

Interplay of Weak Interactions and Structural Features in the Solid State Self-Assembly of Symmetric Diamides

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ABSTRACT: A series of symmetric diamides were synthesized as building blocks and fully characterized to understand the interplay of alkyl chain crystallization, hydrogen bonding, and rigidity of the spacer in the solid state self-assembly process. The nature of self-assembly was investigated using single crystal X-ray diffraction studies. To have a meaningful comparison of the self-assembly process, only spacer groups were changed among the diamide molecules. Diamides **1**, **2**, **4**, and **5** showed trans conformation in the solid lattice with the dodecyl groups on either side of the molecule, whereas **3** and **6** were in the syn conformation. In the crystal lattice, diamide **1** formed Σ -shaped columns, and **3** gave close packed X-shaped dimers. Diamide **6** formed linear ribbons in the solid lattice via intra- and intermolecular hydrogen bonding. In the crystal lattice of **1–5**, alkyl chains were close packed and crystallized. In all crystal lattices described here, the rigidity of the spacer group along with the interplay of hydrogen bonds, alkyl chain crystallization, and packing forces dictate the formation of thermodynamically stable supramolecular architectures with various conformations in the crystal lattice.

Introduction

Investigation of the self-assembly of small molecules and macromolecules allows us to understand the interplay of molecular structure, shape, and presence of functional groups toward the synthesis of multifunctional molecular aggregates.¹ The intra- and intermolecular interactions, such as hydrogen bonding, van der Waals interaction, and π – π stacking play an active role in controlling the self-assembly of molecules in the crystal lattice.² Using elegant design of molecular building blocks and selection of appropriate functional groups, extended molecular arrays including zero dimensional (0D) structures (e.g., capsules³ and squares⁴), one-dimensional (1D) arrays (e.g., tapes,⁵ ribbons,⁶ rods⁷), two-dimensional (2D) networks (e.g., sheets,⁸ honeycombs,⁹ brick walls¹⁰) and three-dimensional (3D) architectures¹¹ have been synthesized and characterized.

Polyamides and oligoamides are attractive model compounds due to their structural similarities with the complex proteins, where both intramolecular and intermolecular hydrogen-bonding ($N-H\cdots O=C<$) play an important role in determining the secondary and tertiary structures.¹² Hamilton and co-workers reported that a series of diamides functionalized with complementary functional moieties gave helical structures due to molecular recognition assisted self-assembly in the solid state.¹³ Gellman's group investigated a few triamide molecules as building blocks and showed the influence of molecular structure on the solid-state self-assembly process.¹⁴

In this paper, five symmetric secondary amides with dodecyloxy groups and one with benzyloxy group as side chains were chosen to investigate the self-assembly of diamide molecules in the crystal lattice. The molecules are designed to understand the significance of the interplay of weak interactions (e.g., hydrogen bonds, van der Waals forces, and alkyl chain crystallization)¹⁵ and

the role of spacer groups between the two amide groups toward the self-assembly in the solid state. These factors are expected to play an important role in stabilizing the supramolecular structures, and a systematic investigation of the self-assembly of diamides (**1–6**) is described. The molecular structures of the target diamides are given in Scheme 1.

Experimental Section

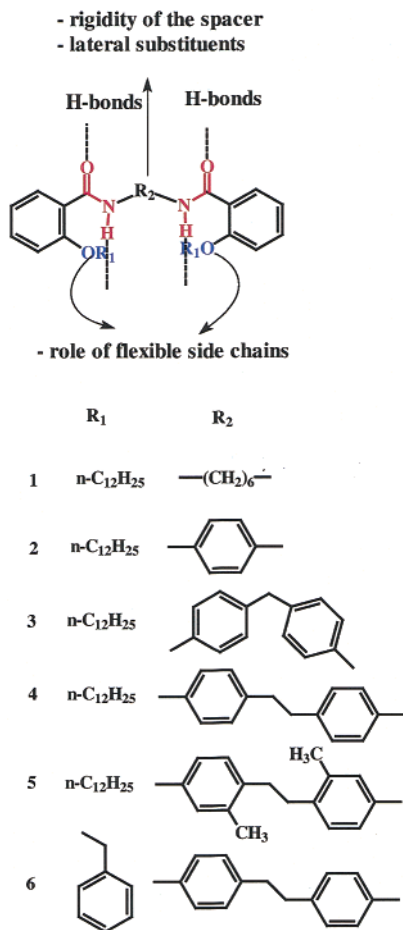
General. All melting points (mp) were determined with a Reichert-Jung Thermo Galen Hot Stage microscope and uncorrected. The ¹H and ¹³C NMR spectra were determined on a Bruker ACF 300 spectrometer with tetramethylsilane as the internal standard. FT-IR spectra were recorded on a Perkin-Elmer 1710 Infrared Fourier Transform spectrophotometer. Mass spectra (MS-ESI) were determined on a Finnigan MAT LCQ or Finnigan TSQ 7000 mass spectrometer at an ion spray voltage of 4.5 kV, and a capillary temperature of 270 or 350 °C. The elemental analyses were performed at the Elemental Analysis Laboratory in the Department of Chemistry.

Single-Crystal X-ray Diffraction Studies. X-ray diffraction data on single crystals were collected on a Bruker AXS SMART CCD 3-circle diffractometer with a Mo–K α radiation ($\lambda = 0.71073$ Å). The software used was SMART¹⁶ for collecting frames of data, indexing reflections and determining lattice parameters; SAINT¹⁶ for integration of intensity of reflections and scaling; SADABS¹⁷ for absorption correction; and SHELX-TL¹⁸ for space group determination, structure solution, and least-squares refinements on F^2 . Structures were solved by direct methods and non-hydrogen atoms refined anisotropically. Hydrogen atoms were introduced at fixed distances from carbon atoms and assigned fixed thermal parameters. All calculations were performed on a Silicon Graphics workstation, using programs provided by Siemens Pvt. Ltd. Some crystal data and structural refinement parameters of diamides **1–6** are given in Table 1.

Materials. All solvents were predistilled before use. Commercially available reagents were used without further purification. Synthesis of 2-benzyloxybenzoic acid was achieved according to the reported method,¹⁹ which involved the alkylation of methyl salicylate with benzyl bromide followed by the hydrolysis of methyl 2-benzyloxybenzoate. The key intermediate 2-dodecyloxybenzoyl chloride²⁰ was synthesized from

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Scheme 1. Molecular Structure of Symmetric Secondary Diamides 1–6



methyl salicylate via alkylation with 1-bromododecane, hydrolysis of the ester group with sodium hydroxide, followed by refluxing with thionyl chloride (Scheme 2).

Methyl 2-Dodecyloxybenzoate. Methyl salicylate (9.1 g, 0.06 mol) and potassium carbonate (24.8 g, 0.18 mol) in DMF (500 mL) was stirred at 80 °C for 1 h under nitrogen atmosphere. 1-Bromododecane (15.5 g, 0.062 mol) was added dropwise and the mixture was stirred for 8 h at 80 °C. After the reaction, the solvent was removed under reduced pressure. The obtained solid was dissolved in hexane (150 mL) and washed with water (100 mL). The organic layer was separated and concentrated to give crude diamide, which was recrystallized in hexane to afford the pure product, methyl 2-dodecyloxybenzoate (yield: 16.91 g, 88%). mp, 38.2–39.5 °C. ¹H NMR (300 MHz, CDCl₃, δ, ppm): 7.79 (d, *J* = 7.8 Hz, 1 H, ArH), 7.45 (t, *J* = 7.5 Hz, 1 H, ArH), 6.89 (m, 2 H, ArH), 4.11 (t, *J* = 6.0 Hz, 2 H, OCH₂), 3.90 (s, 3 H, OCH₃), 1.86 (m, 2 H, CH₂), 1.51–1.16 (m, 18 H, CH₂), 0.87 (t, *J* = 6.0 Hz, 3 H, CH₃). ¹³C NMR (75.4 MHz, CDCl₃, δ, ppm): 167.1 (C=O), 160.1, 133.5, 130.3, 120.1, 116.2, 114.1 (ArC), 72.3 (OCH₂), 50.1 (OCH₃), 32.5, 30.1, 30.0, 26.9, 23.2 (CH₂), 13.9 (CH₃). MS-ESI: *m/z* 320 (M⁺).

