The Elastic Constants of a Nematic Liquid Crystal

Hans Gruler

Gordon McKay Laboratory, Harvard University, Cambridge, Mass. 02138, U.S.A.

(Z. Naturforsch. **30 a**, 230—234 [1975] ; received November 4, 1974)

The elastic constants of a nematic liquid and of a solid crystal were derived by comparing the Gibbs free energy with the elastic energy. The expressions for the elastic constants of the nematic and the solid crystal are isomorphic: $k \propto |\overline{D}|/l$. In the nematic phase $|\overline{D}|$ and l are the mean field energy and the molecular length. In the solid crystal, $|\overline{D}|$ and l correspond to the curvature of the potential and to the lattice constant, respectively. The measured nematic elastic constants show the predicted l dependence.

1. Introduction

The symmetry of a crystal determines the number of non-vanishing elastic constants. In a nematic liquid crystal which is a uniaxial crystal, we find five elastic constants but only three describe bulk properties[1, 2]. Here we calculate the magnitude of these three elastic constants by determining the elastic energy density in two different ways. On the one hand the elastic energy density can be expressed by the elastic constants and the curvature of the optical axis. On the other hand we determine the change of the Gibbs free energy of the deformed state. By comparing these two energy expressions the elastic constants are determined.

2. Mean Field Theory

The phase transition can be described with the Gibbs free energy:

$$G_{\mathrm{N}} = G_{\mathrm{I}} + \Delta U - T\,\Delta S + p\,V \qquad (1)$$

G_{I} is the free energy with an isotropic distribution of the direction of the molecules. $\Delta U = U_{\mathrm{N}} - U_{\mathrm{I}}$ is the increase of the internal energy and $\Delta S = S_{\mathrm{N}} - S_{\mathrm{I}}$ the change of the entropy between the nematic and the isotropic phase. T, p and V are the temperature in °K, the pressure and the volume, respectively. (ΔV_{i} is the change of the volume at the nematic to isotropic phase transition temperature, which will be neglected in the further discussion.) ΔU and ΔS are normally very complicated expressions, but if the interaction energy of one molecule with all others can be described with a mean field, then the problem becomes much easier.

The mean field of the nematic phase was first derived by Maier and Saupe[3]:

$$D(\Theta, \overline{P}_2) = -(A/V_n^2)\,\overline{P}_2 \cdot P_2 \pm \dots \qquad (2)$$

Θ is the angle between the length axis of one molecule and the direction of the preferred axis (optical axis). P_2 is the second Legendre polynomial and $\overline{P}_2$ is one order parameter given by the distribution function $f(\Theta)$:

$$\overline{P}_2 = \int_0^{\pi/2} f(\Theta)\,P_2 \sin\Theta\, d\,\Theta \Big/ \int_0^{\pi/2} f(\Theta) \sin\Theta\, d\,\Theta\,.$$

V_n is the mole volume and A is a coefficient which determines the field of the second Legendre polynomial.

The changes of the internal energy ΔU and the entropy ΔS are[4]:

$$\Delta U = \tfrac{1}{2} N \overline{D} = -\tfrac{1}{2} N (A/V_n^2)\, \overline{P}_2^{\,2}\,,$$

$$T\,\Delta S = N\,\overline{D} + N\,k\,T \ln Z$$

with $Z = \mathrm{const} \int_0^{\pi/2} e^{-D/kT} \sin\Theta\, d\,\Theta$.

The free energy is now:

$$G_{\mathrm{N}} = G_{\mathrm{I}} + \tfrac{1}{2} N (A/V_n^2)\, \overline{P}_2^{\,2} - N\,k\,T \ln Z\,.$$

The order parameter of the nematic phase is determined by

$$\partial G / \partial \overline{P}_2 = 0$$

which leads to:

$$(A/V_n^2)\,\overline{P}_2 = k\,T\,(\partial Z / Z\, \partial \overline{P}_2)\,. \qquad (3\,\mathrm{a})$$

This equation can be solved and fixes $\overline{P}_2$ as a function of T (see [5]). The nematic-isotropic phase transition is given by the following equation:

$$\tfrac{1}{2} (A/V_n^2)\, \overline{P}_2 = k\,T_{\mathrm{NI}} \ln Z\,. \qquad (3\,\mathrm{b})$$

