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Liquid crystals with a 5-phenyltropone core

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Liquid crystals with a 5-phenyltropone structure were prepared. 5-(4-Alkanoylaminophenyl)-tropone derivatives (**5** and **6**) showed smectic A and C phases. From the layer spacing, compound **5q** formed an interdigitated bilayer smectic A phase. The variable temperature FTIR spectra of **5q** indicated the presence of intermolecular hydrogen bonding between the amide carbonyl group and the NH group on the phenyl ring of neighbouring molecules. The amide groups of the 2-alkanoylamino-5-phenyltropones controlled the occurrence of mesophases through not only inter- and intra-molecular hydrogen bonds, but also dipole–dipole interaction with the tropone carbonyl group of neighbouring molecules.

1. Introduction

The most common structure of cores for mesogens is the *para*-substituted phenyl ring as found in the biphenyl subunit with its rigid and extended structure [1]. We are preparing troponoid liquid crystals to investigate the relationship between their molecular structures and mesomorphic properties. Especially noteworthy are the roles of the tropone carbonyl group, which can act as a lateral polar group [2] and play roles in forming inter- [3] and intra-molecular [4, 5] hydrogen bonds, and 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 [6]. For example, 2-(4-alkoxybenzoyloxy)-5-alkylaminotropones (**1**) [3*a*] and 5-alkoxy-2-(4-alkylaminobenzoyloxy) tropones (**2**) [3*b*] show a smectic C phase, and the variable temperature IR spectra indicate the presence of intermolecular hydrogen bonding between the NH and the tropone carbonyl groups, which assists the exclusive formation of the smectic C phase. The corresponding benzenoid systems are non-mesomorpic because of the increased melting point through intermolecular hydrogen bonding [7].

Many papers in the literature discuss the effect of hydrogen bonding interactions on the properties of liquid crystals [8]. We have observed in 5-alkoxy-2-(4-alkoxybenzoylamino) tropones **3** [4] and 5-cyano-2-(4-alkoxybenzoylamino) tropones **4** [5] that intramolecular hydrogen bonding between the tropone carbonyl and the amide NH group at C-2 make the molecules flat and so enhance the mesomorphic properties. In this paper, we report the mesomorphic properties of liquid crystals based on a 5-phenyltropone moiety in 5-(4-alkanoylaminophenyl)-2-alkanoylaminotropones (**5**),

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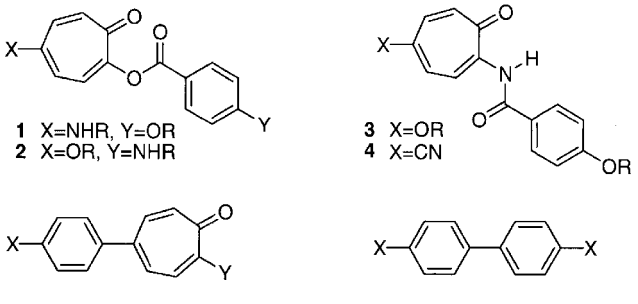
5-(4-alkanoylaminophenyl)-2-alkanoyloxytropones (**6**), 5-(4-alkanoylaminophenyl)-2-alkylaminotropones (**7**), and 2-alkylamino-5-(4-alkylaminophenyl)tropones (**8**).

2. Results

2.1. *Synthesis*

Compounds **5** and **6** [9] were prepared by acylation of 2-amino-5-(4-aminophenyl)tropone (**9**) and 5-(4-aminophenyl)tropolone (**10**) [10]. The ^{1}H NMR spectra of **6** showed a [1, 9] sigmatropy [6] in $CDCl_3$, while those of **5** did not. The ^{1}H NMR spectra of **5** displayed an aromatic proton around δ 9.1 as a doublet ($J = 11$ Hz), which was assigned to H-3. The low field shift was caused by the anisotropy of the adjacent amide C=O group, which is located on the outer side of the molecule because of the intramolecular hydrogen bonding between the tropone C=O and the NH group. The two singlet signals of the NH of **5a** appeared at δ 7.28 and 9.37, of which the latter was assigned to the intramolecularly hydrogen-bonded NH proton. In a D_2O exchange experiment on **5a**, these two NH protons disappeared.

