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An X-Ray Diffraction Study of Nematic Liquid Crystalline and Liquid *p*-Methoxybenzylidene-*p*′-Cyanoaniline[†]

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Abstract—The nemotogenic compound *p*-methoxybenzylidene-*p*′-cyanoaniline in the nematic and isotropic liquid states has been studied by X-ray diffraction. A structure is proposed by comparing calculated intensities of a model with experimental diffraction intensities. The structure is comparable to the "herringbone" packing observed in many organic crystals. The procedure presented in this paper illustrates the practicability of using the method of comparison of experimental intensities with those calculated for a particular structural model. Comparisons of the experimental X-ray diffraction intensities and the radial distribution functions calculated from the intensities at different temperatures indicate an essentially unchanged structure throughout the nematic range but a gross structural change upon passing to the isotropic liquid state.

Introduction

X-Ray diffraction studies of the nematic liquid crystalline structure are few in number. Early workers[1–7] were concerned primarily with qualitative interpretations of the diffraction patterns arising from the nematic structure under various conditions and with comparisons of the nematic and isotropic liquid structures. The first attempt at a direct analysis of the X-ray diffraction pattern from a nematic sample (anisaldazine) was by

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Shaw[8] in 1957. Shaw used the atomic radial distribution function (RDF) technique of Warren, Krutter, and Morningstar,[9] but was unable to obtain sufficient definition of the function in the region of intermolecular interactions and was, therefore, unable to make a definitive structural interpretation. This is a common problem in analyzing X-ray diffraction data from organic samples by electronic or atomic RDF techniques.

If a molecular RDF technique can be applied to a structure, the resolution in the intermolecular region should be much better. Two types of molecular RDF's have been developed; these are the spherical coordinate and the cylindrical coordinate radial distribution functions.

Of the spherical coordinate techniques, only the Menke[10]-Zachariasen[11] technique is directly applicable, and then only to systems composed of independent, spherical molecules.[12–14] The cylindrical coordinate molecular RDF is applicable only in special cases of samples composed of rod-like units which are symmetrical about their long axes. In addition, these units must be mutually parallel in the irradiated volume of the sample. The cylindrical coordinate RDF has been applied by Chistyakov and Vainshtein[15–17] to nematic structures but, even though the parallelism exists between molecules within the nematic clusters, the clusters are randomly oriented, and special techniques are necessary to gain structural information from the X-ray diffraction data of these systems.

The process of postulating a structural model, of calculating the X-ray diffraction intensities that would be produced by this model, and of comparing these intensities with the experimentally observed ones is, in theory, the simplest indirect method for arriving at a structure of a nematic liquid crystal. In practice, however, much labor is involved, but for a nematic system for which partial structural information is known (i.e., the parallelism of the molecules), this method has proven to be practical. This paper presents the results of relating the calculated intensities of a model with the experimental intensities of the nematic state of *p*-methoxybenzylidene - *p*′ - cyanoaniline, $N{\equiv}CC_6H_4N{=}CH{-}C_6H_4OCH_3$, (MBC). Qualitative comparisons of structure as a function of temperature over the nematic range and in the isotropic liquid state are also made from the X-ray diffraction intensities and from electron density (actually atom-pair) RDF's.

Experimental

X-ray diffraction data were taken with a θ–θ diffractometer. The sample was contained in a cup with sample-cavity dimensions of $2 \times 2 \times 0.4$ cm. The cup was inside a heater which maintained the sample temperature within $\pm \frac{1}{4}°$ of the desired temperature. MBC has a low enough vapor pressure in the nematic and liquid (low temperature) states so that no cover on the sample cup was necessary.

MoK$_\alpha$ radiation was used. A Zr–Y balanced filter system (with an additional foil of Al to enhance the balance) was used to monochromate the radiation, and a pulse-height analyzer set to pass 13–22 keV pulses (MoK$_\alpha$ energy 17.5 keV) eliminated wavelengths much removed from the K$_\alpha$ peak where the filters were apt to be poorly balanced. The balanced filters were in the detected beam, and a correction for partially filtered incoherent scattering was applied.[12] The usual polarization and absorption corrections (Milberg [18]) were made.

