curately via a pulse radiolysis technique.[22]

The time-resolved microwave conductivity measurements were carried out by using the same cell design and microwave circuitry reported previously.[18] The solutions, of absorbance at approximately unity, were flash photolyzed at 308 nm by using 10-ns fwhm pulses from a Lambda Physik EMG100 excimer laser with a total incident energy flux per pulse of 6.9 mJ/cm^2 (determined by using (dimethylamino)nitrostilbene[18] as a secondary actinometer). The response time of detection, controlled mainly by the microwave cavity, was 4 ns. The transient changes in detector output were recorded by using a Tektronix-7912 transient digitizer. Calculated fits to the conductivity transients included corrections for the system response function, the shape of the laser pulse, and the geometrical distribution of products in the cell as described previously.[18]

Materials. Spectrograde solvents were obtained from Merck and used without further purification. Compounds **1** and **2** were both synthesized by a Wittig-type condensation from 1-phenyl-4-piperidone (**3**), which was prepared as described previously.[23,24]

1-Phenyl-4-(2-naphthylmethylene)piperidine (1). A solution of triphenyl-2-naphthylphosphonium bromide (41 mmol, prepared from reaction of triphenylphosphine and 2-(bromomethyl)naphthalene (Aldrich)) in 200 mL of tetrahydrofuran was stirred under dry nitrogen and cooled to −60 °C. Of *n*-Butyllithium, 1 equiv (16.3 mL of a 1.6-M solution in *n*-hexane) was slowly added. After 15 min the reaction mixture was warmed to room temperature and **3** (27 mmol) was added. Stirring at room temperature was continued for 60 h, followed by removal of the solvent in vacuo. To the residue 150 mL of HCl (20%) and 300 mL of ether were added. The acid layer were separated and extracted 8 times with ether, made alkaline (pH 13) with NaOH, and again extracted with ether. The latter extracts were dried on $MgSO_4$ and concentrated in vacuo. The residue was purified by chromatography over a short silica column by using ethyl acetate/p.a. 60–80 (1:10 v/v) as eluent, followed by recrystallization from a *n*-pentane/ether mixture: yield, 7.4%, white crystals; mp 87–89 °C; UV (cyclohexane) 249 nm (ϵ 53 000 M^{-1} cm^{-1}), 279 (14 000 M^{-1} cm^{-1}), 288 (13 800 M^{-1} cm^{-1}); ^1H NMR (250 MHz, $CDCl_3$) δ 6.8–7.8 (m, 12 H), 6.5 (s, 1 H), 3.4 (t, 2 H), 3.3 (t, 2 H), 2.7 (t, 2 H), 2.55 (t, 2 H); high-resolution mass spectrum, *m/z* 299.16738. Anal. Calcd for $C_{22}H_{21}N$: 299.1674.

1-Phenyl-4-(4-cyano-1-naphthylmethylene)piperidine (2). Triphenyl-1-(4-cyano)naphthylphosphonium bromide (**4**) was prepared from triphenylphosphine and 4-(bromomethyl)-1-naphthonitrile[25] in refluxing toluene (yield ~90%). A solution of **4** (4.3 mmol) in 3 mL of methanol was poured in 10 mL of aqueous 1 N NaOH. The yellow ylide which precipitated from the solution was separated by immediate extraction with 75 mL of benzene. The benzene extract was washed twice with ice–water, dried on magnesium sulfate, and concentrated in vacuo to about 30 mL. The ketone **3** (4.29 mmol) was then added, and the reaction mixture was refluxed under a nitrogen atmosphere for 28 h. The reaction mixture was transferred into a separating funnel, diluted with benzene (50 mL), washed with water (3 × 20 mL), dried on magnesium sulfate, and concentrated in vacuo. The residue was dissolved in warm ethanol/water (10:1 v/v) from which, after treatment with activated carbon and filtration, **2** crystallized in light yellow needles. The product was purified by repeated crystallization from ethanol: yield, 5%; mp 124–125 °C; UV (cyclohexane) 234 nm (ϵ 52 000 M^{-1} cm^{-1}), 308 (12 000 M^{-1} cm^{-1}); ^1H NMR (250 MHz, $CDCl_3$) δ 6.8–8.3 (m, 11 H), 6.7 (s, 1 H), 3.4 (t, 2 H), 3.2 (t, 2 H), 2.7 (t, 2 H), 2.4 (t, 2 H); high-resolution mass spectrum, *m/z* 324.1627. Anal. Calcd for $C_{23}H_{20}N_2O$: 324.1627.

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Registry No. 1, 91759-51-2; **2**, 91759-52-3.

