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SUSCEPTIBILITIES AND ORDER PARAMETERS OF NEMATIC LIQUID CRYSTALS

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Résumé. — Nous avons mesuré les susceptibilités magnétiques du MBBA, du p-quinquephenyl, et des composés cyano-biphenyl NCB, où N s'échelonne entre 5 et 9, en fonction de température en phase nématique. En phase nématique la susceptibilité est anisotropique et $\Delta\chi = (\chi_{\parallel} - \chi_{\perp})$ devrait être en proportion du paramètre d'ordre S . Nous avons calculé les coefficients de proportionnalité $S/\Delta\chi$ en utilisant des informations que l'on trouve dans la littérature traitant de la susceptibilité de composés organiques semblables. Ces résultats sont en bon accord avec des valeurs obtenues par le procédé, proposé par Haller, qui entraîne l'extrapolation des données expérimentales à une température de zéro, c'est-à-dire, au point où $S = 1$.

Nos résultats correspondant à S rapportés à l'échelle, qui devraient être précis à 3 % près, en termes absolus, sont en accord général avec les résultats correspondant au MBBA obtenus par investigateurs préalables.

Abstract. — The magnetic susceptibilities of MBBA, p-quinquephenyl, and the cyano-biphenyl compounds NCB where N ranges from 5 to 9 have been measured as a function of temperature in the nematic range. In the nematic range the susceptibility is anisotropic and $\Delta\chi = (\chi_{\parallel} - \chi_{\perp})$ should be proportional to the order parameter S . The coefficients of proportionality $S/\Delta\chi$ have been calculated using information available in the literature concerning the susceptibility of similar organic compounds. These results are in good agreement with values obtained by the procedure which Haller has suggested, which involves extrapolation of the experimental data to zero temperature i.e. to $S = 1$.

Our scaled results for S , which should be accurate to within 3 % in absolute terms, are in general agreement with the results of previous investigators in the case of MBBA.

1. Introduction. — Experiments are in progress in our laboratory to measure the Frank stiffness constants of nematic liquid crystals as functions of temperature and pressure, and in order that the results of these experiments may be properly analysed we need information concerning the magnetic anisotropy $\Delta\chi$. This is defined by the equation

$$\Delta\chi = (\chi_{\parallel} - \chi_{\perp}), \quad (1)$$

where χ_{\parallel} and χ_{\perp} are the volume susceptibilities parallel and perpendicular to the so-called director. Measurements of χ_{\parallel} and χ_{\perp} have been initiated to provide the information needed, and in the present paper we describe the results so far obtained, which are for atmospheric pressure only. They are of interest in their own right because from $\Delta\chi$ it is possible to deduce the nematic order parameter S .

For one of the nematic liquids investigated, n-(p-methoxybenzylidene)-p-butylaniline (MBBA), results for $\Delta\chi$ are already available [1], but our success in reproducing these results provides a useful check on the accuracy of our method. No susceptibility

measurements have previously been reported for the other substances, p-quinquephenyl (5P) and five members of the homologous series of 4n-alkyl-4'-cyano-biphenyls distinguished by the number of carbon atoms in the alkyl chain (5CB, 6CB, 7CB, 8CB and 9CB). Quinquephenyl was chosen because it seems to conform more closely than most nematics to the theoretician's ideal of a fluid composed of rigid rods having no permanent electric dipole. Unfortunately, this substance tended to break down under the conditions needed for our experiment, and the results obtained for it are of limited accuracy for this reason. The cyano-biphenyls, however, are well known to be extremely stable.

