

Polymorphism of (*Z*)-4-bromo-*N*-(pent-2-enyl)-*N*-(3-phenylprop-2-ynyl)benzenesulfonamide

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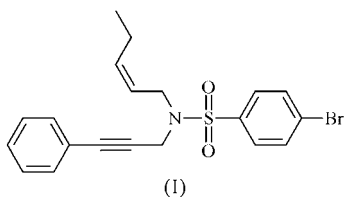
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The title compound, C₂₀H₂₀BrNO₂S, has two polymorphic crystal structures with very similar lattice constants. A number of crystals are composites of the two polymorphs. Both crystal structures contain identical layers of molecules. The packing of the layers, however, is different for the two polymorphs.

Comment

The title compound, (I), was prepared as a starting material for an enantioselective rhodium(I)/BINAP-catalyzed enyne cyclization (Hashmi *et al.*, 2004). The structure of (I) was confirmed by X-ray analysis. During the experiments, it was found that several crystals showed split reflections and these were initially expected to be twinned. Indexing of the reflections of both domains, however, revealed the crystals to be composites of two polymorphs, hereinafter called modifications (*Ia*) and (*Ib*). A total of four crystals of the title compound were measured. One crystal was a pure (*Ia*) polymorph, and three crystals were composites of mainly polymorph (*Ib*) with minor contributions of polymorph (*Ia*). The contributions of the minor polymorph were estimated as 0.30, 0.30 and 0.04, respectively. The second of these three crystals showed the lowest R_{int} and $wR(F^2)$ values after the contributions from (*Ia*) had been subtracted from the observed reflection intensities. Its structure is reported here as the (*Ib*) polymorph and compared with that of the pure (*Ia*) polymorph.



The lattice constants of polymorphs (*Ia*) and (*Ib*) are closely related. The *a* and *b* axes of polymorph (*Ia*) coincide with the *b* and *a* axes of polymorph (*Ib*) in the composite crystals. The

following relationship is found: $a_{(Ib)} = -b_{(Ia)}$, $b_{(Ib)} = -a_{(Ia)}$ and $c_{(Ib)} = -0.395a_{(Ia)} + 0.334b_{(Ia)} - c_{(Ia)}$. The similarity of the unit-cell dimensions suggests that the crystal structures of (*Ia*) and (*Ib*) are also closely related. If the structures were the same then the fractional coordinates of the atoms would be related by $x_{(Ib)} = y_{(Ia)} + 0.334z_{(Ia)}$, $y_{(Ib)} = x_{(Ia)} - 0.395z_{(Ia)}$ and $z_{(Ib)} = z_{(Ia)}$. For the atoms in the asymmetric unit, these relations are indeed confirmed.

The geometries of molecules (*Ia*) and (*Ib*) are almost identical (Fig. 1). The benzene rings are essentially planar. The angle between the planes of the two benzene rings is 49.18 (6)° in (*Ia*) and 49.66 (16)° in (*Ib*). The N atom is non-planar: the sum of the three valence angles about N is 349.9 (2)° in (*Ia*) and 350.0 (4)° in (*Ib*).

The molecules show a number of intramolecular C—H...O and C—H... π contacts. For (*Ia*), these are H6...O1 = 2.50 Å, H7A...O1 = 2.48 Å, H16B...O2 = 2.41 Å, H7B...C17 = 2.71 Å, H16A...C8 = 2.66 Å, H11...C4 = 3.00 Å, H11...C5 = 2.98 Å, H19A...C8 = 3.04 Å and H20C...C8 = 2.93 Å. Very similar contact distances are found in (*Ib*).

