Solvent-free Friedel-Crafts Reaction for Regioselective Synthesis of Ethyl (9-Anthryl)glyoxylate and Chiral Resolution of (±)-(9-Anthryl)hydroxyacetic Acid

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A green chemistry-based highly regioselective synthesis of ethyl (9-anthryl)glyoxylate was achieved by solvent-free Friedel-Crafts reaction at r. t. Several derivatives of ethyl (9-anthryl)glyoxylate were also synthesized. Ethyl (9-anthryl)hydroxyacetate was obtained almost quantitatively by reduction of ethyl (9-anthryl)glyoxylate with $NaBH_4$, and (9-anthryl)methoxyacetic acid was prepared by methylation of ethyl (9-anthryl)hydroxyacetate with CH_3I in the presence of Ag_2O and hydrolysis of ethyl (9-anthryl)methoxyacetate. The hydrolysis of ethyl (9-anthryl)hydroxyacetate gave racemic (9-anthryl)hydroxyacetic acid, and the racemate was successfully resolved by crystallization of the diastereomeric salts resulting from the reaction of (±)-(9-anthryl)hydroxyacetic acid with (–)-ephedrine. As a byproduct, crystals containing racemic (±)-(9-anthryl)hydroxyacetate and protonated (–)-ephedrine were isolated and their structures determined by X-ray diffraction.

Key words: Ethyl (9-Anthryl)glyoxylate, (9-Anthryl)hydroxyacetic Acid, Regioselectivity, Chiral Resolution, X-Ray Structure Analysis

Introduction

In the last decade, the interest in determining the absolute stereochemistry of chiral organic compounds stems from the widely recognized fact that the stereochemistry often determines important chemical, physical, biological, and pharmaceutical properties of the compounds [1]. Several instrumental methods exist for the determination of the absolute configuration of chiral organic compounds, such as X-ray crystallography and chirooptical methods *etc*. Due to appealing advantages based on NMR spectroscopy for these researches, the chiral recognition by NMR known as the "Mosher method" is widely used [2, 3]. The method uses α-methoxy-α-trifluoromethyl-α-phenylacetic acid as the chiral derivatizing reagent for the determination of the absolute configuration of secondary alcohols by NMR [4]. Many efforts to develop chiral derivatizing agents [5] that are useful to assign the absolute configuration of different substrates have been described [6, 7], and arylmethoxyacetic acids (see Fig. 1) containing naphthyl or anthryl systems [8 – 11] are widely used to assign the absolute configuration of chiral organic compounds by NMR with a modified Mosher method [12].

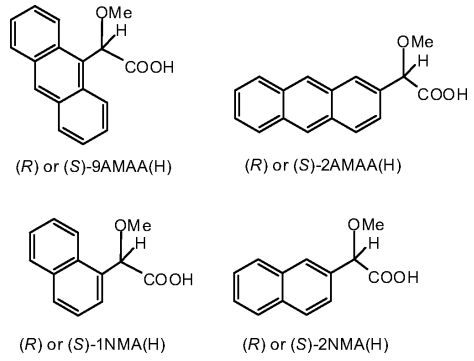
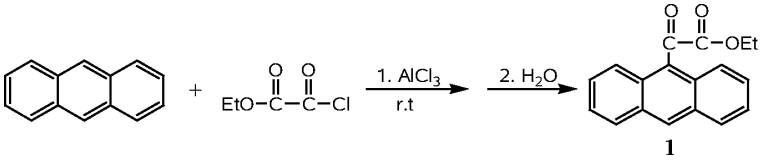


Fig. 1. Structure of some arylmethoxyacetic acids.

In general, all these compounds cause a larger magnetic shielding than α-methoxy-α-phenylacetic acid which was used as the chiral derivatizing reagent in the past [9, 13], thus better separation of the signals in ^{1}H NMR spectra is observed for the enantiomers of a substrate. This effect is particularly important when enantiomerically pure (9-anthryl)methoxyacetic acid (9AMAA(H)) or ethyl (9-anthryl)hydroxyacet-



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Scheme 1. Synthesis of ethyl (9-anthryl)glyoxylate.

