

Synthesis and Structural Analysis of Triphenylmethane-Based Alkanecarboxamides and Their Assembly into Nanometer-Size Fibrous Objects

Hirohiko Houjou,* Tatsuya Koga, Midori Akiizumi, Isao Yoshikawa, and Koji Araki

Institute of Industrial Science, The University of Tokyo, 4-6-1 Komaba, Meguro-ku, Tokyo 153-8505

Received January 7, 2009; E-mail: houjou@iis.u-tokyo.ac.jp

A series of C_3 -symmetric trialkanecarboxamido derivatives was synthesized via a triphenylmethane derivative. The triamides with short alkyl chains (1–6 carbons) crystallized as either prisms or plates, whereas those with long alkyl chains (7–11 carbons) formed gel-like objects composed of fibrous crystals with 100-nm diameters. A discontinuity as a function of alkyl chain length was also observed for the melting points, the vibrational frequencies of the amide groups, and the powder X-ray diffraction patterns of the triamides. On the basis of analysis of the crystal structures of two of the compounds, we make some proposals about the molecular packing and the local structure of the molecular assembly. Our results suggest that there were critical differences in inter-core interactions and in the hydrogen-bonding network, depending on the length of the alkyl chains. We interpret the drastic change in morphology brought about by the tuning of the chain length as a consequence of a change in the mode of molecular assembly.

Systems of multiple hydrogen bonds serve as reversible and flexible cross links in supramolecular polymers and supramolecular elastomers as well as in highly organized biomolecular structures such as proteins and nucleic acids.^{1,2} The reversibility and moderate strength of hydrogen-bonded cross links in these structures are responsible for such characteristic properties as thermal plasticity, viscoelasticity, and the dielectric property.³ Introduction of a network of hydrogen bonds provides supramolecular polymers with practical properties, such as mechanical strength, thermal durability, and non-Newtonian fluidity.^{4–7}

Molecular building blocks that have the potential to form multiple hydrogen bonds are known as supramolecular synthons.⁸ The greater the number of hydrogen bonds a synthon can form, the firmer the resulting supramolecular architecture will be, as a result of the formation of multiple cross links. Many of the supramolecular synthons successfully used to date in, for example, columnar liquid crystals, organogels, fibers, and films,^{9–12} have a common feature: they are C_n -symmetric molecules composed of a rigid core with self-complementary hydrogen-bonding sites and flexible side chains. Because of its energetic stability, hydrogen bonding plays a predominant role in the mode of molecular assembly, and inter-core and inter-chain interactions assist in arranging the architecture.

Systems with aromatic cores prefer an inter-core distance of 3.3–3.5 Å owing to π – π stacking interactions, such as those typically found in graphite. However, a mismatch in distance of stacking cores sometimes arises, because the π – π stacking distance does not always permit the hydrogen-bonding sites to connect to one another. Takasawa et al. utilized a non-aromatic cyclohexane moiety as a core to fabricate supramolecular yarns in which the inter-core and hydrogen-bonding distances were optimized simultaneously.¹³ With an aromatic core, pyrene, the same research group obtained a bistable system, in which they

could control inter-conversion between the core–core interaction mode and the hydrogen-bonded mode.¹⁴

The exploration of new molecules with various aromatic and non-aromatic cores bearing multiple hydrogen-bonding sites is a fascinating area of research. In this study, we designed and synthesized C_3 -symmetric molecules composed of a triphenylmethane core, three amide groups, and alkyl chains with 1 to 11 carbon atoms. The unsubstituted triphenylmethane framework is not planar but parasol shaped, owing to the central sp^3 carbon atom. However, a triphenylmethane with electron-donating groups easily loses its methyne hydrogen by oxidation, and this oxidation results in a virtually planar methylium π -system, which is responsible for the vivid colors of synthetic dyes such as crystal violet and malachite green.¹⁵ The use of a redox-active moiety in a supramolecular system has been shown to lead to such interesting functions as sol–gel conversion that is controlled by oxidation state.¹⁶

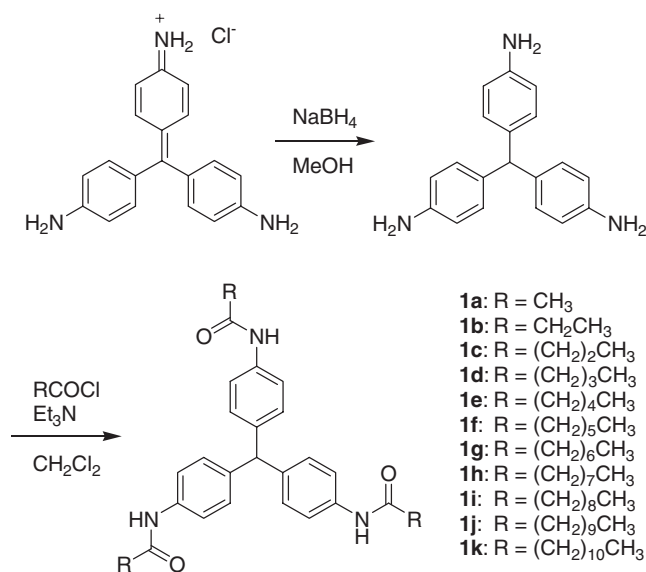
Although triphenylmethane and its related methylium framework can be obtained easily from the above-mentioned artificial dyes, the use of triphenylmethanes in supramolecular chemistry has been rather limited,^{17–23} and little is known about their molecular assembly. Recently, we found that triphenylmethane triamides with long alkyl chains can form a gel-like precipitate in certain solvent systems and that the precipitate is actually a collection of micrometer-thick fibrous objects. In this paper, we describe the synthesis and structural analyses of a series of triphenylmethane trialkanecarboxamides, focusing on the how the structures of their molecular assemblies depended on the length of the alkyl chains.

