

^1H and ^{13}C NMR in Thermotropic Phases

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I. INTRODUCTION

Liquid crystals have been known for more than 90 years, but general interest in these phases has become widespread only during the last 10 years. This development originated in numerous technical applications in electronics, biology, and other fields, and resulted from the synthesis of new compounds with mesophases in quite different temperature ranges. More than 5000 are known today.

Theory does not yet make it possible to predict from the chemical composition alone anything about the existence or the temperature range of liquid crystalline phases. It is experience that proved that the molecules must be elongated, with a rigid central part and a more or less mobile tail at one or both ends, and, to a first approximation, may be regarded as rods. Figuratively speaking, there might exist intermediate phases between the crystalline state and the normal liquid with directional order and restricted freedom for the motion of the centers of mass.

Such kinds of condensed matter are also of interest from a fundamental standpoint, in particular as test specimens for radio-frequency spectroscopy, especially the new methods developed in NMR in recent years.

In what follows, results are presented for some materials which may be typical of results for many

others, and demonstrate that the potentials in this field have not yet been exhausted. All measurements were performed with compounds of the type indicated in Figure 1, which is characteristic of the composition of a large portion of liquid crystals. C is a group such as $-\text{CO}-\text{O}-$, $-\text{NO}=\text{N}-$, $-\text{N}=\text{N}-$, $-\text{CH}=\text{N}-$, which gives the molecule a certain degree of rigidity. A and B are aliphatic or oxyaliphatic groups: $-\text{C}_m\text{H}_{2m+1}$, $-\text{O}-\text{C}_n\text{H}_{2n+1}$, or in one case $-\text{NO}_2$. We shall consider the chemical composition in detail only if necessary to explain particular NMR results.

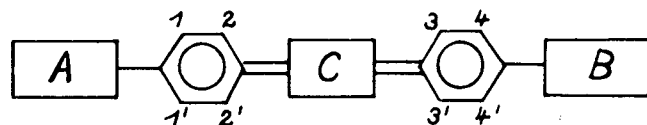


Figure 1. General structure of the compounds used.

II. DIPOLE-DIPOLE COUPLING OF PROTONS

The secular part of the dipole spin Hamiltonian which influences the line shape is

$$H = - \sum_{j>k} \frac{3\gamma_j\gamma_k\hbar^2}{2r_{jk}^3} (I_{jz}I_{kz} - \vec{I}_j\vec{I}_k/3)(3\cos^2\theta_{jk} - 1) \quad (1)$$

The exact evaluation for a system of N spins requires the calculation of 2^N eigenfunctions. Since N is in the range of 10^{20} , the realization is practically impossible. Because of the $1/r_{jk}^3$ dependence and the assumption of uncorrelated motion of different molecules, the influence of remote spins may be neglected and the line shape of 2- or 3-spin systems can be calculated by classical methods. With spin- $1/2$ pairs, the influence of dipolar coupling may be expressed by the splitting of the local field

$$\Delta B_{dip} = \frac{3\mu}{r^3} (3\cos^2\theta - 1) \quad (2a)$$

which in the case of fast rotation (Figure 2) is reduced to

$$\Delta B_{dip} = \frac{3\mu}{r^3} (3\cos^2\theta - 1) (3\cos^2\theta_{PM} - 1)/2 \quad (2b)$$

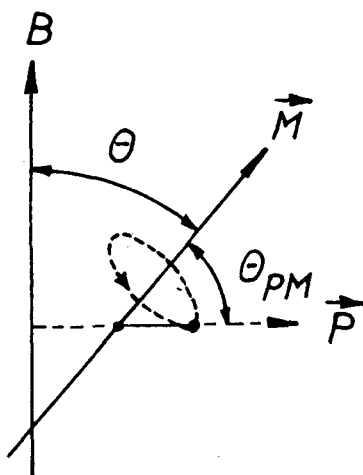


Figure 2. Orientation of the molecule (M) and the proton pair (P) in the magnetic field.

The protons on each side of the benzene rings in Figure 1 (1-2, 1'-2', 3-4, and 3'-4') are such typical spin pairs and hence, the splitting of the proton line in mesophases characterizes the degree of orientation.

In liquid crystal physics,

$$s = \frac{1}{2} (3\cos^2\theta - 1) \quad (3)$$

is used as an order parameter in the nematic phase, θ being the angle between the axis of the molecule and the so-called director, which, in strong magnetic

fields, is parallel to B . A comparison of Eqs. 2 and 3 shows the splitting to be proportional to the order parameter. This implies the existence of a fast rotation of the molecules about their longitudinal axes; the calculation of ΔB_{dip} from molecular data yields the angle θ_{PM} between the molecular axis M and the para-axis P of the benzene rings (Figures 3 and 4).

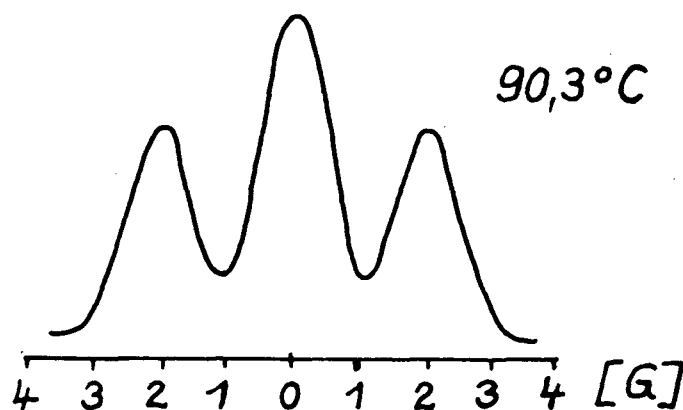


Figure 3. Proton NMR line shape of para-azo-oxy-anisole in the nematic phase (90.3°C).

