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X-ray Photographic Studies of Liquid Crystals†
IV. The Isotropic, Nematic, and Smectic A Phases of Some 4-Alkoxybenzal-4′-Ethylanilines

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Abstract—From X-ray photographs of some 4-alkoxybenzal-4′-ethylanilines ($C_nH_{2n+1}O—C_6H_4—CH{=}N—C_6H_4—C_2H_5$; $n = 5, 6, 7$) we have calculated the average intermolecular distance (D) between neighboring parallel molecules in the isotropic, nematic and smectic A phases, the apparent length (l) of the molecules in the isotropic phase, and the thickness (d) of the smectic layers. All D values for the smectic and nematic phases are between 4.94 and 5.03 Å. In the isotropic phase, the slopes of the D versus t plots for C_6 and C_7 (0.0024 and 0.0028 Å/°C, respectively) are approximately equal to those reported earlier, but for C_5 the slope is somewhat larger (0.0038). The slopes of the D versus t plots for the nematic phase are of the order of 0.01 Å/°C, and for the smectic phase of C_7 the slope is about half of this; for the nematic phases the slope appears to increase with decreasing length of the stability range. All l versus t plots were definitely concave. Extrapolation of the curves to the N–I point yielded l values very close (within 0.4 Å) to lengths calculated from molecular models. For C_7, d is apparently constant, and about 1.5 Å less than the molecular length.

1. Introduction

The work reported in this paper is part of a continuing program for the quantitative determination of molecular parameters in liquid crystals. The two molecular parameters which generally can be determined by X-ray diffraction methods are the apparent length of the molecule (l) or, in the smectic phases, the thickness of the smectic

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layers (d), and the average distance between the long axes of neighboring molecules (D). These parameters are related to the two major diffraction maxima on the X-ray photographs, the " inner ring " and the " outer ring ", respectively. The theory of the relationship between the molecular parameters and the positions of the diffraction maxima has been discussed in previous papers,$^{(1,2)}$ and will not be repeated here.

In this paper we shall concern ourselves with the l, d, and D values obtained from the isotropic, nematic, and smectic A phases of three 4-alkoxybenzal-4′-ethylanilines (ABEA's, for short; the general formula is $RO—C_6H_4—CH{=}N—C_6H_4—C_2H_5$, with R = pentyl, hexyl, and heptyl), with special emphasis on a comparison of the data from these three compounds with each other and also with data obtained previously on other compounds. We shall denote the pentyl compound by " C_5 ", the hexyl compound by " C_6 ", and the heptyl compound by " C_7 ".

2. Experimental Procedures

X-ray diffraction photographs from samples in glass capillaries (0.5 mm diameter) were recorded on flat film, with the camera described earlier,$^{(1)}$ using Ni-filtered Cu radiation. The temperature of the sample was determined with a thermometer calibrated using melting point standards,$^{(2)}$ and the X-ray photographs were analyzed in the usual manner.$^{(2)}$

The preparation of the materials and the temperatures of the various transition points will be reported elsewhere.$^{(3)}$

3. Results

INTERMOLECULAR DISTANCES

With " intramolecular distance ", or " D ", we shall always mean here the average distance between the long axes of neighboring parallel molecules; this D is calculated from the diameter of the outer diffraction ring, using the formula$^{(1)}$ $2D \sin \theta = 1.117\lambda$ where θ is half of the diffraction angle for the outer ring and λ is the wavelength of the radiation used (1.5418 Å). D values were determined, as a function of temperature (*t*), in the isotropic and nematic phases of all three compounds and in the smectic A phase of C_7 (the other two compounds do not have a smectic A phase, only a new type of smectic phase, here called smectic X[(3)]). The data are plotted in Fig. 1. In all isotropic phases, in the nematic phase of C_6, and in the smectic A phase of C_7, three or more values were measured and the

