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Tsunehisa Okuno [a], Satoshi Ikeda [a], Natsuki Kubo [a] & Daniel J. Sandman [b]

[a] Department of Material Science and Chemistry, Wakayama University, Wakayama, Japan

[b] Department of Chemistry and Center for Advanced Materials, University of Massachusetts, Lowell, Massachusetts

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Tsunehisa Okuno
Satoshi Ikeda
Natsuki Kubo
Department of Material Science and Chemistry,
Wakayama University, Wakayama, Japan

Daniel J. Sandman
Department of Chemistry and Center for Advanced Materials,
University of Massachusetts, Lowell, Massachusetts

*Novel ynamine compounds, 5-hydroxy-1-(phenothiazine-10-yl)-1,3-pentadiyne (**1**), its S-oxide (**2**) and S-dioxide (**3**), were prepared. Compound **2** was found to show thermal reactivity to give polydiacetylene, however **1** and **3** did not show any reactivity. Compound **2** stacks along the c axis, forming a columnar structure. The condition of molecular arrangement satisfied Baughman's criterion. Significant intermolecular contact between the oxygen atoms of sulfoxide groups and the adjacent sulfur atoms was recognized.*

Keywords: crystal structure; hydrogen bond; phenothiazine; polydiacetylene; solid-state polymerization; ynamine

INTRODUCTION

Polydiacetylenes (PDAs), which are prepared by solid-state polymerization of diacetylenes [1], are attractive from the viewpoint of their physical properties such as nonlinear optics [2], conductivity [3] and magnetism [4]. It is said that one of the useful ways to increase the

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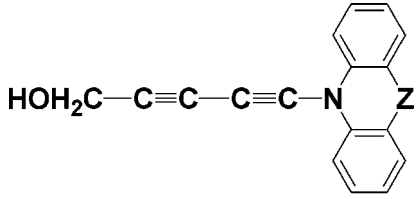
Address correspondence to Dr. Tsunehisa Okuno, Department of Material Science and Chemistry, Wakayama University, 930 Sakaedani, Wakayama 640-8510, Japan. E-mail: okuno@sys.wakayama-u.ac.jp

physical properties of PDAs is to expand the π-conjugated system. However the reactivity of polymerization is known to depend heavily on their crystal structures [5]. Therefore, in order to develop novel PDA systems, control of both crystal arrangement and electronic properties is required.

Diacetylene molecules which incorporate an ynamine moiety are thought to satisfy above mentioned conditions. The π-systems of the PDA backbone and its side chains are conjugated through a nitrogen atom. There are already two reports [6,7] concerning solid-state polymerization of ynamine-incorporating diacetylenes and they showed interesting properties.

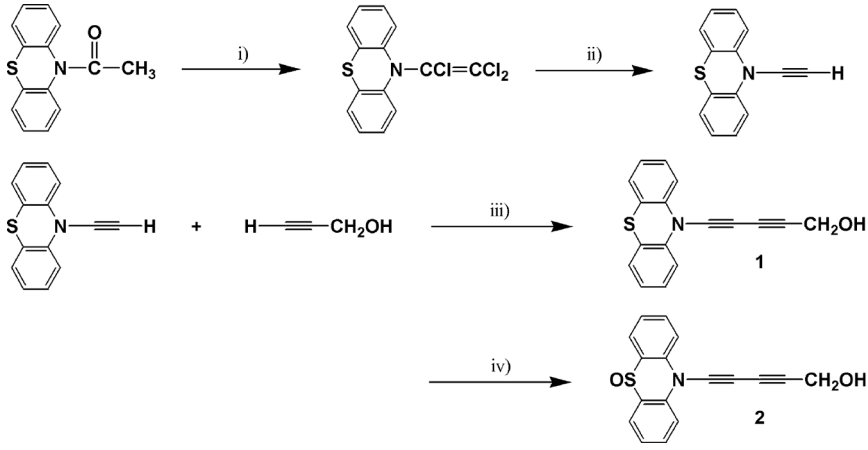
A phenothiazine moiety is also thought to have enough possibilities to satisfy the conditions. The moiety has a low oxidative potential, and is useful for crystal arrangement variations by the chemical modifications on the sulfur atom. We wish to report here preparation and solid-state reactivity of ynamine incorporating diacetylene **1**-**3** based on their crystal structures.