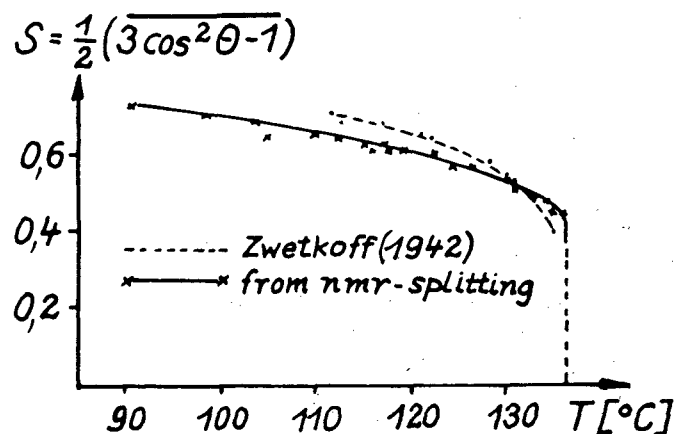


Figure 4. Order parameter from proton-proton splitting compared with the result of optical methods (4).

The linewidth was originally attributed to the orientational distribution of the axes. Small deviations of the order parameter determined in this way from that evaluated by optical or other methods can be explained with different, more detailed models, and especially by the fact that ΔB gives the orientation

only of the central part and not of the molecule at all. The central line in Figure 3 comes from the protons in the tails (A, B—in this case -O-CH₃), which are in quasi-stochastic motion.

Better resolution often shows additional splittings (see Figure 5) which may be due either to spin interaction within each benzene ring or to cracked molecules. From high-resolution ¹³C NMR of liquid crystals (see below), we know that, in nematic phases, the static (or effective) distribution width of the molecular axes is rather narrow. Consequently, the linewidth of the proton resonance requires further discussion.

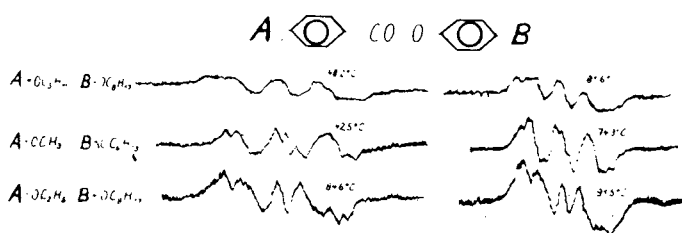


Figure 5. Differentiated lineshapes of some other compounds in nematic phases.

For this reason, a more complete calculation of the lineshape was made (1), starting from Eq. 1. It is, of course, impossible to determine exactly the distribution of resonance frequencies caused by this Hamiltonian if the number of protons is larger than about 5. Nevertheless, such spectra can be evaluated approximately by neglecting the scalar part of Eq. 1, and a computer program has been written to accommodate the coordinates of up to 128 protons. It determines for each proton the additional local field produced by the 16 neighbors with the strongest interactions and constructs the lineshape from these data. The method may be used for rigid molecules in a definite direction, for rotating molecules, or for molecules with rotating groups. To reduce calculation time, some convenient attributes of modern computer languages were omitted, e.g., the floating point. This made the programming more tedious, but made possible the calculation of one spectrum of 128 nuclei, including the influence of 16 neighbors, in 205 seconds with a Bruker-Nicolet NB2 computer.

It is not possible to give the program details in this report, but it is useful to discuss some results. To obtain the coordinates of the protons, monocrystals were grown and analyzed by X rays. In some cases, molecular data were taken from tables.

Figure 6 shows proton spectra from deuterated para-azo-oxy-anisole (CH₃-O-C₆H₄-N=N-C₆H₄-O-CH₃). The good agreement between the experimental and the calculated lineshapes is based on the assumption that the planes of the two benzene rings are perpendicular to each other. This proves that the 4-spin interaction does not suffice to explain the observation.

