

Orientalional ordering in the low-temperature stable phases of deuterated thiophene

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The stable structures of deuterated thiophene C_4D_4S were investigated at 155 (phase III), 115 (phase IV), 100 and 1.5 K (phase V) by neutron powder diffraction. At 155 K, thiophene is orthorhombic with space group $Pbnm$. Although there is some degree of in-plane orientational disorder, molecules begin to order along two symmetrically equivalent main orientations. At 115 K the structure is incommensurate, with a wavevector $\mathbf{q} \simeq 0.55\mathbf{a}^*$. At 100 K and below, there is a doubling of the a cell parameter and the structure space group is $P2_1$. For the first time, it is shown that, unlike C_4H_4S , phase V of C_4D_4S is not an orientational glass: thiophene molecules are perfectly ordered and are oriented within the molecular plane along two alternating directions, corresponding to the two main orientations observed at 155 K. This ordering probably originates in the slowing down of the in-plane reorientational dynamics upon deuteration.

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1. Introduction

Thiophene, C_4H_4S (Fig. 1a), is a heterocyclic ring molecule, which exhibits a very complex phase diagram (see, for example, the calorimetric study of Figuière *et al.*, 1985, illustrated in Fig. 1b), with five stable phases between 235 and 40 K, some of them incommensurate, and three metastable phases. This complexity is generally attributed to the in-plane reorientational motion of the thiophene molecules, which is believed to exist down to 40 K (André & Szwarc, 1991). This reorientational motion originates in the specific shape of the molecule, whose van der Waals envelope can be almost enclosed in a cylinder of radius 3.4 Å, thus allowing easy rotation in the molecular plane.

Phases I and III of thiophene have been previously studied by X-ray diffraction (Abrahams & Lipscomb, 1952; André *et al.*, 1984), and have been described as orthorhombic structures with space groups $Cmca$ and $Pnma$, respectively. In both structures, molecules are packed in a so-called herringbone pattern. According to the authors, both phases show reorientational disorder, the molecular S atom being delocalized over 20 positions for phase I and between 10 positions for phase III.

Phases IV and V have been briefly described by Dunstetter *et al.* (1993): in that work, phase V was found to be a superstructure of phase III, corresponding to a doubling of the a parameter in the $Pbnm$ setting, and was assigned the space group $Pb2_1m$. However, no structural refinement was attempted. Phase IV was found to correspond to an incommensurate superstructure of phase III.

We present here a new neutron powder diffraction investigation of phases III, IV and V of deuterated thiophene (Fig. 2). Phase III is orthorhombic with space group $Pbnm$, but in

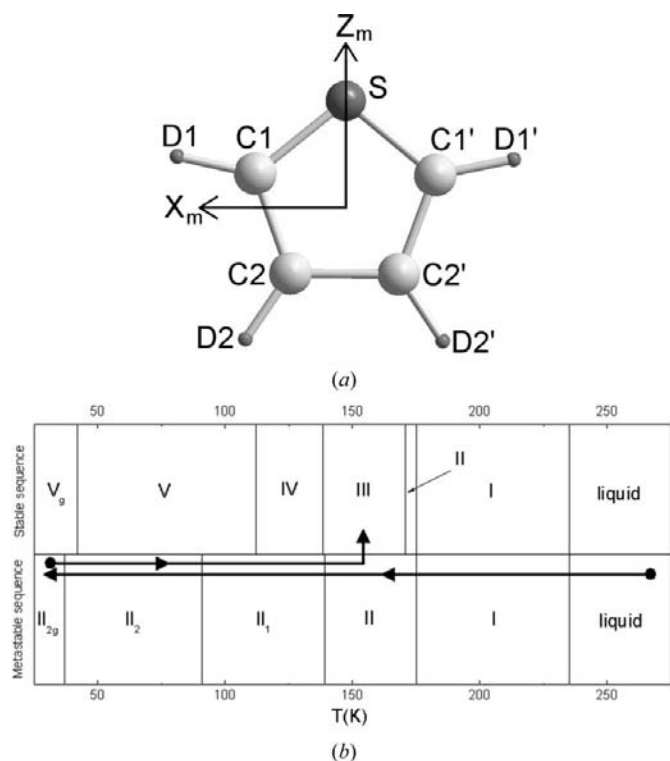


Figure 1
 (a) Scheme of the thiophene molecule; (b) stable and metastable phase-transition sequences of crystalline thiophene at atmospheric pressure. The arrow indicates the procedure to obtain the irreversible metastable phase II to stable phase III transition (from Figuière *et al.*, 1985).

