

^{13}C nuclear spin—lattice relaxation study of anisotropic solvent rotational diffusion in the polystyrene/*trans*-decalin system

Michael E. Moseley and Peter Stilbs

Department of Physical Chemistry, Uppsala University, P.O. Box 532, S-751 21 Uppsala, Sweden
(Received 28 April 1978)

The rotational diffusion tensor for the solvent *trans*-decalin has been determined as a function of temperature (21°–55°C) and polystyrene concentration (0–13% w/w) from ^{13}C spin—lattice relaxation data. The sensitivity of rotational diffusion behaviour of the *trans*-decalin molecule to changes in solution conditions was found to be essentially proportional to the axial ellipticities of the respective principal rotational axes. The degree of anisotropic motion was found to increase strongly upon increasing the polystyrene concentration and decreasing the temperature. Apparent activation energies for rotation about each of the principal axes of inertia have been calculated for the series of polystyrene concentrations.

INTRODUCTION

Determination of molecular mobility through interpretation of nuclear spin—lattice relaxation data offers a uniquely detailed study of microdynamic characteristics of molecules in solution. Woessner¹ has derived equations which enable the determination of the three principal components (R_1 , R_2 , R_3) of the rotational diffusion tensor for asymmetric top molecules in solution, provided that spin—lattice relaxation data are available for at least three different nuclei in the molecule. The method is particularly suited for ^{13}C or ^2H data since spin relaxation of these nuclei is almost exclusively intramolecular^{2,3} and hence directly related to the rotational diffusion rate of the molecule. For ^{13}C nuclei the Woessner equations relate the proton—carbon dipolar relaxation contribution to the ^{13}C relaxation to the rotational diffusion rate. It is possible through parallel studies of the proton—carbon nuclear Overhauser effect (NOE) to determine (and correct for)² the extent to which other relaxation mechanisms contribute to the observed relaxation rates. The method has been successfully applied to simple rigid molecules in solution, particularly by Grant *et al.*^{4,5} and has provided interesting new information about microdynamic behaviour of molecules.

We have found it interesting to investigate the effect of a relatively immobile macromolecule (polystyrene) on the rotational behaviour of a solvent molecule (*trans*-decalin). Polystyrene is known through ^{13}C n.m.r. studies in solution to have a rotational correlation time which is essentially two magnitudes greater⁶ than the rotational correlation time of the solvent in the present study*.

Trans-decalin is a θ solvent for polystyrene at 21°C and approaches the good solvent region at about 40°C⁷. Because of the wide variation in the solution properties from the θ to good solvent conditions it is also of interest to examine

* It is important to note that the n.m.r. correlation time refers to the reorientation rate of individual C—H bond vectors, not to overall molecular reorientation rate (which is an even slower process for non-rigid molecules).

the effects of the temperature parameter on the rotational character of *trans*-decalin.

EXPERIMENTAL

A polystyrene sample with a narrow molecular weight distribution obtained from Pressure Chemical Company ($M = 390\,000$, $\bar{M}_w/\bar{M}_n \leq 1.10$) was used without further purification. The solvent *trans*-decalin (purum) was obtained from Fluka AG. All solutions were prepared by weighing. After addition of solvent, the polymer was allowed to swell for 24 h prior to stirring for several days to ensure solution homogeneity. The measurements were made on non-degassed solutions of varying concentrations of polystyrene (0–13% w/w) at temperatures of 20.6°, 24.9°, 29.6°, 40.9° and 54.8°C. All samples were allowed to equilibrate in the spectrometer at least 30 min prior to measurement. Sample temperatures were determined by means of a very thin copper—constantin thermocouple temporarily placed in the sample and are estimated to be accurate to $\pm 0.5^\circ\text{C}$ if temperature gradients in the tubes are also considered.

