Mesomorphic Properties of 4-Benzoylaminobenzonitrile Derivatives Having an Electron-withdrawing Group with Hydrogen Bonding Ability

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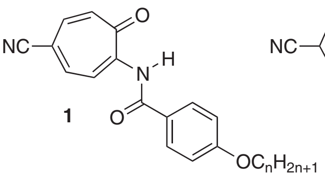
4-Benzoylaminobenzonitrile derivatives having an electron-withdrawing group with hydrogen bonding ability such as a formyl or a nitro group at the C-3 position of the benzonitrile moiety were synthesized. They had the higher transition temperatures than the parent compound. It is explained by the intramolecular hydrogen bonding between the lateral group at C-3 and the amide proton to prohibit the free rotation around the *N*-benzonitrile bond, which made molecules flat to increase transition temperatures.

We have previously reported the mesomorphic properties of 2-(4-alkoxybenzoylamino)- (**1**) and 2-(4-alkoxybenzoyloxy)-5-cyanotropones (**2**).[1] The transition temperatures of amide **1** are higher than those of ester **2** because the single crystallographic analysis of an amide derivative showed that the core structure is almost flat[2] through an intramolecular hydrogen bonding between the tropone carbonyl and the NH group while the core part of an ester derivative is twisted.[3] Furthermore, troponoid amide **1** has higher transition temperatures than the corresponding benzenoid amide **3a**. It must be due to the free rotation around *N*-benzonitrile bond of benzenoid amide **3a**, which reduces an intermolecular overlap between neighboring molecules. It has been already known that an introduction of a hydroxy group into compound **4a**[4] enhanced the transition temperatures, by forming an intramolecular hydrogen bonding in compound **4b**.[5] Similar results were observed in 5-alkyl-2-(4-alkoxyphenyl)pyridines.[5] In this paper, based on the results obtained in troponoid amide **1**, we introduce a lateral group such as a formyl or a nitro group with hydrogen bonding ability at C-3 of the benzonitrile ring of amide **3a** to report the mesomorphic properties.



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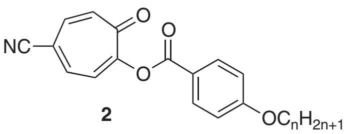

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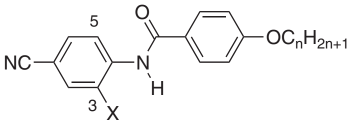
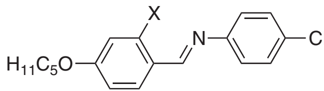
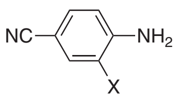


3a: X=H
3b: X=CHO
3c: X=NO_2
3d: X=Br



4a: X=H, Cr • 64 • N • 97 • Iso
4b: X=OH, Cr • 80 • SmA • 81 • N • 124 • Iso



5a: X=H
5b: X=Br
5c: X=CHO
5d: X=NO_2

Aldehyde **3b** was prepared from 4-cyanoaniline (**5a**); bromination of **5a** with *N*-bromosuccinic amide (NBS) gave 2-bromo-4-cyanoaniline (**5b**), which was reacted with 4-alkoxybenzoyl chloride in pyridine in the presence of DMAP to give *N*-(2-bromo-4-cyanophenyl)-4-alkoxybenzamide (**3d**).[6] Consequently, compound **5b** was reacted with *n*-BuLi and with DMF at $-78\,^\circ C$ to give 2-formyl-4-cyanoaniline (**5c**), which gave aldehyde **3b**[6] by the reaction with 4-alkoxybenzoyl chloride. Compound **3c**[6] with a nitro group was prepared by benzoylation of 4-cyano-2-nitroaniline (**5d**) with 4-alkoxybenzoyl chloride. In the ^1H NMR spectrum of aldehyde **3b**, the amide proton [δ 12.17 (1H, br s)] and the aromatic proton [9.12 (1H, d, $J = 8.9$ Hz)] at C-5 appeared at the lower field than parent **3a** [8.22 (1H, br s) and 7.79 (1H, d, $J = 8.0$ Hz)]. Chemical shifts [δ 11.46 (1H, br s) and 9.22 (1H, d, $J = 8.9$ Hz)] of the corresponding protons of compound **3c** are close to those of aldehyde **3b** whereas those [8.58 (1H, br s) and 8.76 (1H, d, $J = 8.9$ Hz)] of compound **3d** are close to parent **3a**. These low field shifts of the amide proton and the ring proton at C-5 of compounds **3b** and **3c** must be due to an intramolecular hydrogen bonding and the anisotropy effect of the benzoyl carbonyl group, respectively. These resulted that they are flat.

