Supporting information for:

The Effect of a Rigid Sulfonamide Bond on Molecular Folding: A Case Study

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1 Crystallography

1.1 Crystal data and data collection parameters

Table S1. Crystal data and data collection parameters of isomorphous solvates to solvates **2I** and **2II**.

	MeCN solvate[a] (solvate **2IB**)	THF solvate[b] (Solvate **2IIB**)
Formula	$C_{32}H_{26}N_4O_6S_2$•$2C_2H_3N$	$C_{32}H_{26}N_4O_6S_2$
M / gmol^{-1}	708.80	626.72
Crystal system	monoclinic	monoclinic
Space group	*C*2/*c*	$P2_1/c$
a / Å	25.153(2)	16.3178(6)
b / Å	7.0022(5)	22.6663(11)
c / Å	20.328(2)	11.7012(8)
β / °	106.073(3)	94.529(2)
V / Å^3	3440.4(4)	4314.3(4)
Z	4	4
ρ_{calc} / g cm^{-3}	1.368	0.965
Meas. reflns	3108	10622
Indep. reflns	2181	6661
R_{int}	0.0915	0.0871
R_1 [$I > 2\sigma(I)$]	0.0703	0.0712
wR_2 [$I > 2\sigma(I)$]	0.1280	0.2572
GooF	1.023	1.026

[a] Low data completeness 74.4%, [b] Low data completeness 86.9%, severely disordered THF electron density masked with Olex^2.[1]

1.2 MeCN solvate of the sulfonamide 2

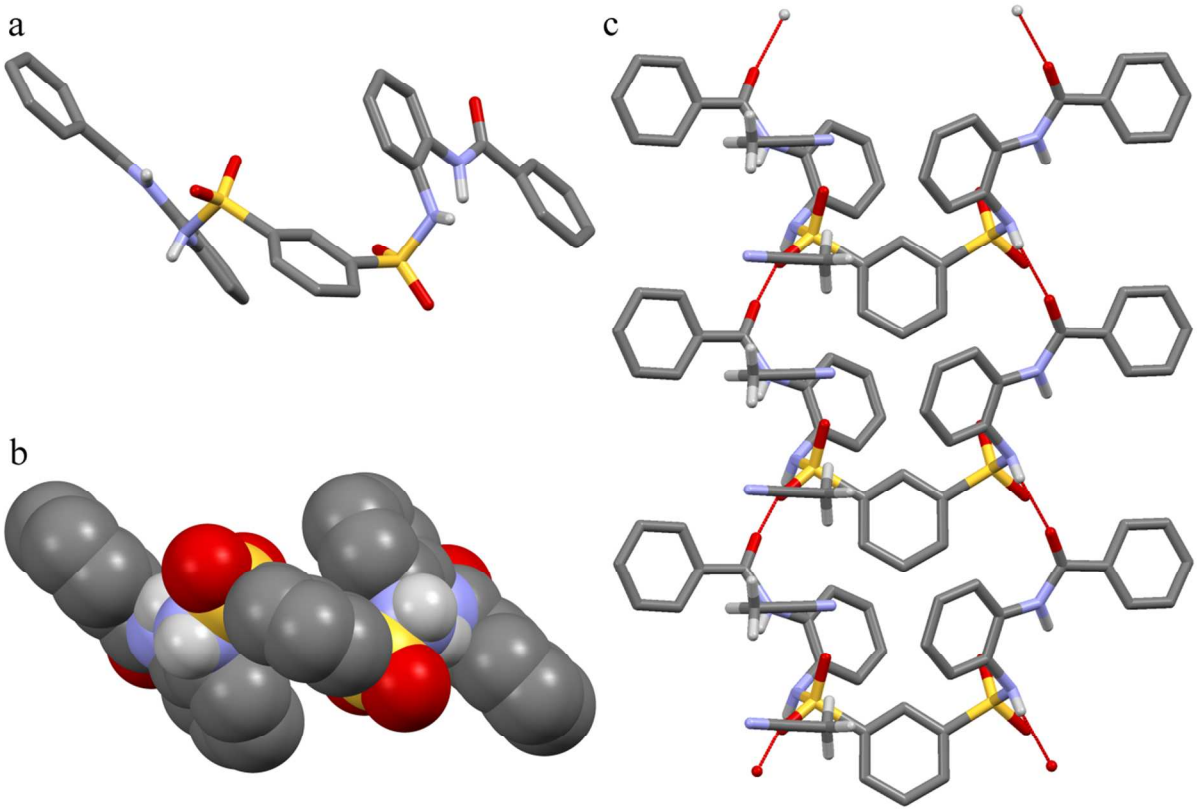


Figure S1. MeCN solvate of the sulfonyl foldamer **2** in a) the unfolded molecular conformation, b) spacefill depiction of the conformation and c) the crystal packing structure with intermolecular hydrogen bonds and MeCN molecules packed inside the solvent channel. Non-amide/sulfonamide hydrogen atoms have been removed for clarity.

1.3 THF solvate of the sulfonamide 2

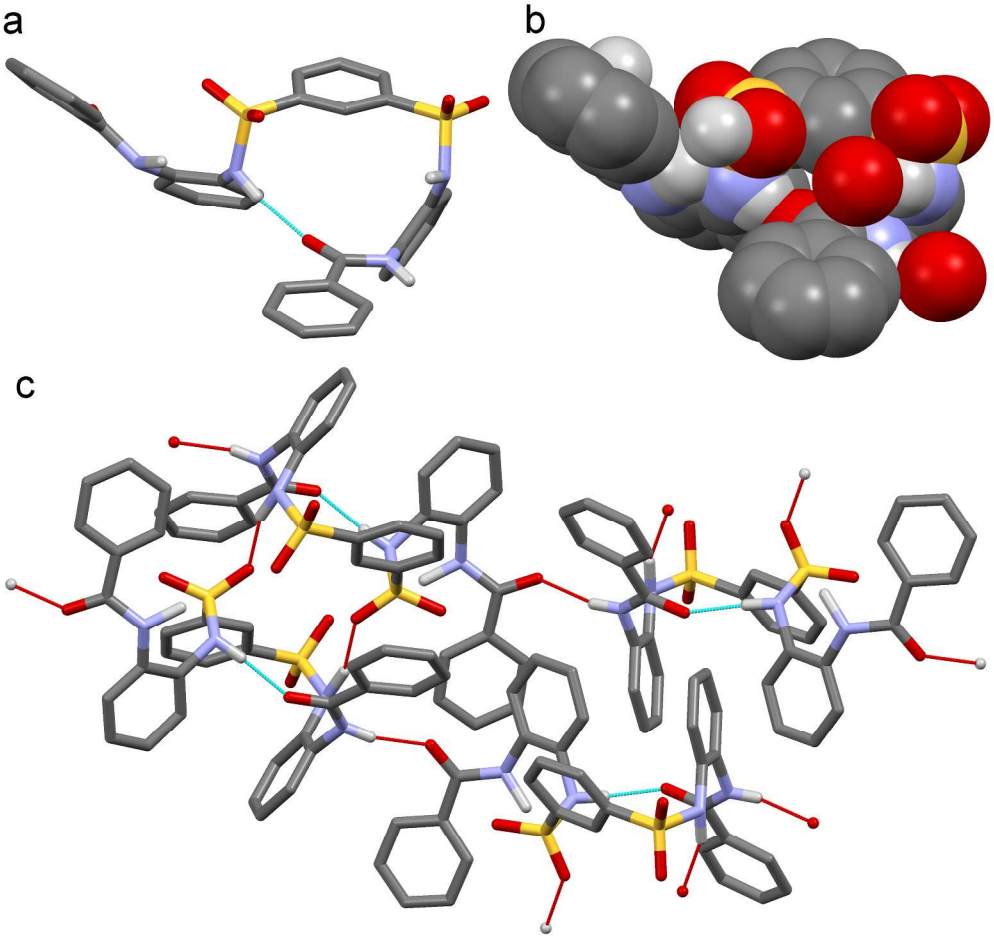


Figure S2. THF solvate of the sulfonyl foldamer **2** in a) a folded molecular conformation showing the intramolecular hydrogen bond, b) spacefill depiction of the conformation and c) the crystal packing structure with intermolecular hydrogen bonds. Non-amide/sulfonamide hydrogen atoms have been removed for clarity. Severely disordered THF solvent molecules were masked by Olex[2].[1]

2 Notes on the Crystallographic Data

EtOAc solvate 2I was crystallized by diffusion from EtOAc solvent and hexane antisolvent as colorless plate crystals. Severely disordered solvent molecules were removed using the SQUEEZE routine of the PLATON program, which caused voids in the structure (197 $Å^3$).[2] The asymmetric unit contains only one half of the sulfonamide **2** molecule.

