Cimetidine, $C_{10}H_{16}N_6S$, form *C*: crystal structure and modelling of polytypes using superspace approach

Alla Arakcheeva,[ab*] Philip Pattison,[ca] Annette Bauer-Brandl,[d] Henrik Birkedal[e] and Gervais Chapuis[a]

[a]Crystallography Competence Center, Ecole Polytechnique Fédérale de Lausanne, 1015 Lausanne, Switzerland, [b]Phase Solution Sarl., Chemin des Mésanges, 7, Lausanne CH-1012, Switzerland, [c]Swiss-Norwegian Beam Lines at ESRF Grenoble BP-220, 38043, France, [d]Department of Physics, Chemistry and Pharmacy, University of Southern Denmark, Campusvej 55, DK-5230 Odense M, Denmark, and [e]Department of Chemistry and iNANO, Aarhus University, Langelandsgade 140, 8000 Aarhus, Denmark.

Corresponding author: allaarakcheeva@gmail.com

SUPPLEMENTARY MATERIALS

Content:

- **Details of the crystal structure of cimetidine form C polytype 6M.**
  - **Atomic parameters.** Tables of atomic coordinates, equivalent and anisotropic ADPs obtained in the supercell model. Coordinates, isotropic displacement parameters and Fourier amplitudes of the displacive modulation function of cimetidine form *C* polytype 6M obtained with the (3+1)D superspace model.
  - **Molecular structure and geometry.** ORTEP plots of three similar molecules consisting the structure. Tables of interatomic distances and angles. Table of characteristics of optimal planes and deviations of individual atoms in three molecules.
  - **Molecule packing.** Table of characteristics of intermolecular hydrogen bonds.
- **Generation of possible polytypes of cimetidine form *C* using the (3+1)D superspace model**
  - **Modelled polytypes 1M, 2M, 3M, 4M and 5M.** Unit cell parameters, space group, atomic positions and molecule packing are present for each polytype.
- **Analysis of XRD patters reported for cimetidine form *C*.**
  - The powder XRD patterns simulated for the modelled 1M, 2M, 3M, 4M, 5M and 6M polytypes are shown in comparison with the published XRD patterns.

Details of the crystal structure of cimetidine form *C* polytype 6M

Atomic parameters

Table S1. Atomic coordinates and equivalent atomic displacement parameters. The first and the second lines stay for values obtained in the 3D supercell and transformed from the (3+1)D superspace models, respectively