For each of the above solution concentrations and temperatures, the ^{13}C spin—lattice relaxation time (T_1) was measured for each of the 3 different carbon signals (C-1, C-2 and C-9) of the *trans*-decalin solvent molecule from standard pulsed inversion—recovery experiments (pulse repetition time $\geq 5 T_1$) on a Jeol FX-100 spectrometer using sets of concentric, thin-walled n.m.r. tubes. The inner tube of 5 mm o.d. contained the polystyrene/*trans*-decalin solution and the outer (10 mm o.d.) tube contained D_2O to provide an 'internal' lock signal (the external ^7Li lock of the spectrometer was found to be far too unstable for the experiments in question and was therefore not used). A parallel determination of proton—carbon nuclear Overhauser enhancement factors (NOE) was made through the gated decoupling technique using pulse repetition times in excess of $10 T_1$ to avoid NOE build-up (see ref 8). Average NOE values for the three ^{13}C signals in the temperature and con-

Table 1 ^{13}C spin-lattice relaxation times, T_1 (sec) for *trans*-decalin in the polystyrene/*trans*-decalin system

% Poly-styrene (w/w)	Carbon position	Temperature ($^{\circ}\text{C}$)				
		20.6	24.9	29.6	40.9	54.8
0	C-9	6.37	6.76	7.24	9.08	10.70
	C-1	4.25	4.47	4.86	5.89	7.03
	C-2	3.70	4.04	4.26	5.20	6.32
1	C-9	5.91	6.63	7.13	8.32	10.52
	C-1	4.14	4.17	4.78	5.69	6.68
	C-2	3.66	3.76	4.17	5.05	5.91
3	C-9	5.38	5.89	6.70	7.88	10.02
	C-1	3.66	3.95	4.43	5.21	6.56
	C-2	3.26	3.51	3.95	4.70	5.79
6	C-9	4.38	5.10	5.57	7.09	8.80
	C-1	3.12	3.58	3.88	4.84	5.94
	C-2	2.79	3.14	3.44	4.29	5.23
10	C-9	3.65	4.23	4.75	6.26	7.82
	C-1	2.76	3.10	3.40	4.29	5.58
	C-2	2.40	2.78	2.96	3.35	4.88
13	C-9	3.14	3.57	4.14	6.02	7.14
	C-1	2.32	2.60	2.94	4.25	5.14
	C-2	2.03	2.33	2.66	3.79	4.55

centration range studied were 2.98 ± 0.12 , 2.98 ± 0.14 and 2.95 ± 0.13 , respectively.

The inversion-recovery data were analysed off-line through a non-linear three-parameter least-squares fitting program to yield the ^{13}C T_1 values. These, together with molecular coordinates (obtained through an iterative molecular mechanics simulation program⁹), were then used as input parameters for a specially developed FORTRAN IV least-squares minimization program (named WOESNR) to obtain the principal components of the rotational diffusion tensor (R_1 , R_2 and R_3) from the original equations of Woessner for dipolar relaxation in a molecule undergoing anisotropic rotational motion. The WOESNR program is in most respects similar to the MOTION program described by Berger *et al.*⁵. Proton-carbon interaction vectors longer than 2.5 Å were neglected in the simulations.

The components R_1 , R_2 and R_3 of the *trans*-decalin rotational diffusion tensor so obtained for five different temperatures (t) at six different polystyrene concentrations (c) were finally fitted to an equation of the form

$$R_i = A + Bc + Cc^2 + Dt + Et^2$$

through a least-squares minimization program.

With the exception of the molecular mechanics program, the general FORTRAN IV minimization routine STEPIT¹⁰ was utilized in all least-squares minimizations.

RESULTS AND DISCUSSION

The experimental T_1 data for each of the different *trans*-decalin carbon signals are given in *Table 1*. Since all NOE values were found to be 3.0 within experimental error, complete dipole-dipole relaxation can be assumed in the analysis of the data², and therefore the T_1 values can be used directly as input values for the WOESNR program. *Table 2* presents the overall best-fit values of the components R_1 , R_2 and R_3 of the rotational diffusion tensor. (The principal

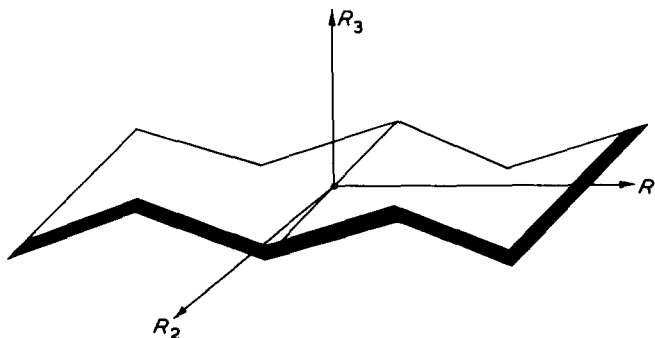
rotational axes are defined in *Figure 1*. The corresponding principal moments of inertia were $I_1 = 207$, $I_2 = 497$ and $I_3 = 655$ a.m.u. Å².)

