May, 1991] © *1991 The Chemical Society of Japan* NOTES *Bull. Chem. Soc. Jpn.*, ***64***, *1679—1681 (1991)* 1679

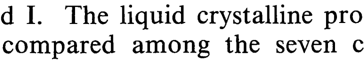
Terminal Polar Substituent Effect on the Liquid Crystalline Properties of a Series of 4-Octyloxy-*N*-(4-substituted benzylidene)anilines

Seiichi Miyajima,* Takehiko Enomoto, Tomohiro Kusanagi, and Takehiko Chiba
Department of Chemistry, College of Humanities and Sciences, Nihon University,
Sakurajosui, Setagaya-ku, Tokyo 156

(Received January 5, 1991)

Synopsis. Mesomorphic properties are studied on the title compounds where substituents are F, Cl, Br, I, NO_2, and CN. Besides the known mesophases, nematic and smectic Ad, in CN and NO_2 homologues, stable smectic A and B phases were observed in either of the Cl and Br derivatives. Metastable nematic and smectic A phases were found in F derivative. The effects of terminal polar substituents, stabilization of the smectic A phase by moderately polar substituents, and of the nematic phase by strongly polar substituents, were confirmed.

The liquid crystalline compound, 4-octyloxy-*N*-(4-cyanobenzylidene)aniline (CBOOA) has been studied extensively as one of the typical compounds having smectic A (S_A) and nematic (N) phases. CBOOA is very popular not only because it exhibits stable S_A and N phases at relatively low temperatures but also because of its interesting physical properties. McMillan's early study[1)] which suggested the existence of a second order S_A–N phase transition in this compound stimulated a good number of experiments on the nature of this phase transition.[2–7)] It is also of particular interest that CBOOA was shown to exhibit a thermotropic reentrant nematic (RN) phase transition at high pressures.[8,9)] It has been conceived until now that this peculiar property is attributable to the strong antiferroelectric intermolecular interaction caused by the cyano end group.[10,11)] Noting that strong polarity of the terminal substituent is essential, Prasad et al.[12)] studied whether RN phase also appeared at high pressures when the cyano group is replaced by nitro group. In this homologue (NBOOA), however, the S_{Ad}/N phase boundary was quite straight in the p–T phase diagram, and the reentrant nematic phase transition did not take place until up to 2 kbar. In this way the kind of terminal substituent delicately affects the liquid crystalline properties. In a recent paper[13)] we showed that terminal polar substituents counteracts on the thermodynamical stability of the S_A state, namely, moderately polar substituents stabilize the S_A state whereas strongly polar substituents relatively stabilize the N state. It was also shown that all of the parameters of the Kobayashi–McMillan's pair and mean field potentials were determined experimentally. In order to further study the terminal polar substituent effect, we prepared a series of compounds, 4-octyloxy-*N*-(4-substituted benzylidene)anilines, where X are H,



F, Cl, Br, and I. The liquid crystalline properties are studied and compared among the seven compounds including the known cyano and nitro derivatives, and the substituent effect is compared with the results obtained in the three-ring systems.[13)] Although the conventional namings XBOOA may also be used, the symbols [X] are used for short in this paper.

Experimental

The materials were synthesized through dehydration condensation of 4-X-substituted benzaldehyde with 4-octyloxy aniline, the latter of which was prepared from potassium 4-acetamidophenoxide by Williamson's method.[14)] Chemical analyses gave good agreement with the formulae.

Dipole moment of the molecule was determined with heterodyne beat method in dilute benzene solutions at 25 °C. 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 zone-refined biphenyl, and the transition enthalpy was calibrated by the solid–solid phase transition of potassium nitrate and the melting transitions of gallium, indium, tin, and biphenyl. Smectic layer spacings were determined from the first order quasi-Bragg reflection of copper *Kα* radiation. The scattering angle was calibrated by the (001) peak of the monoclinic c-polytype powder of stearic acid. Proton NMR lineshape was recorded in [Cl] and [Br] to assess the molecular alignments in the smectic phases with a laboratory-made Fourier-transform NMR spectrometer. The liquid crystalline phases were identified with the aids of texture observation, X-ray diffraction, proton NMR spectrum, and the DSC experiments.