Atom	x	y	z	Ueq
Molecule *I*				
S1a	0.503019(10)	0.05176(19)	0.61024(5)	0.0138(3)
	0.503	0.0517	0.6102	0.01378
N1a	0.45295(3)	0.1772(6)	0.78800(16)	0.0142(10)
	0.4529	0.1776	0.7881	0.01444
N2a	0.45888(4)	-0.0063(6)	0.67547(16)	0.0143(10)
	0.4589	-0.0063	0.6755	0.01421
N3a	0.54751(3)	0.2528(6)	0.46456(16)	0.0151(10)
	0.5475	0.2525	0.4646	0.01513
N4a	0.56680(3)	0.5967(6)	0.42323(16)	0.0148(10)
	0.5668	0.5967	0.4232	0.01481
N5a	0.55565(4)	0.5129(6)	0.55095(16)	0.0156(10)
	0.5556	0.5131	0.551	0.01562
N6a	0.57153(4)	0.9033(7)	0.58504(16)	0.0176(11)
	0.5716	0.9032	0.585	0.01721
C1a	0.44866(4)	-0.0087(8)	0.74282(20)	0.0164(13)
	0.4487	-0.0086	0.7429	0.01618
C2a	0.47058(4)	0.1973(7)	0.67842(19)	0.0130(12)
	0.4706	0.1972	0.6784	0.01309
C3a	0.46708(4)	0.3119(7)	0.74755(19)	0.0120(12)
	0.4671	0.3116	0.7475	0.012080
C4a	0.47599(4)	0.5288(8)	0.7794(2)	0.0164(13)
	0.476	0.5289	0.7792	0.01642
C5a	0.48484(4)	0.2673(7)	0.61338(18)	0.0140(11)
	0.4848	0.2674	0.6135	0.01404
C6a	0.51809(4)	0.2386(8)	0.53785(18)	0.0133(11)
	0.5181	0.239	0.5377	0.01339
C7a	0.53519(4)	0.1049(8)	0.52267(19)	0.0142(12)
	0.5352	0.105	0.5227	0.01453
C8a	0.55690(4)	0.4559(7)	0.47886(19)	0.0124(12)
	0.5569	0.4561	0.479	0.01255
C9a	0.56919(4)	0.5228(8)	0.34649(19)	0.0167(13)
	0.5692	0.5243	0.3463	0.01729
C10a	0.56450(4)	0.7213(8)	0.56566(19)	0.0151(12)
	0.5645	0.7218	0.5656	0.01534
H1n1a	0.4477	0.2065	0.8342	0.0170
H1n3a	0.5487	0.2055	0.4187	0.0182
H1n4a	0.5721	0.7398	0.4335	0.0178
H1c1a	0.4392	-0.1296	0.7581	0.0197
H1c4a	0.4837	0.4424	0.8026	0.0197
H2c4a	0.482	0.6483	0.7405	0.0197
H3c4a	0.468	0.6346	0.8155	0.0197
H1c5a	0.4815	0.2428	0.5687	0.0168
H2c5a	0.4878	0.4577	0.616	0.0168
H1c6a	0.5144	0.2381	0.4934	0.0160
H2c6a	0.5188	0.4262	0.5531	0.0160

H1c7a	0.5345	-0.083	0.5078	0.0171
H2c7a	0.5388	0.1037	0.5672	0.0171
H2c9a	0.5736	0.3389	0.3383	0.0200
H1c9a	0.5769	0.649	0.3156	0.0200
H3c9a	0.5586	0.5315	0.3346	0.0200
Molecule *II*				
