Crystal packing of compounds 4a, 8b, 13a, 14a, 5b·(Me₂SO) and 15a·(Me₂SO).

In compound **4a** a H-bond between N(1)-H(1n) and the oxygen atom O(2) of a symmetry related molecule (see Table S1) gives rise to a chain extending along the *x* axis. In the crystal lattice of compound **8b** a sort of trimer is formed due to the hydrogen-bond interactions (weaker[1] than in **4a**) between the H-bond donors N(1) and N(2) and the oxygen atoms of two symmetry related molecules (see Table S1). In addition the hydrogen atom bonded to N(2) further interacts with a symmetry related oxygen atom O(1) (x-1,+y,+z) so that a chain is formed by the repetition of the trimer unit along the *x* axis (Scheme S1). Finally in compounds **13a** and **14a**, in addition to an intermolecular hydrogen bond interaction involving the hydrogen atom bonded to N(1) and a symmetry related oxygen atom (O(1) and O(3) for **13a** and **14a**, respectively) (see Table S1) a $\pi-\pi$ interaction between an aromatic ring [C(7)-C(12) and C(1)-C(6) in compounds **13a** and **14a**, respectively] and its symmetry related image (see Table S2) there exists (Scheme S1).

Finally, in the crystal lattices of compounds **5b·(Me₂SO)** and **15a·(Me₂SO)** the oxygen atom O(1s) of the crystallization Me₂SO (DMSO) molecule acts as a bidentate acceptor of H-bonds with respect to the hydrogen atoms bound to N(1a) and N(1b) (see Table S1). No additional intermolecular interactions are present in the 3D-arrangement of **5b·(Me₂SO)**; while in compound **15a·(Me₂SO)** a dimer is formed due to a $\pi-\pi$ interaction between the symmetry related aromatic rings A and A" (" =-x+1, -y+1, -z+1) (Scheme S1 and Table S2).

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[1]   G. R. Desiraju, T. Steiner, *The weak hydrogen bond*, IUCr Monographs on Crystallography, Oxford Science Publications, 1999.

Table S1 Intermolecular hydrogen bonds in compounds **4a**, **8b**, **13a**, **14a**, **5b·(Me₂SO)** and **15a·(Me₂SO)**

	X-H···Y	X···Y (Å)	H···Y (Å)	X-H···Y (°)
4a	N(1)-H(1n)···O(2)'	2.904(3)	1.99(4)	166(3)
8b	N(2)-H(2n)···O(2)''	3.090(4)	2.36(4)	150(4)
	N(1)-H(1n)···O(1)'''	3.001(5)	2.37(4)	158(4)
	N(2)-H(2n)···O(1)'ᵛ	3.137(4)	2.64(4)	121(3)
13a	N(1)-H(1n)···O(1)ᵛ	2.920(3)	2.22(3)	173(3)
14a	N(1)-H(1n)···O(3)ᵛ'	3.056(7)	2.27(6)	156(6)
5b·(Me₂SO)	N(1a)-H(1na)···O(1s)	2.808(5)	1.97(5)	163(5)
	N(1b)-H(1nb)···O(1s)	2.815(6)	2.03(6)	165(5)
15a·(Me₂SO)	N(1a)···O(1s)*	2.98(1)		
	N(1b)···O(1s)*	3.26(1)		

' = x-1/2,-y+3/2,+z; '' = -x+1,-y+1,-z+2; ''' = -x+2,-y+2,-z+2; 'ᵛ = x-1,+y,+z; ᵛ = x-1/2,-y+1/2,+z

ᵛ' = -x+2,-y+2,-z+2; * = in compound **15a·(Me₂SO)** the hydrogen atoms bonded to N(1a) and (N1b) were not experimentally found.

Table S2 $\pi-\pi$ Interactions in the crystal packing of compounds **13a**, **14a** and **15a·(Me₂SO)**

		Distance between the centroids of the aromatic rings (Å)
13a	C(7)-C(12)/C(7)-C(12)'	4.052(3)
14a	C(1)-C(6)/C(1)-C(6)''	3.785(6)
15a·(Me₂SO)	C1b-C6b/C1b-C6b''	3.66(1)

' = -x, -y, -z+1; '' =-x+1, -y+1, -z+1.

Table S3 Most relevant geometrical parameters (distances (A°), angles (°)) as derived from ab-initio geometry optimizations (HF/6-311+G(d,p) level of theory) of the **4a-I**, **4a-II**, **4a-III** modelled species.[a] Those derived from X-ray diffraction data of **4a** have been also reported for comparative purposes.

