chirality polynomials underline the importance of the concept of *chirogenic center* used for their definition. This concept circumvents some of the difficulties in the conventional CIP characterization of chirality and provides a natural tool for the analysis of chirality associated with tetrahedral centers.

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Coupling between the Rotation of the Methyl Group and the Proton Exchange in 5-Methyl-9-hydroxyphenalen-1-one

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Abstract: Introduction of a methyl group in the symmetric position in 9-hydroxyphenalen-1-one couples the rotation of the methyl group with the oscillation of the intramolecularly hydrogen bonded proton if the frequencies of the two motions are of the same order of magnitude. This coupling produces two apparently paradoxical effects. On the one hand, the barrier splitting increases; on the other hand, the proton flux through the barrier decreases. If the motions of the methyl group and the proton were uncoupled, the energy levels would be a superposition of the gerade–ungerade eigenvalues of the double-minimum potential and the rotational manifold of the methyl group. However, the coupling between the two motions is observed to split those levels of the methyl rotation which are multiples of three, producing two manifolds, each consisting of six closely spaced energy levels with D_{3d} symmetry, which is that of the two-dimensional potential energy levels for the coupled motion. The calculated average separation between the two manifolds is in good agreement with the assigned experimental value. The fact that with the methyl in position five two closely spaced manifolds are obtained would explain the increase observed in the relaxation of the excited vibrational state in 5-methyl-9-hydroxyphenalen-1-one.

Laser-induced fluorescence (LIF) of 9-hydroxyphenalen-1-one (9-HPLN, Figure 1, I and its 5-methyl derivative (5-M-9-HPLN, Figure 1, II) in a neon matrix at 4 K shows[1] fully relaxed vibrational transitions; this allows the determination of the barrier splitting for the proton exchange in both the ground and the excited states. A barrier splitting of 92 cm^{-1} for 5-M-9-HPLN was found for the ground state, an increase from 69 cm^{-1} for 9-HPLN, the parent compound. In the excited states the splittings were of 311 cm^{-1} for the parent compound and 431 cm^{-1} for the 5-methyl derivative.

If the methyl group in position five rotated freely, the double-minimum potential for the proton exchange would remain symmetric, and the increase in the barrier splitting would denote a decrease in barrier height both in the ground and in the excited states.[1] This barrier reduction could have been caused by the inductive effect of the methyl group through the π-electron system in the molecule or by the proximity of the neon atoms.

The possibility of barrier reduction as the reason for the increase in the barrier splitting seems to be challenged by the NMR spectra as their interpretation seems to indicate a reduced barrier penetration with the addition of a methyl group.[2]

Increased splitting indicates barrier reduction only if the double-minimum potential remains symmetric. It was recently shown[3] that the introduction of a slight asymmetry in a symmetric double-minimum potential increases the splitting of the gerade–ungerade pair and at the same time decreases drastically the penetration through the barrier.

Restricted rotation of a methyl group, if it is in the symmetric position five, will be coupled with the large-amplitude nonharmonic oscillation of the intramolecularly hydrogen bonded proton. As was proposed in a previous publication,[4] when one of the C–H bonds of the methyl group is perpendicular to the plane of the molecule, the double-minimum potential remains symmetric. Rotation of the methyl group from this position destroys the symmetry, thus reducing drastically the tunneling rate.[5] This effect couples the motion of the hydrogen bonded proton with the rotation of the methyl group. The potential energy surface for the coupled motion is now two-dimensional, and, as proposed previously, the eigenstates will belong to the D_{3d} symmetry group, to which the Hamiltonian belongs. A similar Hamiltonian was successfully used to calculate the energy levels for the coupled motion in 2-methyl-3-hydroxyacrolein.

To determine why the barrier splitting increases when the methyl group is attached, the extent of the coupling between the proton exchange and the methyl rotation was evaluated from the potential energy surface.

Calculations

Ab initio SCF molecular orbital calculations were performed for the electronic energy[6] at the STO-3G level[7] with convergence on the density matrix set at 10^{-7} au.

