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Fourier transform Raman spectroscopy of 1,3-dithiole-2-thione and related compounds

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Abstract—The Raman spectra of 1,3-dithiole-2-thione and a series of related compounds were recorded on a fourier transform Raman spectrometer using near-infrared laser excitation. The spectra proved, with limited exception, to be of high quality. With the help of measured depolarisation ratios it has proved possible to make assignments for the stronger peaks in the spectrum of 1,3-dithiole-2-thione, thereby resolving ambiguities and disagreements in the results of previous workers. These assignments have been used to aid in the interpretation of the very characteristic spectra of substituted thiones. The value of these spectra for analytical purposes is discussed.

INTRODUCTION

THE USE of near-infrared (NIR) laser excitation is, in many cases, the only way to obtain good quality Raman spectra of organic species that are highly conjugated, coloured, or have impurities present after work-up. When an NIR laser source is used in concert with a multiplexing spectrometer such as a Fourier transform spectrometer a powerful tool becomes available to the organic chemist; NIR Fourier transform (FT)-Raman spectroscopy is a technique that affords routine and straightforward collection of vibrational spectra, and provides data that is complementary to that obtained from Fourier transform infrared (FT IR) spectroscopy. NIR FT-Raman spectra have been collected from such diverse organic and bio-organic systems as polymers [1], peptides [2], high explosives and narcotics [3], paint systems [4] and catalysts [5].

The series of compounds studied here are based on the 1,3-dithiole-2-thione ring structure (Fig. 1).

The ten thiones in this study are important precursors in the synthesis of a number of tetrathiafulvalene (TTF) derivatives. TTFs are organic π-donors, and their cation radical salts are of considerable interest because of their ability to form molecular conductors and superconductors [6–8]. The NIR FT-Raman spectrum of one such TTF is discussed later.

NIR FT-Raman spectroscopy has several specific advantages over both conventional Raman and FTIR spectroscopy of thiones and their derivatives. Conventional Raman spectroscopy normally uses a visible wavelength laser as the excitation source. With the exception of **C**, a dark red liquid, the compounds studied were coloured crystalline solids. Coloured samples normally absorb visible laser wavelengths to some extent; this can lead to fluorescence or sample pyrolysis, both of which render the vibrational spectrum difficult, if not impossible, to observe. NIR excitation at a wavelength of 1064 nm gives a photon energy too low to excite fluorescence in the majority of molecules, since most do not have electronic absorbtion bands in the near-infrared. This is the major advantage of NIR excitation, which is realised in this work by using an Fourier transform spectrometer. FTIR spectroscopy generally requires the samples in mull form or pressed into potassium bromide (KBr) discs; the compounds in this study do not mull well, and good quality spectra from KBr discs are difficult to obtain. In comparison, the spectra of **A**–**J** obtained by the FT-Raman technique are generally of high quality.

GAYATHRI DEVI *et al.* [9], and IQBAL and OWEN [10], have undertaken vibrational analyses of **A**. The former reports infrared spectra and the results of a normal-coordinate analysis, whilst the latter provides infrared and Raman data, together with normal

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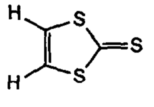

A

Fig. 1. Structure of 1,3-dithiole-2-thione **A**.

coordinate analysis results. Unfortunately, there are significant differences between the results; consequently the assignments must be open to doubt.

The work presented has two objectives. The first is to resolve the ambiguities relating to the vibrational assignment of A. The second is to obtain quality vibrational spectra for the series under study, to assign the spectra, and to evaluate the spectra in an analytical context.

EXPERIMENTAL

Spectra were recorded on Perkin–Elmer model 1710 or 1720 FT-Raman spectrometers. Both were fitted with indium–gallium arsenide (InGaAs) detectors operating at room temperature, quartz beamsplitters, and Barr Associates multilayer dielectric filters. The filters as set in this series of experiments allowed bands down to *ca* 300 cm^{-1} shift to be detected. The excitation source was a Spectron Laser Systems continuous-wave neodinium : yttrium–aluminium garnet (Nd : YAG) laser, operating at a wavelength of 1064 nm, with output stabilisation to provide near-constant intensity. Power levels, as measured at the sample position, varied between 10 and 800 milliwatts. The spectra were recorded at 3 or 4 cm^{-1} resolution, and then corrected for instrumental sensitivity versus wavelength [11].

The laser source used with the 1720 spectrometer is linearly polarised in the vertical plane, so the 1720 spectrometer was used to make depolarisation ratio measurements on **A** and **C**. These experiments involved setting the analyser (Oriel NIR linear polariser) at the virtual J-stop between the output stage of the Michelson interferometer and the detector. Calibration of the experiment was by reference to carbon tetrachloride. **C** was simply loaded into a half-silvered spherical bulb cell, whilst **A** was packed into a bulb cell and then fitted into a hot-cell designed for use with the 180° scattering geometry used on the Perkin–Elmer spectrometers, and heated to *ca* 328 K.

