Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

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Version of record first published: 21 Mar 2007.

To cite this article: Hans Gruler & Gerhard Meier (1973): Investigations on the Elastic Constants of the Nematic Homologous Series of 4,4′-Di(n-Alkoxy) Azoxybenzene, Molecular Crystals and Liquid Crystals, 23:3-4, 261-270

To link to this article: http://dx.doi.org/10.1080/15421407308083376

Molecular Crystals and Liquid Crystals. 1973. Vol. 23, pp. 261–270

Printed in Great Britain

Investigations on the Elastic Constants of the Nematic Homologous Series of 4,4′-Di(*n*-Alkoxy)Azoxybenzene†

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Received December 8, 1972

Abstract—The splay and bend elastic constants of the 4,4′-di(*n*-alkoxy)-azoxybenzenes have been determined by measuring the change in birefringence of parallel oriented samples in a magnetic field. The Maier-Saupe theory shows that the elastic constants should be proportional to S^2 where S is the long range order parameter, but that short range order can also strongly affect these constants. Our measurements on the homologous series do indicate that both long and short range order are important.

The temperature dependence of the bend and splay elastic constants, for example, near the nematic→isotropic transition cannot be explained by the long range order. This dependence corresponds to the pretransitional effects seen in the thermal expansion coefficient in this region, which can only be due to short range order. Our measurements also show that near the nematic→smectic C transition the splay (k_{11}) and bend (k_{33}) elastic constants abnormally increase. This strong temperature dependence of k_{11} and k_{33} can be explained by a pretransitional effect because the planar structure of the smectic C phase requires that k_{11} and k_{33} be very large. This increase is interpreted in terms of de Vries's model of cybotactic groups. A further abnormality in the elastic constants is observed in the region far away from the nematic→isotropic and nematic→smectic C transitions, which is interpreted by changes in the molecular arrangement in the steric units.

The elastic properties of liquid crystals are of theoretical interest and also of practical importance. The theory has mainly been worked out by Oseen,⁽¹⁾ Zocher,⁽²⁾ Frank,⁽³⁾ and Nehring and Saupe.⁽⁴⁾ The technique of measuring elastic constants was developed by Zocher⁽²⁾ and the Russian group around Fréedericksz⁽⁵⁾ and later perfected by Saupe.⁽⁶⁾ In a recent paper Gruler, Scheffer

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† Presented at the Fourth International Liquid Crystal Conference, Kent State University, August 21–25, 1972.

and Meier(7) have discussed these measuring techniques, so it is only necessary here to present a brief summary.

It is possible to determine the elastic constants of a nematic liquid crystal from a deformation of a uniformly aligned sample or single crystal. The nature of the deformation is completely determined by the boundary conditions and the elastic properties of the nematic liquid crystal. A nematic single crystal can be easily prepared between two specially treated parallel glass plates and can undergo formation in a magnetic or electric field. Ratios of the elastic constants can then be determined from the form of the deformation, but it is necessary to know the actual value of the dielectric or diamagnetic anisotropy in order to get the absolute value of the constants.

