

# Kinetic Study of Hydrogen Tunnelling in *meso*-Tetraphenylporphine by Nuclear Magnetic Resonance Lineshape Analysis and Selective $T_{1\rho}$ -Relaxation Time Measurements

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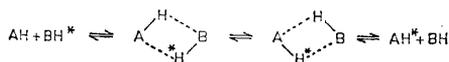
The kinetics of the hydrogen migration between the degenerate tautomers of *meso*-tetraphenylporphine ( $[^1\text{H}_2]\text{TPP}$ ) and of the deuterated species ( $[^2\text{H}_2]\text{TPP}$ ) both dissolved in various media has been studied over a wide range of temperatures by n.m.r.-lineshape analysis and by measurements of the longitudinal relaxation times in the rotating frame,  $T_{1\rho}$ , of selective lines. As proven by the  $^1\text{H}$ -n.m.r.-spectra of  $[^1\text{H}_2\text{-}^{15}\text{N}_4]\text{TPP}$ , the rate constants obtained are entirely due to a random walk of the inner hydrogen atoms between the four nitrogen atoms, and not to intermolecular proton transfer. In the slow exchange range a doublet splitting of the inner proton signal shows that each proton is coupled with one  $^{15}\text{N}$ -spin with a coupling constant of  $J_{^{15}\text{N}-\text{H}} = 101$  Hz. However, in the fast exchange range a pentet splitting is observed with a line distance of  $J_{^{15}\text{N}-\text{H}}/4$ . Consequently, in the slow exchange range, within the n.m.r.-timescale, each proton is localized at a single nitrogen atom. In the fast exchange range, within the n.m.r.-timescale, the inner protons are localised with equal probability at each of the four nitrogen atoms due to rapid random walk. The rate constants do not depend on the type of the solvent used. Their dependence on the temperature is given by

$$k^{\text{H}} = 5.0 \pm 0.5 + \exp(26.5 \pm 1) \exp(-43.4 \pm 1.3) \text{ kJ mol}^{-1}/RT, \quad 160 \leq T \leq 323 \text{ K},$$

$$k^{\text{D}} = \exp(29.7 \pm 0.7) \exp(-57.3 \pm 1.3) \text{ kJ mol}^{-1}/RT, \quad 213 \leq T \leq 305 \text{ K}.$$

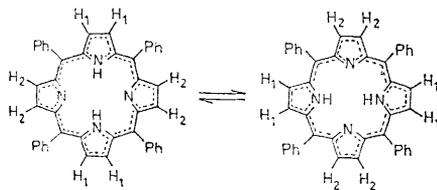
The results cannot be explained in terms of the transition state theory, but only in terms of a vibrational model of tunnelling in a symmetric double minimum potential with quantized vibrational levels along the reaction coordinate. The rate constants are related to the tunnel splittings of barrier-separated degenerate states. The hydrogen motion proceeds by tunnelling between the ground states and the first excited vibrational NH-stretching states, the deuterium motion between the second excited ND-stretching states. It is probable that hydrogen tunnelling in TPP is a synchronous process like hydrogen tunnelling during the inversion of ammonia.

Though there has been much theoretical interest in the mechanisms of coupled proton motion in cyclic hydrogen bonded systems,<sup>1-4</sup> there is little evidence for cyclic exchange mechanisms<sup>5-8</sup> in which two or more protons are transferred during one encounter of the reactants (scheme I). This is mainly due to the experimental difficulties of preparing samples free from impurities which catalyse the proton exchange. Another difficulty that arises if one wants to study coupled proton motion is the short lifetime of cyclic hydrogen bonded intermediates.



Scheme I

The rearrangement of degenerate porphine tautomers such as *meso*-tetraphenylporphine (TPP) is an excellent model for the study of cyclic proton exchange because the "reactants" are held together by the aromatic porphine skeleton (scheme II). The central protons are localised on opposite and not on adjacent nitrogen atoms, as X-ray studies of the trigonal free base porphine<sup>9</sup> and of trigonal TPP<sup>10</sup> reveal.



Scheme II

No tautomerism is observed in these modifications, which indicates that the degeneracy of the tautomers is lifted by the crystal field. By contrast, in the tetragonal forms of porphine<sup>11</sup> and of TPP<sup>12</sup> the protons are randomly distributed among the four nitrogen atoms. The X-ray studies show that the porphine skeletons are planar and that they have almost  $D_{4h}$ -symmetry. The NH...HN arrangement is linear if one neglects slight deflections of the protons from the aromatic plane. This is also supported by Raman-studies of TPP in solution<sup>13</sup> and by *ab initio* calculations of porphine.<sup>14</sup> According to these calculations, there is no preferential hydrogen bonding of the inner protons to either of the adjacent nitrogen atoms. As in the triclinic modification, only one tautomer of TPP is found in foils of polyvinylchloride or isotactic polystyrene<sup>15</sup> at room temperature. By contrast, two non-degenerate tautomers of porphine with NH...HN axes at right angles exist at liquid helium temperature in an *n*-octane Shpol'ski matrix, as shown by fluorescence-<sup>16</sup> and e.s.r.-spectroscopy.<sup>17</sup> The tautomers can interconvert only by photoisomerisation.<sup>18</sup>

In solution TPP shows an entirely different behaviour. The tautomers are degenerate and interconvert rapidly. Storm and Teklu<sup>19</sup> have shown that the rate constants of the tautomeric process can be measured by <sup>1</sup>H-n.m.r.-lineshape analysis. At low temperatures two signals are produced by the aromatic protons H-1 and H-2 (scheme II), which broaden and coalesce with rising temperature. Substitution of the inner protons by deuterons slowed the exchange rates substantially. Similar lineshape effects were also found by Abraham *et al.*<sup>20</sup> in the <sup>13</sup>C-n.m.r.-spectra, and by Gust *et al.*<sup>21</sup> in the <sup>15</sup>N-n.m.r.-spectra of TPP. The following activation parameters for the tautomerism were published by Abraham *et al.*:<sup>22</sup>

$$E_a^H = 38.5 \text{ kJ mol}^{-1}, \Delta S^{*H}(298 \text{ K}) = -42 \text{ J K}^{-1} \text{ mol}^{-1},$$

$$E_a^D = 45.2 \text{ kJ mol}^{-1}, \Delta S^{*D}(298 \text{ K}) = -42 \text{ J K}^{-1} \text{ mol}^{-1}.$$

Very similar parameters were obtained by Eaton and Eaton<sup>23</sup> for the tautomerism in a series of *p*-phenyl substituted TPPs. No significant correlation was found between the type of substituents and the reaction rate constants.

