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Structure and Vibrational Spectra of 2,5-Diiodothiophene: a Model for Polythiophene.

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ABSTRACT

The structure and vibrational spectroscopy of 2,5-diiodothiophene have been described for the first time. The structure is remarkable in that despite the presence of eight molecules in the unit cell, there is almost no evidence for any interaction between them. This is reflected in the spectra that show coincident modes in the infrared, Raman and inelastic neutron scattering (INS) spectra and almost resolution limited linewidths in the INS spectrum, showing that the both the factor group splitting and the phonon dispersion is very small. This property has led to the use of the compound as a calibrant in INS spectroscopy. The deductions from the spectra are confirmed by a periodic-DFT calculation that allows a complete spectral assignment to be made. Comparison to the INS and Raman spectra of polythiophene (for which 2,5-diiodothiophene may be used as a monomer), shows a marked similarity for the former and a marked difference to the latter. The INS spectrum of polythiophene is dominated by the C–H bending modes, which are unchanged on polymerisation. In contrast, the Raman spectrum of polythiophene is dominated by the changed electronic environment which results in strong electron-phonon coupling and a significant upshift of the C=C stretch modes.

INTRODUCTION

Polymeric solar cells are a promising alternative for producing clean and renewable energy due to the possibility of fabricating them onto large areas of lightweight, flexible substrates by solution processing at low cost.¹ In this context, oligothiophenes² and polythiophenes^{3,4} are attracting increasing interest because they offer a range of promising properties. In part, this arises because thiophene chemistry is well-developed⁵ and functionalisation and derivatisation of the C₄H₄S core is possible in many different ways.

Alkyl-substituted polythiophenes are soluble and their use as a starting material allows thin film fabrication⁶ using conventional spin-coating methods. Direct deposition of polythiophene solutions into micro- or nanopatterns on various substrates has also been demonstrated by a variety of methods including inkjet printing.⁷ An alternative approach is to polymerise a monomer on a patterned surface.⁸ 2,5-Diiodothiophene is a promising material for this method because the C–I bonds can be selectively dissociated by ultraviolet irradiation, generating thienyl radicals that polymerise.⁸⁻¹⁰

Vibrational spectroscopy provides a valuable method to characterise the materials and, to this end, the spectra of polythiophene,¹¹⁻¹³ oligothiophenes¹⁴⁻¹⁸ and thiophene¹⁹⁻²¹ have been assigned. However, the spectra of 2,5-diiodothiophene have been little investigated, apart from reports of the infrared spectrum^{9,22} and that of its 2,5- and 3,4- ¹³C isotopomers.²² The assignments were made by comparison to thiophene and polythiophene. The standard method for assigning the spectra, comparison with *ab initio* calculations, is hampered by the absence of structural information about the molecule. In this work, we present a structural characterisation of 2,5-diiodothiophene by single crystal X-ray diffraction and a complete assignment of the vibrational

(infrared, Raman and inelastic neutron scattering (INS)) spectra of the molecule, with the assignments supported by periodic density functional theory (DFT) calculations.

EXPERIMENTAL SECTION

Materials. 2,5-Diiodothiophene was purchased from Aldrich and polythiophene from Rieke Metals and both were used as received.

X-ray Crystallography. An X-ray diffraction experiment on 2,5-diiodothiophene was carried out at 180(2) K on an Oxford Diffraction XCalibur Gemini diffractometer using Mo-K α radiation ($\lambda = 0.71073$ Å). Intensities were integrated and absorption corrections were based on equivalent reflections using the CrysAlisPro software.²³ The structure was solved using olex2.solve²⁴ and refined against F² in SHELXL^{25,26} using OLEX2²⁷. All of the non-hydrogen atoms were refined anisotropically. All of the hydrogen atoms were located geometrically and refined using a riding model. A summary of details of the crystallographic data collection and refinement are given in Table 1.

Crystallographic data for the compound has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC 1537252. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax(+44) 1223 336033, e-mail: deposit@ccdc.cam.ac.uk]

Vibrational Spectroscopy. The INS spectrum was recorded at 20 K with TOSCA²⁸ at ISIS (Didcot, UK).²⁹ The infrared spectrum (500 to 4000 cm⁻¹ at 4 cm⁻¹ resolution) was recorded over the temperature range 113 – 300 K using a Bruker Vertex70 FTIR spectrometer with the sample held in a Specac Low Temperature Golden Gate ATR using 256 scans with a KBr beamsplitter and a DTGS detector. High resolution (1 cm⁻¹) Raman spectra were recorded at room temperature with a Bruker FT-Raman spectrometer using 1064 nm excitation, 200 mW laser power and 1024 scans. Variable

temperature (16 – 300 K) Raman spectra were recorded with a customised³⁰ Renishaw InVia system with 785 nm excitation. Since the initial report,³⁰ the system has been upgraded with new laser rejection filters that enable Raman shifts as small as 40 cm⁻¹ to be observed. A second grating with higher dispersion (1800 lines mm⁻¹ vs. 1200 lines mm⁻¹) has also been added that provides ~3 cm⁻¹ resolution across the 40 - 1800 cm⁻¹ region with 785 nm excitation.