ate (9AHA) are used to assign the absolute configuration of α-chiral secondary alcohols and α-chiral primary amines or α-chiral carboxylic acids by comparing the ^{1}H NMR spectra of the diastereomeric products from the reaction of these chiral substrates with (*R*)- and (*S*)-9AMAA(H), or (*R*)- and (*S*)-9AHA, respectively. The $\Delta\delta^{RS}$ values obtained are 3 – 4 times higher than those with other chiral derivatizing reagents [13]. Therefore, simple and effective methods for the synthesis of the excellent chiral derivatizing reagents 9-AMAA(H), 9-AHA and acquirement of their pure enantiomers are required. In this paper we present an efficient solvent-free Friedel-Crafts reaction for a highly regioselective synthesis of ethyl (9-anthryl)glyoxylate (**1**), a precursor of 9AHA and 9AMAA(H), and the chiral separation of its derivative (9-anthryl)hydroxyacetic acid (9AHAA(H)) using chemical methods, in order to supply an important auxilliary for preparing pure (*R*)- and (*S*)-9AMAA(H), and (*R*)- and (*S*)-9AHA.

Results and Discussion

*The synthesis of ethyl (9-anthryl)glyoxylate (**1**) and its derivatives **2** – **5***

Ethyl (9-anthryl)glyoxylate is the precursor of 9AHA and 9AMAA(H). Though Riguera *et al.* have reported that **1** can be prepared from anthracene and ethyl oxalyl chloride [13], they have not described the procedure in detail and have not mentioned whether the reaction was conducted in solution or in the solid phase. We attempted to find a convenient and environmentally friendly way to prepare the precursor of these reagents. Initially, we synthesized **1** using the traditional liquid method. Due to low solubility of anthracene in most organic solvents, it was found that this synthesis method exhibited some drawbacks: the use of noxious organic solvents, such as CS_2 *etc.*, a big reaction volume, the long reaction time and the low yield ($< 10\,\%$). In addition, some byproducts, such as ethyl (1-anthryl)glyoxylate and ethyl (2-anthryl)glyoxylate, were found.

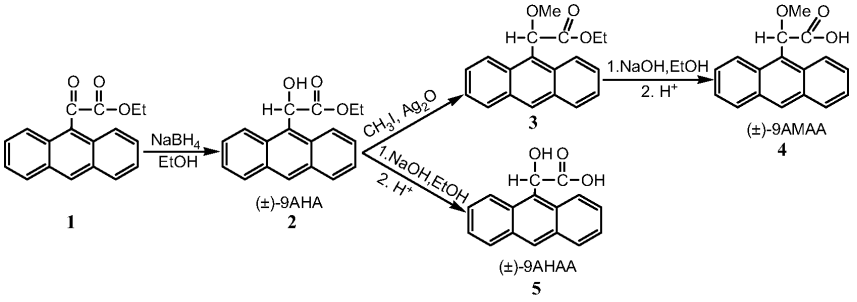
In the face of demands for green and ecologically friendly organic synthesis, solvent-free techniques hold a strategic position as solvents are very often toxic, expensive, problematic to use and to remove. In the absence of solvent, however, reaction pathways, as well as the products formed, may be modified significantly. Ghiaci *et al*. reported that a solvent-free reaction can shorten the reaction time and increase the yield [14]. In order to avoid the drawbacks of the traditional synthesis in liquid phase, our laboratory adopted the method of the solvent-free Friedel-Crafts acylation reaction of anthracene to prepare **1** (Scheme 1).

Initially, the yield (30 – 40 %) was not as high as expected, but we found that when 0.2 – 0.5 equivalents of 1-methyl-2-pyrrolidone were added to the reaction system as an assistant catalyst, a highly regioselective synthesis of **1** was achieved in 92.5 % yield without producing other isomers, such as ethyl (1-anthryl)glyoxylate and ethyl (2-anthryl)glyoxylate. In previous reports, most Friedel-Crafts acylation reactions were conducted in organic solvents. Our method is an efficient solvent-free Friedel-Crafts acylation reaction which can be performed successfully at r. t.

We used the reduction of **1** to obtain 9AHA (**2**), then transformed 9AHA to 9AMAA(H) (**4**) and 9AHAA(H) (**5**) by methylation and hydrolysis reactions (Scheme 2). Compound **1** was reduced almost quantitatively with $NaBH_4$in EtOH at r. t. to give racemic 9AHA. Ethyl (9-anthryl)methoxyacetate was prepared by methylation of 9AHA(H) with CH_3I in the presence of Ag_2O. 9AMAA(H) and 9AHAA(H) were obtained by hydrolysis of their precursors. All these reactions were achieved in high yield.

