and the disappearance of maxima at 275 mμ (shoulder) and 296 mμ (characteristic of IVa) were observed after varied heating periods.

(c) **From IVa (Na Salt) in Dimethylformamide without Copper.**—Heating 3.4 g. (8.8 mmoles) of IVa and 0.40 g. (9.2 mmoles) of sodium amide overnight in 40 ml. of benzene afforded only the sodium salt of IVa. The solvent was decanted from the cooled reaction mixture, and IVa (sodium salt) was heated under reflux in 25 ml. of dimethylformamide. After 1 hr. of heating approximately 65% of Ia (free base) was formed, estimated by ultraviolet at $\lambda_{max}^{CH_3OH}$ 328 mμ. Approximately 80% of Ia was formed after 4.5 hr. of heating. The reaction mixture was heated for 23 hr., but no significant change in yield was observed after 7 hr. The product, Ia (free base), 2.4 g. (91% yield) was isolated from the reaction mixture as described above.

(d) **From IVa and Potassium Carbonate in Benzene without Copper.**—IVa, 2.5 g. (6.5 mmoles), and 0.45 g. (3.3 mmoles) of potassium carbonate were heated under reflux in 25 ml. of benzene. After 4.5 hr. of heating no conversion to Ia was observed (by ultraviolet). Approximately 80% of Ia was formed after 22 hr. of heating, estimated by ultraviolet at $\lambda_{max}^{CH_3OH}$ 328 mμ. There was no significant change in yield after 41 hr. of heating.

(e) **From *N*′-[2-(*o*-Bromophenoxy)-5-chlorophenyl]-*N*,*N*-dimethyl-1,3-propanediamine[1b] (IIIa); Route A$_1$ without Copper.**—IIIa, 5.2 g. (0.014 mole) and 2.0 g. (0.015 mole) of potassium carbonate in 40 ml. of dimethylformamide were heated under reflux with stirring for 48 hr.[11] The reaction mixture was worked up as described above (see a) to give 3.8 g. (90% yield) of Ia (free base). Infrared and ultraviolet spectra of this product as well as the hydrochloride were identical with those prepared by the above procedures.

3-Chloro-10-(3-dimethylaminopropyl)phenoxazine Hydrochloride (Ih), from Va; Route B.[1b]—A reaction mixture of 26.7 g. (0.075 mole) of *o*-(3-dimethylaminopropylamino)-phenol dihydrobromide,[1b] 14.4 g. (0.075 mole) of 1,4-dichloro-2-nitrobenzene and 12.8 g. (0.225 mole) of sodium methylate (95% pure) in 500 ml. of absolute alcohol was heated under reflux for 20 hr. and the cooled reaction mixture was filtered. The filtrate was evaporated to dryness, and the residue was dissolved in 500 ml. of ether and was extracted with 500 ml. of 1 *N* hydrochloric acid in several portions. The combined acidic extracts were washed with ether, made alkaline with potassium carbonate, and extracted several times with ether. The combined ethereal extracts were washed with water, dried over magnesium sulfate, and evaporated to dryness. The residual oil, 9.2 g. (40% yield), was dissolved in 200 ml. of petroleum ether (b.p. 60–90°) and allowed to stand at room temperature for 2 days. The supernatant was decanted from 0.3 g. of a black tar, and the clear solution was cooled for 0.5 hr. in a Dry Ice–acetone bath. This caused a red crystalline solid to separate (Va; see below). The cooled petroleum ether solution was decanted and the supernatant allowed to stand for several days (no more of Va separated during this time). The solution was evaporated to dryness under vacuum. The residual oil was dissolved in ether, decanted from a small amount of an insoluble gum and again evaporated to dryness. The residue, 7.1 g. (31% yield), was distilled and 4.1 g. of purified base was obtained (see Table I).

Compound Ii was also obtained by an analogous procedure (see Table I).