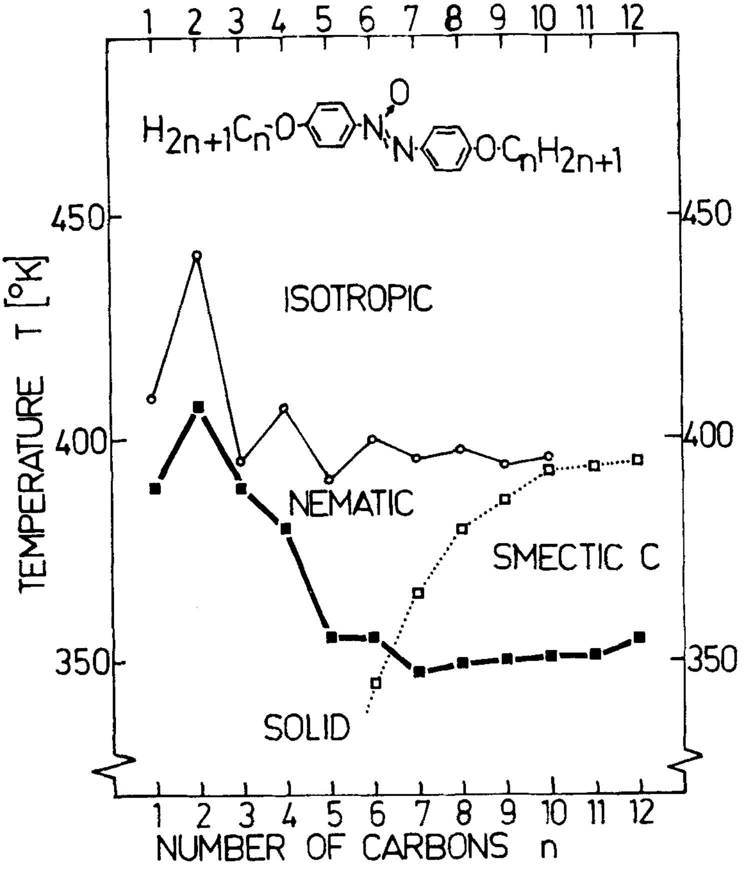

Figure 1. Phase diagram for the 4,4′-di(n-alkoxy)azoxybenzenes.

For the geometry where the optical axis of the single crystal is parallel to the glass surfaces with a magnetic field being applied perpendicular to the glass plates, there exists a threshold field below which the nematic single crystal is not deformed. The splay elastic constant can be determined from this threshold field, H_0.

$$k_{11} = \Delta\chi(H_0 x_0/\pi)^2 \tag{1}$$

where $\Delta\chi$ is the diamagnetic susceptibility anisotropy and x_0 is the thickness of the cell. Information about the form of the deformation can be determined from the change of birefringence of the nematic film, because nematic liquid crystals are optically uniaxial and strongly birefringent. The ratio of the bend to splay elastic constant k_{33}/k_{11} can be determined directly from the shape of the change in the birefringence curve measured as a function of the magnetic field Before discussing the actual elastic constants of the 4,4′-di(*n*-alkoxy)-azoxybenzenes it is helpful to first consider a phase diagram for this series (Fig. 1). For the purpose of later discussion it is important to note that a smectic C phase exists for $n = 6$ and higher homologs. Extrapolating this smectic C phase boundary curve back to small chain lengths it can be seen that the $n = 1$ and 2 homologs must be quite far from any smectic C phase.

In Fig. 2 the measured values of the splay elastic constant k_{11} for the homologous series is plotted against the reduced temperature Θ

$$\Theta = \frac{T}{T_c}\left(\frac{V}{V_c}\right)^2$$

which was defined by Maier and Saupe.⁽⁸⁾ T_c is the nematic → isotropic phase transition temperature in °K and V_c is the mole volume of the nematic phase at the nematic–isotropic transition temperature as defined in Ref. 8. The diamagnetic susceptibility was measured only for the $n = 1$ homolog, but since $\Delta\chi$ is determined mainly by ring currents of the aromatic system, the molar $\Delta\chi$ is to a very good approximation the same for all members of the homologous series at a given reduced temperature.

From Fig. 2 it is seen that the splay elastic constant increases with decreasing temperature, and that the magnitude of this effect becomes larger for the longer chain length compounds. Saupe⁽⁶⁾

