Symmetry and Tunneling in the Intramolecular Proton Exchange in Naphthazarin, Methylnaphthazarin, and Dimethylnaphthazarins

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Abstract: The ^{1}H NMR spectra of naphthazarin and of 2,6- and 2,7-dimethylnaphthazarin in solution show only one signal for the ring hydrogens down to −95 °C, while for monomethylnaphthazarin two lines, corresponding to the quinonoid and to the benzenoid hydrogens, are found. Ab initio SCF calculations on the four compounds indicate the existence of two minimum energy structures with two asymmetric hydrogen bridges and with both hydroxyls on the same ring. For naphthazarin and the two dimethylnaphthazarins these two structures have the same energy, while for monomethylnaphthazarin the tautomer that has the methyl attached to the benzenoid ring is 0.9 kcal/mol above the 2-methyl tautomer. The potential energy surface for the exchange of the two protons has C_{2v} symmetry for naphthazarin and C_h for 2,6- and C_2 for 2,7-dimethylnaphthazarin, while that of monomethylnaphthazarin has no symmetry at all. The surfaces each have an absolute maximum ~28 kcal/mol above the minima and two saddle points at 25 kcal/mol above the minima. The absolute maximum corresponds to the barrier for the concerted proton transfer between the two minimum energy tautomers, while the saddle points constitute the barriers for the stepwise transfers with the structure of 4,8-dihydroxy-1,5-naphthoquinone. The calculated rates of proton exchange for naphthazarin and the two dimethyl derivatives are found to be from 20 to 40 MHz for the normal (H) species and about 1 kHz for the deuterated species. No exchange occurs in monomethylnaphthazarin. These rates would explain the ^{1}H NMR spectra of the four compounds. They also illustrate how destruction of the symmetry in a potential energy surface with high barrier may eliminate tunneling.

For tunneling of the proton in symmetric double minimum potentials an explanation has been proposed[1,2] different from that for asymmetric ones. In the latter, tunneling occurs only when the barrier is low and the interminimal distance is small. In symmetric cases, tunneling is found to occur whenever the barrier and the interminimal distance are finite. Tunneling in symmetric profiles is due to the indistinguishability of the wells.

Theoretical studies for the motion of the proton in the double-minimum potentials provided by various hydrogen-bonded water and methyl alcohol species[1] show that in symmetric cases the rate of proton exchange is several orders of magnitude larger than the theoretical values derived with the semiclassical WKB method.[3] The latter has been successfully used in asymmetric profiles and unbound systems. While our previous theoretical results for water and for methanol were consistent with experimental values for the liquid and solid state, we did not pursue the applicability of the model to condensed phases.

The interpretation of the microwave spectra of β-hydroxyacrolein and α-methyl-β-hydroxyacrolein provides additional evidence of the importance of the symmetry of the intramolecular proton exchange profile for tunneling. Both theoretical[4,5] and experimental[6-8] results indicate that the rate of proton exchange in α-methyl-β-hydroxyacrolein is one order of magnitude smaller than that in β-hydroxyacrolein. The difference is attributed to the strong coupling of the proton exchange with the rotation of the methyl group. This strong coupling exists because the proton will exchange only when the conformation of the methyl group leads to a symmetric double minimum profile. The use of microwave spectra for the interpretation of tunneling has advantages and disadvantages. One advantage is that the interaction between the proton exchange and the surrounding molecules is very small. One disadvantage is that the tunneling rate is estimated indirectly from the separation of relevant energy levels and not determined directly.

