

8-Bromonaphthalene-1-carbaldehyde (4-methylphenylsulfonyl)hydrazone

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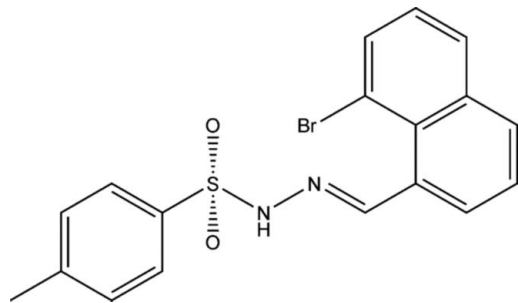
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Key indicators: single-crystal X-ray study; $T = 223$ K; mean $\sigma(\text{C}-\text{C}) = 0.005$ Å; R factor = 0.055; wR factor = 0.151; data-to-parameter ratio = 17.8.

The title compound, $\text{C}_{18}\text{H}_{15}\text{BrN}_2\text{O}_2\text{S}$, was obtained as a by-product during the synthesis of dihalonaphthalenes. The hydrazone and naphthyl units are twisted away from each other by 35 (1°). The bromine substituent and the C center attached to the hydrazone group are twisted out of the plane of the naphthalene system by 6 (1°) and 7 (1°), respectively. Intermolecular hydrogen bonding and π - π stacking hold the molecules together. The average distance between stacked naphthyl ring planes is 3.7 (1) Å.

Related literature

Sulfonylhydrazone (tosyl) derivatives of the general formula $p\text{-CH}_3\text{Ph}-\text{SO}_2-\text{NH}-\text{N}=\text{CH}-R$ have been used to probe the structural features of R -substituents, especially their less stable conformers. Thus, for instance, the conformations of carbocyclic acids and silacyclic ring substituents (Boss *et al.* 1998; Ojala & Gleason, 1998; Ojala *et al.* 1998; Sim 1990; Negron *et al.* 1993) and intramolecular hydrogen bonding (Maas & Hoge, 1980) in tosylates have been studied. For details of the synthesis, see: Bailey *et al.* (1983).



Experimental

Crystal data

$\text{C}_{18}\text{H}_{15}\text{BrN}_2\text{O}_2\text{S}$
 $M_r = 403.29$
Monoclinic, $P2_1/c$
 $a = 12.2464$ (8) Å
 $b = 18.7781$ (12) Å
 $c = 7.4984$ (5) Å
 $\beta = 94.241$ (2°)
 $V = 1719.64$ (19) Å³
 $Z = 4$
Mo $K\alpha$ radiation
 $\mu = 2.52$ mm⁻¹
 $T = 223$ (2) K
 $0.46 \times 0.10 \times 0.08$ mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (SADABS; Sheldrick, 2001)
 $T_{\min} = 0.390$, $T_{\max} = 0.824$
11977 measured reflections
3941 independent reflections
2581 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.033$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.055$
 $wR(F^2) = 0.151$
 $S = 1.06$
3941 reflections
221 parameters
H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\text{max}} = 0.87$ e Å⁻³
 $\Delta\rho_{\text{min}} = -1.08$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{N2}-\text{H2}\cdots\text{O1}^{\text{i}}$	0.86 (4)	2.15 (4)	3.012 (4)	174 (3)

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

Data collection: SMART (Bruker, 1997); cell refinement: SAINT (Bruker, 1997); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997a); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997a); molecular graphics: SHELXTL (Sheldrick, 1997b); software used to prepare material for publication: SHELXTL.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: KP2101).

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supplementary materials

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I. Novak, W. Li and L. J. Harrison

Comment

The crystal structure of (I) is nonplanar with the planes of phenyl and naphthyl moieties inclined at 71° angle (Fig.1). The bromine substituent and C11 center are twisted out of the naphthalene plane by $5(1)^\circ$, presumably due to the steric repulsion between bromine and hydrogen situated at C11. (I) exhibits eclipsed *anti* conformation along N1—N2—S1—O2 linkage with the torsional angle of $177.3(3)^\circ$.

