Role of Symmetry in the Tunnelling of the Proton in Double Minimum Potentials

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Tunnelling has been successfully used to explain the fast rate of exchange in certain inter- and intramolecular proton transfers. A simple concept may help to understand the origin of tunnelling in some cases. When the initial and final structures are identical, the potential energy profile representing the transfer is bound, is symmetric, and has two minima. Here, tunnelling will always occur except with infinitely high or wide barriers. It is a consequence of the indistinguishability of the two states between which the system is exchanging. A slight change in the structure of either the initial or the final state destroys the symmetry of the profile, practically eliminating tunnelling except for low and narrow barriers. This concept has been used to explain the effect of the rotation of the methyl group in the intermolecular proton transfer in methanol and the intramolecular proton exchange in α-methyl-β-hydroxyacrolein. It also can explain why the introduction of one methyl group in naphthazarin eliminates the interconversion between two tautomers.

Tunnel Effect in Chemical Kinetics

The role of tunnelling in chemical kinetics became evident when the theory of absolute reaction rates was introduced.[1] The progress of a reaction is followed by the displacement of the system along the reaction coordinate. In its transition from reactants to products, the system must overcome a potential energy barrier V_0. For the barrier to be crossed, classical mechanics requires that the energy E of the system be equal to or greater than V_0. Quantum mechanics shows, however, that there is a probability $G(E)$ that a system with energy $E \leq V_0$ will "leak" through the barrier. For unbound systems, such as the one shown in Figure 1, this probability has been calculated by using the semiclassical WKB method.

$$G(E) = \exp\left[-\frac{2(2m)^{1/2}}{\hbar}\int_{x_1}^{x_2}[V(x) - E]^{1/2}\mathrm{d}x\right] \quad (1)$$

The use of $G(E)$ in the calculation of the rate constant for a chemical reaction may explain a departure from linearity in an Arrhenius plot. Such departures, together with the effect of the substitution of hydrogen by deuterium, have been used as evidence of tunnelling.

The formalism commonly employed to evaluate the effect of tunnelling on the rate constant requires that the system move from the space on the left (Figure 1), representing the reactants, where it is unbound and where the energy may vary continuously, to the space on the right, where it is equally unbound and where the energy levels also form a continuum. Such formalisms are useful in most gas-phase and in some liquid-phase reactions.

Bound Symmetric and Asymmetric Double Minimum Potentials

The inversion of ammonia was the first system for which the tunnel effect was invoked in order to explain the splitting of the lines in its vibrational spectrum. The potential for this inversion (Figure 2A) is bound, has discrete energy levels, has two minima, and is symmetric. The symmetry is the result of the indistinguishability of the two geometries between which the molecule oscillates. The energy levels of both wells have the same values and occur in pairs. The separation of a pair increases as the energy approaches the top of the barrier. The eigenfunctions are delocalized, extending over both wells, with even (g) or odd (u) character, reflecting the symmetry of the profile.

The intramolecular proton exchange in 1,3 asymmetrically substituted malonaldehyde (Figure 2B) provides an example of a bound and asymmetric double minimum potential. Unlike the ammonia inversion, the energy levels do not occur in pairs, and, except in a case of accidental degeneracy, the energies in one well are different from those in the other. The eigenfunctions near the bottom are localized in their respective wells (except when the barrier is low), but levels close to the top of the barrier may extend through the classically forbidden region into the other well.

The treatment of bound profiles of the kind just described is different from that commonly used for unbound systems. For the former a full quantum mechanical treatment is possible, while for the latter semiclassical methods are used.

The quantum mechanical study of the motion of the proton in double minimum potentials first requires the determination of the profile for the proton exchange; it can be obtained from ab initio selfconsistent-field calculations. A suitable function is fitted to this profile, using one of the various analytical forms available to represent the potential.[2-6] For this function, the ei-

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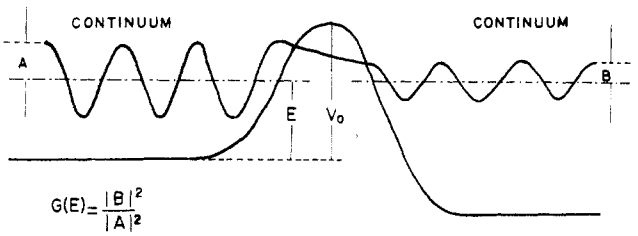

Figure 1. Tunnelling in unbound sytems: the leak through the barrier occurs from a continuum set of energies for the incoming wave to a continuous set for the outgoing wave.