2-Dodecyloxybenzoic Acid. A mixture of methyl 2-dodecyloxybenzoate (16.0 g, 0.05 mol) and sodium hydroxide (2.4 g, 0.06 mol) in ethanol–water (2:1, in volume, 250 mL) was allowed to reflux for 4 h. Excess solvent was removed under reduced pressure, and the residue mixed with water (50 mL) and then acidified with 2 M HCl to get crude product, which was recrystallized in methanol (yield: 11.64 g, 76%). mp, 51.0–52.5 °C. ¹H NMR (300 MHz, CDCl₃ + DMSO-*d*₆, δ, ppm): 8.04 (d, *J* = 7.8 Hz, 1 H, ArH), 7.49 (t, *J* = 7.8 Hz, 1 H, ArH), 6.96 (m, 2 H, ArH), 3.98 (t, *J* = 6.0 Hz, 2 H, OCH₂), 1.84 (m, 2 H, CH₂), 1.52–1.16 (m, 18 H, CH₂), 0.88 (t, *J* = 6.0 Hz, 3 H, CH₃). ¹³C NMR (75.4 MHz, CDCl₃ + DMSO-*d*₆, δ, ppm): 169.5

(C=O), 160.0, 133.4, 130.2, 120.0, 116.4, 114.6 (ArC), 73.5 (OCH₂), 32.5, 30.3, 30.0, 26.7, 23.1 (CH₂), 13.9 (CH₃). MS-ESI: *m/z* 305 (M – 1).

2-Dodecyloxybenzoyl Chloride. This diamide was obtained by refluxing 2-dodecyloxybenzoic acid with thionyl chloride according to the general procedure.²⁰ Yield: 73%, pale yellow oil. ¹H NMR (300 MHz, CDCl₃, δ, ppm): 8.16 (d, *J* = 8.0 Hz, 1 H, ArH), 7.56 (t, *J* = 7.5 Hz, 1 H, ArH), 7.06 (m, 2 H, ArH), 4.11 (t, *J* = 6.0 Hz, 2 H, OCH₂), 1.88 (m, 2 H, CH₂), 1.55–1.14 (m, 18 H, CH₂), 0.87 (t, *J* = 6.0 Hz, 3 H, CH₃). ¹³C NMR (75.4 MHz, CDCl₃, δ, ppm): 172.1 (C=O), 160.4, 134.0, 130.4, 120.5, 116.4, 114.0 (ArC), 72.4 (OCH₂), 32.1, 30.1, 30.0, 26.9, 23.3 (CH₂), 13.9 (CH₃).

General Procedure for Synthesis of Diamides 1–5. A mixture of diamine (12.5 mmol) and triethylamine (5.06 g, 50 mmol) in THF (300 mL) was stirred and cooled to 0 °C. A solution of 2-dodecyloxybenzoyl chloride (8.12 g, 25 mmol) dissolved in dry THF (50 mL) was added dropwise over 30 min, allowed to warm to room temperature, and stirred for another 4 h. The excess solvent was removed under reduced pressure, dissolved in dichloromethane (100 mL), and washed with 1 M sodium bicarbonate solution (100 mL), followed by water (100 mL). The organic layer was concentrated to give crude compound, which was recrystallized in appropriate solvents to afford diamides 1–5.

***N,N*-bis(2-dodecyloxybenzoyl)-1,6-diaminohexane (1).** Recrystallized from methanol, yield: 90%. mp, 75.0–76.8 °C. ¹H NMR (300 MHz, CDCl₃, δ, ppm): 8.21 (d, *J* = 7.5 Hz, 2 H, ArH), 8.04 (t, *J* = 7.2 Hz, 2 H, ArH), 7.40 (t, *J* = 7.2 Hz, 2 H, ArH), 7.05 (t, *J* = 6.0 Hz, 2 H, CONH), 6.93 (d, *J* = 7.5 Hz, 2 H, ArH), 4.11 (t, *J* = 6.0 Hz, 4 H, OCH₂), 3.46 (m, 4 H, NCH₂), 1.86 (m, 4 H, CH₂), 1.62 (m, 4 H, CH₂), 1.55–1.16 (m, 40 H, CH₂), 0.87 (t, *J* = 6.0 Hz, 6 H, CH₃). ¹³C NMR (75.4 MHz, CDCl₃, δ, ppm): δ 165.3 (C=O), 156.9, 132.0, 132.1, 121.4, 121.1, 112.0 (ArC), 68.9 (OCH₂), 39.9 (NCH₂), 31.8, 29.4, 26.8, 26.1, 22.5 (CH₂), 14.0 (CH₃). MS-ESI: *m/z* 692 (M⁺). Anal. Calc for C₄₄H₇₂N₂O₄ (693.05): C, 76.25; H, 10.47; N, 4.04. Found: C, 76.20; H, 10.48; N, 4.41.

***N,N*-bis(2-dodecyloxybenzoyl)-1,4-diaminobenzene (2).** Recrystallized from THF solution, yield: 61%. mp, 115.2–116.7 °C. ¹H NMR (300 MHz, CDCl₃, δ, ppm): 10.08 (s, 2 H, CONH), 8.32 (d, *J* = 7.5 Hz, 2 H, ArH), 7.68 (s, 4 H, ArH), 7.47 (t, *J* = 7.2 Hz, 2 H, ArH), 7.12 (t, *J* = 7.2 Hz, 2 H, ArH), 7.02 (d, *J* = 7.5 Hz, 2 H, ArH), 4.21 (t, *J* = 6.0 Hz, 4 H, OCH₂), 1.80 (m, 4 H, CH₂), 1.56–1.11 (m, 36 H, CH₂), 0.86 (t, *J* = 6.0 Hz, 6 H, CH₃). ¹³C NMR (75.4 MHz, CDCl₃, δ, ppm): 163.0 (C=O), 156.7, 134.7, 133.1, 132.4, 121.6, 121.4, 120.5, 112.3 (ArC), 69.4 (OCH₂), 31.8, 29.5, 26.1, 22.6 (CH₂), 14.0 (CH₃). MS-ESI: *m/z* 684 (M⁺). Anal. Calc for C₄₄H₆₄N₂O₄ (684.99): C, 77.15; H, 9.42; N, 4.09. Found: C, 76.84; H, 9.35; N, 4.45.

***N,N*-bis(2-dodecyloxybenzoyl)-4,4'-diaminodiphenylmethane (3).** Recrystallized from THF, yield: 70%. mp 79.5–80.7 °C. ¹H NMR (300 MHz, CDCl₃, δ, ppm): 10.03 (s, 2 H, CONH), 8.30 (d, *J* = 7.5 Hz, 2 H, ArH), 7.59 (d, *J* = 7.5 Hz, 4 H, ArH), 7.46 (t, *J* = 7.2 Hz, 2 H, ArH), 7.18 (d, *J* = 7.5 Hz, 4 H, ArH), 7.11 (t, *J* = 7.2 Hz, 2 H, ArH), 7.00 (d, *J* = 7.5 Hz, 2 H, ArH), 4.19 (t, *J* = 6.0 Hz, 4 H, OCH₂), 3.96 (s, 2 H, ArCH₂-Ar), 1.97 (m, 4 H, CH₂), 1.55–1.12 (m, 36 H, CH₂), 0.87 (t, *J* = 6.0 Hz, 6 H, CH₃). ¹³C NMR (75.4 MHz, CDCl₃, δ, ppm): 164.3 (C=O), 158.4, 138.8, 136.5, 136.1, 134.1, 132.4, 122.7, 121.5, 120.2, 112.0 (ArC), 68.9 (OCH₂), 41.9 (ArCH₂Ar), 30.8, 29.8, 29.1, 26.3, 22.1 (CH₂), 13.9 (CH₃). MS-ESI: *m/z* 774 (M⁺). Anal. Calc for C₅₁H₇₀N₂O₄ (775.11): C, 79.03; H, 9.10; N, 3.61. Found: C, 78.81; H, 9.07; N, 3.79.

