

Short Note

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Short Note

# 2-(5,6-Diphenyl-1,2,4-Triazin-3-yl)Pyridinium Dichloroiodate (I)

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**Abstract:** 2-(5,6-diphenyl-1,2,4-triazin-3-yl)pyridinium dichloroiodate (I) (**1**) was synthesized by reacting 3-(2-pyridyl)-5,6-diphenyl-1,2,4-triazine with ICl in dichloromethane solution. The structural characterization of **1** by SC-XRD analysis was accompanied by elemental analysis, FT-IR, and FT-Raman spectroscopy measurements.

**Keywords:** 3-(2-pyridyl)-5,6-diphenyl-1,2,4-triazine; polypyridyl donors; SC-XRD

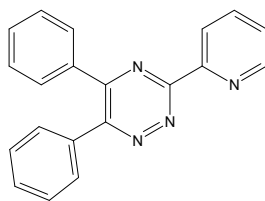
## 1. Introduction

Polypyridine donors react with interhalogens XY and dihalogens X<sub>2</sub> (X, Y = Cl, Br, I) to give a variety of products whose nature depend on the nature of the donor, the interhalogen, and the reaction conditions.[1–4] Among the possible reaction products, Charge-Transfer adducts containing the N...X–Y linear group,[5,6] halonium compounds featuring a N...X<sup>+</sup>...N moiety[7,8] or salts where a N-protonated pyridinium cation is counterbalanced by discrete or extended[9] (poly)halide anions can be mentioned. FT-Raman spectroscopy can provide useful information on the nature of the resulting products.[10] In simple CT-adducts, the adduct formation results in an elongation of the perturbed X–Y moiety with respect to the free halogen/interhalogen. When polyhalides are formed, the peculiar stretching vibrations of the interacting synthons, such as neutral (inter)halogens and tri(inter)halides, can be detected in the low-energy region of the FT-Raman spectrum.

3-(2-Pyridyl)-5,6-diphenyl-1,2,4-triazine[11,12] has been often reported as an efficient donor towards a variety of metal ions.[13–16] This notwithstanding the reactivity of this donor towards halogens or interhalogens has not been described to date. Pursuing our interest towards the reactivity of polypyridyl substrate towards ICl, we report here on the synthesis and structural and vibrational characterization of the novel salt 2-(5,6-diphenyl-1,2,4-triazin-3-yl)pyridinium dichloroiodate (I) (**1**; Scheme 1).

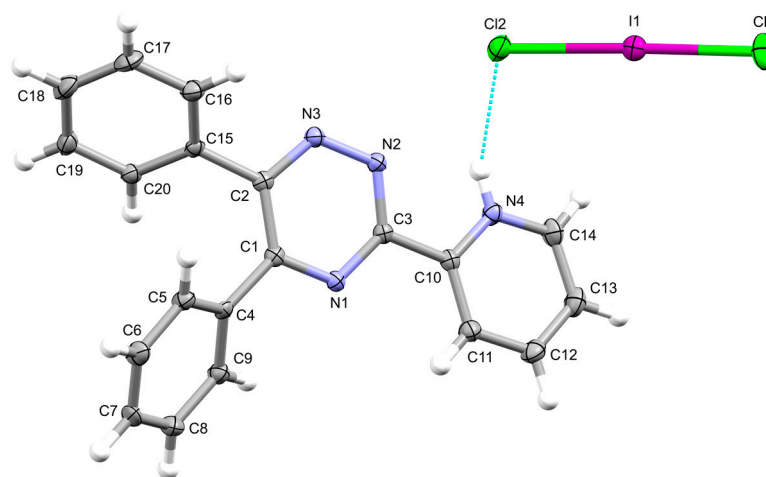
## 2. Results

The reaction of 3-(2-pyridyl)-5,6-diphenyl-1,2,4-triazine (**L**; Scheme 1) with ICl in molar ratios 0.5:1, 1:1, 1:2, and 1:5 in CH<sub>2</sub>Cl<sub>2</sub> yielded products featuring the same microanalytical (elemental analysis, melting point determination) and spectroscopic (FT-IR, FT-Raman) features. Single crystal X-ray diffraction analysis revealed the reaction product to be (HL)[ICl<sub>2</sub>] (**1**).



**Scheme 1.** Molecular scheme of 3-(2-pyridyl)-5,6-diphenyl-1,2,4-triazine (**L**).

Compound **1** crystallizes in the monoclinic space group  $P2_1/c$  with four molecules in the unit cell.