S1b	0.338982(11)	0.09204(19)	0.61518(5)	0.0163(3)
	0.339	0.092	0.6152	0.01636
N1b	0.29041(4)	0.1555(6)	0.79823(16)	0.0168(11)
	0.2904	0.1551	0.7983	0.01673
N2b	0.29538(4)	0.0224(6)	0.68163(16)	0.0169(11)
	0.2954	0.0224	0.6817	0.01723
N3b	0.38369(4)	0.3006(6)	0.47484(16)	0.0154(10)
	0.3837	0.3008	0.4749	0.01562
N4b	0.40329(3)	0.6413(7)	0.43255(15)	0.0156(11)
	0.4033	0.6416	0.4326	0.01550
N5b	0.39189(4)	0.5630(6)	0.56047(16)	0.0160(11)
	0.3919	0.5632	0.5605	0.01634
N6b	0.40831(4)	0.9462(7)	0.59387(16)	0.0183(11)
	0.4083	0.9463	0.5939	0.01862
C1b	0.28580(5)	-0.0114(8)	0.7498(2)	0.0195(13)
	0.2858	-0.0117	0.7497	0.01914
C2b	0.30688(4)	0.2243(7)	0.68787(19)	0.0140(12)
	0.3069	0.2242	0.6879	0.01397
C3b	0.30389(4)	0.3079(7)	0.75956(19)	0.0152(12)
	0.3039	0.3083	0.7596	0.01558
C4b	0.31248(5)	0.5144(8)	0.7953(2)	0.0193(14)
	0.3125	0.5141	0.7953	0.01943
C5b	0.32082(4)	0.3171(7)	0.62429(19)	0.0155(12)
	0.3208	0.317	0.6244	0.01586
C6b	0.35421(4)	0.2883(8)	0.54696(19)	0.0159(12)
	0.3543	0.289	0.547	0.01594
C7b	0.37128(4)	0.1538(8)	0.53229(19)	0.0161(12)
	0.3713	0.1537	0.5323	0.01670
C8b	0.39318(4)	0.5036(7)	0.4890(2)	0.0144(13)
	0.3932	0.5038	0.4888	0.014620
C9b	0.40568(4)	0.5657(8)	0.3558(2)	0.0206(14)
	0.4057	0.5653	0.3559	0.020047
C10b	0.40095(4)	0.7682(8)	0.57503(19)	0.0150(12)
	0.4009	0.7682	0.575	0.01489
H1n1b	0.2857	0.1649	0.8456	0.0202
H1n3b	0.385	0.2529	0.429	0.0185
H1n4b	0.4087	0.7835	0.4425	0.0187
H1c1b	0.2767	-0.1395	0.7632	0.0234
H1c4b	0.3045	0.5979	0.8364	0.0231
H2c4b	0.321	0.4244	0.8127	0.0231
H3c4b	0.3175	0.654	0.76	0.0231
H1c5b	0.3238	0.5032	0.6326	0.0186
H2c5b	0.3173	0.3095	0.5796	0.0186
H1c6b	0.3509	0.296	0.5018	0.0191
H2c6b	0.3548	0.4725	0.5648	0.0191
H1c7b	0.3748	0.1515	0.5771	0.0194
H2c7b	0.3706	-0.034	0.5173	0.0194
H2c9b	0.4132	0.6939	0.3246	0.0247
H1c9b	0.4103	0.3833	0.3476	0.0247
H3c9b	0.3951	0.5698	0.3441	0.0247
Molecule *III*				
S1c	0.667026(11)	-0.01787(19)	0.60291(5)	0.0166(3)
	0.667	-0.0177	0.6029	0.01648