*Resolution of racemic 9AHAA (**5**) by crystallization with (–)-ephedrine*

Several methods exist for the resolution of racemates, such as separation by chiral chromatography, enzymatic resolution and separation *via* diastereomeric adducts *etc.* [15]. We attempted to use inexpensive (–)-ephedrine, a natural chiral alkaloid, as a resolving agent to separate racemic 9AMAA(H) and racemic 9AHAA(H) *via* diastereomeric salts formed in the reactions of these racemates with (–)-ephedrine, respectively. Unfortunately, optically pure 9AMAA(H)



Scheme 2. Synthesis of the derivatives of ethyl (9-anthryl)glyoxylate.

could not be obtained by this method, but racemic 9AHAA(H) was successfully isolated. When equivalents of racemic 9AHAA(H) and (–)-ephedrine were refluxed in ethanol and subsequently cooled to r. t., the salt of $[(+)\text{-}9AHAA]^-$ with $[(-)\text{-ephedrine(H)}]^+$ could be precipitated as a yellow solid. The optically pure (+)-9AHAA(H) was obtained by acidification of the aqueous solution of the salt $[(+)\text{-}9AHAA]^-$ $[(-)\text{-ephedrine(H)}]^+$ due to its water solubility. The successful resolution has been confirmed by chiral capillary electrophoresis. Though (+)-9AHAA(H) is not a new chiral compound, its specific rotation was not reported. We found its $[\alpha]_D^{20}$ to be $+169°$ ($c = 0.2197$, methanol).

Crystal structure of $[(\pm)\text{-}9AHAA]^-$ $[(-)\text{-ephedrine(H)}]^+ \cdot 0.5H_2O$

After filtering off the crystals of the salt $[(+)\text{-}9AHAA]^-$ $[(-)\text{-ephedrine(H)}]^+$, crystals containing racemic $[9AHAA]^-$ with $[(-)\text{-ephedrine(H)}]^+$ were obtained from the mother liquid by slow evaporation of the solvent at r. t. These crystals were recrystallized from 95 % ethanol to give light-yellow single crystals of composition $[(\pm)\text{-}9AHAA]^-$ $[(-)\text{-ephedrine(H)}]^+ \cdot 0.5H_2O$ suitable for X-ray diffraction analysis. The structure determination revealed that racemic 9AHAA anions, two protonated ephedrine cations and a water molecule combine into a structural unit (Fig. 2). The compound crystallizes in the non-centrosymmetric space group $P2_1$ with $Z = 4$. The peculiar composition makes it necessary that there are two crystallographically independent anions of $[(\pm)\text{-}9AHAA]^-$ with opposite chirality while two independent homochiral $[(-)\text{-ephedrine(H)}]^+$cations are their counterparts. As Fig. 2 shows, these molecules are grouped together in a tight arrangement in which the heterochiral $[(\pm)\text{-}9AHAA]^-$ anions seem to be related by a non-crystallographical center of inversion whereas the homochiral ephedrine cations obviously

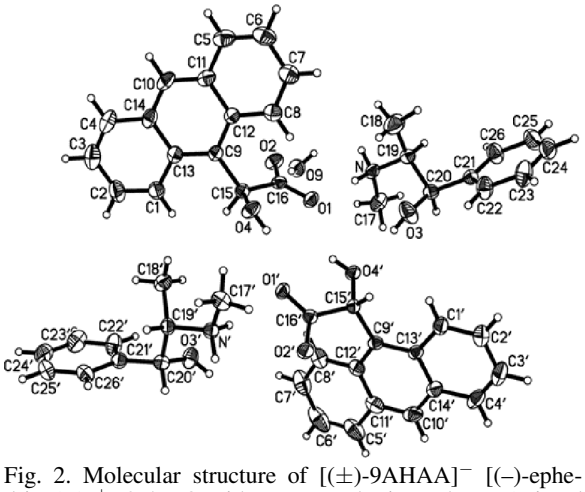


Fig. 2. Molecular structure of $[(\pm)\text{-}9AHAA]^-$ $[(-)\text{-ephedrine(H)}]^+ \cdot 0.5H_2O$ with atom-numbering scheme (primed atoms are used to number the crystallographically independent ions).

are prohibitive for a center of inversion. This assembly is completed by the water molecule, also shown in Fig. 2, which only occurs once.