2. Experimental method. — The magnetic susceptibility was measured by the Faraday-Curie method [2], i.e. by measuring the magnetic force on a sample suspended in a strong inhomogeneous field. The apparatus was similar to that described by Stewart and Rizutto [3]. The specimens were contained in small buckets, which were suspended in an argon atmosphere from a Beckman LM600 electronic micro-

balance. For low temperature measurements on MBBA and the cyano-biphenyls, the buckets were made of PTFE, propylene or delrin, had masses of 0.21-0.37 gm, and contained about 0.85 gm of sample material. The nematic range of 5P being above 380 °C, however, a metal container was needed for this material. Cells were machined from high purity (6N) copper. They were closed before use by screw-on copper caps and sealed by electron-beam welding to prevent evaporation. These copper cells had masses of 1.5-2.0 gm and contained only about 0.25 gm of 5P. The inhomogeneous, transverse magnetic field was provided by an iron-cored electromagnet, fed by a stabilized ($\pm 0.03\%$) current supply, and it was adjusted and monitored with the aid of an NMR spectrometer. Despite the stabilization, the field fluctuated a little, and eddy currents induced in the copper cells made it more difficult to obtain accurate readings during the experiments on 5P. In several preliminary experiments, and in all measurements on 5P, the field (B) was varied between zero and 0.92 T and it was verified that, within the limits of error, the magnetic force was proportional to B^2 . For measurements on MBBA and the cyano-biphenyls, however, a fixed value was chosen for the field, though naturally the magnet was switched on and off periodically to find the magnetic force. The balance was then operated in its servo mode, which ensured that the position of the specimen container was also fixed; calculations showed that variations in container height due to thermal expansion in the silica fibre used to support it could be safely ignored. The servo output, together with the output from a thermocouple in close proximity to the specimen, was recorded on a chart recorder. The temperature was varied continuously by means of heating coils which entirely surrounded the tube inside which the specimens were suspended. The rate of variation was very slow, of the order of 1 K per hour in general and less than that in the neighborhood of the nematic-isotropic transition temperature T_c .

To distinguish the magnetic force on the specimen from the magnetic force on its container, we repeated each run with the container empty. The two forces were roughly equal when the copper cells were used, but when plastic buckets were used the force on the specimen was 4 to 5 times greater than that on the bucket. The apparatus was calibrated by using pure water as the specimen, since accurate measurements for the susceptibility of water are available in the literature [4]. A solution of NiCl_2 proved less satisfactory for calibration purposes because of its paramagnetic nature, and glycerol, which was also tried, proved to contain an unacceptably high concentration of magnetic impurities.

Care had to be taken to avoid magnetic impurities, including oxygen, in the specimens. They were all out-gassed *in situ* for several hours before measurements were made. The water was redistilled before

use in an oxygen-free environment, and it was subsequently exposed to the atmosphere, during transfer to the apparatus, for no more than a few seconds.

For MBBA and the cyano-biphenyls, T_c remained constant and the results were completely reproducible. For 5P, however, the transitions were not very sharp to begin with, and T_c was observed to fall by 8-10 K during the first day at a high temperature, remaining fairly steady thereafter. These observations suggest that 5P was undergoing chemical decomposition during use, and indeed the specimens of this material were found to be dirty afterwards; they contained small specks of what appeared to be carbon and copper. To check on the stability of 5P, some samples were heated in sealed quartz ampoules and then, after several hours at temperatures of up to 400 °C, subjected to analysis by mass spectrometer. They proved to contain quaterphenyl and terphenyl in particular, though these impurities were present only in minute quantities in the material as received from the supplier. These observations were repeated with small copper strips added to the 5P, and the results strongly suggest that the breakdown of 5P is catalysed by copper.

