Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

Roles of sigmatropic migration of a benzoyl group and intermolecular hydrogen bonding between a tropone carbonyl and an NH group on the mesomorphic properties of 2-(4-alkoxybenzoyloxy)-5-alkylaminotropones and 5-alkoxy-2-(4-alkylaminobenzoyloxy)tropo

Akira Mori; Nobuo Kato; Hitoshi Takeshita; Ryuko Nimura; Masahiro Isobe; Chihiro Jin; Seiji Ujiie

Online publication date: 06 August 2010

To cite this Article Mori, Akira , Kato, Nobuo , Takeshita, Hitoshi , Nimura, Ryuko , Isobe, Masahiro , Jin, Chihiro and Ujiie, Seiji(2001) 'Roles of sigmatropic migration of a benzoyl group and intermolecular hydrogen bonding between a tropone carbonyl and an NH group on the mesomorphic properties of 2-(4-alkoxybenzoyloxy)-5-alkylaminotropones and 5-alkoxy-2-(4-alkylaminobenzoyloxy)tropo', Liquid Crystals, 28: 9, 1425 — 1433
To link to this Article: DOI: 10.1080/02678290110067245
URL: http://dx.doi.org/10.1080/02678290110067245

LIQUID CRYSTALS, 2001, VOL. 28, NO. 9, 1425–1433

Roles of sigmatropic migration of a benzoyl group and intermolecular hydrogen bonding between a tropone carbonyl and an NH group on the mesomorphic properties of 2-(4-alkoxybenzoyloxy)-5-alkylaminotropones and 5-alkoxy-2-(4-alkylaminobenzoyloxy)tropones

AKIRA MORI*, NOBUO KATO, HITOSHI TAKESHITA†

Institute of Advanced Material Study, 86 Kyushu University, Kasuga-koen, Kasuga, Fukuoka 816-8580, Japan

RYUKO NIMURA, MASAHIRO ISOBE

Graduate School of Engineering Sciences, 39 Kyushu University, Kasuga-koen, Kasuga, Fukuoka 816-8580, Japan

CHIHIRO JIN

Japan Spectroscopic Co. Ltd., Hachioji, Tokyo 192-8537, Japan

and SEIJI UJIIE

Department of Material Science, Interdisciplinary Faculty of Science and Engineering, Shimane University, Matsue 690-8504, Japan

(*Received 22 January 2001; in final form 23 March 2001; accepted 23 April 2001*)

The mesomorphic properties of 2-(4-alkoxybenzoyloxy)-5-alkylaminotropones and 5-alkoxy-2-(4-alkylaminobenzoyloxy)tropones are discussed on the basis of results obtained by X-ray crystallographic and X-ray diffraction studies, as well as temperature-dependent FTIR spectral measurements. The X-ray crystallographic analysis of 2-(4-dodecylaminobenzoyloxy)-5-tetradecyloxytropone (**2f**) indicated that it formed a head-to-tail dimer through an intermolecular hydrogen bond between the NH and the tropone carbonyl group. The X-ray diffraction study of compound **2f** suggested that the molecules formed interdigitated bilayer smectic C phases with a tilt angle of as much as *c*. 40° to a layer plane. The corresponding benzenoids, however, were non-mesomorphic, with higher melting points than the troponoids. In the troponoids, sigmatropic migration of the benzoyl group weakened the intermolecular hydrogen bonding and assisted the occurrence of mesomorphic properties.

1. Introduction

Non-covalent interactions such as hydrogen bonds, dipole–dipole interactions, and π-π interactions are quite important for ordering molecules. Among them, hydrogen bonds have been given much attention since they not only induce mesomorphic properties, but also stabilize mesophases as reported for aromatic acids [1], monosaccharides [2], and 2-alkylcyclohexylpropane-1,3-diols [3], which form stable dimers that exhibit mesophases. At the same time, however, hydrogen bonds can be less favourable for the appearance of mesophases since they sometimes raise melting points above the mesophase–isotropic transition temperature and hide mesophases.

We are preparing liquid crystals with a tropone ring as a core [4]. One of the most important structural characteristics of troponoids is the presence of the carbonyl group, on which we concentrate attention since it acts as a lateral polar substituent to induce mesomorphic properties and plays a decisive role in inducing the migration of an acyl group of 2-acyloxytropones between the oxygen atom at C-2 and the carbonyl oxygen atom at C-1 [5].

*Author for correspondence; e-mail: mori-a@cm.kyushu-u.ac.jp
†Deceased on 1 October 1998.

Liquid Crystals ISSN 0267-8292 print/ISSN 1366-5855 online © 2001 Taylor & Francis Ltd
http://www.tandf.co.uk/journals
DOI: 10.1080/02678290110067245

We recently prepared troponoid liquid crystals, 2-(4-alkoxybenzoyloxy)-5-alkylaminotropones (**1**) [6] and 5-alkoxy-2-(4-alkylaminobenzoyloxy)tropones (**2**) [7], which show a smectic C (SmC) phase dominantly. We observed in the temperature dependent FTIR spectra that the intermolecular hydrogen bonds between the NH group and both the tropone and the ester carbonyl groups played an important role in the occurrence of the SmC phases. On the other hand, the corresponding benzenoids, 4-alkoxyphenyl 4-alkylaminobenzoates, were not mesomorphic. They had higher melting points than the corresponding troponoids, these higher melting points being due to intermolecular hydrogen bonds. Both troponoids **1** and **2** have an alkylamino group, which could possibly raise the melting points through intermolecular hydrogen bonds to hide the mesomorphism. However, this was not the case. In this paper, we discuss the mesomorphic differences between troponoids and benzenoids by considering the molecular structure in a single crystal and the molecular packing model in the mesomorphic state.

