

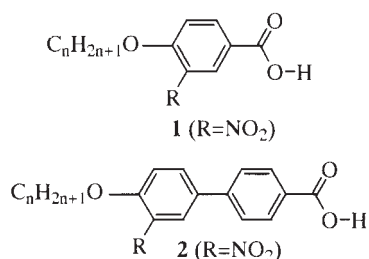
Liquid Crystal Properties of 4-Alkoxy-3-nitrobenzoic Acids

Takeyasu Tasaka, Hiroaki Okamoto,* Yuki Morita, Kazuo Kasatani, and Shunsuke Takenaka
 Department of Materials Science and Engineering, Faculty of Engineering, Yamaguchi University,
 2557 Tokiwadai, Ube, Yamaguchi 755-8611

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For the homologous series of 4-alkoxy-3-nitrobenzoic acids the nonyloxy and the higher members exhibit a smectic A phase, where the layer spacings are 1.5–1.6 times of the fully extended molecular lengths.

It is well known that polar substituents such as nitro and cyano groups in liquid crystal (LC) molecules sometimes play some important roles for the smectic properties.^{1–3} For example, such polar groups at the terminal position of the LC core frequently cause the complex polymesomorphism involving reentrant phases. The lateral polar group is also expected to increase the local specific interactions, causing abnormal phase behavior. In this connection, we are interested in the mesomorphic properties of 4-alkoxy-3-nitrobenzoic acids, **1** (R = NO₂).



The homologous series of the hydrogen derivative of **1** (R = H) is known to exhibit nematic (N) phase as well as smectic C (Sm C) one, when the alkoxy chain is suitably long,⁴ where the hydrogen-bonded dimers are supposed to be formed and responsible for the formation of LC phases. The fluoro and chloro derivatives (R = F or Cl)⁵ are also known to exhibit N and Sm C phases even in the higher members (n = 16), while the transition temperatures are fairly low compared with the corresponding hydrogen derivatives. The related compounds, **2**, have been known to exhibit an interesting mesomorphic behavior.⁶ In this work, we are interested in the polar effect of the lateral nitro group on mesomorphic properties for compounds **1** (R = NO₂).

The transition temperatures and latent heats for the homologous series of **1** are summarized in Table 1. The hexyloxy and heptyloxy homologs are non-mesogenic, and N phase was not formed through the homologs. The homologous series exhibits one kind of mesophase from the nonyloxy member. The mesophase tends to show a focal conic fan texture on the glass surface treated with polyimide. The mesophase has an optically uniaxial nature under a homeotropic alignment. Therefore, the mesophase is assumed to have a layer structure with an orthogonal arrangement.

The mesophase–isotropic transition temperature increases on ascending the homolog, and tends to become constant around

Table 1. Transition temperatures (T/°C) and latent heats (kJ mol⁻¹) for compounds **1**

n	Transition temperatures			Latent heats	
	C	Sm A	I	ΔH_{mp}	ΔH_{SmA-I}
8	•	120	—	•	29.6
9	•	96	(• 83)	•	24.6 ^a
10	•	98	(• 88)	•	20.8
11	•	91	(• 90)	•	22.6
12	•	92	• 94	•	30.8
13	•	89	• 95	•	33.8
14	•	96	• 97	•	45.9
15	•	95	• 97	•	50.1
16	•	98	• 98	•	57.7

^aThe latent heat could not be calculated because of a large exotherm for recrystallization.

98 °C. The mesophase–isotropic transition temperatures appear to exhibit a weak odd-even alternation.

The mesophase phase was further characterized by an X-ray examination. The X-ray profiles for the undecyloxy to hexadecyloxy homologs show a sharp reflection peak around $2\theta = ca. 2^\circ$ and a broad and weak one around 20° . These are attributable to the reflection peaks from the smectic layer and disordered molecular arrangement within the layer.

From the X-ray results and microscopic observation, it is concluded that the smectic phase is assigned to the smectic A (Sm A) modification. A similar alternation of the phase transition behavior has been known in the substituent effect on the mesomorphic properties for 4-alkoxy-3-R-biphenyl-4'-carboxylic acids (**2**), that is, 4-alkoxy-3-nitrobiphenyl-4'-carboxylic acids exhibit an Sm A phase as well as N, Sm C, and smectic D (Sm D) ones,⁷ while the hydrogen (R = H),⁶ halogens (R = Cl or Br), and methoxy derivatives (R = OCH₃)⁷ of **2** exhibit only N and Sm C phases.

