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BRIEF COMMUNICATION

# The Structure and Characterization of 3,4,5-Triiodo-2-Methylthiophene: An Unexpected Iodination Product of 2-Methylthiophene

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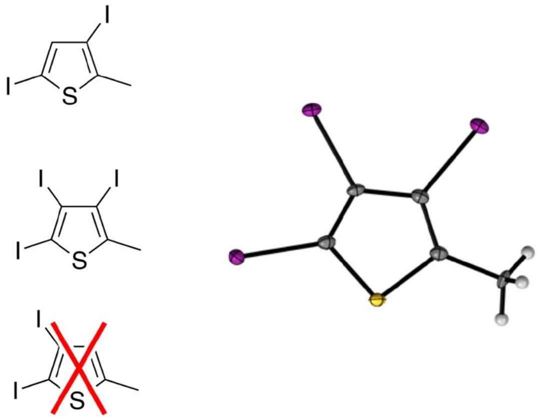
## Abstract

We report the structure and characterization of 3,4,5-triiodo-2-methylthiophene, obtained as an unexpected, unreported, and significant side product from the iodination of 2-methylthiophene using iodine and iodic acid. Identity of this unexpected product was confirmed by X-ray crystallography and $^{1}$H and $^{13}$C NMR. The compound crystallizes in the P2$_1$/c space group with unit cell parameters $a=16.4183(10)$ Å, $b=4.1971(3)$ Å, $c=14.3888(9)$ Å, $\beta=111.4442(14)$, $Z=4$, and $D_{calc}=3.425$ g cm$^{-3}$. Analysis of residual electron density maps indicated the presence of crystallographic disorder between the 2-methyl and 5-iodo positions leading to a model of two distinct molecules of 3,4,5-triiodo-2-methylthiophene where the atoms of these two groups were exchanged. Non-covalent iodine–iodine and sulfur–iodine interactions are observed.

### Graphical Abstract

Three products, two of which are constitutional isomers, are possible when installing multiple iodine atoms on 2-methylthiophene; X-ray structural analysis and spectral characterization show that the 4,5-diiodo isomer is not formed and that the 3,4,5-triiodo isomer is unexpectedly obtained. Halogen and chalcogen bonding are clearly observed.



**Keywords** Iodination reaction · Thiophene · Iodothiophene · Halogen bonding · Sigma-hole · Chalcogen bonding

## Introduction

Iodinated aromatic compounds are valuable synthetic intermediates with reactivity higher than that of the corresponding brominated and chlorinated aryl species, specifically in metalation reactions and metal catalyzed coupling reactions [1, 2]. Typically, however, iodinated intermediates are more

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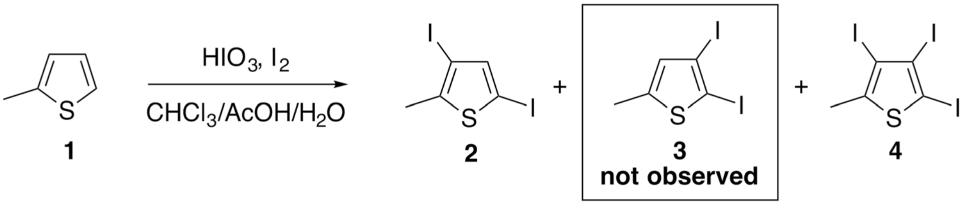

**Scheme 1** The iodination of **1** can give a pair of diiodinated regioisomers **2** and **3**. A triiodinated side product, **4**, however, is unexpectedly observed while compound **3** is not observed

expensive than their brominated and chlorinated analogues.[1] In some cases, the desired iodine compounds are not commercially available [3]. Consequently, research aimed at obtaining aromatic iodides has received much attention.

