins

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High resolution proton nuclear magnetic resonance spectra are reported for eight porphyrins: the methyl esters of coproporphyrin-1 and -3, uroporphyrin-1, protoporphyrin-9, mesoporphyrin-9, hematoporphyrin-9 and phylloerythrin; and the di-cation form of tetra-benz-tetra-aza-porphin. The spectra are interpreted in terms of ring currents in the π -electron system. The equivalence of the four pyrrole rings in coproporphyrin-1 is demonstrated, and the proposal made that this equivalence results from a tautomerism of the NH protons at a rate much greater than 200 sec.⁻¹. Detailed assignments of the spectral lines to functional groups in the molecules are presented and analytical applications of the n.m.r. technique discussed.

High resolution proton nuclear magnetic resonance (n.m.r.) is being applied increasingly to the study of the structure of complex organic molecules, but thus far there has been only limited

application to porphyrins.^{2,3} The present work reports n.m.r. spectra of eight molecules containing

(2) E. D. Becker and R. B. Bradley, *J. Chem. Phys.*, **31**, 1413 (1959).

(3) J. Ellis, A. H. Jackson, G. W. Kenner and J. Lee, *Tetrahedron Letters*, No. 2, 23 (1960).

(1) (a) National Institutes of Health. (b) University of Minnesota.

porphyrin rings, together with assignments of peaks to protons in the molecules and a discussion of the effects of the electronic structure of porphyrins on the n.m.r. spectra.

Experimental

N.m.r. spectra were obtained with a Varian Associates, V-4300-2, spectrometer operating at 60 mc./sec. Spectra were scanned from low to high field at rates of 60 to 400 c.p.s./min. In all cases except phthalocyanine the porphyrin sample was dissolved in CDCl_3 at a concentration of ca. 0.05 M .⁴ Tetramethylsilane (TMS) was used as an internal reference, and benzene or chloroform in a precision coaxial tube was used as an external reference. (Phthalocyanine was dissolved in concentrated D_2SO_4 and only the external reference used.) Positions of the major spectral peaks were measured by superposition of an audio sideband and are accurate to ± 0.5 c.p.s.; positions of weaker peaks were measured by interpolation on the spectral trace and should be accurate to ± 1 c.p.s. (For broad peaks accuracy is, of course, lower.) Data are reported in terms of the frequency independent unit δ

$$\delta = (\nu - \nu_{\text{TMS}})/60 \text{ p.p.m.}$$

with the positive sign given to peaks at lower field than TMS.⁵ Most experiments were conducted at room temperature, with sample temperature estimated to be $27 \pm 3^\circ$. The single low temperature experiment was carried out with the Varian V-4340 variable temperature apparatus.

Uro- and coproporphyrin-1 were obtained from the urine of a patient having erythropoietic (congenital) porphyria. The method of isolation and crystallization as the methyl esters has been described previously⁶; m.p., uro-1, 291–292°, copro-1 248–250°. Coproporphyrin-3 was obtained from the residue of diphtheria bacilli after harvest of toxin⁷; methyl ester m.p. 142°, 166° (dimorphic). Protoporphyrin-9 (isomer series III) was prepared from hemoglobin by Grinstein's method⁸; the methyl ester melted at 224°. Meso-9 was prepared from proto- by catalytic hydrogenation⁹; m.p. 212°. Hematoporphyrin methyl ester was prepared according to H. Fischer and Orth.¹⁰ Phytyloerythrin was isolated from bovine feces¹¹; methyl ester m.p. 266–267°. All of the above samples were homogeneous by column and paper chromatography and spectrophotometry except for the hematoporphyrin which probably has never been obtained entirely pure.

Results and Discussion

Effect of Ring Currents.—Figure 1a shows the spectrum of a typical porphyrin, the methyl ester of coproporphyrin-1. The resonance frequencies of the protons on or near the porphyrin ring are influenced markedly by "ring currents"^{12,13} of π -

(4) This concentration represents ca. 10 mg. of porphyrin in 0.3 ml. Good recognizable spectra probably could have been obtained with about half that amount. Extension to the range of tenths of milligrams (important for application to many naturally occurring porphyrins) should be possible with improved instrumentation, especially with digital data recording and computer averaging of a large number of spectra.