Three temperatures were investigated; these were 107°, 117° and 120°C. The nematic range of MBC is 106–118°C. The temperatures investigated thus represent the extremes of the nematic range and the isotropic liquid just beyond the nematic–isotropic point. Figure 1 shows the intensities of diffraction as a function of angle at the three temperatures.

Results and Discussion

The intensity calculations for proposed structural models having n atoms were made with the Debye equation

$$I(s) = \sum_{1}^{n} \sum_{1}^{n} f_i f_j \frac{\sin sr_{ij}}{sr_{ij}} \qquad (1)$$

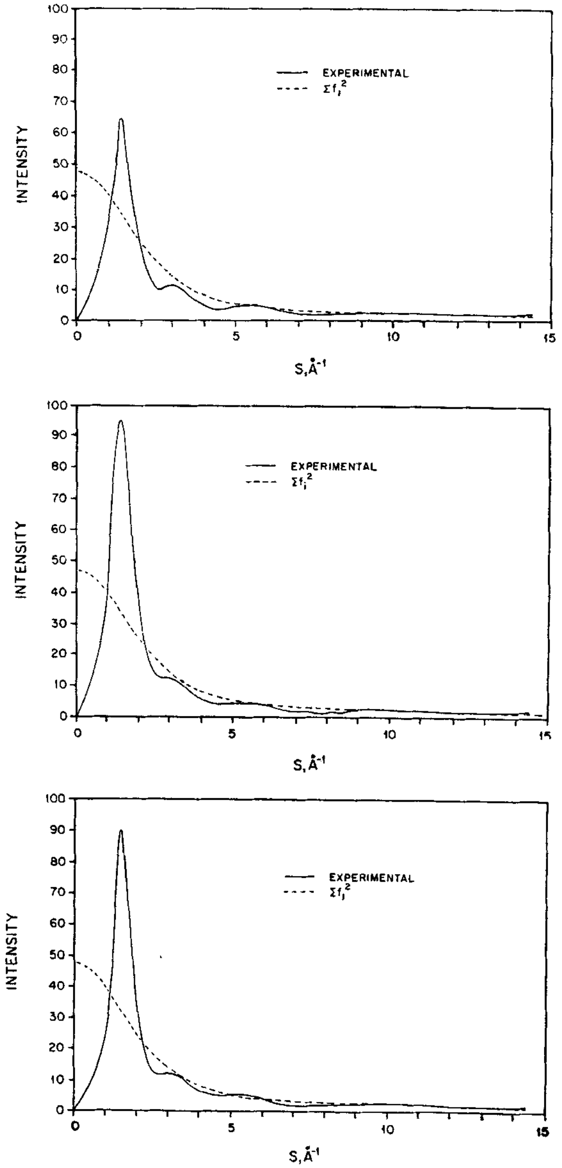


Figure 1. Experimental intensities for MBC at 107°, 117°, and 120°. The temperature increases upward with the bottom figure representing a temperature of 107°.

in which the f's are the atomic scattering factors, $s=(4\pi/\lambda)\sin\theta$, and r_{ij} is the distance between the ith and jth atoms. It is expedient to separate the terms for which $i\neq j$, giving Eq. (2),

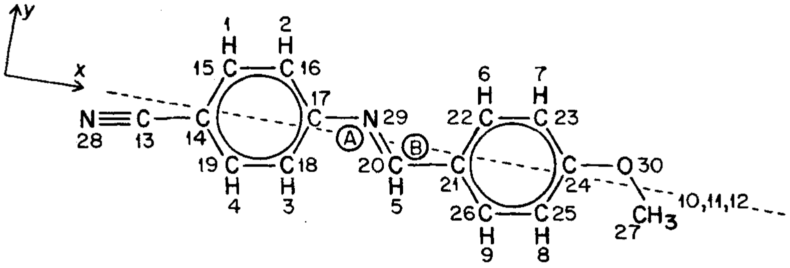
$$I(s) = \sum_1^n f_i^2 + \sum_{\substack{1 \\ i\neq j}}^n \sum_1^n f_i f_j \frac{\sin sr_{ij}}{sr_{ij}} \tag{2}$$

Since the ijth term and the jith term are equal, the number of terms is reduced from n^2 in Eq. (1) to $(n^2+n)/2$ in Eq. (2).

