organic compounds

4-[(Z)-2-(Methylsulfanyl)ethenyl]-1-phenyl-1H-1,2,3-triazole: an order–disorder (OD) interpretation of twinning

Berthold Stöger,[a]* Daniel Lumpi[b] and Johannes Fröhlich[b]

[a]Institute for Chemical Technologies and Analytics, Division of Structural Chemistry, Vienna University of Technology, Getreidemarkt 9/164-SC, A-1060 Vienna, Austria, and [b]Institute of Applied Synthetic Chemistry, Division of Organic Chemistry, Vienna University of Technology, Getreidemarkt 9/163, A-1060 Vienna, Austria
Correspondence e-mail: bstoeger@mail.zserv.tuwien.ac.at

The title compound, $C_{11}H_{11}SN_3$, crystallizes as twins with a twin volume fraction of 0.4232 (13). An order–disorder (OD) interpretation gives a plausible explanation of the crystallization behaviour. The structure is a polytype with a maximum degree of order (MDO). The contact plane is interpreted as being composed of a fragment of the second MDO polytype. The planes of the triazole and phenyl rings are twisted by 36.88 (6)°. Molecules are connected via C—H···N hydrogen bonds, forming layers parallel to (100). The layers can be arranged in geometrically different but energetically virtually equivalent ways, giving rise to polytypism.

Comment

The order–disorder (OD) theory was conceived in the 1950s (Dornberger-Schiff, 1956) to explain unusual X-ray diffraction effects in minerals like wollastonite (Jeffery, 1953) and in isostructural inorganic compounds such as Maddrell's salts and sodium polyarsenates (Dornberger-Schiff *et al.*, 1955). It is based on the geometric equivalence of pairs of layers, which also implies energetic equivalence. Structures in which equivalent sides of a layer can connect to another layer only in a way where all resulting layer pairs are equivalent fulfil the vicinity condition (Dornberger-Schiff & Grell-Niemann, 1961). A fundamental result of OD theory states that structures fulfilling the vicinity condition need not be equivalent or even ordered. If the vicinity condition gives rise to different stacking possibilities, one speaks of proper OD structures. These stacking possibilities are said to belong to the same OD family. Neglecting interactions between atoms separated by more than one layer width, all polytypes of an OD family are energetically equivalent.

Since its inception, OD theory has been developed into a versatile theory for the explanation of polytypism, diffuse scattering, noncrystallographic extinctions and twinning, and as a means of classifying structures by symmetry principles. For example, all dense sphere packings can be considered to belong to the same OD family. OD theory has been successfully applied to all major classes of compounds. In the field of minerals and inorganic synthetic compounds, it has been very helpful in solving structural problems by suggesting reliable structural arrangements (Ferraris *et al.*, 2004). It has also been applied, though less frequently, to organic salts and molecular compounds [*e.g.* urotropin azelate (Bonin *et al.*, 2003), tris-(bicyclo[2.1.1]hexeno)benzene (Birkedal *et al.*, 2003; Ferraris *et al.*, 2004) and nonactin (Dornberger-Schiff, 1966)], and recently even to proteins (Pletnev *et al.*, 2009).

Since OD theory is based on geometric relations, it is not uncommon that OD layers do not correspond to layers in the crystallochemical sense. In this work, layers according to OD description will be designated by a letter *A*, according to the layer notation of Grell & Dornberger-Schiff (1982), whereas layers derived from crystallochemical considerations are denoted *B*.

During our systematic studies of a novel class of organic materials exhibiting nonlinear optical properties (Lumpi *et al.*, 2011), we obtained crystals of the title compound, (I). Although they do not fulfil the basic requirements for second harmonic generation, since they crystallize in the centrosymmetric space group $P2_1/c$, they are interesting from a crystallographic point of view because they are systematically twinned and can be described as OD twins.

