where R is the gas constant and F the Faraday constant. The origin of the factor of 1/4 is the equation (b),

$$\frac{1}{2}O_{2,g} + 2e^{\ominus}_{M} \rightleftharpoons O^{2\ominus}_{\text{surface of metal oxide}} \qquad \text{(b)}$$

from which it can be seen that one electron equates with one quarter of an O_2 molecule.

Previous studies[8,9] of the thermoelectric power of the stabilized δ-phase of Bi_2O_3 in the system $Y_2O_3 \cdot Bi_2O_3$ show that the solid solutions are purely ionic, and plots of θ versus $\ln p_{O_2}$ do indeed have the expected slope $1/4(R/F)$ with θ itself being essentially temperature dependent. We find that the thermoelectric power of the δ-phase of pure Bi_2O_3 exhibits ionic behaviour for $p_{O_2} > 2 \times 10^{-3}$ atm, but not so at lower pressures.

In the present study, samples of $Nb_2O_5 : Bi_2O_3$ (1:60) were prepared as pressed pellets (ca. 1 mm thick, 13 mm diameter) by mixing the pure component oxides and sintering in air at 1023 K for prolonged periods. Gold foil sheets (0.01 mm thick) were pressed onto the faces of a sample and the sandwich so formed was placed between the platinum electrodes of a conductivity cell. The temperature at each face was determined by Pt-Pt/13% Rh thermocouples spot welded to each electrode. The thermocouple EMF at each electrode was monitored with a digital voltmeter and the voltage across the sample was measured with a high impedence electrometer.[10] The pressure of air in the cell could be varied from 10^{-8} to 1 atm. The sign convention used is that θ is positive if the polarity of the hotter electrode is positive. Initial experiments showed that ΔV versus ΔT plots passed through the origin so that rapid measurements of θ could be determined from a single value of ΔT. Additional measurements of conductivity were taken using AC techniques. The sample was annealed in the cell at 1000 K for ca. 12 h to ensure a good electrical contact between it and the electrodes.

The conductivity measurements showed a transition at 900 K, decreasing by two orders of magnitude with decreasing temperature, which indicates the change from high temperature δ-phase to low temperature β-phase. The transition was very slow when the sample was held a few degrees above or below 900 K and it took several hours for the conductivity to reach a constant value.

The plot of θ versus $\ln p_{air}$ for a sample in the δ-phase at 1033 K (Fig. 2) is very similar to that observed for pure Bi_2O_3 showing a slope of $1/4(R/F)$ at high p_{air}, suggesting predominantly ionic conduction. The plot reverses slope at low p_{air}. With the β-phase, however, the results were very unusual. A typical plot for θ versus in $\ln p_{air}$ is shown in Figure 2 for a sample at 768 K. The slope is $4.7(R/F)$ and the results were reversible and characterized by a rapid response (the voltage settles after a few seconds on cycling p_{air}). Similar results were observed down to 573 K.

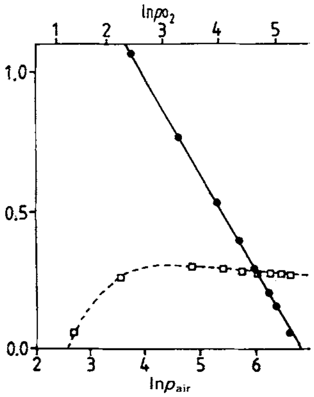

Fig. 2. The dependence of the thermoelectric power θ on air pressure p [torr] for $Nb_2O_5 : Bi_2O_3$ (1:60). Empty squares: δ-phase at 1033 K; filled circles: β-phase at 768 K.

We do not know the origin of the observed dependence of θ on $\ln p_{air}$ in the β-phase. The exponent of 4.7 is too large to be explained on the basis of any simple reaction involving gaseous O_2 and defects. The phenomenon is presumably associated with the generation of electronic carriers either within the sample or at the sample-electrode interfaces.

Although the origin of the observations for the β-phase is at present unclear, the magnitude, speed and reproducibility of the changes in thermoelectric power with varying p_{air} points to potential application in oxygen monitoring. The enhanced response of $Nb_2O_5 : Bi_2O_3$ solid solutions make them attractive materials as oxygen sensors, and worthy of future investigation.

