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ORIGINAL PAPER

Structure of Methyl *N*-(4-methoxyphenylmethyl)-*N*′-cyanocarbamimidothioate and Methyl *N*-[1-(phenylmethyl)-4-piperidinyl]-*N*′-cyanocarbamimidothioate

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Abstract The title compounds, Methyl *N*-(4-methoxyphenylmethyl)-*N*′-cyanocarbamimidothioate, **I**, and Methyl *N*-[1-(phenylmethyl)-4-piperidinyl]-*N*′-cyanocarbamimidothioate, **II**, have been designed and synthesized for use as new potential organic molecular electronic materials. The crystal structure of **I** and **II** were determined with crystal data (**I**: Monoclinic, $P2_1/c$, $a = 4.746(2)$ Å, $b = 5.737(3)$ Å, $c = 17.399(7)$ Å, $\beta = 91.667(7)^\circ$, $R_{\mathrm{all}} = 0.0703$; **II**: Orthorhombic, $Pna2_1$, $a = 18.209(8)$ Å, $b = 11.463(5)$ Å, $c = 7.539(3)$ Å, $\beta = 90.00\ ^\circ$, $R_{\mathrm{all}} = 0.0481$). N–H···N hydrogen bonds were responsible for the formation of one-dimensional zigzag molecular chains of **I**, and trifurcated hydrogen-bonded molecular chains were indicated in structure of **II**. C–H···π and C–H···N hydrogen bonds were found in both structures. All these types of interaction together form an extended three-dimensional network and stabilize the title crystals.

Keywords *N*-cyanocarbamimidothioate · Molecular assemblies · Hydrogen bonds · X-ray diffraction

Introduction

Replacing the traditional inorganic semiconductor with the organic semiconducting materials to modify the electric and optical signals shows great prospect, according to the excellent property of the organic materials [1–3]. Much attention has been paid to organic electronic devices based on the organic molecular and polymer materials. Donor-π-Acceptor heterocyclics have recently attracted considerable attention due to their applications in ultrafast and ultrasensitive molecular electronic devices and ultra-high density data storage [4–7]. Sandwich structure devices Metal/Organic/Metal are manufactured, where “Organic” can be *N*-cyanocarbamimidothioate [8, 9]. Systematic study of the crystal structure of differently substituted *N*-cyanocarbamimidothioate should make it possible to understand the formation of certain structure elements desired for electronic applications. Besides, the knowledge of the bulk structure will be helpful to understand the formation of thin layers, which are needed for microelectronic devices. Herein, the synthesis [10], ^{1}H NMR spectroscopy, FT-IR spectroscopy and crystal structure of the title compounds, methyl *N*-(4-methoxyphenylmethyl)-*N*′-cyanocarbamimidothioate (**I**) and methyl *N*-[1-(phenylmethyl)-4-piperidinyl]-*N*′-cyano-carbamimidothioate (**II**), are reported.

Experimental

Melting points were determined in open capillaries and are uncorrected. IR spectra were recorded on a Nicolet Avatar-360IR spectrometer. ^{1}H NMR spectra were measured on a Bruker DMX500 spectrometer using TMS as internal standard. All chemical reagents were obtained from Aldrich, Merck, Lancaster, or Fluka and used without further purification.

Synthesis of Methyl N-(4-methoxyphenylmethyl)-N′*-cyanocarbamimidothioate* (**I**)

To a solution of dimethyl cyanocarbonimidodithioate (0.1460 g, 1 mmol) in ethanol (5 mL) was added 4-methoxyyphenylmethylamine (0.137 g, 1 mmol), and the

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reaction mixture was stirred at room temperature for 4 h. Thereafter, the reaction mixture was filtered and precipitate was washed with EtOAc to give methyl *N*-(4-methoxyphenylmethyl)-*N*′-cyanocarbamimidothioate (0.224 g, 90%). m.p. 154–156 °C; ^{1}H NMR (DMSO-d_6, 500 MHz): δ 2.60 (s, 3 H, SCH_3), 3.81 (s, 3 H, OCH_3), 4.41–4.56 (d, 2 H, $J = 5.8$ Hz, $PhCH_2$), 7.21–7.46 (m, 5 H, ArH), 8.83 (s, 1 H, NH). IR (KBr) ν: 3008, 2965, 2922, 2211, 1665, 1572, 1437, 1245, 1193, 1010, 861, 766 cm^{-1}.