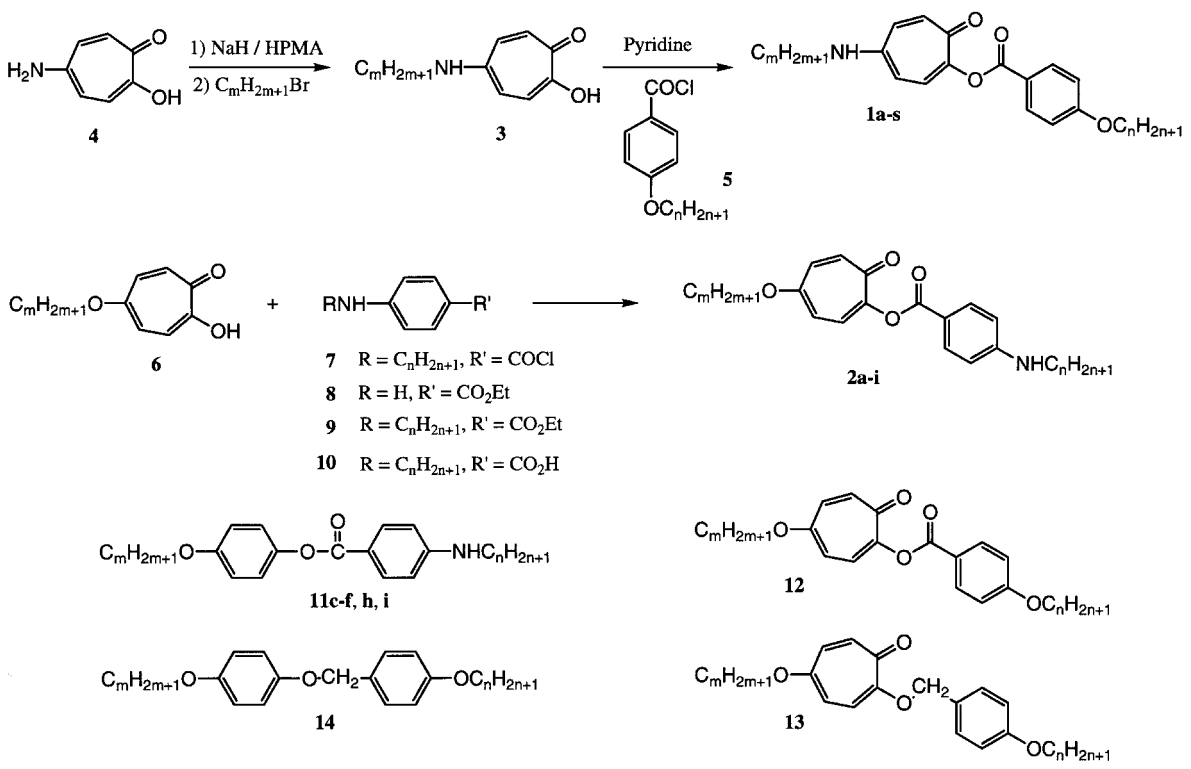
2. Results and discussion

2.1. *Synthesis*

5-Alkylaminotropolones (**3**) were selectively prepared by the reaction of 5-aminotropolone (**4**) [8] and one molar equivalent of alkyl bromide in the presence of sodium amide in hexamethylphosphoric triamide (HMPA). Next, a pyridine solution of **3** was reacted with an equivalent of 4-alkoxybenzoyl chloride (**5**) to give **1**. Similarly, benzoylation of the 5-alkoxytropolone (**6**) [5] with a 4-alkylaminobenzoyl chloride (**7**), prepared from ethyl 4-aminobenzoate (**8**) via ethyl 4-alkylaminobenzoate (**9**) and 4-alkylaminobenzoic acid (**10**), gave **2**. The structures of **1** and **2** were identified by the spectral data: the NMR spectra of **1** were similar to those of 2-benzoyloxytropone, which showed broad signals due to the [1, 9] sigmatropy [9, 10]. It is known that reversible migrations of an acyl and a benzoyl group of tropolone derivatives have been observed by NMR spectroscopy and that the shapes of the signals are changed depending on the structure and the temperature of measurement [10]. For example, the ^{1}H NMR spectrum of **1a** showed broad signals of the tropone ring protons at δ 5.8 (1H), 6.7 (1H), and 7.1 (2H) and of NH at 5.17 (1H) together with two sharp doublets at δ 6.92 (2H) and 8.08 (2H). The ^{13}C NMR spectrum of **1a** showed some broad carbon signals in the sp^2-carbon region and one carbon signal was missing.

2.2. *Mesomorphic Properties of 1 and 2*

The phase transition temperatures were measured by differential scanning calorimetry (DSC) and the mesomorphic phases were observed by polarizing optical



Scheme.

microscopy using a hot stage. The transition temperatures of **1** are summarized in table 1 and those of **2** and the corresponding benzene derivatives, 4-alkoxyphenyl 4-alkylaminobenzoates (**11**), which were prepared similarly from hydroquinone, are summarized in table 2. Interestingly, the compounds **1** and **2** showed only SmC phases, which were assigned by their schlieren optical textures with four brushes, as well as from the results of X-ray diffraction (XRD) studies as shown later. Since the corresponding 5-alkoxy-2-(4-alkoxybenzoyloxy)tropones (**12**) [9] showed nematic (N), smectic A (SmA) and SmC phases, the hetero-atoms changed the mesomorphic properties.

2.3. *Temperature-dependent FTIR spectra*

In the heating process for the temperature-dependent FTIR spectra of 2-(4-dodecylaminobenzoyloxy)-5-tetradecyloxytropone (**2f**), the absorption band of the tropone carbonyl group appeared at 1578 cm^{-1} in the liquid crystalline state and shifted to combine with the C=C absorption band around 1610 cm^{-1} in the isotropic liquid state. In the cooling process, the tropone carbonyl absorption band separated from the C=C absorption band to appear at 1586 cm^{-1} around 105°C, which is the transition temperature to the liquid crystalline state [7]. This means that the hydrogen bond between the NH and the tropone carbonyl group is more strongly operative in the liquid crystalline state.

From the temperature-dependent FTIR spectra of 5-(dodecylamino)-2-(4-dodecyloxybenzoyloxy)tropone (**1g**), which exhibited a monotropic SmC phase, pronounced spectral changes were observed in the NH absorption around 3400 cm^{-1}, in the ester carbonyl absorption around 1700–1730 cm^{-1}, and in the tropone carbonyl and C=C absorption bands around 1500–1600 cm^{-1} [6]. These observations indicated the existence of an intermolecular hydrogen bond between the NH and the ester and/or the tropone carbonyl groups in the liquid crystalline state. In fact, the NH absorption appeared at 3287 cm^{-1} in the liquid crystalline state and shifted to 3387 cm^{-1} in the crystalline state. While the absorption band of the ester carbonyl group of **1g** shifted to higher wavelengths from 1705 to 1734 cm^{-1} in the liquid crystalline state, the spectral change was different from those involving the NH and the tropone carbonyl groups, where the intensities of the absorptions around 1500–1550 cm^{-1} assigned to the tropone carbonyl group were increased with decreasing intensity of the absorption at 1583 cm^{-1} in the liquid crystalline state. It is therefore concluded that the interaction between the NH and the ester carbonyl groups is decreasing and the intermolecular hydrogen bond between the NH and the tropone carbonyl groups is becoming more effective in the liquid crystalline state.