genvalues E_n and eigenfunctions $\Phi_n(x)$ of the stationary Hamiltonian are calculated by the variational method. In an isolated system in which the Hamiltonian does not contain time explicitly, the state function $\Psi(x,t)$ is a function of time and can be expressed as a linear combination of the stationary eigenfunctions multiplied by the pertinent time-dependent exponential:

$$\Psi(x,t)=\sum_n C_n\Phi_n(x)\ \exp\left(-\frac{i}{\hbar}E_nt\right) \qquad (2)$$

where $C_n = \langle\Phi_n(x)|\Psi_0(x,0)\rangle$. The function $\Psi_0(x,0)$ is a Gaussian which represents the proton at $t = 0$.[6] It corresponds to the ground state of the harmonic oscillator defined by the initial well treated as if it were isolated (Figure 3). The probability densities are obtained from the coefficients C_n. They are shown, as functions of time, in Figures 3A and 3B for symmetric and asymmetric double-minimum potentials, respectively.

The time evolution of the proton's position cannot be given with certainty for a system in which the energy is known exactly, since the position operator and the Hamiltonian do not commute. The motion of the proton is more conveniently studied by calculating the expectation, or "average", value of the position of the proton as a function of time:

$$\langle x\rangle = \langle\Psi(x,t)|x|\Psi(x,t)\rangle = \sum|C_n^2|\langle\Phi_n(x)|x|\Phi_n(x)\rangle + 2\sum_n\sum_{m<n} C_n^*C_m\langle\Phi_n(x)|x|\Phi_m(x)\rangle(\cos\omega_{n,m}t) \qquad (3)$$

where $\omega_{n,m} = (E_n - E_m)/\hbar$. Similar calculation of the expectation value of the square of the proton's position gives the indeterminacy of the proton. Both the expectation value of the position and its indeterminacy are used to represent the time evolution of the proton in Figure 3.

For symmetric potentials (Figure 2A), it is impossible to have the initial state coincide with one the eigenstates; as a result, several terms in the expansion given by eq 2 are needed. Because of the symmetry, the first term on the right of eq 3 vanishes. Consequently, the expectation value of the proton's position will oscillate between the wells. This oscillation is described by the second term in eq 3 (Figure 3A).

In asymmetric cases, it is possible to have the initial state coinciding or almost coinciding with the lowest eigenstate of the potential (Figure 2B). Then only one coefficient, C_1, will be close to unity, while the remaining coefficients will be zero or very small. In such cases the state function will remain confined to the well in which it was initially located (Figure 3B). It should be noted that the indeterminacy of the proton increases as it moves into the classically forbidden region, within the barrier.

Intermolecular Proton Exchange

The quantum mechanical description of the motion of the proton in double minimum potentials was first applied[7] to the calculation of the rates of exchange

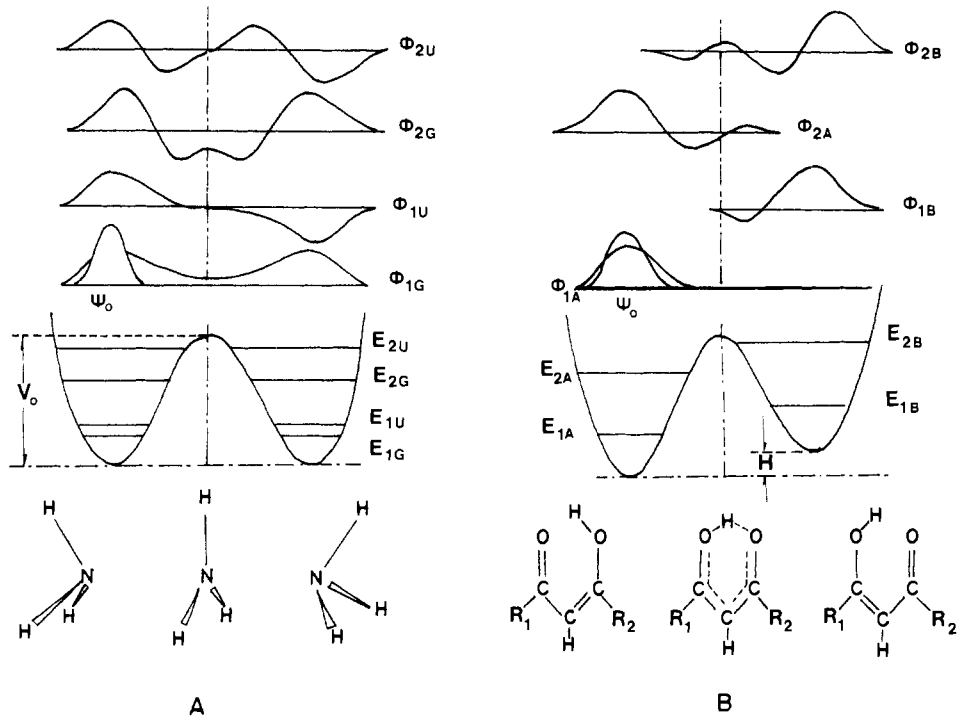

Figure 2. Tunnelling in bound systems: (A) energy levels and eigenfunctions for the potential representing the inversion of ammonia; (B) energy levels and eigenfunctions for a bound asymmetric double minimum potential (R_1 and R_2 differ from each other).