In the 9AHAA anion, both the plane of the carboxylate group and the plane of the anthracene ring form a dihedral angle of 68.8°. In the crystal, intermolecular H bonds together with the electrostatic interactions of 9AHAA anions and protonated ephedrine cations assemble anion, cation, and water molecules into a three-dimensional network. These H bond interactions are presented in Fig. 3, and the respective parameters are listed in Table 1.

Experimental Section

Reagents and techniques

Anthracene was bought from Alfa Aesar (98 %), the other chemicals were analytical grade reagents. The NMR spectra were recorded with a Bruker AVANCE300 spectrometer at 300 MHz for ^{1}H and at 75 MHz for ^{13}C. Chemical

Table 1. H bond geometry (Å, deg) in the crystal of $[(\pm)\text{-9AHAA}]^-$ $[(-)\text{-ephedrine(H)}]^+ \cdot 0.5H_2O$.

D–H···*A*	*D*–H	H···*A*	*D*···*A*	*D*–H···*A*
O4–H4O···O1′	0.82	2.05	2.827(3)	158.0
O4′–H4′O···O1	0.82	2.08	2.776(2)	143.0
O3–H3O···O4′	0.82	2.00	2.795(3)	163.6
O3′–H3′O···O9	0.82	1.93	2.744(3)	171.2
N–HOA···O1	0.90	1.86	2.750(3)	168.1
N–HOB···O2′	0.90	1.83	2.729(3)	172.5
N′–H′B···O1′	0.90	2.19	2.994(3)	148.6
N′–H′A···O2	0.90	1.85	2.750(3)	178.1
O9–H9OA···O2	0.839(10)	1.945(18)	2.758(3)	163(5)
O9–H9OB···O2′	0.829(10)	2.28(3)	2.921(3)	135(4)

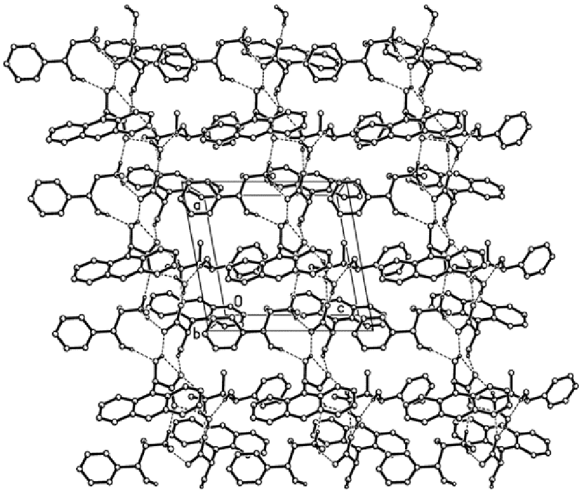


Fig. 3. Intermolecular H bonds in the crystal of $[(\pm)\text{-9AHAA}]^-$ $[(-)\text{-ephedrine(H)}]^+ \cdot 0.5H_2O$; the H bonds are indicated by dashed lines; some H atoms were omitted for clarity.

shifts are reported in ppm using TMS as an internal standard. The IR spectra were recorded with a Nicolet 170SX FT-IR spectrometer using KBr pellets. Elemental analyses were performed with a VarioEL CHNS Elementaranalysensystem. The optical rotations were measured with a JASCO-20C polarimeter. The melting points (uncorrected) were determined using a WRS-113 digital melting point instrument.