Relatively mild iodination methods using iodic acid in conjunction with iodine or potassium iodide have been employed with thiophene and thiophene derivatives [4–6] in order to iodinate the less reactive three and four positions needed for the synthesis of organic materials [7–10] and in particular diarylethene photochromes [11–16]. Other electron rich substrates are also employed [4–6]. The attempt at diiodination of 2-methylthiophene (**1**), as illustrated in Scheme 1, presents a method for acquisition of the highly desirable 3,5-diiodo-2-methylthiophene (**2**), expected to be more reactive than the bromine analogue [17, 18]. The constitutional isomer 4,5-diiodo-2-methlthiophene (**3**) has been posited as another diiodinated product [4], but it was not observed in our hands. Here we report the synthesis and characterization of 3,4,5-triiodo-2-methylthiophene (**4**), an unexpected byproduct of the diiodination of 2-methylthiophene. Crystallographic data shows the presence of halogen and chalcogen bonding.

## Materials and Experimental Details

All chemicals were obtained commercially and used as received. $^1$H and $^{13}$C NMR spectra were acquired using a Varian Inova NMR spectrometer operating at 400 MHz for proton NMR and 100 MHz for carbon NMR. All spectra are referenced to the residual solvent peak of chloroform-*d* at 7.26 ppm. Reagents were combined in air and the reaction was refluxed under a nitrogen atmosphere. Silica gel used for chromatography was 70–230 mesh. Melting points were obtained using a ThermoFisher Scientific IA9000 series digital melting point apparatus and are uncorrected.

## General Synthetic Procedures

### Small-Scale Synthesis of 3,5-Diiodo-2-Methylthiophene (2) and 3,4,5-Triiodo-2-Methyl Thiophene (4)

This procedure is identical to that reported by Sevez and Pozzo [4]. To a 25 mL round bottom flask with reflux condenser was added 2-methylthiophene (0.500 g, 5.09 mmol), acetic acid (3.75 mL), chloroform (3.75 mL), and iodine (1.290 g, 5.09 mmol). With stirring, iodic acid (0.448 g, 2.55 mmol) previously dissolved in water (1.25 mL) was added in portions over 5 min and the reaction was refluxed, under nitrogen, at 80 °C for 24 h. After cooling to room temperature, the reaction was diluted with hexane (30 mL). The hexane phase was collected and the aqueous phase was diluted with water (30 mL) and extracted with hexane (2 × 30 mL). The combined hexane phases were washed with water (30 mL), saturated aqueous sodium bicarbonate (1 × 30 mL), 10 wt% aqueous sodium thiosulfate (30 mL), and finally brine (30 mL). After drying over $MgSO_4$, filtration, and removal of solvent, a clear, brown oil was obtained. By $^1$H NMR, the product yield was quantitative and two products, based on methyl peaks, were present. The products were adsorbed onto silica and separated by column chromatography on silica eluting with hexane. The NMR spectra obtained for compound **2** were consistent the literature report as was the approximate yield [4]. White, needle-like X-ray quality crystals of **4** were obtained by slow evaporation of hexane. For compound **4**: $^1$H NMR (500 MHz, $CDCl_3$) δ 2.55 (s, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 146.36, 106.59, 92.43, 78.23, 20.70.

### Large-Scale Synthesis of 3,5-Diiodo-2-Methylthiophene (2) and 3,4,5-Triiodo-2-Methyl Thiophene (4)

Larger scale reactions (one order of magnitude greater) can be run with product mixtures and spectral data identical to that obtained from the small scale reaction. Running a larger scale reaction presents the problem of separating compounds **2** and **4**, which have similar $R_f$ values when chromatographing on silica eluting with hexanes.

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[1] A price comparison can be found in Table S3.