Received: July 4, 1988 [Z 2845 IE]
German version: *Angew. Chem. 101* (1989) 69

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Investigation of the Tautomerism of ^{15}N-Labeled Hydroporphyrins by Dynamic NMR Spectroscopy[**]

By *Martin Schlabach*, *Helmut Rumpel*, and *Hans-Heinrich Limbach*[*]

The problem of the mechanism of the thermal- and light-induced tautomerism of porphyrin, P (Fig. 1, top left) and its derivatives is of current interest.[1-10] Information about the different reaction pathways shown in Figure 1 (top left) has mainly been obtained from dynamic NMR studies of kinetic HH/HD/DD isotope effects[4,5] and of solid state effects,[8] as well as from theoretical studies.[10] Unfortunately, it has not yet been possible so far to significantly increase or decrease the reaction barrier by variation of the chemical structure,[2,5,7] a technique which

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[**] This work was supported by the Deutsche Forschungsgemeinschaft, the Stiftung Volkswagenwerk and the Fonds der Chemischen Industrie. We thank Prof. Dr. *H. Fritz* for time on the Bruker AM400 NMR spectrometer of Ciba-Geigy AG, Basel, Switzerland.

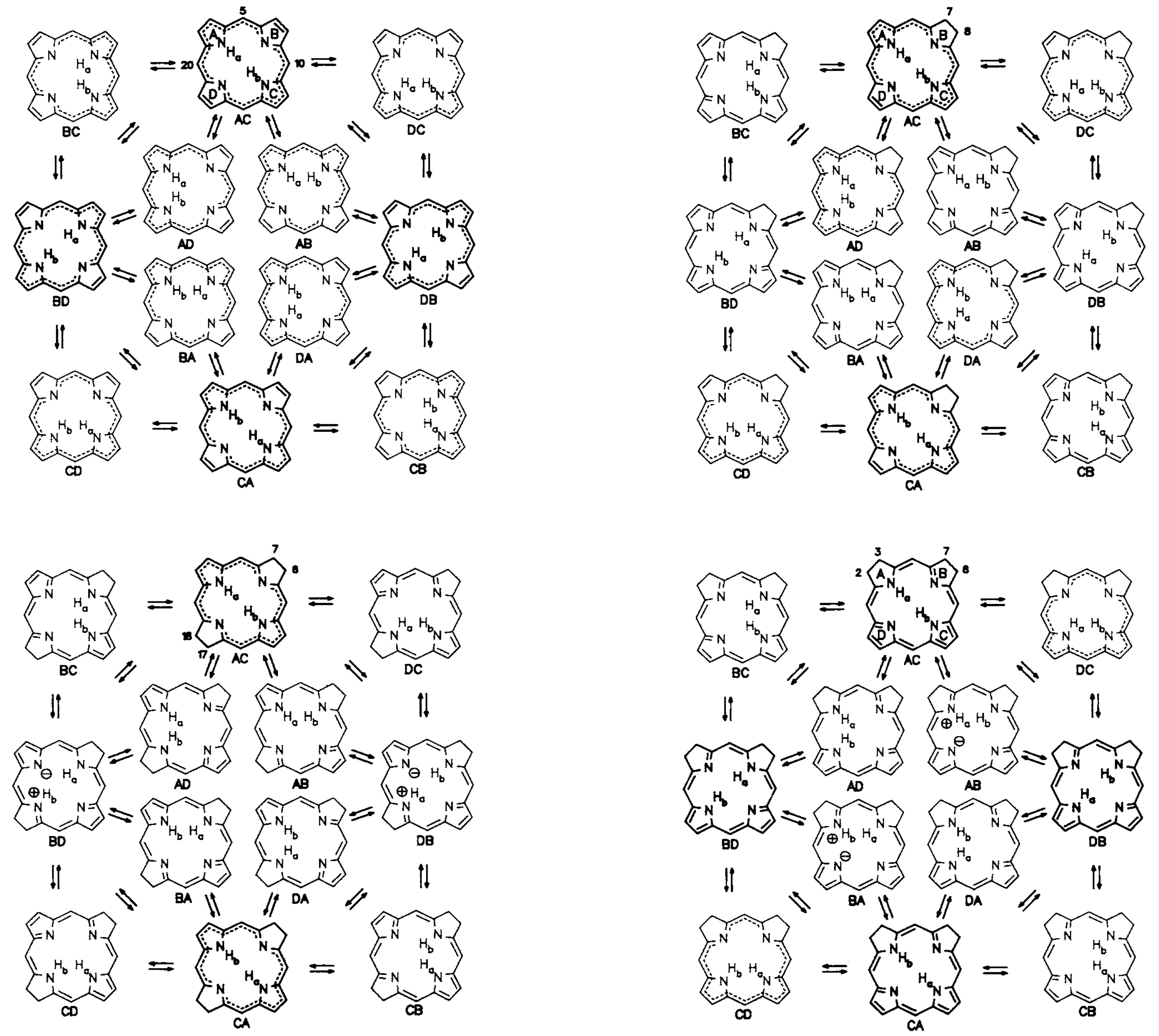

Fig. 1. Proton transfer pathways in the parent compounds porphyrin (formerly porphine [27]) (top left), chlorin (top right), bacteriochlorin (bottom left), and isobacteriochlorin (bottom right). The different pyrrole rings are labeled clockwise with the capital letters A to D. The nitrogen atoms in these rings are labeled as N-21, N-22, N-23 and N-24. The various tautomers are represented here, in a way similar to that proposed in [18], by the pairs XY, with X, Y = A-D. X refers to the pyrrole ring on which the inner proton H$_a$ is located and Y characterizes the location of H$_b$. All tautomers XY and YX are degenerate with exception of the case where one proton is substituted by deuterium. Tautomeric structures which have been spectroscopically assigned are boldfaced. The dashed lines indicate, as usual, "aromatic" 18 π electron delocalization pathways [3, 7]. Only one zwitterionic structure is shown for the tautomers BD and DB and for AB and BA in Figures 1c and 1d.

usually provides interesting insights into reaction mechanisms. We show here that this goal can be achieved by specific hydrogenation of the pyrrole rings of porphyrins, which leads to the biologically important hydroporphyrins chlorin, C (Fig. 1, top right), bacteriochlorin, Bc (Fig. 1, bottom left) and isobacteriochlorin, iBc (Fig. 1, bottom right).