***o*-[4-Chloro-*N*-(3-dimethylaminopropyl)-2-nitroanilino]-phenol (Va).**—The red crystalline solid obtained during the synthesis of Ih (above) was recrystallized from 5 ml. of hot alcohol with a charcoal treatment and 100 ml. of petroleum ether (b.p. 60–90°) to give 1.3 g. (4.7% yield) of crystalline product, m.p. 167–172°. A second recrystallization from 10 ml. of alcohol yielded 0.9 g. (3.3%) of analytically pure material, m.p. 172–173°.

Anal. Calcd. for $C_{17}H_{20}ClN_3O_3$: C, 58.4; H, 5.76; Cl, 10.1; N, 12.0. Found: C, 58.1; H, 5.92; Cl, 10.4; N, 11.8.

Acknowledgment.—We are indebted to L. Brancone and associates for the microanalyses; to C. Pidacks and associates for the chromatographic purifications; to Mrs. K. M. Ostrom and J. Nocera for their technical assistance; to W. Fulmor and associates for infrared, ultraviolet, and n.m.r. data, and to Dr. J. S. Webb and Dr. J. E. Lancaster for their generous interpretation of the n.m.r. data.

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[11] The optimum reaction time for this cyclization was not studied in detail as that from IVa. The actual time for cyclization may be much less, paralleling IVa → Ia.

An Analog Computer for Pyrrole, Porphyrin, and Chlorophyll Strains[1]

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An analog computer made up of specially prepared springs has been constructed to examine distortions in the pyrrole and porphyrin systems. The model permits estimation of changes in bond angles produced by changes in hybridization, those caused by the introduction of a small chelating atom into the center of the porphyrin system, the sliding motion produced by van der Waals repulsions of the central hydrogens, the "wrist action" caused by the introduction of an N-methyl group in the porphyrin ring, and the distortions produced by closure of the isocyclic ring in chlorophyll derivatives.

The usual Stuart-Brieglieb models of porphyrins are adequate to indicate that crowding exists in the γ-position of chlorophyll porphyrins and some chlorins. These models are incapable of showing tensions and warpages in molecules due to strains, however. To permit an assessment of the strains caused by the introduction of large and small groups and by the closure of the isocyclic ring in chlorophyll, phylloerythrin, and similar compounds, a simple analog computer has been constructed.

The principle used in the construction of our computer is based on observations by Kettering, Shutts, and Andrews.[2] The vibrating models

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[1] Porphyrin Studies. XXIII. Paper XXII, P. E. Wei, A. H. Corwin, and R. Arellano, *J. Org. Chem.*, **27**, 3344 (1962).

[2] C. F. Kettering, L. W. Shutts, and D. H. Andrews, *Phys. Rev.*, **36**, 531 (1930).

which they constructed had springs to represent bonds and balls with proper weights to represent atoms. Such models exhibit ratios between characteristic frequencies corresponding to those found in Raman and infrared spectra, thus establishing the general validity of the dynamic model approach to the representation of molecules.

For the purpose of studying strains only, the models can be simplified by the omission of the balls at the atomic positions. Springs are constructed having the approximate ratios of stretching to bending constants observed in similar molecules. These are then joined at predetermined bond angles to form a model of the molecule under investigation. Since the porphyrin ring is planar, the model may be mounted on glass. By providing a frame for the glass, the surface may be levelled. A vibrator made from an electric doorbell and making contact with the lower surface of the glass serves to relieve the model of strains so that the points of attachment of the springs, representing the atoms, will find their equilibrium positions. Substituents which introduce strains may then be added and the new equilibrium positions determined. The change in equilibrium positions gives a graphic representation of the warpage introduced by the strain. The precision of the computations which could be based on such a model would depend upon the accuracy with which angles, distances, and force constants were known, among other factors. Since none of these factors is now known with great precision, great refinement in the construction of such a computer is not now justified.

