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]

ALSOPH H. CORWIN AND PETER ENTIEN WEI[2]

Chemistry Department of The Johns Hopkins University, Baltimore 18, Maryland

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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

(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).

phenol at moderately elevated temperatures is a suitable solvent for the equilibration. At 100°, phenol will partially remove magnesium from metallochlorins and porphyrins, magnesium phenate will partially introduce magnesium into these materials, and equilibrium can be reached from either side (equation I). Exchanges of magnesium between various ligands can also be secured (equation II).

$$PH_2 + Mg(OC_6H_5)_2 \rightleftharpoons PMg + 2C_6H_5OH \quad (I)$$

$$PH_2 + P'Mg \rightleftharpoons PMg + P'H_2 \quad (II)$$

For the estimation of the relative stabilities of magnesium chelates, it is possible to start with either of the ligands in the free state and the other chelated to magnesium. Determination of the position of the equilibrium in these cases requires the simultaneous spectrophotometric determination of four components or else a preliminary separation by chromatography. It was found simpler to equilibrate each ligand with magnesium in phenol, using the phenol as the standard in each case. By the determination of a series of equilibrium constants with respect to phenol, relative stabilities can easily be calculated. Results are given in Table I.

TABLE I

DISSOCIATION CONSTANTS OF MAGNESIUM CHELATES

	Porphyrin ligands	Constants		
1.	Etioporphyrin II	17.35		
2.	Vinyl phylloerthyrin ester	1.45		
3.	Vinyl chloroporphyrin-e_6 ester	0.439		
4.	Tetramethyl-tetracarbethoxy	Small		
	Chlorin ligands		Ratios	
5.	Etiochlorin II	355	(5)/(1)	20.5
6.	Pyropheophorbide-a ester	7.75	(6)/(2)	5.3
7.	Chlorin-e_6 ester	3.79	(7)/(3)	8.6

The reproducibility of the experiments is of the order of 2–3%. Statistical examination of experiments run at different concentrations shows a significant drift of the order of 5% for a threefold change in concentration. This may be ascribed to a deviation from ideality of the solutions of the magnesium complex in phenol.

Discussion

Bond Type.—Compounds 2 and 3 are more polar than compound 1, and compound 4 is very much more polar. In the chlorin series, compounds 6 and 7 are more polar than compound 5. In each series, the compounds with the more electron-attracting group are consistently less dissociated than the less polar, alkyl-substituted etioporphyrin and chlorin. This is the order of stabilities to be expected if the bonding to magnesium were covalent. Accordingly, we conclude that the application of the stability criterion indicates that the magnesium to nitrogen bonds in both porphyrins and chlorins are essentially covalent.

The change in bond type in N–Mg bonds indicated here[4] on going from dipyrrylmethenes to porphyrins may be attributed to the change in geometry. While the two methene molecules can adjust themselves in space to the characteristic bond length of the magnesium ion, the more rigid porphyrin and chlorin skeletons happen to be of about the right size to fit the covalent magnesium bond distance.[1]

Porphyrin–Chlorin Relationship.—In Table I, chlorins 5, 6, and 7 correspond in structure to porphyrins 1, 2, and 3. It will be seen that each metallochlorin is less stable than the corresponding metalloporphyrin. This is the finding which would be predicted on the basis of the reduced resonance possibilities of the metallochlorin system as compared to the metalloporphyrin system. While there are twelve normal bond "Kekulé structures" for metalloporphyrins, excluding double bonds to the metal, there are only nine such structures for the metallochlorins.

Effect of the Isocyclic Ring.—Compound 2 is a porphyrin with a closed five-membered ring similar to that in chlorophyll. Compound 3 is the structurally related porphyrin with the ring opened. The measurements show that closing the ring diminishes the stability of the chelate. Compounds 6 and 7 are the structurally related substances in the chlorin series. Again it will be seen that the chelate with the closed isocyclic ring, 6, is the less stable. This reasoning assumes that the electronic effects of the carbomethoxy groups in compounds 3 and 7 is closely similar to those of the keto groups in compounds 2 and 6.