A deficiency of the former studies is that possible intermolecular mechanisms of the tautomeric exchange which can affect the measured rate constants have not been taken into account. This is necessary since it has been shown by Abraham *et al.*<sup>24</sup> that the dication of TPP is formed in the presence of proton donors such as carboxylic acids. It should be remembered that in the studies cited deuterium was incorporated into TPP by adding [<sup>2</sup>H<sub>1</sub>]methanol or D<sub>2</sub>O to the n.m.r.-samples. In order to maintain identical conditions methanol was added, therefore, to the [<sup>1</sup>H<sub>2</sub>]TPP samples

too. If one considers the association of porphines in solution,<sup>25</sup> intermolecular proton exchange between different TPP-molecules cannot be excluded *a priori* either.

It has been argued<sup>19, 23</sup> that a synchronous proton motion implies the loss of the zero point energies of two NH-stretching vibrations in the symmetrical transition state, which would explain the enhanced kinetic isotope effect found in this reaction. Yet, Bell and Critchlow<sup>6</sup> have pointed out that in synchronous proton transfer only one normal mode is converted into the reaction coordinate. The zero point energy of the other mode is retained more or less in the transition state, which produces normal kinetic isotope effects.

The possibility of explaining the high isotope effect by the mechanism of tunnelling<sup>26</sup> was either not discussed,<sup>19, 22</sup> or rejected,<sup>23</sup> because, first, the Arrhenius curves were found to be linear and, secondly, the frequency factors of the hydrogen and the deuterium migration were not significantly different. However, the range of temperatures for which rate constants were obtained was not wide enough to prove the absence of tunnelling.

A detailed study of the exchange kinetics and an answer to the following questions, which are of great importance for the understanding of cyclic proton motions, are, therefore, still lacking. (1) Can it be proved that the tautomeric process observed in TPP is entirely intramolecular, or are the rate constants affected by intermolecular proton transfer? (2) Is the proton motion accompanied by a rearrangement of the porphine skeleton? (3) Does the transition state theory apply, or do the protons tunnel through the potential wall? (4) Do the protons move simultaneously or in succession? By a combination of the n.m.r.-lineshape analysis and the measurement of the longitudinal relaxation time in the rotating frame,  $T_{1\rho}$ , of selective n.m.r.-signals—which overcomes the uncertainties of the rate determination in the fast and in the slow exchange range—and using an improved sample preparation technique, we have been able to determine new rate constants for the tautomerism of TPP for a wide range of temperatures and solvents.

## EXPERIMENTAL

### PREPARATION OF SAMPLES

[<sup>14</sup>N<sub>4</sub>]TPP and [<sup>15</sup>N<sub>4</sub>]TPP was synthesized<sup>27</sup> from benzaldehyde and [<sup>14</sup>N<sub>1</sub>]pyrrole or [<sup>15</sup>N<sub>1</sub>]pyrrole (CIS, Orsay, France). [<sup>2</sup>H<sub>8</sub>]Tetrahydrofuran ([<sup>2</sup>H<sub>8</sub>]THF) and [<sup>2</sup>H<sub>8</sub>]toluene (Sharp & Dohme, Munich) were dried over anthracene-potassium, and [<sup>2</sup>H<sub>1</sub>]chloroform over alumina (Woelm, Eschwege). [<sup>2</sup>H<sub>2</sub>]TPP was prepared as follows: the solvent and [<sup>2</sup>H<sub>1</sub>]ethanol, previously dried over molecular sieve (Merck, 3 Å), were condensed on solid [<sup>1</sup>H<sub>2</sub>]TPP, which then dissolved. After evaporation the process was repeated several times. The n.m.r.-samples were prepared by condensing the solvent on solid TPP and by filtering the solution through a frit into the n.m.r.-tube which was then sealed off afterwards. All operations, including the preparation of [<sup>2</sup>H<sub>2</sub>]TPP, were carried out *in vacuo* using a whole glass apparatus, in order to exclude air and moisture that might cause catalytic proton transfer reactions. That glassware which came into contact with gaseous or liquid [<sup>2</sup>H<sub>1</sub>]chloroform was darkened with a diffusion colour in order to prevent the photochemical formation of hydrogen chloride.<sup>28</sup> The usual standard tetramethylsilane was added to the solvents before drying (1-2 vol. %).

### LINESHAPE STUDIES

The <sup>1</sup>H-n.m.r.-spectra were measured using a Varian HA-100 spectrometer equipped with a time averaging computer C-1024. The rate constants were obtained by adapting the theoretical lineshape calculated using McConnell's formalism<sup>29</sup> to the digitalized experimental spectra. Fig. 1 illustrates some typical experimental and calculated lineshapes of

the H-1/H-2 signal of TPP in  $[^2\text{H}_8]\text{toluene}$ . The static line width,  $W_0$ , of liquid samples is the sum of the natural line width,  $W_{\text{nat}}$ , and the inhomogeneity,  $\Delta H_0$ , of the magnetic field,  $H_0$ :

$$W_0 = W_{\text{nat}} + \gamma \Delta H_0 / 2, \quad (1a)$$

where

$$W_{\text{nat}} = (\pi T_2^2)^{-1} = (\pi T_1)^{-1}. \quad (1b)$$

The longitudinal relaxation time,  $T_1$  and the intrinsic transverse relaxation time,  $T_2^2$ , are equal for liquids under the condition of motional narrowing.  $\gamma$  is the gyromagnetic ratio.  $W_0$  was obtained as a function of the temperature by the interpolation of the line widths of the H-1/H-2 signal of  $[^2\text{H}_2]\text{TPP}$  at very low and at high temperatures, where the signals do not contain any exchange broadening. As will be shown below,  $W_0$  cannot be determined from the lineshape of the H-1/H-2 signals of  $[^1\text{H}_2]\text{TPP}$  in the slow exchange range since these signals contain an exchange broadening of about 1.6 to 1.8 Hz even at low temperatures. The signal of H-1 in  $[^1\text{H}_2]\text{TPP}$  contains an additional static broadening of 0.5 Hz due to an unresolved coupling with the central protons;<sup>19</sup> this broadening has been taken into account in the calculations. The chemical shifts,  $\nu_1$  and  $\nu_2$ , of H-1 and H-2, show a weak linear dependence on the temperature. The values established for the slow exchange range were extrapolated to the fast exchange range.

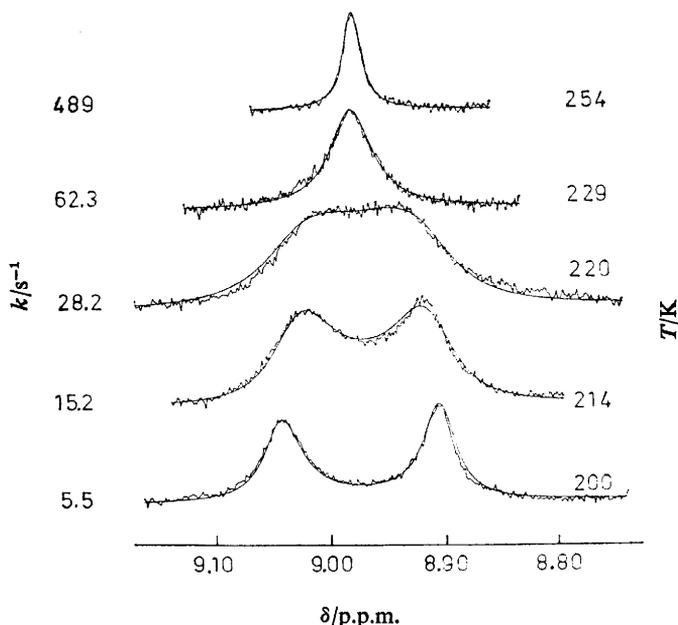


FIG. 1.—Experimental and calculated lineshapes of the  $^1\text{H}$ -n.m.r.-signal of the H-1/H-2 protons of  $[^1\text{H}_2]\text{TPP}$  (see scheme II) at 100 MHz in  $[^2\text{H}_8]\text{toluene}$ .  $k$  is the calculated rate constant.