For these investigations, springs of three different types were constructed by varying the number of turns. The material used was annealed beryllium-copper wire which was $^1/_{16}$ in. in diameter, wound to helices 23 mm. in diameter, and subsequently was heat-treated. These springs had the following lengths and ratios of stretching to bending force constants:

TABLE I

Spring type	Length, mm.	k_s/k_b	k_s/k_{s1}
1	76	14	1.00
2	81	16	0.91
3	85	19	0.63

Templates were constructed for 120° and 109.5° bond angles and with holders mounted in slots to accommodate the springs of varying lengths.

Bak, *et al.*[3], have measured the bond angles and distances of unsubstituted pyrrole with precision by microwave spectra. They find that, on the average of several possible models, the bond at nitrogen is 108 $^2/_3$°, that at the alpha position is 108 $^1/_3$° and that in the beta position is 107 $^1/_2$°. Bond lengths, on the average, are 1.39 Å. for the two N—C bonds, 1.37 Å. for the two C_2–C_3 bonds, and 1.43 Å. for the C_3—C_4 bond. These place the bond rigidities in the order

$$C_3\text{—}C_4 \leqq N\text{—}C < C_2\text{—}C_3$$

We have investigated variations in bond angle by means of our analog computer, varying both the bond strengths and bond lengths by patterns which preserved the central plane of symmetry of the pyrrole ring. These investigations lead to the conclusion that as long as 120° templates are used for all angles, variation of bond lengths and strengths leads to relatively small changes in the angle at nitrogen. Using bond type 1 for the two C_2—C_3 bonds and type 2 for the other three bonds, the following angles were found: N, 106°; alpha, 108°; beta, 109°. If, on the other hand, the angle at nitrogen was set at the tetrahedral angle, using the same bond distribution as before, the computer model gave angles of: N, 98°; alpha, 114°; and beta, 107°. We conclude, as did Bak and his collaborators, that, in pyrrole, the nitrogen is distorted from an atom which originally possessed trigonal symmetry and that, consequently, the hydrogen is coplanar with the pyrrole ring.

Following these indications, a porphyrin model was constructed with all beta-beta bonds and all C—N—C bonds made of type 2 springs and all alpha-beta bonds of type 1. All bond angles were set with the 120° template. When used, exterior C—C bonds were made of type 3. In a chlorin model, the three C—C bonds of ring IV were made of type 3 springs and the two angles of the beta-positions in this ring were set at 109.5°. To facilitate measurement, each N was represented by a flat-headed screw with a fiducial cross centrally engraved upon it. Measurements were made with a horizontal cathetometer mounted on an optical bench to eliminate parallax.

Distortions of the Porphyrin Ring.—Robertson,[4] in his classical studies of the X-ray diffraction of phthalocyanine and its metallic complexes, found that the bond angles in the pyrrole rings of the metal-free molecule were: N, 108.5°; alpha, 109.5–111.5°; beta, 104–106.5°. These differ slightly from those found later by Bak for pyrrole. In spite of this, Robertson concluded that the imine hydrogen atoms probably were not coplanar with the ring, a hypothesis which gave rise to the possibility of two isomers, *cis* and *trans*, with respect to the positions of the two imine hydrogens. On symmetry grounds, Robertson decided that his crystals were *trans*. In contrast to the metal-free compound, the nickel complex had the following angles: N, 99°; alpha, 115°; beta, 105°. Crute,[5] in his study of the crystal structure of nickel etioporphyrin, also found the angle at nitrogen to be less than 100° and the alpha angles to be larger

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(3) B. Bak, D. Christensen, L. Hansen, and J. Rastrup-Andersen, *J. Chem. Phys.*, **24**, 720–25 (1956).

(4) J. M. Robertson, *J. Chem. Soc.*, 1195 (1936).

(5) M. B. Crute, *Acta Cryst.*, **12**, 24 (1959).