These two equations define A/V_{n}^2 and $\overline{P_2(T_{\mathrm{NI}})}$ at the phase transition as:

Reprint requests to: Experimentelle Physik III der Universität Ulm, *D-7900 Ulm*, Oberer Eselsberg, West-Germany.

$$A/V_n^2 = 4.54 \cdot k\,T_{\mathrm{NI}}\,, \quad \overline{P}_2 = 0.44\,. \tag{3 c}$$

If A is independent of the temperature then the order parameter $\overline{P}_2$ is for a reduced temperature $(T/T_{\mathrm{NI}})\,(V_n/V_n(T_{\mathrm{NI}}))^2$ a universal curve[5].

3. Elastic Constants

a) Nematic Liquid Crystal

The change of Gibbs free energy which is produced by a small deformation, can be expressed with a deformation angle α similar to the description of Nehring and Saupe[1] and Frank[2]:

$$\Theta \rightarrow \Theta_0 + \alpha\,.$$

Θ_0 is the angular distribution of the undeformed state. The deformation angle, α, at a position, $\boldsymbol{r}$, can be expressed with the spatial derivative of the deformed optical axis at the origin. The orientation of the optical axis $\mathbf{L}(\boldsymbol{r})$ at $\boldsymbol{r}$ is (see Fig. 1):

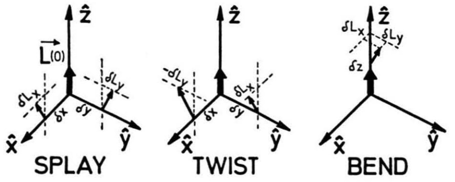

Fig. 1. Illustration of the spatial derivatives of $\boldsymbol{L}(0)$.

$$\begin{aligned}\mathbf{L}(\boldsymbol{r}) = \hat{Z} &+ (L_{x,x}\,X + L_{x,y}\,Y + L_{x,z}\,Z)\,\hat{X}\\ &+ (L_{y,x}\,X + L_{y,y}\,Y + L_{y,z}\,Z)\,\hat{Y} + \ldots\end{aligned}$$

The undisturbed optical axis points into the Z-direction. The deformation angle α is defined by

$$\begin{aligned}\alpha^2 = &(L_{x,x}\,X + L_{x,y}\,Y + L_{x,z}Z)^2\\ &+ (L_{y,x}\,X + L_{y,y}\,Y + L_{y,z}\,Z)^2 + \ldots\end{aligned} \tag{4}$$

If we assume that, owing to the rapid decay of the van der Waals interaction, we have only a nearest or next nearest neighbor interaction, the small deformation approximation will remain valid.

The change of the Gibbs free energy caused by a deformation can now be expressed as:

$$\delta G = \alpha^2 \cdot \tfrac{3}{4}\,N\,\overline{P}_2 \cdot k\,T\,\frac{\partial Z}{Z\,\partial \overline{P}_2} + \ldots \tag{5}$$

By introducing Eq. (3) into Eq. (5), we receive

$$\delta G = -\alpha^2 \cdot \tfrac{3}{4}\,N\,\overline{D} = \tfrac{3}{4}\,\alpha^2\,N\,(A/V_n^2)\,\overline{P}_2^{\,2}\,. \tag{6}$$

The deformation energy can also be described with phenomenological coefficients where the number of coefficients is determined by the symmetry of the system[1, 2]. The elastic energy density of a nematic liquid crystal is then:

$$\begin{aligned}G_{\mathrm{ela}} = &\tfrac{1}{2}\,k_{11}\,(L_{x,x} + L_{y,y})^2 + \tfrac{1}{2}\,k_{22}\,(L_{x,y} - L_{y,x})^2\\ &+ \tfrac{1}{2}\,k_{33}\,(L_{x,z}^2 + L_{y,z}^2)\\ &- (k_{22} + \mathrm{k}_{24}) \sum_{i<j}^{3} (L_{i,i}\,L_{j,j} - L_{i,j}\,L_{j,i})\\ &+ k_{13}\,\mathrm{div}\,(\mathbf{L} \cdot \mathrm{div}\,\mathbf{L})\,.\end{aligned} \tag{7}$$

k_{11}, k_{22} and k_{33} are the splay, twist and bend elastic constants respectively (Figure 2). A comparison of Eqs. (6) and (7) leads to the elastic constants:

