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Depolarized Rayleigh scattering and ^{13}C NMR studies of anisotropic molecular reorientation of aromatic compounds in solution*

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Measurements of reorientational relaxation times of simple aromatic compounds have been made by both depolarized Rayleigh light scattering and ^{13}C NMR spin-lattice relaxation. Combination of the reorientation times determined by these techniques makes it possible to extract the reorientation times about the different molecular axes. The viscosity dependence of reorientation times about the individual molecular axes has been measured for benzene, mesitylene, toluene, and nitrobenzene. The viscosity dependence, which is highly anisotropic, is discussed in terms of a "slip" model of reorientational motion.

I. INTRODUCTION

In previous papers¹⁻³ (hereafter referred to as I, II, and III), we have presented measurements of reorientational relaxation times by depolarized Rayleigh scattering for a variety of molecules in solution. However, for all molecules previously studied we have been able to measure only one relaxation time from the depolarized Rayleigh spectrum which in general corresponds to some over-all rotational motion of the molecule. We have not been able to analyze the depolarized Rayleigh spectra for anisotropic rotational motion with different reorientational relaxation times about the individual axes. Recently, Gillen and Griffiths⁴ have obtained both rotational diffusion coefficients for a symmetric top molecule, benzene, by combining two experimental quantities, the reorientational relaxation times from both the Raman line shape and the deuterium spin-lattice NMR relaxation time. Several other techniques are also available for studying reorientational relaxation of small molecules. These techniques include dielectric dispersion and relaxation,⁵ nuclear magnetic^{6,7} and nuclear quadrupole relaxation,^{8,9} electron spin resonance line shapes,¹⁰ picosecond pulse techniques,¹¹ sound¹² and infrared absorption,¹³ and neutron scattering.¹⁴ In this paper we discuss results obtained by several techniques. We show that by comparing the reorientational relaxation time obtained from depolarized Rayleigh scattering to the reorientational relaxation time obtained from the nuclear magnetic resonance carbon-13 spin-lattice relaxation times, it is possible to deduce both rotational diffusion coefficients for symmetric top molecules and all three rotational diffusion coefficients for asymmetric molecules. The combination of these two techniques is particularly useful, since for both these techniques the reorientational relaxation time is easily obtained. Neither technique requires isotopic substitution, and neither is limited to those molecules for which the quadrupolar coupling constant is known. Generally, the natural abundance of ^{13}C in a molecule (1.1%) is sufficiently great to perform the NMR experiment. In this paper, the combination of light scattering and ^{13}C NMR is used to calculate the reorientation times τ_1 and τ_{\parallel} for benzene and mesitylene. For these molecules, τ_1 is the reorientation time for rotation about an axis in the plane of the ring

(perpendicular to the symmetry axis); τ_{\parallel} is the reorientation time for rotation about the symmetry axis. The viscosity dependence of both τ_1 and τ_{\parallel} has also been determined. We also use the reorientational relaxation times obtained from the two techniques to calculate τ_x , τ_y , and τ_z for toluene and nitrobenzene. For these molecules, τ_x is the reorientation time about the axis which is in the plane of the ring and passes through the substituent, τ_y is the reorientation time about the axis which is in the plane of the ring and is perpendicular to x , and τ_z is the reorientation time about the axis perpendicular to the plane. The viscosity dependence of τ_x , τ_y , τ_z is also presented, and it is discussed in terms of reorientational motion with slip boundary conditions.

II. THEORY

Pecora and Steele¹⁵ have presented a formal molecular theory of light scattering from a fluid composed of optically anisotropic molecules. Pecora¹⁶ later considered the case of a dilute solution of optically anisotropic molecules in an isotropic solvent. Keyes and Kivelson¹⁷ have derived expressions for the depolarized light scattering spectrum when pair correlations become significant. The results of these theories have been summarized in I and II.

In the rotational diffusion approximation for dilute solutions of cylindrically symmetric molecules, it is easy to show^{15,16} that the spectral density at frequency change ω associated with the depolarized component of the scattered field, $I_{\text{VH}}(\omega)$, is given by

$$I_{\text{VH}}(\omega) = \frac{AN}{15\pi} \left(\frac{n^2 + 2}{3} \right)^2 \beta^2 \frac{6\Theta_1}{\omega^2 + (6\Theta_1)^2}, \quad (1)$$

where A is a constant, N is the solute number density, n is the solution refractive index, β is the molecular optical anisotropy, and Θ_1 is the rotational diffusion coefficient about an axis perpendicular to the molecular symmetry axis. The light scattering reorientational relaxation time τ_{LS} is given by $\tau_{\text{LS}} = 1/6\Theta_1$. For molecules with C_{2v} symmetry such as toluene and nitrobenzene the theoretical light scattering spectrum consists of the sum of two Lorentzians whose relative intensities depend on the polarizabilities and rotational diffusion coefficients about the different molecular axes and whose widths are given

by $6\Theta_s + 2\Delta$, where $\Theta_s \equiv \frac{1}{3}(\Theta_x + \Theta_y + \Theta_z)$ and,

$$\Delta \equiv [(\Theta_x - \Theta_y)^2 + (\Theta_z - \Theta_y)(\Theta_z - \Theta_x)]^{1/2}. \quad (2)$$

