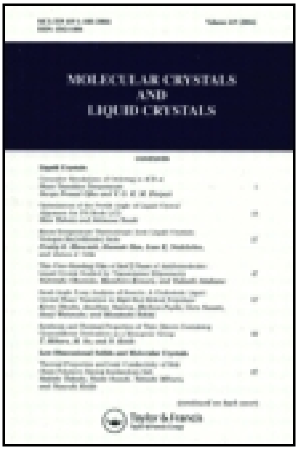

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Importance of Steric Effects in the Isotropic Phase of Nematogenic Compounds

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Importance of Steric Effects in the Isotropic Phase of Nematogenic Compounds[†]

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The dielectric spectra of some mesomorphic substances in their isotropic phase are reported. The measurements are carried out from the radio frequencies up to the far infrared region. We have investigated several substances such as azoxybenzenes, cyanophenylcyclohexanes, azomethines, tolanes and biphenyls. Two special cases appear with the last two series where the dipole moment is directed either perpendicular or parallel to the long molecular axis respectively. The dielectric spectra show different absorption connected with rotational movements around or perpendicular to the long axis. The influence of the molecular surrounding on the dielectric properties is also studied by investigating the influence of dilution. The results have been discussed by using a computer simulation of molecular dynamics of fluid systems containing ellipsoidal particles which interact pair-wisely, assuming the interactions to be governed mainly by steric effects.

INTRODUCTION

Recently, we have reported some dielectric investigations of different mesogenic substances in their nematic phase.[1] The experimental dielectric absorptions have been related to the molecular structures of the compounds. We report here dielectric studies of the same substances in the isotropic phase, showing clearly the influence of steric effects on the relaxation mechanisms. Conversely, the other results we report in the far

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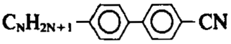
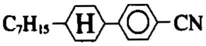
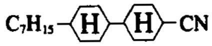
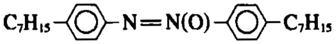
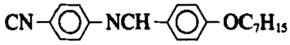
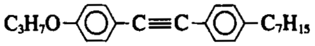
[†] Presented at the Ninth International Liquid Crystal Conference, Bangalore, December 6–10, 1982.

TABLE I

Substances studied

Designation chemical formula	Abbreviation		Transition *T*°C	References
4-alkyl-4′-cyanobiphenyl 	CBn	0	C91I	1
		4	C46I	
		5	C22N35I	
		6	C15N30I	
		7	C29N42I	
		8	S_A32N40I	
1-heptyl-4-(4′cyanophenyl)cyohexane 	PCH7		C30N57I	2
1-heptyl-4-(4′-cyanocyclohexyl)cyclo-hexane 	CCH7		C71N83I	2
4,4′-di-heptylazoxybenzene 	HEPTAB		S_A54N71I	3
4-heptyloxybenzilidene-4′-cyanoani-line 	HBCA		C86N115I	4
4-propoxy-4′-heptyltolane 	PHT		C41N63I	5

1. BDH Chemicals LtD, Poole, Dorset (England).
2. E. Merck, Darmstadt (R. F. A.).
3. C. R.P. P., Talence (France).
4. Collège de France, Paris (France).
5. SEAC (France).

infrared region show that the absorption mechanisms observed are here mainly governed by intramolecular vibrations. Such effects are also clearly seen by looking at the effects of dilution.

