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Self-ordered states derived from 2-benzoyloxy- and 2-benzoylamino-5-cyanotroponoids and their corresponding benzenoids: formation of hexagonal self-assembly of liquid crystalline 2-trialkoxybenzoylamino-5-cyanotroponoids in gel states through intramolecular hydrogen bonding and π–π interaction*

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Two ring systems constructed by a cyanotropone ring and a benzoyl group with a mono-, di-, and tri-alkoxyl group, linked by an ester or amide group, and the corresponding benzenoids were synthesised to investigate mesomorphic properties. Both troponoid esters and amides with a monoalkoxybenzoyl group and the corresponding benzenoids had smectic A phases. Troponoid esters and amides with a di- and trialkoxybenzoyl group exhibited smectic A and hexagonal columnar phases, respectively. However, the corresponding benzenoids with a di- and trialkoxybenzoyl group did not exhibit any mesophases. Interestingly, only the mesomorphic troponoid amides with a trialkoxybenzoyl group showed gelling ability. Non-mesomorphic troponoid amides with a trialkoxybenzoyl group, troponoid amides with mono- and dialkoxyl groups, all troponoid esters and all benzenoid esters and amides were not gelators. It was observed that gel formation is strongly related to the formation of a hexagonal columnar phase. An X-ray diffraction study of octanol gels showed that hexagonal packing is involved in gel formation. NMR titration experiments and IR spectral observation of octanol gels supported the fact that intramolecular hydrogen bonding between the tropone carbonyl and the NH group made the core part flat to induce effective π–π interactions, which are driving forces of gelling ability.

Keywords: gel formation; intramolecular hydrogen bonding; π–π interaction; troponoid derivatives; hexagonal columnar phase

1. Introduction

Usually molecules form soft-ordered states through intermolecular interactions such as dispersion forces, π–π interactions, hydrogen bonding, electrostatic and charge-transfer interactions, etc. (*1*). To form self-organising systems like liquid crystalline and gelling states, it is necessary to control these interactions precisely. Typical structures of liquid crystals consist of a core and a flexible part (*2*). The core has at least two rings, such as benzene or cyclohexane rings, to induce rigidity into molecules. Alkoxyl or alkyl groups are used for the flexible part to induce softness. Furthermore, polar substituents, such as a cyano or a nitro groups, introduce polarisability into molecules. To induce liquid crystalline states, for example, soft side chains are introduced to a hard core by preventing crystallisation while hardness is added into molecules to prevent them from becoming liquid. On the other hand, to form low-molecular-weight gelators, molecules are required to have functional groups such as amide, urea, hydroxyl, and carboxyl groups. The latter play roles in the formation of network structures through hydrogen bonding (*3*). Other than these, it is known that aromatic compounds without these functional groups also form gel states through π–π interactions (*4*). Furthermore, chiral molecules are used to prevent tight packing structures to form gels (*5*).

We are currently focusing our attention on preparation of new soft materials like liquid crystals (*6*) and organogels (*7*) by using seven-membered rings as a new central core structure because they have a large dipole moment, which should make layer structures more feasible by forming a head-to-tail arrangement. Additionally, the carbonyl group of troponoids assists in assembling molecules through inter- and intramolecular hydrogen bonding (*8*).

Previously, we have observed that monocyclic 2-acyloxy-5-alkoxytropones, 2,5-diacyloxytropones, and 5-acyloxy-2-alkoxytropones (*9*) exhibited monotropic smectic A (SmA) phases, whereas the corresponding monocyclic benzenoids were not mesomorphic. We have proposed that in troponoids with an alkanoyloxy group at the C-2 position, the alkanoyl group

*Dedicated to the late Professor Naomi Hoshino-Miyazima.

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migration between the two oxygen atoms of the C-2 position and the carbonyl group, so-called [1,9]-sigmatropy, kept the position of the alkanoyl group within the core width to extend the core structure by forming a pseudo-two-ring system (*9, 10*). Furthermore, when non-polar side chains were introduced into the polar troponoid core (*11*), high intramolecular contrast in polarity induces microsegregation to form layer structures. Additionally, a head-to-tail structure should be formed to cancel repulsive dipole–dipole interactions, which also assisted in forming a layer alignment. We have observed that troponoids are mesomorphic, whereas the corresponding benzenoids are not (*9, 12*) or are less thermally stable (*13*) in some cases. Thus, high contrast in polarity in troponoid derivatives is quite important to induce mesophases.

In this paper, we discuss the self-organising properties of 5-cyanotroponoids (*14*) with mono-, di- and trialkoxybenzoyloxy and with mono-, di-, and trialkoxybenzoylamino groups because the cyano group is one of the most useful substituents in benzenoid liquid crystals, as observed, for example, in cyanobiphenyls (*15*). We have reported that 5-cyanotroponoids with a monoalkoxybenzoyloxy and a monoalkoxybenzoylamino group exhibited SmA phases with higher transition temperatures than the corresponding benzenoids and nematic (N) phases with lower transition temperatures than the benzenoids (*14*). 5-Cyanotroponoids with a dialkoxylated benzoyl group exhibited mesophases, whereas the corresponding benzenoids were not mesomorphic. Similarly, 5-cyanotroponoids with a trialkoxylated benzoyl group exhibited hexagonal columnar (Col_h) phases, whereas the corresponding benzenoids did not show any mesophases. Furthermore, only mesomorphic 2-(3,4,5-trialkoxybenzoylamino)-5-cyanotroponoids showed gelling ability (*7, 16*). In these organogels, the columnar order observed in the liquid crystal state is retained, although the lattice parameters of the gels are slightly larger than those of the Col_h phases obtained from 2-(3,4,5-trialkoxybenzoylamino)-5-cyanotroponoids. This paper clarifies the direct correlation between the formation of the liquid crystalline states and the gel formation (*7*), where the hexagonal packing structure contributes to the appearance of soft-ordered states. Such evidence is not so common, although there have been some studies concerning the gel formation ability of liquid crystalline molecules (*4, 17*).

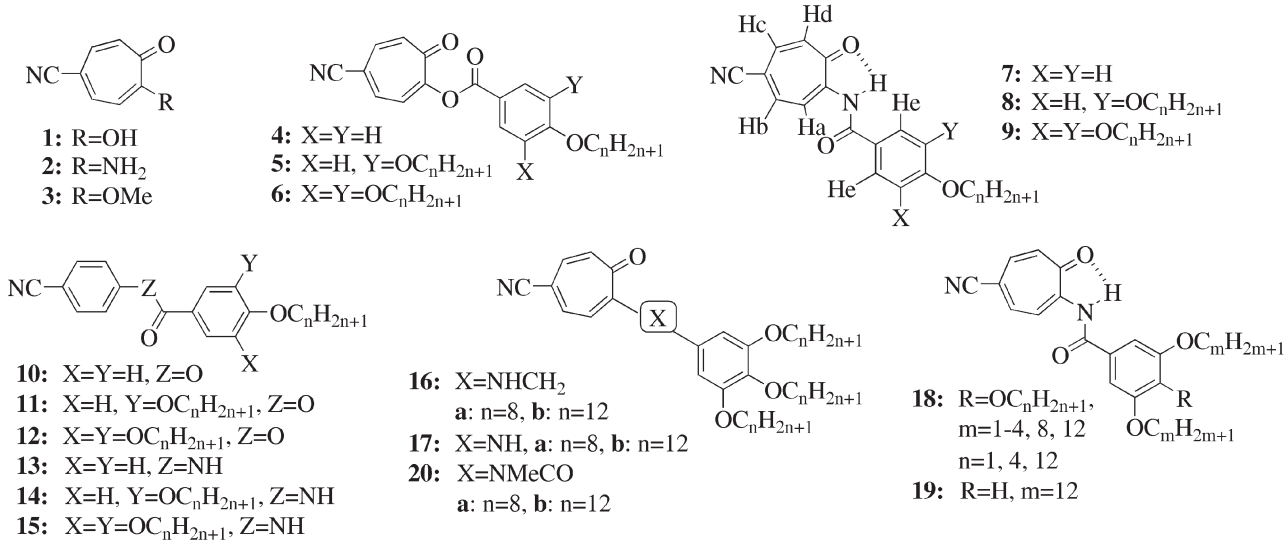
2. Results and discussion

Synthesis

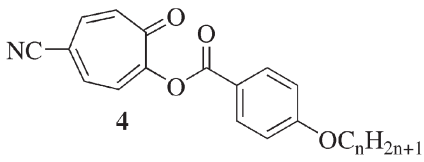
5-Cyanotropolone (**1**) was prepared by a modified method of the known procedure (*18*). 2-Amino-5-cyanotropone (**2**) was synthesised in 92% yield by amination of 5-cyano-2-methoxytropone (**3**), which was obtained by reaction with **1** and diazomethane. Benzoylation of **1** and **2** with mono-, di-, and trialkoxybenzoyl chlorides gave 5-cyanotropone derivatives **4**–**9**, **18** and **19** in reasonable yields. The corresponding benzenoids (**10**–**15**) were similarly synthesised. Reactions of **3** with 3,4,5-trialkoxybenzylamine and 3,4,5-trialkoxyaniline gave **16** and **17**, respectively. The syntheses are summarised in Scheme 1.

Mesomorphic properties

The transition temperatures and thermal behaviour of the compounds investigated were determined using a



Scheme 1.



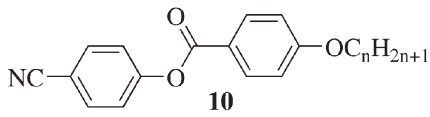
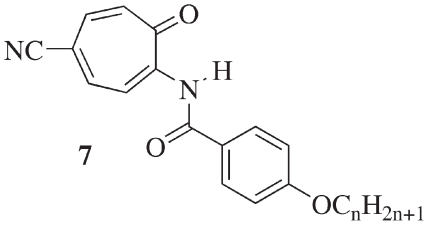


Table 1. Transition temperatures of troponoid ester **4** and benzenoid ester **10** with an alkoxy group.

4	n	Transition temp./°C	**10**	n	Transition temp./°C
a	1	Cr • 142.6 • (N • 50.2 •) Iso	**a**	2	Cr • 121.0 • (N • 105.0 •) Iso
b	2	Cr • 122.3 • (N • 56.8 •) Iso	**b**	4	Cr • 92.0 • N • 104.0 • Iso
c	4	Cr • 116.4 • (N • 55.5 •) Iso	**c**	5	Cr • 87.0 • N • 96.0 • Iso
d	5	Cr • 112.7 • (N • 57.2 •) Iso	**d**	6	Cr • 70.5 • N • 81.0 • Iso
e	6	Cr • 106.0 • (SmA • 54.2 • N • 57.1 •) Iso	**e**	8	Cr • 75.6 • N • 88.0 • Iso
f	8	Cr • 106.5 • (SmA • 80.5 • N • 84.7 •) Iso	**f**	9	Cr • 62.0 • (SmA • 59.0 •) N • 84.0 • Iso
g	9	Cr • 109.4 • (SmA • 95.3 •) Iso	**g**	10	Cr • 80.0 • (SmA • 78.0 •) N • 85.0 • Iso
h	10	Cr • 107.0 • (SmA • 105.7 •) Iso	**h**	12	Cr • 73.0 • SmA • 89.5 • Iso
i	12	Cr • 102.1 • SmA • 116.9 • Iso	**i**	14	Cr • 73.9 • SmA • 89.4 • Iso
j	14	Cr • 101.5 • SmA • 122.6 • Iso	**j**	16	Cr • 83.2 • SmA • 96.3 • Iso
k	16	Cr • 102.4 • SmA • 125.5 • Iso			

polarising optical microscope equipped with a hot stage, as well as X-ray diffraction (XRD) studies. Troponoid esters **4** and amides **7** exhibited SmA phases when the alkoxyl chain was long and they exhibited nematic (N) phases when the alkoxyl chain was short. The SmA phase was determined from observation of focal-conic fan and homeotropic textures. The N phase was assigned from observation of schlieren textures. The results are summarised in Tables 1 and 2 together with those of the corresponding benzenoid esters **10** and amides **13**. Troponoids **4** exhibited N phases with lower thermal stabilities than benzenoids **10** (*15*) and SmA phases with higher thermal stabilities than **10**. This is similar to the results for the mesomorphic properties of 2,5-dibenzoyloxytroponoids and their corresponding benzenoids (*19*).

In order to elucidate the molecular packing structure of the SmA phase of **7**, we measured the XRD pattern of **7h**. The smectic layer spacing (*d*) was observed to be *ca.* 40 Å. Since the calculated molecular length (*l*) by the AM 1 method is 34 Å, the layer spacing is 1.2 times longer than the molecular length. On the other hand, the layer spacing of the corresponding benzenoid **13g** was 45 Å, which is longer than that (40 Å) of **7h**, although the calculated molecular lengths of **7h** and **13g** are almost identical. The *d*/*l* (1.3) value of **13g** is similar to the value (1.4) of the benzenoids (*20*). This indicates that troponoid **7h** forms a tighter packing structure in its SmA phase than benzenoid **13g**. We proposed an anti-parallel packing model, as shown in Figure 1. In the case of **7h**,



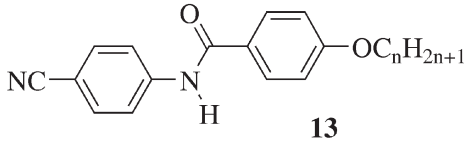


Table 2. Transition temperatures of troponoid amide **7** and benzenoid amide **13** with an alkoxy group.