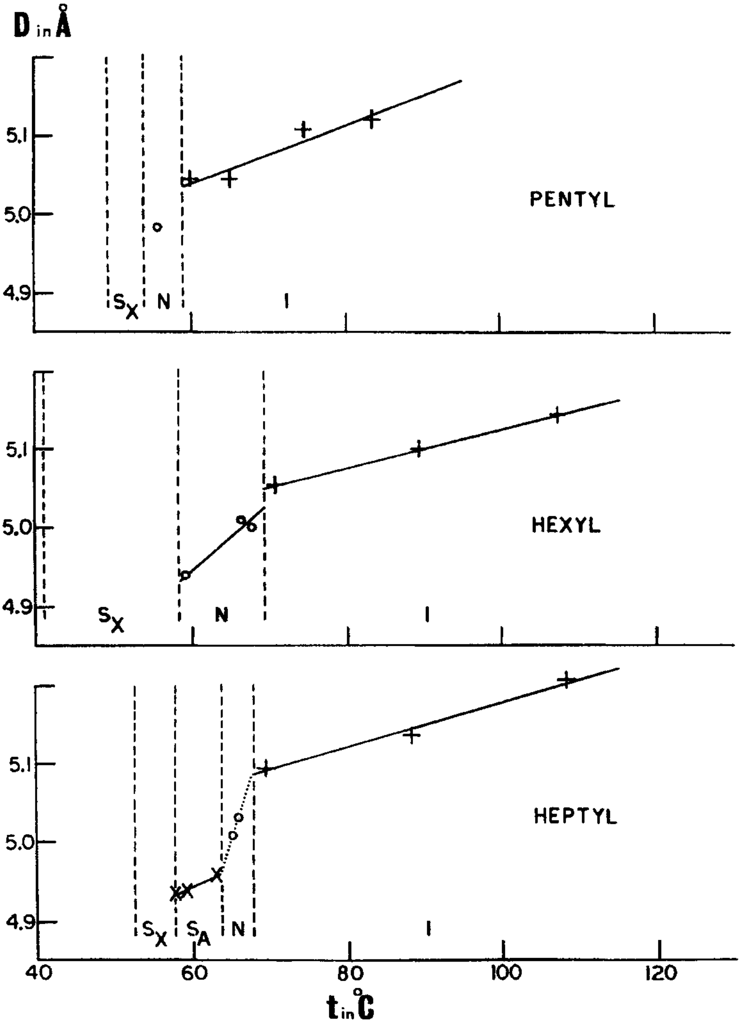

Figure 1. Plots of *D* versus *t* for C_5, C_6 and C_7. The dashed lines mark the transition temperatures; the symbols S_X, S_A, N, and I denote the phase types.

best straight line was calculated with the least-squares method; in all cases the straight lines appeared to give an adequate representation of the variation of *D* with *t*. In the graph for C_7 a dotted line is drawn from the end of the line in the smectic A phase to the beginning of the line in the isotropic phase. This line does not necessarily give a correct indication of the variation of *D* with *t* in this nematic phase,

