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^{13}C NMR Relaxation Rates: Separation of Dipolar and Chemical Shift Anisotropy Effects

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The process of obtaining molecular reorientational dynamics from ^{13}C spin−lattice relaxation data is simplified for aromatic carbons in viscous solutions. Spin−lattice relaxation times (^{13}C) are used to determine pseudorotational correlation times for the ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF6]). The pseudorotational correlation times are used to calculate corrected maximum nuclear Overhauser effect (NOE) factors from a combined isotropic dipolar and NOE equation. These corrected maximum NOE factors are then used to determine the dipolar relaxation rate part of the total relaxation rate for each ^{13}C nucleus in the imidazolium ring. A consequence of this analysis is that a plot of the maximum NOE factors and the total spin−lattice relaxation times have minima at similar temperatures. Chemical shift anisotropy values, $\Delta\sigma$, for the aromatic carbons in the imidazolium cation are temperature dependent with maximum $\Delta\sigma$ values at ca. the same temperature as observed for the spin−lattice relaxation times. The average $\Delta\sigma$ values for the imidazolium ring carbons are similar to those of pyrimidine in liquid crystal solutions.

Introduction

The further development of models and theories of the liquid state is of considerable importance and general interest to workers in science and technology. For example, these models and theories should provide a better understanding of molecular interactions relative to each other and their dynamic behavior in solution. The model often used to describe molecular reorientational processes in the liquid state is the rotational diffusion model.[1] The use of nuclear spin−lattice relaxation rates to obtain information on reorientational dynamics has generally been restricted to the extreme narrowing region where the product of the resonance frequency and the rotational correlation time is less than unity. Unfortunately, many systems of interest are viscous such that one is outside of the region of extreme narrowing and relaxation rates are frequency dependent. Typical systems include biological macromolecules and ionic liquids (room-temperature molten salts), to name a few.

The correlation equations that are useful to the investigator include those developed by Abragam and others,[2−8] which describe rotational molecular motion and its relationship with intramolecular events. Dipolar relaxation can be directly related to rotational motion with the use of spherical harmonic functions. Solution of the resulting autocorrelation functions produces spectral density functions, assuming exponential decay. The spectral density equations are correlation time dependent at a set frequency.[2−4] These equations describe spin−lattice (longitudinal, $R_1 = 1/T_1$) and spin−spin (transverse, $R_2 = 1/T_2$) relaxation mechanisms that include dipole−dipole, chemical shift anisotropy (CSA), spin rotation, scalar relaxation, and quadrupole relaxation.

It should be pointed out that the model of intramolecular rotation is isotropic in nature. In the case of anisotropic motion, these equations do not hold and must be modified to account for different motional characteristics. For example, the correlation function representing relaxation caused by random translational diffusion is not a single exponential. Another limitation is the possibility of a distribution of correlation times caused by internal motion in a macromolecule. Despite these potential limitations, evidence reported previously[9] indicates that the isotropic model can be used successfully to study a significant number of molecular and ionic systems in solution.

There are several models that can be used to interpret experimental nuclear relaxation data. These include (1) the classical dipolar nuclear spin model described elsewhere,[2−7] (2) the continuous distribution of correlation times by Cole and Davidson,[10] (3) the model-free approach of Lipari and Szabo[11] that is a generalization of the two-step model of Wennerström et al.,[12] and (4) the Tricomi[13] function of Zeidler.[14] These different models and theories are described elsewhere.[15,16]

In this report, we outline a method for determining ^{13}C NMR dipolar and CSA relaxation rates while using the classical dipolar relaxation model and nuclear Overhauser effect (NOE) factors to study the imidazolium ring of the 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF6]) ionic liquid. The theoretical gas-phase structure[17] of 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF6]) is shown in Figure 1. The strong hydrogen bonds between the C2 hydrogen and PF_6^- in Figure 1 are further supported by a recent molecular dynamics study of [BMIM][PF6].[18] This ionic liquid ([BMIM][PF6]) has recently been analyzed using the Cole−Davidson[10] and Lipari−Szabo[11] functions to describe molecular reorientational dynamics using ^{13}C NMR spin−lattice relaxation rates and NOE factors.[16]