DCE solvate 2II was crystallized from DCE by slow evaporation as colorless block crystals. DCE molecule is disordered over two positions. The bond lengths between the chloride and carbon atoms were restrained using DFIX (Cl–C 1.79 Å and C–C 1.54 Å).

MeCN solvate 2IB was crystallized from MeCN by slow evaporation as colorless plate crystals. Low data completeness (74.4 %) is caused by poor crystal quality. The asymmetric unit contains only one half of the sulfonamide molecule **2** and one MeCN molecule.

THF solvate 2IIB was crystallized from THF by slow evaporation as colorless plate crystals. Low data completeness (86.9 %) is caused by poor crystal quality. Severely disordered solvent molecules were masked by Olex[2] leaving very large solvent accessible voids in the structure.[1] This also lowers the calculated density of the crystal below 1 g cm^{-3}. The data quality is very poor at resolution over 0.95 Å. The high wR_2 factor and the large number of $(I_{obs}–I_{calc})/\Sigma w > 10$ outliers are also most likely caused by the poor crystal quality.

3 Hydrogen Bonding Parameters

Table S2. Hydrogen bonding parameters for the crystal structures.

Solvate 2I

Intramolecular			Intermolecular		
Bond	**d(D…A)**	**<(DHA)**	**Bond**	**d(D…A)**	**<(DHA)**
-	-		N2–H2N…O1	2.793(3)	172(3)

Solvate 2IB

Intramolecular			Intermolecular		
Bond	**d(D…A)**	**<(DHA)**	**Bond**	**d(D…A)**	**<(DHA)**
N3–H3N…O1	2.774(3)	158(3)	N1–H1N…O6	2.833(3)	159(3)
			N2–H2N…O4	3.080(3)	158(3)

Solvate 2II

Intramolecular			Intermolecular		
Bond	**d(D…A)**	**<(DHA)**	**Bond**	**d(D…A)**	**<(DHA)**
-	-		N1–H1N…O1	2.796(7)	166(6)

Solvate 2IIB

Intramolecular			Intermolecular		
Bond	**d(D…A)**	**<(DHA)**	**Bond**	**d(D…A)**	**<(DHA)**
N3–H3N…O1	2.754(10)	171(13)	N1–H1N…O6	2.856(11)	150(10)
			N2–H2N…O4	3.207(11)	159(8)

Table S3. Hydrogen bonding parameters for the optimized structures.

2I

Intramolecular			Intermolecular		
Bond	**d(D…A)**	**<(DHA)**	**Bond**	**d(D…A)**	**<(DHA)**
N–H…O	2.869	154.12	-	-	-
N–H…O	2.869	154.11			

2I dimeric pair (heading h, tailing t)

Intramolecular			Intermolecular		
Bond	**d(D…A)**	**<(DHA)**	**Bond**	**d(D…A)**	**<(DHA)**
N–H…O (h)	2.809	154.25	N–H…O	2.869	168.72
N–H…O (h)	2.869	153.51	N–H…O	2.944	147.98

2II

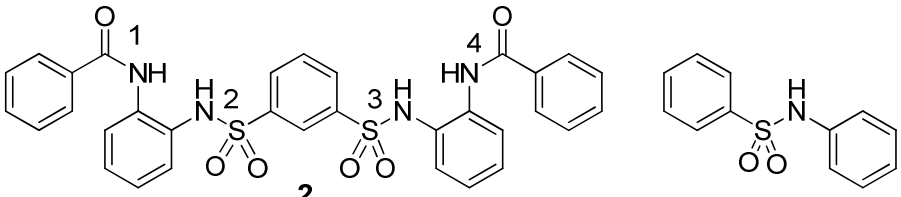
Intramolecular			Intermolecular		
Bond	**d(D…A)**	**<(DHA)**	**Bond**	**d(D…A)**	**<(DHA)**
N–H…O	2.842	155.39			

2III

Intramolecular			Intermolecular		
Bond	**d(D…A)**	**<(DHA)**	**Bond**	**d(D…A)**	**<(DHA)**
N–H…O	3.066	157.64	-	-	-
N–H…O	2.714	141.43			
N–H…O	2.714	141.43			
N–H…O	3.066	157.64			

4 Sulfonamide and Amide Torsion Angles

Scheme S1. Amide/sulfonamide bond numbering in compounds **2** and **3**, and structural fragments used in the CSD searches (right).[3]



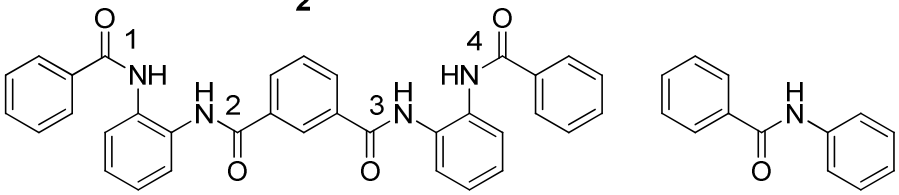


Table S4. Amide and sulfonamide torsion angles (C^{Ar}–C/S–N–C^{Ar}).

Structure:			**Bond (°)**	
Compound 2:	1	2	3	4
2 Solvate 2I	171.74	–68.23	–68.23	171.74
2 Solvate 2IB	169.07	–66.63	–66.63	169.07
2 Solvate 2II	169.60	49.72	–67.32	–166.11
2 Solvate 2IIB	168.67	51.26	–63.49	–165,30
Compound 3:				
3-Form I	–171.78	-169.00	167.17	173.42
3-DMSO I	171.71	165.92	175.14	–171.81
3-DMSO II	175.53	173.08	174.76	172.44
Calculated conformers:				
2I	–168.40	–47.15	–47.21	–168.21
2II	–179.82	–51.58	49.90	178.78
2III	169.78	80.35	80.35	169.78
2I dimeric pair - heading	–170.88	–49.98	–53.89	–175.74
2I dimeric pair - tailing	–177.47	–73.83	–72.10	177.57
Comparison structures from the literature:				
4	-	–55.99	59.56	-
5_1	-	53.73	54.56	-
5_2	-	55.65	57.43	-
6	-	–66.70	60.97	-
7 (C^{Ar}–S–N–C^{Al})	-	–59.35	–74.34	-

In crystal structures, the sulfonamide bond prefers a conformation where the C^{Ar}–S–N–C^{Ar} torsion angle is ±63±11°; an aromatic amide bond prefers C^{Ar}–C–N–C^{Ar} torsion

angle of ±176±5°. These numbers were obtained from the analysis of two CSD searches (Scheme S1, right). The sulfonamide search yielded 598 structures that were used in the analysis, whereas the amide search found 1244 structural hits. The results are the median values for an individual analysis of the positive and negative values of the torsion angle. There were 36 structures that had a torsion angle near 0° which were excluded from the analysis.