(5) For the study of phthalocyanine in D_2SO_4 , where an internal reference could not be used, chloroform was employed as an external reference and a correction applied (for details see, for example, reference 13, p. 79) with published susceptibility data ("Handbook of Chemistry and Physics," 40th Ed.). Finally, the observed frequency of CHCl_3 in porphyrin solutions, $\delta 7.23$ (see Table I), was used to place the resonance frequencies on the δ scale.

(6) C. J. Watson, M. H. Berg, V. E. Hawkinson and I. Bossenmaier, *Clin. Chem.*, **6**, 71 (1960). (Method IVB).

(7) S. Schwartz and M. Keprios (unpublished).

(8) M. Grinstein, *J. Biol. Chem.*, **167**, 515 (1947).

(9) (a) S. Granick, *ibid.*, **172**, 717 (1948); (b) J. Wittenberg and D. Shemin, *ibid.*, **185**, 103 (1950).

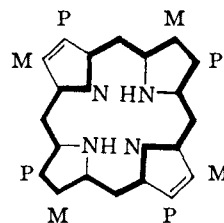
(10) H. Fischer and H. Orth, "Die Chemie des Pyrrols," Akad. Verlagsgesellschaft, Leipzig, Bd. II, Erste Hälfte, 1937.

(11) Ref. 10, Zweite Hälfte, 1940.

(12) J. A. Pople, *J. Chem. Phys.*, **24**, 1111 (1956).

(13) (a) C. E. Johnson, Jr., and F. A. Bovey, *ibid.*, **29**, 1012 (1958); (b) J. S. Waugh and R. W. Fessenden, *J. Am. Chem. Soc.*, **79**, 846 (1957).

electrons about the closed conjugated path indicated by heavy lines ($M = \text{CH}_3$; $P = \text{CH}_2\text{CH}_2\text{-COOCH}_3$). The line at lowest field ($\delta 9.96$)



is assigned to the four methine protons, while the broad peak at $\delta - 3.89$ is attributed to the N-H protons. The methine peak is 2.7 p.p.m. lower in field than the analogous peak in benzene, and the N-H peak is 13 p.p.m. higher in field than the N-H proton resonance in pyrrole. The strong, sharp line at $\delta 3.67$ is due to the methyl groups of the ester substituents and is at exactly the field expected from other molecules (e.g., methyl acetate, $\delta(\text{CH}_3\text{O}) = 3.65$).¹⁴ The methyl groups attached directly to the ring give rise to the line at $\delta 3.55$, which is significantly shifted from the expected position for methyl groups attached directly to unsaturated carbon atoms (e.g., $\text{CH}_2=\text{C}(\text{CH}_3)\text{CH}=\text{CH}_2$, $\delta 1.84$).¹⁴ The two triplets at $\delta 3.20$ and 4.35 are clearly assigned to the methylene groups of the propionic ester substituents. The splitting of ca. 7.6 c.p.s. is typical for protons attached to adjacent tetrahedral carbons. The triplet at $\delta 4.35$ is assigned to the CH_2 group adjacent to the porphyrin rings, since in the absence of ring currents both a $=\text{C}-\text{CH}_2$ group and a CH_2COO group display resonances in the same region (e.g., γ -butyrolactone, $\text{CH}_2\text{C}=\text{O}$, $\delta 2.31$; $\text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}_2-\text{CH}=\text{CH}_2$, $\delta 2.12$),¹⁴ and the effect of ring currents on the resonance frequencies is known to diminish rapidly with distance from the ring.^{12,13} Although the ring current concept furnishes a convenient qualitative and even semi-quantitative explanation of the chemical shifts in porphyrins, it is obviously an oversimplification of the actual situation in the geometrically and electronically complex porphyrin ring. Previous attempts to apply the ring current models^{12,13} to porphyrins have disclosed the quantitative limitations of the model.^{2,3}