2.4. *X-ray crystallographic analysis*

A single crystal of compound **2f** was obtained by recrystallization from dichloromethane. The result of the

Table 1. Transition temperatures (°C) of troponoids **1**.

	m	*n*	**1**
a	6	12	Cr • 102 • I
b	8	12	Cr • 100 • I
c	11	1	Cr • 137 • I
d	11	12	Cr • 94 • (SmC • 91 •) I
e	12	1	Cr • 133 • I
f	12	4	Cr • 95 • I
g	12	12	Cr • 96 • (SmC • 95 •) I
h	14	10	Cr • 101 • SmC • 102 • I
i	14	12	Cr • 99 • SmC • 104 • I
j	14	18	Cr • 95 • SmC • 102 • I
k	16	10	Cr • 99 • SmC • 106 • I
l	16	12	Cr • 100 • SmC • 107 • I
m	16	18	Cr • 95 • SmC • 104 • I
n	18	1	Cr • 113 • I
o	18	4	Cr • 97 • (SmC • 88 • SmA • 95 •) I
p	18	6	Cr • 97 • SmC • 103 • I
q	18	10	Cr • 97 • SmC • 107 • I
r	18	12	Cr • 98 • SmC • 105 • I
s	18	18	Cr • 96 • SmC • 106 • I

( ) means monotropic transition.

Table 2. Transition temperatures (°C) of troponoids **2**, benzenoids **11**, and the selected troponoids **1**.

	m	*n*	**2**	**11**	**1**
a	6	12	Cr • 115 • (SmC • 90 •) I		Cr • 102 • I
b	8	12	Cr • 108 • (SmC • 100 •) I		Cr • 100 • I
c	12	8	Cr • 108 • (SmC • 90 •) I	Cr • 130 • I	
d	12	10	Cr • 112 • (SmC • 98 •) I	Cr • 115 • I	
e	12	12	Cr • 108 • (SmC • 108 •) I	Cr • 119 • I	Cr • 96 • (SmC • 95 •) I
f	14	12	Cr • 109 • SmC • 115 • I	Cr • 119 • I	Cr • 99 • SmC • 104 • I
g	18	4	Cr • 112 • I		Cr • 97 • (SmC • 88 • SmA • 95 •) I
h	18	12	Cr • 108 • SmC • 111 • I	Cr • 116 • I	Cr • 98 • SmC • 105 • I
i	18	18	Cr • 111 • (SmC • 111 •) I	Cr • 115 • I	Cr • 96 • SmC • 106 • I

( ) indicates monotropic transition.

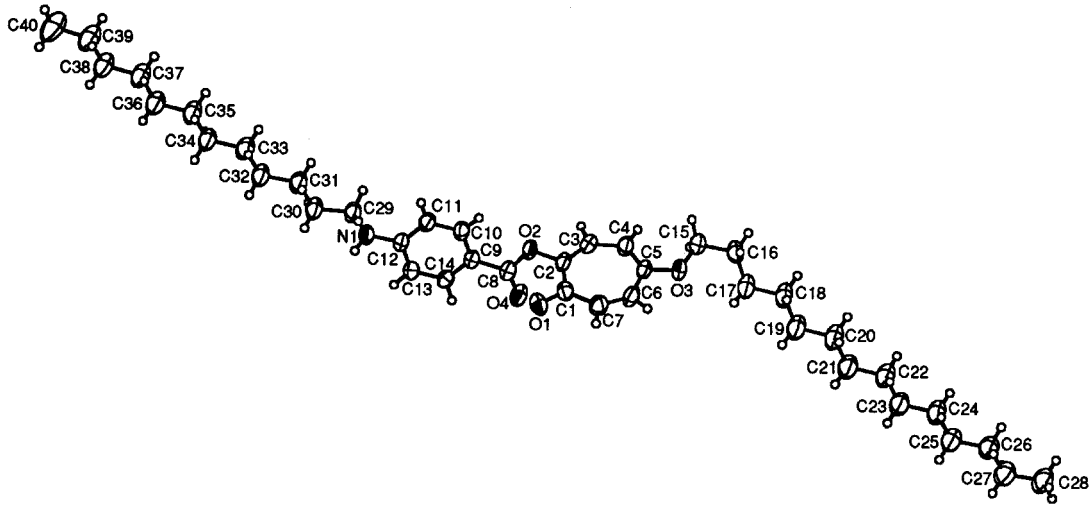


Figure 1. X-ray crystallographic analysis of troponoid **2f**.

crystallographic analysis is shown in figure 1. Compound **2f** formed a head-to-tail dimer. The distance between the tropone carbonyl group and the hydrogen atom of the NH group is 2.138 Å, which indicates the presence of an intermolecular hydrogen bond between them as observed in the temperature-dependent FTIR spectra. Figure 2 shows that the angle between the least-squares plane of the seven-membered ring and that of the linking ester group is 76.5°, and that the linking ester group leans towards the tropone carbonyl group. The shape of molecules is close to the conformation of the transition state of the [1, 9] sigmatropic rearrangement.

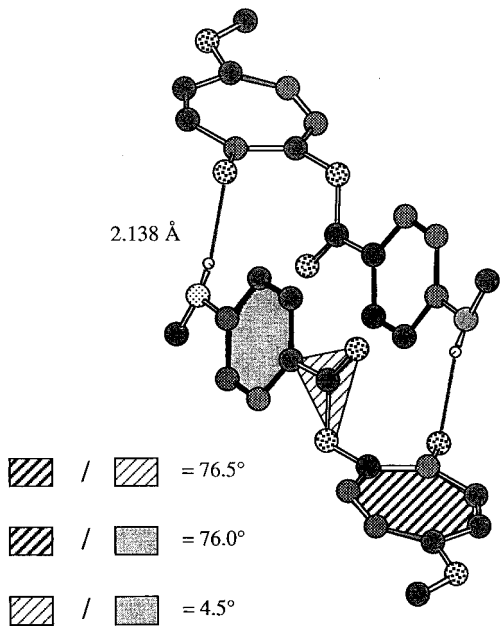


Figure 2. Angles between least-squares planes of the aromatic rings and the linking ester groups and the intermolecular distance between NH and C=O groups.

2.5. *X-ray diffraction analysis*

XRD data for an annealed sample of compound **2f** were measured at 110°C. The scattering peak located at 4.1° indicated the existence of a smectic layer whose spacing (*d*) is calculated from this value to be 21.6 Å. From the X-ray crystallographic analysis, compound **2f** forms a head-to-tail dimer through hydrogen bonding between the NH and the carbonyl groups, a conclusion also supported by the temperature-dependent FTIR spectra. From these results, we estimate that the greatest molecular length (*l*) of the dimer was 50.8 Å in the mesophase. The packing model of **2f** is shown in figure 3, where alkyl chains are interdigitated. From this model, the tilt angle was determined to be as much as *c.* 40°. A mean intermolecular lateral separation is estimated to be 3.9 Å from a broad peak at 22.9°.