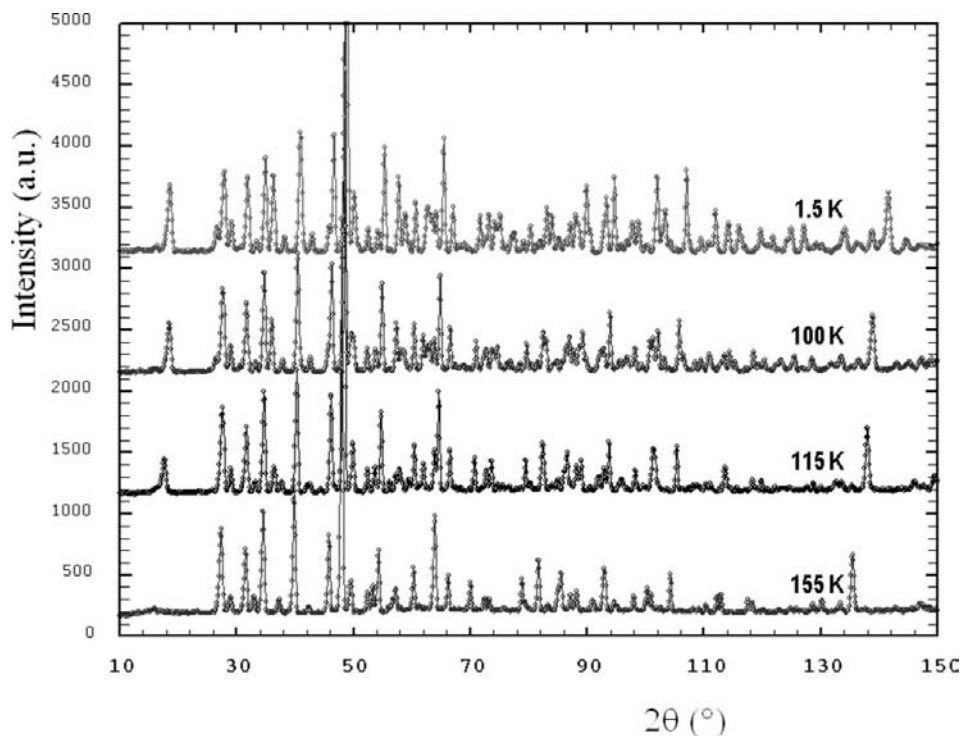


Figure 2
 Neutron powder diffraction patterns of C_4D_4S at 155, 115, 100 and 1.5 K.

Table 1
 Rigid-body intramolecular distances (in Å) and angles (in °), from Harshbarger & Bauer (1970) (see Fig. 1a for atom labels).

S—C1	1.717	C1—S—C1	91.90
C1=C2	1.368	S—C1—C2	112.0
C2—C2	(1.442)	S—C1—D1	121.0
C1—D1	1.072	C1—C2—C2	120.0

contrast with previous results on C_4H_4S , where the thiophene molecule was described as delocalized over 10 in-plane orientations, our refinements show that close to 90% of the molecules orient along two main directions, which are symmetrically equivalent. The structural refinements of the low-temperature phase V at 100 and 1.5 K are also reported: to the best of our knowledge, they show for the first time that below 100 K C_4D_4S molecules order in the structure, with two main in-plane orientations alternating along a . This result contrasts with the commonly accepted image of a glassy state (corresponding to a freezing of the molecule's reorientational motion) for C_4H_4S at low temperature.

2. Experimental

The synthesis of deuterated thiophene was performed as described in Dunstetter *et al.* (1993). Neutron data were collected on the D1A ($\lambda = 2.45$ Å) diffractometer at LLB (Saclay, France) at 1.5, 100, 115 and 155 K upon heating. The sample was first cooled quickly down to 1.5 K (metastable phase sequence, Fig. 1), then heated up to 160 K, at which temperature it was kept for a few hours until the transformation from metastable phase II to stable phase III was complete (Fig. 1b).

