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Coulombic screening in polydiacetylene crystals

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The strong colour of polydiacetylene polymer crystals is due to the backbone exciton. The energy of the exciton is strongly affected by Coulombic interactions with the surrounding crystalline environment. X-ray diffraction and optical absorption measurements of the blue phase polymer crystals of 4BCMU show that a change in the energy of the polydiacetylene backbone exciton can be related to a change in the inter-backbone spacing within the crystals. Over the range of inter-backbone spacings measured, this variation is in very good agreement with Coulombic screening theory. It is calculated from these results that inter-backbone Coulombic screening lowers the value of the exciton energy in the blue phase polymer crystals of 4BCMU by −0.362 eV, which is 15.4% of the total exciton energy. Coulombic screening is shown to have an important effect on the optical absorption properties of other polydiacetylene derivatives. Calculations and resonant Raman spectroscopy measurements show that a combination of a low level of Coulombic screening and strain in the crystal lattice accounts for the red colour of the polymer crystals of PTS-12 and TCDU.

(Keywords: polydiacetylene; polymer crystal; thermal lattice expansion)

INTRODUCTION

Polydiacetylenes are highly conjugated polymers which can be produced by the thermal, ultra-violet or gamma-ray initiated polymerization of diacetylene single crystals[1], Langmuir–Blodgett films[2], liquid crystals or isotropic melts[3,4]. High quality chain extended polymer crystals can be formed by the solid state topochemical polymerization (*Figure 1*) of macroscopically sized single monomer crystals[1]. Polydiacetylenes are strongly absorbing in the visible region of the spectrum due to their highly delocalized π-bonding system which extends along the whole length of the backbone. A whole range of different coloured polydiacetylenes can be produced both in the solid state and in solution[2,5,6]. The lowest energy π to π^* transition in polydiacetylenes is excitonic in nature, where the energy of the exciton E as measured by optical absorption spectroscopy varies between about 2.0 eV in the blue phase polymer crystals to about 2.7 eV in the yellow polymer solutions[7,8]. These variations in E are caused by both changes in the conformation of the polymer backbone and changes in the local environment surrounding the backbone[5,6,8].

Continuous uniform distortion of the polymer backbone can cause continuous variations in the energy of the π to π^* transition. Polydiacetylene polymer crystals which are strained in tension along the main chain direction show an increase in E of 0.037 eV per 1% applied chain strain[9]. Continuous shifts in E of up to 0.6 eV are observed when partially polymerized monomer crystals (conversion less than 1%) are heated so that the few polymer chains present are stretched or compressed by the thermal expansion of the monomer crystal lattice[10].

Similarly, abrupt distortion or twisting of the polymer backbone can cause abrupt changes in the value of E. Soluble polydiacetylene derivatives are found to undergo dramatic blue to yellow and red to yellow solvatochromic and thermochromic transitions where E changes abruptly from 2.0 to 2.7 eV and from 2.3 to 2.7 eV respectively[11,12]. These transitions can be shown to involve a rigid rod to random coil conformational transition of the polydiacetylene backbone[13,14]. When heated, the fully polymerized crystals of some derivatives undergo a blue to red crystallographic phase transition followed by a red to yellow melting transition which involve similar abrupt changes in the value of E[15–19]. The crystallographic transition can be shown to involve the distortion of the backbone by the disordering of the adjacent side-group units, while the melting transition can be shown to involve the disintegration of the crystal structure and the release of the backbone into a more twisted conformation[18–22].

The variation of the energy of the π to π^* transition with conformation can be related to changes in the overall level of electron delocalization along the backbone. As the conformation becomes more distorted, twisted and non-planar, the overall level of electron delocalization decreases, increasing the value of E[5,8]. Two different models have been proposed to explain this effect. The first envisages that deforming the backbone produces abrupt conformational defects such as exact 90° bond rotations about the backbone single bonds, which break

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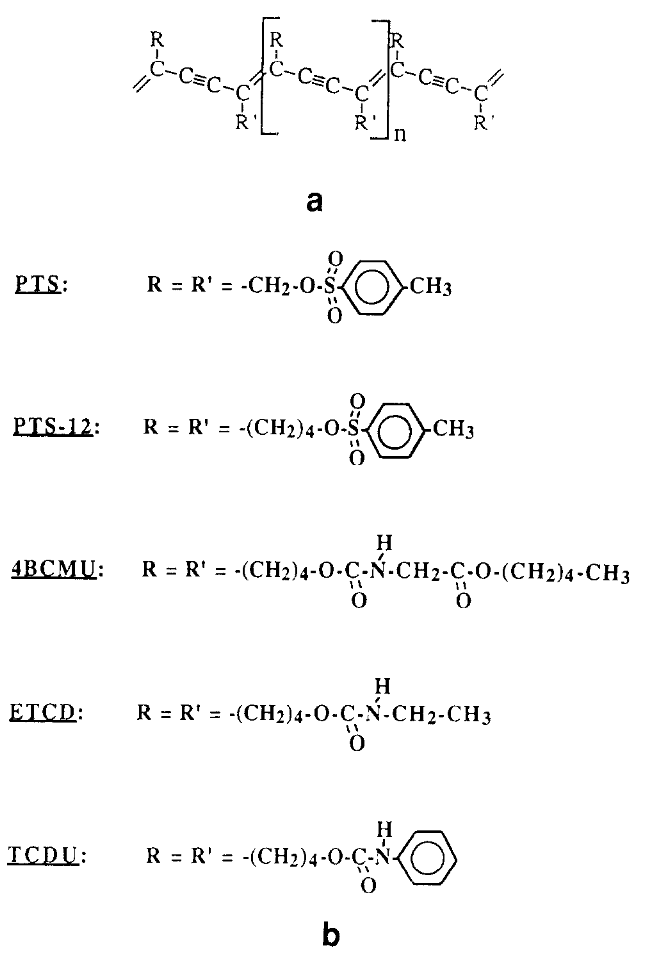

Figure 1 Polydiacetylene structures: (a) structure of the polydiacetylene polymer backbone; (b) structure of the polydiacetylene sidegroups R and R′ attached to the backbone in (a)

the backbone's delocalized electronic system into a series of discrete but fully conjugated segments[11,14,23,24]. The second model envisages that deforming the backbone causes it to take up a smooth and continuous curved conformation by slightly distorting and twisting each bond so that the electronic system tends to localize on the stronger, less distorted triple and double backbone bonds[7,14,25,26]. As previously discussed, experimental and theoretical results from the yellow polymer solutions favour the second model[27].

Variations in E can also be caused by changes in the local environment surrounding the backbone[5,7,8]. The polydiacetylene backbone exciton will undergo polarization interactions with its surrounding environment which will decrease its energy. This type of Coulombic screening will involve interactions with its own sidegroups, with the backbone and sidegroups of neighbouring polydiacetylene chains if in a crystal, or with neighbouring solvent molecules if in solution. Due to the extremely high polarizability of the electronic system on the polydiacetylene backbone and the conjugated units found in the sidegroups of many derivatives, the Coulombic screening from neighbouring chains is expected to be considerable. High-pressure experiments[28] on PTS polymer crystals show a continuous decrease in E with increasing pressure at a steady rate of $-0.07\,\mathrm{eV\,GPa^{-1}}$. When combined with the mean linear compressibility of the crystals, it is estimated that interchain Coulombic screening is lowering the value of E at zero pressure by $-0.32\,\mathrm{eV}$. Electroreflectance measurements also suggest that Coulombic screening from the backbone and conjugated sidegroup units of neighbouring chains should easily cause variations in E which are of the same order of magnitude as those produced by conformational changes[7]. It has also been suggested that a decrease in the level of interchain Coulombic screening is responsible for the blue to red colour change at the crystallographic phase transition in the polymer crystals of ETCD[29].

Apart from the value estimated in the high-pressure experiments, no measurements have been made of the exact amount by which Coulombic screening changes the value of E within polydiacetylene crystals or how this value varies with interchain separation. The present work was undertaken to make these measurements and to explore how Coulombic screening affects the optical properties of the polymer crystals of a variety of different polydiacetylene derivatives.

THEORY

The energy of an exciton E in a molecular crystal with two molecules per unit cell is given by:

$$E = E_0 + D + W + S \pm L \qquad (1)$$

where E_0 is the excitation energy of the free molecule, D is the difference in the van der Waals interaction energy of a molecule in the ground state and the excited state, W arises from dispersion forces due to two electron excitations, and S and L arise from the exchange of excitations between translationally equivalent and inequivalent molecules respectively[8,28]. W gives the lowering of E by the polarization of the surrounding medium and is usually negative. $D+W$ is known as the gas-to-crystal or solvent shift, S is known as the exciton shift and $2L$ is the Davydov splitting. In polydiacetylenes the molecules are effectively of infinite length, and as a result E_0 must be described by an energy band in which it becomes a function of the exciton wavevector. E_0 must also include the effects of the translational symmetry along the polymer chain and the effects of conformational changes on the backbone's electronic structure.

In polydiacetylenes it is estimated that $D < 0.012\,\mathrm{eV}$, $2L < 0.005\,\mathrm{eV}$, and $S \approx L$[8]. Therefore, the sum of $D+S+L$ should be less than 0.017 eV. The value of W estimated from the high-pressure experiments in the literature[28] is $-0.320\,\mathrm{eV}$. The sum of $D+S+L$ is therefore less than 5% of the value of W. As a first approximation D, S and L can be ignored, and equation (1) can be rewritten for polydiacetylenes as:

$$E = E_0 + W \qquad (2)$$

In polydiacetylene crystals essentially two different types of surrounding 'molecule' will provide a substantial contribution to W. These are the highly conjugated polymer backbones of neighbouring chains, and any large conjugated units which are present in the sidegroups of the chain itself or in the sidegroups of neighbouring chains. Hence:

$$W = W_B + W_{SG} \qquad (3)$$

where W_B is the contribution to the level of Coulombic screening from the surrounding polymer backbones of neighbouring chains, and W_{SG} is the contribution from any large conjugated sidegroup units.

