

Short Note

2-(5,6-Diphenyl-1,2,4-Triazin-3-Yl)pyridinium Dichloroiodate (I)

M. Carla Aragoni ¹, Vito Lippolis ¹, Annalisa Mancini ¹, Anna Pintus ¹, Enrico Podda ^{1,2*}, James B. Orton ³, Simon J. Coles ³, and Massimiliano Arca ^{1*}

¹ Dipartimento di Scienze Chimiche e Geologiche, Università degli Studi di Cagliari, S.S. 554 bivio Sestu, Monserrato, 09042 Cagliari, Italy

² Centro Servizi di Ateneo per la Ricerca (CeSAR), Università degli Studi di Cagliari, S.S. 554 bivio Sestu, Monserrato, 09042 Cagliari, Italy

³ UK National Crystallography Service, School of Chemistry, Faculty of Engineering and Physical Sciences, University of Southampton, Southampton SO17 1BJ, UK

* Correspondence: enrico.podda@unica.it (E. P.); marca@unica.it (M. A.)

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

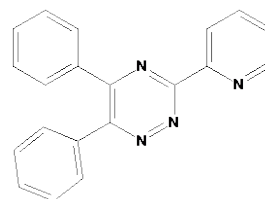
1. Introduction

Polypyridine donors react with interhalogens XY and dihalogens X₂ (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.^{1,2,3,4} Among the possible reaction products, Charge-Transfer adducts containing the N...X–Y linear group,^{5,6} halonium compounds featuring a N...X...N moiety^{5,7,8} or salts where a N-protonated pyridinium cation is counterbalanced by discrete³ or extended⁹ (poly)halide anions can be mentioned. FT-Raman spectroscopy can provide useful information on the nature of the resulting products.^{1,3,9,10} In simple CT-adducts, the adduct formation results in an elongation of the perturbed X–Y moiety with respect to the free halogen/interhalogen.^{3,4} 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.^{1–4}

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.^{13,14,15,16} 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,^{1–4} 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 CH₂Cl₂ 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)[ICl₂] (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.

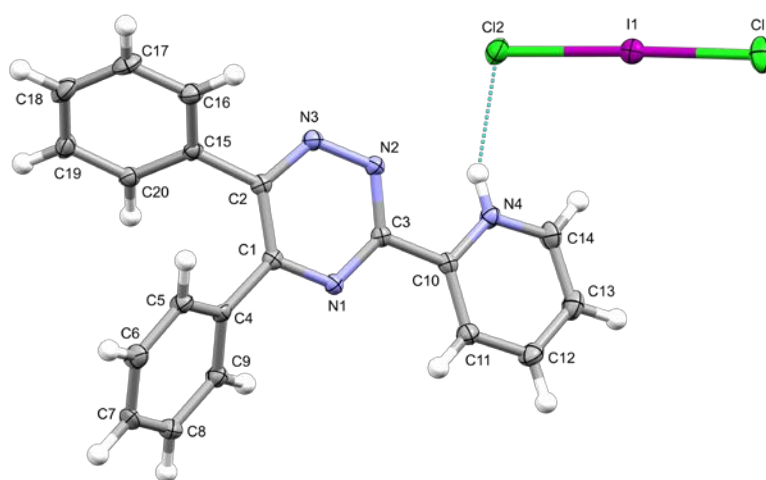


Figure 1 Ellipsoid plot of compound **1** with the numbering scheme adopted viewed along the b -axis. Displacement ellipsoids are drawn at 50% probability level.

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} $[\text{ICl}_2]^-$ 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.¹

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 HEWLOL and HEWLOL01) reported for **L** [phenyl torsions: $32.4(1)$ and $53.6(1)^\circ$; pyridine torsion $1.0(1)^\circ$ for HEWLOL;¹¹ $32.2(2)$, $56.2(2)$, and $9.1(2)^\circ$, respectively, for HEWLOL01¹²] and the corresponding values optimized at density functional theory (DFT)^{19,20} level for **L** (phenyl torsion, 29.6 and 34.6° ; pyridine torsion, 6.1°) and HL^+ (phenyl torsion, 30.9 and 38.1° ; pyridine torsion, 4.4°), suggesting that electronic factors rather than crystal packing interactions are responsible for the nonplanar conformation of the ligand.

The Cl2 terminal atom of the $[\text{ICl}_2]^-$ 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 $[\text{ICl}_2]^-$ anion [Cl1–I1, 2.4856(8); Cl2–I1, 2.6005(6) Å; Cl1–I1–Cl2, 178.27(2)°]. The Cl1 and Cl2 atoms further interact with the H20ⁱ and H13ⁱⁱ protons of different symmetry-related adjacent units (interactions *b* and *c* in Table 1 and Figure 2; ⁱ $= 1 - x, -\frac{1}{2} + y, \frac{3}{2} - z$; ⁱⁱ $= x, \frac{3}{2} - y, -\frac{1}{2} + z$). These interactions, along a set of weak C–H⋯N contacts (Table 1) generate the crystal packing, seen along the *b*-axis in Figure 2.