**Table 1** Summary of X-ray crystallographic data for 3,4,5,-triiodo-2-methylthiophene (**4**)

| CCDC no. | |
|---|---|
| Empirical formula | $C_5H_3I_3S$ |
| Formula weight (g mol$^{-1}$) | 475.83 |
| Temperature (K) | 90 |
| Wavelength (A) | 0.71073 |
| Crystal system | Monoclinic |
| Space group | $P2_1/c$ |
| Unit cell dimensions | |
| *a*, Å | 16.4183(10) |
| *b*, Å | 4.1971(3) |
| *c*, Å | 14.3888(9) |
| β, ° | 111.4442(14) |
| Volume (Å$^3$) | 922.88(10) |
| *Z* | 4 |
| $D_{calc}$ (g cm$^{-3}$) | 3.425 |
| $\mu(\mathrm{MoK}_\alpha)$ mm$^{-1}$ | 10.307 |
| *F*(000) | 832.0 |
| 2θ range (°) | 5.332–62.018 |
| Index ranges | $-23 \leq h \leq 23$<br>$-5 \leq k \leq 5$<br>$-20 \leq l \leq 19$ |
| Reflections collected/unique ($R_{int}$) | 18,676 |
| Data/parameters | 2760/0/103 |
| Goodness-of-fit on $F^2$ | 1.092 |
| Refinement method | Least-squares minimization |
| Final *R* indices [$I > 2\sigma(I)$] | $R_1 = 0.0188$, $wR_2 = 0.0438$ |
| R indices (all data) | $R_1 = 0.0203$, $wR_2 = 0.0448$ |
| Largest diff. peak and hole (e/Å$^3$) | 1.23/– 1.20 |

## X-ray Crystallography

A single crystal of **4** was mounted on a glass fiber using Paratone oil under atmospheric conditions. X-ray diffraction data was collected on a Bruker SMART APEX2 CCD diffractometer installed on a rotating anode source (MoKα radiation, $\lambda = 0.71073$ Å), and equipped with an Oxford Cryosystems (Cryostream700) nitrogen gas-flow apparatus. The data were collected by the rotation method with a 0.5° frame-width (ω scan). Three sets of data (360 frames in each set) were collected, nominally covering complete reciprocal space. The structure was solved in the Olex2 [19] crystallography program using the XT structure solution program [19] using the Intrinsic Phasing method and refined using the SHELXL refinement package [20] using least-squares minimization. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were placed at idealized positions and then allowed to be freely refined. Analysis of residual electron density maps from initial refinements indicated the presence of crystallographic disorder between the 2-methyl and 5-iodo positions. The atoms of these two groups were exchanged leading to two distinct molecules of **4**. The positions of the disordered groups were freely refined. The occupancies of the disordered methyl and iodo groups were constrained to be equivalent in each of the distinct molecules with the additional constraint that the sum of the occupancies for both distinct molecules must sum to 1.0. Ultimately, the occupancies for the two disordered parts was determined to be approximately 0.55 and 0.45. A summary of the crystallographic data and details of the structure refinements are listed in Table 1.

## Results and Discussion

When the reaction illustrated in Scheme 1 is examined by TLC (polyester backed silica stationary phase, hexane mobile phase), two spots of similar $R_f$ are clearly observed. However, the $^1$H NMR spectrum of the crude reaction (Fig. 1) does not match the expected pattern if those spots were due to a mixture of compounds **2** and **3**; were this the case, two singlets should appear in the aromatic region. Only one singlet is observed at 7.08 ppm, which is consistent with the spectrum reported by Sevez and Pozzo [4] for compound **2**. However, two prominent singlets are observed in the aliphatic region at 2.55 ppm and 2.42 ppm with a ratio of 1:4.6, respectively. The peak at 2.42 ppm correlates with that of the methyl peak expected from compound **2** when integration is taken into account and according to the work by Sevez and Pozzo. However, the source for the peak at 2.55 ppm could not be immediately identified. While the $^1$H NMR spectra of various iodinated thiophenes has previously been reported, these spectra were run in carbon tetrachloride using a low field instrument in contrast to the 400 MHz instrument and chloroform-*d* solvent used in these experiments [21].

Fortuitously, a crystalline solid forms from the initially obtained viscous oil. While the obtained solid was impure, dissolution of the crude mixture and adsorption on silica followed by chromatography on silica eluting with 100% hexanes allowed isolation this compound, which we observed had limited solubility in hexane and crystallized slowly as fractions were collected. The compound has a melting point of 97–98 °C, close to the reported melting point of approximately 100–101 °C reported separately by Steinkopf and Takahashi for 3,4,5,-triiodo-2-methylthiophene [21, 22] and identical to that reported by Gronowitz [23]. The obtained crystals were of X-ray quality and subjected to X-ray diffraction analysis, which showed that the anomalous product was indeed triiodinated compound **4** (Fig. 2). Compound **4** has no aromatic protons and the $^1$H NMR spectrum correlates with the crystal structure obtained from pure **4**.