(I)
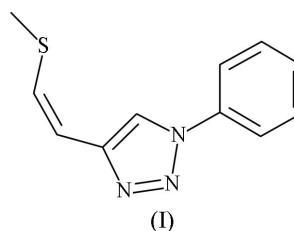
In crystals of (I), one crystallographically unique molecule (Fig. 1) is located on a general position. All interatomic distances are within the ranges of expected values (Allen *et al.*, 2006). The phenyl and triazole rings are planar [maximum
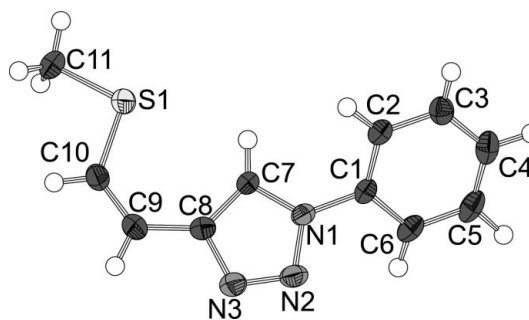

Figure 1
The molecular structure of (I), showing the atom-numbering scheme. C, N and S atoms are represented by dark-, medium- and light-grey ellipsoids, respectively, drawn at the 75% probability level.

distances from the respective least-squares plane = 0.0045 (10) Å for atom C3 and 0.0042 (9) Å for atom C7]. They are twisted about the N1—C1 bond by 36.88 (6)°. This twist is explained by repulsive steric forces between the 5- and *ortho*-H atoms of the triazole and phenyl rings. In comparable 4-alkyl-1-phenyl-1*H*-1,2,3-triazoles, not *ortho*-substituted on the phenyl ring, the twist is generally less pronounced, with angles < 30°. For example, in the closely related propenyl analogue (Lumpi *et al.*, 2011), the twist angle is 8.87 (5)°. An exception is 2,6-bis[1-(4-dimethylaminophenyl)-1*H*-1,2,3-triazol-4-yl]-4-(3,6,9-trioxadeca-1-yloxycarbonyl)pyridine (Meudtner *et al.*, 2007), exhibiting an exceptionally large twist angle of 42.7 (2)°. Interestingly, the second 4-phenyl-1*H*-1,2,3-triazole moiety of the same molecule is close to being planar [twist angle = 0.72 (18)°]. There are a number of such nearly planar 4-phenyl-1,2,3-triazoles, *e.g.* 4-difluoromethyl-1-(4-methylphenyl)-1*H*-1,2,3-triazole (Costa *et al.*, 2006), with a twist angle of 0.34 (14)°. Moreover, in 1-(4-methoxyphenyl)-4-(trifluoromethyl)triazole (Stepanova *et al.*, 1989), the molecule is located on a mirror plane, thus resulting in planarity. A similar phenomenon has been observed and intensely investigated in the room-temperature phase of biphenyl (Trotter, 1961); the biphenyl molecule is located on a centre of inversion and is therefore planar. The preference for a flat geometry, despite the steric repulsive interaction of the *ortho*-H atoms, was explained by a π–π interaction between the connected aromatic rings and by intermolecular interactions (Cailleau *et al.*, 1979).

The –CH=CH—S– group in (I) is nearly coplanar with the triazole ring [dihedral angle between the least-squares planes = 5.14 (13)°], whereas the *S*-methyl group is located distinctly off the molecular plane [torsion angle = 168.40 (15)°]. Only a few crystal structures of compounds with a similar methylsulfanylvinyl side chain are known. For all of them, similar torsion angles are observed, *viz.* 171.2 (3)° in 2-(2-methylsulfonylprop-1-enyl)-4-methylsulfonylthiophene (Mereiter *et al.*, 2000) and 159.57 (14)° in 5-methylsulfanyl-3-(morpholin-4-yl)hexa-2,4-dienenitrile (Mereiter *et al.*, 2001).

The molecules of (I) are connected *via* nonclassical hydrogen bonds (Table 1). The phenyl rings are connected *via* C2—H2···N3 hydrogen bonds to the triazole rings, forming extended chains running along [001]. These chains are, in turn, connected by C11—H113···N2 hydrogen bonds, forming crystallochemical *B* layers with symmetry $P(1)2_1/c1$ (Fig. 2). Adjacent *B* layers connect only *via* van der Waals interactions between the phenyl rings. The shortest interlayer C—H contacts [C4—H4···C1 and C5—H5···C2, with H···C distances of 2.93 (2) and 3.01 (2) Å, respectively] are too long for C—H···π interactions. Given a *B* layer, an adjacent layer can appear in two orientations, related by mirroring at (001). These two possibilities result in virtually identical inter- and intramolecular interactions, which explains the observed twinning and can be described by purely geometric considerations according to OD theory, as follows.

