

# Theoretical Analysis of Mesogenic Properties of Benzalazine and Benzopyran Derivatives

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Mesogenic behaviors of 4,4'-di-*n*-alkoxybenzalazine (**1**) and 3-phenyl-4*H*-4-[one]-benzopyran (**2**) derivatives are analyzed using theoretical models. A general phase diagram including smectic and nematic phases is explained by McMillan's model which is the extension of the model of Maier and Saupe. Some of the fundamental features of **1** and **2** are reproduced by the model, while there are also some discrepancies between the experimental and theoretical results. This may be ascribed to the lack of ordering caused by rigid-body repulsive interaction in the model. In order to investigate the nematic phases in more detail, Kimura's model is applied. The electronic properties of **1** and **2** are calculated by a semiempirical molecular orbital method (AM1). It has turned out that **1** has high polarizability and small permanent dipole moments, while **2** has low polarizability and large permanent dipole moments. The higher temperature for nematic–isotropic transition ( $T_{NI}$ ) of **2** than **1** must be due to more flexibility of **1** or larger permanent dipole moment of **2**.

## I. Introduction

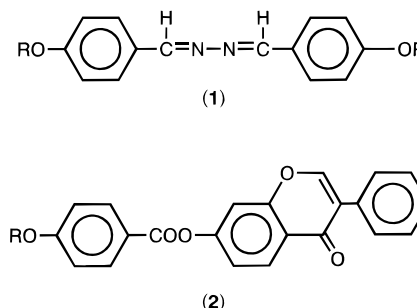
Recently Chudgar *et al.* reported the synthesis and mesogenic properties of 4,4'-di-*n*-alkoxybenzalazines (**1**) and 3-phenyl-4*H*-4-[one]benzopyran derivatives (**2**) shown in Scheme 1.<sup>1,2</sup> Although both of these compounds exhibit attractive properties as liquid crystals giving both nematic and smectic phases, these properties have not been fully understood from the theoretical point of view. In this study, therefore, we have examined the thermodynamic behavior of **1** and **2** using theoretical models. In the first place, McMillan's model<sup>3</sup> is used to interpret qualitatively the smectic and nematic phases. Next, we concentrate on the nematic phase using a more detailed theory (Kimura's model<sup>4</sup>). The electronic properties of **1** and **2** are calculated by a semiempirical molecular orbital method (AM1) and the nematic–isotropic transitions of these compounds are correlated to the electronic properties and the geometry of the molecules.

## II. Methods

**General Molecular Model for Smectic and Nematic Phases.** In order to understand the qualitative properties of smectic and nematic phases, we used McMillan's model<sup>3</sup> which was extended from the theory of Maier and Saupe.<sup>5</sup> The former model has a physical parameter ( $\alpha$ ) acting as a dimensionless interaction strength for smectic A phase, while in the latter model only an orientational parameter is introduced. In the present study, we used the numerical data calculated by McMillan to explain the mesogenic properties of **1** and **2**.

**Detailed Molecular Model for Nematic Phase.** Kimura presented a model which deals with nematic phase in view of both the ordering due to the anisotropic part of dispersion forces

## SCHEME 1. Structures of Liquid Crystal Molecules



between molecules and the ordering due to the rigid-body repulsions.<sup>4</sup> To analyze the present results with this model, we calculated ionization potential, polarizability, and permanent dipole moment of **1** and **2** by AM1 method (MOPAC version 6 in the CAChe system, Sony Tektronix Co.). In the case of **2**, two conformers (**2-1** and **2-2**) shown in Figure 1(b,c) were taken into account, since these conformers turned out to exist in a similar probability in view of the total energy calculated by MM2. The structures of **1**, **2-1**, and **2-2** (Figure 1a–c) were optimized by MM2 before AM1 calculation.

**Transition Temperatures and Transition Entropies.** The data of transition temperatures for nematic–isotropic ( $T_{NI}$ ), smectic–nematic ( $T_{SN}$ ) and smectic–isotropic ( $T_{SI}$ ) transitions, and the corresponding data for transition entropies ( $\Delta S_{NI}$ ,  $\Delta S_{SN}$ , and  $\Delta S_{SI}$ ) were cited and calculated from the literatures,<sup>1,2</sup> where temperatures and enthalpies of transition were measured by both microscopic and DSC methods.

