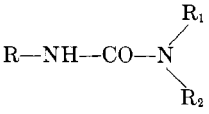
TABLE III
DISUBSTITUTED BUTYL- OR ARYLUREAS



R	R_1	R_2	Yield, %	M.p., °C.	B.p., °C. (mm.)	Calcd., % C	Calcd., % H	Calcd., % N	Found, % C	Found, % H	Found, % N
$CH_3(CH_2)_3$	C_2H_5	C_2H_5	87	...	104–105 (0.001)	62.74	11.70	16.26	62.81	11.71	16.20
$CH_3(CH_2)_3$	$CH_3(CH_2)_2$	$CH_3(CH_2)_2$	78	...	109–110 (0.001)	65.95	12.08	13.99	65.99	12.12	13.91
$CH_3(CH_2)_3$	$(CH_3)_2CH$	$(CH_3)_2CH$	90	...	128–130 (15)	65.95	12.08	13.99	65.70	12.15	13.90
$CH_3(CH_2)_3$	CH_3	C_6H_{11}[a]	80	...	135–138 (0.005)	67.88	11.39	13.19	68.16	11.60	13.32
$CH_3(CH_2)_3$	$CH_2CH_2CH_2CH_2$		91	52–53[b]	...	63.49	10.66	16.46	63.67	10.78	16.59
$CH_3(CH_2)_3$	$CH_2CH_2CH_2CH_2CH_2$		87	63–64[b]	...	65.17	10.94	15.20	65.31	11.02	14.97
$CH_3(CH_2)_3$	$CH_2CH_2OCH_2CH_2$		90	68[b]	...	58.03	9.74	15.04	57.74	9.62	15.20
$CH_3(CH_2)_3$	$CH_2CH_2N(CH_3)CH_2CH_2$		86	54–56[b]	112–115 (0.001)	60.26	10.62	21.08	60.32	10.48	21.04
C_6H_5	$CH_3(CH_2)_2$	$CH_3(CH_2)_2$	85	73[c]	...	70.87	9.15	12.72	70.82	9.12	12.86
4-$C_2H_5OC_6H_4$	C_2H_5	C_2H_5	86	95–96[c]	...	66.07	8.53	11.86	65.80	8.54	11.72

[a] Cyclohexyl. [b] Crystallized from petroleum ether, (60–68°). [c] Crystallized from a benzene-petroleum ether mixture.

Experimental[9]

Preparation of Ureas.—1,1-Diethyl-3-(*o*-aminophenyl)urea was prepared by catalytic reduction of the corresponding nitro compound. The other ureas used were prepared according to a previously reported method.[10] The previously unknown ureas are listed in Table III.

Preparation of Formamidines. Procedure A.—A solution of 0.02 mole of the urea in 150 ml. of anhydrous benzene was added, dropwise, to a well-stirred suspension of 0.03 mole of LAH in 150 ml. of dry ether. The reaction mixture was refluxed for 14 hr. Then, the mixture was cooled and the reaction product and the excess LAH were decomposed by slow addition of water, 15% aqueous NaOH, and water, in succession.[11] After vigorous stirring for 20 min., the mixture was filtered and the precipitate was repeatedly washed with ether. The initial solution and the ether used for washing were combined and shaken with a concentrated solution of tartaric acid. The organic phase, after evaporation of the solvent, gave the unreacted urea; the aqueous phase, after cooling, was made alkaline with potassium carbonate and extracted with ether. The resulting ether solution was dried on anhydrous sodium sulfate, and then evaporated. The residue was then distilled under reduced pressure.

Procedure B.—A solution of 0.02 mole of the urea in 150 ml. of dry benzene was added, dropwise and with stirring, to a suspension of 0.02 mole of LAH in 150 ml. of anhydrous ether. When the addition was finished, the mixture was heated under reflux for 14 hr. The cooled mixture was, successively, worked up as in procedure A.

Procedure C.—This was identical with procedure A, except for the refluxing time (4 hr.).

Procedure D.—A solution of 0.05 mole of the urea in 100 ml. of toluene was added, slowly and under stirring, to a suspension of 0.05 mole of LAH in 100 ml. of *n*-butyl ether. After the addition was complete, the mixture was refluxed for 5 hr. After cooling, the reaction mixture was decomposed and worked up as in procedure A.

Procedure E.—This was similar to procedure B and differed only in the heating time (4 hr.).