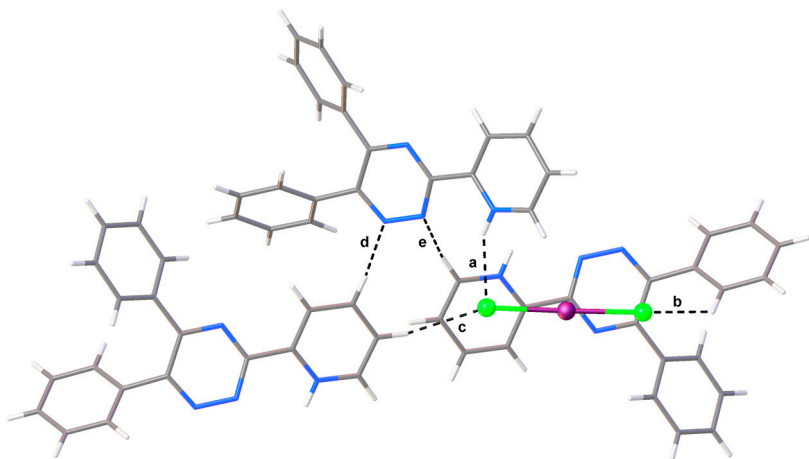
**Figure 1.** Ellipsoid plot of compound **1** with the numbering scheme adopted viewed along the  $b$ -axis. Displacement ellipsoids are drawn at 50% probability level.

Crystal data for compound **1**:  $C_{20}H_{15}Cl_2IN_4$ , ( $M_r = 509.16 \text{ g mol}^{-1}$ ) monoclinic,  $P2_1/c$  (No. 14),  $a = 17.7427(13) \text{ \AA}$ ,  $b = 7.4326(5) \text{ \AA}$ ,  $c = 15.5351(12) \text{ \AA}$ ,  $\beta = 100.659(7)^\circ$ ,  $\alpha = \gamma = 90^\circ$ ,  $V = 2013.3(3) \text{ \AA}^3$ ,  $T = 120(2) \text{ K}$ ,  $Z = 4$ ,  $Z' = 1$ ,  $\mu(\text{Mo K}\alpha) = 1.868 \text{ mm}^{-1}$ , 19110 reflections measured, 4624 unique ( $R_{int} = 0.0302$ ) which were used in all calculations. The final  $wR_2$  was 0.0634 (all data) and  $R_1$  was 0.0270 [ $F^2 \geq 2 \sigma(F^2)$ ].

The asymmetric unit of compound **1** consists of a donor molecule protonated at the N4 pyridine nitrogen atom counterbalanced by a classical[17,18]  $[ICl_2]^-$  anion. Protonation of (poly)pyridyl donors as a result of the reaction with dihalogens or interhalogens is not unusual and it has been attributed to solvolysis or reaction with incipient moisture.<sup>Error! Bookmark not defined.</sup>

In the  $HL^+$  cation, the two phenyl rings of the donor are rotated by  $38.3(3)$  and  $47.7(3)^\circ$  relative to the plane of the triazine, and the pyridine by  $12.6(3)^\circ$ . Quite surprisingly, notwithstanding no crystal structures featuring the  $HL^+$  cation have been deposited to date, these torsion angles can be compared to those featured by the two polymorphs (CSD codes HEWL0L and HEWL0L01) reported for **L** [phenyl torsions:  $32.4(1)$  and  $53.6(1)^\circ$ ; pyridine torsion  $1.0(1)^\circ$  for HEWL0L;<sup>Error! Bookmark not defined.</sup>  $32.2(2)$ ,  $56.2(2)$ , and  $9.1(2)^\circ$ , respectively, for HEWL0L01<sup>Error! Bookmark not defined.</sup>] and the corresponding values optimized at density functional theory (DFT)[19,20] level for **L** (phenyl torsion,  $29.6$  and  $34.6^\circ$ ; pyridine torsion,  $6.1^\circ$ ) and  $HL^+$  (phenyl torsion,  $30.9$  and  $38.1^\circ$ ; pyridine torsion,  $4.4^\circ$ ), suggesting that electronic factors rather than crystal packing interactions are responsible for the nonplanar conformation of the ligand.

The Cl2 terminal atom of the  $[ICl_2]^-$  anion is involved in a hydrogen bonding (HB) interaction with the pyridinium moiety [interaction  $a$  in Figure 2 and Table 1]. The HB interaction results in a remarkable asymmetry of the  $[ICl_2]^-$  anion [Cl1–I1,  $2.4856(8)$ ; Cl2–I1,  $2.6005(6) \text{ \AA}$ ; Cl1–I1–Cl2,  $178.27(2)^\circ$ ]. The Cl1 and Cl2 atoms further interact with the H20<sup>i</sup> and H13<sup>ii</sup> protons of different symmetry-related adjacent units (interactions  $b$  and  $c$  in Table 1 and Figure 2; <sup>i</sup>  $= 1 - x, -\frac{1}{2} + y, \frac{3}{2} - z$ ; <sup>ii</sup>  $= x, \frac{3}{2} - y, -\frac{1}{2} + z$ ). These interactions, along a set of weak C–H $\cdots$ N contacts (Table 1) generate the crystal packing, seen along the  $b$ -axis in Figure 2.