2.6. *Comparison of mesomorphic properties of troponoids and benzenoids*

As shown in table 2, compounds **2** showed SmC phases, whereas the corresponding compounds **11** were non-mesomorphic. The mesomorphic property is dependent

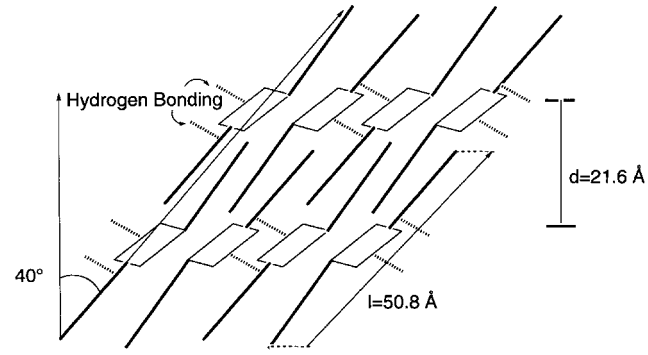


Figure 3. Packing model of troponoid **2f**.

on the core structure, i.e. the presence of the tropone carbonyl group. It is expected that the tropone carbonyl group with a permanent dipole moment (3.5 D) [11] plays a role in stabilizing the smectic phase by increasing the attractive dispersion force [12] between molecules as has been observed for 5-alkoxy-2-(4-alkoxybenzyl oxy)-tropones (**13**) and the corresponding benzene derivatives (**14**). The former were mesomorphic while the latter were not [13].

Additionally, mesomorphic compounds **2**, which have a [1, 9] sigmatropic system [5, 9], have lower melting points than the corresponding non-mesomorphic benzenoids **11**, which have no such a system. This is parallel to the results that 2-acyloxy monocyclic derivatives have lower melting points than 2-alkoxy ones [14].

We have observed that the angle between the benzoyl and the 4-cyanophenyl groups of 4-cyanophenyl 4-docecyloxybenzoate is 47.2° by X-ray crystallographic analysis [15]. Since the angle between the benzoyl group and the tropone ring of **2f** is 76.5°, as shown in figure 2, the planarity of the core part of **2f** should be worse than that of the corresponding benzenoids. The crystal packing of compound **2f** should therefore be more loose in order to give rise to the lower melting points than the benzenoids **11**, since it is anticipated that **2f** and **11** would crystallize retaining the conformations present in the isotropic liquid state.

Comparing the thermal stabilities between troponoids **1** and **2**, the latter **2** have a higher transition temperatures as shown in table 2. Their FTIR spectra indicated that both have hydrogen bonding between the NH and the tropone carbonyl groups. Figure 4 shows the schematic dimeric structures of troponoids **1** and **2**. The core part of troponoids **2** is more extended than that of **1**, because the rigid core length of the molecular long axis of the dimer structure is longer through intermolecular hydrogen than for troponoids **1**.

Finally, figure 5 shows the ^{13}C NMR spectra of compounds **1h** and **2i** at 27°C. Some signals of compound **1h** are broader than those of compound **2i**, which indicates that the rate of the [1, 9] sigmatropy of compound **1h** is faster than that of compound **2i**. The sigmatropic rate would be accelerated by the alkylamino group at C-5, which is a better electron donating substituent than an alkoxy group, and the rate for troponoids **2** would be reduced by the alkylamino group on the migrating benzoyl group [10].

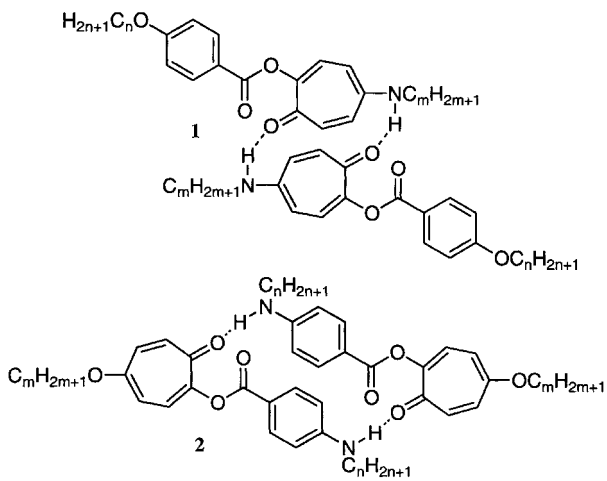


Figure 4. Schematic dimer structures of troponoids **1** (upper) and **2** (lower).

3. Conclusion

Two types of troponoid liquid crystals with an alkylamino group were prepared. They have SmC phases, whose thermal stabilities are dependent on the rigid core length of the molecular long axis of the dimer structures. Comparing the mesomorphic properties between troponoids **1** and **2** and benzenoids **11**, the troponoids were mesomorphic, while the corresponding benzenoids **11** were not. The reason why the benzenoids are not mesomorphic is that the benzenoids have higher melting points than the troponoids due to intermolecular hydrogen bonding. In the troponoids, migration of the benzoyl group in the mesophase made intermolecular hydrogen bonding too weak to influence the mesomorphic properties. This is a characteristic property of the troponoids.

4. Experimental

Elemental analyses were obtained at the elemental analysis laboratory of Kyushu University. Melting points were obtained on a Yanagimoto Micro Melting Point Apparatus and are uncorrected. NMR spectra were measured on a GSX 270H Model spectrometer in $CDCl_3$; the chemical shifts are expressed in δ units. Mass spectra were measured with a JEOL 01SG-2 spectrometer. IR spectra were recorded on a JASCO IR-A102 spectrometer using KBr disks for crystalline compounds. The stationary phase for column chromatography was Wakogel C-300 and the eluent was a mixture of ethyl acetate, chloroform, and hexane. Transition temperatures were measured using a differential scanning calorimeter (Seiko DSC 200) and the mesomorphic phase was observed using a polarizing microscope (Olympus BHSP BH-2) equipped with a hot stage (Linkam TH-600RMS). The XRD 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. Temperature-dependent FTIR spectra were measured by a JASCO FT/IR-8300 and Micro-10 equipped with Mettler FP 84 hot stage.