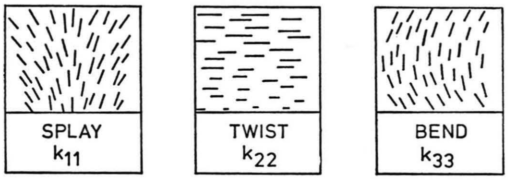

Fig. 2. The main deformations in a nematic liquid crystal.

$$\delta G = \int_{V_n} G_{\mathrm{ela}}\,\delta\tau\,.$$

The volume integrals over the forms which are connected to $(k_{22} + k_{24})$ and k_{13} can be transformed into surface integrals and therefore these terms do not contribute to the Euler-Lagrange differential equations[1]. Now we will solve for k_{11}, k_{22} and k_{33}.

For a pure bend deformation, we get the following relation:

$$\tfrac{1}{2}\,k_{33}\,(L_{x,z}^2 + L_{y,z}^2) = (L_{x,z}^2 + L_{y,z}^2)\,Z^2\,\tfrac{3}{4}\,(N/V_n)\,(-\overline{D})$$

or

$$k_{33} = Z^2\,\tfrac{3}{2}\,(N/V_n)\,(-\overline{D})\,. \tag{8 a}$$

For a pure splay and twist deformation in a planar configuration[1], we get:

$$k_{11} = k_{22} = X^2\,\tfrac{3}{2}\,(N/V_n)\,(-\overline{D})\,. \tag{8 b}$$

The elastic constants are proportional to the packing density (N/V_n), to the average of the main field energy $\overline{D}$ and to the square of a characteristic length.

The square of the distances Z^2 and $X^2\,(=Y^2)$ is only defined within a certain distance R_0 which depends on the anisotropic van der Waals interaction. Supposing only nearest neighbors interaction we can take for R_0 the dimensions of the space one molecule occupies. Example: for PAA (4,4′-di(methoxy) azoxybenzene, $l \sim 17$ Å, $w \sim 4.5$ Å),

$$k_{11} : k_{22} : k_{33} = 1 : 1 : 20\,.$$

This value is far away from the measured values [6, 7]

$$k_{11} : k_{22} : k_{33} = 1.6 : 1 : 3.5\,.$$

If we calculate the volume which one molecule occupies, we get ~ 7.2 Å for the width, assuming that the box has the length of a molecule ($l \sim 17$ Å). The elastic constants now become:

$$k_{11} : k_{22} : k_{33} = 1 : 1 : 5.5\,.$$

If we assume, as Saupe [6] did, that m molecules form a steric unit in order to reduce the steric hindrance, we find, for $m = 2$:

$$k_{11} : k_{22} : k_{33} = 1 : 1 : 1.4\,.$$

The calculated value of k_{33} is:

$$k_{33} = 2.7 \cdot 10^{-6}\ \text{dyne}$$

for

$$A = 13 \cdot 10^{-9}\ [\text{erg cm}^6]^{(3)}\,,\quad V_n = 2.25\ \text{cm}^{3(3)}\,,$$
$$\overline{P}_2 = 0.6\,,\quad m = 2 \quad \text{and} \quad Z^2 \sim (17\ \text{Å})^2\,.$$

The measured value of k_{33} is approximately $1.2 \cdot 10^{-6}$ dyne [6, 7].

Another approach can be made if we introduce a unit cell which describes the short range order structure. Then we get for the mole volume

$$V_n = (x^2 \cdot z)\,L/m\,. \tag{9}$$

In this formula m describes the number of molecules per unit cell and x and z are appropriate average distances in the x, y ($=x$) and z direction. If we assume that only the nearest neighbor interaction is important, then with Eqs. (8) and (9) we are able to find two sets of equations.

