

Fluoren-9-one 4-toluenesulfonylhydrazone:
hydrogen-bonded $R_2^2(8)$ dimers are linked
into sheets by π - π stacking interactionsChristopher Glidewell,^{a*} John N. Low,^b Janet M. S. Skakle^b and James L. Wardell^c^aSchool of Chemistry, University of St Andrews, St Andrews, Fife KY16 9ST, Scotland, ^bDepartment of Chemistry, University of Aberdeen, Meston Walk, Old Aberdeen AB24 3UE, Scotland, and ^cInstituto de Química, Departamento de Química Inorgânica, Universidade Federal do Rio de Janeiro, 21945-970 Rio de Janeiro-RJ, Brazil

Correspondence e-mail: cg@st-andrews.ac.uk

Key indicators

Single-crystal X-ray study
 $T = 120$ K
Mean $\sigma(\text{C}-\text{C}) = 0.002$ Å
 R factor = 0.036
 wR factor = 0.090
Data-to-parameter ratio = 16.5For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.Molecules of the title compound, $\text{C}_{20}\text{H}_{16}\text{N}_2\text{O}_2\text{S}$, are linked into centrosymmetric $R_2^2(8)$ dimers by paired $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds [$\text{H}\cdots\text{O}$ 2.14 Å, $\text{N}\cdots\text{O}$ 2.9951 (15) Å and $\text{N}-\text{H}\cdots\text{O}$ 164°]. Two distinct π - π stacking interactions link the dimers into chains along $[10\bar{1}]$ and $[001]$, respectively, hence forming (010) sheets.

Comment

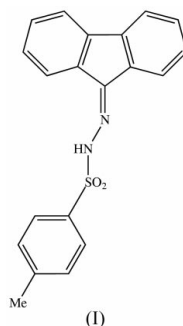
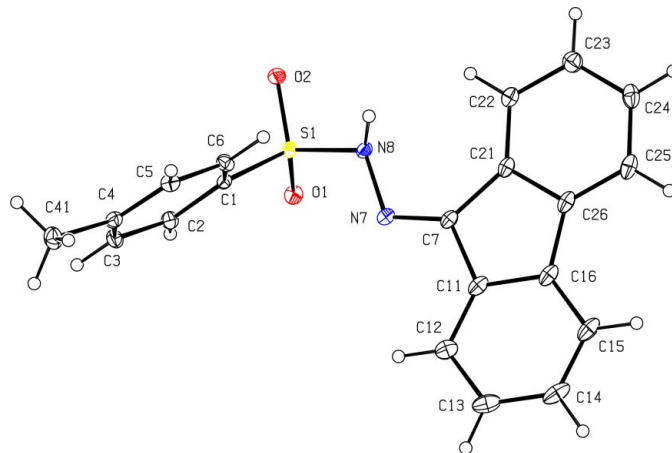
4-Toluenesulfonylhydrazones, $R^1R^2\text{C}=\text{NNHC}_6\text{H}_4\text{Me}$, are not only important derivatives of carbonyl compounds, $R^1R^2\text{C}=\text{O}$, but are also very useful precursors of diazo compounds, $R^1R^2\text{CN}_2$, (Jonczyk & Wlostowska, 1978), as exemplified by the title compound, (I) (Fig. 1).The molecules of (I) are linked by paired $\text{N}-\text{H}\cdots\text{O}=\text{S}$ hydrogen bonds into centrosymmetric dimers, with the reference dimer centred at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ (Fig. 2). The associated $R_2^2(8)$ (Bernstein *et al.*, 1995) motif has been observed previously in a

Figure 1

The molecule of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

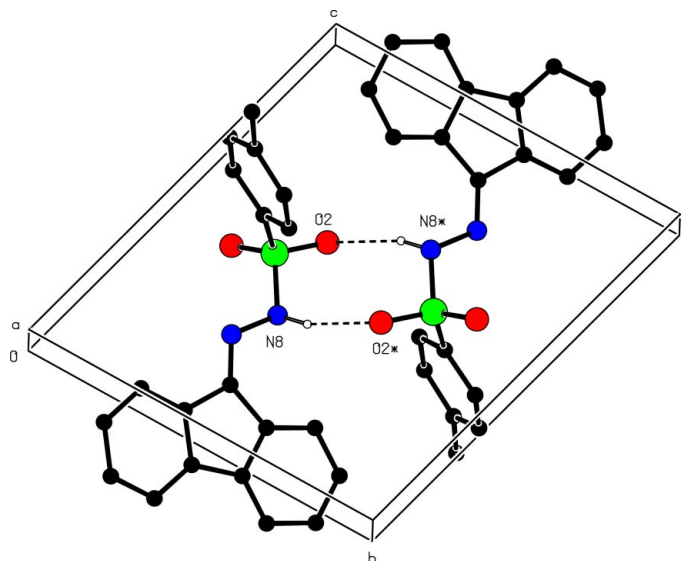


Figure 2
Part of the crystal structure of (I), showing the formation of an $R_2^2(8)$ dimer. For the sake of clarity, H atoms bonded to C atoms have been omitted. The atoms marked with an asterisk (*) are at the symmetry position $(1-x, 1-y, 1-z)$.