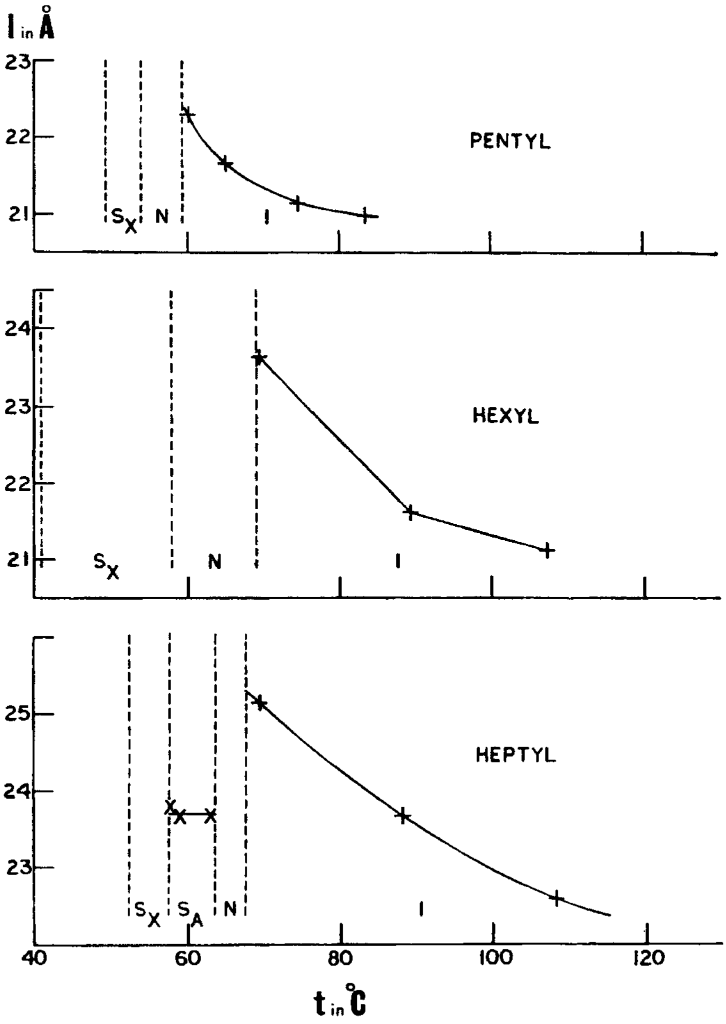

Figure 2. Plots of l versus t for C_5, C_6 and C_7 (see also legend of Fig. 1).

but it is rather remarkable that the two measured values lie so close to this line.

Apparent Molecular Length

With the "apparent molecular length" (l) in the isotropic or nematic phase we mean the average distance between the electron density minima at the ends of the molecule (the electron density of a molecule, as projected onto its long axis, has minima at the ends because there we find only hydrogen atoms and possibly some open space before the beginning of the next molecule(2)); l is calculated from the diameter of the inner diffraction ring, using the formula(2) $2l \sin \theta = 1.229\lambda$. In the nematic phase it is usually not possible to determine l because the direction and the degree of preferred orientation of the molecules generally is not known.(2)

The l values for the isotropic phases of all three compounds are given in Fig. 2. In all cases l decreases with increasing t, but the curves are definitely concave.

For the smectic A phase of C_7 the "l" data in Fig. 2 are actually values of d (the thickness of the smectic layers); d is calculated with $2d \sin \theta = n\lambda$, where n is the order of the diffraction maximum used (usually $n = 2$).

4. Discussion

In this section our main emphasis will be on a comparison of the data from the three homologues with each other and with available data from other compounds. We will discuss first the isotropic phase, next the smectic A phase, and then the nematic phase.

Isotropic Phase

Extrapolation of the l versus t curves (Fig. 2) to the N–I point gives the values of l at this point. These values are listed in Table 1, together with the l values for three other compounds and the molecular lengths (l_c) calculated from molecular models (for these models we assume the aliphatic chains to be in a zig-zag conformation, coplanar with the benzene rings; for details see Ref. 2). From Table 1 a close correlation between l and l_c is apparent. The good agreement between the l and l_c values for the three ABEA's provides additional

TABLE 1 Measured and Calculated Molecular Lengths in the Isotropic Phase at the N–I Point

Compound†	l	l_c
Pentyl	22.4 Å	22.8 Å
Hexyl	23.7	23.9
Heptyl	25.3	25.2
EEB(2)	22.0	21.6
HABP(4)	26.5	27.3
HAMP(6)	22.8	23.6

†EEB = ethyl-*p*-ethoxybenzal-*p*-aminobenzoate,
HABP = *p*-*n*-hexyloxybenzylidene-5-amino-2-butoxypyridine,
HAMP = *p*-*n*-hexyloxybenzylidene-5-amino-2-methoxypyridine.

support for our theory(2) relating the diameter of the inner diffraction ring to the molceular length, since this theory forms the basis for the calculation of l. Assuming this theory to be correct, the near equality between l and l_c indicates that in the isotropic phase at the N–I point most molecules have the same extended conformation as is generally assumed to exist in the liquid crystalline phases, and the decrease of l with t (Fig. 2) means that the molecular conformation starts deviating more and more from the extended conformation. The initial slope of the curve appears to become steeper as the molecule gets shorter (Fig. 2), but the downward trend continues longer for the longer molecules, the net result being that the total observed decrease in l increases with the chain length. This last result would be expected, since the decrease in l may be assumed to be caused by an increasing departure of the aliphatic chains from the original planar zig-zag conformation, and thus would be largest for the longest chains. Why the initial slope is largest for the shortest chain is not clear. In EEB, which has an even smaller total chain length than C_5, the initial slope† was much smaller, smaller, in fact, than the slope for any of the three ABEA's.

