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Carbon-13 NMR of liquid crystal solutions with magic-angle spinning. Hindered rotation in 6-(dialkylamino)fulvenes

Jalees Afzal and B. M. Fung^{a)}

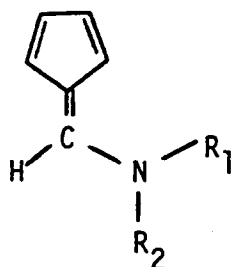
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With magic-angle spinning, the carbon-13 NMR spectra of nematic liquid crystals having positive anisotropy of the magnetic susceptibility show sharp peaks. Solutes which have carbon-13 peaks in the "window" regions of the solvent spectra can be conveniently studied. The hindered rotation of the dialkylamino group in 6-(dimethylamino)fulvene, 6-(diethylamino)fulvene, and 6-(*N*-piperidyl)fulvene in a liquid crystal solvent (E8) has been investigated by carbon-13 NMR with magic-angle spinning. The results are compared with those obtained in isotropic solutions of the same compounds in CDCl₃ and CDCl₃ + E8. The free energy of activation (ΔG^\ddagger) of each compound in the three solvents is the same within experimental error.

I. INTRODUCTION

The dynamic behavior of many molecular systems can be conveniently studied by NMR spectroscopy.^{1,2} However, there have not been extensive dynamic NMR studies on liquid crystal solutions. The main reason for this is the complexity of the proton and carbon-13 NMR spectra of liquid crystal solutions due to nonzero static dipolar interactions. One way to avoid this problem is to study the deuterium NMR of specially deuterated compounds.³ This technique has a large dynamic range³ but is limited by the requirement of special deuteration. We have recently shown that it is possible to study natural-abundance carbon-13 NMR of liquid crystal solutions by using a spin-echo sequence to reduce solvent interference⁴ and applying special phase-alternating proton decoupling to increase the decoupling efficiency.^{4,5} The application of these methods to investigate the hindered rotation in 4-(dimethylamino)pyrimidine has been reported.⁶ In this article, we present the use of magic-angle spinning to investigate the dynamic carbon-13 NMR of 6-(dialkylamino)fulvenes (I–III) in liquid crystal solutions.



I: $R_1 = R_2 = \text{CH}_3$

II: $R_1 = R_2 = \text{CH}_2\text{CH}_3$

III: $\text{N} + R_1 + R_2 = \text{piperidyl}$

The purpose of this study is to examine whether or not a liquid crystal solvent would affect the barrier to the internal rotation in a solute. A systematic change in the size and geometry of the R group serves as a check on the comparison of activation parameters in different solvents.

Magic-angle spinning (MAS) is a powerful technique routinely used in solid-state NMR.^{7,8} The spinning of a ne-

matic liquid crystal sample at or near the magic angle can greatly simplify its NMR spectrum.^{9–11} When a nematic liquid crystal is rapidly spun (≥ 1 kHz at $B_0 = 7$ T) along an axis forming an angle θ with respect to B_0 , the director of the principal axis of the liquid crystal molecule aligns either along or perpendicular to the spinning axis, depending on the signs of the anisotropy of the magnetic susceptibility ($\Delta\chi$) and the factor $f = (3 \cos^2 \theta - 1)/2$.^{9,10} For $\Delta\chi > 0$ and $f > 0$ ($\theta < 54.7^\circ$), the director aligns along the spinning axis and the carbon-13 spectra of liquid crystals show sharp, well-resolved peaks with only nominal proton decoupling power.^{10,11} The peaks of solutes are even sharper.¹¹ Thus, if the solute peaks appear in window regions where there are no solvent peaks, they can be clearly identified and their temperature dependence can be conveniently studied.

II. EXPERIMENTAL SECTION

All carbon-13 NMR measurements were performed on a Varian XL-300 spectrometer at 75.4 MHz. Spectra of liquid samples were measured using a standard 5 mm probe and those of liquid crystal samples were measured using a variable-angle probe manufactured by Dotty Scientific, Columbia, SC. The temperatures of the probes were calibrated with ethylene glycol under the same condition as those at which the spectra were taken (same flow rates of air or nitrogen, and same proton decoupling power and duty cycle). The proton signals of ethylene glycol were observed for the temperature calibration; the receiver was off when the decoupler was on.

