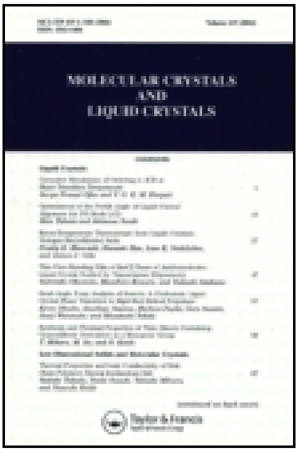

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Liquid Crystals Showing a Molecular Rearrangement: A Dynamic NMR Study of a 2-Benzoyloxytropone Mesogen

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Liquid Crystals Showing a Molecular Rearrangement: A Dynamic NMR Study of a 2-Benzoyloxytropone Mesogen

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The [1, 9] sigmatropic rearrangement has been studied by Dynamic NMR spectroscopy for a 2-benzoyloxytropone mesogen. The proton spectra of the compound in $CDCl_3$ and C_6D_6 as isotropic solvents have been recorded in the ranges 238–328 K and 277–343 K, respectively, and the rate constants for the dynamic process have been determined by line shape analysis. One-dimensional ^2H NMR spectra of the compound in its own mesophases and in the nematic phase E63, recorded between 300–330 K and 298–353 K respectively, show that the exchange process is in the slow limit for this kind of spectra and allow the study of orientational order. The values of the rate constants in anisotropic environments were yielded by the analysis of two-dimensional exchange ^2H NMR spectra in the range 310–330 K for the pure compound and 328–348 K for the compound in E63. The trends of the kinetic constants against temperature, analyzed by the Eyring equation, give the activation parameters of the rearrangement. The activation enthalpies are lower in the isotropic than in the anisotropic phases, and the activation entropies result, respectively, slightly negative and about zero. The frequency of the exchange in the mesophases of the pure compound is significantly lower than the typical frequency of molecular reorientation in nematic and S_C phases.

Keywords: Liquid crystals, dynamic NMR troponoidic compounds

1. INTRODUCTION

In the last few years a wide number of mesogenic compounds has been synthetized with 2-acyloxy-5-alkoxytropone cores.[1–3] The type and stability of the mesophases formed (N, S_A or S_C) strictly depend on the substituents. In particular, 5-alkoxy-2-benzoyloxytropones[3] with long linear terminal chains exhibit enantiotropic S_C (or S_A) phases, while 2-(2-alkenoiloxy)-5-alkoxytropones and 2-alkanoiloxy-5-alkoxytropones generally show a monotropic S_A phase.[1,2]

The molecular rearrangement, called [1, 9] sigmatropy, characteristic of 2-acyloxytropones,[4,5] that is the migration of the acyl substituent between the oxygen atoms at C-1 and C-2 (see Figure 1), is expected to condition the mesogenic properties of these compounds. In order to understand the possible connection between the intramolecular exchange and the formation of liquid crystal phases, it is first of all necessary to define the range of frequencies characteristic of the dynamic process in different mesogens.

The kinetic constants of the [1, 9] sigmatropy have been recently determined for two troponoidic mesogens in a wide range of temperatures and in two solvents, $CDCl_3$

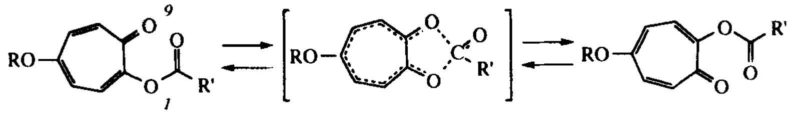


FIGURE 1 [1, 9] sigmatropic rearrangement mechanism.

(isotropic) and E63 (anisotropic).[6] In the first compound (2-(4′-heptylbenzoyloxy)-5-[(4′-heptylperdeuterophenyl)azo]tropone), which exhibits an enantiotropic nematic phase and two monotropic smectic phases, the rate constant is estimated between $7.8 \cdot 10^3$ Hz and $5.5 \cdot 10^4$ Hz in the range $81 \div 115$°C, where the pure compound is nematic or smectic *C*. In the second compound (5-dodecyloxy-2-tridecanoyloxytropone) the rate constant should be of the order of 10^3 Hz between 41°C and 47°C, where the compound forms a monotropic S_A phase.