In order to achieve an OD description, the structure is 'sliced' into OD layers with higher symmetry than required by the space-group symmetry. Accordingly, the structure of (I) is
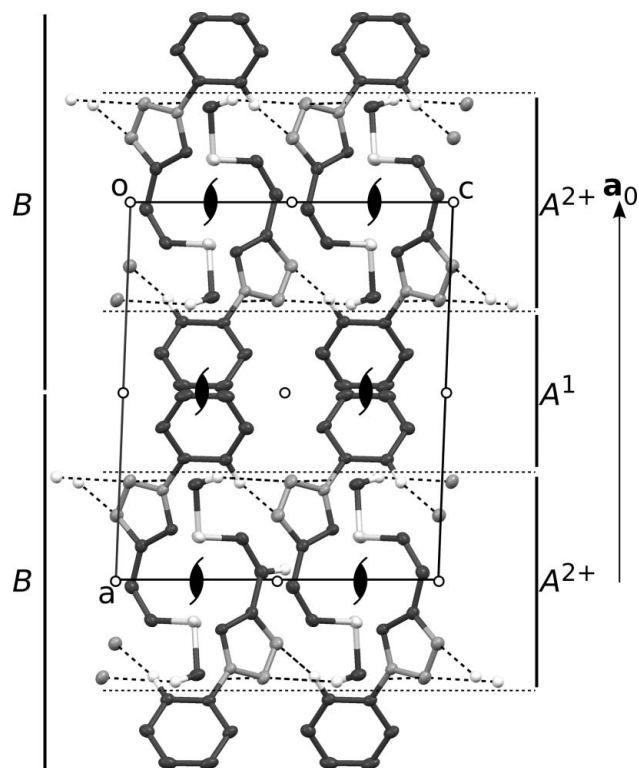

Figure 2
The major polytype ($P2_1/c$) of (I), viewed down [010]. Atom shading is as in Fig. 1 and ellipsoids are drawn at the 60% probability level. H atoms, with the exception of those involved in hydrogen bonds, have been omitted for clarity. Hydrogen bonds are indicated by dashed lines. Layers according to the OD interpretation (A^1 and A^2) are separated by dashed lines. Layer names of OD and crystallochemical layers are indicated to the right and left, respectively. Symmetry elements of the whole polytype are indicated by symbols according to *International Tables for Crystallography* (Hahn, 2006).

decomposed into two kinds of nonpolar (with respect to the stacking direction [100]) layers, *viz.* A^1 (phenyl rings, without H2) and A^2 (H2, triazole ring and aliphatic chain), which possess $P(b)cm$ and $P(1)2_1/c1$ symmetry, respectively (Fig. 2).

The origins of two adjacent layers are related by a translation along $1/2\mathbf{a}_0 \pm s\mathbf{c}$, where $\mathbf{a}_0$ is the vector normal to the layer planes connecting two equivalent layers, and $s = -0.02$ (determined from the lattice parameters of the twin components). Thus, the OD family of the crystal structure of (I) belongs to category IV, characterized by the presence of two kinds of nonpolar OD layers. The OD groupoid family symbol according to the notation of Grell & Dornberger-Schiff (1982) reads as

$$\begin{array}{cc} A^1 & A^2 \\ P(b)cm & P(1)2_1/c1 \\ \multicolumn{2}{c}{[0, s]} \end{array}.$$