EXPERIMENTAL

To see the various inter- or intra-molecular movements, the probe will be the effective dipole moment according to its position and orientation in the molecular structure. The different substances investigated are given in Table I with their transition temperatures. In particular we have studied a

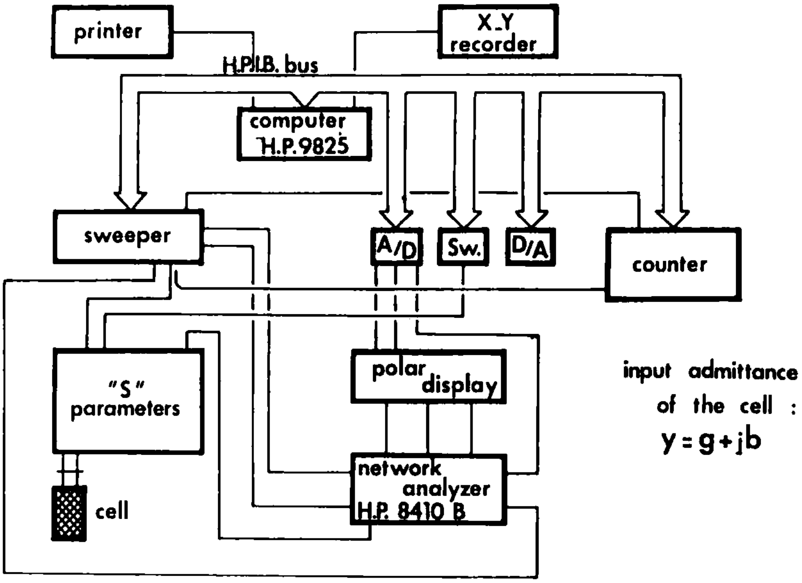


FIGURE 1 Experimental set-up (1 GHz–18 GHz).

cyanobiphenyl series which includes mesomorphic and non-mesomorphic derivatives.

The dielectric permittivities were measured using new techniques developed in our laboratory. Their main features are the following:

- first it is possible to characterize isotropic or anisotropic liquids and solids;
- second, on account of the small quantities of substances available, only a small sample is necessary;
- finally, all the measurements are entirely automatic. This brings new interest to bear upon dielectric techniques, which were previously long and very difficult to work out.

The use of a computer makes it all the easier to obtain:

- a large number of experimental points;
- a strict resolution of basic equations;
- high speed of measurement, each measurement being faster than 30 s for each temperature;
- finally, it makes it possible to do real time analysis, by plotting directly, for example, the Cole-Cole diagram for a given temperature or the dipole correlation function.

For the highest frequencies (1 GHz–18 GHz), the basic device is a network analyzer. The experimental set-up is shown in Figure 1. The measurement procedure and the cell description is given in a previous paper.[2] For the frequencies lying between 1 MHz and 1 GHz, the device is an impedance analyzer (Figure 2), while for the lowest frequencies, more classical bridges are used. In these frequency ranges the experimental cell is a parallel plate capacitor located at the end of a coaxial line. The sample volume is lower than 50 mm^3. The detailed description of this cell and the measurement procedure is published elsewhere.[3]

The temperature of samples is kept constant to within ±0.05°C using an electronically regulated heating stage. Measurements at temperatures up to 200°C can be achieved.

As for classical dielectric techniques, the overall accuracy is estimated to be less than 2% for the permittivity ε', and 5% for ε'' (dielectric loss).

Concerning the far infrared experiments, two systems are used—an automatic diffraction grating spectrometer or a submillimetric laser. The latter makes it possible to carry out measurements with anisotropic samples. These techniques are also described in another publication.[4]

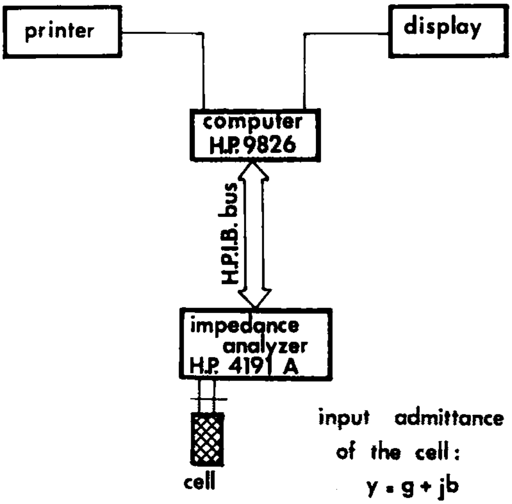


FIGURE 2 Experimental set-up (1 MHz–1 GHz).