Models of the commensurate structures were refined using the *FullProf* suite (Rodríguez-Carvajal, 1993). In all the refinements, the deuterated thiophene molecule C_4D_4S was considered to be a planar rigid-body with symmetry $mm2$ (C_{2v}). The rigid-body intramolecular distances and angles (Table 1) were taken from a gas-phase electron diffraction study carried out on hydrogenated thiophene at 248 K under 10^{-5} torr by Harshbarger & Bauer (1970). Intramolecular distances are likely to change with temperature; however, this is impossible to determine within the resolution of the neutron diffraction experiment and it was therefore decided to keep the intramolecular distances constant from 300 to 1.5 K, as a first

approximation. The position and orientation of the C_4D_4S rigid-body are fully determined in the structure by using the following six parameters: the (x, y, z) coordinates of the centre of mass M_0 and the Euler angles θ , φ and χ . The Euler angles are defined as follows: we denote (X_o, Y_o, Z_o) the axes of the

orthonormal cell system (in our case X_o is parallel to a and Y_o is within the ab plane) and (X_m, Y_m, Z_m) the axes of the rigid-body internal molecular system (Fig. 1*a*). The total rotation labelled by the (θ, φ, χ) angles corresponds to the following combinations of rotations (all are anticlockwise when viewed

from the positive direction of the axis to the origin) applied to the rigid body (it is supposed that both systems coincide when all angles are zero): χ is a rotation of the (X_m, Y_m, Z_m) system around Z_o , θ corresponds to a rotation around Y_o , so θ is the angle between Z_o and Z_m and finally φ corresponds to a rotation around Z_o . In this way the pair of angles (φ, θ) corresponds to the polar coordinates of the Z_m axis with respect to the (X_o, Y_o, Z_o) frame. The (X_m, Y_m, Z_m) internal orthogonal frame was defined using the following procedure: M_0 is the centre of the frame, the Z_m axis is determined by the vector from M_0 to the S atom, and the (X_m, Z_m) plane is the molecular plane. The X_m axis is determined by the vector from M_0 to the projection of the C1 atom onto a line perpendicular to Z_m within the molecular plane (see Fig. 1*a*). The molecular thermal motion of the rigid body was refined by means of the appropriate molecular displacement tensors, the so-called TLS matrices (Schomaker & Trueblood, 1968).

For the refinement of the incommensurate structure, the JANA2000 program (Dušek *et al.*, 2001) was employed, using the same rigid-body description as for the commensurate structures, and isotropic displacement parameters rather than a TLS matrix.

3. Results and discussion

3.1. Phase III (155 K)

The structural refinement using the neutron powder diffraction data collected at 155 K (Fig. 3) confirms that C_4D_4S is orthorhombic ($Pbnm$) with cell parameters $a = 5.552$ (1), $b = 7.620$ (1) and $c = 10.268$ (2) Å. In this space

