is in as good agreement with the data as is the syn isomer. The number of degrees of freedom is 16 − 4 = 12. The minimum value of the R-factor ratio to reject the hypothesis at the 0.5% level is 1.407; the experimental ratio, 0.341/0.092 = 2.89, is large enough to strongly reject the hypothesis. We conclude that the epoxide ring is in the syn arrangement, but we cannot distinguish the planar from the nonplanar cyclobutane model at the 0.5% level.

In one of our early attempts to fit the LIS spectrum of 5-methylbicyclo[3.2.0]hept-3-en-2-one (4) the methyl
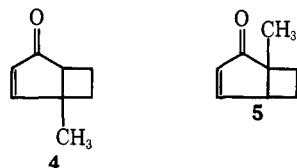
group was misplaced at carbon 1 (5), giving a best fit of R = 0.129. When the methyl group was correctly placed at carbon 5, the R value obtained was 0.080. The 1-methyl possibility can be rejected in favor of the 5-methyl isomer at about the 5% level, using the significance tests.

It should be noted that this method of significance testing gives a *statistical* measure of the confidence at which certain hypotheses can be rejected. Any other information which can be brought to bear on the problem must also be used. For example, our confidence in rejecting the 1-methyl isomer in the choice between structures 4 and 5 is further heightened by the observation that the improbably short O–Eu distance of 2.0 Å was necessary to obtain the 0.129 fit. We must also note that the method does not test whether the model accepted is the *best possible* model—only whether it is preferred, at a determined confidence level, over another proposed model. For instance, even though the planar syn model of 3 is preferred at the 2.5% level, it is still possible that a statistically better fit would be obtained with another conformation of the syn structure or with some mixture of several conformations.

The foregoing applications are illustrative of the power of the method and suggest several obvious extensions. It is already clear to us that monofunctional compounds need not have a complete set of proton LIS data and that refinement of partial sets of data can be used to define local stereochemistry and to identify unassigned resonances. Polyfunctional molecules are also amenable to this general treatment. The technique will prove useful in conformational analysis of flexible molecules, since the R-factor ratio test assesses the validity of several conformational models. Finally, appropriate statistical treatment provides an approach to the frequently perplexing question about whether the LIS method perturbs conformational equilibria. These problems are presently under investigation.

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Nitrogen–Hydrogen Tautomerism in Porphyrins and Chlorins

Sir:

The question of N–H tautomerism in porphyrins has been under active consideration ever since the first definition of the basic porphyrin structure by Fisher and Küster. A variety of spectroscopic[1] and chemical[2] methods have been used in attempts to decide as to what is the most appropriate way to represent the porphyrin structure. Currently structures 1 and 2 are most favored, being in rapid equilibrium, although structure 3 is still used by some authors.[3]
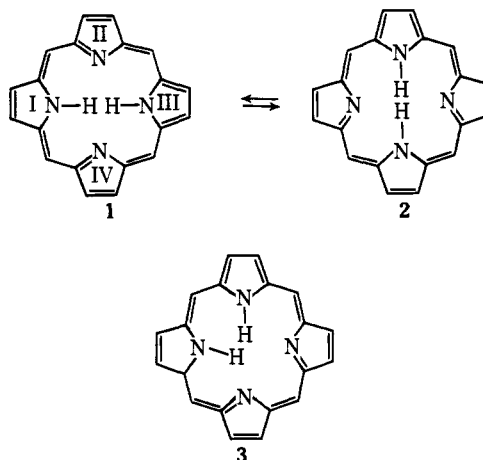
We wish to report here the results of low-temperature proton magnetic resonance (pmr) studies which indicate that we have frozen out the tautomerism between 1 and 2. Furthermore, it appears that a similar facile isomerism takes place in chlorins, a possibility not previously considered to our knowledge.