Naphthazarin and its mono- and disubstituted derivatives provide an excellent system in which the influence of symmetry on proton tunneling in a double minimum potential can be studied. The ^{1}H NMR spectra of naphthazarin and of 2,6- and 2,7-dimethylnaphthazarin show only one signal for the ring hydrogens. Comparing the ^{1}H NMR, IR, and X-ray crystallographic data, Bratan et al.[9] concluded that in naphthazarin the presence of a single line is due to the fast interconversion between the two minimum energy tautomers. The single line is resolved only at −190 °C in the crystal state.[10] Not enough data are available to justify similar conclusions for the dimethylnaphthazarins, where the presence of only one line can also be due to symmetric hydrogen bonds or to asymmetric bridges in a 4,8-dihydroxy-1,5-naphthoquinone type structure.

The ^{1}H NMR spectra of the monosubstituted naphthazarins show two signals for the ring hydrogens. Interpretation of these spectra led Moore and Scheuer[11] to conclude that one of two possible tautomers exists predominantly. Substitution by an ethyl, hydroxyl, methoxyl, or acetoxyl group gives the 2-substituted tautomers, while acetyl gives the 7-substituted compound.

Ab initio SCF calculations can be performed to determine whether the presence of only one line for the dimethylnaphthazarins is due to (a) a symmetric hydrogen bond, (b) a 4,8-dihydroxy-1,5-naphthoquinone structure, or (c) fast exchange between two minimum energy tautomers having the 5,8-dihydroxy-1,4-naphthoquinone structure, as in naphthazarin. Calculations can also be performed on methylnaphthazarin to determine why for it, unlike for the others, the signal of the ring hydrogens is resolved.

Experimental Section

Naphthazarin and methylnaphthazarin were obtained in low yields by Friedel–Crafts acylation of hydroquinone or methylhydroquinone with

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Table I. ^{1}H NMR Absorption Peaks, in ppm, of Naphthazarin (A), 2-Methylnaphthazarin (B), 2,6-Dimethylnaphthazarin (C), and 2,7-Dimethylnaphthazarin (D)

	position			signal		
	2	6	7	H	CH3	OH
A	H	H	H	7.13		12.43
B	CH3	H	H	7.19 6.89^b	2.22^a	12.41 12.53
C	CH3	CH3	H	6.96	2.22	12.72
D	CH3	H	CH3	6.96	2.20	12.48 12.96

^{a} Doublet with J = 1.4 Hz. ^{b} Quartet with J = 1.4 Hz.

maleic or citraconic anhydrides according to published procedures.[9,12-14] When either hydroquinone and citraconic anhydride or methylhydroquinone and maleic anhydride were condensed, only one tautomeric methylnaphthazarin was obtained,[10] with the methyl group attached to the quinonoid ring. Both 2,6- and 2,7-dimethylnaphthazarin were obtained from Friedel-Crafts acylation of methylhydroquinone with citraconic anhydride.[14] These isomers were separated by recrystallization from acetone containing 1% water. The identity and purity of the compounds were confirmed by thin layer chromatography, ^{1}H NMR, mass spectrometry, and elemental analysis. All ^{1}H NMR spectra were determined in methylene-d^2 chloride solution, with either Me_4Si or methylene chloride (5.31 ppm) as internal standard, on a Perkin-Elmer R-32 instrument with a low-temperature accessory.

Results

The chemical shifts of the various protons in naphthazarin and the methylnaphthazarins are shown in Table I. As reported previously,[9,10] for naphthazarin only one signal is obtained from the ring protons. This signal remains unresolved at -90 °C.

The chemical shifts for methylnaphthazarin, not previously reported, show two distinct hydroxylic hydrogen signals and two signals for the ring protons, a singlet at 7.19 and a quartet at 6.89 ppm (J = 1.4 Hz), with areas in a 2:1 proportion. The signal for the methyl group appears as a doublet at 2.21 ppm with the expected J = 1.4 Hz. The quinonoid and methyl hydrogen signals are decoupled by double resonance. Each becomes a sharp singlet with no evidence of any other signal.

Only one signal, at 6.96 ppm, is obtained for the ring protons of both 2,6- and 2,7-dimethylnaphthazarin; the methyl signals appear at 2.22 and 2.20 ppm respectively. The half-width of each signal remains constant when the temperature is lowered to -95 °C. Neither the ring hydrogen nor the methyl hydrogen signals show any fine structure, indicating that the expected multiplets may have collapsed.