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Intramolecular Proton Exchange in 9-Hydroxyphenalen-1-one and Methyl-9-hydroxyphenalen-1-one

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Abstract: A recent ^{13}C NMR study indicates that the fast proton exchange in 9-hydroxyphenalen-1-one is not eliminated when the symmetry of the potential energy profile for the exchange is destroyed by adding a methyl group to form methyl-9-hydroxyphenalen-1-one. Ab initio SCF calculations on 9-hydroxyphenalen-1-one confirm the existence of two equivalent minimum-energy structures with an asymmetric hydrogen bridge. The interconversion between these two structures occurs through a symmetric (C_{2v}) intermediate which is 5.20 kcal/mol above the minimum-energy C_s structures. A 0.64-Å interminimal distance for the resulting double-minimum potential produces a gerade–ungerade splitting of 105.5 cm^{-1} for the hydrogen and 15.8 cm^{-1} for the deuterated species, in good agreement with the experimental results of a laser-excited fluorescence and fluorescence-excitation study. Calculations for methyl-9-hydroxyphenalen-1-one gave a 0.46-kcal/mol energy difference between the two tautomers, in agreement with fluorescence results. The change of the probability density of the proton as a function of time is used to calculate the maximum fraction of the proton that leaks through the barrier. We found that only one-third of the proton will leak to the other well, and this with the frequency increased to 165 cm^{-1}.

In an intramolecular proton exchange, if the initial and final structures are identical, the double-minimum potential for the exchange is symmetric and tunneling will occur whenever barrier and distance between minima are finite.[1-4] When a change in structure destroys the symmetry of the double-minimum potential, the proton will tunnel only if the barrier is low and the interminimal distance is small, or if the energy difference between the minima is very small.[5] This approach has been used to explain

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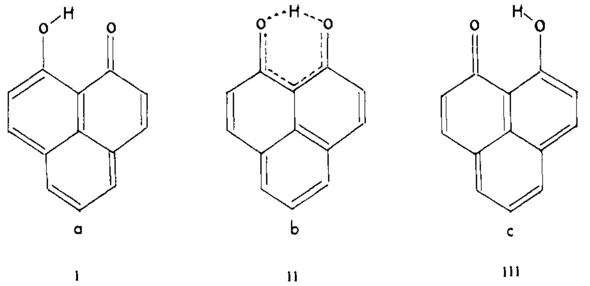

Figure 1. (I) Initial structure, (II) transition-state structure, and (III) final structure.

the fast interconversion between equivalent tautomers which occurs in naphthazarin despite high barriers of about 25 and 28 kcal/mol for concerted and stepwise proton exchanges, respectively, but the absence of interconversion between the nonequivalent methyl-substituted tautomers which differ in energy by about 0.9 kcal/mol.[6]

9-Hydroxyphenalen-1-one, shown in Figure 1, has a very strong intramolecular hydrogen bond,[7] but it shows no absorption for the O–H stretching vibration in its infrared spectrum.[8] X-ray crystallography at 298 K[9] and ^{1}H and ^{13}C NMR[10] studies indicate either that the hydrogen bond is symmetric, as in Figure 1b, or that a rapid interconversion occurs between the two asymmetrically hydrogen bonded structures, as in Figure 1, parts a and c. X-ray photoelectron,[11] deuteron quadrupole,[12] and vibronically resolved laser-excited fluorescence and fluorescence excitation in an argon matrix at 4 K[13] indicate that the hydrogen bond is asymmetric and that intramolecular proton exchange occurs between two equivalent tautomers. The barrier for the double-minimum potential was estimated to be 23 ± 12 kcal/mol.[13] This estimate was made on the basis of the 9 ± 1 cm^{-1} gerade–ungerade splitting of the deuterated species and an interminimal distance of 0.4 Å. This interminimal distance was, however, not obtained from any direct measurement but was estimated from general crystallographic data which provide a statistical correlation between the oxygen–oxygen distance and the position of the hydrogen in a hydrogen bridge. With a barrier of this height, the destruction of the symmetry of the double-minimum potential would eliminate tunneling. This destruction of the symmetry can be accomplished by attaching a methyl group in the 2 or 8 position. However, a ^{13}C NMR study[14] indicates rapid interconversion between the 2- and 8-methyl tautomers of methyl-9-hydroxyphenalen-1-one. The fact that the double-minimum potential is asymmetric is confirmed by fluorescence data[15] which put the energy difference between the tautomers at 180 cm^{-1}.

To determine why, unlike for naphthazarin, the introduction of a methyl group does not stop fast intramolecular proton exchange, an ab initio quantum-mechanical study was performed on 9-hydroxyphenalen-1-one and its 2- and 8-monomethyl-substituted tautomers. Calculations were performed to determine the extent of asymmetry, if any, in the hydrogen-bonded bridge, the height of the barrier, and the interminimal distance.