For a molecule of polarizability α_m and an electronic transition of dipole moment M and energy E, W can be related to the polarizability of the surrounding medium by:

$$W=\sum_{i}^{n}(1/6)\alpha_s(R_i)^{-6}[M^2+(E\alpha_m/4)] \qquad (4)$$

where the surrounding medium consists of n other molecules of polarizability α_s which lie at distances R_i[7]. For a polydiacetylene chain in a polymer crystal, the contribution to the level of Coulombic screening from the surrounding polymer backbones of neighbouring chains can be written as:

$$W_B=\sum_{i}^{m}K_B(R_i)^{-6} \qquad (5)$$

where the polymer backbone is surrounded by m other backbones which lie at distances R_i. K_B is a negative constant which is proportional to the polarizability of the polymer backbone. Likewise, the contribution to the level of Coulombic screening from any large conjugated sidegroup units can be written as:

$$W_{SG}=\sum_{j}^{n}K_{SG}(R_j)^{-6} \qquad (6)$$

where the polymer backbone is surrounded by n large conjugated sidegroup units which lie at distances R_j, and where K_{SG} is a negative constant which is proportional to the polarizability of the large conjugated sidegroup units.

Conformational changes in the physical structure of the backbone will cause variations in the excitation energy of the free molecule E_0. Such conformational changes are normally split into a homogeneous and an inhomogeneous component. The homogeneous component is uniform strain in the polymer crystal lattice, ε, which results in an increase or a decrease in E_0 when the backbone is respectively stretched or compressed. The inhomogeneous component is disorder or non-uniform twisting, where the displacement of backbone atoms from their mean positions is not identical on consecutive repeat units. An increase in the level of disorder or twisting results in an increase in E_0. If each backbone atom has a mean position r in the highly ordered blue phase polymer crystals, then the average level of disorder or non-uniform twisting can be quantified in terms of an average displacement $\langle\Delta r\rangle$. Therefore, E_0 is a function of both the strain in the lattice ε and the level of disorder $\langle\Delta r\rangle$. Equation (2) can be combined with equation (3) and rewritten as:

$$E=E_0(\varepsilon,\langle\Delta r\rangle)+(W_B+W_{SG}) \qquad (7)$$

Thus, any change in the exciton energy E can be related to either a change in the level of uniform strain on the backbone ε, a change in the level of disorder of the backbone $\langle\Delta r\rangle$ or a change in the level of Coulombic screening within the polymer crystals from the surrounding backbones W_B or conjugated sidegroup units W_{SG}.

EXPERIMENTAL PROGRAMME AND ANALYSIS

In the high-pressure experiments on PTS polymer crystals no variation occurred in the value of E_0, so that all changes in the value of E as a function of pressure could be ascribed to changes in the value of (W_B+W_{SG}) (ref. 28). However, the experimental results did not allow separate values of W_B and W_{SG} to be obtained[28]. Furthermore, no measurements could be made of the precise variation of the backbone to backbone distance or the backbone to conjugated sidegroup unit distance as a function of pressure, so that W_B and W_{SG} could not be calculated from equations (5) and (6).

However, in the case of the blue phase polymer crystals of 4BCMU it should be possible to solve these problems because the polymer has no large conjugated sidegroup units ($W_{SG}=0$), and the simple arrangement of the chains within the crystal lattice makes it relatively easy to determine the variation of W_B with inter-backbone distance R_i in equation (5).

The blue phase polymer crystals of 4BCMU have a monoclinic unit cell with the unit cell parameters as listed in *Table 1*[30]. *Figure 2* shows the 4BCMU crystal structure, based on the X-ray diffraction results[30], in the form of a projection onto the a–b plane with the main chain direction (the c lattice direction) nearly normal to the page. The backbone and sidegroups form flat ribbons stabilized by inter-sidegroup hydrohen bonding which lie in vertical stacks forming a herring-bone like structure (*Figures 2* and *3*).

In this type of structure the distance between equivalent points on the polymer backbone within each stack ($a=0.537$ nm) is much smaller than the distance between the backbones in neighbouring stacks ($b/2=2.725$ nm). Because W_B is proportional to $1/R_i^6$, the contribution to W_B from the nearest backbone in the neighbouring stack will only be 5.9×10^{-5} of that from the nearest backbone within the stack, and can be ignored. Also, the contribution from the next nearest-neighbour backbones within

Table 1 Crystal unit cell parameters of different polydiacetylene derivatives

Polydiacetylene	a(nm)	b(nm)	c(nm)	α(deg)	β(deg)	γ(deg)	Reference
4BCMU	0.537	5.45	0.489[a]	90	85	90	30
PTS	1.4493	0.4910[a]	1.4936	90	118.14	90	34, 35
PTS-12	2.013	0.611	0.491[a]	95.1	93.7	88.7	36
TCDU	0.489[a]	3.917	0.619	90	106.3	90	39
ETCD(blue)	1.813	0.489[a]	1.081	90	94	90	45
ETCD(blue)	1.89	0.483[a]	1.089	90	91	90	45

[a] Lattice direction along which polymer backbone lies

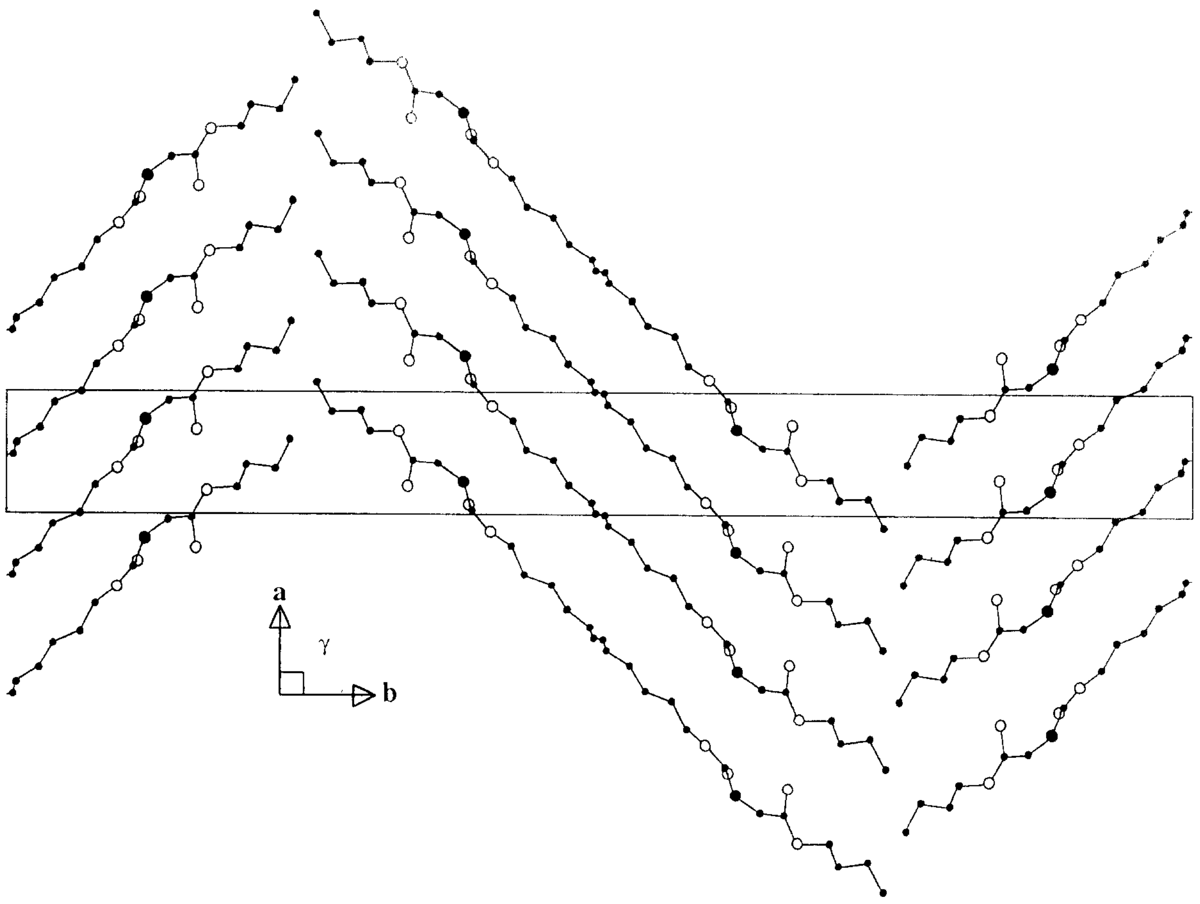

Figure 2 Crystal structure of the 4BCMU blue phase crystals projected on the *a–b* plane with the main chain direction (the *c* lattice direction) nearly normal to the page[30]

each stack which lie at a distance of 2*a*, 3*a* and 4*a* will be 1.6×10^{-2}, 1.4×10^{-3} and 2.4×10^{-4} respectively of that from the nearest-neighbour backbone which lies at a distance of *a*. Given an estimated accuracy in the measurement of *E* of 0.04% (from the error in the optical absorption spectroscopy results), the contribution to W_B from nearest-neighbour backbones beyond 3*a* can also be ignored. Therefore, as the nearest-neighbour backbones lie in equidistant pairs above and below each individual backbone in the stack, it is only necessary to sum equation (5) over the six nearest-neighbour backbones. Thus, for the blue phase polymer crystals of 4BCMU, equation (5) can be rewritten in the form:

$$W_B = \sum_{i=1}^{n=6} K_B(R_i)^{-6} = 2K_B(a)^{-6}(1+(2)^{-6}+(3)^{-6}) \quad (8)$$

This means that the level of Coulombic screening, W_B, produced by neighbouring backbones within the polymer crystals can be related by a simple equation to only one variable, which is the size of the unit cell lattice parameter *a*. If a means can be found to cause variations in *a*, such as temperature or pressure, then variations should occur in the value of W_B. Given that the 4BCMU sidegroups contain no large conjugated units, equation (7) has the form:

$$E = E_0(\varepsilon, \langle \Delta r \rangle) + W_B \quad (9)$$

Therefore, variations in the lattice parameter *a* will result in variations in the exciton energy *E*.

