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Short Note

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<https://doi.org/10.3390/M1801>

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1,4-Diiodotetrafluorobenzene 3,5-di-(pyridin-4-yl)-1,2,4-thiadiazole <1/1>

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Abstract: The reactivity of 3,5-di-(pyridin-4-yl)-1,2,4-thiadiazole (**L1**) with 1,4-diiodotetrafluorobenzene (**1,4-DITFB**) was explored and the halogen-bonded 1:1 co-crystal (**1**) was successfully isolated and structurally characterized.

Keywords: dipyridyl-1,2,4-thiadiazole; polypyridyl donors; halogen bonding; SC-XRD

1. Introduction

1,2,4-Thiadiazoles have been recognized as effective scaffolds in medicinal chemistry, since many derivatives are biologically active and very promising candidates in drug design [1]. Inspired by Cefozopran [2], the first 1,2,4-thiadiazole derivative to enter the market as an antibiotic, extensive synthetic efforts led to the isolation of numerous 1,2,4-thiadiazoles with potential biomedical applications, such as high cytotoxicity against human myeloid leukemia cells [3], inhibitors of Factor XIIIa in the blood coagulation process [4], neuroprotectors, [5] and in the treatment of Alzheimer's disease [6]. The synthesis of 1,2,4-thiadiazoles is typically achieved starting from thioamides, whose oxidation is followed by cyclization, and several methods have been reported using a range of oxidants and reaction solvents [7,8]. A valid protocol reported the use of alcoholic thioamide solutions, which can be easily oxidized by molecular dihalogens, leading to the corresponding thiadiazole in good yields [9].

1,2,4-Thiadiazoles featuring pyridyl substituents, such as 3,5-di-(pyridin-4-yl)-1,2,4-thiadiazole (**L1**) and 3,5-di-(pyridin-3-yl)-1,2,4-thiadiazole (**L2**) (Scheme 1), have been successfully used as building blocks in supramolecular chemistry by exploring their reactivity towards metal ions in the preparation of coordination polymers and polygons [10,11]. The versatility of donors **L1** and **L2** as supramolecular synthons became evident when their reactivity towards dihalogens, interhalogens, and other halogenated derivatives was investigated [12,13]. In this regard, the reaction of **L1** and **L2** with dihalogens and interhalogens was previously reported by our research group [12], and the self-assembly outcomes are summarized in Scheme 1. The results showed that donors **L1** and **L2** can give either Charge-Transfer (CT) adducts or salts with variable degrees of N-protonation (e.g., HL⁺, H₂L²⁺) depending on the solvent polarity and the experimental setup (Scheme 1). The reaction of **L2** with diiodine in CH₂Cl₂ resulted in the bis-adduct **L2·2I₂** with a short N···I bond distance (2.505 Å) and a linear N···I-I fragment as typically observed in CT-adducts. Notably, the reaction of **L1** with diiodine under the same experimental conditions did not produce a crystalline product and its nature as **L1·2I₂** was established by microanalytical determinations and Raman spectroscopy [12].



Citation: Podda, E.; Pintus, A.; Lippolis, V.; Isaia, F.; Slawin, A.M.Z.; Carpenter-Warren, C.L.; Woollins, J.D.; Aragoni, M.C. 1,4-Diiodotetrafluorobenzene 3,5-di-(pyridin-4-yl)-1,2,4-thiadiazole <1/1>. *Molbank* **2024**, *2024*, M1801. <https://doi.org/10.3390/M1801>

