Table 2. *Selected geometric parameters (Å, °) for (2)*

S1—O1	1.423 (2)	C4—C5	1.380 (3)
S1—O2	1.439 (2)	C4—C9	1.392 (3)
S1—N2	1.637 (2)	C5—C6	1.391 (3)
S1—C4	1.753 (2)	C6—C7	1.382 (3)
N1—N2	1.410 (2)	C7—C8	1.394 (3)
N1—C1	1.278 (3)	C7—C10	1.500 (3)
C1—C2	1.499 (3)	C8—C9	1.375 (3)
C1—C3	1.488 (3)		
O1—S1—O2	119.63 (9)	S1—C4—C5	119.6 (2)
O1—S1—N2	108.0 (1)	S1—C4—C9	119.6 (2)
O1—S1—C4	109.02 (9)	C5—C4—C9	120.8 (2)
O2—S1—N2	103.22 (9)	C4—C5—C6	118.6 (2)
O2—S1—C4	108.33 (9)	C5—C6—C7	121.8 (2)
N2—S1—C4	108.01 (9)	C6—C7—C8	118.4 (2)
N2—N1—C1	115.8 (2)	C6—C7—C10	120.9 (2)
S1—N2—N1	114.1 (1)	C8—C7—C10	120.8 (2)
N1—C1—C2	125.6 (2)	C7—C8—C9	120.9 (2)
N1—C1—C3	116.9 (2)	C4—C9—C8	119.6 (2)
C2—C1—C3	117.5 (2)		
S1—N2—N1—C1	174.4 (2)	O2—S1—C4—C9	35.5 (2)
O1—S1—N2—N1	53.3 (2)	N1—N2—S1—C4	−64.5 (2)
O1—S1—C4—C5	−14.2 (2)	N2—S1—C4—C5	102.9 (2)
O1—S1—C4—C9	167.2 (2)	N2—S1—C4—C9	−75.7 (2)
O2—S1—N2—N1	−179.1 (1)	N2—N1—C1—C2	−1.4 (3)
O2—S1—C4—C5	−145.9 (2)	N2—N1—C1—C3	177.9 (2)

For both compounds, data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1985); program(s) used to solve structures: *SHELXS*86 (Sheldrick, 1985); program(s) used to refine structures: *TEXSAN*; molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *TEXSAN*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SX1030). Services for accessing these data are described at the back of the journal.

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By-products from the Preparation of Acetone Tosylhydrazone: 4,5-Dihydro-3,5,5-trimethyl-1-[(4-methylphenyl)sulfonyl]-1*H*-pyrazole and 1,2-Bis(*p*-toluenesulfono)hydrazide

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Abstract

The title compounds, 4,5-dihydro-3,5,5-trimethyl-1-[(4-methylphenyl)sulfonyl]-1*H*-pyrazole, $C_{13}H_{18}N_2O_2S$, and 1,2-bis(*p*-toluenesulfono)hydrazide, $C_{14}H_{16}N_2O_4S_2$, are both obtained as by-products in the preparation of acetone tosylhydrazone from acetone and toluenesulfonohydrazide. In the pyrazole, one of the S—O bonds is nearly eclipsed with the aryl ring [torsion angle 7.2 (2)°]. In the hydrazide, hydrogen bonding between the N—H groups and the S—O groups of the neighboring glide-related molecule [N···O distances of 2.921 (5) and 2.847 (5) Å] links the molecules into chains extending along the *c* axis.

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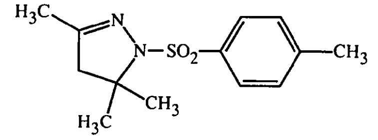
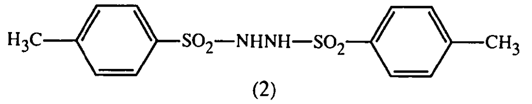
Comment

The title pyrazole compound, (1), was obtained during an attempt to prepare acetone tosylhydrazone by prolonged refluxing of toluenesulfonohydrazide in acetone. Another compound isolated in attempts to prepare this same tosylhydrazone, 1,2-bis(*p*-toluenesulfono)-hydrazide, (2), is reported to be a by-product in the preparation of toluenesulfonohydrazide itself (Bamford & Stevens, 1952). The ostensibly straightforward preparation of one of the simplest tosylhydrazones thus leads to at least four crystalline products. In the previous communication (Ojala *et al.*, 1998), we describe the crystal structures of the two polymorphs of acetone tosylhydrazone we have obtained thus far.