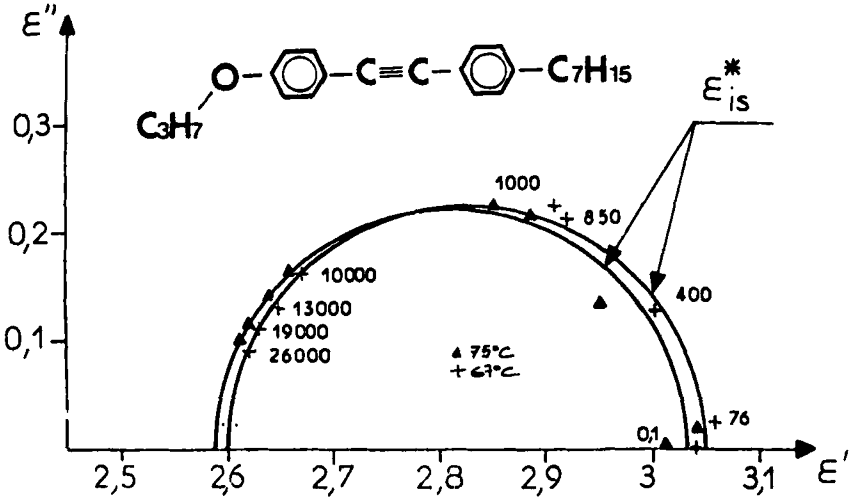


FIGURE 3 Cole-Cole diagram of ε^*_{is} in the isotropic phase of PHT.

RESULTS

The experimental results will be discussed in two parts: (i) the frequency variation of the complex dielectric permittivity $\varepsilon^* = \varepsilon'' - j\varepsilon''$ and (ii) the far infrared absorption α as a function of the input signal wavelength.

(i) Dielectric permittivity

The molecules studied being highly elongated, we could expect that molecular movements around the long axis or around a transverse axis would occur on a quite different time scale. The results shown in Figures 3 and 4 confirm this assumption. With the tolane derivative (Figure 3), the Cole-Cole diagram shows a pure Debye relaxation mechanism whose critical frequency appears in the microwave range ($f_c \sim 3$ GHz). In this case, the molecular dipole moment, mainly located in the alkoxy chain, lies perpendicular to the long axis.[5] Then, the relaxation mechanism, related to a molecular rotation around the long axis will appear at high frequency. Conversely, with a cyanobiphenyl derivative whose dipole moment lies

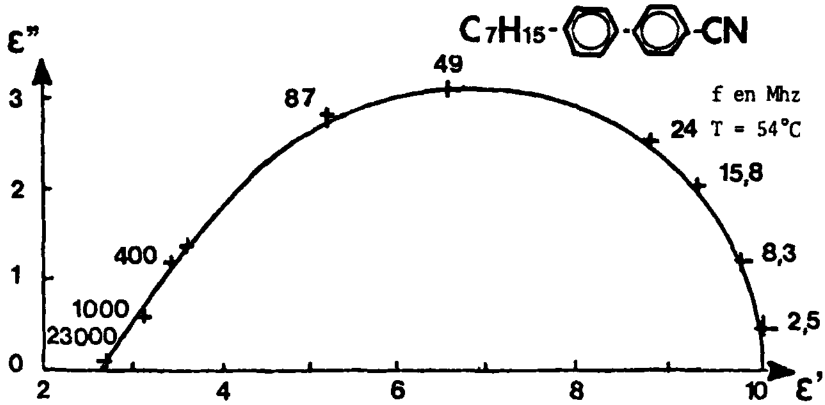


FIGURE 4 Cole-Cole diagram of $\varepsilon_{\parallel}^{*}$ in the isotropic phase of CB7.

along the long axis,[5] the mechanism, involving a rotation around a transverse axis is almost pure (Figure 4). Its critical frequency is about one hundred times smaller ($f_c \sim 50$ MHz).