Results[31] from PTS show that in polydiacetylene polymer crystals the linear thermal expansion coefficient along the main chain direction is only 0.21×10^{-5}/°C. Thus, if the 4BCMU polymer crystals are heated the resultant change in temperature would be expected to have a negligible effect on the magnitude of E_0. Hence, equation (9) can be rewritten and combined with

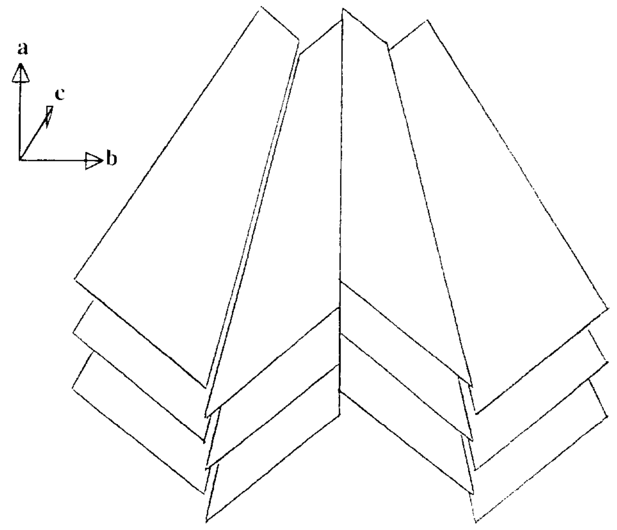

Figure 3 Stacking arrangement within the crystal structure of the flat hydrogen-bonded ribbons formed by the 4BCMU backbone and sidegroups. The ribbons lie in vertical stacks along the *a* lattice direction. The main chain direction lies along the *c* lattice direction[30]

equation (8) to give:

$$E=E_0+2K_B(a)^{-6}(1+(2)^{-6}+(3)^{-6}) \qquad (10)$$

where both E_0 and K_B are constant.

If the 4BCMU polymer crystals are heated and the thermal expansion coefficient along the a lattice direction is sufficiently large, then E should increase with temperature due to the decrease in the level of inter-backbone Coulombic screening as the lattice undergoes thermal expansion. E can be measured using optical absorption spectroscopy and a can be measured using X-ray diffraction. If both the variation of E with temperature and the variation of a with temperature can be measured, then the two results can be combined to give the variation of E with a. Then it should be possible to see whether the results obey equation (10), and if they do, the magnitudes of E_0 and K_B can be calculated.

Furthermore, if the value of K_B can be determined, then the level of inter-backbone Coulombic screening, W_B, can be calculated for the polymer crystals of other polydiacetylene derivatives. This is especially important for PTS since the combined value of (W_B+W_{SG}) is already known and hence would allow the calculation of the magnitudes of W_{SG} and K_{SG} for the phenyl units which lie at the end of the PTS sidegroups.

As various other polydiacetylene derivatives (PTS-12 and TCDU) have phenyl units which lie at the end of their sidegroups, (W_B+W_{SG}) could then be calculated for these. The effect of strain in the lattice and backbone disorder on the magnitude of E_0 can be measured using resonant Raman spectroscopy (TCDU) or calculated from results in the literature (PTS-12). This should make it possible to determine how the different effects of strain, disorder and Coulombic screening produce the particular values of E for the polymer crystals of a variety of different derivatives.

It is for these purposes that the crystals described below were prepared and used in the optical absorption spectroscopy, X-ray diffraction and resonant Raman spectroscopy experiments.

EXPERIMENTAL

To investigate the effect of interchain Coulombic screening polydiacetylene polymer crystals of 4BCMU and TCDU were synthesized and polymerized as described in the literature[32,33]. Polymerization was achieved using 45 Mrad of γ-ray (^{60}Co) irradiation. The 4BCMU optical absorption spectroscopy samples were prepared by evaporating drops of filtered 10^{-2} M monomer solution in acetone onto a glass slide until a thin layer was formed covering an area of about 2 cm × 2 cm. The samples were then immediately placed in an oven and melted at 80°C (4BCMU monomer $T_m=73$°C). The samples were then allowed to recrystallize at 10°C below T_m for 20 h before being cooled to room temperature and polymerized. The resultant film had a dark green-gold colour which under the transmission optical microscope consisted of thin grey crystals of uniform thickness with average dimensions of 100 μm × 200 μm × 1 μm. The 4BCMU sample used in the X-ray diffraction and resonant Raman spectroscopy experiments was crystallized by evaporating a 10^{-2} M monomer solution in acetone and hexane at room temperature to form dark green-gold coloured crystals with average dimensions of 1 mm × 0.5 mm × 0.1 mm. The TCDU sample was crystallized by evaporating a 10^{-2} M monomer solution in acetone and ethyl acetate at room temperature to form dark red coloured crystals with average dimensions of 5 mm × 2 mm × 2 mm.

Optical absorption spectroscopy was used to determine the variation of E with temperature. E is inversely proportional to the wavelength of the peak maximum in the optical absorption spectrum, λ_{max}. The optical absorption spectra were recorded at GEC Marconi Research at Chelmsford, UK using a Perkin-Elmer Lambda 9 UV/VIS/NIR Spectrophotometer operated between 700 and 400 nm. λ_{max} was measured at the point of maximum intensity of the main peak (see *Figure 4*). λ_{max} could be measured to an accuracy of ±0.25 nm. The 4BCMU sample was heated in a purpose built hot-cell which was filled with nitrogen to stop oxidation. The glass slides upon which the optical absorption spectroscopy samples were prepared were stained brown due to the production of trap centres by the γ-ray radiation during polymerization. The spectrum of the trap centres remains unchanged below 130°C, and was subtracted from the sample spectrum by placing an identical glass slide which had been exposed to the same level of radiation in the reference beam of the spectrophotometer.

X-ray diffraction was used to determine the variation of the lattice parameter a with temperature. The X-ray diffraction results were recorded at the University of London X-Ray Facility at Birkbeck College, UK using Cu $K_{\alpha 1}$ and $K_{\alpha 2}$ radiation (average wavelength of

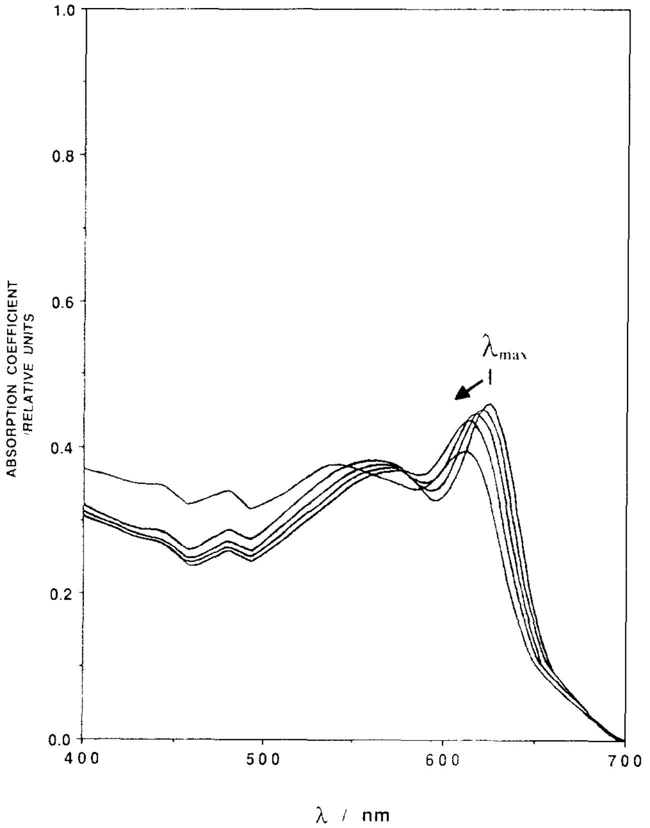

Figure 4 Optical absorption spectra of the 4BCMU blue phase crystals heated between 21 and 90°C. The five individual spectra are recorded at temperatures of 21, 42, 58, 76 and 90°C. The wavelength of the peak maximum, λ_{max}, moves to shorter wavelengths with increasing temperature

0.154184 nm) from an X-ray tube operated at 30 mA/40 kV by a Siemens K710 generator and mounted on a standard Siemens D-500 goniometer with a specially designed θ-circle containing a high temperature rotating stage and fittings allowing it to accommodate a high temperature environmental cell. The diffractometer was controlled and the results analysed using a Siemens Difrac-11 Fortran Software System for X-Ray Diffraction. The cell was filled with nitrogen to avoid oxidation of the samples during heating. The temperatures of the X-ray diffraction experiments were calibrated relative to the optical absorption spectroscopy experiments using the starting temperature and the temperature of the blue to red/yellow crystallographic phase transition, which occurs in the 4BCMU polymer crystals at a temperature of 95°C as measured by optical absorption spectroscopy.

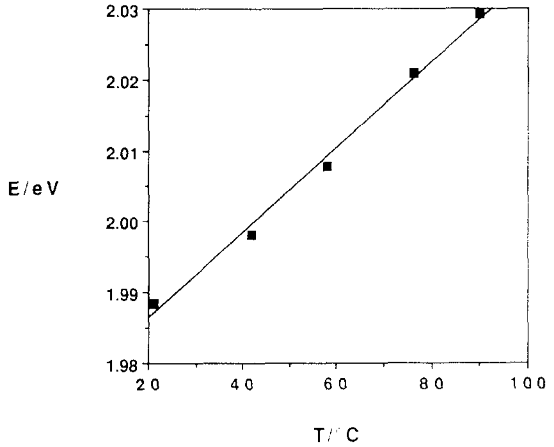

Figure 5 Exciton energy E (calculated from $\lambda_{\max}$) as a function of temperature for the 4BCMU blue phase crystals

Resonant Raman spectroscopy was used to measure the molecular conformation and the level of lattice strain and backbone disorder in TCDU, from which the magnitude of E_0 could be calculated. The resonant Raman spectroscopy results were recorded using an air-cooled HeNe laser with an output at 15808 cm^{-1} (632.8 nm) and a Spex 1401 double-grating monochromator attached to a RCA 31034A photomultiplier. Spectra were recorded between 600 and 1700 cm^{-1} and between 2040 and 2200 cm^{-1}. Power levels were kept below 2 mW at the sample.