Thus, the light scattering reorientation time for such molecules depends on a combination of all three rotational diffusion coefficients. In theory we could measure both the combinations given above by light scattering, but this would not give us enough information to determine all three rotational diffusion coefficients. In any case, in practice, as we discussed in III, it is difficult to detect more than one Lorentzian using interferometry unless certain stringent conditions are met. Unless these conditions are satisfied we can measure only a weighted average of the two reorientation times. We discuss this point further in Sec. V.

In neat liquids and concentrated solutions pair correlations may become important.² Using a simple set of assumptions based on Mori's¹⁸ statistical mechanical theory of fluctuations, Keyes and Kivelson¹⁷ derived an expression for $I_{VH}(\omega)$ for a neat liquid composed of cylindrically symmetric molecules,

$$I_{VH}(\omega) = \frac{AN}{15\pi} \left(\frac{n^2 + 2}{3} \right)^2 \times \beta^2(1+fN) \frac{[(1+gN)/(1+fN)]6\Theta_L}{\omega^2 + \{[(1+gN)/(1+fN)]6\Theta_L\}^2}, \quad (3)$$

where f is a measure of the average static orientational correlation between a pair of solute molecules and g is a measure of time displaced angular momentum correlation between a pair of molecules. The quantity f can be determined from total intensity measurements, and Keyes and Kivelson^{17,19} have argued that time displaced correlations between angular momenta of different molecules are small and therefore $gN \approx 0$. This has been shown to be the case for the only two molecules studied to date, nitrobenzene ($gN = 0.1 \pm 0.1$ for the neat liquid) and chloroform ($gN = 0.0 \pm 0.1$).² Thus it is usually a straightforward procedure to determine the "single particle" reorientation time $1/6\Theta_L$ from the light scattering reorientation time $[(1+fN)/(1+gN)]1/6\Theta_L$. For molecules such as toluene or nitrobenzene where the single particle spectrum consists of two Lorentzians, we expect that when orientational correlations are present there will still be only two Lorentzians whose widths have been modified by the static and dynamic correlation factors.

The ^{13}C NMR spin-lattice relaxation time T_1 can be related to the reorientational relaxation time τ_{NMR} . The dipole-dipole contribution to the ^{13}C spin-lattice relaxation time is given by²⁰

$$T_{1d}^{-1} = \frac{n\gamma_C^2\gamma_H^2\hbar^2}{r_{CH}^6} \tau_{\text{NMR}}, \quad (4)$$

where n is the number of protons directly attached to the carbon, γ_C and γ_H are the magnetogyric ratios for carbon and hydrogen, respectively, and r_{CH} is the carbon-hydrogen bond distance. Other relaxation mechanisms may also contribute to T_1 , but for carbons with directly bound protons the dipole-dipole contribution is usually dominant except when τ_{NMR} becomes very small. When this happens, the other major mechanism, spin-rotation,

becomes important. Fortunately the dipole-dipole contribution to T_1 can be separated from other contributions by measuring the nuclear Overhauser enhancement (NOE). T_{1d} is related to T_1 by the NOE,²⁰

$$T_{1d}/T_1 = 1.998/\text{NOE}, \quad (5)$$

where 1.998 is the maximum possible NOE. Thus by measuring both T_1 and the NOE, τ_{NMR} can be determined. Huntress²¹ has related τ_{NMR} to the components of the rotational diffusion tensor for anisotropic rotational diffusion. For symmetric top molecules such as benzene and mesitylene which have C-H bonds perpendicular to the symmetry axis,

$$\tau_{\text{NMR}} = 1/24\Theta_L + 3/4(2\Theta_L + 4\Theta_{\parallel}). \quad (6)$$

Note that $\tau_{\perp} = 1/6\Theta_L$ and $\tau_{\parallel} = 1/6\Theta_{\parallel}$.