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(9) Melting points were determined on a Fisher-Johns apparatus and are uncorrected.

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Proton Magnetic Resonance Evidence for Ligand–Porphyrin Interaction in Magnesium Porphyrins[1]

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Recently Corwin, *et al.*,[3,4] proposed that the appearance of a new absorption peak in the near ultraviolet (Soret) region of the electronic spectra of metalloporphyrins in the presence of strong ligands is due to a steric interference between the ligand and the π-electron system of the porphyrin ring. Caughey and Iber[5] recently showed that in N-methyl and N-ethyletioporphyrin II (etio II) the position of the N-alkyl resonance is shifted to considerably higher field due to the ring-current effects at the center of the aromatic porphyrin system. We have observed large chemical shifts to high field from their normal position in the case of ligands bound to magnesium in magnesium etioporphyrin II (Mg etio II) and magnesium tetraphenylporphin (Mg TPP). This permits one to determine the number of ligands interacting with the metalloporphyrin and to gain a qualitative view of how tightly the ligand is bound to the metalloporphyrin system.

Table I presents a comparison of the chemical shifts of pyridine in the Mg etio II complex, Mg TPP complex, and some model pyridine complexes. In both the pyridinium hydrochloride and the magnesium hexapyridinate diiodide the pyridine protons are shifted to slightly lower field, a paramagnetic shift expected from the de-

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TABLE I

P.M.R. SHIFTS OF PYRIDINE AND SOME COMPLEXES

	α-H	Shift[a]	β-H	Shift	γ-H	Shift
C_5H_5N[b]	1.42		2.79		2.38	
$C_5H_5N \cdot HCl$	1.12	−0.30	2.03	−0.76	1.50	−0.88
$MgI_2 \cdot 6C_5H_5N$	1.34	−0.08	2.70	−0.09	2.34	−0.04
Mg etio II $\cdot 2C_5H_5N$	5.10	3.68	3.95	1.14	3.35	0.97
Mg etio II $\cdot 1C_5H_5N$	7.15	5.73	4.60	1.81	3.89	1.51
Mg TPP $\cdot 2C_5H_5N$	5.10	3.68	3.80	1.01	3.27	0.89
Mg TPP $\cdot 1C_5H_5N$	6.99	5.57	4.29	1.50	3.53	1.15

[a] Difference in parts per million from free ligand. [b] "High Resolution NMR Spectra Catalog," Varian Associates, Palo Alto, Calif.

TABLE II

P.M.R. SHIFTS OF N-ALKYLPORPHYRIN AND -PYRROLE DERIVATIVES

		τ	Shift
Pyrrole	NH[a]	2.0	
Etio II	NH	13.8	11.8
N-Methylpyrrole	NCH_3[b]	6.34	
N-Methyl etio II	NCH_3	14.89	8.55
	NH	13.1	11.1
N-Ethylpyrrole	NCH_2CH_3	6.12	
	NCH_2CH_3	8.65	
N-Ethyl etio II	NCH_2CH_3	15.16	9.04
	NCH_2CH_3	12.37	3.72

[a] See Table I, ref. b. [b] See ref. 5.

shielding effect of a positive or partial positive charge. In contrast, the pyridine protons in the magnesium porphyrin complexes show diamagnetic shifts many times larger than the shifts in the model complexes. The effect is largest on the α-protons and progressively decreases with the β- and γ-protons. This is consistent with a physical picture of the porphyrin ring-current field interacting through space with the pyridine ligand.

The positions of the pyridine proton resonances are dependent on the amount of pyridine present in solution. Figure 1 shows the dependence of the chemical shifts of the pyridine α-protons on the total amount of pyridine present in solution, both complexed and uncomplexed. The limiting value is the chemical shift of the free pyridine. This type of dependence is consistent with the pyridine ligand exchanging rapidly with the magnesium porphyrin. What is observed is an average of the chemical shifts of the free ligand and of the mono- and diligand–magnesium porphyrin complexes weighted according to their relative concentrations. P.m.r. studies as low as −50° have been carried out in an attempt to observe the true chemical shift of the magnesium porphyrin dipyridinate. No line broadening has been observed for the ligand resonance and evidently the exchange remains facile even at that low temperature. The chemical shifts of the porphyrin protons are unaffected by the pyridine concentration.