Corwin, Walter, and Singh[1] have shown that closing the isocyclic ring on models of metalloporphyrins and metallochlorins produces a strain that warps the molecule. This warpage shortens the metal nitrogen bonds to rings 1 and 3 and lengthens those to rings 2 and 4. The effect of such changes in bond length on the stability of the chelate depends upon the relationship between the "normal" bond distance for the metal in question and the distance available in the particular chelate. In the case of magnesium, the covalent bond radius is estimated to be 1.30 Å.[9] The size of the hole in the porphyrin ring is variable and can change to accommodate atoms of different dimensions and different bond strengths.[10] The N–Me–N distance in the phthalocyanine ring, which should be roughly comparable in rigidity, expands from 3.65 Å. to 3.95 Å. on changing the metal from nickel

(9) M. L. Huggins, *Phys. Rev.*, **28**, 166 (1926). The distance of 1.40 Å. given in L. Pauling, "The Nature of the Chemical Bond," 2nd ed., 1940, p. 179, is based on the measurement of magnesium telluride and probably is too large due to the repulsions of the Te atoms. See L. Pauling and M. L. Huggins, *Z. Krist.*, **87**, 205 (1934).

(10) J. M. Robertson, "Organic Crystals and Molecules," Cornell University Press, Ithaca, N. Y., 1953, pp. 268–269.

to platinum.[11] We may thus assume that the Mg–N distance in a porphyrin without warping substituents would equilibrate at the optimum value for this system and that any increase or decrease in bond length caused by warpage would diminish the stability of the metal to nitrogen link.

The magnitudes of the changes in bond length caused by the closure of the isocyclic ring may be estimated by the use of the model. Since no reliable data exist on the strength of the N–Mg bond, however, these changes cannot be translated with precision into changes in chelate stability. A rough approximation may be obtained by assuming that the change in bond energy of the N–Mg bond is a constant fraction of that of the H–H bond, whose characteristics are well known. Following the changes in bond distance on the Morse curve for hydrogen, it may be calculated that the energy change associated with them should be 1920 cal. for the closing of the isocyclic ring in the metalloporphyrin case. The observed value, from compounds 2 and 3, is 1000 cal. We may thus set the conversion factor equal to the ratio, or 0.52. In the case of the metallochlorin the calculated value, on the assumption that the metalloporphyrin bond distances are optimum, would be 1015 cal. on the hydrogen curve. Using the factor 0.52, we might expect a value of 530 cal. for the change in stability due to the closing of the isocyclic ring on a metallochlorin. The observed value, from compounds 6 and 7, is 580 cal., in excellent agreement with the calculated value. We see thus that the differences in warpage between the two types of compound, due to the differences in bond distributions, are sufficient to account consistently for the differences in stability of the chelates.

Effect of Crowding.—Stuart–Brieglieb models of vinylchloroporphyrin-e_6 show that the side-chain on the bridge is crowded. Because of the nonplanarity of ring 4 in the chlorins[12] and the fact that the substituents on this ring are in the *trans* positions,[13] this crowding is partially relieved in the chlorin system.[14] Examination of the direction of the warpage produced by side-chain crowding[1] shows that the N–Mg bonds would be somewhat lengthened by this effect. Our models do not permit us to estimate the magnitude of the effect but the agreement shown above between values for the porphyrin and chlorin leads to the conclusion that crowding due to substituents on the γ-bridge should displace the nitrogens much less than the warpage due to the closure of the isocyclic ring.

Experimental

Magnesium Etioporphyrin II.—Five hundred milligrams of etioporphyrin II was added to magnesium viologen reagent[15] through a side arm in the flask. Refluxing was continued for 2 min. Two drops of the solution was drawn out, diluted with ether, and inspected in a Hartridge reversion spectroscope for disappearance of the characteristic porphyrin bands. The flask was cooled and the solution filtered with suction on a thin layer of magnesol–cellulose mixture. The flask was washed with 50 ml. of chloroform and the washings were added to the filtrate. The adsorbent then was washed free from the red magnesium complex with more chloroform. The solvent was removed under vacuum and the residual solid was dissolved in 100 cc. of U.S.P. ether and chromatographed over magnesol–cellulose mixture with ether. The red ether solution was concentrated to 50 ml. and centrifuged at 6000 r.p.m. for 20 min. and filtered. The filtrate was further concentrated to 15 ml. and 15 ml. of petroleum ether was added and allowed to evaporate slowly. Crystals formed and were dried at 110° at 1 mm. for 4 hr.; yield, 465 mg.