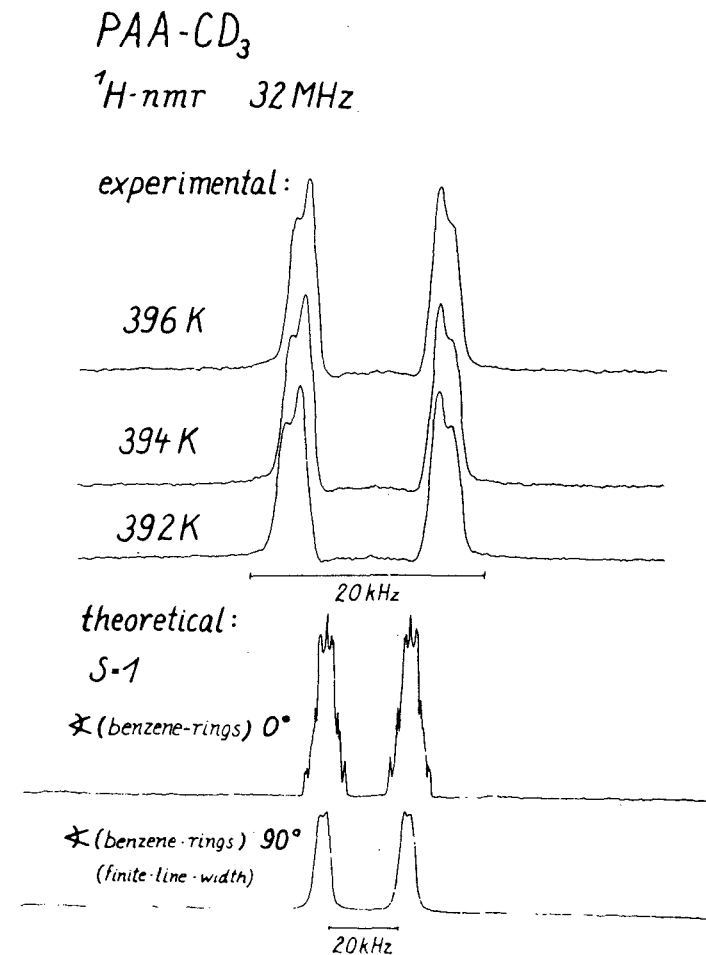


Figure 6. Comparison of calculated and measured proton spectra from deuterated para-azo-oxy-anisole (PAA-CD₃), and the influence of the orientation of the benzene rings.

The influence of the axis of rotation is demonstrated in Figure 7. Rotation about the C-O-bond, obvious from other considerations, gives the best fit to the experimental curve.

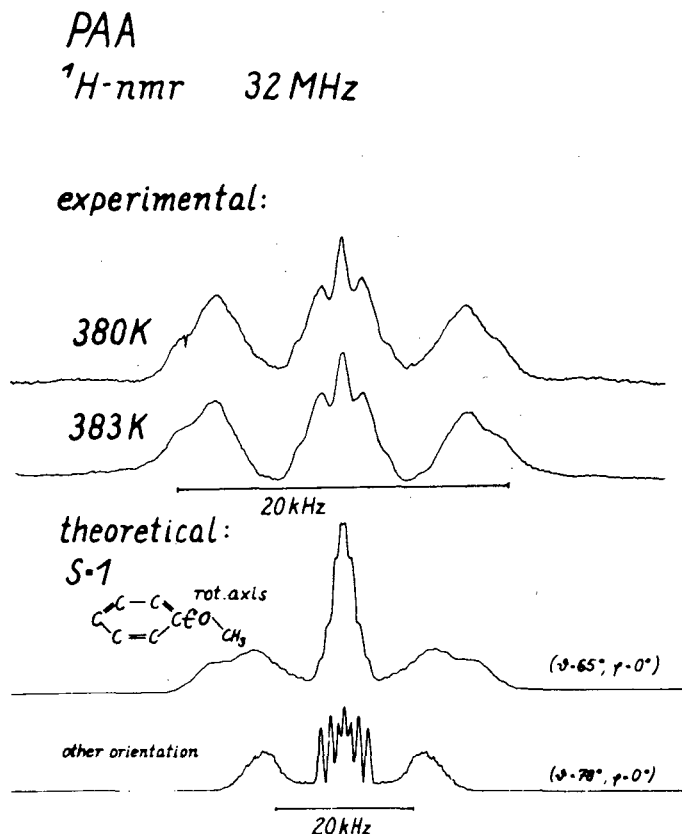


Figure 7. Comparison of calculated and measured spectra from para-azo-oxy-anisole (PAA), and the influence of the orientation of the rotational axis.

The program is also validated by monocrystal spectra in different directions (Figure 8). The narrow central line in the experimental spectra is due to inclusions and impurities, respectively, introduced during crystal growth.

These examples are meant to demonstrate that classical dipole-dipole coupling yields more information when treated with computer techniques. More details will be discussed in papers still in preparation.

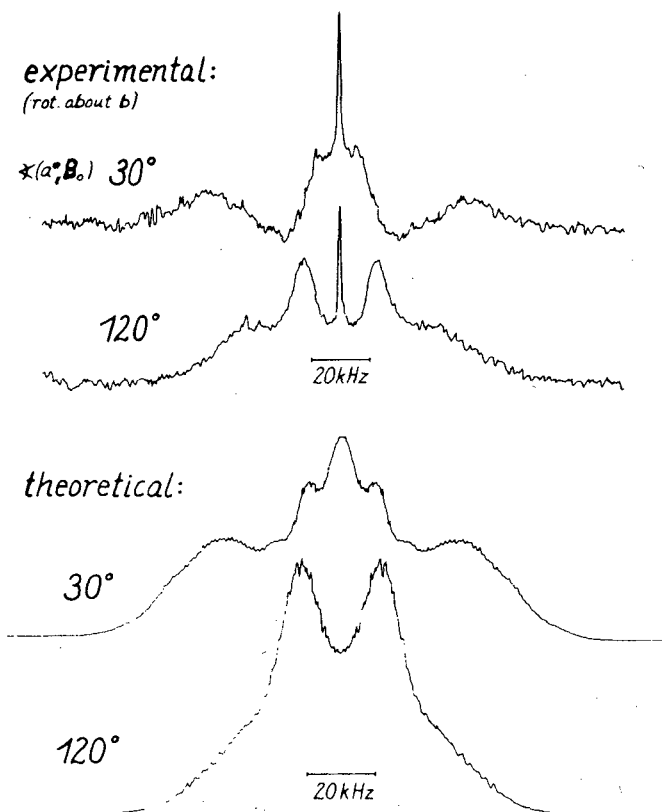
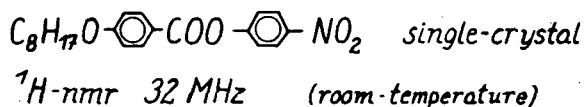


Figure 8. Angular dependence of the ^1H NMR line shape from monocrystals.