As pointed out under " Results ", the variation of D with t in the

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† A decrease of l with t now being well established for C_5, C_6, and C_7, we feel that most probably the correct interpretation of the l versus t data of EEB (Fig. 5 in Ref. 2) is also a curve which initially decreases with t. This curve gives for l at the N–I point the value of 22.0 Å (Table 1) which is somewhat larger than the value of 21.4 Å reported earlier.(2)

TABLE 2 Slopes† of the Least-Squares Lines for D as a Function of t, in Units of 10^{-3} Å/°C

Compound‡	Isotropic	Nematic	Smectic A
Pentyl	3.8 ± 0.9	—	—
Hexyl	2.4 ± 0.5	8.3 ± 2.2	—
Heptyl	2.8 ± 0.4	28.0 ± 22.0	4.8 ± 1.6
EEB(2)	2.5 ± 0.3	1.6 ± 1.5	0.9 ± 1.0
HABP(4)	2.2	—	4.6
BOCP(1,6)	2.7	3.3	—

† The errors given are standard deviations.

‡ BOCP = bis-(4′-*n*-octyloxybenzal)-2-chloro-1,4-phenylenediamine; for other abbreviations see Table 1.

isotropic phase (Fig. 1) could always be represented by a straight line. The slopes of these lines are listed in the second column of Table 2, together with the slopes for three other compounds. These data show that there is little difference between the various compounds. Only C_5 is somewhat of an exception, and it is interesting to note that this compound not only has the largest slope but also the largest error in the slope. This might indicate that the straight line relationship between D and t is not appropriate in this case, but more data are needed to settle this point.

In the discussion of the l data, the N–I point turned out to be of special significance because at this temperature most molecules appeared to have the extended conformation. For this reason, we have also extrapolated the D versus t lines to the N–I point and we have listed the D values so obtained in Table 3. One finds a slight increase, going from C_5 to C_6 to C_7, but all these values are still well within the range set by the values for the other compounds. If one excludes the value for EEB, there is a remarkable correlation between D and n (Table 3); the correlation coefficient for the least-squares line is 0.9994, and its slope is 0.0265 Å/atom. Data on another compound (which is at present under study) indicate, however, that EEB is not the only exception to this relationship.

From this discussion of the l and D values, the isotropic phase of the three ABEA's appears to fit in well with those of previously studied liquid crystals. This similarity is further confirmed by the values of the calculated densities at the N–I point (obtained from

TABLE 3 Values of D in the Isotropic Phase at the N–I Point

Compound	D	t_{N-I}	n†
Pentyl	5.034 ± 0.013 Å	59.0 °C	8
Hexyl	5.051 ± 0.012	69.0	9
Heptyl	5.085 ± 0.012	67.5	10
EEB(2)	4.955‡ ± 0.015	87.6	7
HABP(4)	5.134	100	12
BOCP(6)	5.296	179	18

† n = total namber of C and O atoms in the main chains in the para positions at the ends of the molecule.

‡ This value is based on the data for the isotropic liquid only; the value of 4.950 reported in Ref. 2 was based on the combined data from the nematic and the isotropic phase.

D and l, assuming six nearest neighbors(2)). We find 1.00 (C_5), 0.98 (C_6), and 0.95 gr/cm (C_7), in good agreement with other reported values.(2,7)

SMECTIC A PHASE

The slope of the D versus t line for the smectic A phase of C_7 has already been given in Table 2, together with the slopes for the smectic A phases of two other compounds, EEB and HABP. Further data on these three compounds are given in Table 4. Only one d value is given here for each compound, since we have never observed yet a significant variation of d with t for smectic A phases.