Anal.[16] Calcd. for $C_{32}H_{36}N_4Mg$: C, 76.71; H, 7.24. Found: C, 77.3; 76.77; H, 7.26; 7.26.

Acid treatment regenerated a substance having the spectrum of etioporphyrin II.

Magnesium etiochlorin II was prepared by the method used for the porphyrin except that final crystallization was from petroleum ether; yield, 425 mg. from 500 mg.; spectrum: I, 620; II, 578; III, 567.5; IV, 512; intensities: I > II > IV > III.

Anal. Calcd. for $C_{32}H_{38}N_4Mg$: C, 76.40; H, 7.62. For $C_{32}H_{38}N_4Mg \cdot H_2O$: C, 73.77; H, 7.74. Found: C, 74.00, 73.89; H, 8.00, 8.08.

Acid treatment regenerated a substance having the spectrum of etiochlorin II.

Magnesium Chlorin-e_6 Trimethyl Ester.—The preparation was the same exept that acetone petroleum ether was used for the crystallization and the reaction was protected by dry nitrogen; yield, 195 mg. from 225 mg.; spectrum: I, 645; II, 600; III, 566; IV, 529; intensities: I > II > IV > III.

Anal. Calcd. for $C_{37}H_{40}O_6N_4Mg$: C, 67.23; H, 6.10. Calcd. for $(C_{37}H_{40}O_6N_4Mg)_2 \cdot H_2O$: C, 66.30; H, 6.16. Found: C, 66.67; H, 6.06.

Acid treatment regenerated a substance having the spectrum of chlorin-e_6 trimethyl ester.

Magnesium Pyropheophorbide-a Monomethyl Ester.—The preparation was performed under nitrogen. The chromatogram was developed with ethylene dichloride, hexane, methanol, 10:20:3. Crystallization from ether, petroleum ether; yield, 385 mg. from 430 mg.; spectrum: I, 663; II, 615; III, 579; IV, 535; V, 495; intensities: I > II > III > IV > V.

Anal. Calcd. for $C_{34}H_{34}O_3N_4Mg$: C, 71.53; H, 6.00. Found: C, 71.34; H, 5.83.

Acid treatment regenerated a substance having the spectrum of pyropheophorbide-a ester.

Magnesium Vinylchloroporphyrin-e_6 Trimethyl Ester.—Preparation as for magnesium pyropheophorbide above. Chromatographed with ethylene dichloride, 7.5, hexane, 10, pyridine, 2. Crystallized from hot pyridine, isoöctane and dried under vacuum; yield, 150 mg. from 175 mg.; spectrum: I, 605; II, 560; intensities: II > I.

Anal.[17] Calcd. for $C_{37}H_{38}O_6N_4Mg \cdot 2(C_5H_5N)$: C, 69.07; H, 5.92. Found: C, 68.43; H, 6.04.

Acid treatment regenerated a substance having the spectrum of vinylchloroporphyrin-e_6 trimethyl ester.

Magnesium vinylphylloerythrin monomethyl ester was prepared in the same way as magnesium pyropheophor-

(11) J. M. Robertson and I. Woodward, *J. Chem. Soc.*, 221 (1937); *ibid.*, 40 (1940).

(12) H. Fischer and H. Wenderoth, *Ann.*, **537**, 170 (1939).

(13) G. E. Ficken, R. B. Johns, and R. P. Linstead, *J. Chem. Soc.*, 2272, 2280 (1956).

(14) R. B. Woodward, *Angew. Chem.*, **72**, 651 (1960).