[11-22] Although some evidence for tautomerism[1a] and phototautomerism[21] of chlorins, and for phototautomerism of isobacteriochlorins[22] has been reported, the proton transfer processes occurring in these compounds have not yet been characterized. The different reaction dynamics of hydroporphyrins observed here can be explained by the gain or loss of aromatic resonance energy during the different reaction steps shown in Figures 1. In particular, we have performed ^{1}H NMR line shape analyses of the ^{15}N-labeled hydroporphyrins TPC,[23] TPBc,[24] and TPiBc[25] dissolved in organic solvents.

The ^{1}H NMR spectra of TPC in $C_2D_2Cl_4$ contain only one signal at $\delta \approx -1.5$ ppm for the two inner protons H$_a$ and H$_b$. This δ-value signifies that TPC experiences an aromatic, porphyrin-type ring current.[28] As shown in Figure 2, the signal is split at room temperature into a ^{1}H-^{15}N doublet. These results are consistent only with the presence of the two degenerate tautomers AC and CA which exchange slowly at room temperature within the NMR timescale. For the case of fast exchange, the signal should exhibit a triplet structure as found for other $^{15}\mathrm{NH}\cdots{}^{15}\mathrm{N} \rightleftharpoons {}^{15}\mathrm{N}\cdots\mathrm{H}^{15}\mathrm{N}$ proton transfer systems.[4,29] In fact, a doublet→triplet interconversion is observed at elevated temperatures (Fig. 2, top).[30] The rate constants were obtained by line shape analysis [Eq. (a)].[31]

$$k_{\mathrm{AC}\rightarrow\mathrm{CA}} \cong 10^{11.8}\exp(-61.3\ \mathrm{kJ\,mol^{-1}}/RT) \qquad \text{(a)}$$

Thus, the energy of activation of the tautomerism increases to about 20 kJ mol^{-1} upon hydrogenation of one

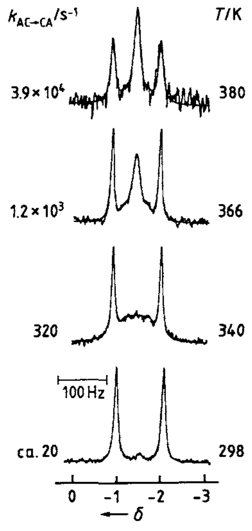

Fig. 2. Superposed experimental and simulated 90.02 MHz ^1H NMR spectra of 95% ^{15}N-enriched TPC [23], dissolved in $C_2D_2Cl_4$, as a function of temperature T. 4 μs π/2 pulses, 2 kHz spectral width, 2.1 s repetition time, 2000 scans on average.

pyrrole ring of porphyrin, an effect which can be explained by the loss of the aromatic resonance energy during the course of the reaction AC→CA.

The ^1H-^{15}N doublet of the inner protons of TPBc dissolved in [D$_8$]toluene appears at $\delta \approx -1.25$ ppm. Thus, this compound also experiences a porphyrin-type ring current. This finding confirms the model of the aromatic electron delocalization pathways[3,7] indicated in Figure 1 by dashed lines. In contrast to TPC, however, the TPBc ^1H-^{15}N doublet does not show any sign of conversion into a triplet even at 140°C. Thus, the process AC→CA must be much slower in TPBc than in TPC. This is understandable because not only is aromatic resonance energy lost during the interconversion AC→CA (Fig. 1, bottom left), there is also the additional energy required for charge separation, when the formally zwitterionic intermediates BD and DB are formed.

