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Effect of terminal polar substituents on the nature of smectic A liquid crystals of a series of 4-(4″-octyloxybenzoyloxy)benzylidene-4′-substituted anilines

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The nature of smectic A liquid crystals and the phase transitions from smectic A to nematic phases are studied in the homologous series of 4-(4″-octyloxybenzoyloxy)benzylidene-4′-substituted anilines, in which the substituents are H, F, Cl, Br, I, NO_2 and CN. Measurements have been performed for the dipole moment of the molecule, the smectic A lattice period, the temperatures and the entropies of phase transitions, and the temperature dependence of the orientational order parameter, all of which provide information on the intermolecular pair potentials. It is shown that the introduction of a terminal polar substituent brings about counteracting contributions to the stability of the smectic A state. It is suggested that the reentrant nematic phase transition can appear in the strongly polar mesogens if the extent of antiparallel association of the molecules increases on lowering the temperature.

1. Introduction

Numerous investigations of the relationship between molecular structure and the thermodynamic stability of the liquid-crystalline states have been reported. However, it is now recognized that even a fundamental problem such as predicting the relative tendency of forming nematic and smectic A phases is not an easy task. Although it is a complex problem there are a number of empirical rules which have been conceived from systematic studies on homologous series of compounds. One such rule is found on the effect of the length of terminal alkyl or alkoxy chains [1–3]. When the chain length is increased in a homologous series, the S_A state is stabilized relative to the N state, and this fact was successfully explained by, for example, the attractive potential theory of Kobayashi and McMillan [4–6]. According to this theory, the relative stability of the S_A state is enhanced when the one dimensional lattice period, d, becomes large compared with the range of the intermolecular dispersion force, r_0. The tendency of forming the S_A phase with increasing chain length is well explained by this theory, assuming that the lattice period is determined by the size of the molecule along its long axis, and r_0 remains constant within the homologous series [5, 7]. While this approach mainly investigates the effect of molecular geometry on the liquid-crystalline properties, an alternative approach is possible which examines the effect of substituents, such as halogen atoms [8–10] at the para-position of the terminal phenyl group. The alternative method is advantageous in that the change in polarizability and dipole moment can be induced by substitution while preserving the geometry and freedom of the internal motion of the molecule. Namely, we can study how the change

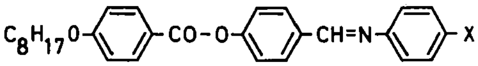

Figure 1. Molecular structure of 4-(4″-octyloxybenzoyloxy)-benzylidene-4′-substituted anilines.

in intermolecular forces alone affects the liquid-crystalline properties. However, this kind of approach has been less common and little is known on the relationship between the kind of terminal substituents and the relative stability of the S_A and N states, except the well-known fact that strongly polar substituents like the cyano group incorporates strong antiferroelectric intermolecular couplings, and then destabilizes the S_A state [11]. It is very interesting in this regard that Weissflog *et al.* prepared a series of mesogens, 4-(4″-octyloxybenzoyloxy)benzylidene-4′-substituted anilines (figure 1) and examined the trends in S_A–N and N–I phase transition temperatures [8], and showed that the substitution by halogens at the 4′-position of the aniline ring remarkably stabilizes the S_A state relative to N and I states. Our interest here is to clarify the origin of this substitution effect with the aid of molecular statistical theory.

This paper reports some of the physical properties of the seven derivatives of the compound shown in figure 1 with X = H, F, Cl, Br, I, NO_2 and CN. Although this series may usually be abbreviated as OBBX, [X] is used for short in this paper. Measurements of the molecular dipole moment, period of one dimensional smectic A lattice, temperatures and the entropies of phase transitions, and the temperature dependence of the orientational order parameter for each of the mesogens are described. Information on the anisotropic intermolecular forces are extracted from these experimental results by applying the mean field theory of Kobayashi–McMillan (K–M). It is stressed that all the parameters which appear in K–M's two particle and mean field potentials are determined from the experiments.

Among the seven compounds [CN] has attracted much interest since the first reports in 1980 [12, 13] that this compound, often called OBBC, exhibits enantiotropic reentrant phase transition, nematic–smectic A–reentrant nematic (RN) on lowering the temperature. Thermal anomalies related to these transitions were analysed [14] in terms of the optimal density theory [15]. The orientational order parameter and the modes of molecular motion were examined by NMR spectroscopy [16, 17]. The successive phase transitions were revealed to be almost of second order [14, 16, 17]. It was also reported from the NMR relaxation measurements [17] that the partially bilayered smectic A (S_{Ad}) state of this compound is characterized by its strong orientational fluctuation. An infrared study was also reported [18]. Synthesis of [H] has been reported in [19], [Cl] in [8, 10], and [Br] and [NO_2] in [8], but up to this date measurements have not been reported on the physical properties except for transition temperatures. The compound [I] was prepared for the first time during the present study.