The magnetic field intensity, B, along a line normal to and passing through the center of a closed current loop may be expressed as $B = (\mu_0 i \sin \alpha R)/4\pi r^2$, where R is the radius of the loop, r the distance from the loop to the point considered, and α the angle formed between r and the axis of the loop.[6] Since the chemical shift is a linear function of the field strength, a plot of the difference in chemical shift between the N-alkylporphyrins and the corresponding N-alkylpyrroles against $1/r^2$ as measured on Dreiding and Stuart Breiglieb models might be expected to give a straight line. Table II presents a comparison of the chemical shifts of the N-alkylporphyrins and -pyrroles. Using the dimensions given by Abraham,[7] a radius of 2.2 Å. for the inner edge of the porphyrin current loop, and the chemical shifts given in Table II, the result given in Fig. 2 is obtained. If the distance from the plane of the porphyrin ring to the point considered is denoted by s, then $r^2 = R^2 + s^2$. For N-methyl etio II the N-methyl group is 1.7 Å. above the plane; for N-ethyl etio II, the N-ethyl CH_2 is at 1.6 Å., the N-ethyl CH_3 is at 3.5 Å. The positions of the pyridine protons in the magnesium etio II monopyridinate may then be determined from this line and the data given in Table I. The positions for the pyridine protons are α = 2.6 Å., β = 5.6 Å., and γ = 6.1 Å. These distances are consistent with those indicated in the Stuart Brieglieb models.

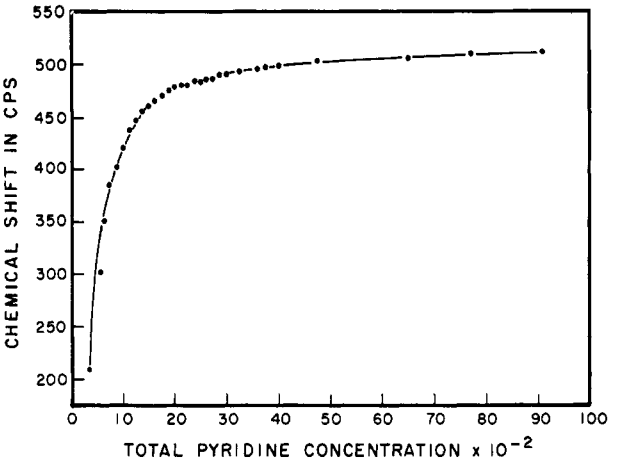

Fig. 1.—A plot of the chemical shift of the α-pyridine protons in cycles per second against the total molar concentration of pyridine in solution.

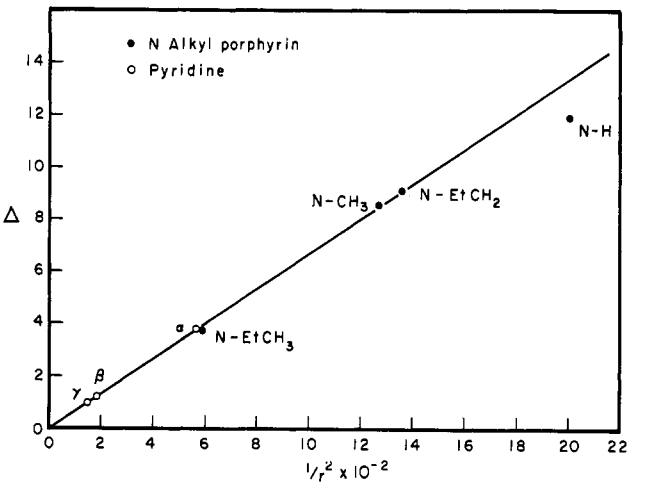

Fig. 2.—A plot of the difference in chemical shift between N-alkyletioporphyrin II and the corresponding N-alkylpyrrole against the square of the reciprocal of the distance of the alkyl group from the current loop. This line is then used to fix the distance of the pyridine protons.

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In Table III the Mg etio II–methanol complex is compared to free methanol. Closs, *et al.*,[8] recently reported a similar but smaller effect in methanol chlorophyl b complexes. The methanol being less tightly bound than the pyridine exhibits a smaller shift to high field.

TABLE III
P.M.R. SHIFTS OF
Mg ETIO II–METHANOL COMPLEX

	CH_3	Shift	OH	Shift
CH_3OH[a]	6.72		5.73	
Mg etio II–CH_3OH	11.00	4.28	10.82	5.09

[a] *Ca.* 0.4 *M* in benzene.