III. RESULTS

The carbon-13 spectrum of 6-(piperidyl)fulvene in the liquid crystalline solvent E8 at 308 K with magic-angle spinning is shown in Fig. 1. Signals of the α carbons in the piperidyl ring can be easily identified. These two peaks gradually merge into one as the temperature is raised, and the spectra are shown in Fig. 2. The spectra of the same compound in CDCl₃ are also shown in Fig. 2 for comparison. CH₃ groups in I and α -CH₂ groups in II give rise to signals similar to

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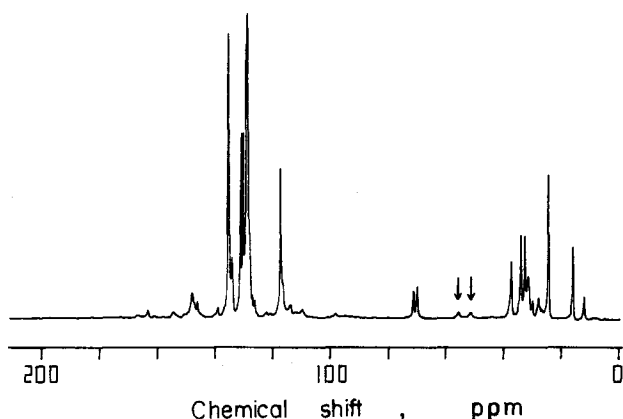


FIG. 1. Carbon-13 NMR spectrum of 6% 6-(*N*-piperidyl)fulvene in E8 at 308 K and 75.4 MHz. The sample was spun along the magic angle at a rate of 1.5 kHz. The arrows indicate peaks of the α carbons in the piperidyl ring.

those shown in Figs. 1 and 2, except with chemical shifts $I < II < III$ and different transition temperatures.

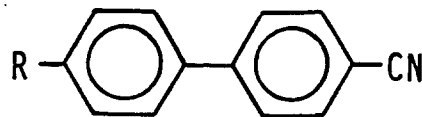
The rate of hindered rotation of the dialkylamino group at each temperature was obtained by the method of total line shape analysis. The spectral amplitudes were fitted to the Gutowsky-Holme equation¹² with least-squares analyses. In the calculation, it was assumed that the intrinsic linewidth at each temperature was the same as the average linewidths of other carbons in the same molecule. The hindered rotation of the 1-6 double bond has a much higher barrier¹³ and is not considered. Results of the total line shape analyses for I-III in $CDCl_3$, E8, and $CDCl_3 + E8$ (2:8) are presented in Fig. 3 as Eyring plots. Thermodynamic param-

eters of the activation processes of the hindered rotation are given in Table I.

IV. DISCUSSION

In a previous study of the hindered rotation of the dimethylamino group in 4-(dimethylamino)pyrimidine,⁶ the liquid crystal was spun slowly (15 Hz) along the magnetic field (B_0) in the conventional way. Solvent interference was reduced by using a spin-echo sequence⁴ and the efficiency of proton decoupling was improved by using a phase-alternating decoupling sequence.⁵ In the case of dialkylaminofulvenes, complete proton decoupling was not achieved with a decoupling power of $\gamma B_1/2\pi = 13$ kHz. This was evidenced by nonequal intensities of the peaks of the two α carbons under the condition of slow exchange. Higher decoupler power would increase solvent interference and might cause an appreciable temperature gradient in the liquid crystal sample. On the other hand, it has been shown that magic-angle spinning is a very useful technique in studying carbon-13 NMR of liquid crystals.^{10,11} Since the nematic director is oriented along the spinning axis and dipolar couplings are reduced by a factor of $(3 \cos^2 \theta - 1)/2$,⁹ only a nominal proton decoupling power ($\gamma B_1/2\pi \lesssim 8$ kHz) needs to be applied to obtain well-resolved carbon peaks (Fig. 1).

The liquid crystal solvent E8 is a mixture of cyanobiphenyls.



$R = C_3H_{11}$, 43%; $R = C_3H_7O$, 17%;
 $R = C_5H_{11}O$, 13%; $R = C_8H_{17}O$, 17%;
 $R = p$ -(*n*-pentyl)phenyl, 10%.

