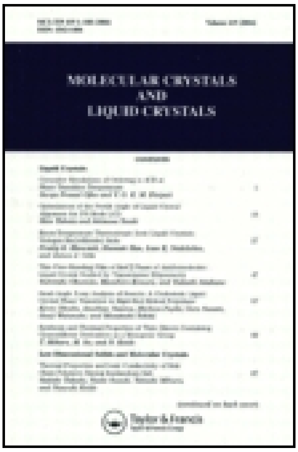

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Liquid Crystals Showing a Molecular Rearrangement: A Dynamic NMR Study of a 2-Acyloxytropone Mesogen and Two Related Compounds

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LIQUID CRYSTALS SHOWING A MOLECULAR REARRANGEMENT: A DYNAMIC NMR STUDY OF A 2-ACYLOXYTROPONE MESOGEN AND TWO RELATED COMPOUNDS

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Abstract The [1,9] sigmatropic rearrangement has been studied by Dynamic NMR spectroscopy for two 2-acyloxytropone mesogens and for 2-acetyloxytropone. The proton spectra of the compounds in $CDCl_3$ have been recorded in the range 213-328 K and the rate constants for the dynamic process determined by line-shape analysis. Evidences of the same rearrangement were found in the ^2H NMR spectra of the three molecules in the nematic phase E63 between 293 and 350 K. Values of the rate constants were yielded also by 2D-exchange spectra in the slow rate limit (300-320 K). The trends of the kinetic constants against temperature, analyzed by the Eyring equation, give the activation parameters of the rearrangement. The activation energies in the nematic solvent are slightly higher than the corresponding ones in $CDCl_3$. By extrapolating these results, we can infer a range of values for the frequency of the process in the liquid-crystalline phases of compounds I and II.

INTRODUCTION

In the last 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 monotropic S_A phases[1,2].

The formation of liquid crystalline phases is at first sight unexpected in molecules with only one aromatic ring as rigid or semi-rigid core. Certainly, the characteristic molecular rearrangement (called [1,9] sigmatropy[4,5]), that is the migration of the acyl substituent between the oxygen atoms at C-1 and C-2 (see Figure 1), plays an important role to this respect.

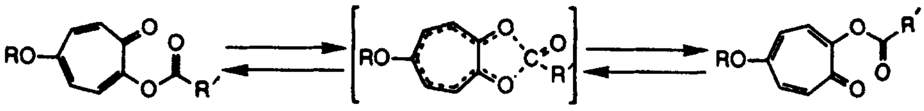


FIGURE 1 [1,9] sigmatropic rearrangement mechanism

This can be true also in the case of compound I (see Figure 2), where the azobenzene group at C-5 already sustains the formation of mesophases.

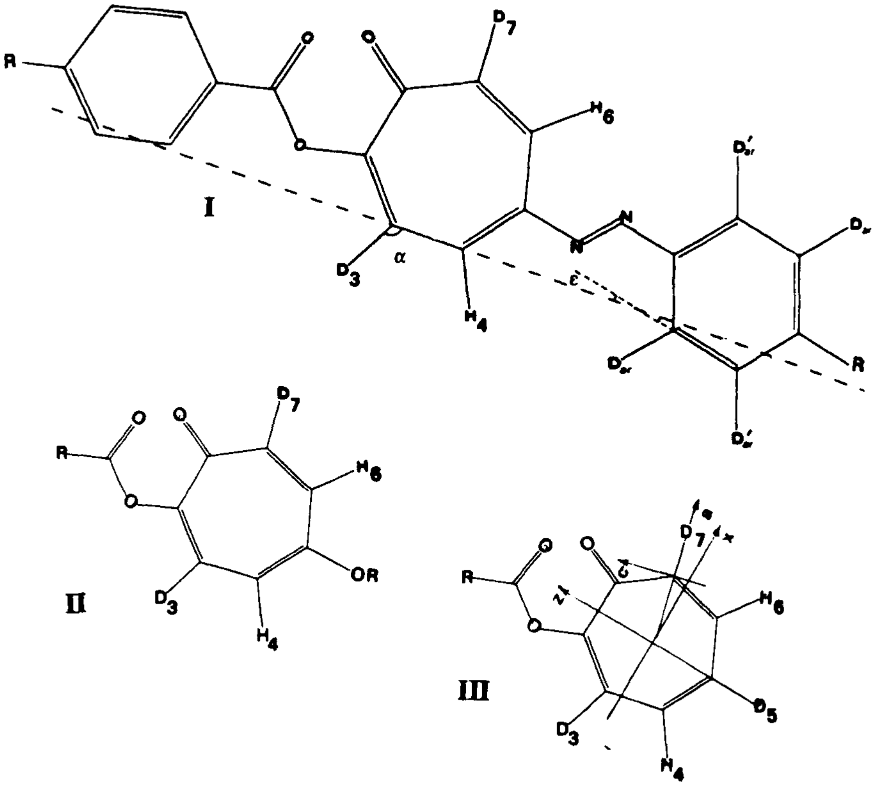


FIGURE 2 Molecular structures of I ($R=C_7H_{15}$), II ($R=C_{12}H_{25}$) and III ($R=CH_3$)

In effects, this compound exhibits an enantiotropic nematic and two monotropic smectic phases according to the scheme:

$$\begin{tikzcd}
Cr \arrow[r, "92^\circ C"] & N \arrow[r, shift left, "152^\circ C"] \arrow[d, "85^\circ C"] & I \arrow[l, shift left] \\
S_I \arrow[u, "72^\circ C"] & S_C \arrow[l, "80^\circ C"] &
\end{tikzcd}$$

The termal behaviour of **I** and its ordering, as monitored by the ordering of the phenyl ring of the azobenzene substituent, has been studied in a previous work[6]. For the present work, besides the benzene ring, also the tropone ring has been deuterated in positions 3, 7; this has allowed to extend the study of the orientational order to a wider molecular fragment and, expecially, to tackle the rate constants determination for the [1,9] sigmatropy with the methods of the dynamic NMR in liquid crystalline phases, as described below.