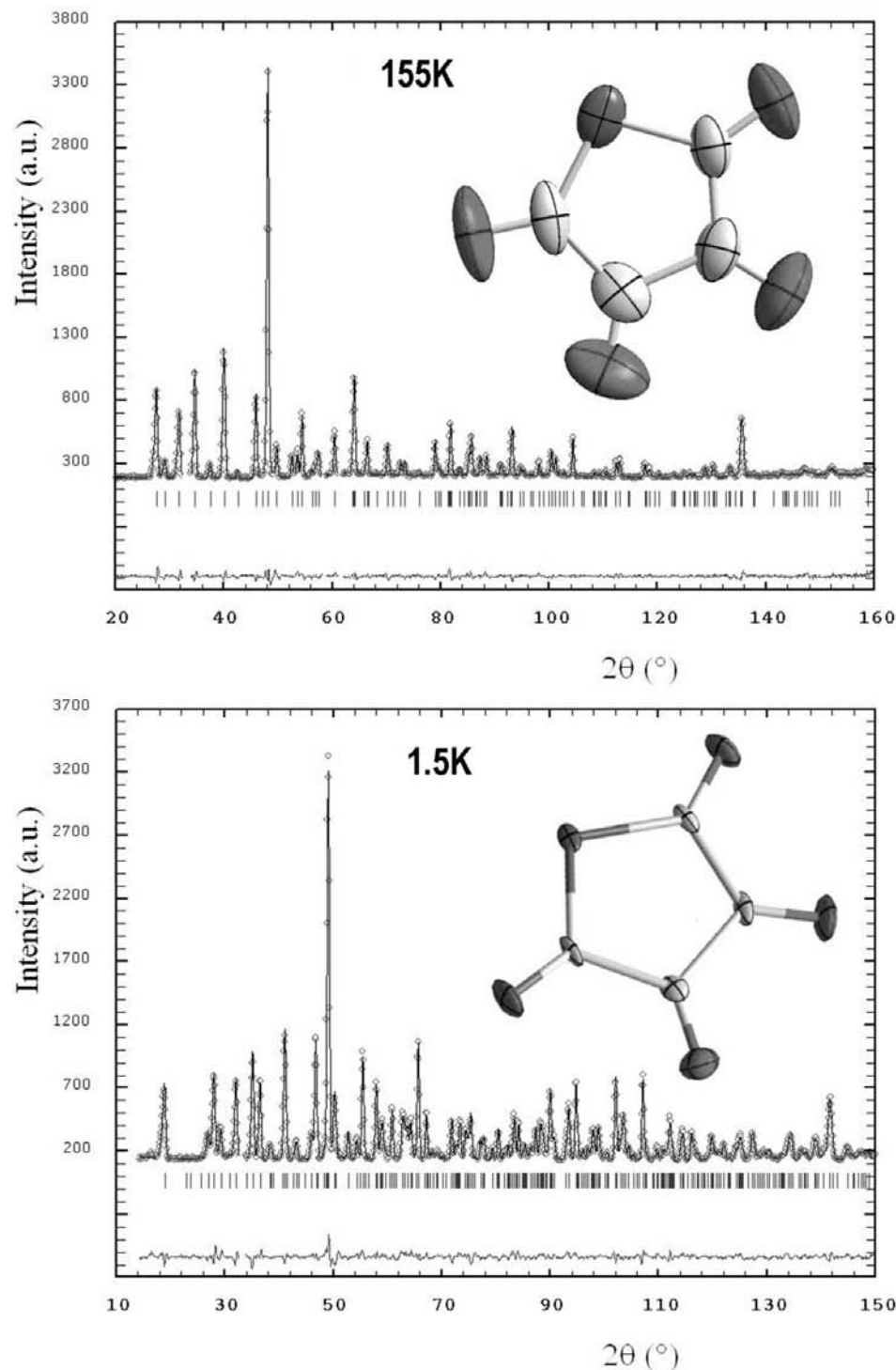


Figure 3 Rietveld refinement of the neutron diffraction patterns of C_4D_4S at (a) 155 K and (b) 1.5 K (experimental data: open circles, calculated profile: continuous line, allowed Bragg reflections: vertical marks; the difference between the experimental and calculated profiles is displayed at the bottom of each graph). Insets: corresponding thiophene C_4D_4S unit showing the displacement ellipsoids, calculated from the TLS matrix coefficients, at 50% probability.

Table 2

Rietveld refinement using the neutron powder diffraction data of C₄D₄S at 1.5, 100 and 300 K.

	1.5 K	100 K	300 K
Crystal data			
Chemical formula	C ₄ D ₄ S	C ₄ D ₄ S	C ₄ D ₄ S
<i>M_r</i>	88	88	88
Cell setting, space group	Monoclinic, <i>P2</i> ₁	Monoclinic, <i>P2</i> ₁	Orthorhombic, <i>Pbnm</i>
Temperature (K)	1.5	100	300
<i>a</i> , <i>b</i> , <i>c</i> (Å)	11.02171 (18), 7.42951 (10), 10.09755 (18)	11.05278 (19), 7.50396 (9), 10.1632 (2)	5.52260 (10), 7.62000 (9), 10.2688 (2)
β (°)	89.989 (5)	89.996 (6)	90
<i>V</i> (Å ³)	826.85 (2)	842.93 (2)	432.13 (1)
<i>Z</i>	8	8	4
Refinement			
<i>R</i> factors	<i>R_p</i> = 0.04542, <i>R_{wp}</i> = 0.05758, <i>R_{exp}</i> = 0.01838, <i>R_B</i> = 0.05051	<i>R_p</i> = 0.03706, <i>R_{wp}</i> = 0.04731, <i>R_{exp}</i> = 0.01827, <i>R_B</i> = 0.05592	<i>R_p</i> = 0.02788, <i>R_{wp}</i> = 0.03756, <i>R_{exp}</i> = 0.01756, <i>R_B</i> = 0.03919
Wavelength of incident radiation (Å)	2.450	2.450	2.450
Excluded region(s)	32.6, 33.75	32.40, 33.75	32.30, 33.75 and 58.05, 58.75
Profile function	Pseudo-Voigt	Pseudo-Voigt	Pseudo-Voigt
No. of parameters	41	40	31
(Δ/σ) _{max}	< 0.0001	< 0.0001	< 0.0001
Preferred orientation correction	None	None	None