2. Experimental

The materials were prepared in three steps: 4-octyloxybenzoic acid was chlorinated with thionyl chloride, and esterified with 4-hydroxybenzaldehyde in dry pyridine. The ester was then condensed with 4-substituted aniline while azeotropically distillating off the water with benzene. The compounds were purified by repeated recrystallization and by molecular distillation. Chemical analyses; Found/%(Calcd./%): [H] C 78·26(78·29), H 7·17(7·27), N 3·19(3·26), [F] C 75·12(75·14), H 6·80(6·76), N 3·17(3·13),

[Cl] C 72·61(72·48), H 6·50(6·52), N 2·89(3·02), Cl 7·67(7·64), [Br] C 66·33(66·14), H 5·98(5·95), N 2·79(2·75), Br 15·31(15·72), [I] C 60·63(60·55), H 5·29(5·44), N 2·70(2·52), I 23·12(22·85), [NO_2] C 70·59(70·87), H 6·12(6·37), N 5·71(5·90), [CN] C 76·84(76·63), H 6·58(6·65), N 6·16(6·16). The compounds [Br], [I], and [NO_2] were found to be chemically unstable at high temperatures. A fresh specimen was used for every measurement because these compounds decomposed after some of the heating–cooling cycles.

The dipole moment of the molecule was determined with the heterodyne beat method in dilute benzene solutions at 25°C. The one dimensional lattice period in the S_A state was determined from the first order quasi-Bragg reflection of copper Kα radiation at 15°C above the crystal to smectic A transition point of each compound. The scattering angle was calibrated by the (001) peak of the monoclinic c-polytype powder of stearic acid. The temperatures and the entropies of phase transitions were measured with a Seiko Electronics DSC 20 calorimeter. The temperature was calibrated by the melting of high purity indium and tin, and the transition enthalpy was calibrated by the solid–solid phase transition of potassium nitrate and the melting transitions of gallium, tin and lead. The liquid-crystalline phases were identified with the aid of texture observation, X-ray diffraction and DSC experiments. Focal conic textures were observed in the S_A phases of all the compounds. The orientational order parameter was calculated from the dipolar splitting of the proton NMR line recorded with a homemade Fourier-transform NMR spectrometer.

3. Experimental results

3.1. *Dipole moment of the molecule*

Values of the dipole moments, μ, of the molecules are given in table 1. Since the value of μ in [H], 3·74 D, measures contributions from the linkage groups, –CO–O– and –CH = N–, the larger values for the other six compounds show that a permanent dipole, parallel to the long molecular axis, is formed by the polar substituent. The halogeno compounds exhibit values in the range 5·00 ± 0·17 D and [NO_2] and [CN] have values greater than 7 D.

Table 1. Results of the dipole moment and X-ray measurements. The dipole moment, μ, of the molecule, observed one-dimensional lattice period $d_{\mathrm{obs.}}$, expected molecular length l_{expected}, and the parameter of interdigitation, $\gamma \equiv d_{\mathrm{obs.}}/l_{\mathrm{expected}}$, are tabulated.

Compound	μ/Debye	$d_{\mathrm{obs.}}$/Å	l_{expected}/Å	γ
[H]	3·74	28·61	28·61	1·000
[F]	4·84	29·05	28·98	1·002
[Cl]	5·03	29·63	29·83	0·993
[Br]	4·99	29·77	30·13	0·988
[I]	5·17	30·94	30·53	1·013
[NO_2]	7·45	32·62	29·82	1·094
[CN]	7·82	37·95	30·29	1·253

3.2. *The phase transition behaviour*

Phase transition sequences are summarized in table 2 and compared in figure 2. The most significant feature is that the temperature range of the S_A phase is widened in halogeno and nitro compounds while only a very narrow S_A range exists in the

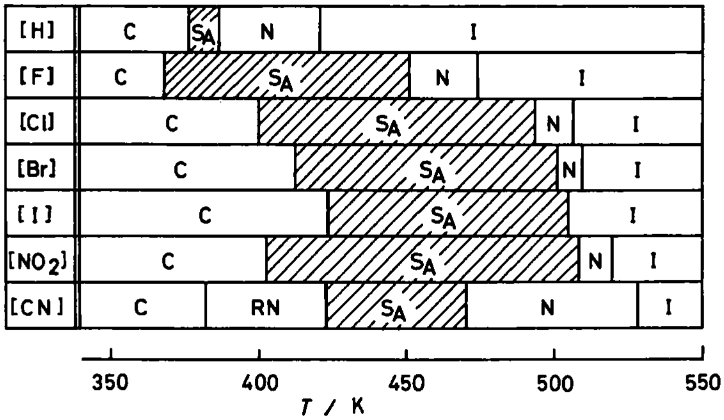

Figure 2. Phase transition behaviour of 4-(4″-octyloxybenzoyloxy)benzylidene-4′-substituted anilines.