First we eliminate the mole volume V_n so that we obtain an equation which de Gennes [8] derived from dimensional analysis

$$k_{11} = \tfrac{3}{2}\,(-\overline{D}/z)\,,$$
$$k_{33} = \tfrac{3}{2}\,(z/x)^2\,(-\overline{D}/z)\,. \tag{10}$$

These equations can be very helpful for estimating the absolute value of the elastic constants from molecular properties, as we will show later. But the temperature dependence of the elastic constants can be better discussed if only (z/x) occur in the formula because then the effect of thermal expansion at a constant symmetry is eliminated. In this case we derive from Eqs. (8) and (9) a reduced elastic constant which first was introduced by Saupe [6].

$$C_{ii} = k_{ii}\,V_n^{7/3}\,\overline{P}_2^{\,-2} = 3/2\,(L \cdot m^{-1} \cdot \gamma_{ii}^{-2})^{1/3} \cdot A$$
$$i = 1, 2, 3 \tag{11}$$
$$\gamma_{11} = \gamma_{22} = z/x \qquad \gamma_{33} = (x/z)^2\,.$$

This reduced elastic constant, C_{ii}, is independent of the temperature if there are no abnormal changes in long range order ($A = \text{const}$) and if there are no structural changes in short range order ($m = \text{const}$ and $\gamma_{ii} = \text{const}$). The curvature elastic constants k_{ii} of a nematic liquid crystal are therefore proportional to the square of the order parameter and inversely proportional to the mole volume with the power 7/3.

If we are far enough away from the nematic to isotropic as well as the nematic to smectic phase transitions, only small changes in short range order structure may be expected; therefore C_{ii} should be independent of temperature. Near phase transitions where rearrangements of short range order can occur, we expect a temperature dependence in C_{ii}. For 4,4′-di(methoxy)-azoxybenzene (PAA) the elastic constants as well as the reduced elastic constants are shown in Fig. 3 as a function of temperature [7]. As we see, the reduced elastic constants are independent of the temperature far away from the nematic to isotropic phase transition, as expected.

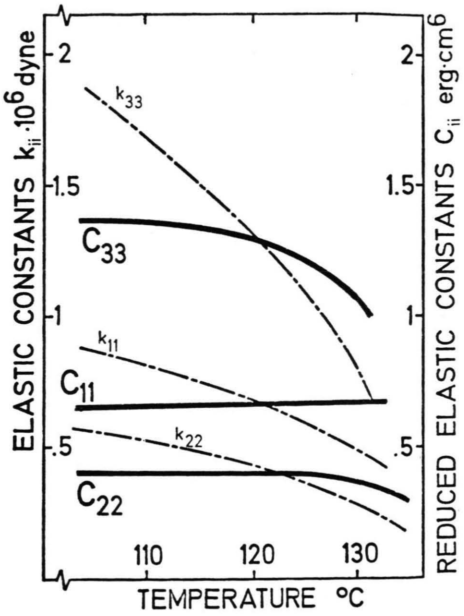

Fig. 3. Elastic and reduced elastic constants of PAA versus temperature (see Ref. 7).

Near the nematic to isotropic phase transition, C_{33} shows a large temperature dependence, whereas C_{11} and C_{22} are almost temperature independent. This strong temperature dependence of C_{33} can be

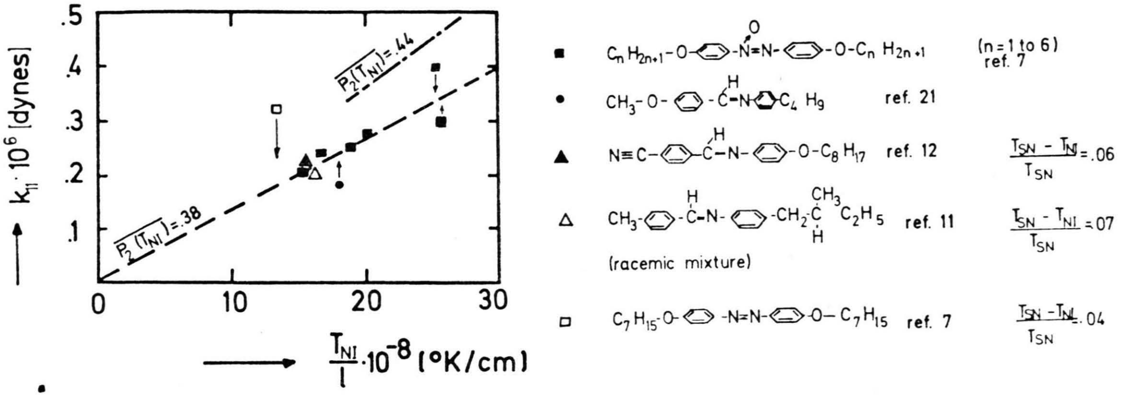

Fig. 4. Comparison between the measured splay elastic constant k_{11} at T_{NI} and the calculated k_{11} as a function of the molecular length.

explained because structural changes in short range order are more strongly weighted in C_{33} than in C_{11} and C_{22} [see Equation (11)]. The predicted temperature dependence of C_{33} is in accordance with experiment, but on the other hand C_{11} and C_{22} should increase with increasing temperature. However, experiments show only a small temperature dependence of C_{11} which is actually opposite to be aforementioned description.

