neously. It is unlikely that the potential energy along the reaction path shown in Fig. 4 of Ref. 7, which should be accompanied by considerable repulsive energy, amounts only up to 0.5 eV. Furthermore, their potential function with such low barrier, in which the first excited state of N–H stretching is close to the barrier top, would give large anharmonic effect and lower the energy level considerably. But this is contradicting the IR result,[1] which indicated that such anharmonicity is absent and that the energy level falls into usual range of N–H stretching. The IR result rather suggests that the first excited state should be well below the barrier top.

Finally, Limbach *et al.*[1] supported the synchronous proton migration[7] from the observation that the N–H stretching motions are correlated. Although the result is interesting, it is not yet clear whether the two protons migrate in phase or not, since there is no direct evidence that the reaction coordinate of proton migration is contributed only by the N–H stretching mode. They argued that if the N–H bending states contribute to the tunneling, the kinetic isotope effect in which $k^{\mathrm{HH}} \simeq 10k^{\mathrm{HD}}$, $k^{\mathrm{HD}} \simeq k^{\mathrm{DD}}$ at 298 K[9] may not be explained. I would like to point out that the isotope effect is a quite delicate problem, the transfer rate being extremely sensitive to the shape of barrier, the energy levels of proton and deuteron, and the reaction path. In the absence of detailed information on these quantities, it is premature to specify the mechanism from available experimental data. Further experimental and theoretical studies will be necessary to elucidate the mechanism of proton migration in porphines.

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Reply to a "Comment on 'IR-spectroscopic study of isotope effects on the NH/ND stretching bands of meso-tetraphenylporphine and vibrational hydrogen tunneling"'

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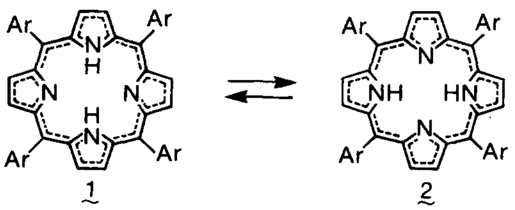
The solution kinetics of the hydrogen migration in meso-tetraphenylporphine (TPP) and other free-base porphines (scheme I) have first been interpreted with transition state theory (TST).[1] We have measured for the first time the HH/HD/DD kinetic isotope effects[2–5] which could not be explained with TST. IR measurements[6] revealed a coupling of the two NH oscillators and—for a proton transfer system—surprisingly sharp NH/ND stretching bands. These experimental results were in favor of a thermally activated HH tunneling process.[2–4,6] Although we were aware that tunneling in such a reaction must be a multidimensional problem, we have discussed the simplest possible tunneling model. In this model, the HH reaction proceeds by tunneling between the first excited NH stretching states and the HD and DD reaction between the second excited states which lie close to the top of the barrier. The energies of activation E_a are identified with the energies of the NH/ND stretching states.[2–4,6]

In two recent theoretical papers, the concept of a thermally activated tunneling process in free-base porphines has also been adopted by Sarai.[7] His CNDO calculations indicated that the skeleton shows a small deviation from C_{4h} vs C_{2h} symmetry, induced by the protons via the pseudo-Jahn–Teller effect. In terms of a two-dimensional tunneling model, it was predicted that half of the energy of activation is used for the rearrangement of the heavy atoms, in contrast to our model. Our proposal[6] that this mechanism should lead to

Scheme I



TPP: Ar ≡ phenyl
TTP Ar ≡ p-tolyl

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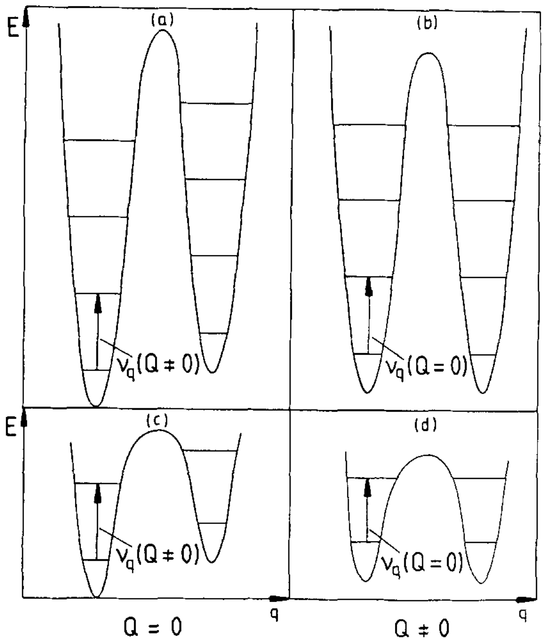