Equivalence of the Four Pyrrole Rings.—As shown above, the only closed completely conjugated path passes through the outer portion of the pyrrole rings containing the N-H group and through the N atoms in the other two rings. The CH_3 groups attached to the two types of pyrrole ring will then be at different distances from the circulating π -electron current and should experience a different local field. Actually the methyl groups are all magnetically equivalent, as indicated by the single sharp CH_3 line in Fig. 1a. This observation can be explained either by a rapid tautomerism of the N-H protons, rendering all four pyrrole rings equivalent on a time average basis, or by an electronic structure (not conveniently represented by resonating single and double bonds) in which

(14) G. V. D. Tiers, "Table of N.M.R. shielding values" (unpublished).

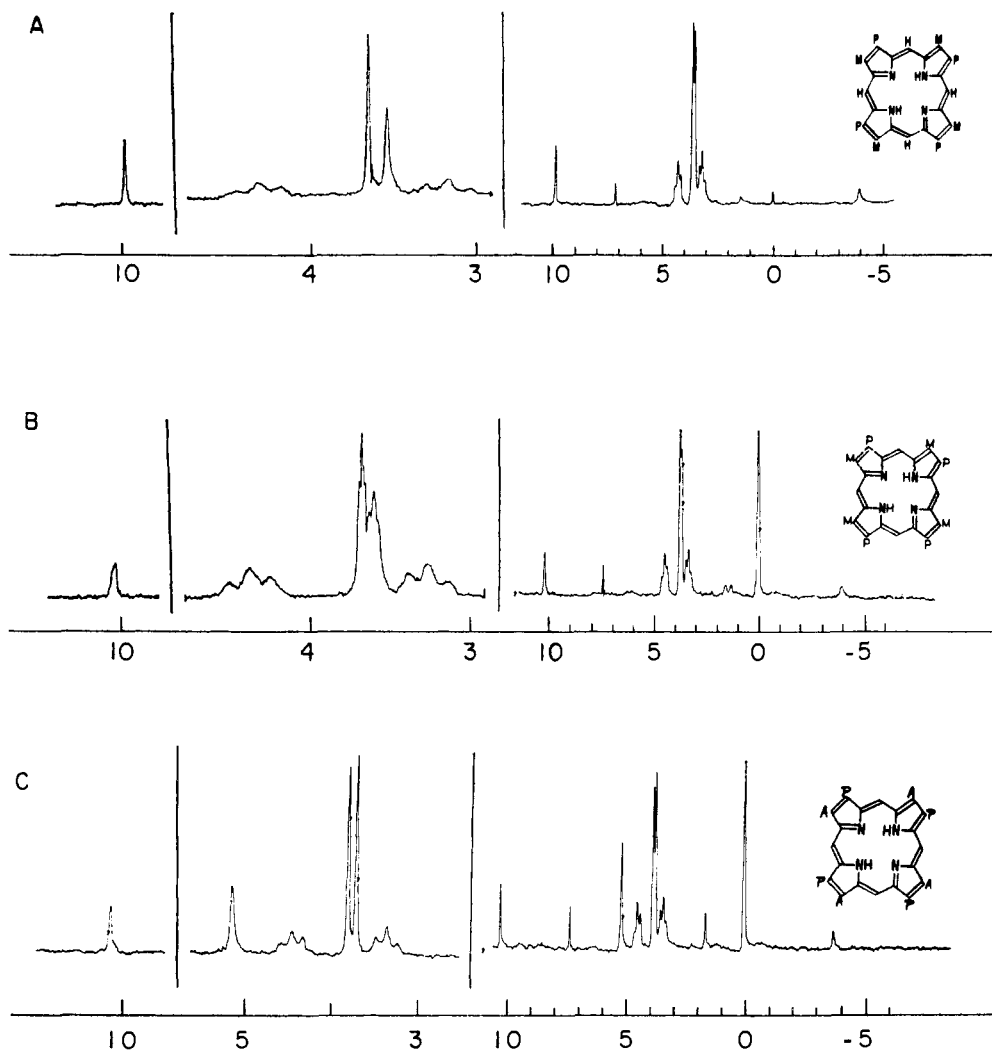


Fig. 1.—Spectra of porphyrin esters: left and center portions, slow scans through selected regions; right portion, rapid scan through entire spectral range: (a) Coproporphyrin-1; (b) Coproporphyrin-3; (c) Uroporphyrin-1; M, CH₃; E, C₂H₅; P, CHCH₂COOCH₃; A, CH₂COOCH₃; V, CH=CH₂; Y, CHOCH₃.

all four rings are electronically equivalent and the N-H protons are held in ionic or bifurcated form. The latter structure is hard to rationalize with infrared spectra, which show a band at 3316 cm.⁻¹, consistent with a normal covalently bound N-H, possibly hydrogen bonded to another N atom. Erdman and Corwin¹⁵ previously rejected the symmetric structure on the basis of their interpretation of the electronic absorption spectrum. They concluded that tautomers exist with a lifetime greater than 10⁻¹² sec. but proposed that the interconversion is "rapid."