Rearranging Eq. (6) we find that

$$\tau_{\parallel} = \frac{4\tau_{\text{NMR}} - \tau_{\text{LS}}}{5 - 2(\tau_{\text{NMR}}/\tau_{\text{LS}})}. \quad (7)$$

Thus $\tau_{\perp} (= \tau_{\text{LS}})$ may be measured directly from the light scattering spectrum (after correcting for contributions from pair correlations), and τ_{\parallel} may be obtained by combining τ_{NMR} and τ_{LS} .

For planar asymmetric molecules the expression for τ_{NMR} becomes

$$\tau_{\text{NMR}} = \frac{3}{4} \frac{1}{\Theta_r} \left\{ (\Theta_x + \Theta_s) \cos^2\varphi + (\Theta_y + \Theta_s) \sin^2\varphi - \frac{(\Theta_x - \Theta_y)^2}{(\Theta_x + \Theta_s)} \sin^2\varphi \cos^2\varphi \right\}, \quad (8)$$

where φ is the angle from the x axis (axes defined in Sec. I) in the plane, Θ_s is defined by Eq. (2) and $\Theta_r = 3(\Theta_x\Theta_y + \Theta_y\Theta_z + \Theta_x\Theta_z)$. For toluene and nitrobenzene we can measure two different NMR reorientation times: $\tau_{\text{NMR}}^{\text{para}}(\varphi = 0)$ and $\tau_{\text{NMR}}^{\text{ortho,meta}}(\varphi = \pi/3)$. These two quantities, when combined with the light scattering reorientation times, $[1/(6\Theta_s - 2\Delta)]$ or $1/(6\Theta_s + 2\Delta)$ or both, contain sufficient information to determine all three rotational diffusion coefficients.

A knowledge of the reorientational relaxation times about all axes will better enable us to evaluate a rotational diffusion model, based on the Stokes-Einstein equation, which we proposed in I. The Stokes-Einstein equation²² relates the rotation diffusion coefficient Θ to the frictional coefficient ζ , and $\Theta = kT/\zeta$, where $\zeta = 8\pi\eta a^3$ for a spherical particle of radius a in a medium of viscosity η . For ellipsoidal particles the theory is more complicated. Perrin²³ has derived equations for the two frictional coefficients of an ellipsoidal particle in terms of the medium viscosity and particle dimensions. Each of these frictional coefficients is proportional to the viscosity.

These theories use the hydrodynamic approximation, i.e., hydrodynamic equations are used to calculate the friction on a large particle immersed in a "continuum" fluid. It is assumed, furthermore, that at the surface of the rotating large particle the solvent fluid rotates with the particle. This is called the "stick" boundary condition. There is reason to expect that the results of

TABLE I. Reorientation times in mesitylene by light scattering.

% Mesitylene by volume	% Solvent by volume	Viscosity (cP)	$\tau_{LS} = \tau_1$ (psec)
20	80 <i>i</i> -C ₅ H ₁₂	0.272	5.43
20	30 <i>i</i> -C ₅ H ₁₂ ; 50 CCl ₄	0.552	8.95
20	80 CCl ₄	0.872	12.5
20	30 CCl ₄ 50 <i>c</i> -C ₈ H ₁₆	1.14	15.6
20	80 <i>c</i> -C ₈ H ₁₆	1.45	18.0
100	...	0.707	11.3

the hydrodynamic theories may be valid even for solute molecules immersed in a fluid of similarly sized molecules.^{1,24} However, the stick boundary condition may not apply. In fact computer calculations,²⁴ have shown that the Stokes-Einstein equation derived under slip boundary conditions is a good model for predicting the *translational* diffusion coefficients of hard sphere liquids. From our previous experimental results¹ it appears that the Stokes-Einstein model using slip boundary conditions would at least qualitatively describe the measured *rotational* diffusion coefficients of benzene derivatives in solution. The ultimate validity of this model can only be tested by quantitative calculations. Zwanzig is currently performing such calculations.²⁵ A direct consequence of this model is that for a sphere rotating under perfect slip conditions the reorientational relaxation time would have no viscosity dependence, and therefore the sphere would reorient inertially.²⁶ As the molecule becomes less spherical the viscosity dependence of the reorientational relaxation time will become greater. Thus rotational diffusion depends strongly on the size and shape of the rotating molecule.^{1,27}

Both the light scattering and NMR results were derived under the assumption that molecular reorientation may be described by the rotational diffusion equation. A rough criterion of the validity of this assumption can be obtained by comparing the measured reorientation

time with the reorientation time of a classical free rotor.²⁸ The free rotor reorientation time is given by $\tau_{fr} = 2\pi / 9(I/kT)^{1/2}$, where I is the moment of inertia about the axis considered.²⁹ If the measured reorientation time is much longer than τ_{fr} , then the rotational diffusion assumption is probably valid. If, however, the measured reorientation time is comparable to τ_{fr} , then inertial effects are probably dominant and the use of Eqs. (1)–(8) may not be completely valid. The qualitative conclusions should remain the same but the results may not be quantitatively correct.⁴