The two S—O bond lengths differ by only 0.007\AA which suggests that there is no delocalization of N2 lone pair into the sulfonyl group; the two moieties being in *gauche* conformation with respect to each other. This is different from the cyclopentanone tosylhydrazone where such delocalization had been proposed (Ojala & Gleason, 1998). The phenyl ring is in the *gauche* conformation at $20(2)^\circ$ versus the SO_2 group.

The crystal packing of (I) is dominated by two kinds of intermolecular interactions: $\text{NH}\cdots\text{O}$ hydrogen bonding and aryl (naphthalene) ring stacking (Fig. 2). The interplanar distance pertinent to $\pi\cdots\pi$ stacking is $3.619(8)\text{\AA}$. The length of hydrogen bonding which is $2.16(4)\text{\AA}$ suggests that $\pi\cdots\pi$ stacking is more important of the two. This is similar to the results obtained for cyclohexanone tosylhydrazone (Ojala & Gleason, 1998) where hydrogen bond length is $2.17(2)\text{\AA}$.

Experimental

The synthesis of (I) was performed according to the procedure reported perviously by Bailey *et al.* (1983). The single crystals were grown from the methanol solution.

Refinement

H atoms were positioned geometrically ($\text{C—H} = 0.94\text{\AA}$) and refined as riding with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. The highest peak is located 0.869\AA from atom Br1 and the deepest hole is located -1.081\AA from atom Br1.

Figures

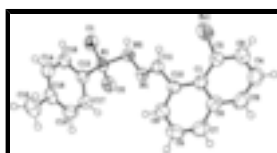


Fig. 1. The molecular structure of (I), with atom labels and 50% probability displacement ellipsoids for non-H atoms.

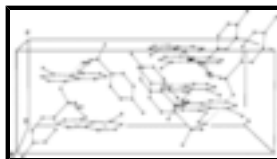


Fig. 2. The packing of (I), viewed down the *a* axis. H atoms have been omitted.

8-Bromonaphthalene-1-carbaldehyde (4-methylphenylsulfonyl)hydrazone

Crystal data

$C_{18}H_{15}BrN_2O_2S$	$F_{000} = 816$
$M_r = 403.29$	$D_x = 1.558 \text{ Mg m}^{-3}$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
Hall symbol: -P2ybc	$\lambda = 0.71073 \text{ \AA}$
$a = 12.2464 (8) \text{ \AA}$	Cell parameters from 2105 reflections
$b = 18.7781 (12) \text{ \AA}$	$\theta = 2.2\text{--}22.9^\circ$
$c = 7.4984 (5) \text{ \AA}$	$\mu = 2.52 \text{ mm}^{-1}$
$\beta = 94.241 (2)^\circ$	$T = 223 (2) \text{ K}$
$V = 1719.64 (19) \text{ \AA}^3$	Needle, colourless
$Z = 4$	$0.46 \times 0.10 \times 0.08 \text{ mm}$

Data collection

Bruker SMART CCD area-detector diffractometer	3941 independent reflections
Radiation source: fine-focus sealed tube	2581 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{\text{int}} = 0.033$
$T = 223(2) \text{ K}$	$\theta_{\text{max}} = 27.5^\circ$
ω scans	$\theta_{\text{min}} = 1.7^\circ$
Absorption correction: multi-scan (SADABS; Sheldrick, 2001)	$h = -15 \rightarrow 14$
$T_{\text{min}} = 0.390$, $T_{\text{max}} = 0.824$	$k = -23 \rightarrow 24$
11977 measured reflections	$l = -9 \rightarrow 9$

Refinement

Refinement on F^2	H atoms treated by a mixture of independent and constrained refinement
Least-squares matrix: full	$w = 1/[\sigma^2(F_o^2) + (0.062P)^2 + 1.172P]$
$R[F^2 > 2\sigma(F^2)] = 0.055$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.151$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.06$	$\Delta\rho_{\text{max}} = 0.87 \text{ e \AA}^{-3}$
3941 reflections	$\Delta\rho_{\text{min}} = -1.08 \text{ e \AA}^{-3}$
221 parameters	Extinction correction: none
Primary atom site location: structure-invariant direct methods	
Secondary atom site location: difference Fourier map	
Hydrogen site location: inferred from neighbouring sites	