The lineshape of the signal of the inner protons in  $[^{15}\text{N}_4]\text{TPP}$  was calculated as a function of the rate constant,  $k_{\text{intra}}$ , of the intramolecular hydrogen migration using the formalism of Kubo<sup>30</sup> and Sack.<sup>31</sup> This formalism could be applied since the  $^{15}\text{N}_4\text{H}_2$ -spin system was found to be of first order. The lineshape equation is then the sum of six terms corresponding to six four-site problems. Each site corresponds to a four-spin product function,  $|\gamma(1)\gamma(2)\gamma(3)\gamma(4)\rangle$ , of the  $^{15}\text{N}_4$  group. The sites interconvert by permutations of the spins in these functions:

$$\mathbf{P}|\gamma(1)\gamma(2)\gamma(3)\gamma(4)\rangle = \frac{1}{2}|(4)\gamma(1)\gamma(2)\gamma(3)\rangle + \frac{1}{2}|\gamma(2)\gamma(3)\gamma(4)\gamma(1)\rangle.$$

The first spin,  $\alpha$  or  $\beta$ , determines the frequency of the site,  $+J^{15\text{N-H}}/2$  or  $-J^{15\text{N-H}}/2$ . The Kubo-Sack matrices are easily constructed according to the rules given by Johnson *et al.*<sup>32</sup> For example, the matrix of the spin system which contains one  $\alpha$ - and three  $\beta$ -spins reads:

$$A = \begin{pmatrix} \alpha\beta\beta\beta & \beta\beta\beta\alpha & \beta\beta\alpha\beta & \beta\alpha\beta\beta \\ -k - \pi W_0 + i\pi J & k/2 & 0 & k/2 \\ k/2 & -k - \pi W_0 - i\pi J & k/2 & 0 \\ 0 & k/2 & -k - \pi W_0 - i\pi J & k/2 \\ k/2 & 0 & k/2 & -k - \pi W_0 - i\pi J \end{pmatrix}$$

The lineshape of the species  $[^1\text{H}_2\text{-}^{14}\text{N}_1\text{-}^{15}\text{N}_3]\text{TPP}$  present in a mole fraction of 8% was calculated in a similar way and superimposed on the spectrum of the mean species, taking the frequency of the sites with  $\gamma(1) = \gamma(^{14}\text{N})$  as zero.

Rate constants from  $^{14}\text{C}$ -spectra were determined as in ref. (22).

#### SELECTIVE $T_{1\rho}$ -RELAXATION TIME MEASUREMENTS

The measurement of the longitudinal relaxation time,  $T_{1\rho}$ , in the rotating frame<sup>33</sup> provides essentially the same information on the rate constants of an exchanging system as does the spin-echo technique.<sup>33</sup> The advantage of the  $T_{1\rho}$ -method is that it can be applied to systems whose n.m.r.-spectra consist of more than one line if a F.T.-n.m.r.-pulse spectrometer is used.<sup>34</sup> In the  $T_{1\rho}$ -experiment the magnetisation is converted into the transverse plane by a  $90^\circ$ -pulse. Immediately afterwards a second pulse is applied with a phase shift of  $90^\circ$ . This pulse corresponds to a rotating magnetic field,  $H_1$ , which is static and collinear to the transverse magnetisation,  $M_y$ , in the rotating frame. If the decay of  $M_y$  in the presence of  $H_1$  obeys an exponential law

$$M_y(t) = M_y(0) \exp(-t/T_{1\rho}),$$

a single relaxation time,  $T_{1\rho}$ , is obtained by measuring  $M_y$  as a function of the time,  $t$ .  $M_y$  is measured by collecting the free induction decay signal (FID) following the second pulse and by Fourier transformation. Examples of selective  $T_{1\rho}$ -measurements of the proton signal H-1/H-2 of  $[^1\text{H}_2]\text{TPP}$  are given in fig. 2 and 3.

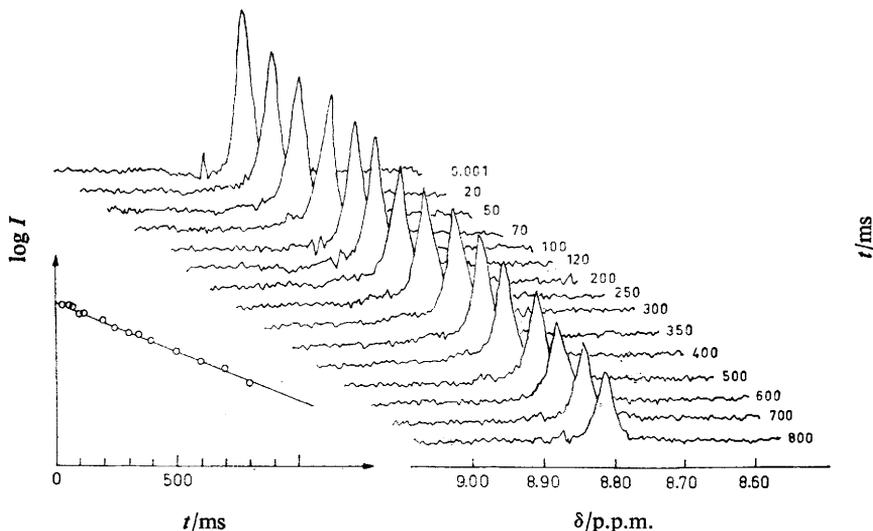


FIG. 2.—Selective  $T_{1\rho}$ -experiment on the coalesced signal of H-1/H-2 at 290 K in  $[^2\text{H}_8]\text{THF}$ .  $I$  is the line intensity. The little peak on the left of the signal corresponds to the irradiating frequency.