For tautomerism to be effective in averaging two configurations to give a single sharp n.m.r. line, the rate must be rapid compared with the difference in resonance frequency between the two forms. The ring current models,^{12,13} which are reliable enough to use for an order of magnitude calculation, predict a difference in resonance frequency of *ca.* 3.5 p.p.m. or *ca.* 200 c.p.s. In order to reduce the rate of tautomerism and possibly

resolve lines due to the separate forms, we lowered the temperature of coproporphyrin-1 in CDCl₃ but observed no significant change in the shape of the CH₃ line to -63°, the freezing point of chloroform. Evidently, the tautomerism rate is still much greater than *ca.* 200 exchanges per second even at this temperature.

Other Features of Porphyrin Spectra.—The spectra of six porphyrin esters are presented in Figs. 1 and 2, and chemical shift data are given in Table I. The effect on the spectra of the symmetry of substitution is shown in Fig. 1a and b, where the spectra of coproporphyrin-1 and -3 are compared. Although the general features of the spectra are quite similar, a slow scan discloses differences, with both the methine and methyl peaks split in coproporphyrin-3 but not in coproporphyrin-1. Since no observable spin coupling effects are expected for these groups, the multiplet structure is evidently due to chemical non-equivalences, which result either from effects transmitted through space from one portion of the molecule to another or through an influence on the electronic structure and possible

(15) J. G. Erdman and A. H. Corwin, *J. Am. Chem. Soc.*, **68**, 1885 (1946).