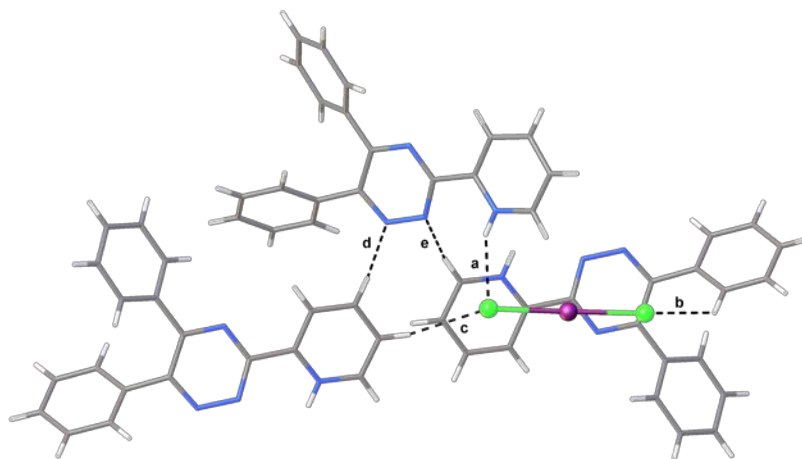


Figure 2 Section of the crystal packing of compound **1** seen along the *b*-axis. Labelled contacts are described in Table 1.

The FT-Raman spectrum of compound **1** shows the expected band due to the symmetric stretching mode peculiar to the $[\text{ICl}_2]^-$ ion at 278 cm^{-1} in the FT-Raman spectrum (Figure 3), in excellent agreement with the corresponding values calculated at hybrid-DFT level [$\nu(\sigma_g) = 257$, $\nu(\sigma_u) = 238 \text{ cm}^{-1}$]. The π_u bending mode is calculated at 108 cm^{-1} 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^{-1} (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 $[\text{ICl}_2]^-$ anions, for which the stretching and the bending modes were reportedly in the range 265–285 cm^{-1} and 85–90 cm^{-1} , respectively.^{1–4,21}

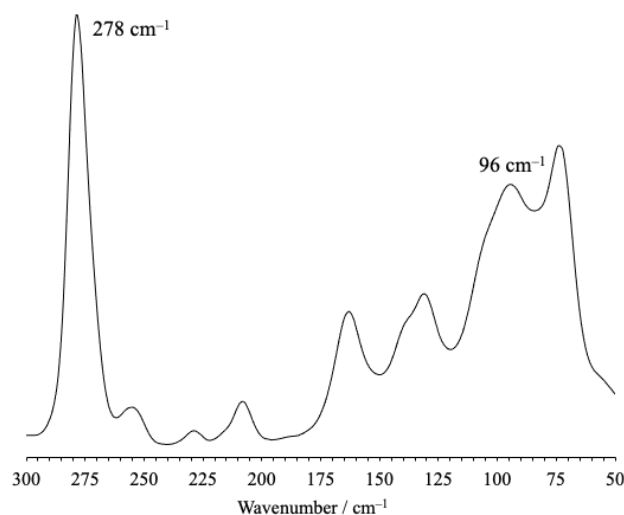


Figure 3 FT-Raman spectrum recorded for compound **1** in the solid-state.

Table 1: Intermolecular interactions of compound 1.

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

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

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 cm⁻¹) spectra (resolution 2 cm⁻¹) were recorded as polythene pellets with a Mylar beam-splitter and polythene windows. Middle IR spectra (resolution 2 cm⁻¹) were recorded as KBr pellets, with a KBr beam-splitter and KBr windows. FT-Raman spectra were recorded (resolution of 2 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 φ and ω scans with a Bruker Nonius KappaCCD area detector situated at the window of a rotating anode (graphite Mo-K α radiation, $\lambda = 0.71073$ Å). The structure was solved with the ShelXT²² solution program using dual methods and the model was refined with ShelXL²³ 2018/3 using full matrix least squares minimization on F^2 . Olex2 1.5²⁴ was used as the graphical interface. DFT^{19,20} calculations were carried out both on **L**, HL⁺, and [ICl₂]⁻ at DFT level with the commercial suite of programs Gaussian 16²⁵ 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 [ICl₂]⁻ ion, respectively. Vibrational frequencies were calculated at the optimized geometries. GaussView²⁹ and PyFreq³⁰ 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 CH₂Cl₂ solution of 3-(2-pyridyl)-5,6-diphenyl-1,2,4-triazine (26 mg, 8.4×10⁻⁵ 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, 4.2×10⁻⁵ mol; 1.6 mL, 8.4×10⁻⁵ mol; 3.1 mL, 1.7×10⁻⁴ mol; 7.8 mL, 4.2×10⁻⁴ 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 C₂₀H₁₅N₄ICl₂: 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 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 cm⁻¹. FT-FIR (polythene pellet, 500–50 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 cm⁻¹. FT-Raman (500–50 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) 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: 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.

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

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

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