The five geometries pertinent to the system (Figure 2) were optimized with the proper geometrical constraints until all analytical nuclear cartesian forces[8] were less than 0.0005 au/Bohr. As in the case of the parent compound, all atoms, except two or three hydrogens of the methyl group, are in a plane. The structure with minimum energy, an absolute minimum, is represented by structure A (Figure 2). In this structure one C–H bond of the methyl group is in the plane of the molecule and cis with respect to the O–H. There is another absolute minimum, 1.05 kJ/mol above the previous one, in which again one methyl C–H is in the plane but now trans with respect to the O–H (structure C, Figure

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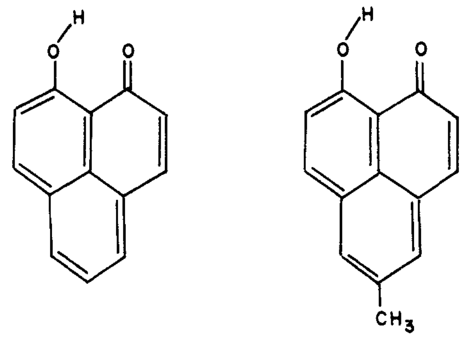

I II

Figure 1. Structures: I, 9-hydroxyphenalen-1-one (9-HPLN), and II, 5-methyl-9-hydroxyphenalen-1-one (5-M-9-HPLN).

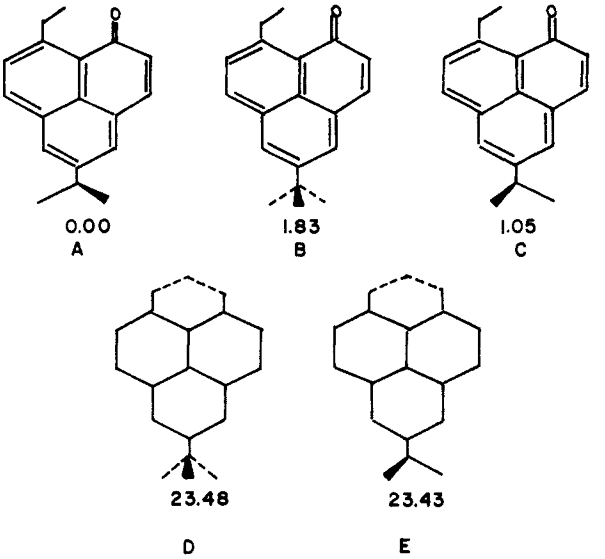

Figure 2. Energies in kJ/mol of the five significant structures of 5-M-9-HPLN. Structures A and C are absolute minima, B is a saddle point, and D and E are maximum energy structures. D and E represent the intermediate for the proton exchange with its energy independent of the angle of rotation of the methyl group.

2). In both these minima the hydrogen bond is asymmetric. The intermediate for the proton transfer, with this proton symmetrically placed and with one methyl C–H bond in the plane, corresponds to structure E; its energy is 23.4 kJ/mol above that of C. This barrier is not significantly different from that of the parent compound. In structure B one of the methyl C–H bonds is perpendicular to the plane of the molecule. The energy for this structure is 1.85 kJ/mol higher than A and 0.80 kJ/mol higher than C. It is not intermediate between the energies of A and C in contrast with 2-methyl-3-hydroxyacrolein for which the structure with one methyl C–H perpendicular to the plane of the molecule (structure IV, Table I, ref 3) has an energy intermediate between the two absolute extremes (I and III, Table I, ref 3). This result is not surprising as 5-M-9-HPLN is aromatic, and the structures in which one methyl C–H is in the plane of the molecule are more stable than any others, including those in which one methyl C–H is perpendicular to that plane. In structure D one methyl C–H is in the plane of the molecule, and the proton is equidistant to the two oxygens. This optimized geometry is 23.5 kJ/mol above that of A. There is no significant barrier for the rotation of the methyl group when the proton is maintained at the intermediate position (structure E).