7	n	Transition temp./°C	**13**	n	Transition temp./°C
a	1	Cr • 251.0 • Iso	**a**	4	Cr • 161.7 • Iso
b	4	Cr • 185.0 • Iso	**b**	6	Cr • 143.0 • Iso
c	6	Cr • 157.5 • (SmA • 150.9 •) Iso	**c**	8	Cr • 123.8 • Iso
d	8	Cr • 166.4 • (SmA • 161.6 •) Iso	**d**	10	Cr • 129.0 • Iso
e	10	Cr • 158.9 • SmA • 167.0 • Iso	**e**	12	Cr • 122.4 • (SmA • 107.5 •) Iso
f	12	Cr • 152.4 • SmA • 169.2 • Iso	**f**	14	Cr • 131.0 • (SmA • 118.4 •) Iso
g	14	Cr • 150.3 • SmA • 168.7 • Iso	**g**	16	Cr • 126.4 • (SmA • 123.7 •) Iso
h	16	Cr • 145.1 • SmA • 166.3 • Iso			

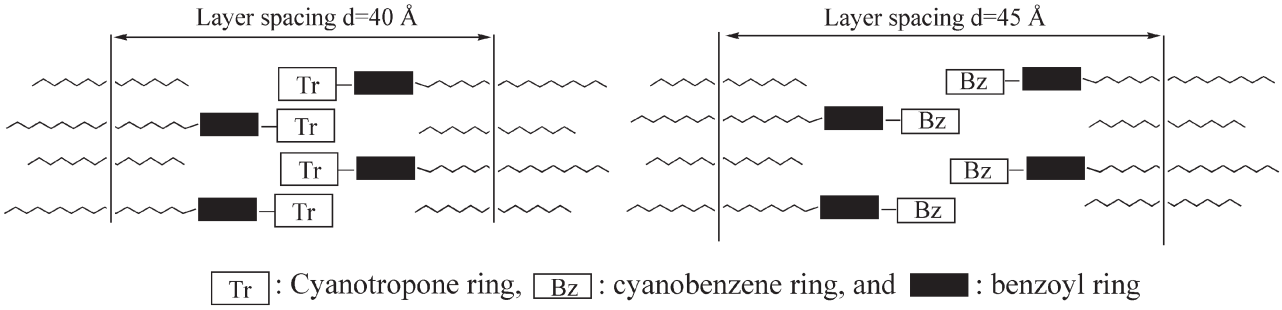
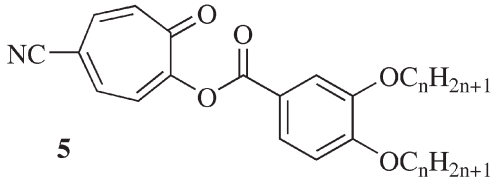


Figure 1. Packing models of compounds **7h** (left) and **13g** (right).

the troponoid cores faced closely, whereas the cyano groups faced closely in **13g**. The core area of the packing model of **13g** is longer than that of **7h**, which caused that **13g** has larger voids than **7h** to result that **13g** has weaker core interactions than **17h**. These observations support the result that **7h** has the higher transition temperatures of the SmA phase than **13g**.

We added an additional alkoxyl group at the C-3 position on the benzoyl group. The transition temperatures and the thermal behaviour of troponoid esters **5** and amides **8** and benzenoid esters **11** and amides **14** with a dialkoxylated benzoyl group are summarised in Tables 3 and 4. Troponoids exhibited the typical focal-conic fan texture of SmA phases. XRD studies of compound **5c** indicated that troponoids formed interdigitated bilayer SmA phases because the layer spacing (d=32 Å) was determined to be 1.3 times longer than the molecular length (l=24 Å) calculated by the MM2 method. Compared with their thermal stabilities of the troponoids, amide derivatives **8** were more stable than ester derivatives **5**. These results are similar to those for the monoalkoxylated troponoids shown in Tables 1–2. As summarised in Tables 3–4, benzenoids **11** and **14** did not exhibit any mesophases. Benzenoid ester **11** with two alkoxyl groups has higher melting points than troponoid ester **5**, which hides any mesophases. In the case of amides **8** and **14**, although both have comparable melting points, the former (**8**) is mesomorphic and the latter (**14**) is not. The benzenoid core structure has not enough strength to make aggregates through π–π interactions when two alkoxyl groups are introduced into the benzene core.

Furthermore, one more alkoxyl group was added into the benzoyl group. Although polarising optical microscopy (POM) observations of troponoid esters **6**, for example, showed unclear, nogeometrical textures, they had viscous, birefringent mesophases. Tables 5 and 6 show the transition temperatures of troponoid esters **6** and amides **9**, in which liquid crystalline properties arise at a certain chain length and amides **9** have higher transition temperatures than esters **6**. The corresponding benzenoid esters **12** and amides **15** were non-mesomorphic.



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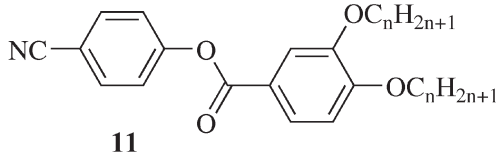
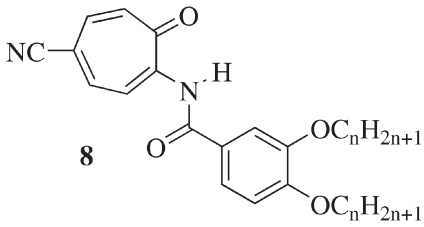


11

Table 3. Transition temperatures of troponoid ester **5** and benzenoid ester **11** with two alkoxy groups.

5	n	Transition temp./°C	**11**	n	Transition temp./°C
a	4	Cr•91.6•Iso	**a**	4	Cr•94.4•Iso
b	6	Cr•57.4•(SmA•55.3•) Iso	**b**	6	Cr•93.0•Iso
c	8	Cr•74.8•(SmA•72.8•) Iso	**c**	8	Cr•93.9•Iso
d	10	Cr•80.6•(SmA•78.2•) Iso	**d**	10	Cr•94.8•Iso
e	12	Cr•85.1•(SmA•80.6•) Iso	**e**	12	Cr•98.3•Iso
f	14	Cr•89.4•(SmA•80.8•) Iso	**f**	14	Cr•98.6•Iso
g	16	Cr•95.7•Iso	**g**	16	Cr•101.5•Iso



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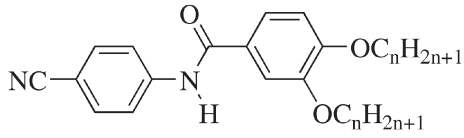
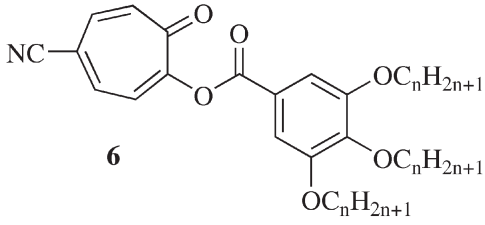


14

Table 4. Transition temperatures of troponoid amide **8** and benzenoid amide **14** with two alkoxy groups.

8	n	Transition temp./°C	**14**	n	Transition temp./°C
a	4	Cr • 156.7 • Iso	**a**	4	Cr • 154.9 • Iso
b	6	Cr • 131.3 • (SmA • 120.2 •) Iso	**b**	6	Cr • 134.8 • Iso
c	8	Cr • 130.7 • (SmA • 118.5 •) Iso	**c**	8	Cr • 130.3 • Iso
d	10	Cr • 131.4 • (SmA • 114.2 •) Iso	**d**	10	Cr • 127.8 • Iso
e	12	Cr • 129.4 • (SmA • 111.1 •) Iso	**e**	12	Cr • 125.9 • Iso
f	14	Cr • 129.4 • Iso	**f**	14	Cr • 124.7 • Iso
g	16	Cr • 124.3 • Iso	**g**	16	Cr • 122.4 • Iso



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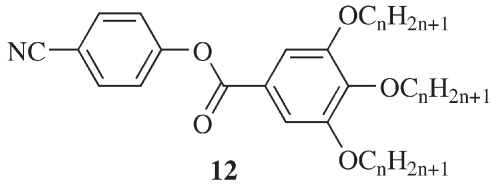


12

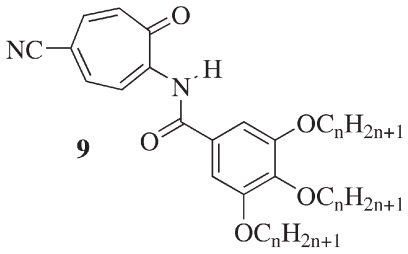
Table 5. Transition temperatures of troponoid ester **6** and benzenoid ester **12** with three alkoxy groups.

6	n	Transition temp./°C	**12**	n	Transition temp./°C
a	4	Cr • 104.5 • Iso	**a**	4	Cr • 74.3 • Iso
b	6	Cr • 72.2 • Iso	**b**	6	Cr • 60.1 • Iso
c	8	Cr • 63.2 • (Col_h • 62.2 •) Iso	**c**	8	Cr • 45.0 • Iso
d	10	Cr • 75.8 • (Col_h • 74.3 •) Iso	**d**	10	Cr • 46.6 • Iso
e	12	Cr • 73.0 • (Col_h • 72.5 •) Iso	**e**	12	Cr • 58.1 • Iso
f	14	Cr • 78.4 • Col_h • 78.7 • Iso	**f**	14	Cr • 68.2 • Iso
g	16	Cr • 84.9 • Col_h • 85.7 • Iso	**g**	16	Cr • 74.5 • Iso

The X-ray diffractogram of **9c** taken at 72°C showed a diffuse halo at 4.2 Å in the wide-angle region and three reflections corresponding to spacings of 39.0, 22.5 and 19.5 Å in the small-angle region, as shown in Figure 2 (*7*). They are in the ratio of $1 : 1/\sqrt{3} : 1/2$, which is in good agreement with the (100), (110) and (200) reflections of a hexagonal packing. The calculated molecular length of **9c** is 23.2 Å, as obtained by MM2 method, and the diameter (45 Å) of a column of the Col_h phase is reasonable to the calculated molecular length if an interdigitated arrangement, as shown in Figure 2, is assumed. Since the number of molecules in a disk was calculated to be about eight by assuming that the density of **9c** is 1 g cm^{-3} (*7, 21*), the packing model of the Col_h phase is shown in Figure 2. Similarly, the XRD data of troponoid ester **6e** are summarised, together with results for **9c**, in Table 7 to confirm that **6e** also has a Col_h phase.

Conformational analysis of troponoid esters and amides

We have already discussed an interesting NMR behaviour of troponoid esters, where the alkanoyl or benzoyl group at the C-2 position of the tropone ring migrates between the tropone carbonyl group and the oxygen atom at the C-2 position both in solution and in mesophases (*9*). This suggested that the C–O bond of the alkanoyloxy or benzoyloxy group is almost parallel to the π-orbitals of the tropone ring. On the other hand, we have observed



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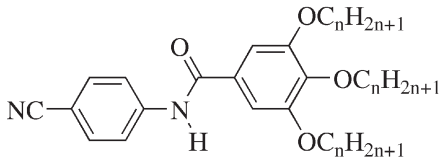


15

Table 6. Transition temperatures of troponoid amide **9** and benzenoid amide **15** with three alkoxy groups.

