

[9] $^1\text{H-NMR}$ see Table 1; $^{13}\text{C-NMR}$ (75.5 MHz, CDCl_3): $\delta = 32.14$ (C-2), 36.21 (C-3), 106.54 (C-20), 109.66 (C-9), 117.18 (C-19), 118.91 (C-10), 119.25 (C-16), 121.97 (C-13), 124.16 (C-7), 125.54 (C-6), 126.11 (C-12), 128.16 (C-17), 129.02, 131.18, 133.66, 134.03, 142.86, 144.00, 158.35, 166.84 (quaternary C); MS (70 eV): m/z 312 (M^+ , 100%), 311 ($M^+ - \text{H}$, 25), 156 (M^{2+} , 40); UV/VIS (benzene): $\lambda = 360$ nm ($\epsilon = 71400$), 382 (51700), 402 (74400), 532 (11300) sh, 548 (15300) sh, 560 (17100), 575 (23800), 595 (29900); IR (KBr): $\tilde{\nu} = 3095, 2921, 1558, 1350, 1213, 1169, 1038, 966, 898, 802$ cm^{-1} .

[10] E. Vogel, M. Balci, K. Pramod, P. Koch, J. Lex, O. Ermer, *Angew. Chem.* 99 (1987) 909; *Angew. Chem. Int. Ed. Engl.* 26 (1987) 928.

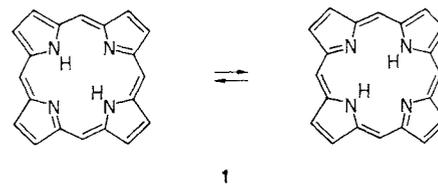
[11] $^1\text{H-NMR}$ (300 MHz, CDCl_3 , saturated solution, 20°C): $\delta = 9.81$ (9.62) [H-10,15], 8.99 (8.92) [H-5,20], 9.04 (9.03) [H-12,13], 9.20 (8.63) [H-8,17], 8.87 (8.52) [H-7,18], 4.74 (4.25) [H-2,3], -2.41 (-2.75) [N-H]. Values in parentheses taken from K. N. Solov'ev, V. A. Mashenkov, A. T. Gradyushko, A. E. Turkova, V. P. Lezina, *J. Appl. Spectrosc. USSR* 13 (1970) 1106 (see also: H. Scheer, J. J. Katz in K. M. Smith: *Porphyrins and Metalloporphyrins*, Elsevier, Amsterdam 1975, p. 442). The observed deviations might be due to differences in concentration.

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[13] **3**: m.p. $> 300^\circ\text{C}$, crystals from chloroform; monoclinic, space group $P2_1/c$, $Z = 4$; $a = 10.369(1)$, $b = 14.456(3)$, $c = 10.535(2)$ Å, $\beta = 102.91(1)^\circ$; $\rho_{\text{calc}} = 1.348$ g cm^{-3} ; intensities measured on a four-circle diffractometer [room temperature, $\lambda_{\text{Mo}} = 0.71069$ Å, $\theta_{\text{Mo}}(\text{max}) = 27^\circ$]; refinement (C, N anisotropic, H isotropic) including the 1403 reflections with $F_0 > 4\sigma(F_0)$; $R = 0.038$, $R_w = 0.042$. For the two inner H-atoms, four positions were refined with half-weights. Further details of the crystal structure investigation are available on request from the Fachinformationszentrum Energie, Physik, Mathematik GmbH, D-7514 Eggenstein-Leopoldshafen 2 (FRG), on quoting the depository number CSD-52593, the names of the authors, and the journal citation.

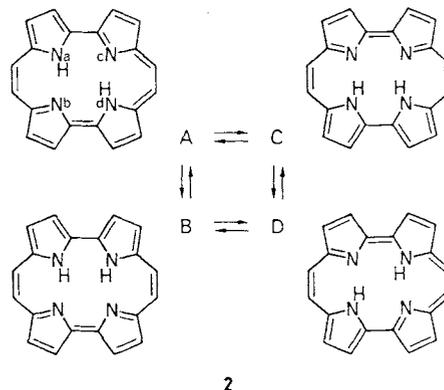
[14] The crystal structure of unsubstituted, metal-free chlorin **1** has hitherto not been described. In the crystals of a highly-substituted chlorin derivative (phytylchlorin ester) the partially hydrogenated pyrrole ring is not planar; this may be attributed in part to steric interactions of the substituents; W. Hoppe, G. Will, J. Gassmann, H. Weichselgartner, *Z. Kristallogr.* 128 (1969) 18.