For the intermediate cases where the molecular dipole moment is tilted with respect to the long molecular axis, but is not perpendicular to it, the existence of the two movements with different critical frequencies leads to distributed absorption domains, as can be seen in Figure 5 for a Schiffs base and in Figure 6 for a cyclohexane derivative. In the case of an azoxybenzene (Figure 7), the two mechanisms involved are almost completely separated.

The influence of steric effects on the dielectric absorption is also evident if we look at the results that we obtained with homologous series of cyanobiphenyl derivatives CBn, where *n* is the number of carbon atoms in the alkyl chain. The substances exhibit enantiotropic mesophases for *n* higher than 4. Figure 9 shows the variation of the critical frequencies of the relaxation mechanism observed (Figure 8) as a function of the reciprocal temperature. One observes a decrease of the relaxation domain amplitude and a decrease of the relaxation frequency with respect to the increasing number of carbon atoms in the chain. On the contrary, the activation energy of the process, given by the slope of the straight lines (Figure 9), remains almost constant. The decrease of the amplitude as *n* increases is probably

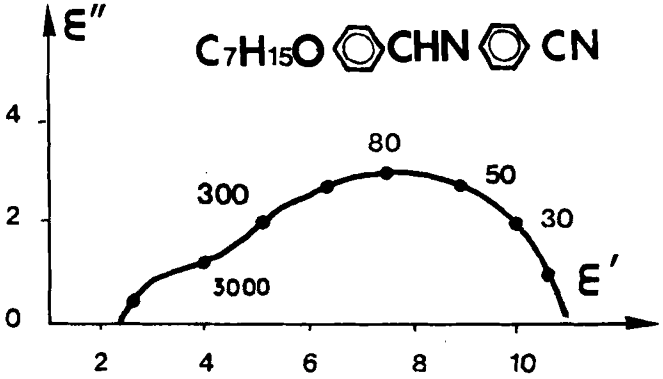


FIGURE 5 Cole-Cole diagram of $\varepsilon_{\parallel}^{*}$ in the isotropic phase of HBCA.

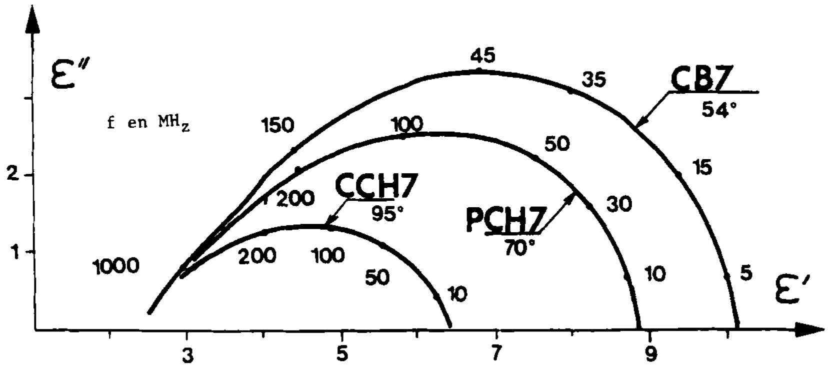


FIGURE 6 Cole-Cole diagram of $\varepsilon_{\parallel}^{*}$ in the isotropic phase of CCH7, PCH7 and CB7.

due to the increase of anti-parallel short range interactions. This leads to a smaller and smaller apparent dipole moment. The effects of dilution in *n*-octane on the dielectric properties of CB7 are shown in Figures 10, 11. As expected, the relaxation range amplitude decreases as the concentration decreases. At the same time, the correlation time decreases. We find again such a variation with the cyclohexane derivative PCH7.