Next, the compounds **7** were prepared by selective acylation of **9** with a half molar amount of an acyl chloride and subsequent alkylation. Similarly, compounds **8** were prepared by alkylation of **9**. The position of the acylation of **7** was shown to be on the phenyl ring from the chemical shift of H-3 of the tropone ring, which appeared at δ 6.62 with the vicinal coupling constant 11.0 Hz. The assignment of the protons on the seven-membered ring was supported by the value of the vicinal coupling constant [11]. The phase transition temperatures were determined using differential scanning calorimetry (DSC), and the mesophases were observed using a polarizing microscope equipped with a hot stage.



Scheme 1.

2.2. *Mesomorphic properties*

Compounds **5** showed a smectic A phase, whereas compounds **6** gave smectic A and C phases when the alkyl chains were long. Compounds **5** showed lower isotropic transition temperatures and somewhat higher melting points than the compounds **6**. The mesomorphic properties and the transition temperatures of **5** and **6** arise from the difference in the heteroatom at C-2 of the tropone nucleus. The results are summarized in tables 1 and 2; the transition temperatures of **7** and **8** are summarized in tables 3 and 4. Compounds **5** and **8** were mesomorphic, whereas the compounds **7** were not. The

Table 1. Transition temperatures and enthalpy changes for troponoids **5**. Cr: crystal, SmA: smectic A phase, I: isotropic liquid; data in square brackets refer to monotropic phase transitions.

	R_1	R_2	Transition temp./°C (ΔH/kJ mol^{-1})
5a	C_7H_{15}	C_7H_{15}	Cr 162 (56.8) [SmA 142 (7.3)] I
5b		C_9H_{19}	Cr 155 (46.7) [SmA 146 (7.6)] I
5c		$C_{11}H_{23}$	Cr 156 (48.1) [SmA 151 (7.9)] I
5d		$C_{13}H_{27}$	Cr 157 (49.5) [SmA 154 (7.9)] I
5e		$C_{15}H_{31}$	Cr 153 SmA 157 I
5f		$C_{17}H_{35}$	Cr^1 132 (3.8) Cr^2 145 (39.7) SmA 158 (8.5) I
5g	C_8H_{17}	C_8H_{17}	Cr 161 (49.2) [SmA 145 (8.9)] I
5h	C_9H_{19}	C_9H_{19}	Cr^1 145 (6.9) Cr^2 151 SmA 154 (8.4) I
5i		$C_{15}H_{31}$	Cr 151 (46.0) SmA 156 (8.0) I
5j		$C_{17}H_{35}$	Cr 150 SmA 156 I
5k	$C_{10}H_{21}$	$C_{10}H_{21}$	Cr 145 (35.3) SmA 155 (8.1) I
5l	$C_{11}H_{23}$	$C_{11}H_{23}$	Cr^1 133 (6.4) Cr^2 150 (36.1) SmA 157 (7.3) I
5m		$C_{13}H_{27}$	Cr 153 SmA 157 I
5n		$C_{15}H_{31}$	Cr 147 (47.3) SmA 156 (7.8) I
5o	$C_{12}H_{25}$	$C_{12}H_{25}$	Cr^1 122 (6.0) Cr^2 150 (38.1) SmA 158 (7.7) I
5p	$C_{13}H_{27}$	C_7H_{15}	Cr 143 (32.0) SmA 158 (8.3) I
5q		$C_{13}H_{27}$	Cr 148 (37.2) SmA 155 (6.3) I
5r	$C_{15}H_{31}$	C_7H_{15}	Cr^1 107 (5.1) Cr^2 138 (30.2) SmA 159 (8.6) I
5s		$C_{11}H_{23}$	Cr 143 (45.7) SmA 156 (7.7) I
5t		$C_{15}H_{31}$	Cr^1 130 (1.4) Cr^2 142 (41.5) SmA 154 (7.0) I
5u	$C_{17}H_{35}$	$C_{17}H_{35}$	Cr^1 129 (2.0) Cr^2 142 (51.5) SmA 151 (6.0) I

Table 2. Transition temperatures and enthalpy changes for troponoids **6**.

	R	Transition temp./°C (ΔH/kJ mol^{-1})
6a	C_7H_{15}	Cr 152 (32.6) SmA 183 (11.2) I
6b	$C_{10}H_{21}$	Cr 143 (32.3) SmC 167 SmA 181 (11.2) I
6c	$C_{11}H_{23}$	Cr^1 98 (19.6) Cr^2 148 SmC 159 SmA 178 (8.4) I
6d	$C_{13}H_{27}$	Cr 140 (38.0) SmC 155 (0.3) SmA 169 (10.9) I

Table 3. Transition temperatures for troponoids **7**.