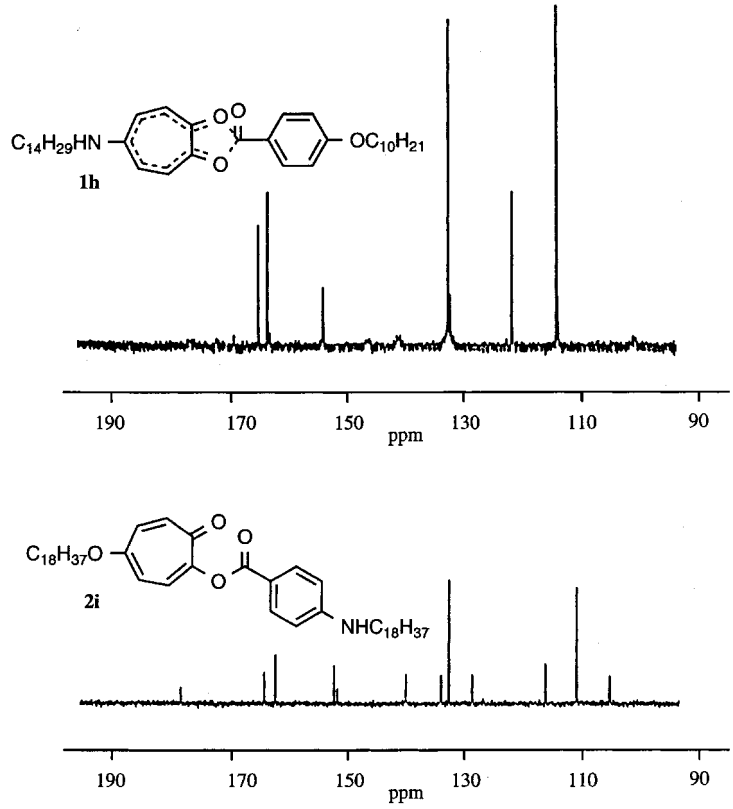


Figure 5. ^{13}C NMR spectra of troponoids **1h** and **2i** in $CDCl_3$ at 27°C.

4.1. *Preparation of 5-hexylaminotropolone (**3a**)*

To a stirred anhydrous suspension of HMPA (hexamethylphosphoric triamide) (5 cm^3), NaH (*c.* 60% dispersion in mineral oil, 120 mg) and 5-aminotropolone (**4**, 274 mg) were added at 0°C under nitrogen. The temperature was allowed to rise slowly to room temperature. 1-Bromohexane (330 mg) was added slowly and stirred at room temperature for 4 h. The mixture was poured into an ice-cooled HCl solution (2 mol dm^{-3}) and shaken with $CHCl_3$. The organic layer was washed with water, dried with $MgSO_4$, and evaporated under reduced pressure. The precipitates were collected and recrystallized from CCl_4 to give 84 mg (19%) of **3a**, yellow needles, m.p. 140°C; ^1H NMR (CD_3OD) δ 0.92 (3H, t, $J = 7.0$ Hz), 1.2–1.55 (6H, m), 1.72 (2H, quint, $J = 7.0$ Hz), 3.36 (2H, t, $J = 7.0$ Hz), 7.32 (2H, dm, $J = 12.5$ Hz), and 7.76 (2H, dm, $J = 12.5$ Hz); ^{13}C NMR (CD_3OD) δ 14.4, 23.6, 27.7, 29.0, 32.6, 44.8, 124.8 (2C), 136.3 (2C), 155.1, and 161.1 (2C); IR (KBr) *v*: 3450, 3220, 2940, 2860, 1642, 1588, 1515, 1470, 1415, 1385, 1370, 1300, 1245 and 1180 cm^{-1}; MS *m/z* (%) 221 (M^+, 66), 150 (55), and 122 (100); found 221.1417, calc for $C_{13}H_{19}NO_2$ 221.1416.

Other **3** compounds were prepared in a similar manner. **3b**: pale yellow needles, m.p. 140°C, yield 41%; found 249.1731, calc for $C_{15}H_{23}NO_2$ 249.1728. **3c**: yellow needles, m.p. 136°C, yield 50%; found 291.2196, calc for $C_{18}H_{29}NO_2$ 291.2198. **3d**: yellow needles, m.p. 143°C, yield 57%; found 305.2356, calc for $C_{19}H_{31}NO_2$ 305.2355. **3e**: yellow needles, m.p. 143°C, yield 32%; found 333.2661, calc for $C_{21}H_{35}NO_2$ 333.2668. **3f**: yellow needles; m.p. 141°C, yield 35%; found 361.2972, calc for $C_{23}H_{39}NO_2$ 361.2981. **3g**: yellow needles, m.p. 109°C, yield 35%; found C 77.05, H 11.08, N 3.60; calc for $C_{25}H_{43}NO_2$ C 77.07, H 11.12, N 3.60%. **3h**: yellow needles, m.p. 89°C, yield 30%; found 445.3920. calc for $C_{29}H_{51}NO_2$ 445.3920.

4.2. *Preparation of ethyl 4-butylaminobenzoate (**9a**)*

To a stirred anhydrous suspension of HMPA (20 cm^3), NaH (*c.* 60% dispersion in mineral oil, 120 mg) and ethyl 4-aminobenzoate (**8**, 5 g) were added at 0°C under nitrogen. The temperature was allowed to rise slowly to room temperature. 1-Bromobutane (4.1 g) was added slowly and stirred at room temperature for 4 h. The mixture was poured into an ice-cooled HCl solution (2 mol dm^{-3}) and shaken with $CHCl_3$. The organic layer was washed with water, dried with $MgSO_4$, and evaporated under reduced pressure. The residue was purified by silica gel chromatography ($CHCl_3$) to give 2 g (30%) of **9a**, colourless prisms, m.p. 66°C; ^1H NMR δ 0.88 (3H, t, $J = 7.3$ Hz), 1.25–1.50 (5H, m), 1.60 (2H, quint,

$J = 7.3$ Hz), 3.14 (2H, t, $J = 7.3$ Hz), 4.31 (2H, q, $J = 7.3$ Hz), 6.53 (2H, dm, $J = 8.8$ Hz), and 7.86 (2H, dm, $J = 8.8$ Hz); ^{13}C NMR δ 13.9, 14.5, 20.2, 31.4, 43.1, 60.1, 111.3 (2C), 118.3, 131.5 (2C), 152.1 and 166.9; IR (KBr) *v*: 3400, 2970, 2890, 1685, 1600, 1535, 1480, 1365, 1340, 1280, 1170, 1125, 1115, 1025 and 775 cm^{-1}; MS *m*/*z* (%) 221 (M^+, 34), 178 (100), and 150 (21); found C 70.62, H 8.63, N 6.23; calc for $C_{13}H_{19}NO_2$ C 70.56, H 8.65, N 6.33%.

Other **9** compounds were prepared in a similar manner. **9b**: colourless plates, m.p. 82°C, yield 30%; found C 75.82, H 10.46, N 3.93; calc for $C_{21}H_{35}NO_2$ C 75.63, H 10.58, N 4.20%. **9c**: colourless crystals, m.p. 88°C, yield 98%; found C 77.55, H 11.19, N 3.15; calc for $C_{27}H_{47}NO_2$ C 77.64, H 11.34, N 3.35%.