RESULTS AND DISCUSSION

Coulombic screening in 4BCMU polymer crystals

Figure 4 shows the optical absorption spectrum of the blue phase polymer crystals of 4BCMU recorded at five different temperatures as the crystals are heated between 21 and 90°C. The main transition peak in the absorption spectrum at 620 nm is due to the creation of the polydiacetylene backbone exciton, which at 21°C has an energy of 1.989 ± 0.001 eV. In the spectrum recorded at 90°C the increase in the absorption of the region between 500 and 400 nm and the decrease in the absorption of the main transition peak is due to the onset of the blue to red/yellow crystallographic phase transition which occurs in the optical absorption experiments at 95°C[19]. The main transition peak shows a continuous shift to shorter wavelengths ($\lambda_{\max}$ decreases) as the temperature increases. This shift is fully reversible if the polymer crystals are cooled.

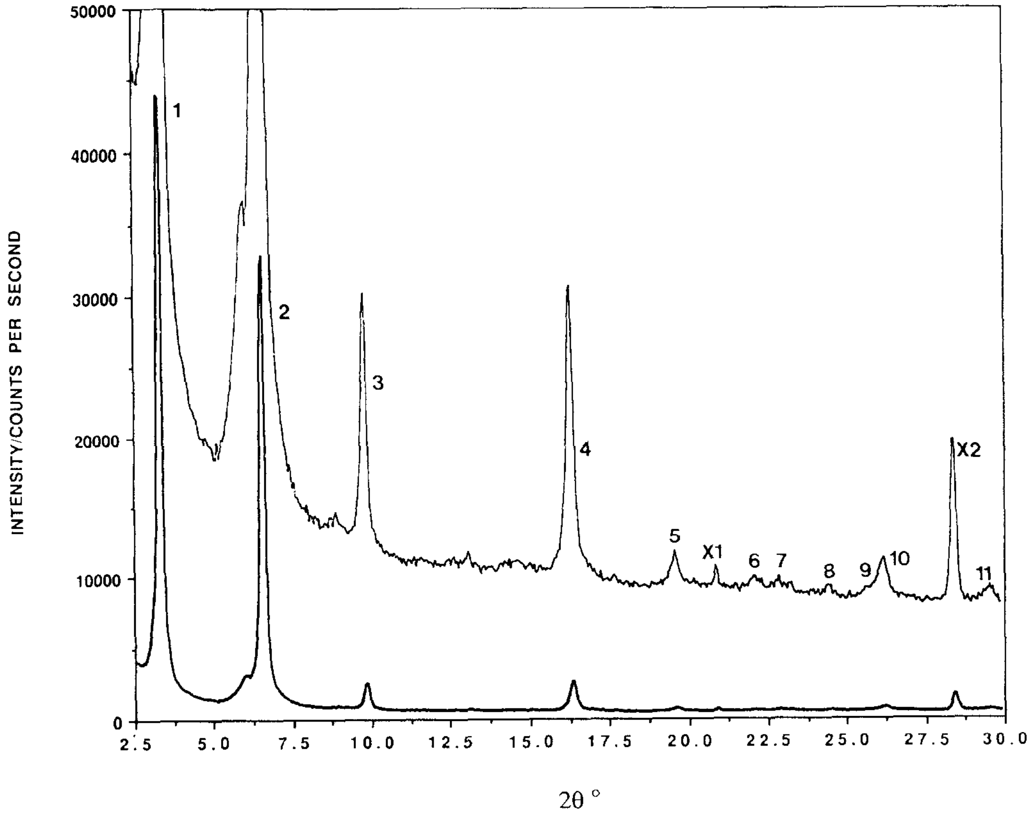

Figure 6 X-ray diffraction spectrum from 4BCMU blue phase crystals between 2θ values of 2.0° and 30.0°

Figure 5 shows the shift in the main transition peak with temperature in terms of the exciton energy E, which shows a continuous and steady increase with increasing temperature at a rate of 6.03×10^{-4} eV/°C. This increase in E with increasing temperature is exactly what would be expected if thermal expansion was increasing the interchain spacing and therefore lowering the level of Coulombic screening within the 4BCMU polymer crystals.

Figure 6 shows the complete X-ray diffraction spectrum of the 4BCMU polymer crystals between 2θ values of 2.0° and 30.0°. The intensity scale on the y-axis of the figure corresponds to the lower curve. The upper curve is identical except that the intensity has been multiplied by 12 to show the small peaks which occur in the spectrum at the relatively larger values of 2θ. The peaks at about 20.9° and 28.5° (peaks X1 and X2) are from the silicon sample holder. *Table 2* shows a complete list of the 2θ, d-spacing and intensity values of all of the diffraction peaks in *Figure 6* which can be identified as being from the blue phase polymer crystals of 4BCMU. These were indexed using the unit cell parameters found in the literature[30] and the resultant (hkl) values are listed in *Table 2*. Three small peaks in *Figure 6* at 2.978°, 5.929° and 8.802° can be identified as the (020), (040) and (060) peaks from the 4BCMU red/yellow phase, which is sometimes produced on the surface of the blue phase polymer crystals when they are washed in acetone to remove any residual monomer immediately after polymerization[19]. These three peaks are not listed in *Table 2*.

As shown by equation (8), variations in the level of inter-backbone Coulombic screening W_B will be due to changes in the magnitude of the lattice parameter a. It is not possible to calculate a directly from a single X-ray diffraction peak, but it is possible to calculate a from a combination of peaks which are present in *Figure 6*. The d-spacing values of a monoclinic unit cell can be calculated using:

$$1/d^2 = h^2/(a.\sin\beta)^2 + k^2/b^2 + l^2/(c.\sin\beta)^2 + 2hl.\cos\beta/(ac.(\sin\beta)^2) \qquad (11)$$

For reflections where $h = 1$ and $l = 0$ equation (11) can be rewritten as:

$$1/d^2 = 1/(a.\sin\beta)^2 + k^2/b^2 \qquad (12)$$

Therefore, by calculating b from the $(0k0)$ series of peaks (peaks 1, 2, 3, 4, 5, 10 and 11 in *Figure 6* and *Table 2*) and by measuring the d-spacing values of any one of the $(1k0)$ peaks (peaks 6, 7, 8 and 9), using equation (12) it is possible to calculate the value of a.

Table 2 X-ray diffraction peak data for peaks in *Figure 6*

Peak	2θ	d (nm)	Intensity (counts s^{-1})	(hkl)
1	3.231	2.732	202 040	(0 2 0)
2	6.474	1.364	158 370	(0 4 0)
3	9.725	0.9087	9615	(0 6 0)
4	16.275	0.5442	13 720	(0 10 0)
5	19.541	0.4539	2530	(0 12 0)
6	22.083	0.4022	950	(1 9 0)
7	23.198	0.3831	265	(1 10 0)
8	24.404	0.3644	375	(1 11 0)
9	25.648	0.3470	420	(1 12 0)
10	26.160	0.3404	2280	(0 16 0)
11	29.611	0.3014	710	(0 18 0)

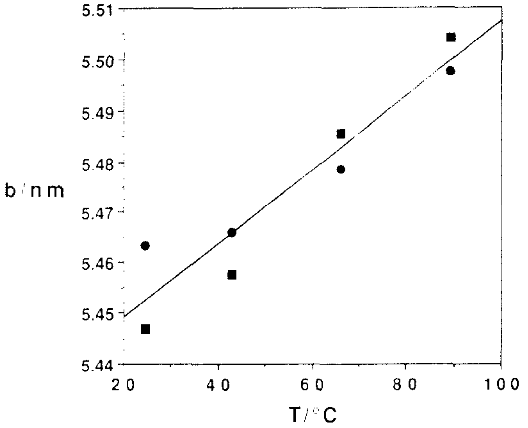

Figure 7 Variation of the magnitude of the b lattice parameter with temperature for the 4BCMU blue phase crystals, calculated from the change with temperature of the d-spacing values of the (020) (●) and (040) (■) peaks in the X-ray diffraction results

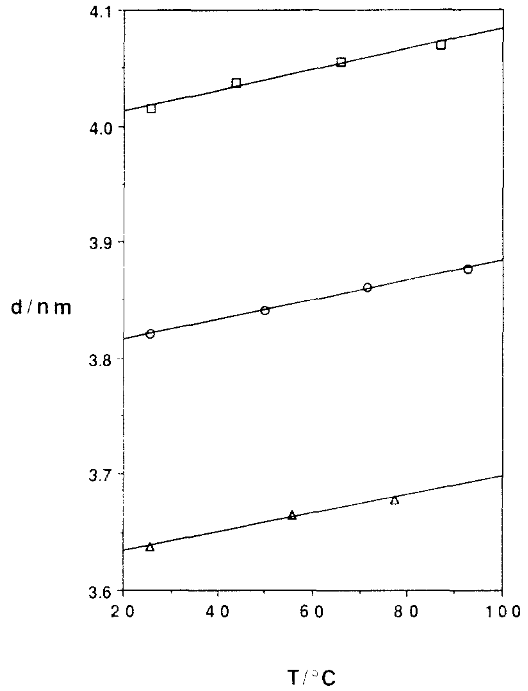

Figure 8 Variation of the magnitude of the d-spacings of the (190) (□), (1 100) (○) and (1 110) (Δ) peaks with temperature for the 4BCMU blue phase crystals

The 2θ values of the (020) and (040) diffraction peaks (peaks 1 and 2) were recorded at four different temperatures between 24°C and 90°C. The resultant values of b calculated from the d-spacings of the two peaks using equation (11) are plotted against temperature in *Figure 7*. The results give a linear thermal expansion coefficient for the 4BCMU blue phase polymer crystals in the b lattice direction of 1.45×10^{-4}/°C, which is about three times as large as that found in PTS polymer crystals perpendicular to the main chain direction[31]. The 2θ values of the (190), (1 100) and (1 110) diffraction peaks (peaks 6,7 and 8) were also recorded at three or four different temperatures between 25°C and 93°C and the