The greatest surprise is, however, provided by the temperature dependent signals of the inner protons of TPiBc, shown in Figure 3. At −100°C, two exchange broadened ^1H-^{15}N doublets[32] of equal intensity are observed at $\delta = 4.6$ and 6.1. This low-field shift of the inner proton signals indicates that the porphyrin-type ring current is largely suppressed in TPiBc.[28] The observation that H_a and H_b are inequivalent[33] can only be explained by the presence of the degenerate non-aromatic *trans*-forms AC, DB, CA and BD (Fig. 1, bottom left). As the temperature is raised, however, coalescence of the H_a and H_b doublets into a single exchange-broadened triplet is observed (Fig. 3, middle). These signal changes are expected for the processes AC→DB (and CA→BD). The processes AC→BD (and CA→DB) would not render H_a and H_b equivalent but would lead to two ^1H-^{15}N triplets at $\delta = 4.6$ and 6.1. It is, however, surprising that the latter processes are not completely suppressed but lead at higher temperatures to a triplet→quintet interconversion of the ^1H-^{15}N signal (Fig. 3, top). The rate constants were obtained by line shape analysis [Eqs. (b) and (c)].[34]

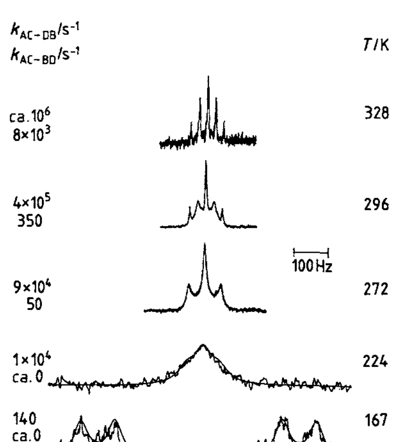

Fig. 3. Superposed experimental and simulated 400.12MHz ^1H NMR spectra of 95% ^{15}N-enriched TPiBc [25], dissolved in [D$_8$]toluene, as a function of temperature T. 3 μs π/2 pulses, 7 kHz spectral width, 2.1 s repetition time, 8000 scans on average.

$$k_{AC\to DB} \cong 10^{10.3}\exp(-27\,\mathrm{kJ\,mol^{-1}}/RT) \qquad \text{(b)}$$

$$k_{AC\to BD} \cong 10^{11.1}\exp(-49.2\,\mathrm{kJ\,mol^{-1}}/RT) \qquad \text{(c)}$$

^1H NMR spectra of deuterated and partly deuterated TPiBc showed that both processes are affected by major kinetic HH/HD/DD isotope effects. In addition, preliminary experiments using the ^{15}N CP/MAS NMR technique[8a–f] indicate that the process AC→DB also takes place in the solid state. These results establish TPiBc as the first intramolecular proton transfer system characterized by two symmetric double minimum potentials of unequal height.

The finding that in TPiBc the process AC→DB is much faster than the process AC→BD could perhaps be explained in terms of weak hydrogen bonds between the rings A and D and between C and B although there is no evidence at present for such phenomena in this class of compounds.[12,15,16] The assumption of a step-wise rather than a concerted reaction mechanism provides, however, a more plausible explanation of the experimental results. According to Figure 1 (bottom right), one expects the process AC→DC in TPiBc to be assisted by a considerable gain of resonance energy in the two transition states separating the aromatic *cis*-intermediate DC from the non-aromatic *trans*-tautomers AC and DB. Such a stabilization is neither expected for pathway AC→BD nor for the concerted proton transfer steps. Further experimental and theoretical studies are, however, necessary in order to confirm the first experimental indications for a stepwise reaction mechanism for the tautomerism of porphyrins obtained in this work.

Received: August 2, 1988 [Z 2898 IE]
German version: *Angew. Chem. 101* (1989) 84

CAS Registry Numbers:
TPC, 118070-81-8; TPBc, 118102-31-1; TPiBc, 118102-32-2; TPP, 71771-09-0.

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[23] TPC (= 5,10,15,20-tetraphenyl[$^{15}N_4$]chlorin = 5,10,15,20-tetraphenyl-[$^{15}N_4$]-7,8-dihydroporphyrin) was prepared, in a similar way as described in [11] for the unlabeled material, from TPP (= 5,10,15,20-tetraphenyl[$^{15}N_4$]porphyrin); TPP was prepared according to [26], [^{15}N]pyrrole synthesized as described in [8d]. Note that the name 5,10,15,20-tetraphenyl[$^{15}N_4$]-2,3-dihydroporphyrin proposed in the IUPAC recommentations [27] is not consistent with the findings of this study. The ^{15}N labeling of all compounds in this study was performed in order to obtain reliable results which are not affected by intermolecular proton exchange and ^{14}N quadrupole relaxation.