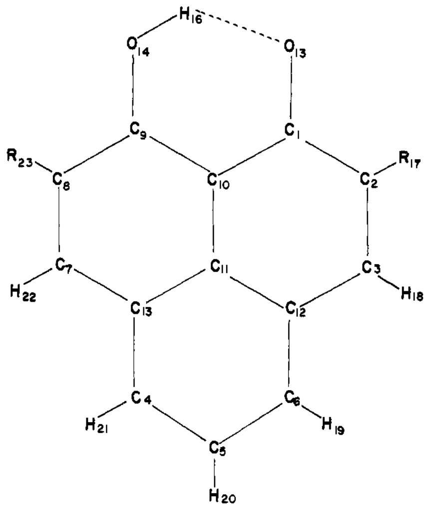

Figure 2. Diagram with thhe identities of the atoms and the numbers by which they are referred to in the text and in the tables for 9-hydroxyphenalen-1-one and the 2-methyl and 8-methyl tautomers of methyl-9-hydroxyphenalen-1-one.

Table I. Energies in Atomic Unit of the Optimized Structures Depicted in Figure 1

9-Hydroxyphenalen-1-one	
SCF energy of minimum energy C_s structure	−638.5949931
energy relative to minimum	
initial and final states, C_s	0.0000000
transition state, C_{2v}	0.0082929
Methyl-9-hydroxyphenalen-1-one	
minimum energy structure	2-methyltautomer with methyl group staggered to C=O
SCF energy of minimum energy structure	−677.1805910

	2-methyl tautomer	transition State	8-methyl tautomer
methyl staggered to C=O			
energy rel to min.	0.0000000	0.0086471	0.0007355
energy barrier	0.0086471		0.0079116
methyl eclipsed to C=O			
energy rel to min.	0.0013516		0.0019671
barrier to rotation	0.0013516		0.0012316
average barrier to rotation of methyl group: 0.0012916			

Calculations

Ab Initio SCF Calculation of the Potential Energy Profile. Ab initio SCF molecular orbital calculations were used for the electronic energy[16,17] at the STO-3G level[18] with convergence on the SCF density matrix set at 1 × 10^{-7} hartree. The significant geometries, two absolute minima and one maximum for 9-hydroxyphenalen-1-one, were determined by using energy gradient optimization methods[19] with the proper symmetry as a constraint. All geometries turned out to be planar. The geometry for the intermediate structure, which has C_{2v} symmetry, was optimized to a structure corresponding to a col in the potential energy surface.

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Table II. Bond Distances in Angstroms of the Significant Structures Depicted in Figure 2 for 9-Hydroxyphenalen-1-one and the 2- and 8-Methyl Tautomers of Methyl-9-hydroxyphenalen-1-one

	initial and final states A, B	transition state C
Bond Lengths		
C(11)–C(10)	1.4271	1.4201
C(9)–C(10)	1.3814	1.4246
C(8)–C(9)	1.4403	1.4707
C(7)–C(8)	1.3487	1.3381
C(13)–C(7)	1.4394	1.4629
C(13)–C(11)	1.4041	1.4125
C(1)–C(10)	1.4891	1.4246
C(2)–C(1)	1.4984	1.4707
C(3)–C(2)	1.3244	1.3381
C(12)–C(3)	1.4793	1.4629
C(11)–C(12)	1.4294	1.4125
C(6)–C(13)	1.4204	1.3942
C(5)–C(6)	1.3627	1.3876
C(5)–C(4)	1.4124	1.3876
C(4)–C(12)	1.3705	1.3942
O(15)–C(9)	1.3658	1.2954
O(14)–C(1)	1.2425	1.2954
H(22)–C(7)	1.0843	1.0855
H(21)–C(6)	1.0835	1.0842
H(20)–C(5)	1.0818	1.0813
H(19)–C(4)	1.0837	1.0842
H(18)–C(3)	1.0850	1.0855
H(16)–O(15)	1.0027	1.1704
H(16)–O(14)	1.5893	1.1704
Interoxygen Distance		
O(14)–O(15)	2.5216	2.3065
For 9-Hydroxyphenalen-1-one		
H(23)–C(8)	1.0816	1.0814
H(17)–C(2)	1.0821	1.0814
For 2-Methyl-9-hydroxyphenalen-1-one, Staggered and Eclipsed		
C(17)–C(2)	1.524	1.524
H(23)–C(8)	1.0816	1.0814
H(Me)–C(17)	1.085	1.085
For 8-Methyl-9-hydroxyphenalen-1-one, Staggered and Eclipsed		
C(23)–C(8)	1.524	1.524
H(17)–C(2)	1.0821	1.0814
H(Me)–C(23)	1.085	1.085