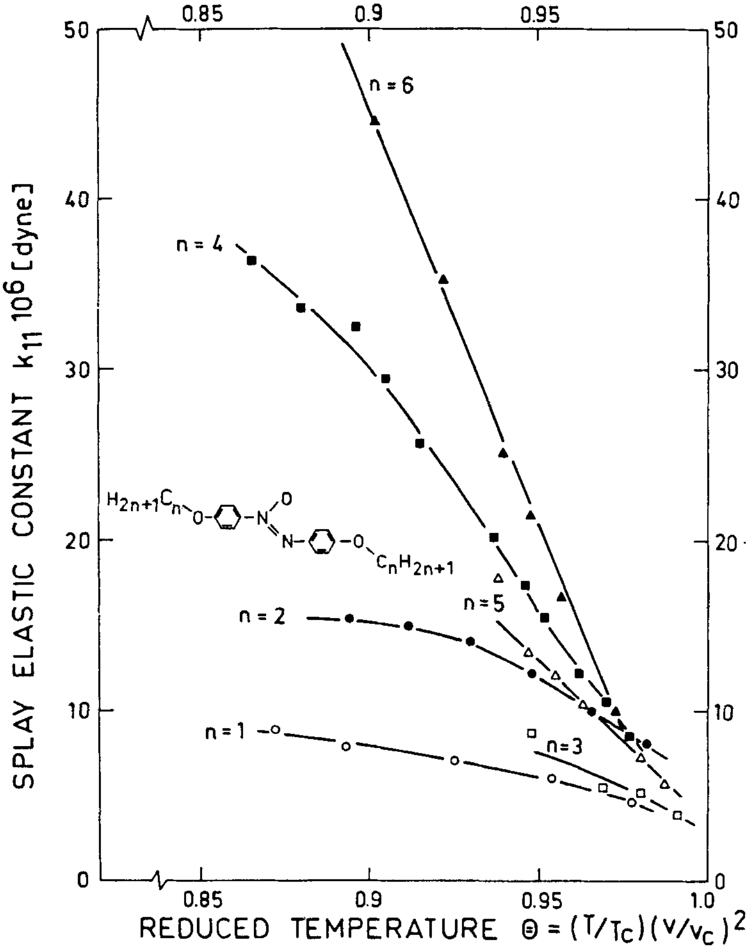

Figure 2. Splay elastic constant k_{11} as a function of reduced temperature.

defines a reduced elastic constant C_{11}

$$C_{11} = k_{11} \cdot \frac{V^{7/3}}{S^2}. \tag{2}$$

C_{11} should be independent of temperature if no change in short range order structure occurs. The effect of simple thermal expansion on the elastic constant is taken care of by the mole volume term in this equation. The order parameter S describes the influence of long range order on the elastic properties. We will show that there are many cases where C_{11} still has a temperature dependence. The order parameter S was not measured for all homologs because it is a good approximation to take the same order parameter S for all of them on a reduced temperature scale.

The reduced splay elastic constant C_{11} of the homologous series is plotted vs. reduced temperature in Fig. 3. C_{11} is nearly temperature independent for the homologs $n = 1$, 2, and 3. This implies that the

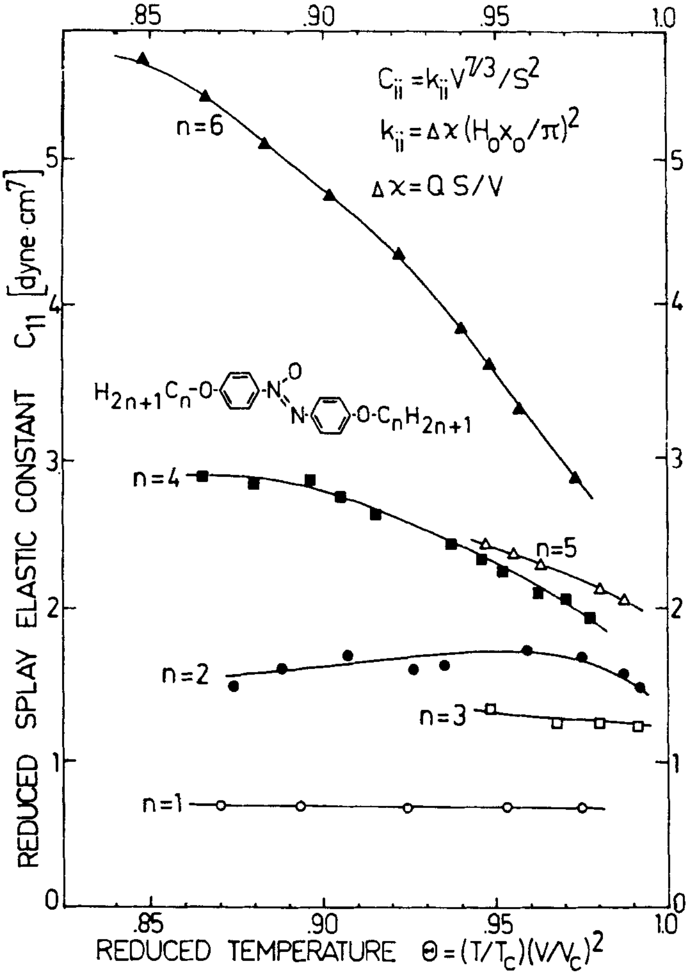

Figure 3. Reduced splay elastic constant C_{11} as a function of reduced temperature.

temperature dependence of the splay elastic constant can be explained only by changes in mole volume and long range order for these compounds. The reduced splay elastic constant is no longer temperature independent for the higher homologs, however, meaning that the assumptions made in the derivation of Eq. 2 are no longer valid. The temperature dependence of the reduced elastic constants C_{11} of the higher homologs can be explained by a change in short range order structure.