It has been shown by Deverell *et al.*<sup>35</sup> that a line which is produced by the coalescence of two signals due to fast exchange between two equally populated sites has a relaxation time,  $T_{1\rho}$ , which is given by

$$T_{1\rho}^{-1} = T_1^{-1} + \frac{\pi^2(v_1 - v_2)^2}{2k} \left( \frac{1}{1 + \omega_1^2/4k^2} \right); \quad \omega_1 = \gamma H_1. \quad (2)$$

$k$  is the rate constant and  $v_1 - v_2$  the separation in hertz, between coalesced lines. For  $H_1 \rightarrow 0$ ,  $T_{1\rho}$  becomes equal to the transverse relaxation time  $T_2$ . Eqn (2) is strictly valid only if the spin locking condition,

$$\Delta \ll \frac{\gamma H_1}{2\pi} \quad (3)$$

is fulfilled.  $\Delta$  is the offset in hertz between the irradiating frequency and the frequency of the observed line. Since the FT-n.m.r. pulse spectrometer Bruker CXP-100 used in this study was equipped with a quadrature detection device, the offset could be minimized to values

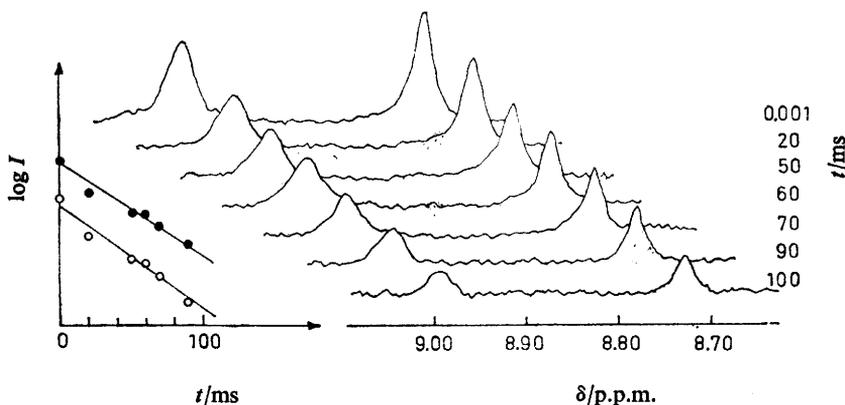


FIG. 3.—Selective  $T_{1\rho}$ -experiment on the signals of H-1 and H-2 in the slow exchange range at 184 K in  $[^2\text{H}_8]\text{THF}$ . The irradiating frequency lay between the two lines.  $I$  is the line intensity.

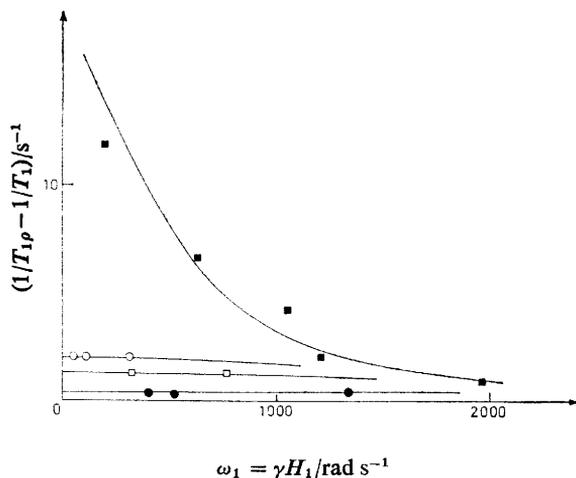


FIG. 4.— $T_{1\rho}^{-1} - T_1^{-1}$  as a function of the strength of the rotating field  $H_1$ . ■, 250; ○, 270; □, 280; ●, 290 K.

of a few hertz; thus eqn (3) was fulfilled even at low  $H_1$ -fields. The relaxation times  $T_{1\rho}$  obtained by this procedure are, therefore, "on resonance" values.  $H_1$  was measured by determining the duration  $t_{180^\circ}$ , the time required to invert the magnetisation. In the case of fast exchange, where  $T_{1\rho}^{-1}(H_1 \rightarrow 0) \gg T_1^{-1}$ , the rate constant,  $k$ , and the difference,  $\nu_1 - \nu_2$ , can be obtained from eqn (2) by measuring  $T_{1\rho}$  as a function of  $H_1$ , and by additional determination of  $T_1$  in the usual way.<sup>33</sup> In the case of very fast exchange, where  $T_{1\rho}^{-1}(H_1 \rightarrow 0) \approx 2 T_1^{-1}$ , only the quotient,  $(\nu_1 - \nu_2)^2/k$ , can be determined fairly precisely. Yet, if  $\nu_1 - \nu_2$  is known,  $k$  can be obtained. Fig. 4 shows some examples of the dependence of  $T_{1\rho}^{-1} - T_1^{-1}$  on the strength of the rotating field  $H_1$ . The theoretical curves shown in fig. 4 were obtained by a non-linear least squares fitting procedure. The varied parameters were  $\nu_1 - \nu_2$  and  $k$  for the upper curve, and  $k$  for the lower curves. Due to the inhomogeneity of  $H_1$  the scattering of the data is more pronounced in the fast exchange region, where  $T_{1\rho}$  is more sensitive to changes of  $H_1$ , than in the very fast exchange region.

For the first time, selective  $T_{1\rho}$ -relaxation experiments were carried out in the slow exchange limit as shown in fig. 3. In this range,  $T_{1\rho}$  does not depend on  $H_1$ , and coincides, therefore, with  $T_2$ . Since the rate constant is given by

$$k = T_2^{-1} - (T_2^0)^{-1},$$

one obtains

$$k = T_{1\rho}^{-1} - T_1^{-1}. \quad (4)$$

This method is, therefore, a powerful alternative to or complement of the Forsén and Hoffmann method.<sup>36</sup>

## RESULTS

In order to establish whether the observed rate constants,  $k_{\text{obs}}$ , of the tautomerism are entirely due to an intramolecular mechanism or whether they contain an intermolecular term,

$$k_{\text{obs}} = k_{\text{intra}} + k_{\text{inter}}, \quad (5)$$

we measured the  $^1\text{H}$ -n.m.r.-signal of the inner protons in  $[\text{}^1\text{H}_2\text{}^{15}\text{N}_4]\text{TPP}$ . The rate constants,  $k_{\text{intra}}$  and  $k_{\text{inter}}$ , can be evaluated from the lineshape of this signal because intermolecular proton transfer results in a decoupling of the  $^{15}\text{N}$ - and  $^1\text{H}$ -spins, in

