

Two isomorphous benzenesulfonamide crystal structures determined by intermolecular C—H···O, C—H··· π and C—H···Cl interactions

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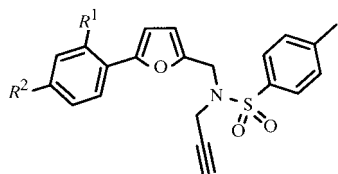
Received 11 May 2001

Accepted 6 June 2001

The title compounds, *N*-[5-(4-chlorophenyl)furan-2-ylmethyl]-4-methyl-*N*-(prop-2-ynyl)benzenesulfonamide, (*Ia*), and *N*-[5-(2-chlorophenyl)furan-2-ylmethyl]-4-methyl-*N*-(prop-2-ynyl)benzenesulfonamide, (*Ib*), both $C_{21}H_{18}ClNO_3S$, have isomorphous crystal structures. The crystal packing is mainly determined by intermolecular C—H···O and C—H··· π interactions. These interactions are very similar in (*Ia*) and (*Ib*). Additional intermolecular C—H···Cl interactions appear less important and are different in (*Ia*) and (*Ib*). The different positions of the Cl atoms result in small variations of the crystal packing of the two compounds.

Comment

The title compounds, (*Ia*) and (*Ib*), were prepared as test substrates for the gold-catalysed conversion of furans bearing terminal alkyne groups to highly substituted biaryl compounds (for background material, see Hashmi *et al.*, 2000).



(*Ia*) $R^1 = H$, $R^2 = Cl$
(*Ib*) $R^1 = Cl$, $R^2 = H$

Compounds (*Ia*) and (*Ib*) have isomorphous crystal structures, despite the different positions of the Cl substituents. The conformations of molecules (*Ia*) and (*Ib*) are very similar; differences of about 2° are found for the torsion angles about the N—C11 and C6—C7 bonds, while a difference of about 5° is found for the torsion angle about the C10—C11 bond. There is a short intramolecular contact distance of 2.65 Å between Cl and H8 in (*Ib*). This distance is considerably shorter than the H···Cl distances of about 2.85 to 3.15 Å generally observed for intermolecular C—H···Cl contacts. The widening of the

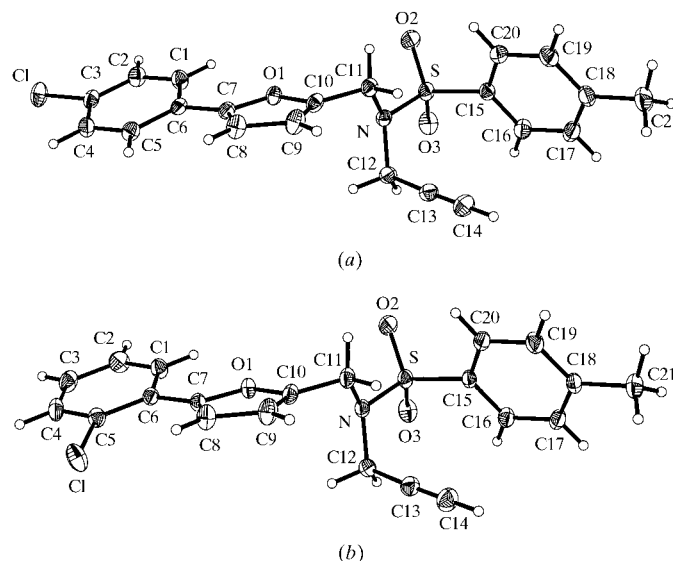


Figure 1
The molecule of (*a*) (*Ia*) and (*b*) (*Ib*). Displacement ellipsoids are drawn at the 50% probability level and H atoms are drawn as small circles of arbitrary radii.

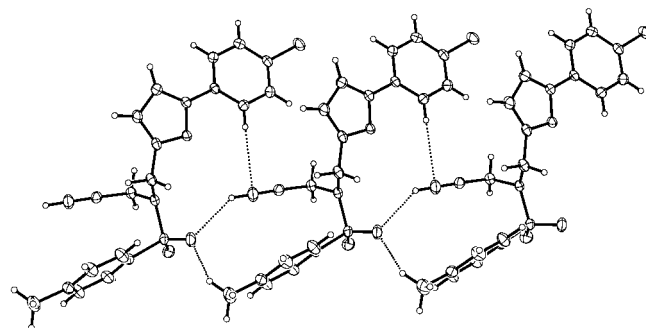


Figure 2
Molecules of (*Ia*) connected in the *a* direction (horizontal direction in figure) into chains by C—H···O and C—H··· π interactions. Similar chains occur in (*Ib*).