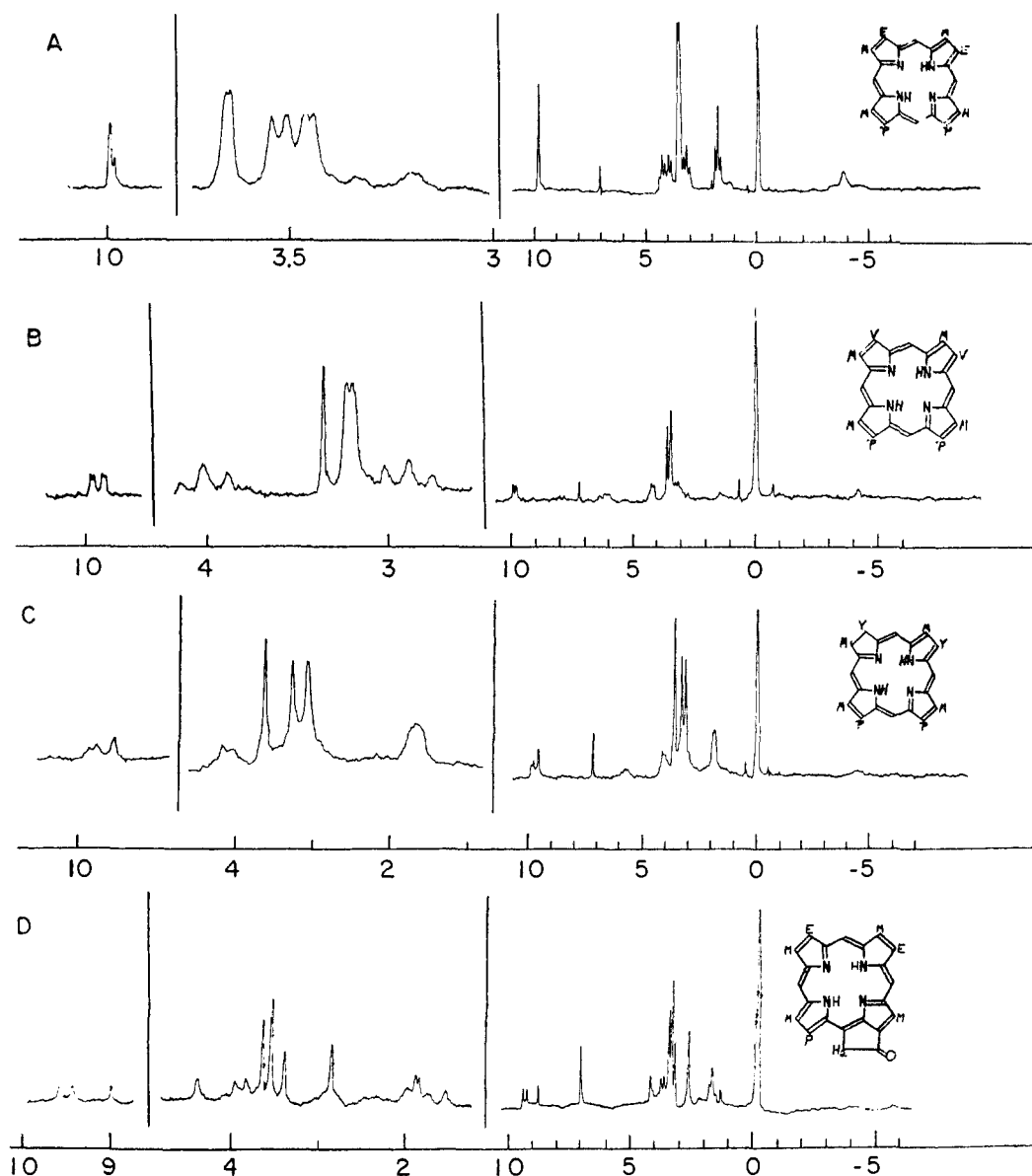


Fig. 2.—Spectra of porphyrin esters, arranged and coded as in Fig. 1: (a) Mesoporphyrin-9; (b) Protoporphyrin-9; (c) Hematoporphyrin-9; (d) Phylloerythrin.

effect on ring currents. We feel that, at present, there are insufficient data to warrant an assignment of spectral lines to protons at specific positions on the porphyrin ring.

Each of the first six porphyrins listed in Table I contains propionic ester groups, the CH_3 resonance of which varies only slightly ($\delta 3.66 \pm 0.03$) among the six compounds. In uroporphyrin-1 the acetic ester CH_3 resonance is assigned to the line at $\delta 3.78$, consistent with the expectation that the closer approach of the methyl group to the ring might result in a small ring current effect on its resonance.

Figure 3 shows a general trend from one compound to another among the resonance frequencies of all the substituent groups common to these six porphyrins (except for the ester CH_3 , which is far removed from electronic effects of the ring). This consistent variation in resonance frequencies

may be related partially to changes in the electronic configuration in the porphyrin ring induced by substituents. This variation does not represent merely a changing magnitude of ring current, since the shift of the N-H resonance parallels those of protons outside the ring. The general shift of resonances to lower field with increased number of carboxylate substituents suggests that the magnetic anisotropy of the carbonyl group may be exerting an influence.