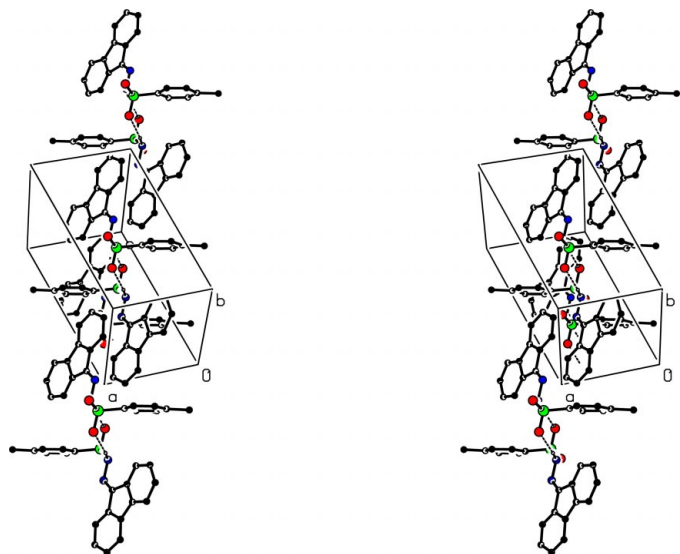


Figure 3
A stereoview of part of the crystal structure of (I), showing the formation of a $[10\bar{1}]$ chain of π -stacked dimers. For the sake of clarity, H atoms bonded to C atoms have been omitted.

number of sulfonamido species (Klug, 1968; Blaschette *et al.*, 1986; Tremayne *et al.*, 1999, 2002; Kelly *et al.*, 2002; Clark *et al.*, 2003). While there are no soft hydrogen bonds of either C—H...O or C—H... π (arene) types present in the structure of (I), the dimeric aggregates are linked into sheets by two distinct π – π stacking interactions, one involving aryl rings and the other involving the fulvene portion of the fluorenone hydrazone.

The C11–C16 aryl rings of the molecules at (x, y, z) and $(2-x, 1-y, -z)$ are parallel, with an interplanar spacing of $3.427(2)$ Å; the centroid separation is $3.725(2)$ Å, corre-

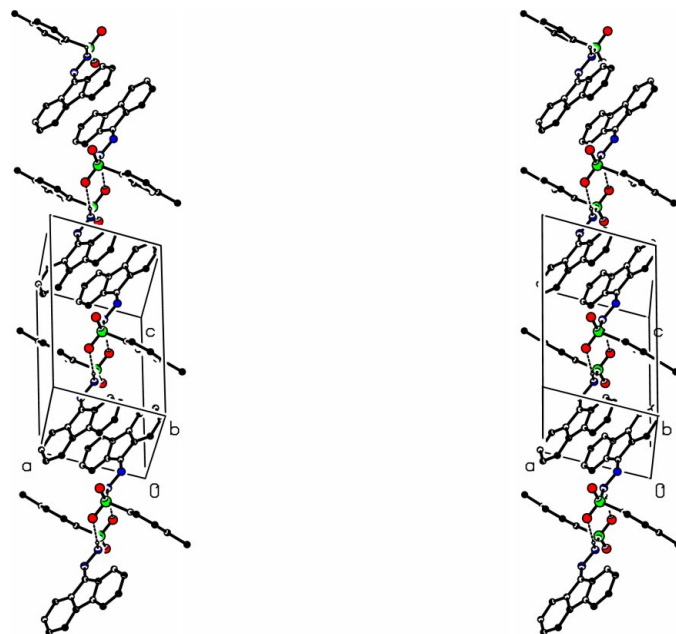


Figure 4
A stereoview of part of the crystal structure of (I), showing the formation of an $[001]$ chain of π -stacked dimers. For the sake of clarity, H atoms bonded to C atoms have been omitted.

sponding to a centroid offset of $1.460(2)$ Å. These two molecules lie in the $R_2^2(8)$ dimers centred at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ and $(\frac{3}{2}, \frac{1}{2}, -\frac{1}{2})$, respectively, so that propagation by inversion of this π – π interaction generates a chain of π -stacked dimers running parallel to the $[10\bar{1}]$ direction (Fig. 3).

The fulvene-type rings (C7/C11/C16/C26/C21) of the molecules at (x, y, z) and $(1-x, 1-y, -z)$, which lie in the $R_2^2(8)$ dimers centred at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ and $(\frac{1}{2}, \frac{1}{2}, -\frac{1}{2})$, respectively, are also parallel; the interplanar spacing is $3.419(2)$ Å and the centroid separation is $3.451(2)$ Å, corresponding to a centroid offset of only $0.473(2)$ Å. Propagation by inversion of the interaction generates a second chain of π -stacked dimers, in this case running parallel to the $[001]$ direction (Fig. 4). The combination of the $[001]$ and $[10\bar{1}]$ chains generates an (010) sheet.