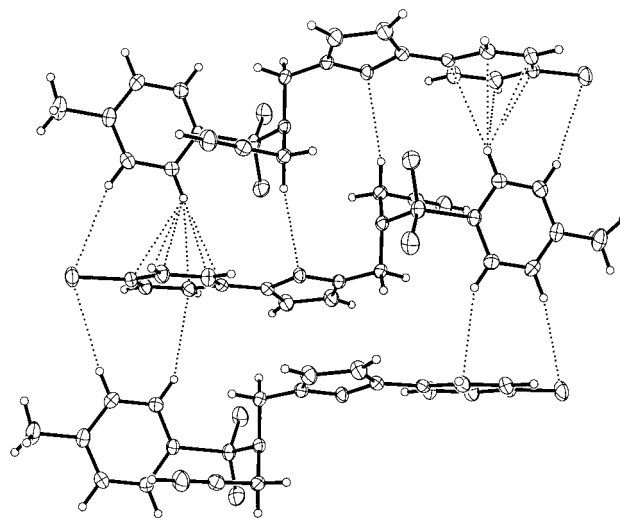


Figure 3
Molecules of (*Ia*) connected in the *b* direction (vertical direction in figure) by C—H··· π , C—H···O and C—H···Cl interactions. Similar chains, but with different C—H···Cl interactions, occur in (*Ib*).

C5—C6—C7 and C6—C7—C8 angles in (*Ib*) by 5 and 3°, respectively, compared with the values in (*Ia*) shows the H8···Cl contact to be probably repulsive. This repulsion is balanced by resonance between the π systems of the furan ring and the adjacent phenyl ring. Atom C6 deviates by 0.047 (3) Å from the furan plane in (*Ib*) and by only 0.015 (3) Å in (*Ia*). Nevertheless, the angle between the plane of the furan ring and the plane of the phenyl group attached to C7 is very similar in both compounds, *i.e.* 13.51 (7)° in (*Ia*) and 13.91 (7)° in (*Ib*).

The N atom is considerably non-planar; the sum of the three valence angles about N is 347.4 (1)° in (*Ia*) and 347.7 (1)° in (*Ib*). The S atom shows a significant displacement from the plane of the phenyl ring to which it is attached: 0.134 (5) Å in (*Ia*) and 0.110 (4) Å in (*Ib*). This out-of-plane deformation may result from intermolecular interactions.

The crystal packing of both compounds shows two distinct features, which are represented in Figs. 2 and 3, respectively. The ethynyl group is involved in a short C—H···O interaction with an H14···O2 distance of 2.41 Å in (*Ia*) and 2.38 Å in (*Ib*) (Tables 1 and 2), resulting in hydrogen-bonded chains of molecules parallel to the *x* axis (Fig. 2). The ethynyl group also acts as an acceptor of a weak C—H··· π contact. The C1—H1··· π_{ethynyl} contact points more closely to the terminal C14 atom than to the centre of the ethynyl group. Similar π interactions involving ethynyl groups have been summarized by Desiraju & Steiner (1999). The molecules are connected parallel to the *y* axis by various intermolecular interactions (Fig. 3), namely two $C_{\text{phenyl}}\text{—H}\cdots\pi_{\text{phenyl}}$ interactions, *viz.* C16—H16···Cg2ⁱⁱⁱ and C20—H20···C5^v (Cg2 represents the centroid of the C1—C6 phenyl ring), a weak C—H···O interaction, *viz.* C12—H12B···O1ⁱⁱⁱ, and C—H···Cl interactions. The latter are different in (*Ia*) and (*Ib*); C17—H17···Clⁱⁱⁱ and C19—H19···Cl^v interactions are observed in (*Ia*), whereas a C20—H20···Cl^v interaction is observed in (*Ib*) (see Tables 1 and 2 for symmetry codes).

Both compounds show a number of additional intermolecular C—H···Cl interactions. A C4—H4···Clⁱⁱ interaction is found in both compounds. Due to the different positions of the Cl atoms, however, the intermolecular C4···Clⁱⁱ vectors differ considerably in (*Ia*) and (*Ib*). Two further C—H···Cl interactions occur in (*Ib*), *i.e.* C19—H19···Cl^{vi} and C21—H21B···Cl^{vi}. Corresponding interactions are missing in (*Ia*). The isomorphism of (*Ia*) and (*Ib*) suggests that the crystal packing of (*Ia*) and (*Ib*) is determined by the intermolecular C—H···O and C—H··· π interactions, rather than by the intermolecular C—H···Cl interactions. The minor importance of the latter interactions is in agreement with the observation of Aullón *et al.* (1998) that the Cl—C group is a very poor hydrogen-bond acceptor. The C—H···Cl contacts observed in (*Ia*) and (*Ib*) are rather long, with H···Cl distances between 2.97 and 3.13 Å. An inspection of 329 randomly selected chlorophenyl-containing structures from the Cambridge Structural Database (Allen & Kennard, 1993) shows that the majority of intermolecular C—H···Cl contacts have H···Cl distances around 3.0 Å. With a few exceptions, there are no intermolecular C—H···Cl contacts with H···Cl

distances shorter than 2.8 Å. These contacts may be characterized as weak electrostatic interactions rather than weak hydrogen bonds. The different positions of the Cl atoms in (*Ia*) and (*Ib*) result in small variations of the crystal packing, leading to significant differences in the lattice constants of (*Ia*) and (*Ib*). The largest difference is observed for the β values.