UV-vis Spectroscopy. The UV-vis spectrum was recorded in diffuse reflectance at room temperature using a Shimadzu UV-1800 spectrometer.

Computational Methods. DFT calculations were carried out with the plane-wave pseudopotential method as implemented in CASTEP.³¹ For the initial structure, the crystal structure as determined by X-ray diffraction in this work was used. The lattice parameters were fixed at the experimental values and the molecular geometry was optimised. The generalised gradient approximation (GGA) Perdew-Burke-Ernzerhof (PBE) functional was used in conjunction with optimised norm-conserving pseudopotentials. The plane-wave cut-off energy was 750 eV and a 4×4×8 (16 k-points) Monkhorst-Pack grid was used. All of the calculations were converged so that the residual forces were less than |0.005| eV Å⁻¹. After geometry optimisation, the vibrational spectra (INS, infrared and Raman) were calculated in the harmonic approximation using density-functional perturbation-theory.^{32,33} This procedure generates the vibrational eigenvalues and eigenvectors, which allows visualisation of the modes within Materials Studio³⁴ and is also the information needed to calculate the INS spectrum using the program ACLIMAX.³⁵ Transition energies for isotopic species were calculated from the dynamical matrix that is stored in the CASTEP checkpoint file using the PHONONS utility.³⁶ We emphasise that none of the transition energies have been scaled.

RESULTS AND DISCUSSION

Solid State Structure. The crystal structure of 2,5-diiodothiophene at 180 K as determined by single crystal X-ray diffraction is shown in Figure 1. The structure is orthorhombic, *Pbca* (no. 61), with eight molecules in the primitive cell, which are all on general sites (C_1 symmetry). However, as may be seen from Table 2, that lists selected bond distances and angles, the molecule is almost planar with approximate C_{2v} symmetry. The experimental geometry is well-reproduced by the CASTEP calculations; all of the bond distances and angles agree to within 0.1 Å and 1 ° respectively. The only exception is for the C–H bond distance which, as is usually found, is underestimated in the X-ray determination. A comparison of the complete observed and calculated structures was performed with the Crystal Packing Similarity facility in MERCURY³⁷ and the result is shown in Figure S1. Omitting the hydrogens gives an rms difference of 0.032, showing a very high level of agreement. (Inclusion of the hydrogen atoms results in an rms difference of 0.088). The calculations do produce a somewhat more symmetrical molecule.

The molecules within the unit cell are effectively isolated, the closest intermolecular contact is at 3.0 Å and is between H1 and H2' on adjacent molecules. This is beyond the sum of the van der Waals radius of hydrogen (2.4 Å).³⁸ Bifurcated I···I contacts of 3.731(1) and 3.837(1) Å were identified at both ends of the molecule between symmetry related molecules forming chains of I···I contacts in the *c* direction and creating 2D planes parallel to the *ac* plane. The distances are within twice van der Waals radius of iodine, 2.04 Å,³⁸ so this is probably the interaction responsible for the stability of the crystal. There is no evidence for π - π stacking.

Figure 1: Solid state structure of 2,5-diiodothiophene as determined by single crystal X-ray diffraction at 180 K.

Vibrational Spectroscopy. Figure 2 compares the low temperature infrared (113 K), Raman (16 K) and INS (20 K) spectra of 2,5-diiodothiophene. The spectra emphasise the complementarity of, and the need for all three types of spectroscopy in order to observe all of the modes.

It can be seen that there is a remarkable degree of concurrence between all three spectra. Since the space group is centrosymmetric, coincident modes in the infrared and Raman spectra would not be expected. With eight molecules in the unit cell it would be expected that the factor group splitting would result in distinct differences between the spectra as the individual factor group components would have different infrared and Raman intensities while the INS spectrum would be a sum of all the components (since there are no selection rules in INS spectroscopy). The presence of modes at the same

transition energy in the infrared and Raman spectra demonstrates that the factor group splitting is very small, a few wavenumbers or so.

Figure 2: Low temperature vibrational spectra of 2,5-diiodothiophene. (a) Infrared at 113 K, (b) Raman at 20 K and (c) INS at 20 K.

Figure 3 shows the low energy Raman spectra as a function of temperature in the range 16 – 300 K, this region is displayed because it is the only one that shows any significant change with temperature. (Extended range Raman spectra 40 – 1800 cm^{-1} are shown in Figure S2 and infrared spectra at 111, 180 and 300 K are shown in Figure S3). Three groups of bands are present: at 40 – 60 cm^{-1} , $\sim 80 \text{ cm}^{-1}$ and 100 – 130 cm^{-1} , on the basis of the periodic-DFT calculations to be described in the next section, these are assigned as: mixed translational and librational modes, librational modes and the C–I bending modes (out-of-plane at 100 – 110 cm^{-1} and in-plane at 110 – 130 cm^{-1}) respectively. The translational and librational modes harden and sharpen as the temperature is reduced, exactly as would be expected as the lattice contracts. The C–I

bending modes behave similarly; the major peak at 106 cm^{-1} shifts slightly to 107.5 cm^{-1} , the pronounced shoulder at $\sim 109\text{ cm}^{-1}$ shifts to 111.4 cm^{-1} and becomes a distinct peak. The very weak in-plane C–I bending modes, that are only present as a weak shoulder at 300 K, are clearly resolved at 16 K. All of these changes are continuous from room temperature to 16 K, thus we conclude that there are no phase transitions between 300 and 16 K and that the 180 K crystal structure is maintained in this temperature range.