Results and Discussion

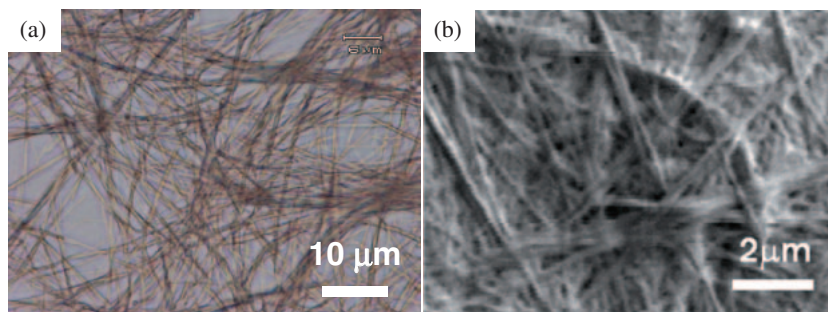
Triphenylmethane-based trialkanecarboxamides **1a–1k** were prepared in moderate yield and then characterized (Scheme 1). The products were roughly categorized into groups by

morphology: **1a–1f** (1–6 carbons per chain) were obtained as either prismatic or platelet microcrystals, whereas **1g–1k** (7–11 carbons per chain) were obtained as thin needles. By examining several recrystallization conditions for these compounds, we found that **1g–1k**, the group with the longer alkyl chains, formed gel-like objects when recrystallized from mixtures of moderately polar (e.g., THF and ethyl acetate) and protic (e.g., methanol and ethanol) solvents. Similar objects also formed when solutions of **1g–1k** in certain hydrophobic solvents (e.g., chloroform and dichloromethane) were emulsified by vigorous shaking with a water phase. Figures 1a and 1b show typical optical and scanning electron microscope images, respectively, of these objects. The images indicate that the gel-like objects were actually micrometer-thick collections of tangled fibers, with each fiber consisting of a bunch of thinner fibers with thicknesses of 100–200 nm.

The drastic change in morphology observed as a result of the transition from a short side chain to a long side chain suggests differences in the structures of the molecular assemblies originating in hydrogen bonding among the amide moieties and in inter-core interactions between the triphenylmethane moieties. To obtain insight into the structure of the molecular assemblies, we measured melting points, infrared spectra, and powder X-ray diffraction patterns of **1a–1k**. In the preparation of the samples for these measurements, we standardized the



Scheme 1.

Figure 1. (a) Optical micrograph and (b) scanning electron micrograph of **1i** obtained from a dichloromethane–water emulsion.

recrystallization system (DMF–ethanol–water) to minimize the effects of environmental differences during crystal growth. Using this procedure, we obtained samples of **1a–1g** as crystals with micro- to millimeter dimensions, and we obtained **1h–1k** as gel-like objects.

Differential scanning calorimetry (DSC) was employed to determine melting points. We identified each endothermic peak as either a melting point or a solid-to-solid phase-transition temperature by referring to the optical microscopy images. For **1e**, DSC showed two endothermic peaks (at 151 and 194 °C) that corresponded to the melting points of two different polymorphs (platelets and prisms, respectively). Triamide **1f** also showed two endothermic peaks (at 186 and 206 °C); the former was a solid–solid transition (prisms to platelets) point, and the latter was the melting point of the platelets. For **1g–1i**, a small endothermic peak ($\Delta H = 2.3$ – 4.1 J g^{-1}) was recorded at about 20 °C lower than the melting points of the triamides, but no morphological change was observed. In view of the relatively small enthalpy changes, we attributed these small peaks to the partial melting of the alkyl chains. The phase-transition temperatures are summarized in Figure 2.

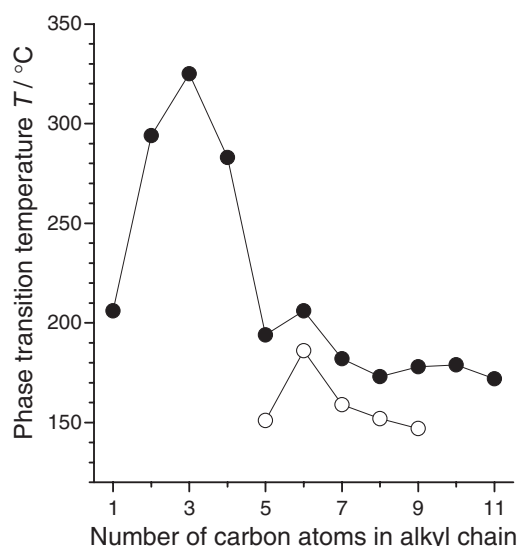


Figure 2. Plot of phase-transition temperatures of **1a–1k** as a function of the number of carbon atoms in the alkyl chains. Solid circles denote melting points, and open circles denote solid–solid transitions (for **1e** and **1f**) and undetermined transitions (for others).

For **1a–1f**, the melting point varied from 190 to 350 °C depending on the length of the alkyl chains, whereas for **1g–1k** the melting point was almost constant at around 160 °C ($\Delta_m H = 76\text{--}85\text{ J g}^{-1}$). This uniformity implies that the predominant contributions to the intermolecular forces were similar for **1g–1k** and were independent of the chain length. We can assume that the melting enthalpies of **1g–1k** were determined mostly by the dissociation of intermolecular hydrogen bonds, whereas those of **1a–1f** involved some other intermolecular forces such as inter-core CH/ π interactions.