Compound **II** belongs to the series of 2-alkanoiloxy-5-alkoxytropones already mentioned[1,2], but presents a new combination of alkyl chains in the substituents, and, as expected, forms a monotropic S_A phase. The molecule deuterated in positions 3, 7 has been also prepared in order to perform the kinetic study.

However, in neither cases of compounds **I** and **II** was it possible to follow the rearrangement directly on the mesophases. In fact, the S_A phase of **II** is highly unstable and cannot be investigated by NMR spectroscopy; as far as **I** is concerned, the signals relative to the deuterons on the tropone ring could not be detected on the whole range of temperature investigated (354÷388 K), where the signals of the aromatic deuterons are present. The absence of these signals can be attributed to the [1,9] sigmatropic rerrangement itself, if its rate is in an intermediate range between the slow and fast limits properly defined for this kind of spectra; in this case the signals could become very broad, even undetectable. This hypothesis must be confirmed by a quantitative kinetic study, expecially because of the relatively wide range of temperatures studied and the lack of any reference for the quadrupolar splittings of the exchanging deuterons in the slow exchange limit, needed to define the 'intermediate' dynamic range.

In compounds **I** and **II** the [1,9] sigmatropic rearrangement has been studied by lineshape analysis of ^1H NMR spectra[7] in $CDCl_3$ and ^2H NMR spectra in a nematic phase[8], and also by analysis of 2D-exchange ^2H NMR[9,10] in the same solvent. This allows to get the rate constants of the dynamic process in different enviroments and to establish the possibility of extrapolating their behaviour to the temperature ranges where **I** and **II** show mesophases. The same kind of study has been performed also on **III**, a small non mesogenic molecule which can be considered as a sort of prototype for the rearrangement under investigation, since the [1,9] sigmatropy has been already studied on tropolone acetate in isotropic solvents.[5] The deuteration allows to extend the study to the anisotropic phase and to a wider range of temperature.

Analogous series of experiments are reported in the literature for other intramolecular processes, such as conformational interconversions in s-trioxane[11,12], cycloexane[8] and cis-decaline[13] and the Cope rerrangement in bullvalene.[14] In all cases the activation parameters are found to be independent on the solvent (isotropic or anisotropic); a minor isotopic effect is detected only in the case of s-trioxane. Of course, the situation could be different for other types of dynamic processes, particularly when they involve bulky, mesogenic molecules as compounds **I** and **II**.

EXPERIMENTAL

Preparations

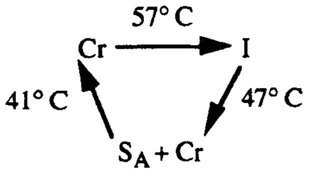
[3,7-$^2H_2$]-2-(4-heptylbenzoyloxy)-5-[(4'-heptylperdeuterophenyl)azo]tropone (**I**) was perpared following previously described procedures[6,15]. 4-Heptylbenzoylchloride (0.519 g, 2.10 mmol) was added to [3,7-$^2H_2$]-2-hydroxy-5-[(4-heptylperdeuterophenyl)azo] tropone (0.684 g, 2.07 mmol) in dry pyridine (18.6 ml) in the presence of a few crystals of DMAP. The mixture was stirred at room temperature for 24 hr, then water was added. **I** was obtained by filtration and purified by recrystallization from acetone, as orange red crystals (0.777 g, 1.09 mmol, 53%). ^1H NMR ($CDCl_3$) 21° C δ_{TMS} 0.89 (t, J=7 Hz, 6 H), 1.30 (m, 16 H), 1.65 (m, 4 H), 2.69 (t, J=7.5 Hz, 4 H), 7.31 (d, J=8.06 Hz, 2 H), 7.96 (brs, 2 H), 8.11 (d, J=8.06 Hz, 2 H). ^{13}C NMR ($CDCl_3$) 21° C δ_{TMS} 14.14, 22.70, 29.22, 31.23, 31.29, 35.96, 36.18, 126.00, 127.72, 130.69, 149.78.