Figure 1 presents the pmr spectra of the β-pyrrole hydrogens of $\alpha,\beta,\gamma,\delta$-tetraphenylporphin (TPP) at several temperatures.[4] At 30° a single fairly sharp peak is obtained (δ 8.72) for the eight β-pyrrole protons, suggesting a C_4 axis for the molecule, rather than the C_2 axis indicated by 1. As the temperature is lowered the peak broadens, reaching a coalescence point at −40° and giving two distinct peaks at −80° (δ 8.61, 8.90). The peak at δ 8.90 is assigned to the protons on pyrrole rings I and III in 1 and the peak at δ 8.61 is assigned to the protons on rings II and IV in 1. The broadening of the δ 8.90 peak is due to long-range coupling between an N–H proton and the β-pyrrole protons. Figure 2 shows the result of a double resonance experiment, at −80°, where the N–H protons (δ −3.33) were irradiated while observing the β-pyr-

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(4) The pmr spectra were obtained at 100 MHz on a 0.005 M solution in a 12-mm sample tube using CS_2 as a solvent. The temperature was calibrated using CH_3OH. Chemical shifts are reported in parts per million using the δ scale relative to TMS internal standard (TMS = δ 0). At this dilution the chemical shift of the porphyrin protons showed no temperature dependence.
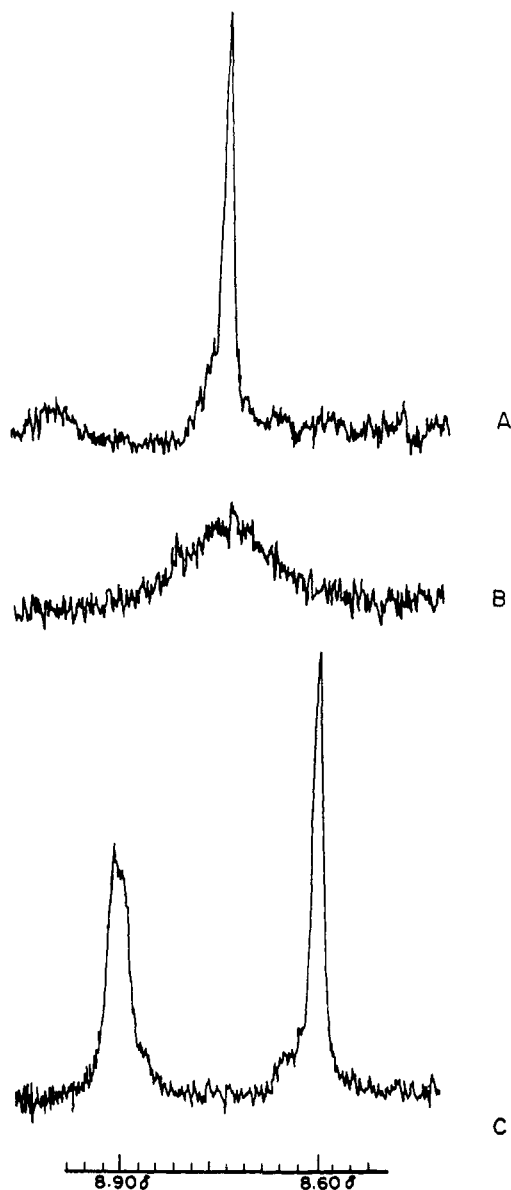
Figure 1. The pmr spectra of the β-pyrrole protons of TPP at several temperatures: A, 30°; B, −40°; C, −80°. The conditions are as given in ref 4.

Figure 2. The pmr spectrum of the β-pyrrole protons of TPP at −80° observed while simultaneously irradiating the NH protons at δ −3.33.