1: Z = S, 2: Z = SO, 3: Z = SO_2

RESULTS AND DISCUSSION

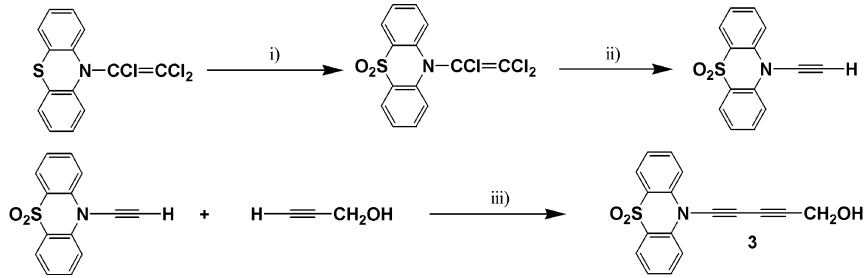
Preparations of compound **1**–**3** are shown in Schemes 1 and 2. Treatment of 10-acetylphenothiazine with phosphorus pentachloride afforded 10-(1, 2, 2-trichloroethenyl)phenothiazine in 44% yield. This compound was transformed into 10-ethynylphenothiazine by treatment of *n*-BuLi in THF. Compound **1** was obtained by an oxidative coupling reaction [8] between 2-propyne-1-ol and 10-ethynylphenothiazine. The oxidation reaction of **1** with hydrogen peroxide in ethanol to give compound **2** in 46% yield [9]. However, compound **3** was not prepared by the literature's method [9] because the ynamine moiety is not stable under acidic conditions. Compound **3** was prepared by an oxidative coupling reaction between 2-propyne-1-ol and 10-ethynylphenothiazine-5, 5-dioxide, which was prepared in 2 steps from 10-(1, 2, 2-trichloroethenyl)phenothiazine as shown in Scheme 2 [10].



SCHEME 1 Syntheses of diacetylene derivatives **1** and **2**. (i) PCl_5/Benzene; (ii) *n*-BuLi/THF, −78°C; (iii) O_2, CuCl, TMEDA/Acetone; (iv) H_2O_{2aq}/ethanol.

Compound **1** and **2** gave single crystals with sufficient quality for X-ray structural analysis. Crystal data of **1** and **2** are summarized in Table 1. Figure 1 shows the crystal structure of compound **1**. The phenothiazine moiety has a bent structure and the dihedral angle between two benzene rings is 141.2°. This value is almost the same that of a previously reported analog [11]. The central six-membered ring has a boat conformation. The structure around the nitrogen atom is almost planar [Fig. 1(a)].

The crystal packing is shown in Figure 1(b). The molecules make dimeric intermolecular hydrogen bonds. The distance between the two oxygen atoms is 2.65 Å, showing that the H-bond is rather strong. The dimers stack along the *b* axis. The crystal packing is



SCHEME 2 Synthesis of diacetylene derivative **3**. (i) H_2O_{2aq}/acetic acid; (ii) *n*-BuLi/THF, −78°C; (iii) O_2, CuCl, TMEDA/Acetone.

TABLE 1 Crystal Data of Compounds **1** and **2**

	1	**2**
Formula	$C_{17}H_{11}S_1O_1N_1$	$C_{17}H_{11}S_1O_2N_1$
Molar mass [g mol^{-1}]	277.34	293.34
Crystal system	Monoclinic	Triclinic
Space group	*C*2/*c*	*P*-1
a [Å]	38.791(8)	11.512(3)
b [Å]	7.738(6)	13.994(5)
c [Å]	9.208(7)	4.506(1)
α[°]	90	92.59(3)
β[°]	94.96(5)	101.00(2)
γ[°]	90	82.50(3)
Z	8	2
V [Å^3]	2753(2)	706.3(4)
ρ_{calcd} [Mgm^{-3}]	1.338	1.379
No. of reflections	2299	3640
No. of unique data	2156	3229
R1($I > 1\sigma(I)$, all data)	0.120, 0.282	0.064, 0.119
wR2($I > 1\sigma(I)$, all data)	0.048, 0.060	0.065, 0.073
Goof($I > 2\sigma(I)$, all data)	1.58, 1.26	1.51, 1.37

not appropriate for polymerization. Actually, compound **1** did not show solid-state reactivity. In order to control the crystal packing, introduction of S-O···S interaction by an oxidation of *S*-position was examined.