III. EXPERIMENTAL

All light scattering spectra were obtained using an apparatus described in I. All solutions were prepared from reagent or spectroquality liquids and were filtered through 0.2 μ Millipore Solvint filters to remove dust. The mesitylene was distilled before use. Viscosities were measured with a Cannon-Ubbelohde viscometer. The ¹³C spin-lattice relaxation times were measured with a Varian Associates XL-100-15 NMR Spectrometer by the method described in II [the pulse sequence used in these experiments was $(T-180^\circ-t-90^\circ)_x$]. NOE measurements were also made on this machine using a "gated" decoupler. The Varian program was modified so the decoupler could be turned on during the acquisition time and then turned off. In this way the ¹³C spectra could be decoupled without the enhancement. As long as the acquisition time $\ll T_1$ there is minimal enhancement, and by correcting for this small enhancement it is possible to measure the NOE simply and accurately by comparing the intensity obtained with the decoupler on continuously with that obtained with the decoupler on only during the acquisition time. An acquisition time of 0.5 sec was normally used (the T_1 's were in the range 10–30 sec). All solutions were degassed by three or more freeze-pump-thaw cycles. All experiments were run at $23 \pm 2^\circ\text{C}$.

IV. REORIENTATION IN BENZENE AND MESITYLENE

Light scattering data for mesitylene are presented in Table I. All light scattering spectra were found to fit well to one Lorentzian. Linewidths were found to be re-

TABLE II. Reorientation times in benzene and mesitylene: τ_1 and $\tau_{||}$.

% Benzene by volume	Solvent	Viscosity (cP)	T_1 (sec)	NOE	τ_{NMR}^a (psec)	$\tau_1 = \tau_{LS}^b$ (psec)	$\tau_{ }^c$ (psec)
50	<i>i</i> -C ₅ H ₁₂	0.350	24.3	1.2	1.2 ± 0.15	2.1 ± 0.05	0.7 ± 0.15
50	<i>c</i> -C ₈ H ₁₆	0.853	22.4	1.7	1.8 ± 0.2	3.85 ± 0.15	0.8 ± 0.4
50	<i>c</i> -C ₈ H ₁₁ OH	2.10	16.7	1.95	2.8 ± 0.2	8.24 ± 0.4	0.7 ± 0.3
100	...	0.607	25.2	1.6	1.5 ± 0.1	2.9 ± 0.1	0.8 ± 0.2
% Mesitylene							
50	<i>i</i> -C ₅ H ₁₂	0.369	9.3	2.0	4.9 ± 0.2	6.9 ± 0.3	3.7 ± 0.4
50	<i>c</i> -C ₈ H ₁₆	0.932	5.2	2.0	8.7 ± 0.3	13.0 ± 0.8	5.9 ± 0.7
50	<i>c</i> -C ₈ H ₁₁ OH	2.74	3.1	2.0	14.8 ± 1.0	32.0 ± 1.5	6.8 ± 1.2
100	...	0.707	5.7	2.0	8.0 ± 0.3	11.0 ± 0.5	5.9 ± 0.7

^aSee Eqs. (4) and (5).

^b τ_{LS} is derived from a least-squares fit to data in Ref. 1 for benzene and to data in Table I for mesitylene.

^cSee Eq. (7).

TABLE III. Viscosity dependence of τ_{\perp} and τ_{\parallel} for benzene and mesitylene.

Benzene	τ_{\perp}	τ_{\parallel}
Experimental slope (psec/cP) ^a	3.5 ± 0.1	0.0 ± 0.1
Experimental intercept (psec), τ_0^a	0.8 ± 0.5	0.7 ± 0.1
τ_{fr} (psec)	0.45	0.64
Mesitylene		
Experimental slope (psec/cP), C^a	10.6 ± 0.8	1.0 ± 0.5
Experimental intercept (psec), τ_0^a	3.2 ± 1.0	4.4 ± 1.0
τ_{fr} (psec)	0.8	1.2

^aFrom a least-squares fit to $\tau = C\eta + \tau_0$.

producible to $\pm 5\%$. Linewidths were derived from a non-linear least-squares fitting program³⁰ and corrected for instrumental broadening by the procedure described in I. One of the main results of our earlier work is that in the absence of strong solute-solvent interaction (e.g., H bonding, dimerization) the solute reorientation time depends only on the solution viscosity and not on the particular choice of solvent.¹⁻³ Thus, once the viscosity dependence of the reorientation time for a given concentration of solute is determined, it is possible to predict the reorientation time of the solute at this concentration in different solvent mixtures simply by measuring the viscosity of the solution. It is necessary to maintain constant solute concentration, since pair correlations (which are concentration dependent) may be important. However, if the reorientation times of the solute at different concentrations happen to have the same viscosity dependence then it can be argued that pair correlation effects are not important and that the reorientation time depends only on solution viscosity and not on either solute concentration or solvent composition. This is in fact the