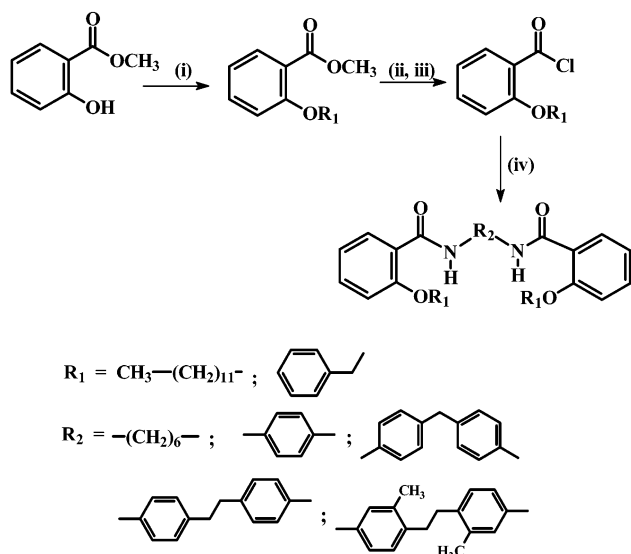
***N,N*-bis(2-dodecyloxybenzoyl)-4,4'-diaminodiphenylethane (4).** Recrystallized from acetone, yield: 89%. mp 113.8–115.0 °C. ¹H NMR (300 MHz, CDCl₃, δ, ppm): 10.04 (s, 2 H, CONH), 8.23 (d, *J* = 7.5 Hz, 2 H, ArH), 7.59 (d, *J* = 7.5 Hz, 4 H, ArH), 7.47 (t, *J* = 7.2 Hz, 2 H, ArH), 7.19 (d, *J* = 7.5 Hz, 4 H, ArH), 7.12 (t, *J* = 7.2 Hz, 2 H, ArH), 7.01 (d, *J* = 7.5 Hz, 2 H, ArH), 4.20 (t, *J* = 6.0 Hz, 4 H, OCH₂), 2.90 (s, 4 H, ArCH₂-CH₂Ar), 1.99 (m, 4 H, CH₂), 1.58–1.11 (m, 36 H, CH₂), 0.87 (t, *J* = 6.0 Hz, 6 H, CH₃). ¹³C NMR (75.4 MHz, CDCl₃, δ, ppm): 163.0 (C=O), 156.7, 137.5, 136.4, 133.2, 132.4, 128.8, 121.7,

Table 1. Selected Crystal Data and Structural Refinement Parameters for Diamides 1–6

| | diamide 1 | diamide 2 | diamide 3 | diamide 4 | diamide 5 | diamide 6 |
|---|---|---|---|---|---|---|
| formula | C ₄₄ H ₇₂ N ₂ O ₄ | C ₄₄ H ₆₄ N ₂ O ₄ | C ₅₁ H ₇₀ N ₂ O ₄ | C ₅₂ H ₇₂ N ₂ O ₄ | C ₅₄ H ₇₆ N ₂ O ₄ | C ₄₂ H ₃₆ N ₂ O ₄ |
| FW | 693.04 | 684.97 | 775.09 | 789.12 | 817.17 | 632.73 |
| <i>T</i> , K | 293(2) | 293(2) | 293(2) | 293(2) | 293(2) | 223(2) |
| system | monoclinic | monoclinic | monoclinic | monoclinic | triclinic | monoclinic |
| space | <i>C2/c</i> | <i>P2₁/c</i> | <i>P2₁/c</i> | <i>P2₁/n</i> | <i>P</i> $\bar{1}$ | <i>C2/c</i> |
| <i>a</i> , Å | 37.165(3) | 13.543(3) | 21.114(11) | 6.122(5) | 7.924(5) | 22.470(2) |
| <i>b</i> , Å | 5.0701(4) | 10.098 | 13.428(7) | 13.001(1) | 10.243(7) | 9.064(8) |
| <i>c</i> , Å | 23.508(2) | 15.048 | 16.665(9) | 29.596(2) | 16.805(1) | 19.952(18) |
| α (°) | 90 | 90 | 90 | 90 | 103.33(2) | 90 |
| β (°) | 101.754(2) | 93.253(1) | 95.151(1) | 92.197(1) | 93.400(2) | 123.93(2) |
| γ (°) | 90 | 90 | 90 | 90 | 108.45(2) | 90 |
| <i>V</i> , Å ³ | 4336.8(6) | 2054.8(6) | 4706.3(4) | 2354.3(3) | 1246.2(1) | 3371.7(5) |
| <i>Z</i> | 4 | 2 | 4 | 2 | 1 | 4 |
| <i>D</i> , g/cm ³ | 1.061 | 1.107 | 1.094 | 1.113 | 1.089 | 1.246 |
| θ , (°) | 1.77–25.0 | 2.43–29.46 | 1.80–25.0 | 1.71–25.0 | 2.17–26.37 | 2.18–25.0 |
| final, <i>R</i> ₁ ^a | 0.0831, | 0.0609 | 0.1034 | 0.0818 | 0.1188 | 0.0573 |
| <i>wR</i> ₂ ^b | 0.1409 | 0.1647 | 0.3045 | 0.1541 | 0.2247 | 0.1511 |
| all data <i>R</i> ₁ | 0.1770 | 0.1022 | 0.2270 | 0.1322 | 0.1867 | 0.1067 |
| <i>wR</i> ₂ | 0.1729 | 0.1891 | 0.3756 | 0.1758 | 0.2591 | 0.1724 |

$$^a R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad ^b wR_2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}, \quad w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP.$$

Scheme 2. Synthetic Route for Target Diamides 1–6^a



^a (i) CH₃(CH₂)₁₁Br, K₂CO₃/DMF, 80 °C; (ii) NaOH, CH₃OH/H₂O; (iii) SOCl₂, refluxing; (iv) H₂N-R₂-NH₂, Et₃N.

121.4, 120.0, 112.2 (ArC), 69.4 (OCH₂), 37.5 (ArCH₂), 31.8, 29.4, 26.1, 22.7 (CH₂), 14.0 (CH₃). MS-ESI: *m/z* 788 (M⁺). Anal. Calc for C₅₂H₇₂N₂O₄ (789.14): C, 79.14; H, 9.20; N, 3.55. Found: C, 78.88; H, 9.10; N, 3.17.

***N,N*-bis-(2-dodecyloxybenzoyl)-4,4'-diamino-2,2'-dimethyldiphenylethane (5).** Recrystallized from acetone, yield: 92%. mp 99.2–101.0 °C. ¹H NMR (300 MHz, CDCl₃, δ , ppm): 10.01 (s, 2 H, CONH), 8.31 (d, *J* = 7.5 Hz, 2 H, ArH), 7.48 (m, 6 H, ArH), 7.13 (m, 4 H, ArH), 7.01 (d, *J* = 7.5 Hz, 2 H, ArH), 4.21 (t, *J* = 6.0 Hz, 4 H, OCH₂), 2.83 (s, 4 H, ArCH₂-CH₂Ar), 2.35 (s, 6 H, ArCH₃), 1.99 (m, 4 H, CH₂), 1.59–1.14 (m, 36 H, CH₂), 0.87 (t, *J* = 6.0 Hz, 6 H, CH₃). ¹³C NMR (75.4 MHz, CDCl₃, δ , ppm): 163.1 (C=O), 156.7, 136.6, 136.5, 135.9, 132.9, 132.3, 129.3, 121.8, 121.6, 121.3, 117.8, 112.2 (ArC), 69.4 (OCH₂), 33.7 (ArCH₂), 31.8, 29.5, 26.2, 22.6 (CH₂), 19.5 (ArCH₃), 14.0 (CH₃). MS-ESI: *m/z* 816 (M⁺). Anal. Calc for C₅₄H₇₆N₂O₄ (817.19): C, 79.34; H, 9.37; N, 3.43. Found: C, 79.08; H, 9.05; N, 3.47.

***N,N*-bis-(2-benzyloxybenzoyl)-4,4'-diaminodiphenylethane (6).** 2-Benzyloxybenzoic acid (5.71 g, 0.025 mol), 1,3-dicyclohexylcarbodiimide (6.19 g, 0.03 mol), and 4-(dimethylamino)pyridine (3.05 g, 0.025 mol) in dichloromethane (300 mL) were allowed to cool below 5 °C, and 4,4'-ethylenedianiline

(2.55 g, 0.012 mol) dissolved in THF (50 mL) was added dropwise over 30 min. The reaction mixture was allowed to warm to room temperature while stirring overnight, filtered, and the filtrate was washed with 1 M sodium bicarbonate solution, followed by water, then precipitated with cold methanol, and recrystallized from acetone. Yield: 2.73 g (36%). mp 212.2–213.8 °C. ¹H NMR (300 MHz, CDCl₃, δ , ppm): 9.93 (s, 2 H, CONH), 8.34 (d, *J* = 7.5 Hz, 2 H, ArH), 7.52–7.46 (m, 8 H, ArH), 7.20–7.12 (m, 12 H, ArH), 7.01 (d, *J* = 7.5 Hz, 4 H, ArH), 5.23 (s, 4 H, PhCH₂), 2.80 (s, 4 H, ArCH₂CH₂Ar). ¹³C NMR (75.4 MHz, CDCl₃, δ , ppm): 165.2 (C=O), 160.9, 140.9, 135.8, 135.4, 132.9, 128.8, 128.3, 128.1, 127.4, 127.4, 120.9, 120.3, 119.1, 114.2 (ArC), 77.5 (OCH₂Ph), 36.4 (ArCH₂). MS-ESI: *m/z* 632 (M⁺). Anal. Calc for C₄₂H₃₆N₂O₄ (632.75): C, 79.72; H, 5.73; N, 4.43. Found: C, 79.44; H, 5.53; N, 4.45.