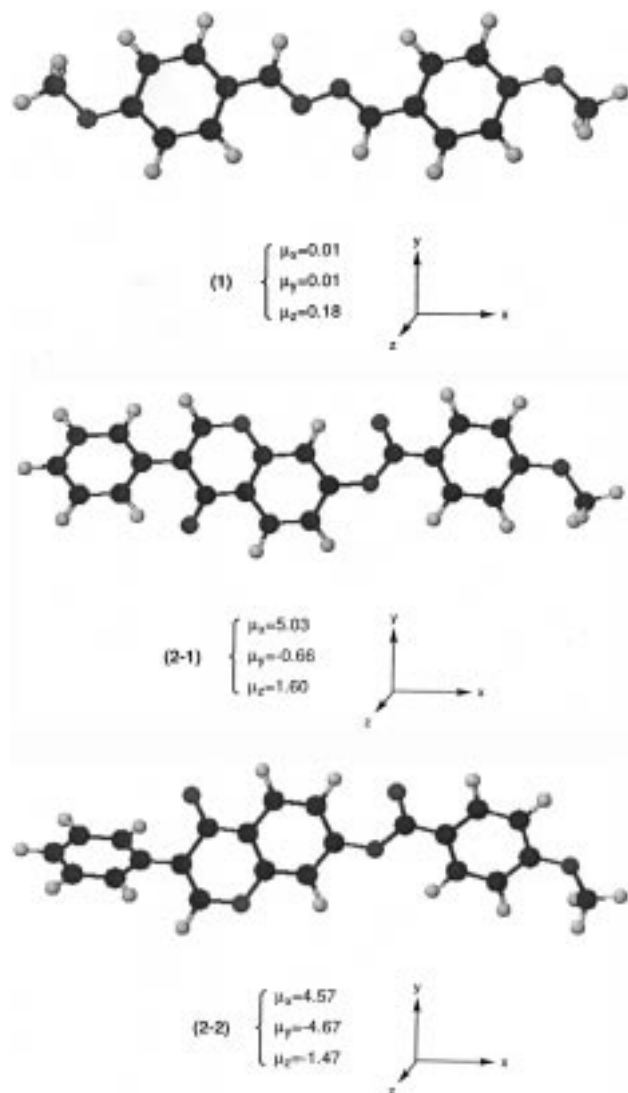
## III. Results

**Qualitative Interpretation of Mesogenic Behavior.** Since the success of the molecular theory for nematic–isotropic transition by Maier and Saupe, their theory has been extensively used to interpret the thermodynamic behavior of nematic–

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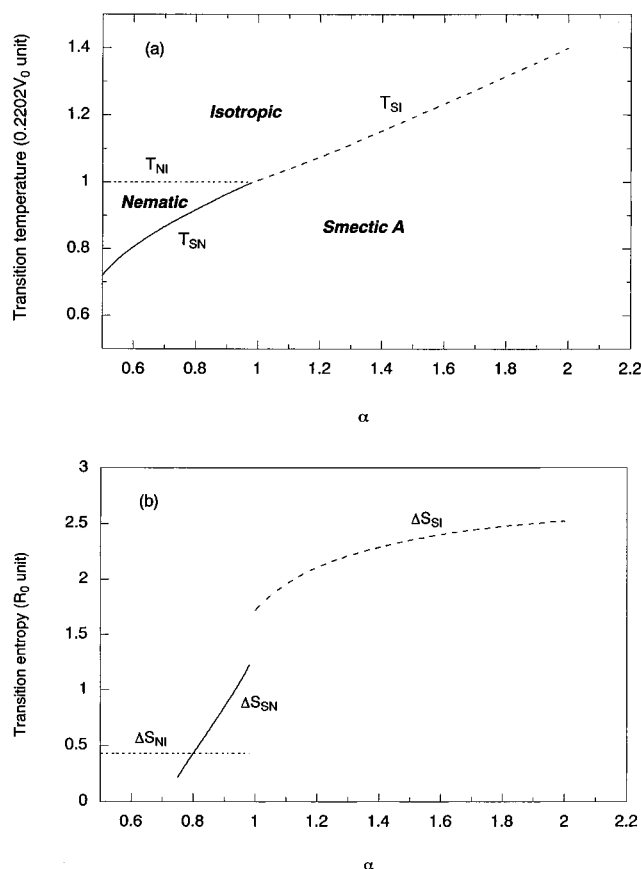
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**Figure 1.** Structures and calculated permanent dipole moments of (a) **1**, (b) **2-1**, and (c) **2-2**.