Methodology

^{13}C NMR Relaxation Studies. The relaxation of ^{13}C in medium-sized molecules at moderate magnetic fields is usually caused by dipolar interactions with directly bonded protons. When the relaxation times are measured under ^{1}H decoupling conditions, the cross-relaxation term vanishes and the intramo-

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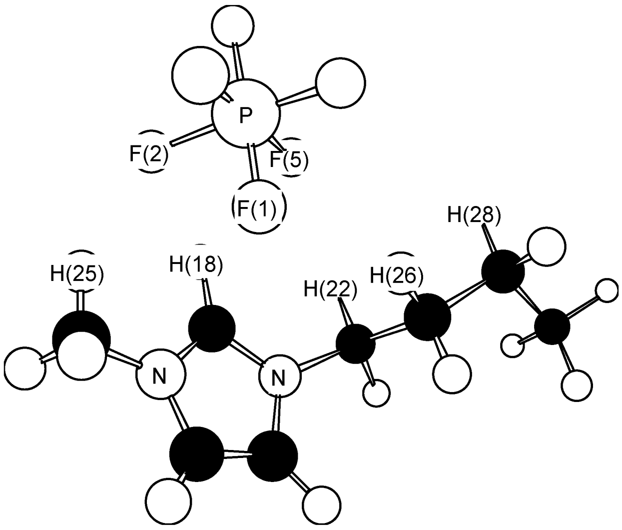

Figure 1. Molecular Structure of [BMIM][PF6] (B3LYP/6311 + G(2d,p)). Hydrogen bonds include: F2−H25 = 2.286 Å; F2−H18 = 2.089 Å; F1−H18 = 2.509 Å; F5−H18 = 2.121 Å; F5−H22 = 2.450 Å; F1−H26 = 2.493 Å; F5−H26 = 2.700 Å.

lecular dipolar longitudinal (spin−lattice) relaxation rate ($R_1^{\mathrm{DD}} = 1/T_1^{\mathrm{DD}})_i$ for the relaxation of ^{13}C nucleus i by N_{H} protons j is connected to the molecular reorientations by[2−7]

$$\left[\frac{1}{T_1^{\mathrm{DD}}}\right]_i = [1/20]\mathrm{N_H}[2\pi D_{ij}]^2[J(\omega_{\mathrm{C}} - \omega_{\mathrm{H}}) + 3J(\omega_{\mathrm{C}}) + 6J(\omega_{\mathrm{C}} + \omega_{\mathrm{H}})] \quad (1)$$

where the dipolar coupling constant is $D_{ij} = (\mu_0/4\pi)\gamma_{\mathrm{C}}\gamma_{\mathrm{H}}(h/2\pi)r_{ij}^{-3}$, μ_0 is the permeability of vacuum, γ_{C} and γ_{H} are the magnetogyric ratios of the ^{13}C and ^{1}H nuclei, respectively, and r_{ij} is the length of the internuclear vector between i and j (C−H = 1.09 Å). $J(\omega)$ are the spectral densities with ω_{C} and ω_{H}, the resonance frequencies of the ^{13}C and ^{1}H nuclei, respectively.

NOE. The NOE factor η_i of carbon atom i relaxed by N_{H} protons j is given by[2−7,19]

$$\eta_i = \gamma_{\mathrm{H}} \sum \sigma_{ij}/[\gamma_{\mathrm{C}} \sum (\rho_{ij} + \rho_i^*)] \quad (2)$$

where $\sum$ includes from $j = 1$ to N_{H}, σ_{ij} is the cross-relaxation rate, ρ_{ij} is the dipolar relaxation rate, and ρ_i^* is the leakage term that represents the contribution of all other relaxation mechanisms to the relaxation of a ^{13}C nucleus i, thus reducing the NOE factor. Usually, intermolecular dipolar contributions can be neglected for ^{13}C nuclei with directly bonded protons. Under ^{1}H decoupling conditions, the sum of ρ_{ij} over all N_{H} interacting protons gives the dipolar spin lattice relaxation rate ($R_1^{\mathrm{DD}} = R_1^{\mathrm{dipolar}} = 1/T_1^{\mathrm{dipolar}})_i$. The relaxation of ^{13}C exclusively via intramolecular dipolar interaction implies a leakage term $\rho_i^* = 0$. Thus the NOE factor reaches its maximum value and depends only on reorientational molecular dynamics[2−7,19]