Academic Editor: Rodrigo Abonia

Received: 15 February 2024

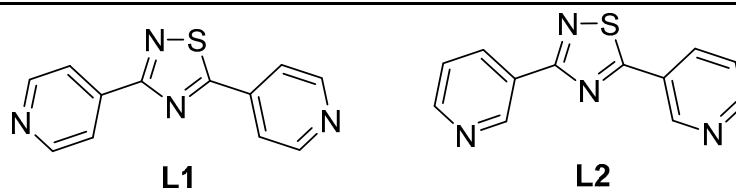
Revised: 24 March 2024

Accepted: 26 March 2024

Published: 1 April 2024



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CT adducts	Ref.		Ref.	
	L1·2I ₂ *	[12] *	L2·2I ₂	[12] (WEDHUK)
Ionic compounds	(HL1 ⁺)(IBr ₂ ⁻)	[12] (WEDHOE)	(HL2 ⁺)(IBr ₂ ⁻)	[12] (WEDHEU)
	(HL1 ⁺)(I ₃ ⁻)	[12] (WEDHIY)	(HL2 ⁺)(I ₃ ⁻)	[12] (WEDGUJ)
	(H ₂ L1 ²⁺)(I ₃ ⁻) ₂ ·2H ₂ O	[13] (XEKTAM)	(HL2 ⁺)(I ₅ ⁻)	[12] (WEDHAQ)
	(H ₂ L1 ²⁺) ₂ (Bi ₈ I ₂₈ ⁴⁻)·4CH ₃ CN	[13] (XEKVIW)	(HL2 ⁺)(I ⁻)·4CH ₃ CN	[13] (XEKTEQ)
	[(H ₂ L1 ²⁺)(HL1 ⁺)](Bi ₂ I ₉ ³⁻)·3H ₂ O	[13] (XEKVOC)	(H ₂ L2 ²⁺)(I ₃ ⁻) ₂ ·L2	[13] (XEKTIU)
			(H ₂ L2 ²⁺)(I ⁻) ₂ ·L2·2CHI ₃	[13] (XEKTOA)
			(H ₂ L2 ²⁺) ₂ (Bi ₄ I ₁₆ ⁴⁻)·2CH ₃ CN·2I ₂	[13] (XEKVUI)
		(H ₂ L2 ²⁺) ₂ (Bi ₆ I ₂₂ ⁴⁻)·2CH ₃ OH	[13] (XEKWAP)	

* Note: L1·2I₂ was not structurally characterized.

Scheme 1. CT adducts and ionic compounds isolated from the reactions between N-donors **L1** and **L2** and halogenated species. Refcodes are given in parentheses.

The role of the solvent becomes crucial when considering the products obtained from the reactions between **L1** or **L2** and I₂ or IBr in ethyl alcohol, where the following ionic compounds were obtained: (HL1⁺)(IBr₂⁻), (HL1⁺)(I₃⁻), (HL2⁺)(IBr₂⁻), (HL2⁺)(I₃⁻), (H₂L2²⁺)(I₃⁻)₂·L2, (HL2⁺)(I₅⁻) (Scheme 1) [12,13]. These structures share cations HL1⁺ or HL2⁺ with only one of the two pyridyl nitrogen atoms being protonated, resulting in the formation of head-to-tail polymeric arrays held by NH⁺···N hydrogen bonds (d_{N...N} distances up to 2.770 Å), whose motif is shaped by the geometrical features of the former donors: wavy chains for cations HL1⁺ and either helices or zig-zag chains in the case of cations HL2⁺ [12]. The only exception among these ionic compounds is represented by (H₂L2²⁺)(I₃⁻)₂·L2, where the donor **L2** appears in both the neutral and the doubly charged HL2²⁺ form.

When acetonitrile was used as a solvent and the donors **L1** and **L2** were reacted with I₂, (H₂L1²⁺)(I₃⁻)₂·2H₂O and (HL2⁺)(I⁻)·4CH₃CN were isolated [13]. Moreover, the reaction of **L2** with I₂ in an iodoform/acetone mixture produced compound (H₂L2²⁺)(I⁻)₂·L2·2CHI₃ [13]. To further investigate the reactivity of **L1** and **L2** toward dihalogens, Pennington and coworkers introduced bismuth triiodide as a building block, producing self-assembled salts with formula (H₂L1²⁺)₂(Bi₈I₂₈⁴⁻)·4CH₃CN, [(H₂L1²⁺)(HL1⁺)](Bi₂I₉³⁻)·3H₂O, (H₂L2²⁺)₂(Bi₄I₁₆⁴⁻)·2CH₃CN·2I₂, and (H₂L2²⁺)₂(Bi₆I₂₂⁴⁻)·2CH₃OH, whose crystal structures show **L1** and **L2** in their mono- or diprotonated forms along with four unusual polyiodobismuthate counterions [13].

On the contrary, the interaction of **L1** and **L2** with the halogen atoms of halo-organic compounds has not yet been reported. This interaction falls into the realm of halogen bonding because it involves a halogen atom acting as an electrophilic site and the lone pair of a pyridine nitrogen atom as a nucleophilic site [14–16]. Following our interest in the study of σ-hole interactions between halogen-rich compounds and pyridine tectons [17,18], we report here on the synthesis and characterization of the novel halogen-bonded 1:1 co-crystal (**1**) formed between **L1** and 1,4-diiodotetrafluorobenzene (**1,4-DIFTB**). In this halo-organic compound, the σ-hole effect for the iodide atoms is enhanced by the presence of the four electronegative fluorides, and numerous co-crystals formed by the halogen bonding between **1,4-DIFTB** and pyridine donors can be found in the literature [14,19–23].