Compound **4** crystallizes in a herringbone type structure and exhibits crystallographic disorder between the 2-methyl and 5-iodo positions. This leads to a model of two

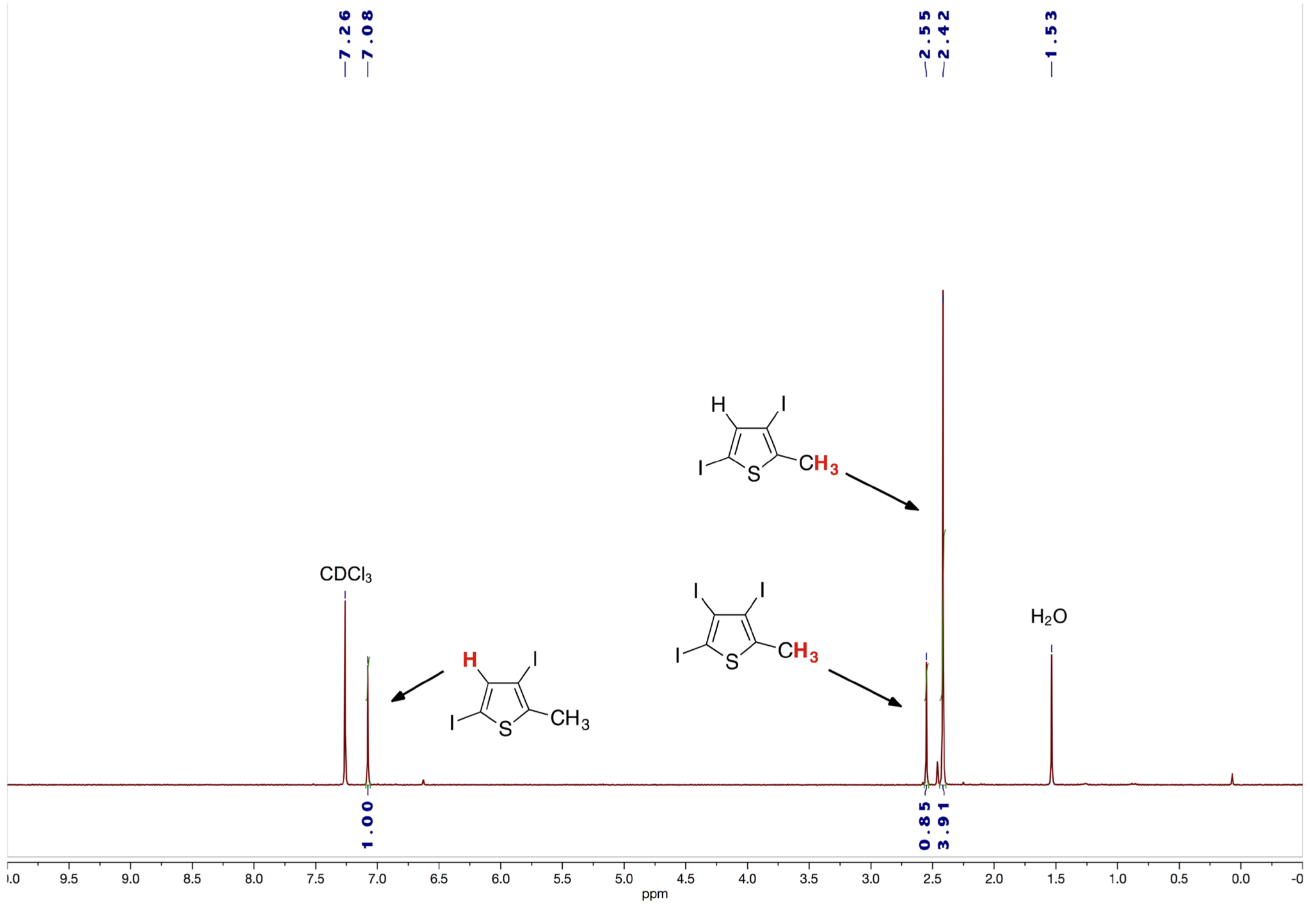


**Fig. 1** Crude $^1$H NMR of the iodination reaction of 2-methylthiophene with proton peaks, integration, and chemical shifts labeled. The residual solvent peak is used as an internal standard