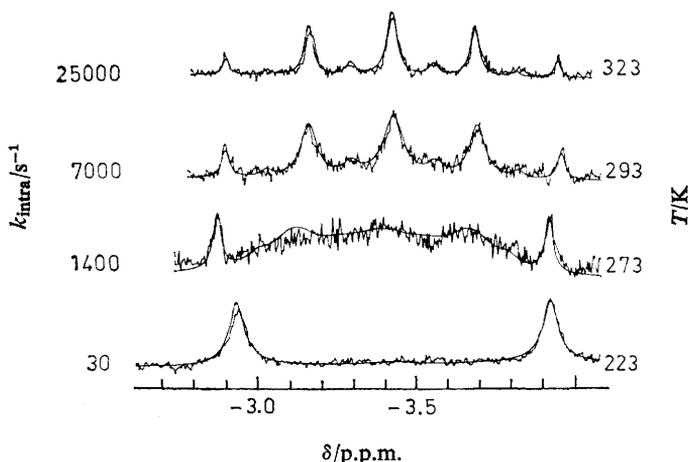


FIG. 5.—Experimental and calculated lineshapes of the  $^1\text{H}$ -n.m.r.-signal of the inner protons of  $[\text{}^1\text{H}_2\text{}^{15}\text{N}_4]\text{TPP}$  (92 %) and  $[\text{}^1\text{H}_2\text{}^{14}\text{N}_1\text{}^{15}\text{N}_3]\text{TPP}$  (8 %) at 90 MHz in  $[\text{}^2\text{H}_8]\text{THF}$  at different temperatures. The mole fractions of the isotopes were determined by simulation of the spectra.

contrast to intramolecular exchange. The corresponding signal of [ $^1\text{H}_2^{14}\text{N}_4$ ]TPP does not give this information because there is decoupling of the  $^{14}\text{N}$ - and the  $^1\text{H}$ -spins by the quadrupole relaxation mechanism. The results of the measurements are shown in fig. 5. The signal appears at high field because the protons are located inside the strong ring current induced in the aromatic porphine skeleton by the magnetic field.<sup>19</sup> At low temperatures the signal is split into a doublet, with a coupling constant  $J_{^{15}\text{N}-\text{H}} = 101 \text{ Hz}$ .<sup>39</sup> At high temperatures the signal consists of a sharp quintet, with a line distance which equals  $\frac{1}{4}$  of the coupling constant. The

TABLE 1.—RATE CONSTANTS  $k$  OF THE TAUTOMERISM IN TPP AND N.M.R.-PARAMETERS OF TPP

(a) [ $^1\text{H}_2$ ]TPP					
$T/\text{K}$	method	solvent	$\delta/\text{p.p.m.}$	$T_1^{-1}/\text{s}^{-1}$	$k/\text{s}^{-1}$
323	2	C	—	—	25 000
308	3 <sup>a</sup>	A	—	—	11 400
306	5	C	0.219 <sup>x</sup>	0.62	13 400
301	3	A	—	—	13 433
293	5	C	0.226 <sup>x</sup>	0.66	6 093
293	2	C	—	—	7 000
290	5	C	0.227 <sup>x</sup>	—	7 240
280	5	C	0.233 <sup>x</sup>	0.87	1 740
273	2	C	—	—	1 400
270	5	C	0.238 <sup>x</sup>	0.87	1 120
254	1	D	0.045 <sup>x</sup>	—	489
250	5	C	0.25±0.03	1.06	243
249	1	A	0.174 <sup>x</sup>	—	389
248	1	C	0.195 <sup>x</sup>	—	355
244	1	B	0.220 <sup>x</sup>	—	180
241	1	C	0.250 <sup>x</sup>	—	129
240	5	C	0.26±0.03	1.09	166
237	1	C	0.250 <sup>x</sup>	—	74.1
234	1	B	0.220 <sup>x</sup>	—	89.5
229	1	D	0.105 <sup>x</sup>	—	62.3
229	1	A	0.078 <sup>x</sup>	—	66.0
228	1	B	0.219 <sup>x</sup>	—	40.5
227	1	A	0.175 <sup>x</sup>	—	40.5
223	2	C	—	—	30.0
223	1	B	0.220 <sup>x</sup>	—	32.0
220	1	D	0.123 <sup>x</sup>	—	28.2
216	1	C	0.263	—	20.0
214	1	D	0.127 <sup>x</sup>	—	15.2
211	1	B	0.224	—	9.4
209	1	D	0.130	—	7.9
206	1	C	0.275	—	9.3
202	1	B	0.220	—	7.2
200	1	A	0.073	—	7.9
200	1	D	0.143	—	5.5
195	1	D	0.153	—	5.5
191	1	D	0.161	—	5.5
184	4,1	C	—	1.5±0.2	5.8
174	4,1	C	—	1.6±0.2	5.1
164	4,1	C	—	1.8±0.2	5.7

TABLE 1.—(continued)

(b)  $[^2\text{H}_2]\text{TPP}$ 

$T/\text{K}$	method	solvent	$\delta/\text{p.p.m.}$	$T_1^{-1}/\text{s}^{-1}$	$k/\text{s}^{-1}$
305	1	C	0.218 <sup>x</sup>	—	1050
299	1	C	0.222 <sup>x</sup>	—	1000
296	1	C	0.230 <sup>x</sup>	—	602
288	1	C	0.228 <sup>x</sup>	—	310
279	1	D	0.041	—	100
276	1	D	0.040	—	128
270	1	A	0.174	—	67.3
267	1	D	0.059	—	60.0
265	1	C	0.244	—	34.7
258	1	D	0.070	—	17.0
255	1	C	0.240	—	15.1
255	1	A	0.258	—	12.9
254	1	C	0.249	—	10.0
252	1	D	0.070	—	11.0
252	1	A	0.159	—	12.9
245	1	C	0.253	—	5.3
213	4	A	—	$2.0 \pm 0.2$	$< 0.3$

$\delta$  Difference of the chemical shifts of the signals of H-1 and H-2 (see scheme II).  $T_1$ , longitudinal relaxation time of the H-1/H-2 signals; in the slow exchange range  $T_1(\text{H-1})$  and  $T_1(\text{H-2})$  were equal. 1, lineshape analysis of the H-1/H-2 signals at 100 MHz. 2, lineshape analysis of the signal of the inner protons in  $[^1\text{H}_2^{15}\text{N}_4]\text{TPP}$ . 3,  $^{13}\text{C}$ -lineshape analysis of the signals of the carbon atoms which are adjacent to the nitrogen atoms. 4,  $T_{1\rho}$ -experiment at 90 MHz using eqn (1). 5,  $T_{1\rho}$ -experiment using eqn (3). A,  $\text{CDCl}_3$ , B,  $\text{CDCl}_3/\text{CS}_2$  1:1, C,  $[^2\text{H}_8]\text{tetrahydrofuran}$ , D,  $[^2\text{H}_8]\text{toluene}$ . <sup>a</sup> Values from ref. (22). <sup>x</sup> Extrapolated values.