1,3-Dithiole-2-thione **A** was purchased from the Aldrich Chemical Company, and recrystallised from hexane. The bis-benzoyl thioester **F** was prepared by benzoylation of the zinc complex **H** [2]. Treatment of **F** with sodium ethoxide gave the bis-sodium thiolate [12] which was treated with dibromoethane to give **D**, with 1,2-dibromophenylethane to give **E**, or with 2,4-dinitrochlorobenzene to give **G**. Direct alkylation of **H** with methyl iodide gave **B**, and with ethyl iodide gave **C**. Treatment of **B** with mercuric acetate gave **I** [13], and coupling either **B** or **I** using triethyl phosphite produced the TTF **J**. All the compounds were purified by recrystallisation or chromatography. New compounds under study were characterised by proton nuclear magnetic resonance (^{1}H-NMR) and mass spectroscopy.

The compounds required no special sampling; a simple tube solid cell and a bulb liquid cell were used, with a hot-cell for the depolarisation ratio measurement on **A**. Alignment of the cells was achieved requiring less than a minute in most cases, such is the ease of sample positioning, which is due to the 180° backscattering collection geometry. The amount of sample available varied, the minimum being *ca* 25 mg. This presented no problem as regards the quality of the spectra obtained.

The only problem encountered experimentally was the decomposition of **H** in the laser beam. The laser is focused to a diameter of *ca* 0.5 mm; reducing the power and defocusing the beam had little effect. The effect of sample pyrolysis was to produce a thermal emission background, which obscured nearly all other spectral features.

RESULTS AND DISCUSSION

The Raman spectrum of 1,3-*dithiole-*2-*thione* (**A**)

Since analogues and derivatives of **A** (Fig. 2) have been shown to contain planar or near-planar thione rings by X-ray crystallography (see [14], for instance) we follow the

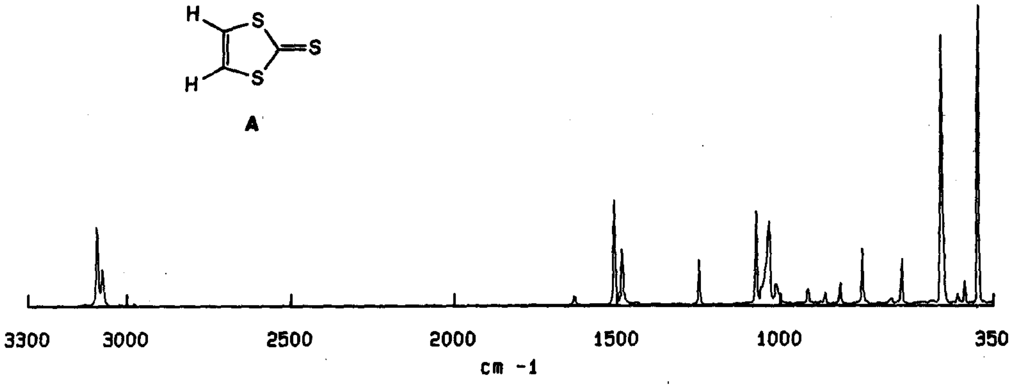

Fig. 2. Spectrum of A.

convention established in previous work [8, 9] by assuming A is planar despite the lack of an experimentally derived crystal structure. According to basic group theory, 18 fundamental modes of vibration ($7A_1$, $2A_2$, $6B_1$, and $3B_2$) are expected in this molecule of C_{2v} symmetry. All but the two A_2 modes are expected to be jointly Raman and infrared-active, the A_2 modes being infrared inactive. More than 18 bands are observed; some of these are weak, and possibly attributable to overtones, combinations, and solid-state effects. The primary purpose of this present study has been to assign the fundamental modes. From group frequency arguments one expects νC–H (3100–3000 cm^{-1}), νC=C (1680–1600 cm^{-1}), νC=S (1200–1050 cm^{-1}), and νC–S (650–500 cm^{-1}) in the Raman spectrum with some intensity. Bending motions of the C=S and C–H groups as well as modes associated with ring deformations are also expected.

The C–H stretch does indeed manifest itself in the expected region, with strong sharp features at 3092 and 3075 cm^{-1}. The shift to above 3000 cm^{-1} may also be indicative of aromaticity in the structure as a whole, and not simply because the hydrogen atoms are ethylenic.