III. DYNAMICS OF THE ORDERING PROCESS IN THE NEMATIC PHASE

The attainment of equilibrium in the nematic phase takes time (from 0.01 s to several seconds). The classical observation of this effect was made first by Zwetkow (2) and later by Weber and Lippmann (3). At low rotation frequencies Ω , no difference from the static case was found because the directors could follow the momentary direction of the magnetic field. However, at a critical frequency $\Omega_{crit} = 1/\tau_{or}$, a change in the signal was observed.

Because, in general,

$$\tau_{or} \gg T_2 \quad (4)$$

it should be possible to follow the process of reorientation by pulse methods. According to a suggestion made by Grande (4), the specimen with the nematic substance was flipped by an angle α for a duration

$$\tau_f \ll \tau_{or} \quad (5)$$

at $t = 0$. At a time t , a 90° pulse was applied and the FID signal observed. After Fourier transformation, the splitting d appeared, which is a measure of the orientation. In this way, d could be determined as a function of t . Figure 9 shows some measurements for different α . The relation between d and the orientation can be obtained from Eq. 2a. Greater accuracy is achieved if the substance also has a smectic-A phase. Then the correlation between the splitting and the orientational dependence on the time can be

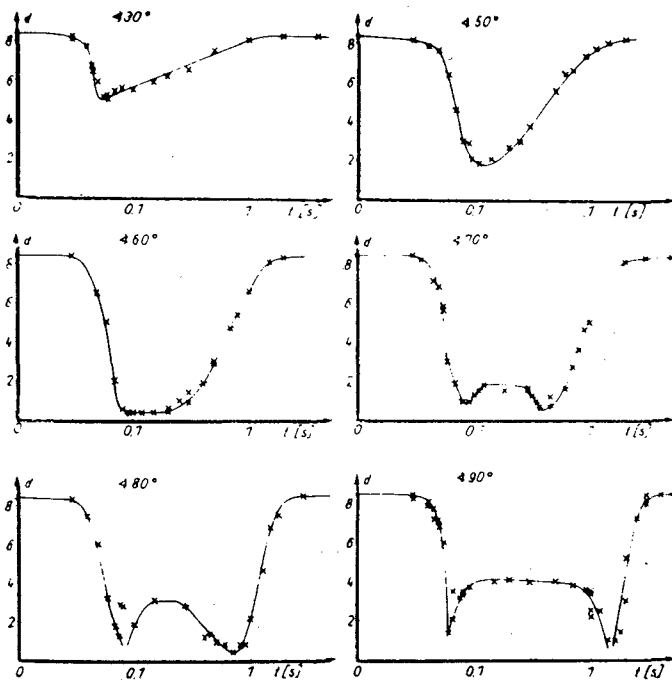


Figure 9. Line splitting during reorientation of nematic phases after an α -degree pulse (4).

found. Figure 10 shows $\log \tan \phi$ to be proportional to t , which means that an equation like

$$\tan \phi = \tan \phi_0 \exp(t/\tau_{or}) \quad (6)$$

describes the experiment rather well.

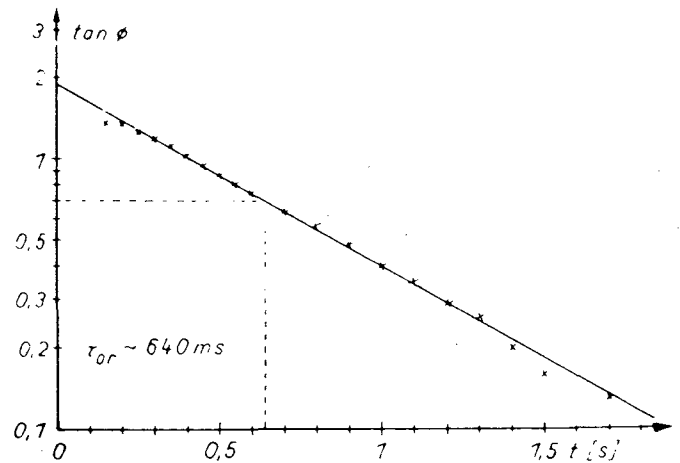


Figure 10. Time dependence of $\tan \phi$ determined from d (4).

The theoretical description starts with the equation of motion of particles of rotational viscosity η in a viscous medium influenced by an external magnetic field

$$C\eta \frac{d\phi}{dt} + \Delta\chi B_0^2 \sin\phi \cos\phi = 0 \quad (7)$$

The solution of Eq. 7 has the form of Eq. 6 with

$$\tau_{or} = \frac{C\eta}{\Delta\chi B_0^2} \quad (8)$$

where C is a constant (of the order of 1) which depends on the shape of the particle, and $\Delta\chi$ is the anisotropy of the magnetic susceptibility. This relation, especially $\tau_{or} \sim 1/B_0^2$, has been proved experimentally. The temperature dependence is not explicit, but is caused only by that of η or $\Delta\chi$. In a quite general case, one would expect the equation of motion (5)

$$C\eta \frac{df}{dt} = \frac{1}{\sin\phi} \frac{\partial}{\partial\phi} [\sin\phi (kT \frac{\partial f}{\partial\phi} - M)] \quad (9)$$

to which an exact solution is impossible. For normal liquids, Debye gave an approximate solution by omitting the effect of the orienting moment M on the distribution function f . For example, this solution

describes the dielectric relaxation of polar molecules in solutions quite well. We note here that neglecting kT gives another approximation which suffices for nematics. Since $\Delta\chi$ is also determined by similar methods, it is possible to measure the rotational viscosity η by magnetic experiments alone.