The intermolecular contacts are reported in Tables 1 and 2. The molecules form centrosymmetric dimers connected by two symmetry-related intermolecular C—H...Br contacts, with a H...Br distance of 2.89 Å in (*Ia*) or 2.87 Å in (*Ib*). These dimers are connected by two intermolecular C—H...O contacts and two intermolecular C(benzene)—H... π (benzene) interactions to form layers parallel to the 001 plane. The layers with $-\frac{1}{4} < z < \frac{1}{4}$ are identical in (*Ia*) and (*Ib*), as shown in Figs. 2 and 3. Neighbouring layers, however, are arranged differently in (*Ia*) and (*Ib*). In both structures, the segments of the unit cell between $-\frac{1}{4} < z < \frac{1}{4}$ and $\frac{1}{4} < z < \frac{3}{4}$ are related by a *c*-glide plane. The direction of the symmetry axis, however, is different in the two structures and is a result of different intermolecular interactions between the layer structures in (*Ia*) and (*Ib*). A weak intermolecular C20—H20B...C18(1 - x , $\frac{1}{2} + y$, $\frac{1}{2} - z$) interaction is observed in (*Ia*), while a weak intermolecular interaction between the C17—H17 bond and the C17=C18 double bond at (1 - x , $y - \frac{1}{2}$, $\frac{1}{2} - z$) is observed in (*Ib*). The only other interaction between

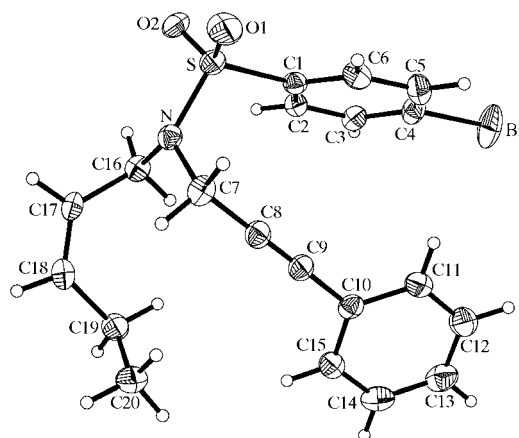


Figure 1
The structure of (*Ia*) at 157 K, shown with 50% probability displacement ellipsoids. The structure of (*Ib*) is similar.

the layers is an intermolecular C18—H18···O2 contact, with a H···O distance of 2.78 Å in (Ia) and 2.73 Å in (Ib). This interaction also acts differently in (Ia) and (Ib). The long H···O distances show this interaction to be very weak.

The similarity of the unit-cell parameters of (Ia) and (Ib) results from the occurrence of identical two-dimensional structural domains in both polymorphs. The arrangement of adjacent domains in the *c* direction, however, is different in (Ia) and (Ib). Variations in the packing of the domains result in composite crystals. The occurrence of composite crystals consisting of two polymorphs is very rare; of over 1000 crystal structures determined in our laboratory, this is only the second example. The other case is the crystal structure of (2*E*,4*S*,5*S*,15*R*)-4,5-dihydroxyhexadec-2-en-15-olide [Cambridge Structural Database (Allen, 2002) refcode JOKSAD]. There, the reflection data resulted from a combination of an orthorhombic lattice, with *a* = 10.797 (1) Å, *b* = 5.440 (3) Å and *c* = 28.390 (4) Å, and a monoclinic lattice, with *a* = 10.796 (1) Å, *b* = 5.440 (3) Å, *c* = 14.48 (2) Å and β = 100.40 (10)°. Both cells have the *a* and *b* axes in common. As that crystal structure was determined long before area detectors came into general use, only the structure of the major orthorhombic polymorph was determined (Quinkert *et*

al., 1991). Another example of a composite crystal of two polymorphs with very similar crystal structures was reported by Freer & Kraut (1965).

Experimental

The synthesis of the title compound was reported by Hashmi *et al.* (2004). Colourless plates were obtained from a solution of (I) in dichloromethane by diffusion of *n*-hexane.