(1)



(2)

*ORTEP*II (Johnson, 1976) views showing the molecular conformations and atom-numbering schemes of the two by-products described here are given in Fig. 1 for (1) and in Fig. 2 for (2). In (1), one of the S—O bonds is nearly eclipsed with the aryl ring [O1—S1—C7—C8 7.2 (2)°]. There are no additional eclipsing interactions involving the S—O bonds and either the aryl or the heterocyclic ring. In (2), there are no eclipsing interactions involving the S—O bonds and either of the two aryl rings. Views of the crystal packing are shown in Fig. 3 for (1) and in Fig. 4 for (2). In contrast to (1), where aryl ring stacking appears to be the major factor in determining the packing, the dominant intermolecular interaction in (2) is a hydrogen bond from each of the N—H groups to a different O atom of the neighboring glide-related molecule, the hydrogen-bonded groups of atoms forming a ten-membered ring (Table 3). Participation in this hydrogen-bonding motif requires that both N—H bonds (as well as the S—O bonds involving the acceptor O atoms) be directed approximately in the **c** direction, which gives the molecules a less than fully extended conformation [S1—N1—N1*A*—S1*A* −121.9 (3)°] and approximate twofold symmetry. The hydrogen bonds link the molecules into chains extending along the *c* axis.

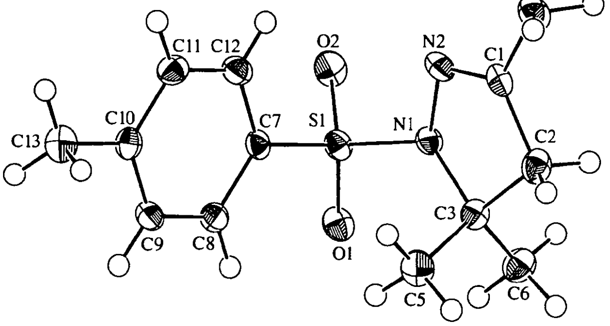


Fig. 1. *ORTEP*II (Johnson, 1976) view of (1) showing the atom numbering. Non-H atoms are represented as 50% probability ellipsoids.

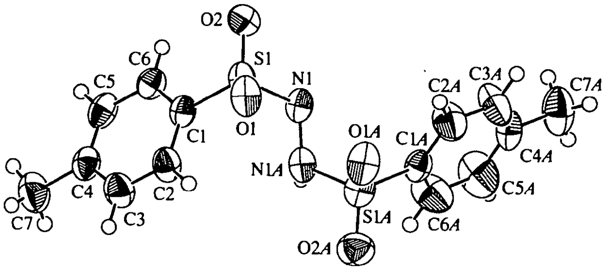


Fig. 2. *ORTEP*II (Johnson, 1976) view of (2) showing the atom numbering. Non-H atoms are represented as 50% probability ellipsoids.

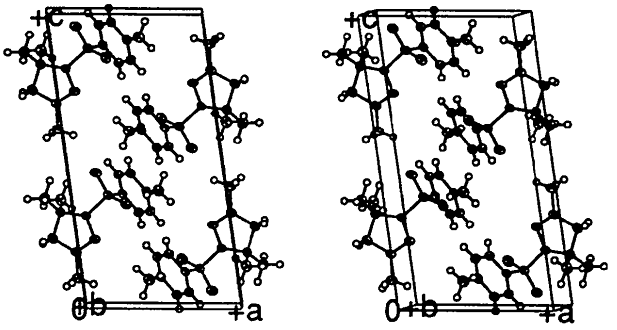


Fig. 3. The molecular packing in (1) viewed along the *b* axis

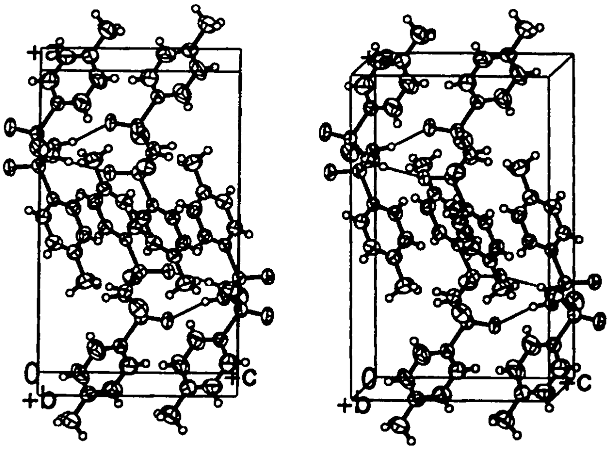


Fig. 4. The molecular packing in (2) viewed along the *b* axis. Hydrogen bonds are indicated by narrow lines.