$$\eta_{i,\max} = \gamma_{\mathrm{H}}[6J(\omega_{\mathrm{C}} + \omega_{\mathrm{H}}) - J(\omega_{\mathrm{C}} - \omega_{\mathrm{H}})]/\gamma_{\mathrm{C}}[J(\omega_{\mathrm{C}} - \omega_{\mathrm{H}}) + 3J(\omega_{\mathrm{C}}) + 6J(\omega_{\mathrm{C}} + \omega_{\mathrm{H}})] \quad (3)$$

Spectral Densities. Assuming isotropic tumbling, the spectral densities can be connected to the effective correlation times, τ_{c}, for reorientation of the corresponding internuclear ^{13}C−^{1}H vectors by

$$J(\omega) = 2\tau_{\mathrm{c}}/[1 + (\omega\tau_{\mathrm{c}})^2] \quad (4)$$

In theory, τ_{c} is the time required for a molecule (i.e., vector connecting the interacting nuclei) to rotate through the angle of one radian; however in fact, the correlation time is the integral with respect to time from 0 to ∞ of the normalized autocorrelation function[2,6] and is actually τ_2, the time constant for the exponential decay of the second-rank Legendre polynomial P_2. In the extreme narrowing case (low viscosity solutions − unlike ionic liquids), the product of $\omega\tau_{\mathrm{c}}$ is much less than unity and $J(\omega) = 2\tau_{\mathrm{c}}$.

CSA. Aromatic ^{13}C nuclei relax even in moderate magnetic fields partially via the CSA mechanism. The corresponding longitudinal relaxation rate of ^{13}C nucleus i is given by[2−7]

$$R_1^{\mathrm{CSA}} = [1/15]\gamma_{\mathrm{C}}^{2}H_{\mathrm{o}}^{2}(\Delta\sigma_i)^2[1 + (\eta_{\mathrm{CSA}}^{2}/3)]J(\omega_{\mathrm{C}}) \quad (5)$$

with the magnetic field strength H_0, the CSA $\Delta\sigma$ for an axially symmetric chemical shift tensor, and the asymmetry parameter, η_{CSA}. The $[1 + \eta_{\mathrm{CSA}}^2/3]$ term usually represents a correction factor of less than 5% and is therefore ignored.

Solution of the Combined Dipolar and NOE Equations

In the case of ring (aromatic) carbons, it is assumed that dipolar relaxation and CSA make up the overall relaxation rate

$$R_1^{\mathrm{total}} = R_1^{\mathrm{dipolar}} + R_1^{\mathrm{CSA}} \quad (6)$$

The dipolar (R_1^{dipolar}) and CSA (R_1^{CSA}) spin−lattice relaxation rates for aromatic carbons may be obtained as follows: (1) the experimental T_1 values are assumed to be completely dipolar and eq 1 is solved for a pseudorotational correlation time, (2) eqs 1 and 3 are combined to form eq 7, and (3) the experimental T_1 values and the pseudorotational correlation times are then used in eq 7 to determine $\eta_{\max}$

$$\eta_{\max} = N_{\mathrm{H}}[T_1^{\mathrm{DD}}/20](\gamma_{\mathrm{H}}/\gamma_{\mathrm{C}})(2\pi D_{ij})^2[6J_+ - J_-] \quad (7)$$

where $J_+ = [2\tau_{\mathrm{c}}/[1 + (\omega_{\mathrm{C}} + \omega_{\mathrm{H}})^2\tau_{\mathrm{c}}^2]]$ and $J_- = [2\tau_{\mathrm{c}}/[1 + (\omega_{\mathrm{C}} - \omega_{\mathrm{H}})\tau_{\mathrm{c}}^2]]$.

The corrected ring carbon R_1^{dipolar} is then calculated using the experimental T_1 values as follows

$$R_1^{\mathrm{dipolar}} = (\mathrm{NOE}/\mathrm{NOE_{max}})/T_1^{\mathrm{total}} \quad (8)$$

The result obtained from eq 8 is then used to solve eq 1 to determine a corrected rotational correlation time (τ_{c}) for each aromatic carbon. Finally, the aromatic carbon CSA (R_1^{CSA}) spin−lattice relaxation rates are determined from eq 6. Equation 5 is then used to calculate the CSA ($\Delta\sigma$) for an axially symmetric chemical-shift tensor.