Table III. Bond Angles in Degrees of the Significant Structures Depicted in Figure 2 for 9-Hydroxyphenalen-1-one and the 2- and 8-Methyl Tautomers of Methyl-9-hydroxyphenalen-1-one

	initial and final states A, B	transition state C
Bond Angle		
C(9)–C(10)–C(11)	120.398	121.832
C(1)–C(10)–C(11)	120.631	121.832
C(10)–C(9)–C(8)	119.603	117.422
C(9)–C(8)–C(7)	120.128	120.207
C(8)–C(7)–C(13)	121.590	122.899
C(7)–C(13)–C(11)	118.403	117.863
C(10)–C(11)–C(13)	119.878	119.777
C(10)–C(1)–C(2)	116.262	117.422
C(1)–C(2)–C(3)	121.408	120.207
C(2)–C(3)–C(12)	122.950	122.899
C(3)–C(12)–C(11)	118.326	117.863
C(10)–C(11)–C(12)	120.424	119.777
C(11)–C(13)–C(6)	119.054	118.859
C(13)–C(6)–C(5)	120.697	120.755
C(6)–C(5)–C(4)	120.214	120.327
C(11)–C(12)–C(4)	119.429	118.859
C(12)–C(4)–C(5)	120.907	120.755
O(15)–C(9)–C(10)	122.172	119.309
O(14)–C(1)–C(10)	120.894	119.309
H(16)–O(15)–C(9)	103.711	102.340
H(16)–O(14)–C(1)	101.745	102.340
H(23)–C(8)–C(9)	118.070	118.022
H(22)–C(7)–C(13)	118.226	117.274
H(21)–C(6)–C(13)	118.828	119.507
H(20)–C(5)–C(4)	119.289	119.837
H(19)–C(4)–C(12)	119.818	119.507
H(18)–C(3)–C(12)	116.691	117.274
H(17)–C(2)–C(1)	116.739	118.022
O- -H- -O Bridge Angle		
O(15)–H(16)–O(14)	152.507	160.367
For 9-Hydroxyphenalen-1-one		
H(22)–C(8)–C(9)	118.070	118.022
H(17)–C(2)–C(1)	116.739	118.022
For 2-Methyl-9-hydroxyphenalen-1-one, Staggered and Eclipsed		
H(22)–C(8)–C(9)	118.070	118.022
C(17)–C(2)–C(3)	122.88	122.79
H(Me)–C(17)–C(2)	110.65	110.65
For 8-Methyl-9-hydroxyphenalen-1-one, Staggered and Eclipsed		
H(17)–C(2)–C(1)	116.739	118.022
C(22)–C(8)–C(7)	122.31	122.79
H(Me)–C(22)–C(8)	110.65	109.65
H(Me)–C(Me)–H(Me)	120.00	120.00

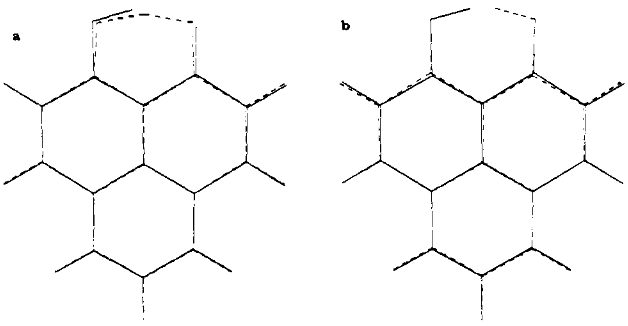

Figure 3. Positions of the atoms in the optimized geometries relative to the center of mass and the mutual rotational axes for proton transfer in 9-hydroxyphenalen-1-one. (a) Initial (C_s symmetry) and transition (C_{2v} symmetry) states; (b) initial (C_s symmetry) and final (C_s symmetry) states.

All analytical nuclear Cartesian forces[17] for the optimized geometries were less than 0.0005 hartree/Bohr.

For methyl-9-hydroxyphenalen-1-one, a methyl group was added to the optimized STO-3G structures of 9-hydroxyphenalen-1-one at the minima and in the transition state. The positions of the hydrogens in the bridges and of the atoms in the methyl group were then optimized and the corresponding SCF energies determined. Two conformations of the methyl group, eclipsed and staggered, were considered.

The structures with their energies are given in Table I. The configurations are shown in Figure 1. The bond lengths and angles are given in Tables II and III. Table IV gives the Cartesian coordinates of the initial, intermediate, and final states, referred to the center of gravity, and after all the rotations have been eliminated. Computer-generated plots of the relative positions of these geometries are depicted in Figure 3.