9	n	Transition temp./°C	**15**	n	Transition temp./°C
a	4	Cr•122.6•Iso	**a**	4	Cr•137.5•Iso
b	6	Cr•87.3•(Col_h•80.5•) Iso	**b**	6	Cr•94.0•Iso
c	8	Cr•87.9•(Col_h•81.5•) Iso	**c**	8	Cr•65.0•Iso
d	10	Cr•93.9•Col_h•98.7•Iso	**d**	10	Cr•64.6•Iso
e	12	Cr•94.9•Col_h•107.0•Iso	**e**	12	Cr•78.0•Iso
f	14	Cr•94.5•Col_h•101.4•Iso	**f**	14	Cr•83.6•Iso
g	16	Cr•93.1•Col_h•99.6•Iso	**g**	16	Cr•66.1•Iso

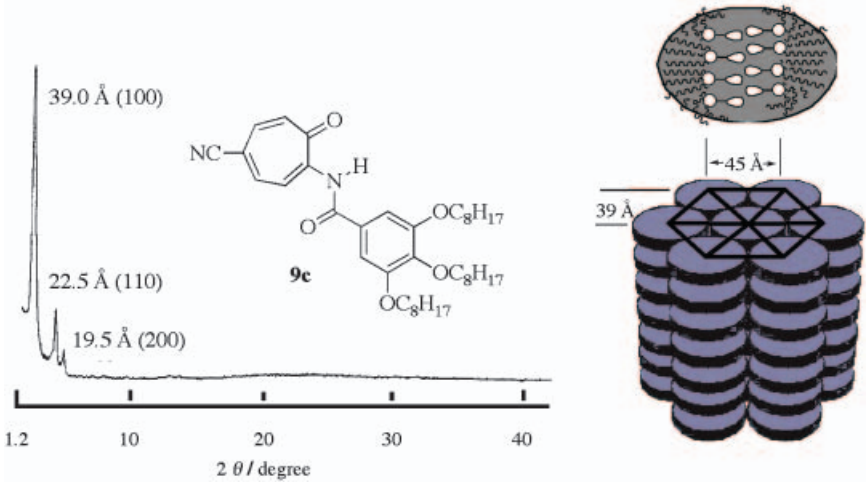


Figure 2. X-ray diffraction pattern and packing model of **9c**.

that troponoid amides form an intramolecular hydrogen bonding between the amide proton and the tropone carbonyl group to make a flat core (*22*). These observations are supported by the crystal structures of a troponoid ester and amide. An X-ray crystallographic analysis of 5-tetradecyloxy-2-(4-dodecylaminobenzoyloxy)tropone (**A**) has been reported, showing in Figure 3 that the core part is twisted by 76.5° (*23*), whereas the core part of 5-butoxy-2-(4-methoxybenzoylamino)tropone (**B**) is observed to be almost planar by X-ray crystallographic analysis (*8*). From ^{1}H NMR spectral observations, it is also reported that troponoid amide **B** has a flat core structure (*8b*). The ^{1}H NMR spectrum of troponoid amide **7a** showed that the tropone ring proton Ha at the C-3 position and the

Table 7. XRD data of liquid crystalline and gel states.

	d_{100} (Å)	d_{110} (Å)	d_{200} (Å)	d_{001} (Å)	Temp. (°C)	a^a
Troponoid amide **9c**	39.0	22.5	19.5	4.2	72	45.1
Troponoid ester **6e**	46.5	26.9	23.4	4.0	40	53.8
Gel of **9c**	40.7	23.0	20.1		72	47.1

[a]Hexagonal lattice parameter (Å).

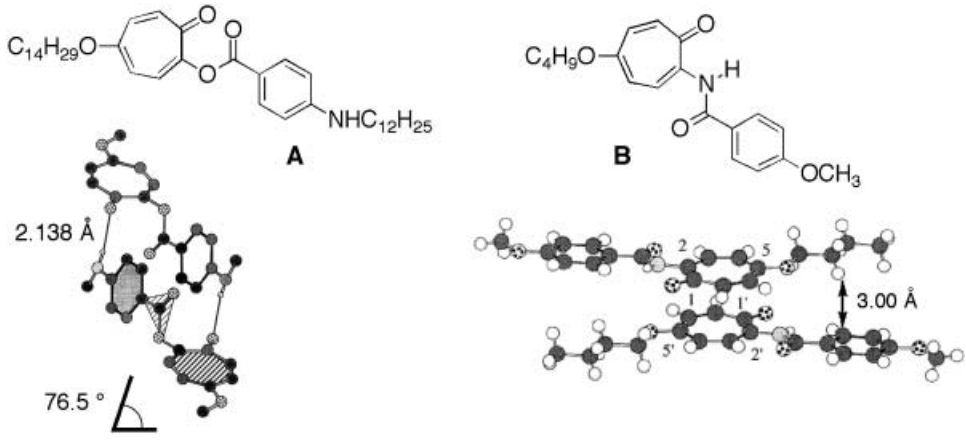


Figure 3. Partial X-ray crystallographic structure of 5-tetradecyloxy-2-(4-dodecylaminobenzoyloxy)tropone (**A**) and X-ray crystallographic structure of 5-butoxy-2-(4-methoxybenzoylamino)tropone (**B**).

NH proton appeared at δ 9.18 as a doublet (J=10.5 Hz) and at 10.36 as a broad singlet as like as compound **B** (*8b*), which indicated that **7a** has also a flat core structure. Consequently, since the structure of troponoid esters is twisted and that of troponoid amides is planar, the planar molecule could form the more tight packing models to induce more thermally stable mesophases, as observed in Tables 1–6.

Gel formation

During purification of synthesised compounds by recrysallisation, we encountered an unexpected, interesting behaviour that troponoid amides with three alkoxyl groups solidified the whole liquids in a test tube, so-called organogellations. They could gel solvents with different polarity such as alcohols, hydrocarbons and aprotic polar solvents. The minimum gel concentrations are summarised in Table 8 together with those of the typical organogellators **C** (*5a*) and **D** (*24*). Troponoid amides **9** are good gelators not only to DMSO, MeOH and MeCN but also to non-polar hydrocarbons. They could not gel aromatic hydrocarbons, halogeno solvents and ethers. Although the reference compounds (**C** and **D**) show gelling ability to a wide variety of solvents, troponoid amides are better gelators than **C** and **D** to alcohols and hydrocarbons.

Interestingly, only mesomorphic compound **9** with an amide group gelled organic solvents. Non-mesomorphic troponoid amides **9**, troponoid amides **7** and **8**, all troponoid esters **6**, benzenoid esters **12** and amides **15** did not gel any organic solvents. Figure 4 shows an optical micrograph of the octanol gel phase of **9c** in (10.1% w/w) taken at 44°C on cooling process from an isotropic liquid state. Highly intertwined, rod-like fibers were observed in a network structure (*7*). Micrographs of hexane xerogels and octanol gels (3% w/w) of **9c** were taken by an environmental scanning electron microscope (ESEM) (*25*) to show the presence of fibres and rod-like strands, respectively, as shown in Figure 4 (*7*).

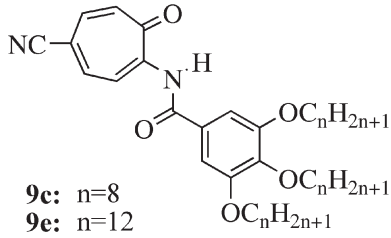
As shown in Figure 5, XRD studies of octanol gels (10.1% w/w) of **9c** taken at 40°C on cooling indicated that three reflections are observed at 40.7, 23.0 and 20.1 Å in the small-angle region, which correspond to a hexagonal packing (*26*). The data are summarised in Table 7. In the wide-angle region, only a very diffuse scattering is observed, so that the diffraction pattern is very similar to that of a Col_h phase. The slightly larger diameter (47 Å) of the column than that (45 Å) of the Col_h phase indicated incorporation of octanol molecules into the periphery of the columns. Based on these observations, we propose that columns including only a few solvent molecules self-organise to assemblies with hexagonal lattice parameters to make elementary fibres. The fibres aligned to form network structures through bundles with a diameter of ca. 200 nm, which are visible by ESEM at a 5000 × instrumental magnification. From these observations, the bundle structure would be composed of about 40 columns.

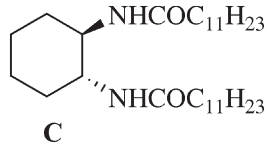
Effect of the connecting group on induction of mesophases and gelling ability

Comparison of thermal stability between amides and esters demonstrated that both troponoid and benzenoid amides were more stable than the esters. The mesomorphic state of amides, however, disappeared when the length of alkoxyl side chains was short. This is due to hydrogen bonding, which raised melting points to hide the mesomorphic states. We synthesised cyanotroponoids with a different type of a

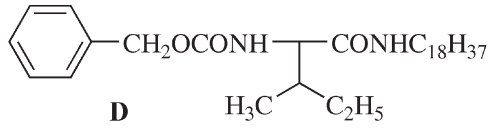
Table 8. Minimum gel concentration (MGC/gL^{-1}).

Solvent	9c	9e	C	D
Hexane	5	10	6	–
Dodecane	10	40	–	–
MeOH	4	6	20	9
2-PrOH	4	15	40	19
Octanol	20	23	–	–
DMSO	4	5	12	3
DMF	25	Cry	10	18
$CHCl_3$	Sol	Sol	–	–
CH_2Cl_2	Sol	Sol	–	–
Benzene	Sol	Sol	20	4
Toluene	Sol	Sol	12	14
Diethyl ether	Sol	Sol	–	–
THF	Sol	Sol	Sol	–
1,4-Dioxane	Sol	Sol	12	18
Cyclohexane	16	26	11	5
Decalin	9	27	–	–
Tetralin	Sol	Sol	–	–
Acetone	35	Cry	10	5
2-Butanone	95	Sol	15	–
3-Pentanone	93	44	–	–
CH_3CN	17	Cry	5	8
Water	Insol	Insol	–	–





C

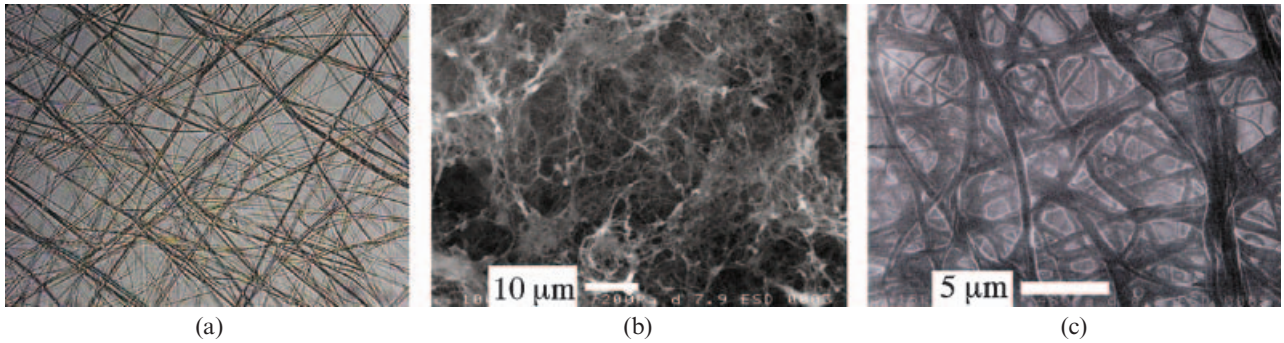


D

connecting group to investigate the effect on soft-ordered states. The thermal behaviours are shown in Table 9. As mentioned above, troponoid amides **9** with Col_h phases gelled organic solvents, whereas troponoid esters **6** with Col_h phases did not show any gelling abilities. The observation indicated that the presence of an amide group is essential to induce gelling ability. When we synthesised *N*-methyl derivative **20** of **9**, they did not show any gelling abilities. These evidences confirmed that hydrogen bonding of the NH group plays a role to induce mesophases and gelling ability. In the ^{1}H NMR spectrum of **20a**, the doublet of the proton at the C-3 position appeared at a higher field (δ 7.03) than that (δ 9.14) of **9a**, which indicated the loss of coplanarity of the core part. On the other hand, when the carbonyl group of the amide connecting group was replaced by the methylene group or was removed, compounds **16** and **17** lost both mesophases and gelling abilities. The ^{1}H NMR spectrum of **16** indicated that the NH proton appeared at δ 8.03 as a triplet to show an existence of intramolecular hydrogen bonding between the tropone carbonyl group and the NH proton. Thus, only intramolecular hydrogen bonding is not enough to induce mesophases. The presence of the carbonyl group would be essential to induce the coplanarity of the core structure.

NMR titration

We measured the ^{1}H NMR spectra of **9c** in $CDCl_3$ by changing the concentration of the gelling solvent, cyclohexane-d_{12}. The results are summarised in Table 10. The chemical shift of the NH proton at δ



(a) (b) (c)

Figure 4. Optical microscope (a) of octanol gel (10.1% w/w) at 44°C and ESEM images of hexane xerogels (b) and octanol gels (3% w/w) (c) of **9c**.

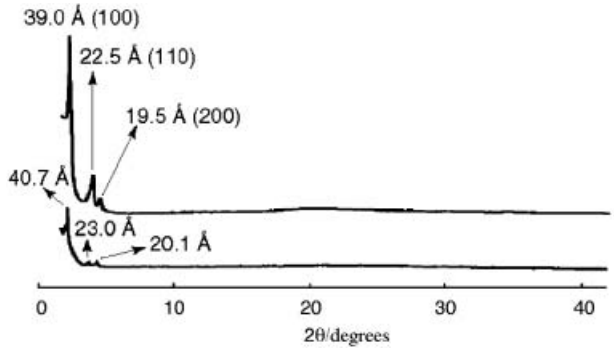


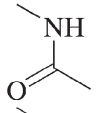
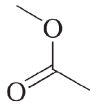
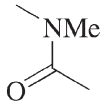
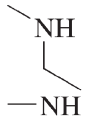
Figure 5. XRD patterns of the Col_h phase of **9c** at 72°C (upper) and octanol gels (10.1 wt.-%) of **9c** at 40°C (lower).