This point is borne out by the 100 cm^{-1} downshift in the frequency of the C=C stretching mode to 1512 cm^{-1}. The C=C stretch is A_1 in character; in C_{2v} this should lead to a polarised Raman band. The symmetric stretch of C–C in an aromatic compound would also be expected to be strongly Raman-active (compare to the 1591 cm^{-1} band of *cis*-1,2-dichloroethene). Both the depolarisation ratio of $\rho_1 = 0.2$ and the relative intensity of the band at 1512 cm^{-1} agree with this. This seems a rather low value for ν(C=C); however, several features support its assignment.

Gayathri Devi *et al.* [9] point out there might be a downshift in frequency due to aromaticity of the ring. This is due to the delocalisation of the bonding electrons around the ring-system. On the basis of infrared data, they assign a reasonably strong band at 1396 cm^{-1} to be the C=C stretch. However, a shift of more than 200 cm^{-1} seems doubtful, even without the benefit of other data. Iqbal and Owen [10] claim that the 1508 cm^{-1} band is C–H bend, whilst the 1634 cm^{-1} band is C=C stretch. This is curious, as the 1634 cm^{-1} band is very much weaker than the 1512 cm^{-1} band; the assignment seems to contradict previous arguments. Also, the 1634, 1512, and 1488 cm^{-1} bands of A are all polarised (ρ_1 *ca* 0.2); this is expected only if the modes of vibration are of A_1 symmetry.

If the band at 1634 cm^{-1} were the C=C stretch it would be reasonable to anticipate such a band throughout the series, possibly shifted by the combined mass and electronic effect of having four sulphur atoms instead of two sulphur and two hydrogen around the double bond. This is not observed. There is, however, a strong sharp band at *ca* 1480 cm^{-1} throughout the series. Applying the same logic concerning the possible shifting of the bands, this tallies well to the 1512 cm^{-1} band of the thione. The only bands in evidence around 1600 cm^{-1} are in those members of the series which have other C=C functionalities, that generally appear at the expected shifts. Other members of the series studied would not be expected to show a band at close to 1510 cm^{-1} if the mode was due to C–H stretching, as they have four sulphur atoms around the C=C bond and no hydrogen atoms; the fact that they all do show a strong sharp band in this region is more indicative that this is the C=C stretch and that the 1634 cm^{-1} band in **A** is of other origin. Comparison to *cis*-1,2-dichloroethene again shows a correlation to the approximate shape of the spectrum in the 1700–1550 cm^{-1} range. The bands are also all polarised. This could possibly be an aid to assigning the 1634 and 1488 cm^{-1} bands in the thione **A**. The 1252 cm^{-1} band in **A**, which disappears on substitution of SMe and similar groups for the hydrogen atoms, is likely to be a C–H bending mode.

The bands at 1077 cm^{-1} and 1038 cm^{-1} are associated with the C=S stretching motion and its coupling to S–C–S motions, although the exact assignment is unclear. BELLAMY [15] comments that C=S is prone to shifts in frequency, and also couples significantly to other modes.

The assignment of bands below 1000 cm^{-1} becomes even more complex; coupling between modes becomes more frequent so the unequivocal assignment of a single band to any one mode of vibration is unlikely. Modes such as C=S bending and C=C torsion will lie in this region, as will C–S stretch and numerous ring-related modes. There are several possible explanations for the intense band at 512 cm^{-1}. It is possibly due to a stretching mode associated with the C–S bond in the –S–(CS)–S– unit; this is plausible because replacement of the hydrogen atoms with other functionalities only shifts the band a little. An alternative view is that it is a ring-breathing mode, similar to that in benzene at 992 cm^{-1}. A similar dual assignment is possible for the 400 cm^{-1} band: as a stretching motion of the C–S bond in the –S–(CC)–S– region, or possibly as a ring mode. There is little reason to assume that the carbon–sulphur stretching vibrations in the –S–(C=S)–S– and –S–(C=C)–S– units will occur at the same frequency. If the 400 cm^{-1} band is due to the S–(C=C)–S entity, changes in the band due to substituting the hydrogen atoms for other groups might be expected; changes are certainly observed. The C–S stretch is not normally seen as low as 400 cm^{-1}, however; so the idea of a ring-related mode is possible. The two previous papers are in considerable disagreement in this region, despite the fact that both include normal-coordinate analyses. The present work, however, includes depolarisation ratio measurements. Depolarisation ratio measurements show that the 512 cm^{-1} band of **A** is highly polarised, with a ρ_l value of *ca* 0.1, and must be due to an A_1 mode; for such a strong, low-frequency mode this would indicate a symmetric ring-breathing motion. Comparison of the depolarisation ratio to that of the 500 cm^{-1} band in **C** shows that the band remains highly polarised, with a ratio of *ca* 0.2. Thus the 512 cm^{-1} band is characteristic of the thione ring itself, in the same way that a strong peak at around 1680 cm^{-1} is indicative of the C=C bond conjugated in the thione ring. The ρ_l value of the 400 cm^{-1} band is 0.4, and therefore indicates a polarised band; however, the assignment of this band is ambiguous, and it would not be appropriate to go further at this stage.