Experimental

The pyrazole derivative (1) was crystallized from acetone. The melting point (Fisher–Johns melting-point apparatus, uncorrected) was found to be 437–445 K, consistent with the literature value of 435–439 K (Engel *et al.*, 1978). Fine needles of the hydrazide (2) were obtained in addition to crystals of acetone tosylhydrazone during an attempt to prepare acetone tosylhydrazone by slow evaporation of a solution of toluenesulfonohydrazide in acetone at room temperature. The melting point of (2) was found to be 495–503 K (dec.), consistent with the literature value of 493–495 K (Bamford & Stevens, 1952).

Compound (1)

Crystal data

$C_{13}H_{18}N_2O_2S$
$M_r = 266.36$
Monoclinic
$P2_1/c$
$a = 8.544\ (2)$ Å
$b = 9.308\ (1)$ Å
$c = 16.603\ (2)$ Å
$\beta = 98.21\ (1)^\circ$
$V = 1306.9\ (3)$ Å^3
$Z = 4$
$D_x = 1.354$ Mg m^{-3}
D_m not measured
Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å
Cell parameters from 25 reflections
$\theta = 46.4$–49.6°
$\mu = 2.13$ mm^{-1}
$T = 173\ (2)$ K
Prism
$0.36 \times 0.18 \times 0.06$ mm
Colorless

Data collection

AFC-6*S* diffractometer
$\omega/2\theta$ scans
Absorption correction:
  ψ scans (North, Phillips & Mathews, 1968)
  $T_{\min} = 0.654$, $T_{\max} = 0.880$
3612 measured reflections
2626 independent reflections
2466 reflections with $I > 0$
$R_{\rm int} = 0.020$
$\theta_{\max} = 70.07^\circ$
$h = 0 \rightarrow 10;\ -8 \rightarrow 0$
$k = 0 \rightarrow 11;\ -7 \rightarrow 0$
$l = -20 \rightarrow 20;\ -10 \rightarrow 13$
3 standard reflections every 150 reflections intensity decay: none

Refinement

Refinement on F^2
$R(F) = 0.052$
$wR(F^2) = 0.073$
$S = 1.62$
2466 reflections
218 parameters
Only coordinates of H atoms refined
$w = 4F_o^2/\sigma^2(F_o^2)$
$(\Delta/\sigma)_{\max} = 0.006$
$\Delta\rho_{\max} = 0.39$ e Å^{-3}
$\Delta\rho_{\min} = -0.39$ e Å^{-3}
Extinction correction: Zachariasen (1963) type 2 Gaussian isotropic
Extinction coefficient: 0.279×10^{-5}
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. *Selected geometric parameters (Å, °) for (1)*

S1—O1	1.433 (1)	C3—C5	1.523 (3)
S1—O2	1.436 (1)	C3—C6	1.521 (3)
S1—N1	1.650 (1)	C7—C8	1.393 (2)
S1—C7	1.766 (2)	C7—C12	1.387 (2)
N1—N2	1.423 (2)	C8—C9	1.388 (3)
N1—C3	1.521 (2)	C9—C10	1.388 (3)
N2—C1	1.280 (2)	C10—C11	1.398 (3)
C1—C2	1.494 (3)	C10—C13	1.503 (3)
C1—C4	1.489 (3)	C11—C12	1.386 (3)
C2—C3	1.536 (2)		
O1—S1—O2	119.92 (8)	N1—C3—C5	111.8 (1)
O1—S1—N1	105.04 (8)	N1—C3—C6	110.7 (1)
O1—S1—C7	108.59 (8)	C2—C3—C5	110.8 (2)
O2—S1—N1	106.46 (8)	C2—C3—C6	111.6 (2)
O2—S1—C7	106.77 (8)	C5—C3—C6	112.3 (2)
N1—S1—C7	109.82 (8)	S1—C7—C8	119.6 (1)
S1—N1—N2	113.4 (1)	S1—C7—C12	120.1 (1)
S1—N1—C3	125.5 (1)	C8—C7—C12	120.3 (2)
N2—N1—C3	111.2 (1)	C7—C8—C9	119.2 (2)
N1—N2—C1	107.3 (2)	C8—C9—C10	121.4 (2)
N2—C1—C2	114.5 (2)	C9—C10—C11	118.4 (2)
N2—C1—C4	122.4 (2)	C9—C10—C13	120.5 (2)
C2—C1—C4	122.9 (2)	C11—C10—C13	121.1 (2)
C1—C2—C3	103.9 (1)	C10—C11—C12	120.9 (2)
N1—C3—C2	98.9 (1)	C7—C12—C11	119.7 (2)