Table 2. Temperatures and entropies of phase transitions. Observed phases are designated by *. The figures represent the temperatures of phase transition in Kelvin, and the figures in parentheses stand for the discontinuities of entropy at the phase transitions in units of $J K^{-1} mol^{-1}$.

Compound	Crystal		RN		S_A		N		I
[H]	*			376·8 (109)	*	386·9 (2·65)	*	421·2 (2·80)	*
[F]	*			368·2 (84·8)	*	450·9 (2·10)	*	474·1 (2·31)	*
[Cl]	*			400·1 (54·1)	*	493·5 (3·95)	*	506·4 (3·19)	*
[Br]	*			412·5 (48·8)	*	501·1 (5·62)	*	509·4 (2·84)	*
[I]	*			423·6 (50·1)	*			504·9 (13·1)	*
[NO_2]	*			402·7 (96·2)	*	508·3 (1·54)	*	519·1 (2·78)	*
[CN]	*	381·0 (95·1)	*	423 (~0)	*	470 (~0)	*	530·2 (2·09)	*

unsubstituted compound. This suggests that polar substituents enhance the thermodynamical stability of the S_A phase more than the N and I phases. In the iodo compound the S_A phase fully smears out the N phase. It is also recognized, however, that the S_A phase is made unstable relative to the N phase in [CN], leading to the emergence of the reentrant nematic phase, although this compound has the most polar substituent.

3.3. *Period of one dimensional S_A lattice*

Quasi-Bragg peaks were observed in the S_A phases of the mesogens. Only the first order peak was detected in [CN], whereas in the other compounds the second order peak was observed. It has been reported [20, 21] that in the S_{A_d} mesophase of cyano mesogens the smectic periodicity is a sinusoidal modulation of the density. Our observation supports this picture, namely, only [CN] is in the sinusoidally modulated S_A while the others have more distinct modulations.

The period of one dimensional lattice, *d*, is shown in table 1. The shortest period, 28·61 Å, was observed for [H], and the longest was 37·95 Å for [CN]. In the case of polar mesogens, there is a possibility of molecular association making the translational period of the S_A lattice longer than the molecular length (interdigitation). In order to evaluate the extent of this interdigitation, we take here an assumption that the value observed for [H], $d = 28{\cdot}61$ Å, is equal to the molecular length of this compound, l, because [H] has non-polar ends with no reason to favour the interdigitated structure. It should be noted that this value coincides with the estimated molecular length of [H] in its extended alkyl form. We can calculate the expected values of molecular lengths of the other compounds, l_{expected}, by correcting the l of [H] for the C–X bond length and the van der Waals radius of X. An important structural parameter, γ, which is a measure of interdigitation of the molecules along its molecular axis, is defined as the ratio

$$\gamma \equiv d_{\text{obs.}}/l_{\text{expected}}. \tag{1}$$

The quantities of l_{expected} and γ are given in table 1, and γ is plotted against the molecular dipole moment in figure 3. It is readily seen that the S_A states of the halogeno compounds and [CN] are of S_{A_1} and S_{A_d}, respectively; [NO_2] has a small extent of interdigitation.

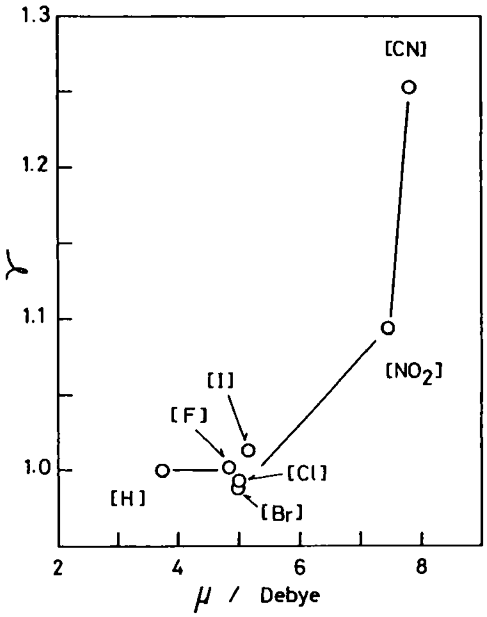

Figure 3. Interdigitation parameter, $\gamma = d_{\text{obs.}}/l_{\text{expected}}$, as a function of the dipole moment of the molecule, μ. The solid line is only a guide for the eyes.

3.4. *The entropies of phase transitions*

The entropies of phase transitions, ΔS_{tr}, are summarized in table 2 together with the transition temperatures. Since the six compounds, except [I], exhibit smectic A to nematic and nematic to isotropic phase transitions, ΔS_{AN} and ΔS_{NI} are plotted separately in figures 4 and 5 against $T_{\text{AN}}/T_{\text{NI}}$ and T_{NI}, respectively. It is seen that ΔS_{AN} depends strongly on the substituents, while ΔS_{NI} takes similar values.