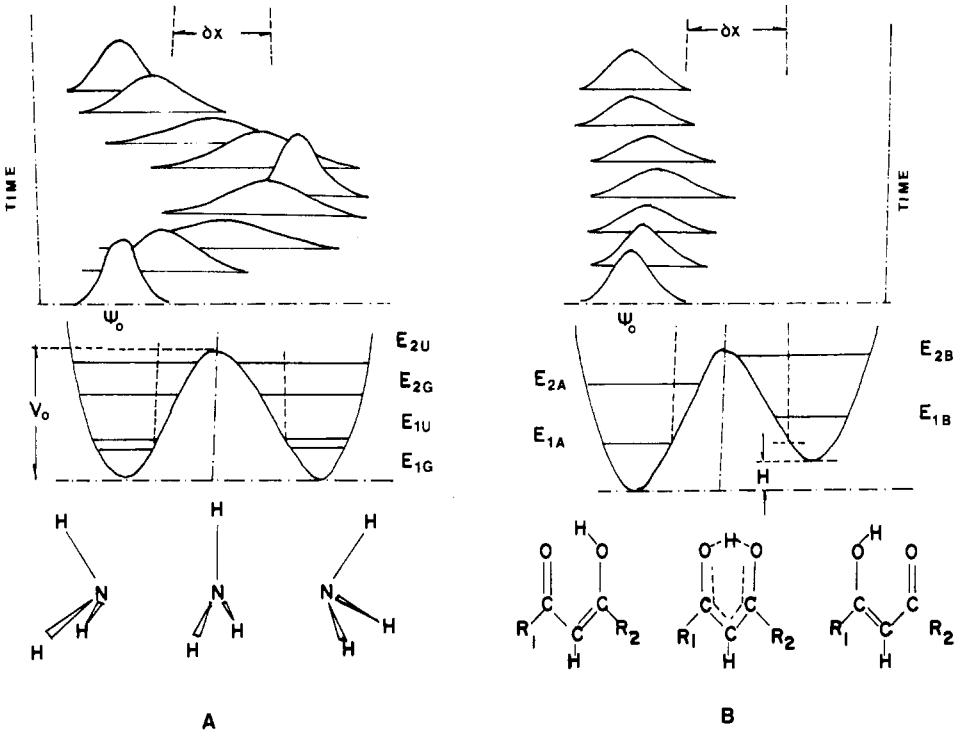

Figure 3. Time evolution of the state function representing the motion of the proton in a symmetric and in an asymmetric double minimum potential.

Table I
Parameters for Symmetric (S) and Asymmetric (A) Intermolecular Proton Exchange in Water and Methyl Alcohol Systems and for Intramolecular Proton Exchange in β-Hydroxyacrolein along the Reaction Coordinate (RC) and Direct Transfer (DT) Paths[a]

			D	V_0	m	tunnelling frequency
CH_3OHOCH_3	S	DT	0.384	9.49	1.0	4.00^{11}
CH_3OHOCH_3	A	DT	0.384	9.49	1.0	none
$CH_3OHHHOCH_3$	S	DT	0.374	8.61	1.0	7.00^{11}
CH_3OHOCH_3	A	DT	0.374	8.61	1.0	none
$H_2OH_2OHOH_2OH_2$	S	DT	0.365	7.60	1.0	1.00^{12}
$H_2OH_2OHOH_2OH_2$	A	DT	0.364	7.60	1.0	none
β-hydroxyacrolein	S	RC	0.457	11.60	4.3	2.27^{10}
β-hydroxyacrolein	S	DT	0.877	15.95	1.0	7.10^{10}

[a] Energy barrier V_0 in kcal/mol, effective mass m in amu, interminimal distance D in Å, and calculated frequencies in Hz.

between methanol and methoxide ion (eq i), between methyloxonium ion and methanol (eq ii), and between hydronium ion and water (eq iii). For selected con-

$$CH_3OH + {}^-OCH_3 = CH_3O^- + HOCH_3 \quad \text{(i)}$$

$$CH_3OH_2^+ + HOCH_3 = CH_3OH + {}^+H_2OCH_3 \quad \text{(ii)}$$

$$H_2O{\cdot}H_2OH^+ + OH_2{\cdot}OH_2 = H_2O{\cdot}H_2O + {}^+HOH_2OH_2 \quad \text{(iii)}$$

formations of the methyl group in (i) (Figure 4 A), and in (ii), the profile for the proton exchange is symmetric.[7] Energy barriers from 8.6 to 9.5 kcal/mol (Table I) were found with calculated rates of exchange from 3.98×10^{11} to 6.31×10^{11} Hz. Rotation of one methyl group in these geometries destroys the symmetry of the profile (Figure 4B), the wells are no longer indistinguishable, the eigenfunctions for the lower eigenstates are localized in their respective wells, and the expectation value of the proton's position fails to leak through the barrier.