isotropic transition. In spite of its qualitative usefulness, however, it cannot deal with other mesogenic phases such as smectic, since only an orientational order parameter was taken into account in their theory. To extend the Maier–Saupe model to the smectic A phase, McMillan introduced a new order parameter. In the nematic phase the centers of mass are randomly situated, while the long axes are parallel to a preferred axis. In the smectic phase, on the other hand, the centers of mass are located on planes perpendicular to a preferred axis with the long axes being parallel to the preferred axis. In the theory of smectic phase, therefore, a positional parameter is needed in addition to an orientational parameter.

Figure 2, a and b, respectively, shows the transition temperature and transition entropy predicted from the model of McMillan, where the calculated data were cited from his article.<sup>3</sup> Here the transition temperature and transition entropy are given in  $0.2202V_0$  unit and  $R_0$  ( $=8.31 \text{ J K}^{-1} \text{ mol}^{-1}$ ) unit, respectively. Figure 3a,b shows the observed transition temperature and transition entropy of compound **1**. Figure 4a,b also exhibits those quantities of compound **2**. Parameter  $\alpha$  is used in Figure 2, while the alkyl chain length is used in Figures 3 and 4. Since  $\alpha$  is known to increase with increasing alkyl chain length,<sup>3</sup> we can qualitatively compare the theoretical (Figure 2) and the experimental (Figures 3 and 4) results. Some essential features



**Figure 2.** Theoretical dependency of (a) transition temperature and (b) transition entropy on parameter  $\alpha$  (data are cited from ref 3).

of the observed diagram of **2** (Figure 4) are well reproduced by the theoretical model in the following points, although the results for **1** (Figure 3) do not show as clear a similarity as **2**.

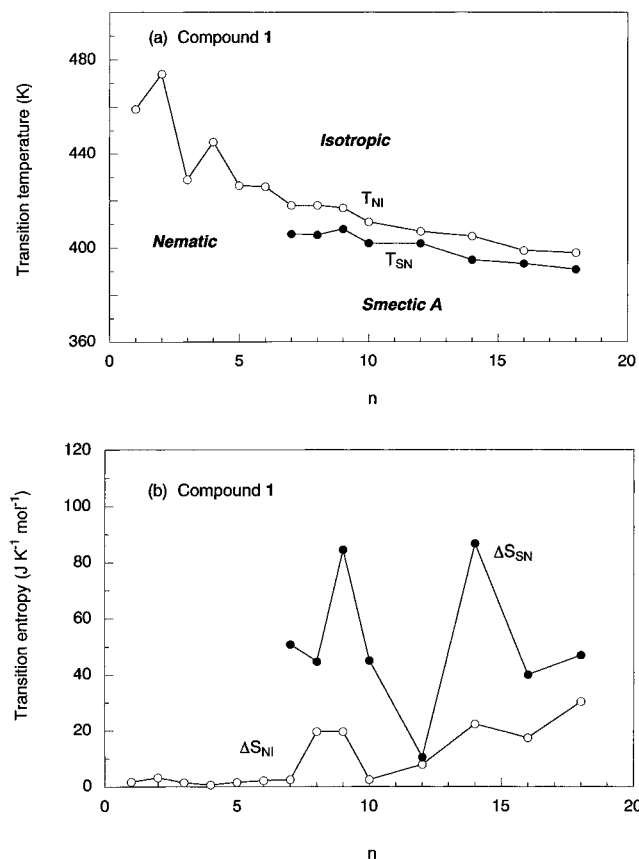
1. In the region of short alkyl chains, both nematic and smectic phases are present. In the region of longer alkyl chains, however, the nematic phase disappears and only the smectic A phase remains.
2.  $T_{SN}$  increases with increasing alkyl chain length.
3.  $T_{SN}$  and  $T_{NI}$  curves coalesce to  $T_{SI}$  curve.
4.  $\Delta S_{NI}$  is as a whole constant, while  $\Delta S_{SN}$  tends to increase with increasing alkyl chain length and is larger than  $\Delta S_{NI}$ .
5.  $\Delta S_{SI}$  is much larger than  $\Delta S_{SN}$ , and it increases with increasing alkyl chain length. The discontinuity of  $\Delta S_{SN}$  and  $\Delta S_{SI}$  is also observed in both the theoretical and the experimental diagrams.