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Scheme 1. Tautomerism of Porphine 1.

Whereas double minimum potentials have been found by dynamic NMR spectroscopy for dissolved^[3] and crystalline^[4,5] porphyrins the problem of tautomerism in crystalline porphine **1** has not yet been solved. Two X-ray structure analyses of **1**^[6,7] also indicate a double minimum potential but are contradictory with respect to the phenomenon of order or disorder of the inner hydrogen atoms.



Scheme 2. Tautomerism of Porphycene 2.

$^{15}\text{N-CPMAS-NMR}$ Study of the Problem of NH Tautomerism in Crystalline Porphine and Porphycene**

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In contrast to porphine **1** (Scheme 1) and many of its derivatives the novel porphine isomer porphycene **2**^[1] (Scheme 2) is distinguished by the presence of strong $\text{N-H}\cdots\text{N}$ hydrogen bonds and by an apparently extremely fast NH tautomerism, as indicated by the $^1\text{H-NMR}$ and IR spectra of **2**. This finding agrees with model considerations because the compound can obviously be formally classified with respect to the arrangement of the $\text{N-H}\cdots\text{N}$ groups and the short NN distances as a double seven-membered ring H-chelate.^[2] Similarly as in the case of such chelates it is also difficult to establish for **2** whether the inner H-atoms are located in a single minimum potential or whether they move along a double minimum potential. An X-ray structure analysis of **2** - although subject to some uncertainties with regard to the position of the H-atoms - indicates a multiple minimum potential.^[1]

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In view of the experimental^[3-8] and theoretical^[9] importance of NH tautomerism in the chemistry of porphyrins and related pyrrolic macrocycles we have now investigated the localization and transfer of the N-protons in **1** and **2** using variable-temperature high-resolution $^{15}\text{N-CPMAS-NMR}$ spectroscopy - which has already proven useful in the chemistry of macrocycles.^[4,5,10,11]

Figure 1 shows a superposition of the experimental and calculated 9.12-MHz $^{15}\text{N-CPMAS-NMR}$ spectra of ^{15}N -enriched^[13] **1** as a function of temperature. At low temperatures we observe a singlet at $\delta_{\text{NH}} = 107$ ppm for the imino and a singlet at $\delta_{\text{N}} = 215$ ppm for the azomethine nitrogen atoms.^[14] As the temperature is raised the signals broaden and coalesce into one sharp singlet at 161 ppm. From these findings it follows that the proton transfer is very fast at room temperature, but "frozen" at low temperatures. A nitrogen atom *m* involved in a fast tautomeric process gives rise to a line *m* in the $^{15}\text{N-NMR}$ spectra at the position

$$\delta_m = p_m \delta_{\text{NH}} + (1 - p_m) \delta_{\text{N}} \quad (a)$$

p_m is the average proton density on atom *m*. The observation of only one average line at $\delta = (\delta_{\text{NH}} + \delta_{\text{N}})/2$ means, therefore, that all nitrogen atoms in crystalline **1** are characterized within the margin of error by the same average proton density $p = 1/2$. This result contradicts the proposition of localized inner H-atoms,^[7] but supports a disordered structure with two tautomers of almost equal energy^[6] shown in Scheme 1. Such a symmetric situation is, however, the exception^[4,5,10] rather than the rule, and has

been observed so far only in the case of *meso*-tetratolylporphyrin (TTP).^[4,15] In the case of triclinic *meso*-tetraphenylporphyrin (TPP) it was found by ¹⁵N-CPMAS-NMR spectroscopy that the equilibrium in Scheme 1 was disturbed by crystal effects.^[4] By simulation of the experimental spectra (Fig. 1) in the temperature range between 200 and 350 K an energy of activation of 39 kJ mol⁻¹ and a frequency factor of 10¹¹ s⁻¹ were obtained for the exchange in Scheme 1. These values agree well with those found previously for dissolved TPP^[3] and crystalline TTP.^[4] It is still unclear as to whether the proton motion in **1** takes place along a synchronous pathway or along an asynchronous pathway via tautomers with protons on adjacent nitrogen atoms, and as to whether each inner proton migrates between only two or – as in solution^[3] – between all four nitrogen atoms.

