New Troponoid Liquid Crystalline Compounds, 5-Alkoxy-2-(4-alkoxybenzoylamino)tropones

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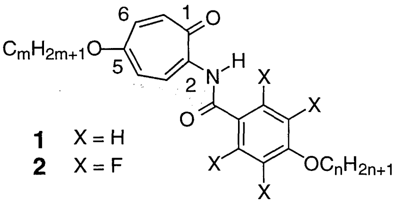
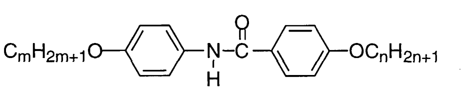
The X-ray crystallographic structural analysis of 5-butoxy-2-(4-methoxybenzoylamino)tropone, a liquid crystalline compound, revealed to form the head-to-tail dimer, in which a CH-π interaction between the benzoyl π-system and the β-hydrogen of the 5-butoxy group on the tropone ring of the neighboring molecule as well as intermolecular π-π stacking interactions with the two tropone systems. On the other hand, 2-(4-alkoxybenzoylamino)-5-methoxytropone lacking the β-hydrogen and the corresponding benzenoid, *N*-(4-alkoxyphenyl)-4-alkoxybenzamide were non-mesogenic.

During our recent study on the troponoid liquid crystals,[1] we have discovered a new type of compounds, 5-alkoxy-2-(4-alkoxybenzoylamino)tropone **1** (m, n),[2] which was prepared from 5-alkoxy-2-aminotropone and 4-alkoxybenzoyl chloride by conventional methods.[3] The X-ray crystallographic structural analysis indicated a CH-π interaction between the benzoyl π-system and the β-hydrogen of the alkyl group on the tropone ring of the neighboring molecule as well as intermolecular π-π stacking interactions with the two tropone systems. In this paper, we describe the role of the intermolecular interactions on the exhibition of the mesophase.



1 X = H
2 X = F



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The phase transition temperatures of **1** and their enthalpy changes were determined by differential scanning calorimetry. The appearance of the mesophases was determined with a polarizing microscope equipped with a hot stage. Compound **1** (4, 1) showed simultaneous occurrence of schlieren textures with droplets. The clearing point enthalpy change (ΔH) of **1** (4, 1) was 0.7 kJ/mol, which is similar to the ordinary nematic (N) phase. The X-ray diffraction study of **1** (4, 1) also supported N phase. Interestingly, **1** (2, 1) was mesogenic, whereas **1** (1, 2) was not. The length of the side chains on the tropone ring was required to be longer than the ethoxy group for the appearance of the mesophase.

The X-ray crystallographic analysis of a single crystal of **1** (4, 1)[4] disclosed that the overall shape of the molecule was angular due to intramolecular hydrogen bonding between the tropone carbonyl group and the NH group and **1** (4, 1) formed the dimeric head-to-tail structure as shown in Figure 1, in which the two tropone rings faced each other with a slight slip. The distances between the carbonyl carbon and the hydrogen at C-4 and between C-6' and the hydrogen at C-3 were 3.451 and 3.382 Å, respectively. They were not close each other. The distance between the carbon atom at C-2 of a tropone ring and the carbon atom at C-5' of the other tropone ring is 3.522 Å, which is close to the sum (3.4 Å) of the van der Waals radii of two aromatic carbons to indicate that two tropone rings are forming a π-π stacking structure.[5] Furthermore, the intermolecular distance between one of the methylene hydrogen atoms at the β-carbon of the butoxy group on the tropone ring and the benzene ring of another molecule is 3.003 Å, which is also close to the sum (2.9 Å) of their van der Waals radii. Therefore, it should be suggestive of a CH-π interaction[6] between them. These crystal structural characteristics are compatible with the results that the alkyl chain length of the tropone ring was critical whether they were mesogenic or not since **1** (1, 2), which has no close hydrogen atom to interact with the benzene ring, was non-mesogenic, while **1** (2, 1) with the close hydrogen atom was mesogenic.