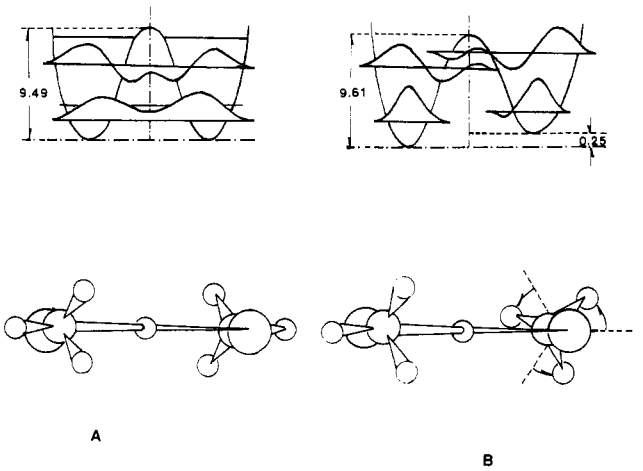

Figure 4. Eigenstates for the intermolecular proton exchange for the methyl alcohol system. Rotation of the methyl group destroys the symmetry of the profile, quenching tunnelling.

The results indicate that the rate of proton exchange for these systems is determined by the rate of rotation of the methyl group.

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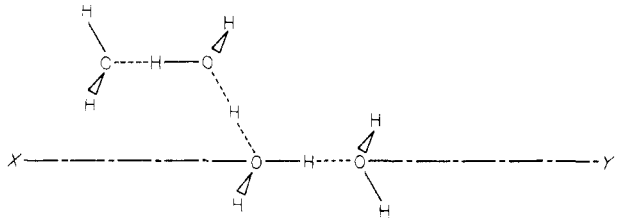
Table II
Parameters for the Coupled Motion of the Proton Exchange and the Methyl Group Rotation in α-Methyl-β-hydroxyacrolein[a]

						hydrogen		deuterium	
RC	m(H)	m(D)	D	V_0	V_3	A_{1g},A_{2u}	E_u,E_g	A_{1g},A_{2u}	E_u,E_g
RC	4.3	5.1	1.022	11.60	1.1	2.19 (08)	1.08 (08)	9.94 (07)	2.94 (07)
DT	1.1	2.1	0.811	17.93	1.1	3.77 (10)	1.88 (10)	1.94 (09)	0.94 (09)
experimental						3.77 (10)	1.88 (10)	1.94 (09)	0.94 (09)

[a] Energy barriers V_0 and V_3 in kcal/mol, effective mass m in amu, interminimal distance D in Å, energy differences in Hz. Significant energy levels in the two-dimensional potential were calculated by using the direct transfer (DT) and the reaction coordinate (RC) paths for the proton exchange.

The profile for the proton exchange between water molecules (reaction iii) is symmetric when the arrangement of the molecules is that of ice, for which the barrier is 7.6 kcal/mol, with an exchange rate of 1.0×10^{12} Hz.

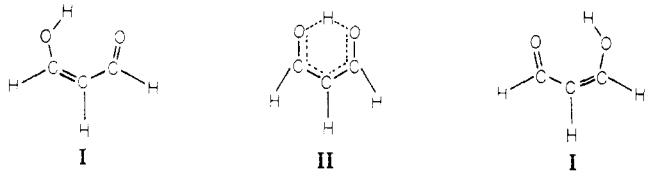


Rotation of one of the molecules around the axis xy destroys the symmetry of the profile. The expectation value of the proton's position fails to leak through the barrier, indicating that departure from the structure of ice reduces the rate of exchange between the water molecules. This result is consistent with the fact that experimentally the rate of proton transfer in ice is ten times faster than that in water.[8]

Intramolecular Proton Exchange

The theoretical studies for the methanol and water systems are meaningful for isolated systems, but their applicability to condensed phases is open to question. This might be settled by experimental evidence from microwave spectra, in which the interaction between a molecule and its surroundings is minimal.