Results and Discussion

Basic Assumptions. The basic assumption in this analysis is that the maximum value of the ^{13}C NOE in eq 3 is determined by the dipolar rotational correlation time obtained from the measured relaxation rate. In other words, eq 1 is solved for the rotational correlation time, assuming that the measured ^{13}C relaxation rate is completely dipolar. This rotational correlation time is then used with eq 7 to determine a maximum NOE value (≤1.988 for ^{13}C). This maximum NOE value is then compared with the measured NOE value, and eq 8 is used to generate a new (corrected) value of the dipolar relaxation rate. This new value of the ^{13}C dipolar relaxation rate is used to solve eq 1 for the final (corrected) rotational correlation time. Finally, eq 6 is

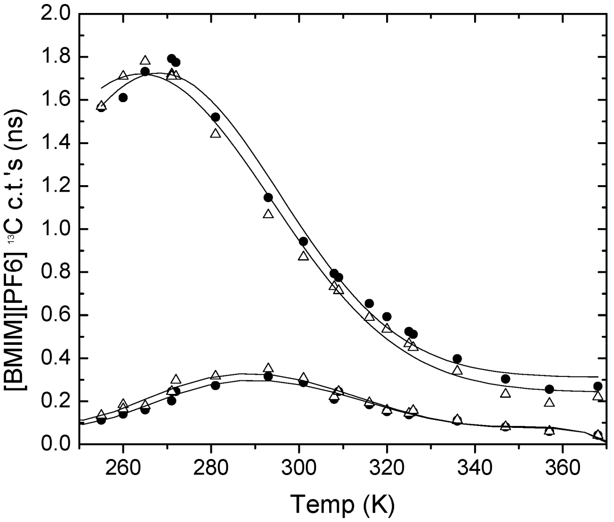

Figure 2. Corrected (upper curves) and initial (lower curves) correlation times (ns) for [BMIM][PF6] ionic liquid vs temperature. (●) Imidazolium ring C2 carbon; (△) average of imidazolium ring C4 and C5 carbons.

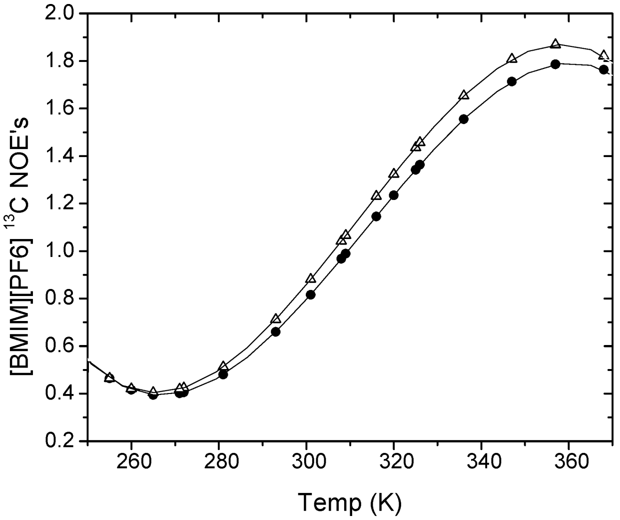

Figure 3. Experimental ^{13}C imidazolium ring NOE factors for [BMIM][PF6] ionic liquid vs temperature. (●) Imidazolium ring C2 carbon; (△) average of imidazolium ring C4 and C5 carbons.

used to determine the amount of the experimentally determined ^{13}C relaxation rate that is due to CSA.