The layer spacings are plotted against the carbon number in Figure 1, where the calculated molecular lengths are also indicated. The molecular lengths were estimated from a semi-empirical molecular orbital calculation (MOPAC97), where the most stable conformation was obtained by the AM1 method, and the results are shown in Figure 2.

It would be reasonable to assume that the rotation around the ether bond is strongly restricted because of the large steric hindrance between the methylene chain and the nitro group, so that the entire molecular shape is bent a little, as shown in Figure 2. The molecular lengths, d , in Table 1 are calculated from the model conformation. In such model, the molecular length is expected to extend by 1.25 Å/methylene unit, if the average alkoxy chain arranges normal to the smectic layer plane. In general, the benzoic acid derivatives are known to form hydrogen-bonded dimers. It would be reasonable to assume that

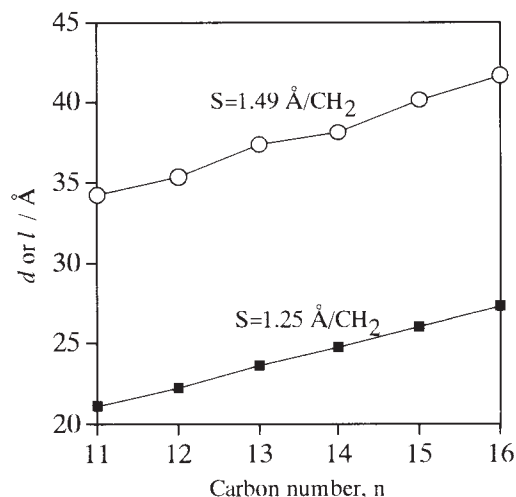


Figure 1. Plots of layer spacings (○) and calculated molecular lengths (■) against the carbon number.

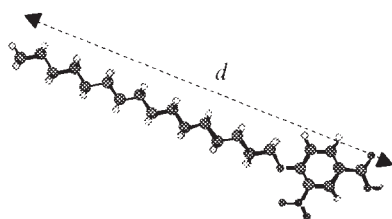


Figure 2. A possible molecular structure of the hexadecyloxy homolog of **1**, calculated by the AM1 method (MOPAC).

such dimers are also formed in compounds **1**, so that the layer spacings are expected to be twice of the calculated molecular lengths. If the molecules form the hydrogen-bonded dimers and the alkoxy chains are normal to the smectic layer in Sm A phase, the layer spacings are expected to increase 2.50 Å (twice of 1.25 Å).

The observed layer spacings for the homologs in Figure 1 show a linear correlation with the carbon number, while the plot shows a little uneven, suggesting that the long hydrocarbon chain extends almost linearly without distorting in whole members. Interestingly, the observed layer spacings are longer than the calculated molecular lengths for the monomers and fairly shorter than twice. In addition, the slope for the observed layer spacings

in Figure 1 (1.49 Å/methylene unit) is larger than the slope for the calculated molecular lengths (1.25 Å) and smaller than twice (2.50 Å). From these results, it is apparent that the molecular arrangement in the Sm A phase is not a monolayers type of the dimers.

Generally, LC materials having a terminal polar group such as a nitro or a cyano group show an interesting phase transition behavior involving N and Sm A phases, where the layer spacings for the Sm A phase is larger than the calculated molecular lengths.¹⁻³ In such systems, strong polar interactions around the terminal polar groups have been supposed to play important role for the abnormal phase transition behavior. Although, in the present system, the nitro group is not located at the terminal position of the LC core but the lateral one, the similar polar interactions might affect the layer structure.

In 4-alkoxy-3-nitrophenyl-4'-carboxylic acids (**2**), the higher homologs show the mesomorphic sequence of a Sm C–Sm D–Sm A type.⁷ The Sm D phase has been known scarcely to form in conventional LC materials, and the structure of Sm D phase for **2** has been clarified in more detail.^{8,9} There is no doubt that the lateral nitro group plays important role for the complex phase transition behavior. In the present homologs the Sm C and D phases could not be observed.

Further examination is now underway.

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