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ARTICLES

Anisotropic Reorientational Dynamics of Toluene in Neat Liquid. A ^{13}C Nuclear Magnetic Relaxation Study

Laszlo Sturz and Andreas Dölle*

Institut für Physikalische Chemie, Rheinisch-Westfälische Technische Hochschule, 52056 Aachen, Germany

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The reorientational motion of toluene in neat liquid was examined by using ^{13}C nuclear magnetic relaxation. The temperature-dependent dipolar spin−lattice relaxation rates and cross-correlation rates between the dipolar and the chemical-shift anisotropy relaxation mechanisms were measured for different ^{13}C nuclei in the molecule over a temperature range of 253 to 318 K. Assuming the molecular frame to show an anisotropic rotational motion, we found three different rotational diffusion constants about the molecular rotation axes. Reorientation velocities about the C_2 axis and the axis perpendicular to the molecular plane were of comparable magnitude, but change their ratio in the temperature range investigated in this study. The reorientation about the axis in the molecular plane and perpendicular to the C_2 axis was found to be approximately 2 to 3 times slower. The rotational diffusion constants were fitted to an Arrhenius equation, and activation energies from 3.5 to 9.1 kJ mol^{-1} were found. Furthermore, correlation times for the reorientation of different ^{13}C−^{1}H bonds, spin−lattice relaxation rates for the chemical-shift anisotropy and spin-rotation mechanisms were also derived for the different ^{13}C nuclei.

Introduction

Toluene is a common solvent used in a variety of technical processes, and an investigation on its rotation dynamics will be helpful in the understanding of its solvation properties. Furthermore, comparing the rotational motion of different substituted benzenes with benzene will give information on the effect of substituents on the overall dynamics of the molecules. Several authors[1−7] have investigated the rotational dynamics of toluene with NMR and light-scattering techniques. With NMR, ^{13}C or ^{2}H spin−lattice relaxation is used to assess the dipolar or quadrupolar contribution to relaxation, respectively, from which a correlation time for the reorientation of the respective ^{13}C−^{1}H/^{2}H bond can be obtained. In general, i.e., for anisotropic rotational motion of toluene, three different rotational diffusion constants will be obtained that are a measure of the reorientational velocity about the molecular axes.

If the NMR signals of different ^{13}C nuclei in the aromatic ring cannot be resolved, the rotational motion may be interpreted in terms of an averaged isotropic model.[1,2] Even if different spin−lattice relaxation times are observed for monosubstituted benzenes, there is still the problem of the relaxation times of the ^{13}C nuclei in ortho and meta positions being quite similar to each other due to the molecular symmetry. In effect, only two equations can be used to evaluate the three unknown rotational diffusion constants. Treating toluene as a symmetric-top molecule, Levy et al.,[3] Hamza et al.,[5] and Lambert et al.[6] obtained results for the anisotropy of its rotational dynamics.

Combining NMR correlation times with correlation times obtained from depolarized Rayleigh scattering measurements, Bauer et al.[4] obtained three correlation times for the reorientation of toluene about its principal axes. Bluhm[7] reported the first

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* To whom correspondence should be addressed. E-mail: doelle@rwth-aachen.de.

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results obtained by using only measurements of NMR relaxation data and assuming fully anisotropic motion. However, this derivation of three different rotational diffusion constants from the dipolar relaxation rates of the carbon nuclei has the drawback that the similarity of these rates for the carbon nuclei at meta and ortho positions introduces a large error into the calculations as described above. Thus, when only conventional NMR relaxation data from the dipolar or quadrupolar pathway are used, there are doubts about the reliability of these results.

Other mechanisms important for the relaxation of ^{13}C nuclei in toluene are the chemical-shift anisotropy and spin-rotation mechanism. Separating the relaxation rates is difficult in the first case, because it requires measurements at different resonance frequencies, i.e., magnetic fields.[8] In the second case, reliable values on the coupling constants between spin system and the lattice are not reported in the literature. Another possibility to gain information about molecular tumbling is the cross-correlation of the dipolar and chemical-shift anisotropy mechanisms. This cross-correlation, which can be observed in coupled ^{13}C spectra, causes relaxation asymmetries of the split multiplet lines, and cross-correlation rates can be calculated from the evolution of these asymmetries. In the present study, the ^{13}C dipolar relaxation rates and one cross-correlation rate of the aromatic ring were used to determine the three rotational diffusion constants. In a forthcoming publication the internal rotation of the methyl group will be treated by applying the results of the present paper and using an anisotropic model for reorientational motions of toluene.