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2 , conventional R-factors R are based on F, with F set to zero for negative F^2 . The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Br1	0.40011 (4)	0.08029 (3)	0.73517 (11)	0.1087 (3)
S1	0.07404 (7)	0.31733 (5)	0.78451 (12)	0.0485 (2)
O1	0.1068 (2)	0.34964 (14)	0.9527 (3)	0.0593 (7)
O2	-0.0310 (2)	0.28498 (15)	0.7576 (4)	0.0655 (7)
N1	0.2709 (2)	0.27425 (15)	0.7687 (4)	0.0460 (6)
N2	0.1611 (2)	0.25271 (16)	0.7556 (4)	0.0470 (7)
H2	0.144 (3)	0.226 (2)	0.664 (5)	0.049 (11)*
C1	0.5391 (3)	0.20422 (19)	0.6797 (4)	0.0478 (8)
C2	0.5315 (3)	0.1286 (2)	0.6893 (5)	0.0567 (9)
C3	0.6192 (4)	0.0852 (2)	0.6796 (6)	0.0734 (12)
H3	0.6100	0.0356	0.6864	0.088*
C4	0.7231 (4)	0.1134 (3)	0.6596 (6)	0.0776 (13)
H4	0.7831	0.0828	0.6495	0.093*
C5	0.7369 (3)	0.1844 (3)	0.6547 (6)	0.0736 (12)
H5	0.8074	0.2032	0.6446	0.088*
C6	0.6471 (3)	0.2313 (2)	0.6646 (5)	0.0565 (9)
C7	0.6657 (4)	0.3053 (2)	0.6644 (6)	0.0692 (11)
H7	0.7371	0.3227	0.6559	0.083*
C8	0.5826 (4)	0.3513 (2)	0.6763 (7)	0.0759 (12)
H8	0.5962	0.4006	0.6776	0.091*
C9	0.4761 (3)	0.3262 (2)	0.6868 (6)	0.0623 (10)
H9	0.4190	0.3593	0.6942	0.075*
C10	0.4517 (3)	0.25488 (18)	0.6868 (4)	0.0463 (8)
C11	0.3349 (3)	0.23599 (18)	0.6834 (4)	0.0460 (8)
H11	0.3080	0.1960	0.6188	0.055*
C12	0.0890 (3)	0.38028 (18)	0.6158 (4)	0.0449 (8)
C13	0.0225 (3)	0.37623 (19)	0.4594 (5)	0.0507 (8)
H13	-0.0334	0.3419	0.4466	0.061*
C14	0.0386 (3)	0.42278 (19)	0.3226 (5)	0.0533 (9)
H14	-0.0068	0.4201	0.2161	0.064*
C15	0.1207 (3)	0.47362 (19)	0.3389 (5)	0.0512 (9)
C16	0.1855 (3)	0.4770 (2)	0.4967 (5)	0.0571 (9)
H16	0.2410	0.5115	0.5097	0.069*