Figure 3: Variable temperature Raman spectra of 2,5-diiodothiophene in the 30 – 130 cm^{-1} region. Red: 300 K, olive 180 K, purple 100 K, blue 50 K and black 16 K.

A comparison of the observed and calculated INS, infrared and Raman spectra are shown in Figures 4-6. It can be seen that in all cases the agreement is essentially quantitative for both the transition energies and relative intensities. For the infrared spectrum, Figure 5, while the calculation correctly reproduces the positions and intensities of the major peaks, there are also a number of additional peaks. These are due to overtones and combinations which are the result of anharmonicity. This is

beyond the scope of the work as the phonon calculations assume a harmonic potential. It is somewhat surprising that they are observed with such intensity, these seems to be a feature of the use of the ATR technique. The derivative-like line shape is a result of the Christiansen effect, caused by the particle size. We note that the 785 nm excitation used for the Raman spectrum is well outside the absorption envelope (see inset in Figure 6), thus resonance or pre-resonance effects are absent and the calculated relative intensities well-match those observed. Table S1 lists the calculated vibrational transition energies at the Γ -point, their symmetries and the infrared and Raman intensities of 2,5-diiodothiophene in the solid state in space group *Pbca* with factor group D_{2h} . As previously deduced from the spectra, the calculations show that the factor group splitting is very small; generally only a few wavenumbers.

Table 3 lists the observed bands and their assignments. It can be seen that the modes fall into distinct groups: external modes below 100 cm^{-1} , the C–I bend and stretch modes in the range $100 - 365\text{ cm}^{-1}$, ring torsions at $450 - 550\text{ cm}^{-1}$, C–S stretches at $650 - 750\text{ cm}^{-1}$, out-of-plane C–H bending modes at $750 - 900\text{ cm}^{-1}$, the in-plane ring deformations at $900 - 1000\text{ cm}^{-1}$, the in-plane C–H bending modes at $1050 - 1200\text{ cm}^{-1}$, C–C and C=C stretches at $1250 - 1500\text{ cm}^{-1}$ and the C–H stretches at $>3100\text{ cm}^{-1}$.

Figure 4: Observed (a) and CASTEP calculated (b) INS spectra of 2,5-diiodothiophene at 20 K.

Figure 5: Observed (a) and CASTEP calculated (b) infrared spectra of 2,5-diiodothiophene at 300 K.

Figure 6: Observed (a) and CASTEP calculated (b) Raman spectra of 2,5-diiodothiophene at 16 K. The inset shows the diffuse reflectance UV-vis spectrum of the compound at room temperature.

As a further check on the calculation, the infrared spectra of the ¹³C isotopomers²² 2,5-diiodo-2,5-¹³C-thiophene and 2,5-diiodo-3,4-¹³C-thiophene were also generated³⁶ from the dynamical matrix that is created as part of the CASTEP vibrational analysis.^{32,33} Figure 7 compares observed and calculated spectra for the isotopomers and excellent agreement is obtained.

Figure 7: Left: observed²² and right: CASTEP calculated infrared spectra of 2,5-diiodothiophene isotopomers at 300 K. (a) 2,5-diiodothiophene, (b) 2,5-diiodo-3,4-¹³C-thiophene and (c) 2,5-diiodo-2,5-¹³C-thiophene. The left part of the figure is reproduced with permission from John Wiley and Sons, Inc.

Infrared and Raman spectra are measured at the Γ -point in the Brillouin zone *i.e.* (almost) zero wavevector. In contrast, INS spectra are measured at all wavevectors and the calculated INS spectrum in Figure 4 is generated from a calculation of the transition energies as a function of wavevector (dispersion) across the entire Brillouin zone. Figure 8 shows the dispersion plot for 2,5-diiodothiophene. The modes are noticeable for being almost dispersionless: even the optic whole-body (external) modes are almost flat, Figure 8a. This is clearly seen for the C–H stretch modes, Figure 8b, and the in-plane ring deformation modes, Figure 8c, where the dispersion is less than the factor group splitting. This is the spectral consequence of the absence of any significant

intermolecular interaction that is apparent from the structural determination. The result is that the INS modes are very sharp and on many instruments are resolution limited, (although not on TOSCA).³⁹ This has led to 2,5-diiodothiophene becoming the compound of choice for both resolution and wavenumber calibration.^{23,40,41} The low temperature INS, infrared and Raman spectra are available as images and as ASCII files from the INS database (<http://www.isis2.isis.rl.ac.uk/INSdatabase/>).

Figure 8: CASTEP calculated dispersion curves of 2,5-diiodothiophene: (a) the fingerprint region, (b) C–H stretch region and (c) expanded view of the in-plane ring deformation modes.