The depolarisation ratios of the major bands in **A** are presented in Table 1.

Compounds related to 1,3-*dithiole*-2-*thione* (**A**)

The C–H *stretch region*. Throughout the series the expected positions of the C–H modes are observed. **B–E** all contain aliphatic hydrogen atoms, which exhibit shifts in the 2900–3000 cm^{-1} range, whereas bands due to aromatic C–H occur at between 3000 and 3100 cm^{-1}. A good example is **E**, where there are two groups of shifts, one characterising each kind of C–H linkage; aliphatic at 2965, 2937, and 2917 cm^{-1}, with aromatic at 3068, 3053, and 3039 cm^{-1}. **A** exhibits stretching at 3092 and 3076 cm^{-1}, higher than normal for –(C=C)–H; this is possibly due to the aromatic nature of this particular C=C, since the thione is thought to possess a high degree of conjugation via delocalisation. **G** has weak C–H bands, relative to other compounds containing aromatic hydrogen atoms. The spectrum of 2,4-dinitrobenzene shows similar behaviour, implying that the presence of nitro groups on the benzene ring reduces the intensity of the aromatic C–H bonds.

Table 1. Depolarisation ratios of the major bands of **A**

Band position (cm^{-1})	Depolarisation ratio (ρ_l)
3092 (3081)	0.23
3076 (3066)	?
1634	0.22
1512 (1510)	0.23
1488 (1485)	0.22
1252 (1262)	0.74
1077 (1090)	0.22
1038 (1046)	0.21
1015 (1018)	0.20
919 (920)	0.15
820 (819)	0.71
753 (751)	0.19
633 (625)	0.71
512 (510)	0.17
440	0.70 (?)
400	0.42

The band position column contains values for the solid state, and in parentheses for the liquid state, which is achieved by heating the sample to above 50°C.

The C=C *stretch region*. A strong band is in evidence in nearly all spectra at *ca* 1470 cm^{-1} which is assigned as the C=C stretch. This is quite characteristic of the series. Even in **H** a peak is discernable in the 1450 cm^{-1} area. In **A** the band occurs at 1512 cm^{-1}; this is probably because the double bond has two sulphur atoms and two hydrogen atoms attached, as opposed to four sulphur atoms as in all other compounds. Thus a change from $-S_2(C{=}C)H_2$ to $-S_2(C{=}C)S_2-$ results in a frequency shift of *ca* 30–40 cm^{-1} downwards for the double bond. In **G** the intensity of the band is much lower. The anomalous behaviour of **G** has already been noted; it seems that dinitrophenyl groups tend to be so strongly Raman-active that they even dominate other strongly scattering groups, such as C=C.

Other features in the 1800–1000 cm^{-1} *region*. There are two points of note in this region. The first is the disappearance of the bands at 1488 cm^{-1} and 1252 cm^{-1} apparent in **A** but not in the other compounds. This lends support to the view that these are C–H bending modes. It would be expected that C–H bending and similar modes of the side-groups lie in this region; this appears to be true, as the spectra of **B** and **C**, for instance, exhibit such bands. The second point of note concerns those compounds which have

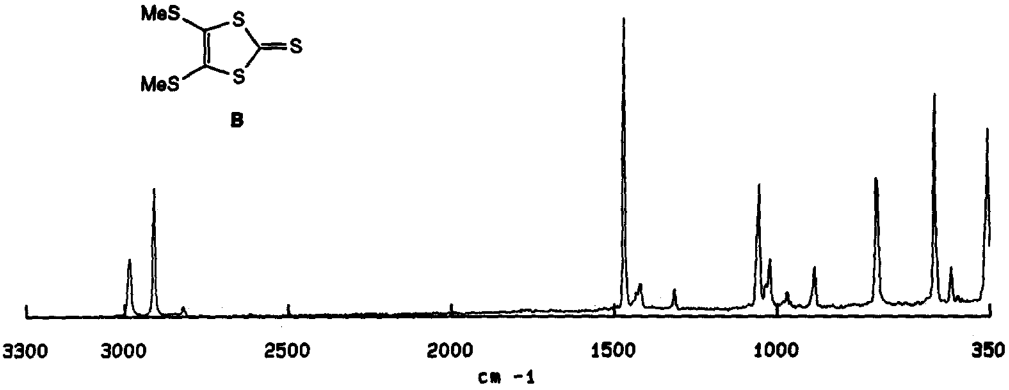

Fig. 3. Spectrum of **B**.