[24] TPBc (= 5,10,15,20-tetraphenyl[$^{15}N_4$]bacteriochlorin) was prepared, in a way similar to that described in [11] for the unlabeled material, from TPP.

[25] TPiBc (= 5,10,15,20-tetraphenyl[$^{15}N_4$]isobacteriochlorin) was prepared, in a way similar to that described in [11] for the unlabeled material, from TPP.

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[30] Intermolecular proton transfer would lead to breakdown of the ^{1}H-^{15}N splitting pattern [29].

[31] The activation parameters were obtained from a total of 16 spectra of TPC in $C_2D_2Cl_4$ and [D_8]toluene in the temperature range 298 to 406 K; no solvent effects were observed.

[32] In monodeuterated TPiBc, these signals are sharp at −100°C due to a kinetic HH/HD isotope effect which indicates that the broadening in the bottom spectrum of Figure 3 stems from proton transfer and not from slow rotational diffusion [6].

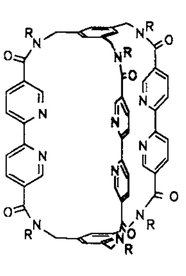
[33] We tentatively assign the signal at $\delta = 4.6$ to H-21 and the signal at $\delta = 6.1$ to H-23. For the atomic numbering scheme see legend to Figure 1.

[34] $k_{AC \rightarrow DB}$ was obtained from 7 spectra between 170 and 280 K, $k_{AC \rightarrow BD}$ from 4 spectra between 270 and 320 K. Note that the line shape of the outer proton signals, which are not shown here, is sensitive only to the process AC→DB and not to the process AC→BD.

Selective Molecular Recognition of Trihydroxybenzenes[**]

By *Frank Ebmeyer* and *Fritz Vögtle*[*]

The complexation of organic molecules in nonaqueous media is currently being intensively investigated.[1] We report here on the synthesis and complexation properties of the macrobicyclic compounds **2**–**4**,[2] which exhibit a remarkable selectivity for phenolic substrates, in particular trihydroxybenzenes. Although the bipyridine ligand **1**, synthesized in 1986, strongly complexes small metal cations,[3] it does not bind organic molecules. The successive expansion of the host cavity with the C_3-symmetric spacers introduced by us[4] leads to the new complex-forming molecules **2**–**4** having larger cavities.



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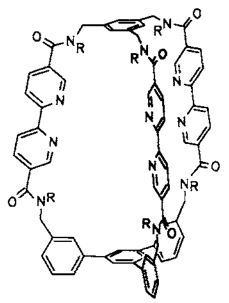

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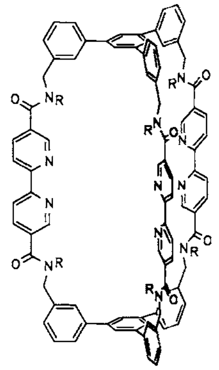

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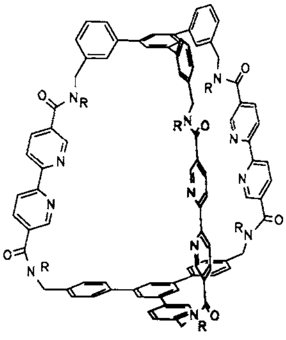

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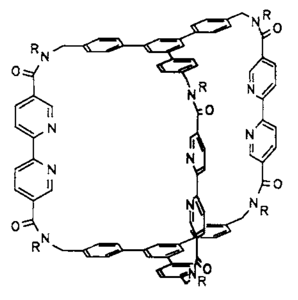

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R = Benzyl

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[**] This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie and by Bayer AG, Leverkusen, BASF AG, Ludwigshafen, Hoechst AG, Frankfurt, and Degussa AG, Hanau (donation of chemicals). *F. E.* thanks the Stiftung Volkswagenwerk for a Kekulé Stipendium. We thank Dr. *J. Peter-Katalinić* (Physiologisch-chemisches Institut der Universität Bonn) and Finnigan/MAT (Bremen) for FAB mass spectra, Dr. *G. Eckhart* and *C. Schmidt* for EI mass spectra and NMR spectra, respectively, Dipl.-Chem. *Ch. Seel* for the drawings, and Mrs. *A. Bail* for assistance.