Table I[a]

E	0.008264		
d	1.21300		
k	0.143731		
I	17468.0		
A_2	0.056487	A_0	0.000200
v_0	0.061707	A_3/x_0	0.00030
α	1.729329	A_6/x_0^2	0.00139
$\langle 1g\vert x\vert 1u\rangle$	0.63780	$\langle 2g\vert x\vert 1u\rangle$	0.25661
$\langle 2g\vert x\vert 2u\rangle$	0.49154	$\langle 3g\vert x\vert 2u\rangle$	0.47809
$\langle 1g\vert x^2\vert 1g\rangle$	0.43015	$\langle 1u\vert x^2\vert 1u\rangle$	0.474567
$\langle 2g\vert x^2\vert 2g\rangle$	0.329840	$\langle 2u\vert x^2\vert 2u\rangle$	0.483839
e_{1g}	0.00384358	e_{1u}	0.00424782
e_{2g}	0.00977868	e_{2u}	0.0129430

[a] Values of the parameters used in the calculation: E, d and k are the energy barrier, the interminimal distance, and the curvature at the minima of the symmetric double-minimum potential. I is the calculated moment of inertia for the methyl group. All the values are given in atomic units. A_0, v_0 and α are the constants of the parabola-Gaussian function for the symmetric double-minimum potential. A_0, A_3, and A_6 are the parameters of the potential given in eq 1, while e_g and e_u are the eigenvalues for the symmetric double-minimum potential.

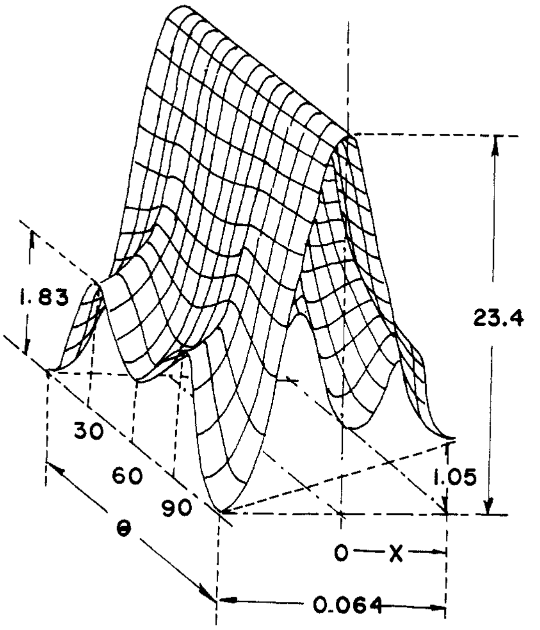

Figure 3. Potential energy surface representing the coupled motion of the intramolecularly hydrogen bonded proton and the rotation of the methyl group. The energies, in kJ/mol, correspond to the structures given in Figure 2. The interminimal distance is in nm.

Potential Energy Surface

The potential energy surface representing the coupled motion of the proton and the methyl group is represented in Figure 3. The surface has its maximum, which is independent of the angle of rotation of the methyl group, at $x = 0$. The minimum energy structures, which are absolute minima, occur at $\theta = 2n(\pi/3)$ for $x = x_0$ and at $(2n + 1)(\pi/3)$ for $x = -x_0$. The structure of 1.05 kJ/m above that of the minimum occurs at $(2n + 1)(\pi/3)$ for $x = x_0$ and $2n(\pi/3)$ for $x = -x_0$. The saddle points occur when the methyl C–H is perpendicular to the plane, and they are located at $\theta = (2n + 1)(\pi/6)$ at $x = +x_0$. The values for the barrier E and interminimal distance d are given in Figure 3 in SI units. These values, along with the curvature k of the one-dimensional symmetric double-minimum potential are given in Table I in au. The proper functional representation for the two-dimensional potential is

$$V(x) + A_0 + A_3(x/x_0)\cos(3\theta) + A_6(x/x_0)^2\sin^2 3\theta \quad (1)$$

$V(x)$ is the symmetric double-minimum potential which gives the best fit for the value of k, here the sum of a parabola and a Gaussian. The values of A_0, A_3, and A_6 are given in Table I. It should be noted that the coupling potential for 5-M-9-HPLN differs from that for 2-methyl-3-hydroxyacrolein in that the last term in eq 1 has been added in order to provide for the saddle points obtained when the methyl C–H is perpendicular to the plane of the molecule. However, this addition does not alter the D_{3d}