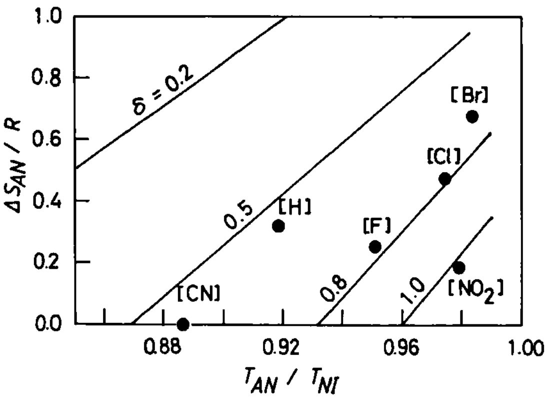

Figure 4. Discontinuity of the entropy at the smectic A to nematic phase transition, plotted against T_{AN}/T_{NI}. The solid curves represent the results of mean field calculation by Kventsel *et al.* [25] for a number of different values of δ.

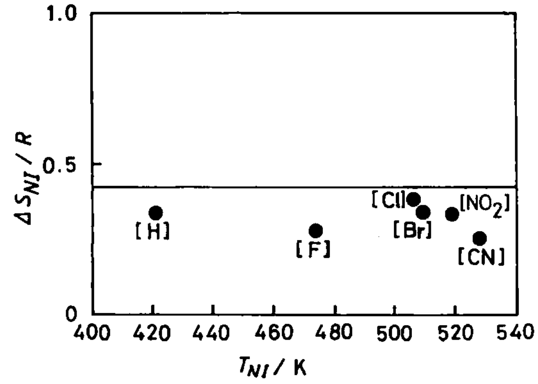

Figure 5. Discontinuity of the entropy at the nematic to isotropic phase transition, plotted against T_{NI}. The solid line shows the prediction of the mean field theory.

3.5. *The temperature dependence of the orientational order parameter*

NMR dipolar splitting, $\Delta\nu$, of the phenyl protons gives the orientational order parameter η via the equation

$$\Delta\nu = (3/2\pi)\gamma_p^2\hbar r^{-3}p_2(\cos\phi)\eta, \qquad (2)$$

where γ_p is the gyromagnetic ratio of the proton, and $p_2(x)$ is the Legendre polynomial of rank two. In evaluating η, the interproton distance of $r = 2{\cdot}45$ Å and the angle of $\phi = 10°$ between the long molecular axis and the interproton vector were taken. Examples of the results, η versus T/T_{NI}, are shown in figure 6 for [H] and [Cl]. Discontinuities of η at the A–N and N–I transitions, $\Delta\eta_{AN}$ and $\Delta\eta_{NI}$, are given in table 3 and figures 7 and 8. $\Delta\eta_{AN}$ in [Br] and $\Delta\eta_{NI}$ in [Br] and [NO$_2$] could not be determined due to decomposition. It is noticed from figures 4 and 7 that the nature of the A–N phase transition is strongly affected by the terminal substituents. In the following section we extract information on the anisotropic intermolecular forces from the experimental data.