Double-Minimum Potential Energy Profile. The sum of a parabola and a Gaussian is used to represent the double-minimum potential (eq 1, ref 5). From the values of the barrier, the interminimal distance, and the curvatures at the minima, the parameters a_2, V_0, α, and x_0 of the function were determined. The interminimal distance was taken as the length of the arc connecting the initial and final geometries and was calculated from the values given in Table IV. The curvatures at the stationary points were determined from the change in the energy of the molecule as its geometry changes along the reaction coordinate. The value of the effective mass was taken as the nominal value for the proton or deuteron, as if the proton transfers directly from the initial to the final state through tunneling, independently from the motion of the remaining atoms in the molecule, as is plausible from various

Table IV. Cartesian Coordinates for the Optimized Geometries of the Initial and Final (C_{2s} Symmetry) and the Transition (C_{2v} Symmetry) States of 9-Hydroxyphenalen-1-one Referred to the Center of Mass and Mutual Rotational Axes after Separation of Rotational Dispalcements[a]

atom		initial	transition	final	S(I,T)	S(I,F)
C(10)	X	0.02362	0.00000	−0.02362	0.03163	0.04725
	Z	−0.86429	−0.84326	−0.86429		
C(11)	X	0.01645	0.00000	−0.01645	0.02162	0.03290
	Z	0.56281	0.57683	0.56281		
C(9)	X	1.21866	1.21030	1.25388	0.03823	0.08027
	Z	−1.55731	−1.59461	−1.62944		
C(8)	X	2.46235	2.47430	2.51310	0.01679	0.05255
	Z	−0.83094	−0.84273	−0.81733		
C(7)	X	2.45861	2.46172	2.48049	0.02268	0.02455
	Z	0.51778	0.49531	0.50664		
C(13)	X	1.23043	1.22599	1.21971	0.01087	0.01611
	Z	1.26839	1.27831	1.28041		
C(1)	X	−1.25388	−1.21030	−1.21866	0.05579	0.08027
	Z	−1.62944	−1.59461	−1.55731		
C(2)	X	−2.51310	−2.47430	−2.46235	0.04638	0.05255
	Z	−0.81733	−0.84273	−0.83094		
C(3)	X	−2.48049	−2.46172	−2.45861	0.02193	0.02455
	Z	0.50664	0.49531	0.51778		
C(12)	X	−1.21971	−1.22599	−1.23043	0.00662	0.01611
	Z	1.28041	1.27831	1.26839		
C(6)	X	1.20288	1.20365	1.20281	0.01623	0.03772
	Z	2.68851	2.67230	2.65080		
C(5)	X	0.01789	0.00000	−0.01789	0.01794	0.03578
	Z	3.36128	3.36266	3.36128		
C(4)	X	−1.20281	−1.20365	−1.20288	0.02152	0.03772
	Z	2.65080	2.67230	2.68851		
O(15)	X	1.26782	1.15327	1.25333	0.11932	0.05230
	Z	−2.92218	−2.88876	−2.87193		
O(14)	X	−1.25333	−1.15327	−1.26782	0.10147	0.05230
	Z	−2.87193	−2.88876	−2.92218		
H(23)	X	3.38312	3.39897	3.44606	0.01664	0.07095
	Z	−1.39837	−1.40344	−1.36561		
H(22)	X	3.39438	3.39832	3.40290	0.02183	0.01502
	Z	1.06554	1.04407	1.07791		
H(21)	X	2.14181	2.13852	2.13632	0.00860	0.02862
	Z	3.22929	3.22134	3.20120		
H(20)	X	0.00068	0.00000	−0.00068	0.00119	0.00136
	Z	4.44299	4.44397	4.44299		
H(19)	X	−2.13632	−2.13852	−2.14181	0.02026	0.02862
	Z	3.20120	3.22134	3.22929		
H(18)	X	−3.40290	−3.39832	−3.39438	0.03415	0.01502
	Z	1.07791	1.04407	1.06554		
H(17)	X	−3.44606	−3.39897	−3.38312	0.06041	0.07095
	Z	−1.36561	−1.40344	−1.39837		
H(16)	X	0.30284	0.00000	−0.30284	0.32100	0.60568
	Z	−3.19476	−3.08831	−3.19476		

[a] All distances are in angstrom units. The column labeled S(I,T) gives the linear dispacement between the initial and transition states. The column labeled S(I,F) gives the linear displacement between the initial and final states.

Table V. Values Used to Calculate the Parameters of the Function Fitted to the One-Dimensional Double-Minimum Potential, the Eigenvalues of the Lower Eigenstates in au, the Frequency of Oscillation of the probability Density in Hz, and the Fraction of the Tunneling Nucleus That Reaches the Other Well for the Normal and Deuterated Species of 9-Hydroxyphenalen-1-one and the 2- and 8-Methyl Tautomers of Methyl-9-hydroxyphenalen-1-one

energy barrier	0.008293
interminimal distance	1.2128
energy difference between minima	0.007355
mass in amu for proton	1.000
mass in amu for deuteron	2.000
A_2	0.05673
V_0	0.06195
α	1.72995
x_0 (asymmetric case)	0.005346