2. Results

The slow evaporation of a chloroform solution of **L1** and **1,4-DITFB** in 1:1 molar ratio at room temperature afforded colorless crystals, established by means of X-ray diffraction analysis as a 1:1 halogen-bonded co-crystal with formula **L1·1,4-DITFB** (compound **1**; Figure 1). Compound **1** crystallizes in the triclinic space group $P\bar{1}$ with two units in the unit cell (see Table S1 for structural data and refinement parameters).

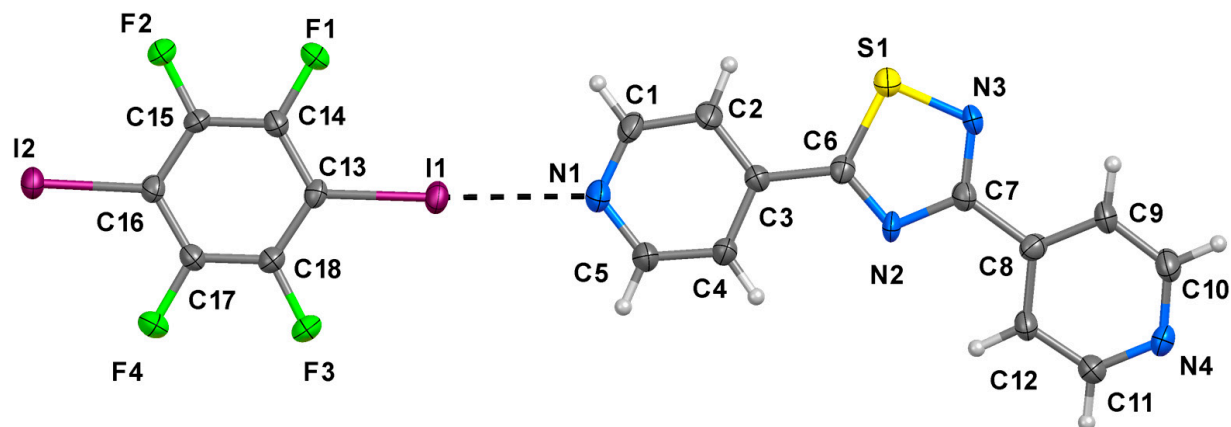


Figure 1. X-ray crystal structure of compound **1** with the numbering scheme adopted. Displacement ellipsoids were drawn at the 50% probability level.

Crystal data for compound **1**: $C_{18}H_8F_4I_2N_4S$, ($M_r = 642.14 \text{ g mol}^{-1}$) triclinic, $P\bar{1}$, $a = 5.6690(4) \text{ \AA}$, $b = 12.3300(9) \text{ \AA}$, $c = 14.1339(9) \text{ \AA}$, $\alpha = 91.644(6)^\circ$, $\beta = 96.314(6)^\circ$, $\gamma = 92.400(6)^\circ$, $V = 980.54(12) \text{ \AA}^3$, $T = 173(2) \text{ K}$, $Z = 2$, $\rho_{\text{calc}} = 2.175 \text{ g/cm}^3$, $\mu(\text{Mo K}\alpha) = 3.363 \text{ mm}^{-1}$. The final R_1 was 0.0333 [$F^2 \geq 2 \sigma(F^2)$], wR_2 was 0.0960 (all data), and the $\text{Goof} = 1.043$.

The **1,4-DITFB** molecules interact with **L1** to form neutral adducts at both N-pyridyl atoms with $d_{\text{N}\cdots\text{I}}$ distances of 2.801(5) and 2.947(4) \AA and C–I \cdots N angles of 177.4(2) and 168.3(2) $^\circ$ for N1 \cdots I1 and N4 \cdots I2ⁱ, respectively (entries *a* and *b* in Figure 2; ⁱ = 2 + x, –1 + y, –1 + z; Tables S2 and S3). These values are similar to the average N \cdots I value of 2.9(2) \AA retrieved from the CSD database (version 5.43, three updates) for the structurally characterized compounds in which **1,4-DITFB** interacts with pyridyl-based donors (the search was constrained to N \cdots I distances up to the sum of the atomic van der Waals radii: 3.53 \AA).

The resulting $(\text{L1}\cdot\text{1,4-DITFB})_\infty$ 1D-chains propagate approximately along the $[\bar{2}11]$ direction and pack into 2D sheets via weak C–H \cdots F interactions (entries *c*–*e* in Figure 2 and Table 1) [23]. The FT-IR spectrum (Figure S1) recorded for compound **1** showed a shift towards lower frequency of the $\nu(\text{C–I})$ stretching mode from 760 to 748 cm^{-1} on passing from free **1,4-DITFB** to the co-crystal, as a consequence of the halogen bonding between the two species [14].