Figure 3. The pmr spectra of the NH protons of chlorin e_6 trimethyl ester at several different temperatures: A, 60°; B, 30°; C, 20°; D, 10°. The conditions are as given in ref 7.

role hydrogens. The δ 8.90 peak becomes much sharper; the δ 8.61 peak is unchanged. When TPP is titrated with 2 mol of trifluoroacetic acid to form $TPPH_2^{2+}$ a coupling constant of 1.5 Hz is observed between the β-pyrrole protons and the N–H protons. Other similar couplings have been observed in pyrroles and acetone pyrrole.[5]

Further support for this assignment was obtained by replacing the two central hydrogens with deuterium to give TPP-d_2.[6] This compound shows a coalescence temperature of 0° for the β-pyrrole protons, at 60 MHz,[7] giving two equally sharp peaks at −30°. The rise of some 50° in the coalescence temperature indicates a large isotope effect on the rate

of tautomerism. It is apparent that it will be best to search for this type of tautomerism in other porphyrins using the deuterated forms.[1c,8]

Chlorin e_6 trimethyl ester shows a similar temperature-dependent behavior. The N–H protons on rings I and III in structure 4 are not equivalent; however, at 40° only one rather broad N–H peak (δ −1.38) is observed. On cooling to 10° two distinct N–H protons are observed (δ −1.35, −1.42), as shown in Figure 3. The N–H protons can only be exchanged through an intermediate such as 5.

This structure can maintain the 18π-electron aromatic system by using the unshared pair of electrons on the sp^2-hybridized nitrogen in the chlorin ring. The fact

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(7) The pmr spectra at 60 MHz were obtained on 0.06 M solutions using $CDCl_3$–CS_2 mixed solvent. At these higher concentrations some temperature dependence of the chemical shift of the porphyrin protons was observed. This is undoubtedly due to intermolecular aggregation, as has been reported many times before.
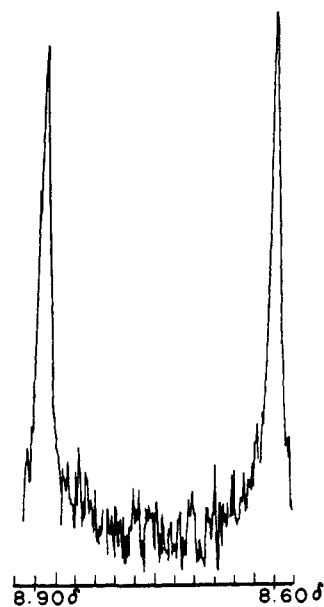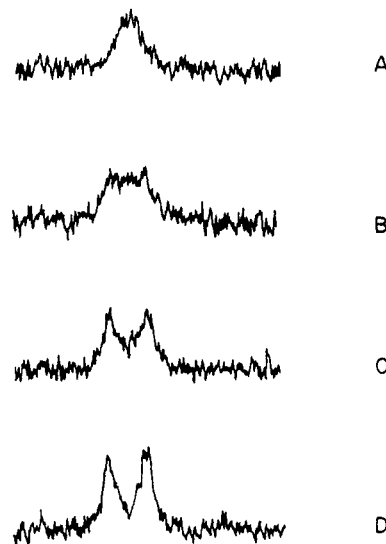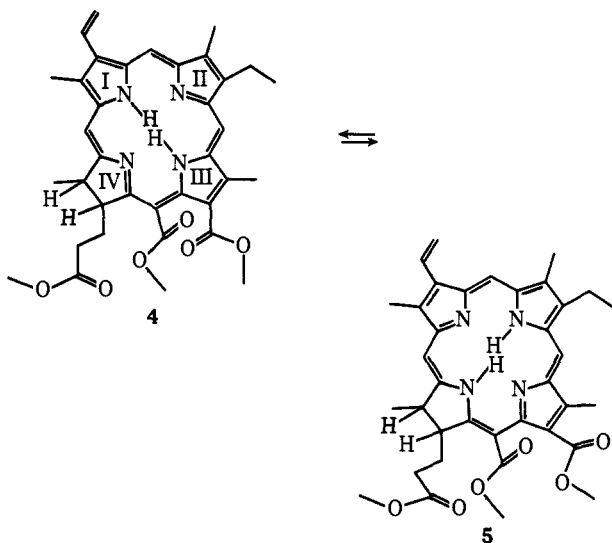
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4