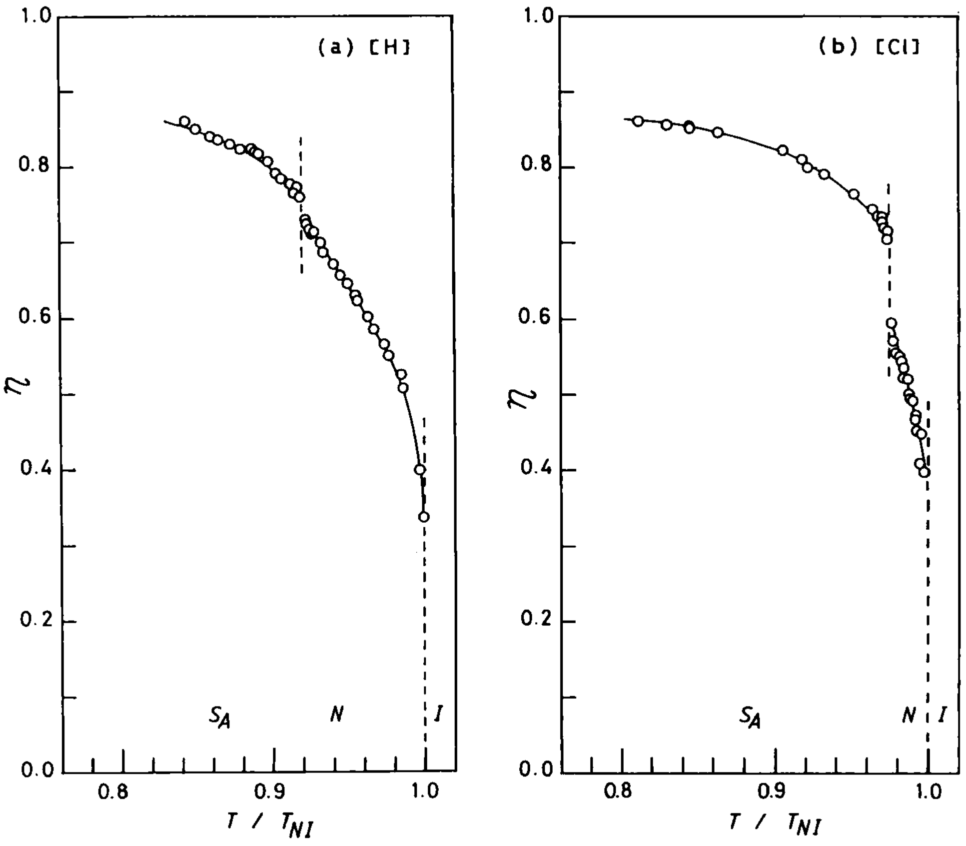

Figure 6. Variation of the orientational order parameter, η, with temperaure T/T_{NI} for (*a*) unsubstituted compound and (*b*) chloro compound.

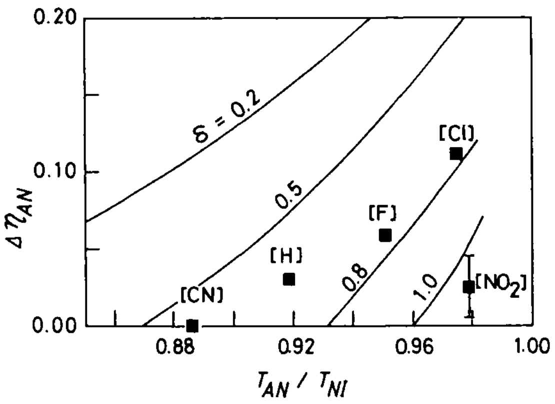

Figure 7. Discontinuity of the orientational order parameter at the smectic A to nematic phase transition, $\Delta\eta_{AN}$, plotted against T_{AN}/T_{NI}. The solid curves represent the results of the mean field calculation by Kventsel *et al.* [25] for a number of different values of δ.

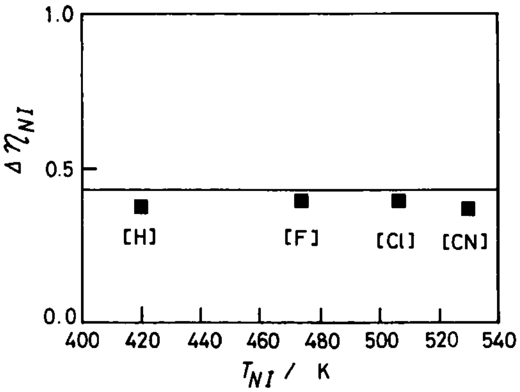

Figure 8. Discontinuity of the orientational order parameter at the nematic to isotropic phase transition, $\Delta\eta_{NI}$, plotted against T_{NI}. The solid line shows the prediction of the mean field theory.

Table 3. Discontinuities of the orientational order parameter, η at the phase transitions.

Compound	RN/S$_A$	S$_A$/N	S$_A$/I	N/I
[H]	-	0·030	-	0·375
[F]	-	0·059	-	0·365
[Cl]	-	0·111	-	0·399
[Br]	-		-	
[I]	-	-	0·713	-
[NO$_2$]	-	0·025 ± 0·020	-	
[CN]	~0	~0	-	0·362

4. Discussion

It is well known that, among the theoretical attempts to elucidate the smectic A state and the A–N phase transition [22], the first successful molecular statistical theory is the one developed by Kobayashi [4] and McMillan [5, 6]. This theory assumes an attractive pair potential between the rod-like molecules in the form

$$V_{12}(r_{12}, \cos\theta_{12}) = -V_0(r_0^3\pi^{3/2})^{-1} \exp[-(r_{12}/r_0)^2][p_2(\cos\theta_{12}) + \delta], \quad (3)$$

where r_{12} and θ_{12} are the distance between the centres of mass of the molecules and the angle between the two molecular axes, respectively. Three parameters are introduced here: V_0 (potential depth), r_0 (the range where intermolecular force acts), and δ (magnitude of isotropic potential relative to the anisotropic one). If a density modulation with a period d is applied along the z axis, parallel to the director, the averaged one particle potential felt by a molecule can be expressed by

$$V_1(z,\theta) = -V_0[\eta p_2(\cos\theta) + \alpha\sigma\cos(2\pi z/d)p_2(\cos\theta) + \alpha\delta\tau\cos(2\pi z/d)], \quad (4)$$

where θ is the tilt angle of the molecule with respect to the z axis. The order parameters, η (orientational), τ (translational), and σ (mixed), are defined by the following ensemble averages:

$$\eta = \langle p_2(\cos\theta)\rangle, \quad (5)$$

$$\tau = \langle\cos(2\pi z/d)\rangle, \quad (6)$$

and

$$\sigma = \langle p_2(\cos\theta)\cos(2\pi z/d)\rangle. \tag{7}$$

In equation (4) a new potential parameter

$$\alpha = 2\exp[-(\pi r_0/d)^2], \tag{8}$$

is introduced, which has an effect of controlling the relative stability of the S_A and N states. Kobayashi and McMillan obtained the solutions corresponding to the S_A, N and I phases by solving the self-consistent ternary simultaneous equations, and discussed the nature of the phase transitions among these phases. It is known that various experimental facts can be explained fairly well by this simple theory. For example, the stabilization of the S_A state with lengthening the alkyl chain was ascribed to the increase in α. It was also shown that this increase in α brings about the increase in the discontinuities of entropy and order parameters, and enhances the first order nature of the A–N phase transition. Similar tendencies were deduced later from more complicated theoretical treatments including both attractive and repulsive potentials [23, 24], but a merit of the attractive potential theory still lies in its simplicity. Especially, the recent recalculation by Kventsel *et al.* [25] by applying the decoupling approximation $\sigma = \eta\tau$ instead of equation (7), made the comparison with the experimental data easier. In this section, therefore, our experimental data are analysed according to this theory. A practical advantage of this analysis is that all of the three parameters in the starting pair potential can be determined from the experimental quantities, T_{NI}, T_{AN}/T_{NI} and ΔS_{AN}. The last quantity can be replaced by $\Delta\eta_{AN}$. Another parameter, α, in the averaged one particle potential is determined by d from the X-ray experiment. It is to be noted here that the experimental values of ΔS_{NI} and $\Delta\eta_{NI}$ can serve as tests for the validity of this treatment, because McMillan pointed out that the nature of the N–I phase transition does not depend on the details of the intermolecular pair potential, and that the universal values, $\Delta S_{NI} = 0{\cdot}42\,R$ and $\Delta\eta_{NI} = 0{\cdot}43$, of the Maier–Saupe theory [26] still apply to the mesogens which exhibit S_A–N–I phase sequences. Our experimental results of ΔS_{NI} in figure 5 and $\Delta\eta_{NI}$ in figure 8 are indeed independent of the substances, although the experimental values are generally a little smaller than the theoretical prediction; this validates the present treatment.

Let us now proceed to the analysis of the A–N phase transitions of the compounds studied here. The calculations by Kventsel *et al.* [25] are shown in figure 4 and 7 for ΔS_{AN} and $\Delta\eta_{AN}$, respectively, against T_{AN}/T_{NI} for a number of different values of δ. The procedure of determining the four parameters is as follows: δ is first determined from figures 4 and 7 separately, and α is then determined from the T_{AN}/T_{NI} versus $\alpha\delta$ plot in figure 4 of [25], and r_0 is calculated from equation (8) by using d from table 1. The potential depth V_0 is determined from T_{NI}. The parameters determined are summarized in table 4 and are plotted against μ in figure 9 to show the effect of the molecular dipole moment on the intermolecular potential. Two sets of the three parameters, r_0, δ and α, were obtained for [H], [F], [Cl] and [NO_2], using either ΔS_{AN} or $\Delta\eta_{AN}$. Definite values were not obtained in [I] and [CN] because [I] did not exhibit A–N transition, and ΔS_{AN} and $\Delta\eta_{AN}$ were immeasurably small in [CN]. Inspection of figure 9 brings about the following four correlations; (i) the increase in molecular dipole moment increases the depth of the potential V_0, and enhances the stability of the liquid-crystalline states relative to the isotropic liquid state, (ii) the anisotropy of the pair potential is reduced (δ increases) as μ increases, (iii) r_0 increases with