Methyl N-[1-(phenylmethyl)-4-piperidinyl]-N′-cyanocarbamimidothioate (**II**) was prepared in the same manner as **I**, yield: 85%, m.p. 160–1162 °C; ^{1}H NMR (DMSO-d_6, 500 MHz): δ 1.52–2.45 (m, 9H, *piperidinyl*-H), 2.60 (s, 3 H, SCH_3), 3.52 (s, 2 H, $PhCH_2$), 7.20–7.36 (m, 5 H, ArH), 7.84 (d, 1 H, $J = 7.8$ Hz, NH). IR (KBr) ν: 3280, 2985, 2910, 2170, 1540, 1515, 1417, 1265, 1001, 869, 776 cm^{-1}.

Crystal Structure Determinations and Refinements

Single crystals of **I** and **II** suitable for X-ray analysis were obtained by slow evaporation from ethanol. Single crystalline samples of **I** and **II** are yellow prisms. The experimental data were obtained at room temperature using MoKα-radiation and a graphite monochromator ($\lambda = 0.7107$ Å) with Bruker SMART diffractometer using phi and omega scans technique. The structures were solved by direct methods and refined by a full matrix least-squares procedure in the anisotropic approximation for non-hydrogen atoms. H atoms were refined as riding atoms in ideal positions. The isotropic refinement of the H atoms was likely also constrained to be 1.2 Ueq of their parent atom. For both structures, multi-scan was used for absorption correction (SADABS; Sheldrick, 1996) [11]. All calculations were carried out with a personal computer using the Bruker SHELXTL program package [12, 13]. Drawing of these molecules was obtained with the ORTEP program [14].

CCDC-745940 (**I**) and CCDC-745941 (**II**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at http://www.ccdc.cam.ac.uk/const/retrieving.html or from the Cambridge-Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 (0) 1223–336033 or e-mail: deposit@ccdc.cam.ac.uk.

Results and Discussion

Important details of the data collection and structure refinement are summarized in Table 1. Selected geometric parameters and hydrogen bonding geometry are presented in Table 2. Structures of **I** and **II** are shown in Fig. 1. It is noteworthy that the presence of a push–pull imine unit, with the methylthio group as electron donor and the cyano group as an electron acceptor, most probably leads to diverse attractive close interactions in their crystal structures [15].

Table 1 Crystal data and structure refinement for **I** and **II**

	I	**II**
CCDC deposit no.	745940	745941
Color/Shape	Yellow/prism	Yellow/prism
Empirical formula	$C_{11}H_{13}N_3OS$	$C_{15}H_{20}N_4S$
Formula weight	235.30	288.42
Temperature, K	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/c$	$Pna2_1$
Absorption correction	Multi-scan (SADABS)	Multi-scan (SADABS)
Unit cell dimensions		
a (Å)	4.746(2)	18.209(8)
b (Å)	5.737(3)	11.463(5)
c (Å)	42.22(2)	7.539(3)
β (°)	91.667(7)	90.00
Density (calculated) (Mg/m^3)	1.360	1.217
μ (mm^{-1})	0.264	0.202
F (000)	496	616
Crystal size (mm)	0.40 × 0.20 × 0.20	0.25 × 0.15 × 0.14
Θ range for data collection (°)	2.896–27.040	2.857–26.326
Ranges of *h*, *k*, *l*	$-6 \leq h \leq 6$	$-21 \leq h \leq 18$
	$-7 \leq k \leq 7$	$-12 \leq k \leq 13$
	$-53 \leq l \leq 29$	$-8 \leq l \leq 8$
Reflections collected	4811	6112
Reflections observed	2108	2365
Independent reflections	2418	2753
Data/parameters	2418/145	2753/181
GOF (F^2)	1.160	1.047
Final R_1/wR_2 indices [$I > 2\sigma(I)$]	0.0620/0.1513	0.0382/0.0859
Final R_1/wR_2 indices (for all)	0.0703/0.1552	0.0481/0.0906
Largest diff. Peak/hole (e.Å^{-3})	0.503/−0.257	0.165/−0.164

