Electronic Supporting Information†

Polymorphism and Isostructurality in Sulfonylhydrazones

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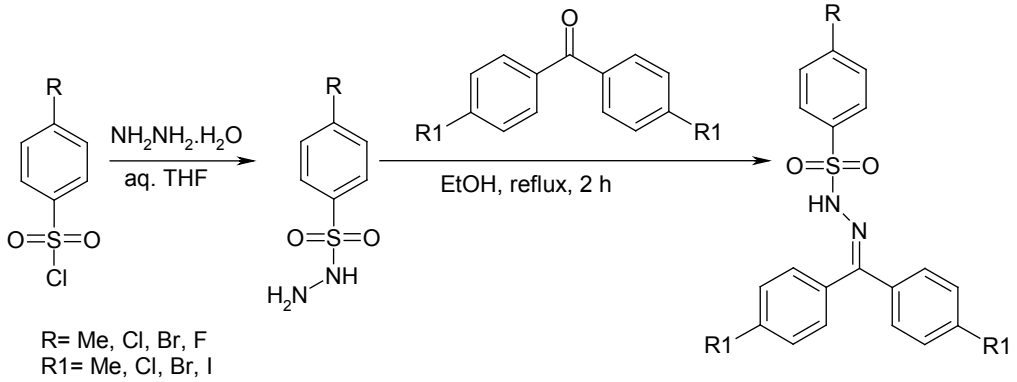
Experimental Section

Sulfonylhydrazones were synthesized using the following procedure (Scheme S1) and purified by recrystallization from ethanol. Melting points were determined in Fischer-Jones apparatus.



Scheme S1 Reaction procedure used to synthesize Sulfonylhydrazones.

CMSH: To a stirred solution of *p*-chlorosulfonyl chloride (5.0 g, 23 mmol) in 25 mL THF was added hydrazine hydrate (2.5 g, 49 mmol) drop wise at 0°C. The reaction was continued for 30 min and the product extracted with ether to give *p*-chlorosulfonyl hydrazine. To a well stirred solution of *p*-chlorosulfonyl hydrazine (500 mg, 2.42 mmol) in 10 mL ethanol was added equimolar amount of 4,4′-dimethyl benzophenone (508.87 mg, 2.42 mmol) and was refluxed for 2 h. Cooling the reaction mixture afforded crystalline bis(*p*-tolyl)ketone *p*-chlorosulfonyl hydrazone as precipitate which was then filtered, washed with cold ethanol and recrystallized from hot ethanol.

^{1}H NMR (500 MHz, DMSO-D6, δ ppm): 2.28 (3H, s), 2.39 (3H, s), 7.10 (4H, d, J 10), 7.32 (2H, d, J 10), 7.71 (4H, d, J 10), 7.91 (2H, d, J 10), 10.46 (1H, s).

FT-IR (KBr, cm^{-1}): 3188, 1585, 1346, 1167.

M. p.: 161-162 °C.

TCSH, **TBSH**, **FMSH** and **MISH** were synthesized using the above procedure.

TCSH:

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.39 (4H, d, J 8), 7.52 (2H, d, J 8), 7.71 (4H, d, J 8), 7.90 (2H, d, J 8).

FT-IR (KBr, cm^{-1}): 3194, 1587, 1352, 1168.

M. p.: 203-205 °C.

TBSH:

^{1}H NMR (500 MHz, DMSO-D6, δ ppm): 7.2 (4H, d, J 10), 7.55 (2H, d, J 10), 7.73 (4H, d, J 10), 7.8 (2H, d, J 10), 10.8 (1H, s).

FT-IR (KBr, cm^{-1}): 3192, 1589, 1346, 1170.

M. p.: 236-239 °C.

FMSH:

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 2.30 (6H, s), 6.98 (4H, d, J 8), 7.21 (2H, d, J 8), 7.41 (4H, d, J 8), 7.63 (2H, d, J 8). The NH proton could not be located in the usual 0-10 ppm range.

FT-IR (KBr, cm^{-1}): 3184, 1585, 1317, 1176.

M. p.: 139-143 °C.

MISH:

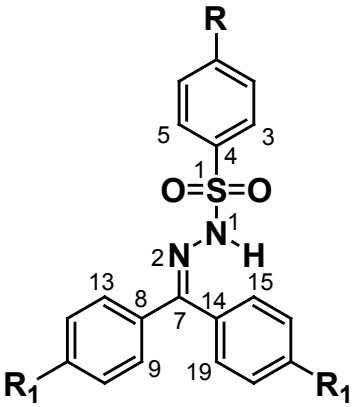
^{1}H NMR (500 MHz, DMSO-D6, δ ppm): 2.39 (3H, s), 7.41 (4H, d, J 10), 7.71 (2H, d, J 10), 7.77 (4H, d, J 10), 7.88 (2H, d, J10), 10.66 (1H, s).

FT-IR (KBr, cm^{-1}): 3186, 1595, 1346, 1167.