Comparison to polythiophene. Figure 9 compares the INS spectra of 2,5-diiodothiophene and polythiophene. It is seen that there is considerable similarity for the region $> 500 \text{ cm}^{-1}$. This is as expected because the lattice modes of the polymer and the molecule will be different character, while the range $100 - 365 \text{ cm}^{-1}$ region of 2,5-diiodothiophene is dominated by the C–I bend and stretch modes (Table 3). The strong bands in the $800 - 1200 \text{ cm}^{-1}$ region are C–H bending modes and these are almost unchanged on going from the “monomer” to the polymer.

Figure 9: Comparison of the INS spectra of: (a) 2,5-diiodothiophene and (b) polythiophene at 16 K.

The similarity in the INS spectra is in marked contrast to that of the Raman spectra. Figure 10 compares the high resolution (1 cm^{-1}) FT-Raman spectra of the two materials. Except for the C–H in-plane bending mode at $\sim 1050\text{ cm}^{-1}$ there are almost no coincident modes. The C=C stretch mode has shifted up to 1456 cm^{-1} from 1383 cm^{-1} and has broadened from 4 cm^{-1} to 14 cm^{-1} full width at half height, both effects are a result of the sequence length in polythiophene as previously noted.⁴²

It is also striking that there are very few modes apparent and that the C–H stretch modes are absent in the polythiophene spectrum. This is similar to what is observed in β -carotene,^{43,44} (which contains an all-*trans* sequence of alternating C=C and C–C bonds and is a model compound for polyacetylene), in this case the effect was ascribed to electron-phonon coupling.⁴⁵

Figure 10: Comparison of the 1 cm^{-1} resolution FT-Raman spectra of: (a) 2,5-diiodothiophene and (b) polythiophene at room temperature.

CONCLUSIONS

The structure and vibrational spectroscopy of 2,5-diiodothiophene have been described for the first time. The structure is remarkable, in that despite the presence of eight molecules in the unit cell, there is almost no evidence for any interaction between them. This is reflected in the spectra that show coincident modes in the infrared, Raman and INS spectra and almost resolution limited linewidths in the INS spectrum, showing that both the factor group splitting and the phonon dispersion are very small. This property has led to the use of the compound as a calibrant in INS spectroscopy.

Comparison to the INS and Raman spectra of polythiophene (for which 2,5-diiodothiophene may be used as a monomer), shows that the INS spectrum of polythiophene is dominated by the C–H bending modes, which are unchanged on polymerisation. In contrast, the Raman spectrum of polythiophene is dominated by the changed electronic environment which results in strong electron-phonon coupling and a

significant upshift of the C=C stretch modes.

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Notes

The authors declare that there are no conflicts of interest.

ASSOCIATED CONTENT

Supporting Information

Table of calculated vibrational transition energies at the Γ -point, Raman and infrared spectra as a function of temperature for the 0 – 1600 cm^{-1} range.

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Table 1. Crystal data and structure refinement details for 2,5-diiodothiophene.

Empirical formula	C ₄ H ₂ I ₂ S
Formula weight	335.92
Temperature / K	180(2)
Crystal system	Orthorhombic
Space group	<i>Pbca</i>
Space group number	61
a / Å	14.9443(9)
b / Å	18.2941(15)
c / Å	5.2541(3)
α / °	90
β / °	90
γ / °	90
Volume / Å ³	1436.43(17)
Z	8
ρ _{calc} / g cm ⁻³	3.107
μ / mm ⁻¹	8.933
F(000)	1184.0
Crystal size / mm ³	0.1 × 0.06 × 0.02
Radiation	MoKα (λ = 0.71073)
2θ range for data collection / °	5.89 to 52.744
Index ranges	-18 ≤ h ≤ 18, -22 ≤ k ≤ 21, -6 ≤ l ≤ 6
Reflections collected	7641
R _{int} / R _{sigma}	0.0731 / 0.0499
Data / restraints / parameters	1466 / 0 / 64
Goodness-of-fit on F ²	1.123
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0647, wR ₂ = 0.1754
Final R indexes [all data]	R ₁ = 0.0741, wR ₂ = 0.1824
Largest diff. peak / hole / e Å ⁻³	2.81 / -1.45

Table 2. Comparison of selected observed and calculated bond distances and angles in 2,5-diiodothiophene.

	Observed	Calculated
Bond distance / Å		
S–C1	1.699	1.727
S–C4	1.738	1.727
C1–C2	1.314	1.378
C2–C3	1.434	1.422
C3–C4	1.359	1.378
C1–I1	2.102	2.064
C4–I2	2.049	2.066
C2–H1	0.931	1.088
C3–H2	0.931	1.088
Bond angle / °		
S–C1–C2	113.6	112.0
C1–C2–C3	113.1	112.4
C2–C3–C4	111.2	112.3
C3–C4–S	111.5	112.0
C4–S–C1	90.5	91.3
S–C1–I1	120.9	121.9
S–C4–I2	120.4	120.9
Dihedral angle / °		
S–C1–C2–C3	-0.9	-0.4
C1–C2–C3–C4	-0.2	0.4
C2–C3–C4–S	0.5	-0.3
C3–C4–S–C1	0.8	0.0
C2–C1–I1–S	1.5	1.1
C3–C4–I2–S	0.6	1.3

Table 3. Observed and calculated transition energies of 2,5-diiodothiophene in the solid state.