In Fig. 4 the second experimentally measured quantity k_{33}/k_{11} is displayed. If the temperature dependence of the elastic constants k_{11} and k_{33} is determined only by the temperature dependence of the order parameter S and thermal expansion coefficient then the ratio k_{33}/k_{11} should be independent of temperature. Figure 4 shows that this is generally not the case. This is a direct indication that the elastic constants of nematic liquid crystals depend on short range order as well as on long range order.

To a first simple approximation we assume that the nematic range

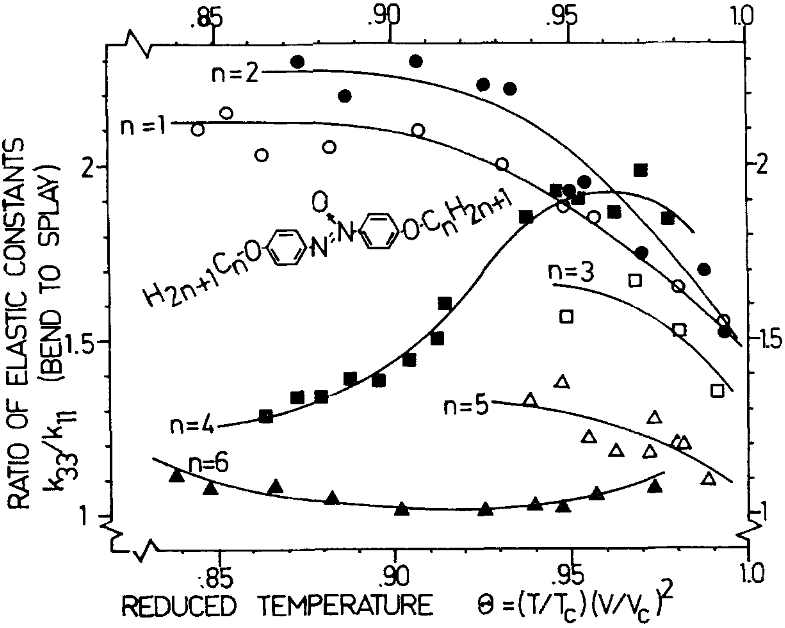

Figure 4. Ratio of elastic constants k_{33}/k_{11} (bend to splay) as a function of reduced temperature.

can be broken up into 4 regions, each having its own characteristic short range order structure and corresponding k_{33}/k_{11} ratio (Fig. 5). A more detailed discussion of this point is given in an additional paper.(9) We presume that these curves are generally valid for any nematic substance having a large enough temperature range.

X-ray scattering data(10) indicate that cybotactic groups having a smectic-like structure exist in the nematic phase on region IV near the smectic phase transition. The elastic properties of the nematic

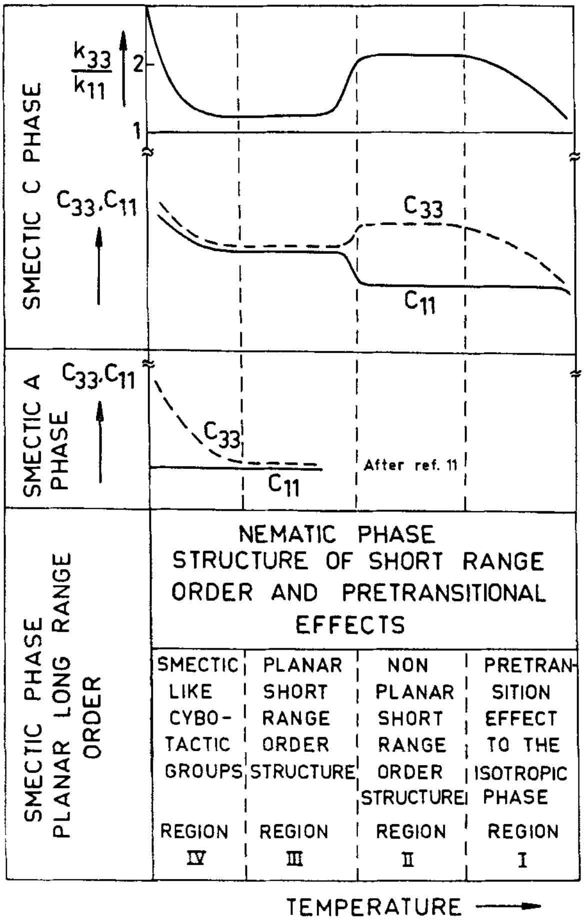

Figure 5. Elastic properties k_{33}/k_{11} (bend to splay), C_{33} and C_{11} (reduced bend and splay constant) in the nematic phase as a function of temperature and short range order.