In Table IV the positions of the porphyrin complex chemical shifts are compared to the resonance positions in the free bases. Caughey and Koski[9] have noted that the introduction of a metal ion normally results in a general shift to higher field for those protons affected by the ring current. The effect of the magnesium and the various ligands is slight and in no case is any nonequivalence of any of the porphyrin protons induced.

TABLE IV
P.M.R. SHIFTS OF
ETIO II, TPP, AND MAGNESIUM COMPLEXES

	CH_3	CH_2CH_3	CH_2CH_3	Methine
Etio II[a]	6.38	8.13	5.90	−0.13
Mg etio II·$2C_5H_5N$	6.35	8.13	5.88	−0.15
Mg etio II·$1C_5H_5N$	6.37	8.14	5.88	−0.11
Mg etio II·$1CH_3OH$	6.40	8.17	5.94	−0.03

	Phenyl hydrogens		
	β-H	o-H	m- and p-H
TPP	1.05	1.70	2.20
Mg TPP·$2C_5H_5N$	1.05	1.70	2.20
Mg TPP·$1C_5H_5N$	1.05	1.70	2.23

Experimental

The spectra were recorded on a Varian A-60 n.m.r. spectrometer in $CDCl_3$ solution at *ca.* 0.05 *M* concentrations. Neither the etio II nor TPP nor their magnesium derivatives show concentration dependence of their chemical shifts such as have been reported for porphyrins containing polar functional groups.[8,10] The τ-values were determined from the calibrated paper relative to tetramethylsilane internal standard, τ 10. All spectra were recorded at 35°.

The magnesium diiodide hexapyridinate, magnesium porphyrin mono- and dipyridinates, and Mg etio II monomethanolate were prepared by the method of Wei, Corwin, and Arellano.[11] The electronic spectra of the magnesium porphyrins corresponded to those reported in the literature.[11,12] The number of ligands attached to the magnesium porphyrin were determined by proton integration.

The N-alkylpyrroles were synthesized from potassium pyrrole and the alkyl diiodide[13,14] and distilled, and the p.m.r. spectra were taken in $CDCl_3$.

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The Structure of Acetonepyrrole[1]

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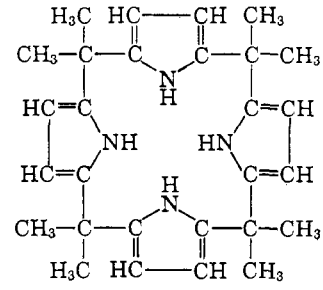
Acetonepyrrole (**1**), the acid-catalyzed condensation product of acetone and pyrrole, was first reported by A. Baeyer[3] in 1886. A structure was proposed by Chelintzev and Tronov[4] and named α,β,γ,δ-octamethylporphinogen by H. Fisher.[5] Rothemund and Gage[6] recently investigated the structure by hydrogenolysis and pyrolytic degradation. Their conclusion was that at least three of the four bridge carbons were linked to the α-positions of the pyrrole nuclei but that the nature



1
acetonepyrrole

of the linkage of the fourth bridge carbon remained in doubt. Examination of Stuart–Breiglieb molecular models reveals that either the α- or β-linkage is sterically feasible.

The proton magnetic resonance (p.m.r.) spectrum of a molecule is sensitive to both the electronic environment of the proton, as shown by the chemical shift, and the symmetry of the molecule, as shown by spin–spin interactions. The p.m.r. spectrum of acetonepyrrole shows only three peaks. A sharp singlet at δ 1.53 is assigned to the eight bridge methyl groups. A doublet at 6.00 (J = 2.80 c.p.s.) is assigned to the eight protons at the β-positions on the pyrrole rings. Abraham and Bernstein[7] have observed coupling between the protons at the 1- and 3-positions in β-free pyrroles. In the cases they investigated the coupling constant was 2.43 c.p.s. The slightly larger coupling constant in the case of acetonepyrrole may be due to the lack of intermolecular hydrogen bonding in this molecule. In alkyl-substituted pyrroles the chemical shifts of the α- and β-protons are separated by *ca.* 0.5 p.p.m. with the β-protons falling in the region of δ 6.[8] If any β-linkages were present the α-proton would then be observed in the region of δ 6.5. A broad peak at δ 7.1 is assigned to the

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