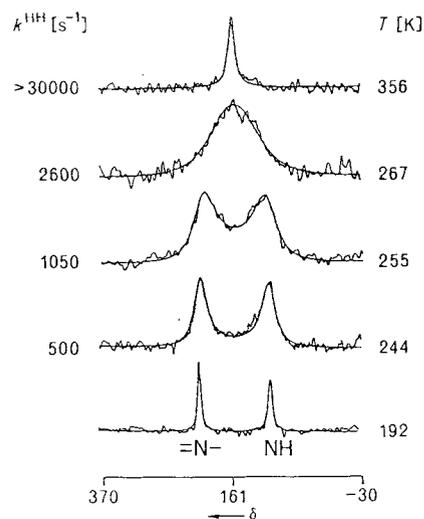
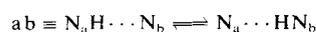


Fig. 1. Superposed experimental and calculated ¹⁵N-CPMAS-NMR spectra of 95% ¹⁵N-enriched porphine **1** at 9.12 MHz as a function of temperature. 3 to 6 ms CP-time, 7 kHz spectral width, 2.1 s repetition time. Reference: external ¹⁵NH₄Cl. The spectra were obtained with a Bruker CXP-100 NMR spectrometer equipped with a Doty-spinner [12] and a low temperature heat exchanger described previously [5]. k^{1H} is the rate constant of the tautomerism in a symmetric double-minimum potential. The additional simulation parameters, $W_0(N) = 57$ Hz and $W_0(NH) = 75$ Hz (halfwidth in absence of exchange) were taken from the low-temperature spectra.

A comparison of the ¹⁵N-CPMAS-NMR spectra of **2** (Fig. 2) at elevated temperatures with the spectra of **1** surprisingly reveals virtually no differences, i.e. at high temperatures a very fast proton transfer apparently takes place not only in **1** but also in **2**. However, in contrast to **1**, **2** does not show line-broadening as the temperature is lowered, i.e. no “freezing” of the proton motions, but a splitting into four sharp singlets a–d, which continuously drift away from each other with decreasing temperature. The upfield shift of line a (and of d) matches the downfield shift of line b (and of c). This observation proves the presence of two non-equivalent asymmetric proton transfer systems



and



in which the exchange is still fast with respect to the NMR time-scale even at 107 K. The shifts of the signals with de-

creasing temperature can be explained in terms of Equation (a) with an increasing proton density p_a on atom a at the expense of the proton density p_b on atom b. The same is true for the system dc, where, however, the effect is less pronounced. Since temperature-dependent proton densi-

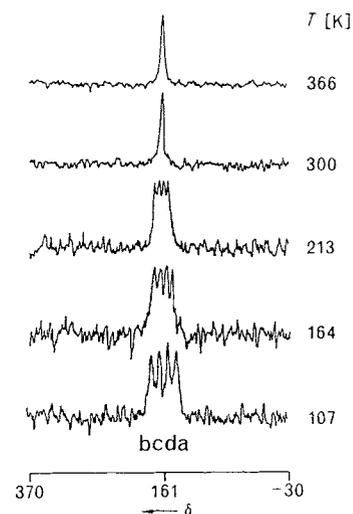


Fig. 2. ¹⁵N-CPMAS-NMR spectra of 95% ¹⁵N-enriched porphycene **2** at 9.12 MHz as a function of temperature. 6 ms CP-time, 5 kHz spectral width, 2.7 s repetition time. Reference: external ¹⁵NH₄Cl. Average number of scans: 1200. The low-temperature spectra were obtained with a pulse sequence for minimizing artifacts from long radiofrequency pulses [16] by which—as we find here—also acoustic ringing [17] is suppressed.