The number of stacking possibilities is formally derived using the *NFZ* relationship (Ďurovič, 1997). It is based on those layer symmetry operations which leave intact the orientation with respect to the stacking direction. For A^1 layers, these form the group $P(2)cm$. Since the mirror plane does not apply to A^2 layers, given the position of the former,
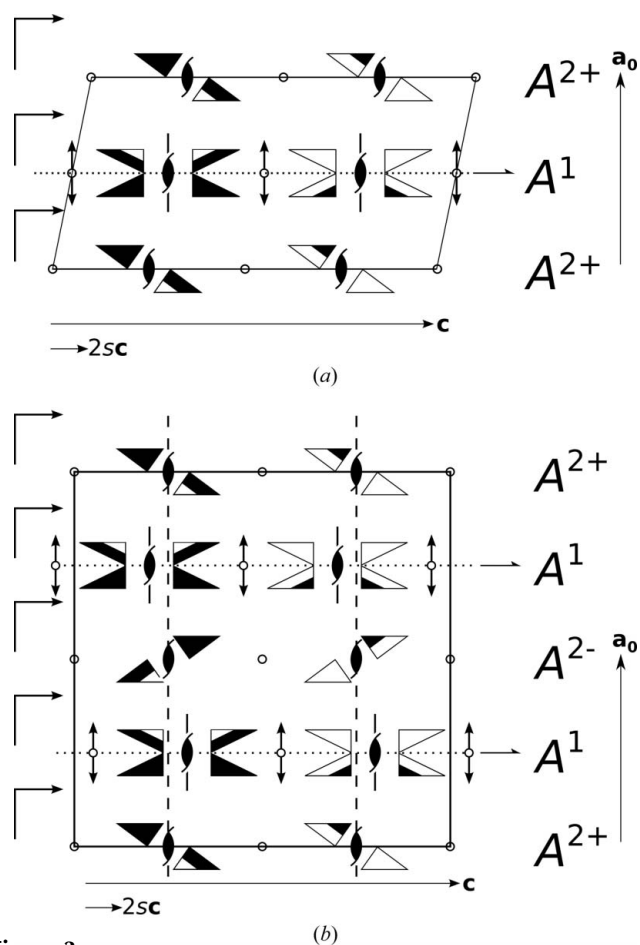
organic compounds

Figure 3
Global and local symmetry of the (a) MDO_1 ($P2_1/c$) and (b) MDO_2 (*Pbcm*) polytypes of (I), represented schematically by two non-equivalent triangles which are black on one side and white on the other. A small triangle of opposite shading indicates translation along $\frac{1}{2}\mathbf{b}$. Symmetry elements are as in Fig. 2.

the latter can appear in two orientations related by the mirror operation, which will be denoted A^{2+} and A^{2-}. The twofold rotation generates the same pair of orientations and the *c*-glide applies to A^2 layers as well and therefore does not produce additional possible orientations. For A^2 layers, on the other hand, the operations to be considered are the members of $P(1)c1$. All of them apply to adjacent A^1 layers. Thus, given the position of the former, the position of the latter is fixed. These stacking possibilities give rise to two polytypes with a maximum degree of order (MDO) (Dornberger-Schiff & Grell, 1982). For MDO_1: $P2_1/c$, $\mathbf{a} = \mathbf{a}_0 + 2s\mathbf{c}$ and all A^2 layers appear in the same orientation. For MDO_2: *Pbca*, $\mathbf{a} = 2\mathbf{a}_0$, and A^2 layers appear alternately as A^{2+} and A^{2-}.

A common feature in OD structures is desymmetrization of layers (Ďurovič, 1979). Indeed, the symmetry of A^1 layers is reduced from $P(b)cm$ to $P(1)2_1/c1$ and $P(b)c2_1$ in MDO_1 and MDO_2, respectively. The symmetry of A^2 layers, on the other hand, is retained in both MDO polytypes. The local and global symmetries of both MDO polytypes are shown schematically in Fig. 3.

As mentioned previously, crystals of (I) are twins. The twin components are of the MDO_1 polytype, appearing in two

different orientations related by the mirror operation of A^1 layers. Polytype MDO_2 is only evidenced indirectly by the twinning operation. At the contact plane, at least one $A^{2+}A^1A^{2-}$ triple layer of MDO_2 exists.

In all polytypes, the configuration and conformation of the molecules is identical and intermolecular interaction is confined to A^2 layers. The polytypes only differ in the relative orientation of molecules which are loosely connected by the phenyl rings. However, independent of the orientation, the arrangement of the phenyl rings is virtually identical, due to the higher symmetry of A^1 layers. Thus, the OD interpretation is valid and gives a plausible explanation of the observed twinning.