IV. PROTON NMR IN THE SMECTIC PHASE

Smectic phases are more viscous than nematic ones so we expect similar spectra. This assumption was confirmed by experiments. The viscosity of smectics is so high that the degree of order is scarcely influenced by magnetic fields. By careful cooling down of the nematic phases in strong magnetic fields, it is possible to produce specimens similar to monocrystals. This enables observation of the angular dependence of the ^1H lineshape. In the smectic-A phase, a dependence varying with $(3\cos^2\theta - 1)$ is found, where θ is the angle between the magnetic field B and the normal to the planes of the smectic layers. Figure 11 shows a typical curve of the second moments. At the magic angle $\theta \simeq 55^\circ$, the linewidth is very narrow, and the ratio of ΔB^2 at $\theta = 0^\circ$ to its value at $\theta = 90^\circ$ is 4:1, according to a simple theory. This fact can be explained only by assuming that all smectic layers are almost perfectly parallel to each other (a distribution width less than 5°) and that all molecular units are rotating very quickly about the normal to these planes. This cannot be the case for smectic-C phases since here the minimum is much shallower and is shifted to larger angles.

The consequences of these observations with respect to the phase structure belong more to the field of liquid crystal physics and will not be discussed here.

V. HIGH-RESOLUTION ^{13}C NMR IN LIQUID CRYSTALS

The observation of ^{13}C NMR lines in such phases is rather difficult due to strong dipole-dipole coupling with adjacent protons and to the low natural abundance of ^{13}C nuclei (1.1%). However, proton decoupling by strong RF fields and the nuclear Overhauser effect enable us to observe high-resolution spectra in crystal-like systems (6) and thus to determine chemical shifts.

The screening of the external magnetic field may be described by a symmetric 2nd rank tensor the principal axes of which are determined by the directions of the chemical bonds

$$\hat{\sigma}_p = \begin{pmatrix} \sigma_{11} & \text{H} & \text{O} & \text{O} \\ \text{O} & \sigma_{22} & \text{O} & \text{O} \\ \text{O} & \text{O} & \sigma_{33} & \text{O} \\ \text{O} & \text{O} & \text{O} & \sigma_{33} \end{pmatrix} \quad (10)$$

These values must be transformed into the molecular frame (x, y, z) by

$$\hat{\sigma}_M = R \cdot \hat{\sigma}_p \cdot R \quad (11)$$

The transformation matrix R is given by Eulerian angles. Assuming fast rotation about the z axis, we have $\sigma_{xx} = \sigma_{yy}$. These values must be transformed by a similar transformation into the laboratory frame (X, Y, Z) . We are interested only in its Z value, which can be written

$$\sigma_{ZZ} = \langle \sigma \rangle + \frac{\sigma_{zz} - \sigma_{xx}}{3} (3\cos^2\theta_{MH} - 1) \quad (12)$$

where $\langle \sigma \rangle = (\sigma_{11} + \sigma_{22} + \sigma_{33})/3$ is the isotropic part normally being measured in liquids. Here, it can be found at the magic orientation $(3\cos^2\theta_{MH} - 1) = 0$.

The experimentally detected lines are sufficiently narrow to enable the observation of each carbon atom. The correlation between the carbon atoms and the lines can be found by comparison with other spectra from similar compounds and from the amplitude ratio (Figure 12).

The width of the lines is small, showing that the axes of the molecules are effectively almost parallel with a distribution width of 5° in the nematic as well as in the smectic phase. "Effectively" implies that this is not necessarily a static arrangement. The axes may actually fluctuate about much larger angles so fast that only the averaged directions become effective.

It is not possible to distinguish the lines, from carbon atoms, which are symmetric about the paraxial axis. This also confirms the fast rotation of all molecules about this axis.

In this way it is possible to observe separately the orientation of each carbon atom (Figure 13).

The carbons of the central parts all have the same temperature dependence in the nematic phase, *i.e.*, this part must be rather rigid. The curve corresponds to that expected from ^1H splitting or other methods. However, the shift of the chain carbons behaves differently, remaining practically constant, then changing suddenly at the transition point to the isotropic