Theoretical Calculations

Potential Energy Surfaces for the Proton Exchange. Ab initio SCF molecular orbital calculations with minimal basis set[15,16] were performed to determine the structures of minimum energies for the molecules of naphthazarin, monomethylnaphthazarin, and 2,6- and 2,7-dimethylnaphthazarin. Each of the four compounds has two geometries for which the energy is an absolute minimum, corresponding to the structure in which the two hydroxyls are on the same ring (structures A and B, Figure 1). For naphthazarin, the two structures are degenerate; that is, they are equivalent. For the two dimethylnaphthazarins, the two structures A and B are also equivalent if the methyl groups have the proper orientation. For the two monomethylnaphthazarin tautomers, the structure in which the methyl group is on the benzenoid ring, 7-methylnaphthazarin, is 0.9 kcal/mol above the energy of the 2-methyl tautomer when one of the C-H bonds of the methyl group is in the trans position with respect to the C-O bond. The difference is the same when the bonds are in the cis position.

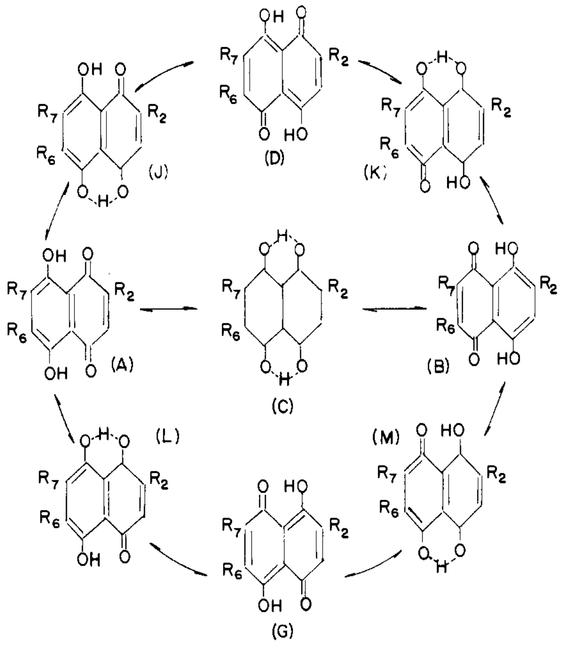

Figure 1. Schematic representation of the various proton transfer pathways in naphthazarin and its methyl derivatives. The path A-C-B represents the concerted exchange of both protons. A-G-B and A-D-B show the stepwise exchanges. For each compound, A and B are absolute minima, C is an absolute maximum, and D and G are saddle points.

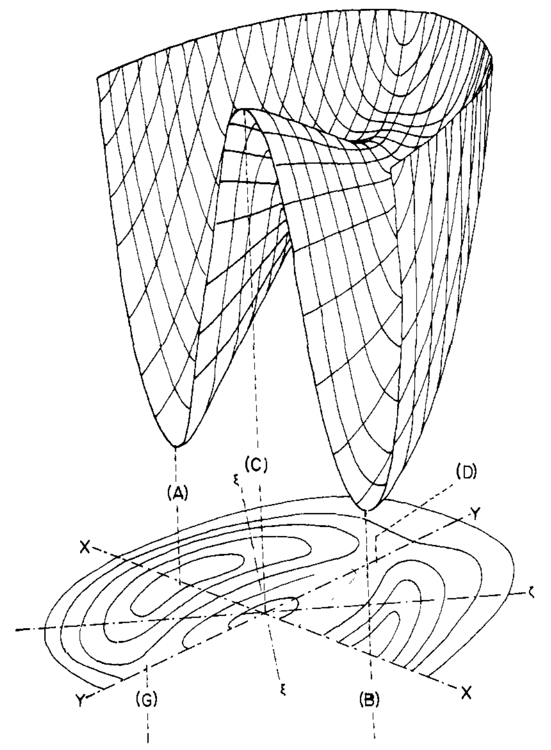

Figure 2. The potential energy surface represents the variation of the total energy of the system as it goes from one absolute miminum structure (A) to the other (B). The surface has an absolute maximum (C), which represents the barrier for the concerted proton exchange between A and B, and two saddle points, D and G, representing the intermediates in the stepwise proton exchange.