Sources of Error. As indicated in an earlier section, there are questions of biexponential behavior and the use of an isotropic model to describe anisotropic motion. First of all, there appear to be few (if any) examples of biexponential behavior in the literature as far as viscous solutions of this type are concerned. Despite its inherent assumptions, the isotropic model has proved to be reasonably successful in describing a wide range of viscous solutions and providing useful physical information concerning these systems.[9]

However, there are other problems that should be considered including scalar relaxation and chemical exchange that are easily detected.[20] In this study, scalar relaxation will not be a factor as it arises only when the Larmor frequencies are similar (carbon bonded to bromine) or when a slow-relaxing nucleus is bonded to a fast-relaxing nucleus (carbon bonded to aluminum). Another relaxation mechanism that can contribute to line broadening is that of chemical exchange. Chemical exchange is generally present when the observed NMR peak broadens out with increasing temperature and then separates into two or more peaks when the exchange rate between species is faster than the NMR time scale. Temperature studies of [BMIM][PF6] have failed to indicate any of the above relaxation mechanisms in this ionic liquid ([BMIM][PF6]).

Finally, there is the question of molecular mobility using the isotropic model. A detailed analysis of this system using isotropic and related models provides a reasonable description of molecular mobility.[16] This analysis was recently supported by a molecular dynamics study of [BMIM][PF6].[18] In a theoretical study[21] of homonuclear NOEs as probes of molecular mobility, it was concluded that, in general, NOEs are insensitive to internal mobility and depend solely on overall molecular mobility. The extension of this conclusion to heteronuclear systems is supported to a limited extent by the correlation between diffusion coefficients and ^{13}C relaxation rates in viscous solutions.[22−24]

Correlation Times. Figure 2 contains initial rotational (assuming complete dipolar relaxation, eq 1) and corrected rotational correlation times (ns) for the imidazolium ring carbons of the [BMIM][PF6] ionic liquid vs temperature. The initial rotational correlation times are determined from eq 1 (assuming complete dipolar relaxation), and the corrected rotational correlation times are determined from eqs 7, 8, and 1 again, as outlined in the previous sections. The corrected (final) rotational correlation times are predicted to be considerably longer (numerically greater) than the initial rotational correlation times, as the total relaxation rate is now separated into both dipolar relaxation and a second contribution (CSA). This is shown in Figure 2 as is the shift of the correlation time maximum from ca. 293 to 273 K as the correlation times are corrected. The correlation time maxima observed in Figure 2 are typical for ^{13}C relaxation rate studies of ionic liquids and are generally located near (but not at) the NOE minima (Figure 3) for these and related systems.[15,16,22−24]

Corrected Maximum NOE Factors and Spin−Lattice Relaxation Times. The experimental NOE factors for systems outside of the region of extreme narrowing ($\omega^2\tau^2 > 1$) seldom have the same minima as the total spin−lattice relaxation times. Figure 3 contains measured NOE factors for the ring carbons in the [BMIM][PF6] ionic liquid vs temperature.[10] The experimental NOE minimum is located at ca. 265 K.

The imidazolium ring ^{13}C T_1 values have a minimum at 293 K, as shown in Figure 4. Figure 4 also contains the corrected maximum NOE factors that reach an apparent minima at ∼293 K, thus matching the minima for the imidazolium ring ^{13}C T_1 values.

The matching of the maximum NOE factor minima with the minima obtained for the T_1 values from the same nuclei is a fortuitous consequence of combining eqs 1, 3, and 7 to obtain a corrected maximum NOE factor. The final (corrected) NOE factors are such that the minimum in the NOE curve is located at a temperature similar to that obtained for measured ^{13}C T_1 values. We can offer no particular explanation for this matching of minima; however, it may (or may not) serve as a useful check on the correct application of these equations in solving similar problems.

CSA. The CSA (eq 5) is typically defined as

$$\Delta\sigma = |\sigma_{\parallel} - \sigma_{\perp}| = \sigma_{zz} - (\sigma_{xx} + \sigma_{yy})/2 \qquad (9)$$

with $|\sigma_{zz}| \geq |\sigma_{yy}| \geq |\sigma_{xx}|$. The asymmetry parameter, η_{CSA}, is generally ignored (as mentioned previously) in CSA analysis, as it would normally result in less than a 5−10% correction, as shown in solid-state[19] isotropic studies. By use of the convention