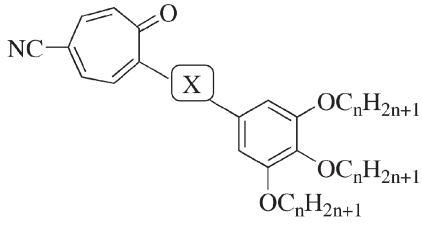
10.31 and two benzene ring protons (He) at 7.15 did not change, whereas the tropone ring protons except for the proton Ha of the C-3 position at δ 9.14 shifted to the higher field ($0.1 \sim 0.12 \times$ ppm) by increasing the concentration of cyclohexane-d_{12}. The chemical shift of the NH proton, which formed intramolecular hydrogen bonding, is independent on the concentration of the gelling solvent. Furthermore, the IR spectra of crystalline **9c** and octanol gels (10.1%) of **9c** were measured as KBr disks and as liquid films inserted between NaCl plates, respectively, to observe that the absorption bands between 1685 and 1500 cm^{-1} were almost identical, which also supported the fact that intramolecular hydrogen bonding contributed in both crystal and gelling states. Both NMR and IR spectral investigations suggested that intramolecular hydrogen bonding of the NH group is the major driving force for gellation rather than intermolecular hydrogen bonding. Troponoid amides with three alkoxyl groups did not gel halogeno solvents, aromatic hydrocarbons and ethers. We have deduced that the fundamental structure of the octanol gel consists of columns with a hexagonal packing structure through π–π interactions between the aromatic core structures. In aromatic hydrocarbons, therefore, they could insert to the space between the aromatic core structures of hexagonal columns to break the π–π interactions between the aromatic cores.

Effect of the number and length of the alkoxyl group on induction of mesophases and gel states

We summarise thermal stabilities of some monoalkoxylated **4** and **7** and dialkoxylated troponoids **5** and **8** in Table 11. The former has the higher transition temperatures than the latter. An XRD study of troponoid **8c** with two alkoxyl side chains was performed. The lateral distances of compounds **7h** and **8c** in their SmA phases were determined to be 3.7 and 4.2 Å, respectively. Compound **7h**, thus, has the

Table 9. Effect of the connecting group on transition temperatures (°C) and gelling ability.

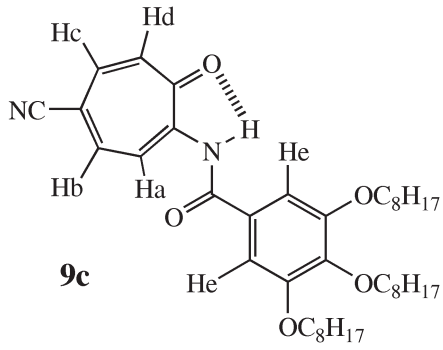
X	n=8	n=12	Gelling ability
	**9c:** Cr • 87.9 • (Col_h • 81.5 •) Iso	**9e:** Cr • 94.9 • Col_h • 107.0 • Iso	Yes
	**6c:** Cr • 63.2 • (Col_h • 62.2 •) Iso	**6e:** Cr • 73.0 • (Col_h • 72.5 •) Iso	No
	**20a:** Cr • 58.2 • Iso	**20b:** Cr • 68.6 • Iso	No
	**16a:** Cr • 71.1 • Iso	**16b:** Cr • 87.9 • Iso	No
	**17a:** Cr • 63.4 • Iso	**17b:** Cr • 82.0 • Iso	No



16: X=$NHCH_2$
a: n=8, **b**: n=12
17: X=NH, **a**: n=8, **b**: n=12
20: X=NMeCO
a: n=8, **b**: n=12

Table 10. NMR titration of troponoid amide **9c.**

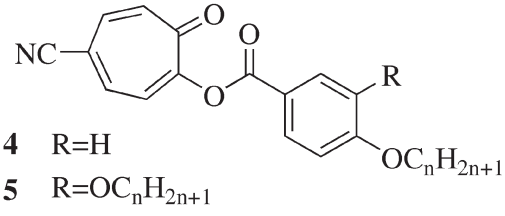
$CDCl_3$: cyclohexane-d_{12}	NH	Ha	Hb	Hc	Hd	He
100 : 0	δ 10.31	9.14	7.71	7.46	7.35	7.15
2 : 1	10.32	9.16	7.67	7.43	7.33	7.16
1 : 1	10.33	9.16	7.64	7.39	7.30	7.17
1 : 2	10.32	9.14	7.59	7.34	7.25	7.15
0 : 100	10.26	9.07	7.46	7.00	7.12	7.10



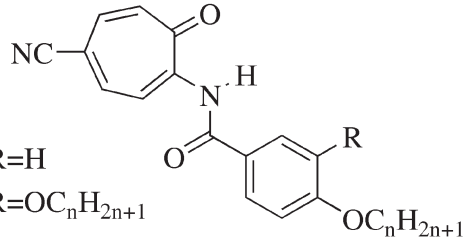
shorter lateral distance than compound **8c**, which indicates that **7h** with a single side chain has the tighter packing structure than **8c** with two side chains. A loose packing model of **8c** would come from the existence of the additional alkoxyl group at the C-3 position of the benzoyl group, which would disturb the tight packing to decrease the transition temperatures.

On the other hand, the corresponding benzenoids (**11** and **14**) with two side chains were not mesomorphic, as summarised in Tables 3 and 4. The benzenoid core structure could not keep mesomorphic states when the number of the side chain increased. When we introduced three alkoxyl side chains into the benzoyl group, the troponoids exhibited Col_h phases. However, benzenoids could not induce any mesophases, as shown in Tables 5 and 6. Usually, when the number of alkoxyl side chains increased, the volume occupied by the chains increased to develop a mismatch between the volumes of chains and the core, as shown in Scheme 2. This generates a curved interface to break lamellar structures to form a fundamental unit leading to the columnar phases (*27*). In the present case, eight molecules formed a disk to make columns. In the case of the benzenoids with two and three alkoxyl groups, the alkoxyl groups introduced increased the lateral width of molecules to diminish the interaction of the core parts between the neighboring molecules. They failed to form architectures because the benzenoid core structure is not flat due to rotation around the connecting bond (*28*). Troponoid amides have a flat core structure because they form intramolecular hydrogen bonding between the tropone carbonyl group and the NH group. In the case of troponoid esters, they showed mesophases when two and three alkoxyl groups are introduced on the benzoyl group. It should be due to the [1,9]-sigmatropic migration, which expands the area of the core part (*9*) and restricts the number of the conformers (*10*) to assist the appearance of mesophases.

Next, we synthesised troponoid amides **18** with a trialkoxylated benzoyl group, which have the different length of the alkoxyl groups to investigate the effect of the length of the alkoxyl groups on the thermal stability of the mesophases and the gelling ability. The transition temperatures and the minimun gel concentrations are shown in Table 12. When the length (n) of the alkoxyl groups at the C-3 and C-5 positions is fixed



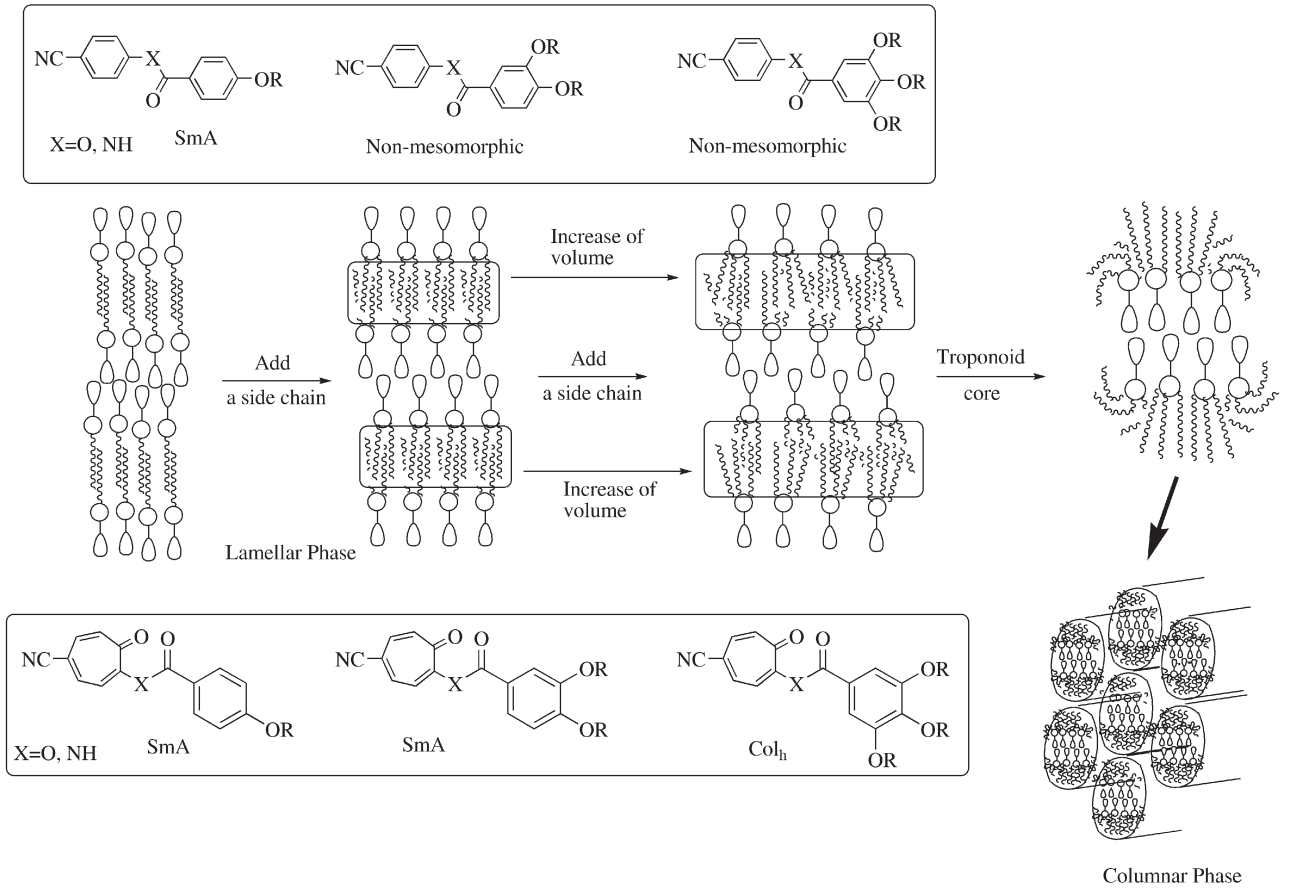
4 R=H
5 R=OC_nH_{2n+1}



7 R=H
8 R=OC_nH_{2n+1}

Table 11. Comparison of transition temperatures between troponoids with an alkoxyl group (upper) and those with two alkoxyl groups (lower).

	n	Transition temp. (°C)		n	Transition temp. (°C)
4f	8	Cr•106.5•(SmA•80.5•N•84.7•) Iso	**7d**	8	Cr•166.4•(SmA•161.6•) Iso
4i	12	Cr•102.1•SmA•116.9•Iso	**7f**	12	Cr•152.4•SmA•169.2•Iso
			7h	16	Cr•145.1•SmA•166.3•Iso
5c	8	Cr•74.8•(SmA•72.8•) Iso	**8c**	8	Cr•130.7•(SmA•118.5•) Iso
5e	12	Cr•85.1•(SmA•80.6•) Iso	**8e**	12	Cr•129.4•(SmA•111.1•) Iso
			8g	16	Cr•124.3•Iso



Scheme 2.

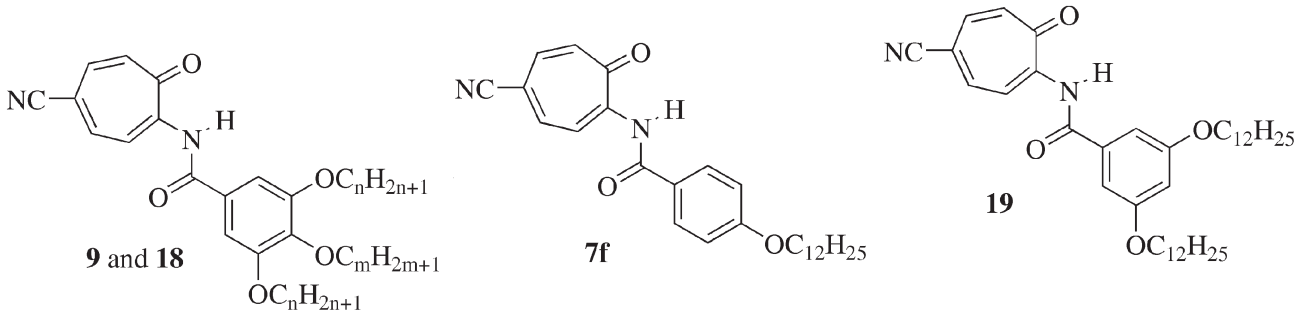


Table 12. Transition temperatures of troponoid amides and minimum gel concentration (g/L) to DMSO.

	n	m	Transition temp. (°C)	Minimum gel concentration
18a	1	12	Cr•116.7•(SmA•109.1•) Iso	Crystals
18b	2	12	Cr•150.8•Col$_h$•159.0•Iso	8
18c	3	12	Cr•127.0•Col$_h$•143.9•Iso	6
18d	4	12	Cr•82.3•Col$_h$•92.0•Iso	4
18e	8	12	Cr•75.8•Col$_h$•94.9•Iso	3
9e	12	12	Cr•94.9•Col$_h$•107.0•Iso	5
18f	12	4	Cr•93.4•Col$_h$•100.9•Iso	2
18g	12	1	Cr•101.0•(Col$_h$•94.0•) Iso	2
19			Cr•69.1•(Col$_h$•63.0•) Iso	Crystals
7f			Cr•152.4•SmA•169.2•Iso	Crystals

to $OC_{12}H_{25}$, and that (m) at the C-4 position is increased, the thermal stability of the Col_h phases increased. Compound **19** without any substituents at the C-4 position had a Col_h phase. Next, the length at the C-4 position is fixed to $OC_{12}H_{25}$ and n is changed. Troponoid amide **18a** with two methoxyl group showed a SmA phase and amide **18b** with two ethoxyl groups had a Col_h phase with the highest transition temperature. When the length of the side chains at the C-3 and C-5 positions increased, the transition temperatures of the Col_h phase decreased and the temperature increased again around $n=8$. The transition temperature of the SmA phase of amide **18a** with two methoxyl groups decreased by 60°C when compared with troponoid amide **7f**. This could be explained by the effect of the two lateral methoxyl groups, which decreased the lateral overlapping in the lamellar layer structure. It is rather surprising that compound **18b** with two ethoxyl groups had the highest clearing point of the Col_h phase.