N1c	0.61657(4)	0.1521(6)	0.77287(17)	0.0191(11)
	0.6166	0.1517	0.7729	0.01888
N2c	0.62296(4)	-0.0478(6)	0.66253(17)	0.0176(11)
	0.6229	-0.0478	0.6626	0.01790
N3c	0.71249(4)	0.1272(6)	0.45911(16)	0.0159(10)
	0.7125	0.1274	0.4592	0.01594
N4c	0.73337(4)	0.4505(7)	0.42261(16)	0.0208(11)
	0.7334	0.4506	0.4226	0.02080
N5c	0.72165(4)	0.3496(7)	0.54827(16)	0.0192(11)
	0.7217	0.3497	0.5484	0.01964
N6c	0.73844(5)	0.6945(9)	0.59302(19)	0.0387(14)
	0.7384	0.6943	0.5931	0.03868
C1c	0.61237(5)	-0.0409(8)	0.7290(2)	0.0190(13)
	0.6124	-0.0407	0.7289	0.01936
C2c	0.63485(4)	0.1540(8)	0.66499(19)	0.0159(12)
	0.6349	0.1538	0.6651	0.01624
C3c	0.63107(4)	0.2794(7)	0.73266(19)	0.0153(12)
	0.6311	0.2793	0.7326	0.01533
C4c	0.63974(5)	0.4965(8)	0.7645(2)	0.0203(14)
	0.6397	0.4964	0.7646	0.02049
C5c	0.64958(4)	0.2117(8)	0.60153(19)	0.0157(12)
	0.6495	0.2117	0.6015	0.01615
C6c	0.68308(4)	0.1477(8)	0.53083(19)	0.0155(12)
	0.6831	0.148	0.5308	0.01559
C7c	0.69950(4)	-0.0129(8)	0.51493(19)	0.0154(12)
	0.6995	-0.013	0.5149	0.01560
C8c	0.72277(4)	0.3112(8)	0.47635(19)	0.0142(12)
	0.7228	0.3115	0.4763	0.01407
C9c	0.73508(5)	0.4086(9)	0.3445(2)	0.0288(15)
	0.735	0.408	0.3445	0.02876
C10c	0.73124(5)	0.5373(9)	0.5676(2)	0.0227(14)
	0.7312	0.5365	0.5676	0.02168
H1n1c	0.6111	0.1894	0.8183	0.0229
H1n3c	0.7136	0.0896	0.4127	0.0190
H1n4c	0.7397	0.5745	0.4351	0.0250
H1c1c	0.6028	-0.1593	0.7445	0.0228
H1c4c	0.645	0.6247	0.7264	0.0243
H2c4c	0.6481	0.4126	0.7846	0.0243
H3c4c	0.6317	0.5922	0.8031	0.0243
H1c5c	0.653	0.3999	0.6038	0.0188
H2c5c	0.6465	0.1868	0.556	0.0188
H1c6c	0.6794	0.1592	0.4865	0.0186
H2c6c	0.6848	0.3319	0.5459	0.0186
H1c7c	0.6978	-0.1945	0.4978	0.0185
H2c7c	0.7029	-0.0301	0.5597	0.0185
H2c9c	0.7439	0.5234	0.316	0.0346
H1c9c	0.7248	0.456	0.3336	0.0346
H3c9c	0.7377	0.2187	0.3321	0.0346