Computer programs: *FULLPROF* (Rodríguez-Carvajal, 1993), *DIAMOND* (Crystal Impact, 1998).

group a thiophene molecule statistically occupies either of two equivalent positions related to one another by a mirror plane perpendicular to the molecular ring. Earlier work on C₄H₄S by André *et al.* (1984) concluded that the thiophene molecule was delocalized over at least ten positions; several models were therefore investigated to account for this enhanced in-plane delocalization. The first model was based on one ‘average’ molecule with five equivalent atoms corresponding to a mean atom (1/5 sulfur + 4/5 carbon), to simulate complete delocalization over ten positions. In a similar way, the second model consisted of five molecules sharing the same centre of mass but having different θ , φ and χ orientations. Both these models failed to give even tolerable results. The best model that was eventually found was based on three molecules having different orientations and different occupancy factors on the same site. The refinement results based on this model are satisfactory (top of Fig. 3, Table 2¹). They show that for the three molecules the molecular plane is roughly parallel to *c* and forms a $\sim 32^\circ$ angle with the *a* axis. Within this plane, 88% of the molecules (molecule 1 in Table 3) are oriented along two mirror-like directions forming a 20.7° angle with the *c* axis. Two other in-plane orientations (molecules 2 and 3 in Table 3) have low occupancies, with only 7.6 and 4.4% of the remaining molecules. The orientation of molecule 2 could not actually be determined precisely, as θ (in-plane) rotations within 30° of the value given in Table 3 gave identical refinement results. Phase III is illustrated in Fig. 4. The molecular packing has a herringbone pattern reminiscent of that found for phase I (André *et al.*, 1984), with a higher density. The TLS matrix coefficients and atomic isodensity contours (Fourier maps)

show that there is a slight in-plane rotation of the molecule, and confirm that the molecule is not fully delocalized (inset of top of Fig. 3, Fig. 5*a*). The slightly different ellipsoid on the S atom is thought to result from the fact that the molecule is disordered with the preferred orientation. As already reported (Abrahams & Lipscomb, 1952) for phase I, the molecules in the structure are not especially closely packed, with the shortest intermolecular distance between an S atom and a C atom of an adjacent molecule being 3.70 Å.

The cell parameters obtained for phase III at 155 K are close to those obtained by André *et al.* (1984) [*a* = 5.45 (2), *b* = 7.57 (2) and *c* = 10.20 (10) Å] on a single crystal of C₄H₄S studied by X-ray diffraction at 296 K under 435 MPa (these

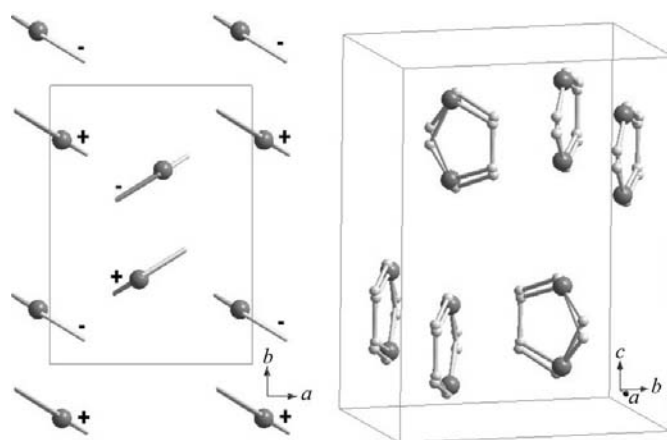


Figure 4
(001) projection and unit cell of the structure of phase III of C₄D₄S (155 K). (–) and (+) signs refer to molecules at *z* = 0.25 and *z* = 0.75, respectively. For the sake of clarity, only molecule 1 (see text and Table 3) is shown, and D atoms have been omitted.

¹ Supplementary data for this paper are available from the IUCr electronic archives (Reference: KD5024). Services for accessing these data are described at the back of the journal.

Table 3

Orientations ($^{\circ}$) of the three independent C_4D_4S molecules sharing the same site in phase III (155 K), along with the corresponding occupancy factors.

The centre of mass of the three molecules is located at $[-0.002$ (2), 0.167 (2), 0.240 (3)].