From Tables 2 and 4 emerges a close similarity between C_7 and HABP: the D versus t slopes are virtually identical, the same holds for the D values at the higher temperature given in each case (i.e., at the upper limit of the stability range of the smectic A phase), and the calculated densities are similar. EEB, on the other hand, is seen to differ significantly from the other two compounds in all three aspects. The reason for these differences lies almost certainly in the stronger lateral forces in EEB, created by the permanent dipole of the carboalkoxy group.(5) Stronger lateral forces would result in a more compact packing (smaller D, higher density) and a smaller lateral expansion (dD/dt), which is what we observe for EEB. These same forces may also be responsible for EEB's low value of D at the N–I point (Table 3), although it should be noted that its dD/dt in the

TABLE 4 Data on Smectic A Phases†

Compound	D	d	l_c	$l_c - d$	n	Density	t
Heptyl	4.935 ± 0.005 Å	23.71 ± 0.04 Å	25.2 Å	1.5 Å	10	1.074 gr/cc	57.5 °C
	4.963 ± 0.007					1.062	63.5
HABP(4)	4.903	25.42	27.3	1.9	12	1.112	86
	4.968					1.083	100
EEB(2)	4.890 ± 0.007	19.942 ± 0.008	21.6	1.7	7	1.196	71.5
	4.898 ± 0.004					1.192	80.4

† For n, see Table 3; the densities are calculated from D and d, assuming that the molecules stand perpendicular to the layers.

isotropic phase is apparently " normal " (Table 2). Interesting in this regard is that, notwithstanding the differences between EEB and C_7 and HABP, the difference in calculated density between the smectic A phase at its high temperature limit and the isotropic phase at its low temperature limit is essentially the same for all three compounds (0.11 gr/cm^3 for C_7, 0.11 for HABP, 0.13 for EEB).

Comparing the D values of C_7 (Table 4) with the width and the thickness of a benzene ring (6.7 and 3.6 Å, respectively) one sees that in C_7, just as in EEB,(2) there is no room for rotation of the molecules around their long axes. From the D value in Table 3 this also appears to be true even in the isotropic phases of the ABEA's, at least at temperatures not too far above the N–I point.

Another point of interest in Table 4 is the close similarity between the values for $l_c - d$. Apparently there is no correlation with the lengths of the aliphatic chains (n) nor with the density of the packing (D). We consider this as evidence in support of our earlier contention(2) that the difference between l_c and d is caused by a slight penetration of the ends of the molecules in each smectic layer into the two adjacent layers, rather than by folding of the aliphatic chains or tilting of the molecules.

Special attention should be called to the large values of $\mathrm{d}D/\mathrm{d}t$ for C_7 and HABP (Table 2). These values are about twice as large as those measured for the corresponding isotropic phases, whereas normally one would expect a larger expansion for the *higher* temperature phase. A similar effect has been observed by Demus *et al.*(8) in density measurements on 4-(4-n-propylmercaptobenzalamino)-azobenzol: they found for the smectic B phase a much greater thermal expansion than for the corresponding isotropic phase.

NEMATIC PHASE

As in the case of EEB,(2) values obtained for l in the nematic phases of the ABEA's varied widely, thus indicating that these nematic phases are classical nematic phases,(9) i.e., nematic phases without any order except for the near parallelism of neighboring molecules.

The D data (Fig. 1 and Table 2) indicate for the ABEA's much larger slopes of the plots of D versus t in the nematic phases than in the isotropic phases. This is in contrast with the data on EEB and BOCP (Table 2) which give essentially identical slopes for the two phases. Moreover, the slope for C_7, which has a very short stability range for the nematic phase, appears to be considerably greater than for C_6, which has a longer stability range.

These *D* data indicate that, whereas the smectic A phase and the isotropic phases of the three ABEA's appeared to be very similar to those of other compounds, the nematic phases show a different behavior. A further investigation of these phases, with X-rays as well as with other techniques, would seem to be quite worthwhile.