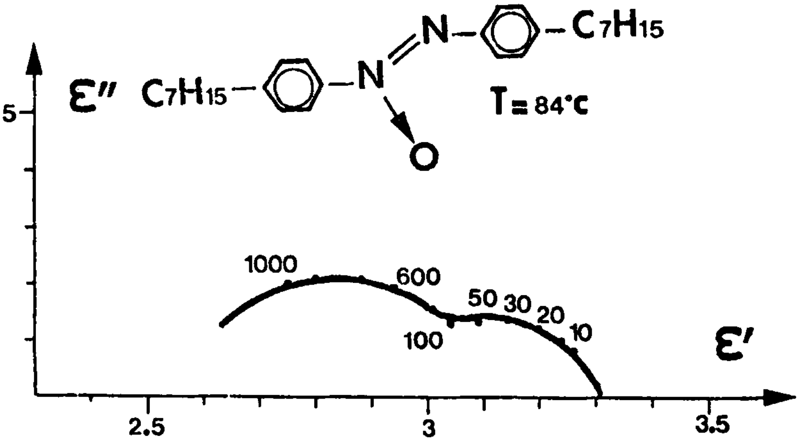


FIGURE 7 Cole-Cole diagram of ε^*_{ii} in the isotropic phase of HEPTAB.

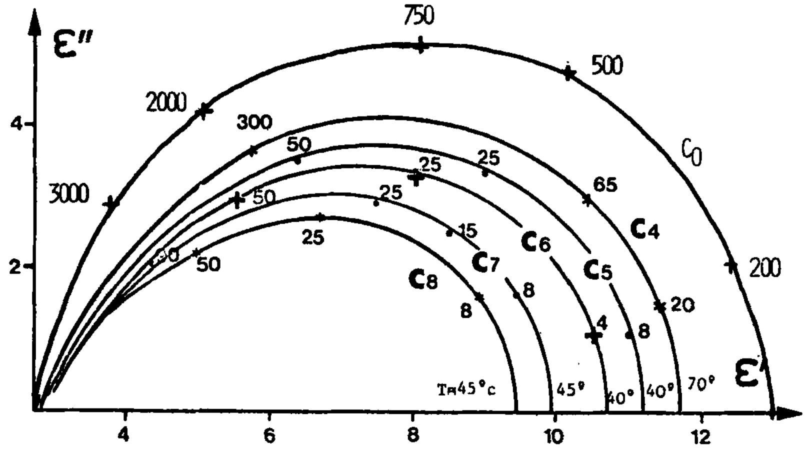


FIGURE 8 Cole-Cole diagram of ε^*_{ii} in the isotropic phase of homologous series CBn.

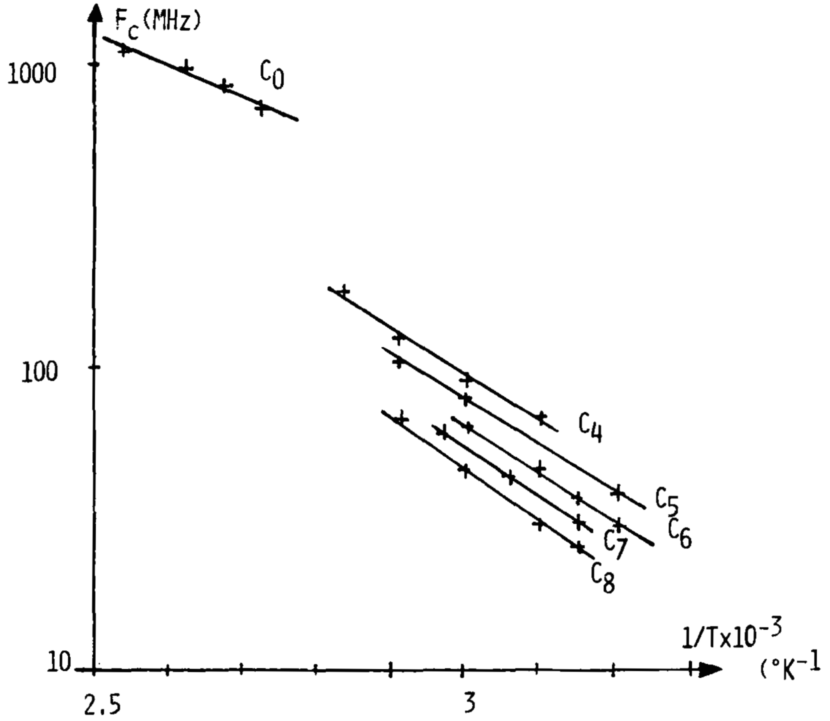


FIGURE 9 The critical frequencies as a function of the reciprocal temperature.