Experimental

Synthesis of (*Ia*): 5-(4-chlorophenyl)furan-2-carbaldehyde (705 mg, 3.41 mmol), prop-2-ynylamine (188 mg, 3.41 mmol) and MgSO₄ (800 mg, 6.56 mmol) were stirred in dichloromethane. After 24 h, the solvent was removed *in vacuo*, the residue taken up in methanol and NaBH₄ (70.3 mg, 1.86 mmol) added. After 16 h, an aqueous work-up and column chromatography on silica gel (hexane/ethyl acetate, 3:1) provided 351 mg (42%) of [5-(4-chlorophenyl)furan-2-ylmethyl]-prop-2-ynylamine. The latter amine (300 mg, 1.22 mmol), *p*-toluenesulfonyl chloride (233 mg, 1.22 mmol), triethylamine (234 mg, 1.22 mmol) and 4-(*N,N*-dimethylamino)pyridine (7.5 mg, 61.4 μ mol) in dichloromethane were stirred for 16 h. After aqueous work-up and column chromatography on silica gel (hexane/ethyl acetate/dichloromethane, 20:1:1), 176 mg (36%) of (*Ia*) was obtained as colourless crystals with a melting point of 415–417 K. Single crystals were obtained from a hexane/dichloromethane mixture at 277 K. Synthesis of (*Ib*): 5-(2-chlorophenyl)furan-2-carbaldehyde (1.00 g, 4.84 mmol), prop-2-ynylamine (265 mg, 4.84 mmol), MgSO₄ (1.00 g, 83.1 mmol) and NaBH₄ (91.6 mg, 2.42 mmol) were treated as

Table 1

Hydrogen-bonding geometry (Å, °) for (*Ia*).

Cg2 represents the centroid of the C1—C6 phenyl ring.

<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>
C2—H2···O3 ⁱ	0.95	2.64	3.519 (2)	153
C4—H4···Cl ⁱⁱ	0.95	3.01	3.821 (2)	144
C12—H12B···O1 ⁱⁱⁱ	0.99	2.73	3.703 (2)	169
C14—H14···O2 ^{iv}	0.95	2.41	3.227 (3)	144
C17—H17···Cl ⁱⁱⁱ	0.95	2.97	3.900 (2)	165
C19—H19···Cl ^v	0.95	3.05	3.977 (2)	166
C21—H21A···O2 ^{iv}	0.98	2.61	3.423 (2)	140
C16—H16···Cg2 ⁱⁱⁱ	0.95	2.60	3.457 (2)	150
C20—H20···C5 ^v	0.95	2.86	3.733 (2)	154
C1—H1···C14 ^{vi}	0.95	2.87	3.812 (2)	174

Symmetry codes: (i) 2 - *x*, 1 - *y*, 1 - *z*; (ii) 2 - *x*, 2 - *y*, -*z*; (iii) 1 - *x*, 1 - *y*, 1 - *z*; (iv) *x* - 1, *y*, *z*; (v) 1 - *x*, 2 - *y*, 1 - *z*; (vi) 1 + *x*, *y*, *z*.

Table 2

Hydrogen-bonding geometry (Å, °) for (*Ib*).

Cg2 represents the centroid of the C1—C6 phenyl ring.

<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>
C2—H2···O3 ⁱ	0.95	2.74	3.479 (2)	135
C4—H4···Cl ⁱⁱ	0.95	3.13	3.974 (2)	148
C12—H12B···O1 ⁱⁱⁱ	0.99	2.71	3.679 (2)	165
C14—H14···O2 ^{iv}	0.95	2.38	3.242 (2)	150
C20—H20···Cl ^v	0.95	3.07	3.949 (2)	154
C19—H19···Cl ^{vi}	0.95	3.05	3.865 (2)	145
C21—H21A···O2 ^{iv}	0.98	2.80	3.620 (2)	142
C21—H21B···Cl ^{vi}	0.98	3.08	4.016 (2)	159
C16—H16···Cg2 ⁱⁱⁱ	0.95	2.66	3.484 (2)	145
C20—H20···C5 ^v	0.95	2.90	3.777 (2)	154
C1—H1···C14 ⁱⁱⁱ	0.95	2.78	3.694 (2)	162