The two-dimensional potential energy surface representing the interconversion of the two minimum energy tautomers has one absolute maximum and two saddle points (Figure 2). The absolute maximum corresponds to structure C (Figure 1), in which the two hydrogen-bonded protons are equidistant from the two oxygens. At the two saddle points (structures D and G, Figure 1) the two hydroxyls are on different rings and the structure is that of 4,8-dihydroxy-1,5-benzoquinone (see Figure 3 for num-

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Table II. Energies of the Five Significant Structures Depicted in Figure 1 for the Four Molecules Studied[a]

		energy, kcal/mol						
compd	sym	A	B	C	D	G	1-D[b]	2-D[c]
naphthazarin	C_{2v}	0.0	0.0	28.0	25.0	25.0	20.5	20.5
2,6-dimethylnaphthazarin	C_h	0.0	0.0	27.2	24.7	24.7	25.5	
2,7-dimethylnaphthazarin	C_2	0.0	0.0	27.3	24.5	24.5	24.9	
2-methylnaphthazarin	none	0.0	0.9	28.1	25.7	25.7	none	

[a] The calculated frequencies for the proton exchange are given in MHz. [b] One dimension. [c] Two dimensions.

Table III. Bond Distances (Å) of the Significant Structures Depicted in Figure 1[a]

	structure		
bond	A, B	D, G	C
C(1)-C(2)	1.508	1.485	1.492
C(2)-C(3)	1.320	1.347	1.334
C(1)-C(9)	1.500	1.462	1.398
C(8)-C(9)	1.403	1.439	1.398
C(7)-C(8)	1.413	1.447	1.492
C(6)-C(7)	1.374	1.347	1.334
C(9)-C(10)	1.407	1.407	1.430
C(1)-O(11)	1.239	1.239	1.298
C(8)-O(14)	1.378	1.378	1.298
O(14)-H(19)	0.995	0.995	1.204
O(11)-H(19)	1.577	1.574	1.204
C(2)-H(15)	1.088	1.097	1.085
C(7)-H(18)	1.085	1.083	1.085

[a] The distances given describe only the upper portion of each structure. The distances not listed can be found from the symmetry of each structure: A, B belongs to point group C_{2v}; D, G belongs to point group C_{2h}; C belongs to point group D_{2h}.

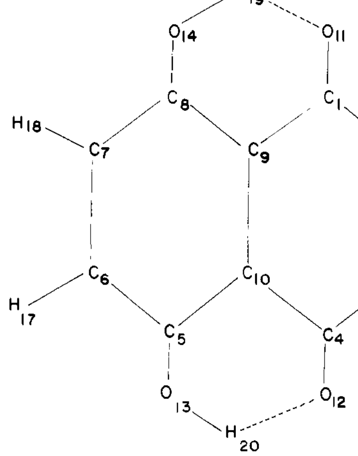

Figure 3. Diagram with the identities of the atoms and the numbers by which they are referred to in the text and in the tables.