Here we present a similar study performed on 2-(4′-dodecyloxybenzoyloxy)-5-hexyloxytropone (**1**) and on its deuterated analogue 3,7-dideutero-2-(4′-dodecyloxy benzoyloxy)-5-hexyloxytropone (**2**, Figure 2). Compound **1** is known to form an enantiotropic nematic phase and a monotropic S_C one.[3] As a general rule, the presence of the benzoyloxy group allows the formation of stable liquid crystal phases by this kind of troponoidic compounds. Here the semi-rigid core of the mesogenic unit should consist of the benzoyloxytropone fragment and just inside this fragment the exchange process occurs.

For compound **1** the rate constants have been determined in $CDCl_3$ and C_6D_6 as isotropic solvents by lineshape analysis of the ^1H NMR spectra.[7] In the mesophases of the pure compound and in the nematic phase E63 the rate constants could be determined only by an analysis of the two-dimensional exchange ^2H NMR spectra[8,9] of compound **2**. This constitutes the first application of such a technique to a pure mesogen.

2. EXPERIMENTAL

2.1 Preparations

The synthesis of 2-(4′-dodecyloxybenzoyloxy)-5-hexyloxytropone (**1**) was carried out as described in Refs. 1 and 2. 5-hydroxytropone (0.36 g, 6.9 mmol) was treated with

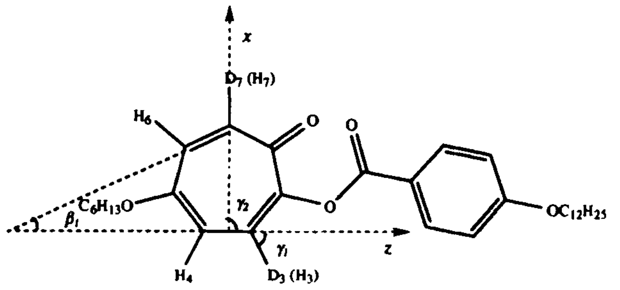


FIGURE 2 Molecular structures of **1** and **2**, local reference frame and numbering of atoms.

NaH (0.17 g, 6.9 mmol) in dry hexamethylphosphoric triamide (9.5 ml) at 0°C for 30 min. 1-Bromohexane (0.36 ml, 2.7 mmol) was added to the resultant solution at 0°C. The mixture was kept at room temperature overnight, then acidified. The solid was filtered and recrystallized from $CHCl_3$ to give 5-hexyloxytropolone (0.48 g, 2.2 mmol, 84%).

0.48 g (2.2 mmol) of 5-hexyloxytropolone were dissolved in dry pyridine (10 ml) and added to 4-dodecyloxybenzoic chloride (prepared from 2.6 mmol of 4-dodecyloxybenzoic acid with a slight excess of oxalyl chloride in C_6H_6 at 40°C) in the presence of a few crystals of DMAP, at 0°C. The mixture was stirred overnight at room temperature, then added to water and the product extracted into diethylic ether. The residue obtained after evaporation was subjected to SiO_2 TLC with Et_2O/petroleum ether (3:2). The R_f 0.59 fraction was collected to give **1** as white-ivory crystals (0.39 g, 0.8 mmol, 35%).

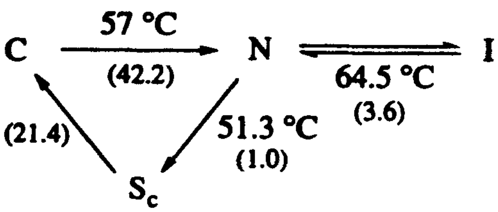
^1H NMR ($CDCl_3$): $\delta_H = 0.85$–0.97 (m, 6H, $-C\underline{H}_3$); 1.24–1.41 (m, 24H, $-C\underline{H}_2-$); 1.83 (m, 4H, $-C\underline{H}_2-CH_2-O$); 3.94 (t, 2H, $J = 6.6$, $-C\underline{H}_2-O$ of hexyloxy-group); 4.03 (t, 2H, $J = 6.6$, $-C\underline{H}_2-O$ of dodecyloxy-group); 6.25 (brs, 1H, H_4 or H_6); 6.94 (d, 2H, $J = 9.0$, aromatics); 7.16 (brs, 1H, H_4 or H_6); 7.24 (d, 2H, $J = 11.8$, H_3 and H_7); 8.13 (d, 2H, $J = 8.8$, aromatics);

^{13}C NMR ($CDCl_3$); $\delta_C = 14.14$ ($-\underline{C}H_3$); 22.67–31.70 ($-\underline{C}H_2-$); 68.31, 68.48 ($-\underline{C}H_2-O$); 105.91, 134.11 (troponic C_4 and C_6); 114.22 (aromatic C_3 and C_5); 128.70, 140.18 (troponic C_3 and C_7); 132.57 (aromatic C_2 and C_6); 163.55 (aromatic C_4).