As shown in Table 12, compound **18g** and **18f** with the shorter alkoxyl group at the C-4 position showed lower critical gel concentration to DMSO whereas **18b** with the ethoxyl groups at the C-3 and C-5 positions had the highest critical gel concentration. The length of the alkoxyl group at the C-4 position is responsible to the thermal stability of the Col_h phase and the length of the alkoxyl groups at the C-3 and C-5 positions to the critical gel concentration. Except for compound **19**, the compounds with a lamellar phase are not suitable for organogelators.

3. Conclusion

We have observed that both troponoids and benzenoids with a monoalkoxylated benzoyl group were mesomorphic. The clearing points of the nematic phases of benzenoid esters are higher than those of troponoid esters, whereas those of the SmA phases of troponoid esters and amides are higher than benzenoids. These results indicate that a polar troponoid core favours formation of lamellar structures. When an alkoxyl group was introduced on the benzoyl group, benzenoids with two alkoxyl side chains did not exhibit any mesophases and troponoids showed SmA phases. As discussed, troponoid amides have a flat core, which plays a role in formation of lamellar structures. In the case of troponoid esters, they have the [1,9]-sigmatropic system to expand the core structure.

When one more alkoxyl group was added into the benzoyl group, troponoids with three alkoxyl chains exhibited Col_h phases. Increasing the number of the side chains, it is reported that lamellar phases disappeared to exhibit columnar phases or not to induce any mesophases (*27*). In the case of benzenoids with three alkoxyl side chains, they did not exhibit any mesophases. Increase of the side chains disturbed induction of mesomorphic states in the benzenoids where lateral interactions of the core structures are not sufficient to form aggregates. This is a remarkable contrast to the troponoids, which could keep mesomorphic states when the number of the side chain increased.

The present study has demonstrated the relationship between mesomorphic properties and gelling abilities of new types of low-molecular-weight gelators with Col_h phases. The intramolecular hydrogen bonding between a tropone carbonyl group and an NH group of amides is a major factor to make molecules flat, which gives rise to strong $\pi-\pi$ interactions, and hence to induce more stable columnar phases (*29*) and gelling abilities. Formation of columnar molecular assemblies through macroscopic phase separation played a crucial role for gelling procedures (*26b, 30*).

4. Experimental

Characterisation

Elemental analyses were performed at the elemental analysis laboratory of Kyushu University. NMR spectra were measured on JEOL GSX 270H, LA 400, and LA 600 spectrometers in $CDCl_3$; the chemical shifts are expressed in δ units. Mass spectra were measured with JEOL 01SG-2 and LMS-700 spectrometers. IR spectra were recorded using a JASCO IR Report 100 spectrometer with KBr disks. The stationary phase for column chromatography was Wako gel C-300 and the eluant was a mixture of ethyl acetate, chloroform and hexane. Transition temperatures were measured using a differential scanning calorimeter (Seiko DSC 200, heating and cooling rate was $5°C\,min^{-1}$) and the mesomorphic phase was observed with a polarising optical microscope (Olympus BHSP BH-2) equipped with a hot stage (Linkam TH-600RMS). X-ray powder diffraction measurements were carried out with a Rigaku Rint 2100 system using Ni-filtered Cu K_α radiation at various temperatures. The measuring temperatures were controlled with a Linkam HFS-91 hot stage.

Syntheses

*Synthesis of 5-cyano-2-methoxytropone (**2**).*

An ether solution of CH_2N_2 was added dropwise to a $CHCl_3$ solution of 5-cyanotropolone (160 mg, 0.1 mmol) (*18*) in an ice bath. After standing at room temperature, the solvent was removed under reduced

pressure. The residue was chromatographed on a silica-gel column to give 5-cyano-2-methoxytropone (139 mg, 81%), m.p. 184°C. ^{1}H NMR: δ 4.05 (3H, s), 6.74 (1H, J=10.5 Hz), 7.18 (1H, d, J=12.7 Hz), 7.29 (1H, dd, J=12.7, 1.5 Hz), 7.54 (1H, dd, J=10.5, 1.5 Hz). ^{13}C NMR: δ 57.2, 110.1, 119.3, 135.1, 137.8, 140.2, 168.1, 179.1. M/z: found 161.0476; calculated for $C_9H_7NO_2$, 161.0477.

*Synthesis of 2-amino-5-cyanotropone (**3**).*

A methanol suspension of 5-cyano-2-methoxytropone (100 mg, 0.58 mmol) and 28% aqueous NH_3 solution was reacted at room temperature. The solvent was removed and the residue was purified to give 2-amino-5-cyanotropone (79 mg, 92%), m.p. 249°C (dec). ^{1}H NMR (DMSO-d_6): δ 6.81 (1H, d, J=12.2 Hz), 6.87 (1H, d, J=11.0 Hz), 7.40 (1H, dd, J=12.2, 1.7 Hz), 7.57 (1H, dd, J=11.0, 1.7 Hz). M/z: found 146.0479; calculated for $C_8H_6N_2O$, 146.0480.

*Synthesis of 2-(4-alkoxybenzoyloxy)-5-cyanotropones (**4**).*

An HMPA solution (1 ml) of 5-cyanotropolone (20.8 mg, 0.14 mmol) and 60% NaH (6.5 mg, 0.16 mmol) was stirred under nitrogen atmosphere. After 1 h, 4-methoxybenzoyl chloride (50 mg, 0.29 mmol) was added and the reaction mixture was stirred for 6 h at room temperature. The reaction was quenched by 2M HCl solution in an ice bath. The reaction mixture was extracted with AcOEt. The organic layer was washed with sat. NaCl solution and dried on $MgSO_4$. The solvent was evaporated and the residue was chromatographed on a silica-gel column to obtain colourless crystals **4a** (22.6 mg, recrystallisation in AcOEt-hexane): yield 57%. ^{1}H NMR: δ 3.90 (3H, s), 6.99 (2H, d, J=8.0 Hz), 7.30 (2H, br), 7.43 (2H, br), 8.10 (2H, d, J=8.0 Hz). ^{13}C NMR: δ 55.60, 114.06, 117.24, 118.48, 120.19, 132.86, 163.04, 164.49. MS (FAB$^+$): m/z 282 (M^++1, 3%), 135 (39%). Elemental analysis: found, C 68.07, H 3.97, N 4.93%; calculated for $C_{16}H_{11}NO_4$, C 68.32, H 3.94, N 4.98%.

For **4b**: yield 51%. Elemental analysis: found, C 68.97, H 4.53, N 4.70%; calculated for $C_{17}H_{13}NO_4$, C 69.15, H 4.44, N 4.74%. For **4c**: yield 54%. Elemental analysis: found, C 70.48, H 5.31, N 4.36%; calculated for $C_{19}H_{17}NO_4$, C 70.58, H 5.30, N 4.33%. For **4d**: yield 65%. Elemental analysis: found, C 71.14, H 5.71, N 4.14%; calculated for $C_{20}H_{19}NO_4$, C 71.20, H 5.68, N 4.15%. For **4e**: yield 58%. Elemental analysis: found, C 71.72, H 6.04, N 3.98%; calculated for $C_{21}H_{21}NO_4$, C 71.78, H 6.02, N 3.99%. For **4f**: yield 61%. Elemental analysis: found, C 72.58, H 6.65, N 3.72%; calculated for $C_{23}H_{25}NO_4$, C 72.80, H 6.64, N 3.69%. For **4g**: yield 83%. Elemental analysis: found, C 73.20, H 6.87, N 3.56%; calculated for $C_{24}H_{27}NO_4$, C 73.26, H 6.92, N 3.56%. For **4h**: yield 70%. Elemental analysis: found, C 73.71, H 7.20, N 3.49%; calculated for $C_{25}H_{29}NO_4$, C 73.69, H 7.17, N 3.44%. For **4i**: yield 66%. Elemental analysis: found, C 74.21, H 7.62, N 3.28%; calculated for $C_{27}H_{33}NO_4$, C 74.45, H 7.64, N 3.22%. For **4j**: yield 77%. Elemental analysis: found, C 74.92, H 8.02, N 3.08%; calculated for $C_{29}H_{37}NO_3$, C 75.13, H 8.04, N 3.02%. For **4k**: yield 42%. Elemental analysis: found, C 75.64, H 8.45, N 2.91%; calculated for $C_{31}H_{41}NO_4$, C 75.73, H 8.41, N 2.85%.

*Synthesis of 2-(4-alkoxybenzoylamino)-5-cyanotropones (**7**).*

An HMPA solution (1 ml) of 2-amino-5-cyanotropolone (10.2 mg, 0.07 mmol) and 60% NaH (4 mg, 0.1 mmol) was stirred under nitrogen atmosphere. After 1 h, 4-methoxybenzoyl chloride (20 mg, 0.12 mmol) was added and the reaction mixture was stirred for 6 h at room temperature. The reaction was quenched by 2M HCl solution in an ice bath. The reaction mixture was extracted with AcOEt. The organic layer was washed with sat. NaCl solution and dried on $MgSO_4$. The solvent was evaporated and the residue was chromatographed on a silica-gel column to obtain colourless **7a** (15.8 mg, recrystallisation in AcOEt–hexane): yield 81%. ^{1}H NMR: δ 3.91 (3H, s), 7.01 (2H, d, J=8.0 Hz), 7.36 (1H, d, J=12.0 Hz), 7.46 (1H, dd, J=12.0, 1.5 Hz), 7.70 (1H, dd, J=10.5, 1.5 Hz), 7.95 (2H, d, J=8.0 Hz), 9.18 (1H, d, J=10.5 Hz), 10.36 (1H, br). ^{13}C NMR: δ 55.63, 113.22, 114.39, 117.68, 119.31, 125.56, 129.81, 135.22, 137.15, 142.90, 150.28, 163.72, 165.79, 178.66. MS (70 eV): m/z 280 (M^+, 100%). Elemental analysis: found, C 68.31, H 4.36, N 10.00%; calculated for $C_{16}H_{12}N_2O_3$, C 68.56, H 4.32, N 9.99%.

For **7b**: yield 81%. Elemental analysis: found, C 70.68, H 5.65, N 8.77%; calculated for $C_{19}H_{18}N_2O_3$, C 70.79, H 5.63, N 8.69%. For **7c**: yield 56%. Elemental analysis: found, C 71.96, H 6.34, N 8.03%; calculated for $C_{21}H_{22}N_2O_3$, C 71.98, H 6.33, N 7.99%. For **7d**: yield 73%. Elemental analysis: found, C 72.95, H 6.91, N 7.44%; calculated for $C_{23}H_{26}N_2O_3$, C 72.99, H 6.92, N 7.40%. For **7e**: yield 81%. Elemental analysis: found, C 73.71, H 7.43, N 6.93%; calculated for $C_{25}H_{30}N_2O_3$, C 73.86, H 7.44, N 6.89%. For **7f**: yield 73%. Elemental analysis: found, C 74.35, H 7.88, N 6.50% Calcd for $C_{27}H_{34}N_2O_3$, C 74.62, H 7.89, N 6.45%. For **7g**: yield 77%. Elemental analysis: found, C 75.42, H

8.28, N 6.13%; calculated for $C_{29}H_{38}N_2O_3$, C 75.29, H 8.28, N 6.06%. For **7h**: yield 59%. Elemental analysis: found, C 75.81, H 8.59, N 5.75%; calculated for $C_{31}H_{42}N_2O_3$, C 75.88, H 8.63, N 5.71%.