Results and Discussion

Synthesis. The diamides 1–5 were obtained from treatment of 2-dodecyloxybenzoyl chloride with the corresponding diamine (e.g., 1,6-diaminohexane, 1,4-diaminobenzene, 4,4'-diaminodiphenylmethane, 4,4'-diaminodiphenylethane, and 4,4'-diamino-2,2'-dimethyldiphenylethane) in anhydrous tetrahydrofuran using triethylamine as base (Scheme 2).

2-Benzyloxybenzoic acid was synthesized according to the reported procedure,¹⁹ purified, and reacted with 4,4'-diaminodiphenylethane in the presence of 1,3-dicyclohexylcarbodiimide (DCC) and 4-(dimethylamino)pyridine (DMAP) in dichloromethane to afford diamide 6 in 36% yield. All diamides (1–6) were purified and fully characterized using ¹H and ¹³C NMR spectroscopy, mass spectrometry, elemental analysis, and single-crystal X-ray data.

Crystal Structure of *N,N*-bis-(2-dodecyloxybenzoyl)-1,6-diaminohexane (1). Single crystals of 1 (Figure 1) were obtained from methanol solution using slow evaporation of solvent at ambient conditions and examined using single-crystal X-ray diffraction methods. It gave a monoclinic crystal lattice with a *C2/c* space group. All bond distances and angles of the molecule are normal. All hydrogen atoms of diamide 1 were fixed at a given assigned positions. Selected crystal data and structural refinement parameters of diamide 1 are given in Table 1.

Diamide 1 showed no centrosymmetry in the solid state and gave a *Z*-shaped conformation with *C*₂ symmetry (Figure 1a).

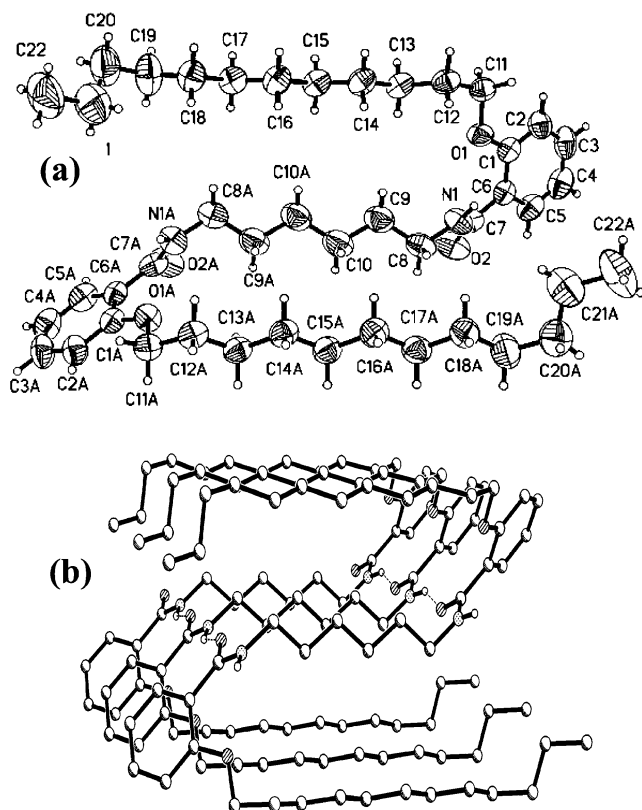


Figure 1. (a) ORTEP view of diamide **1**, letter A refers to symmetry code: $-x, y, -z + 1/2$. (b) Molecules are organized parallel to each other along the b -axis via intermolecular hydrogen bonding in the crystal lattice of **1** and the distance between two neighboring molecules is ca. 4.2 Å. Displacement ellipsoids are shown at the 50% probability level. H-bonds are represented as dotted lines.

The dihedral angle between two phenyl rings of the same molecule is ca. 96°. The dodecyl groups at each end of the molecule are folded (at C11 and C11A) and packed parallel to the flexible hexamethylene spacer group at the center. Strong intermolecular hydrogen bonds, $N-H\cdots O$ with $d(N\cdots O)$ of 2.855 (3) Å and the angle $N-H\cdots O$ of ca. 143° are formed between the amide groups of the adjacent molecules along the b -axis (Figure 1b) which gave rise to a linear 1D hydrogen bonded chain inside the crystal lattice, similar to the observed amide H-bonding motifs.²¹ All molecules stack parallel to each other along the hydrogen bonded chain axis to form a column and the distance between the adjacent molecules along the column is ca. 4.2 Å.

The end methyl and the adjacent methylene groups of the dodecyl chains are folded toward the columnar axis to achieve a close packed lattice (Figure 2). It is clear that an interplay of strong intermolecular hydrogen bonding, alkyl chain crystallization, and π - π stacking²² of the aromatic rings influence the self-assembly of diamide (**1**) in the crystal lattice. In diamide **2**, a rigid 1,4-disubstituted benzene moiety is incorporated as spacer and linear dodecyl groups at each end of the molecule.

Crystal Structure of *N,N*-bis-(2-dodecyloxybenzoyl)-1,4-diaminobenzene (2**).** Single crystals of **2** (Figure 3a) were obtained from methanol solution using a slow evaporation method at ambient conditions. The observed crystal lattice belongs to a monoclinic system

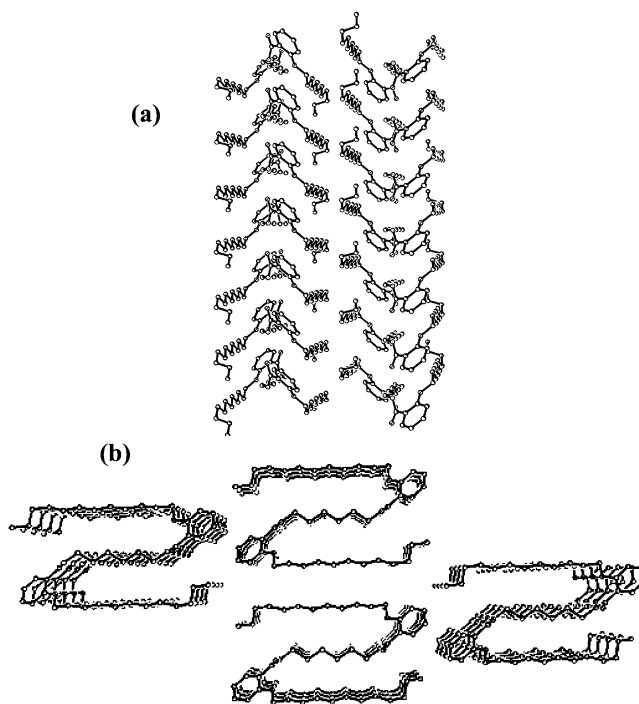


Figure 2. (a) Packing of two hydrogen-bonded columns of diamide **1** (view in the bc -plane) and (b) the organization of the adjacent Z -shaped columns along the b -axis (view in the ac -plane). Hydrogen atoms are omitted for clarity.

with $P2_1/c$ space group. Selected data and structure refinement parameters of diamide **2** are given in Table 1. Diamide **2** gave a Z -shaped conformation in the crystal lattice and showed centrosymmetry with a center of inversion at the middle of the 1,4-disubstituted benzene ring.

Strong intramolecular hydrogen bonding (e.g., $N1-H1\cdots O1$ with $d(N\cdots O)$ of 2.635 (4) Å) was observed between the $N-H$ of the amide moiety and the oxygen atom of the ether group in the crystal lattice of **2** (Figure 3a). The observed $N1-H1\cdots O1$ angle was ca. 144°. Such strong intramolecular hydrogen bonds enhance the planarity of the molecule by keeping the end benzene rings and the dodecyl chains in one plane (the dihedral angle between the end benzene ring and the center benzene ring was ca. 9°). As a result, the molecular structure showed a planar Z -shaped conformation in the crystal lattice. Two $C-H\cdots O$ intermolecular hydrogen bonds with $d(C\cdots O)$ of 3.381 (4) Å were formed between the oxygen atoms of the amide group and the hydrogen atoms on the central phenyl ring from an adjacent diamide molecule in the crystal lattice (Figure 3b). The observed $C-H\cdots O$ angle was ca. 150°. As a result, 1D planar ribbons were formed and both intermolecular and intramolecular hydrogen bonds facilitated the packing of the diamide units in a staggered, but parallel fashion to achieve alkyl chain crystallization. The alkyl chains were interdigitated and packed between the hydrogen-bonded 1D ribbons of the diamides to form a close packed 2D sheet in the crystal lattice (Figure 3c).