Results and Discussion

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], 1.77 D (1 D=1 Debye=3.3356×10^{-30} C m), measures contributions from the linkage groups, –CH=N– and –O–, 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 of 2.60±0.08 D, and [NO_2] and [CN] have values greater than 5 D.

Identification of the Liquid Crystalline Phases. In the known compound, [CN] and [NO_2],[12,15,16)] the reported mesophases, S_A and N, were confirmed from the microscopic texture observations. Differential scanning calorimetry and the texture observation revealed that no liquid crystalline phases appear in [H] and [I]. [F] showed metastable N and S_A phases of only narrow temperature ranges on cooling from the isotropic (I) phase. In either of [Cl] and [Br], two liquid crystalline phases were found, both of which were of smectic type in microscopic appearances. DSC study revealed that the smectic-to-smectic and the smectic-to-isotropic phase transitions were strongly of first order, and the entropy of the former transition was about half in mag-

Table 1. Dipole Moment μ of the Molecule, and the Smectic Layer Spacings, d, in the S_B and S_A Phases

Compound	μ/Debye	d/Å (S_B)	d/Å (S_A)
[H]	1.77	—	—
[F]	2.52	—	—
[Cl]	2.56	25.1	24.7
[Br]	2.68	25.8	25.4
[I]	2.65	—	—
[NO_2]	5.14	—	31.9
[CN]	5.21	—	35.7

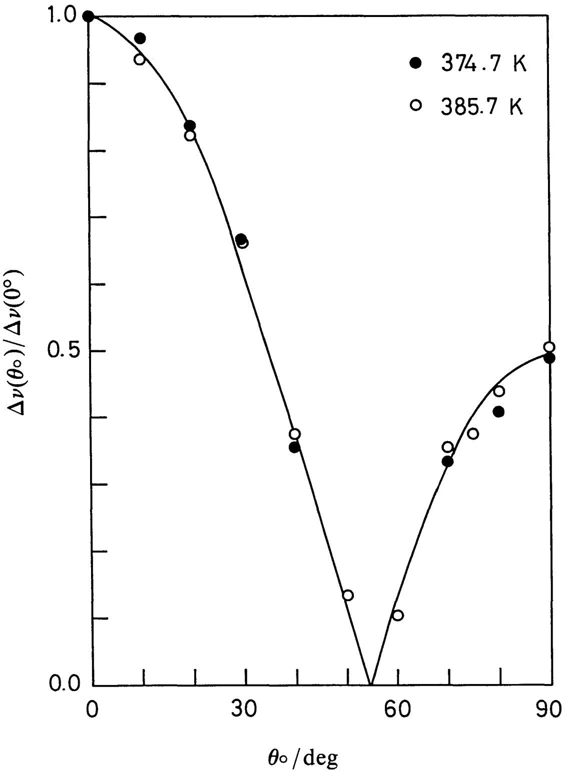


Fig. 1. The angular dependence of the proton NMR splitting frequency normalized to that taken at $\theta_o=0°$ in the high (○) and low (●) temperature smectic phases of [Br]. Each phase is assigned to S_A and S_B in the text. θ_o is the angle between the external magnetic field and the averaged direction of the director. The solid line represents $p_2(\cos\theta_o)$ where p_2 is the Legendre polynomial of rank two.

nitude that of the latter transition. More decisive results in identifying these phases were obtained from the angular dependence studies of the proton NMR lines. Figure 1 shows the angular dependence of the dipolar splitting of the phenyl protons in [Br]. The open and the filled circles show the data taken in the high and low temperature smectic phases, respectively. If the smectic states are of the orthogonal type (in which the averaged direction of the molecular long axis is not tilted from the layer normal), the dipolar splitting frequency is given by the equation,17)

$$\Delta\nu(\theta_o)/\Delta\nu(0°) = |p_2(\cos\theta_o)|, \qquad (1)$$

irrespective of the magnitude of orientational order parameter. Here θ_o is the angle between director and the external magnetic field, and p_2 (x) is the Legendre polynomial of rank two. Figure 1 clearly show that the experimental results follow Eq. 1, and the dipolar splitting vanishes as θ_o approaches the magic angle (54.7°). Both of the smectic phases are thus revealed to be of orthogonal type. The result in [Cl] was quite similar to that of [Br]. Judging also from the textures, DSC, and X-ray results, the high and low temperature mesophases were concluded to be S_A and S_B, respectively. The phase transition behaviors of all the compounds studied are summarized in Table 2.