ERRORS IN THE DATA

The relationships between *D* and *t* have been given by us as straight lines. In a previous publication in this series(2) we gave for all such plots the standard deviation of the data points (σ_D) and the standard deviation of the slope (σ_A); both σ_D and σ_A were obtained from the least-squares treatment of the data, the relationship between them being $\sigma_A = \sigma_D/[\sqrt{\Sigma t_i^2 - (1/n)(\Sigma t_i)^2}]$, where t_i is the temperature of the i-th data point. For a small number of data points, however, the σ_D obtained from the least-squares analysis is not a good indication of the accuracy of the data; e.g., with two data points $\sigma_D = 0$, independent of the error in the measurements. To obtain a better measure of the error in the data when the number of data points is small, we have calculated σ_D as the root mean square error in *D*. This error is calculated from the differences between repeated measurements of each D_i, which are usually measurements of the same film in different directions. When this new value of σ_D was larger than the old one (obtained from the least-squares analysis), we used this new σ_D in the formula given above for the calculation of a new value for σ_A. When the new σ_D was smaller than the old one, we kept the old value of σ_A.

The values of σ_A given in Table 2 were obtained in the manner described above, combining the data from C_5, C_6 and C_7 to give one average σ_D for the nematic phases (0.014 Å) and one for the isotropic phases (0.012 Å) of these compounds. For the smectic phase of C_7 the σ_D was 0.006 Å. The data for EEB were analyzed separately and gave $\sigma_D = 0.009$ and 0.019 for the nematic and the isotropic phase, respectively.

To obtain the error in a *D* value (calculated from the least-squares line) at a given temperature t_t, we expressed the temperatures of the data points in terms of their values relative to this temperature t_t and performed the least-squares calculation; the constant B in $D = At + B$ (the formula for the least-squares line) is then equal to D at t_t, and the error in this D value is the σ_B obtained from the least-squares calculation. As described above for σ_A, we calculated a correspondingly larger σ_B if the root mean square error σ_D was larger than the σ_D obtained from the least-square analysis.

For the determination of the error in l (Fig. 2, Table 1) we calculated the root mean square error in l in the way described above, again combining the data from C_5, C_6 and C_7. The result was $\sigma_l = 0.2$ Å. For the d measurements we could not use the same procedure, however, since repeated measurements gave identical results. Assuming that d does not change with temperature, we obtained an estimate of the error by comparing the three d measurements (Fig. 2) with each other. For the average of the three measurements we obtained a root mean square error of 0.04 Å, the same value as the error obtained from the least-squares analysis of a large number of data points for EEB.(2)

It should be noted that none of the errors given above takes into account the effect of systematic errors.

5. Summary

On the basis of a comparative study of the D, d, and l values of three ABEA's and other compounds, the smectic A, nematic, and isotropic phases of the ABEA's have been discussed. The smectic A phase of C_7 is very similar to one studied earlier, and shows a relatively large increase of D with t, almost twice as large as in the corresponding isotropic phase. The nematic phases appear to be of the classical nematic type, but have very large values of dD/dt; the largest value is found for the phase with the shortest stability range. The isotropic phases show a linear increase of D with t similar to that in other compounds, and a non-linear decrease of l with t.

REFERENCES

1. de Vries, A., *Mol. Cryst. and Liq. Cryst.* **10**, 219 (1970).
2. de Vries, A., *Mol. Cryst. and Liq. Cryst.* **11**, 361 (1970).
3. Fishel, D. L. and de Vries, A., to be published.

4. de Vries, A., Annual Report to the U.S. Army under Contract DA-44-009-AMC-1074(T) (1969).
5. Gray, G. W., *Molecular Structure and the Properties of Liquid Crystals*, Academic Press, London, 1962, Chapter VIII.
6. de Vries, A., unpublished work.
7. Price, F. P. and Wendorff, J. H., *J. Phys. Chem.* **75**, 2839 (1971); ibid. **75**, 2849 (1971).
8. Demus, D., Klapperstück, M., Rurainski, R. and Marzotko, D., *Z. Phys. Chem.* (Leipzig) **246**, 385 (1971).
9. de Vries, A., *Mol. Cryst. and Liq. Cryst.* **10**, 31 (1970).