Theoretical Background

The formalism by Grant et al.[9,10] and Canet[11] is used to describe the relaxation in coupled $^{13}C-^{1}H$ systems. In this formalism the longitudinal relaxation is given by the time dependence of the magnetization modes $\boldsymbol{\nu}(t)$ with

$$\frac{d\boldsymbol{\nu}(t)}{dt} = -\boldsymbol{\Gamma}\boldsymbol{\nu}(t) \tag{1}$$

where $\boldsymbol{\Gamma}$ is the relaxation matrix and the vector $\boldsymbol{\nu}(t)$ contains the orthonormal magnetization modes. In a two-spin-$^1/_2$ system the latter are given by the equations

$$\begin{aligned} \boldsymbol{\nu}_1(t) &= \overline{\langle \hat{I}_z \rangle} - I_z^{eq} \\ \boldsymbol{\nu}_2(t) &= \overline{\langle \hat{S}_z \rangle} - S_z^{eq} \\ \boldsymbol{\nu}_3(t) &= \overline{\langle 2\hat{I}_z\hat{S}_z \rangle} \\ \boldsymbol{\nu}_4(t) &= \overline{\langle \hat{E}/2 \rangle} \end{aligned} \tag{2}$$

Here, $\boldsymbol{\nu}_1(t)$ and $\boldsymbol{\nu}_2(t)$ correspond to the total ^{13}C and ^{1}H polarizations after subtraction of their thermal equilibrium values, $\boldsymbol{\nu}_3(t)$ to the longitudinal two-spin order of the coupled ^{13}C and ^{1}H spins, and $\boldsymbol{\nu}_4(t)$ to the summation over the populations of all energy levels in the $^{13}C-^{1}H$ spin system. $\langle \hat{I}_z \rangle$ and $\langle \hat{S}_z \rangle$ are the ensemble averages over the expectation values for the z components of the ^{13}C and ^{1}H spin operators, respectively, and $\hat{E}$ is the identity operator.

The relaxation matrix is symmetric ($\Gamma_{ij} = \Gamma_{ji}$), and the matrix elements are linear combinations of the spectral densities. The elements Γ_{4n} and Γ_{m4} cancel out, while $\Gamma_{23} = \Gamma_{32}$ can be assumed to be very small compared to the remaining elements.[12] Following the notation by Grant et al.,[9,10] and when the extreme narrowing condition ($\omega\tau \ll 1$) holds, the remaining elements for toluene are

$$\begin{aligned} \Gamma_{11} &= \frac{1}{T_1^{\ DD}} + \frac{1}{T_1^{\ CSA(I)}} + ... = \frac{5}{6}J^{DD} + J^{CSA(I)} + ... \\ \Gamma_{12} &= \Gamma_{21} = \frac{5}{12}J^{DD} = \frac{1}{2}\frac{1}{T_1^{\ DD}} \\ \Gamma_{22} &= \frac{1}{T_1^{\ DD}} + \frac{1}{T_1^{\ CSA(S)}} + ... = \frac{5}{6}J^{DD} + J^{CSA(S)} + ... \\ \Gamma_{13} &= \Gamma_{31} = J^{DD-CSA(I)} \\ \Gamma_{33} &= -\Gamma_{11} - \Gamma_{22} + \frac{14}{5}\Gamma_{12} \end{aligned} \tag{3}$$

in which Γ_{11} is the longitudinal relaxation rate of the ^{13}C nucleus I, Γ_{22} is the longitudinal relaxation rate of the ^{1}H nucleus S, Γ_{12} is the cross-relaxation rate between the nuclei I and S, Γ_{13} is the cross-correlation rate between the dipolar and the chemical-shift anisotropy mechanisms for nucleus I, and J^{DD}, J^{CSA}, and J^{DD-CSA} are the spectral densities for the dipolar and chemical-shift anisotropy autocorrelation functions and the cross-correlation function, respectively.