Table 1. Transition temperatures (°C) and enthalpy changes (kJ/mol) of **1**

(m, n)	C		N		Iso
1, 1	•	174 (32.4)	-		•
1, 2	•	156 (30.1)	-		•
1, 12	•	114 (38.1)	-		•
2, 1	•	135 (30.1)	•	137	•
2, 2	•	146 (22.8)	•	151 (1.3)	•
2, 12	•	102 (46.2)	•	112 (1.0)	•
4, 1	•	96	•	114	•
6, 12	•	62 (35.1)	•	108 (1.7)	•

C: Crystal, N: Nematic C phase, Iso: Isotropic liquid. Numbers in parentheses are enthaly changes.

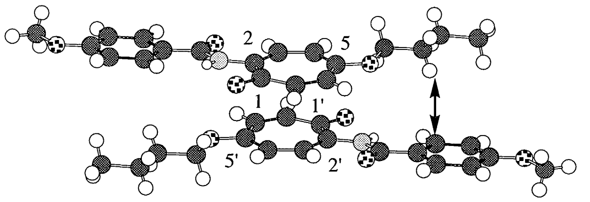

Figure 1. Side view of the head-to-tail dimer of **1** (4,1). The double-headed arrow indicates the CH-π interaction.

Next, perfluorobenzene derivatives **2** (m, n) were prepared to compare their properties with **1**. However, they were not mesogenic even in **2** (4, 1) and **2** (6, 12) with longer alkyl chains.[7] Since the electron density of the benzene ring of **2** is more lowered by electron withdrawing fluorine atoms than that of **1**, the CH-π interaction in **2** should be reduced. A more precise description of the structure of **2** has to await a structural determination by X-ray crystallography.

Finally, the corresponding benzenoid derivatives **3** (4, 4), **3** (6, 12), and **3** (9, 4) were not mesogenic.[8] It is easily understood that the higher melting point of **3** than the corresponding **1** was caused by the intermolecular hydrogen bond between the NH and the amido carbonyl groups. In the case of **1**, however, the NH group took a part in the intramolecular hydrogen bond to reduce an intermolecular hydrogen bond and to make melting point lower. These remarkable properties are undoubtedly due to the tropone carbonyl group.

In conclusion, the mesogenic properties of troponoids can be rationalized by both π-π stacking and CH-π interactions[9] and by reduction of intermolecular hydrogen bonding. Electron-withdrawing substituents on the benzene ring depressed CH-π interactions to make them non-mesogenic. The substituent effect on the mesogenic properties should be explored and further investigations on the unique troponoid liquid crystals are continued.

Table 2. Transition temperatures (°C) of **2**

(m, n)	C		Iso
1, 1	•	186	•
4, 1	•	162	•
6, 12	•	89	•

References and Note

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2 m and n denote carbon numbers of alkoxy groups on the 5-position of the tropone and the 4-position of benzoyl moieties.

3 Synthesis of these compounds will be described in a full paper.

4 Crystal data: $C_{19}H_{21}O_4N$, M=327.38; monoclinic, space group $P2_1/n$; a=13.196(3), b=12.673(1), c=10.788(1) Å, β=107.55(2)°; V=1720.3(5) Å^3; Z=4; λ(Cu Kα)=1.54184 Å, R=0.049, Rw=0.072.

5 a) C. A. Hunter and J. K. M. Sanders, *J. Am. Chem. Soc.*, **112**, 5525 (1990). b) M. Fujita, Y. J. Kwan, S. Washizu, and K. Ogura, *J. Am. Chem. Soc.*, **116**, 1151 (1994).

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7 Perfluorobenzene derivatives **2** (4, 1) and **2** (6, 12) have the higher melting points at 169 °C and 92 °C than the corresponding **1** series.

8 The melting points of **3** (4, 6), **3** (6, 12), and **3** (9, 4) were 153 °C, 150 °C, and 146 °C, respectively.

9 K. Miyamura, A. Mihara, T. Fujii, Y. Gohshi, and Y. Ishii, *J. Am. Chem. Soc.*, **117**, 2377 (1995).