Figure 2 shows the crystal structure of compound **2**. The molecular structure is almost the same with that of compound **1** except for the dihedral angle of two benzene rings (Fig. 2(a)). The angle is 145°, which is slightly wider than that of compound **1**. The oxygen atom of sulfoxide group occupies an axial position. Molecules stack along the *c* axis making regular one-dimensional columns [Fig. 2(b)]. Stacking intervals of the molecules are 4.51 Å. The molecules incline about 49° with the stacking axis. The distance between C(13) and the adjacent C(16) is 3.64 Å. Intermolecular distance of S-O···S contact is 3.13 Å, which is shorter than the sum of van der Waals radii. The hydroxyl groups also make intermolecular hydrogen bonds with the oxygen atoms of sulfoxide groups. The distance is 2.72 Å, suggesting the bonds are not so weak, which reflects on the increase of melting point. The S-O···S short contact is reported in thianthrene 10-oxide derivatives or thioxanthone 10-oxide [12], however the position of the oxygen atoms are very different. The central six-membered rings of these three heterocyclic compounds usually have boat conformations. The oxygen atom of compound **2** occupied the axial position of

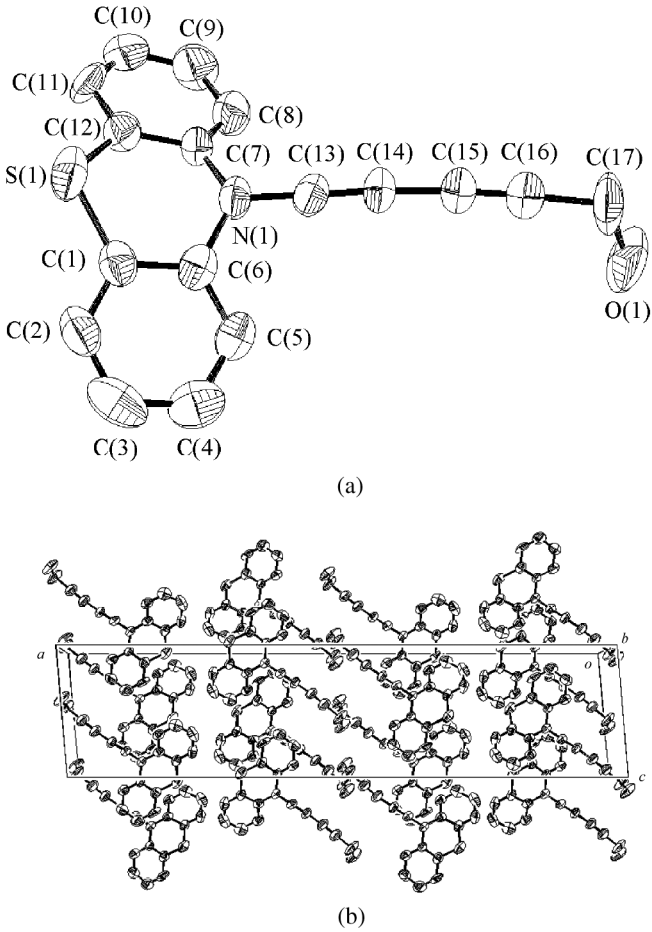


FIGURE 1 Crystal structure of the compound **1**: (a) Molecular structure (b) Unit cell viewed from the *b* axis.

the ring. But that of thianthrene or thioxanthone system occupies the equatorial one.

According to Baughman's suggestions [5], polymerization can proceed when the stacking intervals is between 4.8 Å and 5.6 Å, and the inclination angle is between 40° and 50°. Compound **2** satisfies this condition and has the possibility to polymerize in the solid state. Compound **2** showed polymerization reactivity by thermal annealing above 130°C or by irradiation. Thermal polymerization of **2** proceeded smoothly at 150°C. The monomer disappeared within 24 hours, and