*Ethyl (9-anthryl)glyoxylate (**1**)*

A mixture of anthracene (17.82 g, 0.10 mol), anhydrous $AlCl_3$ (26.67 g, 0.20 mol) and 1-methyl-2-pyrrolidone (1.98 g, 0.02 mol) was triturated in a porcelain mortar placed in an anhydrous operator chest with change-color silica gel for absorbing moisture and as a moisture indicator, and solid NaOH for absorbing the HCl gas released from the reaction process. To the mixture was added ethyl oxalyl chloride (20.48 g, 0.15 mol) at 3 – 6 drops per minute with adequate trituration. After allowing the dark green mixture to react for 4.5 h, crushed ice (130.00 g) was added. After the ice had thawed, the mixture was filtered to give a brown solid raw product **1**. It was recrystallized from acetone to yield a yellow solid **1** (25.70 g, 92.5 % yield). M. p. 83.8 – 84.7 °C. – ^{1}H NMR (300 MHz, [D$_6$]-acetone): δ = 1.30 (t, 3 H), 4.37 (q, 2 H), 7.61 (m, 2 H), 7.67 (m, 2 H), 7.99 (m, 2 H), 8.19 (m, 2 H), 8.79 (t, 1 H). – ^{13}C NMR (75 MHz, [D$_6$]-acetone): δ = 14.3, 63.5, 124.8, 126.8, 129.1, 130.0, 130.1, 131.2, 131.9, 132.1, 162.8, 193.1. – IR (KBr): ν = 3051, 2948, 2301, 1725, 1600, 1451, 1400, 1302, 1250, 1100 cm^{-1}. – $C_{18}H_{14}O_3$ (278.30): calcd. C 77.68, H 5.07; found C 77.74, H 4.97.

Table 2. Crystal and structure refinement data for $[(\pm)\text{-9AHAA}]^-$ $[(-)\text{-ephedrine(H)}]^+ \cdot 0.5H_2O$.

Empirical formula	$C_{26}H_{28}NO_{4.50}$
Formula weight	426.49
Crystal size, mm	$0.54 \times 0.40 \times 0.34$
Temperature, K	296(2)
Wavelength, Å	0.71073
Crystal system	monoclinic
Space group	$P2_1$
a, Å	9.484(1)
b, Å	21.915(4)
c, Å	10.988(2)
β, deg	100.87(2)
Volume, Å^3	2242.9(6)
Z	4
Calculated density, Mg m^{-3}	1.263
Absorption coefficient, mm^{-1}	0.086
F(000), e	908
Theta range for data collection, deg	1.86 – 28.25
Limiting indices	$0 \le h \le 12$, $0 \le k \le 29$, $-14 \le l \le 14$
Reflections collected	6249
Independent reflections	5697
R_{int}	0.015
Absorption correction	none
Data/restraints/parameters	5697 / 3 / 585
Goodness-of-fit on F^2	0.809
Final R indices [$I \ge 2\sigma(I)$]	$R1$ = 0.037, $wR2$ = 0.058
R indices (all data)	$R1$ = 0.079, $wR2$ = 0.064
Absolute structure parameter x	0.01(1)
Extinction coefficient	0.0195(6)
Largest diff. peak/hole, e Å^{-3}	0.156/−0.126

*Ethyl (9-anthryl)hydroxyacetate (9AHA, **2**) and (9-anthryl)hydroxyacetic acid (9AHAA(H), **5**)*

To the ethanol solution (350 mL) of **1** (10.00 g) was added 1.00 g of $NaBH_4$ gradually with stirring in an ice-water bath until **1** was exhausted. The process was tracked by TLC. Then 10 mL of dilute hydrochloric acid was slowly added, and the mixture was stirred for 10 min. Ethanol was removed *in vacuo* and a yellow solid was obtained, which was dissolved in acetone and filtered. The acetone was re-

moved *in vacuo*, 9.81 g 9AHA was obtained as a straw yellow solid in 97.4 % yield. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.05 (t, 3 H), 3.71 (s, 1 H), 4.16 (m, 2 H), 6.61 (s, 1 H), 7.55 (m, 4 H), 8.03 (m, 2 H), 8.37 (m, 2 H), 8.51 (m, 1 H). – $C_{18}H_{16}O_3$ (280.31): calcd. C 77.12, H 5.75; found C 77.07, H 5.63.

9AHAA(H) was obtained by the hydrolysis of 9AHA. To the ethanol solution (100 mL) of 9AHA (6.00 g) was added a 30 % aqueous solution of NaOH (20 mL) and the mixture was refluxed until 9AHA was consumed (TLC). Ethanol was removed *in vacuo*. After acidification with dilute hydrochloric acid, 5.17 g of a straw yellow solid was filtered off (95.8 % yield). – ^{1}H NMR (300 MHz, [D$_6$]-DMSO): δ = 6.18 (s, 1 H), 6.55 (s, 1 H), 7.53 (m, 4 H), 8.11 (d, 2 H), 8.57 (m, 3 H), 12.69 (s, 1 H). – ^{13}C NMR (75 MHz, [D$_6$]-DMSO): δ = 67.4, 125.4, 125.6, 126.3, 128.1, 129.3, 130.0, 131.6, 132.7, 175.5. – $C_{16}H_{12}O_3$ (252.26): calcd. C 76.18, H 4.79; found C 76.11, H 4.89.