In the structure of **I**, the C10–N3 distance shows predominantly triple-bond character, whereas the C10–N2, N2–C9 and C9–N1 distances suggest that they are partial double bonds. Together with the quasilinear N2–C10–N3 angle of the cyano group, this pattern is typical of the $N{\equiv}C{-}N{=}C(SCH_3){-}N$ group of methyl *N*-cyanocarboximidothioate compounds [16]. Further examination of the

Table 2 Selected geometric parameters (Å, °), hydrogen-bonding geometry (Å, °) and short intermolecular contacts (Å) for **I** and **II**

I		**II**	
N3–C10	1.144(4)	N4–C15	1.157(3)
N2–C10	1.315(4)	N3–C15	1.324(3)
N2–C9	1.317(3)	N3–C13	1.326(3)
N1–C9	1.312(3)	N2–C13	1.328(3)
S1–C11	1.787(3)	S1–C14	1.804(3)
O1–C1	1.403(5)	N1–C7	1.456(3)
N3–C10–N2	172.3(3)	N4–C15–N3	174.3(3)
C10–N2–C9	119.7(2)	C15–N3–C13	119.0(2)
N1–C9–N2	119.1(2)	N3–C13–N2	119.7(2)
C9–N1–C8	122.1(2)	C13–N2–C10	124.4(2)
N1–H1d···N3^{i}	3.000(4)	N2–H2b···N4$^{\#i}$	3.145(3)
	150.8		144.0
C1–H1a···O1^{ii}	3.410(3)	C11–H11a···N4$^{\#i}$	3.605(3)
	140.6		141.7
C4–H4···N2^{iii}	3.526(4)	C14–H14···N4$^{\#i}$	3.629(4)
	160.8		165.2
C8–H8b···C4^{iv}	3.697(3)	C11–H11b···*Ct*1$^{\#ii}$	3.646(3)
(phenyl)	162.0	(phenyl, C1···C6)	173.0
S1···S1^{v}	3.297(4)	C8–H8b···C15$^{\#iii}$	3.667(4)
		(cyano)	163.6

Note Symmetry code: (i) $x + 1, y + 1, z$; (ii) $-x, y + 1/2, 3/2 - z$; (iii) $x, y + 1, z$; (iv) $x + 1, y, z$; (v) $-x + 1, -y, -z + 2$; (#i) $-x + 3/2, y + 1/2, z - 1/2$; (#ii) $x, y, z + 1$; (#iii) $x, y, z - 1$. *Ct* refers to the centroid of the C1···C6 phenyl ring

crystal structure of **I** reveals the existence of several possible C–H···N, C–H···O, C–H···π (C4, phenyl) and N–H···N interactions (Table 2), as described in the literature [17, 18]. Intermolecular N1–H1d···N3^{i} hydrogen bonds [symmetry code: (i) $x + 1, y + 1, z$] form zigzag molecular chains propagating along the b axis direction, as shown in Fig. 2. The S1···S1^{v} [symmetry code: (v) $-x + 1, -y, -z + 2$] non-bonded separation is 3.297 (2) Å, lower than the sum of the van der Waals for the corresponding atoms, which indicates a strong intermolecular interaction between these atoms.

In the structure of **II**, there also exists the similar N≡C–N=C(SCH_3)–N group as compound **I**. The six-membered piperidinyl ring adopts a chair conformation. Examination of the crystal structure of **II** reveals the existence of several possible C–H···N and N–H···N interactions (Table 2). A view down the *b* axis of the unit cell (Fig. 3) reveals hydrogen-bonded zigzag molecular chains, which are formed by cyano-N···H2b intermolecular bonds. This same cyano N atom also accepts other hydrogen bonds that crosslinks neighboring hydrogen-bonded rings via N···H14 and N···H11a bonds. Thus, the terminal cyano N atom is a trifurcated hydrogen-bond acceptor as shown in Fig. 4. Two kinds of C–H···π intermolecular interactions were shown in structure of **II**, they are C11–H11b···*Ct*1 (*Ct* refers to the centroid of the C1···C6 phenyl ring) and C8–H8b···C15 (cyano group C15≡N4) hydrogen bonds.