In spite of these agreements, there are also some discrepancies between the theoretical and the observed behaviors such as the following:

1. In the observed diagram (Figure 4a),  $T_{NI}$  decreases with increasing alkyl chain length, although it remains constant in the theoretical model (Figure 2a). This is ascribed to the fact that only the ordering due to the *anisotropic part of intermolecular forces* is considered in McMillan's model. As will be described in Discussion, the decrease in  $T_{NI}$  can be accounted for by the ordering due to the *rigid-body repulsive interactions*.

2. Figure 4a shows that  $T_{SI}$  increases up to the chain length 12 and then decreases with increasing the chain length, whereas it monotonously increases in the theoretical model (Figure 2a). The lack of the ordering by the rigid-body repulsive interaction may also account for this disagreement.

**Relation between Molecular Properties and Transition Temperature of Nematic–Isotropic.** As mentioned above,



**Figure 3.** Observed dependency of (a) transition temperature and (b) transition entropy on alkyl chain length ( $n$ ) for compound **1** (data are cited from ref 1).

there are two factors affecting the thermodynamic properties of liquid crystals. One is ordering due to the anisotropic part of dispersion forces between molecules which was first treated by Maier and Saupe,<sup>3</sup> and the other factor is ordering by the rigid-body repulsions pointed by Onsager.<sup>6</sup> One of the theories which treat with both of these factors was proposed by Kimura.<sup>5</sup> The finally derived equation is

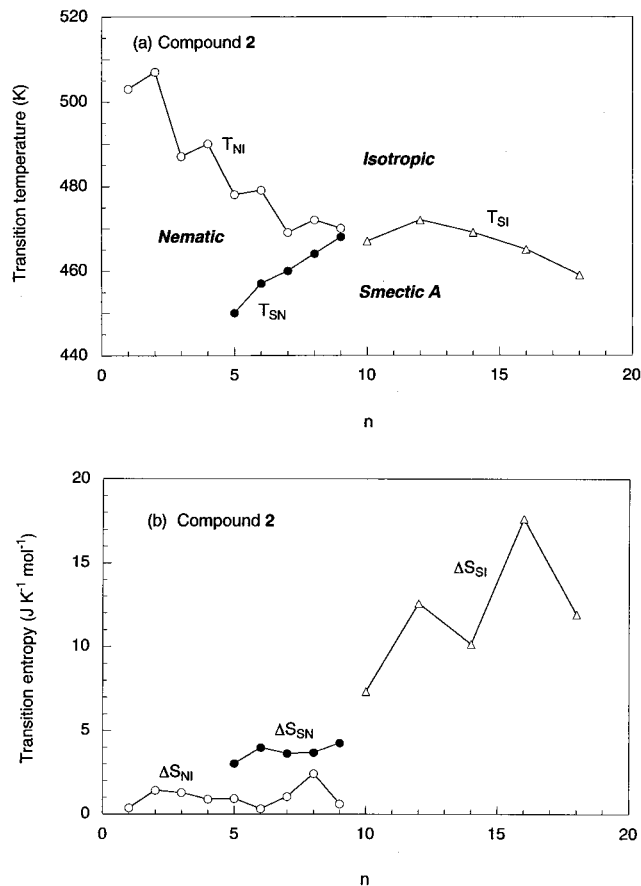
$$T_{NI} = (64A/5\pi^2 kD^6) \{ (5.21 - L/D)(L/D - 0.426)(L/D - 0.333) \}^{-1} \quad (1)$$

where  $A$  is the quantity related to the strength of dispersion forces,  $k$  is the Boltzmann constant,  $D$  is the diameter of the rigid spherocylinders having radius  $r$  and cylindrical length  $l$ , and  $L = l + 2r$ . Using the simple Drude model, the quantity  $A$  is approximately given by eq 2, where  $I$  is the