Extraction of the desired susceptibility from the measurements is not entirely straightforward, since the magnetic force depends upon an integral of $d(B^2)/dz$ over the volume of the specimen and corrections for thermal expansion are required. The masses of the nematic specimen and of the water used for calibration purposes were adjusted so as to make them as nearly equal in volume as possible. Knowing these masses, which were determined by weighing before and after each run, and knowing the densities $\rho(T)$ of the nematic and of water as functions of temperature, we were able to calculate a temperature T_0 at which the two volumes should be identical. Then if $F_1(T)$ is the magnetic force on the nematic specimen at temperature T , where its susceptibility is $\chi_1(T)$, and $F_2(T)$ and $\chi_2(T)$ are equivalent quantities for water, we may write

$$\frac{F_1(T)}{F_2(T_0)} = \frac{\chi_1(T) - \chi_0(T)}{\chi_2(T_0) - \chi_0(T_0)} \frac{\rho_1(T_0)}{\rho_1(T)} (1 + C), \quad (2)$$

where

$$C = \frac{1}{2}(T - T_0) ((\beta_1 - 2\alpha)d - 2\alpha D)(B'/B). \quad (3)$$

In equation (2), χ_0 is the volume susceptibility of the argon atmosphere; fortunately, χ_1 and χ_2 were sufficiently close to one another in practice, and sufficiently large compared with χ_0 , for this to be ignored. In equation (3), β_1 and α are respectively the volume expansion coefficient of the nematic and the linear expansion coefficient of the bucket; d is the depth of the liquid in the bucket; D is the distance from the bottom of the bucket to the point where it is attached to the silica fibre; B' is the field gradient dB/dz , which to a good approximation was indepen-

dent of z in our apparatus; and B is the magnitude of the field at the midpoint of the specimen. The correction factor C is not very significant, since it changed our values for χ_1 by less than 0.1 %, and it was applied only to the cyano-biphenyl data. For the cyano-biphenyl compounds we had available accurate density data, kindly supplied by Dr. D. Dunmur.

Since the magnetic field was strong enough to align the director, the procedure described above yields χ_{\parallel} rather than χ_{\perp} for a nematic. To obtain the latter quantity we made use of measurements of χ_{iso} , the susceptibility of the isotropic phase above T_c . The mass susceptibility of the isotropic phase,

$$\chi_{\text{iso}}^{(m)} = \chi_{\text{iso}}/\rho_{\text{iso}}, \quad (4)$$

should be, and was in practice, independent of temperature, and it should be equal to the average mass susceptibility of the nematic. Hence we have

$$\chi_{\parallel}^{(m)}(T) + 2\chi_{\perp}^{(m)}(T) = 3\chi_{\text{iso}}^{(m)}, \quad (5)$$

or

$$\Delta\chi^{(m)}(T) = \frac{3}{2}(\chi_{\parallel}^{(m)} - \chi_{\text{iso}}^{(m)}). \quad (6)$$

It is the anisotropy in the mass susceptibility, $\Delta\chi^{(m)}$, that should be proportional to the nematic order parameter S [5] rather than the anisotropy in the volume susceptibility, and it is $\Delta\chi^{(m)}$ that is plotted in the curves below.

3. Scaling the order parameter. — It is readily shown that if α_1 , α_2 and α_3 are the three principal components of the magnetic polarisability tensor for an individual molecule, and the 3 axis is the long axis of the molecule, then in the nematic phase

$$M\Delta\chi^{(m)} = N_A(\alpha_3 - \frac{1}{2}(\alpha_1 + \alpha_2))S, \quad (7)$$

where M is the molecular weight and N_A is Avagadro's number, while in the isotropic phase

$$M\chi_{\text{iso}}^{(m)} = N_A\frac{1}{3}(\alpha_1 + \alpha_2 + \alpha_3). \quad (8)$$

It follows from (7) and (8) that the required scaling factor is given by

$$\begin{aligned} S/\Delta\chi^{(m)} &= \frac{2}{3}(N_A\alpha_3/M - \chi_{\text{iso}}^{(m)})^{-1} \\ &= \frac{2}{3}(\chi_3^{(m)} - \chi_{\text{iso}}^{(m)})^{-1}, \end{aligned} \quad (9)$$

where $\chi_3^{(m)}$ is the mass susceptibility that would be measured in the 3 direction if the molecules could be perfectly aligned.