Symmetry codes: (i) 2 - *x*, 1 - *y*, 1 - *z*; (ii) 2 - *x*, 2 - *y*, -*z*; (iii) 1 - *x*, 1 - *y*, 1 - *z*; (iv) *x* - 1, *y*, *z*; (v) 1 - *x*, 2 - *y*, 1 - *z*; (vi) *x* - 1, *y*, 1 + *z*; (vii) 1 + *x*, *y*, *z*.

described above for (Ia). Column chromatography on silica gel (hexane/ethyl acetate/dichloromethane, 5:1:1) provided [5-(2-chlorophenyl)furan-2-ylmethyl]prop-2-ynylamine (572 mg, 48%). From the latter amine (572 mg, 2.33 mmol), *p*-toluenesulfonyl chloride (533 mg, 2.80 mmol), triethylamine (290 mg, 2.87 mmol) and 4-(*N,N*-dimethylamino)pyridine (14.2 mg, 283 mmol) by the method described for (Ia) after column chromatography (hexane/ethyl acetate/dichloromethane, 20:1:1), 531 mg (57%) of (Ib) were obtained as colourless crystals with a melting point of 404–405 K. Single crystals were obtained from a hexane/dichloromethane mixture at 277 K.

Compound (Ia)

Crystal data

C₂₁H₁₈ClNO₃S
M_r = 399.87
 Triclinic, *P* $\bar{1}$
a = 7.5309 (16) Å
b = 9.5789 (14) Å
c = 13.893 (2) Å
 α = 80.234 (9)°
 β = 82.252 (14)°
 γ = 73.959 (10)°
V = 945.1 (3) Å³
Z = 2
D_x = 1.405 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 139 reflections
 θ = 3–23°
 μ = 0.33 mm⁻¹
T = 140 (2) K
 Plate, colourless
 0.50 × 0.24 × 0.08 mm

Data collection

Siemens SMART CCD diffractometer
 ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 2000)
T_{min} = 0.923, *T_{max}* = 0.974
 19065 measured reflections
 5805 independent reflections
 4256 reflections with *I* > 2σ(*I*)
 R_{int} = 0.037
 θ_{max} = 30.9°
 h = -10 → 10
 k = -13 → 13
 l = -20 → 20
 234 standard reflections
 frequency: 600 min
 intensity decay: none

Refinement

Refinement on *F*²
 $R[F^2 > 2\sigma(F^2)] = 0.047$
 $wR(F^2) = 0.107$
S = 1.03
 5805 reflections
 246 parameters
 H atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.04P)^2 + 0.50P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.51 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\text{min}} = -0.40 \text{ e } \text{Å}^{-3}$
 Extinction correction: SHELXL97
 Extinction coefficient: 0.0049 (13)

Compound (Ib)

Crystal data

C₂₁H₁₈ClNO₃S
M_r = 399.87
 Triclinic, *P* $\bar{1}$
a = 7.6526 (13) Å
b = 9.679 (2) Å
c = 13.6308 (19) Å
 α = 79.910 (13)°
 β = 75.152 (13)°
 γ = 74.435 (12)°
V = 934.0 (3) Å³
Z = 2
D_x = 1.422 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 160 reflections
 θ = 3–23°
 μ = 0.34 mm⁻¹
T = 140 (2) K
 Plate, colourless
 0.50 × 0.16 × 0.12 mm

Data collection

Siemens SMART CCD diffractometer
 ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 2000)
T_{min} = 0.921, *T_{max}* = 0.960
 19124 measured reflections
 6133 independent reflections
 4738 reflections with *I* > 2σ(*I*)
 R_{int} = 0.029
 θ_{max} = 31.5°
 h = -11 → 10
 k = -14 → 13
 l = -18 → 20
 276 standard reflections
 frequency: 600 min
 intensity decay: none

Refinement

Refinement on *F*²
 $R[F^2 > 2\sigma(F^2)] = 0.041$
 $wR(F^2) = 0.094$
S = 1.04
 6133 reflections
 246 parameters
 H atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.03P)^2 + 0.52P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.36 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\text{min}} = -0.47 \text{ e } \text{Å}^{-3}$
 Extinction correction: SHELXL97
 Extinction coefficient: 0.0045 (12)

The H atoms were taken from a difference Fourier synthesis. They were refined with fixed individual displacement parameters [$U(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ and $U(\text{H}) = 1.5U_{\text{eq}}(\text{C}_{\text{methyl}})$] using a riding model with fixed C–H distances of 0.98 Å for methyl, 0.99 Å for secondary, and 0.95 Å for phenyl and alkyne H atoms. The torsion angles about the C–C bond of the methyl groups were refined.

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: XP in SHELXTL (Sheldrick, 1996); software used to prepare material for publication: CIF in SHELXL97.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1466). Services for accessing these data are described at the back of the journal.

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