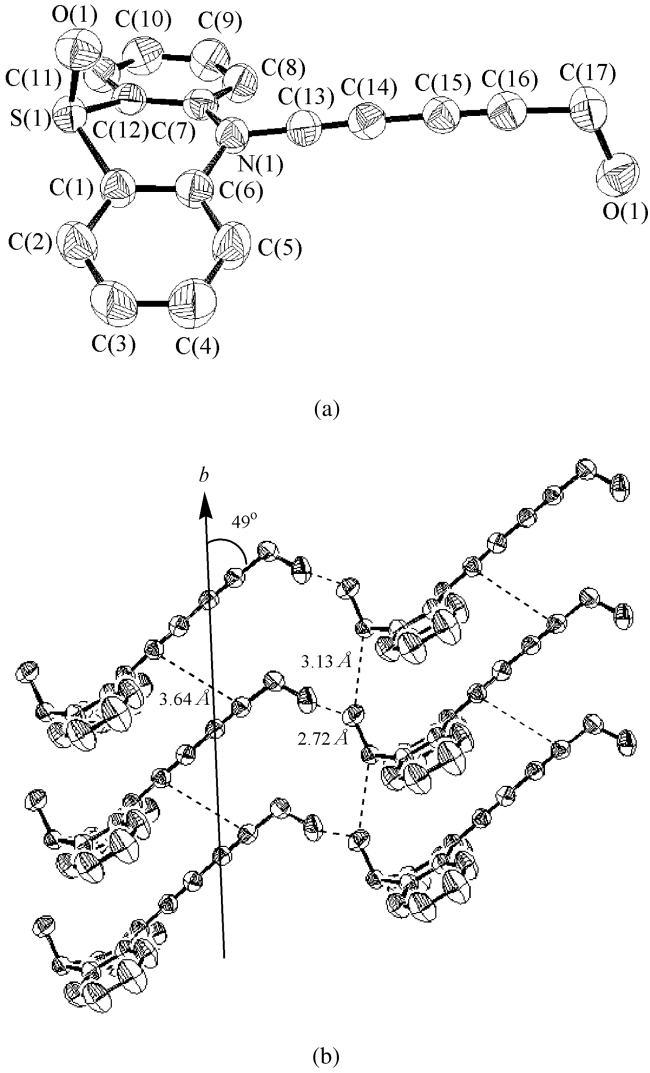


FIGURE 2 Crystal structure of the compound **2**: (a) Molecular structure (b) Molecular stacking along the *c* axis.

insoluble polymer was obtained. However, mostly monomer remained under UV or γ-ray irradiation. The conversion of the monomers was ca. 10% in both cases (UV: 24 hours, γ-ray: 50 Mrad). The lattice mismatch between the monomer crystal and the polymer one may suppress further polymerization. The electronic spectrum of the

polymer gave a broad band at around 630 nm, which was assigned to an excitonic transition.

In summary, we prepared novel three diacetylenes which incorporated ynamine moiety. We could succeed in structural analyses of **1** and **2**. Judging from the crystal structure, molecular stacking of **2** satisfies the Baughman's suggestions, and the compound showed polymerization reactivity. The short contact of S-O $\cdots$ S was found to play a crucial role in the molecular arrangement.

EXPERIMENTAL PART

General

Infrared spectra were recorded on a JASCO FT/IR-420 spectrometer with samples in compressed KBr discs. UV/Vis spectra were measured on a HITACHI U-2010 spectrometer. 1H and 13 C NMR spectra were measured on a JEOL JNM-AL300. Tetramethylsilane was used for an internal standard. Gel permeation chromatography (GPC) was performed on Japan Analytical Industry Co., Ltd. LC-918 equipped with JAIGEL 1H-2H. Melting point was measured on a Yanako Model MP and temperature was not corrected.

X-ray diffraction data were collected on RIGAKU AFC-5R automatic four-circle diffractmeter using graphite-monochromatic Mo Kα radiation. Crystal structures were solved by using Texsan. Anisotropic thermal parameters were introduced for all non-H atoms. Hydrogen atoms were not refined.