4.3. *Preparation of 4-butylaminobenzoic acid (**10a**)*

To an EtOH solution of ethyl 4-butylaminobenzoate (2 g), an aqueous KOH solution (50 cm^3) was added and the mixture boiled for 10 h. After the EtOH was evaporated off under reduced pressure, the mixture was acidified and the product extracted with $CHCl_3$ and recrystallized from AcOEt to give 1.3 g (74%) of **10a**, colourless crystals, m.p. 150°C; ^{1}H NMR (50.0°C) δ 0.97 (3H, t, $J = 7.4$ Hz), 1.44 (2H, sext, $J = 7.4$ Hz), 1.63 (2H, quint, $J = 7.4$ Hz), 3.18 (2H, t, $J = 7.4$ Hz), 6.55 (2H, dm, $J = 8.7$ Hz), and 7.91 (2H, dm, $J = 8.7$ Hz); ^{13}C NMR (50.0°C) δ 13.8, 20.2, 31.5, 43.2, 111.5 (2C), 117.3, 132.4 (2C), 152.9 and 171.5; IR (KBr) *v*: 3440, 3390, 2990, 2950, 1665, 1605, 1575, 1530, 1410, 1320, 1295 and 1175 cm^{-1}; MS *m*/*z* (%) 193 (M^+, 23) and 150 (100); found C 68.28, H 7.78, N 7.11; calc for $C_{11}H_{15}NO_2$ C 68.37, H 7.82, N 7.25%.

Other **10** compounds were prepared in a similar manner. **10b**: colourless plates, m.p. 125°C, yield 55%; found C 74.51, H 10.11, N 4.49; calc for $C_{19}H_{31}NO_2$ C 74.71, H 10.23, N 4.59%. **10c**: colourless plates, m.p. 107°C, yield 95%; found C 77.35, H 10.80, N 3.77; calc for $C_{25}H_{43}NO_2$ C 77.07, H 11.13, N 3.60%.

4.4. *Preparation of 4-alkylaminobenzoyl chlorides (7)*

4-Alkylaminobenzoyl chlorides (**7**) were prepared by the reactions between 4-alkylaminobenzoic acids and thionyl chloride in pyridine.

4.5. *Preparation of 2-(4-dodecyloxybenzoyloxy)-5-hexylaminotropone (**1a**)*

To an anhydrous pyridine solution (3 cm^3) of 5-hexylaminotropolone (**3a**, 111 mg), 4-dodecyloxybenzoyl chloride (153 mg) was added in the presence of DMAP (4-*N*,*N*′-dimethylaminopyridine) under nitrogen at room temperature. After stirring for 12 h, the mixture was poured into aqueous $KHSO_4$ solution and extracted with $CHCl_3$. The organic layer was washed with water, dried with $MgSO_4$, and evaporated under reduced pressure. The residue was purified using silica gel chromatography (AcOEt : hexane = 1) to give 248 mg (97%) of **1a** yellow powder; ^{1}H NMR δ 0.88 (6H, m), 1.10–1.70 (26H, m), 1.83 (2H, quint, $J = 6.6$ Hz), 2.96 (2H, br s), 4.01 (2H, t, $J = 6.6$ Hz), 5.71 (1H, br s), 6.22 (2H, br s), 6.91 (2H, dm, $J = 8.8$ Hz), 7.07 (1H, br s), and 8.08 (2H, dm, $J = 8.8$ Hz); ^{13}C NMR δ 14.0, 14.1, 22.6, 22.7, 26.0, 26.8, 27.9, 29.1, 29.4 (2C), 29.6 (3C), 29.7, 31.5, 31.9, 43.6, 68.3, 100.9 (br), 114.1 (2C), 121.6, 132 (br), 132.4 (2C), 140.8 (br), 146.4 (br), 154.1, 163.4, 165.0, and 176.6 (br); IR (KBr) *v*: 3370, 2950, 2860, 1708, 1605, 1574, 1543, 1508, 1464, 1435, 1405, 1282, 1250, 1185, 1170, 1100, 845 and 760 cm^{-1}; MS *m*/*z* (%) 509 (M^+, 15), 290 (21), and 289 (100); found C 75.36, H 9.25, N 2.64; calc for $C_{32}H_{47}NO_4$ C 75.40, H 9.29, N 2.75%.

Other **1** compounds were prepared in a similar manner. **1b**: yellow powder, yield 53%; found C 76.15, H 9.51, N 2.52; calc for $C_{34}H_{51}NO_4$ C 75.94, H 9.56, N 2.60%. **1c**: yellow powder, yield 43%; found C 73.32, H 8.22, N 3.01; calc for $C_{26}H_{35}NO_4$ C 73.38, H 8.29, N 3.29%. **1d**: yellow powder, yield 72%; found C 76.39, H 9.78, N 2.22; calc for $C_{37}H_{57}NO_4$ C 76.64, H 9.91, N 2.42%. **1e**: yellow needles, yield 35%; found C 73.50, H 8.27, N 2.90; calc for $C_{27}H_{37}NO_4$ C 73.77, H 8.48, N 3.19%. **1f**: yellow powder, yield 19%; found C 74.97, H 8.85, N 2.74; calc for $C_{30}H_{43}NO_4$ C 74.81, H 9.00, N 2.91%. **1g**: yellow powder, yield 71%; found C 76.96, H 9.90, N 2.33; calc for $C_{38}H_{59}NO_4$ C 76.85, H 10.01, N 2.36%. **1h**: yellow powder, yield 96%; found C 76.88, H 9.74, N 2.22; calc for $C_{38}H_{59}NO_4$ C 76.85, H 10.01, N 2.36%. **1i**: yellow powder, yield 97%; found C 77.51, H 10.01, N 2.33; calc for $C_{40}H_{63}NO_4$ C 77.25, H 10.21, N 2.25%. **1j**: pale yellow powder, yield 77%; found C 78.27, H 10.45, N 2.16; calc for $C_{46}H_{75}NO_4$ C 78.25, H 10.71, N 1.98%. **1k**: yellow powder, yield 90%; found C 77.59, H 9.97, N 2.16; calc for $C_{40}H_{63}NO_4$ C 77.25, H 10.21, N 2.25%. **1l**: yellow powder, yield 84%; found C 77.85, H 10.14, N 2.14; calc for $C_{42}H_{67}NO_4$ C 77.61, H 10.39, N 2.16%. **1m**: yellow powder, yield 77%; found C 78.25, H 10.55, N 2.01; calc for $C_{48}H_{79}NO_4$ C 78.53, H 10.85, N 1.91%. **1n**: yellow needles, yield 10%; found C 75.23, H 9.26, N 2.29; calc for $C_{33}H_{49}NO_4$ C 75.68, H 9.43, N 2.67%. **1o**: pale yellow powder, yield 23%; found C 76.48, H 9.66, N 2.47; calc for $C_{36}H_{55}NO_4$ C 76.42, H 9.80, N 2.48%. **1p**: yellow powder, yield 45%; found C 76.91, H 9.97, N 2.43; calc for $C_{38}H_{59}NO_4$ C 76.85, H 10.01, N 2.36%. **1q**: yellow powder, yield 73%; found C 77.84, H 10.25, N 2.27; calc for $C_{42}H_{67}NO_4$ C 77.61, H 10.39, N 2.15%. **1r**: yellow powder, yield 36%; found C 77.60, H 10.28, N 2.10; calc for $C_{44}H_{71}NO_4$ C 77.94, H 10.55, N 2.07%. **1s**: yellow powder, yield 62%; found C 78.48, H 10.63, N 1.71; calc for $C_{50}H_{83}NO_4$ C 78.79, H 10.98, N 1.84%.