Table 1. Compound **1** intermolecular interactions.

	C–I \cdots N	$d_{\text{C–I}}$ (\AA)	$d_{\text{I}\cdots\text{N}}$ (\AA)	$\alpha_{\text{C–I}\cdots\text{N}}$ ($^\circ$)	
<i>a</i>	C13–I1 \cdots N1	2.101(5)	2.801(5)	177.4(2)	
<i>b</i>	C16 ⁱ –I2 ⁱ \cdots N4	2.092(5)	2.947(4)	168.3(2)	
	C–H \cdots F	$d_{\text{C–H}}$ (\AA)	$d_{\text{H}\cdots\text{F}}$ (\AA)	$d_{\text{C}\cdots\text{F}}$ (\AA)	$\alpha_{\text{C–H}\cdots\text{F}}$ ($^\circ$)
<i>c</i>	C2–H2 \cdots F2 ⁱⁱ	0.95	2.450	3.307(6)	150
<i>d</i>	C4–H4 \cdots F3 ⁱⁱⁱ	0.95	2.607	3.142(6)	122
<i>e</i>	C5–H5 \cdots F3 ⁱⁱⁱ	0.95	2.505	3.111(6)	116

Symmetry codes: ⁱ = 2 + x, –1 + y, –1 + z; ⁱⁱ = 1 – x, 2 – y, 1 – z; ⁱⁱⁱ = –x, 1 – y, 1 – z.