Polymorph (Ia)

Crystal data

C₂₀H₂₀BrNO₂S
M_r = 418.34
 Monoclinic, *P*₂₁/*c*
a = 6.3199 (6) Å
b = 7.3333 (9) Å
c = 40.438 (7) Å
 β = 93.571 (12)°
V = 1870.5 (4) Å³
Z = 4

D_x = 1.486 Mg m⁻³
 Mo K α radiation
 Cell parameters from 193 reflections
 θ = 3–23°
 μ = 2.32 mm⁻¹
T = 157 (2) K
 Plate, colourless
 0.48 × 0.30 × 0.07 mm

Data collection

Siemens SMART 1K CCD area-detector diffractometer
 ω scans
 Absorption correction: numerical (SHELXTL; Sheldrick, 1996)
T_{min} = 0.441, *T_{max}* = 0.848
 21 361 measured reflections

5721 independent reflections
 4562 reflections with *I* > 2 σ (*I*)
R_{int} = 0.068
 θ_{max} = 31.5°
h = -9 → 9
k = -10 → 9
l = -56 → 60

Refinement

Refinement on *F*²
R [*F*² > 2 σ (*F*²)] = 0.058
wR(*F*²) = 0.101
S = 1.19
 5721 reflections
 227 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.02P)^2 + 2P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} = 0.001$
 $\Delta\rho_{max} = 0.46 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{min} = -0.84 \text{ e } \text{Å}^{-3}$

Table 1

Hydrogen-bond geometry (Å, °) for (Ia).

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
C13—H13···Br ⁱ	0.95	2.89	3.588 (3)	132
C16—H16A···O1 ⁱⁱ	0.99	2.56	3.448 (3)	149
C18—H18···O2 ⁱⁱⁱ	0.95	2.78	3.607 (3)	147
C20—H20A···O2 ^{iv}	0.98	2.67	3.616 (3)	163
C3—H3···C14 ^v	0.95	2.95	3.841 (4)	157
C3—H3···C15 ^v	0.95	2.83	3.524 (4)	130
C14—H14···C1 ^{iv}	0.95	2.88	3.557 (4)	130
C14—H14···C2 ^{iv}	0.95	2.94	3.835 (3)	157
C20—H20B···C18 ^{vi}	0.98	2.96	3.525 (4)	118

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

Polymorph (Ib)

Crystal data

C₂₀H₂₀BrNO₂S
M_r = 418.34
 Monoclinic, *P*₂₁/*c*
a = 7.3219 (18) Å
b = 6.3291 (17) Å
c = 40.535 (17) Å
 β = 93.419 (12)°
V = 1875.1 (10) Å³
Z = 4

D_x = 1.482 Mg m⁻³
 Mo K α radiation
 Cell parameters from 73 reflections
 θ = 3–23°
 μ = 2.32 mm⁻¹
T = 156 (2) K
 Plate, colourless
 0.40 × 0.30 × 0.04 mm

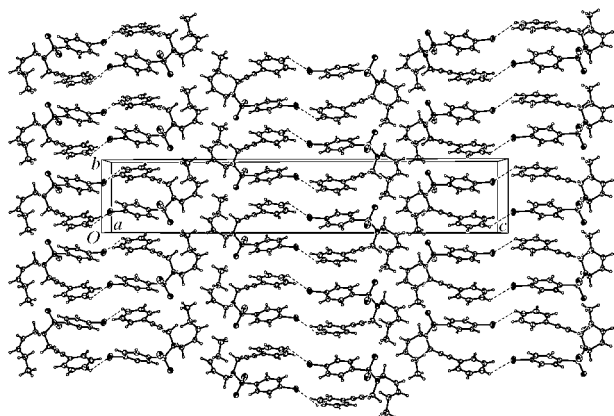


Figure 2
 The crystal packing of (Ia) at 157 K, viewed down *a*. The intermolecular C—H···Br contacts are indicated by dashed lines.