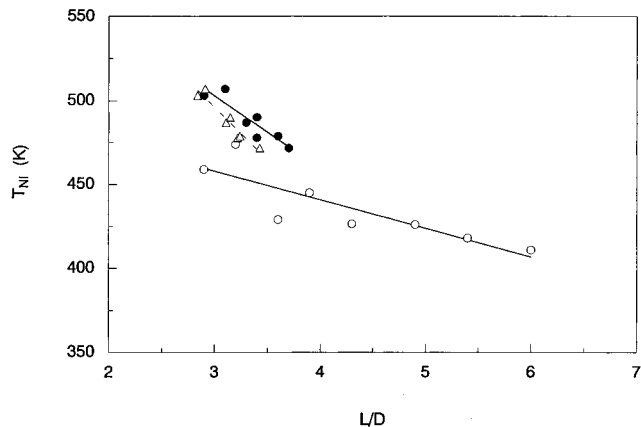
$$A = (I/4) \{ \alpha_{||}(0) - \alpha_{\perp}(0) \}^2 \quad (2)$$

ionization energy of a molecule and  $\alpha_{||}(0)$  and  $\alpha_{\perp}(0)$  are respectively the parallel and perpendicular components of electronic static polarizability of a molecule.<sup>5</sup> Equation 1 qualitatively indicates that  $T_{NI}$  is dominated by  $A$ ,  $D$ , and  $L/D$ . Thus we first investigated the effect of  $L/D$  on  $T_{NI}$  (Figure 5). The structures of **1**, **2-1**, and **2-2** used for the estimation of  $L/D$  are shown in Figure 1a–c. As predicted by eq 1,  $T_{NI}$  has a tendency to decrease with increasing  $L/D$  in the region of small  $L/D$  for **1** and **2** (Figure 5), although the agreement is qualitative.

In order to obtain coefficient  $A$  using eq 2, we calculated  $I$ ,  $\alpha_{||}(0)$ , and  $\alpha_{\perp}(0)$  by the AM1 method. The dependence of  $I$

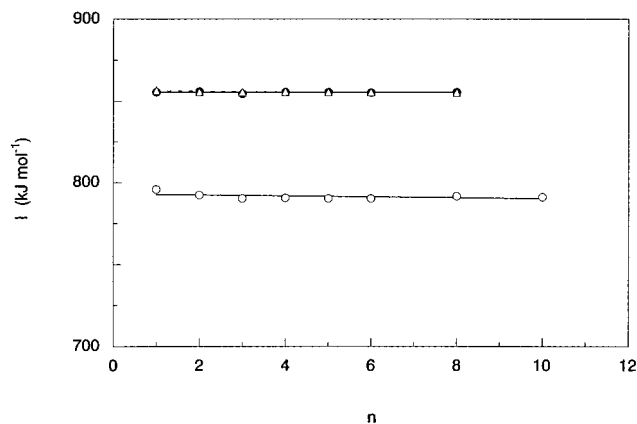


**Figure 4.** Observed dependency of (a) transition temperature and (b) transition entropy on  $n$  for compound **2** (data are cited from ref 2).