5 Solvate 2I solvent channels

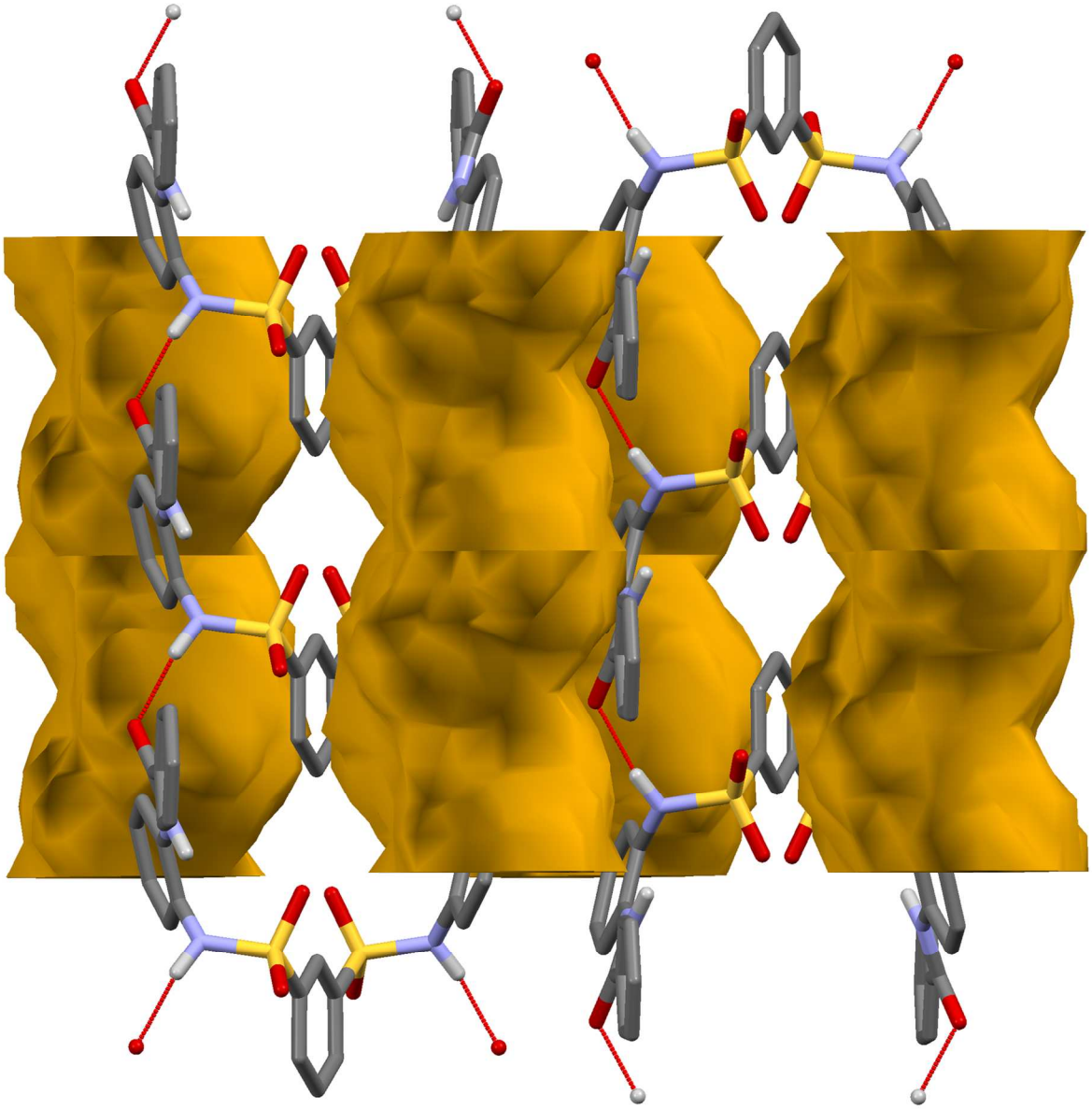


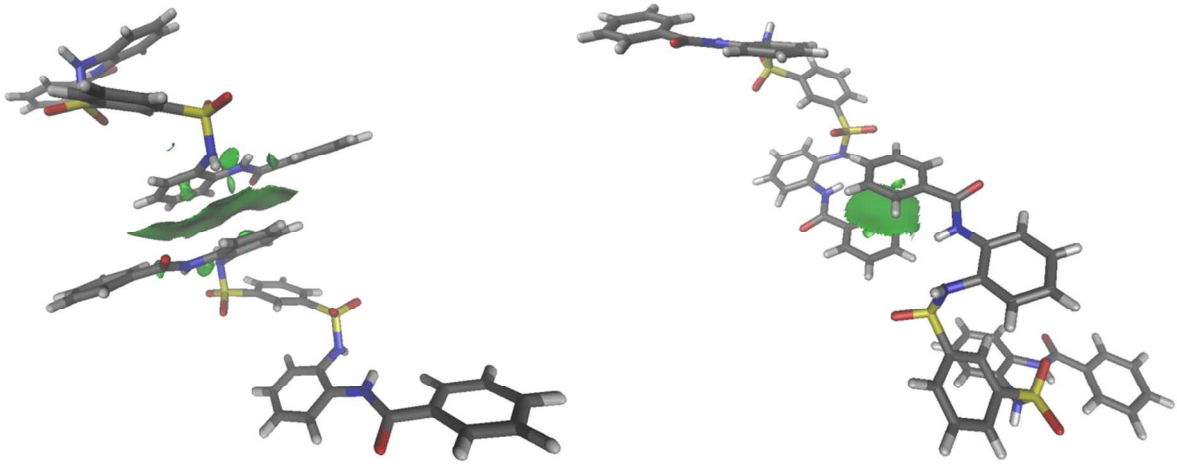
Figure S3. A packing figure of solvate **2I** showing the solvent accessible voids in yellow. The voids are created when the electron density of the severely disordered solvents is removed from the structure with SQUEEZE.[2] The voids were calculated with Mercury.[4]

6 π-π Stacking Interactions

Isosurface representations of the π–π stacking interactions in the crystal packing of the solvate **2I** and solvate **2II** were calculated with NCIplot[5] and visualized with VMD.[6]

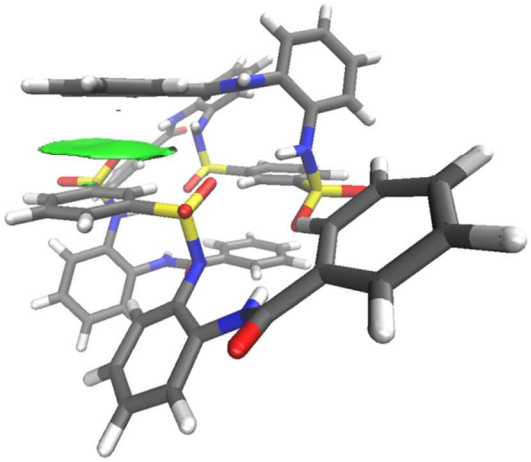
6.1 Solvate 2I

Each side of **2** forms two different π–π stacking interactions with the aromatic side chains.



6.2 Solvate 2II

In addition to the $R_2^2(16)$ motif hydrogen bonds the molecular pairs of **2** are stabilized by a parallel displaced π–π stacking interaction. The surface is calculated for only one of the two identical interactions.



7 Energies and geometries (gas phase) of calculated structures

Table S5. Energies of calculated structures **2I**, **2I***, **2II** and **2III**.[a]

	Energy (a.u.)			Enthalpy (a.u.)		
	gas phase	DCE	EtOAc	gas phase	DCE	EtOAc
2I	-2701.933710	-2701.958113	-2701.954946	-2701.355439	-2701.379241	-2701.376095
2I*	-2701.918310	-2701.945749	-2701.942253	----------	----------	----------
2II	-2701.936862	-2701.961116	-2701.958163	-2701.358197	-2701.383172	-2701.380271
2III	-2701.952760	-2701.971585	-2701.969187	-2701.373198	-2701.392736	-2701.390538

[a] The energies for structure **2I*** are calculated as single point runs using the structure of the "tailing" molecule in the optimized dimeric pair of **2I**.

Structure of **2I** in *xyz*-format

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C	4.215009	-1.754472	-0.291557
H	4.246765	-0.887197	-0.938724
C	5.288732	-2.002845	0.548734
H	6.136080	-1.329325	0.547136
C	5.274543	-3.105268	1.389538
H	6.109150	-3.291425	2.053787
C	4.190530	-3.971890	1.375262
H	4.175477	-4.833918	2.029841
C	3.124384	-3.734038	0.525595
H	2.270879	-4.399011	0.501400
C	3.122738	-2.615935	-0.301845
C	1.892354	-2.394614	-1.132762
C	0.462236	-0.562034	-1.981507
C	-0.746525	-1.258236	-1.938865
H	-0.757508	-2.249047	-1.514717
C	-1.907353	-0.701985	-2.440351
H	-2.829664	-1.265886	-2.375943
C	-1.897047	0.565910	-2.998689
H	-2.805065	1.008555	-3.384410
C	-0.710172	1.270714	-3.038716
H	-0.681864	2.271570	-3.453782
C	0.467213	0.721038	-2.545770
C	1.018031	3.231509	-0.630809
C	0.005614	2.528117	-0.000222
H	0.002313	1.448271	-0.000816
C	0.013698	5.309771	0.001505
H	0.016935	6.391545	0.002206
C	1.024990	4.618149	-0.647504
H	1.826080	5.141732	-1.151868
N	1.637016	-1.082305	-1.428672
H	2.271485	-0.398787	-1.042109
N	1.672135	1.489516	-2.654983
H	1.736668	2.039134	-3.500111
O	1.179627	-3.317543	-1.463539
O	2.760364	1.361337	-0.428955
O	3.251237	3.242107	-1.980294
S	2.329512	2.322923	-1.398806
C	-4.223790	-1.734925	0.287715
H	-4.252838	-0.866373	0.933307
C	-5.296068	-1.978699	-0.555787
H	-6.139642	-1.300472	-0.557999
C	-5.285125	-3.082418	-1.394954
H	-6.118437	-3.264817	-2.061871
C	-4.205978	-3.954978	-1.375772
H	-4.193411	-4.818048	-2.029031
C	-3.141444	-3.721760	-0.522818
H	-2.291708	-4.391371	-0.494877
C	-3.136382	-2.602417	0.302948
C	-1.907046	-2.386550	1.136900
C	-0.466474	-0.560699	1.981980
C	0.738358	-1.263597	1.938439
H	0.743174	-2.254828	1.515105
C	1.903068	-0.713363	2.437547
H	2.822259	-1.282316	2.371501
C	1.900528	0.555003	2.994931
H	2.811482	0.993182	3.378812
C	0.717511	1.266260	3.036204
H	0.695381	2.267565	3.450570
C	-0.463607	0.722712	2.545309
C	-1.002642	3.236642	0.631283
C	-1.001526	4.623265	0.649756
H	-1.799450	5.150821	1.155007
N	-1.644479	-1.075061	1.430323
H	-2.274554	-0.388579	1.041815
N	-1.664193	1.497826	2.655466
H	-1.725115	2.047937	3.500538
O	-1.200691	-3.312868	1.471735
O	-2.753916	1.374734	0.429913
O	-3.235269	3.257897	1.981508
S	-2.318212	2.334312	1.399620