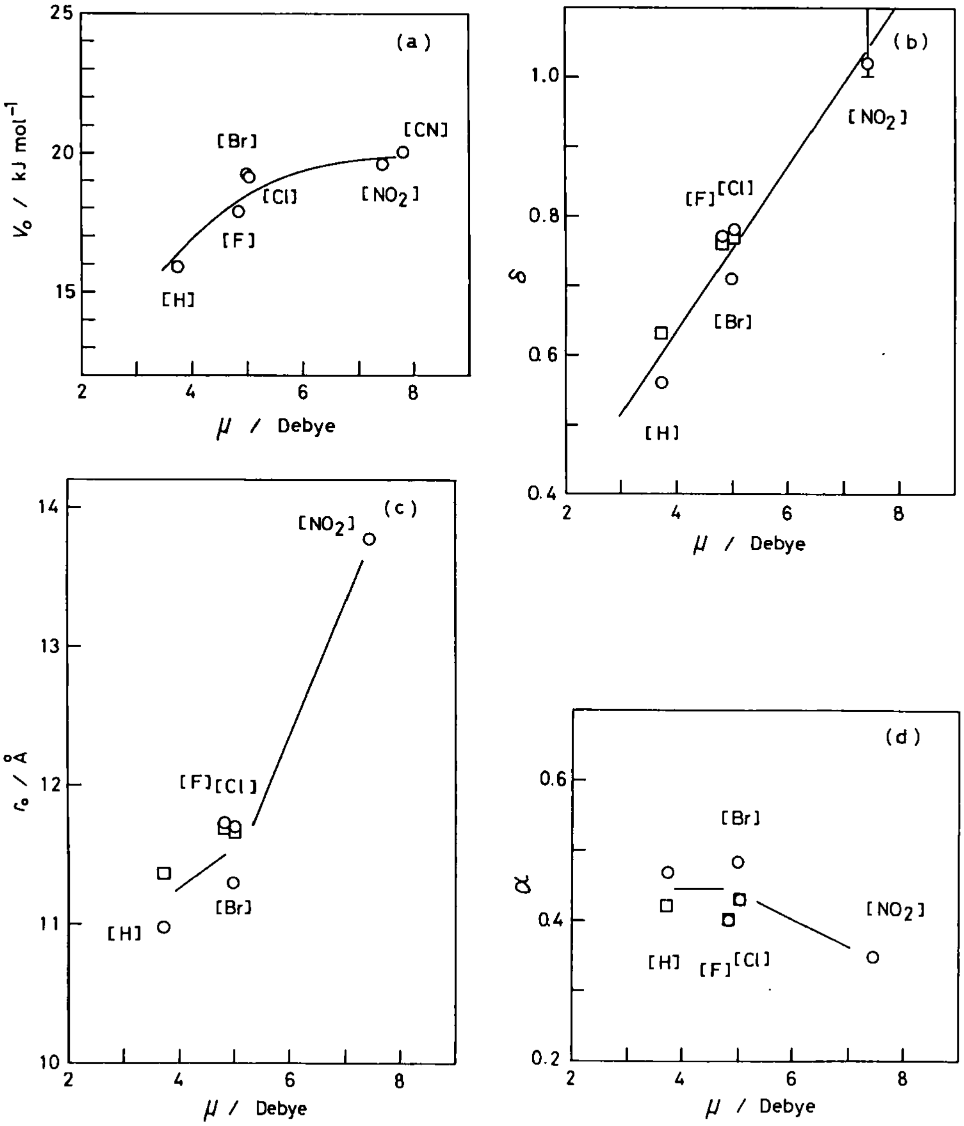

Figure 9. Parameters of Kobayashi-McMillan potential determined from the present experiments, (*a*) V_0, (*b*) δ, (*c*) r_0 and (*d*) α, plotted against μ. The circles and squares represent the parameters determined from the DSC and NMR experiments, respectively. The solid lines are guides for the eyes.

increasing polarity of the substituents, and (iv) α remains roughly constant in [H] and the halogeno compounds (increase in r_0 is compensated by the increase in d) but is smaller for [NO$_2$] (increase in r_0 exceeds that in d). According to the calculation by Kventsel *et al.* [25], the increase in δ for a given α makes T_{AN} rise almost linearly with δ while T_{NI} is quite insensitive to the change in δ, and so this increase in δ shifts the relative thermodynamic stability from N to S_A within the liquid-crystalline state. The decrease in α, however, is not favoured in stabilizing the S_A state, and so this mesophase in [NO$_2$] has a potential instability. It is interesting to note that the factors (ii) and (iv) counteract on the stability of the S_A state. It is often seen that terminally

Table 4. Parameters of the Kobayashi–McMillan potential determined from the present experiments. The parameters determined from the NMR experiments are indicated by †, while those based on DSC measurements are not specified.

Compound	V_0/kJ mol^{-1}	r_0/Å	δ	α
[H]	15·90	11·0	0·56	0·47
		11·4†	0·63†	0·42†
[F]	17·89	11·7	0·77	0·40
		11·7†	0·76†	0·40†
[Cl]	19·11	11·7	0·78	0·43
		11·7†	0·77†	0·43†
[Br]	19·22	11·3	0·71	0·48
[NO$_2$]	19·59	13·8	1·02	0·34
[CN]	20·01	–	–	–

halogenated compounds possess stable S_A phases while in the cyano or nitro compounds, in which the polarity is strongly enhanced, the N state is relatively stabilized [9, 10], sometimes bringing about the reentrant nematic phase.

Let us consider then the origin of these changes in potential parameters. The Kobayashi–McMillan's pair potential, which is for non-polar liquid crystals, consists of the zeroth and second rank Legendre polynomials without taking into account the odd rank terms. In the case of the polar mesogens of interest here, intermolecular dipole–dipole and dipole–induced dipole interactions act as perturbations to the theory. Considering that the dipole moment and polarizability are both anisotropic in these polar mesogens, the anisotropy of the intermolecular attractive force might be expected to increase, however, the μ dependence of δ in figure 9 (*b*) conflicts with this. A possible explanation is the association of the molecules. It seems plausible that antiparallel pairing of the molecules reduces the effective dipole moment and the anisotropy of the polarizability, and increases the value of δ. Antiparallel pairing would also make the effective shape of the molecules more or less bulkier and increase r_0. The introduction of moderately polar substituent atoms such as halogens thus enhances the S_A stability mainly through the effect of increasing V_0 and δ. If, however, an extremely strong polar end group is incorporated, a significant increase in r_0 caused by antiparallel association exceeds the increase in d, and hence reduces α. The S_A state is destabilized compared with N by this decrease in α.