Table IV. Bond Angles (Degrees) of the Significant Structures Depicted in Figure 1

	structure		
angle	A, B	D, G	C
C(2)-C(1)-C(9)	117.55	116.11	115.90
C(1)-C(2)-C(3)	122.10	112.67	122.01
C(1)-C(9)-C(10)	120.35	121.22	121.12
C(7)-C(8)-C(9)	118.48	120.10	115.90
C(6)-C(7)-C(8)	121.02	120.23	122.01
C(8)-C(9)-C(10)	120.50	119.66	121.12
O(11)-C(1)-C(9)	120.35	121.22	121.12
O(14)-C(8)-C(9)	120.50	119.66	121.12
H(19)-O(14)-C(8)	100.50	104.44	100.21
H(15)-C(2)-C(1)	117.9	116.75	118.91
H(18)-C(7)-C(8)	119.09	120.41	118.91

Table V. Bond Distances (Å) for Three of the Methylnaphthazarin Structures Given in Figure 1[a]

	structure		
bond	A	B	C
C(2)-C(21)	1.531		1.530
C(7)-C(21)		1.529	
H(22)-C(21)	1.090	1.090	1.090
H(23)-C(21)	1.090	1.090	1.090
H(24)-C(21)	1.090	1.090	1.090

[a] Only the values different from those for the corresponding structures in Table III are given. The methyl carbon and hydrogens have numbers 21-24.

Table VI. Bond Angles (Degrees) of Three of the Structures Depicted in Figure 1

	structure		
angle	A	B	C
C(3)-C(2)-C(21)	120.00		120.00
C(2)-C(21)-H(22)	109.47		109.47
C(2)-C(21)-H(23)	109.47		109.47
C(2)-C(21)-H(24)	109.47		109.47
C(6)-C(7)-C(21)		120.00	
C(7)-C(21)-H(22)		109.47	
C(7)-C(21)-H(23)		109.47	
C(7)-C(21)-H(24)		109.47	

bering). The energies of the absolute maximum and of the two saddle points for each of the four compounds are given in Table II. The absolute maximum C represents the intermediate for the concerted proton exchange between the minimum energy tautomers A and B, while the saddle points D and G are the intermediates for the stepwise proton exchange. The energy of the absolute maximum of each compound varies from 27.7 kcal/mol above the minima in 2,7-dimethylnaphthazarin to 28.1 kcal/mol in 2-methylnaphthazarin. For the saddle points, the energy is found to be between 24.5 and 25.7 kcal/mol. On principle, the energies for the two saddle points for monomethylnaphthazarin, and also for 2,6-dimethylnaphthazarin, should differ from each other. However, the difference is found to be of the order of 0.01 kcal/mol (Table II), too small to be significant in these calculations. The schematic representation of the various other strucures involved in the stepwise proton exchange is also shown in Figure 1. From these structures and from the energy values reported in Table II, it follows that the surface representing the interconversion between tautomers A and B has C_{2v} symmetry for naphthazarin, C_h symmetry for 2,6-dimethylnaphthazarin, C_2 symmetry for 2,7-dimethylnaphthazarin, and no symmetry for monomethylnaphthazarin.

The bond lengths and bond angles of the intermediates vary, reflecting the interconversions between the benzenoid and quinonoid rings and between the carbonyl and hydroxyl groups. The differences are, however, not large enough to increase significantly the value of the effective mass involved in the exchange. Tables III–VI show the lengths in angstroms and the bond angles in degrees for naphthazarin and monomethylnaphthazarin. The bond lengths and angles for the dimethylnaphthazarins are very close to those for naphthazarin and monomethylnaphthazarin. The small differences are within the precision expected from the calculations.

Determination of the Rates of Proton Exchange. The potential energy surface for the motion of the two hydrogen-bonded protons in naphthazarin (Figure 2) is a function of two variables, ξ and ζ, the distance each proton has from its position in structure C.

Table VII. Values of the Energy Barriers, E_0 and E_1, and the Interminimal Distance, D, Used To Calculate the Parameters of the Potential Energy Surface Given by Eq 1[a]

$E_0 = 0.0446$	$A_2 = 0.166382$
$E_1 = 0.0408$	$A_4 = 0.155173$
$D = 1.4640$	$B_2 = 0.014176$
	$B_4 = 0.013221$
	$C = 0.168394$

[a] All the values are given in atomic units.