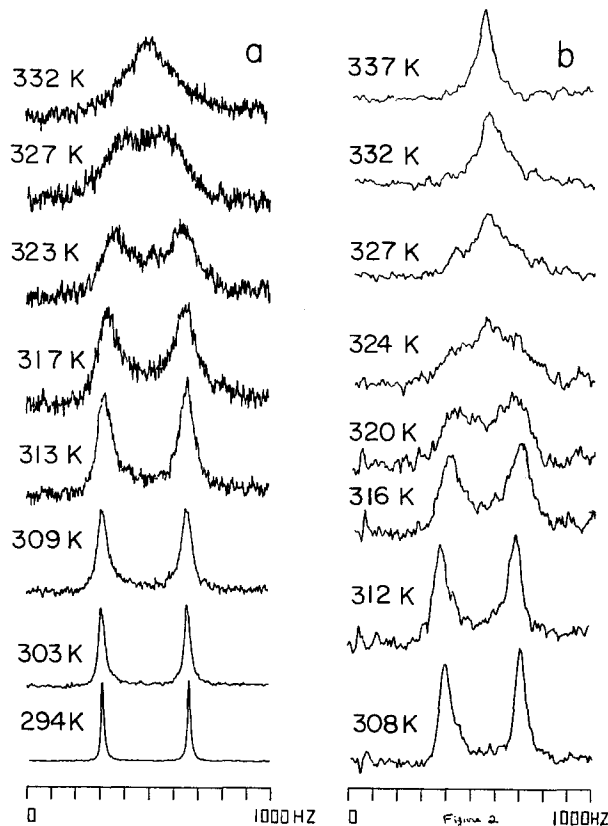


FIG. 2. Carbon-13 NMR spectra of the α carbons of 6-(*N*-piperidyl)fulvene at 75.4 MHz. (a) In $CDCl_3$, (b) In E8 with magic-angle spinning.

It was used in this work because it has an appropriate liquid crystalline range (-12 – 71 °C) and shows no carbon-13 peaks in the region where the peaks of the α carbons of the solutes appear. For isotropic solvents, $CDCl_3$ was used either alone or mixed with E8 in a ratio of 2:8 so that any possible effect due to substantial changes in the molecular structure of the solvents would be accounted for.

The results obtained from the Eyring plots are presented in Table I. In this table, the values of ΔG^\ddagger at 298 K rather than those at the coalescence temperatures are listed, because the coalescence temperature (the temperature at which the two NMR peaks merge to one) is not clearly defined in these cases and is dependent on the spectrometer frequency. At any rate, the coalescence temperatures of the C-13 spectra of I-III at 75.4 MHz are close to 298 K, and the values of ΔG^\ddagger are not very sensitive to changes in T over a range of 10–20 K in the present cases. The results show that ΔG^\ddagger for each compound is solvent independent within experimental error. Their values are comparable to those obtained from proton NMR.¹³ The results that

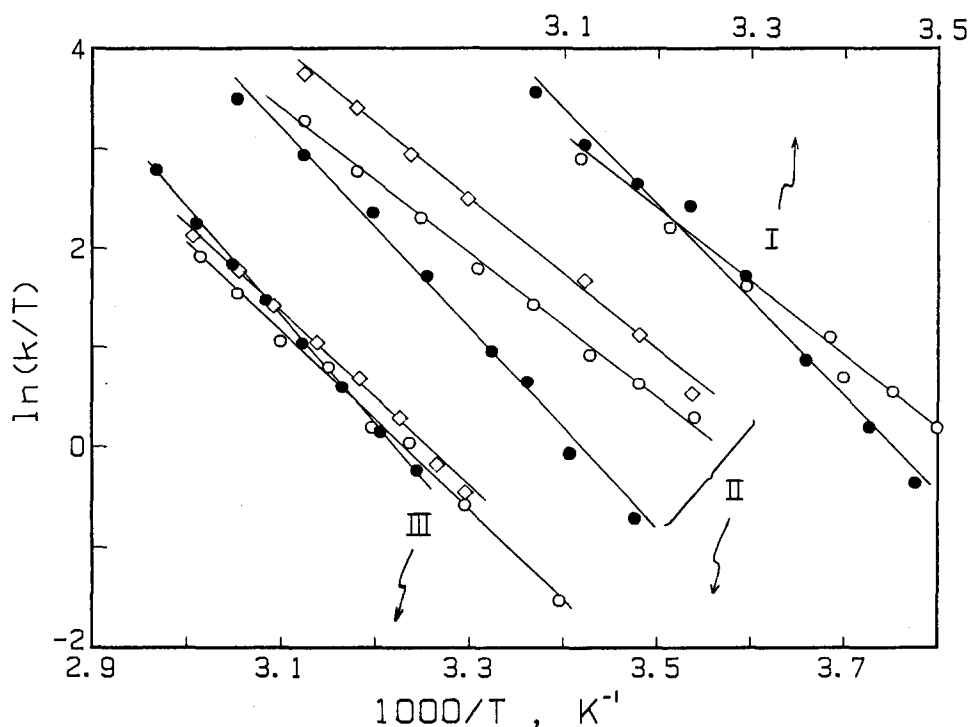


FIG. 3. Eyring plots for hindered rotation of the dialkylamino group in 6-(dimethylamino)fulvene (I), 6-(diethylamino)fulvene (II), and 6-(*N*-piperidyl)fulvene (III) and in three solvents: \circ , CDCl_3 ; \square , $\text{CDCl}_3 + \text{E8}$ (2:8, isotropic); \bullet , E8 (liquid crystalline). The abscissa for I is shifted to avoid overlapping. The straight lines were drawn from results of weighted least-squares calculations.

$\Delta G^\ddagger(\text{III}) > \Delta G^\ddagger(\text{I}) \approx \Delta G^\ddagger(\text{II})$ is likely due to the electronic effect of the piperidyl ring in III.