	R_1	R_2	Transition temp./°C
7a	C_9H_{19}	$C_{10}H_{21}$	Cr 130 I
7b		$C_{14}H_{29}$	Cr 130 I
7c		$C_{16}H_{33}$	Cr 130 I
7d	$C_{13}H_{27}$	$C_{10}H_{21}$	Cr 132 I
7e		$C_{16}H_{33}$	Cr 131 I

Table 4. Transition temperatures and enthalpy changes for troponoids **8**.

	R	Transition temp./°C (ΔH/kJ mol^{-1})
8a	C_6H_{13}	Cr 109 I
8b	C_8H_{17}	Cr 119 I
8c	$C_{12}H_{25}$	Cr 104 (58.2) [SmC 72] I
8d	$C_{16}H_{33}$	Cr 104 (69.4) [SmC 80] I

Table 5. Transition temperatures for benzenoids **12** and **13**. N: nematic phase, SmI: smectic I phase, SmC: smectic C phase.

	X	Transition temp./°C
12	$NHCOC_{15}H_{31}$	Cr 242 I
13a	NHC_6H_{13}	Cr_1 65.8 Cr_2 69.2 Cr_3 93.6 N 103.0 I
13b	NHC_8H_{17}	Cr_1 87.3 Cr_2 96.0 Cr_3 99.0 [SmI 98.1] SmC 110.0 N 110.4 I
13c	$NHC_{12}H_{25}$	Cr_1 83.7 Cr_2 96.4 SmI 113.5 SmC 117.8 I
13d	$NHC_{16}H_{33}$	Cr_1 71.0 Cr_2 97.0 Cr_3 103.0 SmI 115.6 I

structural differences among them depend upon whether the amide group is present or not and the number of amide groups they have.

2.3. *X-ray diffraction study of* **5q**

The X-ray diffraction patterns of **5q** were measured to determine the molecular packing model of the smectic A phase. The layer spacing (d) was observed to be 36.2 Å. Since the molecular length (l) of **5q** was calculated to be 43 Å, the d/l ratio is 0.84, which indicates an interdigitated bilayer smectic A phase. The ^{1}H NMR spectrum of **5q** in $CDCl_3$ showed intramolecular hydrogen bonding between the tropone carbonyl and the NH group. From these results, we propose the packing model shown in figure 1, where the molecules form a head-to-tail alignment. The amide NH group at C-2 forms an intramolecular hydrogen bond and the amide carbonyl group at C-2 forms an intermolecular hydrogen bond with the amide NH group of a neighbouring phenyl group. Additionally, the dipole moments of a tropone carbonyl and an amide carbonyl group at C-2 cancel one another.

2.4. *IR spectral measurements*

The variable temperature FTIR spectra of **5q** show two amide absorptions at 1672 and 1695 cm^{-1} in the crystal state. The latter was assigned to the amide group on the tropone ring, since the amide absorption of 2-acetylaminotropone was observed at 1692 cm^{-1}. The former absorption at 1672 cm^{-1} for the amide group on the phenyl ring shifted to higher wavelengths in the liquid crystalline state, coalescing with the absorption at 1695 cm^{-1}, and finally the combined absorption appeared at 1712 cm^{-1} in the isotropic state. The IR spectrum of **7e** showed an amide absorption at 1658 cm^{-1} in the crystal state. The lower amide absorption of **7e** indicates that the amide group of **7e** gives a stronger intermolecular hydrogen bond than in **5q**, and this removes the mesomorphic properties of **7e**. The difference between mesomorphic **5** with a higher melting point and non-mesomorphic **7** is that **5** has two amide groups and **7** has one. In the case of **5**, the amide carbonyl group at C-2 interacts through dipole–dipole interaction with the tropone carbonyl group of neighbouring molecules to align molecules. The dipole–dipole interaction assists in making an intermolecular hydrogen bond possible. The amide absorption in the crystal state of an oxygen