When the model of small-step diffusion is applied,[13] the relation between the longitudinal relaxation times and the rotational diffusion constants are given according to Grant et al.[10] or Huntress[14]

$$\begin{aligned} \frac{1}{T_1^{\ DD}} &= \frac{10}{12}J^{DD} = \\ & K_{DD}^2\left[\frac{11R_x^{\ 2} + 58R_xR_y + 11R_y^{\ 2} + 88(R_x + R_y)R_z + 32R_z^{\ 2}}{96(R_x + R_y + 4R_z)(R_xR_y + R_xR_z + R_yR_z)}\right] + \\ & K_{DD}^2\left[\frac{12(R_x - R_y)(R_x + R_y + 4R_z)\cos(2\Theta) - 9(R_x + R_y)^2\cos(4\Theta)}{96(R_x + R_y + 4R_z)(R_xR_y + R_xR_z + R_yR_z)}\right] \end{aligned} \tag{4}$$

$$\begin{aligned} \frac{1}{T_1^{\ CSA(I)}} &= J^{CSA(I)} = \\ & K_{CSA(I)}^2\left[\frac{2(R_x + R_y + 4R_z)^2 + (R_x^{\ 2} + 6R_xR_y + R_y^{\ 2} + 8(R_x + R_y)R_z)\eta_{CSA(I)}^2}{180(R_x + R_y + 4R_z)(R_xR_y + R_xR_z + R_yR_z)}\right] + \\ & K_{CSA(I)}^2\left[\frac{(R_x - R_y)\eta_{CSA(I)}(4(R_x + R_y + R_z)\cos(2\Theta) + (R_x - R_y)\eta_{CSA(I)}\cos(4\Theta))}{180(R_x + R_y + 4R_z)(R_xR_y + R_xR_z + R_yR_z)}\right] \end{aligned} \tag{5}$$

$$\begin{aligned} \Gamma_{13} &= J^{DD-CSA(I)} = \\ & -K_{DD}K_{CSA(I)}\left[\frac{2(R_x + R_y + 4R_z)^2 + 3\eta_{CSA(I)}(R_x^{\ 2} + 6R_xR_y + R_y^{\ 2} + 8(R_x + R_y)R_z)}{120(R_x + R_y + 4R_z)(R_xR_y + R_xR_z + R_yR_z)}\right] - \\ & K_{DD}K_{CSA(I)}\left[\frac{2(R_x - R_y)(R_x + R_y + R_z)(3 + \eta_{CSA(I)})\cos(2\Theta) + 3(R_x - R_y)^2\cos(4\Theta)}{120(R_x + R_y + 4R_z)(R_xR_y + R_xR_z + R_yR_z)}\right] \end{aligned} \tag{6}$$

Here, R_x, R_y, and R_z are the rotational diffusion constants, Θ is the angle between the x axis of the rotational diffusion system and the C−H bond in question (see Figure 1). K_{DD} and $K_{CSA(I)}$ are the coupling constants for the dipolar and the chemical-shift anisotropy interaction, respectively. They are given by $K_{DD} = (\mu_0/4\pi)(\gamma_C\ \gamma_H\hbar/r^3)$ and $K_{CSA(I)} = \omega_C\Delta\sigma_{CSA(I)}$, with $\Delta\sigma_{CSA(I)}$ and $\eta_{CSA(I)}$ as the chemical-shift anisotropy and asymmetry of the ^{13}C nucleus, respectively. Following the convention $|\sigma_{zz}| \geq |\sigma_{yy}| \geq |\sigma_{xx}|$, the chemical-shift anisotropy and asymmetry are given by $\Delta\sigma = \sigma_{zz} - (^1/_2)(\sigma_{xx} + \sigma_{yy})$ and $\eta = (^3/_2)(\sigma_{xx} - \sigma_{yy})/\Delta\sigma$. The principal interaction axes are shown in Figure 2 for the para ^{13}C nucleus as an example. For the other nuclei the z

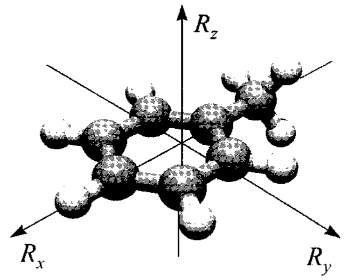

Figure 1. Orientation of the rotational diffusion principal axis system for the optimized structure of toluene.