INS / cm ⁻¹	Raman/ cm ⁻¹	Infrared* / cm ⁻¹ 1	CASTEP† / cm ⁻¹	Description
			19	Acoustic + optic translation
			28	Libration
40w‡			38	Translation
55w	50w		46	Libration
60w	56w		53	Translation
80s	80s		66	Libration
112w,br	110s	104w	108	C–I in-phase out-of-plane bend
	119m		115	C–I in-phase in-plane bend
185w	187s	187w	187	C–I symmetric stretch
228m	227w	232w	224	C–I out-of-phase out-of-plane bend
240m	243w		238	C–I out-of-phase in-plane bend
360s	361w	358m	361	C–I antisymmetric stretch
457m	458w	456s	451	Out-of-plane ring deformation (C–S torsion)
538s			537	C2–C3 torsion

638w	639s		632	C1–S + C4–S in-phase stretch
730m	731w	731w	717	C1–S + C4–S out-of-phase stretch
793s		789s	776	In-phase C–H out-of-plane bend
874s			870	Out-of-phase C–H out-of-plane bend
926m	917vw	924m	913	Symmetric in-plane ring deformation (in-phase C1=C2–C3 + C4=C3–C2 bend)
950m	927w	948m	932	Antisymmetric in-plane ring deformation (out-of-phase C1=C2–C3 + C4=C3–C2 bend)
1057m	1053w/1058sh		1058	C–H in-plane symmetric bend
1203m	1203w		1187	C–H in-plane antisymmetric bend
1291m	1293m		1280	(C1=C2 + C3=C4 in-phase stretch) + (C2–C3 stretch)
	1385s	1387s	1380	C2–C3 stretch + (C1=C2 + C3=C4 in-phase stretch)
		1497m	1475	C1=C2 + C3=C4 out-of-phase stretch
	3067w	3068w,sh	3123	Out-of-phase C–H stretch
	3078w	3077w	3133	In-phase C–H stretch

† Values < 400 cm⁻¹ are taken from the 300 K data (Figure S3a), those at > 400 cm⁻¹ from the 111 K data (Figures 5a and S3c).

*Calculated values are the average of the factor group split octet at the Γ -point from the solid state calculation, the complete list is given in Table S1.

‡ w = weak, m = medium, s = strong, sh = shoulder, v = very, br = broad.

Table of Contents graphic.

Supplementary Information for:

Structure and Vibrational Spectra of 2,5-Diiodothiophene: a Model for Polythiophene.

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Table S1. Complete list of calculated vibrational transition energies at the Γ -point, symmetries, infrared and Raman intensities of 2,5-diiodothiophene in the solid state in space group *Pbca* with factor group *D*_{2h}.

Transition energy / cm ⁻¹	Symmetry	Infrared intensity / km mol ⁻¹	Raman intensity / Å ⁴ amu ⁻¹	Description†
0	<i>B</i> _{2u}	0.00	0.00	Acoustic mode
0	<i>B</i> _{1u}	0.00	0.00	Acoustic mode
0	<i>B</i> _{3u}	0.00	0.00	Acoustic mode
14	<i>B</i> _{2g}	0.00	0.00	Translation
16	<i>A</i> _g	0.00	0.00	Translation
18	<i>B</i> _{2u}	0.08	0.00	Translation
23	<i>A</i> _u	0.00	0.00	Translation
23	<i>B</i> _{1g}	0.00	2.59	Translation
25	<i>B</i> _{1u}	0.00	0.00	Libration
25	<i>B</i> _{3g}	0.00	11.60	Translation
26	<i>B</i> _{3g}	0.00	1.93	Translation
29	<i>A</i> _u	0.00	0.00	Libration
29	<i>B</i> _{3u}	2.01	0.00	Libration

31	B_{2g}	0.00	5.05	Libration
31	B_{1u}	0.15	0.00	Libration
31	A_g	0.00	20.67	Libration
33	A_u	0.00	0.00	Translation
35	B_{3u}	0.80	0.00	Translation
36	B_{3g}	0.00	0.00	Translation
39	B_{2g}	0.00	36.53	Translation
39	B_{1g}	0.00	0.00	Translation
40	B_{3u}	21.44	0.00	Libration
41	A_g	0.00	5.62	Translation
43	B_{2u}	0.05	0.00	Libration
44	B_{2u}	0.14	0.00	Translation
45	B_{3u}	0.50	0.00	Libration
45	B_{1u}	3.14	0.00	Libration
46	B_{1g}	0.00	2.33	Libration
46	A_g	0.00	101.80	Libration

47	B_{2g}	0.00	6.09	Translation
47	A_u	0.00	0.00	Libration
48	B_{1g}	0.00	0.00	Translation
48	B_{1u}	8.66	0.00	Libration
50	B_{3g}	0.00	0.00	Libration
52	B_{2u}	0.00	0.00	Libration
52	B_{2g}	0.00	37.30	Translation
53	B_{1g}	0.00	0.00	Translation
55	B_{3g}	0.00	4.02	Translation
55	A_g	0.00	36.22	Translation
56	B_{3u}	0.26	0.00	Libration
57	A_u	0.00	0.00	Libration
58	B_{2u}	0.06	0.00	Libration
58	A_u	0.00	0.00	Libration
61	B_{1u}	0.00	0.00	Libration
71	A_g	0.00	8.91	Libration