According to Krishnan, Guha and Banerjee [6] the molecules are perfectly aligned in the crystalline phases of biphenyl, terphenyl and quaterphenyl and these authors have measured $\chi_3^{(m)}$ for these three compounds. Since the results vary only slightly from one member of the series to the next, and the variation is linear, one may confidently extrapolate the data to find $\chi_3^{(m)}$ for quinquephenyl. Hence to find $S/\Delta\chi^{(m)}$ for this material presents no problem. We estimate it to be 2.83 ± 0.01 gm.

No results are available for crystalline specimens of cyanobiphenyls. According to Pascal's rule, however, which is known to be quite accurately obeyed by organic substances [7], the magnetic polarisability of a molecule can be evaluated by adding together the characteristic polarisabilities of the groups of which it is composed. To estimate $\chi_3^{(m)}$ for 5CB, say, we may therefore start with $\chi_3^{(m)}$ for biphenyl, as given by the work of Krishnan *et al.*, deduct from this the small contribution made by the two terminal hydrogen atoms (which may be estimated from the difference in between biphenyl and terphenyl), and add terms to represent the longitudinal polarisabilities of the —CN group and the —C₅H₁₁ groups. The average polarisabilities characteristic of these two groups are well known [4], and the anisotropy of the polarisability for the —CN group may be deduced from the work of Flygare [8]. We have assumed the relatively small contribution made by the —C₅H₁₁ group to be isotropic.

Our theoretical values for $S/\Delta\chi^{(m)}$, as given by equation (9), are listed in the second column of table I. For 5P, the error should not exceed about 1 %. For the cyano-biphenyls, it may be as much as 2 %. A figure has been included for MBBA, but $\chi_3^{(m)}$ cannot be predicted quite so confidently for this material, so the error in $S/\Delta\chi^{(m)}$ could perhaps be as much as 5 %.

TABLE I

Scaling factors and isotropic susceptibilities of nematics

| 1. Nematic substance | 2. $10^{-6} S/\Delta\chi^{(m)}$ (gm) (calculated) | 3. $10^{-6} S/\Delta\chi^{(m)}$ (gm) (Haller) | 4. $10^6 \chi_{\text{iso}}^{(m)}$ (gm ⁻¹) (calculated) | 5. $10^6 \chi_{\text{iso}}^{(m)}$ (gm ⁻¹) (measured) |
|----------------------|---|---|--|--|
| 5P | 2.83 | 2.6 | 0.658 0 | 0.651 8 |
| 5CB | 5.33 | 5.5 | 0.673 6 | 0.671 1 |
| 6CB | 5.63 | 5.8 | 0.681 6 | 0.680 0 |
| 7CB | 5.93 | 6.3 | 0.685 5 | 0.689 1 |
| 8CB | 6.23 | — | 0.691 6 | 0.693 1 |
| 9CB | 6.53 | — | 0.696 5 | 0.700 0 |
| MBBA | 4.95 | 5.1 | 0.650 0 | 0.643 7 |

As a check on the arguments outlined above, we have used them to calculate $\chi_{\text{iso}}^{(m)}$ for all the materials investigated, with results that are compared with experiment in columns 4 and 5 of the table. The agreement is good. As a further check, we have estimated the scaling factor by the quite different method which Haller has suggested [9], which involves extrapolating the measurements of $\Delta\chi^{(m)}$, on a logarithmic plot, to zero temperature, where S should be unity. Here again, as may be seen from column 3 of the table, the agreement is satisfactory.