All bond distances and angles in the benzene rings, methylene groups, methyl groups, ether groups, and amide groups are normal. All hydrogen atoms of diamide **2** were located from the Fourier difference map.

To further explore the role of the rigidity of the spacer group, we used 4,4'-diaminodiphenyl methane as a base

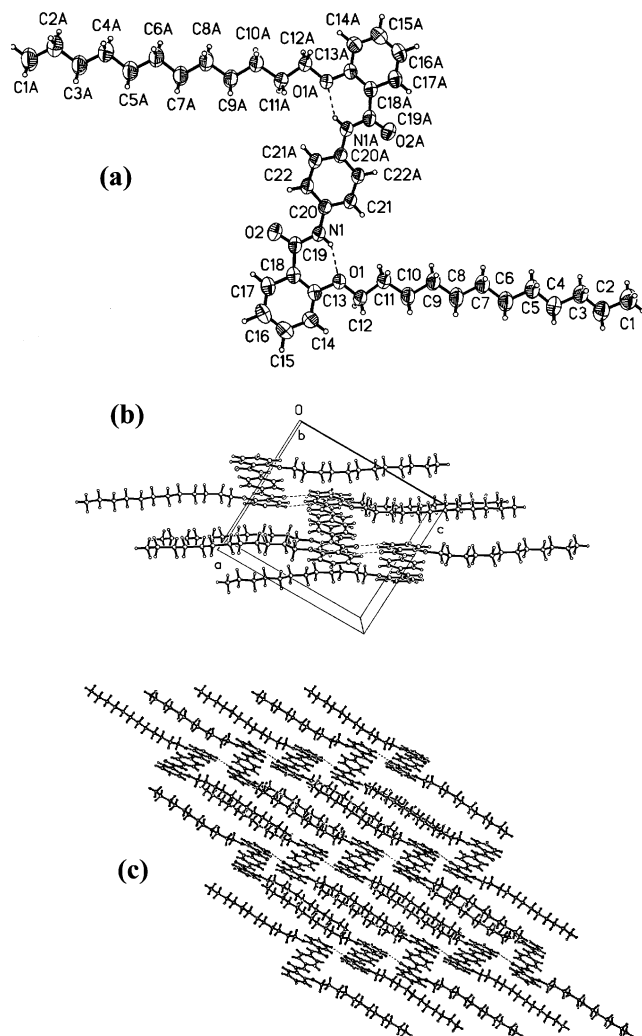


Figure 3. (a) ORTEP view of **2**, symmetry code: $-x, y + 1/2, -z + 1/2$. (b) organization of diamide molecules via intermolecular hydrogen bonds in the crystal lattice of **2**. (c) An infinite sheet formed via hydrogen bonding and alkyl chain interdigitation viewed in the *ac*-plane. Displacement ellipsoids are shown at the 50% probability level. Broken lines indicate hydrogen bonds.

to synthesize the diamide **3**. Due to the incorporation of methylene group at the center, diamide **3** is expected to be less rigid.

Crystal Structure of *N,N*-bis-(2-dodecyloxybenzoyl)-4,4'-diaminodiphenylmethane (3**)**. Single crystals of diamide **3** (Figure 4) were obtained from methanol solution using a slow evaporation method at ambient conditions. Selected geometric parameters for the crystal lattice of **3** are listed in Table 1. Crystals of **3** were formed with the monoclinic crystal lattice ($P2_1/c$ space group), and all bond distances and angles of the molecule were normal. All hydrogen atoms of **3** are fixed at the given assigned positions. Due to the sp^3 hybridized methylene group at the center, the diamide molecules in the crystal lattice were folded into a V-shaped conformation with a C_2 symmetry through the central methylene carbon (C26) as shown in Figure 4. A strong intramolecular $N1-H1\cdots O1$ hydrogen bond with $d(N\cdots O)$ of 2.632(3) Å and the $\angle N1-H1\cdots O1$ of ca. 142° was formed between the N-H site of amide group and the oxygen atom of the ether group in the crystal lattice

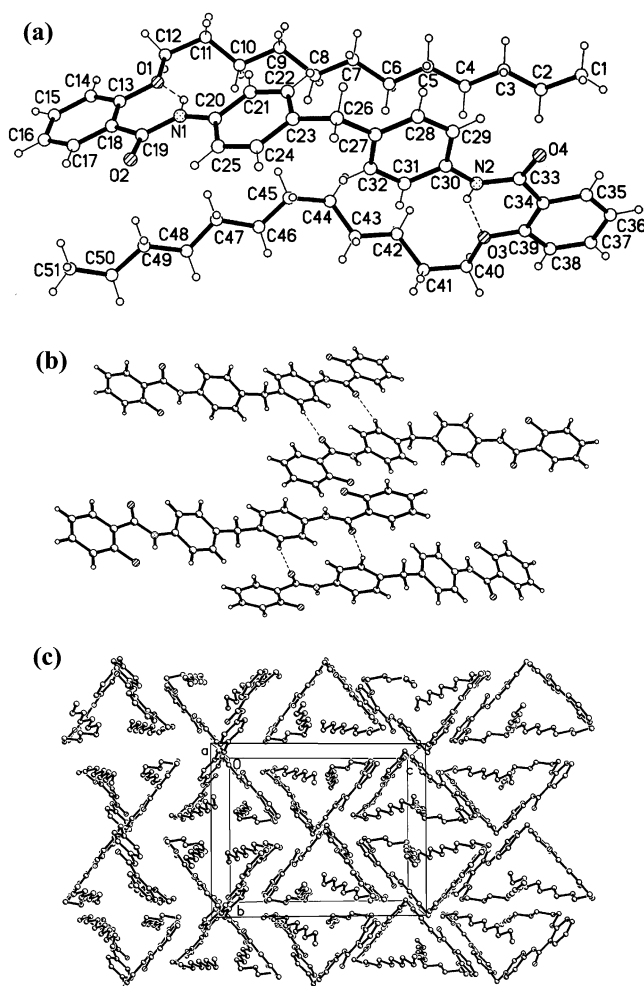


Figure 4. (a) Molecular structure with the atom numbering scheme of **3** (b) two independent dimers of **3** showing intermolecular C-H...O hydrogen bonds as dotted lines (viewed along the side ways, alkoxy side chains are omitted for clarity) and (c) the packing of X-shaped discrete dimers in the crystal lattice (the hydrogen atoms are omitted for clarity).

of **3**. This allowed the planarization of the two benzene rings connected to each amide group with a dihedral angle of ca. 6° . The angle $C23-C26-C27$ at the central methylene group is ca. 95° , smaller than the expected tetrahedral angle (Figure 4a). The two neighboring V-shaped molecules form a dimer via intermolecular C-H...O hydrogen bonds with $d(C\cdots O)$ of 3.321(5) Å between the $O=C<$ moiety of the amide group from one molecule and the hydrogen atom of the benzene ring of an adjacent diamide molecule (Figure 4b,c). The $\angle C-H\cdots O$ is ca. 158° . Interestingly, only one of the two diamide groups on the same molecule participates in the intermolecular C-H...O bond formation. No interdigitation of alkyl chains was observed in the lattice. The alkyl chains fold to fill the empty spaces inside the V-shaped molecule. To explore further the relationship between the flexibility of the molecule (i.e., spacer group) and the crystal structure, the methylene group in diamide **3** was replaced with an ethylene group in diamide **4**. Single crystals of **4** were grown and analyzed using single-crystal X-ray analyses.

Crystal Structure of *N,N*-bis-(2-dodecyloxybenzoyl)-4,4'-diaminodiphenylmethane (4**)**. Single crystals