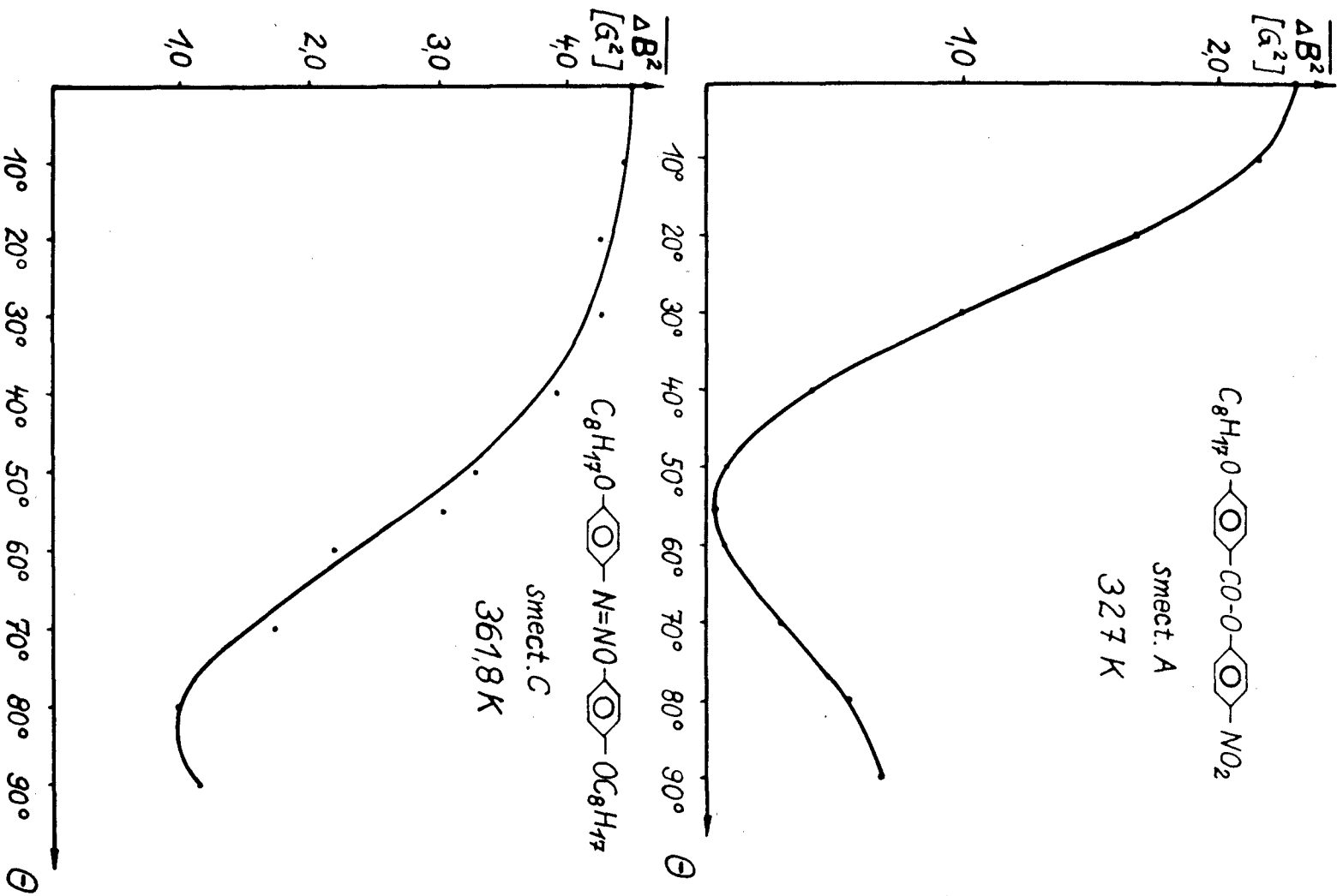


Figure 11. Angular dependence of the second moments: (a) in smectic-A phases. (b) in smectic-C phases.