distinct molecules of **4** where the atoms of the 5-iodo and the 2-methyl groups are exchanged. When measuring the bond lengths of C(3)–I(1) and C(4)–I(2), distances of 2.085(12) Å and 2.081(2) Å, respectively, are observed. These lengths are identical to those reported by Allen and coworkers for $C_{ar}$–I bonds when standard deviations are taken into account [24]. The bonds C(2)–I(3A) and C(5)–I(3) are shorter at 2.012(2) Å and 2.026(2) Å, respectively, likely due to the effects of non-covalent interaction between sulfur atoms and neighboring iodine atoms.

When examining short contacts and the resultant bond angles, evidence supporting halogen bonding [25] and chalcogen bonding [26] is observed. The first set of halogen and chalcogen bonds forms a tetramer of **4** (Fig. 3). At 3.673 and 3.826 Å, the non-covalent I2–I3 and I3–I3 interactions, respectively, are shorter than the sum of the van der Waals radii [27] at 3.96 Å for an iodine–iodine interaction. With a C5–I3–I2 bond angle of 168.01°, the interaction is consistent with the σ-hole [28] of I3 interacting with the lone pairs on I2. The remaining close contact of the tetramer is formed between S1 and I2 with a distance of 3.615 Å—shorter than the van der Waals distance of 3.78 Å for S–I. The C4–I2–S bond angle of 171.37° suggests that the sulfur lone pair are interacting with the σ-hole of I2.

The tetramers also exhibit lateral short I1–I1 contacts of 3.771 Å (Fig. 4). These interactions form a zig-zag chain that propagates parallel to (010). Similar to above, the σ-hole of I1 appears to be interacting with the lone pairs on the neighboring I1 atoms.

## Conclusions

Using X-ray crystallography and standard spectroscopic techniques, we were able to correct an oversight in the literature. As shown in Scheme 1, the literature supposes that the products obtained from iodination of 2-methylthiophene are **2** and **3** as opposed to **2** and **4**. The presence of **4** is confirmed by single crystal diffraction methods while the absence of **3** is determined by the $^1$H NMR spectrum of the crude product mixture. As iodinated compounds are useful intermediates and starting material, we imagine that compound **4**, obtained by relatively mild methods, could find use in the field of organic materials. The observed halogen and chalcogen bonds will add to our understanding of these non-covalent interactions and potentially find applications in materials engineering [29–31], biological applications [32–34], and recently in separation methods [35].

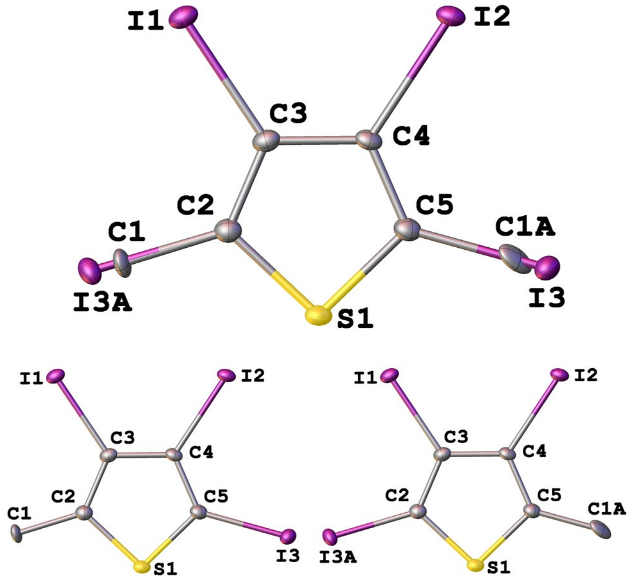
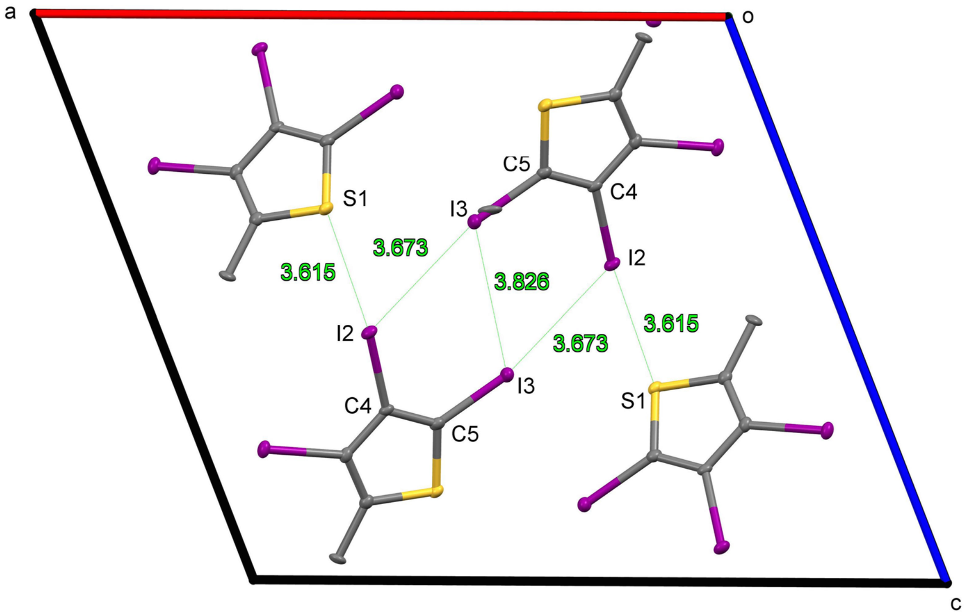