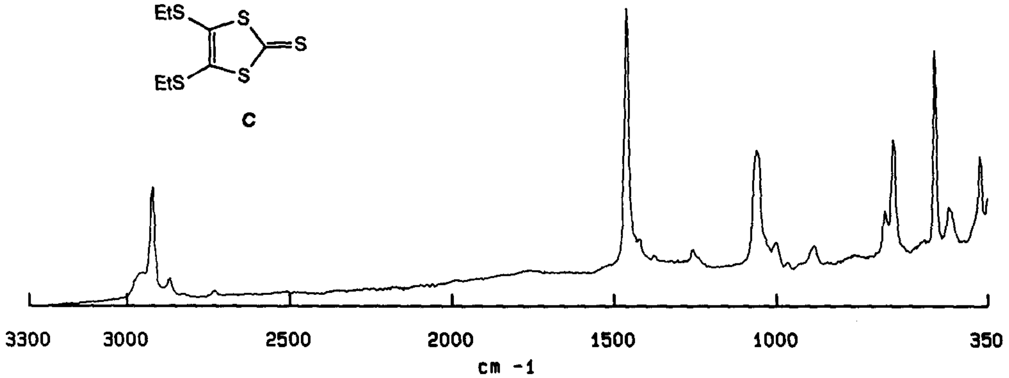

Fig. 4. Spectrum of C.

functional groups that give rise to bands in the 1800–1000 cm^{-1} region, such as C=O bonds, phenyl rings, and nitro groups. Generally these features are at shifts predicted by group frequency arguments; in cases where assignment is difficult due to lack of specific information, comparison of the spectra of the compound in question with a chemically and structurally closely related species may be of use. Comparison of **G** with 2,4-dinitrobenzene, for instance, aids the identification of the $-S(C_6H_3(NO)_2)$ bands in the spectrum of **G**.

The C=S *stretch region*. Ethylene trithiocarbonate has ν(C=S) at 1074 cm^{-1} [16]; considering the similarity of the thione ring structure (see Fig. 12), and the fact that C=S stretch generally falls into the 1200–1050 cm^{-1} region, the assignment of a band around 1070–1060 cm^{-1} as to the stretching mode of the exocyclic C=S bond is fairly sound. The series studied all show not one but several peaks in this region. This may imply that coupling of the C=S stretch occurs in other modes, as BELLAMY suggests. IQBAL and OWEN report that for **A** the three Raman bands in the area at 1076(w), 1038(m), and 1008 cm^{-1}(w) are due to C=S stretch, a combination of –S–(CS)– stretch and –S–(CS)– in-plane bend, and –S–(CS)– stretch, respectively. DEVI and SATHYANARAYANA report that the infrared bands at 1079, 1050, and 1015 cm^{-1} are due to out-of-plane C–H bend with C=S stretch, C=S stretch with –S–(CS)– stretch and ring deformation, and unassigned respectively. These disagreements underline the difficulty in making unambiguous assignments. Nevertheless, it does seem that the 1070–1000 cm^{-1} region is indicative of the C=S stretch and modes unassigned concerning the ring, and is therefore useful in fingerprinting each of the series.

The C–S *stretch region*. It would perhaps be better to call this region the true fingerprint region of the spectrum, because, apart from a strongly Raman-active band at 510–530 cm^{-1} in all compounds, there is strikingly little in common between the spectra.

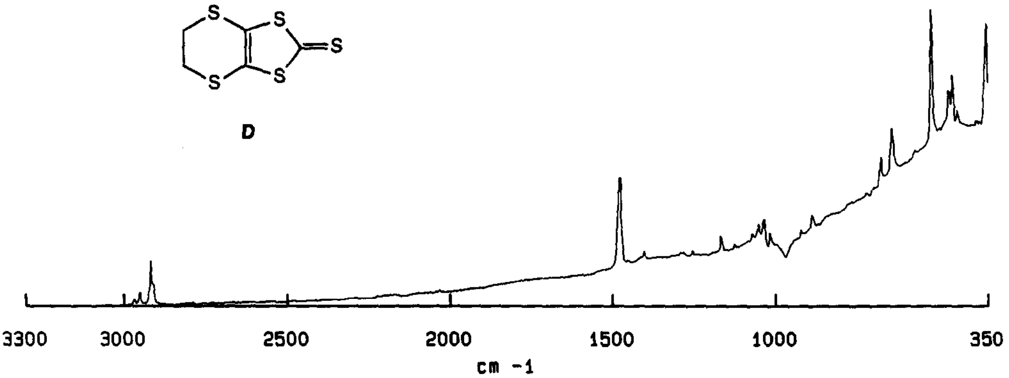

Fig. 5. Spectrum of D.