corresponding signal of the isotope  $[^1\text{H}_2^{14}\text{N}_1^{15}\text{N}_3]\text{TPP}$  gives rise to a quartet which appears between the lines of the quintet. At intermediate temperatures, line broadening is observed accompanied by the appearance of three new lines which sharpen to form a quintet at high temperatures. Consequently, in the slow exchange range, within the n.m.r.-timescale, each proton is localised at a single nitrogen atom. In the fast exchange range, within the n.m.r.-timescale, the inner protons are localised with equal probability at each of the four nitrogen atoms due to rapid random walk. As is shown in fig. 5, the fit between the experimental and the calculated spectra is very satisfactory. Since no line broadening due to intermolecular proton exchange is observed at 323 K the rate constant  $k_{\text{inter}}$  (323 K) of an intermolecular mechanism cannot exceed  $\sim 1 \text{ s}^{-1}$ , a value which corresponds to the lower limit of rate constants detectable by n.m.r.-lineshape analysis. The maximum rate constant,  $k_{\text{max}}^{\text{inter}}$ , of intermolecular proton transfer is limited by the rate of diffusion of the reactants. It has been shown<sup>31</sup> that  $k_{\text{inter}}^{\text{max}}$  is proportional to  $T/\eta$ , where  $T$  is the temperature and  $\eta$  the viscosity of the solvent.  $T/\eta$  is proportional to  $\exp(-a/T)$ , where  $a$  lies between 1000 and 1500 K for organic solvents.<sup>38</sup> Therefore,  $k_{\text{inter}}$  is given by the equation:  $k_{\text{inter}} \leq 24 \exp(-10^3/T)$ . Table 1, which contains the observed rate constants,  $k_{\text{obs}}$ , shows that  $k_{\text{obs}} \gg k_{\text{inter}}^{\text{max}}$  for all temperatures. Thus, all rate constants measured are due entirely to an intramolecular process.

In the  $^1\text{H}$ -n.m.r. spectra of  $[^1\text{H}_2^{15}\text{N}_4]\text{TPP}/\text{CDCl}_3$ -samples which we had exposed to daylight only a broad  $^{15}\text{N}$ -H signal was found at 323 K, thus indicating the presence of intermolecular proton exchange in the order of  $10^2 \text{ s}^{-1}$ . The resulting term,  $k_{\text{inter}} \approx 2500 \exp(-10^3/T)$ , is within the margin of error of  $k_{\text{obs}}$  in eqn (5) at high temperatures, and can, therefore, be neglected. But this is not the case at low temperatures, where  $k_{\text{inter}}$  is of the same order as  $k_{\text{intra}}$  in this sample. This intermolecular exchange is probably due to traces of deuterium chloride formed by the photolysis of  $\text{CDCl}_3$ .<sup>28</sup> Therefore, the observation of a singlet for the central protons of  $[^{15}\text{N}_4]\text{octaethylporphin}$  dissolved in  $\text{CDCl}_3$ <sup>39</sup> at room temperature can be explained by the presence of intermolecular proton transfer.

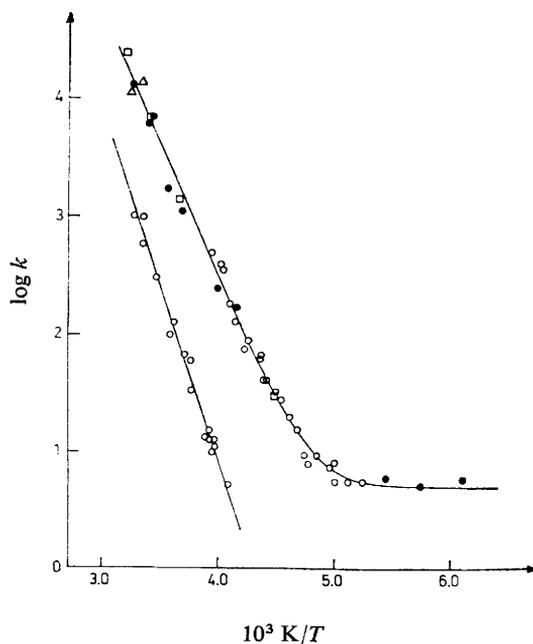


FIG. 6.—Arrhenius diagram of the hydrogen motion (see scheme II) in  $[^1\text{H}_2]\text{TPP}$  (upper curve) and of the deuteron motion in  $[^2\text{H}_2]\text{TPP}$  (lower curve).  $\circ$ , from the lineshape analysis of the signals of H-1 and H-2;  $\square$ , from the lineshape analysis of the signal of the inner protons;  $\triangle$ , from the lineshape analysis of the  $^{13}\text{C}$ -signals of the carbon atoms which are adjacent to the nitrogen atoms;  $\bullet$ , from selective  $T_{1\rho}$ -relaxation experiments.

Table 1 shows a close agreement between our rate constants obtained by various methods and the value obtained by Abraham *et al.*<sup>22</sup> from  $^{13}\text{C}$ -n.m.r.-lineshape analysis. Table 1 also contains all other parameters used in the evaluation of rate constants.

At low temperatures we found that  $k^{\text{H}}$  became independent of the temperature. This was proved by lineshape analysis and selective  $T_{1\rho}$ -experiments as follows.

Since H-2 and the inner hydrogen atoms are separated by a distance of  $5 \text{ \AA}$  these atoms are coupled neither directly nor indirectly. Therefore, the chemical and the magnetic environment of H-2 is not changed when the inner hydrogen atoms are replaced by deuterium atoms. Thus, we found that, for example

$$T_1(\text{H-2}, [^1\text{H}_2]\text{TPP}) = T_1(\text{H-2}, [^2\text{H}_2]\text{TPP}).$$

Yet, a temperature independent difference,  $\Delta W$ , between the linewidths of the H-2 signal in  $[^1\text{H}_2]\text{TPP}$  and  $[^2\text{H}_2]\text{TPP}$ ,  $\Delta W = W(\text{H-2}, [^1\text{H}_2]\text{TPP}) - W(\text{H-2}, [^2\text{H}_2]\text{TPP}) = 1.7 \pm 0.2$  Hz, was observed below 200 K. Since  $k^{\text{D}} \ll 1 \text{ s}^{-1}$  in this temperature range,  $\Delta W$  must be an exchange broadening due to the hydrogen migration and  $k^{\text{H}} = \pi \Delta W \approx 5 \text{ s}^{-1}$ .

This result was confirmed by the selective  $T_{1\rho}$ -experiments mentioned above. An example of these experiments was shown in fig. 3. The strength of the rotating magnetic field,  $H_1$ , was varied between  $400 < \gamma_{\text{H}} H_1 < 2000 \text{ rad s}^{-1}$ , but no change in  $T_{1\rho}(\text{H-2}, [^1\text{H}_2]\text{TPP})$  was observed. Within the margin of error the relaxation was found to be exponential. The temperature independent difference,

$$\Delta R(\text{H-2}, [^1\text{H}_2]\text{TPP}) = T_{1\rho}^{-1}(\text{H-2}, [^1\text{H}_2]\text{TPP}) - T_1^{-1}(\text{H-2}, [^1\text{H}_2]\text{TPP}) = k^{\text{H}} \approx 5 \text{ s}^{-1},$$