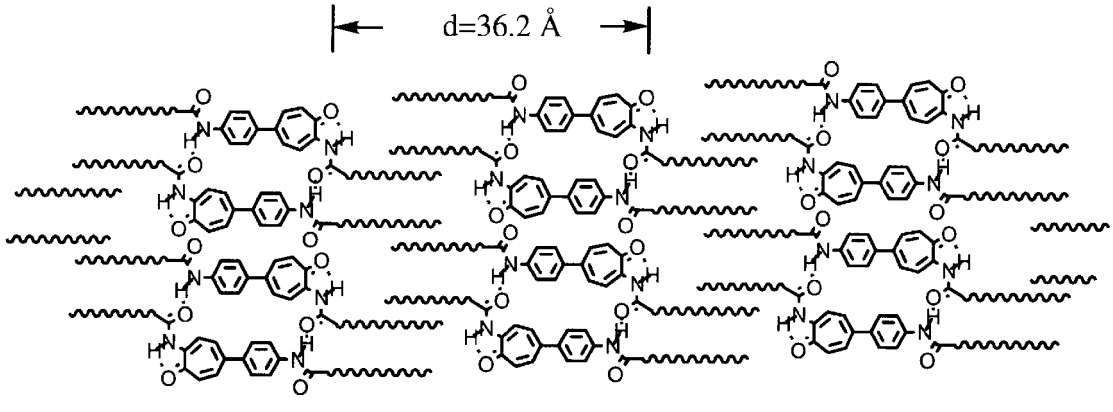


Figure 1. Packing model for the smectic A phase of compound **5q**.

analogue (**6d**) of **5b** was observed in the variable temperature FTIR spectra at a longer wavelength (1710 cm^{-1}) than those of diamide **5q** and monoamide **7e**.

3. Discussion

It is known that an amide group raises the melting point [12] and promotes smectic properties [13] through intermolecular hydrogen bonding. Thus, the compounds **5** with two amide groups have the highest melting points among the series studied. Although compounds with a higher melting point are generally less likely to be liquid crystals [14], in the present series, the compounds **5** with a higher melting point showed an enantiotropic smectic A phase, whereas compounds **7** with a lower melting point were non-mesomorphic.

As observed in the IR spectra, the compounds **6** have an absorption of the amide group at 1710 cm^{-1}, which is a longer wavelength than for the others. Compound **6** could also form a head-to-tail arrangement, where the intermolecular hydrogen bonding between the tropone carbonyl and the amide NH group would be weakened because the tropone carbonyl group of sigmatropic systems acts as an acceptor of the acyl group at C-2. On the other hand, the IR spectra of the compounds **7** indicate that the molecules form tight, intermolecular hydrogen bondings through the amide groups, which raise the melting point. Furthermore, since the conformation of the alkylamino group of **7** is flexible, a head-to-tail alignment would be disturbed, so losing the appearance of mesophases.

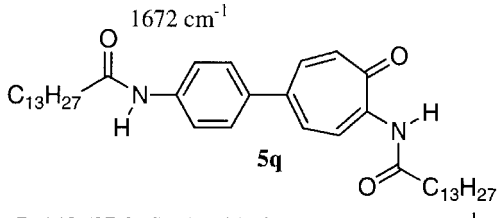
Thus, the amide carbonyl group at C-2 of **5** could assume the role of an interface to prevent the molecules being too close to each other. The tropone carbonyl group acts not only as an acceptor of intramolecular hydrogen bonding in **5**, **7**, and **8**, but also as a dipolar substituent in **5**. This is one of the characteristic features of troponoid liquid crystals [14].

Next, we prepared the ^{N}-methyl derivative (**11**) of **5q** to prove the contribution of intramolecular hydrogen bonding. Compound **11** was not mesomorphic. The benzene carbonyl group of **11** would direct towards the tropone carbonyl group because the tropone ring proton of H-3 at δ 9.10 in **5q** shifted to higher field at 7.13 which indicates that intramolecular hydrogen bonding plays a role in inducing mesomorphic properties.