The assignments of resonance lines to other substituents in certain porphyrins (e.g., vinyl, ethyl) are straightforward. The data are given in Table I. The broad lines in hematoporphyrin-9 probably result both from slow exchange of the O-H proton and from impurities present in this sample.

Phylloerythrin.—The lower symmetry of phylloerythrin leads to a more complex spectrum than

TABLE I
N.M.R. DATA FOR PORPHYRINS
 δ (ppm.)

Porphyrin	CH	NH	Ester CH ₃ O	Ester CH ₂	Ester CH ₃	Ring- CH ₂	Acetate CH ₃	Ethyl CH ₂	Ethyl CH ₃	Vinyl	Isocyclic CH ₂	Acetate CH ₃ O (solvent)	CHCl ₃	C ₆ H ₆ (external)
Coproporphyrin-1	9.96	-3.89	3.67	4.35	3.20	3.55							7.23 7.25	6.41 ₁ 6.41 ₁
Coproporphyrin-3	10.06	-3.92	3.687 3.671 3.652	4.38	3.25	3.624 3.596 3.567								
Uroporphyrin-1	10.14	-3.65	3.69	4.42	3.33		5.11					3.78	7.25	6.41 ₀
Mesoporphyrin-9	9.977 9.921	-3.91	3.652 3.636	4.28	3.21	3.541 3.504 3.459 3.441		1.83	3.93				7.19	6.40 ₈
Protoporphyrin-9	9.932 9.897 9.810 9.775	-4.12	3.63	4.30	3.17	3.511 3.481				6.1-6.4 (mult.)			7.24	6.40 ₆
Hematoporphyrin-9	9.915 9.824 9.609	-4.13	3.65	4.13	?	3.33 3.13		1.83					7.23	6.40 ₅
Phylloerythrin	9.62 9.47 9.02	?	3.68	?	?	3.58 3.42 2.87		1.864 1.817	3.93		4.43		7.26	...
Tetra-benz-tetra- aza-porphin	9.59 8.52													

those of most of the other porphyrins, as shown in Fig. 2d. Although we cannot at present arrive at a completely satisfactory interpretation of the entire spectrum, we are able to present a reasonably complete, though somewhat tentative, analysis. The three methine protons are clearly responsible for the lines at δ 9.02, 9.47 and 9.62. The line at δ 3.68 is due to the ester CH₃. The CH₃'s of the two ethyl groups are expected to be only slightly affected by ring currents and will resonate at high field. The features at δ 1.73-1.97 are almost certainly attributable to the two 1:2:1 triplets arising from these CH₂ groups. The centers of the triplets are displaced from each other as a result of a small chemical non-equivalence. The four remaining CH₂ groups are expected at lower field and should be unsplit. The strong lines at δ 2.87, 3.42 and 3.58 must be due to these four methyl groups, with the most intense line (3.58) presumably accounting for two CH₃'s. The line at 2.87 is at higher field than the resonances found in other porphyrins for CH₃ groups attached to the ring. This shift may well represent the effect of the isocyclic ring in altering the π -electron distribution and changing the ring current effects at specific points around the ring. We tentatively assign the line at 3.58 to the CH₃ groups in rings I and II, since they should be least affected by the isocyclic rings. The line at δ 4.43 is tentatively assigned to the methylene group in the isocyclic ring. Its area is appropriate to two protons, it is unsplit, and its frequency is reasonable for a group adjacent to both the porphyrin ring and the carbonyl group. The CH₂'s of the ethyl groups are expected to have lines (1:3:3:1 quartets) in the region of δ 4.0. The lines observed at δ 3.87, 4.00 and 4.12 (separation 7.5 c.p.s.) are attributed to these two CH₂ groups, with the fourth line of the quartet partially hidden under the CH₃O line. From the other porphyrin data, the lines due to the two methylene groups in the propionic ester substituent are expected near δ 3.4 and 4.5. The un-

resolved lines near δ 3.0 may account for one of these groups, but the location of the resonance of the other is in doubt. It may be hidden under the methylene and CH₃O peaks near δ 4.0, but we see no evidence of its presence there. It might