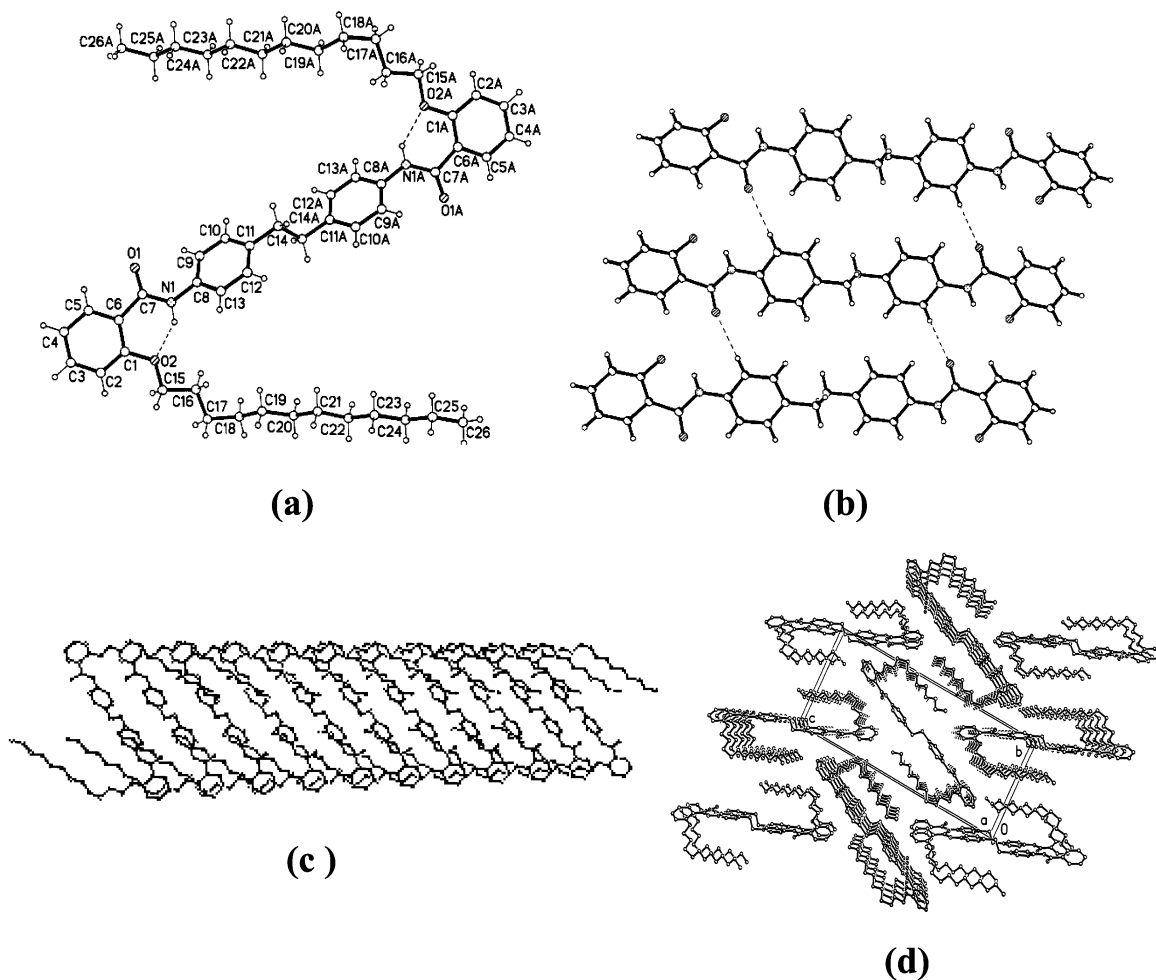


Figure 5. (a) Molecular structure of **4** with the atom numbering scheme, symmetry code: $-x + 1/2, y + 1/2, -z + 1/2$. (b) Intermolecular hydrogen bonding diagram between neighboring diamide molecules in the crystal lattice of **4**, dodecyl groups are omitted for clarity. (c) S-shaped column of 1D hydrogen-bonded network in the crystal lattice of **4** along the *a*-axis. (d) two orientations of S-shaped 1D hydrogen-bonded ribbons observed in the crystal lattice (view in the *bc* plane).

tals of **4** were obtained in tetrahydrofuran solution using the slow evaporation method at ambient conditions. Due to the flexibility of the ethylene spacer, the diamide **4** adopted a *trans* conformation at the center ethylene group in the crystal lattice and thus formed an S-shaped topology. Diamide **4** showed a crystallographic centrosymmetry with the center of inversion at the middle point of the C14–C14A bond (Figure 5a). All bond distances and angles in the molecule are normal. Selected geometric parameters for **4** are listed in Table 1. Crystal **4** gave a monoclinic crystal lattice with a $P2_1/n$ space group (Table 1).

Strong intramolecular hydrogen bonds between the hydrogen bond donor sites (N–H) of amide groups and the oxygen atoms of the ether moiety (e.g., N1–H1···O2 with $d(\text{N} \cdots \text{O})$ of 2.676 (3) Å and the $\angle \text{N} \cdots \text{H} \cdots \text{O}$ of ca. 133°) are observed on both ends of the molecule (Figure 5a).

The alkyl chains were folded toward the center of the molecule to form an S-shaped conformation in the crystal lattice. Intermolecular C–H···O hydrogen bonds with $d(\text{C} \cdots \text{O})$ of 3.362(5) Å and the $\angle \text{C} \cdots \text{H} \cdots \text{O}$ of ca. 167° were formed between the O=C< group of the amide moiety and the C–H of the benzene ring of an adjacent diamide molecules in the crystal lattice (Figure 5b). The

distance between two neighboring molecules along the columnar stack of the S-shaped molecules is ca. 4.8 Å (Figure 5c). All alkyl chains were organized parallel to each other to form a column, and such columns packed close to each other in the crystal lattice (Figure 5d). No strong interactions between the adjacent columns or alkyl chain interdigitation were observed. Due to the increased flexibility of the center ethylene group, both intermolecular C–H···O hydrogen bonds and the intramolecular N–H···O bonds were observed in the lattice.

It is clear that the incorporation of an ethylene group provided considerable flexibility for diamide **4** and the molecule adopted an S-shaped conformation in the crystal lattice. The flexible ethyl group at the center is in *anti* conformation and provides space for accommodating additional functional groups. This prompted us to explore the effect of lateral methyl groups attached to central benzene rings of **4**. We anticipated that the introduction of the methylene groups near the center ethylene bridge may freeze the conformational freedom of the molecule and influence the self-assembly in the crystal lattice.

Crystal Structure of *N,N*-bis-(2-dodecyloxybenzoyl)-4,4'-diamino-2,2'-dimethyldiphenyl-methane (5). Single crystals of **5** (Figure 6) were obtained

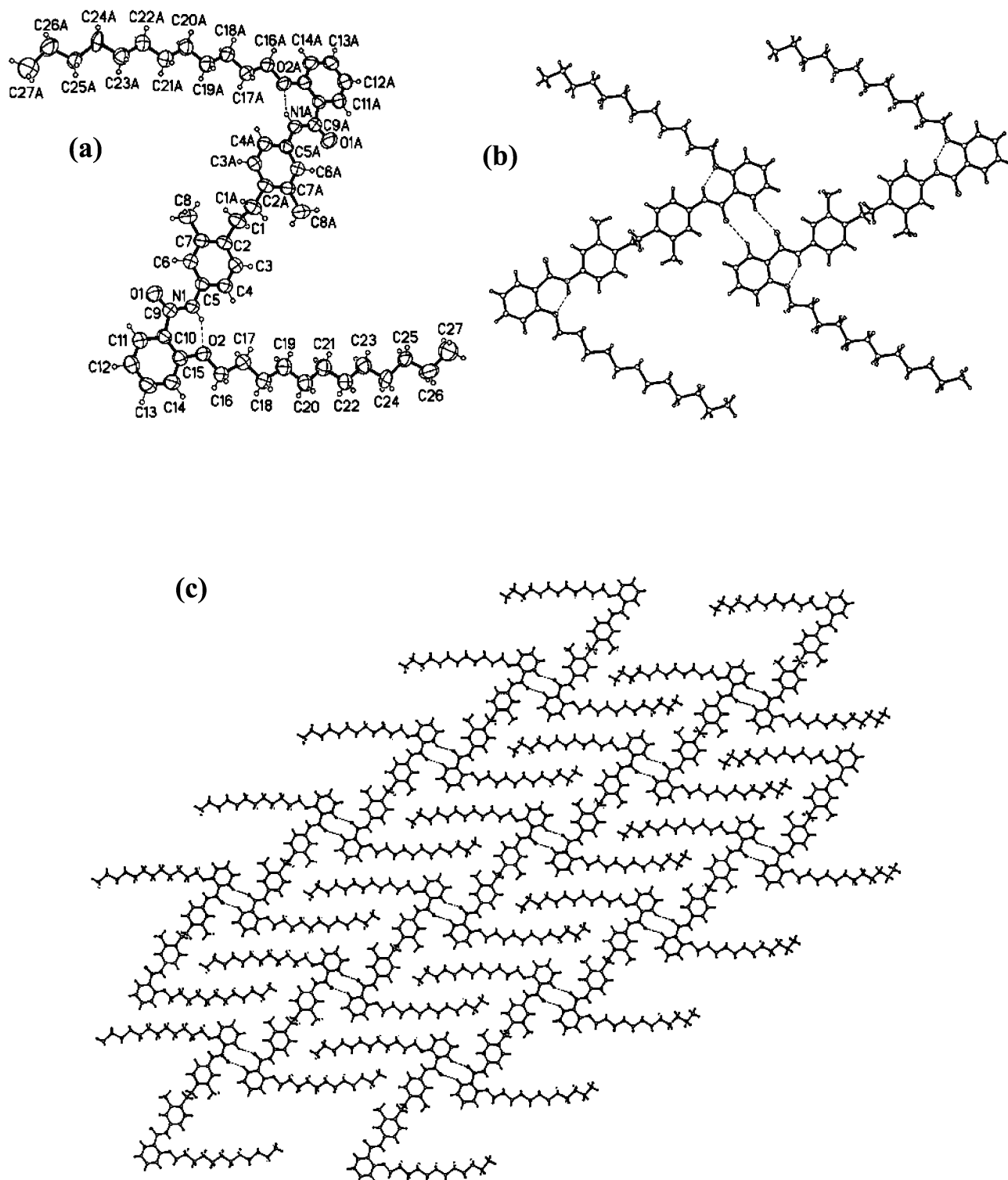


Figure 6. (a) ORTEP view of **5**, symmetry code: $-x, -y, -z$. Displacement ellipsoids are shown at the 50% probability level. (b) Intermolecular hydrogen bonding diagram between two neighboring diamide molecules in the crystal lattice of **5**. Broken lines denote hydrogen bonds. (c) The interdigitated **Z**-shaped 2D sheet of diamide **5** in the crystal lattice. Note the planarity and the close packed nature of the sheet.