The transition temperatures of **3** are summarized in Table 1. Polarizing microscopic observations showed that aldehyde **3b** ($n = 8$) had schlieren textures at 159.6 °C and focal-conic and homeotropic textures at 152.6 °C, which indicated that they were nematic and smectic A phases, respectively. The X-ray diffraction studies of aldehyde **3b** ($n = 16$) and bromide **3d** ($n = 16$) derivatives showed that the ratio of the layer spacing (d) and the calculated molecular length (l) by MM2 is 1.3 for **3b** and 1.3 for **3d**, which concluded that they had an interdigitated bilayer structure.

When a formyl group was introduced at the C-3 of the benzonitrile ring, the transition temperatures were increased. Although the melting points were increased by 22 °C as the maximum temperature, the clearing points were increased by 43–61 °C, which are close to those of troponoid amide **1**.[1] It is explained by the prohibition of the free rotation between the *N*-

Table 1. Transition temperatures of 4-benzoylaminobenzonitriles[a]

	n	Transition temp./°C		n	Transition temp./°C
3a	4	Cr·161.7·Iso	**3c**	**4**	Cr·113.0·Iso
	8	Cr·123.8·Iso		8	Cr·98.0·SmA·101.4·Iso
	12	Cr·122.4·(SmA·107.5·)Iso		12	Cr·97.6·SmA·119.6·Iso
	14	Cr·131.0·(SmA·118.4·)Iso		14	Cr·103.7·SmA·124.5·Iso
	16	Cr·126.4·(SmA·123.7·)Iso		16	Cr·101.5·SmA·126.1·Iso
3b	**4**	Cr·155.7·N·165.0·Iso			
	8	Cr·145.5·SmA·156.7·N·160.0·Iso	**3d**	**8**	Cr·95.7·(N·82.0·)Iso
	12	Cr·135.9·SmA·168.6·Iso		12	Cr·97.7·(SmA·85.8·N·86.8·)Iso
	14	Cr·131.8·SmA·166.8·Iso		14	Cr·96.8·(SmA·92.3·)Iso
	16	Cr·131.6·SmA·166.8·Iso		16	Cr·99.3·(SmA·95.6·)Iso

[a]Cr: crystals, SmA: smectic A phase, N: nematic phase, Iso: isotropic liquid. ( ) means monotropic transition.

benzonitrile ring. An intramolecular hydrogen bonding between the formyl group and the amide proton made the core part flat, which increased the thermal stability of the smectic A phase. Although the intramolecular hydrogen bonding played a role to prohibit intermolecular hydrogen bonding, the tight overlapping between flat molecules increased the melting points as well as the clearing points. When the length of the alkoxy side chain of **3b** is short, an nematic phase appears.

Next, a nitro group was introduced at the C-3 position. The transition temperatures of nitro compound **3c** were reduced when compared with those of aldehyde **3b**. This should be due to the repulsive force of ionic nitro groups, which made intermolecular interactions weaker to reduce the transition temperatures although the core part of nitro compound **3c** is flat. When compared the transition temperatures of compounds **3b** and **3c** with parent **3a**, the melting points of **3c** were reduced while those of **3b** and their clearing points of compounds **3b** and **3c** were increased.

Finally, we introduced a bromine atom at the C-3 position. Both melting and clearing points were decreased to induce an nematic phase as observed in **3d** ($n = 8$). These results are consistent with the views that the lateral substituent has a large effect on melting point and the thermal stability of the smectic phases and has a less pronounced effect on the nematic clearing point.[7]

The molecular breadths of **3** were calculated by MM2 as follows; **3a**; 6.6 Å, **3b**; 8.0 Å, **3c**; 8.5 Å, and **3d**; 8.1 Å. Although compound **3c** with the widest molecular breadth is less favorable to exhibit mesogenic properties, they had higher transition temperatures than bromide **3d**. This should be attributable to the intramolecular hydrogen bonding ability of the nitro group.

By introducing an electron-withdrawing group with intramolecualr hydrogen bonding ability, the transition temperatures were increased. The lateral group at C-3 took part in prohibiting the free rotation around the *N*-benzonitrile moiety through intramolecular hydrogen bonding to induce mesogenic properties.

References and Notes

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6 All new compounds gave satisfactory spectral data. The selected elemental analysis data are shown: **3b** ($n = 12$): Found: C, 74.62; H, 7.89; N, 6.45%. Calcd for $C_{27}H_{34}N_2O_3$: C, 74.62; H, 7.86; N, 6.40%. **3c** ($n = 12$): Found: C, 69.33; H, 7.36; N, 9.41%. Calcd for $C_{26}H_{33}N_3O_4$: C, 69.16; H, 7.37; N, 9.31%. **3d** ($n = 12$): Found: C, 64.37; H, 6.81; N, 5.80%. Calcd for $C_{26}H_{33}BrN_2O_2$: C, 64.33; H, 6.85; N, 5.77%.

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