M. p.: 249-253 °C.

X-ray Crystallography

X-ray reflections were collected on a Bruker SMART APEXCCD equipped with a graphite monochromator and Mo-K_α fine-focus sealed tube (λ = 0.71073 Å). Data reduction was performed using Bruker SAINT software.[1] Intensities for absorption were corrected using SADABS.[2] Structure solution and refinement were carried out using Bruker SHELXTL.[3] The hydrogen atoms were refined isotropically and the heavy atoms were refined anisotropically. N–H hydrogens were located from difference electron density maps and C–H hydrogens were fixed using HFIX command in SHELXTL. A check of thefinal CIF file using PLATON[4] did not show any missedsymmetry. CIF files of all the crystal structures containrefinement details under _refine_special_details. Packing diagrams were prepared usingX-Seed.[5]



Scheme S2 The labeled atoms of sulfonylhydrazone for dihedral angles measurements. **CMSH**: R =CH_3, R_1 = Cl; **TCSH**: R = R_1 = Cl; **TBSH**: R = R_1 = Br; **FMSH**: R = F, R_1 =

CH_3; **MISH**: R = CH_3, R_1 = I. The labeling of atoms is different depending on the symmetry in the crystal structure.

Table S1 Dihedral angle of sulfonylhydrazones.

Compound	Atom[a]	Dihedral Angle
CMSH-I	C5−C4−S1−N1	64.41(1)
	C3−C4−S1−N1	116.96(1)
	N2−C7−C14−C15	1.68 (1)
	N2−C7−C14−C19	179.73 (1)
	N2−C7−C8−C9	78.12 (1)
	N2−C7−C8−C13	99.07(1)
CMSH-II	C3−C4−S1−N1	61.38 (3)
	C5−C4−S1−N1	120.08 (3)
	N2−C7−C8−C13	5.05 (4)
	N2−C7−C8−C9	173.29 (3)
	N2−C7−C14−C19	75.12 (4)
	N2−C7−C14−C15	100.59 (4)
TCSH	C5−C4−S1−N1	64.42 (1)
	C3−C4−S1−N1	116.28 (1)
	N2−C7−C14−C15	0.05 (2)
	N2−C7−C14−C19	179.64 (1)
	N2−C7−C8−C9	77.03 (2)
	N2−C7−C8−C13	100.26 (1)
TBSH	C3−C4−S1−N1	63.46 (2)
	C5−C4−S1−N1	116.97 (2)
	N2−C7−C8−C13	2.22 (3)
	N2−C7−C8−C9	176.91 (2)
	N2−C7−C14−C19	75.35 (3)
	N2−C7−C14−C15	100.91 (3)

FMSH	C3−C4−S1−N1	61.19 (1)
	C5−C4−S1−N1	120.76 (1)
	N2−C7−C14−C15	4.15 (2)
	N2−C7−C14−C19	177.36 (1)
	N2−C7−C8−C13	74.20 (2)
	N2−C7−C8−C9	102.86 (2)
MISH	C5−C4−S1−N1	54.90 (1)
	C3−C4−S1−N1	124.84 (1)
	N2−C7−C14−C15	6.73 (1)
	N2−C7−C14−C19	171.49 (1)
	N2−C7−C8−C9	72.49 (1)
	N2−C7−C8−C13	106.17 (1)

[a] Labeling of atoms is different depending on the symmetry in the crystal structure.

Table S2 Comparison between crystallographic parameters of CMSH-I and CMSH-II with reported isomorphous aryl sulfonylhydrazone derivatives.

	CMSH-I (in this study)	**TMSH form 1** (reported)[16b]	**MCSH** (reported)[16b]	**CMSH-II** (in this study)	**MBSH** (reported)[16b]
Chemical formula	$C_{21}H_{19}ClN_2O_2S$	$C_{22}H_{22}N_2O_2S$	$C_{20}H_{16}Cl_2N_2O_2S$	$C_{21}H_{19}ClN_2O_2S$	$C_{20}H_{16}Br_2N_2O_2S$
Formula weight	398.89	378.48	419.31	398.89	508.23
Crystal system	Monoclinic	Monoclinic	Monoclinic	Orthorhombic	Orthorhombic
Space group	*C2/c*	*C2/c*	*C2/c*	*Pbca*	*Pbca*
T/K	298(2)	298(2)	100(2)	298(2)	100(2)
a/Å	22.305(2)	22.250(3)	22.4996(17)	11.726(5)	11.4666(7)
b/ Å	12.0112(12)	12.1201(15)	11.4602(7)	15.488(7)	15.5694(9)
c/ Å	15.3336(15)	15.2891(19)	15.4310(9)	22.317(10)	22.2113(13)
α/°	90	90	90	90	90
β/°	100.953(2)	100.538(2)	102.552(2)	90	90
γ/°	90	90	90	90	90
Z	8	8	8	8	8
V/ Å^3	4033.1(7)	4053.5(9)	3883.8(4)	4053(3)	3965.3(4)
D_{calc}/g cm^{-3}	1.314	1.240	1.434	1.307	1.703
μ /mm^{-1}	0.311	0.178	0.460	0.309	4.212
R1[I > 2(I)]	0.0514	0.0501	0.0317	0.0451	0.0241
wR2 (all)	0.1270	0.1307	0.0833	0.1141	0.0589
Goodness-of-fit	1.039	1.037	1.057	1.050	1.031

Ref. 16(b) S. Roy and A. Nangia, *Cryst. Growth Des.*, 2007, **7**, 2047.