Even though MBC is one of the simplest of nematogenic compounds, it contains thirty atoms (including the hydrogens). Thus, for a model containing, say, seven molecules, there are 210 atoms, and the number of terms involved in Eq. (2) at each value of s is 22155. It is obvious that a high speed computer is essential to make these calculations practical.

A computer program system was developed to make the intensity calculations and the comparisons. The first step in the computer program system was to calculate the coordinates of all atoms in the structural model from the coordinates of the atoms in a reference molecule and the translations and rotations of all other molecules with respect to this molecule. The second step was to calculate the $(n^2+n)/2$ interatomic distances, the third to calculate the intensities, and the fourth to normalize the calculated intensities to the experimental intensities for comparison. The four steps were performed automatically.

In order to make the intensity calculations as described above, the coordinates of all atoms in the reference molecule, and thus its configuration, must be known. The configurations of molecules similar to MBC (i.e., aromatic anils) have been reported.[19-22] The most direct evidence (X-ray crystal structure analysis of *N*-5-chlorosalicylideneaniline [22]) indicates that MBC is a planar molecule as shown in Fig. 2. *N*-5-Chlorosalicylideneaniline is structurally quite similar to MBC. The atomic coordinates for the reference molecule of MBC (cf. Fig. 2 for the numbering system) are listed in Table 1. These coordinates are based on the bond lengths and angles given in Table 2. The three methyl hydrogens were assumed to be at the average position for a freely rotating methyl group.



$N{\equiv}CC_6H_4N{=}CHC_6H_4OCH_3$

p-methoxybenzylidene-p'-cyanoaniline

Figure 2. Molecular configuration of MBC. The molecular axis is indicated.

The final model chosen as a possible structure of nematic MBC was suggested by the "herringbone" packing found in many organic crystals. The model is shown in Fig. 3, and the molecular translations and rotations relative to the reference molecule (#1) are given in Table 3. In Fig. 3, the view is into the long axes of the

TABLE 1 Atomic Coordinates for *p*-Methoxybenzylidene-*p*′-Cyanoaniline

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
1	−1.600	1.895	0	16	0.477	1.317	0
2	0.845	2.339	0	17	1.382	0.251	0
3	1.614	−1.892	0	18	0.910	−1.064	0
4	−0.831	−2.336	0	19	−0.467	−1.315	0
5	3.329	−1.514	0	20	3.689	−0.503	0
6	4.732	2.877	0	21	5.146	−0.239	0
7	7.191	3.324	0	22	5.613	1.076	0
8	8.136	−1.870	0	23	7.000	1.328	0
9	5.676	−2.317	0	24	7.900	0.262	0
10	10.125	−1.016	0	25	7.433	−1.053	0
11	10.126	−1.016	0	26	6.046	−1.305	0
12	10.124	−1.016	0	27	9.950	−0.723	0
13	−2.791	−0.507	0	28	−3.931	−0.714	0
14	−1.373	−0.249	0	29	2.819	0.512	0
15	−0.900	1.066	0	30	9.239	0.505	0

TABLE 2 Pertinent Bond Lengths and Angles

C—H (all)	1.084	C—C (phenyl)	1.395	C—C (ϕ-C≡N)	1.440
C—C (ϕ-C=N)	1.407	C—N (ϕ-N=C)	1.450	C=N	1.340
C≡N	1.158	C—O (ϕ-O)	1.360	C—O (CH_3—O)	1.420

All bond lengths are in Ångströms.

All bond angles were taken to be 120° except for the ϕ—C≡N (180°) and the ϕ—O—CH_3 (109°).