*Synthesis of 4-(4-alkoxybenzoylamino)benzonitriles (**13**).*

A thionyl chloride (1 ml) solution of 4-butoxybenzoic acid (197 mg, 1.0 mmol) was refluxed for 5 h. An HMPA soution (1 ml) of 4-aminobenzonitrile (100 mg, 0.847 mmol) and 60% NaH (40 mg, 1 mmol) was stirred under nitrogen atmosphere. After 1 h, 4-butoxybenzoyl chloride prepared above was added and the reaction mixture was stirred for 6 h at room temperature. The reaction was quenched by 2M HCl solution in an ice bath. The reaction mixture was extracted with AcOEt. The organic layer was washed with sat. NaCl solution and dried on $MgSO_4$. The solvent was evaporated and the residue was chromatographed on a silica-gel column to obtain colourless **13a** (185.2 mg, recrystallisation in AcOEt–hexane: yield 74%. ^{1}H NMR: δ 0.99 (3H, t, J=7.0 Hz), 1.50 (2H, sex, J=7.0 Hz), 1.80 (2H, quin, J=7.0 Hz), 4.02 (2H, t, J=7.0 Hz), 6.95 (2H, d, J=8.0 Hz), 7.62 (2H, d, J=8.0 Hz), 7.78 (2H, d, J=8.0 Hz), 7.83 (2H, d, J=8.0 Hz), 8.11 (1H, brs). ^{13}C NMR: δ 13.82, 19.19, 31.12, 68.05, 106.97, 114.60, 118.94, 119.87, 125.85, 129.11, 133.28, 142.36, 162.64, 165.46. MS (70 eV): m/z 294 (M^+, 11%), 177 (100%). Elemental analysis: found, C 73.45, H 6.16, N 9.59%; calculated for $C_{18}H_{18}N_2O_2$, C 73.45, H 6.16, N 9.52%.

For 1**3b**: yield 81%. Elemental analysis: found, C 74.48, H 6.89, N 8.74%; calculated for $C_{20}H_{22}N_2O_2$, C 74.51, H 6.88, N 8.69%. For **13c**: yield 98%. Elemental analysis: found, C 75.41, H 7.49, N 8.06%; calculated for $C_{22}H_{26}N_2O_2$, C 75.40, H 7.48, N 7.99%. For **13d**: yield 78%. Elemental analysis: found, C 76.13, H 8.03, N 7.43%; calculated for $C_{24}H_{30}N_2O_2$, C 76.16, H 7.99, N 7.40%. For **13e**: yield 88%. Elemental analysis: found, C 76.76, H 8.42, N 7.03%; calculated for $C_{26}H_{34}N_2O_2$, C 76.81, H 8.43, N 6.89%. For **13f**: yield 66%. Elemental analysis: found, C 77.25, H 8.81, N 6.52%; calculated for $C_{28}H_{38}N_2O_2$, C 77.38, H 8.81, N 6.45%. For **13g**: yield 82%. Elemental analysis: found, C 78.00, H 9.18, N 6.13%; calculated for $C_{30}H_{42}N_2O_2$, C 77.88, H 9.15, N 6.05%.

*Synthesis of 2-(3,4-dialkoxybenzoyloxy)-5-cyanotropones (**5**).*

A thionyl chloride (1 ml) solution of 3,4-dibutoxybenzoic acid (58.5 mg, 0.22 mmol) was refluxed for 5 h. An HMPA soution (1 ml) of 5-cyanotropolone (28.1 mg, 0.19 mmol) and 60% NaH (8.3 mg, 0.21 mmol) was stirred under nitrogen atmosphere. After 1 h, 3,4-dibutoxybenzoyl chloride prepared above was added and the reaction mixture was stirred for 6 h at room temperature. The reaction was quenched by 2M HCl solution in an ice bath. The reaction mixture was extracted with AcOEt. The organic layer was washed with sat. NaCl solution and dried on $MgSO_4$. The solvent was evaporated and the residue was chromatographed on a silica-gel column to obtain colourless **5a** (45.8 mg, recrystallisation in AcOEt–hexane): yield 61%. ^{1}H NMR: δ 0.98 (3H, t, J=7.0 Hz), 1.00 (3H, t, J=7.0 Hz), 1.46 (4H, m), 1.83 (4H, m), 4.05 (2H, t, J=7.0 Hz), 4.09 (2H, t, J=7.0 Hz), 6.92 (1H, d, J=8.0 Hz), 7.30 (2H, br), 7.40 (2H, br), 7.60 (1H, d, J=2.2 Hz), 7.76 (1H, dd, J=8.0, 2.2 Hz). ^{13}C NMR: δ 13.83, 13.86, 19.18, 19.21, 31,04, 31.19, 68.84, 69.09, 112.01, 114.87, 117.23, 118.49, 119.86, 125.13, 148.82, 154.52, 163.22. MS (70 eV): m/z 395 (M^+, 1%), 283 (26%), 249 (100%). Elemental analysis: found, C 69.63, H 6.34, N 3.48%; calculated for $C_{23}H_{25}NO_5$, C 69.86, H 6.37, N 3.54%.

For **5b**: yield 62%. Elemental analysis: found, C 71.75, H 7.39, N 3.02%; calculated for $C_{27}H_{33}NO_5$, C 71.82, H 7.37, N 3.10%. For **5c**: yield 55%. Elemental analysis: found, C 73.20, H 8.15, N 2.79%; calculated for $C_{31}H_{41}NO_5$, C 73.34 H, 8.14, N 2.76%. For **5d**: yield 53%. Elemental analysis: found, C 74.41, H 8.75, N 2.49%; calculated for $C_{35}H_{49}NO_5$, C 74.57, H 8.76, N 2.48%. For **5e**: yield 87%. Elemental analysis: found, C 75.52, H 9.26, N 2.27%; calculated for $C_{39}H_{57}NO_5$, C 75.57, H 9.27, N 2.26%. For **5f**: yield 81%. Elemental analysis: found, C 76.31, H 9.67, N 2.10%; calculated for $C_{43}H_{65}NO_5$, C 76.40, H 9.69, N 2.07%. For **5g**: yield 51%. Elemental analysis: found, C 77.06, H 10.01, N 1.94%; calculated for $C_{47}H_{73}NO_5$, C 77.11, H 10.05, N 1.91%.

*Synthesis of 4-(3,4-dialkoxybenzoyloxy)benzonitriles (**11**).*

A thionyl chloride (1 ml) solution of 3,4-dibutoxybenzoic acid (86.5 mg, 0.325 mmol) was refluxed for 5 h. An HMPA soution (1 ml) of 4-hydrobenzonitrile (32.1 mg, 0.27 mmol) and 60% NaH (12.4 mg, 0.31 mmol) was stirred under nitrogen atmosphere. After 1 h, 3,4-dibutoxybenzoyl chloride prepared above was added and the reaction mixture was stirred for 6 h at room temperature. The reaction was quenched by 2M HCl solution in an ice bath. The reaction mixture was extracted with AcOEt. The organic layer was washed with sat. NaCl solution and dried on $MgSO_4$. The solvent was evaporated and the residue was chromatographed on a silica-gel column

to obtain colourless **11a** (54.8 mg, recrystallisation in AcOEt–hexane): yield 55%. ^{1}H NMR: δ 0.996 (3H, t, J=7.0 Hz), 1.003 (3H, t, J=7.0 Hz), 1.54 (4H, m), 1.84 (4H, m), 4.08 (2H, t, J=7.0 Hz), 4.10 (2H, t, J=7.0 Hz), 6.94 (1H, d, J=8.0 Hz), 7.36 (2H, d, J=8.0 Hz), 7.63 (1H, d, J=2.2 Hz), 7.73 (2H, d, J=8.0 Hz), 7.80 (1H, dd, J=8.0, 2.2 Hz). ^{13}C NMR: δ 13.85, 13.87, 19.19, 19.22, 31.05. 31.20, 68.83, 69.12, 109.58, 111.96, 114.63, 118.37, 120.53, 123.03, 124.67, 133.67, 148.80, 154.36, 154.51, 164.19. MS (70 eV): m/z 367 (M^+, 20%), 249 (100%). Elemental analysis: found, C 71.98, H 6.89, N 3.84%; calculated for $C_{22}H_{25}NO_4$, C 71.91, H 6.86, N 3.81%.

For **11b**: yield 44%. Elemental analysis: found, C 73.68, H 7.85, N 3.34%; calculated for $C_{26}H_{33}NO_4$, C 73.73, H 7.85, N 3.31%. For **11c**: yield 71%. Elemental analysis: found, C 75.09, H 8.58, N 2.94%; calculated for $C_{30}H_{41}NO_4$, C 75.12, H 8.62, N 2.92%. For **11d**: yield 68%. Elemental analysis: found, C 76.16, H 9.17, N 2.66%; calculated for $C_{34}H_{49}NO_4$, C 76.22, H 9.22, N 2.61%. For **11e**: yield 67%. Elemental analysis: found, C 77.12, H 9.68, N 2.41%; calculated for $C_{38}H_{57}NO_4$, C 77.11, H 9.71, N 2.37%. For **11f**: yield 68%. Elemental analysis: found, C 77.89, H 10.11, N 2.20%; calculated for $C_{42}H_{65}NO_4$, C 77.85, H 10.11, N 2.16%. For **11g**: yield 55%. Elemental analysis: found, C 78.34, H 10.42, N 2.01%; calculated for $C_{46}H_{73}NO_4$, C 78.47, H 10.45, N 1.99%.

*Synthesis of 2-(3,4-dialkoxybenzoylamino)-5-cyanotropones (**8**).*

A thionyl chloride (1 ml) solution of 3,4-dibutoxybenzoic acid 44.7 mg, 0.17 mmol) was refluxed for 5 h. An HMPA soution (1 ml) of 2-amino-5-cyanotropone (20.1 mg, 0.14 mmol) and 60% NaH (6.6 mg, 0.17 mmol) was stirred under nitrogen atmosphere. After 1 h, 3,4-dibutoxybenzoyl chloride prepared above was added and the reaction mixture was stirred for 6 h at room temperature. The reaction was quenched by 2M HCl solution in an ice bath. The reaction mixture was extracted with AcOEt. The organic layer was washed with sat. NaCl solution and dried on $MgSO_4$. The solvent was evaporated and the residue was chromatographed on a silica-gel column to obtain colourless **8a** (38.9 mg, recrystallisation in AcOEt–hexane): yield 72%. IR (KBr, cm^{-1}): 3302, 2956, 2870, 2220, 1717, 1680, 1621, 1578, 1495, 1446, 1368, 1263, 1200, 1132, 1098, 1025, 968, 871, 847, 800. ^{1}H NMR: δ 1.00 (6H, t, J=7.0 Hz), 1.53 (4H, sex, J=7.0 Hz), 1.85 (4H, m), 4.09 (2H, t, J=7.0 Hz), 4.10 (2H, t, J=7.0 Hz), 6.95 (1H, d, J=8.0 Hz), 7.35 (1H, d, J=12.0 Hz), 7.46 (1H, dd, J=12.0, 1.7 Hz), 7.52 (1H, d, J=2.2 Hz), 7.53 (1H, dd, J=8.0, 2.2 Hz), 7.70 (1H, dd, J=10.5, 1.7 Hz), 9.16 (1H, d, J=10.5 Hz), 10.36 (1H, br). ^{13}C NMR: δ 13.87, 19.19, 19.22, 31.05, 31.17, 68.89, 69.12, 112.10, 112.80, 113.13, 117.58, 119.33, 120.93, 125.48, 135.14, 137.15, 142.90, 149.33, 150.29, 153.70, 165.95, 178.64. MS (70 eV): m/z 394 (M^+, 22%), 249 (100%). Elemental analysis: found, C 69.80, H 6.61, N 7.11%; calculated for $C_{23}H_{26}N_2O_4$, C 70.03, H 6.64, N 7.10%.

For **8b**: yield 79%. Elemental analysis: found, C 71.82, H 7.57, N 6.32%; calculated for $C_{27}H_{34}N_2O_4$, C 71.97, H 7.61, N 6.22%. For **8c**: yield 88%. Elemental analysis: found, C 73.49, H 8.34, N 5.55%; calculated for $C_{31}H_{42}N_2O_4$, C 73.49, H 8.36, N 5.53%. For **8d**: yield 61%. Elemental analysis: found, C 74.74, H 8.99, N 5.02%; calculated for $C_{35}H_{50}N_2O_4$, C 74.70, H 8.95, N 4.98%. For **8e**: yield 65%. Elemental analysis: found, C 75.58, H 9.43, N 4.51%; calculated for $C_{39}H_{58}N_2O_4$, C 75.69, H 9.45, N 4.53%. For **8f**: yield 87%. Elemental analysis: found, C 76.59, H 9.90, N 4.23%; calculated for $C_{43}H_{66}N_2O_4$, C 76.51, H 9.86, N 4.15%. For **8g**: yield 79%. Elemental analysis: found, C 77.04, H 10.17, N 3.86%; calculated for $C_{47}H_{74}N_2O_4$, C 77.21, H 10.20, N 3.83%.