Structure of **2I** dimeric pair in *xyz*-format

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C	-2.809348	6.370390	-1.120249
H	-3.722544	6.012942	-1.580670
C	-2.843153	7.573359	-0.435810
H	-3.775067	8.117186	-0.353318
C	-1.686406	8.077467	0.137371
H	-1.714345	9.016772	0.674936
C	-0.493316	7.380355	0.017119
H	0.411936	7.770880	0.463185
C	-0.457152	6.181624	-0.671549
H	0.470567	5.635155	-0.766123
C	-1.616371	5.661653	-1.237161
C	-1.512033	4.356113	-1.956481
C	-2.918251	2.433414	-2.674959
C	-1.966256	1.713086	-3.392476

H	-0.984055	2.133533	-3.525100
C	-2.285998	0.476056	-3.923882
H	-1.526335	-0.070769	-4.467265
C	-3.548175	-0.070462	-3.762395
H	-3.786505	-1.041638	-4.173720
C	-4.506248	0.645393	-3.065322
H	-5.504572	0.245819	-2.934472
C	-4.203226	1.885899	-2.527707
C	-6.362776	1.034903	0.007903
C	-5.631685	-0.133955	0.134569
H	-4.552579	-0.112796	0.075420
C	-8.413613	-0.161214	0.320353
H	-9.492710	-0.172505	0.394991
C	-7.748449	1.032124	0.096967
H	-8.289805	1.964527	0.010441
N	-2.685042	3.681550	-2.103054
H	-3.472639	4.050243	-1.598003
N	-5.207102	2.666352	-1.871795
H	-6.026393	2.905431	-2.410817
O	-0.445634	3.936281	-2.378121
O	-4.243178	2.466202	0.382552
O	-6.430536	3.617330	0.018721
S	-5.511329	2.564165	-0.261285
C	-2.516855	-6.490012	1.151655
H	-3.327998	-6.027765	1.701888
C	-2.704536	-7.761990	0.638133
H	-3.655291	-8.260531	0.774497
C	-1.675033	-8.393454	-0.042494
H	-1.824179	-9.385528	-0.449580
C	-0.454826	-7.753735	-0.201282
H	0.350584	-8.241627	-0.734574
C	-0.261963	-6.486104	0.318783
H	0.680618	-5.975898	0.184000
C	-1.294799	-5.840779	0.989496
C	-1.031758	-4.470061	1.528152
C	-2.276722	-2.403145	2.175370
C	-1.201566	-1.587942	2.512383
H	-0.202800	-1.957538	2.371030
C	-1.413667	-0.305798	2.986396
H	-0.555284	0.314270	3.213374
C	-2.696058	0.194409	3.139208
H	-2.857434	1.204160	3.489757
C	-3.773438	-0.612786	2.818230
H	-4.786019	-0.246095	2.934854
C	-3.575355	-1.898298	2.338779
C	-6.315527	-1.317596	0.366208
C	-7.699464	-1.340528	0.461044
H	-8.203773	-2.280795	0.637152
N	-2.142617	-3.695868	1.668557
H	-2.996793	-4.088467	1.312944
N	-4.690727	-2.750009	2.050034
H	-5.333282	-2.936100	2.806085
O	0.093703	-4.093507	1.809634
O	-4.359110	-2.836978	-0.386357
O	-6.361442	-3.884899	0.669716
S	-5.410631	-2.826275	0.579466
C	4.041975	3.364753	3.447105
H	3.093760	3.501325	2.943282
C	4.096943	3.550752	4.819568
H	3.198867	3.826048	5.357690
C	5.293788	3.384320	5.499237
H	5.332361	3.524493	6.572328
C	6.442863	3.043340	4.800445
H	7.380987	2.913373	5.324774
C	6.391747	2.867919	3.428669
H	7.277025	2.606400	2.864426
C	5.190606	3.016003	2.743269
C	5.228595	2.755492	1.263104
C	3.804216	2.008511	-0.610919
C	4.795982	1.353198	-1.340582
H	5.770693	1.227039	-0.895824
C	4.542203	0.879777	-2.614166
H	5.329021	0.366545	-3.152266
C	3.292610	1.040389	-3.189135
H	3.089373	0.658463	-4.180307
C	2.299023	1.677482	-2.472393
H	1.311629	1.812219	-2.895551
C	2.541769	2.169523	-1.195727
C	-0.013409	0.651809	0.006496
C	0.921264	-0.351412	-0.184781
H	1.964148	-0.179843	0.037184
C	-1.764237	-0.782316	-0.754379
H	-2.804382	-0.966322	-0.981525
C	-1.354618	0.454030	-0.282269
H	-2.066239	1.252320	-0.113517
N	4.022448	2.462128	0.696355
H	3.222039	2.405914	1.308417
N	1.485494	2.879468	-0.537924
H	0.873696	3.360939	-1.200902
O	6.276677	2.784337	0.651996
O	1.412381	1.893808	1.743698
O	-0.561236	3.070664	0.806945

S	0.558124	2.203226	0.631214
C	5.822592	-2.832324	-2.932649
H	4.938378	-3.321080	-2.545394
C	6.174067	-3.041951	-4.256242
H	5.560666	-3.681875	-4.877499
C	7.304864	-2.436189	-4.781355
H	7.573192	-2.596397	-5.818123
C	8.093159	-1.628638	-3.973855
H	8.979304	-1.156301	-4.378383
C	7.748513	-1.426096	-2.648637
H	8.354302	-0.805243	-2.001842
C	6.603925	-2.015314	-2.121643
C	6.278156	-1.714028	-0.685250
C	4.355136	-1.584365	0.868151
C	4.908071	-0.668604	1.765217
H	5.830773	-0.177446	1.498673
C	4.307403	-0.409224	2.983202
H	4.760285	0.309869	3.653733
C	3.141059	-1.063105	3.340288
H	2.673764	-0.880233	4.298580
C	2.569275	-1.952272	2.451955
H	1.669635	-2.490198	2.717681
C	3.147079	-2.208800	1.214426
C	0.491999	-1.575801	-0.668031
C	-0.847314	-1.804026	-0.943577
H	-1.165948	-2.770490	-1.310204
N	4.961374	-1.869824	-0.360521
H	4.326004	-2.087959	-1.113820
N	2.499297	-3.180342	0.379361
H	1.894717	-3.795496	0.922081
O	7.136787	-1.344173	0.088571
O	2.642475	-2.214965	-1.909397
O	1.020035	-4.015160	-1.391779
S	1.703069	-2.821238	-1.011424

Structure of **2II** in *xyz*-format

70

O	-1.352201	1.266505	0.850463
O	-4.329100	-0.145165	-2.830636
O	-4.800064	-2.411938	-1.921286
O	0.623701	1.574033	-1.866702
O	2.395797	-0.165509	-1.989355
O	5.585765	-1.747176	1.522751
N	-3.480988	1.289842	1.550810
H	-4.317621	1.826547	1.702217
N	-4.267829	-0.470447	-0.428628
H	-4.201267	0.533417	-0.507667
N	1.242765	0.331927	0.163245
H	0.461148	0.883358	0.518118
N	3.791657	-0.631663	0.663204
H	3.532140	0.190652	0.145220
S	-4.064790	-1.191405	-1.899909
S	1.143458	0.301126	-1.482011
C	-1.577650	3.900750	-0.122168
H	-0.896894	3.239853	-0.645007
C	-1.605034	5.255434	-0.404332
H	-0.941867	5.658047	-1.158667
C	-2.474038	6.091900	0.280680
H	-2.489114	7.152448	0.063778
C	-3.320773	5.574027	1.249510
H	-3.986947	6.228055	1.796730
C	-3.306166	4.217299	1.526388
H	-3.951913	3.833368	2.307554
C	-2.436840	3.375445	0.838774
C	-2.360419	1.908819	1.087559
C	-3.487671	-0.110591	1.817301
C	-3.074349	-0.587208	3.048963
H	-2.764323	0.124938	3.802620
C	-3.034819	-1.947735	3.297081
H	-2.700995	-2.315786	4.257629
C	-3.421625	-2.828384	2.299568
H	-3.401784	-3.895309	2.481453
C	-3.842249	-2.366400	1.064345
H	-4.162826	-3.060825	0.301489
C	-3.868216	-0.999479	0.806647
C	-2.345086	-1.610159	-1.952381
C	-1.964729	-2.934211	-2.104242
H	-2.724128	-3.698222	-2.197112
C	-0.616753	-3.255655	-2.139410
H	-0.311221	-4.285598	-2.264298
C	0.338534	-2.264785	-1.997826
H	1.393520	-2.502813	-2.003175
C	-0.064315	-0.945783	-1.835219
C	-1.402983	-0.602337	-1.821884
H	-1.693580	0.432186	-1.698552
C	1.420943	-0.900380	0.875551
C	0.310874	-1.584378	1.350040
H	-0.673621	-1.169927	1.168885
C	0.461141	-2.768659	2.048075
H	-0.412426	-3.289693	2.416220