Compound (2)

Crystal data

$C_{14}H_{16}N_2O_4S_2$
$M_r = 340.41$
Monoclinic
$P2_1/c$
$a = 15.785\ (1)$ Å
$b = 10.7397\ (9)$ Å
$c = 9.492\ (2)$ Å
$\beta = 90.168\ (10)^\circ$
$V = 1609.3\ (3)$ Å^3
$Z = 4$
$D_x = 1.405$ Mg m^{-3}
D_m not measured
Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å
Cell parameters from 18 reflections
$\theta = 22.5$–52.1°
$\mu = 3.17$ mm^{-1}
$T = 296$ K
Needle
$0.48 \times 0.06 \times 0.04$ mm
Colorless

Data collection

AFC-6*S* diffractometer
$\omega/2\theta$ scans
Absorption correction:
  ψ scans (North, Phillips & Mathews, 1968)
  $T_{\min} = 0.776$, $T_{\max} = 0.881$
6696 measured reflections
2970 independent reflections
2970 reflections with $I > 0$
$R_{\rm int} = 0.05$
$\theta_{\max} = 70.09^\circ$
$h = -19 \rightarrow 19;\ -19 \rightarrow 19$
$k = -13 \rightarrow 0;\ 0 \rightarrow 13$
$l = 0 \rightarrow 11;\ -11 \rightarrow 0$
3 standard reflections every 150 reflections intensity decay: -2.52% (correction applied)

Refinement

Refinement on F^2
$R(F) = 0.082$
$wR(F^2) = 0.121$
$S = 2.06$
2970 reflections
199 parameters
H atoms: see below
$w = 4F_o^2/\sigma^2(F_o^2)$
$(\Delta/\sigma)_{\max} = 0.0260$
$\Delta\rho_{\max} = 0.63$ e Å^{-3}
$\Delta\rho_{\min} = -0.50$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 2. *Selected geometric parameters (Å, °) for (2)*

S1*A*—O1*A*	1.428 (3)	C1*A*—C6*A*	1.361 (7)
S1*A*—O2*A*	1.420 (4)	C2*A*—C3*A*	1.372 (7)
S1*A*—N1*A*	1.646 (4)	C2—C3	1.386 (6)
S1*A*—C1*A*	1.762 (4)	C3—C4	1.393 (7)
S1—O1	1.436 (3)	C3*A*—C4*A*	1.345 (8)
S1—O2	1.430 (4)	C4*A*—C5*A*	1.342 (8)
S1—N1	1.667 (4)	C4*A*—C7*A*	1.493 (7)
S1—C1	1.744 (4)	C4—C5	1.379 (7)
N1—N1*A*	1.413 (5)	C4—C7	1.522 (7)
C1—C2	1.390 (7)	C5—C6	1.414 (6)
C1—C6	1.375 (6)	C5*A*—C6*A*	1.391 (8)
C1*A*—C2*A*	1.350 (7)		