supplementary materials

C17	0.1711 (3)	0.43105 (19)	0.6358 (5)	0.0524 (9)
H17	0.2162	0.4340	0.7425	0.063*
C18	0.1399 (4)	0.5224 (2)	0.1843 (6)	0.0698 (11)
H18A	0.1564	0.4942	0.0813	0.105*
H18B	0.2010	0.5538	0.2174	0.105*
H18C	0.0747	0.5506	0.1548	0.105*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0653 (3)	0.0562 (3)	0.2042 (8)	-0.0074 (2)	0.0086 (4)	0.0218 (3)
S1	0.0445 (5)	0.0489 (5)	0.0527 (5)	0.0059 (4)	0.0085 (4)	0.0051 (4)
O1	0.0676 (16)	0.0624 (16)	0.0491 (14)	0.0143 (13)	0.0116 (13)	-0.0017 (12)
O2	0.0465 (14)	0.0670 (17)	0.0839 (19)	-0.0001 (13)	0.0111 (13)	0.0162 (15)
N1	0.0450 (15)	0.0448 (15)	0.0482 (16)	0.0024 (13)	0.0026 (13)	0.0006 (12)
N2	0.0440 (16)	0.0430 (16)	0.0538 (18)	0.0019 (12)	0.0026 (14)	-0.0014 (14)
C1	0.0463 (18)	0.052 (2)	0.0445 (18)	0.0037 (15)	0.0017 (15)	-0.0029 (15)
C2	0.047 (2)	0.054 (2)	0.068 (2)	0.0006 (17)	0.0014 (18)	-0.0038 (18)
C3	0.069 (3)	0.060 (3)	0.090 (3)	0.016 (2)	-0.001 (2)	-0.011 (2)
C4	0.057 (3)	0.088 (3)	0.088 (3)	0.020 (2)	0.006 (2)	-0.011 (3)
C5	0.040 (2)	0.094 (4)	0.086 (3)	0.001 (2)	0.004 (2)	-0.009 (3)
C6	0.047 (2)	0.065 (2)	0.057 (2)	-0.0039 (18)	-0.0004 (17)	-0.0044 (19)
C7	0.054 (2)	0.073 (3)	0.081 (3)	-0.013 (2)	0.003 (2)	0.002 (2)
C8	0.074 (3)	0.053 (2)	0.101 (3)	-0.017 (2)	0.006 (3)	-0.002 (2)
C9	0.060 (2)	0.050 (2)	0.077 (3)	0.0027 (18)	0.007 (2)	-0.0004 (19)
C10	0.0472 (18)	0.0459 (18)	0.0457 (18)	0.0010 (15)	0.0021 (15)	-0.0062 (15)
C11	0.0492 (19)	0.0438 (18)	0.0444 (18)	0.0052 (15)	-0.0008 (15)	0.0000 (15)
C12	0.0434 (17)	0.0424 (18)	0.0493 (19)	0.0066 (14)	0.0064 (15)	0.0023 (15)
C13	0.0452 (18)	0.050 (2)	0.057 (2)	0.0012 (15)	0.0037 (17)	0.0016 (17)
C14	0.054 (2)	0.058 (2)	0.0473 (19)	0.0097 (17)	-0.0017 (17)	-0.0019 (17)
C15	0.056 (2)	0.0447 (19)	0.055 (2)	0.0145 (16)	0.0134 (18)	0.0029 (16)
C16	0.055 (2)	0.048 (2)	0.069 (2)	-0.0052 (17)	0.007 (2)	-0.0007 (18)
C17	0.052 (2)	0.050 (2)	0.055 (2)	-0.0005 (16)	-0.0038 (17)	-0.0019 (16)
C18	0.078 (3)	0.061 (3)	0.072 (3)	0.010 (2)	0.016 (2)	0.016 (2)

Geometric parameters (\AA , $^\circ$)

Br1—C2	1.900 (4)	C8—C9	1.394 (6)
S1—O2	1.423 (3)	C8—H8	0.9400
S1—O1	1.430 (3)	C9—C10	1.372 (5)
S1—N2	1.640 (3)	C9—H9	0.9400
S1—C12	1.751 (3)	C10—C11	1.472 (5)
N1—C11	1.271 (4)	C11—H11	0.9400
N1—N2	1.400 (4)	C12—C13	1.380 (5)
N2—H2	0.86 (4)	C12—C17	1.386 (5)
C1—C2	1.425 (5)	C13—C14	1.373 (5)
C1—C6	1.430 (5)	C13—H13	0.9400
C1—C10	1.436 (5)	C14—C15	1.385 (5)
C2—C3	1.355 (5)	C14—H14	0.9400