4.6. *Preparation of 2-(4-dodecylaminobenzoyloxy)-5-hexyloxytropone (**2a**)*

To an anhydrous benzene solution (5 cm^3) of 4-dodecylaminobenzoic acid (183 mg), thionyl chloride (2 cm^3) was added and the mixture heated under reflux for 5 h. After the solvents were removed under reduced pressure, pyridine (3 cm^3) was added. To the resultant mixture, 5-hexyloxytropolone (111 mg) was added in the presence of DMAP under nitrogen at room temperature. After stirring for 12 h at room temperature, the mixture was poured into aqueous $KHSO_4$ solution and shaken with $CHCl_3$. The organic layer was washed with water, dried with $MgSO_4$, and evaporated under reduced pressure. The residue was purified using silica gel chromatography ($CHCl_3$: AcOEt = 20) to give 183 mg (72%) of **2a**, colourless plates; ^{1}H NMR δ 0.80–1.00 (6H, m), 1.15–1.50 (24H, m), 1.63 (2H, quint, J = 7.3 Hz), 1.80 (2H, quint, J = 6.6 Hz), 3.16 (2H, t, J = 7.3 Hz), 3.92 (2H, t, J = 6.6 Hz), 6.22 (1H, br d, J = 12.1 Hz), 6.58 (2H, dm, J = 8.8 Hz), 7.10 (1H, br d, J = 12.1 Hz), 7.22 (2H, d, J = 12.1 Hz), and 7.98 (2H, dm, J = 8.8 Hz); ^{13}C NMR δ 14.0, 14.1, 22.5, 22.7, 25.6, 27.1, 28.7, 29.1, 29.4 (2C), 29.6 (4C), 31.4, 31.9, 43.6, 68.7, 105.8, 111.7 (2C), 116.8, 128.7, 132.6 (2C), 134.0, 140.1, 152.1, 152.4, 162.8, 164.6 and 178.5; IR (KBr) ν: 3330, 2930, 2850, 1705, 1605, 1575, 1520, 1245, 1160 and 1075 cm^{-1}; MS m/z (%) 509 (M^+, 5), 289 (22), and 288 (100); found C 75.66, H 9.35, N 2.55; calc for $C_{32}H_{47}NO_4$ C 75.40, H 9.29, N 2.75%.

Other **2** compounds were prepared in a similar manner. **2b**: pale yellow plates, yield 67%; found C 76.11, H 9.64, N 2.59; calc for $C_{34}H_{51}NO_4$ C 75.94, H 9.56, N 2.60%. **2c**: pale yellow plates, yield 12%; found C 75.67, H 9.55, N 2.55; calc for $C_{34}H_{51}NO_4$ C 75.94, H 9.56, N 2.60%. **2d**: pale yellow plates, yield 13%; found C 76.12, H 9.83, N 2.31; calc for $C_{36}H_{55}NO_4$ C 76.42, H 9.80, N 2.48%. **2e**: pale yellow plates, yield 65%; found C 76.88, H 9.89, N 2.15; calc for $C_{38}H_{59}NO_4$ C 76.85, H 10.01, N 2.36%. **2f**: pale yellow plates, yield 67%; found C 77.16, H 10.12, N 2.00; calc for $C_{40}H_{63}NO_4$ C 77.25, H 10.21, N 2.25%. **2g**: pale yellow plates, yield 78%; found C 76.46, H 9.66, N 2.26; calc for $C_{36}H_{55}NO_4$ C 76.42, H 9.80, N 2.48%. **2h**: pale yellow needles, yield 85%; found C 78.17, H 10.42, N 2.03; calc for $C_{44}H_{71}NO_4$ C 77.94, H 10.55, N 2.07%. **2i**: pale yellow plates, yield 66%; found C 78.74, H 10.98, N 2.08; calc for $C_{50}H_{83}NO_4$ C 78.79, H 10.98, N 1.84%.

4.7. *X-ray crystallographic analysis of **2f***

A single crystal of **2f** was obtained as a pale yellow plate having the approximate dimensions 0.50 × 0.17 × 0.07 mm^3 by recrystallization from dichloromethane. The X-ray measurements were made on an Enraf-Nonius FR590 diffractometer with graphite monochromated Cu-K_α radiation (λ = 1.54184 Å). The data were collected at a temperature of 23 ± 2°C using the w-2θ scan technique to a maximum 2θ value of 129.86°. The structure was solved by a direct method (SIR92 [16]), and was refined using full-matrix least squares (SHELXL93 [17]) based on F^2 of all independent measured reflections. All H atoms except a hydrogen on the nitrogen were located at ideal positions and were included in the refinement, but restrained to ride on the atom to which they were bonded. Isotropic thermal factors of these H atoms were held fixed to 1.2 times or 1.5 times (for methyls) U_{eq} of the riding atoms. The hydrogen attached on the amide N atom was located from the difference Fourier map and its positional parameters and the isotropic thermal factor were refined. The selected crystallographic data are listed in table 3†.

Table 3. Crystallographic data for troponoid **2f**.

Formula	$C_{40}H_{63}NO_4$
Formula mass	M_r = 621.94
Crystal colour	Pale yellow
Crystal size/mm^3	0.50 × 0.17 × 0.07
Crystal system	Triclinic
Space group	$P\bar{1}$
a/Å	10.173 (1)
b/Å	21.985 (2)
c/Å	9.385 (1)
α/deg	93.458 (6)
β/deg	112.495 (7)
γ/deg	97.322 (7)
V/Å^3	1909.9 (4)
Z	2
D_{calc}/g cm	1.082
μ/mm^{-1}	0.526
No. of reflections used	6465
No. of obsd refl. [$I > 2\sigma(I)$]	3930
Refined parameters	411
Refinement	F^2 (SHELXL93)
$R[F^2 > 2\sigma(F^2)]$	0.0456
$wR(F^2)$	0.1475

4.8. *X-ray diffraction study of **2f***

The XRD measurements were carried out with a Rigaku Rint 2100 system using Ni-filtered Cu-K_α radiation at various temperatures. Samples placed on a RinKam hot stage (HFS-91) were used for the XRD measurements.