Table S2. Anisotropic displacement parameters

Atom	U11	U22	U33	U12	U13	U23
Molecule *I*						
S1a	0.0105(5)	0.0156(5)	0.0144(5)	-0.0018(4)	-0.0019(4)	0.0031(4)
N1a	0.0121(16)	0.0182(17)	0.0114(16)	0.0007(13)	-0.0016(14)	0.0043(14)
N2a	0.0133(15)	0.0161(17)	0.0138(17)	-0.0017(13)	-0.0039(14)	0.0027(13)
N3a	0.0113(14)	0.0214(17)	0.0128(16)	-0.0035(14)	-0.0033(14)	-0.0017(14)
N4a	0.0134(16)	0.0144(17)	0.0164(17)	-0.0040(13)	-0.0034(14)	-0.0016(14)
N5a	0.0141(15)	0.0173(17)	0.0144(17)	-0.0056(14)	-0.0023(14)	0.0006(13)
N6a	0.0174(16)	0.0182(18)	0.0170(17)	0.0015(15)	-0.0043(14)	-0.0023(14)
C1a	0.014(2)	0.018(2)	0.017(2)	-0.0019(16)	-0.0032(18)	0.0059(17)
C2a	0.0123(18)	0.0130(19)	0.0150(19)	0.0038(16)	-0.0059(16)	0.0034(16)
C3a	0.0078(17)	0.0133(19)	0.0156(19)	0.0046(15)	-0.0043(15)	0.0012(16)
C4a	0.016(2)	0.018(2)	0.016(2)	0.0003(16)	-0.0051(17)	-0.0009(16)
C5a	0.0151(18)	0.0137(19)	0.0131(18)	-0.0011(16)	-0.0036(15)	0.0030(17)
C6a	0.0120(17)	0.0152(19)	0.0126(19)	-0.0018(16)	-0.0032(15)	0.0005(17)
C7a	0.0136(17)	0.0161(19)	0.0143(19)	-0.0007(16)	-0.0059(16)	-0.0017(17)
C8a	0.0068(17)	0.016(2)	0.014(2)	0.0032(16)	-0.0018(16)	-0.0007(16)
C9a	0.014(2)	0.023(2)	0.0124(19)	-0.0030(17)	-0.0037(16)	0.0036(17)
C10a	0.0145(18)	0.020(2)	0.0096(18)	0.0047(19)	-0.0005(16)	0.0041(17)
H1n1a	0.014503	0.021784	0.013621	0.000809	-0.001957	0.005109
H1n3a	0.013531	0.025676	0.015311	-0.004213	-0.003965	-0.002052
H1n4a	0.016114	0.017274	0.019657	-0.004774	-0.004137	-0.001929
H1c1a	0.017219	0.021162	0.02011	-0.002245	-0.003893	0.007118
H1c4a	0.019172	0.0213	0.019159	0.000414	-0.006083	-0.001079
H2c4a	0.019172	0.0213	0.019159	0.000414	-0.006083	-0.001079
H3c4a	0.019172	0.0213	0.019159	0.000414	-0.006083	-0.001079
H1c5a	0.01807	0.016443	0.015703	-0.001352	-0.004328	0.003608
H2c5a	0.01807	0.016443	0.015703	-0.001352	-0.004328	0.003608
H1c6a	0.014429	0.018251	0.015086	-0.002204	-0.003828	0.000639
H2c6a	0.014429	0.018251	0.015086	-0.002204	-0.003828	0.000639
H1c7a	0.0163	0.019297	0.017124	-0.000893	-0.007109	-0.002067
H2c7a	0.0163	0.019297	0.017124	-0.000893	-0.007109	-0.002067
H2c9a	0.017119	0.027998	0.014898	-0.003639	-0.004405	0.004321
H1c9a	0.017119	0.027998	0.014898	-0.003639	-0.004405	0.004321
H3c9a	0.017246	0.027833	0.015414	0.003729	-0.00402	-0.004334
Molecule *II*						
S1b	0.0156(5)	0.0153(5)	0.0171(5)	-0.0032(4)	-0.0030(4)	0.0026(4)
N1b	0.0171(17)	0.0244(18)	0.0084(16)	0.0015(14)	-0.0024(15)	-0.0012(15)
N2b	0.0164(16)	0.0209(18)	0.0126(17)	-0.0048(14)	-0.0024(14)	0.0016(13)
N3b	0.0133(15)	0.0166(17)	0.0150(16)	-0.0042(14)	-0.0015(14)	-0.0013(14)
N4b	0.0139(16)	0.0171(18)	0.0163(17)	-0.0017(14)	-0.0049(14)	-0.0020(15)
N5b	0.0136(15)	0.0163(17)	0.0171(18)	-0.0039(14)	-0.0027(14)	-0.0002(14)
N6b	0.0210(17)	0.0194(18)	0.0147(17)	0.0007(15)	-0.0050(14)	-0.0021(14)
C1b	0.018(2)	0.025(2)	0.017(2)	-0.0031(17)	-0.0064(18)	-0.0009(18)
C2b	0.0131(18)	0.015(2)	0.0135(19)	0.0021(16)	-0.0033(15)	-0.0018(16)
C3b	0.0149(18)	0.015(2)	0.016(2)	0.0013(16)	-0.0057(16)	0.0018(16)
C4b	0.023(2)	0.021(2)	0.016(2)	0.0008(17)	-0.0080(18)	-0.0048(16)
C5b	0.0176(18)	0.014(2)	0.0153(19)	-0.0019(16)	-0.0049(16)	0.0008(16)
C6b	0.0163(18)	0.014(2)	0.0176(19)	-0.0025(16)	-0.0056(16)	0.0017(17)
C7b	0.0174(18)	0.016(2)	0.017(2)	-0.0043(17)	-0.0064(16)	0.0017(17)
C8b	0.0102(18)	0.015(2)	0.018(2)	0.0031(16)	-0.0039(17)	-0.0005(17)
C9b	0.019(2)	0.026(2)	0.018(2)	-0.0030(18)	-0.0057(17)	0.0052(18)
C10b	0.0127(18)	0.019(2)	0.0108(18)	0.0056(18)	0.0013(16)	0.0006(17)
H1n1b	0.020504	0.029306	0.010115	0.001836	-0.002931	-0.001401
H1n3b	0.015986	0.019906	0.017961	-0.005034	-0.001845	-0.001523
H1n4b	0.016738	0.020573	0.019537	-0.002038	-0.005934	-0.002412