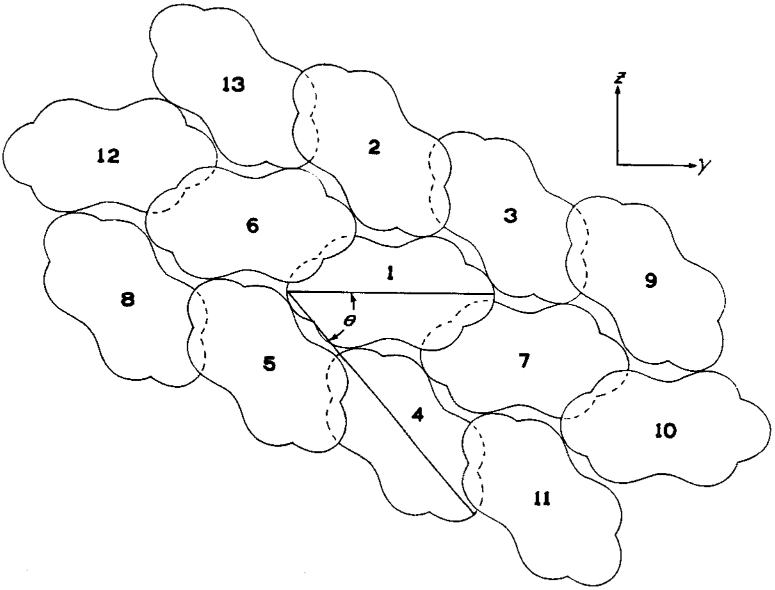


Figure 3. Cross-sectional view of MBC molecules in the "herringbone" packing arrangement. The view is into the long axes from the positive x direction.

molecules from the positive x direction. The long axis of the reference molecule is coincident with the x axis and passes through the centers of both benzene rings (cf. Fig. 2). The relative translations along the long axes were chosen to take maximum advantage of the offset in the molecule caused by the C=N central bond.

In using the Debye equation to calculate intensities, it is common to employ a correction for thermal vibrations of the atoms. For

TABLE 3 Relative Molecular Translations and Rotations for the Basic "Herringbone" Structure

Molecule	Δx (Å)	Δy (Å)	Δz (Å)	θ^0
1	0	0	0	0
2	1.5	−0.6	4.5	49
3	−1.5	3.8	2.4	49
4	−1.5	0.6	−4.5	49
5	1.5	3.8	−2.4	49
6	3.0	−4.4	2.1	0
7	−3.0	4.4	−2.1	0
8	−1.5	−8.3	−0.3	49
9	1.5	8.3	0.3	49
10	0	8.9	−4.2	0
11	1.5	5.1	−6.6	49
12	0	−8.9	4.2	0
13	−1.5	−5.1	6.6	49

the large numbers of atoms involved in models such as used in this work, it is not practical to try to include a correction term to represent the fluctuation of each interatomic distance. Rather, a

TABLE 4 Relative Molecular Translations and Rotations for the "Randomized Herringbone" Structure

Molecule	Δx (Å)	Δy (Å)	Δz (Å)	θ^0
1	0	0	0	0
2	1.7	−0.4	4.4	51.0
3	−1.3	4.0	2.5	49.6
4	−1.4	0.6	−4.5	48.0
5	1.6	−3.8	−2.3	49.6
6	3.2	−4.4	2.0	1.0
7	−2.8	4.6	−2.2	−2.0
8	1.5	8.0	0	45.0
9	−1.5	−8.5	−0.5	50.0
10	0	8.9	−4.3	0.5
11	1.7	5.2	−6.7	49.0
12	0.2	−9.0	4.2	0
13	−1.5	−5.1	6.6	48.0

slight random shift of the molecules from their equilibrium positions (the positions indicated in Table 3) was used. The shifted-molecule positions are given in Table 4.