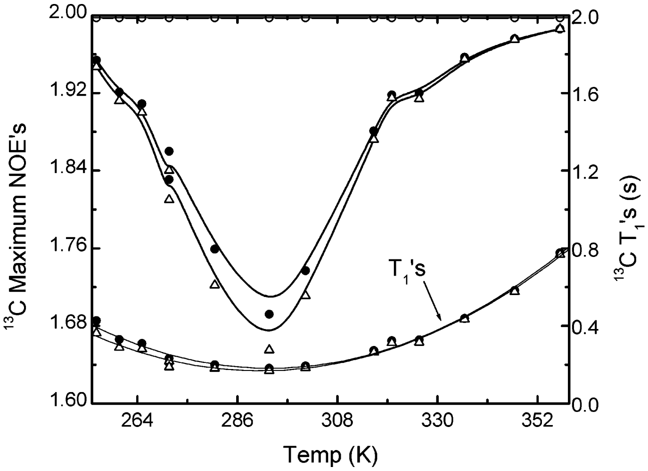

Figure 4. Corrected maximum ^{13}C NOE factors and total spin−lattice relaxation times (T_1) for [BMIM][PF6] ionic liquid vs temperature. (●) Imidazolium ring C2 carbon; (△) average of imidazolium ring C4 and C5 carbons; (○) theoretical NOE ^{13}C maximum of 1.988.

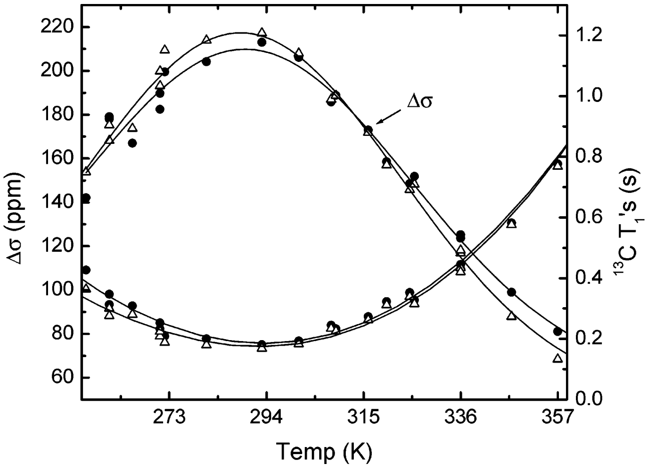

Figure 5. ^{13}C $\Delta\sigma$ and total spin−lattice relaxation times (T_1) for [BMIM][PF6] ionic liquids vs temperature. (●) Imidazolium ring C2 carbon; (△) average of imidazolium ring C4 and C5 carbons.

outlined for eq 9, the asymmetry factor is given by[2−7,25]

$$\eta_{\mathrm{CSA}} = (3/2)(\sigma_{xx} - \sigma_{yy})/\Delta\sigma \qquad (10)$$

Figure 5 contains a plot of CSA and ^{13}C spin−lattice relaxation times vs temperature for the [BMIM][PF6] ionic liquid. In this case, the spin−lattice relaxation times minimum is similar to the maximum for the CSA, $\Delta\sigma$, for the C2, C4, and C5 carbons on the imidazolium cation. In particular, the $\Delta\sigma$ values for the C2 carbon vary from 142 ppm at 255 K to a maximum of 213 ppm at 293 K and then to a value of 81 ppm at 357 K. The averaged $\Delta\sigma$ values for C4 and C5 vary from 154 ppm at 255 K to a maximum of 217 ppm at 293 K and then to a value of 72 ppm at 357 K. The average of the C2 $\Delta\sigma$ values over the entire temperature range is 161 ppm, and the average of the C4 and C5 carbons over the same range is 159 ppm.

The average $\Delta\sigma$ values for the 3 imidazolium ring carbons compare favorably with isotropic values of 159 and 157 ppm for pyrimidine in liquid crystal solutions;[26] however, there is the question of temperature dependence. First of all, it should be emphasized that one is observing a system of ion pairs that undoubtedly possesses equilibrium characteristics. Even in static systems, it has been observed that relatively small changes in the position of a single hydrogen atom can result in major shifts in the tensorial shieldings.[27] It has also been pointed out by Mehring that the isotropic average of the shielding tensor is closely related to the isotropic shift in liquids, showing only a little dependence on packing in the solid state.[25] In view of these observations, the temperature dependence of $\Delta\sigma$ in the [BMIM]-[PF6] ionic liquid is perhaps not unexpected.

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