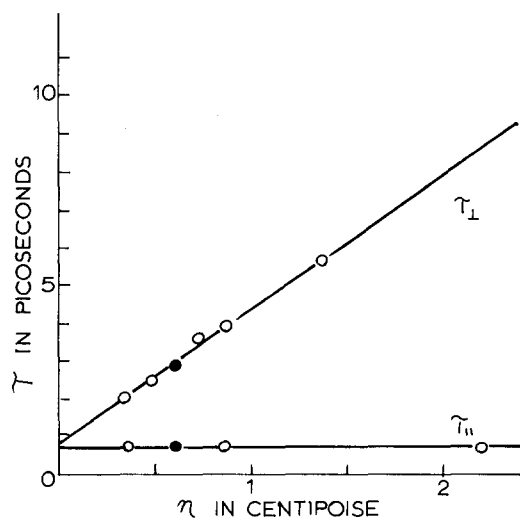


FIG. 1. Reorientational relaxation time τ vs solution viscosity for benzene solutions \circ , and neat benzene \bullet .

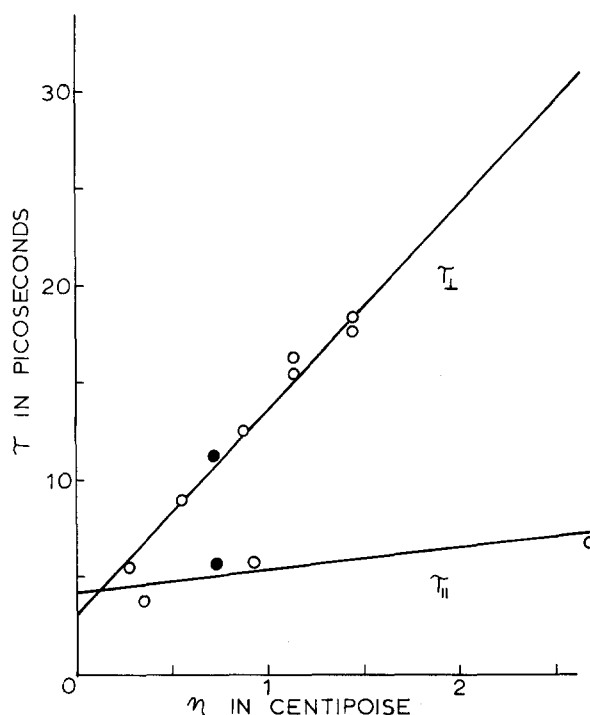


FIG. 2. Reorientational relaxation time τ vs solution viscosity for mesitylene solutions \circ , and neat mesitylene \bullet .

case for both benzene and mesitylene (see Table I and Ref. 1).

Table II presents data on the reorientation times of benzene and mesitylene. Viscosities were reproducible to $\pm 1.0\%$. The NMR T_1 data was reproducible to $\pm 5\%$ and the NOE for benzene was reproducible to ± 0.1 . This gives a total error in τ_{NMR} of about $\pm 10\%$. The NOE for neat benzene agrees well with that obtained by Levy *et al.*³¹ Kuhlmann and Grant³² found the NOE of neat mesitylene at 35°C to be 2.0, the maximum possible enhancement. Since as discussed in Sec. II the other mechanisms become important only for short τ_{NMR} (low viscosity, high temperature) it is clear that the value of the NOE for mesitylene at 23°C must also be 2.0. The NOE for all the mesitylene solutions at 23°C is taken to be 2.0. These estimated values are probably as accurate as can be experimentally determined. The values of τ_{LS} in Table II were not measured directly but are calculated by combining the measured viscosity with the parameters derived from a least-squares fit of the data in Table I (for mesitylene) and Ref. 1 (for benzene) to the straight line $\tau_{LS} = C\eta + \tau_0$. The values of C and τ_0 are listed in Table III.

Figures 1 and 2 show the viscosity dependence of τ_{\perp} and τ_{\parallel} for benzene and mesitylene, respectively. Molecular reorientation in both molecules is highly anisotropic. The slopes and intercepts are given in Table III. For neat benzene at 23° the value of τ_{\parallel} is 0.7 psec, in reasonable agreement with the results of Gillen and Griffiths⁴ who obtained a value of ~ 0.5 psec.