Synthesis

10-(1, 2, 2-Trichloroethenyl)phenothiazine

A benzene solution (40 ml) of 10-acetylphenothiazine (5.00 g, 20.7 mmol) and phosphorus pentachloride (8.62 g, 41.4 mmol) was refluxed for 48 hours under a nitrogen atmosphere. The solution was poured into water, and the organic layer was washed with aqueous Na_2CO_3 and water. It was dried over Na_2SO_4 and the filtrate was concentrated under reduced pressure. The residual oil was purified by column chromatography (SiO_2, hexane) to give colorless oil of 10-(1, 2, 2-trichloroethenyl)phenothizine. (2.91 g, 44%) mp. 67–70°C, ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.85 (*dd*, $J = 1.2$, 8.1 Hz, 2H), 6.96 (*ddd*, $J = 1.2$, 7.2, 8.1 Hz, 2H), 7.10 (*ddd*, $J = 1.8$, 7.2, 7.7 Hz, 2H), 7.30 (*dd*, $J = 1.8$, 7.7 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 115.8, 121.4, 124.4, 126.9, 127.4, 127.7, 129.8, 138.9.

10-Ethynylphenothiazine

To a THF solution (30 ml) of 10-(1, 2, 2-trichloroethenyl)phenothizine (1.00 g, 3.04 mmol) was added dropwise a hexane solution of *n*-butyllithium (7.60 mmol, l, 4.44 ml) at −78°C for 30 minutes. The solution was stirred for 2 hours at −78°C, and allowed to warm to room temperature. The solution was poured into water, and extracted twice with ether. The organic layer was washed with brine, and dried over Na_2SO_4. After filtration, an evaporator removed the solvent. Since the compound was not stable in the solid state, purification was not attempted. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.30(*s*, 1H), 7.01 (*ddd*, $J = 1.2$, 7.5, 8.7 Hz, 2H), 7.10 (*dd*, $J = 1.5$, 7.5 Hz, 2H), 7.20 (*ddd*, $J = 1.5$, 8.1, 8.7 Hz, 2H), 7.46 (*dd*, $J = 1.2$, 8.1 Hz, 2H).^{13}C NMR (75 MHz, $CDCl_3$): δ 62.0, 76.7, 117.5, 122.8, 124.8, 126.9, 127.5, 139.9. IR (KBr/cm^{-1}): 3297($\nu_{\equiv C\text{-}H}$), 2131($\nu_{C\equiv C}$).

5-Hydroxy-1-(Phenothiazine-10-yl) 1, 3-Pentadiyne (1)

A suspension of CuCl (0.25 g, 2.55 mmol) in acetone (15 ml) was stirred under an argon atmosphere. After an addition of *N*, *N*, *N*′, *N*′-tetramethylethylenediamine (0.11 ml, 0.75 mmol) to the suspension and it was stirred for 30 minutes. The supernatant was added dropwise to an acetone solution of 10-ethynylphenothiazine (0.20 g, 0.89 mmol) and 2-propyne-1-ol (0.60 g, 10.74 mmol) under an argon atmosphere. Then the solution was stirred for 24 hours under an oxygen atmosphere. It was poured into water and extracted several times with benzene. The combined benzene solution was washed with water, ammonium hydroxide (4%) and water. It was dried over Na_2SO_4. After filtration, the filtrate was evaporated to dryness under reduced pressure. The residue was purified by the use of GPC to give a white powder of compound **1**. (0.11 g, 46%) mp. 134°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ1.71 (*t*, $J = 6.2$ Hz, 1H), 4.46 (*d*, $J = 6.2$ Hz, 2H), 7.05 (*dt*, $J = 1.2$, 7.8 Hz, 2H), 7.12 (*dd*, $J = 1.2$, 7.8 Hz, 2H), 7.21 (*dt*, $J = 1.2$, 7.8 Hz, 2H), 7.42 (*dd*, $J = 1.2$, 7.8 Hz, 2H). ^{13}C NMR: δ 51.9, 60.1, 70.6, 72.6, 81.6, 117.9, 123.2, 125.4, 127.0, 127.6, 139.1.

5-Hydroxy-1-(Phenothiazine-5-Oxide-10-yl) 1, 3-Pentadiyne (2)

Compound **1** (0.28 g, 1.01 mmol) was dissolved in 10 ml of ethanol. Hydrogen peroxide solution (0.90 ml, 5.8 mmol) was added dropwise to the solution, and it was refluxed for 10 hours. The solution was poured into hot water, and allowed to stand for 1 day to give colorless needles of compound **2**. (0.20 g, 67%) mp. 165–168°C. ^{1}H NMR (300 MHz,$CDCl_3$): δ 2.18 (*s*, 1H), 4.43 (*s*, 2H), 7.42 (*ddd*, $J = 1.2$, 7.2, 7.8 Hz, 2H), 7.70 (*ddd*, $J = 1.5$, 7.2, 8.4, 2H), 7.95 (*dd*, $J = 1.2$, 8.4, 2H), 7.96 (*dd*, $J = 1.5$, 7.8,

2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 51.9, 60.1, 70.54, 72.6, 81.6, 117.9, 123.3, 125.4, 127.0, 127.6, 139.1. IR (KBr/cm^{-1}): 2251 ($\nu_{C\equiv C}$), 3260 (ν_{OH}).