has, therefore, to be identified with  $k^{\text{H}}$  according to eqn (3). Eqn (3) can be applied here because  $\Delta R(\text{H-2}, [^2\text{H}_2]\text{TPP})$  was found to be zero in this temperature range where  $k^{\text{D}} \ll 1 \text{ s}^{-1}$ . One can exclude that  $\Delta R(\text{H-2}, [^1\text{H}_2]\text{TPP})$  is due to relaxation mechanisms other than the hydrogen exchange. These other mechanisms should affect  $\Delta R(\text{H-2}, [^1\text{H}_2]\text{TPP})$  and  $\Delta R(\text{H-2}, [^2\text{H}_2]\text{TPP})$  in the same way. Therefore,  $\Delta R(\text{H-2}, [^1\text{H}_2]\text{TPP})$  and  $\Delta R(\text{H-2}, [^2\text{H}_2]\text{TPP})$  should be equal, which is not the case. Such a relaxation mechanism could be, for example, cross relaxation between the different hyperfine lines of H-2 which might be due to an indirect coupling between H-2 and the nitrogen atoms. It must be recalled that only  $\Delta R(\text{H-2}, [^1\text{H}_2]\text{TPP})$  was found to be independent of the temperature; the values of  $T_1 = T_1(\text{H-2}, [^1\text{H}_2]\text{TPP}) = T_1(\text{H-1}, [^1\text{H}_2]\text{TPP})$  showed a slight dependence on the temperature and the solvent as shown in table 1.

TABLE 2.—KINETIC PARAMETERS FOR THE HYDROGEN MOTION IN TPP ACCORDING TO EQN (5).

$k_{t0}^{\text{H}}/\text{s}^{-1}$	$\ln k_{t1}^{\text{H}}$	$\ln k_{t2}^{\text{D}}$	$(k^{\text{H}}/k^{\text{D}})_{298 \text{ K}}$	$E_1^{\text{H}}/\text{kJ mol}^{-1}$	$E_2^{\text{D}}/\text{kJ mol}^{-1}$
$5.0 \pm 0.5$	$26.5 \pm 1$	$29.7 \pm 0.7$	$11.1 \pm 3$	$43.4 \pm 1.3$	$57.3 \pm 1.3$

Fig. 6 shows the Arrhenius diagram of the hydrogen migration and the deuterium migration in TPP. Deuterium migration obeys a simple Arrhenius law, but hydrogen migration obeys an Arrhenius law only at high temperatures, becoming a horizontal line as the temperature is lowered. The strong deviation from a straight line is already apparent at 220 K where  $k^{\text{H}} \approx 30 \text{ s}^{-1}$ . The calculated lines of fig. 6 were obtained by adapting the experimental data to the equations:

$$k^{\text{H}} = k_{t0}^{\text{H}} + k_{t1}^{\text{H}} \exp(-E_1^{\text{H}}/RT), \quad (6a)$$

and

$$k^{\text{D}} = k_{t2}^{\text{D}} \exp(-E_2^{\text{D}}/RT), \quad (6b)$$

using a non-linear least squares fitting procedure.

Table 2 contains the activation parameters obtained. The errors given in table 2 are the standard errors. Although our rate constants and those given by Abraham *et al.*<sup>22</sup> are equal within the margin of error, the activation parameters extracted from these data are markedly different. This discrepancy is due to the fact that only a few rate constants were measured by these authors and that the form of eqn (6a) could, thus, not be recognized. It is probable that an Arrhenius law similar to eqn (6a) could be established for *p*-phenyl substituted TPPs<sup>23</sup> if more rate constants were measured at low temperatures.

## DISCUSSION

Since we have proved that the observed rate constants of the tautomerism in TPP do not contain any significant term arising from intermolecular proton transfer, the deviation from a linear Arrhenius curve in the case of  $[^1\text{H}_2]\text{TPP}$  can only be explained by the presence of tunnelling following Bell's arguments.<sup>37</sup> Tunnelling occurs even in the high temperature range since the kinetic isotope effect and the quotient of the pre-exponential factors in eqn (6) are beyond the semi-classical limits  $(k^{\text{H}}/k^{\text{D}})_{298\text{K}} \leq 7$  and  $2^{\frac{1}{2}} \leq A^{\text{H}}/A^{\text{D}} \leq \frac{1}{2}$  given in ref. (37). The change of the slope of the Arrhenius curve in fig. 6 or eqn (6a) takes place within one unit of  $10^3 \text{ K}/T$ . Such a sudden change has to our knowledge not been previously observed in proton transfer reactions. The Bell treatment of tunnelling in proton transfer reactions assumes a continuous distribution of energy on both sides of the barrier. This assumption results in gradual changes of the slope of the Arrhenius curve, and, therefore, is unable to accommodate our data. Until now all data concerning tunnelling protons could be explained on the grounds of the Bell model if one allowed for modifications of the barrier shape.<sup>40, 41</sup> The existence of a sudden change of the Arrhenius curve was postulated by Brickmann and Zimmermann<sup>42</sup> on the basis of a double minimum potential with discrete quantized vibrational levels on both sides of the barrier. These authors showed that the tunnel-splitting  $\Delta E_i$  of the degenerate vibrational levels  $i$  of a symmetrical double minimum potential are related to the rate constant,  $k$ , of the isomerization between the two wells in the following way:<sup>43</sup>

$$k = \sum_{i=0}^N k_{ti} [\exp(-E_i/kT)] / [\sum_i \exp(-E_i/kT)], \quad (7)$$

where  $k_{ti}$  is the tunnel frequency between barrier-separated degenerate states  $i$  which are related to the tunnel-splittings  $\Delta E_i = \hbar k_{ti}$ .  $\hbar$  is Planck's constant,  $k$  the Boltzmann constant, and  $T$  the temperature. If  $N \gg 1$  this vibrational model of tunnelling and the Bell model become equivalent. In the low temperature approximation, with  $E_0 = 0$ , it follows using molar energies that

$$k = \sum_{i=1}^N k_{ti} \exp(-E_i/RT) + k_{t0}. \quad (8)$$

Eqn (6a) is understandable only within the scope of this model. Until now tunnel-splittings have never been determined by measuring rate constants but only directly by spectroscopic methods. For example, the tunnel frequencies of the inversion of ammonia lie in the range of  $10^{10}$ - $10^{13} \text{ s}^{-1}$  and have been determined from the fine structure of i.r.-lines.<sup>44</sup> The frequencies of rotational tunnelling of  $\text{XY}_n$ -groups in the solid state which are of the same order have been obtained by inelastic neutron scattering<sup>45</sup> or by measuring longitudinal relaxation times,  $T_1$ , as a function of the temperature.<sup>46</sup> All these methods are inadequate for the determination of such low tunnel frequencies as  $k_{t0} = 5 \text{ s}^{-1}$ , obtained here from the measurement of rate constants.