74	B_{1g}	0.00	97.62	Libration
75	B_{2g}	0.00	0.00	Libration
78	B_{3g}	0.00	123.32	Libration
104	B_{1u}	0.46	0.00	C–I in-phase out-of-plane bend
105	B_{2g}	0.00	0.00	C–I in-phase out-of-plane bend
108	B_{3u}	1.36	0.00	C–I in-phase out-of-plane bend
109	A_g	0.00	20.19	C–I in-phase out-of-plane bend
110	A_g	0.00	336.42	C–I in-phase in-plane bend
110	A_u	0.00	0.00	C–I in-phase out-of-plane bend
110	B_{3g}	0.00	49.24	C–I in-phase out-of-plane bend
112	B_{1u}	0.73	0.00	C–I in-phase in-plane bend
113	B_{1g}	0.00	0.00	C–I in-phase in-plane bend
113	B_{2g}	0.00	223.16	C–I in-phase in-plane bend
114	B_{2u}	0.00	0.00	C–I in-phase out-of-plane bend
115	B_{1g}	0.00	5.39	C–I in-phase out-of-plane bend
116	B_{3u}	0.01	0.00	C–I in-phase in-plane bend

117	A_u	0.00	0.00	C–I in-phase in-plane bend
118	B_{3g}	0.00	8.12	C–I in-phase in-plane bend
119	B_{2u}	1.06	0.00	C–I in-phase in-plane bend
184	A_u	0.00	0.00	C–I symmetric stretch
185	B_{3g}	0.00	3.63	C–I symmetric stretch
186	B_{2u}	2.60	0.00	C–I symmetric stretch
186	B_{1g}	0.00	5.47	C–I symmetric stretch
187	B_{1u}	0.26	0.00	C–I symmetric stretch
187	B_{2g}	0.00	326.63	C–I symmetric stretch
188	B_{3u}	2.22	0.00	C–I symmetric stretch
188	A_g	0.00	608.29	C–I symmetric stretch
220	B_{2u}	0.12	0.00	C–I out-of-phase out-of-plane bend
221	B_{3u}	0.09	0.00	C–I out-of-phase out-of-plane bend
221	B_{1g}	0.00	0.00	C–I out-of-phase out-of-plane bend
223	A_g	0.00	33.43	C–I out-of-phase out-of-plane bend
224	A_u	0.00	0.00	C–I out-of-phase out-of-plane bend

225	B_{1u}	0.21	0.00	C–I out-of-phase out-of-plane bend
227	B_{3g}	0.00	0.00	C–I out-of-phase out-of-plane bend
228	B_{2g}	0.00	46.49	C–I out-of-phase out-of-plane bend
236	A_g	0.00	19.63	C–I out-of-phase in-plane bend
236	B_{1u}	1.45	0.00	C–I out-of-phase in-plane bend
236	B_{2g}	0.00	2.79	C–I out-of-phase in-plane bend
237	B_{3u}	0.24	0.00	C–I out-of-phase in-plane bend
240	A_u	0.00	0.00	C–I out-of-phase in-plane bend
240	B_{3g}	0.00	33.85	C–I out-of-phase in-plane bend
241	B_{1g}	0.00	25.12	C–I out-of-phase in-plane bend
242	B_{2u}	0.21	0.00	C–I out-of-phase in-plane bend
360	B_{3u}	14.46	0.00	C–I antisymmetric stretch
360	A_g	0.00	45.59	C–I antisymmetric stretch
361	B_{2u}	0.94	0.00	C–I antisymmetric stretch
361	B_{1g}	0.00	27.07	C–I antisymmetric stretch
361	B_{1u}	1.78	0.00	C–I antisymmetric stretch

362	B_{2g}	0.00	0.00	C–I antisymmetric stretch
362	A_u	0.00	0.00	C–I antisymmetric stretch
363	B_{3g}	0.00	27.57	C–I antisymmetric stretch
449	B_{1u}	246.89	0.00	Out-of-plane ring deformation (C–S torsion)
450	B_{2g}	0.00	2.35	Out-of-plane ring deformation (C–S torsion)
450	B_{3u}	104.55	0.00	Out-of-plane ring deformation (C–S torsion)
451	A_g	0.00	1.85	Out-of-plane ring deformation (C–S torsion)
451	A_u	0.00	0.00	Out-of-plane ring deformation (C–S torsion)
453	B_{3g}	0.00	9.04	Out-of-plane ring deformation (C–S torsion)
453	B_{2u}	0.67	0.00	Out-of-plane ring deformation (C–S torsion)
454	B_{1g}	0.00	2.06	Out-of-plane ring deformation (C–S torsion)
533	A_u	0.00	0.00	C2–C3 torsion
534	B_{1u}	1.42	0.00	C2–C3 torsion
536	B_{1g}	0.00	0.00	C2–C3 torsion
537	B_{2u}	0.03	0.00	C2–C3 torsion
537	A_g	0.00	10.55	C2–C3 torsion