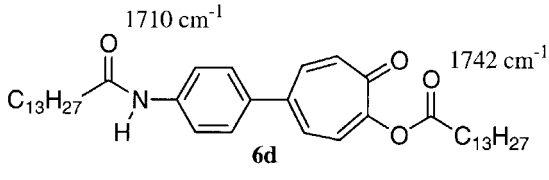
Here, we discuss the role of the tropone carbonyl group on the mesomorphic properties. When compared with the transition temperatures of compound **5t** in table 1 and those of the corresponding benzenoid system **12** [15], the latter had only a melting point at 242°C, which is higher by as much as 100°C than that of **5t**. The intramolecular hydrogen bonding between the amide NH and the tropone carbonyl group prohibits formation of an intermolecular hydrogen bonding, which would raise the melting point. Thus, the tropone carbonyl group enhances the appearance of mesomorphic properties. On the other hand, when compared with the compounds **8**, where the tropone carbonyl group acts as a lateral substituent group, and the corresponding benzenoids **13** [16], the latter had the higher clearing points and the lower melting points. The presence of the tropone carbonyl group would be disadvantageous in this case because of its increasing molecular width.

4. Conclusion

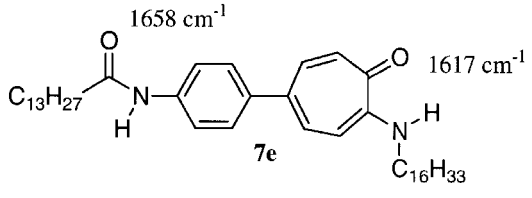
We have prepared liquid crystal materials with a 5-phenyltropone core with amide, ester, and alkylamino



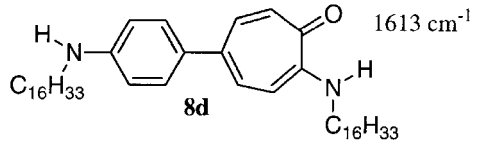
Cr 148 (37.2) SmA 155 (6.3) Iso



Cr 140 (38.0) SmC 155 (0.3) SmA 169 (10.9) Iso



Cr 131 Iso



Cr 104 (69.4) [SmC 80] Iso

Scheme 2.

groups to evaluate their mesomorphic properties. Among the troponoids, ester **6** had the highest clearing point. This is because ester **6** is a [1, 9] sigmatropic system [6], which enhances the occurrence of mesophases. When compared with compounds **5** and **7**, the second amide group of **5** increases the melting point as well as the mesomorphic properties, which also supports the presence of dipole–dipole interactions between the tropone carbonyl group and the amide carbonyl group on the phenyl ring of neighbouring molecules. Furthermore, the amide group of **7** increases the melting points to obscure mesophases, because the bis(alkylamino) derivatives **8** with longer chains are mesomorphic.

5. Experimental

The elemental analyses were made at the elemental analysis laboratory of Kyushu University. The NMR spectra were measured on a GSX 270H Model spectrometer using $CDCl_3$ as solvent; the chemical shifts are expressed in δ units. The mass spectra were measured on a JEOL 01SG-2 spectrometer. The 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 phases were observed using a polarizing microscope (Olympus BHSP BH-2) equipped with a hot stage (Linkam TH-600RMS). The X-ray 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.