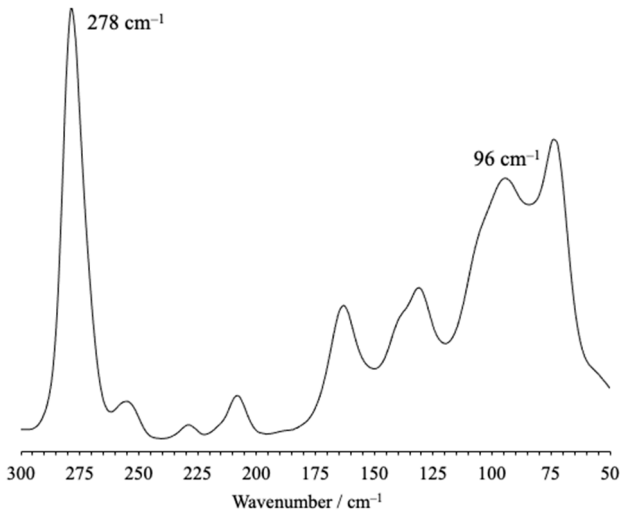
**Figure 2.** Section of the crystal packing of compound **1** seen along the *b*-axis. Labelled contacts are described in Table 1.

**Table 1.** Intermolecular interactions of compound **1**.

Interaction	$d_{D-H}$ (Å)	$d_{H\cdots A}$ (Å)	$d_{D\cdots A}$ (Å)	$\alpha_{D-H\cdots A}$ (°)
<i>a</i> N4–H4 $\cdots$ Cl2	0.85(3)	2.39(2)	3.174(2)	153(2)
<i>b</i> C20 <sup>i</sup> –H20 <sup>i</sup> $\cdots$ Cl1	0.95	2.88	3.541(2)	128.2
<i>c</i> C13 <sup>ii</sup> –H13 <sup>ii</sup> $\cdots$ Cl2	0.95	2.70	3.610(3)	160.9
<i>d</i> C12 <sup>ii</sup> –H12 <sup>ii</sup> $\cdots$ N3	0.95	2.66	3.291(3)	124.5
<i>e</i> C14 <sup>i</sup> –H14 <sup>i</sup> $\cdots$ N2	0.95	2.62	3.425(3)	143.2

$i = 1 - x, -\frac{1}{2} + y, \frac{3}{2} - z; ii = x, \frac{3}{2} - y, -\frac{1}{2} + z.$

The FT-Raman spectrum of compound **1** shows the expected band due to the symmetric stretching mode peculiar to the [ICl<sub>2</sub>]<sup>−</sup> ion at 278 cm<sup>−1</sup> in the FT-Raman spectrum (Figure 3), in excellent agreement with the corresponding values calculated at hybrid-DFT level [ $\nu(\sigma_g) = 257$ ,  $\nu(\sigma_u) = 238$  cm<sup>−1</sup>]. The  $\pi_u$  bending mode is calculated at 108 cm<sup>−1</sup> and can be envisaged both in the FT-Raman and in the FT-FIR spectra within the complex envelope of bands at about 100 cm<sup>−1</sup> (Figure S3). Notably the wavenumbers of the stretching and bending modes are very close to those previously reported for different compounds featuring (poly)pyridinium cations balanced by [ICl<sub>2</sub>]<sup>−</sup> anions, for which the stretching and the bending modes were reportedly in the range 265–285 cm<sup>−1</sup> and 85–90 cm<sup>−1</sup>, respectively.<sup>Error! Bookmark not defined.–Error! Bookmark not defined.,[21]</sup>