Another explanation of the strong temperature dependence of C_{33} near the nematic to isotropic phase transition is the fluctuation of the order parameter $\overline{P_2}$. Such fluctuations give rise to some uncertainty in the preferred direction. Therefore we can expect that those elastic constants which have a connection to the preferred direction should show an abnormal temperature dependence near the nematic to isotropic phase transition. Equation (7) shows that from the main elastic constants only the bend elastic constant k_{33} is connected to the preferred z-direction. Therefore only k_{33} should have an abnormal temperature dependence as it was observed in experiment.

The pretransitional effects of the elastic constants near the smectic phase are not included in this calculation. Theory [9, 10] and experiment were described elsewhere [7, 11–14].

The elastic constants can also be described by the nematic mean field $\bar{D}$ and the dimensions of the unit cell as we see from Equation (10). The average value of the nematic mean field at the nematic to isotropic phase transition is given by the mean field theory [see Eq. (3 c)]. The splay and twist elastic constants depend only on the z-direction of the unit cell which we assume to be proportional to the molecular length. On the other hand the abnormal temperature dependence of k_{11} and k_{22} near the nematic to isotropic phase transition is small so that the extrapolated value $k_{11}(T_{\mathrm{NI}})$ of the experimental data can be compared with the theoretical value.

Figure 4 shows the extrapolated elastic constant k_{11} (T_{NI}) for several different nematic molecules. The length of the molecules was determined from a molecular model. We see that the elastic constant can be rather well described by the inverse of the molecular length. But if we take the order parameter $\overline{P_2(T_{\mathrm{NI}})}$ which the Maier-Saupe theory [3] predicts $\overline{P_2(T_{\mathrm{NI}})} = .44$ then the predicted elastic constants are in general too large as we can see in Figure 4. This is not surprising because the order parameter $\overline{P_2(T_{\mathrm{NI}})}$ predicted by the Maier-Saupe theory is too large compared with measured ones. The enlarged Maier-Saupe theory (Humphries-James-Luckhurst theory) [15] never predicts a universal order parameter for all nematics as the Maier-Saupe theory [3]. Therefore we should have measurements of the order parameter in order to compare theory and experimental values of the elastic constants. But since not enough order parameter measurements are available we make the best fit for $\overline{P_2(T_{\mathrm{NI}})}$ to the elastic constant data, which then gives .38. This value is close to the value which Humphries et al. [15] found for several compounds.

In Fig. 4 there are still deviations of the elastic constants from the straight line which we will discuss in more detail. For the $n = 1$ and 2 homolog of the alkyloxyazoxybenzenes (■) the degree of order of $n=2$ homolog is about 10% higher than for the $n=1$ homolog[5]. This means that the $n=2$ homolog fits the theory much better as shown in Figure 4. For MBBA (●) Jen et al.[16] found an extrapolated value for $\overline{P_2(T_{\mathrm{NI}})}$ of about .32, so that this nematic compound also fits the theory quite well. McMillan's mean field theory[17] for the smectic A phase leads to an enlarged order parameter if the nematic temperature range becomes small enough. Therefore heptyloxyazobenzene (□) with its relatively small nematic temperature range also fits theory better than Fig. 4 illustrates. Figure 4 shows that the measured elastic constants versus molecular length fit quite well the Maier-Saupe theory if the degree of order is known or can be estimated. Now we have the possibility to predict quite well the elastic properties for a nematic molecule where the phase diagramm is known.

However, we have to be careful if the molecules are very long, because we based our calculation on the mean field approximation. For very long molecules the Onsager theory which includes the steric hindrance can describe the nematic phase better than the mean field approximation[18]. For example, for PAA the mean field approximation is quite a good approximation since the measured Grüneisen constant is about 3.7[19]. For pure van der Waals interaction (mean field) we expect a Grüneisen constant of 2 and for hard core interaction (Onsager) infinity[19].