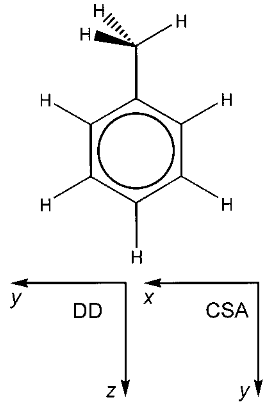

Figure 2. Orientation of the principal axis systems of the dipolar and chemical-shift interactions given for the para ^{13}C nucleus of toluene as an example.

and *y* axes of the DD and CSA interactions are also parallel to the C−H bond. The other symbols have the usual meanings.

The temperature dependence of the rotational diffusion constant about axis *i* is often described by an Arrhenius equation

$$R_i = R_{i0} \exp(-E_{Ai}/RT) \tag{7}$$

Results

The molecular geometry related to the inertial principal axis system is shown in Figure 1. The total longitudinal relaxation rates $1/T_1$, NOE factors η_{C-H}, and DD-CSA cross-correlation relaxation rates $1/T_1^{DD-CSA}$ were measured for the different ^{13}C nuclei of the aromatic ring in a temperature range from 253 to 318 K and at a ^{13}C resonance frequency of 62.89 MHz. The results for the different relaxation rates are given in Figure 3 for the aromatic ortho, meta, and para ^{13}C nuclei as a function of the reciprocal temperature. The rotational diffusion constants obtained are plotted in Figure 4; rotational anisotropies were calculated from the ratio of these values and are shown in a logarithmic plot in Figure 5. The activation parameters from a fit to the data are contained in Table 1.

Discussion

As can be seen from Figure 3, the observed relaxation rates decrease with increasing temperature, which is the typical behavior in the extreme narrowing region, where $\omega\tau \ll 1$ is valid. The reorientational motion becomes faster with increasing temperature and the relaxation interactions less effective. The relaxation rates via the CSA relaxation mechanism were calculated from the rotational diffusion constants by using eq 5 and the values 181.5 ppm and 0.72 for the chemical shift anisotropy $\Delta\sigma_{CSA}$ and asymmetry η_{CSA}, respectively. These values taken from Pines et al.[15] are assumed to be equal for all ^{13}C nuclei. This assumption is supported by the fact that for benzene the same value was obtained (ref 21 and literature cited therein), thus indicating that the methyl group in toluene does not affect the electronic structure of the ring carbons significantly regarding these values. The contribution of the chemical shift anisotropy mechanism to the longitudinal relaxation is 3 to 5%, independent of the position in the ring and temperature. The spin-rotation (SR) relaxation rate is obtained by subtracting the dipolar and chemical shift anisotropy relaxation rate from the total longitudinal relaxation rate. The SR and CSA relaxation rates are also shown in Figure 3. The DD relaxation mechanism dominates in the observed temperature region for all ring nuclei. The CSA and DD-CSA cross-correlation mechanisms contribute at the given field strength constantly to the total relaxation rate by approximately 5 and 15%, respectively, whereas the SR rates increase from being inconsiderable at 253 K to approximately 15% at high temperatures. The latter are the only rates that increase with increasing temperature and lead to a decrease in