The potential, referred to the absolute minimum, can be fitted to the fourth degree polynomial

$$V = E_0 - A_2x^2 + A_4x^4 - B_2y^2 + B_4y^4 + Cx^2y^2 \qquad (1)$$

where the variable x represents the path for the concerted proton transfer between the minimum energy structures A and B and the coordinate y, perpendicular to x, connects the saddle points.

The coefficients for eq 1, calculated from the values of barriers E_0 (the absolute maximum) for the concerted proton transfer and E_1 (the saddle points) for the stepwise transfer, are given by

$$A_2 = 8E_0/D^2 \qquad A_4 = 16E_0/D^4$$
$$B_2 = 8(E_0 - E_1)/D^2 \qquad B_4 = 16(E_0 - E_1)/D^4 \qquad (2)$$
$$C = 16(2E_0 - E_1)/D^4$$

The values of E_0, E_1, and D, together with the coefficients for eq 1, are given in Table VII.

The eigenstates for this potential are calculated by using the variational method. Products of two one-dimensional harmonic oscillator functions, $\chi(k,x)$ and $\chi(l,y)$, centered at the position of the absolute maximum, are used as the basis set

$$\Phi(\mu,x,y) = \sum_k\sum_l b(\mu,k,l)\chi(k,x)\chi(l,y) \qquad (3)$$

where μ indicates the symmetry to which the eigenstate belongs.

symmetry μ	product $\chi(k,x)$	$\chi(l,y)$
A_1	gerade	gerade
A_2	ungerade	ungerade
B_1	ungerade	gerade
B_2	gerade	ungerade

Initially the two protons are placed at the positions they occupy in one of the absolute minimum structures. The product of two one-dimensional Gaussians centered on this minimum is expanded in terms of the stationary eigenfunctions of this system:

$$\Psi_0(x,y,x_0) = \frac{1}{\sqrt{\pi}}(\gamma_1\gamma_2)^{-1/4} \exp\left(-\frac{\gamma_1}{2}(x - x_0)^2 - \frac{\gamma_2}{2}y^2\right) \qquad (4)$$

The values of γ_1 and γ_2 are calculated from the curvatures k_x and k_y at the minima.

The initial state is expanded in terms of the stationary eigenstates:

$$\Psi_0(x,y,x_0) = \sum_\mu\sum_m c(\mu,m)\Phi(\mu,m,x,y) \qquad (5)$$

As Ψ is an even function of y, only the products belonging to the A_1 and B_1 symmetry species of the C_{2v} symmetry group contribute to the expansion. The time evolution of the system is estimated by calculating the expectation value of x and y as a function of time. The expectation value of y, $\langle y\rangle$, equals 0, while the expectation value of x is given by

$$\langle x\rangle = 2\sum_n\sum_m c(A_1,n)c(B_1,m)\langle\Phi(A_1,n)|x|\Phi(B_1,m)\rangle \cos \omega_{n,m}t \qquad (6)$$

where

$$(E_m - E_n)/\hbar = \omega_{n,m} \qquad (7)$$

For naphthazarin, which has a very high energy barrier, only the lowest energy levels of the A_1 and B_1 symmetry species make significant contributions in eq 6; the exchange frequency is given by the difference between them divided by h. These energies, as well as the tunneling frequencies for hydrogen and deuterium, are listed in Table VIII.

Table VIII. Eigenvalues (cm^{-1}) of the Two Lowest Energy Levels for the One- and Two-Dimensional Potential Energy Functions for Hydrogen and Deuterium[a]

one dimension	two dimensions
Hydrogen	
$E_g = 1446.964998$	$E_{A_1} = 2130.021033$
$E_u = 1446.965678$	$E_{B_1} = 2130.019674$
$\nu = 20.37$ MHz	$\nu = 40.77$ MHz
Deuterium	
$E_g = 1029.402471929$	$E_{A_1} = 1517.236302894$
$E_u = 1029.402472217$	$E_{B_1} = 1517.236303487$
$\nu = 0.86$ kHz	$\nu = 17.8$ kHz

[a] Only the symmetry species A_1 and B_1 are significant in the calculation of tunneling times in the two-dimensional profile for naphthazarin.