TABLE II

DISTORTION OF PORPHYRIN RING IN DIFFERENT DIRECTIONS

Force applied	Bond distances and standard deviations (mm.) four observations each			
	Adjacent		Opposite	
	N_1—N_2, N_3—N_4 (av.)	N_2—N_3, N_4—N_1 (av.)	N_1—N_3	N_2-N_4
None	156.0 ± 0.2	159.0 ± 0.6	223.5 ± 1.9	221.75 ± 0.3
2 × 50 g. to opposite β-β bonds	157.6 ± 0.5	159.1 ± 0.2	214.4 ± 0.5	232.4 ± 0.3
Change	+1.6 ± 0.5	+0.1 ± 0.6	−9.1 ± 2.0	+10.7 ± 0.4
2 × 50 g. on bridge angle bisectors	116.3 ± 0.7	197.25 ± 0.7	230.4 ± 0.3	228.4 ± 0.3
Change	−39.7 ± 0.7	+38.3 ± 0.9	+6.9 ± 1.9	+6.7 ± 0.4

than the beta by a somewhat larger ratio than in the case of phthalocyanine. Robertson ascribed this distortion of the ring to attraction for the nitrogen by the nickel, on the assumption that the Ni—N bond distance is less than the size of the hole in the unperturbed phthalocyanine ring. This concept is supported by the fact that the platinum complex shows a 108° angle at N, which is ascribed to a more favorable metal diameter.

Following Robertson's suggestion, we have distorted the porphyrin ring of our model by means of an internally applied strain. Using four type 3 springs locked at right angles at the center as an analog of the nickel atom, sufficient distortion was secured to reduce the angle at nitrogen to 99°, which is that found by Robertson for nickel phthalocyanine. This model gave alpha angles of 113° and beta angles of 107°, in reasonable agreement with the 115° and 105° found by the X-ray method. Thus the model lends support to the concept advanced by Robertson that an internal strain applied by the nickel atom could account for the observed distortion of the phthalocyanine ring. It should be noted, however, that this does not constitute a unique solution to the problem, since the angles found in this model agree also with those formed by using a tetrahedral template at the nitrogen. Thus there are two possible explanations of the bond angles found by Robertson for nickel phthalocyanine: (1) internal stress applied by the nickel atom; (2) alteration of the hybridization at nitrogen due to the presence of nickel. A decision between these must rest on grounds other than the measurement of bond angles. It should also be noted that Crute had difficulty reconciling his X-ray findings on nickel etioporphyrin with a completely planar model and assumed that two nitrogens were slightly above the plane and two slightly below. This would be the shape expected if the hybridization at nitrogen had been altered to tetrahedral by the presence of the nickel.

Robertson also reported that metal-free phthalocyanine is distorted so that two adjacent nitrogens are closer than the next two. This effect was ascribed to hydrogen bonding. Donohue[6] disputed this interpretation and argued that the conditions necessary to stable hydrogen bond formation were lacking in the phthalocyanine ring. Infrared observations on porphyrins and chlorins, on the other hand, support the concept of hydrogen bonding, although a recent discussion points out that this bonding must be of an unusual nature.[7] A weakness in Donohue's argument is the lack of a suitable alternative to the postulate of hydrogen bonding for explaining the results of the X-ray analysis. It is suggested that one alternative that should be explored is that forces of repulsion between opposite hydrogens on the nitrogens distort the phthalocyanine ring. Such forces would exist only if the hydrogens tended to be coplanar with the ring, the most probable model in the metal-free case. Our computer furnishes a method for evaluating the possibility that such forces, if they exist, could account for the observed distortions.

Stuart–Brieglieb models,[8] which are constructed with interference radii smaller than the values of van der Waals radii assigned by Pauling,[9] show opposite hydrogens approximately in contact. When van der Waals radii are used, models show appreciable interference between hydrogen atoms bound to opposite nitrogens in the porphyrin or phthalocyanine ring. One might expect forces exerted by hydrogens in opposite positions to increase the distance between opposite nitrogens, in contrast to the observations of Robertson that it is adjacent nitrogens which have increased N—N distances. Examination of the porphyrin computer, however, shows that adjacent nitrogens are more easily displaced than opposite nitrogens. The pertinent measurements are given in Table II.