The profiles of the IR spectra of **1a–1k** were quite similar to one another, with slight differences in the wavenumbers of the characteristic peaks. In Figure 3, the wavenumbers of the amide I (C=O stretch) and amide II (N–H bend) bands are plotted as a function of the length of the alkyl chains. The wavenumbers of the amide II bands differed clearly between groups **1a–1f** ($1537\text{--}1541\text{ cm}^{-1}$) and **1g–1k** ($1526\text{--}1531\text{ cm}^{-1}$). The trend for the amide I bands was basically the same as

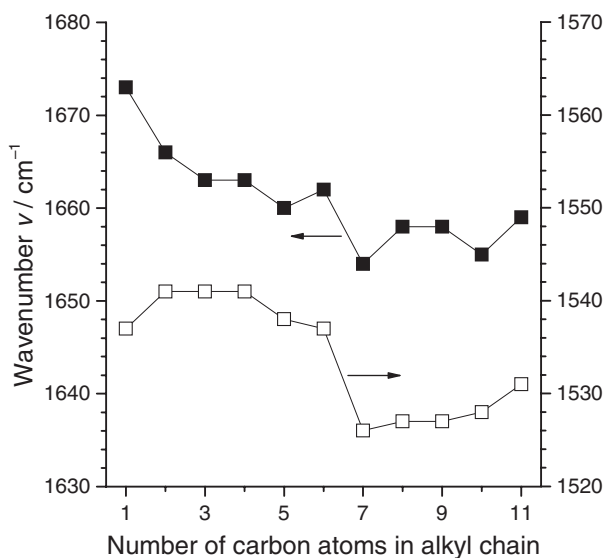


Figure 3. Plot of the wavenumber of the amide I (■, left axis) and II (□, right axis) vibrational bands as a function of the number of carbon atoms in the alkyl chains.

that for the amide II bands, deviating only for a few of the compounds. Similarly, the trend for the N–H stretch vibration bands ($\approx 3290\text{ cm}^{-1}$, not shown) showed a discontinuity (slightly high wavenumber shift) at around **1e** and **1f**. The clear difference in the resonances of the two amide bands indicates that the modes of intermolecular hydrogen bonding were different for **1a–1f** and **1g–1k**. On the basis of the simple relationship between the resonance of the C=O stretch oscillation and the strength of hydrogen bonding, we can assume that the molecular arrangement in **1g–1k** was such that the amide groups formed stronger hydrogen bonds than those in **1a–1f**. On the other hand, the N–H bond oscillation shows quite an opposite trend. Thus, we should confine the interpretation to a qualitative change in hydrogen-bonding mode.

The X-ray diffraction patterns of **1b–1d** were quite similar to one another (Figure 4), which suggests that they had the same crystal system and similar packing. The peak at around 8° of 2θ was characteristic of this group. The patterns for **1h–1k** were also similar to one another, but their crystal system was apparently different from that of **1b–1d**. The patterns for **1h–1k** under the same measurement conditions showed low S/N ratios, which suggests low crystallinity, although there were characteristic peaks in the region of $7^\circ > 2\theta$. The pattern of **1e**, which was not similar to the patterns of any of the other triamides, seemed to be a mixture of the patterns of **1d** and **1f**.

We succeeded in obtaining single-crystal X-ray structures of **1c** and **1d**, which had essentially the same packing structure, although their lattice constants ($a = 18.85\text{ \AA}$ and $c = 13.93\text{ \AA}$ for **1c**; $a = 19.99\text{ \AA}$ and $c = 13.50\text{ \AA}$ for **1d**) differed slightly. Powder patterns simulated from the crystallographic data of **1c** and **1d** agreed sufficiently well with the patterns shown in Figure 4.²⁴ In addition, from the observed powder pattern of **1b**, we estimated that it had a rhombohedral crystal system with lattice constants of $a = 17.7\text{ \AA}$ and $c = 14.0\text{ \AA}$. The ORTEP drawings of **1c** are shown in Figure 5. Additionally, a schematic view of the molecular packing is shown in Figure 6a. The molecule was shaped like a wide-open parasol centered around the central sp^3 carbon atom (the H–C–C(ipso) and C(ipso)–C(H)–C(ipso) angles were 107.2 and 111.7° , respectively). The depth of the molecular parasol was roughly

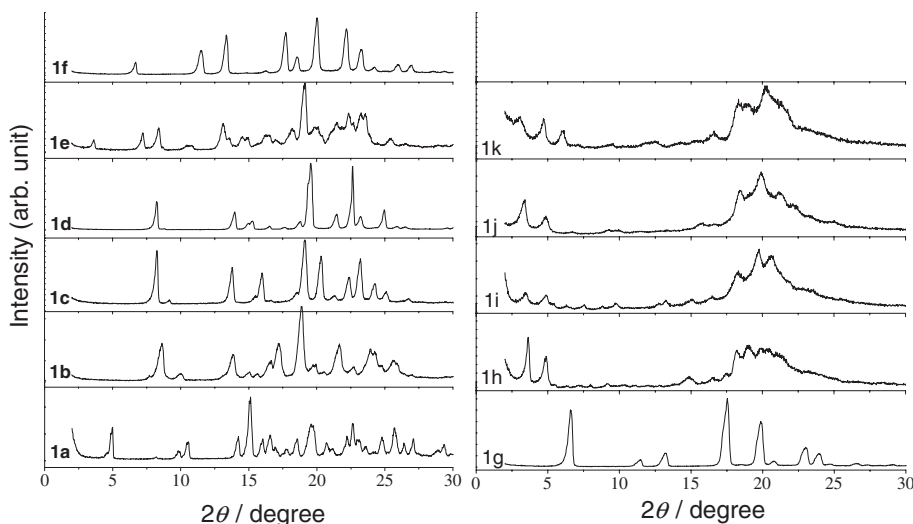


Figure 4. X-ray diffraction patterns for the powder samples of **1a–1k**.