538	B_{3u}	0.06	0.00	C2–C3 torsion
541	B_{3g}	0.00	0.00	C2–C3 torsion
542	B_{2g}	0.00	4.70	C2–C3 torsion
631	B_{3g}	0.00	12.37	C1–S + C4–S in-phase stretch
631	B_{2g}	0.00	154.80	C1–S + C4–S in-phase stretch
632	A_u	0.00	0.00	C1–S + C4–S in-phase stretch
632	A_g	0.00	3108.77	C1–S + C4–S in-phase stretch
632	B_{1u}	3.55	0.00	C1–S + C4–S in-phase stretch
633	B_{1g}	0.00	0.00	C1–S + C4–S in-phase stretch
634	B_{3u}	0.38	0.00	C1–S + C4–S in-phase stretch
636	B_{2u}	1.86	0.00	C1–S + C4–S in-phase stretch
717	A_g	0.00	2.74	C1–S + C4–S out-of-phase stretch
717	B_{3u}	64.90	0.00	C1–S + C4–S out-of-phase stretch
717	B_{2u}	1.08	0.00	C1–S + C4–S out-of-phase stretch
717	B_{1g}	0.00	52.20	C1–S + C4–S out-of-phase stretch
717	B_{3g}	0.00	11.09	C1–S + C4–S out-of-phase stretch

717	B_{2g}	0.00	10.27	C1–S + C4–S out-of-phase stretch
718	A_u	0.00	0.00	C1–S + C4–S out-of-phase stretch
718	B_{1u}	24.34	0.00	C1–S + C4–S out-of-phase stretch
771	B_{1u}	498.48	0.00	In-phase C–H out-of-plane bend
771	A_u	0.00	0.00	In-phase C–H out-of-plane bend
773	B_{3u}	309.30	0.00	In-phase C–H out-of-plane bend
774	B_{2u}	0.11	0.00	In-phase C–H out-of-plane bend
777	A_g	0.00	9.99	In-phase C–H out-of-plane bend
777	B_{1g}	0.00	7.84	In-phase C–H out-of-plane bend
782	B_{2g}	0.00	16.46	In-phase C–H out-of-plane bend
782	B_{3g}	0.00	0.00	In-phase C–H out-of-plane bend
862	A_u	0.00	0.00	Out-of-phase C–H out-of-plane bend
862	B_{1u}	3.08	0.00	Out-of-phase C–H out-of-plane bend
867	B_{1g}	0.00	0.00	Out-of-phase C–H out-of-plane bend
867	A_g	0.00	24.26	Out-of-phase C–H out-of-plane bend
874	B_{2u}	6.30	0.00	Out-of-phase C–H out-of-plane bend

874	B_{3u}	1.97	0.00	Out-of-phase C–H out-of-plane bend
878	B_{3g}	0.00	6.43	Out-of-phase C–H out-of-plane bend
878	B_{2g}	0.00	15.14	Out-of-phase C–H out-of-plane bend
910	B_{2u}	161.64	0.00	Symmetric in-plane ring deformation (in-phase C1–C2–C3 + C4–C3–C2 bend)
911	B_{3g}	0.00	22.89	Symmetric in-plane ring deformation (in-phase C1–C2–C3 + C4–C3–C2 bend)
912	B_{1g}	0.00	11.00	Symmetric in-plane ring deformation (in-phase C1–C2–C3 + C4–C3–C2 bend)
912	A_u	0.00	0.00	Symmetric in-plane ring deformation (in-phase C1–C2–C3 + C4–C3–C2 bend)
913	B_{3u}	1.05	0.00	Symmetric in-plane ring deformation (in-phase C1–C2–C3 + C4–C3–C2 bend)
914	B_{1u}	1.95	0.00	Symmetric in-plane ring deformation (in-phase C1–C2–C3 + C4–C3–C2 bend)
914	B_{2g}	0.00	618.27	Symmetric in-plane ring deformation (in-phase C1–C2–C3 + C4–C3–C2 bend)
914	A_g	0.00	600.22	Symmetric in-plane ring deformation (in-phase C1–C2–C3 + C4–C3–C2 bend)
931	B_{1g}	0.00	5.90	Antisymmetric in-plane ring deformation (out-of-phase C1–C2–C3 + C4–C3–C2 bend)
931	B_{3g}	0.00	0.00	Antisymmetric in-plane ring deformation (out-of-phase C1–C2–C3 + C4–C3–C2 bend)
932	B_{2u}	1.70	0.00	Antisymmetric in-plane ring deformation (out-of-phase C1–C2–C3 + C4–C3–C2 bend)
932	A_g	0.00	11.65	Antisymmetric in-plane ring deformation (out-of-phase C1–C2–C3 + C4–C3–C2 bend)
932	A_u	0.00	0.00	Antisymmetric in-plane ring deformation (out-of-phase C1–C2–C3 + C4–C3–C2 bend)