Table II[a]

A_{1g}	0.0	A_{1g}	0.0
E_u	4.2	E_u	4.4
E_g	14.2	E_g	15.5
A_{2u}	20.6	A_{2u}	23.0
A_{2u}	104.9	A_{2u}	103.6
E_g	100.6	E_g	110.8
E_u	112.3	E_u	126.6
A_{1g}	124.1	A_{1g}	139.6

[a] Energy levels of the two-dimensional potential energy surface for the coupled motion of the proton exchange and the methyl group rotation. The levels are in cm^{-1}. The column on the left is obtained by using 69 cm^{-1}, the experimental value for the splitting in 9-HPLN. For the column on the right the value of 88 cm^{-1} calculated for 5-M-9-HPLN was used.

symmetry of the surface. The eigenstates of this Hamiltonian belong to the A_{1g}, A_{2u}, E_g, and E_u irreducible representations (eq 13–17, ref 3). Each of the six matrices consists of a diagonal $H(n,n)$ and two subdiagonals, $H(n + 1, n)$ and $H(n + 2, n)$. The diagonal elements are readily calculated as the sum of the gerade or ungerade energy levels plus the contribution of the pertinent torsional levels (eq 8, ref 3). There is an additional contribution to the principal diagonal from the last term in eq 1 as $\langle g|x^2|g\rangle$ and $\langle u|x^2|u\rangle$. The subdiagonal $H(n + 1, n)$ has an expression similar to eq 9, ref 3. The $H(n + 2, n)$ elements will all be equal to either $A_6\langle g|x^2|g\rangle$ or $A_6\langle u|x^2|u\rangle$. The values of these transition moments are given in Table I. The effect of the subdiagonal terms is to split the doubly degenerate levels in which m is a multiple of three: the energy of one degenerate level increases while that of the other decreases, as expected in a threefold restricted rotor. If m is not a multiple of three, the nondiagonal elements will increase the separation of the levels of $m = 1$ and $m = 5$ and of $m = 2$ and $m = 4$. The separations will increase with the values of A_3, A_6, and the transition moments.

Discussion

A splitting of 88 cm^{-1} is calculated for the symmetric one-dimensional double-minimum potential. This value compares favorably with the 69 cm^{-1} obtained from the interpretation of the LIF spectrum of 9-HPLN. The energy levels for the coupled motion are listed in Table II. These levels are grouped into two manifolds separated by 80 cm^{-1}. The lower manifold, O_+, forms a narrow band of 23 cm^{-1} containing the A_{1g}, E_u, E_g, and A_{2u} levels. The upper manifold, O_- contains the levels in reverse order within 36 cm^{-1}. The average separation between the two manifolds is 104.2 cm^{-1}, close to the reported 92-cm^{-1} separation for 5-M-9HPLN. The relative positions of the energy levels are depicted in Figure 4.

The coupling between the two motions produces two opposing effects. On the one hand, the separation between the O_+ levels and the O_- levels increases with the rotational barrier, while on the other hand the width of the manifold, given by the separation between the A_{1g} and A_{2u} levels, decreases. This width determines the extent of leakage of the proton through the barrier.[3]

These trends can be qualitatively predicted. In the limit of a very high rotational barrier, the system will consist of 6 equivalent oscillator wells with sixfold degenerate eigenvalues.

The manifolds O_+ and O_- of the ground electronic state S_0 and the O^+ manifold of the upper electronic state S_1 are depicted in Figure 5. The O_+^+ transition produces a sharp signal as O_+ and O^+ have the levels in the same order. However, in the O_-^+ transition the order of the levels is reversed. This produces the broad band shown.

Conclusions

Ab initio SCF calculations do not indicate any significant decrease in the barrier for the proton exchange when the methyl group is attached to the symmetric position in 9-HPLN to form 5-M-9-HPLN.

The calculations do, however, indicate that the rotation of the methyl group has a barrier of 1.83 kJ/mol when the hydrogen bonded proton is at either minimum energy position.