(15) P. E. Wei, A. H. Corwin, and R. Arellano, *J. Org. Chem.*, **27**, 3344 (1962).

(16) Microanalyses performed by Mr. Joseph Walter.

(17) The authors wish to thank Mr. Roberto Arellano for the preparation of the analytical sample of this substance.

TABLE II

ACID REPLACEMENT OF MAGNESIUM IN CHELATES

Compound	Removal pH in dimethylformamide	Vol. acetic in dioxane, cc.
5	5	1.5
1	4.0 (4.5 partial)	2.5
6	4.0	2.5
7	4.0 (partial)	3.5
2	4.0 (partial)	3.5
3	2.0	5.5
4	Stable at 1.0	Stable at 10

bide above. It was chromatographed with ethylene dichloride, 10, acetone, 5, hexane, 2. It was crystallized from hot pyridine, isoöctane, and dried in vacuum; yield, 74 mg. from 100 mg.; spectrum: I, 620; II, 567.5; intensities: I > II.

Anal.[17] Calcd. for $C_{34}H_{32}O_3N_4Mg \cdot 2(C_5H_5N)$: C, 72.6; H, 5.82. Found: C, 72.35; H, 5.48.

Acid treatment regenerated a substance having the spectrum of vinylphylloerythrin methyl ester.

Magnesium 1,3,5,7-tetramethyl-2,4,6,8-tetracarbethoxyporphyrin was prepared as magnesium etioporphyrin II. Chromatography was done with ethylene dichloride, methanol, hexane, 1:1:1. Crystallization was from chloroform–methanol; yield, 28 mg. from 30 mg.; spectrum: I, 612; II, 573; intensities: II > I.

Anal. Calcd. for $C_{36}H_{36}O_8N_4Mg \cdot CH_3OH$: C, 62.94; H, 5.65. Found: C, 62.34; H, 5.72.

Acid treatment regenerated a substance having the spectrum of the starting porphyrin.

Acid Replacement of Magnesium from Complexes.—One hundred fifty cubic centimeters of dimethylformamide was placed in a 400-cc. beaker, fitted with a magnetic stirrer, and connected to a pH meter. Glacial acetic acid was added to pH 5. A 5-cc. aliquot of this solution was drawn out into a shell vial, to which a magnesium complex was added to a strength just sufficient to be examined on the Hartridge spectroscope for absorption bands. The solution then was heated on the water bath with shaking for 30 sec. and then quickly chilled with an ice–water bath and examined in the spectroscope. After all complexes had been examined at this pH, the acidity was increased and the process repeated. Table II shows the results (numbering as in Table I).

Another acid replacement was carried out at room temperature in mixtures of dioxane and glacial acetic acid. Acid and alkali purified dioxane was used. A 5-cc. sample was pipetted into each shell vial containing a magnesium complex. A 1.5-cc. sample of glacial acetic acid then was added to each vial with shaking and the solution was examined after 30 min. Those that did not react were treated with an additional cubic centimeter of glacial acetic acid, shaken, allowed to stand 30 min., and re-examined. This procedure was repeated until all had been converted except no. 4. The results also are given in Table II.