We note that for both benzene and mesitylene τ_{\parallel} has a much smaller viscosity dependence than τ_{\perp} . In fact τ_{\parallel} for benzene is essentially independent of viscosity. Both

TABLE IV. Reorientation times in toluene by ^{13}C NMR and light scattering.

% Toluene by volume	Solvent	Viscosity (cP)		T_1 (sec)	NOE	τ_{NMR} (psec)	τ_{LS}^a (psec)
50	<i>i</i> -C ₅ H ₁₂	0.343	<i>ortho, meta</i> ^b <i>para</i>	22.0 17.3	1.7 1.6	1.78 ± 0.1 2.19 ± 0.1	3.4 ± 0.1
50	<i>c</i> -C ₈ H ₁₆	0.882	<i>ortho, meta</i> <i>para</i>	17.1 12.6	1.95 1.85	2.70 ± 0.2 3.42 ± 0.2	6.35 ± 0.3
50	<i>c</i> -C ₈ H ₁₁ OH	2.00	<i>ortho, meta</i> <i>para</i>	13.2 9.8	2.0 1.85	3.55 ± 0.2 4.42 ± 0.4	12.5 ± 1.0
100	...	0.552	<i>ortho, meta</i> <i>para</i>	17.2 13.6	1.55 1.6	2.25 ± 0.1 2.85 ± 0.2	4.65 ± 0.2

^a τ_{LS} is derived from a least-squares fit to data in Ref. 1.

^b*Ortho* and *meta* data are an average of *ortho* and *meta* carbons. Within experimental error both T_1 and NOE were equivalent for both carbons.

these results are consistent with the slip model of rotational diffusion. Of course they may also be consistent with other models of rotational motion of liquids. They are not, however, consistent with the hydrodynamic stick model since this model predicts that the viscosity dependence of τ_{\parallel} should be greater than that of τ_{\perp} for both benzene and mesitylene.

As was discussed in Sec. II the ratio of the measured reorientation time to the free rotor reorientation time τ_{fr} gives a rough indication of the validity of the rotational diffusion approximation. By comparing the values of τ_{\perp} and τ_{\parallel} in benzene with those of τ_{fr} , we can immediately see that rotation about an axis perpendicular to the symmetry axis can probably be adequately described by rotational diffusion while rotation about the symmetry axis is most likely dominated by inertial effects. For mesitylene the rotational diffusion assumption is reasonably valid for both rotations. The small viscosity dependence of τ_{\parallel} in mesitylene is probably due to steric effects involving the methyl groups.

V. REORIENTATION IN TOLUENE AND NITROBENZENE

Reorientation times for toluene are presented in Table IV. The T_1 's are reproducible to $\pm 5\%$ or better and the NOE's to ± 0.1 . The values of τ_{NMR} are reproducible to $\pm 10\%$. The light scattering times have been derived from the least-squares fit of the data on toluene reported in I to the line $\tau_{\text{LS}} = C\eta + \tau_0$. The value of C is 5.7 ± 0.4 psec/cP and the value of τ_0 is 1.3 ± 0.3 psec. It should be noted that we observed a small concentration effect in toluene. The reorientation time of neat toluene was approximately 10%–15% slower than that of the least-squares line through the "low" concentration points. This is due to a small pair correlation effect. The values of C and τ_0 used to calculate τ_{LS} in Table IV are for the single particle time.

The times, τ_{NMR} and τ_{LS} , for nitrobenzene are taken from II. The values of τ_{NMR} were calculated assuming that the NOE for all nitrobenzene solutions is 2.0 in accordance with the value obtained by Levy *et al.*³¹ for neat nitrobenzene. The values of the single particle light scattering time were calculated from the least-squares

fit single particle slope and intercept and the solution viscosity. As discussed in II, the single particle intercept exhibited a weak concentration dependence. For this reason it is necessary to maintain a constant concentration of nitrobenzene when comparing reorientation times. For the 50% nitrobenzene solutions the single particle slope was 6.0 ± 0.4 psec/cP and the intercept was 5.6 ± 0.8 psec. Due to the necessity of correcting for the large pair correlation effect the values of τ_{LS} for nitrobenzene are estimated to be accurate to $\pm 10\%$.

The theoretical light scattering spectrum for both toluene and nitrobenzene should consist of the sum of two Lorentzians. However, all toluene spectra fit well to one Lorentzian. All nitrobenzene spectra which did not exhibit the "shear doublet" fit well to one Lorentzian. In fact this is not a surprising result. From tables of polarizabilities³³ and values of the reorientation times it is found¹⁸ that the area of the narrow Lorentzian should be approximately 50–100 times greater than that of the wide Lorentzian for both toluene and nitrobenzene. Thus the contribution of the wide Lorentzian is negligible, and the light scattering spectrum will be essentially one Lorentzian with a width given by $6\Theta - 2\Delta$.