The microwave spectrum of β-hydroxyacrolein[9] suggests the existence of a low-amplitude nonharmonic vibration due to the intramolecular hydrogen-bonded proton exchange. The geometry of minimum energy[10,11] corresponds to a conformation (I) in which the hydrogen-bonded proton is covalently bound to one of the oxygens:



I II I

The reaction coordinate for the interconversion of the two tautomers (I) has the intermediate structure II, which is 11.6 kcal/mol higher than the energy of I and has a significantly smaller C–C–C angle.[11] The effective mass for the interconversion is calculated as 4.288 amu for the normal (H) and 5.054 for the deuterated (D) species. The calculated rate of exchange of 2.25×10^{10} Hz is one order of magnitude smaller than the experimentally estimated value[11] (Table I). The experimental ratio $k(H)/k(D)$ of the exchange rates for the normal and deuterated species is much lower than the value predicted theoretically. Closer agreement results when the effective masses of the normal and deuterated species have the ratio of 1:2. This ratio would require a transfer in which the hydrogen isotope moves while the other atoms of the molecule remain in fixed positions. Such a direct transfer is justifiable since there is a difference of 3 orders of magnitude between the vibrational frequencies and the rate of proton exchange. The barrier for the direct transfer is 15.95 kcal/mol[11] with an interminimal distance of 0.877 Å (Table I). The calculated rate of exchange compares satisfactorily with the 7.08×10^{10} to 31.6×10^{10} Hz estimated experimentally.

Substituted β-hydroxyacroleins provide the opportunity to study the role of the symmetry of the profile in proton exchange mechanisms. α-Methyl-β-hydroxyacrolein is the simplest of these systems for which reliable theoretical calculations are feasible. In this molecule, the double minimum potential for the interconversion of the two tautomers will be symmetric only when one C–H bond of the methyl group (Figure 5A) is in a plane perpendicular to the principal plane of the molecule. Departure from this geometry, by rotation of the methyl group, destroys the symmetry of the profile, considerably reducing the rate of proton exchange (Figure 5B). As a result, fast exchange will occur only at selected conformations of the methyl group, and then a strong coupling of the two motions will occur. This coupling has been suggested by Sanders and Wilson[12] from the interpretation of the microwave spectrum of the molecule. A two-dimensional potential energy function was used to represent the coupled motion of the proton and the methyl group:[13]

$$V(x) + (V_3/2)(x_0 - x \cos 3\theta) \qquad (4)$$

x is the distance, along the reaction path, of the proton from its position of maximum energy, and x_0 is the position of the minimum. The function $V(x)$ represents the symmetric double minimum potential for the proton exchange, and V_3 is the torsional barrier for the methyl group. The potential function given by eq 4 belongs to the D_{3d} symmetry group. As in the case of β-hydroxy-

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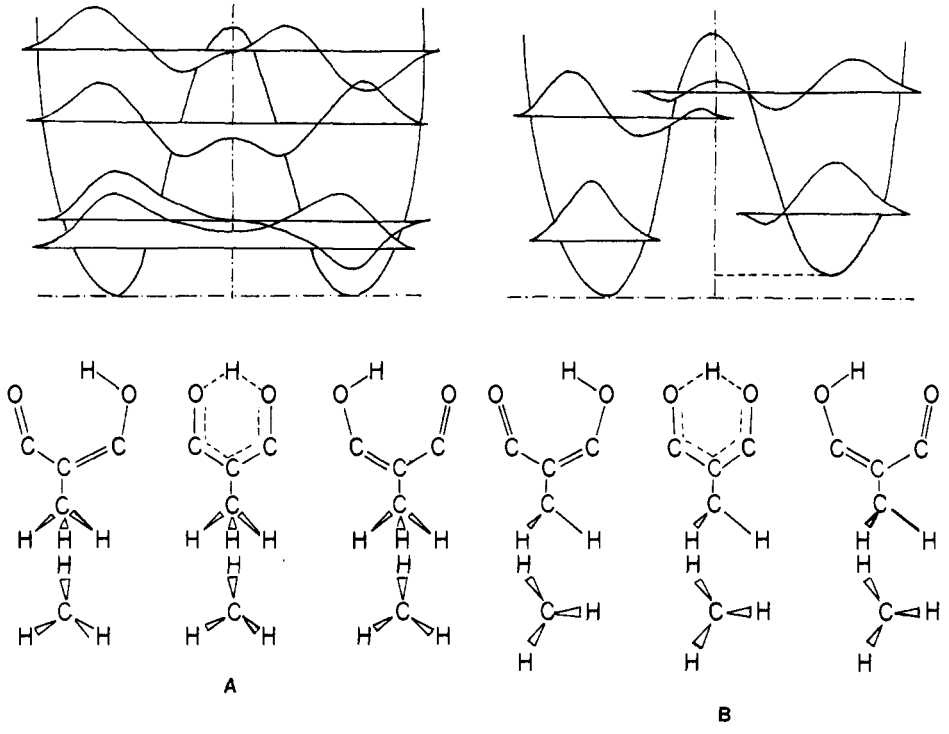