Figure 4 shows the calculated intensities for seven-, nine-, and thirteen-molecule structural models. The solid curve is the experimental X-ray diffraction intensity curve for MBC at 107°. The structures include the molecules one through seven, one through nine, and one through thirteen of Fig. 3 and Table 4. The calculated intensities outside the major peak region are almost identical, and only the thirteen-molecule case is shown in its entirety. The effect of increasing the number of molecules is to produce a better match between the calculated and experimental intensities. The calculations were stopped with thirteen molecules because of limits in the computer memory; the trend is well established, and indicates the proposed structure to be a reasonable one.

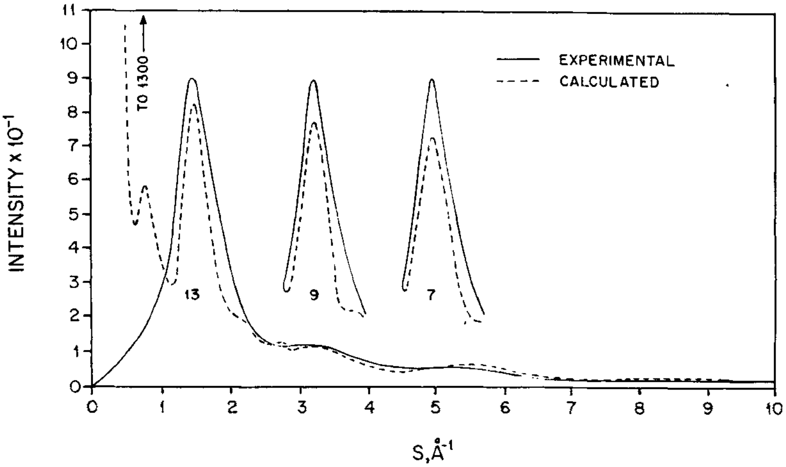


Figure 4. Calculated intensities for seven-, nine-, and thirteen-molecule "herringbone" structures compared to the experimental intensities (107°).

The maximum in the calculated intensity curve of Fig. 4 at about $s = 0.8$ Å^{-1} caused some concern until it was shown that it was due to the omission of the "continuum" of electron density outside the structural unit for which the intensities were calculated.[23] The continuum intensity, I_c, can be calculated approximately from

$$I_c = -\left\{\frac{3\rho V(\sin sR - sr\cos sR)}{(sR)^3}\right\}^2,$$

where ρ is the average electron density, V is the volume and R is the radius of the (spherical) structural unit. Figure 5 shows the continuum intensity curve for an MBC structural unit having a radius of 7.5 Å (a reasonable radius for the structural models considered here). It is obvious that the model which we propose is not spherical, but as we increase the number of molecules in the cluster we approach spherical geometry. The intensities represented in Figs 4 and 5 are not normalized to the same units, but it is evident that the negative peak at about 0.8 $Å^{-1}$ in Fig. 5 would tend to cancel the positive one at the same position in Fig. 4.

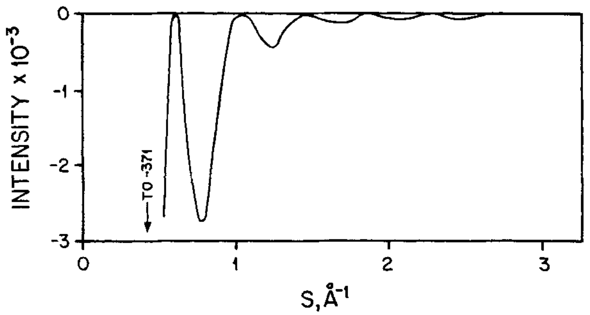


Figure 5. Continuum intensity curve for electron density = 0.345 $e^2/Å^3$ and $R = 7.5$ Å.

We return to Fig. 1 to consider the intensities for the three temperatures investigated. The curves for the system at 107° and 117° are quite similar, but the 120° curve is considerably less intense at the main peak. This suggests that the structure is essentially constant throughout the nematic range except for increased molecular separations due to increased temperature as suggested by the slight shift of the 117° curve to smaller s values and that there is a gross structural change upon passing to the isotropic liquid state.