C	1.734700	-3.271212	2.258209
H	1.869465	-4.204405	2.790521
C	2.854175	-2.593683	1.806004
H	3.844631	-2.975137	1.991759
C	2.714109	-1.387996	1.117765
C	5.128532	-0.841539	0.856320
C	6.020262	0.167454	0.192843
C	7.269807	0.380946	0.765066
H	7.538717	-0.182852	1.648503
C	8.145169	1.296668	0.209450
H	9.111650	1.464696	0.667305
C	7.785357	1.994792	-0.934744
H	8.471667	2.708789	-1.372667
C	6.549752	1.770329	-1.521376
H	6.272274	2.298055	-2.424861
C	5.665286	0.861556	-0.960483
H	4.716686	0.677950	-1.452025

Structure of **2III** in *xyz*-format

70

O	3.706151	1.733900	0.243731
O	0.061765	3.776045	0.972750
O	-1.080253	2.563149	-0.878027
O	1.080253	-2.563149	-0.878027
O	-0.061765	-3.776045	0.972750
O	-3.706151	-1.733900	0.243731
N	2.703312	0.038121	-0.882547
H	2.405344	-0.927533	-0.824649
N	1.381583	2.674012	-0.793892
H	2.225131	2.719942	-0.217278
N	-1.381583	-2.674012	-0.793892
H	-2.225131	-2.719942	-0.217278
N	-2.703312	-0.038121	-0.882547
H	-2.405344	0.927533	-0.824649
S	0.000000	2.682301	0.063050
S	0.000000	-2.682301	0.063050
C	3.654251	0.241139	2.608719
H	3.693154	1.320572	2.668403
C	3.732422	-0.539205	3.748997
H	3.835165	-0.067352	4.717785
C	3.678566	-1.921683	3.649031
H	3.735687	-2.533076	4.540873
C	3.559343	-2.521069	2.404669
H	3.522408	-3.598973	2.317777
C	3.478345	-1.741196	1.263115
H	3.388726	-2.236926	0.305807
C	3.510896	-0.353021	1.359405
C	3.341429	0.567976	0.190254
C	2.228372	0.708510	-2.033530
C	2.337278	0.033844	-3.245452
H	2.847801	-0.920574	-3.261068
C	1.790686	0.554552	-4.401988
H	1.881718	0.007911	-5.331299
C	1.135204	1.775155	-4.367379
H	0.709549	2.195910	-5.268663
C	1.029661	2.459819	-3.172234
H	0.522887	3.413208	-3.118211
C	1.550445	1.933341	-1.997031
C	0.003465	1.191605	1.020354
C	0.007572	1.205087	2.405997
H	0.010238	2.150211	2.931226
C	0.000000	0.000000	3.092067
H	0.000000	0.000000	4.173536
C	-0.007572	-1.205087	2.405997
H	-0.010238	-2.150211	2.931226
C	-0.003465	-1.191605	1.020354
C	0.000000	0.000000	0.325054
H	0.000000	0.000000	-0.755522
C	-1.550445	-1.933341	-1.997031
C	-1.029661	-2.459819	-3.172234
H	-0.522887	-3.413208	-3.118211
C	-1.135204	-1.775155	-4.367379
H	-0.709549	-2.195910	-5.268663
C	-1.790686	-0.554552	-4.401988
H	-1.881718	-0.007911	-5.331299
C	-2.337278	-0.033844	-3.245452
H	-2.847801	0.920574	-3.261068
C	-2.228372	-0.708510	-2.033530
C	-3.341429	-0.567976	0.190254
C	-3.510896	0.353021	1.359405
C	-3.654251	-0.241139	2.608719
H	-3.693154	-1.320572	2.668403
C	-3.732422	0.539205	3.748997
H	-3.835165	0.067352	4.717785
C	-3.678566	1.921683	3.649031
H	-3.735687	2.533076	4.540873
C	-3.559343	2.521069	2.404669
H	-3.522408	3.598973	2.317777
C	-3.478345	1.741196	1.263115
H	-3.388726	2.236926	0.305807

8 Overlay Figures for Compounds 5–7 and optimized structure of 5

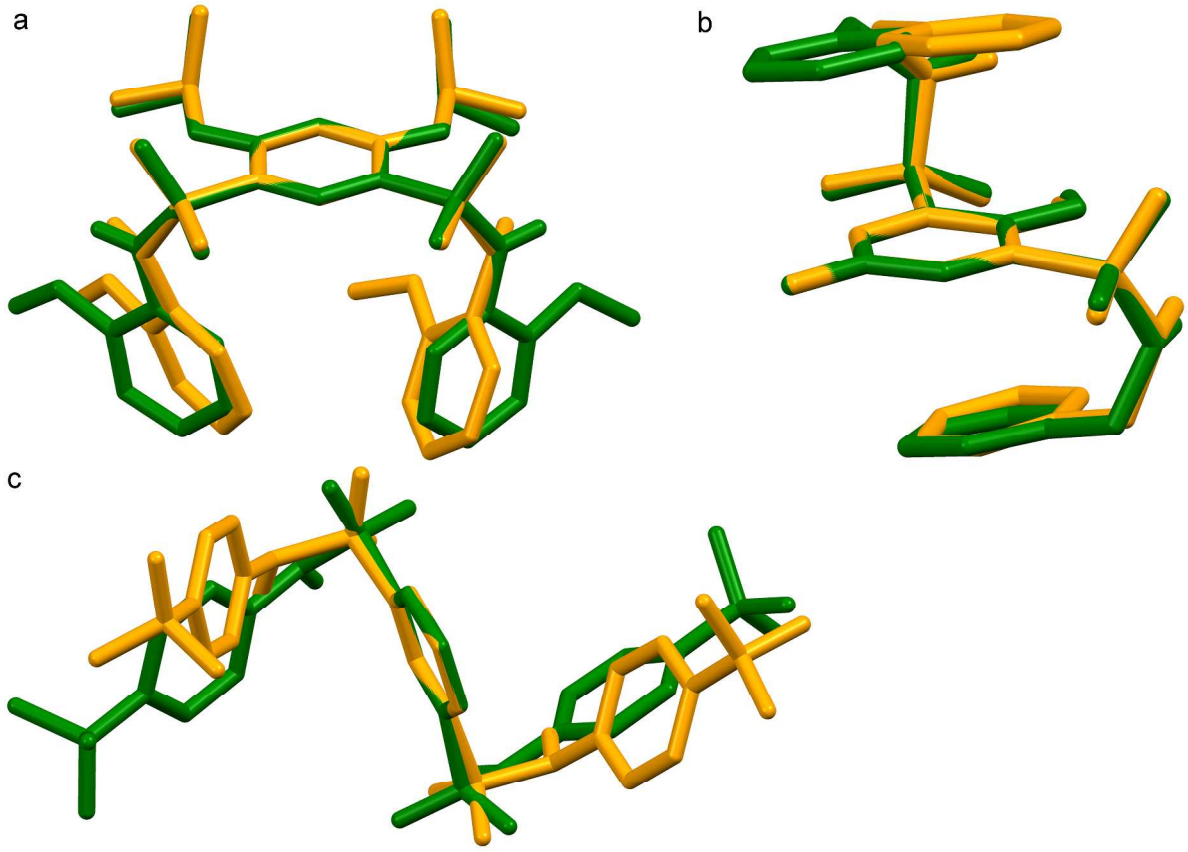


Figure S4. Overlay figures of (a) the crystal structure of **6** and an optimized structure of **6**, (b) the crystal structure of **7** and an optimized structure of **7** and (c) the crystal structure of **5** and an optimized structure of **5**. Crystal structures and calculated structures are shown in green and yellow, respectively. Non-amide/sulfonamide hydrogen atoms have been removed for clarity. Overlay figures were drawn with Mercury.[4]

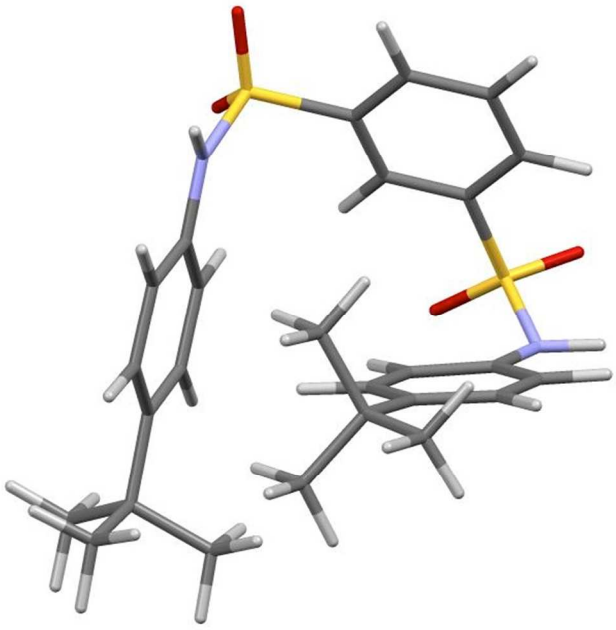


Figure S5. Optimized structure of **5** with aromatic side chains on the same side of the central aromatic ring.