*Synthesis of 4-(3,4-dialkoxybenzoylamino)benzonitriles (**14**).*

A thionyl chloride (1 ml) solution of 3,4-dibutoxybenzoic acid (111.9 mg, 0.42 mmol) was refluxed for 5 h. An HMPA soution (1 ml) of 4-aminobenzonitrile (40.2 mg, 0.34 mmol) and 60% NaH (12.4 mg, 0.31 mmol) was stirred under nitrogen atmosphere. After 1 h, 3,4-dibutoxybenzoyl chloride prepared above was added and the reaction mixture was stirred for 6 h at room temperature. The reaction was quenched by 2M HCl solution in an ice bath. The reaction mixture was extracted with AcOEt. The organic layer was washed with sat. NaCl solution and dried on $MgSO_4$. The solvent was evaporated and the residue was chromatographed on a silica-gel column to obtain colourless **14a** (83.6 mg, recrystallisation in AcOEt–hexane): yield 67%. ^{1}H NMR: δ 0.96 (3H, t, J=7.0 Hz), 0.98 (3H, t, J=7.0 Hz), 1.49 (4H, m,), 1.81 (4H, m), 4.01 (2H, t, J=7.0 Hz), 4.04 (2H, t, J=7.0 Hz), 6.85 (2H, d, J=8.0 Hz), 7.39 (1H, dd, J=8.0, 2.2 Hz), 7.45 (1H, d, J=2.2 Hz), 7.60 (2H, d, J=8.0 Hz), 7.80 (2H, d, J=8.0 Hz), 8.33 (1H, br). ^{13}C NMR: δ 13.85, 19.19, 31.09, 31.19, 68.88, 69.14, 106.84, 112.13, 112.87, 119.00, 119.95, 120.14, 126.23, 133.22, 142.0, 149.14, 152.84, 165.73. MS (70 eV): m/z 366 (M^+, 23%), 249 (100%). Elemental analysis: found, C 72.25, H 7.17, N 7.69%; calculated for $C_{22}H_{25}N_2O_3$, C 72.11, H 7.15, N 7.64%.

For **14b**: yield 72%. Elemental analysis: found, C 73.83, H 8.09, N 6.68%; calculated for $C_{26}H_{34}N_2O_3$, C 73.90, H 8.11, N 6.63%. For **14c**: yield 67%. Elemental analysis: found, C 75.34, H 8.85, N 5.89%; calculated for $C_{30}H_{42}N_2O_3$, C 75.28 H, 8.84, N 5.85%. For **14d**: yield 67%. Elemental analysis: found, C 76.30, H 9.41, N 5.27%; calculated for $C_{34}H_{50}N_2O_3$, C 76.36, H 9.42, N 5.24%. For **14e**: yield 65%. Elemental analysis: found, C 77.30, H 9.91, N 4.79%; calculated for $C_{38}H_{58}N_2O_3$, C 77.24, H 9.89, N 4.74%. For **14f**: yield 56%. Elemental analysis: found, C 77.88, H 10.26, N 4.36%; calculated for $C_{42}H_{66}N_2O_3$, C 77.97, H 10.28, N 4.33%. For **14g**: yield 65%. Elemental analysis: found, C 78.57, H 10.59, N 4.00%; calculated for $C_{46}H_{74}N_2O_3$, C 78.58, H 10.61, N 3.98%.

*Synthesis of 2-(3,4,5-trialkoxybenzoyloxy)-5-cyanotropones (**6**).*

A thionyl chloride (1 ml) solution of 3,4,5-tributoxybenzoic acid (150.5 mg, 0.445 mmol) was refluxed for 5 h. An HMPA soution (1 ml) of 5-cyanotropolone (53.2 mg, 0.36 mmol) and 60% NaH (18.1 mg, 0.45 mmol) was stirred under nitrogen atmosphere. After 1 h, 3,4,5-triibutoxybenzoyl chloride prepared above was added and the reaction mixture was stirred for 6 h at room temperature. The reaction was quenched by 2M HCl solution in an ice bath. The reaction mixture was extracted with AcOEt. The organic layer was washed with sat. NaCl solution and dried on $MgSO_4$. The solvent was evaporated and the residue was chromatographed on a silica-gel column to obtain colourless **6a** (68.8 mg, recrystallisation in AcOEt–hexane): yield 67%. ^{1}H NMR: δ 0.97 (3H, t, J=7.0 Hz), 0.98 (6H, t, J=7.0 Hz), 1.52 (6H, m), 1.74 (2H, m), 1.80 (4H, m), 4.03 (4H, t, J=7.0 Hz), 4.07 (2H, t, J=7.0 Hz), 7.30 (2H, br), 7.35 (2H, s), 7.40 (2H, br). ^{13}C NMR: δ 13.71, 13.75, 19.01, 19.14, 31.18, 32.21, 68.80, 73.13, 108.80, 117.24, 118.35, 122.10, 122.75, 140.75, 143.50, 152.93, 163.09, 172.73. MS (FAB$^+$): m/z 468 (M^++1, 1%), 321 (100%). Elemental analysis: found, C 69.19, H 6.94, N 3.22%; calculated for $C_{27}H_{33}NO_6$, C 69.36, H 7.11, N 3.00%.

For **6b**: yield 46%. Elemental analysis: found, C 71.87, H 8.23, N 2.59%; calculated for $C_{33}H_{45}NO_6$, C 71.84, H 8.22, N 2.54%. For **6c**: yield 34%. Elemental analysis: found, C 73.41, H 9.11, N 2.10%; calculated for $C_{39}H_{57}NO_6$, C 73.67, H 9.04, N 2.20%. For **6d**: yield 46%. Elemental analysis: found, C 74.92, H 9.68, N 1.96%; calculated for $C_{45}H_{69}NO_6$, C 75.06, H 9.66, N 1.95%. For **6e**: yield 45%. Elemental analysis: found, C 76.06, H 10.09, N 1.71%; calculated for $C_{51}H_{81}NO_6$, C 76.17, H 10.15, N 1.74%. For **6f**: yield 52%. Elemental analysis: found, C 77.04, H 10.65, N 1.56%; calculated for $C_{57}H_{93}NO_6$, C 77.07, H 10.55, N 1.58%. For **6g**: yield 53%. Elemental analysis: found, C 77.67, H 10.92, N 1.49%; calculated for $C_{63}H_{105}NO_6$, C 77.81, H 10.88, N 1.44%.

*Synthesis of 4-(3,4,5-trialkoxybenzoyloxy)benzonitriles (**12**).*

A thionyl chloride (1 ml) solution of 3,4,5-tributoxybenzoic acid (173.9 mg, 0.51 mmol) was refluxed for 5 h. An HMPA soution (1 ml) of 4-hydroxybenzonitrile (50.2 mg, 0.42 mmol) and 60% NaH (20.8 mg, 0.52 mmol) was stirred under nitrogen atmosphere. After 1 h, 3,4,5-triibutoxybenzoyl chloride prepared above was added and the reaction mixture was stirred for 6 h at room temperature. The reaction was quenched by 2 M HCl solution in an ice bath. The reaction mixture was extracted with AcOEt. The organic layer was washed with sat. NaCl solution and dried on $MgSO_4$. The solvent was evaporated and the residue was chromatographed on a silica-gel column to obtain colourless **12a** (80.5 mg, recrystallisation in AcOEt–hexane): yield 46%. ^{1}H NMR: δ 0.98 (3H, t, J=7.0 Hz), 0.99 (6H, t, J=7.0 Hz), 1.54 (6H, m), 1.75 (2H, quin, J=7.0 Hz), 1.82 (4H, quin, J=7.0 Hz), 4.06 (4H, t, J=7.0 Hz), 4.10 (2H, t, J=7.0 Hz), 7.50 (2H, d, J=8.0 Hz), 7.39 (2H, s), 7.74 (2H, d, J=8.0 Hz). ^{13}C NMR: δ 13.84, 13.87, 19.14, 19.27, 31.31, 32.34, 69.00, 73.26, 108.68, 109.74, 118.31, 122.91, 123.05, 133.71, 143.52, 153.08, 1154.40, 164.21. MS (70 eV): m/z 439 (M^+, 1%), 321 (100%). Elemental analysis: found, C 71.03, H 7.51, N 3.15%; calculated for $C_{26}H_{33}NO_5$, C 71.05, H 7.57, N 3.19%.

For **12b**: yield 61%. Elemental analysis: found, C 73.55, H 8.73, N 2.66%; calculated for $C_{32}H_{45}NO_5$, C 73.39, H 8.66, N 2.67%. For **12c**: yield 54%. Elemental analysis: found, C 75.10, H 9.48, N 2.31%; calculated for $C_{38}H_{57}NO_5$, C 75.08, H 9.45, N 2.30%. For **12d**: yield 49%. Elemental analysis: found, C 76.40, H 10.15, N 1.91%; calculated for $C_{44}H_{69}NO_5$, C 76.37, H 10.05, N 2.02%. For **12e**: yield 54%. Elemental analysis: found, C 77.19, H 10.43, N 1.78%; calculated for $C_{50}H_{81}NO_5$, C 77.37, H 10.52, N 1.80%. For **12f**: yield 45%. Elemental analysis: found, C 78.17, H 10.90, N 1.66%; calculated for $C_{56}H_{93}NO_5$, C 78.18, H 10.90, N 1.63%. For **12g**: yield 54%. Elemental analysis: found, C 78.80, H 11.21, N 1.51%; calculated for $C_{62}H_{105}NO_5$, C 78.84, H 11.21, N 1.48%.

*Synthesis of 2-(3,4,5-trialkoxybenzoylamino)-5-cyanotropones (**9**).*

A thionyl chloride (1 ml) solution of 3,4,5-tributoxybenzoic acid (280.1 mg, 0.832 mmol) was refluxed for

5 h. An HMPA soution (1 ml) of 5-cyanotropolone (98.5 mg, 0.674 mmol) and 60% NaH (34 mg, 0.85 mmol) was stirred under nitrogen atmosphere. After 1 h, 3,4,5-triibutoxybenzoyl chloride prepared above was added and the reaction mixture was stirred for 6 h at room temperature. The reaction was quenched by 2M HCl solution in an ice bath. The reaction mixture was extracted with AcOEt. The organic layer was washed with sat. NaCl solution and dried on $MgSO_4$. The solvent was evaporated and the residue was chromatographed on a silica-gel column to obtain colourless **9a** (120.3 mg, recrystallisation in AcOEt–hexane): yield 38%. IR (KBr, cm^{-1}): 3280, 2954, 2868, 2214, 1677, 1625, 1580, 1368, 1184, 1128, 879. ^{1}H NMR: δ 0.96 (6H, t, J=7.0 Hz), 1.00 (3H, t, J=7.0 Hz), 1.54 (6H, m), 1.75 (2H, quin, J=7.0 Hz), 1.83 (4H, quin, J=7.0 Hz), 4.06 (2H, t, J=7.0 Hz), 4.08 (4H, t, J=7.0 Hz), 7.15 (2H, s,), 7.35 (1H, d, J=12.0 Hz), 7.46 (1H, dd, J=12.0, 1.7 Hz), 7.70 (1H, dd, J=10.5, 1.7 Hz), 9.14 (1H, d, J=10.5 Hz), 10.31 (1H, br). ^{13}C NMR: δ 13.84, 13.87, 19.13, 19.26, 31.31, 32.32, 69.12, 73.30, 106.20, 113.40, 117.75, 119.25, 128.04, 135.329, 137.20, 142.89, 150.09, 153.42, 166.20, 178.64. MS (FAB^+): m/z 466 (M^++1, 16%), 321 (100%). Elemental analysis: found, C 69.54, H 7.32, N 5.94%; calculated for $C_{27}H_{34}N_2O_5$, C 69.50, H 7.35, N 6.00%.

For **9b**: yield 47%. Elemental analysis: found, C 71.83, H 8.40, N 5.09%; calculated for $C_{33}H_{46}N_2O_5$, C 71.97, H 8.42, N 5.09%. For **9c**: yield 48%. Elemental analysis: found, C 73.55, H 9.21, N 4.44%; calculated for $C_{39}H_{58}N_2O_5$, C 73.78, H 9.21, N 4.41%. For **9d**: yield 54%. Elemental analysis: found, C 75.04, H 9.82, N 3.93%; calculated for $C_{45}H_{70}N_2O_5$, C 75.17, H 9.81, N 3.90%. For **9e**: yield 48%. Elemental analysis: found, C 76.16, H 10.23, N 3.43%; calculated for $C_{51}H_{82}N_2O_5$, C 76.26, H 10.29, N 3.49%. For **9f**: yield 57%. Elemental analysis: found, C 77.07, H 10.71, N 3.16%; calculated for $C_{57}H_{94}N_2O_5$, C 77.15, H 10.68, N 3.16%. For **9g**: yield 62%. Elemental analysis: found, C 78.03, H 11.08, N 2.95%; calculated for $C_{63}H_{106}N_2O_5$, C 77.89, H 11.00, N 2.88%.