932	B_{3u}	218.37	0.00	Antisymmetric in-plane ring deformation (out-of-phase C1–C2–C3 + C4–C3–C2 bend)
934	B_{2g}	0.00	0.00	Antisymmetric in-plane ring deformation (out-of-phase C1–C2–C3 + C4–C3–C2 bend)
935	B_{1u}	46.81	0.00	Antisymmetric in-plane ring deformation (out-of-phase C1–C2–C3 + C4–C3–C2 bend)
1054	B_{1g}	0.00	13.66	C–H in-plane symmetric bend
1055	A_u	0.00	0.00	C–H in-plane symmetric bend
1055	A_g	0.00	416.56	C–H in-plane symmetric bend
1056	B_{1u}	20.39	0.00	C–H in-plane symmetric bend
1060	B_{3g}	0.00	19.89	C–H in-plane symmetric bend
1061	B_{2g}	0.00	43.68	C–H in-plane symmetric bend
1062	B_{2u}	26.24	0.00	C–H in-plane symmetric bend
1063	B_{3u}	2.42	0.00	C–H in-plane symmetric bend
1187	B_{1u}	72.16	0.00	C–H in-plane antisymmetric bend
1187	A_u	0.00	0.00	C–H in-plane antisymmetric bend
1187	B_{3u}	84.57	0.00	C–H in-plane antisymmetric bend
1187	B_{2u}	6.49	0.00	C–H in-plane antisymmetric bend
1187	A_g	0.00	19.26	C–H in-plane antisymmetric bend

1187	B_{1g}	0.00	150.45	C–H in-plane antisymmetric bend
1187	B_{3g}	0.00	133.95	C–H in-plane antisymmetric bend
1188	B_{2g}	0.00	2.61	C–H in-plane antisymmetric bend
1278	B_{2u}	0.47	0.00	C1–C2 + C3–C4 in-phase stretch
1279	B_{3g}	0.00	54.82	C1–C2 + C3–C4 in-phase stretch
1279	A_u	0.00	0.00	C1–C2 + C3–C4 in-phase stretch
1280	B_{2g}	0.00	4.23	C1–C2 + C3–C4 in-phase stretch
1280	B_{3u}	3.46	0.00	C1–C2 + C3–C4 in-phase stretch
1280	B_{1u}	4.99	0.00	C1–C2 + C3–C4 in-phase stretch
1280	B_{1g}	0.00	2.41	C1–C2 + C3–C4 in-phase stretch
1281	A_g	0.00	1936.40	C1–C2 + C3–C4 in-phase stretch
1379	B_{1u}	14.08	0.00	C2–C3 stretch
1379	A_g	0.00	6622.85	C2–C3 stretch
1379	A_u	0.00	0.00	C2–C3 stretch
1379	B_{1g}	0.00	73.40	C2–C3 stretch
1380	B_{3g}	0.00	0.00	C2–C3 stretch

1380	B_{2g}	0.00	1492.25	C2–C3 stretch
1381	B_{2u}	401.10	0.00	C2–C3 stretch
1383	B_{3u}	4.29	0.00	C2–C3 stretch
1475	A_u	0.00	0.00	C1–C2 + C3–C4 out-of-phase stretch
1475	B_{1u}	48.16	0.00	C1–C2 + C3–C4 out-of-phase stretch
1475	B_{1g}	0.00	4.98	C1–C2 + C3–C4 out-of-phase stretch
1475	A_g	0.00	9.98	C1–C2 + C3–C4 out-of-phase stretch
1476	B_{3u}	79.26	0.00	C1–C2 + C3–C4 out-of-phase stretch
1476	B_{2u}	1.47	0.00	C1–C2 + C3–C4 out-of-phase stretch
1476	B_{3g}	0.00	6.12	C1–C2 + C3–C4 out-of-phase stretch
1476	B_{2g}	0.00	9.06	C1–C2 + C3–C4 out-of-phase stretch
3122	B_{3u}	24.71	0.00	Out-of-phase C–H stretch
3122	B_{2u}	0.00	0.00	Out-of-phase C–H stretch
3122	A_u	0.00	0.00	Out-of-phase C–H stretch
3123	B_{3g}	0.00	1344.38	Out-of-phase C–H stretch
3123	B_{2g}	0.00	31.55	Out-of-phase C–H stretch

3123	A_g	0.00	58.01	Out-of-phase C–H stretch
3123	B_{1g}	0.00	2221.87	Out-of-phase C–H stretch
3132	B_{2u}	185.34	0.00	Out-of-phase C–H stretch
3132	B_{3u}	0.00	0.00	In-phase C–H stretch
3133	A_u	0.00	0.00	In-phase C–H stretch
3133	B_{1u}	18.64	0.00	In-phase C–H stretch
3133	B_{3g}	0.00	654.29	In-phase C–H stretch
3133	B_{2g}	0.00	377.38	In-phase C–H stretch
3133	A_g	0.00	13551.08	In-phase C–H stretch
3133	B_{1g}	0.00	64.64	In-phase C–H stretch

† The symmetry allows the translations and librations to mix, thus the description reflects the predominant motion.

Figure S1: Comparison of the experimental and CASTEP optimised structure of 2,5-diiodothiophene. The grey atoms are those of the experimental structure and the green for the calculated structure, the iodine (purple) and sulfur (yellow) are coincident in both structures. As noted in the text, the only significant difference is for the C–H bond distance which, as is usually found, is underestimated in the X-ray determination.

Figure S2: Extended range (30 – 1800 cm^{-1}) variable temperature Raman spectra of 2,5-diiodothiophene.

Figure S3: Infrared spectra of 2,5-diiodothiophene at: (a) 300 K, (b) 180 K and (c) 111 K.