FIG. 1. Potential curves (schematically) of the hydrogen migration in porphines for a coupling of the proton motion to the heavy atoms of the ring skeleton. q: proton motion; Q: heavy atom motion; $\nu_q(Q)$: NH stretching frequency as a function of Q.

large NH/ND stretching bands of TPP has been commented by Sarai.[8] In the following we discuss, therefore, this interesting problem as well as some of our new experimental results on hydrogen migration in solid state porphines.[9]

Figure 1 schematically shows the potential curve of the tautomerism in porphines as a function of the proton coordinate q for the case that the porphine skeleton must rearrange from D_{2h} [Figs. 1(a) and 1(c)] to D_{4h} [Figs. 1(b) and 1(d)] and again to D_{2h} during the process. Q represents the skeletal motion. Proton tunneling occurs when the potential along q is symmetric, i.e., when the skeleton has D_{4h} symmetry at $Q = 0$ [Figs. 1(b) and 1(d)]. The change of Q from D_{2h} to D_{4h} symmetry is associated with the energy E_A. Since in Figs. 1(a) and 1(c) the skeleton has only D_{2h} symmetry, the proton potential is asymmetric. E_M is the energy difference between the two minima. According to the CNDO results of Sarai, E_A is of the order of 0.3 eV and E_M is about 1.2 eV. We consider two cases. In Figs. 1(a) and 1(b), the barrier lies far, in Figs. 1(c) and 1(d), just above the first excited NH stretching state. The CNDO[7] and *ab initio*[8] results predict a situation described by Figs. 1(a) and 1(b), and the preceding comment of Sarai[8] refers to this high barrier case. Since the NH stretching frequencies are not significantly different in Figs. 1(a) and 1(b), the NH stretching band will be sharp. In the low barrier case [Figs. 1(c) and 1(d)], the change of the NH stretching frequency with Q is nonnegligible, which leads to a large or structured NH stretching band as is known from H-bonded systems. This is what we have stated previously.[6] We did not consider the high barrier case because the experimental frequency factors of the HD and the DD migration are about 10^{13} s^{-1}, which is typical for an intramolecular over barrier reaction. Therefore, it is not likely that the HD and the DD migration proceed by tunneling in contrast to the HH migration whose frequency factor is about 10^{11} s^{-1}, indicating tunneling. Thus, the top of the barrier must lie close to the second excited ND stretching state. This experimental result, derived without using the one-dimensional approximation, is not in good agreement with the CNDO[7] and even the *ab initio* calculations.[8] In order to account for the low barrier height and, at the same time, the sharp NH stretching bands we proposed the following. If the porphine skeleton is assumed to be rigid and if its symmetry is close to D_{4h}, E_A and E_M are small as compared to the energy of activation, E_a, and the barrier height. The reaction can then be described in good one-dimensional approximation by the symmetric potential of Fig. 1(d) alone, leading to sharp NH/ND stretching bands. A possible doublet splitting[2,4,6] due to tunneling was expected to be much smaller than the observed bandwidth of 23 cm^{-1}.

We have argued[2] that the one-dimensional proton tunneling probabilities along the synchronous pathway are higher than along the asynchronous pathway if the barrier heights are comparable. Tunneling along the asynchronous pathway will be preferred only if the barrier height is less than half of the value along the synchronous pathway. Since we observed a coupled proton motion already in the potential wells[6] we believe that the synchronous pathway is favored as long as the reaction proceeds by tunneling.