4. Solid Crystal

The elastic constants of a solid crystal can be derived with the lattice theory[20] which is similar to the mean field approximation in a nematic liquid crystal. In this chapter, we will show the isomorphism in the elastic constants between a solid and a nematic liquid crystal.

If the displacement (u_2-u_1) is small in comparison with the lattice constant a, the displacement energy may be written in Hooke's law approximation:

$$\beta/2\,(u_2-u_1)^2+\dots$$

β is the currature of the elastic potential.
The energy density for a homogeneous pure strain is then:

$$u=\tfrac{1}{2}\,a^2\,\frac{L}{V_n}\,\beta\,(e_{xx}^2+e_{yy}^2+e_{zz}^2)+\dots \qquad (13)$$

where e_{xx}, e_{yy} and e_{zz} are strain components. The energy density can also be written with phenomenological coefficients c:

$$u=\tfrac{1}{2}\,c\,(e_{xx}^2+e_{yy}^2+\epsilon_{zz}^2)+\dots \qquad (14)$$

A comparison between Eqs. (13) and (14) gives the elastic constant, c:

$$c=a^2(L/V_n)\,\beta\,. \qquad (15)$$

This expression for the elastic constant c is isomorphic with the expression for the elastic constants of a nematic liquid crystal [Equation (8)]. Equation (15) can be changed

$$c\cong\beta/a \qquad (16)$$

if the mole volume is expressed by the lattice constant. Equation (16) is again isomorphic with Equation (11). Since $\overline{D}$ in Eqs. (8) and (11) and β in Eqs. (15) and (16) have different dimensions, the dimensions of the elastic constants of a solid crystal and a liquid crystal are different.

Acknowledgements

The author would like to thank all members of the Division, especially R. B. Meyer, for their kind hospitality during his stay at Harvard. This research was sponsored by the National Science Foundation and by the Division of Engineering and Applied Physics, Harvard University.

---

[1] J. Nehring and A. Saupe, J. Chem. Phys. **54**, 337 [1971].

[2] F. C. Frank, Disc. Faraday Soc. **25**, 19 [1958].

[3] W. Maier and A. Saupe, Z. Naturforsch. **14a**, 882 [1959]; **15a**, 287 [1960].

[4] See besides Ref. 3 L. D. Landau and E. M. Lifshitz, "Statistical Physics", Addison-Wesley Publishing Comp. Reading, Menlo Park, London 1970.

[5] A. Saupe, Angew. Chem. Internat. Edit. **7**, 97 [1968].

[6] A. Saupe, Z. Naturforsch. **15a**, 810 and 815 [1960].

[7] H. Gruler, Z. Naturforsch. **28a**, 474 [1973].

[8] P. G. de Gennes, "The Physics of Liquid Crystals", Oxford University Press, London 1974.

[9] K. K. Kobayashi, Mol. Cryst. & Liquid Cryst. **13**, 137 [1971].

[10] P. G. de Gennes, Solid State Comm. **10**, 753 [1972].

[11] L. Cheung and R. B. Meyer, Phys. Lett. **43A**, 261 [1973].

[12] L. Cheung, R. B. Meyer, and H. Gruler, Phys. Rev. Lett. **31**, 349 [1973].

[13] P. E. Cladis, Phys. Rev. Lett. **31**, 1200 [1973].

[14] M. Delaye, R. Ribotta, and G. Durand, Phys. Rev. Lett. **31**, 443 [1973].

[15] R. L. Humphries, P. G. James, and G. R. Luckhurst, J. Chem. Soc., Faraday Trans. II. **68**, 1031 [1972].

[16] S. Jen, N. A. Clark, and P. S. Pershan, Phys. Rev. Lett. **31**, 1552 [1973].

[17] W. L. McMillan, Phys. Rev. A **4**, 1238 [1971].

[18] L. Onsager, Ann. N. Y. Acad. Sci. **51**, 6271 [1949].

[19] J. R. McColl, Phys. Lett. **38A**, 55 [1972].

[20] See, for example, C. Kittel, Introduction to Solid State Physics, J. Wiley & Son, Inc., New York 1963, pp. 85.

[21] I. Haller, J. Chem. Phys. **57**, 1400 [1972]; H. Gruler, T. J. Scheffer, and G. Meier, Z. Naturforsch. **27a**, 966 [1972].