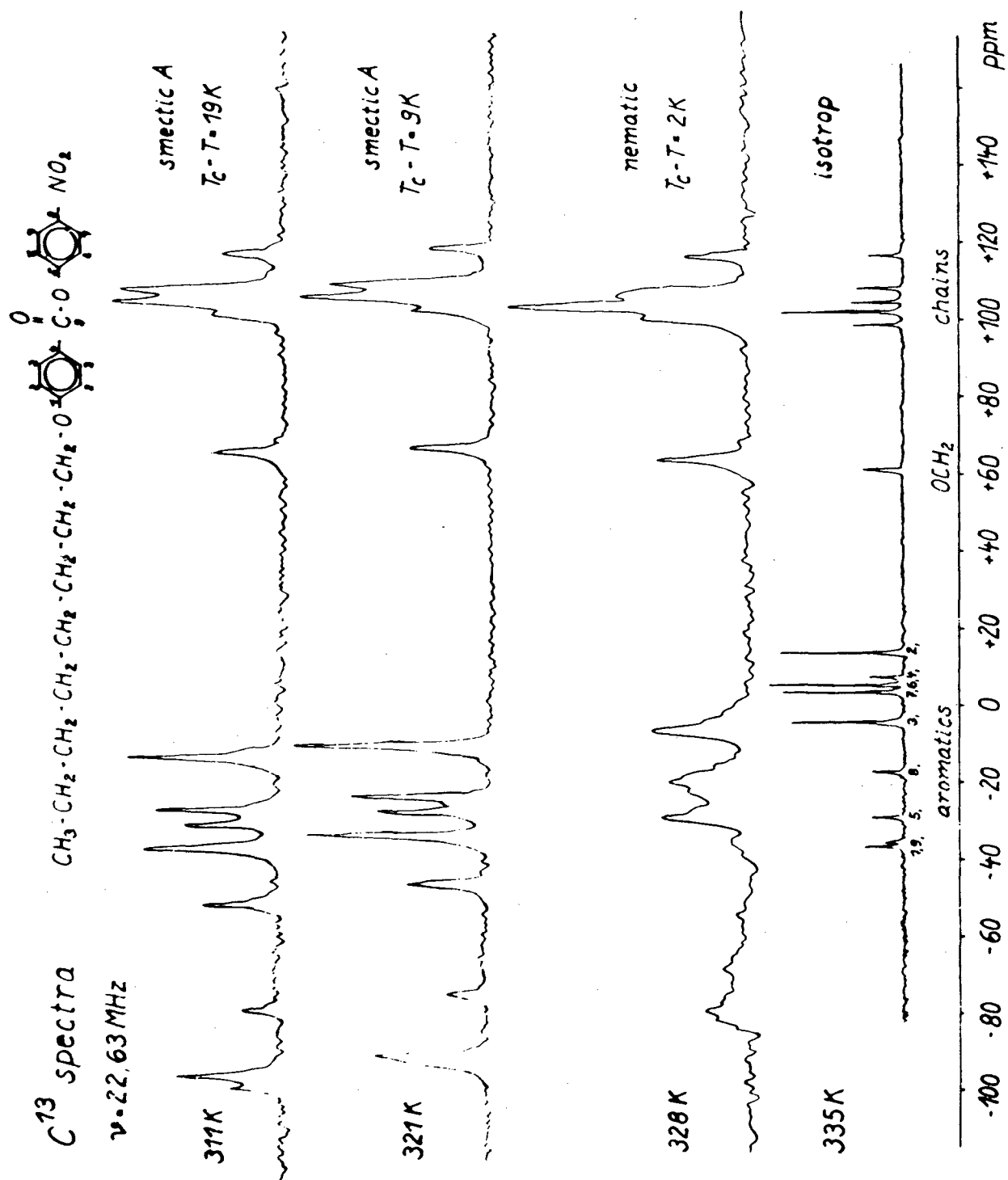


Figure 12. Proton-enhanced ^{13}C NMR spectra in different phases.

phase. This demonstrates that the orientational behavior of the tails differs from that of the central

part. This is an important hint for the theories of liquid crystalline phases.

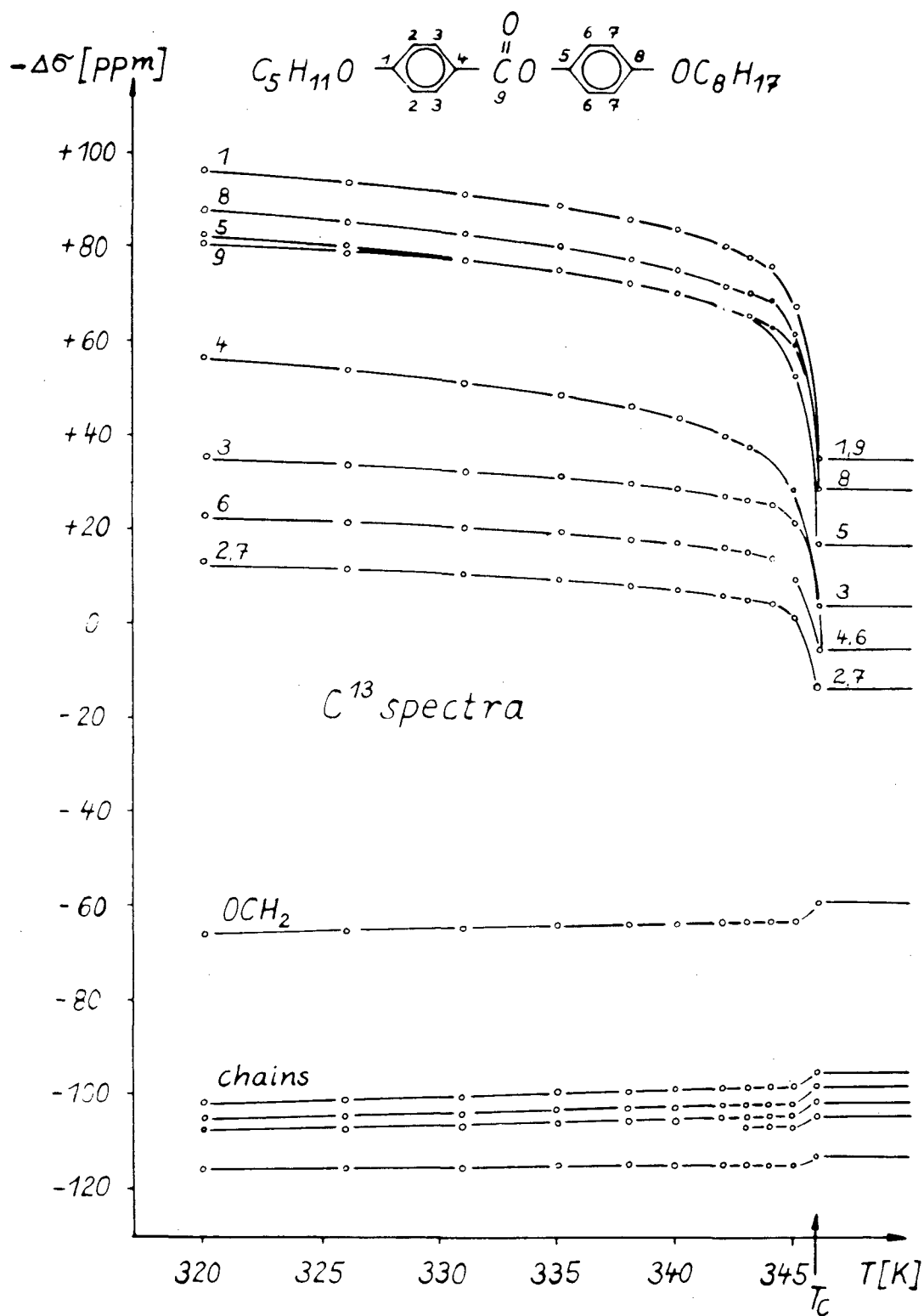


Figure 13. Line shift of ^{13}C NMR spectra in the nematic phase.