In contrast to ΔG^\ddagger , the values ΔH^\ddagger and ΔS^\ddagger of all three compounds in liquid crystal solutions are higher than the corresponding ones in isotropic solutions. In a previous study of the hindered rotation of 4-(dimethylamino)pyrimidine in liquid crystal solutions, we also observed that ΔH^\ddagger is larger in a liquid crystal solution than in an isotropic solution.⁶ Since it has been suggested that ΔG^\ddagger is determined mainly by electronic effect and ΔH^\ddagger may be affected more by intermolecular interaction,^{14,15} we argued that the increase in ΔH^\ddagger might be caused by forces of solvent ordering in the liquid crystalline phase.⁶ The present study was undertaken to examine this hypothesis by systematically varying the size of the solute molecules.

The ground state of the 6-(dialkylamino)fulvenes is essentially planar, except that the β carbons in the alkyl part may have out-of-plane motions. In the transition state, the C–N–C plane in the dialkylamino group is perpendicular to the fulvene ring. When both the molecular structure and the conformational flexibility are taken into account, the molec-

ular volume of the transition state would have the relation $\text{II} > \text{III} > \text{I}$, because the ethyl groups in II can extend farthest into space due to free rotation of the N–C $_{\alpha}$ bond. If the bulkiness of the transition state of the solute contributes to the loss of solvent ordering and the increase in ΔS^\ddagger as previously suggested,⁶ the difference between ΔH^\ddagger in the liquid crystalline phase (E8) and the liquid phase (CDCl_3 or $\text{CDCl}_3 + \text{E8}$) is expected to follow the same order, namely $\text{II} > \text{III} > \text{I}$. However, the data in Table I show that this is not the case: $\Delta H^\ddagger(\text{liquid crystal}) - \Delta H^\ddagger(\text{isotropic})$ has the order $\text{I} > \text{II} > \text{III}$. Furthermore, the Eyring plots in Fig. 3 indicate that the rate of hindered rotation in the liquid crystalline phase is not necessarily lower than that in the liquid phase. These comparisons indicate that ΔH^\ddagger may not be a good parameter to characterize any possible solvent effect on the barrier to hindered rotations in I–III.

In the total line shape analyses, it was assumed that the intrinsic linewidths of the α carbons at each temperature were the same as the average linewidth of other carbons in the same molecule. The values of this parameter in the liquid crystalline phase (10–25 Hz) are considerably larger than

TABLE I. Activation parameters for hindered rotation of the dialkylamino group in 6-(dialkylamino)fulvenes.

	Temperature range (K) ^a	ΔH^\ddagger (kJ mol ⁻¹)	ΔS^\ddagger (J mol ⁻¹ K ⁻¹)	ΔG^\ddagger_{298} (kJ mol ⁻¹)
I in CDCl_3	286–321	50 ± 2	12 ± 8	56 ± 3
E8	288–326	79 ± 4	77 ± 14	56 ± 6
II in CDCl_3	282–320	61 ± 1	20 ± 5	55 ± 5
$\text{CDCl}_3 + \text{E8}$ (2:8)	283–320	63 ± 2	31 ± 6	54 ± 6
E8	288–328	83 ± 3	86 ± 9	57 ± 4
III in CDCl_3	294–332	74 ± 2	41 ± 7	61 ± 3
$\text{CDCl}_3 + \text{E8}$ (2:8)	302–332	74 ± 2	42 ± 6	61 ± 2
E8	307–337	91 ± 4	95 ± 3	62 ± 1

^a This was chosen to obtain spectra for a proper range of line shape analysis for each system and depends on ΔG^\ddagger as well as the difference in the chemical shifts of the two carbon peaks.

those in the liquid phase (4 Hz, including a line broadening factor of 3 Hz in the exponential multiplication for Fourier transform). The former also increases with temperatures while the latter does not. This may be one of the reasons for the differences in ΔH^\ddagger in the two different types of solvent. Another contribution may be some temperature gradient in the liquid crystal samples, which were studied with a Dotty variable-angle probe that has a less stringent temperature regulation than the Varian Dewar-jacketed probe for the study of liquids. At the nematic-to-isotropic transition temperature, both nematic and isotropic signals were observed using the Dotty probe. Therefore, its temperature gradient was estimated to be about 1 K with 50% duty cycle.

In contrast to ΔH^\ddagger , the data in Table I show that ΔG_{298}^\ddagger for each compound is solvent independent within experimental error. Since it has been shown that ΔG^\ddagger obtained from NMR data is subject to less experimental uncertainties than ΔH^\ddagger and ΔS^\ddagger are,¹⁵⁻²⁰ we conclude that solvent ordering in a liquid crystalline solvent has no appreciable effect on the barrier to hindered rotation in compounds I-III.

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