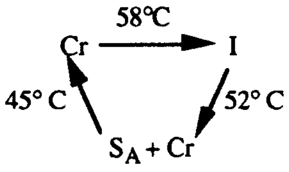
5-dodecyloxy-2-tridecanoiloxytropone (non deuterated analogous of **II**) was prepared in a similar way to the procedures described in ref. 1-3. The monoalkylation at C-5 was carried out treating 0.057 g (0.41 mmol) of 5-hydroxytropolone[16] with NaH (0.025 g, 1.04 mmol) in hexamethylphosphonc triamide (1.5 ml) at 0° C for 15 minutes. 1-Bromododecane (0.095 g, 0.46 mmol) was added to the resultant solution (red-brown) at 0° C and the mixture was acidified; the 5-dodecyloxytropolone precipitated was filtered and recrystallized from $CHCl_3$, to give 0.101 g (0.33 mmol, 81%) of purified product. 0.090 g (0.30 mmol) of 5-dodecyloxytropolone were dissolved in dry pyridine (2 ml) and added to tridecanoic chloride (prepared from 0.35 mmol of tridecanoic acid with slight excess of oxalyl chloride in C_6H_6 at 60° C) together with a few crystals of DMAP, at 0° C. The mixture was kept at room temperature overnight, then water was added and the product was extracted into Et_2O. The residue after evaporation was subject to SiO_2 TLC with Et_2O/petroleum ether (50/50) to give 0.038 g (0.08 mmol, 25%) of product as white-ivory solid. ^1H NMR ($CDCl_3$) δ_{TMS} 0.81 (t, J=8 Hz, 6 H), 1.22 (m, 34 H), 1.69 (m, 6 H), 2.53 (t, J=8.7 Hz, 2 H), 3.85 (t, J=6.1 Hz, 2 H), 6.60 (brs, 2 H), 7.08 (d, J=11.08 Hz, 2 H). ^{13}C NMR ($CDCl_3$) δ_{TMS} 14.15, 22.73, 24.86, 25.98, 28.77, 29.15, 29.33, 29.69, 29.90, 31.95, 33.99, 68.84, 163.01, 166.88, 171.59, 177.15, 202.80. The same procedure was used for preparing [3,7-$^2H_2$]-5-dodecyloxy-2-tridecanoiloxytropone from [3,7-$^2H_2$]-5-hydroxytropolone (0.215 g, 1.53 mmol) obtaining 0.144 g (0.29 mmol, 19%) of product. ^{1}H NMR (CDCl$_3$) δ_{TMS} 0.82 (t, J=8 Hz, 6 H), 1.22 (m, 34 H), 1.70 (m, 6 H), 2.52 (t, J=8 Hz, 2 H), 3.82 (t, J=7 Hz, 2 H), 6.58 (brs, 2 H), 7.08 (d, J=12.1 Hz, 2 H). ^{13}C NMR (CDCl$_3$) δ_{TMS} 14.18, 22.75, 24.89, 25.98, 28.78, 29.17, 29.35, 29.40, 29.55, 29.70, 31.97, 34.01, 68.86, 163.03, 166.88, 171.61.

[3,5,7-^{2}H$_3$]-2-acetyloxytropone was prepared as described in ref. 16. 0.110 g (1.41 mmol) of acetyl chloride were added to 0.202 g (1.62 mmol) of [3,5,7-^{2}H$_3$]-2-hydroxytropone in dry pyridine (0.5 ml). The mixture was stirred at room temperature for 1 hr, then acidified, and the product extracted into CHCl$_3$. The resultant solution was washed with H$_2$O. After evaporation of the solvent, the residue was subject to sublimation (70° C/5 mm Hg) to give 0.150 g (0.85 mmol, 60%) of colourless crystals. ^{1}H NMR (CDCl$_3$) δ_{TMS} 2.35 (s, 3 H), 7.13 (s, 2 H). ^{13}C NMR (CDCl$_3$) δ_{TMS} 20.75, 133.88, 133.93, 177.42.

Optical Observations

The appearance of the mesomorphic phase of compound **II** was determined by a polarizing microscope equipped with a hot stage. The observed sequences of transitions are shown in the following schemes for the non-deuterated and deuterated compound **II**, respectively.





The S_A phase separates from the isotropic liquid as bâtonnets, while the crystallization begins in differents regions of the sample.

NMR experiments

The NMR measurements were made on a Bruker AMX 300 spectrometer equipped with variable temperature control. The ^{1}H NMR spectra were recorded on solutions of **I**, **II** (non deuterated analogous) and **III** in CDCl$_3$ (0.3% wt). The ^{2}H NMR spectra (one and two-dimensional) were performed in the nematic mixture E63 (BDH), with about 20% by weight of compounds **I** and **II**, and 10% by weight of compound **III**. The clearing point of the neat solvent is 87.5° C; the N-I transition temperature reaches 100° C for the solution of **I**. The one-dimesional ^{2}H spectra had a width of 125 kHz and a resolution of 5 Hz/point. The baseline was corrected by substituing the first points of the FID with those computed by a linear prediction routine.[17] For the two-dimensional ^{2}H spectra, the pulse sequence $(\pi/2)$-t_1-$(\pi/2)$-τ_m-$(\pi/2)$-t_2 was used, with the phase cycling suitable to obtain phase sensitive spectra with the States et al. method, described in ref.18. This is equivalent to perform the two experiments referred as "Zeeman-order" and "quadrupolar-order" in ref. 9 and to combine them in equal proportion. In this way, only a partial cancellation of the cross peaks due to the quadrupolar interaction is obtained; anyway, this is enough for confirming the network of the exchange process and the relative signs of the quadrupolar splittings; the intensity ratios between the peaks of interest are the same in both Zeeman- and quadrupolar-order experiments and, therefore, should not be altered by there combination. We must also consider that the 90° pulse width was rather long (9 µs); this could cause considerable deviations of the experimental spectra from those theoretically predicted[19] and makes meaningless any effort to use calibrated pulses (namely of 54.7°) to obtain a perfect cancellation of the unimportant peaks. The relaxation times T_{1Z} and T_{1Q} of the tropone ring deuterons of compound **I** had been evaluated, previously to this experiment, by the method proposed by Wimperis[20] at 313 K; they were found to be 1.26 (±0.28) ms and 1.02 (±0.16) ms, respectively. Mixing times ranging from $4 \cdot 10^{-4}$ to $7 \cdot 10^{-4}$ s were used, so to obtain values around 2.5 for the ratios between the integrals of the diagonal and the exchange peaks. 1024 data points were collected in the t_2 domain, with TPPI quadrature procedure, with sampling intervals of 5 µs. 70 to 128 FID's with increments of 10 µs of t_1 were collected and in any case zero-filled to 128 points before the Fourier transformation. These conditions correspond to a spectral width of 100 kHz in both dimensions. The one and two-dimensional ^2H spectra of **II** and **III** have been recorded under proton decoupling conditions.