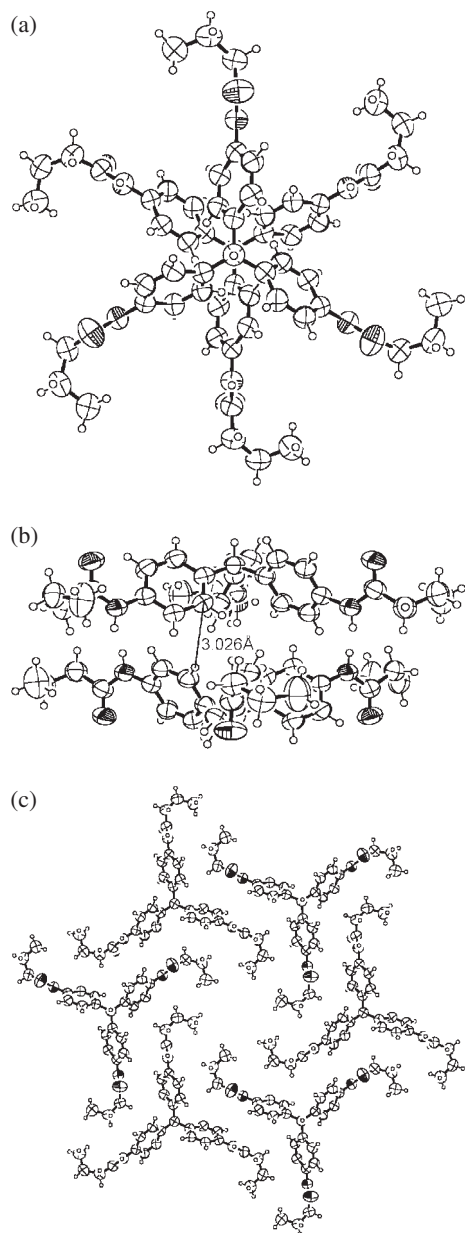


Figure 5. ORTEP drawings of the crystal structure of **1c**: (a) parallel to the *c* axis, (b) parallel to the *a* axis of two proximal molecules, and (c) molecular packing in the *C*-plane. One-third of the molecule is crystallographically independent.

3 Å, and the C=O and N–H groups were nearly parallel to the *c* axis (Figure 5b).

Two proximal parasols of **1c** formed a dimer with alternating ribs; in the dimer, there were some close contacts between the phenyl rings. The shortest distance between H and C atoms was 3.026 Å (denoted by a line in Figure 5b), which suggests a CH/π interaction.²⁵ A sextuple CH/π interaction between two molecules may have contributed to the relatively high melting points of **1b–1d**. The dimer was hexagonally packed with its parasol's "ferrule" coincident with the *c* axis, and consequently the amide groups were arranged in a hydrogen-bonded 3₁-helix parallel to the *c* axis (Figures 6b and 6c). The N...O distance in

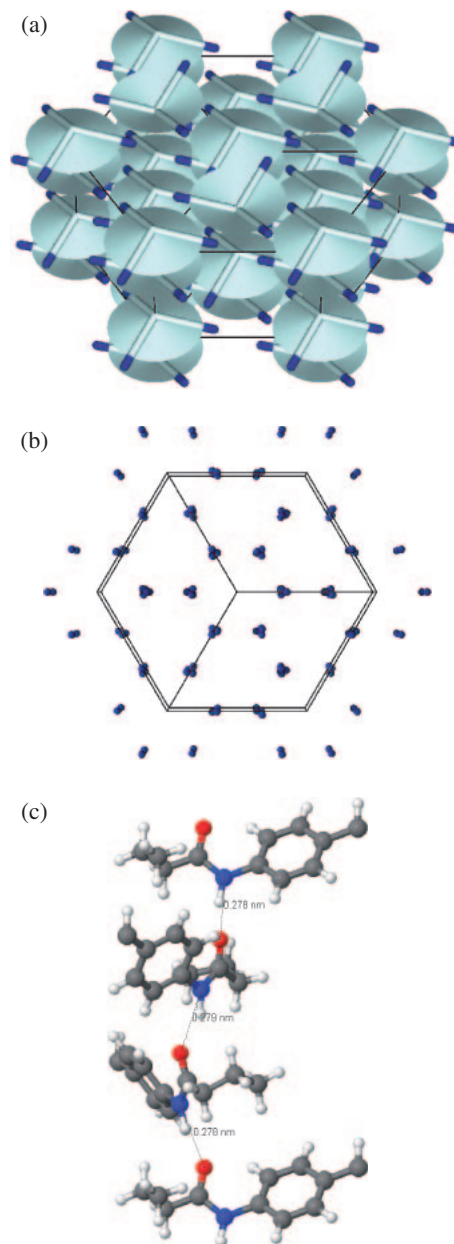


Figure 6. The packing structures of **1b–1d**, where each triple-ribbed parasol represents the unit molecule, and each edge (deep blue) of the rib is a hydrogen-bonding site: (a) bird's-eye view, (b) top view of the hydrogen-bonding sites, and (c) side view of the 3₁-helical hydrogen-bonded chain of **1c**. For clarity, only one-third of the molecule is shown.

each proximal pair was 2.78 Å, which is in the normal range for an amide–amide hydrogen bond.

The alkyl chains formed a vortex in a space surrounded by six molecules of **1c** (Figure 5c). Because of restriction by the hydrogen bonds, the volume of the space that accommodated the alkyl chains could not freely expand. Thus, this type of crystal packing can be expected to become unstable when the number of carbon atoms of the chains is increased to 5 or 6. The polymorphism observed for **1e** and **1f** implies that these compounds were situated at a critical point between the

packing structure of **1b–1d** and another structure suitable for **1g–1k**.

Although relating crystal structure to macroscopic crystal habit is difficult, we can at least assume that the prismatic or platelet habit observed for **1a–1f** was a consequence of the rates of crystal growth that were well-balanced between the *c* axis direction (hydrogen bonding and CH/ π interaction) and the *C*-plane direction (hydrogen bonding).

Compound **1g** was obtained as needles under the given conditions. In contrast, recrystallization of compounds **1h–1k** from all the solvent systems we examined afforded very thin, fibrous objects. This result suggests that for these compounds the rates of crystal growth in the axial direction and the radial direction were markedly unbalanced. Because we did not obtain single-crystal X-ray structures of all the compounds, we attempted to estimate the structure of the molecular assemblies of **1g–1k** based on the analytical results described above. First, the trend in the melting points of **1g–1k** indicate the compounds had a molecular packing in which a certain intermolecular force was the predominant contributor to melting enthalpy. Second, the trend of the IR spectra suggests that **1g–1k** formed stronger (stiffer) hydrogen bonds than did the other triamides. Third, the X-ray powder patterns suggest that the molecular packing of **1g–1k** was definitely different from that of **1b–1d**.