Experimental

The syntheses of (3-bromo-2-thienyl)trimethylsilane (Fröhlich & Kalt, 1990) and azidobenzene (Cwiklicki & Rehse, 2004) were performed according to previously reported methods. All other chemicals were obtained commercially and were used without further purification.

The precursor (*Z*)-trimethyl[4-(methylsulfanyl)but-3-en-1-yn-1-yl]-silane, (II), was prepared by analogy with the pentene compound (Lumpi *et al.*, 2011). To a solution of (3-bromo-2-thienyl)trimethyl-silane (1.88 g, 8.0 mmol) in dry Et_2O (30 ml, 0.3 *M*) under an argon atmosphere at 203 K, *n*-BuLi (3.5 ml, 8.8 mmol; 2.5 *M* solution in hexanes) was added over a period of 15 min and the mixture stirred for 1 h. The mixture was then warmed to 283 K, stirred for 1 h, cooled to 273 K and MeI (2.50 g, 17.6 mmol) was added. After 1 h at room temperature, the mixture was poured onto a half-saturated NH_4Cl solution and extracted with Et_2O. The organic layer was washed with brine, dried over anhydrous Na_2SO_4 and concentrated. Column chromatography [light petroleum, dichloromethane ($1\rightarrow4\%$)] yielded 0.685 g (50%) of (II) as a pale-yellow liquid. ^1H NMR (200 MHz, $CDCl_3$): δ 6.49 (*d*, *J* = 10.0 Hz, 1H), 5.49 (*d*, *J* = 10.0 Hz, 1H), 2.38 (*s*, 3H), 0.20 (*s*, 9H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 143.1 (*d*), 104.5 (*d*), 102.9 (*s*), 101.2 (*s*), 16.8 (*q*), −0.1 (*q*). Analysis calculated for $C_8H_{14}SSi$: m/z 171.0658 $[M + H]^+$; found: MS (APCI): m/z 171.0686 $[M + H]^+$.

The title compound was prepared by analogy with the propenyl compound (Lumpi *et al.*, 2011). To a suspension of (II) (0.427 g, 2.51 mmol, 1.00 equivalent), azidobenzene (0.372 g, 3.12 mmol, 1.25 equivalents), $CuSO_4\cdot5H_2O$ (0.125 g, 0.50 mmol, 20 mol%) and sodium ascorbate (0.200 g, 1.01 mmol, 40 mol%) in *t*-BuOH–H_2O (1:1 *v/v*, 6.3 ml, 0.4 *M*) was added potassium fluoride (0.169 g, 2.91 mmol, 1.16 equivalents). The reaction vessel was sealed and heated at 323 K for 18 h. The reaction mixture was then diluted with water and extracted with Et_2O. The combined organic layers were washed with brine and dried over anhydrous Na_2SO_4. Suction filtration and evaporation of the solvent, followed by column chromatography (light petroleum, Et_2O, 3:1 *v/v*) and crystallization from *n*-hexane, afforded (I) (0.386 g, 71%) as a white solid. Single crystals were obtained by recrystallization from *n*-hexane (m.p. 362.9–362.2 K). ^1H NMR (400 MHz, CD_2Cl_2): δ 8.21 (*s*, 1H), 7.77 (*d*, *J* = 8.0 Hz, 2H), 7.55 (*t*, *J* = 7.8 Hz, 2H), 7.46 (*t*, *J* = 7.4 Hz, 1H), 6.65 (*d*, *J* = 10.8 Hz, 1H), 6.43 (*d*, *J* = 10.6 Hz, 1H), 2.48 (*s*, 3H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ 145.8 (*s*), 137.6 (*s*), 131.3 (*d*), 130.3 (*d*), 129.1 (*d*), 121.0 (*d*), 120.4 (*d*), 114.5 (*d*), 18.6 (*q*). Analysis calculated for $C_{11}H_{11}N_3S$: m/z 218.0746 $[M + H]^+$; found: MS (ESI): m/z 218.0756 $[M + H]^+$.