9 Powder X-Ray Diffraction Data

Powder X-ray diffraction data was collected on a PANalytical X'Pert PRO MPD diffractometer in reflection mode with $CuK_{\alpha 1}$-radiation (1.5406 Å). A 2θ-angle range of 3–35º and step time of 170 s were used with a step resolution of 0.016º. Powder X-ray diffraction samples were pressed to a zero background silicon plate. All figures were drawn with X'Pert Highscore Plus[7] and the calculated PXRD patterns were created with Mercury.[4]

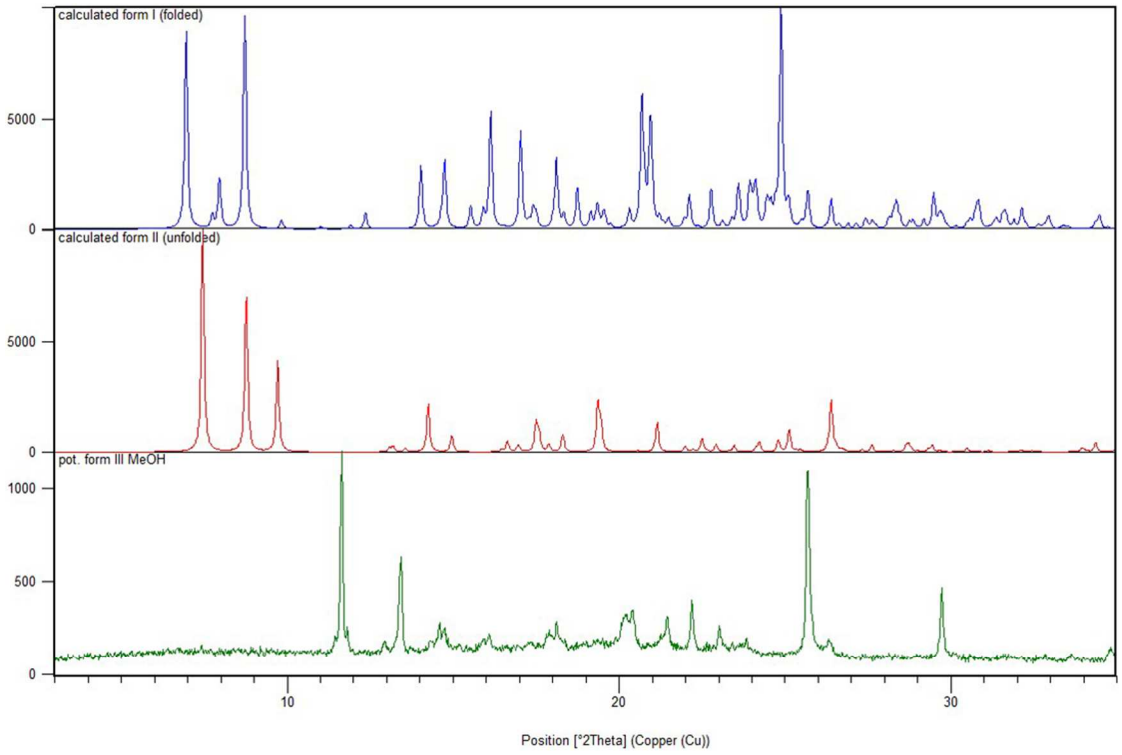
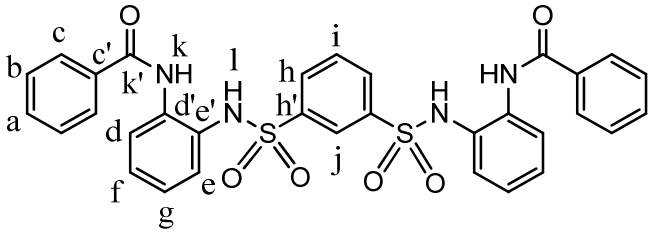


Figure S6. Calculated and measured PXRD patterns of the sulfonamide foldamer **2**. The folded form (solvate **2II**) pattern is blue, unfolded form (solvate **2I**) is red and the unknown form is green.

10 NMR Spectra of the Sulfonamide 2

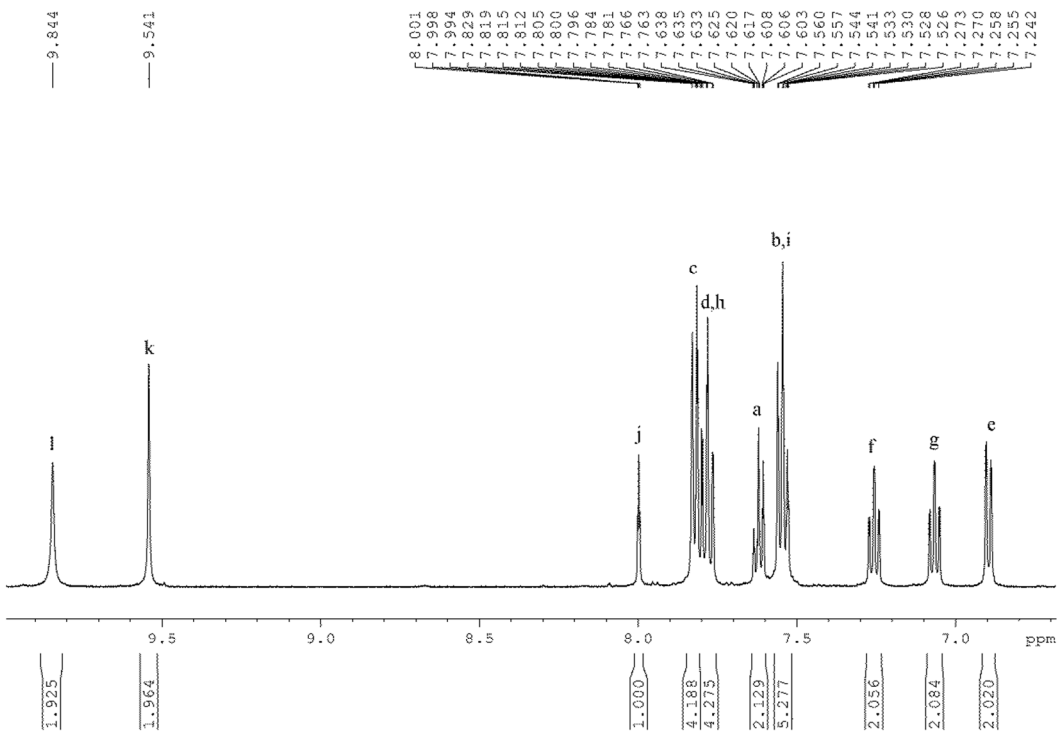
^{1}H, ^{13}C, COSY, HMBC and HMQC spectra were measured for compound **2** in DMSO-d_6. For clarity the spectra have been scaled to display only aromatic and N–H peaks; only the aromatic peaks are shown in case of COSY and HMQC spectra.

A VT-NMR study and a NOESY spectrum of compound **2** were done in acetone-d_6. The NOESY spectrum shows correlation between some of the protons of the outermost aromatic rings and the amide hydrogen atoms of the inner sulfonamide groups.