Electron-density RDF's were calculated for the three temperatures from the following equation.

$$D(r) = 4\pi r^2 \rho_0 + \frac{2r}{\pi} \int_0^{s_m} si(s) \sin rs \, ds$$

In this equation ρ_0 is the average density in electrons^2/Å^3 and $i(s) = (I_{\text{exp}} - \sum f_i^2)\, M(s)$. I_{exp} is the coherent experimental intensity and $M(s)$ is a modification function used to sharpen the peaks of the distribution function. $M(s)$ was found to be useful in the form $[f_C(0)/f_C(s)]^2$, representing the ratio of the squares of the scattering factors for carbon at zero and s.

Comparison of the RDF's in Fig. 6 shows a closer approach of the RDF's to the average (the dashed curves) as the temperature is increased as would be expected, but there is a greater change in going from 117° to 120° than in going from 107° to 117°. When one considers the density change (cf. Fig. 7) in going from 107° to 117° (1.093 − 1.083 = 0.010 g/cm^3) is greater than that in going from 117° to 120° (1.083 − 1.076 = 0.007 g/cm^3, one would expect less change in the latter case than in the former for the same type of structure. This again suggests an essentially constant structure throughout the nematic range and a gross structure change upon passing into the isotropic liquid.

The kind of structural change occurring at the nematic–isotropic transition is still somewhat speculative. It seems likely, however, that the change is essentially one of breaking up the clusters so that there are only a few molecules associated in any ordered group. This conclusion is drawn from the fact that the X-ray diffraction curves for the nematic and isotropic states are similar in all respects except for the intensities of the peaks. On the basis of the trend shown in Fig. 4, a structural model containing fewer than seven molecules would completely explain the intensity curve for 120°.

The molecular packing configuration deduced in this work is not claimed to be a complete structural analysis, but the proposed

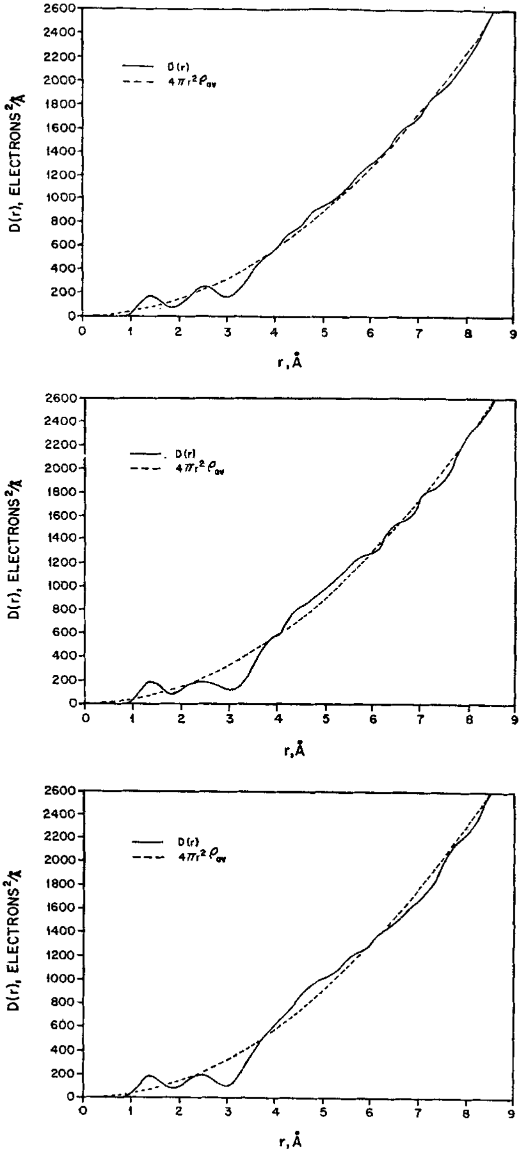


Figure 6. RDF's for MBC at 107°, 117°, and 120°. The temperature increases upward with the bottom figure representing a temperature of 107°.

structure is a reasonable one based on the present knowledge of the nematic state. The practicability of deducing at least a first-approximation structure by the intensity comparison method has been shown. The structure could be verified by more sophisticated and complicated techniques such as discussed by Fournet.[14]