**Fig. 2** The crystal structure of 3,4,5-triiodo-2-methylthiophene (**2**) with both the major and minor species shown superimposed (top) . The structure of the major disorder species where C2–I3A and C5–C1A bonds are not shown (bottom left); the structure of the minor disorder species where C2–I3A and C5–C1A bonds are shown (bottom right). Thermal ellipsoids are shown at 50% and hydrogen atoms are omitted for clarity

## Supplementary Information

NMR spectra, $^{1}$H and $^{13}$C, for 3,4,5-triiodo-2-methyl thiophene. CCDC 1860825 contains the supplementary crystallographic data for this paper; this data can be obtained free of charge via http://www.ccd.cam.ac.uk/conts/retrieving.html or from CCDC, 12 Union Road, Cambridge CB21EZ, UK; Fax: +44-1223-336033; Email: deposit@ccdc.cam.ac.uk.

**Fig. 3** The tetramer of **4** with halogen and chalcogen bonds and bond lengths denoted



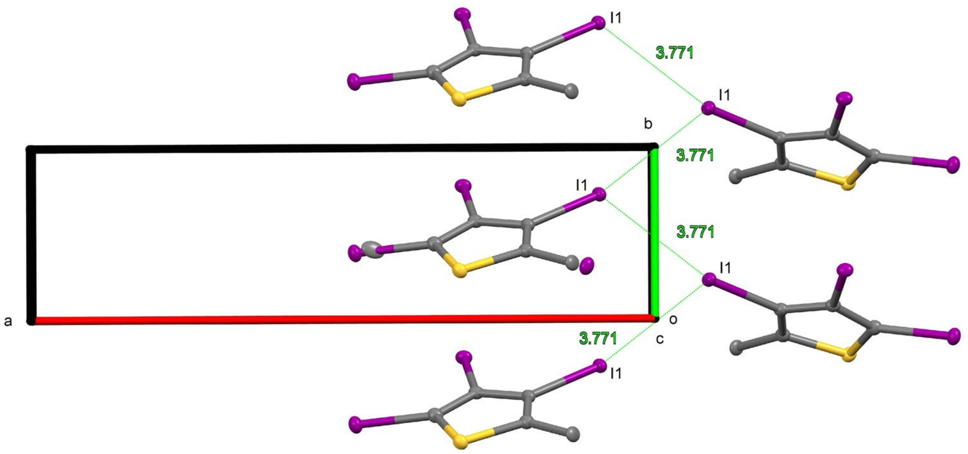


**Fig. 4** Lateral short I1–I1 contacts of 3.771 Å showing a zig-zag chain that propagates parallel to [010] for **4**

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