	4-I	4-II	4-III	4
r_{N1-S1}/Å	1.635	1.635	1.633	1.616(3)
r_{S1-O1}^{b}/Å	1.423	1.423	1.422	1.426(2)
r_{S1-O2}/Å	1.415	1.415	1.419	1.434(2)
r_{N1-H}/Å	0.997	0.997	1.000	0.94(4)
r_{S1-C1}/Å	1.766	1.776	1.783	1.754(3)
r_{N1-C7}/Å	1.417	1.417	1.425	1.420(4)
$\Sigma(<N1)^{c}$/°	354.4	354.4	345.7	359(2)
τ_1^{d}/°	-58.9	-59.0	-55.8	-62.1(3)
τ_2^{e}/°	-121.5	-121.5	-178.8	-122.1(3)
τ_3^{f}/°	12.5/59.9	12.6/59.9	55.7/2.3	16.3(1)/ 58.1(1)
$\Sigma(internal<)^{g}$/°	839.4	839.4	832.8	839.4(2)
$<(A/B)^{h}$/°	48.9	48.9	54.5	45.5(1)
ΔC_s^{i}/°	42.0	42.0	46.3	50.0
Bow^{i}/°	54.5	54.5	55.2	50.6(3)
Stern^{i}/°	30.7	30.7	25.1	40.4(1)

[a] Refer to Figure 3 in the manuscript for molecular models and atom labelling; [b] O1 Is the sulfone oxygen atom closest to the N-bound hydrogen; [c] Summation of the bond angles about the sulfonamide nitrogen atom N1; [d] [C7–N1–S1–C1 Dihedral angle; [e] C6–C1–S1–N1 Dihedral angle; [f] Angles between the plane through N1,S1,Y and the least-squares planes through rings A and B, respectively; [g] Sum of the internal bond angles in the seven-membered ring, which should be about 808° on the basis of the VSEPR rule. [h] Interplanar angle between the aromatic rings. [i] See refs. 23 and 24 in the manuscript for the parameter definitions.

Table S4 Most relevant geometrical parameters (distances (Å), angles (°)) as derived from ab-initio geometry optimizations (HF/6-311+G(d,p) level of theory) of the **8a-I**, **8a-II**, **8a-III** modelled species.[a] Those derived from X-ray diffraction data of **8b** have been also reported for comparative purposes.

	8a-I	8a-II	8a-III	8b
$r_{N1\text{-}S1}$/Å	1.630	1.643	1.630	1.596(4)
$r_{S1\text{-}O1}$[b]/Å	1.423	1.424	1.423	1.435(3)
$r_{S1\text{-}O2}$/Å	1.420	1.423	1.420	1.426(3)
$r_{N1\text{-}H}$/Å	1.000	0.998	1.000	0.67(4)
$r_{S1\text{-}C1}$/Å	1.779	1.761	1.779	1.750(4)
$r_{N1\text{-}C7}$/Å	1.426	1.461	1.426	1.412(5)
$\Sigma(<N1)$[c]/°	347.0	347.0	346.6	359(3)
τ_1[d]/°	-65.0	-84.0	-64.8	-81.3(3)
τ_2[e]/°	-168.1	-145.5	-168.3	-132.0(3)
τ_3[f]/°	55.3/13.8	54.3/38.6	55.3/13.6	39.0(1) / 49.1(2)
$\Sigma(internal<)$[g]/°	841.7	847.7	842.6	857.6(3)
$<(A/B)$[h]/°	44.1	28.6	44.3	21.5(1)
ΔC_s[i]/°	53.6	68.0	53.4	65.7
Bow[i]/°	45.9	23.5	46.1	9.7(4)
Stern[i]/°	19.6	9.1	19.8	28.7(2)

[a] Refer to Figure 3 in the manuscript for molecular models and atom labelling; [b] O1 Is the sulfone oxygen atom closest to the N-bound hydrogen; [c] Summation of the bond angles about the sulfonamide nitrogen atom N1; [d] [C7–N1–S1–C1 Dihedral angle; [e] C6–C1–S1–N1 Dihedral angle; [f] Angles between the plane through N1,S1,Y and the least-squares planes through rings A and B, respectively; [g] Sum of the internal bond angles in the seven-membered ring, which should be about 808° on the basis of the VSEPR rule. [h] Interplanar angle between the aromatic rings. [i] See refs. 23 and 24 in the manuscript for the parameter definitions.