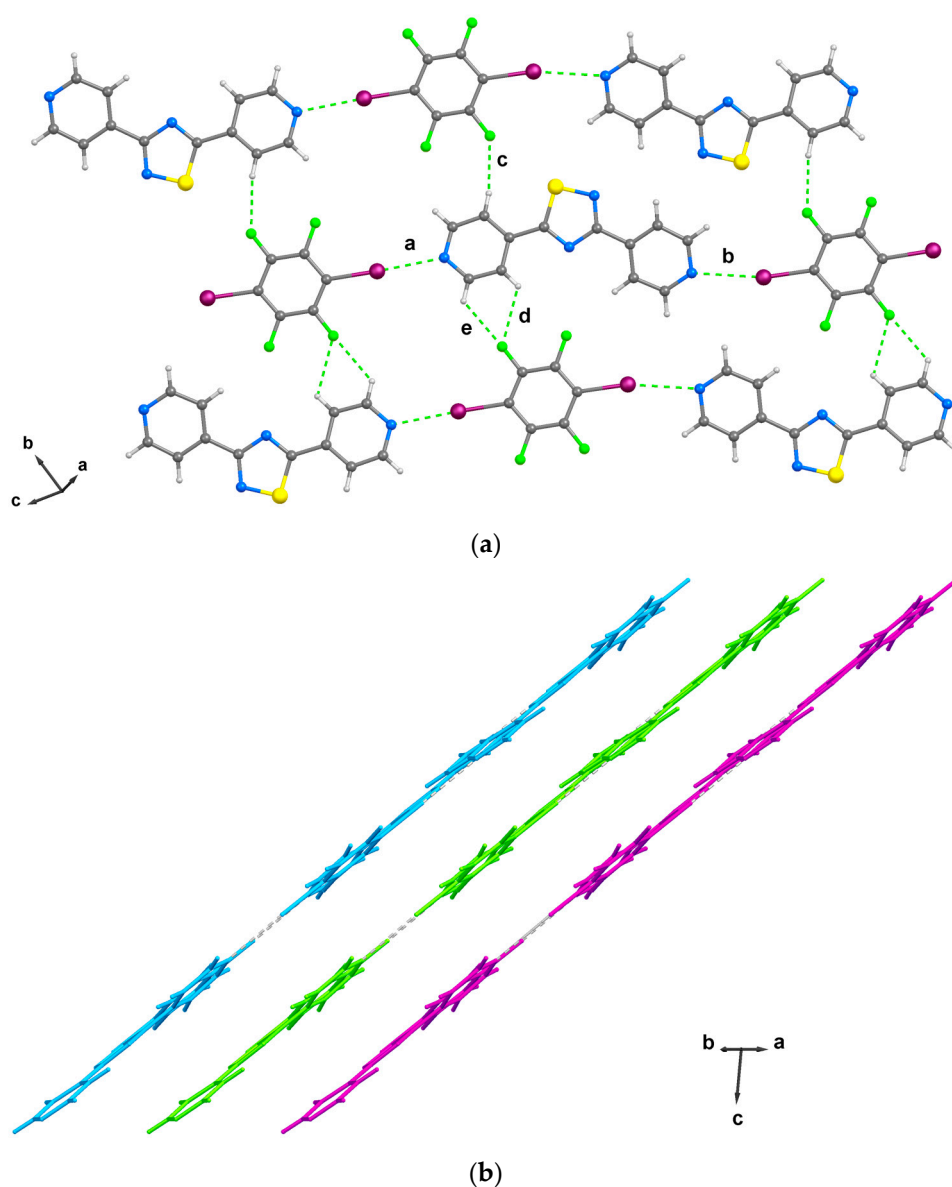


Figure 2. Partial view of the crystal packing of **1** showing (a) a single layer with the relevant intermolecular interactions a–e are labelled according to Table 1, and (b) adjacent layers viewed along the [110] direction.

3. Materials and Methods

3.1. General

L1 was synthesized according to a method in the literature [9]. **1,4-DIFTB** and chloroform were purchased from Merck and used without any further purification. Elemental analysis determinations were performed with a Perkin Elmer EA CHN elemental analyzer. The FT-IR spectra ($4000\text{--}400\text{ cm}^{-1}$) were recorded on KBr pellets on a Thermo Nicolet 5700 spectrometer. Melting point determination was performed on a FALC mod. C apparatus. Single crystal X-ray diffraction data were collected at 173 K on a Rigaku SCX mini diffractometer using graphite monochromated Mo $K\alpha$ radiation (0.71073 \AA). Data collection and processing were carried out using CrysAlisPro [24]. The structure was solved with the ShelXT [25] solution program using dual methods and the model was refined using full matrix least squares minimization on F^2 with ShelXL [26] 2018/3. The crystal was found to be a non-merohedral twin and the model was refined as a two-component twin. Olex2 1.5 [27] was used as the graphical interface.

3.2. Preparation of L1·1,4-DITFB (1)

L1 (12.0 mg; 5.00×10^{-5} mol) and 1,4-DITFB (20.1 mg; 5.00×10^{-5} mol) were dissolved in chloroform (5 mL) and the mixture was stirred at room temperature for 20 min. The resulting solution was filtered through a PTFE filter and the solvent allowed to evaporate slowly to afford compound 1 as colorless crystals suitable for X-ray diffraction analysis (10.8 mg; 1.68×10^{-5} mol; 34%). Elemental analysis calcd (%) for C₁₈H₈F₄I₂N₄S: C 32.67, H 1.26, N 8.73. Found: C 31.88, H 0.66, N 8.21. M.p. = 186 °C. FT-IR (KBr, 4000–400 cm⁻¹): 1599 m, 1458 vs, 1410 s, 1335 m, 1290 m, 1207 m, 1124 m, 1063 m, 995 m, 939 s, 825 ms, 748 m, 733 ms, 712 ms, 677 m, 636 ms, 505 m, 474 w, 422 w cm⁻¹ (Figure S1).

4. Conclusions

The halogen-bonded co-crystal (1) was obtained by the self-assembly of 3,5-di-(pyridin-4-yl)-1,2,4-thiadiazole (L1) and 1,4-diiodotetrafluorobenzene (1,4-DITFB) in chloroform. The crystal structure of 1, determined by means of crystallographic tools, corresponds to the formulation L1·1,4-DITFB. A comparison between the FT-IR spectra of 1 and 1,4-DITFB provided further evidence for the halogen bonding between the two building blocks.

Supplementary Materials: The following supporting information is available online. Figure S1: Solid-state FT-IR spectrum of compound 1 (500–3500 cm⁻¹, KBr pellet); Table S1: Crystal data and structure refinement parameters for compound 1; Tables S2: Bond lengths (Å) for compound 1; Tables S3: Bond angles (°) for compound 1.

Author Contributions: Conceptualization and writing (original draft): E.P., M.C.A.; Data analysis and presentation of results: M.C.A., E.P. and A.P., M.C.A., V.L. and F.I. are experts in the field of halogen bonding and extensively investigated the reactivity of L1 towards various halogenated species. A.M.Z.S., J.D.W. and C.L.C.-W. performed the XRD analysis of compound 1. All authors have read and agreed to the published version of the manuscript.

Funding: The authors acknowledge Fondazione di Sardegna (FdS Progetti Biennali di Ateneo, annualità 2022). The authors acknowledge the Ministero per l'Ambiente e la Sicurezza Energetica (MASE; formerly Ministero della Transizione Ecologica, MITE)—Direzione generale Economia Circolare for funding (RAEE—Edizione 2021).

Data Availability Statement: Crystallographic data were deposited at CCCD (CIF deposition number 2332380).

Conflicts of Interest: The authors declare no conflicts of interest.

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