We have also argued that the kinetic HH/HD/DD isotope effects are not in agreement with a mechanism where the tunnel process occurs from excited bending states.[2,4,6] This does not mean that tunneling between, e.g., the third excited NH bending states whose energy would also correspond to the experimental E_a value does not take place but that this tunnel process does not affect the rate constants as long as the remaining effective barrier height and width is greater in the third NH bending state as compared to the first NH stretching state. In contrast to the experiments, tunneling between the NH bending states should lead to a curvature of the Arrhenius curve. I agree with Sarai[8] that it will be difficult to calculate the HH/HD/DD isotope effects in terms of a two-dimensional tunneling model because such model necessarily contains more parameters than can be verified experimentally. However, in contrary to the one-dimensional NH stretching tunneling model, where one can understand that $k^{\mathrm{HH}} \gg k^{\mathrm{HD}} \approx k^{\mathrm{DD}}$,[4] k^{HD} will always be greater than k^{DD} if the number of available states on both sides of the barrier is increased,[4] e.g., if one assumes that tunneling from excited bending states determines the rate constants.

We come now to the problem of the porphine tautomerism in the solid state. The structure of triclinic TPP[10] has been interpreted in terms of only tautomer 1 in scheme I. We have recently measured ^{15}N NMR spectra of solid TPP and TTP (meso-tetratolylporphine).[9] The exchange broadened spectra indicated that in solids both tautomers were present (1:1 for TTP and 7 : 1 for TPP at 295 K). Thus, the small energy difference (0.06 eV) between the tautomers in triclinic TPP is not caused by the protons via the pseudo-Jahn–Teller effect but by crystal packing forces, because the asymmetry disappears by going from TPP to TTP. In solution, this has no effect on the hydrogen migration rates. Within the margin of error the rate constants of the HH reaction in solid TTP and the backwards rate constant in solid TPP are the same as the rate constants found previously for TPP in solution.[2,4] Since the NH stretching frequency which determines in our view of the reaction the energy of activation, is not significantly different in solution and the solid state, this coincidence is easily explained with the one-dimensional tunneling model.

We conclude that there is, for the moment, no experimental evidence for a coupling of proton tunneling to a skeleton rearrangement in porphines. We may, however, not exclude that future refined experiments on porphines, especially on asymmetric systems, or with a greater chance, on more flexible proton transfer systems will reveal such a coupling.

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Self-diffusion related to shear viscosity at the melting temperature of metals

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In a recent paper, Zwanzig[1] has derived a relation between the self-diffusion coefficient D and the shear viscosity η of liquids, having the form

$$(D7/k_BT)v^{1/3} = 0.0658(2 + \eta/\eta_l) = C', \tag{1}$$

where k_BT is the thermal energy corresponding to temperature T, v is the volume per particle V/N, while η_l is the longitudinal viscosity. While the actual value of C' in Eq. (1) clearly depends on the ratio of η to η_l, which is often not known quantitatively, Zwanzig points out that C' as defined above can vary only between 0.13 and 0.18. He shows that Eq. (1) is consistent with experimental data[2] on tetramethylsilane at $T = 293$ and 373 K, and on benzene at $T = 393$ K.

The present note adds to the above two examples the fact that a relation of the form (1) is obeyed by a variety of liquid metals just above their melting temperature T_m. As with the argument of Zwanzig,[1] Brown and March[3] used the Green–Kubo formulas for D and η. For liquid metals near T_m, they exploited the fact that the self-correlation function $S_s(k,\omega)$ and the van Hove function $S(k,\omega)$, which enter the Green–Kubo formulas for D and η_l, have a rather well-defined frequency range $0 < \omega < \omega_D$, analogous to the Debye frequency in a crystalline solid. Relating ω_D to the melting temperature T_m using Lindemann's law of melting, Brown and March thereby obtained the approximate relations for the atomic transport coefficients at T_m:

$$DM^{1/2}\rho^{1/3}/T_m^{1/2} = \text{constant} \tag{2}$$

and

$$\eta/T_m^{1/2}M^{1/2}\rho^{2/3} = \text{constant}, \tag{3}$$

where M is the atomic mass while ρ is the atomic number density N/V. Forming the quantity $(D\eta/k_BT_m)/\rho^{1/3}$ appearing in Eq. (1), from Eqs. (2) and (3), one immediately finds that it is a constant, in accord with Zwanzig's prediction. Since the formulas (2) and (3) were compared directly with experiment in Ref. 3, we need not go into numerical detail again here.

In conclusion, if we focus attention on the melting temperature T_m, measured atomic transport data for a variety of liquid metals is in accord with the Zwanzig relation (1), with C' approximately constant.

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