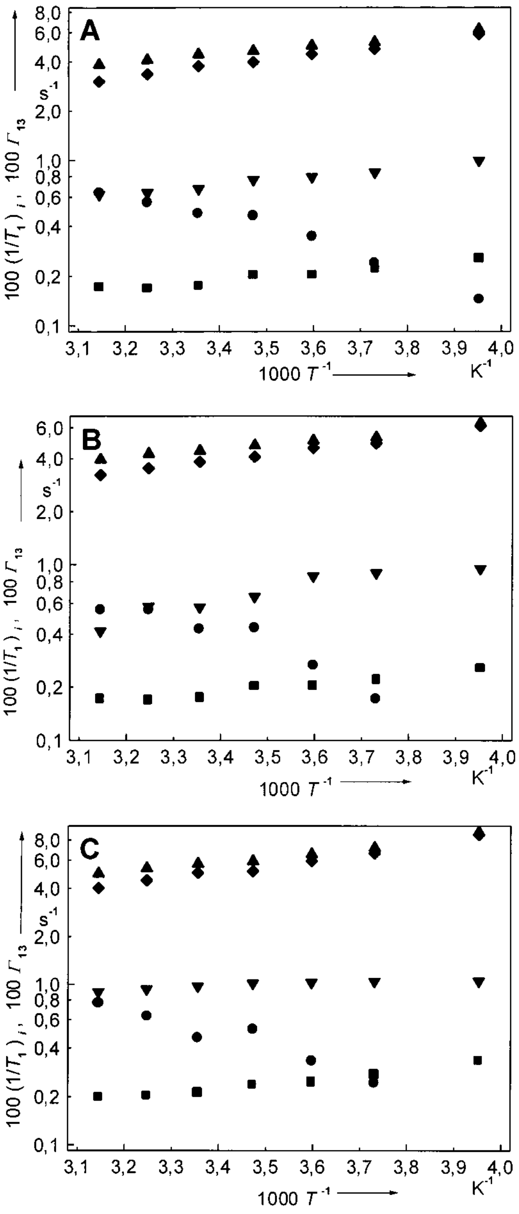

Figure 3. ^{13}C longitudinal relaxation rates $(1/T_1)_i$ of toluene at 62.89 MHz as a function of reciprocal temperature: total (▲), dipolar (♦), spin-rotation (●), chemical-shift anisotropy (■), and cross-correlation DD-CSA (▼) relaxation rates for the ortho (A), meta (B), and para (C) ^{13}C nucleus.

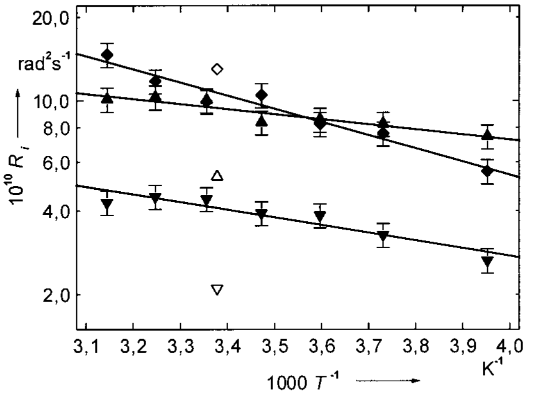

Figure 4. Rotational diffusion constants R_x (▲), R_y (▼), and R_z (♦) of toluene as a function of the reciprocal temperature compared to the values by Bauer et al.[4] (open symbols). The lines represent the fit of the Arrhenius equation to the data of the present study.

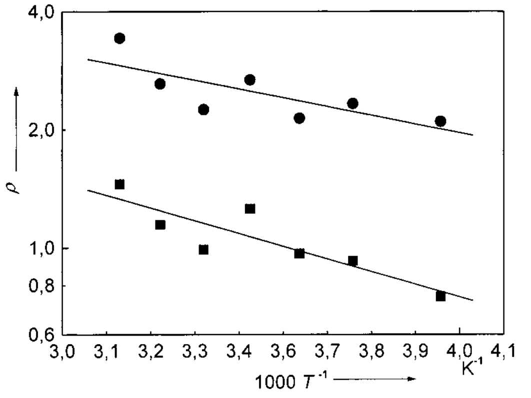

Figure 5. Anisotropies $\rho_x = R_z/R_x$ (■) and $\rho_y = R_z/R_y$ (●) for the reorientational motions of toluene.

TABLE 1: Activation Parameters of Rotational Motion for Toluene in Neat Liquid (Activation Energies E_{Ai} and Preexponential Factors R_{0i})

	$R_{0i}/10^{12}$ s^{-1}	E_{Ai}/kJ mol^{-1}	χ^2
R_x	0.4 ± 0.1	3.5 ± 0.6	4.8
R_y	0.34 ± 0.08	5.2 ± 0.5	10
R_z	4 ± 1	9.1 ± 0.6	11

the absolute value of the slope for the total relaxation rate curve plotted as a function of $1/T$.