RESULTS

Compound I

The dynamic process under investigation is clearly shown by the series of ^1H spectra of **I** in $CDCl_3$ in the range between 223 K and 323 K. At the low temperatures H_4 and H_6 give two narrow signals at $\delta > 7.5$ ppm; the specific assignment is not evident and, anyway, is unessential. Between 223 K and 253 K the line width (≈7.9 Hz) is unaffected by the temperature change, while the chemical shift of the low field signal changes so that the relative distance $\Delta\nu_0$ between the two peaks increases from 106.1 Hz to 108.0 Hz (≈0.63 Hz/K). Above 253 K, the two lines become broader and approach the cohalescence. Beyond 293 K a single line is found, progressively narrowing with increasing temperature. The kinetic constants yielded by the lineshape analysis of the spectra are reported in Table 1, with the corresponding values of $\Delta G^{\#}$, obtained by the

Eyring equation:

$$k = \frac{k_B T}{h} \exp\left(-\frac{\Delta G^{\#}}{RT} \right) \tag{1}$$

The $\Delta H^{\#}$ and $\Delta S^{\#}$ values deduced from the dependence of $\Delta G^{\#}$ on the temperature are shown in Table 2. The negative sign of $\Delta S^{\#}$ is consistent with a preceeding determination of this parameter in related compounds[5] and is the main indication that the [1,9] sigmatropy occurs through a concerted mechanism.

The spectra of **I** in E63, some of which are reported in Figure 3, are important for explaining those recorded on the very mesophases of **I**.

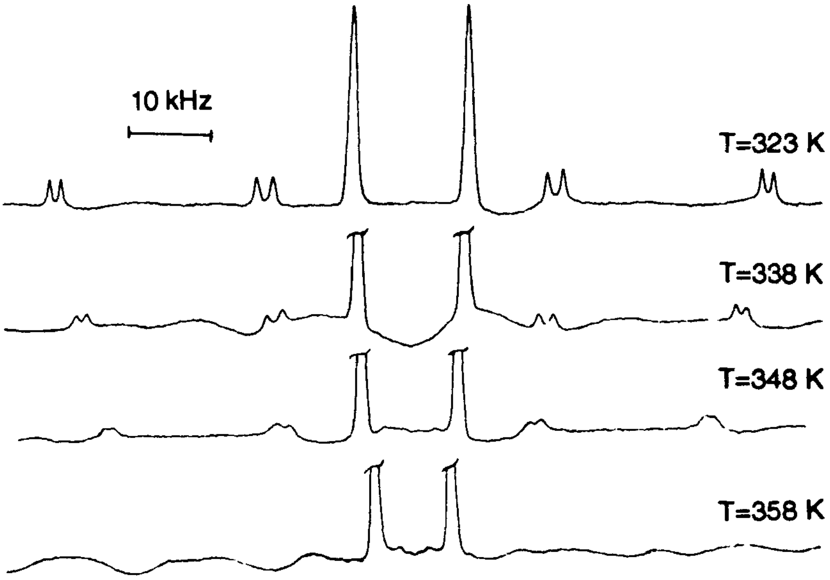


FIGURE 3 ^{2}H NMR spectra of **I** in E63

At 303 K we find a quadrupolar doublet assigned to the four aromatic deuterons and two other quadrupolar doublets, with larger splittings, relative to the two tropone ring deuterons, respectively. Each component of these last doublets is split in two signals by the dipolar coupling between the deuteron and the nearest proton on the tropone ring. All this is consistent with the dynamic process being in the slow exchange limit. Up to 313 K the spectra are affected only by the orientational order reduction, which decreases the quadrupolar and dipolar splittings. Above 313 K the signals due to the troponic deuterons get broader (the half-height line-width ranges from 560 Hz to 1200 Hz) and weaker until, at 353 K, they completely disappear. At 373 K the sample becomes isotropic, before the averaged doublet of the troponic deuterons has emerged from the baseline. The situation found above 353 K is analogous to that charaterizing the spectra of the mesophase between 354 K and 391 K.