The pre-exponential term in eqn (6a) is, then, the tunnelling frequency,  $k_{t1}$ , from the first excited vibrational level. The apparent energy of activation,  $E_1^{\text{H}}$ , in eqn (6a) is the energy gap between the ground state and the excited state. Since  $E_1^{\text{H}}$  corresponds to the energy of the stretching vibration of the NH-bond in TPP<sup>47</sup> ( $\tilde{\nu}_{\text{NHas}} = 3315 \text{ cm}^{-1} = 40 \text{ kJ mol}^{-1}$ ), it is the normal mode of a stretching vibration that becomes the reaction coordinate. It cannot be the normal mode of a bending vibration, since in this case several vibrational states between 0 and  $43.4 \text{ kJ mol}^{-1}$

should exist from which the reaction can proceed. Consequently, eqn (6a) should contain more than two terms.

Within this vibrational model the Arrhenius curve of the deuteron rearrangement must be due to a reaction from an excited level of the ND-stretching vibration. The energy of activation,  $E_2^D$ , is about twice the energy of the ND-stretching vibration<sup>47</sup> ( $\tilde{\nu}_{\text{NDas}} = 2478 \text{ cm}^{-1} = 30 \text{ kJ mol}^{-1}$ ). Therefore, it is probable that the reaction proceeds from the second excited vibrational level. Thus, the high value of  $E_1^H - E_2^D = 14 \text{ kJ mol}^{-1}$ , which is not explicable in terms of the transition state theory, is easily explained. The tunnel frequencies in the vibrational ground state and in the first excited ND-stretching level do not contribute in any significant way to the reaction rate in the temperature range where rate constants have been observed, because tunnelling is hindered by the higher mass of deuterium. The vibrational model of tunnelling in [ $^1\text{H}_2$ ]TPP and [ $^2\text{H}_2$ ]TPP developed here is illustrated in fig. 7.

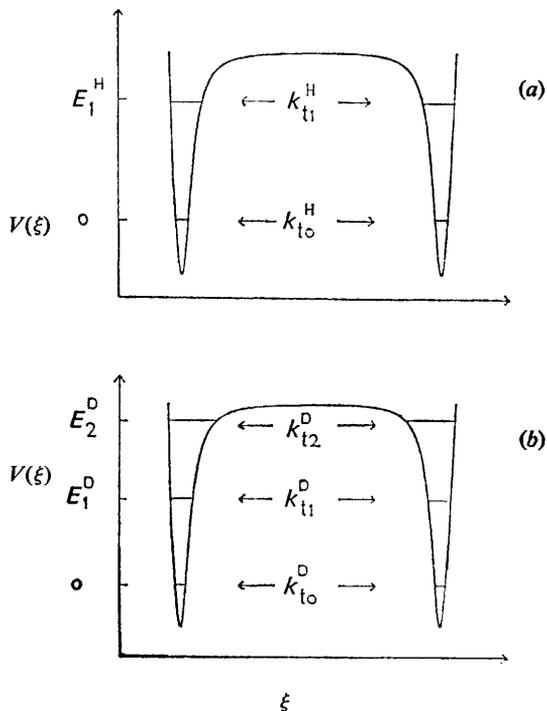


FIG. 7.—Vibrational model of tunnelling in (a) [ $^1\text{H}_2$ ]TPP and (b) [ $^2\text{H}_2$ ]TPP.  $V(\xi)$  is the potential (schematically) along the reaction coordinate,  $\xi$ . Each level  $i$  is split by  $\Delta E_i = \hbar k_{ti}$ , not shown here on account of its smallness.  $k_{ti}$  is the tunnel-frequency between the barrier-separated states  $i$  and  $h$  is Planck's constant.

The observation of tunnelling is in agreement with the observation that the rate constants are independent of the solvent used. No solvent reorganisation which could affect the rate constants need occur during the migration because the inner hydrogen atoms are poorly solvated. This is in agreement with the observation of a very low solubility of free base porphine as compared to TPP. A good solvation of protons about to be transferred increases the effective mass moving during the transfer, thus reducing the probability of tunnelling.<sup>40</sup>

Since the tautomers of TPP are degenerate the hydrogen atoms move in a symmetric double minimum potential,  $V(\xi)$ , as shown in fig. 7. The reaction coordinate,  $\xi$ , is a linear combination of the coordinates of all atoms that move during the reaction. From the crystallographic data<sup>10, 12</sup> of TPP we know that the aromatic porphine skeleton has almost  $D_{4h}$ -symmetry. During an hypothetical rearrangement in the solid state the bond lengths do not change  $>0.03 \text{ \AA}$ . These changes are due in part to the distortion of the molecule by the crystal field. By contrast, each central proton is transported over a distance of  $\approx 1.6$  to  $2.1 \text{ \AA}$ , depending on the reaction pathway. Therefore, the motions of the heavy atoms are not coupled to the proton motion, and the reaction coordinate is a function of only the coordinates of the central protons.

The observation<sup>17</sup> that at 4.2 K the tautomers of porphine incorporated in an n-octane crystal do not interconvert in the electronic ground state at a measurable rate, need not disagree with our observation of a temperature independent tunnel frequency of  $k_{t0} = 5 \text{ s}^{-1}$ . In the solid state the molecule is distorted and the degeneracy of the two tautomers is lifted, as is indicated by a difference in fluorescence of the two tautomers.<sup>17</sup> For even slight distortions of the symmetric double minimum potential the model of Brickmann and Zimmermann<sup>42</sup> predicts a considerable decrease in the tunnel frequencies.

A last comment has to be made on the effective masses,  $\mu_{\text{eff}}^{\text{H}}$  and  $\mu_{\text{eff}}^{\text{D}}$ , transported during the rearrangement of porphines. The relations

$$\mu_{\text{eff}}^{\text{H}} = 1 \text{ a.m.u.} \quad \text{and} \quad \mu_{\text{eff}}^{\text{D}} = 2 \text{ a.m.u.}$$

hold independent of a synchronous or an asynchronous pathway. This is immediately verified by comparing the reduced masses,  $\mu_{\text{XY}_2}$  and  $\mu_{\text{XY}}$ , of the symmetric and the asymmetric vibration in an  $\text{XY}_2$ -molecule and of the vibration in an XY-molecule.<sup>48</sup> For  $m_X \gg m_Y$ ,  $\mu_{\text{XY}_2} = \mu_{\text{XY}} = m_Y$ . The assumption of  $\mu_{\text{eff}}^{\text{H}} = 2$  in ref. (23) is, therefore, not correct. Since there is no mass influence on the degree of coupling of the motion, tunnelling along a pathway along which both hydrogen atoms are moving synchronously must be favoured, because the reaction path is shorter for a synchronous motion than for a step by step motion.<sup>49</sup> The situation is analogous to the inversion of ammonia,<sup>50</sup> which could be considered as a synchronous tunnelling of three protons if the mass of the nitrogen atom were infinitely high.

It should be possible to extract more information on the potential surface of the tautomerism of TPP from the tunnel frequencies measured by a quantitative treatment within the scope of the formalism given by Brickmann and Zimmermann.<sup>42, 43</sup> We hope that we shall be able to present the results of such calculations in the future.

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