4. Results. — Curves for $\Delta\chi^{(m)}$ versus temperature for all seven nematics, derived from the continuous curves plotted by the chart recorder, are reproduced in figures 1-3. Since the results may be of value to others who are engaged, like us, in measurement of the Frank constants for some of these materials, it may be noted that, except in the case of 8CB and 9CB, the curves may be reproduced within the limits of experimental error by the analytic formula

$$\Delta\chi^{(m)}(T) = A_0 + A_1(T_c - T)^n - A_2(T_c - T) + A_3(T_c - T)^2. \quad (10)$$

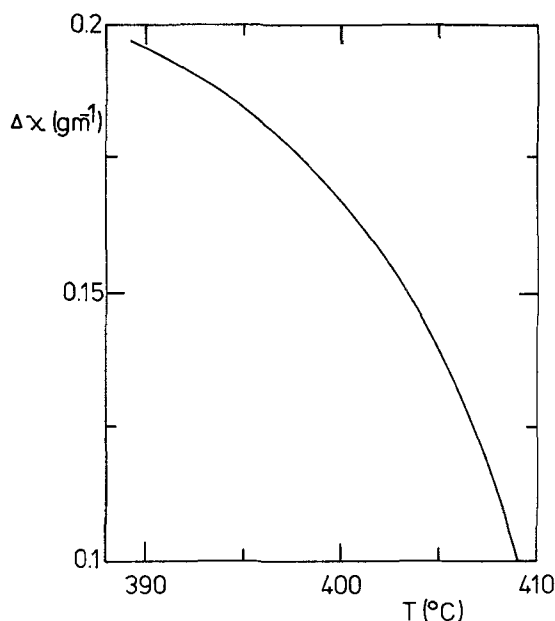


FIG. 1. — Temperature dependence of the anisotropy of the mass susceptibility for 5P.

TABLE II

| Substance | Fitting parameters for $\Delta\chi^{(m)}$ | | | | |
|-----------|---|------------|------------|---------------|---------|
| | $10^8 A_0$ | $10^8 A_1$ | $10^8 A_2$ | $10^{11} A_3$ | n |
| 5P | 9.351 | 41.56 | 39.91 | 1.317 | 0.990 6 |
| 5CB | 7.061 | 2.717 | 1.315 | 5.791 | 0.793 5 |
| 6CB | 5.947 | 3.821 | 2.312 | 3.193 | 0.805 0 |
| 7CB | 6.166 | 2.197 | 7.162 | 5.946 | 0.705 0 |
| MBBA | 6.373 | 2.427 | 0.856 7 | 3.858 | 0.737 6 |

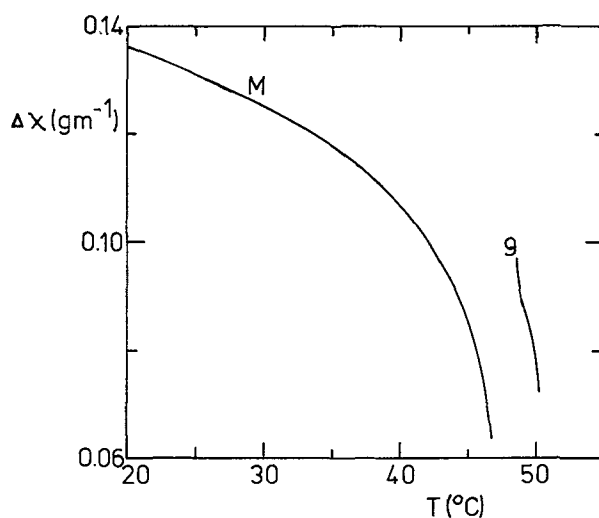


FIG. 2. — Temperature dependence of the anisotropy of the mass susceptibilities of (M)MBBA and (9)9CB.