Finally we would like to comment on the possible microscopic origin of the reentrant nematic phase transition in [CN]. It has been known that the mean field theories of the K–M type cannot explain this unusual phase transition in so far as one assumes that the potential parameters are determined by the molecular structure alone, and have no dependence on temperature. Luckhurst *et al.*, on the other hand, deduced the occurrence of this phase transition by simply assuming that α decreases on lowering the temperature [25, 27]. Although this was the first successful molecular statistical treatment of this phase transition, the origin of this temperature dependence of α was not clear. The present study has shown that α can be lowered by molecular association via the greater increment in r_0 than in d. Within the context of the present analysis, it is reasonable to assume that α decreases with lowering of the temperature since the extent of molecular association may increase with lowering of the temperature.

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References

[1] Gray, G. W., 1979, *The Molecular Physics of Liquid Crystals*, edited by G. R. Luckhurst and G. W. Gray (Academic Press), Chaps. 1 and 12.
[2] Gray, G. W., 1983, *Phil. Trans. R. Soc.* A, **309**, 77.
[3] Levine, A. W., 1976, *Introduction to Liquid Crystals*, edited by E. B. Priestley, P. J. Wojtowicz and P. Sheng (Plenum Press), Chap. 2.
[4] Koyabashi, K. K., 1970, *Physics Lett.* A, **31**, 125; 1970, *J. phys. Soc. Japan*, **29**, 101; 1971, *Molec. Crystals liq. Crystals*, **13**, 137.
[5] McMillan, W. L., 1971, *Phys. Rev.* A, **4**, 1238.
[6] McMillan, W. L., 1972, *Phys. Rev.* A, **6**, 936.
[7] Lee, F., Tan, H. T., Yu Ming Shih, and Chia-Wei Woo, 1973, *Phys. Rev. Lett.*, **31**, 1117.
[8] Weissflog, W., Pelzl, G., and Demus, D., 1981, *Molec. Crystals liq. Crystals*, **76**, 261.
[9] Tsuji, K., Sorai, M., Suga, H., and Seki, S., 1982, *Molec. Crystals liq. Crystals*, **90**, 85.
[10] Vora, A., and Patel, D. N., 1983, *Molec. Crystals liq. Crystals*, **103**, 127.
[11] Longa, L., and de Jeu, W. H., 1982, *Phys. Rev.* A, **26**, 1632.
[12] Weissflog, W., Pelzl, G., Wiegeleben, A., and Demus, D., 1980, *Molec. Crystals liq. Crystals*, **56**, 295.
[13] Tinh, N. H., Zann, A., Dubois, J. C., and Billard, J., 1980, *Molec. Crystals liq. Crystals*, **56**, 323.
[14] Miyajima, S., and Chiba, T., 1985, *J. phys. Soc. Japan*, **54**, 2793.
[15] Pershan, P. S., and Prost, J., 1979, *J. Phys. Lett., Paris*, **40**, L-27.
[16] Miyajima, S., Akaba, K., and Chiba, T., 1984, *Solid St. Commun.*, **49**, 675.
[17] Miyajima, S., and Chiba, T., 1988, *J. phys. Soc. Japan*, **57**, 2550.
[18] Takase, A., and Sakagami, S., 1984, *Jap. J. appl. Phys.*, **23**, 1532.
[19] Dave, J. S., Kurian, G., and Patel, N. R., 1980, *Indian J. Chem.* A, **19**, 1161.
[20] Als-Nielsen, J., Birgenau, R. J., Kaplan, M., Litster, J. D., and Safinya, C. R., 1977, *Phys. Rev. Lett.*, **39**, 1668.
[21] Stamatoff, J., Cladis, P. E., Guillon, D., Cross, M. C., Bilash, T., and Finn, P., 1980, *Phys. Rev. Lett.*, **44**, 1509.
[22] Lubensky, T. C., 1983, *J. Chim. phys.*, **80**, 31.
[23] Hoshino, M., Nakano, H., and Kimura, H., 1979, *J. phys. Soc. Japan*, **47**, 740; 1981, *Ibid.*, **50**, 1067.
[24] Nakagawa, M., and Akahane, T., 1984, *J. phys. Soc. Japan*, **53**, 1951.
[25] Kventsel, G. F., Luckhurst, G. R., and Zewdie, H. B., 1985, *Molec. Phys.*, **56**, 589.
[26] Maier, W., and Saupe, A., 1958, *Z. Naturf.* (*a*), **13**, 564; 1959, *Ibid.*, **14**, 882; 1960, *Ibid.*, **15**, 287.
[27] Luckhurst, G. R., and Timimi, B. A., 1981, *Molec. Crystals liq. Crystals Lett.*, **64**, 253.