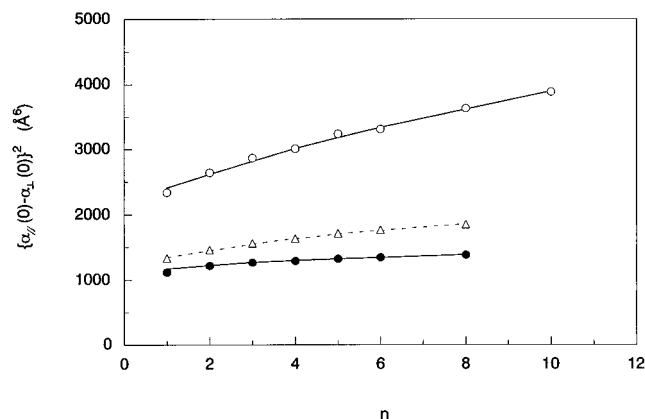


**Figure 5.** Relation between  $T_{NI}$  and  $L/D$ : **1** (○), **2-1** (●), and **2-2** (△).

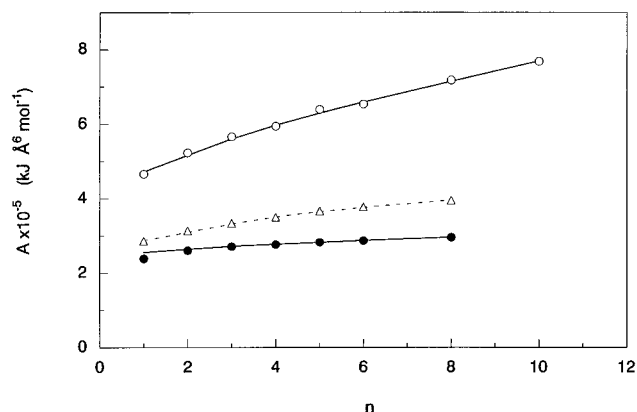
and  $\{ \alpha_{||}(0) - \alpha_{\perp}(0) \}^2$  on the number of carbon atoms of the alkyl chains ( $n$ ) is shown in Figures 6 and 7. The  $I$  values of **2-1** (ca. 850 kJ mol<sup>-1</sup>) and **2-2** (ca. 850 kJ mol<sup>-1</sup>) are slightly higher than that of **1** (ca. 800 kJ mol<sup>-1</sup>) irrespective of  $n$  (Figure 6), while the anisotropy of polarizabilities,  $\{ \alpha_{||}(0) - \alpha_{\perp}(0) \}^2$ , of **1** (2340–3880 Å<sup>6</sup>) is considerably higher than those of **2-1** and **2-2** (1110–1850 Å<sup>6</sup>) and increases with  $n$  (Figure 7). Coefficient  $A$  obtained from these two factors is plotted against  $n$  (Figure 8). It is apparent that the large value of  $A$  in **1** ( $4.65 \times 10^5$  to  $7.68 \times 10^5$  kJ Å<sup>6</sup> mol<sup>-1</sup>) arises from its high polarizability due to its long  $\pi$ -conjugation system. On the other hand, the  $\pi$ -conjugation of **2-1** and **2-2** is not so long as **1**, which accounts for lower polarizability and smaller  $A$  value ( $2.39 \times 10^5$  to  $3.95 \times 10^5$  kJ Å<sup>6</sup> mol<sup>-1</sup>).



**Figure 6.** Relation between calculated ionization potential ( $I$ ) and  $n$ : **1** (○), **2-1** (●), and **2-2** (△).



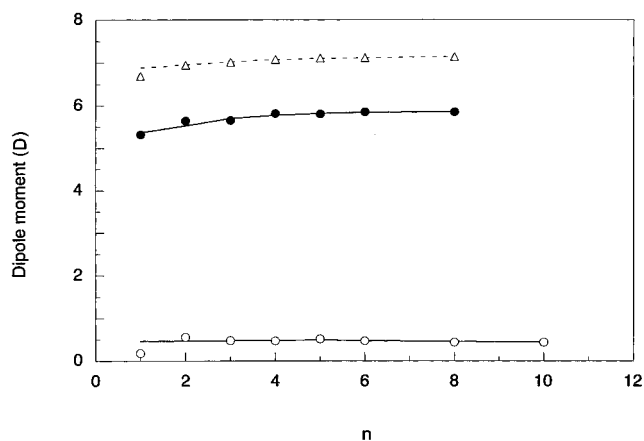
**Figure 7.** Relation between  $\{\alpha_{||}(0) - \alpha_{\perp}(0)\}^2$  and  $n$ : **1** (○), **2-1** (●), and **2-2** (△).



**Figure 8.** Relation between  $A$  and  $n$ : **1** (○), **2-1** (●), and **2-2** (△).

It is concluded qualitatively from eq 1 that the  $D$  value of **1** should be larger than that of **2**, since  $T_{NI}$  of **2** is higher than that of **1** as shown in Figure 5. The greater flexibility of **1** induced by two alkyl chains may account for the larger  $D$  value.