TABLE III

EXCHANGES OF MAGNESIUM CHELATES WITH PORPHYRINS AND CHLORINS

Expt. no.	Reagents	Temp., °C.	Time, min.	Major product	Minor product
1	Mg-1 + 4	190	120	1 + Mg-4[a]	4 + Mg-1[a]
2	Mg-1 + 3	101	15	1 + Mg-3	3 + Mg-1
3	Mg-1 + 2	190	120	1 + Mg-2	2 + Mg-1
4	Mg-1 + 7	100	15	1 + Mg-7	7 + Mg-1
5	Mg-1 + 6	102	15	1 + Mg-6	6 + Mg-1
6	Mg-1 + 5	100	15	5 + Mg-1	1 + ...
7	Mg-3 + 1	103	10	1 + Mg-3	3 + Mg-1
8	Mg-3 + 4	100	15	3 + Mg-4[a]	4 + Mg-3[a]
9	Mg-3 + 2	100	15	2 + Mg-3[a]	3 + Mg-2[a]
10	Mg-3 + 7	102	15	7 + Mg-3	3 + Mg-7
11	Mg-3 + 6	100	15	6 + Mg-3	3 + Mg-6
12	Mg-2 + 1	170	30	1 + Mg-2	2 + Mg-1
13	Mg-2 + 3	100	15	2 + Mg-3	3 + Mg-2
14	Mg-2 + 6	150	30	6 + Mg-2	2 + Mg-6
15	Mg-2 + 7	100	15	7 + Mg-2	2 + Mg-7
16	Mg-7 + 1	100	15	1 + Mg-7	7 + Mg-1
17	Mg-7 + 2	100	15	7 + Mg-2	2 + Mg-7
18	Mg-7 + 3	100	15	7 + Mg-3	3 + Mg-7
19	Mg-7 + 4	110	10	7 + Mg-4[a]	4 + Mg-7[a]
20	Mg-7 + 6	103	15	6 + Mg-7	7 + Mg-6
21	Mg-7 + 5	103	20	5 + Mg-7	7 + ...
22	Mg-6 + 1	102	30	1 + Mg-6	6 + Mg-1
23	Mg-6 + 7	100	15	6 + Mg-7	7 + Mg-6
24	Mg-6 + 2	130	15	6 + Mg-2	2 + Mg-6
25	Mg-6 + 5	100	15	5 + Mg-6	6 + ...
26	Mg-5 + 7	101	15	5 + Mg-7	7 + Mg-5
27	Mg-5 + 6	101	15	5 + Mg-6	6 + Mg-5
28	Mg-5 + 1	100	15	5 + Mg-1	1 + Mg-5
29	Mg-4 + 1	150	30	1 + Mg-4[a]	...[a]

[a] Solvent used for chromatography: $10C_2H_4Cl_2$, $20C_6H_{14}$, $3CH_3OH$.

Acid Replacements with Substituted Pyrroles and Phenols.—It is evident from the acid replacement that the porphyrins and chlorins with carbethoxy groups formed more stable complexes than the ones substituted with ethyl groups. Therefore, orienting experiments were performed with the more acidic pyrroles containing carbethoxy groups as weak acids for the removal of magnesium. Magnesium etioporphyrin II (2 mg.) was mixed with 2,4-dimethyl-3,5-dicarbethoxypyrrole (50 mg.) in a soft glass tube which was evacuated and then sealed. After heating for 30 min. at 180°, the tube was opened and the product examined spectroscopically. No free porphyrin was found. With 2,4-dicarbethoxy-3-methyl-5-carbomethoxypyrrole treated similarly, chromatography of the product showed a trace of free porphyrin. With *p*-nitrophenol, only free porphyrin was found, no magnesium complex remaining. With phenol,

TABLE IV

SPECTRA OF PORPHYRINS AND MAGNESIUM CHELATES

Compound 1 Conc. × 10^5 1.385		Compound 2 2.092		Compound 3 2.684		Compound 4 2.439	
Abs. max. mμ	ε × 10^4	Abs. max. mμ	ε × 10^4	Abs. max. mμ	ε × 10^4	Abs. max. mμ	ε × 10^4
620	(0.440)	640	(0.206)	633	(0.149)	647–650	(0.131)
580	(0.317)	620	(0.125)	605	(0.260)	593–595	(0.300)
567–568	(0.629)	590	(1.190)	580	(0.686)	555	(0.370)
530	(0.952)	567–568	(1.371)	550	(0.965)	520	(0.706)
498	(1.380)	525	(0.679)	512	(1.032)		
Compound Mg-1 Conc. × 10^5 2.132		Compound Mg-2 6.172		Compound Mg-3 3.344		Compound Mg-4 4.720	
Abs. max. mμ	ε × 10^4	Abs. max. mμ	ε × 10^4	Abs. max. mμ	ε × 10^4	Abs. max. mμ	ε × 10^4
580	(1.785)	620	(0.287)	605	(0.622)	612	(0.425)
545	(1.885)	590	(0.139)	560	(0.709)	573	(0.894)
498	(0.226)	567–568	(0.207)	512	(0.155)		