The deuterated analogue **2** was prepared by a similar procedure starting from 3,5,7-trideutero-5-hydroxytropone and 1-bromohexane. In the ^1H NMR spectrum of **2** at room temperature the doublet at δ 7.24 was lacking.

2.2 Optical and Calorimetrical Observations

The measurements of phase transition temperatures and enthalpy changes were carried out using a differential scanning calorimeter (DSC). The mesomorphic phases were observed by a polarizing microscope equipped with a hot stage. The results found for the non-deuterated compound differ slightly from the ones reported in Ref. 3 (± 3°C, ± 1 kJ/mol), but are in good agreement with the sequence of transitions observed for the deuterated compound, shown in the following scheme. Enthalpy changes are reported in brackets as kJ/mol.



A change of the birifringence colours in the *schlieren* texture of the S_C phase observed at 46.4°C suggests a change in the tilt angle.

2.3 NMR Experiments

NMR measurements were made on a Bruker AMX 300 spectrometer, equipped with variable temperature control.

^{1}H NMR spectra were recorded, at various temperatures, on two samples containing **1** dissolved in $CDCl_3$ (0.3% wt) and in C_6D_6 (0.3% wt), respectively, and on a third sample containing **1** and **2** in the ratio 1:0.7 in C_6D_6.

One- and two-dimensional ^{2}H NMR spectra were recorded, at various temperatures, on pure **2** and on a solution of **2** (20% wt) in the nematic mixture E63 (BDH). This last sample presented a clearing point of about 85° C against 87.5°C of the pure solvent. The $\pi/2$ pulse width was 9 μs. The one-dimensional ^{2}H spectra had a width of 100 or 125 kHz and a resolution of 5 Hz/point. In the case of the pure compound, the first points of the FID were substituted with those computed by a linear prediction routine in order to correct the baseline. For the spectra of **2** in E63 the quadrupolar echo pulse sequence was employed with time interval between the pulses of 30 or 50 μs. The relaxation times T_{1Z} for **2** in E63 were estimated by the aperiodic pulse sequence recovery method[10] at 313 and 348 K.

Exchange 2D ^{2}H NMR were recorded using the pulse sequence:[8]

$$\left(\frac{\pi}{2}\right)_{\Phi_1} - t_1 - \left(\frac{\pi}{2}\right)_{\Phi_2} - \tau_m - \left(\frac{\pi}{2}\right)_{\Phi_3} - t_2$$

with a phase cycling suitable to obtain phase sensitive spectra with the States *et al.* method.[11] This procedure, as described in Ref. 6, prevents a perfect combination of the Zeeman and quadrupolar order spectra and the consequent cancellation of the cross peaks due to quadrupolar interactions; nevertheless, the integral values of the interesting peaks are not alterated. Mixing times ranging from 2 to 4 ms were used for pure **2** and from 1.5 to 4 ms for **2** in E63. 512 data points were collected in the t_2 domain, using the TPPI quadrature procedure, with sampling intervals of 5 μs. 64 to 128 FIDs with increments of t_1 of 10 μs were collected and in any case zero-filled to 256 points before the Fourier transformation. These conditions correspond to a spectral width of 100 kHz in both dimensions.

3. RESULTS

3.1 Non-Deuterated Compound 1 in Isotropic Solvents

^{1}H NMR spectra were recorded on **1** dissolved both in $CDCl_3$ and in C_6D_6, between 238–328 K and 277–343 K, respectively. In both series of spectra four doublets (**a**, **b**, **c**, **d**) are present at low temperature; they correspond to the four troponic protons. In the series of spectra run on the sample containing **1** + **2**, two broad singlets are superimposed on the **c**, **d** doublets.

