

Short Note

4-[(1,3-Benzothiazol-2-ylimino)methyl]phenyl Dodecanoate

Sie-Tiong Ha ^{1*}, Teck-Ming Koh ², Yip-Foo Win ¹ and Siew-Teng Ong ¹

¹ Department of Chemical Science, Faculty of Science, Universiti Tunku Abdul Rahman, Jln Universiti, Bandar Barat, 31900 Kampar, Perak, Malaysia

² Department of Science, Faculty of Engineering & Science, Universiti Tunku Abdul Rahman, Jln Genting Kelang, Setapak 53300 Kuala Lumpur, Malaysia

* Author to whom correspondence should be addressed; E-Mail: hast@utar.edu.my or hast_utar@yahoo.com.

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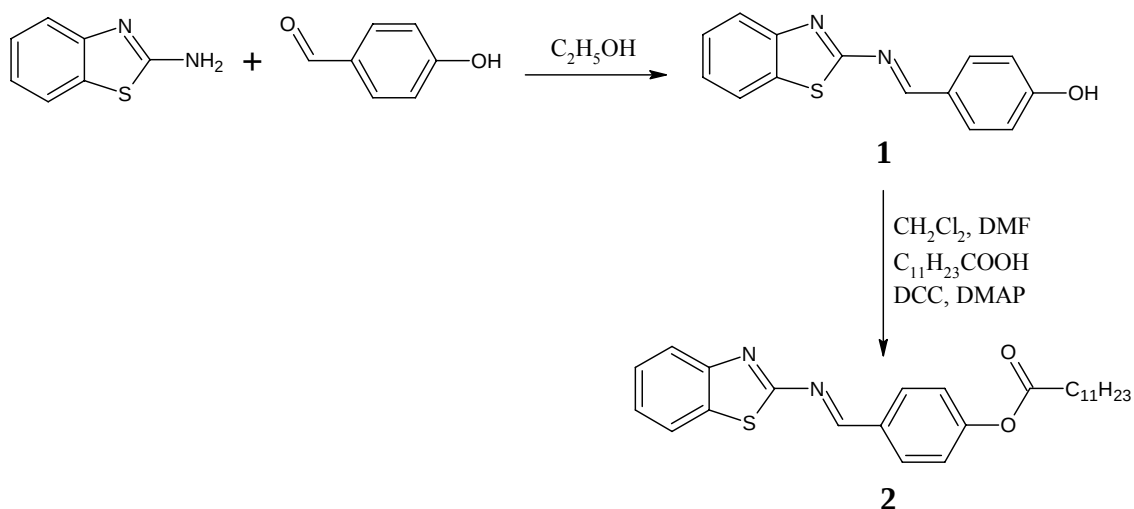
Abstract: A heterocycle, 4-[(1,3-benzothiazol-2-ylimino)methyl]phenyl dodecanoate, was synthesized and its IR, ¹H NMR, ¹³C NMR, elemental analysis and MS spectroscopic data are presented. This new compound exhibited smectic A phase.

Keywords: 4-[(1,3-benzothiazol-2-ylimino)methyl]phenyl dodecanoate; heterocyclic liquid crystal; smectic A

Schiff bases have attracted much attention ever since the discovery of the first room temperature liquid crystal, 4-methoxybenzylidene-4'-butylaniline [1]. Many kinds of heterocyclic structures, such as pyridine [2], furan [3], thiophene [4] and benzothiazole [5–7] have been introduced as core centre in liquid crystalline compounds. In this paper, we report the synthesis of a new Schiff base comprising the benzothiazole moiety: 4-[(1,3-benzothiazol-2-ylimino)methyl]phenyl dodecanoate. This new compound exhibits enantiotropic smectic A phase, as indicated by thermal (DSC) and polarizing optical microscopy studies.