A standard error analysis of the raw R_i data is not possible, since the number of parameters (R_1 , R_2 and R_3) equals the number of observables (the three T_1 values). However, through Monte Carlo simulations, probable error intervals in the R_i values resulting from the estimated uncertainties in the relative T_1 values for the three types of ^{13}C nuclei ($\pm 2\%$) were found to be of the orders: $R_1 \pm 0.2R_1$, $R_2 \pm 0.5R_2$, and $R_3 \pm 0.1R_3$. These figures are similar to the error limits claimed by Grant *et al.*⁴ in their measurements on neat *trans*-decalin and they also agree well with the scatter observed when fitting the (t, c)-surface mentioned above.

The computer-drawn *Figures 2a-2c* give an overall picture of the data in *Table 2*. The general trends of the variations in the R_i with temperature and polystyrene concentration were deemed experimentally significant in comparison with the probable error limits of the R_i values. Several tendencies are worth noting. It is observed that *trans*-decalin does exhibit extensive anisotropy of rotation as seen in the large variation in R_1 , R_2 and R_3 . Rotational diffusion around

Table 2 Components of the rotational diffusion tensor, R_1 , R_2 , R_3 (rad²/nsec) for *trans*-decalin in the polystyrene/*trans*-decalin system

% Poly-styrene (w/w)	Component	Temperature ($^{\circ}\text{C}$)				
		20.6	24.9	29.6	40.9	54.8
0	R_1	38.5	42.0	44.9	52.6	65.1
	R_2	10.2	11.7	12.8	15.2	17.7
	R_3	51.3	55.1	58.3	67.1	82.2
1	R_1	37.0	40.7	43.4	51.0	63.5
	R_2	9.2	10.7	11.8	14.2	16.7
	R_3	51.2	55.0	58.2	67.0	82.0
3	R_1	34.0	37.5	40.4	48.1	60.6
	R_2	7.3	8.8	9.9	12.3	14.9
	R_3	51.1	54.9	58.1	66.9	81.9
6	R_1	29.9	33.5	36.4	44.0	56.5
	R_2	4.9	6.4	7.5	9.9	12.5
	R_3	51.2	55.0	58.2	67.0	82.1
10	R_1	25.2	28.7	31.6	39.3	51.8
	R_2	2.5	4.0	5.1	7.5	10.0
	R_3	52.0	55.8	59.0	67.7	82.8
13	R_1	22.1	25.6	28.6	36.2	48.7
	R_2	1.2	2.7	3.8	6.7	8.8
	R_3	53.0	56.7	59.9	68.7	83.8