At 238 K the four doublets, generated by **1** in $CDCl_3$, are resolved and occur at $\delta = 7.23$ ppm (H_a), $\delta = 7.25$ ppm (H_b), $\delta = 7.11$ ppm (H_c), $\delta = 6.23$ ppm (H_d). The coupling constants are $J_{ac} = 13.3$ Hz and $J_{bd} = 10.7$ Hz. There is also another small coupling resolved between H_c and H_d, with $J_{cd} = 2.3$ Hz. By comparison with the spectrum of the deuterated mesogen in $CDCl_3$, it is possible to relate **a** and **b** to the couple H_3 and H_7. The specific assignment is not evident, but it is not essential anyway. With increasing temperature, the chemical shifts of all protons decrease by -0.2 to -0.5 Hz/K.

Between 243 and 273 K **a** and **b** become closer and coalesce at 283 K. In the meantime **c** and **d** become broader and progressively disappear.

At 277 K, the doublets given by **1** in C_6D_6 are at $\delta = 6.83$ ppm (H_a), $\delta = 6.71$ ppm (H_b), $\delta = 6.26$ ppm (H_c), $\delta = 5.14$ ppm (H_d), with $J_{ac} = 13.2$ Hz and $J_{bd} = 10.4$ Hz as coupling constants. The small coupling between **c** and **d** is estimated of 1–2 Hz, while **c** and **d** were attributed to H_4 and H_6 (or H_6 and H_4). At 318 K **a** and **b** arrive at coalescence, resulting in a single doublet, which becomes narrow with increasing temperature. Meanwhile **c** and **d** become broader, until they disappear in the baseline. These two signals follow a similar evolution in the spectra of the sample containing **1** and **2**.

In all cases, the kinetic constants were obtained by lineshape simulation, performed with the DNMR3 computer program.[12] Good simulations of the spectra of **1** + **2** in C_6D_6 were obtained by superimposing, with the suitable scaling factor, the spectra computed, with the same k value, for **1** and **2**. Moreover, we proved that, in order to have satisfactory simulations, the k values relative to the dynamic process in **1** and **2** must not differ more than about 15%. In short, the kinetic constants for **1** and **2**, at the same temperature, are the same, within the limits of the experimental error. The k values for the two solvents and the corresponding $\Delta G^{\neq}$ values, calculated by the Eyring equation, are reported in Table 1. The $\Delta H^{\neq}$ and $\Delta S^{\neq}$ values deduced from the dependence of $\Delta G^{\neq}$ upon the temperature are shown in Table 2.

3.2 Deuterated Compound 2 in Anisotropic Solvents

The ^{2}H NMR spectra of 2 both pure and in E63 (Figures 3a and 3b), recorded between 300–330 K and 298–353 K respectively, show two quadrupolar doublets at all temperatures. Each component is split in two signals because of the dipolar interaction between the deuteron and the nearest proton on the troponic ring. The linewidths do not increase with increasing temperature. Therefore, the exchange process is in the slow rate limit for this kind of spectra. In the spectra of the pure compound at 320 K and 321 K the coexistence of the nematic and S_C phases is evident. The broadening and disappearing of the inner quadrupolar doublet at low temperature can be explained by a substantial slowing down of the reorientational motions in the smectic phases. This could more dramatically affect the splittings due to deuterons for which the angle between the C-D bond direction and the magnetic field is closer to the magic angle.

The one-dimensional spectra have been used to study the orientational order of **2**, assuming the geometry of Figure 2. We observe that the larger dipolar coupling corresponds to a highly ordered direction ($S_{DH} \approx 0.8$, computed with $r_{DH} = 2.41$ Å), along which we fix the z axis of the local reference frame (see Figure 2). The assignment of the larger and smaller quadrupolar splittings to D_7 and D_3, that is, to the nuclei close to and far from the benzoylic group, respectively, is supported by geometrical considerations. In fact, assuming standard bond angles, the angle between the z axis and the para axis of the aromatic ring is computed to be only about 13°, and the highly ordered z direction do not differ too much from an hypothetical molecular long axis. We fix the x local axis in the plane of the troponic ring; if the X-ray geometry of tropolone[13] is assumed for the troponic ring, the CD_7 bond forms an angle of 86° with the z direction. The order biaxiality is presumably very small or negligible ($S_{xx} - S_{yy} \approx 0$), as is

TABLE 1

Kinetics constants and free activation energies from ^{1}H NMR spectra of **1** in isotropic solvents and ^{2}H NMR spectra of **2** in anisotropic environments*