Figures 4 and 5 show clearly that the reorientational motion of toluene is of anisotropic nature in the neat liquid. Reorientations about the *y* axis are the slowest, and those about the *x* and *z* axes are both faster and become equal to each other for a temperature of about 278 K. However, the activation energy for rotations about the *z* axis is higher, resulting in a changeover of the velocities for rotations about the latter two axes. When these results are compared with those for the symmetric rotator benzene in neat liquid,[16] the effect of the additional methyl group becomes obvious: It slows down the reorientation about all axes; particularly pronounced is the effect for rotation about the *y* and *z* axes, for which the rotational speed is slowed by a factor of 2 to 3 compared to $R_\perp$ or $R_\parallel$ for benzene, respectively. Toluene in contrast to benzene is below and above 278 K an asymmetric rotator, and the reorientation about the *z* axis is only the fastest at higher temperatures, then becoming as fast as that about the C_2 axis (i.e., about *x*), and then at lower temperatures slower than about the *x* direction. The activation energy for rotations about the axis perpendicular to the aromatic ring (*z* axis) is in contrast to benzene now the highest, about *x* it is comparable to the reorientation about the C_6 axis of benzene, and about *y* it is between both reorientational motions of benzene. The results in Figure 5 indicate that the anisotropies increase slightly with increasing temperature.

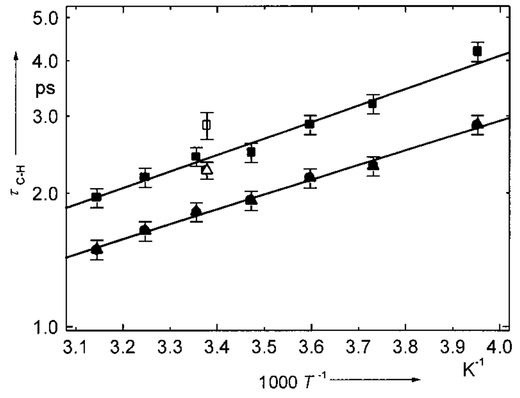

Figure 6. Calculated correlation times of the ortho (●), meta (▲), and para (■) C−H vectors of toluene compared to the values by Bauer et al.[4] (open symbols).

When it is assumed that toluene behaves like a symmetric rotator, the C_2 axis, i.e., the *x* axis, is taken to be the main axis of reorientation with the *y* and *z* axes being equal and perpendicular to it. This assumption leads for toluene, when the method by Levy et al.[3] is applied, to estimated values for the anisotropies ρ between 1.8 and 2.5 rather than 2.1 to 2.8 for R_x/R_y or 0.7 to 1.3 for R_x/R_z in the case of an anisotropically reorienting molecule, as observed in the present study. A symmetric rotator model was also applied by Hamza et al.[5] and Lambert et al.[6] These authors used the Woessner formalism to evaluate the anisotropy of the rotational motion of toluene and yielded independently a value for $\rho = R_\parallel/R_\perp$ of 2.2 at temperatures of 301[5] and 313[6] K (with $R_\parallel = R_x$ and $R_\perp = R_y = R_z$) in accordance with the method by Levy et al. (see above). Thus, methods treating toluene as a symmetric rotator are not sufficiently accurate to describe the rotational anisotropy of toluene in neat liquid properly because in contrast to the assumption of these simplifying models reorientation about *x* is approximately as fast as that about the *z* axis.

Using the method by Levy et al.[3] implies that the dipolar relaxation rates are directly proportional to the correlation times for reorientation of the corresponding $^{13}C-^{1}H$ vectors. Since the dipolar relaxation rates for the ortho and meta ^{13}C nuclei are not the same, different correlation times have to be expected when only the directly bound protons are taken into account in the evaluation of the correlation times. This, however, is physically not reasonable because of the symmetry of the toluene molecule. The relaxation rate for the meta ^{13}C nucleus is slightly larger because it has one more rigid proton in its neighborhood than the ortho ^{13}C nucleus. Therefore, the correlation times were calculated from the rotational diffusion constants and plotted logarithmically against the reciprocal temperature in Figure 6. As can be seen from the figure, the correlation times for the ortho and meta carbon now fall onto each other as expected, whereas the correlation time for the para $^{13}C-^{1}H$ vector is longer.

The reorientational correlation times about the rotational diffusion principal axes *x*, *y*, and *z* obtained by Bauer et al.[4] from combined depolarized Rayleigh light scattering and NMR measurements are recalculated to give the rotational diffusion constants at only one temperature value of 296 K with the values 5.3×10^{10}, 2.1×10^{10}, and 13×10^{10} rad^2 s^{-1}, respectively. The corresponding values of the present study at a temperature of 298 K are 10×10^{10}, 4.4×10^{10}, and 9.9×10^{10} rad^2 s^{-1}, being in contradiction with the former values; i.e., toluene behaves at that temperature like a symmetric rotator. The reason for this discrepancy may be caused by the fact that different spectroscopic techniques were used to evaluate the rotational diffusion constants. The values for the rotational diffusion constants obtained by Bluhm[7] scatter too much and are not further discussed here because of the reasons given in the Introduction.