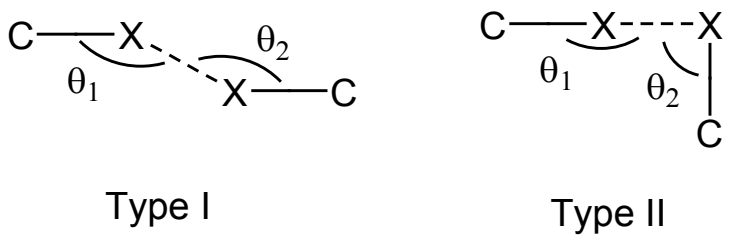
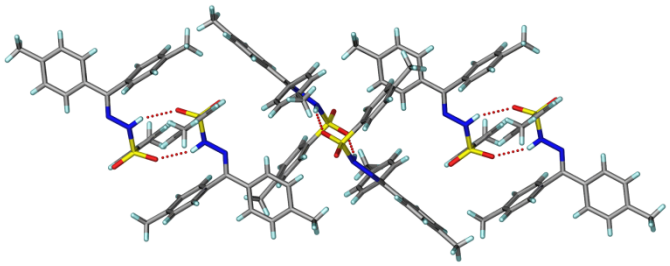
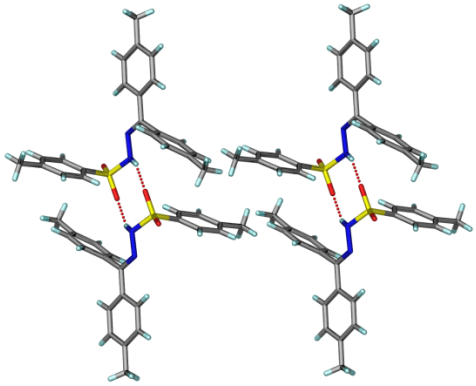


Figure S1 Halogen (X denotes halogen atom) type I (where $\theta_1 = \theta_2$) and type II ($\theta_1 \cong 180°$ and $\theta_2 \cong 90°$) inter-halogen interactions.

TMSH-I

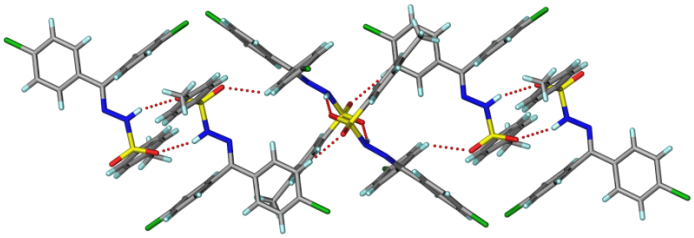


Sulfonamide dimers form 1D tape



Inversion related sulfonamide dimers

MCSH



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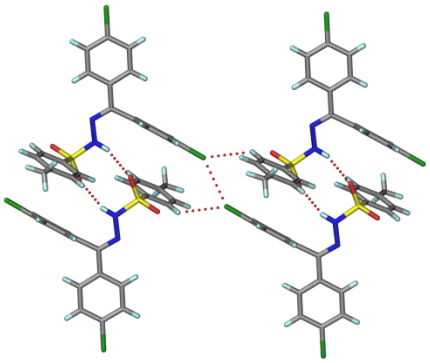
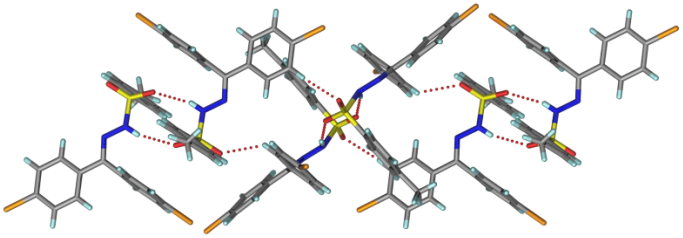
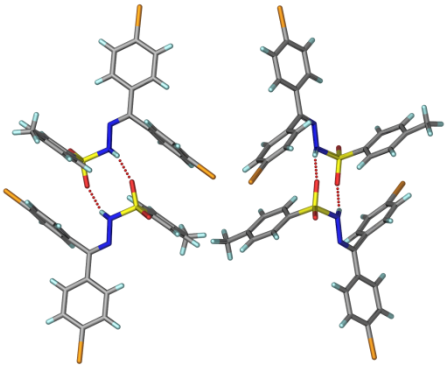


Inversion related sulfonamide dimers

MBSH



Sulfonamide dimers form 1D tape



Glide related Sulfonamide dimers

Figure S2 Sulfonamide dimers and molecular packing in the crystal structures of TMSH-I and MCSH (isomorphous to CMSH-I); and MBSH (isomorphous to CMSH-II).

References

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