5

that the exchange can be slowed down at such a high temperature suggests that structure **5** is of somewhat higher energy than **4**. In the pheophorbide series, where ring V is closed, the distortions[9] introduced into the system prevent intramolecular hydrogen bonding and two distinct N–H absorptions are always observed.[10]

Webb and Fleischer[11] suggested recently that the best description of the aromatic ring current in a porphyrin is one having a 16-membered inner ring, with the four β-pyrrole positions equivalent isolated double bonds. The electronic structure is usually represented as an 18-membered cyclic polyene with two of the β-pyrrole positions isolated from the aromatic system. Our results support the older structure having two distinct types of β-pyrrole positions. The lower field of these at δ 8.90 is the one normally assigned to the aromatic system..

Acknowledgments. We thank E. Sokoloski of the National Institutes of Health for the 100-MHz pmr spectra and the Petroleum Research Fund, administered by the American Chemical Society, and the National Institute of General Medical Sciences for financial support.

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Received November 1, 1971

Is the Concerted "Ene" Mechanism of the $^1\Delta_g$ Excited Oxygen Molecule Reactions with Olefins Really Eliminated? Photooxygenation and Electrolysis in the Presence of Azide Ions[1]

Sir:

Agreement exists that the mechanism of $^1\Delta_g$ O_2 reactions with cyclic 1,3-dienes is a concerted 1,4 addition of singlet oxygen to give endoperoxides.[2]

However, no such agreement exists with regard to the mechanism of $^1\Delta_g$ O_2 reactions with olefins that lead to allylic hydroperoxides. A cyclic cis process was established by stereochemical studies[3] and a large body of evidence has led to the suggestion that the cyclic process is concerted.[2a,c,4-9] In contrast, a two-step mechanism that involves formation of a dioxetane or perepoxide intermediate was postulated by Kearns, *et al.*,[10,11] from the fact that photooxygenation of olefins in the presence of azide ions gave the saturated azido hydroperoxides along with allylic hydroperoxides. They concluded that "these results completely rule out the concerted "ene" mechanism as a route to allylic hydroperoxides."[10,11] We have studied dye-sensitized photooxygenations of 2,3-dimethyl-2-butene (**1**) and α-terpinene (**6**) in the presence of sodium azide, as well as the electrolysis of NaN_3 in oxygen-saturated methanolic and aqueous methanolic solutions in the presence of **1** and **6**. Our results show that the interpretation by Kearns, *et al.*,[10,11] is not warranted.

Irradiation of 1.43 g of **1** in 170 ml of oxygen-saturated methanol, aqueous methanol, or water in the presence of Rose Bengal as described earlier[2b,5,6] gives the allylic hydroperoxide **2a** at rates $(r_{O_2}^0)$ that decrease with increasing water content of the solvent. In the presence of N_3^-, the rates of oxygen consumption (r_{O_2}) decrease with increasing N_3^- concentration up to about 0.1 M N_3^- (Figure 1). The irradiated solutions were reduced with aqueous sodium sulfite and the alcohols **2b** and **3b** were assayed and isolated by

2a, R = OH
b, R = H

3a, R = OH
b, R = H
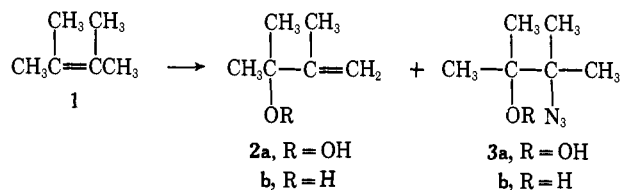
gas chromatography.[12] The production of the azido compound in methanol and in aqueous methanol begins at relatively high N_3^- concentrations where quenching of the oxygen uptake rate is already very appreciable (Figure 1). These results indicate that at least two different intermediates are involved that react with N_3^-. Furthermore, with increasing water content of the solvent, the amount of the azido alcohol **3b** that

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