TABLE V

SPECTRA OF CHLORINS AND MAGNESIUM CHELATES

Compound 5 Conc. × 10^5 1.500		Compound 6 1.001		Compound 7 1.083	
Abs. max. mμ	ε × 10^4	Abs. max. mμ	ε × 10^4	Abs. max. mμ	ε × 10^4
645	(5.010)	667	(5.040)	665	(4.490)
620	(0.335)	663	(3.740)	645	(0.920)
615	(0.370)	609	(0.939)	610	(0.480)
590	(0.392)	560	(0.371)	560	(0.157)
545	(0.158)	540	(1.079)	530	(0.480)
520	(0.370)	510	(1.351)	500	(1.292)
495	(1.148)	475	(0.496)		
Compound Mg-5 Conc. × 10^5 2.540		Compound Mg-6 1.004		Compound Mg-7 1.740	
Abs. max. mμ	ε × 10^4	Abs. max. mμ	ε × 10^4	Abs. max. mμ	ε × 10^4
620	(3.120)	667	(3.860)	665	(0.793)
575–580	(0.571)	663	(4.560)	645	(4.820)
567–568	(0.472)	615	(0.930)	600	(0.925)
512	(0.484)	575–580	(0.502)	575	(0.442)
495	(0.284)	530–535	(0.291)	525	(0.414)
		495	(0.226)		

ture. This affords an alternative method for closing the isocyclic ring in chlorophyll derivatives. A repetition of the experiment at 101° showed that the partial removal of magnesium took place without ring closure. Additional experimentation, recorded below, showed that 100° was adequate for the exchange and equilibration of the remaining magnesium complexes.

Exchange Reactions.—The techniques involved were the same as those described above. It was difficult to weigh the two samples in an exact one to one molar ratio. A pair of equal weight aluminum holders for the balance pans was made to hold the sample tubes and tare tubes which were cut to equal lengths. In adding samples, an aluminum block with a hole to fit the 6-mm. soft glass tubes was used for handling. All reactions were carried out in the absence of air, that is, below 1 mm. in sealed tubes. The resulting mixtures were chromatographed over magnesol–cellulose with ether unless otherwise specified. The amount of phenol was a microspatulaful and was not weighed. The results are given in Table III.

Quantitative Spectra. Samples were prepared by quantitative dilution in spectral grade dimethylformamide. The results of the measurements are given in Tables IV and V.

Equilibria of Magnesium Complexes with Phenol.—The equilibria were studied in 6-mm. soft glass tubes evacuated to 0.2 mm. and sealed. The heater was an insulated aluminum block drilled with ten holes to fit the tubes and was controlled by a variac and a relay. The tubes sealed with samples were heated at 100° and then chilled rapidly in an ice–water bath. The resulting samples were immediately recorded at the selected wave length on a Beckman DU spectrophotometer. The solvent used for the quantitative reference absorption curves contained no phenol, so the dimethylformamide containing phenol was checked against

TABLE VI

EQUILIBRATION OF MAGNESIUM CHELATES IN PHENOL AT 100° FOR 10 MINUTES

Expt.	Comp.	Conc. (moles/mole phenol)	Vol. dimethyl-formamide	Opt. dens.	K
30	Mg-7	0.00562	33⅓	0.408 (665); 0.860 (645)	3.79
31	Mg-6	0.00640	26⅔	1.84 (667); 1.80 (663)	7.75
32	Mg-1	0.00825	26⅔	0.652 (580); 0.344 (498)	17.35
33	Mg-3	0.00725	10	0.750 (605); 0.303 (512)	0.439
34	Mg-3	0.00815	10	0.993 (605); 0.424 (512)	0.450
35	Mg-2	0.00172	10	0.088 (620); 0.202 (590)	1.45
36	Mg-5	0.01653	35	0.655 (620); 0.792 (495)	355.
37	Mg-5	0.00522	50	0.219 (620); 0.561 (495)	329.[a]
38	Mg-5	0.00626	50	0.312 (620); 0.844 (495)	340.
39	Mg-5	0.00420	50	0.217 (620); 0.645 (495)	335.