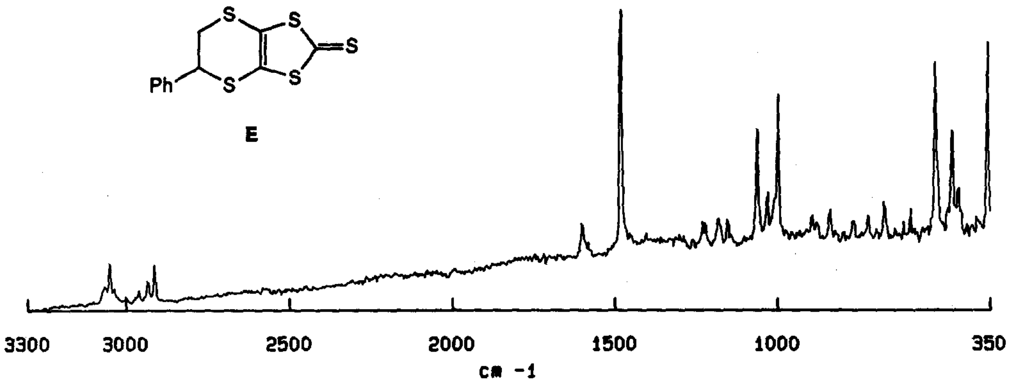

Fig. 6. Spectrum of E.

The methodology here is to look for correlations in intensity, position and band shape between compounds of similar structure such as **B** and **C**. The origin of the band at *ca* 515 cm^{-1} has already been speculated upon; it is almost certainly a ring-breathing mode.

B and **C** group together as do **D** and **E**. Certain features are shared:

(i) 890 cm^{-1} (w),
(ii) 700–670 cm^{-1} (mw),
(iii) 510–530 cm^{-1} (mw-ms),
(iv) 380–320 cm^{-1} (mw).

Feature (iv) is closely replicated between the two pairs **B** and **C**, and **D** and **E**; it comprises a set of two or three peaks; (iii) is always a sharp single peak; (ii) is more difficult to interpret. In **B** it is a sharp close doublet, whereas in **C** it is two peaks of different intensity separated by 28 cm^{-1}. It seems to be two peaks of equal intensity separated by 32 cm^{-1} in **D**, whilst in **E** there appears to be only one peak, although the spectrum of **E** is more complicated than **D** in that region, as is expected from their structural relationship. (i) is apparent as a weak single peak, split in **E** as a weak doublet.

A further characteristic of this region is a weak feature at around 470 cm^{-1}, possibly combined with a very weak feature at lower shifts, around 430 cm^{-1}. Some spectra do not have this feature sufficiently well-resolved or intense.

It may be possible to predict the whereabouts of the C–S stretches of the SMe and SEt derivatives of **A** by analogy to the thiol series, R–SH. This would identify the S–Me frequency as *ca* 700 cm^{-1} and the S–Et as *ca* 650 cm^{-1}, both of which are observed. If this is so, then the nature of the side-groups appended to the ring could be described by analogy to the thiols or similar series, making identification of a specific thione straightforward by identifying the specific side-groups.

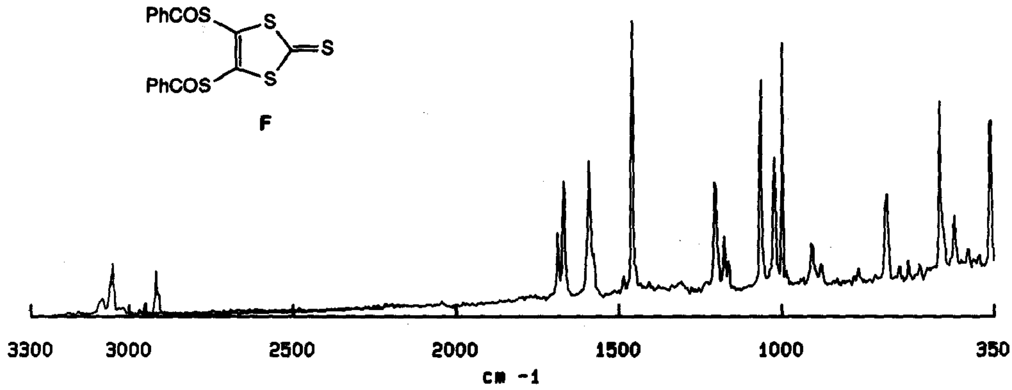

Fig. 7. Spectrum of F.