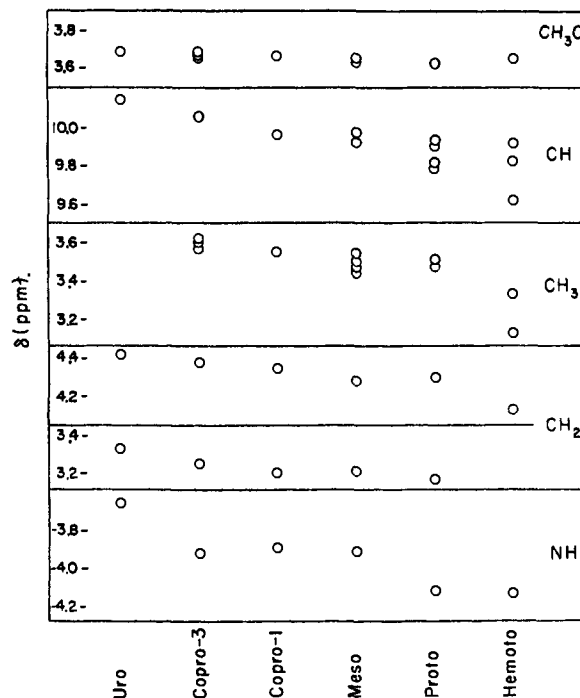


Fig. 3.—Variation of chemical shifts among porphyrin esters.

account for the otherwise unexplained broad absorption at δ 2.5, but this would require a very large alteration in ring current effect. Unlike the other porphyrins studied, there is no line in phylloerythrin at $\delta < 0$ that can be attributed to the N-H protons. However, the quadrupole relaxation effects might well broaden this line beyond

recognition. The alternative assignment of the N-H protons to the otherwise unexplained lines at δ 1.52 or 2.5 is unpalatable since it implies a much larger change in ring current effect than is evidenced by the resonance frequency of the methine protons.

Tetra-benz-tetra-aza-porphin (Phthalocyanine).¹⁶—The spectrum of this compound dissolved in concentrated D₂SO₄ consists of two lines (half-width \sim 15 c.p.s.) at δ 8.52 and 9.59 (measured as described in the Experimental Section). In sulfuric acid solution phthalocyanine is almost certainly in the di-cation form, and the four benz-pyrrole rings are thus equivalent through resonance interaction. The two lines must arise from the non-equivalent protons α and β to the pyrrole ring. Since these protons constitute an A₂B₂ or A₂X₂ system, the lines are expected to be split into complex multiplets.¹⁷ The observed width of

(16) This sample was supplied by Dr. R. Livingston of the University of Minnesota to Dr. E. Charney of the NIH, and Dr. Charney made a portion of it available for this work.

15 c.p.s. is large enough to obscure such splitting; indeed, the width probably results partially from unresolved splitting and partially from hindered molecular rotation in the viscous solvent. No N-H line was observed, presumably due to exchange with deuterium in the solvent.

Applications to Porphyrin Structure Studies.—The tabulation of characteristic chemical shifts for a number of porphyrins opens the way for the use of this technique in structure elucidation of porphyrins and related molecules. The differences shown in the spectra of the closely related isomers coproporphyrin-1 and -3 indicate that in suitable cases n.m.r. will be a powerful analytical tool in porphyrin research. Further studies of known porphyrins may permit the development of a more complete relation between chemical shifts and specific locations of functional groups, thereby considerably extending the utility of the technique.

(17) J. A. Pople, W. G. Schneider and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., New York, N. Y., 1959.