The χ test introduced by Wallach and Huntress[17] gives a criterion for whether the model of small-step rotational diffusion is valid for the investigated rotational motion or whether inertial effects predominate. When the reorientational correlation time τ_i about the ith rotation axis is larger than the mean period $(\tau_f)_i$ of free rotation, the molecular motion is in the regime of rotational diffusion, and the following relation is valid:

$$\chi_i = \left(\frac{\tau}{\tau_f}\right)_i = \frac{5}{18R_i}\sqrt{\frac{kT}{I_i}} \gg 1 \tag{8}$$

with the principal moments of inertia $I_x = 1.53 \times 10^{45}$ kg m^2, $I_y = 3.29 \times 10^{45}$ kg m^2, $I_z = 4.76 \times 10^{45}$ kg m^2, the temperature T, and the Boltzmann constant k. For rotation about the axes x, y, and z the χ_i values ranged from 4.7 to 5.7, 7.5 to 11, and 1.8 to 4.3, respectively. With the classification of the χ_i values given by Gillen and Noggle,[18] the reorientational motion about the x and y axes are in the rotational diffusion regime, whereas that about the z axis cannot be interpreted in terms of a simple rotational diffusion model, since inertial effects are partially involved. Therefore, it appears questionable if the rotational diffusion model is fully applicable for the evaluation of the data. Although approaches like the extended diffusion model exist to treat cases in which inertial effects are becoming important for reorientational motions, they are presently still not capable of representing anisotropic molecular reorientational motion.[8,19]

Conclusions

The reorientational motion of toluene in the neat liquid is clearly anisotropic. Toluene behaves like a symmetric rotator at a temperature of approximately 278 K with the rotations about the C_2 axis and the axis perpendicular to the aromatic plane being equal to each other. Since the activation energies for both rotational modes are slightly different, the reorientation about the axis perpendicular to the aromatic plane is faster at higher and slower at lower temperatures than about the C_2 axis. Rotations about the axis in the aromatic plane perpendicular to the C_2 axis are always the slowest. The activation parameters for the rotational motion are, to the authors knowledge, given in the present study for the first time. The measurement of the DD-CSA cross-correlation relaxation rates proved to be a valuable tool in the investigation of the rotational motions of aromatic molecules.

Methods

The distances and angles necessary for the calculations were obtained using the semiempirical AM1 method[20] implemented in the HyperChem program package.[21] The bond distances between the ^{13}C nuclei and the directly bonded protons are 110.0 pm, and the angles Θ_{meta} and Θ_{ortho} are 60.2° and 119.7°, respectively.

All NMR experiments where performed on a Bruker AM 250 spectrometer ($B_0 = 5.875$ T, $\nu_0(^1\mathrm{H}) = 250.13$ MHz, $\nu_0(^{13}\mathrm{C}) = 62.89$ MHz, lock on ^{2}H of [^{2}H$_6$]acetone in a 10 mm NMR tube surrounding the inner NMR tube with 7.5 mm diameter which contained the degassed toluene). The 8 to 16 transients were collected with a spectral width of 8900 Hz into 16 K time domain points. The 90° pulse length was in the range of 15 μs, and the relaxation delay was 5 T_1 for measurement of the longitudinal ^{13}C relaxation times and 10 T_1 for the measurement of the NOE Factors and DD-CSA cross-correlation rates. ^{1}H broad-band decoupling was achieved by employing a WALTZ sequence.[22]

Measurements of T_1 were carried out with the inversion−recovery pulse sequence. The 180° pulse was replaced by a composite pulse cluster[23,24] $90°_\phi 240°_\phi 90°_\phi$ to improve the quality of spin-inversion. The spin−lattice relaxation times were obtained from the ^{1}H broad-band decoupled ^{13}C spectra by using a three-parameter exponential fit implemented in the spectrometer software. The relaxation data were extracted from the signal heights, the dipolar relaxation rates obtained from

$$\frac{1}{T_1^{\mathrm{DD}}} = \frac{\eta_{\mathrm{C-H}}}{\eta_{\mathrm{C-H,max}}}\frac{1}{T_1} \tag{9}$$

where $\eta_{\mathrm{C-H,max}} = 1.988$ is the maximum nuclear Overhauser factor. The performance of the NOE experiments was tested using the Overhauser factor of cyclooctane, which was $\eta = 2.00$, being within experimental error the maximum Overhauser factor.[25] Two-level broad-band decoupling and using the signals heights yielded in our experiments $\eta = 1.94 \pm 0.01$.