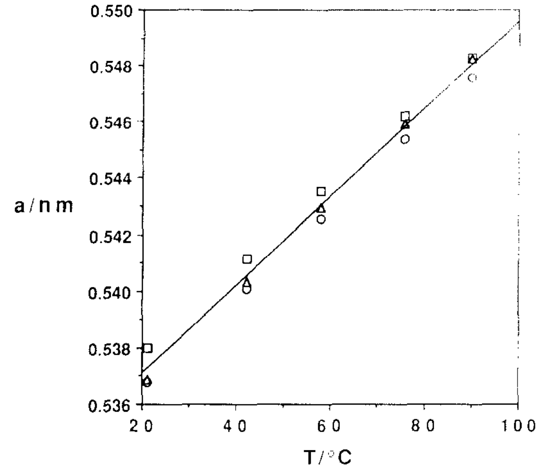

Figure 9 Variation of the magnitude of the *a* lattice parameter with temperature for the 4BCMU blue phase crystals for each of the (1 9 0) (□), (1 10 0) (○) and (1 11 0) (△) peaks

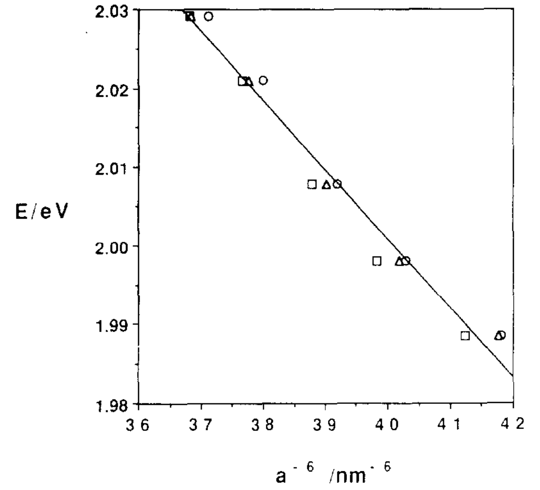

Figure 10 Variation of the exciton energy *E* with the inverse sixth-power of the magnitude of the *a* lattice parameter according to equation (10) for the 4BCMU blue phase crystals

d-spacing values for the three peaks are plotted against temperature in *Figure 8*. Straight line least mean squares fits to the different results shown in *Figures 7* and *8* produce four equations giving the magnitude of the b lattice parameter and the d-spacing values of the (1 9 0), (1 10 0) and (1 11 0) peaks at any given temperature between 21°C and 90°C. Using these equations and equation 12, a value for a is calculated for each of the (1 9 0), (1 10 0) and (1 11 0) peaks at each of the five different temperatures at which the optical absorption spectra shown in *Figure 4* were recorded. The results are plotted in *Figure 9*. This gives a linear thermal expansion coefficient in the a direction of 2.93×10^{-4}/°C, which is about six times as large as that found for PTS[31].

The values of a obtained are plotted against the values of E from the optical absorption spectroscopy experiment in the form of equation (10) (i.e. E *versus* $(a)^{-6}$). This is shown in *Figure 10*. The results lie on a straight line with a correlation coefficient of 0.988. Thus, over the range of interchain spacings explored, within the blue phase polymer crystals of 4BCMU, the Coulombic screening theory explains well the observed variation in the magnitude of E with temperature.

Fitting the results to equation (10) gives:

$$E_0 = 2.351\,\text{eV} \tag{13}$$

$$K_B = -4.305 \times 10^{-3}\,\text{eV nm}^6 \tag{14}$$

for the blue phase polymer crystals of 4BCMU. In the 4BCMU crystals at room temperature $E = 1.989$ eV. Hence, at room temperature and atmospheric pressure:

$$W = W_B = -0.362\,\text{eV} \tag{15}$$

Coulombic screening therefore lowers the total value of E by 15.4% (ratio of W to E_0) in the blue phase polymer crystals of 4BCMU.

This value of W for 4BCMU is very close to the value at room temperature and atmospheric pressure of -0.320 eV estimated from the high-pressure experiments on the polymer crystals of PTS[28]. In PTS Coulombic screening thus lowers the total value of E by 14% (refs 8, 28).

Coulombic screening in PTS polymer crystals

Although the value for W at room temperature and atmospheric pressure is essentially identical for the polymer crystals of PTS and 4BCMU, there are distinct differences in the way Coulombic screening affects both polymers.

The polymer crystals of PTS at room temperature have a monoclinic unit cell with the unit cell parameters as listed in *Table 1*[34,35]. *Figure 11* shows the PTS crystal structure, based on the X-ray diffraction results in the literature[34,35] in the form of a projection onto the a–c plane with the main chain direction (the b lattice direction) normal to the page. The smallest nearest-neighbour inter-backbone distance in the PTS polymer

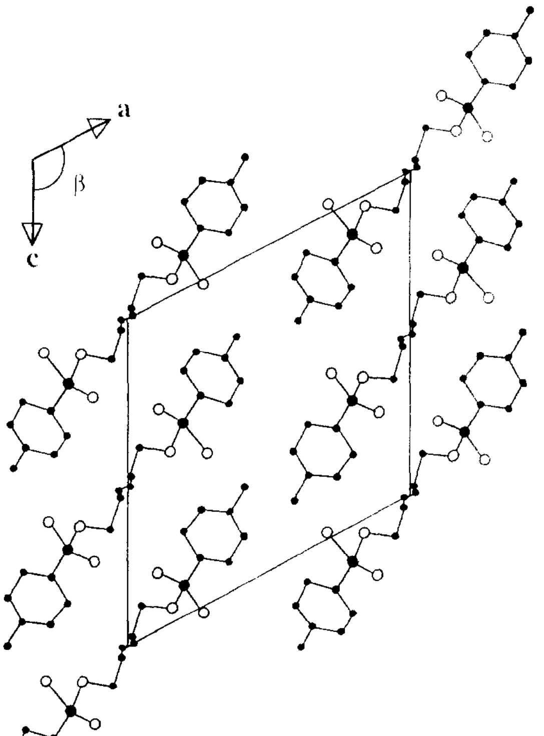

Figure 11 Crystal structure of the blue phase PTS crystals projected on the a–c plane with the main chain direction (the b lattice direction) normal to the page[34,35]

crystals lies along the c lattice direction and is equal to $c/2 = 0.7468$ nm, which is much larger than that found in 4BCMU.

To calculate the contribution to the level of Coulombic screening, W_B, from the surrounding polymer backbones in the PTS polymer crystals, the six nearest-neighbour backbones are used as in the 4BCMU calculations and as will be used when calculating W_B in the polymer crystals of other polydiacetylene derivatives in this paper.

The distances R_i from each backbone to the three nearest-neighbour pairs of backbones are listed in *Table 3*. The results for 4BCMU are also listed for comparison. Using these values and the value for K_B found for 4BCMU, equation (5) is used to calculate that the level of Coulombic screening provided from the surrounding polymer backbones within the polymer crystals of PTS resulting in:

$$W_B = -0.052\,\text{eV} \tag{16}$$

This is only 16% of the total level of Coulombic screening ($W = -0.320$ eV) estimated from the high-pressure experiments[28].

Table 3 Distances R_i and R_j for the polymer crystals of different polydiacetylene derivatives

Polydiacetylene	$R_i{}^a$(nm)	$R_j{}^b$(nm)
4BCMU	0.537 1.074 1.611	– – –
PTS	0.7468 1.2796 1.4493	0.434 0.614 0.940
PTS-12	0.611 1.222 1.833	0.702 0.903 0.963
TCDU	0.619 1.238 1.857	0.810 0.862 1.143
ETCD(blue)	0.537 1.074 1.611	– – –
ETCD(red)	0.545 1.090 1.623	– – –

[a] Distance from each backbone to three nearest-neighbour pairs of backbones

[b] Distance from each backbone to three nearest-neighbour pairs of sidegroup phenyl rings

The remaining contribution to the level of Coulombic screening, W_{SG}, must be provided by the conjugated phenyl units which lie at the end of each sidegroup and are positioned very close to the backbone of adjacent chains in the PTS crystal structure (see *Figure 11*). This is given by:

$$W_{SG} = (W - W_B) = -0.320 - (-0.052) = -0.268\,\text{eV} \tag{17}$$

Thus, in PTS, the major contribution to the level of Coulombic screening is from the phenyl rings which lie at the end of each sidegroup, and not from the surrounding polymer backbones within the crystal structure.

The value of E for the PTS polymer crystals at room temperature and atmospheric pressure is 1.996 eV (from the Kramers-Kronig transformation of the measured optical reflection spectra[7,8]). Therefore, from equation (2), the value of E_0 at room temperature and atmospheric pressure is 2.316 eV. The values of E, W_B, W_{SG}, W and E_0 for PTS are listed in *Table 4*, along with the values for 4BCMU and the other polydiacetylenes analysed in the text.

Having obtained a value for W_{SG} for the phenyl sidegroup units in the PTS polymer crystals, it is now possible to calculate a value for the constant K_{SG} in equation (6) for phenyl units. As for the situation with the backbones, it is assumed that the six nearest-neighbour phenyl rings essentially provide all of the total value of W_{SG}, the contribution from the other phenyl rings within the crystals being negligible. The distance R_j from each backbone to the three nearest-neighbour pairs of phenyl sidegroup units (measured to the centre of each ring) are listed in *Table 3*. Using these values and equation (6), it is calculated that for the phenyl sidegroup units in the polymer crystals of PTS:

$$K_{SG} = -0.786 \times 10^{-3}\,\text{eV nm}^{n} \tag{18}$$

This is about one sixth of the value of K_B found for 4BCMU. Therefore, each phenyl sidegroup unit provides about one sixth of the level of Coulombic screening expected from a polydiacetylene backbone unit placed at the same distance.