In the second and third columns, averages of measurements on adjacent nitrogens are given in groups of two. The second column shows that the application of equal outward forces normal to opposite β-β bonds produces little distortion of the positions of adjacent nitrogens, as might be expected. The fourth and fifth columns show the effect of the same forces on distances between transannular nitrogens, where it should be at a

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(6) J. Donohue, *J. Phys. Chem.*, **56**, 503 (1952).

(7) S. F. Mason, *J. Chem. Soc.*, 979 (1958).

(8) G. Brieglieb in Houben-Weyl, "Methoden der Organischen Chemie," G. Thieme Verlag, Stuttgart, 1955, pp. 549–572.

(9) L. Pauling, "The Nature of the Chemical Bond," 3rd ed., Cornell University Press, Ithaca, N. Y., 1960.

maximum. It will be observed that the increase in one direction is balanced by a nearly equal decrease in the other. When the weights are applied outwardly on the angle bisectors of the bridge carbons, the opposite set of effects is observed. The distortion of adjacent nitrogen distances is at a maximum and the distortion of transannular distances is less, although still an appreciable fraction of that caused by the application of a direct transannular force. The amount of distortion of adjacent distances, in this case, is approximately four times as great as the amount of distortion of transannular distances in the first case, showing that the "sliding" motion of the second type of force application is the more effective in securing accommodation of the interference between opposite hydrogens in the ring.

Robertson found the two closer nitrogens to be 2.65 Å. apart and the two more distant to be 2.76 Å. separated. If we assume that the difference is due to repulsions between hydrogens, the distance between adjacent nitrogens in the doubly charged negative ion, not allowing for expansion due to charge repulsion, would be 2.705 Å. Assuming the N—H bond distance is 1.02 Å. and the van der Waals radius of hydrogen is 1.20 Å., the theoretical overlap for two hydrogens set in such a ring without deformation would be 0.984 cu. Å. If we now allow the repulsions to act at an angle halfway between the two directions given for Table II, one set of adjacent nitrogens would move farther apart and the other would move closer together to give the observed values. A further deformation also would take place to change the angles between three nitrogens from 90°, giving a parallelogram instead of a rectangle. This was the figure actually observed by Robertson. However, he ascribed this deviation to a tilt of the plane of the ring from the projection. The presence and magnitude of this tilt thus become critical data with respect to a decision between the theory advanced here and that of hydrogen bonding. Assuming that the actual figure is a parallelogram with angles of 88° and 92°, still further accommodation of the theoretical overlap would be obtained. Finally, we may assume that a force sufficient to deform the porphyrin ring by 2° would be sufficient to deform the N—O—H bonds by 5°. The sum of all of these deformations would diminish the overlap between opposite hydrogens to 0.590 cu. Å., which is 60% of the original value on the undeformed ring. Some accommodation undoubtedly also would take place by interpenetration of the two fields of force represented by the van der Waals radii.

Our analysis thus leads to the conclusion that van der Waals repulsion between opposite hydrogens would be present to account for the distortion observed in the ring of metal-free phthalocyanine and that the distortion would be in the direction actually observed. Because of the infrared evidence, the most reasonable assumption seems to be that both this repulsion and hydrogen bonding are present in this molecule.

Robertson also observed that the adjacent nitrogens in nickel phthalocyanine appear to differ in their distances by an amount just outside of experimental error and that the central angles at nickel are 89 and 91° instead of being all equal to 90°. While the precision of our computer is not sufficient to resolve this question unequivocally, such a distortion seems unlikely on the basis of a model in which the four nitrogens and the nickel are in a plane. For the sliding distortion of the pyrrole rings produced in accommodating to the larger van der Waals radii of the two internally placed hydrogens, the essential factor was that the forces be applied at only two nitrogens. With an internal stress applied equally at all four nitrogens, symmetrical strain would be expected.