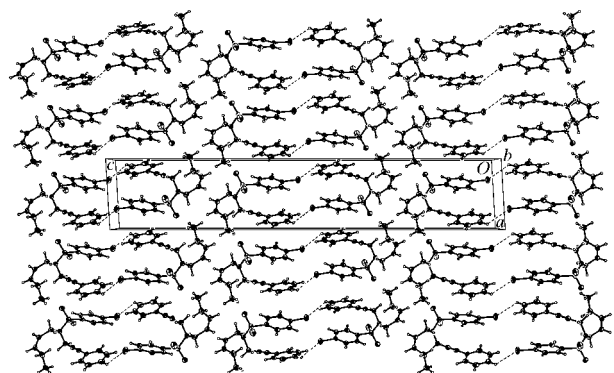


Figure 3
 The crystal packing of (Ib) at 156 K, viewed down *b*. The intermolecular C—H···Br contacts are indicated by dashed lines.

Data collection

Siemens SMART 1K CCD area-detector diffractometer
 ω scans
 Absorption correction: numerical (SHELXTL; Sheldrick, 1996)
 $T_{\min} = 0.450$, $T_{\max} = 0.912$
 12 467 measured reflections

4140 independent reflections
 3013 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.120$
 $\theta_{\text{max}} = 27.5^\circ$
 $h = -7 \rightarrow 9$
 $k = -8 \rightarrow 8$
 $l = -38 \rightarrow 53$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.087$
 $wR(F^2) = 0.171$
 $S = 1.19$
 4140 reflections
 227 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.03P)^2 + 9P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.59 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.66 \text{ e } \text{\AA}^{-3}$

Table 2

Hydrogen-bond geometry (\AA , $^\circ$) for (Ib).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
C13—H13 \cdots Br ⁱ	0.95	2.87	3.579 (7)	132
C16—H16B \cdots O1 ⁱⁱ	0.99	2.56	3.447 (7)	150
C18—H18 \cdots O2 ⁱⁱⁱ	0.95	2.73	3.610 (7)	154
C20—H20A \cdots O2 ^{iv}	0.98	2.64	3.598 (8)	165
C3—H3 \cdots C14 ^v	0.95	2.95	3.850 (9)	158
C3—H3 \cdots C15 ^v	0.95	2.82	3.523 (9)	132
C14—H14 \cdots C1 ^{iv}	0.95	2.87	3.551 (9)	130
C14—H14 \cdots C2 ^{iv}	0.95	2.93	3.821 (9)	157
C17—H17 \cdots C17 ^{vi}	0.95	3.05	3.901 (9)	150
C17—H17 \cdots C18 ^{vi}	0.95	3.00	3.761 (9)	138

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

The measured intensities of (Ib) were corrected for contributions from composite reflections of (Ia). If the positions of both reflections in reciprocal space differ by less than 0.3 reciprocal lattice units, then $I_{Ib, \text{corrected}} = I_{Ib, \text{obs}} - kI_{Ia, \text{obs}}$. Different values for the scaling factor k were tried and the best result was obtained for $k = 0.3$. Thus, 7431 of

the 12 467 measured reflections were corrected. The R_{int} value was 0.152 before the correction and 0.120 afterwards, while $wR(F^2)$ decreased from 0.277 to 0.171. The still rather large value of R_{int} results from incomplete background corrections, due to many partially overlapping reflection profiles. The 0.96-(Ib)/0.04-(Ia) crystal was of poor quality, resulting in broad reflection profiles. Consequently, this crystal had larger $wR(F^2)$ values than the 0.70-(Ib)/0.30-(Ia) crystal. H atoms were positioned geometrically at fixed distances of $C_{sp^2}-H = 0.95 \text{ \AA}$, secondary $C-H = 0.99 \text{ \AA}$ and methyl $C-H = 0.98 \text{ \AA}$, and refined as riding, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ or $1.5U_{\text{eq}}(\text{methyl C})$. The torsion angle about the C—C axis was refined for the methyl group.

For both compounds, data collection: SMART (Siemens, 1995); cell refinement: SMART; data reduction: SAINT (Siemens, 1995); program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL (Sheldrick, 1996); software used to prepare material for publication: SHELXL97.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ1187). Services for accessing these data are described at the back of the journal.

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