10-(1, 2, 2-Trichloroethenyl)phenothiazine-5, 5-Dioxide

Hydrogen peroxide solution (3.0 ml, 20 mmol) was added to a solution of 10-(1, 2, 2-trichloroethenyl)phenothiazine (6.57 g, 20.0 mmol) in acetic acid (67 ml). The solution was refluxed for 30 minutes and poured into water to give white precipitate. The precipitate was filtered off and recrystallized from ethanol to afford white powder. (4.15 g, 58%) ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.85 (*ddd*, $J = 1.2$, 7.8, 8.7 Hz, 2H), 7.05 (*dd*, $J = 1.5$, 7.8 Hz, 2H), 7.20 (*ddd*, $J = 1.5$, 8.1, 8.7 Hz, 2H), 7.46 (*dd*, $J = 1.2$, 8.1 Hz, 2H).

10-Ethynylphenothiazine-5, 5-Dioxide

To a THF solution (200 ml) of 10-(1, 2, 2-trichloroethenyl)phenothizine-5, 5-dioxide (6.60 g, 20.0 mmol) was added dropwise a hexane solution of *n*-butyllithium (50.6 mmol, 29.6 ml) at −78°C for 30 minutes. The solution was stirred for 2 hours at −78°C, and allowed to warm to room temperature. The solution was poured into water, and extracted twice with ether. The organic layer was washed with brine, and dried over Na_2SO_4. After filtration, an evaporator removed the solvent. Since the compound was not stable in the solid state, purification was not executed. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.30 (*s*, 1H), 7.01 (*ddd*, $J = 1.2$, 7.8, 8.7 Hz, 2H), 7.10 (*dd*, $J = 1.5$, 7.8 Hz, 2H), 7.20 (*ddd*, $J = 1.5$, 8.1, 8.7 Hz, 2H), 7.46 (*dd*, $J = 1.2$, 8.1 Hz, 2H).

10-(5-Hydroxy-1, 3-Pentadiynyl)phenothiazine-9, 9-Dioxide (3)

A suspension of CuCl (5.0 g, 51.0 mmol) in acetone (300 ml) was stirred under an argon atmosphere. After an addition of *N*, *N*, *N*′, *N*′-tetramethylethylenediamine (2.20 ml, 15.0 mmol) to the suspension, it was stirred for 30 minutes. The supernatant was added dropwise to an acetone solution of 10-ethynylphenothiazine (5.10 g, 20.0 mmol) and 2-propyne-1-ol (11.58 g, 0.206 mol) under an argon atmosphere. Then the solution was stirred for 24 hours under an oxygen atmosphere. It was poured into water and extracted several times with benzene. The combined benzene solution was washed with water, ammonium hydroxide (4%) and water. It was dried over Na_2SO_4. After filtration, the filtrate was evaporated to dryness under reduced pressure. The residue was purified by the use of GPC to give a white powder of compound **3**. (1.52 g, 27%) mp. 180–182°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.71 (*t*, $J = 6.2$ Hz, 1H), 4.46 (*d*, $J = 6.2$ Hz, 2H), 7.05 (*dt*, $J = 1.2$, 7.5 Hz, 2H), 7.12 (*dd*, $J = 1.5$, 7.5 Hz, 2H), 7.21 (*dt*, $J = 1.5$, 7.5 Hz,

2H), 7.42 (*dt*, $J = 1.5$, 7.5 Hz, 2H). ^{13}C NMR: δ 51.7, 63.5, 67.7, 69.1, 83.2, 118.1, 123.7, 125.3, 125.8, 133.7, 138.1.

Supplementary Data

Supplementary data are available, upon request, from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, quoting the deposition numbers 282618 and 282619.

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