Figure 5. Eigenstates for the intramolecular proton exchange in α-methyl-β-hydroxyacrolein. The proton will tunnel only when the conformation of the methyl group leads to a symmetric profile for the exchange (A), not when the profile is asymmetric (B).

acrolein, two reaction profiles were used to determine the function $V(x)$. The standard reaction coordinate[13] again involves appreciable displacement of the heavy atoms, especially the oxygens. As a result the effective mass is large. The direct transfer has a higher barrier but an effective mass of only 1.0 for the normal (H) species. The energy splitting between the pertinent energy levels as well as the parameters of the potential are given in Table II. The experimentally estimated energy splittings are also listed. As in the case of β-hydroxyacrolein, the direct transfer seems to give a result much closer to the experimental value than the one obtained by using the reaction coordinate.

Naphthazarin and its monomethyl- and dimethyl-substituted derivatives (Figure 6) provide excellent systems for the study of the role of the symmetry of the profile. These systems have two intramolecular hydrogen-bonded protons. It is known from infrared and crystallographic data[14] that the hydrogen bonds are asymmetric. Naphthazarin is reported to undergo, in solution, fast exchange between its two tautomers.[14,15] It has been claimed that the interconversion involves a concerted proton exchange in a symmetric double minimum potential. Monosubstituted naphthazarins[15] exist only as one of two possible tautomers: ethyl, hydroxyl, methoxyl, or acetoxyl groups produce the 2-substitured derivative while the acetyl group gives the 7-substituted derivative. Similarly, only one tautomer is detected in methylnaphthazarin, in which the presence of the methyl group is expected to cause only a small departure from the symmetry of the profile of naphthazarin. Introduction of a second methyl group, on the other ring, reestablishes the symmetry of the profile and, with it, the fast interconversion between the tautomers.

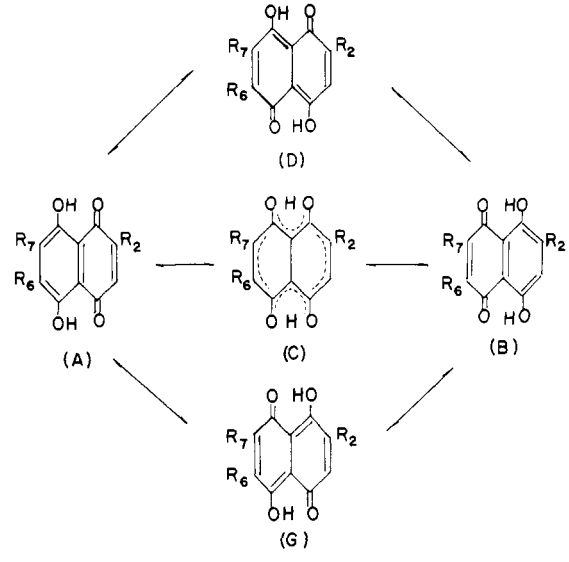

Figure 6. Schematic representation of the various proton transfer pathways in naphthazarin and its methyl derivatives. The path A — C — B represents the concerted exchange of both protons. A — G — B and A — D — B show the stepwise exchanges. In each compound, A and B are absolute minima, C is an absolute maximum, and D and G are saddle points.

Ab initio SCF–MO calculations[16] on naphthazarin, 2,7-, and 2,6-dimethylnaphthazarin, and monomethylnaphthazarin indicate that each has two minimum energy structures with two asymmetric hydrogen bridges with both hydroxyls on the same ring (A and B in Figure 6). For naphthazarin (Figure 7A) and for the two dimethylnaphthazarins, structure A has the same energy as B, while for monomethylnaphthazarin the tautomer that has the methyl attached to the benzenoid