Table 1
Hydrogen-bond geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C11—H113$\cdots$N2^{i}	0.94 (2)	2.62 (3)	3.503 (2)	156 (2)
C2—H2$\cdots$N3^{ii}	0.98 (2)	2.41 (2)	3.3220 (19)	154.6 (17)

Symmetry codes: (i) $-x + 2, -y, -z$; (ii) $x, -y + \frac{1}{2}, z + \frac{1}{2}$.

Crystal data

$C_{11}H_{11}N_3S$
$M_r = 217.29$
Monoclinic, $P2_1/c$
$a = 12.6198$ (3) Å
$b = 7.8465$ (2) Å
$c = 10.7699$ (3) Å
$\beta = 92.2261$ (17)°

$V = 1065.64$ (5) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 0.27$ mm^{-1}
$T = 100$ K
$0.45 \times 0.38 \times 0.22$ mm

Data collection

Bruker APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*TWINABS*; Bruker, 2008)
$T_{min} = 0.888$, $T_{max} = 0.943$

23874 measured reflections
4678 independent reflections
3654 reflections with $I > 2\sigma(I)$
$R_{int} = 0.045$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.048$
$wR(F^2) = 0.111$
$S = 1.03$
4678 reflections

181 parameters
All H-atom parameters refined
$\Delta\rho_{max} = 0.46$ e Å^{-3}
$\Delta\rho_{min} = -0.30$ e Å^{-3}

Figure 4
The ($h1l$) plane of the diffraction pattern of (I), reconstructed from CCD data. Only the $h \geq 0, l \geq 0$ quadrant is shown for clarity. Fully overlapping reflections ($l = 11$) are indicated by a rectangle.
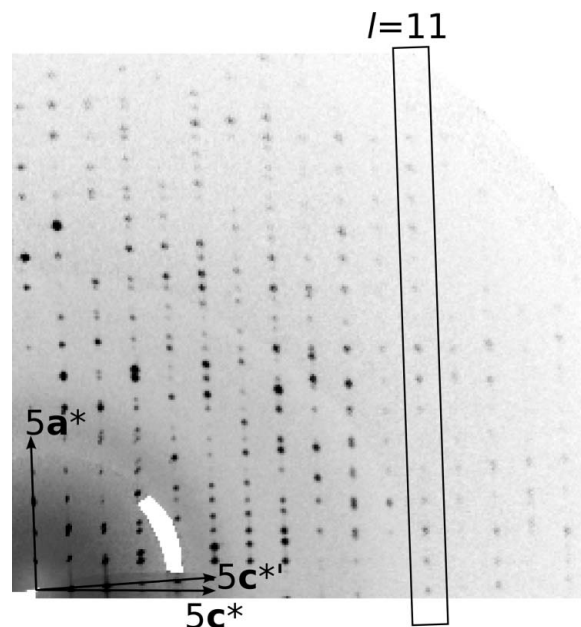
Of five crystals analysed, all were twinned. The reflections of the two twin components were separated using the *RLATT* software (Bruker, 2008). In all cases, the twin domains were related by mirroring at (001). The final unit-cell parameters were refined during data reduction with *SAINT-Plus* (Bruker, 2008). The parameters of both twin domains were restrained to the same values.

The twin index is $10.98 \simeq 11$, although besides reflections $|l| = 0, 11$, reflections $|l| = 1, 2, 9, 10, 12, 13$ are also partially overlapping (Fig. 4). Minor diffuse scattering along **a*** (Fig. 4), indicating disorder in the stacking direction, was neglected.

The structure was solved using direct methods on a data set with averaged equivalent reflections of both twin components. Refinement was performed using the reflections of the major twin domain. All non-H atoms were refined with anisotropic displacement parameters. The parameters of all H atoms were fully refined. No suspicious electron density was found in the difference Fourier maps of the final refinement cycles. The twin volume fraction was refined from overlapping reflections to 0.4232 (13).

Data collection: *APEX2* (Bruker, 2008); cell refinement: *SAINT-Plus* (Bruker, 2008); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ATOMS* (Dowty, 2006) and *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *publCIF* (Westrip, 2010).

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