Coulombic screening in PTS-12 polymer crystals

A derivative with a very similar chemical structure to PTS is PTS-12 (see *Figure 1b*). However, in the fully polymerized crystals of PTS-12, E has a value of 2.32 eV (ref. 14) measured using optical absorption spectroscopy.

Table 4 Measured and calculated values of E, E_0, W_B, W_{SG} and W for different polydiacetylene derivatives

Polydiacetylene	E(eV) (observed)	W_B(eV)	W_{SG}(eV)	W(eV) ($W_B + W_{SG}$)	E_0(eV)	E(eV) ($E_0 + W$)
4BCMU	1.989	−0.362	–	−0.362	2.351	–
PTS	1.996[a]	−0.052	−0.268	−0.320[d]	2.316	–
PTS-12	2.32[b]	−0.168	−0.010	0.178	2.474	2.30
TCDU	2.29[c]	−0.156	−0.010	−0.166	2.407	2.241
ETCD(blue)	1.97[a]	−0.349	–	−0.349	2.319	–
ETCD(red)	2.32[a]	−0.334	–	−0.334	2.319	1.99

[a] Ref. 7

[b] Ref. 14

[c] Ref. 37

[d] Ref. 28

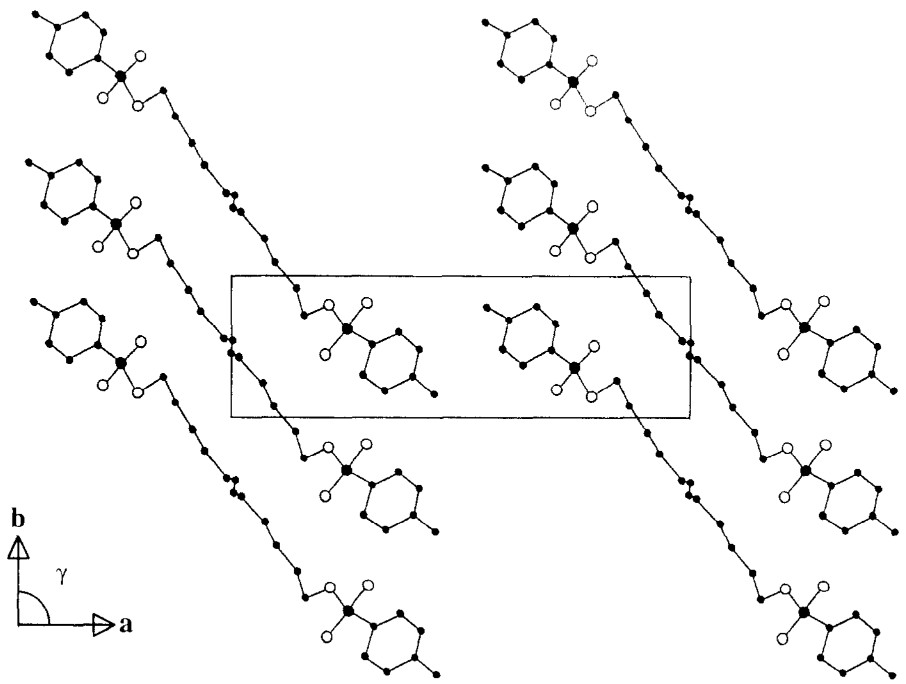

Figure 12 Crystal structure of the red coloured PTS-12 crystals projected on the *a–b* plane with the main chain direction (the *c* lattice direction) nearly normal to the page[36]

This is 0.32 eV below that found in the polymer crystals of PTS. One possible explanation is that the level of Coulombic screening in the PTS-12 crystals is much lower than that in the PTS crystals.

The polymer crystals of PTS-12 at room temperature have a triclinic unit cell with the unit cell parameters as listed in *Table 1*[36]. *Figure 12* shows the PTS-12 crystal structure, based on the X-ray diffraction results in the literature[36], in the form of a projection onto the *a–b* plane with the main chain direction (the *c* lattice direction) nearly normal to the page.

Using the same method as for PTS, the values for R_i and R_j in *Table 3* for PTS-12 and the values for K_B and K_{SG} found for 4BCMU and PTS respectively, it is calculated that for the polymer crystals of PTS-12:

$$W_B = -0.168\,\text{eV} \qquad (19)$$

$$W_{SG} = -0.010\,\text{eV} \qquad (20)$$

Therefore, the total level of Coulombic screening is:

$$W = (W_B + W_{SG}) = -0.168 + 0.010 = -0.178\,\text{eV} \qquad (21)$$

The average value of E_0 in the 4BCMU and PTS-12 polymer crystals is 2.334 eV. If it is assumed that in the PTS-12 polymer crystals E_0 has this average value, then from equation (2):

$$E = E_0 + W = 2.334 - 0.178 = 2.156\,\text{eV} \qquad (22)$$

This is 0.18 eV smaller than the experimentally measured value of E of 2.32 eV (ref. 14).

However, during the initial stages of polymerization of the PTS-12 crystals E is equal to 2.18 eV (refs 14, 36). When the level of conversion increases above about 25% the crystals undergo a crystallographic phase transition which abruptly shifts E discontinuously to 2.32 eV (refs 14, 36). This shift is presumably due to strain in the lattice causing an increase in the value of E_0 of 0.14 eV (refs 14, 36). Therefore, in the fully polymerized polymer crystals of PTS-12, E_0 would be expected to be 0.14 eV greater than that found in the polymer crystals of PTS. Thus, for PTS-12:

$$E_0 = 2.334 + 0.14 = 2.474\,\text{eV} \qquad (23)$$

If this new value of E_0 is then used in equation (2), then:

$$E = E_0 + W = 2.474 - 0.178 = 2.30\,\text{eV} \qquad (24)$$

This is much closer to the experimentally measured value of E of 2.32 eV (ref. 14).

Different red coloured phases in TCDU polymer crystals

Another derivative with a relatively low value of E is TCDU. The freshly polymerized polymer crystals are coloured red and have an E value of 2.29 eV (averaged from the measured optical absorption spectra and the Kramers–Kronig transformation of the measured optical reflection spectra[33,37]).

It was originally proposed that TCDU had a butatrienic rather than an acetylenic backbone structure, but recent X-ray diffraction measurements of the backbone bond lengths, along with theoretical calculations and evidence from PTS oligomers, strongly suggest that the backbone structure must be acetylenic[7,8,33,38,39]. It has also been proposed from ^{13}C n.m.r. results that the low value of E is due to the disordering of the backbone as occurs in the high temperature red phases of ETCD and 4BCMU, but the X-ray diffraction results show that the backbone and sidegroups in the freshly polymerized TCDU crystals are in a highly ordered state[38–40]. The ^{13}C n.m.r. results are probably produced by a disordered phase of TCDU, but this is almost certainly another red phase, normally occurring at higher temperatures in other derivatives, which has been produced during the preparation of the polymer crystals. The appearance of this 'high tempera-

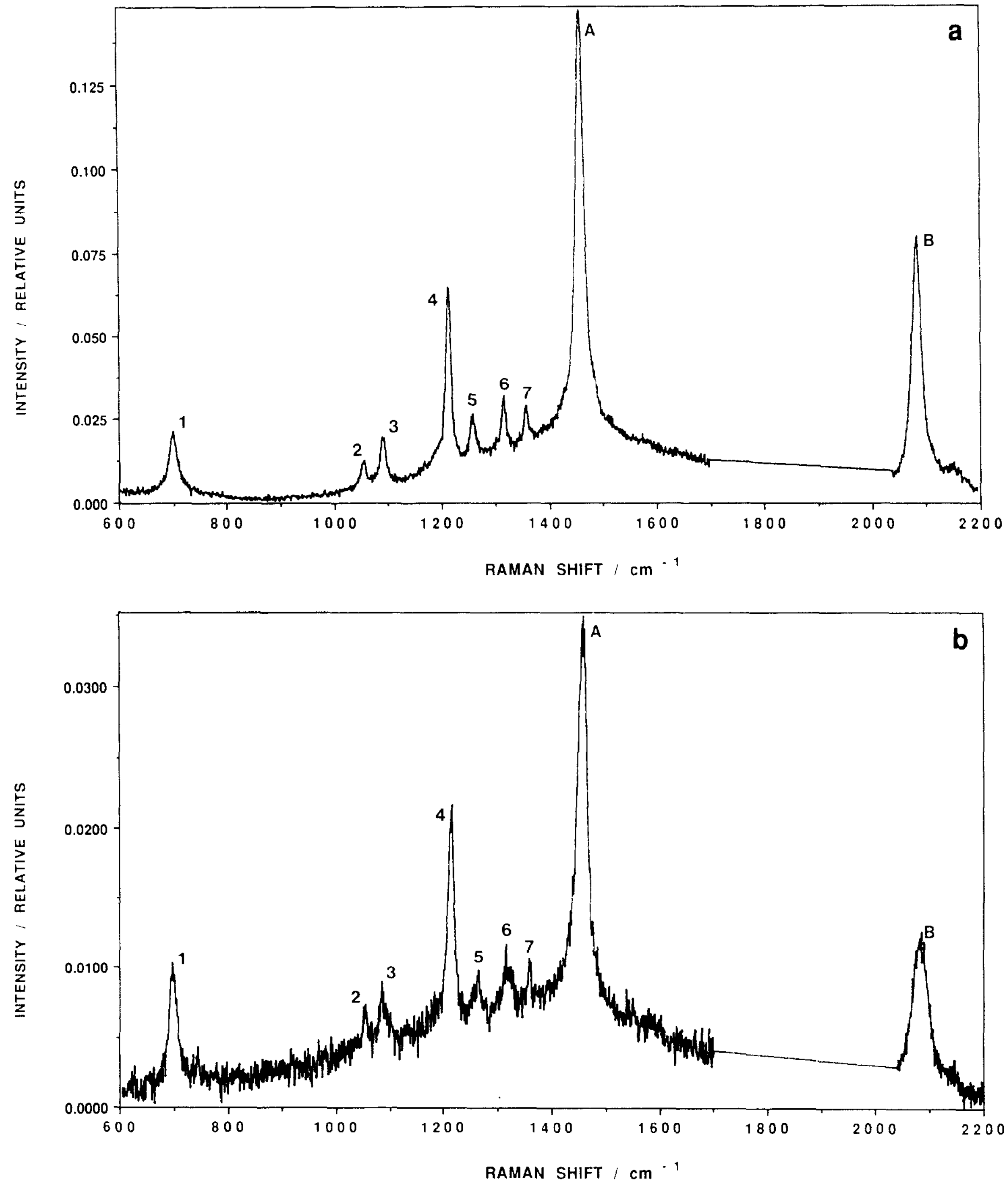

Figure 13 Resonant Raman spectrum from: (a) blue phase 4BCMU crystals; (b) red coloured TCDU crystals

ture' disordered red phase is known to sometimes occur in the preparation of 4BCMU, and it would explain the reported difficulties in obtaining high quality TCDU crystals in the recent X-ray diffraction experiments[19,39]. The low temperature blue phase which is observed in the TCDU polymer crystals is probably similar to that which occurs at low temperatures in PTS and 4BCMU and does not involve any real change to the room temperature backbone conformation[30,35,40,41].