O1*A*—S1*A*—O2*A*	121.0 (2)	S1*A*—C1*A*—C2*A*	120.6 (4)
O1*A*—S1*A*—N1*A*	107.3 (2)	S1*A*—C1*A*—C6*A*	119.3 (4)
O1*A*—S1*A*—C1*A*	107.2 (2)	C2*A*—C1*A*—C6*A*	120.1 (5)
O2*A*—S1*A*—N1*A*	104.5 (2)	C1*A*—C2*A*—C3*A*	118.6 (5)
O2*A*—S1*A*—C1*A*	108.9 (2)	C1—C2—C3	119.7 (5)
N1*A*—S1*A*—C1*A*	107.1 (2)	C2—C3—C4	122.0 (5)
O1—S1—O2	120.3 (2)	C2*A*—C3*A*—C4*A*	122.9 (6)
O1—S1—N1	105.7 (2)	C3*A*—C4*A*—C5*A*	118.0 (5)
O1—S1—C1	108.0 (2)	C3*A*—C4*A*—C7*A*	121.8 (6)
O2—S1—N1	103.0 (2)	C5*A*—C4*A*—C7*A*	120.2 (6)
O2—S1—C1	110.8 (2)	C3—C4—C5	116.8 (5)
N1—S1—C1	108.3 (2)	C3—C4—C7	120.6 (5)
S1—N1—N1*A*	112.8 (3)	C5—C4—C7	122.6 (5)
S1*A*—N1*A*—N1	114.4 (3)	C4—C5—C6	122.8 (5)
S1—C1—C2	119.5 (4)	C4*A*—C5*A*—C6*A*	121.0 (6)
S1—C1—C6	120.0 (4)	C1*A*—C6*A*—C5*A*	119.3 (6)
C2—C1—C6	120.4 (4)	C1—C6—C5	118.3 (5)

Table 3. *Hydrogen-bonding geometry (Å, °) for (2)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1N···O1*A*^{i}	0.95	2.03 (1)	2.921 (5)	155 (1)
N1*A*—H1NA···O1^{i}	0.95	1.95 (1)	2.847 (5)	156 (1)

Symmetry code: (i) $x, \frac{3}{2} - y, \frac{1}{2} + z$.

In (1), the positional parameters of the H atoms were refined [C—H range: 0.91 (2)–1.02 (2) Å]. In (2), all H atoms were placed in calculated positions. In light of the near twofold symmetry of the molecules in (2), a precautionary check for higher symmetry was conducted using the program *MISSYM* (Le Page, 1987); none was found.

For both compounds, data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1985); program(s) used to solve structures: *SHELXS*86 (Sheldrick, 1985); program(s) used to refine structures: *TEXSAN*; software used to prepare material for publication: *TEXSAN*.

We thank the Minnesota Medical Foundation and the Graduate School of the University of Minnesota for partial support of this work.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SX1031). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1998). **C54**, 63–66

Cyclopentanone Tosylhydrazone and Cyclohexanone Tosylhydrazone

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Abstract

The crystal structures of 2-cyclopentylidene-1-(*p*-toluenesulfono)hydrazide [cyclopentanone tosylhydrazone, $C_{12}H_{16}N_2O_2S$, (1)] and 2-cyclohexylidene-1-(*p*-toluenesulfono)hydrazide [cyclohexanone tosylhydrazone, $C_{13}H_{18}N_2O_2S$, (2)] are described. In both structures, the conformation of the N—N—S—O linkage is *anti*, with torsion angles of −173.5 (1)° in (1) and 174.9 (1)° in (2), giving the molecules as a whole a folded appearance. In the cyclopentyl structure, the phenyl ring is twisted away from any eclipsing interaction with either S—O bond, but in the cyclohexyl structure, it is eclipsed with the S—O bond [torsion angle 1.4 (2)°]. In both structures, the packing arrangement features centrosymmetrically hydrogen-bonded pairs of molecules, with the *anti* O atom as the acceptor atom [N···O distance of 2.986 (2) Å in (1) and 2.969 (2) Å in (2)].

Comment

As part of our ongoing study of the interactions between proteins and sulfated carbohydrates, we have previously determined the crystal structures of several sugar derivatives prepared by the reaction of monosaccharides with phenylhydrazine or toluenesulfonhydrazide (Ojala & Gleason, 1996; Ojala, Ojala & Gleason, 1997). Depending on the monosaccharide, such a derivative can assume a cyclic form and exist as an *N*-glycoside or assume an acyclic form and exist as a hydrazone. In an effort to identify bands in the infrared spectra of these derivatives which would be readily diagnostic for a particular form, we have also prepared and examined the tosylhydrazones of non-carbohydrate compounds which must yield hydrazones rather than cyclic structures. Our aim is to be able use their infrared spectra for comparison purposes. In a previous report we have described the crystal structures of two polymorphs of one of these true hydrazones, acetone tosylhydrazone (Ojala, Ojala, Pennamon & Gleason, 1998). We describe here the crystal

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