Erdman and Corwin[10] showed that relatively small shifts in spectral absorption take place on N-methylation of etioporphyrin, indicating that there is no change in bond type or major energy disturbance on N-methylation of the porphyrin ring. Stuart models show that accommodation of the N-methyl group could not take place on a wholly planar model without very serious distortion of the molecule. If one of the pyrrole rings is allowed to rotate at its two bridge junctions slightly so as to bring the nitrogen out of the plane, however, accommodation can take place without serious distortion. This type of rotation would be especially favorable to accommodation because of the "leverage" which would permit a small motion of the pyrrole nitrogen to accompany a larger motion of the methyl carbon. In the cases of the zinc and copper complexes of N-methyletioporphyrin,[11] one seems forced to assume such a "wrist-action" to achieve accommodation. In these compounds the metal and three nitrogens must be nearly coplanar and the fourth nitrogen which bears the methyl group must be forced out of the plane sufficiently to permit the methyl to lie above the ring plane on the metal atom.

To estimate the effectiveness of this type of wrist action on a pyrrole ring, the computer model was suspended vertically in a frame on a stand. The weight of the model was borne by two suspensions at the beta-positions of ring I. Rings II and III then were lightly attached to the frame by thread and springs and ring IV was left free for study. To secure a reference position, two threads were attached to opposite sides of the center of the nitrogen atom and a fiducial mark was made on one of these. Two 59-g. weights then were suspended by the threads over nylon pulleys and the model was vibrated to secure equilibrium. To secure torque, two 25-g. weights were suspended in a similar man-

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

[11] W. K. McEwen, *ibid.*, **68**, 711 (1946).

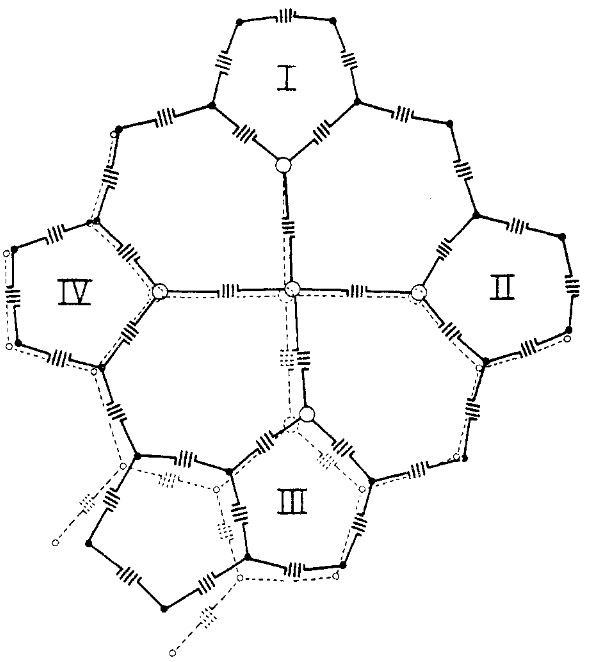

Fig. 1.—Analog computer. Superimposed models showing isocyclic ring open - - - - -, and closed ——.

ner on one side of the model by the two bridge carbons holding ring IV and the 50-g. weight on this side was removed. This secured a balanced torque of 50 g. applied to the ring nitrogen against 50 g. applied equally at the bridge carbons. The resultant linear displacement of the nitrogen was −2.5 mm. but the angular displacement of the pyrrole ring was approximately 45°. This would give an accommodation of 56 mm. at the center of a carbon attached to nitrogen, roughly equivalent to 1 A. It is evident that this mode of accommodation requires less energy than any other.