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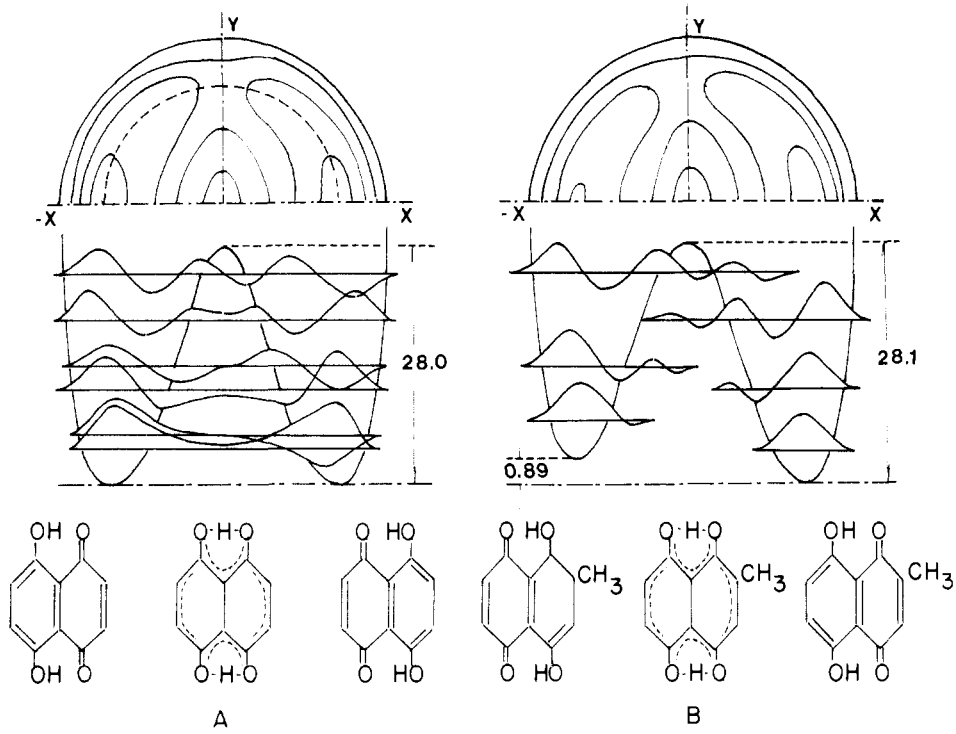

Figure 7. (Top) Two-dimensional potential energy profile for naphthazarin (A), and for monomethylnaphthazarin (B). The coordinate x represents the concerted exchange of both protons while y connects the two saddle points. The broken line represents the stepwise transfer which corresponds to the "reaction coordinate path". (Bottom) One-dimensional potential energy profile for the concerted proton exchanges in naphthazarin (A) and monomethylnaphthazarin (B).

ring is 0.9 kcal/mol above the 2-methyl tautomer (Figure 7B). Each two-dimensional potential energy surface representing the exchange between two structures has one absolute maximum about 28 kcal/mol above the minima and two saddle points at 25 kcal/mol above the minima (Figure 8). The maximum corresponds to the barrier for the concerted proton transfer between the two minimum energy tautomers while the saddle points, with the structure of 4,8-dihydroxy-1,5-naphthoquinone, constitute the barrier for the stepwise proton transfer. While the potential energy surface for the exchange between the two protons has C_{2v} symmetry for naphthazarin and C_{1h} symmetry for 2,6- and C_2 symmetry for 2,7-dimethylnaphthazarin, that for monomethylnaphthazarin has no symmetry at all.

For naphthazarin, the potential energy surface is a polynomial of fourth degree in ξ for one proton, and in ζ (Figure 8) for the other, ξ and ζ being the distance of each proton from the position it has at the absolute maximum. By the appropriate coordinate transformation the polynomial can be written as

$$V = V_0 - A_2x^2 + A_4x^4 - B_2y^2 + B_4y^4 + Cx^2y^2 \quad (5)$$

where the variable x represents the path for the concerted proton transfer between the minimum energy structures, while y, perpendicular to x, connects the two saddle points. The coefficients are obtained from the energy of the absolute maximum V_0, the energy at the saddle points V_1, and the interminimal distance D. The eigenstates of each potential are calculated by the variational method, with products of two-dimensional oscillator functions as basis set. Initially the protons are located at the positions they have in one of the minimum energy structures A or B. A product of

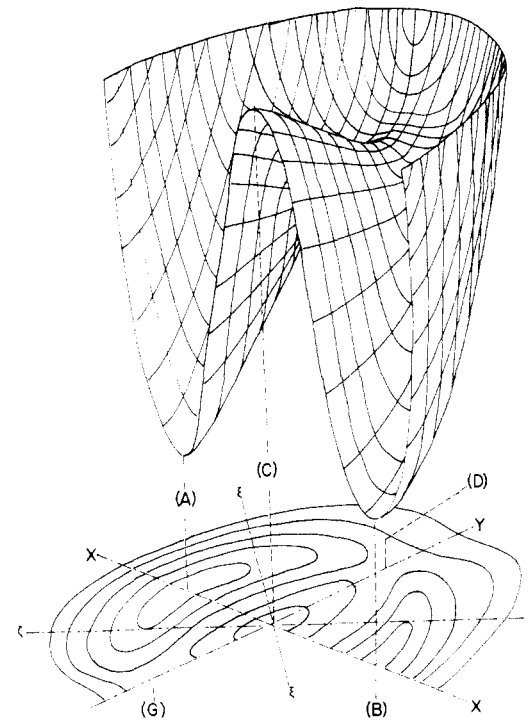

Figure 8. Potential energy surface for the two-dimensional proton exchange in naphthazarin.