	Molecule 1	Molecule 2	Molecule 3
Occupancy factor (%)	87.6	4.9	7.5
θ	159.2 (2)	76 (2)	225 (2)
φ	144.8 (5)	125 (2)	143 (3)
χ	-3.6 (5)	-10 (2)	-27 (2)

conditions correspond to the stability domain of phase III). In these conditions, the authors found that the thiophene molecule was delocalized over five or ten positions. Even if our three-molecule model accounts for some degree of disorder, it is, quite unexpectedly, much less disordered than in André's X-ray study. Our results show that the thiophene molecule is actually far from being completely delocalized: it is, rather, statistically disordered between two positions. As André's work was carried out under very different conditions and on a hydrogenated sample, comparisons with our results are difficult. It is expected, in particular, that the degree of delocalization of the thiophene molecule in phase III varies with temperature and applied pressure. As will be seen in further detail below, deuteration is also likely to affect molecular dynamics.

3.2. Phase V (100 and 1.5 K)

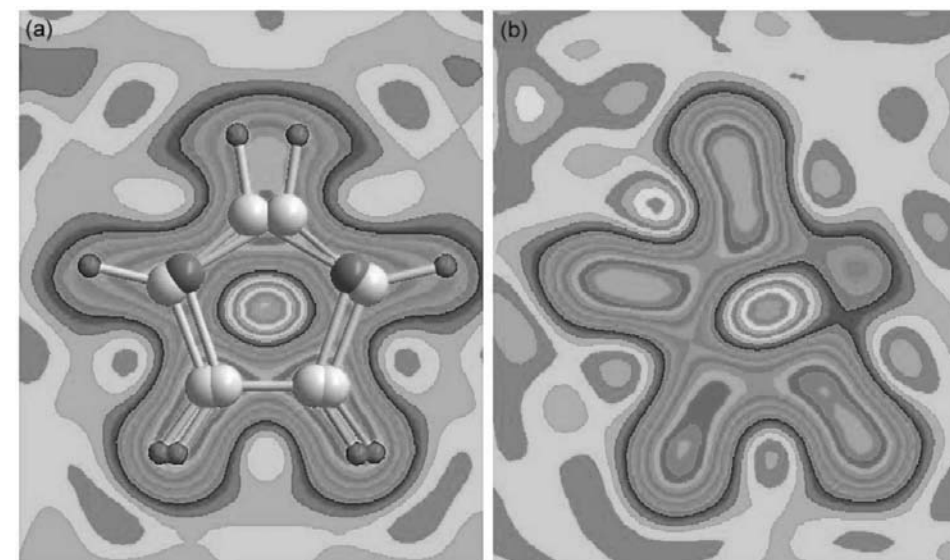
Phase V was easily indexed as a superstructure of phase III involving a doubling of the a lattice parameter. Accordingly, considering group-subgroup relations, the first obvious space group to try was $Pb2_1m$, but all attempts to refine the structure

Table 4

Positions of the centres of mass and orientations ($^{\circ}$) of the four independent C_4D_4S molecules in phase V (1.5 K).

	Molecule 1	Molecule 2	Molecule 3	Molecule 4
x	-0.139 (1)	-0.117 (1)	0.373 (1)	0.382 (1)
y	0.166	-0.179 (2)	0.162 (3)	-0.194 (2)
z	-0.036 (1)	-0.499 (2)	0.019 (1)	-0.493 (2)
θ	154.3 (3)	331.6 (4)	28.6 (3)	150.7 (5)
φ	163 (2)	134 (2)	166 (2)	-57 (2)
χ	15 (2)	16 (2)	163 (2)	-27 (2)

in this space group failed, suggesting the disappearance of the mirror related to the in-plane orientational disorder of the molecules. The monoclinic $Pb11$ space group, in which the in-plane orientations of the molecules are all parallel, also failed to give a convincing result. Eventually, the structure was successfully refined (bottom of Fig. 3) using the monoclinic $P2_1$ space group, in which the two main in-plane molecular orientations observed in phase III now alternate along a . The Fourier map at 100 K (Fig. 5b) shows that thiophene molecules are fully localized, with the S atom clearly noticeable on the isodensity contour. Results of the 100 and 1.5 K refinements are given in Table 2. Note that refining the monoclinic cell β angle did not lead to a significant deviation from 90° . There is a slight decrease of the b and c cell parameters when changing from 100 to 1.5 K, but no major change is observed in the molecules' positions or orientations. Phase V at 1.5 K is pictured in Fig. 6 and the corresponding positions and orientations of the four independent molecules are given in Table 4. In addition to the alternating (along a) in-plane orientations of the molecules, which results from the disappearance of the statistical disorder, it can be seen that the molecular planes are no longer parallel to c , but that the four independent molecules are now tilted with respect to c by an angle of $\sim 31^{\circ}$ varying slightly from one molecule to the other. This effect can also be seen in the TLS matrix coefficients, which do not correspond to an in-plane rotation, as at 155 K, but rather to an out-of-plane vibration (inset of Fig. 3, bottom). The shortest intermolecular distances do not show any significant change with regard to the 155 K structure: the shortest sulfur-carbon distances between adjacent molecules stay in the range 3.55–3.79 Å.