The spectra at 303, 308 and 313 K, where the dynamic process is in the slow limit, are used to study the orientational order of I in E63, assuming the geometry of Figure 2 to be valid. The molecular fragment constituted by the troponic ring and the azo-benzene group is considered planar and rigid, with the exception of the rotations around the C-N bonds. The ordering of this fragment is obtained by means of 5 or 6 local parameters relative to the internuclear directions C-D_3, C-D_7, D_3-H_4, D_7-H_6, C-D_{ar} and D_{ar}-D'_{ar} (where the D_{ar}-D'_{ar} dipolar coupling is available); in turn, such local order parameters can be calculated from the quadrupolar and dipolar splittings resolved in the spectra, using the appropriate relations:

$$\Delta\nu_q = \frac{3}{2}q\left[S_{aa} + \frac{\eta}{3}(S_{cc} - S_{bb})\right] \tag{2}$$

$$\Delta D_{ij} = -4K_{ij}\frac{S_{ij}}{r_{ij}^3} \tag{3}$$

The a,b,c reference frame, where the electric gradient field is diagonal, has its principal axis a along the C-D bond. In the computation, the quadrupolar coupling constant q is assumed 185 kHz and the asymmetry parameter η is neglected in equation (2). Equation (3) is adequate to the case of proton-deuteron dipolar splittings.

We have verified that, assuming regular structures with standard bond lenghts and angles for the arenic and troponic rings, at each temperature (303 K, 308 K, 313 K) the local order parameters S_{ij} or S_{aa} can be simply referred to the one relative to the D_3-H_4 direction, the best oriented among those considered, by equation (4)

$$S_{ij}(aa) = \frac{3\cos^2\beta - 1}{2}S_{D_3H_4} \tag{4}$$

where β is the angle between the ij (or aa) and D_3-H_4 directions. The agreement between the experimental S_{ij} (S_{aa}) values and those computed through equation (4) is excellent if the angles α=116.6° and ε=14.2° (see Figure 2) are assumed, that is accepting minor deviations from the standard geometry initially defined (α=115.7° and ε=12.9°). All this means that, within the limits imposed by the experimental error on the quadrupolar and dipolar splittings, the ordering of the central fragment has a cylindrical symmetry;

however, it must be noted that a biaxiality of about 0.1, as evaluated in ref. 6 for the arene fragment of the same compound, cannot be excluded, especially considering the high experimental uncertainty on the D_{ar}-D'_{ar} dipolar coupling. The principal order parameter, S_{D3H4}, computed under the geometrical assumption described, is 0.70, 0.69, 0.68 at 303 K, 308 K and 313 K, respectively.

Equations (2), (4) and (2) again, used in this sequence, allow to estimate the quadrupolar splittings $\Delta\nu_3$ and $\Delta\nu_7$ of D_3 and D_7 respectively, in the ^2H spectra of the mesophase of compound **I**, using S_{D3H4} calculated from the quadrupolar splittings of the arene deuterons. The difference between the possible values of $\Delta\nu_3$ and $\Delta\nu_7$ is ≈55 kHz at 388 K (the highest temperature investigated). This allows to infer that, at 388 K, the rate constant for the exchange is less than $5 \cdot 10^5$ Hz, since no signals of D_3 and D_7 are present in the spectrum. The rate constant at 354 K (the lowest temperature studied in the mesophase) should be equal or greater than the one evaluated for I in E63 at the same temperature, where the signals disappear. The k values for I in E63 can be estimated from the increase of the line width detected between 318 K and 343 K[8], and have values between 300 s^{-1} and 1500 s^{-1}. However, we must remember that the experimental line width of the exchanging peaks may be severely altered by the inevitable delay before the acquisition of the FID and by the necessary procedure of linear prediction[17] applied to the first few points of the FID. In particular, the line widths of broad signals and, consequently, the k values are probably underestimated.

2D-exchange ^2H spectra, one of which is shown in Figure 4a, make possible an indipendent evaluation of the rate constants for the [1,9] sigmatropy in E63 at the temperature where the exchange is slow. The k values (see Table 1) are calculated from the integral ratios R between diagonal and exchange cross peaks:

$$k = \frac{1}{2\tau_m} \ln \frac{R+1}{R-1} \tag{5}$$

The error on the k constants dramatically increases when R approaches 1; on the other hand, we cannot safely determine the integrals of the exchange cross peaks if they are too weak. Therefore, low and high values of R have been avoided by a suitable choice of τ_m, as already pointed out. Nevertheless, the values of k so determined are to be cautiously considered since the spectra show some incongruities with respect to the theoretical predictions; in partcular, the intensities are not symmetrical with respect to the main diagonal. This can be ascribed to the finite pulse width, as explained in ref 19. The average intensities of the cross and diagonal peaks have been considered for computing the ratios R. Altogether, a 90° pulse of 9 μs could be too long for a precise determination of quantities that, as the rate constants, depend on signal intensities ratios; however, the rough k values we have obtained are in good agreement with those found from the one-dimensional spectra.

The results of $\Delta G^{\#}$ relative to the E63 solvent can be analysed to obtain the $\Delta H^{\#}$ and $\Delta S^{\#}$ values of Table 2.