from tetrahydrofuran solution using a slow evaporation method at ambient conditions. Selected geometric parameters for crystal **5** are listed in Table 1. The molecules adopted a more rigid **Z**-shaped conformation with a centrosymmetry and the center of inversion at the middle point of the C1–C1A bond. All bond distances and angles for the substituted benzene rings, methylene groups, methyl groups, ethylene groups, and

amide groups are normal. Crystal lattice of **5** formed a triclinic system with a $P\bar{1}$ space group (Table 1). Strong intramolecular hydrogen bonds such as N1–H1 \cdots O2 with $d(\text{N}\cdots\text{O})$ of 2.638(3) Å and the angle $\angle\text{N–H}\cdots\text{O}$ of ca. 140° between the hydrogen bond donor sites (N–H) of the amide group and the oxygen atom of the dodecyloxy group were observed in the crystal lattice (Figure 6b).

Two benzene rings connected to the amide group are organized in one plane with a dihedral angle of ca. 4° due to the presence of intramolecular N–H \cdots O hydrogen bonds. Diamide **5** showed Z-shaped rigid conformation in the solid lattice. Intermolecular hydrogen bonds of C–H \cdots O with $d(\text{C}\cdots\text{O})$ of 3.253(4) Å and the angle $\angle\text{C–H}\cdots\text{O}$ of ca. 147° are formed between the oxygen atom of the $>\text{C=O}$ group and the hydrogen atom of an adjacent benzene ring in the crystal lattice (Figure 6b). The linear alkoxy groups from adjacent hydrogen-bonded chains were interdigitated and crystallized to form a 2D sheet (Figure 6c). The difference between the molecular structure of **5** and **4** involve the incorporation of lateral methyl groups, which could fill the empty space in the crystal lattice. In the case of **4**, the benzene rings connected to the amide group were not coplanar. Also, the molecular packing inside the crystal lattice showed significant differences, from close packed S-shaped columns (**4**) to a planar 2D sheet (**5**) structure.

To understand the role of dodecyl chain (i.e., alkyl chain crystallization) in the self-assembly process, diamide **6** was synthesized with rigid and short benzyloxy groups as side chains and all other structural features of diamide **4**.

Crystal Structure of *N,N*-bis(2-benzyloxybenzoyl)-4,4'-diaminodiphenylethane (6**).** Single crystals of **6** were obtained from methanol solution using slow evaporation method at ambient conditions. All bond distances and angles in the substituted benzene rings, methylene groups, methyl groups, ethylene groups, and amide groups are normal. The single crystals showed a monoclinic lattice with a $C2/c$ space group (Table 1). All hydrogen atoms of the molecule were fixed at a given assigned positions.

The packing of the molecules inside the crystal lattice was not centrosymmetric with a C_2 symmetric center at the C21–C21A bond (Figure 7). Strong intramolecular hydrogen bonds such as N1–H1 \cdots O2 with $d(\text{N}\cdots\text{O})$ of 2.634(4) Å and the $\angle\text{N–H}\cdots\text{O}$ of ca. 140° between the N–H group of the amide moiety and the oxygen atom of the benzyloxy groups were observed in the crystal lattice (Figure 7b). Unlike the crystal structures of diamides **1–5**, the benzyloxy groups are organized on the same side of the molecule to give a ω -shape conformation in the crystal lattice.

Intermolecular C–H \cdots O hydrogen bonds with $d(\text{C}\cdots\text{O})$ of 3.234(5) Å and $\angle\text{C–H}\cdots\text{O}$ of ca. 150° were formed between the hydrogen bond acceptor site ($\text{O}=\text{C}<$) of the amide group and the hydrogen atom of the central benzene ring of the adjacent diamide molecule in the crystal lattice (Figure 7b). The intermolecular hydrogen bonds along the a -axis allow the molecules to form linear ribbon with a β -sheet topology (Figure 7c).

Similarities and Differences in the Self-Assembly of Diamides 1–6. Hydrogen Bonding. All diamides (**1–6**) were synthesized to investigate the role of hydrogen bonds, alkyl chain crystallization, and the rigidity of the spacer groups in the self-assembly processes. The symmetric molecules (**1–6**) contain rigid or flexible spacer groups between the two amide functional moieties. Single crystals were grown from various solvents and analyzed using single-crystal X-ray dif-

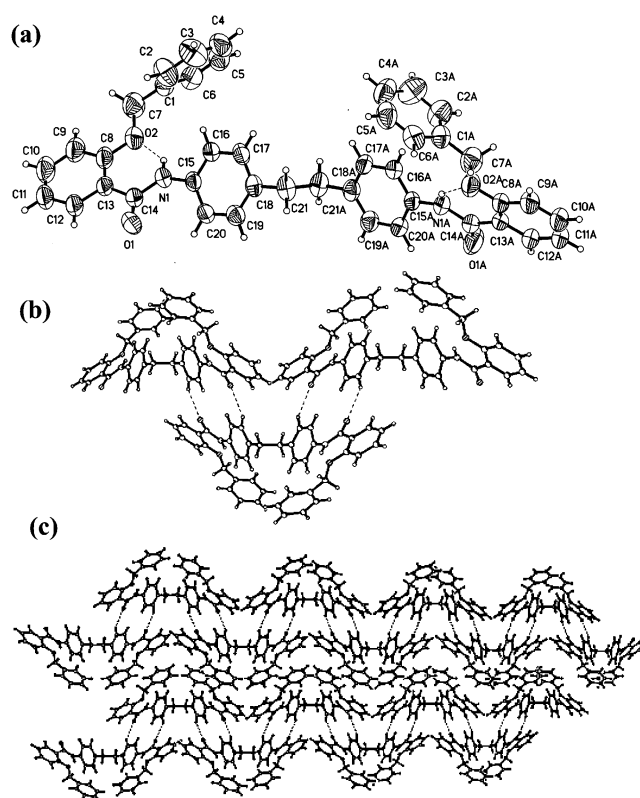


Figure 7. (a) ORTEP view of diamide **6** with atom numbering, symmetry code: $-x, y, -z + 1/2$. Displacement ellipsoids are shown at the 50% probability level. Broken lines denote hydrogen bonds. (b) Intermolecular hydrogen bonding between two neighboring diamide molecules in the crystal lattice of diamide **6**. (c) The β -sheet ribbons and the lattice packing of diamide **6** facilitated via intermolecular hydrogen bonding (viewed in the bc -plane).

Table 2. Intra- and Intermolecular Hydrogen-Bond Distances and Angle for Diamides **1–6**^a

| diamide | D–H \cdots A | D–H (Å) | H \cdots A (Å) | D \cdots A (Å) | $\angle\text{D–H}\cdots\text{A}$ ($^\circ$) |
|----------|----------------------------------|------------|---------------------|---------------------|--|
| 1 | N1–H1 \cdots O2 ⁱ | 0.860 | 2.121 | 2.855 (3) | 143 |
| 2 | N1–H1 \cdots O1 ⁱⁱ | 0.824 | 1.923 | 2.635 (4) | 144 |
| | C–H \cdots O | 1.012 | 2.475 | 3.381 (4) | 150 |
| 3 | N1–H1 \cdots O1 ⁱⁱⁱ | 0.860 | 1.900 | 2.632 (3) | 142 |
| | C–H \cdots O | 0.934 | 2.435 | 3.321 (5) | 158 |
| 4 | N1–H1 \cdots O2 ^{iv} | 0.860 | 2.018 | 2.676 (3) | 133 |
| | C–H \cdots O | 0.934 | 2.445 | 3.362 (5) | 167 |
| 5 | N1–H1 \cdots O2 ^v | 0.860 | 1.918 | 2.638 (3) | 140 |
| | C–H \cdots O | 0.934 | 2.434 | 3.253 (4) | 147 |
| 6 | N1–H1 \cdots O2 ^{vi} | 0.870 | 1.898 | 2.634 (4) | 140 |
| | C–H \cdots O | 0.942 | 2.549 | 3.234 (5) | 150 |

^a Symmetry codes: (i) $x, y + 1, z$ (ii) $-x + 1, -y + 1, -z$; (iii) $-x, 1/2 + y, 1/2 - z$; (iv) $-x + 1, -y + 2, -z$; (v) $-x + 1, -y + 1, -z + 1$; (vi) $-x + 1, y, -z + 1/2$.

fraction studies. In all cases, there were no solvent molecules incorporated in the crystal lattice.