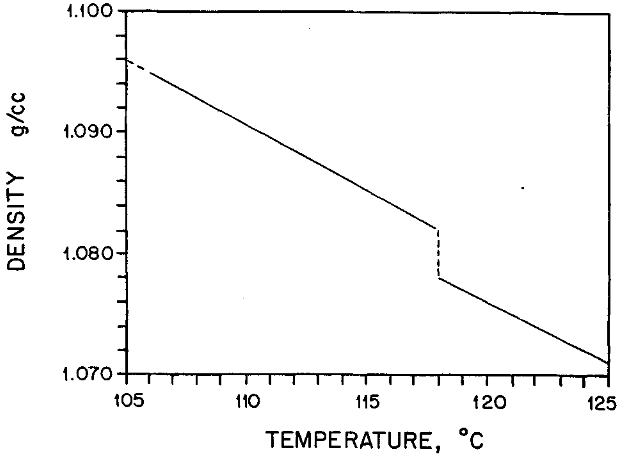


Figure 7. Density of MBC as a function of temperature.

In order to make a completely reliable deduction of the molecular packing in any fluid sample, it is necessary to know the configuration of the atoms within the individual molecules in the state in which they are being investigated. The main concern in the present research is a possible rotation about the central –C=N– bond (cf. Fig. 2). Work is presently being done in our laboratories using nuclear magnetic resonance to elucidate the configuration about the –C=N– group in aromatic anils in the nematic state.

REFERENCES

1. Huckel, E., *Physik. Z.* **22**, 561 (1921).
2. Kast, W., *Naturwissenschaften* **21**, 737 (1933); *Ann. Physik* **19**, 571 (1934); *ibid.* **83**, 418 (1927); *Z. Physik* **71**, 39 (1931).
3. Katz, J. R., *Naturwissenschaften* **16**, 758 (1928).
4. Glamann, P. W., Herrmann, K., and Krummacher, A. H., *Z. Krist.* **74**, 73 (1930).

5. Stewart, G. W., *Trans. Faraday Soc.* **29**, 982 (1934); *J. Chem. Phys.* **4**, 231 (1936); *Phys. Rev.* **38**, 931 (1931).
6. Herrmann, K. and Krummacher, A. H., *Z. Physik* **70**, 758 (1931).
7. Herrmann, K., Krummacher, A. H., and May, K., *Z. Physik* **73**, 419 (1931).
8. Shaw, W. G., Dissertation, Cincinnati, 1957.
9. Warren, B. E., Krutter, H., and Morningstar, O., *J. Am. Ceram. Soc.* **19**, 202 (1936).
10. Menke, H., *Physik. Z.* **33**, 593 (1932).
11. Zachariasen, W., *Phys. Rev.* **47**, 277 (1935).
12. Gulrich, L. W., Dissertation, Kent State University, 1967.
13. de Vries, A., *J. Chem. Phys.* **46**, 1610 (1967).
14. Fournet, G., *Handbuch der Physik* **32**, 238 (1957).
15. Chistyakov, I. G. and Vainshtein, B. K., *Kristallografiya* **8**, 570 (1963).
16. Vainshtein, B. K. and Chistyakov, I. G., *Dokl. Akad. Nauk SSSR* **153**, 326 (1963).
17. Chistyakov, I. G., *Zh. Strukt. Khim.* **5**, 550 (1964).
18. Milberg, M. E., *J. Appl. Phys.* **29**, 64 (1958).
19. Favini, G. and Gamba, A., *J. Chim. Phys.* **62**, 995 (1965).
20. Jaffé, H. H., Yeh, S., and Gardner, R. W., *J. Mol. Spectr.* **2**, 120 (1958).
21. Ebara, N., *Bull. Chem. Soc. Japan* **34**, 1151 (1961).
22. Bregman, J., Leiserowitz, L., and Schmidt, G. M. J., *J. Chem. Soc.* 2068 (1964).
23. de Vries, A., personal communication.