**Figure 5**

Isodensity contours (Fourier maps) in the molecular plane of the thiophene molecule at (a) 155 K (phase III) and (b) 100 K (phase V). A schematic view of the thiophene molecule is superimposed on (a) to illustrate the mirror-symmetry element.

temperature decreases. In addition, below 40 K a glass transition is clearly seen by calorimetric studies, both in the stable and metastable phase sequences (Figuière *et al.*, 1985). These findings contrast with our results: our refinements of the 100 and 1.5 K structures of deuterated thiophene C_4D_4S show that in-plane orientational order is achieved as high as 100 K, and that there is no further phase transition at lower temperature (100 and 1.5 K structures being similar). All the available literature on thiophene molecular dynamics concerns hydrogenated thiophene; to the best of our knowledge, no dynamics study has ever been carried out on deuterated thiophene. It is a proven fact, however, that deuteration modifies molecular dynamics as it increases the inertia of the molecules. This has

been shown for example in methyl rotational dynamics studies (Fillaux *et al.*, 2003). It is therefore likely that the rotational dynamics of C_4D_4S should be slower than those of its hydrogenated counterpart. As, according to dynamics studies, statistical disorder still persists down to 40 K in C_4H_4S and is then followed by a freezing of the molecular reorientational motion in a glass-like state, the case of C_4D_4S would therefore be an interesting example of deuteration-induced molecular ordering. However, this will need to be further investigated and confirmed by a synchrotron powder diffraction study *versus* temperature of the stable sequence of C_4H_4S .

3.3. Phase IV (115 K)

Between 139 and 112 K, phase IV of C_4H_4S has been characterized as incommensurate, with respect to the orthorhombic frame of phase III. C_4D_4S at 115 K indeed shows an incommensurate structure, which can be indexed with a wavevector $\mathbf{q} = 0.55a^*$. Considering the difference between phase III and phase V, this incommensurate state probably results from the progressive in-plane ordering of the thiophene molecules and a refinement was attempted along this line: the 'average structure' was built from the $P2_1$ structure of phase V halved along a , with two independent molecules. At each molecule's site (termed site 1 and site 2 in the following) an additional mirror-like molecule was added, simulating the mirror element of the $Pbnm$ space group of phase III. An occupancy modulation wave was then added to the average

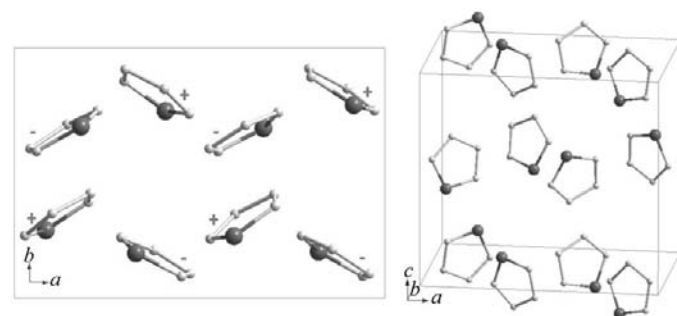


Figure 6
(001) projection and unit cell of the structure of phase V of C_4D_4S (1.5 K). (–) and (+) signs refer to molecules at $z \simeq 0$ and $z \simeq 0.5$, respectively. For the sake of clarity, D atoms have been omitted.