(ii) Far infrared absorption

The measurements were carried out on a cyanobiphenyl series (CBn) and with cyano-substituted derivatives of cyclohexane. Figure 12 shows the experimental absorption of CB7 in the isotropic phase. The absorption in the 50 micron range may be attributed to a vibration mode of the CN group, while the remaining absorption for higher wavelengths is probably connected with vibrational modes of the bond between the two phenyl rings.

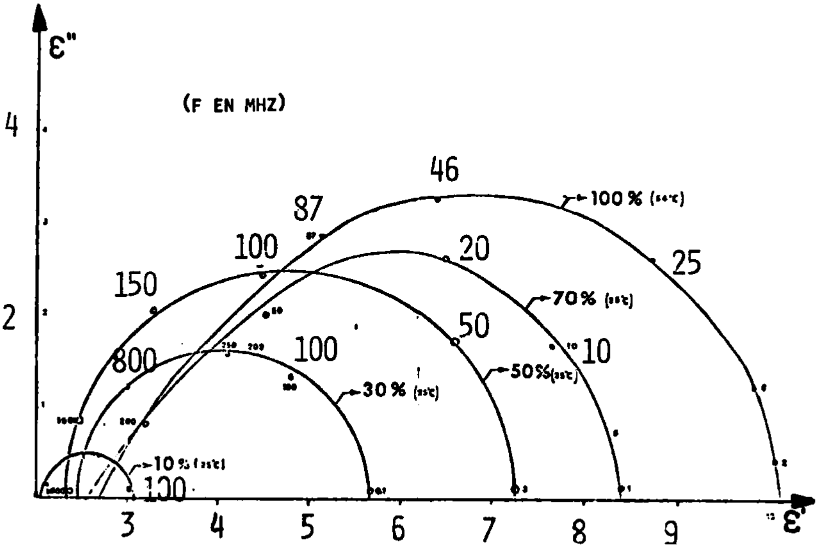


FIGURE 10 Cole-Cole diagram of CB7 diluted in *n*-octane.

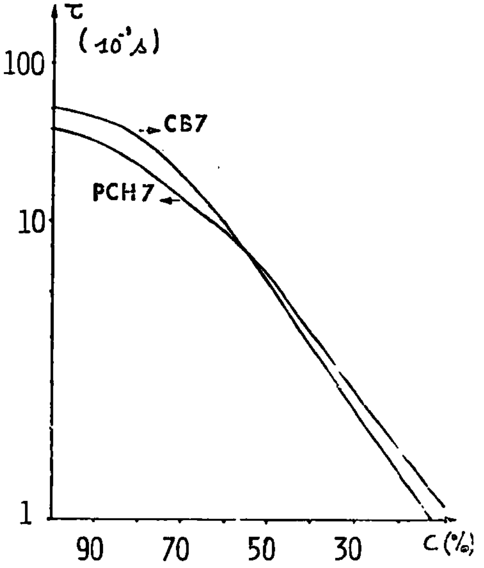


FIGURE 11 Correlation time as a function of concentration of CB7 and PCH7 in *n*-octane.