The values of τ_x , τ_y , and τ_z are related to the experimentally determined quantities, $\tau_{\text{NMR}}^{\text{ortho,meta}}$, $\tau_{\text{NMR}}^{\text{para}}$ and τ_{LS}

TABLE V. Calculated reorientation times in toluene and nitrobenzene, τ_x , τ_y , τ_z .

% Toluene by volume	Solvent	Viscosity (cP)	τ_x^a	τ_y^a	τ_z^a
50	<i>i</i> -C ₅ H ₁₂	0.343	2.45 ± 0.3	5.1 ± 0.5	1.1 ± 0.3
50	<i>c</i> -C ₈ H ₁₆	0.828	4.11 ± 0.5	11.8 ± 1.5	1.3 ± 0.3
50	<i>c</i> -C ₈ H ₁₁ OH	2.00	7.00 ± 1.0	b	1.0 ± 0.5
100	...	0.552	3.14 ± 0.3	7.84 ± 1.0	1.3 ± 0.3
% Nitrobenzene					
50	<i>i</i> -C ₅ H ₁₂	0.703	5.4 ± 0.5	19.0 ± 3.0	4.1 ± 0.5
50	CCl ₄	1.25	6.8 ± 0.7	34.0 ± 6.0	4.5 ± 0.5
50	<i>c</i> -C ₈ H ₁₆	1.70	7.9 ± 1.5	51.0 ± 12.0	4.7 ± 0.7

^aError limits were calculated taking "worst possible" values from Tables IV and V.

^bUndetermined. See discussion.

TABLE VI. Viscosity dependence of τ_x , τ_y , and τ_z for toluene and nitrobenzene.

Toluene	τ_x	τ_y	τ_z
Experimental slope (psec/cP), C^a	3.2 ± 0.4	12.5 ± 1.5	0.0 ± 0.3
Experimental intercept (psec), τ_0^a	1.2 ± 0.5	1.0 ± 1.0	1.2 ± 0.3
τ_{fr} (psec)	0.45	0.67	0.81
Nitrobenzene			
Experimental slope (psec/cP), C^a	2.7 ± 0.5	26.0 ± 5.0	0.6 ± 0.4
Experimental intercept (psec), τ_0^a	3.5 ± 1.0	$2.0^{+0.0}_{-2.0}$	3.7 ± 1.0
τ_{fr} (psec)	0.55	0.96	1.1

^aFrom a least-squares fit to $\tau = C\eta + \tau_0$.

by Eqs. (2) and (8) and the definition $\tau_i \equiv 1/6\theta_i$ (where $i = x, y, z$). The values of τ_x , τ_y , and τ_z were obtained by an iterative procedure which first involves calculating the values τ_y/τ_x and τ_z/τ_x from the experimental values $\tau_{NMR}^{ortho,meta}/\tau_{NMR}^{para}$ and $\tau_{NMR}^{para}/\tau_{LS}$. The absolute values of τ_x , τ_y , and τ_z were then calculated from the experimental value of τ_{LS} . These values are listed in Table V for toluene and the 50% nitrobenzene solutions. The other nitrobenzene solutions would be similar to the 50% solutions with the 20% solutions having, in general, slightly shorter reorientation times. The value of τ_y for the 50% toluene-50% cyclohexanol solution is not tabulated because in this region of highly anisotropic reorientation, the experimental ratios are not very sensitive to the val-

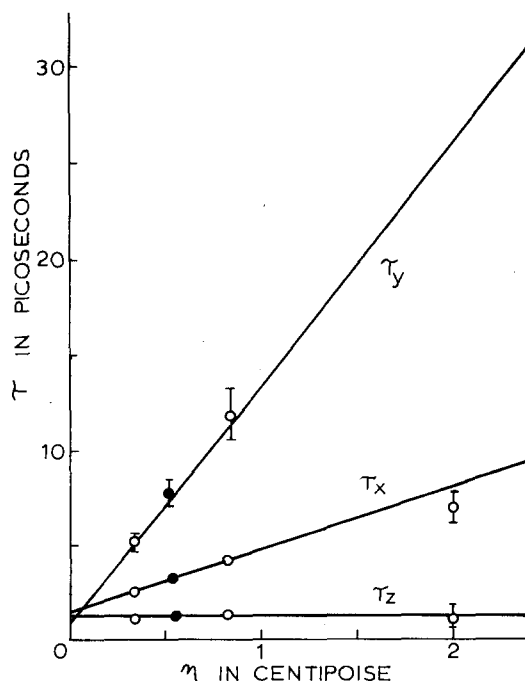


FIG. 3. Reorientational relaxation time τ vs solution viscosity for toluene solutions \circ , and neat toluene \bullet .