These findings suggest that the local structure of the molecular assembly in **1g** is a key to the estimation of the structure of **1h–1k**. By analyzing the powder pattern of **1g** under various boundary conditions, we provisionally determined its crystal system as trigonal ($P\bar{3}$), with lattice constants of $a = 15.4$ and $c = 7.8$ Å, which best reproduces the observed pattern.²⁵ Although a Rietveld analysis of **1g** has not been completed to give the convergence of a structure, we attempted to fit the molecule into this lattice. A triangle with a base of 15.4 Å could just accommodate a triphenylmethane triamide core, although the height of 7.8 Å was not in agreement with the alternating assembly of the dimer (≈ 13.5 Å) observed for **1b–1d**. Therefore, we suggest that the parasol of triphenylmethane stacked in columnar form and that the neighboring pairs of columns ran anti-parallel to each other (Figure 7a). Inside the column, there was sufficient volume for the alkyl chains to fold between the stacked parasols. Packing two molecular units in this cell resulted in a calculated density of 1.39 g cm⁻³, which was in good agreement with the density of common organic compounds, albeit slightly larger than the values for **1c** (1.162 g cm⁻³) and **1d** (1.155 g cm⁻³).

In this model, each lattice point assembled six ribs in S_6 symmetry, by virtue of which the amide groups formed a cyclic hydrogen-bonding network, although we did not determine the detailed structure (Figure 7b). A possible model for such a cyclic hexamer has been reported for the crystal structure of a cyclohexane-1,3,5-tricarboxamide.²⁶ Notably, the hydrogen-bonding interactions in the above model contributed to crystal growth in the lateral (i.e., perpendicular to the *c* axis) direction, whereas for **1b–1d**, the hydrogen bond served as a linker in both axial (i.e., parallel to the *c* axis) and lateral directions. Consequently, we suggest that **1g**, growth in the axial direction was dominated by interactions among alkyl chains and that the obvious difference in crystal habit between **1b–1d** and **1g** is

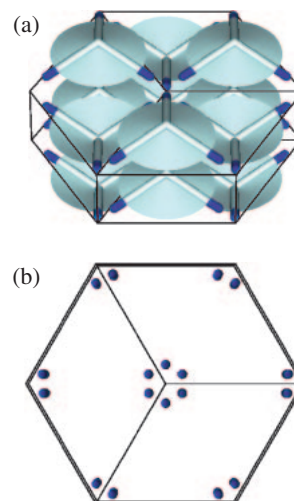


Figure 7. A plausible packing structure of **1g**, where each triple-ribbed parasol represents the unit molecule and the ends of the ribs (dark blue) are hydrogen-bonding sites: (a) bird's-eye view and (b) top view of the hydrogen-bonding sites.

attributable to a difference in the mode of molecular assembly. Taking account of the precipitation conditions adopted, we assumed the following mechanism for the formation of the needles. In a moderately polar medium, the hydrogen-bonded and non-hydrogen-bonded triphenylmethane molecules were in equilibrium with each other. Upon addition of a protic solvent or water, hydrophobic interactions between the alkyl chains promoted crystal growth along the *c* axis, and growth in the direction perpendicular to the *c* axis was suppressed owing to accelerated dissociation of hydrogen bonding. As a result of the difference in growth rate, **1g** formed an assembly with a high axis-to-radius ratio and eventually separated out of solution as needles. This assumption on the growth mechanism is also in agreement of the cylindrical symmetry of the presumed molecular packing.

The X-ray diffraction patterns (Figure 4) of the powder samples of **1h–1k** were similar to one another, which suggests that their packing structures were similar. However, the diffraction patterns showed a low S/N ratio, which indicates that the order of the molecular arrangement was considerably disturbed. For these compounds, as well as for **1g**, the formation of a 3₁-helical hydrogen-bonded chain was impossible, owing to their long alkyl chains. Thus, we can suggest that the predominant force for assembly of the molecules themselves was hydrophobic interactions. It is probable that an extreme difference in the rates of crystal growth resulted in the formation of fibrous objects.

Conclusion

We synthesized a series of triphenylmethane triamides with alkyl chains of various lengths as new synthons for supra-molecular systems. The morphology of the compounds depended on the length of the alkyl chains. Upon recrystallization, the triamides with short alkyl chains (1–6 carbons) gave prismatic or platelet microcrystals, whereas those with long alkyl chains (7–11 carbons) gave gel-like objects composed of

100-nm fibrous crystals. The melting points, the vibrational frequencies of the amide groups, and the molecular packing in the solid state also clearly depended on chain length. The crystal structures of some of the compounds suggested that the compounds with short chains preferred a structure composed of stacked dimers in which a 3_1 -helical hydrogen-bonded chain was formed. However, this structure appeared to be destabilized in compounds with alkyl chains with more than 6 carbons. We propose that these compounds preferred a structure in which the alkyl chains were accommodated between stacked parasols of triphenylmethane. We propose that molecular assembly with a high axis-to-radius ratio resulted from the predominance of hydrophobic interactions during crystal growth. In summary, in this study we demonstrated that a drastic change in macroscopic morphology can be brought about by the tuning of the length of the alkyl side chains, which resulted in a change in the mode of molecular assembly.

Experimental

General. All the chemicals were purchased from Tokyo Chemical Industry, and used without further purification. Thermogravimetric analyses were performed using a Rigaku TG-DTA 8120 and a Perkin-Elmer DSC (sample weight ≈ 20 mg, heating rate 5 K min^{-1} under N_2 flow 20 mL min^{-1}). IR spectra were recorded using a JEOL WINSPEC100 spectrometer, with wavenumber resolution of 0.5 cm^{-1} . ^1H and ^{13}C NMR spectra were measured using a JEOL JNM-AL400 (400 MHz for ^1H nuclei). Powder X-ray diffraction patterns were recorded using a Rigaku RINT2100 diffractometer, $\lambda(\text{Cu K}\alpha) = 1.5418\text{ \AA}$, with scan rate of 4° min^{-1} , and scan step of 0.02° .