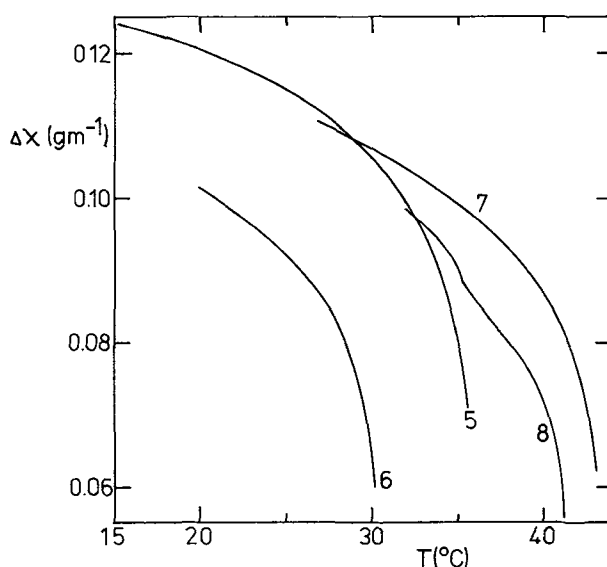


FIG. 3. — Temperature dependence of the anisotropy of the mass susceptibility of (5)5CB, (6)6CB, (7)7CB, and (8)8CB.

Table II shows an appropriate set of values (not unique) for the parameters in this equation, if $\Delta\chi^{(m)}$ is measured in gm^{-1} and $(T_c - T)$ in K. They have been established with the aid of a computer, using a standard fitting programme. In table III, we give

TABLE III

Transition data for nematics

| Substance | T_{SN} (°C) | T_c (°C) | $10^6 \Delta\chi_c^{(m)}$ (gm^{-1}) | S_c |
|-----------|-------------------------|---------------|---|-----------|
| 5P | — | ca. 409.2 | ca. 0.115 | ca. 0.325 |
| 5CB | — | 35.7 | 0.070 8 | 0.377 |
| 6CB | — | 30.2 | 0.059 7 | 0.336 |
| 7CB | — | 43.2 | 0.062 3 | 0.369 |
| 8CB | 34.3 | 41.6 | 0.055 8 | 0.348 |
| 9CB | 48.5 | 50.3 | 0.072 0 | 0.470 |
| MBBA | — | 46.7 | 0.063 8 | 0.316 |

the values we observed for the nematic-isotropic transition temperature, T_c , together with the lowest values we measured, just below this temperature, for $\Delta\chi^{(m)}$. Values for the smectic-nematic transition temperature, T_{SN} , are included for 8CB and 9CB. It is the pretransitional effects just above T_{SN} that make equation (10) inappropriate for 8CB and 9CB. They also, incidentally, make it impossible to carry through the Haller scaling procedure. The transition at T_{SN} is probably a first-order one, though only weakly so, but we were unable in our experiments to detect any discontinuity in $\Delta\chi^{(m)}$.

To convert $\Delta\chi^{(m)}$ into S , we prefer to use the scaling factors in column 2 of table I rather than those in column 3. Scaled curves for S versus reduced temperature, T/T_c , are reproduced in figures 4-5. Table III includes values for S_c , the magnitude of the order parameter at the nematic-isotropic transition.

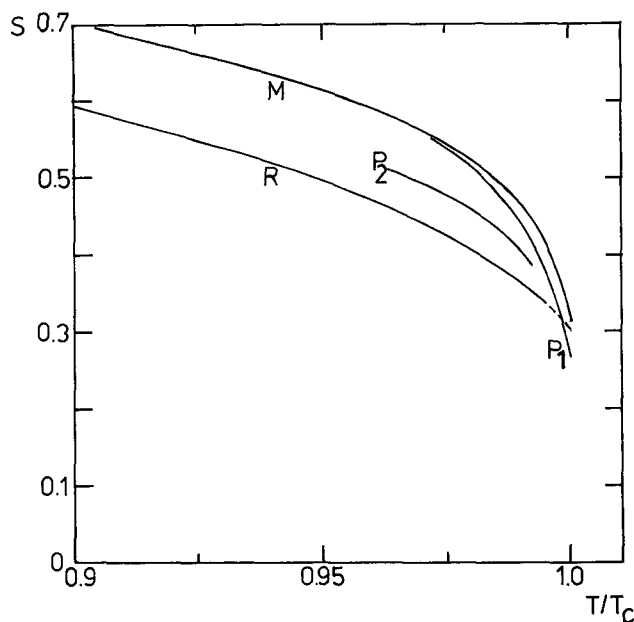


FIG. 4. — Order parameters as a function of reduced temperature for MBBA [(R) ref. [1] and (M) this work] and 5P [(P₁) first run and (P₂) second run].