T(K)	CDCl$_3$		C_6D_6		E63		Pure compound **2**	
	k(s^{-1})	$\Delta G^{\neq}$(kcal/mol)	k(s^{-1})	$\Delta G^{\neq}$(kcal/mol)	k(s^{-1})	$\Delta G^{\neq}$(kcal/mol)	k(s^{-1})	$\Delta G^{\neq}$(kcal/mol)
268	5	15.0						
273	7	15.0						
283	15	15.1						
288	20	15.2						
290			10	15.8				
293	27	15.2		15.8				
296				15.8				
298	40	15.3	20	15.8				
303	50	15.4	27	15.9				
308			35	15.9				
310							41	15.9
313	100	15.5	40	15.9				
315							76	15.8
318			65	15.9				
323	200	15.6	90	16.0				
325							139	15.8
328			140	16.0	83	16.6		
330							234	15.8
333			250	16.0	85	16.6		
338					138	16.6		
343			400	16.1	180	16.5		
348					309	16.5		

* The uncertainty on the rate constants is between 10–20% in all cases. The consequent uncertainty on $\Delta G^{\neq}$ is between 0.1–0.2 kcal/mol.

TABLE 2
Activation enthalpies and entropies

Solvent	ΔH^* (kcal/mol)	ΔS^* (e.u.)
$CDCl_3$	14.2 ± 0.8	− 6 ± 2
C_6D_6	12.2 ± 0.3	− 10 ± 2
E63	17.5 ± 2.3	3 ± 7
–	16.4 ± 2.1	2 ± 6

reported to be for various nematic phases and, in particular, for other troponoidic compounds.[6] Therefore, from simple geometrical considerations it is possible to determine the signs of the smaller dipolar coupling and of the two quadrupolar splittings, which are all negative. The local order parameters S_{xx}, S_{zz}, S_{xz} have been determined, at the various temperatures, from the four or three splittings resolved in each spectrum, using the following equations:

$$\Delta\nu_{q_i} = \frac{3}{2}q\left\{S_{zz}\left[\cos^2\gamma_i + \frac{\eta}{3}(1+\mathrm{sen}^2\gamma_i)\right] + S_{xx}\left[\mathrm{sen}^2\gamma_i + \frac{\eta}{3}(1+\cos^2\gamma_i)\right]\right.$$
$$\left. + S_{xz}\,\mathrm{sen}2\gamma_i\left(1-\frac{\eta}{3}\right)-\frac{\eta}{3}\right\} \tag{1}$$

$$D_{\mathrm{DH}_i} = -2\mathrm{K}_{DH}\frac{1}{\mathrm{r}^3_{DH_i}}\left\{S_{zz}\cos^2\beta_i + S_{xx}\,\mathrm{sen}^2\beta_i + S_{xz}\,\mathrm{sen}2\beta_i\right\} \tag{2}$$

Here η is the asymmetry parameter of the quadrupolar interaction, fixed at 0.04. β_i and γ_i refer to the angles indicated in Figure 2 and, on the base of the geometry of the tropolone molecule, are assumed to be $\beta_1 = 27.3°$, $\beta_2 = 0°$, $\gamma_1 = 63.5°$, $\gamma_2 = 86.0°$; r_{DH_1} and r_{DH_2} are 2.28 Å and 2.41 Å respectively. Small variations of the geometrical assumptions do not affect substantially the resulting order parameters. The values obtained are reported in Figures 4a and 4b for compound **2** in its own mesophases and in E63, respectively. We observe that, in both case, S_{xx} is better defined than S_{zz}, since it mainly depends on the well-determined value of $\Delta\nu_{\mathrm{CD}_7}$, while S_{zz} mainly depends on the rather uncertain $\mathrm{D}_{\mathrm{D_3H_4}}$ dipolar coupling. S_{xz} is found to be ≈ 0 in the pure mesogen, and ≈ -0.05 in the nematic solution. This means that the order matrix is diagonal or almost diagonal in the reference system chosen. The biaxiality is computed to be in the range 0.05 ÷ 0.13 for the pure compound, 0.01 ÷ 0.07 for the E63 solution. In the former case, the order parameters show a discontinuity at 321K, corresponding to the N $\rightarrow S_C$ transition. In the tilted phase, the order parameters S_{zz} and $|S_{xx}|$ increase with decreasing temperature. This indicates that the local director inside the smectic layers aligns with the magnetic field, while the normal to the layers is tilted. Such behaviour contrasts with the one shown by another troponic mesogen in its S_C phase.[14]