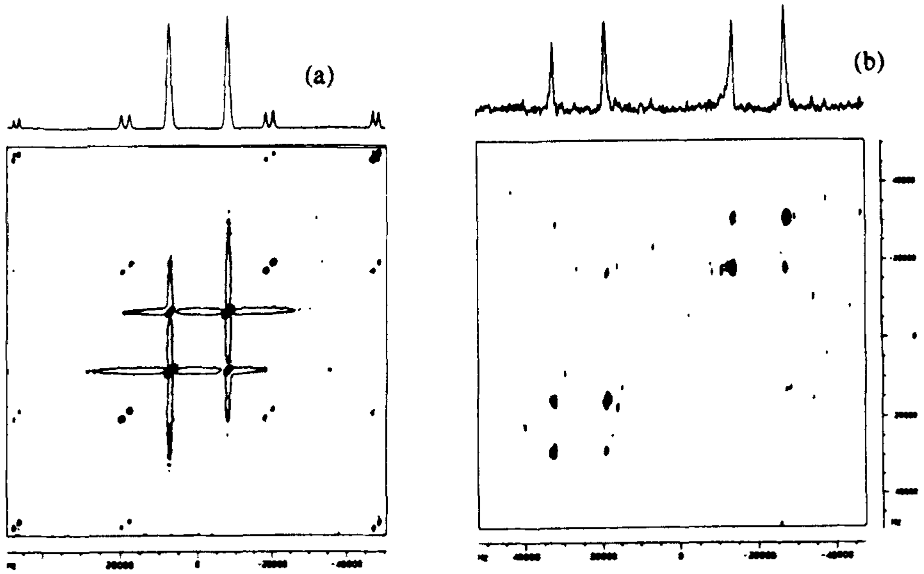


FIGURE 4 2D ^{2}H NMR spectra: (a) I in E63 at T =310 K ($\tau_m = 7\cdot10^{-4}$ s); (b) II in E63 at T =313 K ($\tau_m = 4\cdot10^{-4}$ s)

Compound II

^{1}H NMR spectra are recorded on the non-deuterated analogous of II dissolved in $CDCl_3$, in the temperature range between 203 K and 328 K. At low temperature, four doublets are found, corresponding to the four troponic protons, a, a' and b,b'. At 203 K, three doublets, partially superimposed, occur at δ=7.265 (H_b), 7.226 ($H_{b'}$) and 7.163 ppm (H_a), respectively; the fourth is at 6.277 ppm ($H_{a'}$). With increasing temperature, the chemical shift of all protons decreases with rates ranging between -0.2 Hz/K and -0.4 Hz/K. The resolved couplings are J_{ab}=13.5 Hz and $J_{a'b'}$=10.5 Hz. The simulation of the lineshape, performed with the DNMR3 computer program[21], allows to obtain the rate constants reported in Table 1, with the relative $\Delta G^{\#}$ values. The values of $\Delta H^{\#}$ and $\Delta S^{\#}$ yielded by the analysis of the $\Delta G^{\#}$ trend with temperature (see eq. (1)) are shown in Table 2.

The [1,9] sigmatropy can also be observed in the ^{2}H spectra of II in E63. The spectra, some of which are reported in Figure 5, are recorded from 263 K and 338 K. The peaks progressively loose intensity, until they disappear above 323 K, but do not become sistematically broader; therefore the signal lineshapes cannot be used for an estimate of the rate constants. k values can be obtained from 2D-exchange ^{2}H NMR spectra (see Figure 4b), recorded between 293 K and 313 K by the same procedure described for compound **I**. Table 1 shows the k and $\Delta G^{\#}$ values; in Table 2 the resulting $\Delta H^{\#}$ and $\Delta S^{\#}$ are reported.

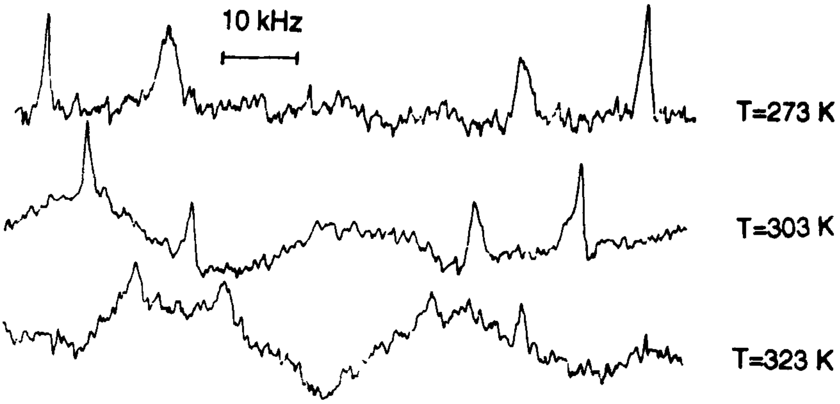


FIGURE 5 ^{2}H NMR spectra of **II** in E63

Compound **III**

The [1,9] sigmatropic rearrangement is evident in the ^{1}H NMR spectra of **III** in $CDCl_3$. These spectra, recorded from 209 K to 293 K, show a behaviour similar to that found for compound **I**. At low temperature the two protons H_4 and H_6 give two narrow signals at δ=7÷7.5 ppm. When the temperature increases, these signals become broader and approach the coalescence. Beyond 223 K, a single line is found, which becomes progressively narrower. The lineshape analysis gives the k values reported in Table 1, with the corresponding values of $\Delta G^{\#}$ obtained with equation (1). From the dependence of $\Delta G^{\#}$ on the temperature, the $\Delta H^{\#}$ and $\Delta S^{\#}$ values shown in Table 2 are determined, in good agreement with the literature[5].