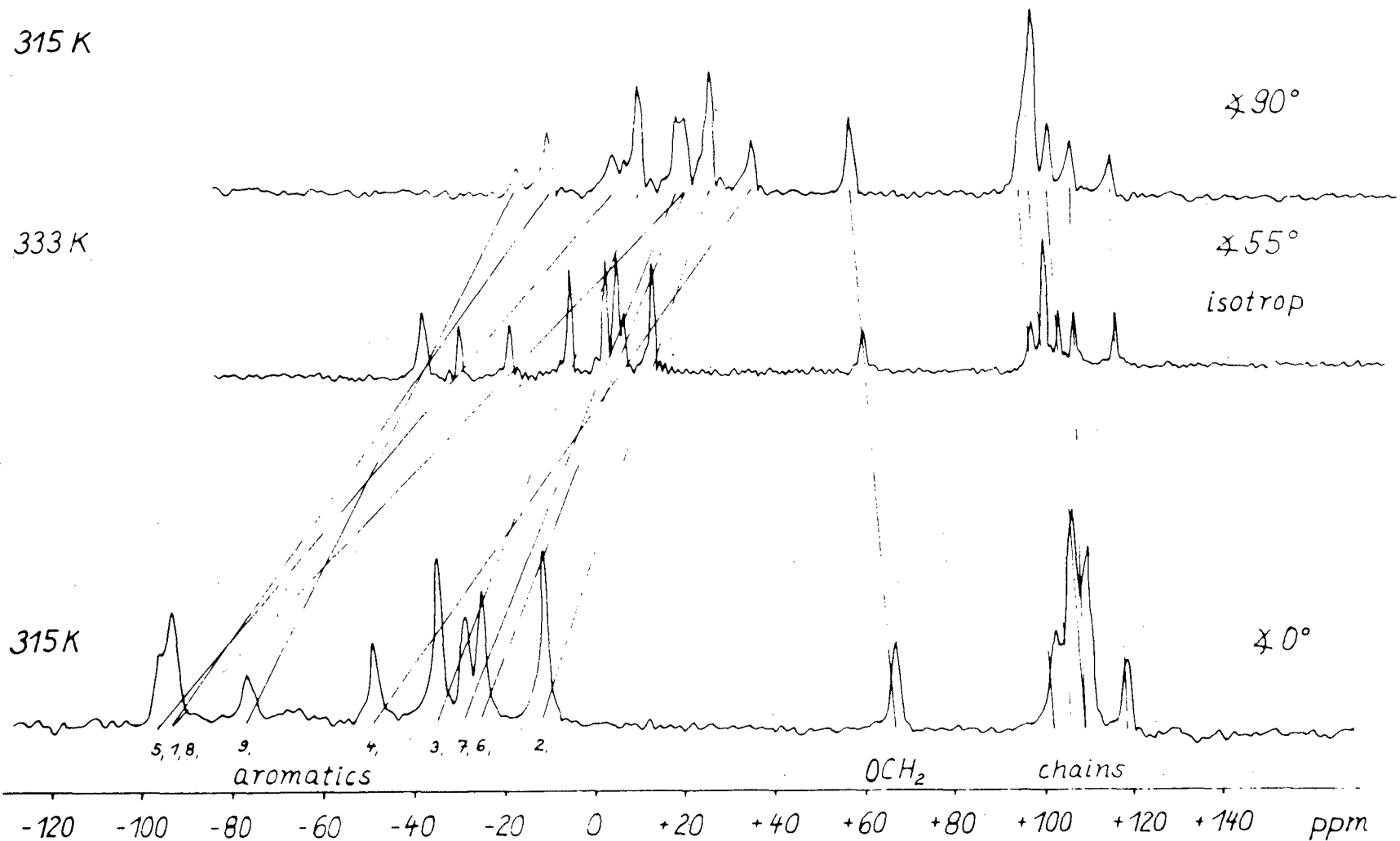
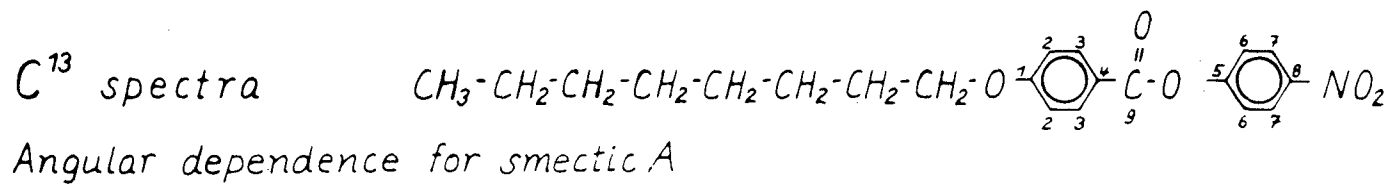


Figure 14. Angular dependence of ^{13}C NMR spectra in the smectic-A phase.

Figure 14 shows the angular dependence of ^{13}C shifts in smectic-A phases.

The few figures presented in this paper are representative for examples of nematic, smectic-A, or smectic-C systems.

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