*(9-Anthryl)methoxyacetic acid (9AMAA(H), **4**)*

14.00 g 9AHA was dissolved in 82 mL of CH_3I, and 8.87 g of Ag_2O was added. The mixture was refluxed until 9AHA had reacted completely. After cooling the mixture to r. t. and separation of unreacted Ag_2O, CH_3I was removed to give 13.30 g ethyl (9-anthryl)methoxyacetate as a yellow solid (90.5 % yield). – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.94 (t, 3 H), 3.39 (s, 3 H), 4.02 (q, 2 H), 6.48 (s, 1 H), 7.55 (m, 4 H), 8.10 (d, 2 H), 8.58 (s, 1 H), 8.65 (m, 2 H). – $C_{19}H_{18}O_3$ (294.34): calcd. C 77.53, H 6.16; found C 77.85, H 6.00.

1.00 g of ethyl (9-anthryl)methoxyacetate was dissolved in 30 mL of ethanol, and 10 mL of a 30 % aqueous solution of NaOH was added. The mixture was refluxed until ethyl (9-anthryl)methoxyacetate had reacted completely. Ethanol was removed *in vacuo*. After acidification with dilute hydrochloric acid, the mixture was filtered to give 0.85 g of a straw yellow solid (93.9 % yield). – ^{1}H NMR (300 MHz, [D$_6$]-DMSO): δ = 3.30 (s, 3 H), 6.04 (s, 1 H), 7.48 (m, 4 H), 8.08 (t, 2 H), 8.53 (s, 1 H), 8.68 (m, 2 H). – $C_{17}H_{14}O_3$ (266.29): calcd. C 76.68, H 5.30; found C 76.55, H 5.28.

Resolution of racemic 9AHAA(H)

4.00 g (20 mmol) of (–)-ephedrine hydrochloride was dissolved in 10 mL of H_2O, and 5 mL of a 40 % aqueous solution of NaOH was added with stirring. The mixture was extracted twice with 10 mL of ethyl ether. The extract was dried with anhydrous Na_2SO_4, and the ethyl ether was removed to give 3.20 g of (–)-ephedrine. To a solution of (–)-ephedrine (3.20 g, 20 mmol) in 30 mL of ethanol, 5.04 g (20 mmol) of racemic 9AHAA(H) was added, and the mixture was refluxed for 2 h. After cooling to r. t., 1.41 g of yellow [(±)-9AHAA]$^-$ [(–)-ephedrine(H)]$^+$ was obtained at r. t. – ^{1}H NMR (300 MHz, [D$_6$]-DMSO): δ = 0.80 (d, 3 H), 2.46 (s, 3 H), 3.18 (m, 1 H), 5.06 (d, 1 H), 6.13 (s, 1 H), 7.30 (m, 5 H), 7.44 (d, 4 H), 8.01 (d, 2 H), 8.47 (s, 1 H), 8.60 (d, 2 H). – $C_{26}H_{27}NO_4$ (417.50): calcd. C 74.80, H 6.52, N 3.35; found C 74.70, H 6.40, N 3.18.

The salt was dissolved in water, and acidified with dilute hydrochloric acid. Filtration gave 0.83 g of a straw yellow solid of (+)-9AHAA(H). – $[\alpha]_D^{20}$ = +169° (c = 0.2197, methanol). – $C_{16}H_{12}O_3$(252.26): calcd. C 76.18, H 4.79; found C 76.08, H 4.61.

X-Ray diffraction data were collected on a Siemens P4 four-circle diffractometer with graphite-monochromated MoK_α radiation (λ = 0.071073 nm). The structure was solved by Direct Methods with SHELXS-97 [16] and refined by full-matrix least-squares on F^2 with SHELXL-97 [17]. All H atoms were added in calculated positions and refined using a riding model. The crystal used for the diffraction study showed no decomposition during data collection. The crystal data, experimental details, and refinement results are summarized in Table 2.

CCDC 641707 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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