**Figure 3.** FT-Raman spectrum recorded for compound **1** in the solid-state.

### 3. Materials and Methods

#### 3.1. General

All the reagents and solvents were purchased from Sigma-Aldrich or Lancaster and used without further purification. Elemental analyses were performed with an EA1108 CHNS-O Fisons instrument. Infrared spectra were recorded on a Bruker IFS55 spectrometer at room temperature using a flow of dried air. Far-IR (500–50  $\text{cm}^{-1}$ ) spectra (resolution 2  $\text{cm}^{-1}$ ) were recorded as polythene pellets with a Mylar beam-splitter and polythene windows. Middle IR spectra (resolution 2  $\text{cm}^{-1}$ ) were recorded as KBr pellets, with a KBr beam-splitter and KBr windows. FT-Raman spectra were recorded (resolution of 2  $\text{cm}^{-1}$ ) on a Bruker RFS100 FT-Raman spectrometer, fitted with an In–Ga–As detector (room temperature) operating with a Nd:YAG laser (excitation wavelength 1064 nm) with a 180° scattering geometry (excitation powder 5 mW). Melting point was determined on a FALC mod. C apparatus. X-ray diffraction data for compound **1** were collected at 120(2) K by means of combined  $\varphi$  and  $\omega$  scans with a Bruker Nonius KappaCCD area detector situated at the window of a rotating anode (graphite Mo- $K_{\alpha}$  radiation,  $\lambda = 0.71073$  Å). The structure was solved with the ShelXT[22] solution program using dual methods and the model was refined with ShelXL[23] 2018/3 using full matrix least squares minimization on  $F^2$ . Olex2 1.5[24] was used as the graphical interface. DFT<sup>Error!</sup> calculations were carried out both on **L**,  $\text{HL}^+$ , and  $[\text{ICl}_2]^-$  at DFT level with the commercial suite of programs Gaussian 16[25] by adopting the mPW1PW hybrid functional.[26] The def2SVP and def2TZVP basis sets[27,28] were adopted for the atomic species of the **L** donor and the  $[\text{ICl}_2]^-$  ion, respectively. Vibrational frequencies were calculated at the optimized geometries. GaussView[29] and PyFreq[30] were used to investigate the Kohn-Sham molecular orbital composition and the vibrational frequencies.

#### 3.2. Synthesis of 2-(5,6-diphenyl-1,2,4-triazin-3-yl)pyridinium dichloroiodate (I) (1)

To 2 mL of a  $\text{CH}_2\text{Cl}_2$  solution of 3-(2-pyridyl)-5,6-diphenyl-1,2,4-triazine (26 mg,  $8.4 \times 10^{-5}$  mol), a 0.054 M solution of ICl in the same solvent was added dropwise in **L**:ICl molar ratios ranging between 1:05 and 1:5 (0.8 mL,  $4.2 \times 10^{-5}$  mol; 1.6 mL,  $8.4 \times 10^{-5}$  mol; 3.1 mL,  $1.7 \times 10^{-4}$  mol; 7.8 mL,  $4.2 \times 10^{-4}$  mol). By slow air evaporation of the resulting mixture a crystalline precipitate was isolated and washed with light petroleum ether and dried under reduced pressure. Elemental analysis calcd. for  $\text{C}_{20}\text{H}_{15}\text{N}_4\text{ICl}_2$ : 47.18; H, 2.97; N, 11.00%. Found: C, 47.23; H, 2.47; N, 11.28%. M.p. 218 °C. FT-MIR (KBr pellet, 4000–400  $\text{cm}^{-1}$ ): 3467m, 2362m, 1624m, 1612s, 1608m, 1538m, 1506m, 1445m, 1410s, 1375m, 1306m, 1227s, 1164s, 1005m, 943m, 783m, 766s, 755s, 736m, 692m, 660s, 539m, 534m, 510m, 443m, 416w  $\text{cm}^{-1}$ . FT-FIR (polytene pellet, 500–50  $\text{cm}^{-1}$ ): 487m, 444m, 416m, 402s, 391m, 366m, 332m, 319m, 310m, 284m, 273s, 260s, 234s, 218s, 199s, 191s, 163m, 145m, 135s, 129s, 103w, 95m, 85m, 67s  $\text{cm}^{-1}$ . FT-Raman (500–50  $\text{cm}^{-1}$ , 5 mW, relative intensities in parentheses related to the highest peak taken equal to 10.0): 278 (10.0), 163 (3.3), 131 (3.8), 94 (6.2), 73 (7.1)  $\text{cm}^{-1}$ .

### 4. Conclusions

2-(5,6-diphenyl-1,2,4-triazin-3-yl)pyridinium dichloroiodate (I) (**1**) was synthesized and fully characterized. Further studies are ongoing in our laboratories to investigate the reactivity of 3-(2-pyridyl)-5,6-diphenyl-1,2,4-triazine towards different dihalogens and interhalogens and its potential role as a building block in the formation of extended supramolecular assemblies.

**Supplementary Materials:** The following supporting information can be downloaded at the website of this paper posted on Preprints.org. Figures S1 and S2: FT-IR; Table S1: Crystal data and refinement parameters; Tables S2, S3: bond lengths and angles; Table S4–S5: DFT-optimized orthogonal Cartesian coordinates.

**Author Contributions:** Conceptualisation: MA, MCA, VL, AM. Data curation: MCA, EP, AP, MA, AM, JBO, SJC. Investigation: MCA, VL, AM, AP, EP, JBO, SJC, MA. Writing (original draft): MA. All authors have read and agreed to the published version of the manuscript.



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**Data Availability Statement:** Crystallographic data were deposited at CCCD (CIF deposition number 2263970).

**Conflicts of Interest:** The authors declare no conflict of interest.

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