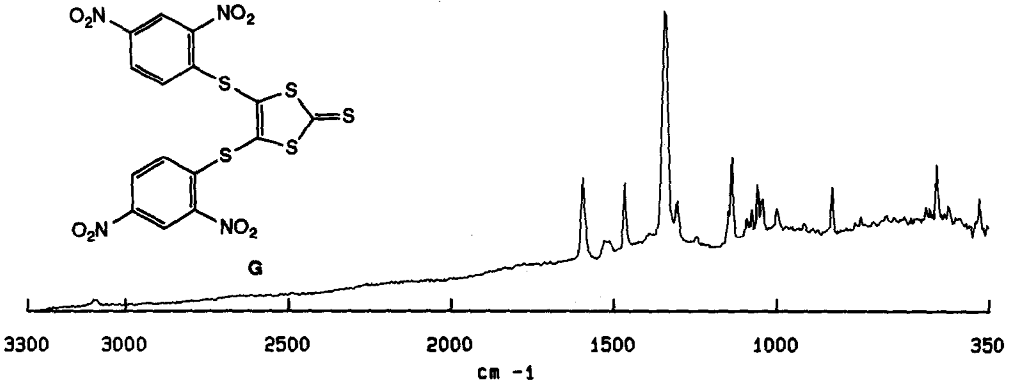

Fig. 8. Spectrum of G.

Other comparisons. **B**, the symmetric SMe analogue of **A**, was compared with the symmetric SMe TTF **J** and the symmetric SMe analogue of 1,3-dithiole-2-one **I**. The structures of these compounds are reproduced in Fig. 13.

Comparison of each major region in the spectra suggests that **B** is more aromatic than **I**, as substituting C=S for C=O raises the C–H stretching frequencies by 2–5 cm^{-1}. **J** does not exhibit such a change. The C=C stretch in **I** is higher than in **B** by 14 cm^{-1}, again reinforcing the idea of reduced aromaticity in **I**. A weak band is in evidence at 1658 cm^{-1} in **I**; this could be a combination or overtone band, or the C=O stretch frequency, which would not be expected to be intensely Raman-active. **J** has a very similar C=C stretching frequency to **B**, and has two peaks at 1554 and 1542 cm^{-1}, the bridging C=C being the probable cause. A possible reason for their occurrence at lower frequencies than normal is the aromatic downshift of the thione ring system. Features present in **B** around 1420 cm^{-1} and 1320 cm^{-1} are still visible in both **J** and **I**; this indicates they are concerned with the SMe groups and probably are due to C–H bending motions. Obviously the C=S stretching region is greatly different in **J** and **I**, and also in the fingerprint region. The peaks at *ca* 700 cm^{-1} in all three are probably due to C–S stretching in the SMe groups, by comparison to the C–S stretch of thio-methanol, MeSH. The most obvious change is the disappearance of the characteristic 510 cm^{-1} band from **B**; in **J** there are bands at 495 and 450 cm^{-1}, and in **I** at 465 and 381 cm^{-1}, but not at around 510 cm^{-1}. The disappearance of this thione ring mode could show that the coupling of two thione rings to produce a TTF was successful.

CONCLUSIONS

It is helpful to collect the information from the above results that is germane in an analytical context. This presents no problem, as several very clear spectra–structure

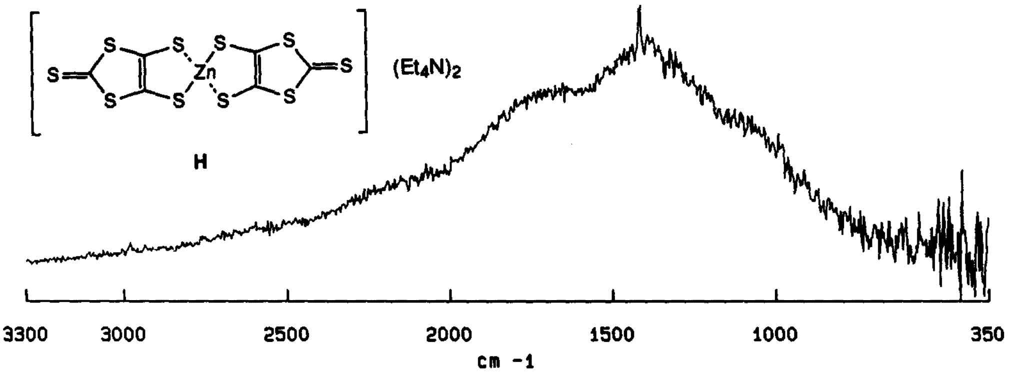

Fig. 9. Spectrum of H.