2D-exchange ^{2}H NMR spectra make it possible to estimate the [1,9] sigmatropy rate constants for **2** both pure and in E63, in the ranges of temperature from 310 to

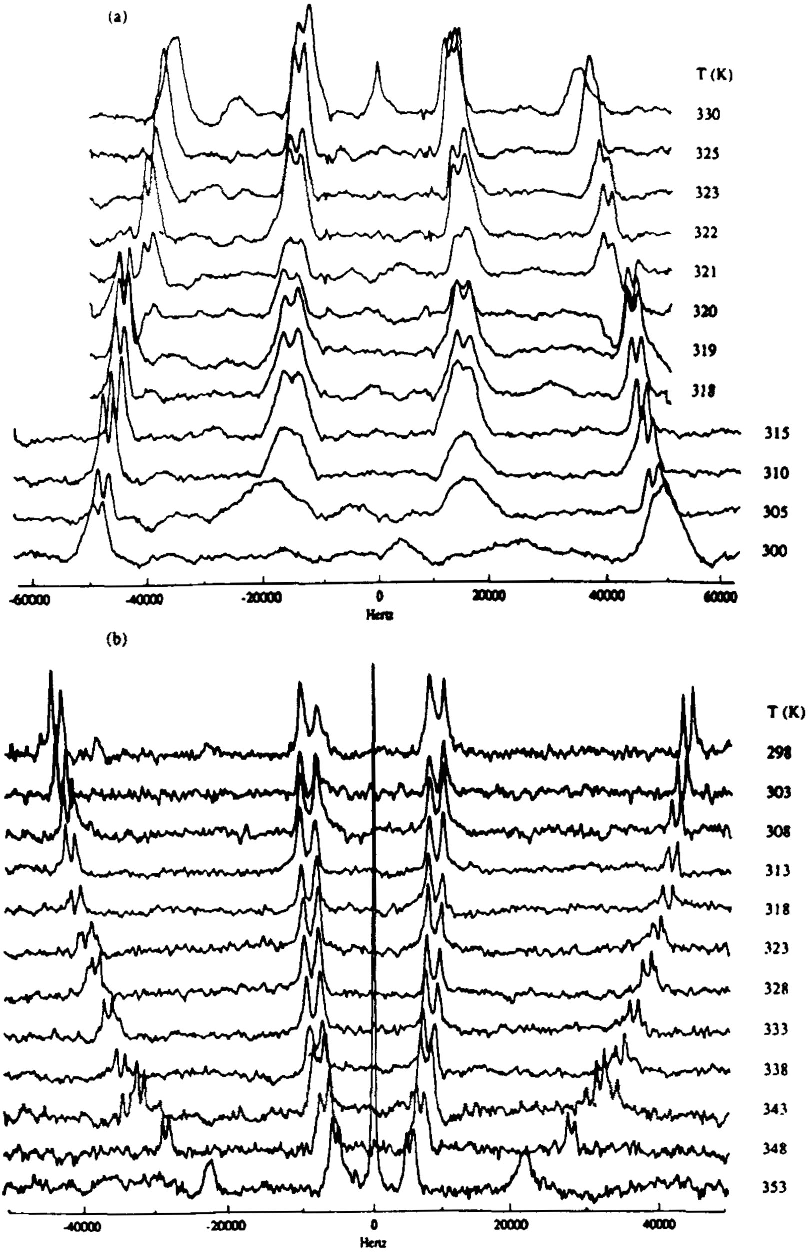


FIGURE 3 ^{2}H NMR spectra of **2** at various temperatures: (a) pure compound; (b) solution in E63.

330 K and from 328 to 348 K, respectively. For allowing a suitable choice of τ_m, T_{1Z} has been previously estimated for **2** in E63 at two different temperatures. Using the saturation recovery pulse sequence, the values shown in Table 3 were obtained.