two-dimensional Gaussians centered at this minimum is the initial state. This product is expanded in terms of stationary states in a manner similar to that for the one-dimensional case. For this choice of initial state, only the A_1 and B_1 symmetry species of the C_{2v} group contribute to the expansion. In naphthazarin the tunnelling frequency is dependent on the difference of the lowest A_1 and B_1 levels. This difference and the energy

Table III
Proton Exchange of the Two Minimum Energy Tautomers of Naphthazarin (IV), 2,6- and 2,7-Dimethylnaphthazarins (V and VI), and Monomethylnaphthazarin (VII)

	R_2	R_6	R_7	symm.	V_0	V_1		V_2	H	one-dim freq	two-dim freq
IV	H	H	H	C_{2v}	28.0	25.0	=	25.0	0.0	20.5 (6)	40.0 (6)
V	CH_3	CH_3	H	C_{1h}	27.2	24.7		24.7	0.0	25.5 (6)	
VI	CH_3	H	CH_3	C_2	27.3	24.5	=	24.5	0.0	24.9 (6)	
VII	CH_3	H	H	none	28.1	25.7		25.7	0.9	none	none

[a] Energy barriers V_0 of the absolute maximum and V_1 and V_2 of the saddle points in kcal/mol, energy difference H between the two absolute minima and the frequency in Hz of the proton exchange of the two minimum energy tautomers of naphthazarin (IV), 2,6- and 2,7-dimethylnaphthazarins (V and VI), and monomethylnaphthazarin (VII).

of each pertinent geometry are given in Table III for naphthazarin and its methyl derivatives.

On a two-dimensional surface (Figure 8), the expectation value of the proton's position is a function of two variables: x and y. With the present choice of initial state, the expectation value of the proton's position will move along the x axis, as $\langle y \rangle = 0$. Classically one would say that only the concerted proton transfer contributes to the exchange. The present quantum mechanical result is a consequence of the fact that for the stepwise transfer the possible trajectories, one through the upper saddle point (D), the other through the lower saddle point (G), are indistinguishable and therefore equally probable (Figure 6).

Tunnelling frequencies for the concerted proton exchanges were calculated by using one-dimensional profiles. The differences between the results in one and in two dimensions indicate that both concerted and stepwise proton exchanges occur. The latter is the principal contributor in deuterated naphthazarin. This is expected since the large effective mass of the deuterated species makes the system behave more classically, following the "reaction coordinate path", in this case the stepwise mechanism.

Monomethylnaphthazarin deserves special attention. The tautomer which has the methyl group attached to the quinonoid ring (2-methylnaphthazarin) is 0.9 kcal/mol more stable than the other tautomer (7-methylnaphthazarin). The small calculated difference between the methylnaphthazarin tautomers would indicate an equilibrium with $K = 0.23$ at room temperature. The calculations also suggest that, if the hydrogen-bonded protons were initially located at the positions they have in 2-methylnaphthazarin, they will stay there and will not move to the positions they would have in 7-methylnaphthazarin. It should be stressed that the confinement of each hydrogen-bonded proton to one position is due to the combination of asymmetry in the potential and great height of the barrier. An exchange rate of 1.17×10^{-9} Hz is calculated by the semiclassical WKB method (formula 2.120 of ref 1), a frequency equivalent to a tunnelling time of 27 years.

The protons' not exchanging would explain the ^1H NMR spectrum of monomethylnaphthazarin, for in it the 2-methyl tautomer seems to be the predominant structure, since there are two signals for ring hydrogens and both the quartet of the quinonoid ring hydrogens and the doublet of the methyl group hydrogens are well defined.

Concluding Remarks

The dependence of tunnelling on the symmetry of the profile for the proton exchange is specially significant in systems with barriers above 10 kcal/mol where the tunnel effect will cease to manifest itself when the symmetry is eliminated.

The symmetry can be eliminated by a very small perturbation such as the one produced by the rotation of the methyl group in the methyl alcohol systems and in α-methyl-β-hydroxyacrolein, where the rates of exchange seem to be determined by the frequency of rotation of the methyl group.

This effect may play a fundamental role in the kinetics of chemical reactions in which the rate-determining step is the transfer of the proton in a hydrogen-bonded intermediate. It is possible that the profile for the proton transfer is symmetric only every time a part of the molecule forming the activated complex attains a particular conformation or geometry, in which case the rate-determining step will depend on the frequency with which such conformation or geometry is attained.