Eigenvalues for 9-Hydroxyphenalene-1-one

	proton	deuteron
g_1	0.0042562531	0.0032518102
u_1	0.0047374172	0.0033242683
g_2	0.0104690903	0.0080835318
u_2	0.0143668981	0.0095462861
Frequency of Oscillation in s^{-1}	0.3166×10^{13}	0.4768×10^{12}
Energy Difference of the Two Lower Eigenstates in cm^{-1}	105.5	15.9
Fraction of the Tunneling Reaching the Other Well	1.0	1.0

Eigenvalues for the Methyl-9-hydroxyphenalen-1-one

	proton	deuteron
g_1	0.0040390690	0.0029817801
u_1	0.0048040357	0.0036693431
g_2	0.0101542106	0.0079288804
u_2	0.0133418273	0.0091433786
Frequency of Oscillation in s^{-1}	5.03×10^{12}	4.52×10^{12}
Energy Difference of the Two Lower Eigenstates	167.8	150.8
Fraction of the Tunneling Nucleus Reaching the Other Well	0.30	<0.03

experimental and theoretical studies.[13,23-26]

The stationary eigenstates of the Hamiltonian operator for the proton or deuteron were calculated by the variational method.[5,21] Computer-generated plots of the profiles with the eigenvalues and the eigenfunctions for the lower stationary states are shown in Figure 4, parts a and c. The parameters for these potentials, the eigenvalues and the difference in energy of the lower two levels for the proton and the deuteron, are given in Table V.

Determination of the Time Evolution of the System. The proton was initially localized in one well, as if it were confined to the position it would have if the system consisted only of one of the minimum-energy structures. This initial state was represented as a normalized Gaussian (eq 13, ref 5). At a given time, the state function of the system is a linear combination of the stationary states multiplied by the corresponding time-dependent factor.[5] To study the motion of the proton we have, in previous publications, used the expectation value of the position of the proton as a function of time (eq 20, ref 5). However, this method does not show that in near symmetric cases the expectation value of the position of the proton may not reach the other well and yet a fraction of the proton may be found in that well. The use of the probability density as a function of time (eq 19, ref 5) improves the description of the motion of the proton in such near-symmetric potentials. The time evolution of the probability density for the state function representing the tunneling nucleus in the symmetric or the asymmetric profiles was determined and plotted as in Figure 4, parts b and d, along with the expectation value of the position of the proton as a function of time.

The average frequency of the large-amplitude nonharmonic vibration is defined as the number of completed oscillations per unit time taken over an extended period of time.

Results and Discussion

9-Hydroxyphenalen-1-one. For 9-hydroxyphenalen-1-one the two configurations of minimum energy correspond to structures

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I and III, one being the mirror image of the other, with no axis of symmetry (symmetry group C_s). When compared to the X-ray crystal structure,[9] most of the bond lengths and angles for the structure of minimum energy were within 0.02 or 0.03 Å or 5° as expected when the STO-3G basis set is used.[19,22]

Structure II represents the intermediate for a proton exchange between the two minimum-energy tautomers and has a twofold axis of symmetry which contains the intervening hydrogen (symmetry group C_{2v}). As can be seen from Table IV and Figure 3, parts a and b, except for the C(9)–C(10), C(1)–C(10), C–O, and O–H bond lengths, the bond lengths and angles of the transition-state structure, as well as those of the final structure, did not differ by more than 0.03 Å or 2°, respectively, from those of the initial structure. This indicates that the interconversion takes place with very little movement of the atoms of the ring system.

The barrier for the interconversion between the two minimum-energy C_s geometries was found to be 5.20 kcal/mol. This barrier height value is considered reliable since the STO-3G basis set is known to be successful in the calculation of differences in energies of structures in which the number of each kind of chemical bond is conserved.[22]

Table IV and Figure 3, parts a and b, show that the C—O—H—O—C atoms move considerably less by moving directly from one structure of minimum energy to the other than by moving along a path that would include the symmetric intermediate. An interminimal distance of 0.64 Å was obtained for this direct transfer path. The effective mass was taken as the nominal value for the proton or deuteron, as if the proton transfers directly from the initial to the final state through tunneling, independently from the motion of the remaining atoms in the molecule, as was found in various experimental and theoretical studies.[13,23-26]

As can be seen in Figure 4a, the two eigenstates which have energies below the barrier form a gerade–ungerade pair with eigenfunctions extending over both wells. The frequencies of the gerade–ungerade splittings were found to be 0.317×10^{13} s^{-1} for the normal and 0.477×10^{12} s^{-1} for the deuterated species, corresponding to wavenumbers of 105.5 and 15.9 cm^{-1}, respectively, in good agreement with the results from fluorescence spectra, measured as 9 ± 1 cm^{-1} for the deuterated species and estimated at 127 ± 10 cm^{-1} for the normal species.[13]

In previous publications,[5,16,21] the motion of a tunneling nucleus in a double-minimum potential was calculated from the expectation value of the position of the proton as function of time. The present method shows that the proton, when its expectation value is within the barrier, should not necessarily be considered as localized in the barrier. In Figure 4b, both the probability density of the proton and the expectation value of the position of the proton are shown as functions of time. It is clear that the probability density in the classically forbidden region is always very small. When the expectation value of the position of the proton is in this region, the probability density has two maxima, one in each well. The description of the tunneling proton is improved by taking into account the weighted average of its density in each well. This density alternately increases and decreases as the system evolves in time. Only the tailing edges of the probability density are found inside the barrier. For normal and deuterated 9-hydroxyphenalen-1-one, all of the tunneling nucleus reaches the other well with the frequency of the respective gerade–ungerade splitting.