5.1. *2-Alkanoylamino-5-(4-alkanoylaminophenyl)tropones (5)*

Octanoyl chloride (54 mg, 0.33 mmol) and a catalytic amount of 4-dimethylaminopyridine (DMAP) were added to a pyridine solution (3 cm^3) of 2-amino-5-(4-aminophenyl)tropone [10] (30 mg, 0.14 mmol) and the mixture was stirred at room temperature for 12 h. Saturated aqueous $KHSO_4$ was added to the reaction mixture which was shaken with $CHCl_3$. The organic layer was dried over $MgSO_4$ and the solvent evaporated. The residue was chromatographed on a silica gel column (hexane : AcOEt = 3 : 1) to give **5a**, m.p. 162°C, yellow crystals, 42 mg, 65%. ^{1}H NMR ($CDCl_3$) δ: 0.89 (6H, t, J = 6.8 Hz), 1.2–1.4 (16H, m), 1.7–1.8 (4H, m), 2.39 (2H, t, J = 7.5 Hz), 2.50 (2H, t, J = 7.5 Hz), 7.28 (1H, br s), 7.41 (1H, d, J = 12.5 Hz), 7.41 (1H, dd, J = 10.6, 2.2 Hz), 7.47 (2H, d, J = 8.8 Hz), 7.63 (2H, d, J = 8.8 Hz), 7.64 (1H, dd, J = 12.5, 2.2 Hz), 9.10 (1H, d, J = 10.6 Hz), 9.37 (1H, s). Mass (m/z): 465 ($M^+ + 1$), 464 (M^+), 338 (base). $C_{29}H_{40}N_2O_3$: C, 74.97 (75.13); H, 8.68 (8.71); N, 6.03 (6.24)%†. **5b**: m.p. 155°C, 56%, $C_{31}H_{44}N_2O_3$: C, 75.57 (75.49); H, 9.00 (9.06); N, 5.69 (5.43)%. **5c**: m.p. 156°C, 60%, $C_{33}H_{48}N_2O_3$: C, 76.11 (76.06); H, 9.29 (9.15); N, 5.38 (5.15)%. **5d**: m.p. 157°C, 74%, $C_{35}H_{52}N_2O_3$: C, 76.60 (76.97); H, 9.55 (9.61); N, 5.10 (4.93)%. **5e**: m.p. 153°C, 71%, $C_{37}H_{56}N_2O_3$: C, 77.04 (77.37); H, 9.78 (9.83); N, 4.86 (5.02)%. **5f**: m.p. 132°C, 69%, $C_{39}H_{60}N_2O_3$: C, 77.44 (77.77); H, 9.99 (10.00); N, 4.63 (4.57)%. **5g**: m.p. 161°C, 56%, $C_{31}H_{44}N_2O_3$: C, 75.57 (75.56); H, 9.00 (8.86); N, 5.69 (5.59)%. **5h**: m.p. 145°C, 72%, $C_{33}H_{48}N_2O_3$: C, 76.11 (76.11); H, 9.29 (9.22); N, 5.38 (5.47)%. **5i**: m.p. 151°C, 81%, $C_{39}H_{60}N_2O_3$: C, 77.44 (77.60); H, 9.99 (9.87); N, 4.63 (4.91)%. **5j**: m.p. 150°C, 65%, $C_{41}H_{64}N_2O_3$: C, 77.80 (77.90); H, 10.19 (10.20); N, 4.43 (4.43)%. **5k**: m.p. 145°C, 74%, $C_{35}H_{52}N_2O_3$: C, 76.60 (76.97); H, 9.55 (9.61); N, 5.10 (4.93)%. **5l**: m.p. 133°C, 61%, $C_{37}H_{56}N_2O_3$: C, 77.04 (76.82); H, 9.78 (9.80); N, 4.86 (4.91)%. **5m**: m.p. 153°C, 76%, $C_{39}H_{60}N_2O_3$: C, 77.44 (77.29); H, 10.00 (9.96); N, 4.63 (4.70)%. **5n**: m.p. 147°C, 84%, $C_{41}H_{64}N_2O_3$: C, 77.80 (78.10); H, 10.19 (10.07); N, 4.43 (4.39)%. **5o**: m.p. 122°C, 57%, $C_{39}H_{60}N_2O_3$: C, 77.44 (77.39); H, 10.00 (9.98); N, 4.63 (4.45)%. **5p**: m.p. 143°C, 39%, $C_{35}H_{52}N_2O_3$: C, 76.60 (76.48); H, 9.55 (9.48); N, 5.10 (5.32)%. **5q**: m.p. 148°C, 42%, $C_{41}H_{64}N_2O_3$: C, 77.80 (77.68); H, 10.19 (10.05); N, 4.43 (4.54)%. **5r**: m.p. 107°C, 71%, $C_{37}H_{56}N_2O_3$: C, 77.04 (77.11); H, 9.78 (9.74); N, 4.86 (4.97)%. **5s**: m.p. 143°C, 54%, $C_{41}H_{64}N_2O_3$: C, 77.80 (77.59); H, 10.19 (10.01), N, 4.43 (4.29)%. **5t**: m.p. 130°C, 22%, $C_{45}H_{72}N_2O_3$: C, 78.44 (78.26); H, 10.53 (10.50); N, 4.07 (3.84)%. **5u**: m.p. 129°C, 12%, $C_{49}H_{80}N_2O_3$: C, 78.98 (78.82); H, 10.82 (10.72); N, 3.76 (3.71)%.