**Figure 1** Principal rotational axes in *trans*-decalin

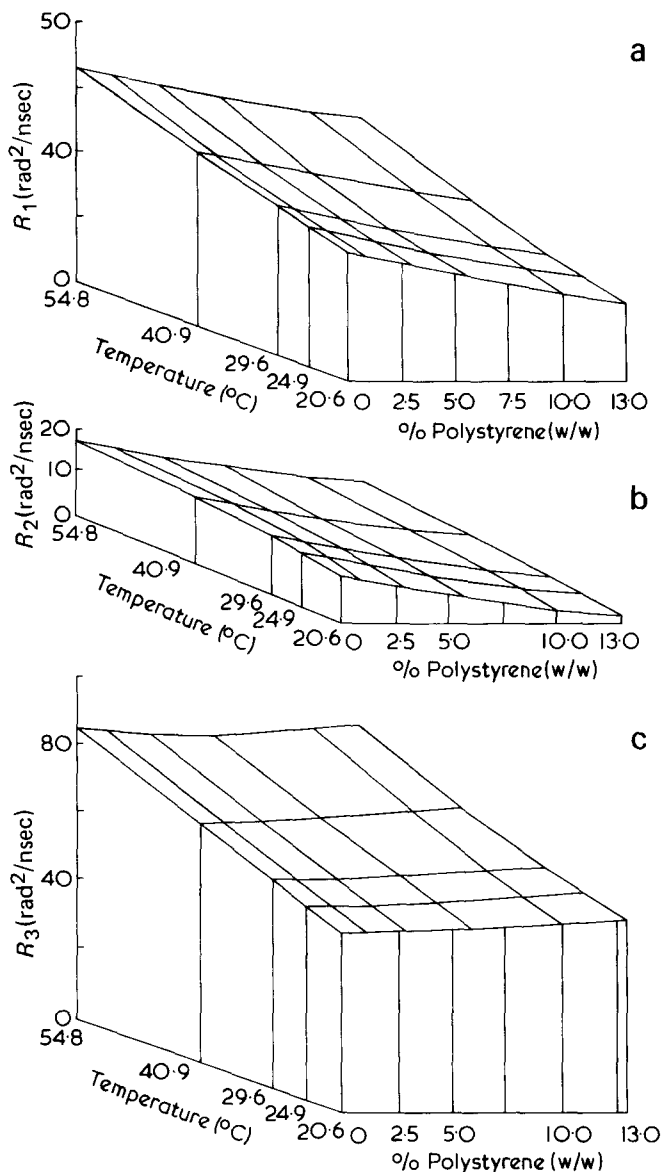


Figure 2 (a)–(c) Components R_1 , R_2 , and R_3 of the rotational diffusion tensor for *trans*-decalin as a function of temperature and polystyrene concentration in the polystyrene/*trans*-decalin system

the I_3 axis is insensitive to polystyrene concentration at all temperatures, while displaying a slight but constant temperature dependence at all concentrations. This is as expected in that this rotation displaces the least solution volume and hence should be least sensitive to the presence of the relatively immobile polystyrene chain structures. Rotational diffusion around the remaining two axes shows both temperature and concentration dependences: R_1 a greater temperature dependence and R_2 (with the largest displaced volume upon rotation) a greater concentration dependence. Grant *et al.*⁴ estimated the volume displaced by rotation about an axis to be proportional to the axial ellipticity (ϵ), which was defined as the ratio of the maximum distance between atoms along the two axes perpendicular to the axis in question and calculated the ratios $\epsilon_1 : \epsilon_2 : \epsilon_3$ to be 1.34:1.85:1 for *trans*-decalin.

The ratio R_1/R_2 has been taken as a measure of the anisotropy of rotation and the effects of temperature and concentration are illustrated in Figure 3. The dominating factor is clearly the sensitivity of R_2 to changes in polystyrene concentration, in that the variation in R_1/R_3 is no larger than a factor of 1.5 throughout the measured temperature

and concentration interval, while the variation in R_2/R_3 approaches a factor of 10. The rotational anisotropy of rate in the absence of polystyrene, but, at higher polystyrene concentrations increases strongly with decreasing temperature. Likewise, the sensitivity of changes in the rotational anisotropy to changes in the amount of polystyrene present in the microenvironment of *trans*-decalin decreases with increasing temperature.

Apparent activation energies of *trans*-decalin rotation about the three axes quantify the temperature dependences and have been determined for each of the polystyrene concentrations. Arrhenius plots of $\ln(R_i)$ vs. $1000/T$ were linear and the results are shown in Figure 4.

CONCLUSIONS

The presence of the polystyrene chains drastically alters the rotational behaviour of *trans*-decalin. The results seem to indicate that the polymeric medium hinders rotation about an axis in proportion to the rotational volume displacement, resulting in increases in the variation among the apparent

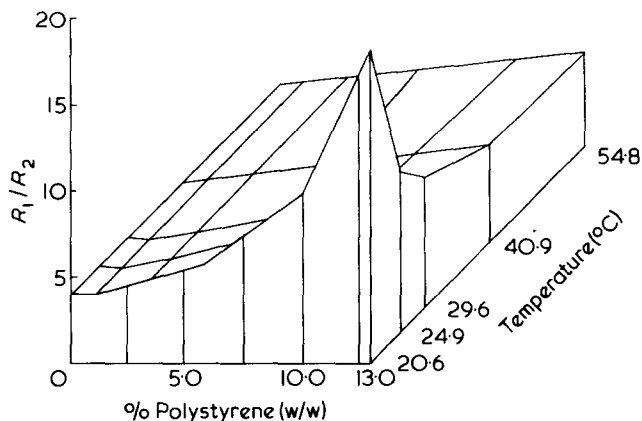


Figure 3 Anisotropic rotation (R_1/R_2) in *trans*-decalin as a function of temperature and polystyrene concentration in the polystyrene/*trans*-decalin system