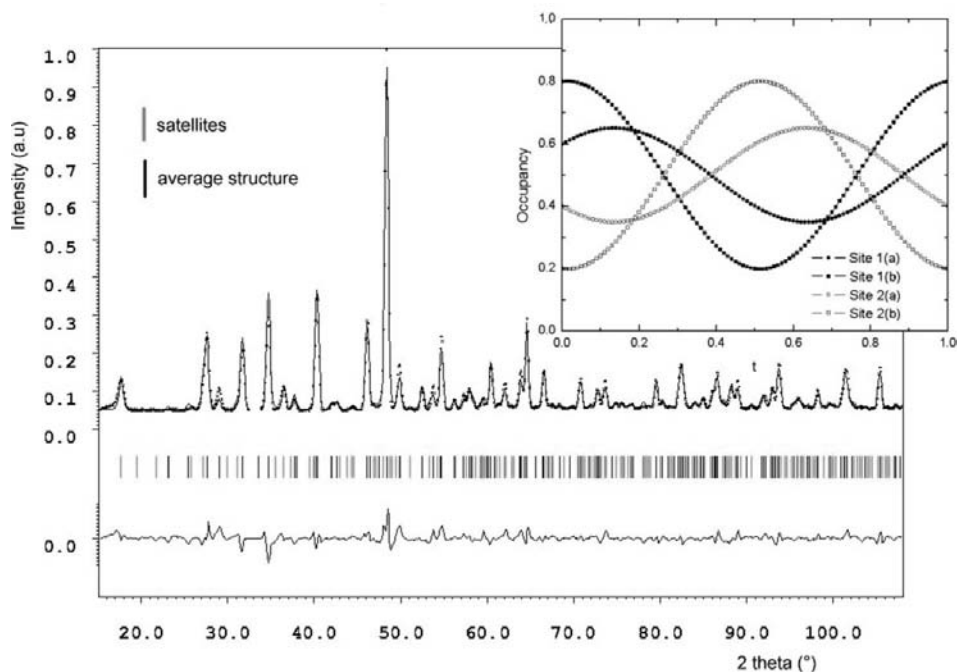


Figure 7
Refinement pattern of the incommensurate structure of deuterated thiophene at 115 K (phase IV; experimental data: open circles, calculated profile: continuous line, allowed Bragg reflections: vertical marks; the difference between the experimental and calculated profiles is displayed at the bottom of each graph). Inset: occupancy plots *versus* internal coordinate $t = x_4 - qr$ (in a four-dimensional space; Dušek *et al.*, 2001). (a) and (b) refer to the two molecules sharing the same site complementarily; site 1 is located at $(-0.2524, 0.1645, -0.0177)$ and site 2 at $(-0.2456, -0.1555, -0.5983)$.

structure to model the progressive in-plane ordering of the molecules, the occupancies of two site-sharing molecules being modulated complementarily so as to keep the total occupancy to 1. In order to improve the refinement, an additional position modulation wave on the (x, y, z) coordinates of the molecules' positions was added. This simple model leads to a fairly satisfactory refinement (Table 5, Fig. 7), which shows that the structural incommensurability results mainly from an occupancy modulation. The corresponding modulation waves are illustrated in the inset of Fig. 7: they tend to show that at 115 K site 1 is more disordered than site 2. A more complete model, however, cannot be reasonably derived from powder data.

4. Conclusion

The pseudo-pentagonal symmetry of thiophene has long been thought to be at the origin of the incom-

Table 5

Rietveld refinement using the neutron powder diffraction data of the incommensurate structure of C₄D₄S at 115 K (phase IV).

C ₄ D ₄ S Phase IV – incommensurate			
Temperature (K)	115	Modulation vector	$q = 0.552(2)a^*$
Crystal system	Monoclinic (1)	Volume (Å ³)	423.1 (2) (1)
Space group	<i>P</i> 2 ₁ (No. 4) (1)	<i>Z</i>	4 (1)
<i>a</i> (Å)	5.516 (1)†	Number of parameters	68
<i>b</i> (Å)	7.533 (1)†	<i>R</i> _p factor	0.0677
<i>c</i> (Å)	10.182 (2)†	<i>R</i> _{wp} factor	0.0878
β (°)	89.996 (6)	χ^2	25.1

† Refers to the average cell.

mensurate and glassy structures observed in its complex phase diagram. Our results on the low-temperature stable phase sequence of deuterated thiophene show that in-plane reorientational ordering starts at 155 K and is complete at 100 K. This suggests that the incommensurability observed at 115 K is probably linked with the disorder resulting from the progressive ordering of the thiophene molecules. The refinements using our neutron diffraction patterns do not provide evidence for any glassy phase in C₄D₄S, in contrast to the reported behaviour of C₄H₄S. This is likely to be due to easier in-plane reorientational motion in the hydrogenated compound, which would prevent the establishment of in-plane ordering, as observed in the deuterated compound.

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