5.2. *2-Alkanoyloxy-5-(4-alkanoylaminophenyl)-tropones (6)*

Octanoyl chloride (54 mg, 0.33 mmol) and a catalytic amount of DMAP were added to a pyridine solution (3 cm^3) of 5-(4-aminophenyl)tropolone [9] (30 mg, 0.14 mmol) and the mixture was stirred at room temperature for 12 h. Saturated aqueous $KHSO_4$ was added to the reaction mixture which was shaken with $CHCl_3$. The organic layer was dried over $MgSO_4$ and the solvent evaporated. The residue was chromatographed on a silica gel column (hexane : AcOEt = 9 : 1) to give **6a**, m.p. 152°C, yellow crystals, 43 mg, 65%. ^{1}H NMR ($CDCl_3$) δ: 0.88 (6H, m), 1.2–1.4 (16H, m), 1.7–1.8 (4H, m), 2.34 (2H, t, J = 7.5 Hz), 2.64 (2H, t, J = 7.5 Hz), 7.27 (2H, d, J = 11.4 Hz), 7.32 (2H, d, J = 11.4 Hz), 7.44 (2H, d, J = 8.8 Hz), 7.62 (2H, d, J = 8.8 Hz). Mass (m/z):

† In all cases, the experimental data for elemental analyses are shown in parenthesis.

465 (M^+), 339 (base), 213 (20). $C_{29}H_{39}NO_4$: C, 74.81 (74.72); H, 8.44 (8.28); N, 301 (2.93)%. **6b**: m.p. 143°C, 45%, $C_{35}H_{51}NO_4$: C, 76.46 (76.59); H, 9.35 (9.21); N, 2.55 (2.61)%. **6c**: m.p. 148°C, 57%, $C_{37}H_{55}NO_4$: C, 76.91 (76.86); H, 9.59 (9.30); N, 2.42 (2.34)%. **6d**: m.p. 140°C, 57%, $C_{41}H_{63}NO_4$: C, 77.68 (77.57); H, 10.02 (10.00); N, 2.21 (2.26%).

5.3. *2-Alkylamino-5-(4-alkanoylaminophenyl)-tropones (7)*

Decanoyl chloride (21 mg, 0.12 mmol) and a catalytic amount of DMAP were added to a pyridine solution (3 cm^3) of 2-amino-5-(4-aminophenyl)tropone (25 mg, 0.12 mmol) and the mixture was stirred at room temperature for 12 h. After evaporating the solvent, a solution of hexamethylphosphoric triamide (HMPA) (3 cm^3) and NaH (5 mg, 0.12 mmol) were added and the mixture was stirred at 0°C for 1 h. 1-Bromodecane (22 mg, 0.098 mmol) was added and the reaction mixture was stirred at 60°C for 12 h. The mixture was poured into 2M HCl and shaken with AcOEt. The organic layer was washed with saturated NaCl solution and dried over $MgSO_4$. The solvent was evaporated and the residue was chromatographed on a silica gel column to give **7a**. m.p. 130°C, 24 mg, 41%, yellow crystals. ^{1}H NMR ($CDCl_3$) δ: 0.88 (6H, m), 1.2–1.4 (26H, m), 1.7–1.8 (4H, m), 2.38 (2H, t, J = 7.5 Hz), 3.34 (2H, dt, J = 7.0, 5.8 Hz), 6.62 (1H, d, J = 11.0 Hz), 7.21 (1H, d, J = 12.1 Hz), 7.41 (2H, d, J = 8.8 Hz), 7.44 (1H, dd, J = 11.0, 2.2 Hz), 7.52 (1H, dd, J = 12.1, 2.2 Hz), 7.59 (2H, d, J = 8.8 Hz). IR (KBr, disc) ν: 3288, 2954, 2918, 2848, 1659, 1618, 1561, 1525, 1470, 1445, 1404, 1348, 1265, 1187, 1138, 1030, 966, 854, 818, 722, 626, 530 cm^{-1}. $C_{33}H_{50}N_2O_2$: C, 78.21 (78.44); H, 9.94 (10.04); N, 5.52 (5.60)%. **7b**: m.p. 130°C, 66%, $C_{37}H_{58}N_2O_2$: C, 78.95 (79.01); H, 10.39 (10.43); N, 4.98 (5.16)%. **7c**: m.p. 130°C, 50%, $C_{39}H_{62}N_2O_2$: C, 79.27 (79.04); H, 10.57 (10.65); N, 4.74 (4.88)%. **7d**: m.p. 132°C, 41%, $C_{37}H_{58}N_2O_2$: C, 78.95 (78.86); H, 10.39 (10.45); N, 4.98 (5.17)%. **7e**: m.p. 131°C, 64%, $C_{43}H_{70}N_2O_2$: C, 79.82 (79.68); H, 10.90 (10.91); N, 4.33 (4.22)%.