C3—C4	1.396 (6)	C15—C16	1.377 (5)
C3—H3	0.9400	C15—C18	1.509 (5)
C4—C5	1.345 (7)	C16—C17	1.374 (5)
C4—H4	0.9400	C16—H16	0.9400
C5—C6	1.416 (6)	C17—H17	0.9400
C5—H5	0.9400	C18—H18A	0.9700
C6—C7	1.408 (6)	C18—H18B	0.9700
C7—C8	1.343 (6)	C18—H18C	0.9700
C7—H7	0.9400		
O2—S1—O1	119.83 (17)	C10—C9—C8	122.3 (4)
O2—S1—N2	104.79 (16)	C10—C9—H9	118.8
O1—S1—N2	106.73 (16)	C8—C9—H9	118.8
O2—S1—C12	109.13 (17)	C9—C10—C1	119.0 (3)
O1—S1—C12	108.24 (16)	C9—C10—C11	116.5 (3)
N2—S1—C12	107.47 (15)	C1—C10—C11	124.4 (3)
C11—N1—N2	115.3 (3)	N1—C11—C10	119.4 (3)
N1—N2—S1	114.0 (2)	N1—C11—H11	120.3
N1—N2—H2	114 (2)	C10—C11—H11	120.3
S1—N2—H2	114 (2)	C13—C12—C17	120.5 (3)
C2—C1—C6	115.1 (3)	C13—C12—S1	119.4 (3)
C2—C1—C10	127.3 (3)	C17—C12—S1	120.0 (3)
C6—C1—C10	117.6 (3)	C14—C13—C12	119.5 (3)
C3—C2—C1	122.8 (4)	C14—C13—H13	120.3
C3—C2—Br1	114.1 (3)	C12—C13—H13	120.3
C1—C2—Br1	123.0 (3)	C13—C14—C15	121.1 (4)
C2—C3—C4	120.6 (4)	C13—C14—H14	119.5
C2—C3—H3	119.7	C15—C14—H14	119.5
C4—C3—H3	119.7	C16—C15—C14	118.4 (3)
C5—C4—C3	119.8 (4)	C16—C15—C18	121.3 (4)
C5—C4—H4	120.1	C14—C15—C18	120.3 (4)
C3—C4—H4	120.1	C17—C16—C15	121.7 (4)
C4—C5—C6	121.1 (4)	C17—C16—H16	119.2
C4—C5—H5	119.5	C15—C16—H16	119.2
C6—C5—H5	119.5	C16—C17—C12	118.9 (4)
C7—C6—C5	119.2 (4)	C16—C17—H17	120.6
C7—C6—C1	120.2 (4)	C12—C17—H17	120.6
C5—C6—C1	120.6 (4)	C15—C18—H18A	109.5
C8—C7—C6	120.7 (4)	C15—C18—H18B	109.5
C8—C7—H7	119.6	H18A—C18—H18B	109.5
C6—C7—H7	119.6	C15—C18—H18C	109.5
C7—C8—C9	120.2 (4)	H18A—C18—H18C	109.5
C7—C8—H8	119.9	H18B—C18—H18C	109.5
C9—C8—H8	119.9		

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$N2-H2\cdots O1^i$	0.86 (4)	2.15 (4)	3.012 (4)	174 (3)

Symmetry codes: (i) $x, -y+1/2, z-1/2$.

Fig. 1

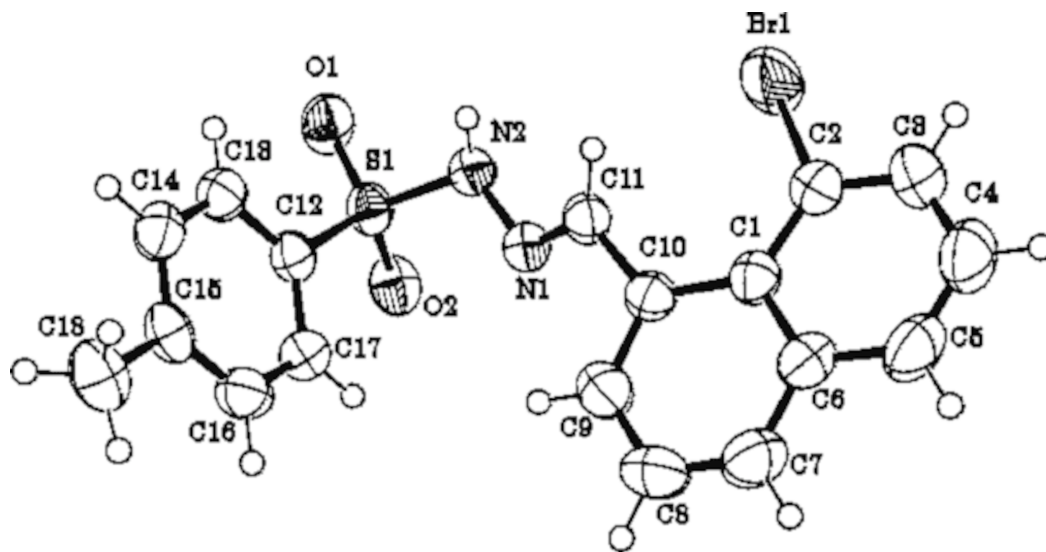


Fig. 2