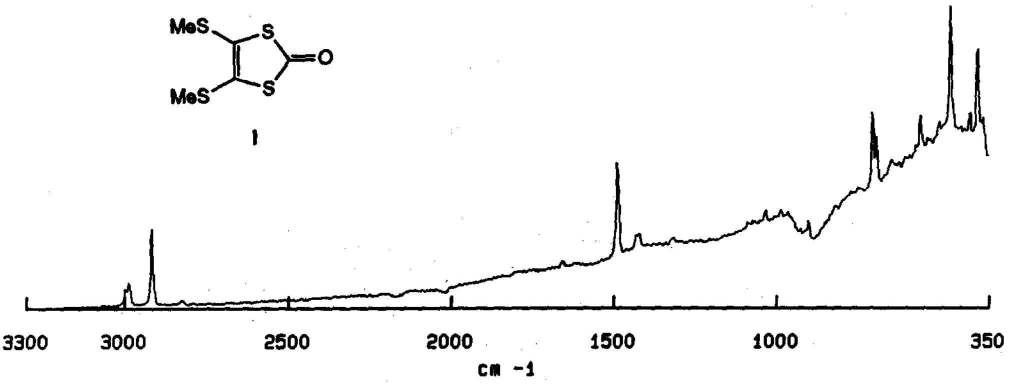

Fig. 10. Spectrum of I.

correlations are evident. The most obvious of these is the shift in the C=C stretch, which lies in the region 1460–1490 cm^{-1}, except for A. It is usually the strongest peak in the spectrum. Both counts make it exceedingly characteristic of the thione ring system. Confirmatory evidence comes from the medium-to-strong peak in the 510–530 cm^{-1} range. The medium intensity peak at around 1060–1070 cm^{-1} is also useful, but can be difficult to identify, particularly if aromatic substituents are present. There are enough additional peaks in all the compounds studied to result in an accurate fingerprint being possible. Combined with the already proven ability of the FT-Raman technique for quantitative analysis [17], it is to be anticipated that the technique will become a major tool in the analysis of substituted thiones and their derivatives.

The major points of note in comparison to other compounds are the easily discernable changes on coupling two thiones to form a TTF and on replacing the exocyclic sulphur atom with oxygen.

In order to be able to assign the vibrational spectra of the substituted thiones completely, the complete and unambiguous assignment of A is required; this in turn requires that both infrared and Raman spectra over the entire 4000–0 cm^{-1} range be obtained. Until this is done a definitive vibrational analysis of A is unlikely. In order to simulate the spectra accurately by normal-coordinate analysis an experimental crystal structure is necessary and will have to be obtained. Further investigation into the electronic structure of the simple thiones may well help reveal why the C=C stretch is of such low frequency in more certain terms, as well as help explain the aromaticity of the ring, and give a computed equilibrium geometry to compare with that derived experimentally.

This work has shown NIR FTR spectoscopy to be a valuable method in the analysis of thione ring systems and their derivatives, and further demonstrates the power of the technique in organic analysis.

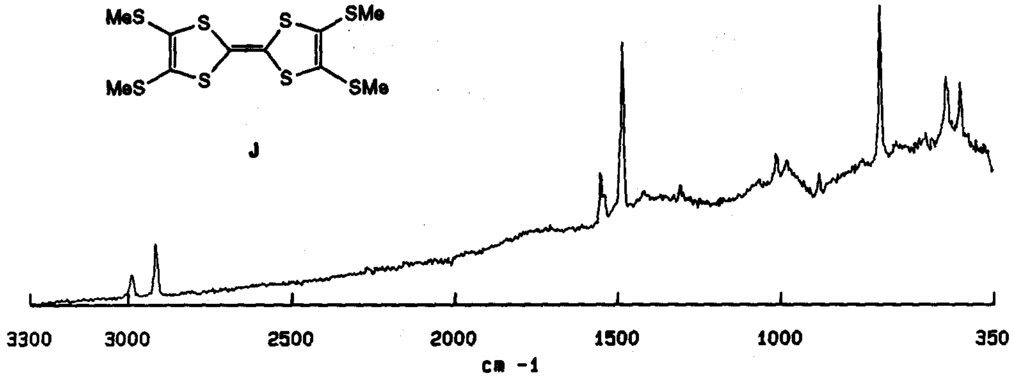

Fig. 11. Spectrum of J.

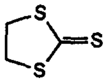

Fig. 12. Structure of ethylene trithiocarbonate.

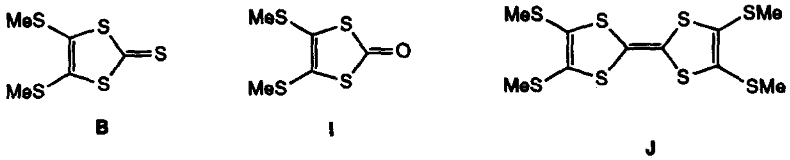

Fig. 13. Structures of **B**, **J** and **I**.

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