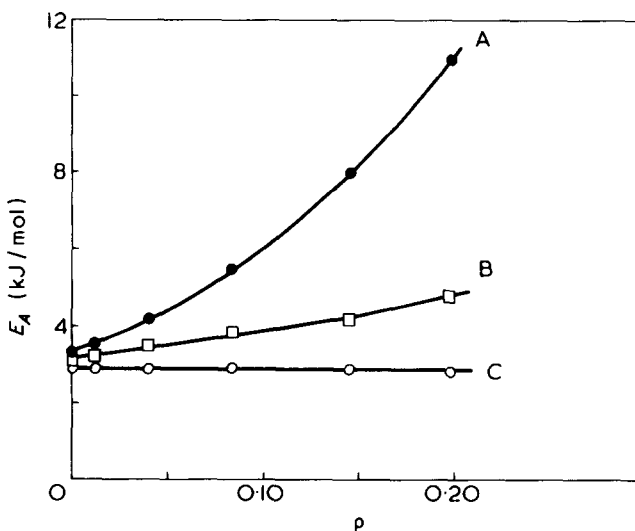


Figure 4 Apparent activation energy (E_a) for axial rotation in *trans*-decalin in the polystyrene/*trans*-decalin system as a function of ρ , the number ratio of monomeric chain segments to *trans*-decalin molecules (13% w/w polystyrene corresponds to $\rho = 0.20$). A, R_2 ; B, R_1 ; C, R_3

rotational activation energies of the three axes and likewise in the overall tumbling anisotropy. The structuring of the microenvironment due to this presence, as manifest in the increased degree of anisotropic rotation in the solvent molecule, becomes more pronounced with increasing polymer concentration and decreasing temperature.

ACKNOWLEDGEMENTS

We are indebted to Professor G. Bergson for putting the spectrometer at our disposal, to Dr U. Obenius for technical assistance and to Dr S. Berger for providing unpublished data for the check-out of the WOESNR program. We are also very grateful to Drs B. Nyström and J. Roots for valuable discussions and assistance and to Professor K. Mislow for making a copy of the molecular mechanics simulation program available to us.

REFERENCES

- 1 Woessner, D. E. *J. Chem. Phys.* 1962, **37**, 647
- 2 Lyerla Jr, J. R. and Levy, G. C. in 'Topics in Carbon-13 NMR Spectroscopy' (Ed. G. C. Levy), Wiley, New York, 1974, Vol. 1
- 3 Mantsch, H. H., Saito, H. and Smith, I. C. P. in 'Progress in Nuclear Magnetic Resonance Spectroscopy' (Eds J. W. Emsley, J. Feeney and L. H. Sutcliffe), Pergamon Press, Oxford, 1977, Vol. 11, part 4
- 4 Grant, D. M., Pugmire, R. J., Black, E. P. and Christensen, K. A. *J. Am. Chem. Soc.* 1973, **95**, 8465
- 5 Berger, S., Kriessel, F. R., Grant, D. M. and Roberts, J. D. *J. Am. Chem. Soc.* 1975, **97**, 1805
- 6 Allerhand, A. and Hailstone, R. K. *J. Chem. Phys.* 1972, **56**, 3718
- 7 Nyström, B. and Roots, J. *Polymer* 1977, **18**, 1289
- 8 Opella, S. J., Nelson, D. J. and Jardetzky, O. *J. Chem. Phys.* 1976, **64**, 2533
- 9 Andose, J. D. and Mislow, K. *J. Am. Chem. Soc.* 1974, **96**, 2168
- 10 Chandler, J. P., Subroutine STEPIT, program 66. Quantum Chemistry Program Exchange, Chemistry Department, Indiana University, Bloomington, Ind. 47401, USA