Synthesis. Pararosaniline hydrochloride salt (3.24 g, 10 mmol) was reduced to the corresponding leuco form, 4,4',4''-triamino-triphenylmethane (**2**), using sodium tetrahydroborate in 100 mL of ethanol solution. The usual work up of the solution afforded grayish white crystalline solid (y. 52%). Three equivalents of an alkanoyl chloride ($\text{C}_n\text{H}_{2n+1}\text{COCl}$, $n = 1\text{--}10$) were allowed to react with **2** in dichloromethane solution in the presence of three equivalents of triethylamine. The reaction mixture was worked up in the usual way, and colorless solid of **1a**–**1j** was isolated. The products were identified by ^1H and ^{13}C NMR, IR, FAB(+) MS, and elemental analysis.

1a: Yield 77%; mp $206\text{--}207^\circ\text{C}$; IR (KBr): 3307 (ν_{NH}), 1673 (ν_{amideI}), 1537 (ν_{amideII}) cm^{-1} ; FAB(+) MS m/z 415.67 (415.19 calcd for M^+); elemental analysis Calcd for $\text{C}_{25}\text{H}_{25}\text{N}_3\text{O}_3 \cdot \text{H}_2\text{O}$: C, 69.27; H, 6.28; N, 9.69%. Found: C, 69.19; H, 6.25; N, 9.61%; ^1H NMR ($\text{DMSO}-d_6$): δ 2.01 (s, CH_3 , 9H), 5.41 (s, Ar_3CH , 1H), 6.99 (d, $J = 8.6\text{ Hz}$, ArH, 6H), 7.47 (d, $J = 8.6\text{ Hz}$, ArH, 6H), 9.90 (s, NH, 3H); ^{13}C NMR ($\text{DMSO}-d_6$): δ 24.8, 80.0, 119.7, 129.8, 138.1, 139.4, 168.8.

1b: Yield 93%; mp $294\text{--}295^\circ\text{C}$; IR (KBr): 3288 (ν_{NH}), 1666 (ν_{amideI}), 1541 (ν_{amideII}) cm^{-1} ; FAB(+) MS m/z 458.61 (458.25 calcd for $\text{M} + \text{H}^+$); elemental analysis Calcd for $\text{C}_{28}\text{H}_{31}\text{N}_3\text{O}_3 \cdot (\text{C}_3\text{H}_7\text{NO})_{1/3}$: C, 72.27; H, 6.97; N, 9.69%. Found: C, 72.21; H, 7.06; N, 9.64%; ^1H NMR ($\text{DMSO}-d_6$): δ 1.06 (t, $J = 7.6\text{ Hz}$, CH_3 , 9H), 2.29 (q, $J = 7.6\text{ Hz}$, $-\text{CH}_2-$, 6H), 5.40 (s, Ar_3CH , 1H), 6.98 (d, $J = 8.6\text{ Hz}$, ArH, 6H), 7.50 (d, $J = 8.6\text{ Hz}$, ArH, 6H), 9.83 (s, NH, 3H); ^{13}C NMR ($\text{DMSO}-d_6$): δ 10.5, 30.3, 55.0, 119.7, 129.8, 138.1, 139.3, 172.5.

1c: Yield 79%; mp $325\text{--}326^\circ\text{C}$; IR (KBr): 3287 (ν_{NH}), 1663 (ν_{amideI}), 1541 (ν_{amideII}) cm^{-1} ; FAB(+) MS m/z 500.44 (500.29 calcd for $\text{M} + \text{H}^+$); elemental analysis Calcd for $\text{C}_{31}\text{H}_{37}\text{N}_3\text{O}_3$: C,

74.52; H, 7.46; N, 8.41%. Found: C, 74.43; H, 7.62; N, 8.69%; ^1H NMR ($\text{DMSO}-d_6$): δ 0.90 (t, $J = 7.4\text{ Hz}$, CH_3 , 9H), 1.59 (sext, $J = 7.4\text{ Hz}$, $-\text{CH}_2-$, 6H), 2.25 (t, $J = 7.4\text{ Hz}$, $-\text{CH}_2-$, 6H), 5.41 (s, Ar_3CH , 1H), 6.99 (d, $J = 8.6\text{ Hz}$, ArH, 6H), 7.51 (d, $J = 8.6\text{ Hz}$, ArH, 6H), 9.84 (s, NH, 3H); ^{13}C NMR ($\text{DMSO}-d_6$): δ 14.6, 19.6, 39.2, 55.1, 119.8, 129.9, 138.2, 139.4, 171.8.

1d: Yield 90%; mp $283\text{--}284^\circ\text{C}$; IR (KBr): 3288 (ν_{NH}), 1663 (ν_{amideI}), 1541 (ν_{amideII}) cm^{-1} ; FAB(+) MS m/z 542.61 (542.34 calcd for $\text{M} + \text{H}^+$); elemental analysis Calcd for $\text{C}_{34}\text{H}_{43}\text{N}_3\text{O}_3$: C, 75.38; H, 8.00; N, 7.76%. Found: C, 75.12; H, 8.17; N, 7.63%; ^1H NMR ($\text{DMSO}-d_6$): δ 0.89 (t, $J = 7.4\text{ Hz}$, CH_3 , 9H), 1.31 (sext, $J = 7.4\text{ Hz}$, $-\text{CH}_2-$, 6H), 1.56 (quint, $J = 7.4\text{ Hz}$, $-\text{CH}_2-$, 6H), 2.27 (t, $J = 7.4\text{ Hz}$, $-\text{CH}_2-$, 6H), 5.41 (s, Ar_3CH , 1H), 6.99 (d, $J = 8.6\text{ Hz}$, ArH, 6H), 7.50 (d, $J = 8.6\text{ Hz}$, ArH, 6H), 9.84 (s, NH, 3H); ^{13}C NMR ($\text{DMSO}-d_6$): δ 15.4, 23.4, 28.9, 37.7, 55.1, 120.5, 130.6, 138.9, 140.2, 172.6.