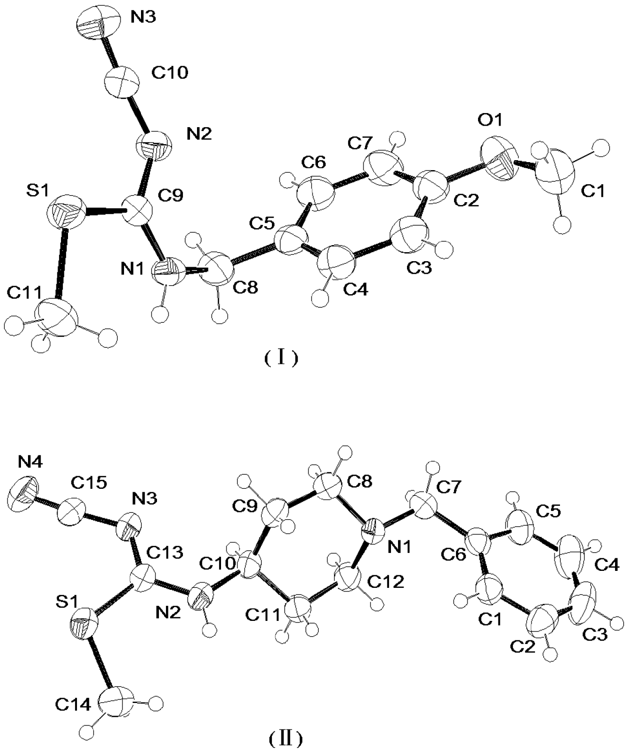

Fig. 1 Molecular structure of **I** and **II**. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii

Comparing crystal **I** to **II**, it can be found that they have the similar cyanocarbamimidothioate moiety, which is responsible for some special electronic properties [19]. N–H···N hydrogen bonds form zigzag molecular chains in both crystals. However, S···S short contacts only existed in structure of **I** and trifurcated hydrogen bonds were merely observed in structure of **II**. C–H···π (phenyl) interactions were revealed in both structures, which can be divided into point to point interactions of **I** and point to face interactions of **II**; and C–H···π (C≡N) interactions were just disclosed in structure of **II**.

In summary, two *N*′-cyanocarbamimidothioates forming molecular chains by intermolecular N–H···N hydrogen bonding interactions, has been characterized. The structural features and the existing similarities and differences are discussed.

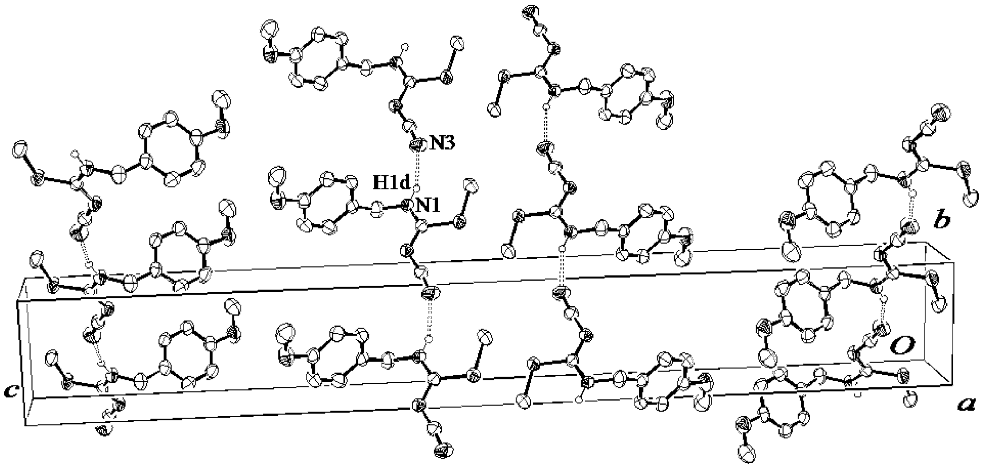

Fig. 2 Projections of molecular packing of **I**. *Dashed lines* indicate N–H···N hydrogen bonds