Since the expectation value of y equals 0, the expectation value of the point that represents the system will move along the x axis. Classically, one would say that only the concerted proton transfer contributes to the exchange. However, in quantum mechanics, the result is a consequence of the fact that, for the stepwise transfer, both possible trajectories, through the upper and lower saddle points, are equally possible, and therefore undistinguishable.

The tunneling frequencies for the concerted proton exchange, also presented in Table VIII, were calculated with previously published techniques for one-dimensional problems. The differences between the results of the one-dimensional and the two-dimensional calculations indicates that both the concerted and the stepwise proton exchanges occur. The stepwise transfer seems to be the principal contributor to the exchange rate when deuterated naphthazarin is used.

Introduction of one methyl group into naphthazarin destroys the symmetry of the potential energy surface. The one-dimensional double-minimum profile for the concerted exchange is slightly asymmetric. The energy difference between the minima is only 0.9 kcal/mol, while the energy barrier of 28.1 kcal/mol is practically the same as for naphthazarin.

The calculated 0.9 kcal/mol energy difference between the minima in monomethylnaphthazarin is less than the systematic reliability for the relative energetics of the ab initio SCF calculations. However, this result would explain the ^{1}H NMR spectrum of methylnaphthazarin, which shows the presence of the tautomer with the methyl group attached to the quinonoid ring and has two signals for the ring hydrogens, which may indicate slow exchange on the ^{1}H NMR time scale.

Conclusion

The results of the calculations indicate that for naphthazarin and for 2,6- and 2,7-dimethylnaphthazarin the structures of minimum energy correspond to two degenerate (equivalent) tautomers with two asymmetric hydrogen bonds in which the two hydroxyls are on the same ring. The structures in which the two hydrogen-bonded protons are equidistant (symmetric hydrogen bonds) are absolute maxima, with energies about 28 kcal/mol above the minima. The structures in which the two hydroxyls are on different rings (4,8-dihydroxy-1,5-naphthoquinone) are saddle points and are about 25 kcal/mol above the minima. The calculated motion of the proton in these three systems indicates fast exchange between the two degenerate tautomers, with exchange rates from 20 to 40 MHz for the normal (H) and 1 to 17 kHz for the deuterated species. Both concerted and stepwise proton exchanges occur. The latter will be the principal mechanism in the deuterated species.

These results may explain the ^{1}H NMR spectra of naphthazarin, and of 2,6- and 2,7-dimethylnaphthazarin, in which only one signal is obtained for the ring hydrogens with no evidence of either the expected quartet of the quinonoid hydrogen or of the doublet for the hydrogens of the methyl group.

In monomethylnaphthazarin the energy of one tautomer is 0.9 kcal/mol above that of the other. This difference destroys the symmetry of the potential surface. Our calculation shows that tunneling will not occur in this system for which the energy barrier is 28.1 kcal/mol for the concerted transfer and 25.0 kcal/mol for the stepwise transfers. If the hydrogen-bonded protons are initially placed in the positions they occupy in 2-methylnaphthazarin, they will remain there, without leaking through the barrier to the well representing 7-methylnaphthazarin. This would explain the ^1H NMR spectrum of monomethylnaphthazarin, in which the 2-methyl tautomer seems to be the predominant structure, with two signals for the ring hydrogens, and in which both the quartet of the quinonoid ring and the doublet of the methyl group hydrogens are well defined.