The dynamic process is also evident in the ^{2}H NMR spectra of **III** in E63 (some are shown in Figure 6), recorded from 253 K to 338 K. Up to 268 K, the [1,9] sigmatropy can be considered in the slow rate limit; therefore the spectra present three quadrupolar doublets corresponding to the three deuterons of **III**. The quadrupolar doublet with the largest splitting is unaffected by the dynamic process and is attibuted to D_5. The evolution of the remaining two doublets, assigned to D_3 and D_7, with increasing temperature indicates that $\Delta\nu_3$ and $\Delta\nu_7$ have opposite signs. To this purpose, the spectrum at 298 K is particularly significant. Above 328 K, an averaged doublet is present. As already said in the case of compound **I** in E63, the lineshape can be altered with respect to the theoretical one by the data acquisition and processing procedures. However, a reliable estimate of the rate constants is allowed, expecially for those temperatures where the spectra show peculiar features. Some rate constants have therefore been determined by lineshape analysis (see Figure 6 for the computed spectra and Tables 1 and 2 for the k and $\Delta G^{\#}$, $\Delta H^{\#}$ and $\Delta S^{\#}$ values). As far as the 2D-NMR spectrum is concerned, since the exchanging quadrupolar splittings have similar absolute values and opposite signs, the exchange cross peaks occur very close to the secondary diagonal and to the signals connecting the two components of each quadrupolar doublet. These last signals are only partially cancelled by the combination of the Zeeman- and quadrupolar-order experiments; this prevents a quantitative determination of rate constants from the intensities ratios.

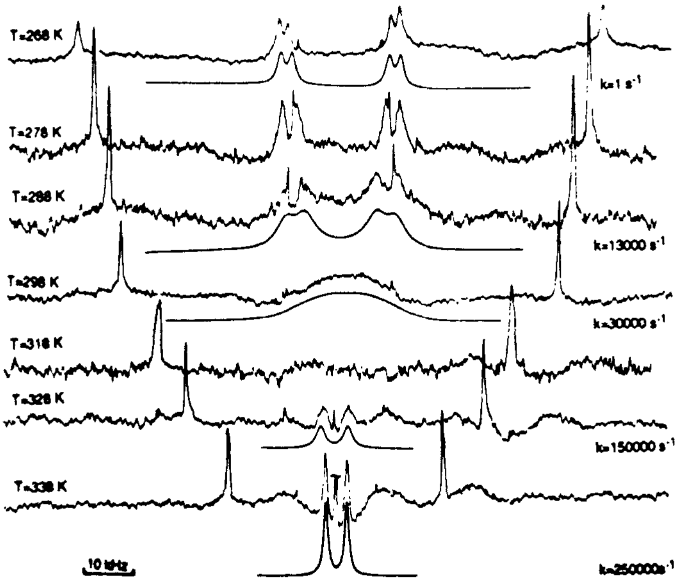


FIGURE 6 Experimental and simulated ^2H NMR spectra of **III** in E63

From the monodimentional spectra of III in E63 at 258 K, 263 K, 268 K the order matrix for the molecule has been determined, using equation (2) for the $\Delta\nu_q$'s of the three deuterons, with q=185 kHz and η=0.04, and expressing the local order parameters S_{aa}, S_{bb} and S_{cc} in terms of S_{zz}, S_{xx} and S_{xz} (see Figure 1 for the reference frames). The negative sign is attributed to the smaller quadrupolar splitting, since only in this way the diagonalization of the order matrix requires the same rotation of the x, y, z reference frame at the three temperatures considered (22.1° toward the C-D bond corresponding to the largest splitting). The principal order axis in the ring plane is almost aligned with one of the two C-O bonds, presumably with the C-$OCOCH_3$ bond. The values of S_{zz}, S_{xx} and S_{xz} obtained with this sign assignment are reported in Table 3.

TABLE I Rate constants and activation energies*.

	I		II		III	
T (K)	k (s^{-1})	ΔG[#] (kcal/mol)	k (s^{-1})	ΔG[#] (kcal/mol)	k (s^{-1})	ΔG[#] (kcal/mol)
Solvent $CDCl_3$						
211					22	10.9
212					28	10.9
213					39	10.9
218					69	10.8
220					100	10.7
223			2	12.6	110	10.8
228					162	10.9
233			7	12.6	259	11.0
238					342	11.1
243			18	12.7	471	11.2
253			55	12.7	768	11.4
263	9	14.2	160	12.7	1137	11.7
273	49	13.8	220	13.0		
283	174	13.6	600	12.9		
298	480	13.8				
303			1600	13.3		
308	853	13.9				
313			2500	13.5		
318	1504	14.0				
320	1778	14.2				
323			4000	13.7		
328			6000	13.6		
Solvent E63						
288					13000	11.4
293			377	13.7		
298					30000	11.3
303			612	13.9		
310	404	14.5				
313	498	14.5	992	14.1		
316	586	14.5				
320	776	14.6				
325	944	14.7				
328					150000	11.5
330	1172	14.8				
338					250000	11.5

*The uncertainty on the rate constants is about 20% or 30% of the k value for determinations in $CDCl_3$ and E63, respectively. The consequent uncertainty on ΔG[#] is between 0.1÷0.2 kcal/mol.

TABLE 2 Activation entalpies and entropies*.