*Synthesis of 4-(3,4,5-trialkoxybenzoylamino)benzonitriles (**15**).*

A thionyl chloride (1 ml) solution of 3,4,5-tributoxybenzoic acid (190.2 mg, 0.56 mmol) was refluxed for 5 h. An HMPA soution (1 ml) of 4-aminobenzonitrile (54.7 mg, 0.46 mmol) and 60% NaH (23.1 mg, 0.58 mmol) was stirred under nitrogen atmosphere. After 1 h, 3,4,5-triibutoxybenzoyl chloride prepared above was added and the reaction mixture was stirred for 6 h at room temperature. The reaction was quenched by 2M HCl solution in an ice bath. The reaction mixture was extracted with AcOEt. The organic layer was washed with sat. NaCl solution and dried on $MgSO_4$. The solvent was evaporated and the residue was chromatographed on a silica-gel column to obtain colourless **15a** (63.3 mg, recrystallisation in AcOEt–hexane): yield 31%. IR (KBr, cm^{-1}): 3276, 2954, 2866, 2224, 1647, 1585, 1519, 1338, 1126, 835. ^{1}H NMR: δ 0.96 (9H, t, J=7.0 Hz), 1.48 (6H, m), 1.74 (6H, m), 3.98 (4H, t, J=7.0 Hz), 4.01 (2H, t, J=7.0 Hz), 7.03 (2H, s,), 7.61 (2H, d, J=8.0 Hz), 7.82 (2H, d, J=8.0 Hz), 8.45 (1H, br). ^{13}C NMR: δ 13.77, 13.82, 19.08, 19.18, 31.28, 32.25, 69.01, 73.17, 105.82, 106.87, 118.96, 120.05, 128.86, 133.15, 141.76, 142.39, 153.16, 166.13. MS (FAB^+): m/z 439 (M^++1, 100%). Elemental analysis: found, C 71.03, H 7.74, N 6.32%; calculated for $C_{26}H_{34}N_2O_4$, C 70.21, H 7.81, N 6.39%.

For **15b**: yield 60%. Elemental analysis: found, C 73.30, H 8.84, N 5.53%; calculated for $C_{32}H_{46}N_2O_4$, C 73.53, H 8.87, N 5.36%. For **15c**: yield 31%. Elemental analysis: found, C 75.24, H 9.67, N 4.64%; calculated for $C_{38}H_{58}N_2O_4$, C 75.21, H 9.63, N 4.62%. For **15d**: yield 53%. Elemental analysis: found, C 76.37, H 10.21, N 3.97%; calculated for $C_{44}H_{70}N_2O_4$, C 76.47, H 10.21, N 4.05%. For **15e**: yield 51%. Elemental analysis: found, C 77.36, H 10.61, N 3.57%; calculated for $C_{50}H_{82}N_2O_4$, C 77.47, H 10.66, N 3.61%. For **15f**: yield 56%. Elemental analysis: found, C 78.03, H 11.06, N 3.29%; calculated for $C_{56}H_{94}N_2O_4$, C 78.27, H 11.03, N 3.26%. For **15g**: yield 67%. Elemental analysis: found, C 78.99, H 11.36, N 3.01%; calculated for $C_{62}H_{105}N_2O_4$, C 78.92, H 11.32, N 2.97%.

*Synthesis of 2-(3,4,5-trialkoxybenzylamino)-5-cyanotropones (**16**).*

A THF solution (5 ml) of 5-cyano-2-methoxytropone (102.6 mg, 0.64 mmol) and 3,4,5-trioctyloxybenzylamine (402.6 mg, 0.82 mmol) was stirred at room temperature for 3 h. The solvent was evaporated and the residue was chromatographed on a silica-gel column to obtain yellow crystals **16a** (345.1 mg, recrystallisation in chloroform–methanol): yield 87% ^{1}H NMR: δ 0.88 (9H, t, J=7.0 Hz), 1.28 (24H, br), 1.45 (6H, m), 1.77 (6H, m), 3.93 (4H, t, J=7.0 Hz), 3.95 (2H, t, J=7.0 Hz), 4.48 (2H, d, J=5.9 Hz), 6.47 (2H, s), 6.50 (1H, d, J=11.1 Hz), 7.06 (1H, d, J=12.2 Hz), 7.37 (1H, dd, J=12.2, 1.6 Hz), 7.48 (1H, dd, J=11.1, 1.6 Hz), 8.03 (1H, t, J=5.9 Hz). ^{13}C NMR: δ 13.95, 22.52, 22.54, 25.92, 29.13, 29.20, 29.38, 30.16, 31.66, 31.75, 47.60, 69.03, 73.30, 104.18, 105.73, 106.90, 120.81, 127.64, 129.69, 137.82, 137.90, 141.44, 153.52, 156.66, 176.37. MS (FAB^+): m/z 621

(M^++1, 22%), 620 (M^+, 51%), 475 (100%). Elemental analysis: found, C 75.39, H 9.68, N 4.56%; calculated for $C_{39}H_{60}N_2O_4$, C 75.44, H 9.74, N 4.51%.

For **16b**: yield 90%. Elemental analysis: found, C 77.56, H 10.73, N 3.52%; calculated for $C_{51}H_{84}N_2O_4$, C 77.61, H 10.73, N 3.55%.

*Synthesis of 2-(3,4,5-trialkoxyphenylamino)-5-cyanotropones (**17**).*

A THF solution (5 ml) of 5-cyano-2-methoxytropone (25.6 mg, 0.16 mmol) and 3,4,5-trioctyloxybenzylamine (87.4 mg, 0.18 mmol) was stirred at room temperature for 3 h. The solvent was evaporated and the residue was chromatographed on a silica-gel column to obtain yellow crystals **17a** (42 mg, recrystallisation in chloroform–methanol): yield 44% ^{1}H NMR: δ 0.89 (9H, t, J=7.0 Hz), 1.29 (24H, br), 1.47 (6H, m), 1.79 (6H, m), 3.94 (4H, t, J=7.0 Hz), 3.99 (2H, t, J=7.0 Hz), 6.46 (2H, s), 6.98 (1H, d, J=11.1 Hz), 7.15 (1H, d, J=12.2 Hz), 7.43 (1H, dd, J=12.2, 1.6 Hz), 7.43 (1H, dd, J=11.1, 1.6 Hz), 9.05 (1H, s). ^{13}C NMR: δ 14.06, 14.07, 22.63, 22.66, 26.01, 26.05, 29.23, 29.30, 29.34, 29.49, 30.28, 31.77, 31.87, 69.35, 73.61, 103.39, 105.62, 108.46, 120.75, 128.76, 131.44, 137.62, 138.07, 141.40, 154.05, 156.05, 176.32. MS (FAB$^+$): m/z 607 (M^++1, 100%), 493 (12%). Elemental analysis: found, C 75.18, H 9.62, N 4.67%; calculated for $C_{38}H_{58}N_2O_4$, C 75.21, H 9.63, N 4.62%.

For **17b**: yield 60%. Elemental analysis: found, C 77.28, H 10.70, N 3.62%; calculated for $C_{50}H_{82}N_2O_4$, C 77.47, H 10.66, N 3.61%.

*Synthesis of 2-(3,4,5-trialkoxybenzoylamino)-5-cyanotropones (**18**).*

A thionyl chloride (3 ml) solution of 4-dodecyloxy-3,5-dimethoxybenzoic acid (287.8 mg, 0.57 mmol) was refluxed for 5 h. An HMPA solution (1 ml) of 2-amino-5-cyanotropolone (105.1 mg, 0.72 mmol) and 60% NaH (30 mg, 0.75 mmol) was stirred under nitrogen atmosphere. After 1 h, 4-dodecyloxy-3,5-dimethoxybenzoyl chloride prepared above was added and the reaction mixture was stirred for 3 h at room temperature. The reaction was quenched by 2M HCl solution in an ice bath. The reaction mixture was extracted with AcOEt. The organic layer was washed with sat. NaCl solution and dried on $MgSO_4$. The solvent was evaporated and the residue was chromatographed on a silica-gel column to obtain colourless **18a** (198.6 mg, recrystallisation in chloroform–methanol): yield 56%. ^{1}H NMR: δ 0.88 (6H, t, J=7.0 Hz), 1.26 (16H, m), 1.46 (2H, m), 1.76 (2H, quin, J=7.0 Hz), 3.94 (6H, s), 4.06 (2H, t, J=7.0 Hz), 7.18 (2H, s), 7.36 (1H, d, J=12.0 Hz), 7.47 (1H, dd, J=12.0, 1.7 Hz), 7.72 (1H, dd, J=10.5, 1.7 Hz), 9.15 (1H, d, J=10.5 Hz), 10.33 (1H, br). ^{13}C NMR: δ 14.11, 22.67, 25.76, 29.34, 29.38, 29.61, 29.66, 30.09, 31.90, 56.38, 73.76, 105.06, 113.48, 117.79, 119.18, 128.20, 135.32, 137.21, 142.08, 142.84, 149.98, 153.75, 166.03, 178.60. MS (FAB$^+$): m/z 495 (M^++1, 8%), 494 (M^+, 13%), 349 (84%), 181 (100%). Elemental analysis: found, C 70.15, H 7.75, N 5.61%; calculated for $C_{29}H_{38}N_2O_5$, C 70.42, H 7.74, N 5.66%.

For **18b**: yield 27%. Elemental analysis: found, C 71.04, H 8.10, N 5.37%; calculated for $C_{31}H_{42}N_2O_5$, C 71.24, H 8.10, N 5.36%. For **18c**: yield 36%. Elemental analysis: found, C 71.67, H 8.36, N 5.12%; calculated for $C_{33}H_{46}N_2O_5$, C 71.97, H 8.42, N 5.09%. For **18d**: yield 49%. Elemental analysis: found, C 72.45, H 8.75, N 4.55%; calculated for $C_{35}H_{50}N_2O_5$, C 72.63, H 8.71, N 4.84%. For **18e**: yield 63%. Elemental analysis: found, C 74.61, H 9.62, N 3.97%; calculated for $C_{43}H_{66}N_2O_5$, C 74.74, H 9.63, N 4.05%. For **18f**: yield 39%. Elemental analysis: found, C 74.59, H 9.66, N 4.01%; calculated for $C_{43}H_{66}N_2O_5$, C 74.74, H 9.63, N 4.05%. For **18g**: yield 28%. Elemental analysis: found, C 74.04, H 9.33, N 4.37%; calculated for $C_{40}H_{60}N_2O_5$, C 74.04, H 9.32, N 4.32%.

For **19**, ^{1}H NMR: δ 0.88 (6H, t, J=7.0 Hz), 1.27 (32H, m), 1.46 (2H, quin, J=7.0 Hz), 1.80 (2H, quin, J=7.0 Hz), 4.00 (2H, t, J=7.0 Hz), 6.67 (1H, t, J=2.0 Hz), 7.15 (2H, d, J=2.0 Hz), 7.35 (1H, d, J=12.0 Hz), 7.45 (1H, dd, J=12.0, 1.7 Hz), 7.70 (1H, dd, J=10.5, 1.7 Hz), 9.15 (1H, d, J=10.5 Hz), 10.30 (1H, br). ^{13}C NMR: δ 14.12, 22.68, 26.00, 29.13, 29.35, 29.59, 29.62, 29.65, 31.90, 68.45, 105.81, 106.04, 113.52, 117.88, 119.21, 135.23, 135.50, 137.05, 142.81, 149.94, 160.75, 166.46, 178.58. MS (FAB$^+$): m/z 619 (M^++1, 5%), 618 (M^+, 5%), 473 (100%). Elemental analysis: found, C 75.71, H 9.50, N 4.34%; calculated for $C_{39}H_{58}N_2O_4$, C 75.69, H 9.45, N 4.53%.

*Synthesis of 2-(3,4,5-trialkoxybenzoylamino)-5-cyano-N-methyltropones (**20**).*

A thionyl chloride (3 ml) solution of 3,4,5-trioctyloxybenzoic acid (202.1 mg, 0.4 mmol) was refluxed for 5 h. An HMPA soution (1 ml) of *N*-methyl-2-amino-5-cyanotropolone (51 mg, 0.32 mmol) and 60% NaH (16 mg, 0.4 mmol) was stirred under nitrogen atmosphere. After 1 h, 3,4,5-trioctyloxybenzoyl chloride prepared above was added and the reaction mixture was stirred for 3 h at room temperature. The reaction was quenched by 2 M HCl solution in an ice bath. The reaction mixture was extracted with AcOEt. The organic layer was washed with sat. NaCl solution

and dried on $MgSO_4$. The solvent was evaporated and the residue was chromatographed on a silica-gel column to obtain colourless **20a** (120.9 mg, recrystallisation in chloroform–methanol): yield 59%. ^{1}H NMR: δ 0.88 (9H, t, J=7.0 Hz), 1.29 (24H, br), 1.42 (6H, m), 1.72 (6H, m), 3.33 (3H, s), 3.83 (4H, t, J=7.0 Hz), 3.93 (2H, t, J=7.0 Hz), 6.63 (2H, s), 7.03 (1H, d, J=12.2 Hz), 7.03 (1H, d, J=10.7 Hz), 7.11 (1H, dd, J=12.2, 1.6 Hz), 7.25 (1H, dd, J=10.7, 1.6 Hz). ^{13}C NMR: δ 14.03, 22.59, 25.95, 29.09, 29.19, 29.23, 29.41, 30.17, 31.73, 31.80, 36.59, 36.61, 68.98, 73.54, 106.56, 116.48, 118.23, 129.72, 129.97, 133.95, 139.13, 139.63, 140.47, 152.77, 158.21, 171.08, 181.40. MS (FAB$^+$): m/z 649 (M^++1, 2%), 648 (M^+, 3%), 489 (100%). Elemental analysis: found, C 73.88, H 9.45, N 4.20%; calculated for $C_{40}H_{60}N_2O_5$, C 74.04, H 9.32, N 4.32%.

For **20b**: yield 70%. Elemental analysis: found, C 76.21, H 10.40, N 3.33%; calculated for $C_{52}H_{84}N_2O_5$, C 76.42, H 10.36, N 3.43%.

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