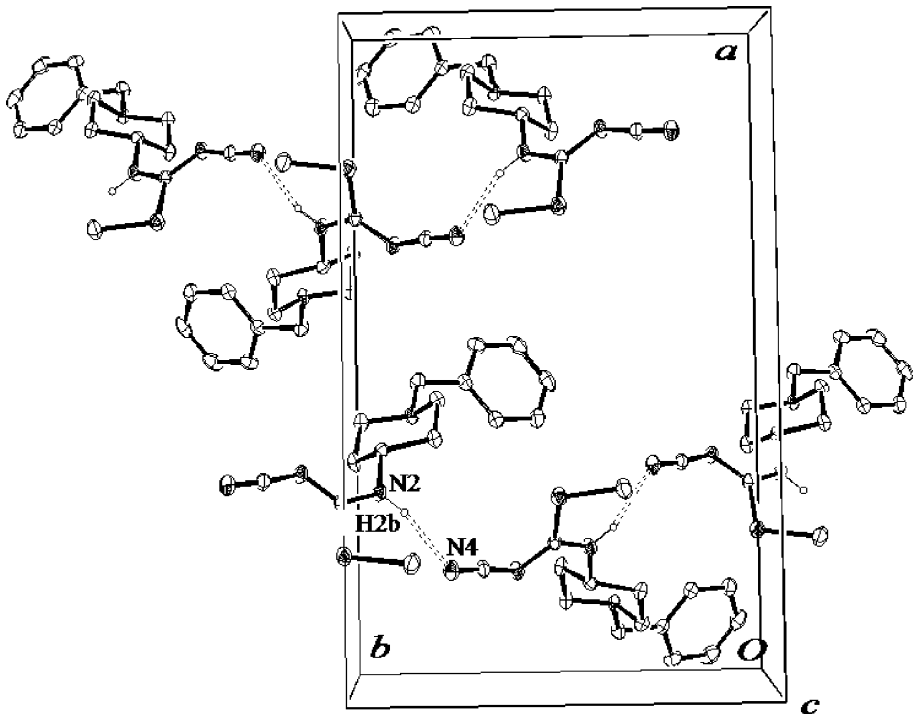

Fig. 3 Projections of molecular packing of **II**. *Dashed lines* indicate N–H···N hydrogen bonds

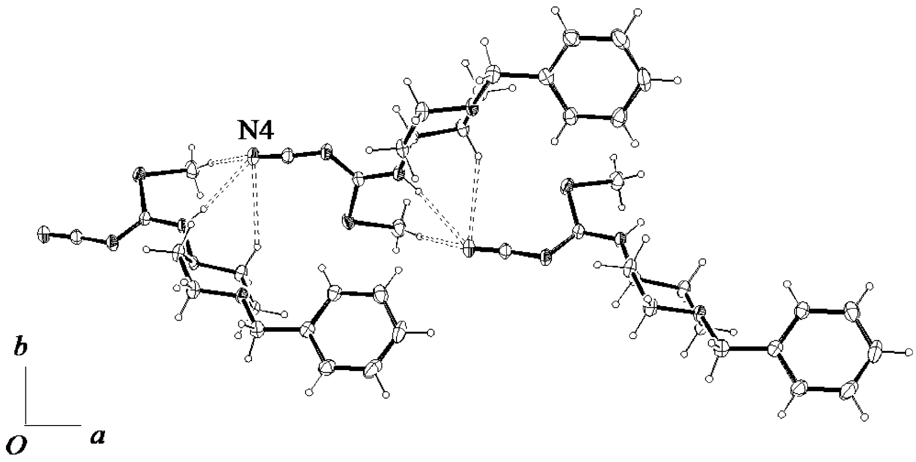

Fig. 4 Trifurcated hydrogen-bonded molecular chains propagating in the *a*-axis direction; dashed lines indicate C11–H11a···N4$^{\#i}$, C14–H14···N4$^{\#i}$ and N2–H2b···N4$^{\#i}$ hydrogen bonds. (Symmetry code as in Table 2)

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