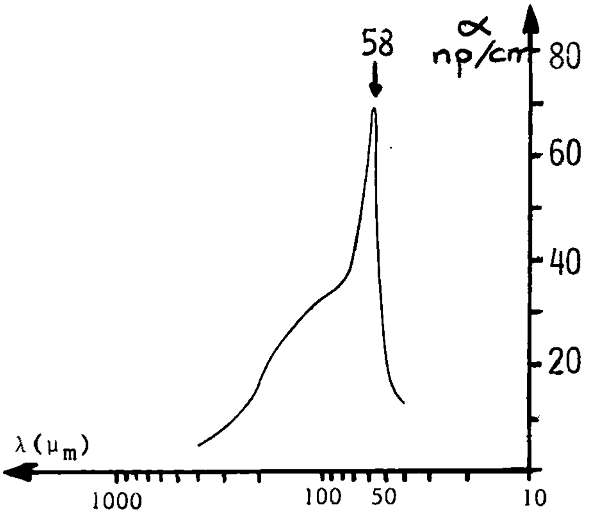


FIGURE 12 Far infrared absorption of CB7; $T = 51°C$.

This interpretation is rather clear if we look at the well-known far infrared absorptions of molecules such as biphenyl, benzonitrile or cyanobiphenyl.[4] The alkyl chain length does not significantly change the absorption observed (Figure 13).

The assumption of the existence of intra-molecular modes in the far infrared region is also clear if we look at the effect of dilution (Figure 14) which does not change the experimental absorption shape. This is shown for the three substances CB7, PCH7 and CCH7.

DISCUSSION

The preceding results have shown that the dielectric absorption of mesogenic rod-like molecules is mainly governed by steric effects. These results can be explained more quantitatively using a numerical simulation model which is detailed elsewhere.[6] The calculation has been done for a system of N rigid prolate ellipsoidal particles. They interact pair-wisely with a modified Lennard Jones potential:

$$V_{ij} = 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right] \quad (1)$$