[a] Equilibrated 30 min.

the magnesium of the complex was partially and appreciably removed. Similar treatment of magnesium tetramethyltetracarbethoxyporphyrin showed no removal of magnesium. In the case of the magnesium complex of vinylchloroporphyrin-e_6 trimethyl ester, partial removal of magnesium was observed, but the products obtained were identified spectroscopically as magnesium vinylphylloerythrin monomethyl ester and the corresponding free porphyrin. Hence ring closure took place at this tempera-

the pure dimethylformamide as a blank at each selected wave length and no absorption was observed. Results are given in Table VI.

Statistical examination of the last four determinations shows a significant correlation with concentration, the equilibrium shifting toward slightly greater dissociation with greater concentration. Correlation coefficient, 0.865. Probability of correlation, about 60 to 1.

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Conformational Analysis. XXXIII. On the Conformation of the Cyclooctane Ring[1,2]

NORMAN L. ALLINGER, S. P. JINDAL, AND MARGARET A. DAROOGE[3]

Department of Chemistry, Wayne State University, Detroit 2, Michigan

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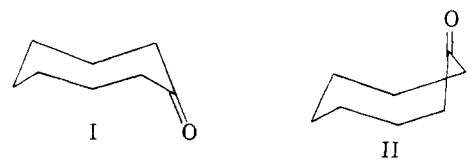
The dipole moments of 5-(*p*-chlorophenyl)-cyclooctane ethylene ketal and appropriate related compounds have been interpreted in terms of a stretched crown conformation for the cyclooctane ring. Reinterpretation of earlier data shows that such a conformation fits all available information. The carbonyl carbon of the ketone prefers to be at a specific location on the crown, while in the ketal a different location is preferred. These results are interpreted in terms of van der Waals and torsional forces.

The basic conformation of the cyclooctane ring appears to be fairly well established as that of a crown.[4-13] The approximate nature of this crown is known in one instance from X-ray diffraction studies.[6] Since cyclooctane and its derivatives in general appear to possess only a single conformation, it seems likely that the same conformation of the ring is to be found in most cases. Such data as are available appear consistent with this idea. There remains the problem in substituted cyclooctanes of the location of the substituents on the different non-equivalent carbons.

Cyclooctanone represents a simple derivative, the geometry of which may be reconsidered in the light of recent work. An earlier interpretation[7] of its conformation appeared to give evidence for a mixture of two conformations (I and II). More recent evidence has shown[5] that the experimental facts are consistent only with I. The structure II



is probably of higher energy than previously realized because of the repulsion between the carbonyl carbon and the C-4 and C-6 methylenes. The recently found small values for the 3-alkylketone effect[14] are consistent with this interpretation.

There appear to be three separate studies in the literature which offer experimental evidence which must be accommodated by any structure for cyclooctanone that is proposed. These are studies on the 5-heterocyclooctanones,[11] on α-bromocyclooctanone,[15] and on 5-*p*-chlorophenylcyclooctanone.[7] If it is assumed that the basic ring structure is the stretched crown (Fig. 1), there remains only the problem of the location of the carbonyl, at C-1, C-2, or C-3. Leonard's dipole moment results[11] show a very small angle between the dipoles of 5-oxacyclooctanone, and are consistent with the carbonyl being at C-1, but not at C-2 or C-3. The dipole moment of 5-(*p*-chlorophenyl)-cyclooctanone[7] is likewise consistent only with the carbonyl being at C-1.

Earlier, the available data on α-bromocyclooctanone was interpreted[15] in terms of an equilibrium involving forms I and II. It was remarked at the time that the data were insufficient to establish that such an equilibrium existed, but it could be shown that the data were consistent with such an equilibrium. Since it is now clear that such an equilibrium does not exist, these data remain to

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(3) Predoctoral U. S. Public Health Service Fellow, General Division of Medical Sciences, 1960–1962.

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