phase in this region should therefore share certain similarities to the elastic properties of the smectic phase. The pure bend and splay elastic deformations are represented schematically in Fig. 6 for the nematic, smectic *A* and smectic *C* phases. Obviously, the bend deformation is inconsistent with the planar structure in both the smectic *A* and smectic *C* phases. The bend elastic constant k_{33} must therefore be very large in both smectic phases in comparison to the nematic phase. The splay elastic deformation, on the other hand, is allowed in the smectic *A* phase because the director **L** is perpendicular to the smectic planes. We therefore expect no big change in the splay elastic constant at the nematic to smectic *A* phase transition. In the smectic *C* phase, however, the director **L** makes a certain angle to the planes and the pure splay deformation is inconsistent with the planar structure. One would therefore expect to measure a correspondingly large increase of the splay elastic constant k_{11} in going from the nematic to smectic *C* phase.

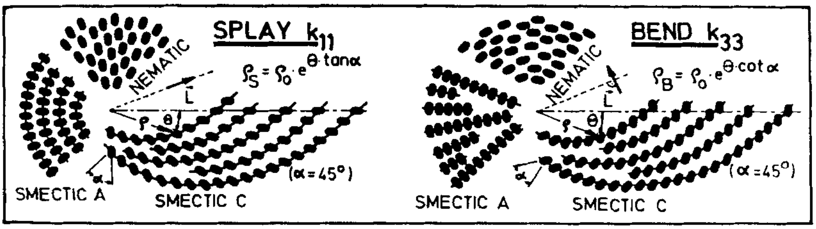

Figure 6. Pure elastic bend and splay deformations in the nematic, smectic *A* and smectic *C* phases.

Cheung and Meyer(11) have measured the splay and bend elastic constants of a nematic liquid crystal near the smectic *A* phase transition. As expected from our simple model, their results show that the bend elastic constant k_{33} anomalously increases at the nematic to smectic *A* transition while the splay elastic constant k_{11} behaves normally. Figures 3 and 4 for the $n = 6$ homolog show that the situation is more complicated at the smectic *C* phase transition. As expected, both splay and bend elastic constants increase near the smectic *C* phase transition. The ratio k_{33}/k_{11} for the $n = 6$ homolog is nearly independent of temperature. We believe that this fact is almost accidental because Gruler(9) found a strong increase in the ratio of k_{33}/k_{11} near the nematic to smectic *C* phase transition in

4,4′-di(*n*-heptyloxy)azobenzene which has a monotropic smectic *C* phase. From Fig. 6 we would expect the same temperature behaviour for the splay and bend elastic constants only for the special case where $\alpha = 45°$.

The cybotactic groups become smaller and smaller with increasing temperature so that the cybotactic groups in region III may consist of only two to four molecules. Saupe(6) called these groups steric units. The tendency for planar ordering of the molecules, however, is still not yet completely lost in region III. Chistyakov and Chaikowsky's(12) X-ray experiments show that the steric units can consist of a planar arrangement of molecules. A planar short range order structure is assumed in region III.

This short range order structure can still be considered as a pretransitional effect to the smectic phase. Since the planar short range order structure is not changed there should also be no change in the reduced elastic constants as is indicated in Fig. 5.

Chistyakov and Chaikowsky(12) indicate that a planar short range order structure does not exist in region II. The short range order structure has to change between regions II and III and therefore the values for the reduced elastic constants must change. In going from region II to region III, C_{33} decreases and C_{11} increases. This is also the experimental result which we found for the $n = 4$ homologs shown in Figs. 3 and 4.

There is probably also a non-planar short range order structure in region I and we expect large pretransitional changes in short range order to the isotropic phase. The anomalous temperature dependence of the thermal expansion coefficient for nematics(8) in region I shows that the short range order structure must be changing. At present we do not have a short range order model for this region.

Acknowledgement

The authors are indebted to Dr. Terry J. Scheffer for many helpful discussions.

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