Applying the inversion−recovery sequence to a ^{13}C−^{1}H spin system without proton decoupling gave a spectrum in which the lines belonging to one nucleus show a difference in the signal heights as a function of the delays between the first and the second pulse of the inversion−recovery sequence. While the signals of the nuclei in meta and para positions partially overlapped in the spectrum, the multiplet resulting from the nuclei in the ortho position was isolated from the first ones and split mainly into two groups. Thus, the obtained FIDs were treated with an exponential multiplication using a line broadening factor of 6 Hz in order to suppress the appearance of the small long-range ^{13}C−^{1}H couplings. Regarding the nucleus in the ortho position, this procedure allows the ^{13}C−^{1}H spin system to be treated as an AX spectrum in a first-order approximation. Then, the time dependence of the two-spin-order $\nu_3(t) = \langle 2\hat{I}_z\hat{S}_z\rangle(t)$ is directly related to the signal height differences of the apparent doublet lines in the coupled spectrum.[12,16,26] In the initial slope approximation, all contributions to ν_3 disappear except those by the DD-CSA cross-correlation

$$\lim_{t\to 0} \dot{\nu}_3(t) = 2\Gamma_{13} I_{\mathrm{C}}^{\mathrm{eq}} \tag{10}$$

The usual approach to extract Γ_{13} from the evolution of $\nu_3(t)$ is to estimate the initial slope from a linear approximation

$$\nu_3(t) = \mathrm{a} + 2\Gamma_{13}t \tag{11}$$

which is the first-order expansion of the triexponential solution of $\nu_3(t)$. Since the assumption of the linear approximation is always limited to an arbitrarily chosen time interval, the next element of the expansion series was also taken into account.[16] Within the time interval of $t = 0$ to 8.6 s the parabolic fit

$$\nu_3(t) = a + 2\Gamma_{13}t + bt^2 \tag{12}$$

was found to be adequate and more precise than the linear approximation. The initial slopes obtained by these two methods varied up to 40%.

The measurements of the spin−lattice relaxation times were repeated 4 times, those for the NOE factors 10 times, and those for the DD-CSA cross-correlation relaxation rates 4 times. The mean standard deviations of the total and dipolar relaxation rates and the NOE factors were below 1% in all cases. The exponential fit to the experimental data showed within the experimental error a full inversion of the magnetization when the composite pulse cluster was applied. The standard deviations of the cross-correlation rates were between 5 and 15%. The accuracy of the temperature measurements is estimated to be ±1 K.

For evaluation of the three rotational diffusion constants, the theoretical expressions (eqs 4 to 6) for the dipolar relaxation rates of the carbons in ortho, meta, and para positions as well as for the cross-correlation rate of the carbon in the ortho position were fitted to the experimental results with the rotational diffusion constants as variable parameters. Since the values for Γ_{13} from the meta and para positions were not accurate enough because of partial overlap in the spectrum (see above), they were omitted from the fitting procedure. While the AX approximation was used for evaluating the cross-correlation rate, the experimental dipolar rates were fitted to the sum of all dipolar components, including interactions between the carbon nucleus under consideration and all protons in the molecule (except those in the methyl group). The results for the rotational diffusion constants were mainly influenced by errors from the cross-correlation rate. Deviations of 5 to 15% resulted for the rotational diffusion constants when using $\Gamma_{13} + \sigma$ and $\Gamma_{13} - \sigma$ in the calculations, where σ is the mean standard deviation of Γ_{13}.

The computation of the activation parameters for the rotational diffusion constants was achieved by a FORTRAN 77 program,[27] which performed a χ^2 fit of the activation parameters to the experimental rotational diffusion constants by the Levenberg−Marquardt method.

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