Another possible explanation for the high  $T_{NI}$  of **2** may be the large permanent dipole moment (5.32–7.14 D) (Figure 9). Although this direct interaction between permanent dipole moments is ruled out in Kimura's model, the interactions between permanent and induced dipole moments can contribute to  $T_{NI}$ . Conformer **2-2** has a large  $y$  component ( $\mu_y = -4.67$  D) as well as large  $x$  component ( $\mu_x = 4.57$  D), although **2-1** actually has only  $x$  component ( $\mu_x = 5.03$  D). The difference in the  $y$ -directed permanent dipole moments between **2-1** and



**Figure 9.** Relation between permanent dipole moment ( $\mu$ ) and  $n$ : **1** (○), **2-1** (●), and **2-2** (△).

**2-2** is caused by the difference in the arrangement of the two carbonyl groups. That is, **2-1** has two antiparallel carbonyl groups directed along the  $y$ -axis, but **2-2** has two parallel carbonyl groups. Contrary to **2-1** and **2-2**, the permanent dipole moment of **1** is quite small (Figures 1a and 9) in spite of its large polarizability. Thus there is a possibility that the large permanent dipole moment of **2** contributes to the intermolecular force and elevate  $T_{NI}$ .<sup>3</sup>

#### IV. Discussion

According to McMillan's model, nematic–isotropic transition should be independent of alkyl chain length ( $n$ ); *viz.*,  $T_{NI}$  and  $\Delta S_{NI}$  are constant irrespective of  $n$  (Figure 2). The observed  $T_{NI}$ , however, decreases as a whole with increasing  $n$  both in **1** and **2** (Figures 3a and 4a). On the other hand, Kimura's model can qualitatively explain the experimental  $T_{NI}$ , which is due to the rigid-body repulsive interactions between alkyl chain tails included in this model. It is generally known that the stability of the nematic phase is dominated by the structures of central cores of liquid crystal molecules and long alkyl chains attached to the central cores weaken the molecular interaction in nematic phase. The findings that the observed  $\Delta S_{NI}$  of **2** (Figure 4b) is as a whole independent of  $n$  are well compatible with McMillan's model. That  $\Delta S_{NI}$  of **1** has a tendency to gradually increase when  $n$  is larger than 10 (Figure 3b) may be due to pronounced flexibility of long alkyl chains.

Compounds **1** and **2** also exhibit smectic A phases. McMillan's model predicts that both  $T_{SN}$  and  $\Delta S_{SN}$  should increase with  $n$  (Figure 2). This prediction qualitatively agrees with the observation for **2** (Figure 4), whereas in compound **1**  $T_{SN}$  shown in Figure 3a decreases gradually with increasing  $n$ . It may be concluded from the above discussion that rigid-body repulsive interactions are not so important in smectic–nematic transition. That is, in smectic–nematic transition the long axis of rodlike molecules is retained in one particular direction and thus there is only small change in the repulsive interaction between rodlike molecules.

We next focus on the difference in compounds **1** and **2**. The electronic properties of **1** and **2** are in contrast to each other; *viz.*, **1** has large polarizability and small permanent dipole moment while **2** has large permanent dipole moment and small polarizability. Two possible interpretations have been presented for the difference in  $T_{NI}$ . Kimura's theory for nematic–isotropic transition suggests that the difference in  $T_{NI}$  between **1** and **2** arises from the difference in the width ( $D$ ) of the molecules. Another possible interpretation is that  $T_{NI}$  depends on the

magnitude permanent dipole moment; *viz.*, the interaction between permanent dipole moment and induced dipole moment of **2** can elevate  $T_{NI}$ . It is also an intriguing finding that the smectic A phase of **2** is more stable than that of **1**. It was reported that the large lateral dipole moment of liquid crystal molecules stabilizes the smectic A phase because of the increase in intermolecular interaction.<sup>7</sup> This is in good agreement with the high stability of the smectic phase in **2**, which has much larger lateral dipole moment than **1** as shown in Figure 1.

## References and Notes

- (1) Chugar, N. K.; Shah, S. N.; Vora, R. A. *Mol. Cryst. Liq. Cryst.* **1991**, *209*, 237.
- (2) Chudgar, N. K.; Bosco, R.; Shah, S. N. *Liq. Cryst.* **1991**, *10*, 141.
- (3) McMillan, W. L. *Phys. Rev.* **1971**, *A4*, 1238.
- (4) Kimura, H. *J. Phys. Soc. Jpn.* **1974**, *36*, 1280.
- (5) Maier, W.; Saupe, A. *Z. Naturforsch.* **1952**, *14a*, 882; **1960**, *15a*, 287; **1961**, *16a*, 816.
- (6) Onsager, L. *Ann. N.Y. Acad. Sci.* **1949**, *51*, 627.
- (7) Nakai, H.; Takenaka, S.; Kusabayashi, S. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 3571.