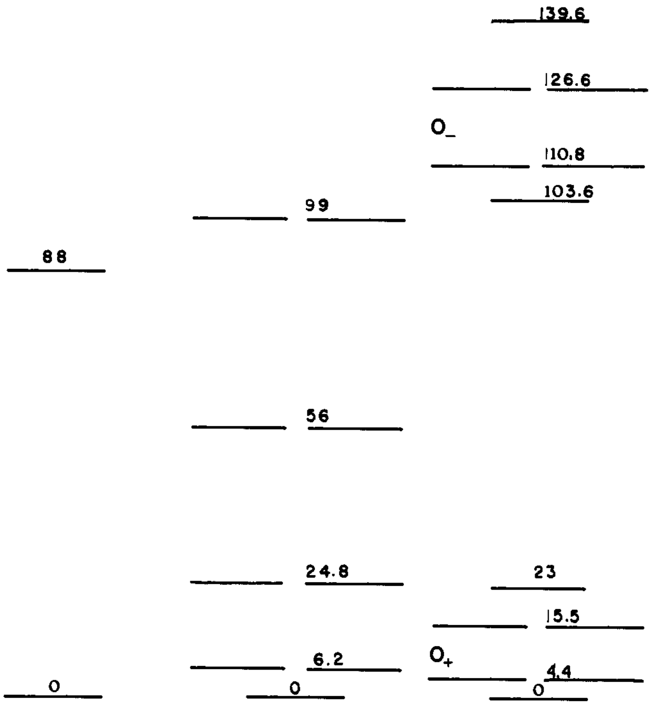

Figure 4. Energy levels, in cm^{-1}, for the coupled motion of the methyl group and the intramolecularly hydrogen bonded proton. The levels on the left are those of the one-dimensional hydrogen bonded proton. In the center are the levels for the free methyl rotation. The levels on the right are those for the coupled motion.

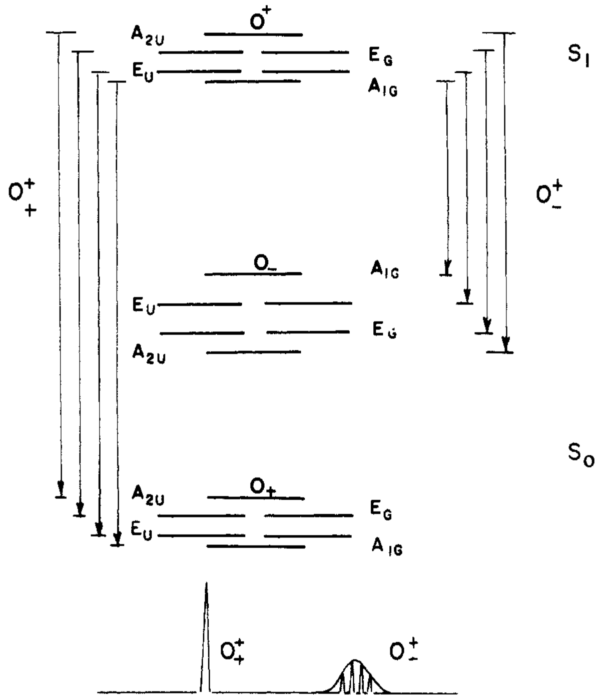

Figure 5. Schematic representation of the O_+ and O_- manifolds of the ground electronic state S_0 and the O^+ manifold of the first excited electronic state S_1. For the transitions between the O^+ and the O_+ manifold the levels with the same symmetry are in the same order. The order of the levels is reversed for the transition from O^+ to O_-.

This barrier couples the rotation of the methyl group with the nonharmonic oscillation of the proton. As a result the energy levels of the coupled motion show the pattern of the D_{3d} symmetry group to which the two-dimensional potential energy surface belongs.

This pattern shows two manifolds of energy levels: the lower one showing the A_{1g} level first, followed by the two degenerate E_u and E_g levels, and the A_{2u} level. The second manifold has the order reversed: A_u first and A_{1g} last.