The following points deserve comment. — (a) Our order parameter curve for MBBA lies well above the curve obtained by Rose [1] for this substance, which is included in figure 4; Rose deduced the magnetic anisotropy from NMR measurements. Except in the neighborhood of T_c , however, the two curves are similar in shape, and most of the discrepancy is attributable to a difference of opinion as regards the scaling factor $S/\Delta\chi^{(m)}$. Other sets of results for the order parameter in MBBA have been assembled by Jen *et al.* [10], but to include them all in figure 4 would confuse the diagram. In general, our value for S_c (0.316) is consistent with the curve fitted to other experimenters, data by Jen *et al.*, but at $T/T_c = 0.9$ that curve passes through 0.65 whereas ours passes through 0.71.

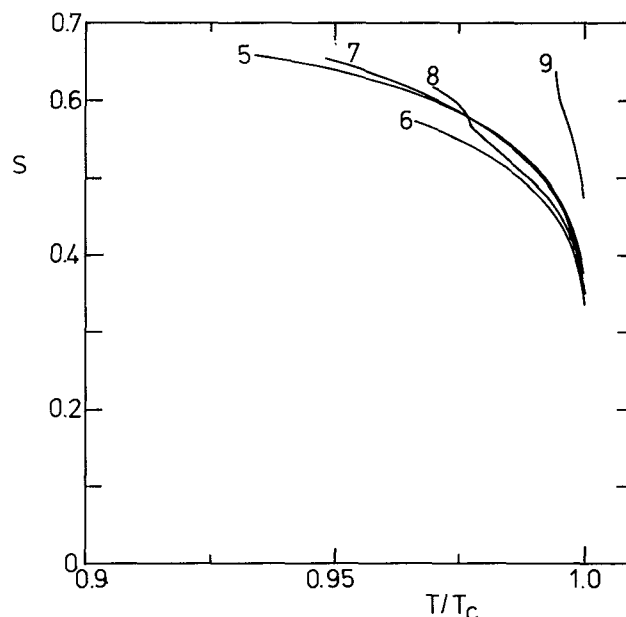


FIG. 5. — Order parameters as a function of reduced temperature for cyano-biphenyls (5)5CB, (6)6CB, (7)7CB, (8)8CB, and (9)9CB.

(b) The two curves for 5P in figure 4 correspond to the results obtained in two different runs using the same sample. The curve for the later run is the lower one, so it seems that the presence of impurities such as quaterphenyl and terphenyl tends to reduce S for a given T/T_c . Since the first run lasted for two days, the impurity concentration must have increased considerably in the course of it, being larger for temperatures close to T_c than well below T_c . It looks as though the order parameter curve for pure 5P may be rather similar to our curve for MBBA.

(c) Our values for the order parameter in 5CB are about 15% higher than those reported by Horn [11], who measured the birefringence of 5CB and scaled his results by the Haller procedure. The discrepancy is perhaps rather larger than would be expected, if order parameters based on two such different quantities as the magnetic anisotropy and the birefringence should be the same. But we agree with Horn that for 5CB, as for other cyano-biphenyls, S falls rather sharply as T_c is approached.

(d) De Jeu and Claasen [5], who have made measurements similar to ours on a homologous series of *pp'*-di-*n*-alkylazoxybenzenes have reported a marked odd-even oscillation in the magnitude of S for given T/T_c . The same effect is apparent in figure 5 for the cyano-biphenyls.

(e) The quantity S_c is surprisingly high for 9CB, a feature that is apparent in the data for $\Delta\chi^{(m)}$ and which cannot be blamed on faulty scaling. For all the other materials S_c is significantly below the value (ca. 0.43) predicted by the theory of Maier and Saupe.

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