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The Crystal and Molecular Structure of S₆ (Sulfur-6)

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An X-ray crystallographic study of rhombohedral sulfur has been carried out. The crystals consist of hexameric molecules, S₆, with symmetry $\bar{3}m$. Fourier and least squares refinement of the atomic parameters give the following structural quantities: S-S bond length, 2.057 ± 0.018 Å., S-S-S bond angle, $102.2 \pm 1.6^\circ$, S-S-S-S torsion angle, $74.5 \pm 2.5^\circ$. These values are compared with those found in orthorhombic sulfur, S₈, and are used in a discussion of the potential function for rotation about the S-S bond together with the S-S-S bending force constant.

Introduction

An allotrope of sulfur discovered by Engel¹ was shown to be a hexamer by Aten.² The results of an incomplete X-ray study by Frondel and Whitfield³ together with the morphological observations of Friedel⁴ prompted Donnay⁵ to suggest that the substance was rhombohedral, space group $R\bar{3}$ (C_{3i}², No. 148) with six atoms in a unit cell having $a = 6.45$ kX., $\alpha = 115^\circ 18'$. The corresponding hexagonal lattice constants are $A = 10.9$ kX., $C = 4.26$ kX. These conclusions were verified in our preliminary note.⁶ We wish now to report the results of our refinement of this structure.

Experimental

Crystals of S₆ were prepared by the method described by Aten.² They were mounted in the usual way, and intensity data were collected for the ($hk0$) and ($0kl$) zones in a Weissenberg camera with unfiltered CuK α radiation. The exposure times were limited to about an hour by the instability of the crystals, but the intensity range of the reflections was increased by using small angles of oscillation. Intensities were estimated visually. The ($hk0$) intensities were corrected for absorption by use of the powder rod formula and the value 0.25 mm. for the radius. No cor-

rection was applied to the ($0kl$) reflections because the crystal used was much smaller.

The lattice constants were determined from a multiple exposure powder photograph. The hexagonal unit cell was chosen for use in this and all calculations in preference to the rhombohedral one.⁷ The powder data, which are given in full elsewhere,⁸ give the following results

$$A = 10.818 \pm 0.002 \text{ \AA.}, C = 4.280 \pm 0.001 \text{ \AA.}$$

$$(\lambda \text{ CuK}\alpha = 1.5418 \text{ \AA.})$$

In agreement with the results of Frondel and Whitfield³ it was found that the axis of symmetry was threefold and that there were no vertical planes of symmetry. As predicted by Donnay,⁵ only those reflections having $-h+k+l = 3n$ were observed. The space group is therefore established as $R\bar{3}$. The calculated density for 18 sulfur atoms per unit cell is 2.21 g. cm.⁻³, as compared with the observed value¹ of 2.14 g. cm.⁻³.

Derivation of the Structure.—The general position of the space group is 18-fold. There are thus three positional parameters to be determined. The required molecular symmetry is $\bar{3}$. Trial values for x and y were obtained by assuming S₆ molecules having bond lengths 2.04 Å. and bond angles 104° and then applying the method of Knott.⁹ F values for the ($hk0$) reflections were calculated, and the signs of all 25 of them could be assigned with confidence. The form factor for

(1) E. C. Engel, *Compt. Rend. Acad. Sci. Paris*, **112**, 866 (1891).

(2) A. Aten, *Z. physik. Chem.*, **88**, 321 (1914).

(3) C. Frondel and R. E. Whitfield, *Acta Cryst.*, **3**, 242 (1950).

(4) C. Friedel, *C. R. Acad. Sci. Paris*, **112**, 834 (1891).

(5) J. D. H. Donnay, *Acta Cryst.*, **3**, 245 (1955).

(6) J. Donohue, A. Caron and E. Goldish, *Nature*, **182**, 518 (1958).

(7) M. J. Buerger, "Elementary Crystallography," John Wiley and Sons, Inc., New York, N. Y., 1956, p. 106.

(8) A. Caron and J. Donohue, *J. Phys. Chem.*, **64**, 1767 (1960).

(9) G. Knott, *Proc. Phys. Soc. Lond.*, **52**, 229 (1940).