Dynamic Features of 2-Allyloxy-naphthalene: Accessing Internal Mobility in Solution via $R_1\rho$

V. B. Riatto, S. A. Fernandes, F. Y. Fujiwara, A. J. Marsaioli*
Instituto de Química-Unicamp, Campinas, SP, Brazil
anita@iqm.unicamp.br

Abstract: *Dynamic features of 2-allyloxy-naphthalene were investigated by measuring ^{1}H NMR rotating frame relaxation rates ($R_1\rho$) upon selective and double-selective excitation of dipolarly connected spin pairs. Hydrogen-hydrogen distances were calculated, and the correlation times were evaluated. The results obtained were compared to spin lattice relaxation rates and NOE data.*

Various ^{1}H NMR techniques have been used to monitor the interaction of supramolecular guest-host complexes in solution.[1] Topology and dynamic features are investigated by measuring ^{1}H NMR spin-lattice relaxation rates (R_1) upon double-selective excitation of dipolarly connected spin pairs of the guest molecule.[2,3] However, this methodology fails for molecules with τ_c ~1, when NOE values are close to zero. This is found to be the case of 1 kDa molecules. In such situations, we propose the use of dipolar relaxation rates in the rotating frame ($R_1\rho$) instead.[4] The proposed method extends the R_1 measurements that have been developed for macromolecules to medium sized molecules with $R_1\rho$ measurements.

We have first optimized $T_1\rho$ experiments and in a second instance we have applied both R_1 (traditional method) and $R_1\rho$ alternative method to 2-allyloxy-naphthalene (**1**) to obtain conformer population and average distance of the methylene belonging to the allyl moiety and the aromatic methine. In short, this dynamic model was used to demonstrate the applicability of the $R_1\rho$ technique to monitor internal motions.

NMR spectra and relaxation data were obtained on a Varian INOVA-500 spectrometer. Nonselective spin-lattice relaxation rates (R_1^{ns}) were measured by the inversion recovery techniques (180°-τ-90°-acq.). Selective spin-lattice relaxation measurements (R_1^s) were carried out applying a selective 180° soft pulse to the signals of interest. After a delay time τ, a non selective 90° hard pulse was applied. Rotating frame spin-lattice relaxation rates ($R_1\rho$) were measured by applying the pulse sequence, 90°$_x$-t(SL)$_y$-Acq, where (SL) denotes spin-locking and t is the mixing time. The relaxation rates measurements were optimized by experimenting different mixing times and spinlock powers. Selective and double selective rotating frame spin-lattice relaxation ($R_1\rho^s$ and $R_1\rho^{ds}$) measurements were carried out by applying a selective 180° soft pulse to the signals of interest followed by a non-selective spin-lock.

The parameters of ^{1}H NMR selective relaxation rate for 2-allyloxy-naphthalene in

$CDCl_3$ solution are summarized in Table 1. These data were then used to estimate the correlation times associated using the diagram R_1^{ns}/R_1^s x $\omega\tau_c$.[5] The parameters of ^1H NMR

rotating frame spin-lattice relaxation rates for 2-allyloxy-naphthalene in $CDCl_3$ solution are summarized in Table 1.

Table 1. ^1H NMR spin-lattice relaxation and rotating frame spin-lattice relaxation rates of 15 mM 2-allyloxy-naphthalene in $CDCl_3$.

	R_1^{ns} (s^{-1})	R_1^s (s^{-1})	τ_c (s)	$R_1\rho^s$ (s^{-1})	$R_1\rho^{ds}_{AC}$ (s^{-1})	$R_1\rho^{ds}_{BC}$ (s^{-1})
A	0.304	0.253	2.54633 x 10^{-10}	0.341	0.417	-
B	0.232	0.202	2.86462 x 10^{-10}	0.326	-	0.360
C	0.426	0.375	2.86462 x 10^{-10}	0.395	0.412	0.405

The dipolar cross-relaxation rates ($\sigma_\rho^{A,C}$ = 0,076 s^{-1} and $\sigma_\rho^{B,C}$ = 0,034 s^{-1}) and the internuclear distances (r_{A-C} = 0.225 nm and r_{B-C} = 0.242 nm) were calculated by equations 1 and 2.[6]

$$\sigma_{ij} = R_i^{i,j} - R_i^s \qquad (eq.1)$$

$$\sigma_{ij} = (1/10) \cdot (\gamma_H^4 \, h^2 / 4\pi^2 r_{ij}^6) \cdot \{ [6\tau_{ij} / (1 + 4\omega_H^2\tau_{ij}^2)] - \tau_{ij} \}, \qquad (eq. 2)$$

where h is the Planck constant, γ_H is the hydrogen magnetogyric constant and ν_H is the hydrogen Larmor frequency.

The dipolar cross-relaxation rates agree with the NOE experiments. Irradiation of H_C led to a 10% enhancement in the H_A signal and 1.8% enhancement in the H_B. There is a larger

dipolar contribution for the A-C vector than for H-B. The values calculated for A-C and B-C distances are consistent with the expected. The distance values obtained by NOE are r_{A-C} = 0,273 nm and r_{B-C} = 0,315 nm, which show the same trend but different absolute values.

These studies demonstrated the feasibility of $R_1\rho$ method to monitor molecular geometric and dynamic features, although more data are required to point out the limitations of the method. Though not precise, it is certainly rapid and convenient for establishing supramolecular interactions of molecules with $\omega\tau_c$ ~1.

Acknowledgements

References

1. J. N. S. Evans, *Biomolecular NMR Spectroscopy*, University Press, Oxford, 1995.

2. G. Valensin, *J. Magn. Res.* **46** (1982) 23.

3. N. Marchettini, G. Valensin, *J. Phys. Chem.* **94** (1990) 4507.

4. Y. S. Wang, S. Ikuta, *J. Am. Chem. Soc.* **111** (1989) 1243.

5. G. Valensin, *J. Mag. Res*. **46** (1982)23.

6. L. Calzolai, E. Gaggelli, A. Maccotta, G. Valensin, *J. Magn. Res. Series B* **112** (1996) 228.