Experimental

The title compound was prepared using the published procedure of Bamford & Stevens (1952) and it was recrystallized from ethanol [m.p. 457–460 K (decomposes); literature m.p. 453–455 K (decomposes)].

Crystal data

$C_{20}H_{16}N_2O_2S$
 $M_r = 348.41$
 Triclinic, $P\bar{1}$
 $a = 7.7487(2)$ Å
 $b = 10.4290(3)$ Å
 $c = 11.2007(3)$ Å
 $\alpha = 71.8482(13)^\circ$
 $\beta = 76.9553(17)^\circ$
 $\gamma = 75.3167(17)^\circ$
 $V = 821.34(4)$ Å³

$Z = 2$
 $D_x = 1.409$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 3744 reflections
 $\theta = 3.1$ – 27.5°
 $\mu = 0.21$ mm⁻¹
 $T = 120(2)$ K
 Block, yellow
 $0.48 \times 0.40 \times 0.26$ mm

Data collection

Nonius KappaCCD area-detector diffractometer
 φ scans, and ω scans with κ offsets
 Absorption correction: multi-scan (SORTAV; Blessing, 1995, 1997)
 $T_{\min} = 0.915$, $T_{\max} = 0.947$
 6955 measured reflections

3744 independent reflections
 3294 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.016$
 $\theta_{\text{max}} = 27.5^\circ$
 $h = -9 \rightarrow 10$
 $k = -13 \rightarrow 13$
 $l = -14 \rightarrow 14$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.036$
 $wR(F^2) = 0.090$
 $S = 1.06$
 3744 reflections
 227 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0355P)^2 + 0.4642P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.33 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.49 \text{ e } \text{\AA}^{-3}$

Table 1

Selected geometric parameters (\AA , $^\circ$).

S1—C1	1.7569 (13)	C7—C11	1.4803 (19)
S1—O1	1.4281 (10)	C7—C21	1.485 (2)
S1—O2	1.4448 (10)	C11—C16	1.403 (2)
S1—N8	1.6375 (11)	C21—C26	1.4140 (19)
N8—N7	1.4038 (16)	C16—C26	1.467 (2)
N7—C7	1.2916 (18)		
C11—C7—N7—N8	178.55 (11)	C7—N7—N8—S1	169.89 (9)

Table 2

Hydrogen-bonding geometry (\AA , $^\circ$).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
N8—H8 \cdots O2 ⁱ	0.88	2.14	2.9951 (15)	164

Symmetry code: (i) $1 - x, 1 - y, 1 - z$.

All H atoms were located using difference maps and subsequently treated as riding atoms, with C—H distances of 0.95 (aromatic) or 0.98 (methyl), and an N—H distance of 0.88 \AA , and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C,N})$, or $1.5U_{\text{eq}}(\text{C})$ for methyl H.

Data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN*; program(s) used to solve structure: *OSCAIL* (McArdle, 2003) and *SHELXS86* (Sheldrick, 1990); program(s) used to refine structure: *OSCAIL* and *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97* and *PRPKAPPA* (Ferguson, 1999).

X-ray data were collected at the EPSRC X-ray Crystallographic Service, University of Southampton, UK; the authors thank the staff for all their help and advice. JNL thanks NCR Self-Service, Dundee, for grants which have provided computing facilities for this work. JLW thanks CNPq and FAPERJ for financial support.

References

- Bamford, W. R. & Stevens, T. S. (1952). *J. Chem. Soc.* pp. 4735–4738.
 Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
 Blaschette, A., Wieland, E., Schomburg, D. & Adelhelm, M. (1986). *Z. Anorg. Allg. Chem.* **533**, 7–717.
 Blessing, R. H. (1995). *Acta Cryst.* **A51**, 33–37.
 Blessing, R. H. (1997). *J. Appl. Cryst.* **30**, 421–426.
 Clark, J. C., McLaughlin, M. L. & Fronczek, F. R. (2003). *Acta Cryst.* **E59**, o2005–o2006.
 Ferguson, G. (1999). *PRPKAPPA*. University of Guelph, Canada.
 Jonczyk, A. & Wlostowska, J. (1978). *Synth. Commun.* **8**, 569–572.
 Kelly, C. J., Skakle, J. M. S., Wardell, J. L., Wardell, S. M. S. V., Low, J. N. & Glidewell, C. (2002). *Acta Cryst.* **B58**, 94–108.
 Klug, H. P. (1968). *Acta Cryst.* **B24**, 792–802.
 McArdle, P. (2003). *OSCAIL for Windows*. Version 10. Crystallography Centre, Chemistry Department, NUI Galway, Ireland.
 Nonius (1997). *KappaCCD Server Software*. Windows 3.11 Version. Nonius BV, Delft, The Netherlands.
 Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
 Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
 Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
 Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.
 Tremayne, M., MacLean, E. J., Tang, C. C. & Glidewell, C. (1999). *Acta Cryst.* **B55**, 1068–1074.
 Tremayne, M., Seaton, C. C. & Glidewell, C. (2002). *Acta Cryst.* **B58**, 823–834.