5.4. *2-Alkylamino-5-(4-alkanoylaminophenyl)-tropones (8)*

An HMPA solution (3 cm^3) of 2-amino-5-(4-aminophenyl)tropone (40 mg, 0.19 mmol) and NaH (14 mg, 0.57 mmol) was stirred at 0°C for 1 h. 1-Bromodecane (75 mg, 0.57 mmol) was added and the reaction mixture was stirred at 60°C for 12 h. The mixture was poured into 2M HCl and shaken with AcOEt. The organic layer was washed with saturated NaCl solution and dried over $MgSO_4$. The solvent was evaporated and the residue chromatographed on a silica gel column (hexane : AcOEt = 5 : 1) to give **8a**, m.p. 109°C, 20 mg, 27%, yellow crystals. ^{1}H NMR ($CDCl_3$) δ: 0.91 (6H, t, J = 7.0 Hz), 1.2–1.4 (12H, m), 1.6–1.7 (2H, m), 1.7–1.8 (2H, m), 3.15 (2H, t, J = 7.1 Hz), 3.33 (2H, dt, J = 6.9, 6.2 Hz), 6.62 (1H, d, J = 11.0 Hz), 6.65 (2H, d, J = 8.8 Hz), 7.10 (1H, br s), 7.22 (1H, d, J = 12.1 Hz), 7.31 (2H, d, J = 8.8 Hz), 7.43 (1H, dd, J = 11.0, 2.2 Hz), 7.55 (1H, dd, J = 12.1, 2.2 Hz). Mass (m/z): 380 (M, base), 381 ($M^+ + 1$), 309 (31). $C_{25}H_{36}N_2O$: C, 78.90 (78.91); H, 9.53 (9.39); N, 7.36 (7.14)%. **8b**: m.p. 119°C, 29%, $C_{29}H_{44}N_2O$: C, 79.77 (79.86); H, 10.16 (10.24); N, 6.42 (6.34)%. **8c**: m.p. 104°C, 36%, $C_{37}H_{60}N_2O$: C, 80.96 (80.81); H, 11.02 (10.81); N, 5.10 (4.81)%. **8d**: m.p. 104°C, 18%, $C_{45}H_{76}N_2O$: C, 81.76 (82.11); H, 11.59 (11.62); N, 4.24 (4.17)%.

5.5. *2-N-Methyl-N-tetradecanoylamino-5-(4-tetradecanoylaminophenyl)tropone (11)*

A THF solution (10 cm^3) of 2-amino-5-(4-aminophenyl)tropone (100 mg, 0.47 mmol) and NaH (150 mg, 1.03 mmol) was stirred at 0°C for 1 h. Methyl iodide (27 mg, 1.13 mmol) was added to the mixture. After the mixture had been heated at 40°C for 12 h, pyridine (3 cm^3), tetradecanoyl chloride (220 mg, 0.89 mmol), and a catalytic amount of DMAP were added and the whole stirred at room temperature for 12 h. The mixture was poured into 2M HCl and then shaken with AcOEt. The solvent layer was dried over $MgSO_4$ and evaporated. The residue was chromatographed on a silica gel column (hexane : AcOEt = 1 : 1) to give **11**, m.p. 133°C, 29 mg, 10%, yellow crystals. ^{1}H NMR ($CDCl_3$) δ: 0.88 (6H, m), 1.2–1.4 (40H, m), 1.6–1.7 (2H, m), 1.7–1.8 (2H, m), 2.18 (2H, t, J = 7.5 Hz), 2.40 (2H, t, J = 7.3 Hz), 3.18 (3H, s), 7.13 (1H, dd, J = 9.9, 1.8 Hz), 7.30 (1H, d, J = 12.8 Hz), 7.41 (1H, d, J = 9.9 Hz), 7.48 (2H, d, J = 8.8 Hz), 7.51 (1H, dd, J = 12.8, 1.8 Hz), 7.66 (2H, d, J = 8.8 Hz). Mass (m/z): 647 ($M^+ + 1$), 646 (M^+), 436 (base). High mass: observed 647.5149; calc for $C_{42}H_{66}N_2O_3$, 647.5152.

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