The average separation between the two manifolds is found to be 104 cm^{-1} if the barrier splitting for the proton exchange of the parent compound is taken as the reported 69 cm^{-1}. This value is in good agreement with the experimentally assigned value of 92 cm^{-1}.

More interesting is that in this system the exchange between the minimum energy tautomers is not given by the splitting between the two manifolds. Also, in this case the proton oscillates anharmonically between the structures of minimum energy. The time evolution of the system is calculated by expanding the initial state in terms of the stationary states and using the coefficients of this expansion to calculate the expectation value of the proton's position as a function of time. When this value is calculated, one finds that only the transition moments between the A_{1g} and A_{2u} levels contribute to the time dependent part. However, only the coefficients of the states belonging to the same manifold contribute significantly to the amplitude of the oscillation, whose frequency corresponds to a separation of 23 cm^{-1}. This amounts to a reduction by more than one half compared to the rate of exchange in the parent compound, 9-HPLN, in line with previous claims that the proton exchange is controlled by the rotation of the methyl group.

This effect may also explain the at least tenfold increase in the rate of vibrational relaxation when the methyl group is attached in the symmetric position of the parent compound. This increase may be due to an increase in the density of states in the manifold, which would favor the transfer of energy to the phonons in the cryogenic matrix.

Transport of Small Molecules in Swollen Polymer Beads[†]

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Abstract: Pulsed-field-gradient spin-echo (PGSE) NMR experiments have been used to determine self-diffusion coefficients of toluene in swollen cross-linked polystyrene beads with 5.7–40% cross-linking. Self-diffusion coefficients were also determined for toluene in linear polystyrene solutions over a concentration range of 0.1–0.7 weight fraction of polymer. The swelling ratios of the cross-linked beads were used to determine the concentration of toluene in the beads by assuming that the increase in volume is due only to solvent uptake. A comparison of solvent diffusion in the cross-linked and the non-cross-linked systems at similar concentrations shows remarkably close agreement. These results suggest that the diffusion rate in the cross-linked polymer beads is not significantly affected by the presence of cross-links and is mainly determined by the concentration of solvent in the bead.

The use of cross-linked polymer beads is widespread in the chemical industry. They are used as supports for catalysts, ion exchange resins, solid-phase peptide syntheses, and packings for chromatography columns. In all of these applications, efficiency may be limited by the rate of transport of low molecular weight species through the polymer matrix. Previous studies have investigated reaction rates of a number of heterogeneous reactions involving polymer-bound catalysts.[1-3] By varying polymer bead size and mixing rate it was shown that in many cases the reaction rate was limited by the rate of transport of reactants in the polymer matrix.

Although there have been a significant number of studies of the dynamics of the polymer chain in these systems, very little is known about the motions of small molecules embedded in the polymer matrix. In some cases the state of the solvent can be probed with NMR since separate resonances for solvent species inside and outside of a bead may be observed in high-resolution proton[4,5] and carbon-13 NMR spectra.[6,7] Carbon-13 spin–lattice relaxation time measurements have been used to probe differences in the rotational mobility of the solvent, and, in favorable cases, these differences can be used to estimate the exchange rate in and out of the beads.[8]

In the present study, we report direct measurement of the self-diffusion coefficients of solvent molecules inside swollen cross-linked polymer beads. This is the first time that such measurements inside cross-linked polymer beads have been reported, although diffusion measurements of solvents in other microporous media, particularly zeolites, have been published previously.[9-12] The method used to probe the self-diffusion behavior of the solvent is the pulsed-field-gradient spin-echo (PGSE) NMR method. The advantage of this method is that the distance scale over which the experiment is sensitive is much less than the size of the polymer beads used. Therefore exchange between adsorbed and interstitial solvent makes a minimal contribution to the experimental results. A detailed theoretical treatment of signal attenuation in the PGSE NMR experiment as a function of diffusion, relaxation, exchange rates, and particle size in heterogeneous systems has been reported.[9-11] A general solution of it is not possible, but solutions for some limiting conditions are available. A comparison of the results of NMR studies with diffusion coefficients determined by sorption techniques[11-12] and neutron scattering[13] indicates that diffusion in the zeolite crystals can be readily determined with the PGSE technique.

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