An example of 2D-exchange ^{2}H NMR for the pure deuterated compound is given in Figure 5. The k values, reported in Table 1, were calculated from the integral ratios

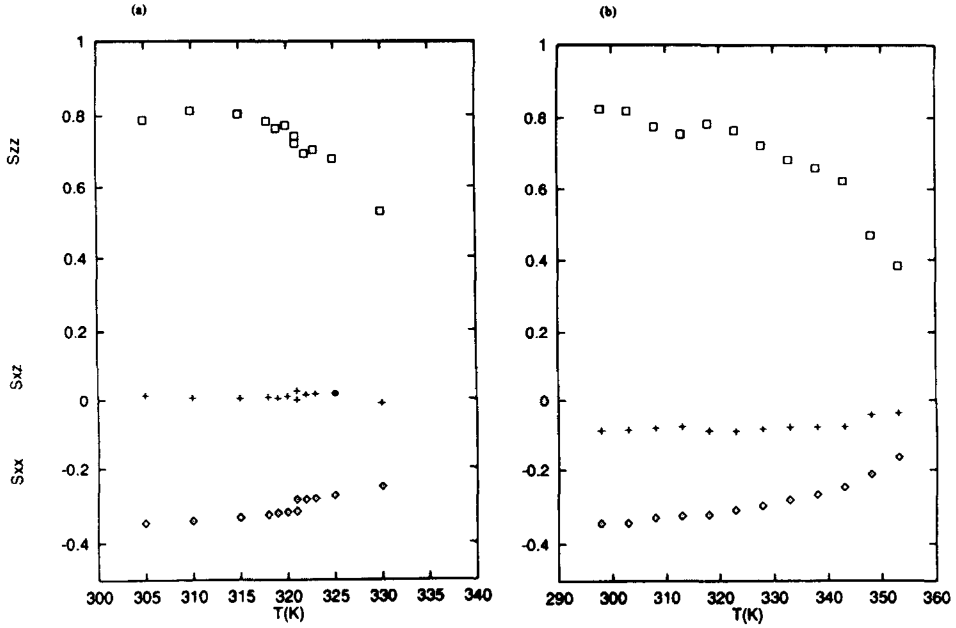


FIGURE 4 S_{xx}(◇), S_{zz}(□) and S_{xz}(+) order parameters of **2**: (a) pure compound; (b) solution in E63. In all cases the uncertainties of S_{xx} and S_{zz} are evaluated about 0.003 and 0.05, respectively, the uncertainty of S_{xz} is about 0.03.

R between exchange cross peaks and diagonal ones through the relation:

$$k = \frac{1}{2\tau_m} \ln \frac{1+R}{1-R}$$

The relative $\Delta H^{\neq}$ and $\Delta S^{\neq}$ values are shown in Table 2.

4. DISCUSSION

The Arrhenius plot in Figure 6 puts in evidence the different trends of the rate constants in the phases studied. The lineshape analysis performed on the spectra of **1** + **2** in C_6D_6 allows exclusion any detectable isotopic effect on the rate of the [1 ,9] sigmatropy, due