Table S5 Most relevant geometrical parameters (distances (Å), angles (°)) as derived from ab-initio geometry optimizations (HF/6-311+G(d,p) level of theory) of the **13a-I**, **13a-II**, **13a-III** modelled species.[a] Those derived from X-ray diffraction data of **13a** have been also reported for comparative purposes.
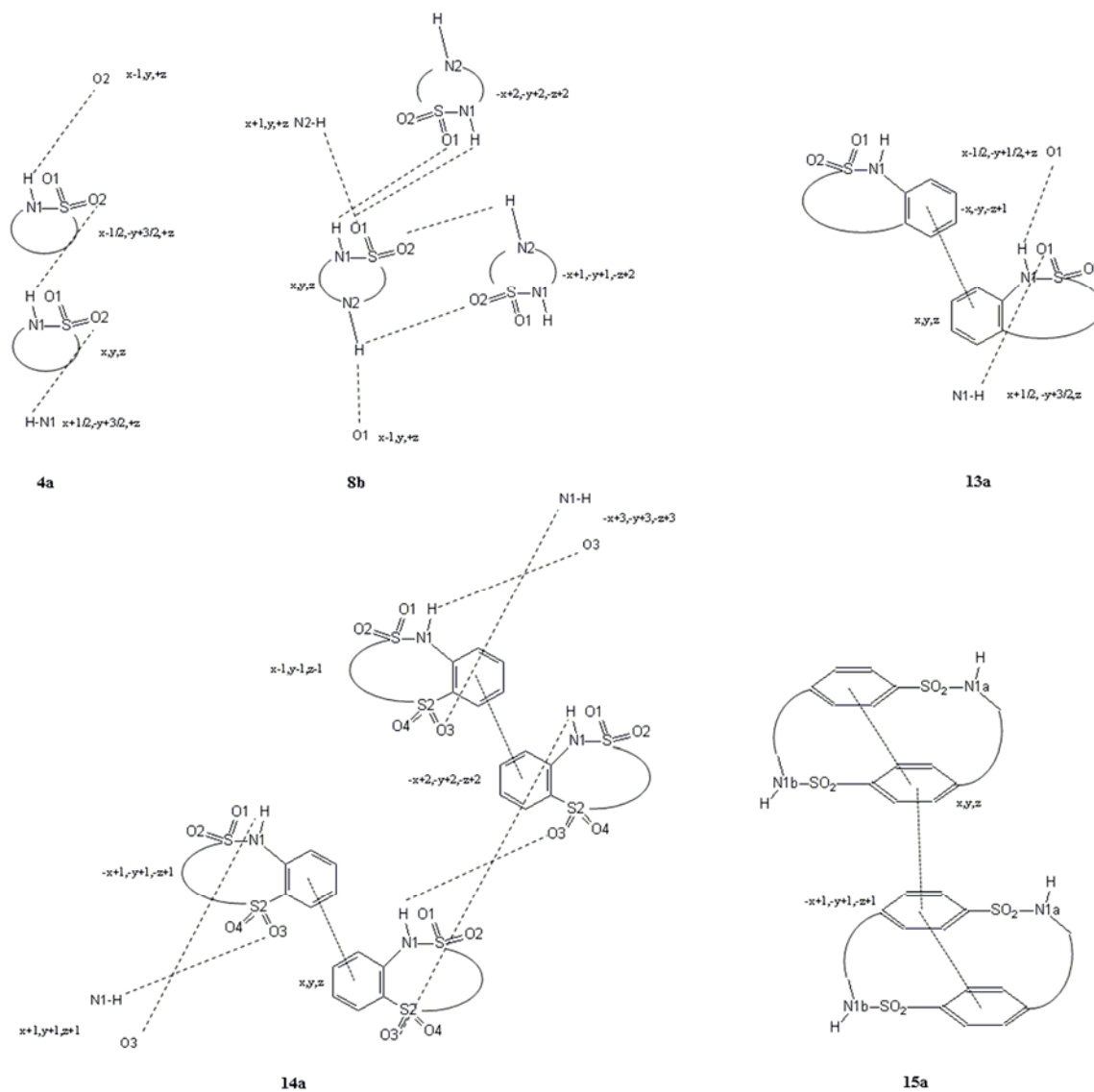
	13a-I	13a-II	13a-III	13a
r_{N1-S1}/Å	1.634	1.634	1.632	1.610(3)
r_{S1-O1}[b]/Å	1.424	1.424	1.422	1.432(2)
r_{S1-O2}/Å	1.415	1.415	1.420	1.428(2)
r_{N1-H}/Å	0.995	0.995	1.000	0.70(3)
r_{S1-C1}/Å	1.773	1.773	1.792	1.769(2)
r_{N1-C7}/Å	1.408	1.408	1.425	1.434(4)
$\Sigma(<N1)$[c]/°	359.3	359.4	346.0	346(2)
τ_1[d]/°	-74.6	-74.1	-53.6	-69.4(2)
τ_2[e]/°	-117.0	-116.9	167.7	-173.0(2)
τ_3[f]/°	18.4/65.0	17.9/65.0	56.9/11.7	58.7(1)/ 7.4(1)
$\Sigma(internal<)$[g]/°	837.5	837.5	822.8	832.1(2)
$<(A/B)$[h]/°	47.9	48.3	68.2	51.6(1)
ΔC_s[i]/°	59.3	59.0	43.7	50.6
Bow[i]/°	42.5	42.7	49.2	43.2(1)
Stern[i]/°	31.9	32.1	33.5	12.1(1)