The probability density of the state function is a superposition of the projections onto each well. For molecules with high tunneling rates, methods such as microwave, infrared, photoelectron, or quadrupole coupling spectroscopy in which the time scale is 10^{-9} s or less, would detect an asymmetric hydrogen bond because they detect the protonic density as being in one well or the other at any given time. However, for experimental methods with slower time scales, such as NMR, the system would appear as if it had a symmetric hydrogen bond.

Methyl-9-hydroxyphenalen-1-one. The introduction of a methyl group destroys the symmetry of the profile. Conformations of the methyl group with a C–H bond staggered to the C=O bond were found to be of lower energy than those of the eclipsed form. The energy for the 8-methyl tautomer is 0.461 kcal/mol or 154 cm^{-1} above that of the 2-methyl tautomer, which has the methyl group attached to the ring with the C=O group, in agreement with the value estimated from fluorescence spectroscopy.[15] This corresponds to an equilibrium constant of 0.459 and a 2- to 8-methyl tautomer ratio of 2:1 at 298 K, in agreement with the ^{13}C NMR study.[14] The top of the barrier for the proton exchange between the tautomers is represented by structure II, with an energy 5.42 kcal/mol above that of the minimum-energy structure.

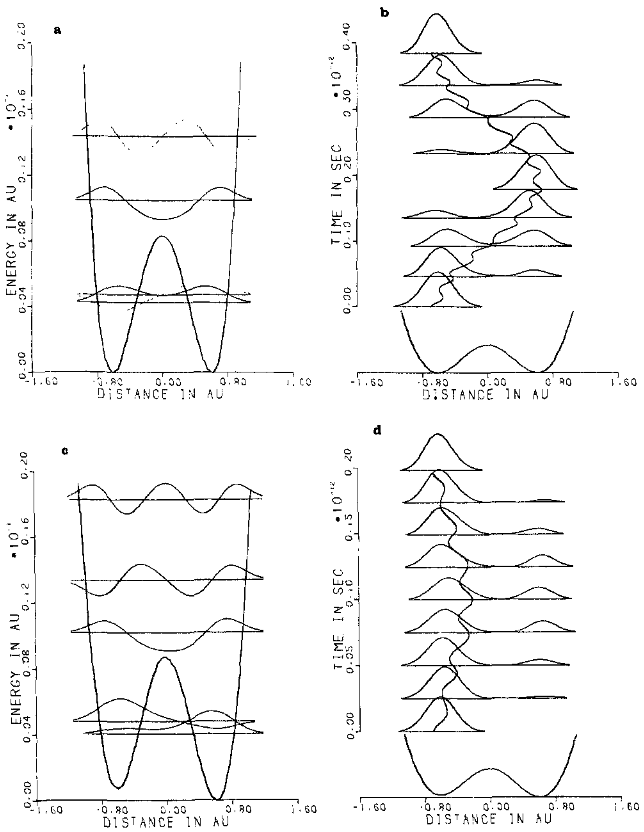

Figure 4. Double-minimum potential energy profiles, some of the lower eigenvalues and the corresponding eigenfunctions of the stationary eigenstates, and the time evolution of the probability density and of the expectation value of the position for the tunneling nucleus initially localized in one well for 9-hydroxyphenalen-1-one (a, b) and methyl-9-hydroxyphenalen-1-one (c, d).

The double-minimum potential for methyl-9-hydroxyphenalen-1-one is slightly asymmetric with an energy difference between the minima of 0.461 kcal/mol and an average barrier of 5.2 kcal/mol. As can be seen in Figure 4c, the eigenfunctions of the two eigenstates which have energies below the barrier, although largely localized in their respective wells by this slight asymmetry, do penetrate into the other well, signifying that tunneling occurs. The energy difference between the two lowest eigenstates is 5.03×10^{12} s^{-1} for the normal and 4.52×10^{12} s^{-1} for the deuterated species, corresponding to wavenumbers of 168 and 151 cm^{-1}, respectively, in agreement with estimates of 199 and 170 cm^{-1}, respectively, from fluorescence spectroscopy results.[15] Figure 4d shows that the expectation value of the position of the tunneling nucleus does not penetrate into the other well, but when the expectation value reaches its maximum inside of the barrier, the probability density of the initially localized state function is divided between the wells. Three-tenths of the proton, but less than three-hundredths of the deuteron, reaches the other well with each oscillation, the frequency of each being equal to the energy difference between its two lowest eigenstates.