Brunings and Corwin[12] pointed out that the bulky methyl group attached to a dipyrrylmethene could best be accommodated by allowing a number of small changes to take place rather than by concentrating the total displacement in one type of change. This principle has since been recognized in other connections.[13,14] It is now evident that the major adjustment which should be made in our models for these strained molecules is the wrist action of the pyrrole ring, leaving a small adjustment to be absorbed by bond bending and interpenetration of van der Waals radii. Experimental investigations examining this point of view by means of n.m.r. spectra will be published soon.[15]

The next set of measurements, Table III, was designed to test the effect of isocyclic ring closure on porphyrin and chlorin symmetry. Four measurements were made for each distance reported and the standard deviations of measurement are given.

TABLE III

TRANSANNULAR N—N DISTANCES IN NON-CHELATED ION MODELS

Isocyclic ring	N_1—N_3 (mm.)	N_2—N_4 (mm.)
	Porphyrin model	
Open	225.73 ± 0.1	222.10 ± 0.14
Closed	219.24 ± 0.17	226.48 ± 0.17
Change	−6.48	+4.38
	Chlorin model	
Open	224.78 ± 0.1	221.68 ± 0.17
Closed	218.00 ± 0.24	225.83 ± 0.1
Change	−6.78	+4.15

Since the closure of the isocyclic ring involved no disturbance of the internal relationships of the bonds forming the porphyrin and chlorin ring models, the change in cross-ring distance with closure of this ring can be determined with some confidence. It will be seen that the distance from ring 1 to the ring with the fused isocyclic ring, ring 3, diminishes while the distance between ring 2 and ring 4, which is the reduced ring in the case of the chlorin, increases. Examination of the model shows that this is mainly due to a strain imposed by the isocyclic ring closure on the ring 3 to γ-bridge bond of the porphyrin or chlorin system. This bond is part of the isocyclic ring and is strained from its normal equilibrium position by being forced to conform to the limitations of bond angles set by its participation in the five-membered ring. It will be noted, further, that differences in rigidity between the porphyrin system and the chlorin system are relatively small.

To secure a closer approximation to the situation prevailing in the magnesium complexes, which can be shown to possess weak covalent bonds from magnesium to nitrogen,[16] a model magnesium atom was constructed with a fiducial cross at the center and four weak springs leading to the nitrogens. These springs had the following characteristics: Ratio of k_s/k_b, 23:1; ratio of k_s to k_s of ring springs, type 1, 1:20. Measurements on models containing "magnesium" are tabulated in Table IV.

Table IV shows that the warpages indicated by Table III are not symmetrically distributed with respect to the center of the porphyrin or chlorin system but are greater on the side toward the isocyclic ring than on the opposite side. This is the behavior to be expected, since the maximum strain is on the ring 3 to γ-bridge bond. In particular, the model shows that the bond from magnesium to the nitrogen of ring 4 will be stretched by the closure of the isocyclic ring. This also is the position at which the properties of the porphyrin ring are modified in chlorophyll by being reduced. The porphyrin metal chelate model was photographed with the

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(12) K. J. Brunings and A. H. Corwin, *J. Am. Chem. Soc.*, **14**, 593 (1942).

(13) T. L. Hill, *J. Chem. Phys.*, **14**, 465 (1946).

(14) F. H. Westheimer and J. L. Mayer, *ibid.*, 733 (1946).

(15) P. K. Iber and W. S. Caughey, to be published.

(16) A. H. Corwin and P. E. Wei, *J. Org. Chem.*, **27**, 4285 (1962).

TABLE IV

BOND DISTANCES IN METAL CHELATE MODELS

Isocyclic ring	N_1—Mg (mm.)	N_2—Mg (mm.)	N_3—Mg (mm.)	N_4—Mg (mm.)
		Porphyrin model		
Open	110.50 ± 0.0	108.43 ± 0.2	109.85 ± 0.17	110.98 ± 0.1
Closed	109.60 ± 0.0	108.85 ± 0.1	107.00 ± 0.14	112.30 ± 0.14
Change	−0.90	+0.42	−2.85	+1.32
		Chlorin model		
Open	111.58 ± 0.17	108.18 ± 0.26	109.73 ± 0.26	110.23 ± 0.3
Closed	109.90 ± 0.0	109.05 ± 0.1	107.38 ± 0.17	111.58 ± 0.33
Change	−1.68	+0.87	−2.35	+1.35

isocyclic ring open and then again with it closed. These photographs were then superimposed and a drawing was prepared, Fig. 1, showing the relative positions of the atoms in the two models.