Figures 13a and *b* show the resonant Raman spectra of the blue phase 4BCMU polymer crystals and the red phase TCDU polymer crystals obtained in this study. The Raman shift of all the peaks in the spectra are listed in *Table 5*. The intense peaks at about 1460 cm^{-1} (peak

Table 5 Raman shift (in cm^{-1}) of the peaks in the resonant Raman spectra of *Figures 13a* and *b* for the 4BCMU blue crystals and the TCDU red crystals

	Peak	4BCMU	TCDU
Single bond region	1	700	694
	2	1056	1051
	3	1092	1080
	4	1214	1210
	5	1258	1261
	6	1318	1315
	7	1360	1356
Double bond region	A	1461	1454
Triple bond region	B	2086	2086

A) and 2080 cm^{-1} (peak B) are due to the vibrational modes of the double and triple backbone bonds respectively[8,42]. The peaks in the region between 600 and 1400 cm^{-1} (peaks 1 to 7) are due to vibrational modes involving the sidegroup units which are coupled to the backbone[42]. In 4BCMU and TCDU these vibrational modes will only involve the 4-methyl sidegroup units which are immediately adjacent to the backbone. This is because the single-bonded oxygen atom which connects the 4-methyl units to the rest of the sidegroup (see structure in *Figure 1b*) will vibrationally decouple the rest of the sidegroup from the backbone. The difference in the intensity of the spectra is due to the fact that the exciting laser line at 632.8 nm is more in resonance with the 4BCMU blue phase crystals ($\lambda_{\max} = 624.5$ nm) than the TCDU red phase crystals ($\lambda_{\max} = 540$ nm).

The resonant Raman spectrum of the red coloured polymer crystals of TCDU is very similar to that of the blue coloured polymer crystals of 4BCMU. The number and relative intensities of the peaks in both spectra are identical, the only difference being some small changes in the Raman shift which occurs for some of the peaks. This indicates that the polydiacetylene backbone and the 4-methyl sidegroup units immediately adjacent to the backbone must have almost exactly the same conformation in both derivatives. This confirms the X-ray diffraction results for TCDU and 4BCMU in the literature[30,38,39], which show that in both derivatives the polydiacetylene backbone is in a highly ordered conformation and that the 4-methyl sidegroup units are in an ordered all-*trans* conformation which lies almost exactly in the same plane as the backbone.

The Raman spectra also confirm that the red colour of the freshly polymerized TCDU crystals cannot be due to disorder, because otherwise the peaks between 600 and 1400 cm^{-1} (peaks 1 to 7) would be broadened and the Raman shift of the double and triple bond peaks (peaks A and B) would be shifted to higher wavenumber values, as occurs in the disordered high temperature red coloured polymer crystals and the disordered yellow coloured polymer solutions of various polydiacetylene derivatives[14,19,22,24,42].

However, it was found that if the intensity of the exciting laser line is increased above the 2 mW used to record the results in *Figure 13b*, a second double bond peak (peak A) started to appear at 1487 cm^{-1}. This is confirmed by resonant Raman spectroscopy results in the literature for the freshly polymerized TCDU crystals recorded with the same exciting laser line at 632.8 nm and with a laser intensity of 15 mW, which show spectra with two double bond peaks at 1460 and 1488 cm^{-1} (ref. 33). Apparently if the intensity of the exciting laser is increased much above 2 mW the polymer crystals are heated so that they undergo a thermochromic phase transition into another structural phase. The fact that the second double bond peak is at higher wavenumber values means that this new phase has a more disordered backbone structure than that in the original polymer crystals.

When the second double bond peak started to appear at 1487 cm^{-1} in the results in this work, three new relatively broad peaks also started to appear in the region between 600 and 1400 cm^{-1} at approximate wavenumber values of 1068, 1184 and 1243 cm^{-1}. These wavenumber values correspond closely to those of the three most intense peaks in the same region in the resonant Raman spectra of the high temperature disordered red/yellow phase of 4BCMU[19]. This high temperature phase is the same as that which occurs in the polymer crystals of ETCD and IPUDO[15,16]. Therefore, TCDU does indeed have a disordered phase which is completely distinct from the ordered phase which occurs in the freshly polymerized red coloured crystals.

Coulombic screening in TCDU polymer crystals

Given that the relatively low value of E in the freshly polymerized TCDU crystals is not due to backbone disorder, the most likely cause is either strain on the backbone or a low level of Coulombic screening.

The level of strain on the backbone can be measured using resonant Raman spectroscopy[43]. The small differences in the Raman shifts of the peaks between 600 and 1400 cm^{-1} (peaks 1 to 7) in the spectra of 4BCMU and TCDU indicates that there are slight differences in the conformation of the 4-methyl sidegroup units immediately adjacent to the backbone in the two derivatives. The double bond peak (peak A) in the TCDU spectrum is also shifted to a lower wavenumber value than that in the 4BCMU spectrum. This indicates that there is a slightly different level of strain on the TCDU backbone than on the 4BCMU backbone, so that there should be a slight difference in the value of E_0 between the two derivatives.

The polydiacetylene polymer crystals of HDEU (Mod I) strained in tension along the main chain direction show a decrease in the wavenumber value of the double bond peak of -4.6 cm^{-1} per 1% of applied chain strain[44]. Hence, the difference in the wavenumber value of the double bond peak of -7 cm^{-1} between the 4BCMU and TCDU polymer crystals indicates a difference in the level of applied chain strain of $+1.52\%$.

The polymer crystals of PTS strained in tension along the main chain direction show an increase in E of 0.037 eV per 1% of applied chain strain[9]. Therefore, $+1.52\%$ of applied chain strain should result in a difference in the value of E_0 between the polymer crystals of 4BCMU and TCDU of $+0.056$ eV. The value of E_0 in the 4BCMU polymer crystals is 2.351 eV. Thus, in the polymer crystals of TCDU:

$$E_0 = 2.351 + 0.056 = 2.407\ \text{eV} \qquad (25)$$

The polymer crystals of TCDU at room temperature have a monoclinic unit cell with the unit cell parameters as listed in *Table 1*[39]. *Figure 14* shows the TCDU crystal structure, based on the X-ray diffraction results in the literature[39], in the form of a projection onto the b–c plane with the main chain direction (the a lattice direction) nearly normal to the page.

Using the same method as described previously and the values in *Table 3*, it is calculated that for the polymer crystals of TCDU:

$$W_B = -0.156\ \text{eV} \qquad (26)$$

$$W_{SG} = -0.010\ \text{eV} \qquad (27)$$

Thus, the total level of Coulombic screening is:

$$W = (W_B + W_{SG}) = -0.156 + (-0.010) = -0.166\ \text{eV} \qquad (28)$$

From equation (2):

$$E = E_0 + W = 2.407 - 0.166 = 2.241\ \text{eV} \qquad (29)$$

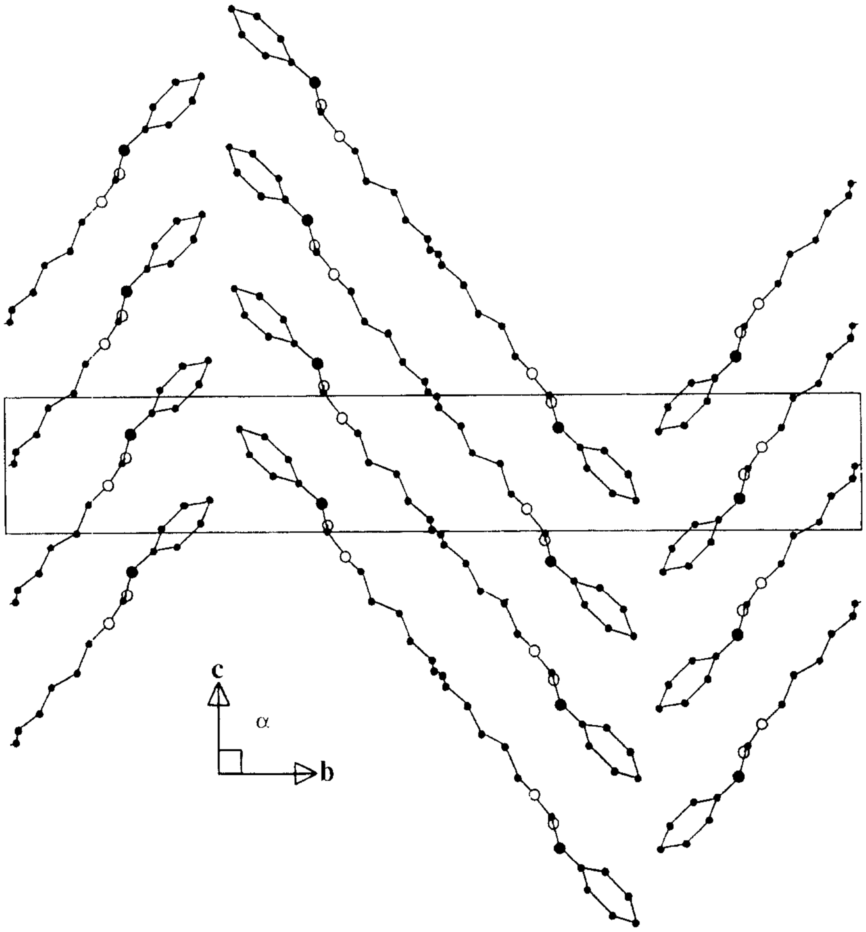

Figure 14 Crystal structure of the red coloured TCDU crystals projected on the *b–c* plane with the main chain direction (the *a* lattice direction) nearly normal to the page[39]

This is in reasonably good agreement with the experimentally measured value of E of 2.29 eV (refs 33, 37).