4.9. *Preparation of 4-octyloxyphenyl 4-dodecylaminobenzoate (**11c**)*

A typical procedure was as follows. To an anhydrous benzene solution (3 cm^3) of 4-octylaminobenzoic acid

† Details of the analysis have been deposited at the Editorial Office as a Crystallographic Information File (CIF).

(100 mg), thionyl chloride (2 cm^3) was added and the mixture heated at reflux for 4 h. After the solvents were removed under reduced pressure, pyridine (1 cm^3) was added. To the resultant mixture, 4-dodecyloxyphenol (120 mg) was added in the presence of DMAP under nitrogen at room temperature. After stirring for 12 h at room temperature, the mixture was poured into aqueous $KHSO_4$ solution and extracted with $CHCl_3$. The organic layer was washed with water, dried with $MgSO_4$, and evaporated under reduced pressure. The residue was purified using silica gel chromatography ($CHCl_3$: AcOEt = 20) to give 64 mg (25%) of **11c**, pale yellow plates; ^{1}H NMR δ 0.86–0.90 (6H, m), 1.11–1.83 (32H, m), 3.18 (2H, t, J = 7.0 Hz), 3.94 (2H, t, J = 6.4 Hz), 4.18 (1H, br s), 6.58 (2H, d, J = 8.8 Hz), 6.90 (2H, d, J = 9.2 Hz), 7.08 (2H, d, J = 8.8 Hz), and 7.99 (2H, d, J = 8.8 Hz); ^{13}C NMR δ 14.1 (2C), 22.6, 22.7, 26.1, 27.1, 29.2, 29.3 (2C), 29.4 (3C), 29.6 (3C), 29.7, 31.8, 43.5, 68.5, 111.6, 115.0 (2C), 115.4, 116.0, 122.6, 132.2 (2C), 144.7, 152.4, 156.6 and 165.7; MS *m/z* (%) 509 (M^+, 6) and 232 (100); found C 77.53, H 10.21, N 2.65; calc for $C_{33}H_{51}NO_3$ C 77.75, H 10.08, N 2.75%. **11d**: pale yellow plates, yield 6%, found C 78.10, H 10.20, N 2.87; calc for $C_{35}H_{55}NO_3$ C 78.16, H 10.31, N 2.60%. **11e**: pale yellow plates, yield 11%, found C 78.40, H 10.27, N 2.25; calc for $C_{37}H_{59}NO_3$ C 78.53, H 10.51, N 2.54%. **11f**: pale yellow plates, yield 16%, found C 78.90, H 10.55, N 2.40; calc for $C_{39}H_{63}NO_3$ C 78.87, H 10.69, N 2.36%. **11h**: pale yellow plates, yield 9%, found C 79.41, H 11.05, N 2.25; calc for $C_{43}H_{71}NO_3$ C 79.45, H 11.01, N 2.15%. **11i**: pale yellow plates, yield 11%, found C 80.34, H 11.38, N 1.98; calc for $C_{49}H_{83}NO_3$ C 80.16, H 11.40, N 1.91%.

References

[1] Gray, G. W., and Jones, B., 1953, *J. chem. Soc.*, 4179; Bryan, R. F., Hartley, P., Miller, R. W., and Shen, M.-S., 1980, *Mol. Cryst. liq. Cryst.*, **62,** 281.

[2] Jeffrey, G. A., 1986, *Acc. chem. Res.*, **19,** 168.

[3] Diele, S., Mädicke, A., Geissler, E., Meinel, K., Demus, D., and Sackmann, H., 1989, *Mol. Cryst. liq. Cryst.*, **166,** 131.

[4] Takemoto, M., Mori, A., and Ujiie, S., 1999, *Chem. Lett.*, 1177; Hashimoto, M., Ujiie, S., and Mori, A., 2000, *Chem. Lett.*, 758.

[5] Mori, A., Takeshita, H., Kida, K., and Uchida, M., 1990, *J. Am. chem. Soc.*, **112,** 8635; Kida, K., Mori, A., and Takeshita, H., 1991, *Mol. Cryst. liq. Cryst.*, **199,** 387.

[6] Mori, A., Nimura, R., and Takeshita, H., 1991, *Chem. Lett.*, 77.

[7] Mori, A., Nimura, R., Isobe, M., and Takeshita, H., 1992, *Chem. Lett.*, 859.

[8] Nozoe, T., Seto, S., Ebine, S., and Itô, S., 1951, *J. Am. chem. Soc.*, **73,** 1895; Nozoe, T., Seto, S., Takeda, H., and Sato, T., 1952, *Sci. Rept. Tohoku Univ., Ser. 1*, **35,** 274.

[9] Mori, A., Uchida, M., and Takeshita, H., 1989, *Chem. Lett.*, 591; Mori, A., Kato, N., Takeshita, H., Uchida, M., Taya, H., and Nimura, R., 1991, *J. mater. Chem.*, **1,** 799.

[10] Masamune, S., Kemp-Jones, A. V., Green, J., Rabenstein, D. L., Yasunami, M., Takase, K., and Nozoe, T., 1973, *J. chem. Soc., chem. Commun.*, 283; Minkin, V. I., Olekhnovich, L. P., Zhdanov, Y. A., Budarina, Z. N., and Metlushenko, V. P., 1974, *Tetrahedron Lett.*, 563; Minkin, V. I., Olekhnovich, L. P., and Zhdanov, Y. A., 1981, *Acc. chem. Res.*, **14,** 210; Takeshita, H., Mori, A., Watanabe, H., Kusaba, T., Sugiyama, S., and Kodama, M., 1987, *Bull. chem. Soc. Jpn.*, **60,** 4335.

[11] Kubo, M., Nozoe, T., and Kurita, Y., 1951, *Nature*, **169,** 688.

[12] Takatoh, K., Sunohara, K., and Sakamoto, M., 1988, *Mol. Cryst. liq. Cryst.*, **164,** 167.

[13] Mori, A., Taya, H., and Takeshita, H., 1991, *Chem. Lett.*, 579.

[14] Mori, A., Takematsu, S., Isobe, M., and Takeshita, H., 1995, *Chem. Lett.*, 15.

[15] Kubo, K., and Mori, A., 2001, *Acta Cryst.*, **E57,** o113.

[16] Altomare, M. C., Burla, M., Camalli, G., Cascarano, C., Giacovazzo, A., Guagliardi, G., and Polidori, J., 1994, *J. appl. Crystallogr.*, **27,** 435.

[17] Sheldrick, G. M., 1993, SHELXL93. Program for the Refinement of Crystal Structures (University of Göttingen, Germany).