Conclusion

A barrier of 5.20 kcal/mol and an interminimal distance of 0.64 Å were found for intramolecular proton exchange in 9-hydroxyphenalen-1-one, with frequencies of gerade–ungerade splittings of 105.5 cm^{-1} for the hydrogenated and 15.9 cm^{-1} for the normal and deuterated species, respectively. The difference in energy between the tautomers of methyl-9-hydroxyphenalen-1-one was found to be 154 cm^{-1}, in good agreement with the results from laser-excited fluorescence and fluorescence-excitation spectroscopy.[13,15] The time evolution of the probability density of the initially localized state function demonstrates that, for the symmetric case, the proton or deuteron reaches the other well at the frequencies of their respective gerade–ungerade splittings. For the asymmetric case, three-tenths of a proton, but less than three-hundredths of a deuteron, reaches the other well with each oscillation of frequency equal to the energy difference between the two lowest eigenstates, 5.03×10^{13} and 4.52×10^{13} s, respectively.

Although the introduction of the methyl substituent destroys the symmetry of the double-mininum potential, the rate is fast because the barrier, the interminimal distance, and the difference in energy between the two tautomers are small for this nearly symmetric potential energy profile. This explains the NMR spectra interpreted as showing that methylnaphthazarin does not have proton exchange, but methyl-9-hydroxyphenalen-1-one does.

Tunneling in near symmetric cases deserves special attention. In symmetric cases, one can calculate tunneling from the energy difference between the gerade–ungerade pair. This is so because the proton will spend equal time in each well, and tunnelling will depend on the frequency with which the proton oscillates between the wells. When the profile is asymmetric, the fraction of the proton that leaks to the other well decreases as the energy difference between the minima increases. It has been found[26] that this fraction depends on the ratio of the energy difference between the minima and the tunneling splitting in the corresponding symmetric case. In the present study the fraction of the proton that leaks to the other well is reduced from unity in the symmetric case to one-third in this nearly symmetric case, while the frequency with which the maximum leakage occurs increases by 60%.

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Two-Dimensional Heteronuclear NOE (HOESY) Experiments: Investigation of Dipolar Interactions between Heteronuclei and Nearby Protons

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Abstract: Heteronuclear 2-D NOE (HOESY) experiments were applied to the study of dipolar interactions between heteronuclei and nearby protons. The dipolar interactions between quaternary carbons and protons were studied in two cases: camphor and fluoranthene. Solvent–solute dipolar interactions between phosphorus and protons were investigated for adenosine triphosphate in water. In D_2O, NOEs were observed between α- and β-phosphates and C5′ protons; the α-phsophorus also shows a weak cross peak with H-8′, consistent with the expected anti conformation for ATP in solution.

The nuclear Overhauser effect arises from changes in spin populations due to dipolar relaxation in the presence of double irradiation. For example, applying wide-band ^{1}H decoupling results in observed ^{13}C signals which are enhanced by a factor (NOEF) of up to 1.98, due to the disturbance of the Boltzman distribution of the ^{13}C and ^{1}H dipolar-coupled spins.[1] NOE not only enhances ^{13}C sensitivity but also provides valuable information for molecular dynamics[2] and structure elucidation. Since NOE is related to $(r_{AB})^{-6}$, the distance between two dipolar interacting spins A and B can in principle be calculated.

Ernst and co-workers[3-5] developed a homonuclear 2-D experiment to observe NOE phenomena. The technique is able to simultaneously resolve many individual spin NOE effects, even in complex systems.[6]

In preliminary reports our group[7] and Rinaldi[8] presented a heteronuclear 2-D NOE experiment for the investigation of heteronuclear dipolar interactions. The pulse sequence for the heteronuclear 2-D NOE experiment is shown in Figure 1A, and the vector model that describes the I spin magnetization is shown Figure 1B. For the simple system of 2 spins, I (^{1}H in this case) and S (observed nucleus: ^{13}C or ^{31}P), the components of I magnetization $M(\alpha)$ and $M(\beta)$ corresponding to the two S spin states can be represented by the vectors α and β. After an initial 90° (I) pulse (Figure 1Ba), the two vectors precess for a period of time, $t_1/2$, and accumulate a relative phase angle of $\pi J t_1$ (Figure 1Bb). Following a 180° pulse on S, the two spin-state labels interchange (Figure 1Bc), and further precess for another $(t_1/2)$ period, causing the two vectors to become refocused (Figure 1Bd). So far, the two I magnetization vectors remain parallel at the end of the evolution period, and no magnetization transfer has occurred; this means that scalar interactions between I and S have

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