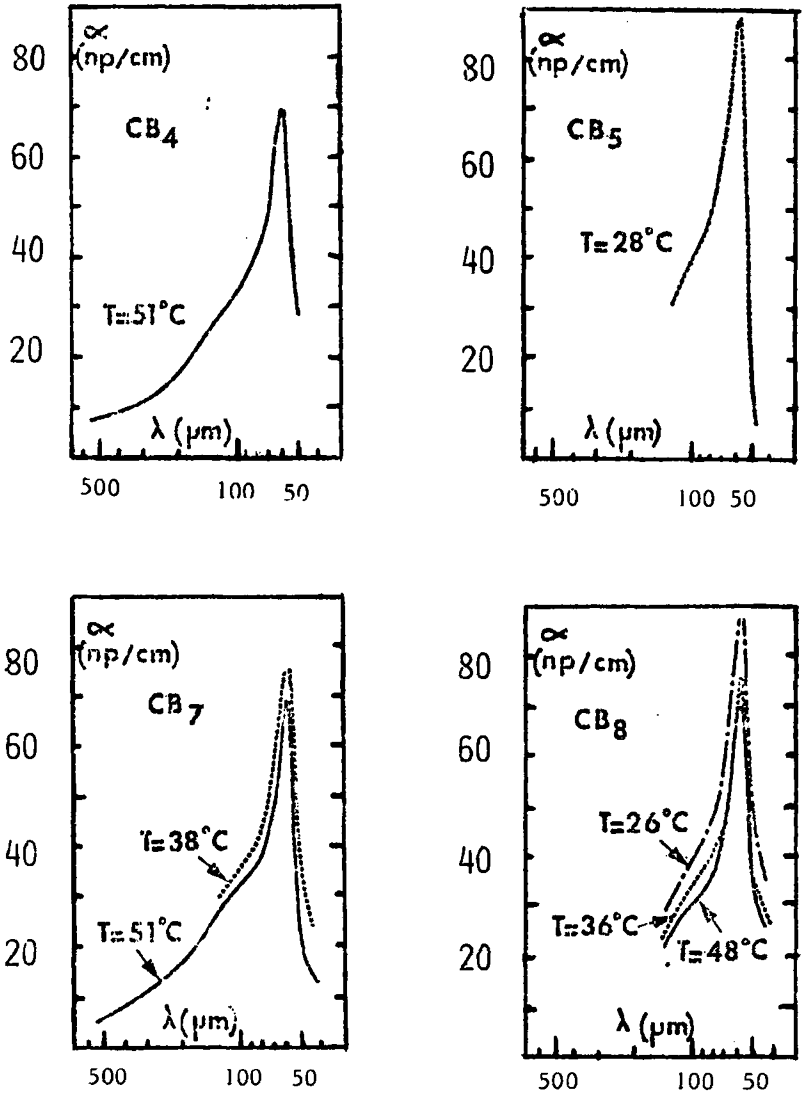


FIGURE 13 Far infrared absorption of CBn: — liquid phase, - - - nematic phase, ··· smectic *a* phase.

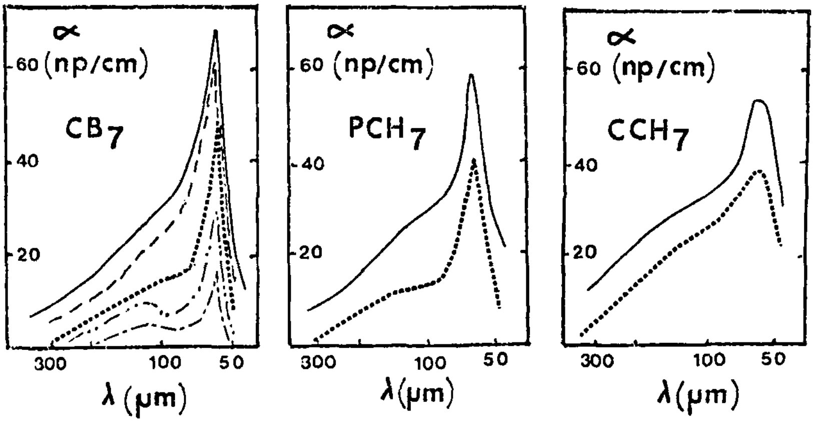


FIGURE 14 Far infrared absorption of CB$_7$, PCH$_7$ and CCH$_7$ diluted in *n*-octane: —pure liquid, ---dilution 70%, ···50%, ———30%, ———10%.

TABLE II

CBn molecular parameters

CBn molecular parameters	
Mass	$m = 4.61\ 10^{-25}$ kg
Inertial moment	$I = 17.5\ 10^{-44}$ kg·m^2
Particle density	$\frac{N}{V} = 2.16\ 10^{27}$ m^{-3}
Potential strength	36.7 K

TABLE III

Influence of molecular length $\sigma_\parallel$ on the critical frequency f_c

$\sigma_\perp = 5.3$ Å	$\sigma_{\parallel 2}/\sigma_{\parallel 1}$	f_{c2}/f_{c1}
Simulation	1.5	0.35
Exp. CB8/CB4	1.5	0.45

TABLE IV

Influence of molecular width $\sigma_\perp$ on the critical frequency

$\sigma_\parallel = 17.9$ Å	$\sigma_{\perp 2}/\sigma_{\perp 1}$	f_{c2}/f_{c1}
Simulation	1.2	0.72

where r_{ij} is the distance between the centers of the two molecules i and j. ε_{ij} and σ_{ij} are functions of the geometrical anisotropy of the ellipsoid, and of the relative orientation of the molecular long axes. The parameters have been chosen to correspond to those of the CBn molecule. They are summed up in Table II.

The results concern only the movement around a transverse axis (dipole moment parallel to the long axis). As expected, the critical frequency f_c decreases as the molecular length $\sigma_{\|}$ increases (Table III) and the results agree quite well with experiment. On the contrary, the influence of the molecular width is rather small (Table IV).

As a conclusion, steric effects seem to be very important for hertzian dielectric absorption. Conversely, they are not perceptible in the far infrared region.

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