In analogy to a recently published procedure [8], a solution of 2-aminobenzothiazole (6.01 g, 40 mmol) and 4-hydroxybenzaldehyde (4.88 g, 40 mmol) in absolute ethanol (60 mL) was heated under reflux for 3 h. The solvent was removed by slow evaporation and Schiff base **1** thus obtained was recrystallized from absolute ethanol. Then, Schiff base **1** (5.09 g, 20 mmol) in dimethylformamide (10 mL), was added to a solution of dodecanoic acid (4.01 g, 20 mmol) and 4-dimethylaminopyridine (1.22 g, 10 mmol) in dichloromethane (70 mL). The resulting mixture was stirred in an ice bath. To this solution, N,N'-dicyclohexylcarbodiimide (4.13 g, 20 mmol) in 10 mL of dichloromethane was

added dropwise while stirring in the ice bath for 1 h. The resulting mixture was subsequently stirred at room temperature for another 3 h. Then, the reaction mixture was filtered and the excess solvent was removed from the filtrate by evaporation. Recrystallization from absolute ethanol gave the Schiff base **1** as yellow solid (44%).

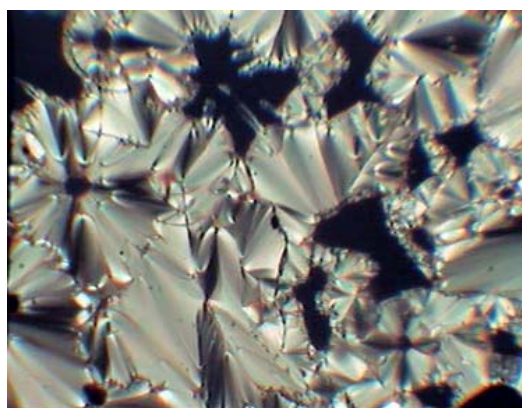


Thermal data obtained from DSC analysis (enthalpy changes, kJ mol^{-1} in bracket):

Heating: Crystal 80.8°C (45.07) Smectic A 85.6°C (7.44) Isotropic.

Cooling: Crystal 52.7°C (37.81) Smectic A 81.7°C (8.17) Isotropic.

Optical photomicrograph showing fan-shaped texture of smectic A phase observed under polarizing optical microscope:



MS (EI): $m/z = 436$ (M^+ , 9.2%), 254 (100), 225 (8.1), 57 (4.9), 43 (6.4).

IR (KBr, cm^{-1}): 3064, 3033 (C-H aromatic), 2922, 2851 (C-H aliphatic), 1747 (C=O ester), 1618 (C=N, imine), 1600 (C=N, thiazole), 1509 (C=C aromatic).

^1H NMR (400 MHz, CDCl_3): δ/ppm 0.88 (t, 3H, $J = 7.0$ Hz, CH_3 -), 1.27-1.43 (m, 16H, CH_3 -(CH_2) $_8$ - CH_2 -), 1.70-1.80 (q, 2H, $J = 7.3$ Hz, $-\text{CH}_2\text{-CH}_2\text{-COO-}$), 2.59 (t, 2H, $J = 7.6$ Hz, $-\text{CH}_2\text{-COO-}$),

7.25 (d, 2H, $J = 6.8$ Hz, Ar-H), 7.37 (t, 1H, $J = 8.3$ Hz, Ar-H), 7.48 (t, 1H, $J = 8.3$ Hz, Ar-H), 7.84 (d, 1H, $J = 8.1$ Hz, Ar-H), 7.99 (d, 1H, $J = 8.1$ Hz, Ar-H), 8.06 (d, 2H, $J = 6.8$ Hz, Ar-H), 9.05 (s, 1H, -N=CH-).

^{13}C NMR (100 MHz, CDCl_3): δ/ppm 171.7 (-COO-), 164.8 (C=N), 154.6, 151.6, 134.63, 134.6, 132.2, 131.5, 126.4, 125.1, 123.0, 122.3, 121.6 for aromatic carbons, 34.4, 31.9, 29.5, 29.4, 29.3, 29.2, 29.0, 24.8, 22.6 for methylene carbons [-COO-(CH₂)₁₀-CH₃], 14.1 (-CH₃).

Elemental analysis: Calculated for C₂₆H₃₂N₂O₂S: C, 71.52%, H, 7.39%, N, 6.42%; Found: C, 71.65%, H, 7.50%, N, 6.53%.

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