This calculated value of E for the red coloured TCDU crystals ($E = 2.24$ eV) is 0.25 eV larger than the experimentally measured value of E for the blue coloured 4BCMU crystals ($E = 1.99$ eV). However, the experimentally measured value of E for the red coloured TCDU polymer crystals ($E = 2.29$ eV) (refs 33, 37) is 0.30 eV larger than that for the blue coloured 4BCMU polymer crystals. Therefore, a combination of a low level of Coulombic screening and strain in the lattice can account for 83% (the ratio of 0.25 eV to 0.30 eV) of the observed difference in the value of E between 4BCMU and TCDU. The remainder is probably due to an underestimation of the level of strain in the lattice. The effect of strain on the backbone which is not exactly parallel to the main chain direction has not been measured using resonant Raman spectroscopy, so sidegroup induced strain perpendicular to the main chain direction cannot be measured or quantified.

Coulombic screening in ETCD polymer crystals

It has been suggested that a decrease in the level of interchain Coulombic screening is responsible for the blue to red colour change at the crystallographic phase transition in the polymer crystals of ETCD[29]. This colour transition involves a change in the value of E from 1.97 eV in the blue phase to 2.35 eV in the red phase (from the Kramers–Kronig transformation of the measured optical reflection spectra[7,15]).

ETCD has a monoclinic unit cell with lattice parameters listed as in *Table 1*[45]. The blue to red colour change involves an expansion in the unit cell volume of 4%[45]. Although the full crystal structure has not been determined for ETCD, the unit cell parameters are very similar to those of other polydiacetylenes such as 4BCMU and TCDU and it is very likely that the chains are packed in the crystals in an almost identical manner[19,45]. If the sidegroups in the blue coloured ETCD polymer crystals have the same conformation as the sidegroups in the blue coloured 4BCMU and red coloured TCDU polymer crystals, then it can be estimated that the flat hydrogen-bonded ribbons which would be formed in the ETCD polymer crystals should have a width of about 2.5 nm. If the ETCD ribbons stack in the polymer crystals at the same angle at which the 4BCMU ribbons stack in *Figure 2*, then the width of the stack in the ETCD crystals should be about 1.78 nm. This is almost identical to the magnitude of the *a* lattice parameter in the ETCD blue phase polymer crystal structure[45]. Also, the magnitude of the *c* lattice parameter in the ETCD polymer crystal structure (1.081 nm) is almost exactly double the magnitude of the *a* lattice parameter in the 4BCMU polymer crystal structure (0.537 nm). Given that the polydiacetylene chain repeat unit is equal to 0.491 nm, the chain direction must lie along the direction of the *b*-axis. Therefore, the most likely form of the ETCD blue phase

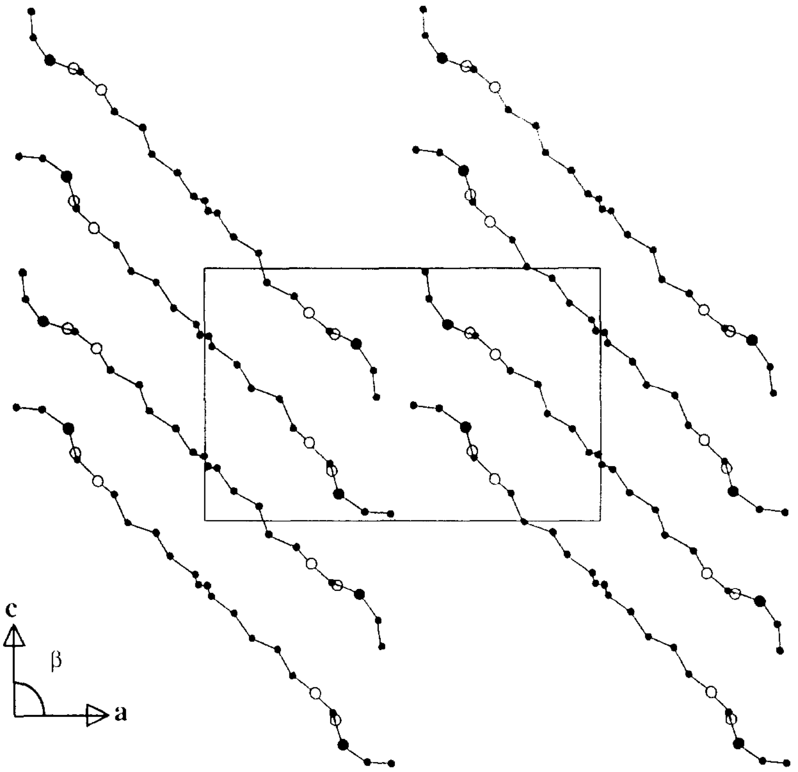

Figure 15 Proposed crystal structure of the ETCD crystals projected on the *a–c* plane with the main chain direction (the *b* lattice direction) normal to the page

polymer crystal structure is shown in *Figure 15*, where the structure is illustrated in the form of a projection onto the *a–c* plane with the main chain direction (the *b* lattice direction) normal to the page.

Using the same method as described previously and the values in *Table 3*, it is calculated that for the blue coloured polymer crystals of ETCD.

$$W = (W_B + W_{SG}) = -0.349 + 0 = -0.349\,\text{eV} \qquad (30)$$

The blue phase ETCD polymer crystals have a measured value of E of 1.97 eV (refs 7, 15). Therefore, from equation (2):

$$E_0 = E - W = 1.97 - (-0.349) = 2.319\,\text{eV} \qquad (31)$$

Using the same method as before, it is calculated that for the red coloured polymer crystals of ETCD:

$$W = (W_B + W_{SG}) = -0.334 + 0 = -0.334\,\text{eV} \qquad (32)$$

If the blue to red colour change in ETCD is not due to a disordering of the backbone or a huge increase in the level of strain in the lattice, then E_0 should have the same magnitude in both the blue and the red coloured crystals. Using the value of E_0 of 2.319 eV found for the blue phase crystals, it is calculated from equation (2) that for the red phase crystals:

$$E = E_0 + W = 2.319 - 0.334 = 1.985\,\text{eV} \qquad (33)$$

This is in complete disagreement with the experimentally measured value of 2.35 eV (refs 7, 15). It is calculated that even if all of the expansion in the volume of the unit cell at the blue to red transition occurred along the *c* lattice direction and caused the maximum expansion in the nearest-neighbour inter-backbone distance, the value of E in the red phase of ETCD would be 2.043 eV, which is still too small compared to the measured value.

Therefore, a change in the level of Coulombic screening cannot be responsible for the blue to red colour change which occurs at the crystallographic phase transition in the polymer crystals of ETCD. The colour change is most likely due to an increase in the value of E_0 by the disordering of the backbone and adjacent inner sidegroup units, as suggested by a variety of different experimental measurements[19,20,40,42,46].

SUMMARY

Measurements of the variation of the X-ray diffraction spectrum and the optical absorption spectrum with temperature show that in the blue phase polymer crystals of 4BCMU an increase in the energy of the polydiacetylene backbone exciton can be related to an increase in the inter-backbone spacing within the crystals. This is exactly what would be expected if coulombic screening is contributing substantially to the value of the exciton energy within polydiacetylene crystals. Over the range of inter-backbone spacings measured, this variation is in very good agreement with a Coulombic screening theory which represents the exciton energy as being proportional to the inverse sixth power of the inter-backbone spacing. On this basis it is shown from the present results that inter-backbone Coulombic screening lowers the value of the exciton energy in the blue phase polymer crystals of 4BCMU by −0.362 eV, which is 15.4% of the total exciton energy. This is very close to the value estimated in the literature from high-pressure experiments, which suggested that Coulombic screening lowers the value of the exciton energy in the blue phase polymer crystals of PTS by −0.320 eV, which is 14% of the total exciton energy.

Using the results from 4BCMU it is shown that due to the relatively large inter-backbone spacings within the PTS polymer crystals, Coulombic screening from nearest-neighbour backbones can only account for −0.052 eV or 16% of the total measured Coulombic screening. It is proposed that the remainder is produced by the conjugated sidegroup phenyl rings, which in the PTS crystal structure pack very closely to the backbones of adjacent chains. It is shown that each phenyl ring provides about one sixth of the level of Coulombic screening expected from a polydiacetylene backbone unit placed at the same distance. It is also shown from the results for 4BCMU and PTS that a combination of a low level of Coulombic screening and strain in the lattice can account for the relatively low value of the exciton energy in the red coloured polymer crystals of PTS-12. The resonant Raman spectroscopy results show that in the freshly polymerized red coloured crystals of TCDU the backbone and inner sidegroup units must have the same level of order and an almost identical conformation to those in the blue coloured polymer crystals of 4BCMU. Therefore, the relatively low value of the exciton energy in the red TCDU crystals cannot be due to disordering of the backbone as has been proposed in the literature. It is shown that 83% of the low value of the exciton energy in TCDU can be accounted for by a combination of a low level of coulombic screening and strain in the crystal lattice. Similar calculations also show that a change in the level of Coulombic screening cannot be responsible for the blue to red colour change which occurs at the crystallographic phase transition in the polymer crystals of ETCD, as has recently been proposed in the literature.

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