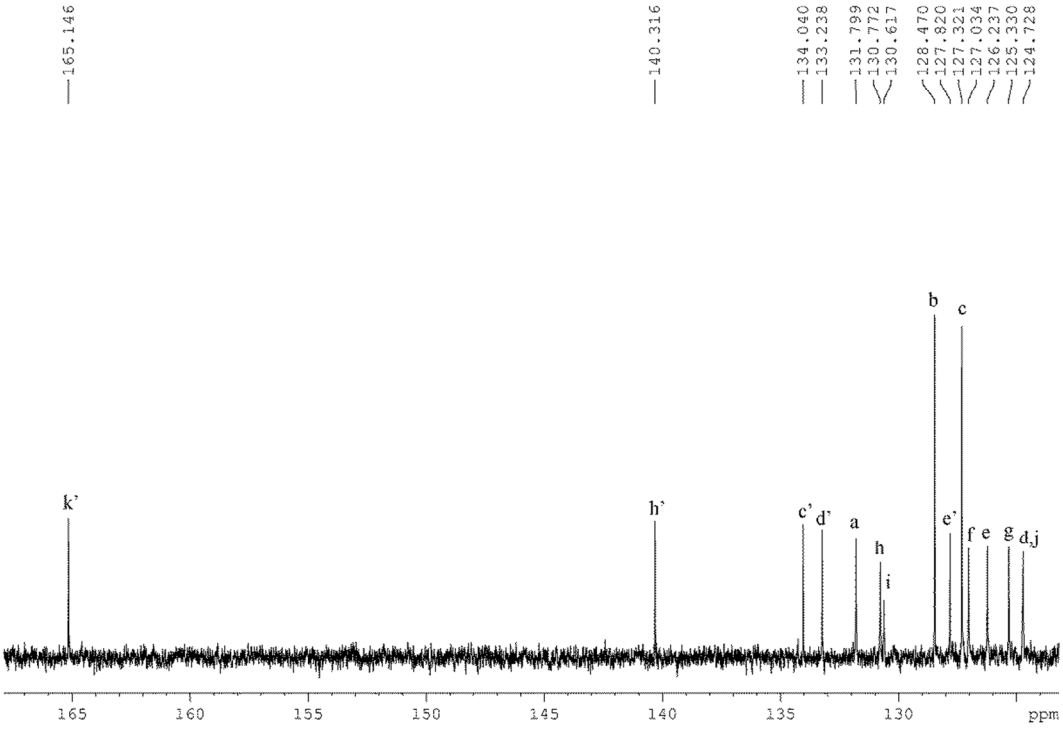


Sulfonamide 2

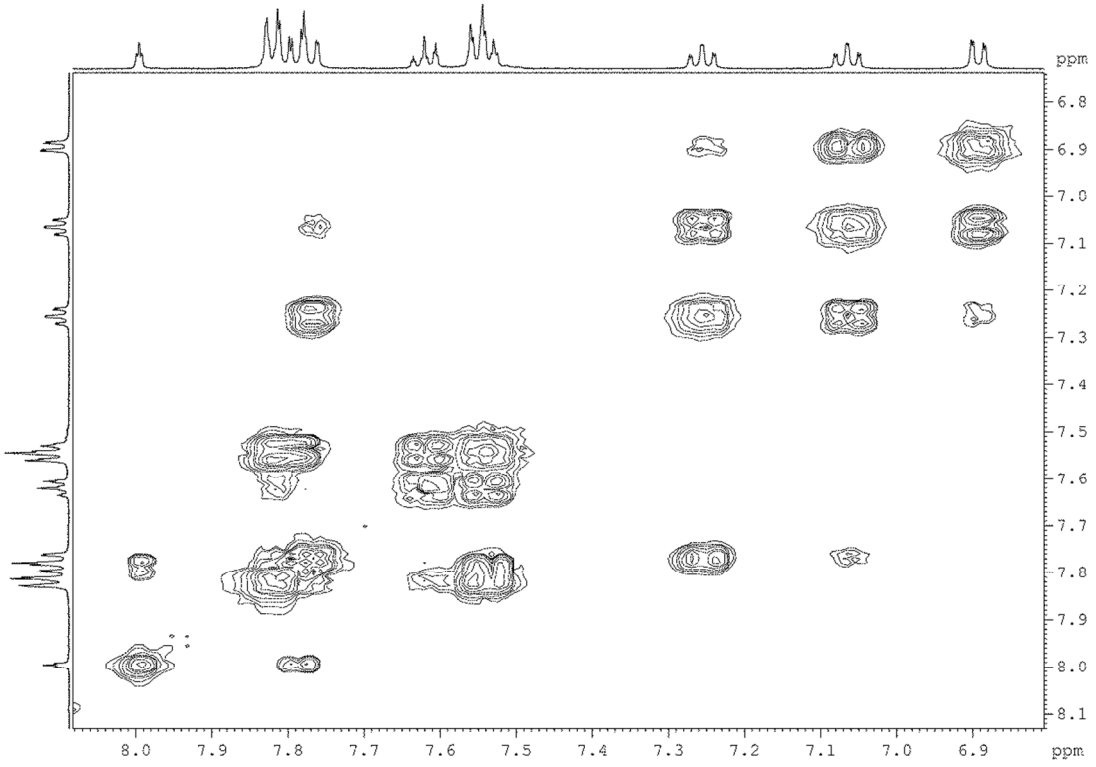
^{1}H



^{13}C



COSY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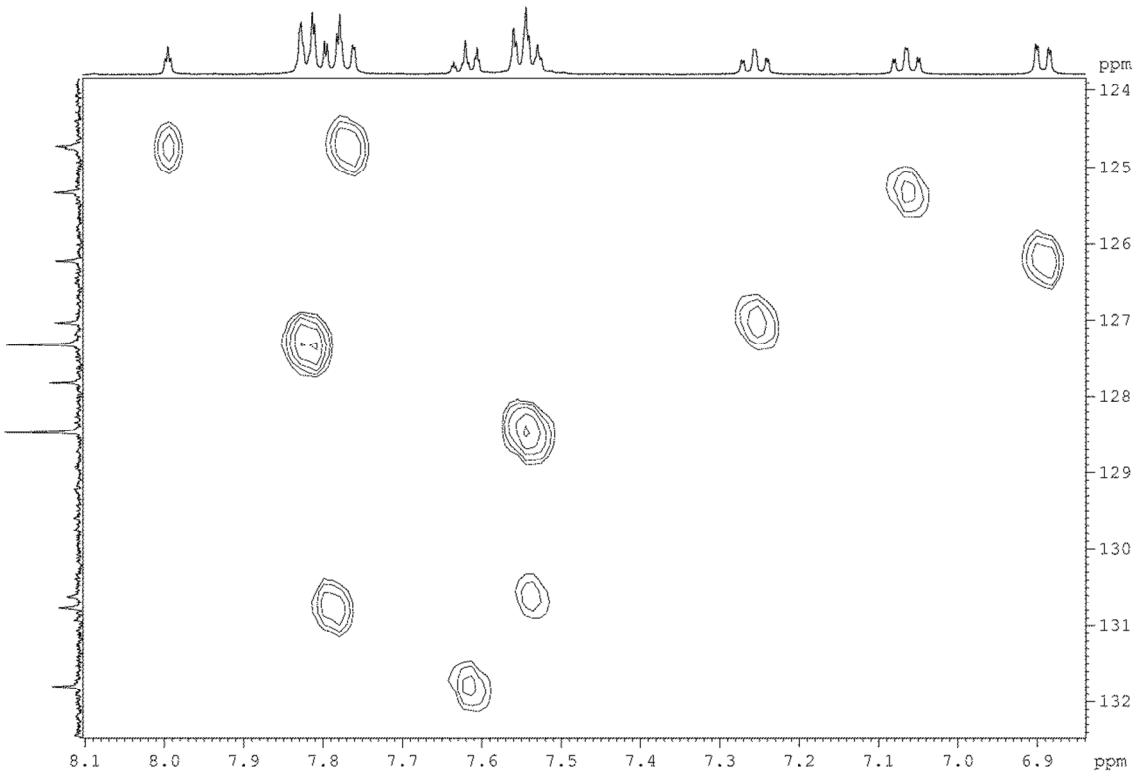
6.9
7.0
7.1
7.2
7.3
7.4
7.5
7.6
7.7
7.8
7.9
8.0
8.1
8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9
ppm