Layer Spacings in the Smectic Phases. The smectic layer spacings were measured in S_A and S_B phases, and are summarized in Table 1. Judging from the stereochemical molecular model, the molecular length along the long axis is 23—24 Å in this series of compounds. The observed values of d in the S_A phases of [Cl] and [Br] shows that these mesophases are of the monolayer type, whereas those in [NO_2] and [CN] belong to S_{Ad} modification, as has been already reported. The observed d in the low temperature smectic (S_B) phase in [Cl] and [Br] is consistent with the monolayer model, and is also consistent with the NMR result.

Entropies of Phase Transitions. The temperatures and the entropies of phase transitions are summarized in Table 2. The entropies of N–I phase transitions, ΔS_{NI}, observed in [NO_2] and [CN] were 0.249 R and 0.273 R, respectively, where R is the gas constant. These are considerably smaller than the universal value of 0.42 R predicted by the statistical theories of Maier and Saupe18) and McMillan.19) On the other hand, the entropies of S_B–S_A transition, ΔS_{BA}, observed in [Cl] and [Br] were 0.908 R and 1.034 R, respectively, both of which are larger than 0.559 R predicted by Meyer and McMillan.20) The S_{Ad}–N transition entropy was too small to be detected in [CN], while it amounted to 0.165 R in [NO_2]. Details on the difference in nature of the two S_{Ad}–N phase transitions will be described elsewhere.21) Table 2 also summarizes the total amount of the entropies of phase transitions in each of the compounds. It is of some interest to point out that the accumulated entropies of phase transitions in each of the compounds amount to like values, 116±8 J K^{-1} mol^{-1}, proving that the entropy of the condensed state in such a rod-like compound is acquired mainly at the phase transitions in a stepwise manner until the isotropic symmetry is finally obtained. This fact was first pointed out by Tsuji et al.22) in the 4-substituted *N*-(4-hexyloxybenzylidene)anilines, analogues to our series having reversed linkage group and shorter alkyl chain, where the accumulated entropy was 93.6±2.5 J K^{-1} mol^{-1}. The latter value is comparable to but a little smaller than our result. The difference (22 J K^{-1} mol^{-1}) is attributable to the difference in chain length because of the following assessment. If three conformations are allowed for each of the methylene group, the conformational entropy shared by the two methylene units is $2R \ln 3=18.3$ J K^{-1} mol^{-1}, which explains the above dif-

Table 2. Temperatures and Entropies of Phase Transitions

Observed stable phases are designated by *. The plain figures represent the temperatures of phase transition in Kelvin, and the parenthesized figures stand for the discontinuities of entropy at the phase transitions in the unit of J K^{-1} mol^{-1}. Accumulated entropy of phase transitions for each compound is shown in the last column.

Compound	CII		CI		S_B		S_A		N		I	($\Sigma\Delta S_{tr}$)
[H]	*	—		—		—		—		342.7 (121)	*	(121)
[F]$^{a)}$	*	—		—		—		—		360.5 (124)	*	(124)
[Cl]	*	—		363.3 (84.7)	*	370.4 (7.55)	*	—		381.4 (16.3)	*	(108.6)
[Br]	*	—		365.5 (80.3)	*	384.8 (8.60)	*	—		388.2 (19.8)	*	(108.7)
[I]	*	378.53 (21.4)	*	—		—		—		392.83 (92.2)	*	(113.6)
[NO$_2$]	*	—		—		336.5 (107)	*	349.3 (0.360)	*	358.5 (2.07)	*	(109.4)
[CN]	*	339.9 (33.19)	*	—		347.0 (85.6)	*	356.2 (ca. 0)	*	382.1 (2.27)	*	(121.1)

a) Metastable N and S_A phases were found on cooling from I.

ference fairly well.