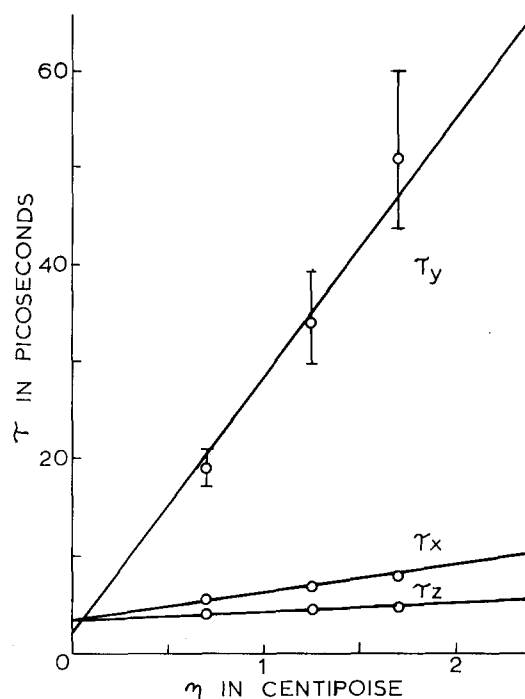


FIG. 4. Reorientational relaxation time τ vs solution viscosity for nitrobenzene solutions.

ue of τ_y . Small errors in $\tau_{NMR}^{para}/\tau_{LS}$ give rise to large errors in τ_y . Considering that it is difficult to maintain the NMR tube to within better than $\pm 2^\circ\text{C}$ it is not surprising that the errors in τ_y are rather large. It is possible to place a lower limit of 20 psec on the value of τ_y . A line drawn through the other three points gives a value of ~ 26 psec.

The viscosity dependences of τ_x , τ_y , and τ_z are shown for toluene and nitrobenzene in Figs. 3 and 4, and the least-squares slopes and intercepts are shown in Table VI. The viscosity dependences are again consistent with the slip model of reorientational motion. In both cases the reorientation about the z axis is fastest and has almost no viscosity dependence. For toluene this rotation most likely is dominated by inertial effects. This rotation takes place almost within the volume of the molecule and does not appreciably disturb the solvent. Reorientation about the x axis has a viscosity dependence which is reasonably similar to that of benzene. This is not surprising, especially for toluene. If the methyl group rotates independently of the benzene ring, one would predict that reorientation about the x axis in toluene should be identical with the perpendicular reorientation in benzene. Reorientation about the y axis is slowest because it involves flipping both the ring and the substituent group. It is interesting to note that the viscosity dependence of τ_y for toluene is very similar to the viscosity dependence of τ_1 in mesitylene. It is rather surprising that the viscosity dependence of τ_y in nitrobenzene is twice that of τ_y in toluene. Perhaps this is evidence for the formation of a "weak" dimer³⁴ which hinders rotation about the y axis.

Other workers have previously measured the reorientational anisotropy for other symmetric or nearly sym-

metric tops.^{4,8,9,35,36} In general the reorientation time τ_{\parallel} is shorter than τ_{\perp} which is in qualitative agreement with the slip model of molecular reorientation—the more “spherical” rotation is the faster. Most notable is the work of Kintzinger and Lehn⁸ on molecular reorientation in pyridine. They analyze the deuterium and ^{14}N quadrupolar relaxation times of selectively deuterated pyridine analogs. They treat pyridine both as a symmetric top and a planar asymmetric top, and report the temperature dependence of the reorientation time about each axis. They find that pyridine can adequately be treated as a symmetric top and that the temperature dependence of τ_{\perp} is greater than the temperature dependence of τ_{\parallel} .

VI. CONCLUSION

We have measured the reorientation times of benzene, mesitylene, toluene, and nitrobenzene by depolarized light scattering and ^{13}C spin–lattice relaxation. We have determined the viscosity dependences of the two reorientation times of benzene and mesitylene and of all three reorientation times of toluene and nitrobenzene. The viscosity dependences of the reorientation times depend strongly on the anisometries in molecular shape. The reorientation that “least disturbs the solvent” [rotates within its own volume] has the least viscosity dependence and is the fastest. The reorientation that “moves” the most solvent has a greater viscosity dependence and is slower. We have qualitatively explained this highly anisotropic reorientation in terms of a slip model of reorientational motion. Of course, a more detailed dynamical theory of reorientation that is easily applicable to experimental results should be formulated.

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