All hydrogen bond distances and angles for diamides **1–6** are summarized in Table 2. In general, the observed intermolecular hydrogen bonds are longer than the intramolecular ones. In the crystal lattices of all diamide molecules, except **1**, intramolecular hydrogen bonds between the hydrogen bond donor sites (N–H) of amide moieties and oxygen atom of the ether groups were observed. Due to the flexibility of hexamethylene spacer in **1**, only intermolecular N–H \cdots O bonds were observed. The N \cdots O distances of the intramolecular hydrogen bonds in **2–6** range from 2.632(3) to 2.676(3)

Table 3. Structural Characters and Packing Arrangements of Diamides 1–6 in Solid State

| diamide | molecular conformation | rigidity of spacer | symmetry | packing arrangement |
|---------|------------------------|--------------------|----------------|---------------------|
| 1 | Z shaped | flexible | C_2 | column |
| 2 | Z shaped | rigid | centrosymmetry | 2D sheet |
| 3 | V shaped | semirigid | C_2 | dimer |
| 4 | S shaped | semirigid | centrosymmetry | column |
| 5 | Z shaped | rigid | centrosymmetry | 2D sheet |
| 6 | ω shaped | semirigid | C_2 | ribbon |

Å (Table 2, column 5), indicating the formation of strong hydrogen bonds. Another motif observed in the crystal lattice of 2–6 involves the observation of intermolecular C–H...O bonds between the hydrogen bond acceptor site (O=C<) of the amide group and the hydrogen atom of the benzene ring of the adjacent molecules.

Spacer Group. Different spacer groups such as hexamethylene, the 1,4-disubstituted benzene ring, and 4,4'-disubstituted diphenylethylene groups were incorporated into the two diamide moieties. Diamide 1 has a flexible hexamethylene spacer, whereas diamides 2–6 contain rigid or semirigid spacer groups. It is interesting to note that changing the spacer and keeping dodecyl groups in diamides (1–5) affected the strength and geometry of the hydrogen bond, molecular conformation, and packing of molecules in the lattice. The flexible hexamethylene spacer allows diamide 1 to pack in a column and form intermolecular hydrogen bonds between the adjacent molecules. In all other cases (2, 3, 4, 5, and 6), both intramolecular (N–H...O) and intermolecular (C–H...O) hydrogen bonding motifs (Table 2) and significant packing differences in the crystal lattice were observed. The molecular structure of diamides 4 and 5 are similar, except the presence of two lateral methyl groups in 5. However, this translates into a columnar structure in 4 to a planar 2D lattice structure in 5. It is conceivable that the two lateral methyl groups increase the rigidity of diamide 5 and force it to be planar. Interdigitation of alkyl chains gives rise to a planar 2D lattice. Unlike the trans conformation seen in the lattice of other diamides, 6 showed a syn arrangement of the short benzyl side groups. Some features of the packing of diamides in the crystal lattice are given in Table 3.

In the case of 2, the rigid 1,4-disubstituted benzene ring facilitated the diamide molecule to organize with a Z-shaped conformation. Diamide 3 adopted a V-shaped structure, possibly due to the tetrahedral angle at the central methylene group. In diamides 4 and 5, the central ethylene group allows the molecules to pack in a Z-shaped conformation. The lateral methyl groups attached to the spacer in diamide 5 was useful to fill the empty space as well as to reduce the rotational freedom around the central ethylene group. Diamide 6 is unique due to the absence of alkyl chains and the syn packing of benzyl groups.

Alkyl Chain Crystallization. In the crystal lattices of 1–5, the dodecyl groups were well organized and crystallized. For diamides 1, 2, 4, and 5, the side chains of the adjacent molecules interact in the 3D lattice and pack parallel to each other. Diamides 2 and 5 showed centrosymmetry with a Z-shaped arrangement in the crystal lattice. The intermolecular C–H...O hydrogen bonds facilitated the organization of the diamide molecules, and two neighboring 1D hydrogen-bonded chains

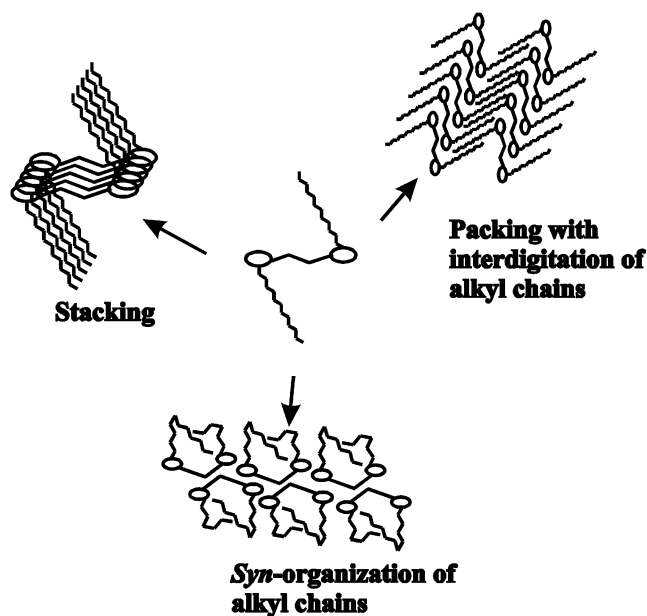


Figure 8. Schematic representation of the observed packing motifs of diamides 1–6 in the crystal lattice.

were closely packed due to the interdigitation of the alkyl chains of the dodecyl groups to form 2D sheets in the crystal lattice. No alkyl chain interdigitation was found in the crystal lattices of 1, 3, and 4. Diamide 4 gave an S-shaped 1D ribbon network without interdigitation of alkyl chain. Diamide 1 gave Z-shaped columns, while 3 formed X-shaped structures through the dimerization of two V-shaped individual molecules in the crystal lattice. Diamide 6 with no alkyl chains showed close packing of ω -shaped molecules giving a ribbon-type arrangement via C–H...O intermolecular hydrogen bonding. We did not observe significant disorder in the crystal lattices of diamides 1–6. A schematic representation of the observed molecular packing from our diamide building blocks is given in Figure 8.

Thermal properties of all the above crystals were analyzed using a differential scanning calorimeter, and only melting transitions were observed. Even though diamides 1–5 have both rigid segments and soft segments, they did not show mesophases.

Conclusions

The self-assembly of symmetric diamides 1–6 in the solid state were investigated using single-crystal X-ray diffraction techniques. Diamide 1 gave Z-shaped columns and diamide 3 showed X-type dimer in the crystal lattice. The Z-shaped self-assembled 2D sheets were formed in the crystal packing arrangements of diamides 2 and 5 via hydrogen bonding of amide groups and interdigitation of long alkyl chains. Diamide 4 gave S-shaped hydrogen-bonded columns in the crystal lattice, whereas 6 showed hydrogen-bonded ribbons of ω -shaped molecular structure using both intra- and intermolecular hydrogen bonds. The Z-shaped conformation (trans conformation) was favorable for the symmetric diamides, but this preference was subject to disruption by the geometric factors. Both intermolecular and intramolecular hydrogen bonds also influence the conformation of the individual molecules. Since the

dodecyl group is the same for diamides **1–5**, it is important to note that the changes in self-assembly observed in the crystal lattice could only be due to the nature (i.e., flexibility and length) of the spacer and the packing interactions. Since the final structure formed in the crystal lattice was the thermodynamically stable structure, optimal arrangements of molecules were obtained due to the interplay of multiple interactions such as hydrogen bonding, alkyl chain crystallization, π – π stacking interaction, rigidity of spacer groups, geometric properties of molecules, and packing forces in the crystal lattice.

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Supporting Information Available: Details of crystal coordinates and torsion angles for diamides **1–6** as a CIF file. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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