HMQC


ppm
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125
126
127
128
129
130
131
132
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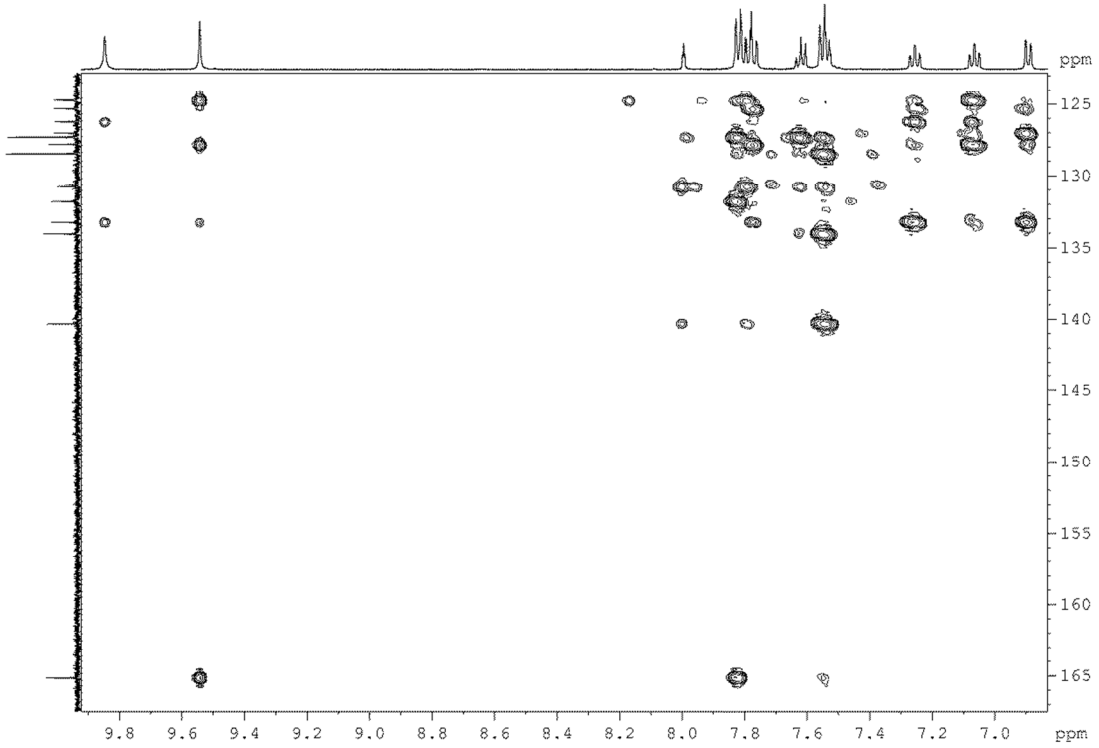
ppm

HMBC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130
135
140
145
150
155
160
165
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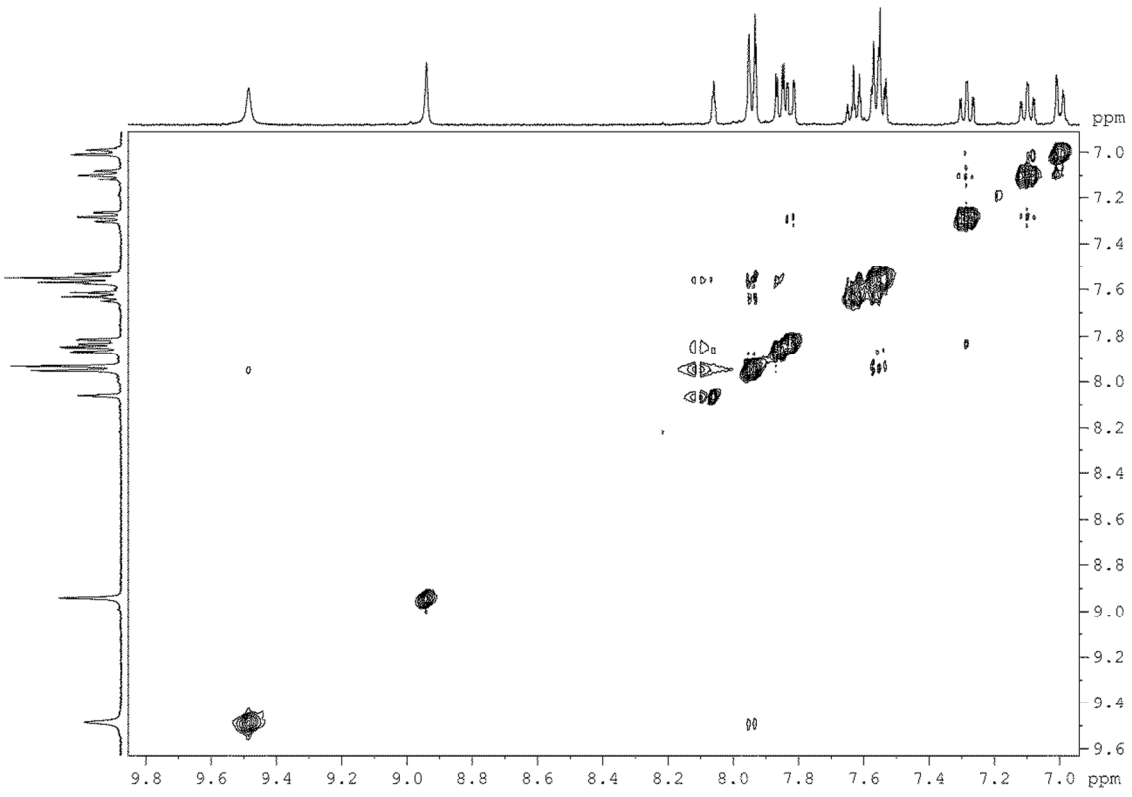
ppm

NOESY


ppm
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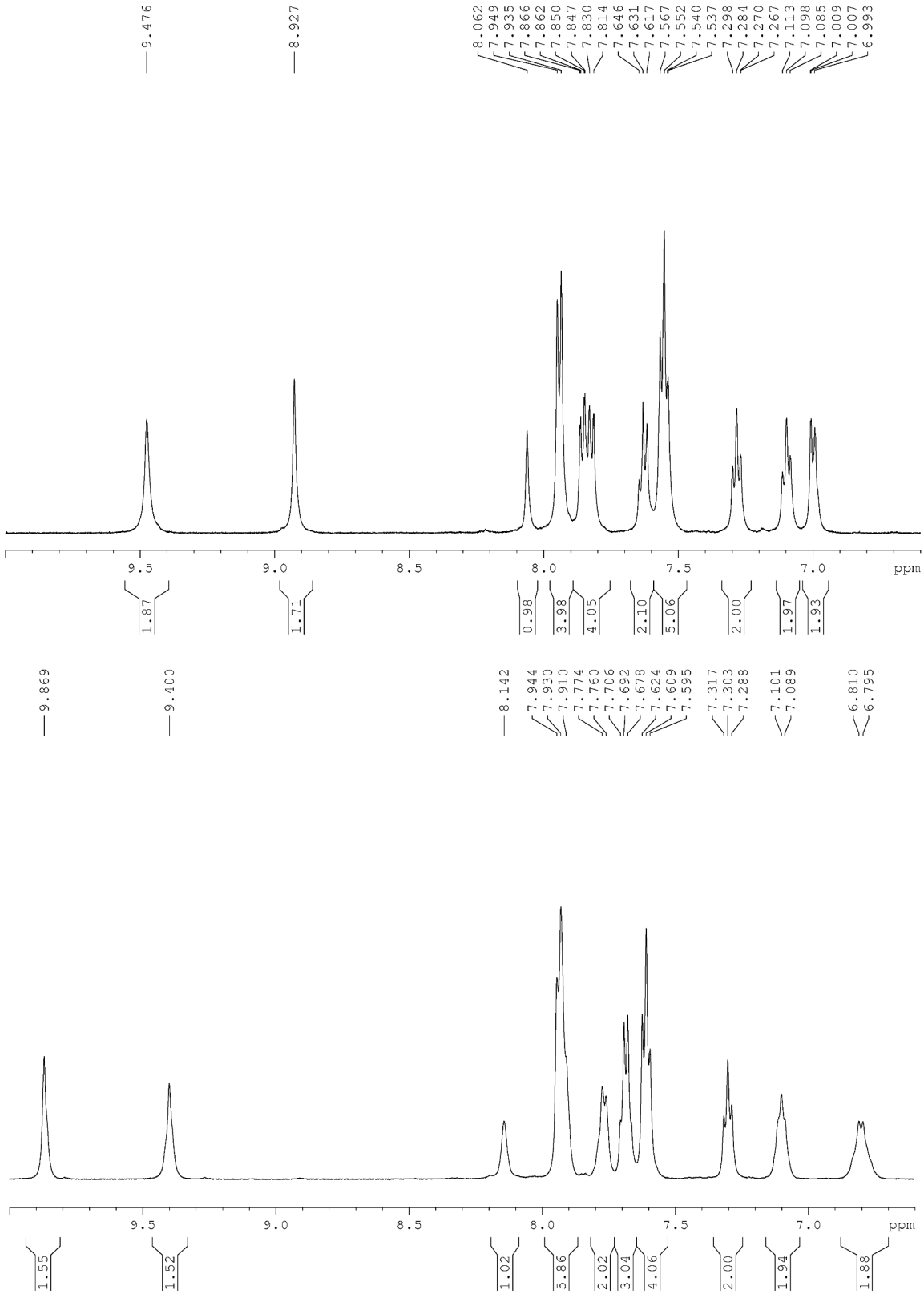
7.2
7.4
7.6
7.8
8.0
8.2
8.4
8.6
8.8
9.0
9.2
9.4
9.6
9.8 9.6 9.4 9.2 9.0 8.8 8.6 8.4 8.2 8.0 7.8 7.6 7.4 7.2 7.0 ppm

VT-NMR in acetone-d_6; 30°C (top) and −80°C (bottom)



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