ties are characteristic for double- or multiple-minimum potentials one can, therefore, exclude the possibility of a single minimum potential for the inner hydrogen atoms of **2**. Note that in the case of a symmetric double minimum potential the proton densities are also independent of temperature, a fact which makes it very difficult in the case of symmetric molecules in the liquid state to distinguish between single- and multiple-minimum potentials by NMR. As shown here for **2**, this distinction is possible nowadays by CPMAS-NMR spectroscopic examination of the molecules in the solid state where symmetries are generally perturbed. In order to calculate values for K_{ab} and K_{dc} in terms of Equation (a) it is necessary to assume values of the unknown quantities δ_{NH} and δ_N . Since the high-temperature ¹⁵N-NMR line positions of **1** and **2** agree exactly one can take these values in approximation from **1**. Thus, we obtain from the temperature dependence of K_{ab} and K_{dc} for the tautomerism of crystalline **2** the very small reaction enthalpies $\Delta H_{ab} = 0.69$ kJ mol⁻¹ and $\Delta H_{dc} = 0.2$ kJ mol⁻¹, but no entropy differences, i.e. $\Delta S_{ab} \approx \Delta S_{dc} \approx 0$. It cannot be excluded that there are also small energy differences between the two tautomers in crystalline **1** which, however, cannot be observed because of severe dynamic line-broadening when the temperature is lowered.

For an assignment of the nitrogen lines a–d in Figure 2 to atom positions in the unit cell two possibilities are consistent with the NMR spectra: (i) there are two non-equivalent porphycene molecules in the crystal at low temperatures, each of which contains either two equivalent ab or dc proton transfer systems, i.e. has access to only two tautomeric states; (ii) all porphycene molecules in the crystal are equivalent, but each molecule contains both proton transfer systems ab and cd, i.e. exists in all of the four fast interconverting tautomeric states A to B shown in Scheme 2. In both cases the degeneracy of the two tautomers with a

transverse arrangement and of those with a vicinal arrangement of the inner protons is removed in the crystal due to intermolecular interactions.^[18] Since only one type of porphycene molecules is observed in the crystal at room temperature,^[11] there is a high probability that case (ii) is realized.^[19] If one further assumes that the state of lowest energy is characterized by a transverse arrangement of the inner hydrogen atoms one can, tentatively, assign the observed nitrogen lines to the atom positions shown in Scheme 2. The observation that $K_{ab} = p_b/p_a$ and $K_{dc} = p_c/p_d$ are different means that the proton motion in both proton transfer units is asynchronous. A similar situation has been found recently for a tetraaza[14]annulene derivative.^[10]

We conclude that the two inner H-atoms in crystalline porphine **1** move with measurable rates in a double minimum potential which is symmetric within the margins of experimental error. In the seven-membered ring H-chelate porphycene **2** an energy barrier exists between the four NH tautomers, which, however, is very small because of the short NH...N distances. The pairwise equivalence of the tautomers is destroyed due to crystal effects. In contrast to the case of **1**, the mutual interconversion of the tautomers is, therefore, so fast that it is no longer possible to measure rate constants for the proton motion by lineshape analysis of the ¹⁵N-CPMAS-NMR spectra.

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$$K_{ab} = K_{AC}(1 + K_{CD})/(1 + K_{AB}); \quad K_{dc} = K_{AB}(1 + K_{BD})/(1 + K_{AC}).$$

[19] A differentiation of both cases by two-dimensional spin diffusion experiments as in the case of 5,14-dihydro-6,8,15,17-tetramethyl-5,9,14,18-tetraazadibenzo[*a,h*]cyclotetradecene(tetramethylidibenzotetraaza[14]annulene) [10] will be attempted in a future study.

BOOK REVIEWS

Ostwalds Klassiker der exakten Wissenschaften 265. Jacobus Henricus van't Hoff: Studien zur chemischen Dynamik (Etudes de dynamique chimique) 1884. Translated by L. Dunsch. Akademische Verlagsgesellschaft Geest & Portig, Leipzig 1985. 236 pp., paperback, DM 31.00.—

In the report "Opportunities in Chemistry" (the Pimentel Report, a successor to the Westheimer Report), published recently in the USA, the first item in a list of the most important chemical research tasks suggested for intensive study in the rest of this century is: "Understanding chemical reactivity (... clarification of factors that control the rates of reactions ... to sustain international leadership for the US at the major fundamental frontier of chemis-

try)". The award of the Nobel Prize for Chemistry last year to D. Herschbach, Y. Lee and J. Polanyi for their work on the dynamics of chemical reactions underlines this view of the importance of reaction kinetics.

J. H. van't Hoff's "Etudes de dynamique chimique" was published in 1884. These studies of the dynamics of chemical processes are probably the first comprehensive account of reaction kinetics. It is a happy circumstance that this classic work has now been published again (for the first time in German), and it provides a good opportunity to look back on 100 years of growth in the quantitative understanding of chemical reactions, an understanding which, as indicated above, is still open to much further improvement.