We conclude that analog computers of the sort described have great utility in attempts to correlate experimentally observed properties of molecules with internal stresses and resultant strains.

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Stabilities of Magnesium Chelates of Porphyrins and Chlorins[1]

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Magnesium phenate has been found to equilibrate with porphyrins and chlorins in phenol solutions at 100°. The dissociation constants of the magnesium complexes of several synthetic and analytic porphyrins and chlorins have been determined. It is concluded that in these substances the magnesium is covalently bonded to nitrogen and that magnesium porphyrins are more stable than magnesium chlorins with identical substituents. The closure of the five-membered isocyclic ring in chlorophyll-like structures produces a warpage of the porphyrin or chlorin system that decreases the stability of the magnesium complex.

Earlier investigators[3,4] have concluded that the bonding of magnesium in most chelates is primarily ionic. MacKinney and Joslyn,[5] however, concluded from relative rates of replacement of magnesium by hydrogen in chlorophylls *a* and *b* that the magnesium–nitrogen bond is highly covalent. The question is capable of resolution if equilibrium constants of chelates with varied peripheral substituents can be measured instead of rates. Corwin and Melville[4] did not succeed in finding conditions suitable for this equilibration. The present paper describes the successful outcome of this earlier line of experimentation and the measurement of selected equilibrium constants.

Equilibration of Magnesium Chelates.—Previous attempts to equilibrate magnesium with chlorophyll derivatives generally have not been successful. Thus Ruben, Frenkel, and Kamen[6] could not exchange radioactive magnesium in purified chlorophyll solutions. Becker and Sheline[7] found, however, that petroleum ether-soluble plant materials permitted the exchange to proceed. This procedure does not give promise of general utility in magnesium exchanges. Corwin and Melville[4] tried unsuccessfully to secure magnesium exchanges between porphyrins and chlorins in acetic acid systems.

Caughey and Corwin[8] showed that the removal of copper from a porphyrin required four protons. Assuming that the principle of microscopic reversibility applies, equilibration of a metal with a porphyrin should take place with the acid salt of the ligand and should be promoted by an acidic medium. Following this reasoning, a variety of acid cleavage experiments was performed in the hope of finding an equilibrating solvent. The use of so strong an acid as acetic acid invariably gave cleavage. With varying strengths of acetic acid it was possible, however, to distinguish between the chelates with respect to ease of cleavage and the results obtained are parallel to those found on true equilibration. A group of very weakly acidic materials was then tried and it was discovered that

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[1] Porphyrin Studies. XXIV. Paper XXIII, A. H. Corwin, A. Walter, and Ranbir Singh, *J. Org. Chem.*, **27**, 4280 (1962).

[2] Abstracted from the doctoral dissertation of P. E. Wei, The Johns Hopkins University, 1958.

[3] W. E. Evans and R. Pearson, *J. Am. Chem. Soc.*, **64**, 2867 (1942).

[4] A. H. Corwin and M. H. Melville, *ibid.*, **77**, 2755 (1955).

[5] G. MacKinney and M. A. Joslyn, *ibid.*, **62**, 231 (1940).

[6] S. Ruben, A. W. Frenkel, and M. D. Kamen, *J. Phys. Chem.*, **46**, 710 (1942).

[7] R. S. Becker and R. K. Sheline, *J. Chem. Phys.*, **21**, 946 (1953).

[8] W. S. Caughey and A. H. Corwin, *J. Am. Chem. Soc.*, **77**, 1509 (1955).