TABLE 3

Zeeman relaxation times for compound **2** in E63

T(K)	T_{1Z}(ms)	
	D_7	D_3
313	2.6 ± 0.2	3.8 ± 0.6
348	5.2 ± 0.5	7.1 ± 0.6

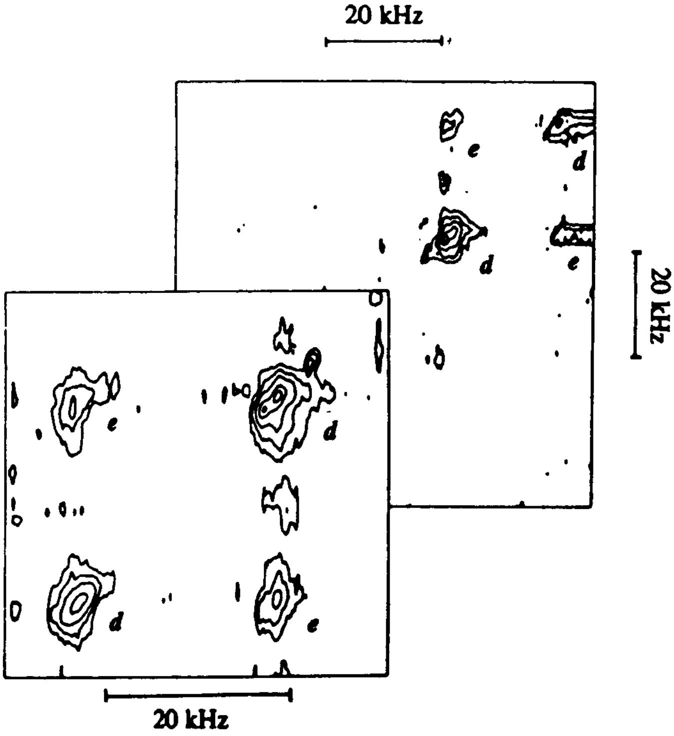


FIGURE 5 Two-dimensional ^2H NMR exchange spectrum of pure compound **2** at 330 K, using a mixing time of 2 ms. The left quadrant at the bottom is expanded. *d* diagonal peaks; *e* exchange peaks.

to the partial deuteration of the troponic ring. The [1,9] sigmatropy is systematically slower in C_6D_6 than in $CDCl_3$. The trend of ln k against $1/T$ for the pure compound in its mesophases excellently fits those relative to the isotropic solvents, whereas the kinetic in E63 is the slowest. The same solvent effect had already been found for two other troponoidic mesogens in E63. As far as the activation parametes are concerned, from the data collected in Table 2, we can infer that (i) $\Delta H^{\neq}$ is lower in the isotropic than in the anisotropic environment; (ii) $\Delta S^{\neq}$ is slightly negative or about 0 in the isotropic and anisotropic environments, respectively. A negative value of $\Delta S^{\neq}$ is reported in the literature for the [1,9] sigmatropy in other troponoidic compounds, independently of the isotropic solvent used, and was the main evidence of a concerted mechanism for the exchange process.

The most interesting comparison, however, can be made between the results presented in this work and those reported in Ref. 6 for two other troponoidic mesogens. Whenever the comparison is possible (in $CDCl_3$ or E63, at the same temperatures), the rate of the sigmatropy is significantly slower and the activation free energy is higher for the compound studied here than for the other two. The same conclusion is reached by comparing rate constants and activation free energies relative to the ranges of temperature where the mesophases are formed. This excludes the possibility of associating the formation of stable liquid crystal phases by troponoidic compounds to specific, or at least comparable, exchanging rates. Finally we remark that the k values

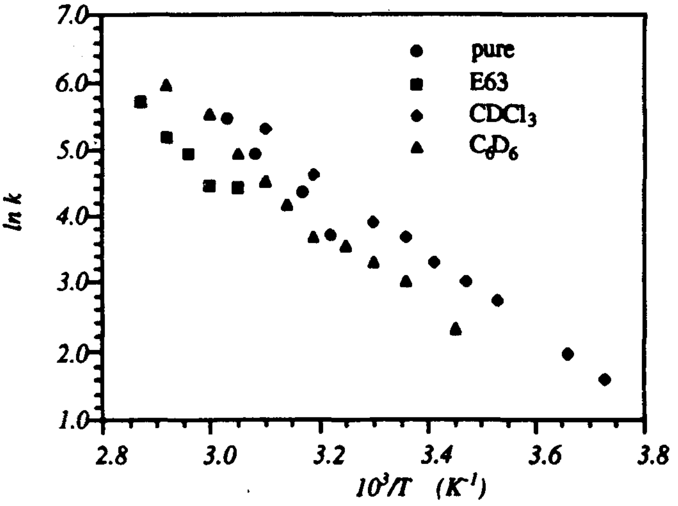


FIGURE 6 Arrhenius plot for the rate of the [1,9] sigmatropy in compounds 1 and 2, in isotropic and anisotropic environments, respectively.

estimated for the present compound are lower than $3 \cdot 10^2$ Hz, while k values in Ref. 6 are much higher, up to a maximum of $2.5 \cdot 10^5$ Hz. However, in all cases, the frequency of the sigmatropic exchange is much lower than the typical frequencies for molecular reorientation in nematic and smectic phases S_A and S_C.[15] In the molecule studied here, in particular, the exchange can be considered as frozen with respect to any reorientational and conformational motion. On the other hand, the frequency range $10^3 \div 10^5$ Hz seems to be characterized by the nematic and smectic director fluctuations[15] and the intramolecular exchange might influence this kind of collective motion. In this case, the different exchange rates found for the compound here studied and the first one presented in Ref. 6 could also be related to the different kind of alignment assumed by the respective S_C phases in the magnetic field.

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