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Surface Tension of Ternary Polymeric Solution

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Abstract: Assuming a ternary mixture to be made up of three binary mixtures, Flory's statistical theory has been extended to obtain a relationship for the surface tension of a ternary liquid mixture. In the light of above extension, the surface tension of a ternary mixture of hexane–decane–hexadecane polymer homologues has been predicted at 303.16 K, over a wide range of composition. There is reasonable agreement between theory and experiment.

Introduction

Patterson et al.[1-3] have drawn attention to the close connection between the Flory theory of mixtures[4,5] and the corresponding states theory[6] of Prigogine by employing a simple cell model of the liquid state. Flory's statistical theory has been used, successfully,[7-10] to evaluate the surface tension of pure liquid and binary liquid mixtures through the use of suitable characteristic parameters (i.e., reduction parameters), p^*, v^*, and T^*, for pressure, volume, and temperature, respectively. Recently Pandey[11] and Mishra[12] have also have shown the applicability of Flory's theory to predict sound velocity and surface tension at elevated pressure. It appears from the literature that no adequate theory is available for predicting the surface tension values in ternary liquid mixtures. In this connection the extension of the relationships for the surface tension of binary mixtures to the case of ternary systems is of interest. In the present paper Flory's statistical theory has been extended to evaluate the characteristic parameters of ternary liquid mixture, which in turn have been employed to predict the surface tension of hexane–decane–hexadecane polymer homologues at 303.16 K.

Theoretical Section

Patterson and Rastogi[7] in their extension of the corresponding states theory dealt with the surface tension by using as the reduction parameter

$$\sigma^* = k^{1/3}p^{*2/3}T^{*1/3} \tag{1}$$

called the characteristic surface tension of the liquid. Here k is the Boltzmann constant. Starting from the work of Prigogine and Saraga,[13] they derived a reduced surface tension equation which in the case of a van der Waals liquid can be written as

$$\tilde{\sigma}(\tilde{v}) = M\tilde{v}^{5/3} - \frac{\tilde{v}^{1/3} - 1}{\tilde{v}^2} \ln \frac{\tilde{v}^{1/3} - 0.5}{\tilde{v}^{1/3} - 1} \tag{2}$$

where M is the fraction of nearest neighbors that a molecule loses on moving from the bulk of the liquid to the surface. Its most suitable value[7] is 0.29, which is used in our calculations. Thus surface tension of a liquid in terms of Flory theory can be described by the expression

$$\sigma = \sigma^*\tilde{\sigma}(\tilde{v}) \tag{3}$$

The characteristic and reduced parameters involved in the above equation of surface tension can be evaluated by the following procedure in the case of a ternary mixture.

The intermolecular energy E_0 for the liquid is expressed by[4]

$$E_0 = Nrs\eta/2v \tag{4}$$

where N is the number of molecules, v is the volume per segment, rs is the number of contact sites, and η is a constant characterizing the energy of interaction for a pair of a neighboring sites.

The reduced equation of state derived from the resulting partition function is given by[4]

$$\frac{\tilde{p}\tilde{v}}{\tilde{T}} = \frac{\tilde{v}^{1/3}}{\tilde{v}^{1/3} - 1} - \frac{1}{\tilde{v}\tilde{T}} \tag{5}$$

The reduced quantities $\tilde{p}$, $\tilde{v}$, and $\tilde{T}$ are given by

$$\tilde{p} = p/p^* = 2pv^{*2}/s\eta \tag{6}$$

$$\tilde{T} = T/T^* = 2v^*ckT/s\eta \tag{7}$$

$$\tilde{v} = v/v^* = V/V^* \tag{8}$$

Thus

$$p^* = ckT^*/v^* \tag{9}$$

where $V = rv$ is the molar volume. The isobar at zero pressure is

$$T^* = \frac{T\tilde{v}^{1/3}}{\tilde{v}^{1/3} - 1} \tag{10}$$

From which

$$\tilde{v}^{1/3} = \frac{\alpha T}{3(1 + \alpha T)} + 1 \tag{11}$$

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