[a] Refer to Figure 3 in the manuscript for molecular models and atom labelling; [b] O1 Is the sulfone oxygen atom closest to the N-bound hydrogen; [c] Summation of the bond angles about the sulfonamide nitrogen atom N1; [d] [C7–N1–S1–C1 Dihedral angle; [e] C6–C1–S1–N1 Dihedral angle; [f] Angles between the plane through N1,S1,Y and the least-squares planes through rings A and B, respectively; [g] Sum of the internal bond angles in the seven-membered ring, which should be about 808° on the basis of the VSEPR rule. [h] Interplanar angle between the aromatic rings. [i] See refs. 23 and 24 in the manuscript for the parameter definitions.

Table S6 Most relevant geometrical parameters (distances (A˚), angles (°)) as derived from ab-initio geometry optimizations (HF/6-311+G(d,p) level of theory) of the **14a-I**, **14a-II**, **14a-III** modelled species.[a] Those derived from X-ray diffraction data of **14a** have been also reported for comparative purposes.

	14a-I	**14a-II**	**14a-III**	**14a**
r_{N1-S1}/Å	1.638	1.638	1.627	1.594(7)
$r_{S1-O1}{}^b$/Å	1.421	1.420	1.417	1.424(4)
r_{S1-O2}/Å	1.412	1.412	1.419	1.446(6)
r_{N1-H}/Å	0.996	0.996	1.001	0.84(7)
r_{S1-C1}/Å	1.774	1.774	1.798	1.773(8)
r_{N1-C7}/Å	1.406	1.406	1.426	1.463(9)
$\Sigma(<N1)^c$/°	355.2	355.2	347.5	348(2)
$\tau_1{}^d$/°	-86.6	-86.7	-60.7	-62.9(6)
$\tau_2{}^e$/°	-120.4	-120.5	174.8	178.0(5)
$\tau_3{}^f$/°	31.5/65.5	31.6/65.5	25.8/38.4	59.1(3)/ 2.9(2)
$\Sigma(internal<)^g$ /°	840.1	840.0	825.8	827.7(3)
$<(A/B)^h$/°	39.9	39.8	64.1	60.5(2)
$\Delta C_s{}^i$/°	45.6	45.6	50.3	53.4
Bow[i]/°	32.3	32.2	48.8	45.8(3)
Stern[i]/°	27.4	27.4	28.4	20.4(4)

[a] Refer to Figure 3 in the manuscript for molecular models and atom labelling; [b] O1 Is the sulfone oxygen atom closest to the N-bound hydrogen; [c] Summation of the bond angles about the sulfonamide nitrogen atom N1; [d] [C7–N1–S1–C1 Dihedral angle; [e] C6–C1–S1–N1 Dihedral angle; [f] Angles between the plane through N1,S1,Y and the least-squares planes through rings A and B, respectively; [g] Sum of the internal bond angles in the seven-membered ring, which should be about 808° on the basis of the VSEPR rule. [h] Interplanar angle between the aromatic rings. [i] See refs. 23 and 24 in the manuscript for the parameter definitions.

Scheme S1 Schematic representation of the intermolecular interactions in **4a**, **8b**, **13a**, **14a** and

15a·(Me₂SO)