1e: Yield 95%; mp $194\text{--}195^\circ\text{C}$; IR (KBr): 3297 (ν_{NH}), 1660 (ν_{amideI}), 1538 (ν_{amideII}) cm^{-1} ; FAB(+) MS m/z 584.55 (584.39 calcd for $\text{M} + \text{H}^+$); elemental analysis Calcd for $\text{C}_{37}\text{H}_{49}\text{N}_3\text{O}_3 \cdot (\text{H}_2\text{O})_{1/3}$: C, 75.35; H, 8.49; N, 7.12%. Found: C, 75.73; H, 8.52; N, 7.14%; ^1H NMR (CDCl_3): δ 0.87 (t, $J = 7.0\text{ Hz}$, CH_3 , 9H), 1.30–1.33 (m, $-\text{CH}_2-$, 12H), 1.67–1.71 (m, $-\text{CH}_2-$, 6H), 2.33 (t, $J = 7.6\text{ Hz}$, $-\text{CH}_2-$, 6H), 5.36 (s, Ar_3CH , 1H), 6.93 (d, $J = 8.4\text{ Hz}$, ArH, 6H), 7.39 (d, $J = 8.4\text{ Hz}$, ArH, 6H), 7.81 (s, NH, 3H); ^{13}C NMR (CDCl_3): δ 14.3, 22.8, 25.8, 31.8, 38.0, 55.4, 120.2, 129.9, 136.5, 139.8, 172.0.

1f: Yield 80%; mp $205\text{--}206^\circ\text{C}$; IR (KBr): 3298 (ν_{NH}), 1662 (ν_{amideI}), 1537 (ν_{amideII}) cm^{-1} ; FAB(+) MS m/z 626.68 (626.43 calcd for $\text{M} + \text{H}^+$); elemental analysis Calcd for $\text{C}_{40}\text{H}_{55}\text{N}_3\text{O}_3$: C, 76.76; H, 8.86; N, 6.71%. Found: C, 76.48; H, 8.86; N, 6.52%; ^1H NMR (CDCl_3): δ 0.85 (t, $J = 6.8\text{ Hz}$, CH_3 , 9H), 1.25–1.35 (m, $-\text{CH}_2-$, 18H), 1.68 (quint, $J = 7.5\text{ Hz}$, $-\text{CH}_2-$, 6H), 2.33 (t, $J = 7.5\text{ Hz}$, $-\text{CH}_2-$, 6H), 5.36 (s, Ar_3CH , 1H), 6.93 (d, $J = 8.4\text{ Hz}$, ArH, 6H), 7.39 (d, $J = 8.4\text{ Hz}$, ArH, 6H), 7.83 (s, NH, 3H); ^{13}C NMR (CDCl_3): δ 14.4, 22.9, 26.1, 29.3, 31.9, 38.1, 55.4, 120.2, 129.9, 136.6, 139.8, 172.0.

1g: Yield 78%; mp $182\text{--}183^\circ\text{C}$; IR (KBr): 3285 (ν_{NH}), 1654 (ν_{amideI}), 1526 (ν_{amideII}) cm^{-1} ; FAB(+) MS m/z 668.82 (668.48 calcd for $\text{M} + \text{H}^+$); elemental analysis Calcd for $\text{C}_{43}\text{H}_{61}\text{N}_3\text{O}_3$: C, 77.32; H, 9.20; N, 6.29%. Found: C, 77.12; H, 9.30; N, 6.79%; ^1H NMR (CDCl_3): δ 0.87 (t, $J = 6.9\text{ Hz}$, CH_3 , 9H), 1.26–1.32 (m, $-\text{CH}_2-$, 24H), 1.70 (quint, $J = 7.4\text{ Hz}$, $-\text{CH}_2-$, 6H), 2.33 (t, $J = 7.4\text{ Hz}$, $-\text{CH}_2-$, 6H), 5.40 (s, Ar_3CH , 1H), 6.97 (d, $J = 8.4\text{ Hz}$, ArH, 6H), 7.40 (d, $J = 8.4\text{ Hz}$, ArH, 6H), 7.47 (s, NH, 3H); ^{13}C NMR (CDCl_3): δ 14.5, 23.0, 26.1, 29.5, 29.7, 32.1, 38.2, 55.4, 120.1, 130.0, 136.5, 139.9, 171.8.

1h: Yield 85%; mp $173\text{--}174^\circ\text{C}$; IR (KBr): 3289 (ν_{NH}), 1658 (ν_{amideI}), 1527 (ν_{amideII}) cm^{-1} ; FAB(+) MS m/z 710.94 (710.53 calcd for $\text{M} + \text{H}^+$); elemental analysis Calcd for $\text{C}_{46}\text{H}_{67}\text{N}_3\text{O}_3$: C, 77.81; H, 9.51; N, 5.92%. Found: C, 77.58; H, 9.60; N, 6.09%; ^1H NMR (CDCl_3): δ 0.86 (t, $J = 6.8\text{ Hz}$, CH_3 , 9H), 1.25–1.32 (m, $-\text{CH}_2-$, 30H), 1.69 (quint, $J = 7.6\text{ Hz}$, $-\text{CH}_2-$, 6H), 2.33 (t, $J = 7.6\text{ Hz}$, $-\text{CH}_2-$, 6H), 5.39 (s, Ar_3CH , 1H), 6.95 (d, $J = 8.4\text{ Hz}$, ArH, 6H), 7.40 (d, $J = 8.4\text{ Hz}$, ArH, 6H), 7.61 (s, NH, 3H); ^{13}C NMR (CDCl_3): δ 14.5, 23.0, 26.1, 29.5, 29.7, 29.7, 32.2, 38.1, 55.4, 120.1, 129.9, 136.5, 139.8, 171.9.