	I		II		III	
SOLVENT	$\Delta H^{\#}$ (kcal/mol)	$\Delta S^{\#}$ (u.e)	$\Delta H^{\#}$ (kcal/mol)	$\Delta S^{\#}$ (u.e)	$\Delta H^{\#}$ (kcal/mol)	$\Delta S^{\#}$ (u.e)
CDCl3	10.0	-13	10.2	-10	8.0	-13
E63	10.1	-14	8.3	-18	10.4	-3
CDCl3 and E63					9.5	-6
Ref. 5					8.2	-11

*The uncertainties on $\Delta H^{\#}$ and $\Delta S^{\#}$ are estimated of tenths of kcal/mol and of some e.u., respectively.

TABLE 3 Order parameters* of the tropone ring of compound **III** in E63

T(K)	S_{xx}	S_{zz}	S_{yy}	S_{xz}
258	-0.030	0.385	-0.355	0.203
263	-0.025	0.369	-0.344	0.192
268	-0.021	0.358	-0.336	0.184

*The estimated uncertainty is of some units of the last digit quoted.

DISCUSSION

The values of the activation parameters reported in Table 2 show that, in all the cases examined, $\Delta H^{\#}$ is about 10 kcal/mol and $\Delta S^{\#}$ is negative. Some of this data are not completely reliable, owing to the described difficulties connected with the determination of the k values from the spectra. In the case of **II** in E63, only three k values are available for the determination of two activation parameters.

A global view of the k dependence on temperature can be given through the Arrhenius plots of Figure 7. It is evident that, for both compounds **I** and **II**, distinct trends are found for the two solvents: the corresponding best-fit straight lines are about parallel. As far as compound **III** is concerned, the measurements relative to the two solvents refer to different ranges of temperature and the comparison with the other cases cannot be direct. Figure 7c shows that the best-fit straight lines are not parallel. In the temperature range relative to the CDCl3 measurements, lower rate constants are predicted in E63, just as found for compounds **I** and **II**. However, in the case of **III**, if we consider the high error on the k constants determined in E63 and tolerate a bad reproduction of the highest experimental k's found in $CDCl_3$, a common trend could be recognized, connecting the k values in the two solvents and corresponding to quite acceptable activation parameters (see Table 2).

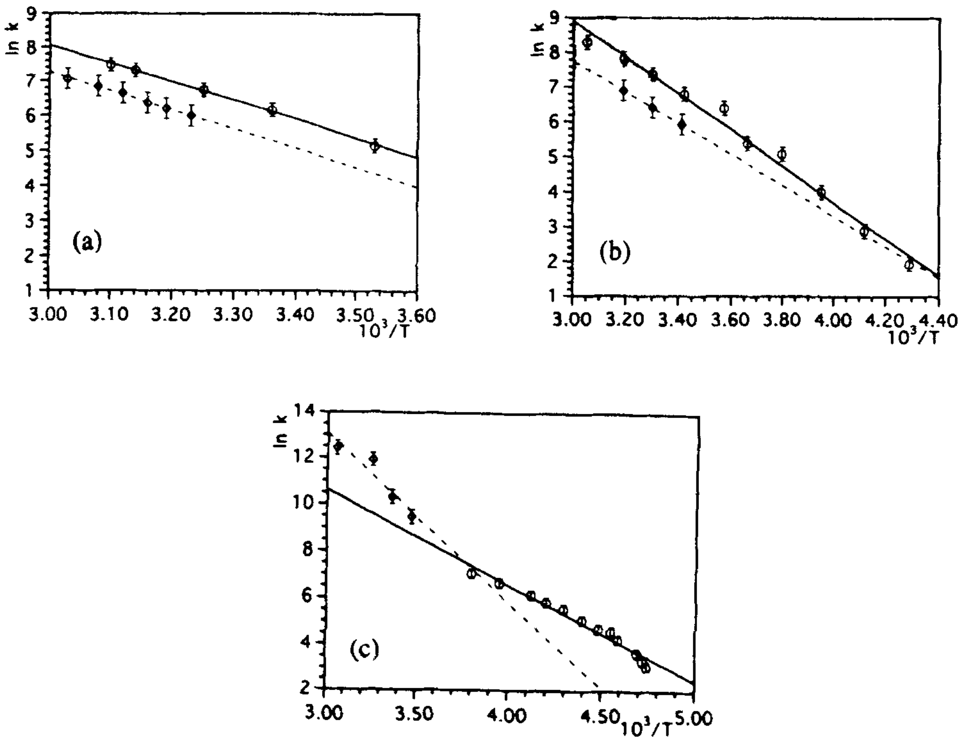


FIGURE 8 Arrhenius plots for compounds I (a), II (b) and III (c): measurements in $CDCl_3$ ( ) and E63 ( )

By extrapolating the k values found in E63 for I and II to the temperatures where the mesophases appear, we infer that in the stable liquid crystalline phases of I the rate of the [1,9] sigmatropy ranges from 7800 s^{-1} to 55000 s^{-1}; in the unstable S_A phase of II, k should be about 1000 ÷ 1400 s^{-1}.

CONCLUSION

The [1,9] sigmatropy is found to be slower in the anisotropic nematic environment of E63 than in $CDCl_3$, in the temperature range examined, for two 2-acyloxytropone mesogens.

This is not necessarily true for the smaller compound **III**, where the solvent effect could be reduced or absent, as reported for exchanges processes in cyclic molecules.[8,11-14]

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