Effect of Terminal Polar Substituents on the Liquid Crystalline Properties. It was shown by the present authors[13)] that terminal polar substituents bring about increase in the intermolecular attractive force, and also bring about counteracting contributions to the stability of the S_A phase in the homologous series of 4-substituted *N*-[4-(4-octyloxybenzoyloxy) benzylidene]anilines (OBBX series). In that case, the tendency of liquid crystal formation was strongly enhanced in the homologous compounds with polar end groups compared with the unsubstituted one. It was also shown that moderately polar substituents like halogens significantly stabilized the S_A phase, but extremely polar substituents such as cyano group relatively stabilized the N phase. The general conclusions still hold in the present series: namely, the liquid crystalline nature is enhanced in [Cl], [Br], [NO$_2$], and [CN] compared with the non-mesogen [H]. It is also recognized that N phase is relatively stabilized in [NO$_2$] and [CN], whereas destabilized and lost in [Cl] and [Br]. It is the expected tendency that the halogeno compounds favor the S_A state. It should be noted, however, that two-ring compounds generally have less tendency of forming the liquid crystalline phase than three-ring compounds, and it is the major difference in the phase transition behaviors of the present and the OBBX series. The survival of the high temperature crystalline phase up to above 390 K in [I] and the existence of only metastable N and S_A phases in [F] will be attributable to this general tendency.

We thank Dr. Hatsumi Mori for her kind advice and collaboration in DSC measurements.

References

1) W. L. McMillan, *Phys. Rev. A,* **7**, 1419 (1973).

2) P. E. Cladis, *Phys. Rev. Lett.,* **31**, 1200 (1973).

3) S. Torza and P. E. Cladis, *Phys. Rev. Lett.,* **32**, 1406 (1974).

4) K. C. Chu and W. L. McMillan, *Phys. Rev. A,* **11**, 1059 (1975).

5) R. A. Wise, A. Olah, and J. W. Doane, *J. Phys. [Paris], Colloq.,* **36**, C1-117 (1975).

6) M. F. Achard, F. Hardouin, G. Sigaud, and H. Gasparoux, *J. Chem. Phys.,* **65**, 1387 (1976).

7) D. Armitage and F. P. Price, *Mol. Cryst. Liq. Cryst.,* **38**, 229 (1977).

8) P. E. Cladis, R. K. Bogardus, and D. Aadsen, *Phys. Rev. A,* **18**, 2292 (1978).

9) D. Guillon, P. Cladis, D. Aadsen, and W. B. Daniels, *Phys. Rev. A,* **21**, 658 (1980).

10) L. Longa and W. H. de Jeu, *Phys. Rev. A,* **26**, 1632 (1982).

11) J. Prost and P. Barois, *J. Chim. Phys. (Paris),* **80**, 65 (1983).

12) S. Krishna Prasad, S. Pfeiffer, G. Heppke, and R. Shashidhar, *Z. Naturforsch., A,* **40**, 632 (1985).

13) S. Miyajima, K. Nakazawa, K. Niikura, Y. Ujiiye, M. Yashiro, and T. Chiba, *Liq. Cryst.,* **8**, 707 (1990).

14) P. Keller and L. Liebert, "Solid State Physics," ed by F. Seitz and D. Turnbull, Academic Press, New York (1978), Supplement Vol. 14, pp. 19—76.

15) R. A. Vora and N. Dixit, "Liquid Crystals," ed by S. Chandrasekhar, Heydon, London (1980), pp. 585—588.

16) P. C. Jain, S. R. S. Kafle, R. A. Vora, and N. Dixit, *Mol. Cryst. Liq. Cryst.,* **103**, 287 (1983).

17) C. A. Veracini, "Nuclear Magnetic Resonance of Liquid Crystals," ed by J. W. Emsley, D. Reidel Publ. Co., Dordrecht (1985), Chap. 5, pp. 99—121.

18) W. Maier and A. Saupe, *Z. Naturforsch., A,* **13**, 564 (1958); *ibid.,* **14**, 882 (1959); *ibid.,* **15**, 287 (1960).

19) W. L. McMillan, *Phys. Rev. A,* **4**, 1238 (1971); *ibid.,* **6**, 936 (1972).

20) R. J. Meyer and W. L. McMillan, *Phys. Rev. A,* **9**, 899 (1974).

21) S. Miyajima and T. Chiba, unpublished result.

22) K. Tsuji, M. Sorai, H. Suga, and S. Seki, *Mol. Cryst. Liq. Cryst.,* **90**, 85 (1982).