1i: Yield 92%; mp $177\text{--}178^\circ\text{C}$; IR (KBr): 3292 (ν_{NH}), 1658 (ν_{amideI}), 1527 (ν_{amideII}) cm^{-1} ; FAB(+) MS m/z 752.94 (752.58 calcd for $\text{M} + \text{H}^+$); elemental analysis Calcd for $\text{C}_{49}\text{H}_{73}\text{N}_3\text{O}_3$: C, 78.25; H, 9.78; N, 5.59%. Found: C, 78.18; H, 9.91; N, 5.86%; ^1H NMR (CDCl_3): δ 0.87 (t, $J = 6.9\text{ Hz}$, CH_3 , 9H), 1.25–1.32 (m, $-\text{CH}_2-$, 36H), 1.70 (quint, $J = 7.6\text{ Hz}$, $-\text{CH}_2-$, 6H), 2.33 (t, $J =$

7.6 Hz, $-\text{CH}_2-$, 6H), 5.41 (s, Ar_3CH , 1H), 6.99 (d, $J = 8.4$ Hz, ArH, 6H), 7.35 (s, NH, 3H), 7.41 (d, $J = 8.4$ Hz, ArH, 6H); ^{13}C NMR (CDCl_3): δ 14.5, 23.1, 26.1, 29.7, 29.7, 29.8, 29.9, 32.3, 38.2, 55.4, 120.1, 130.1, 136.5, 139.8, 171.7.

1j: Yield 80%; mp 178–179 °C; IR (KBr): 3290 (ν_{NH}), 1655 (ν_{amideI}), 1528 (ν_{amideII}) cm^{-1} ; FAB(+) MS m/z 795.01 (794.62 calcd for $\text{M} + \text{H}^+$); elemental analysis Calcd for $\text{C}_{52}\text{H}_{79}\text{N}_3\text{O}_3$: C, 78.64; H, 10.03; N, 5.29%. Found: C, 78.68; H, 10.22; N, 5.46%; ^1H NMR (CDCl_3): δ 0.87 (t, $J = 6.9$ Hz, CH_3 , 9H), 1.24–1.30 (m, $-\text{CH}_2-$, 42H), 1.68 (quint, $J = 7.6$ Hz, $-\text{CH}_2-$, 6H), 2.33 (t, $J = 7.6$ Hz, $-\text{CH}_2-$, 6H), 5.42 (s, Ar_3CH , 1H), 7.00 (d, $J = 8.5$ Hz, ArH, 6H), 7.25 (s, NH, 3H), 7.41 (d, $J = 8.5$ Hz, ArH, 6H); ^{13}C NMR (CDCl_3): δ 14.5, 23.1, 26.2, 29.7, 29.7, 29.8, 29.9, 30.0, 32.3, 38.1, 55.4, 120.2, 129.9, 136.6, 139.8, 172.1.

1k: Yield 89%; mp 171–172 °C; IR (KBr): 3290 (ν_{NH}), 1659 (ν_{amideI}), 1528 (ν_{amideII}) cm^{-1} ; FAB(+) MS m/z 836.84 (836.67 calcd for $\text{M} + \text{H}^+$); elemental analysis Calcd for $\text{C}_{55}\text{H}_{85}\text{N}_3\text{O}_3$: C, 78.99; H, 10.24; N, 5.02%. Found: C, 79.12; H, 10.48; N, 5.18%; ^1H NMR (CDCl_3): δ 0.87 (t, $J = 6.9$ Hz, CH_3 , 9H), 1.24–1.31 (m, $-\text{CH}_2-$, 48H), 1.69 (quint, $J = 7.6$ Hz, $-\text{CH}_2-$, 6H), 2.33 (t, $J = 7.6$ Hz, $-\text{CH}_2-$, 6H), 5.38 (s, Ar_3CH , 1H), 6.95 (d, $J = 8.4$ Hz, ArH, 6H), 7.40 (d, $J = 8.4$ Hz, ArH, 6H), 7.63 (s, NH, 3H); ^{13}C NMR (CDCl_3): δ 14.5, 23.1, 26.2, 29.7, 29.8, 29.8, 29.9, 30.0, 30.0, 32.3, 38.0, 55.4, 120.3, 129.8, 136.6, 139.8, 172.3.

X-ray Crystal Structure Analysis. For X-ray diffraction of single crystals, data were collected on a MacScienceDIPLabo Imaging Plate diffractometer, $\lambda(\text{Cu K}\alpha) = 1.5418 \text{ \AA}$. The structure was solved by direct methods and expanded using Fourier techniques. All calculations were performed with the crystallographic software package SHELX-97.²⁷ Crystallographic data have been deposited with Cambridge Crystallographic Data Centre: Deposition numbers CCDC-723047 and -723048 to compounds No. **1c** and **1d**. Copies of the data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html> (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, U.K.; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

1c: $\text{C}_{31}\text{H}_{37}\text{N}_3\text{O}_3$, $M_r = 499.64$, rhombohedral, $a = 18.8490(6)$, $c = 13.927 \text{ \AA}$, $V = 4285.14(14) \text{ \AA}^3$, $D_{\text{calcd}} = 1.162 \text{ g cm}^{-3}$, $T = 233 \text{ K}$, space group $R\bar{3}$ (#143), $Z = 6$, $\mu(\text{Cu K}\alpha) = 5.9 \text{ cm}^{-1}$, 12848 reflections measured and 1385 unique ($2\theta_{\text{max}} = 146.1^\circ$, $R_{\text{int}} = 0.033$), which were used in all calculations. $R = 0.080$, $R_w = 0.168$.

1d: $\text{C}_{34}\text{H}_{43}\text{N}_3\text{O}_3$, $M_r = 541.71$, rhombohedral, $a = 19.9890(5)$, $c = 13.500 \text{ \AA}$, $V = 4671.39(12) \text{ \AA}^3$, $D_{\text{calcd}} = 1.155 \text{ g cm}^{-3}$, $T = 298 \text{ K}$, space group $R\bar{3}$ (#143), $Z = 6$, $\mu(\text{Cu K}\alpha) = 5.8 \text{ cm}^{-1}$, 13799 reflections measured and 1677 unique ($2\theta_{\text{max}} = 146.7^\circ$, $R_{\text{int}} = 0.029$), which were used in all calculations. $R = 0.083$, $R_w = 0.207$.

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