H1c1b	0.021803	0.029486	0.019997	-0.003678	-0.007641	-0.00107
H1c4b	0.027288	0.02518	0.018867	0.000929	-0.009561	-0.005798
H2c4b	0.027288	0.02518	0.018867	0.000929	-0.009561	-0.005798
H3c4b	0.027288	0.02518	0.018867	0.000929	-0.009561	-0.005798
H1c5b	0.021143	0.016548	0.018403	-0.00232	-0.005833	0.000976
H2c5b	0.021143	0.016548	0.018403	-0.00232	-0.005833	0.000976
H1c6b	0.019502	0.017312	0.021117	-0.002991	-0.006678	0.002031
H2c6b	0.019502	0.017312	0.021117	-0.002991	-0.006678	0.002031
H1c7b	0.020893	0.018653	0.01984	-0.005207	-0.007717	0.002056
H2c7b	0.020893	0.018653	0.01984	-0.005207	-0.007717	0.002056
H1c9b	0.022323	0.031243	0.021038	-0.003586	-0.006882	0.006198
H2c9b	0.022323	0.031243	0.021038	-0.003586	-0.006882	0.006198
H3c9b	0.022323	0.031243	0.021038	-0.003586	-0.006882	0.006198
Molecule *III*						
S1c	0.0148(5)	0.0164(5)	0.0173(5)	-0.0025(4)	-0.0021(4)	0.0051(4)
N1c	0.0183(17)	0.0255(18)	0.0119(17)	0.0014(15)	-0.0015(14)	0.0032(15)
N2c	0.0163(16)	0.0177(17)	0.0185(18)	-0.0012(14)	-0.0041(15)	0.0057(14)
N3c	0.0151(15)	0.0230(18)	0.0085(16)	-0.0064(14)	-0.0016(14)	-0.0025(14)
N4c	0.0219(18)	0.0263(19)	0.0133(17)	-0.0138(15)	-0.0031(15)	-0.0022(15)
N5c	0.0223(17)	0.0226(18)	0.0120(17)	-0.0096(15)	-0.0036(14)	-0.0015(14)
N6c	0.041(2)	0.055(3)	0.0173(18)	-0.030(2)	-0.0021(17)	-0.0047(19)
C1c	0.016(2)	0.019(2)	0.022(2)	-0.0015(17)	-0.0043(19)	0.0095(18)
C2c	0.0182(19)	0.015(2)	0.015(2)	-0.0003(16)	-0.0058(17)	0.0064(16)
C3c	0.0143(18)	0.015(2)	0.016(2)	0.0027(16)	-0.0040(16)	0.0049(17)
C4c	0.019(2)	0.026(2)	0.017(2)	0.0030(17)	-0.0079(18)	0.0016(17)
C5c	0.0186(18)	0.015(2)	0.0129(18)	-0.0021(16)	-0.0037(15)	0.0001(17)
C6c	0.0177(18)	0.0140(19)	0.0141(19)	-0.0048(16)	-0.0029(16)	0.0008(17)
C7c	0.0166(18)	0.016(2)	0.014(2)	-0.0106(16)	-0.0060(16)	0.0028(17)
C8c	0.0109(18)	0.020(2)	0.0094(19)	-0.0012(17)	0.0021(15)	-0.0016(16)
C9c	0.028(2)	0.040(3)	0.015(2)	-0.021(2)	-0.0021(18)	-0.0027(19)
C10c	0.020(2)	0.034(3)	0.010(2)	-0.007(2)	0.0029(18)	-0.0019(19)
H1n1c	0.021921	0.030654	0.014293	0.001706	-0.001772	0.003843
H1n3c	0.018155	0.027638	0.01017	-0.007644	-0.001922	-0.003026
H1n4c	0.026331	0.031598	0.015901	-0.016518	-0.003716	-0.002622
H1c1c	0.01865	0.023201	0.02613	-0.001812	-0.005106	0.011348
H1c4c	0.023323	0.03155	0.020154	0.00365	-0.009498	0.001905
H2c4c	0.023323	0.03155	0.020154	0.00365	-0.009498	0.001905
H3c4c	0.023323	0.03155	0.020154	0.00365	-0.009498	0.001905
H1c5c	0.022328	0.018324	0.015469	-0.002469	-0.004429	0.000077
H2c5c	0.022328	0.018324	0.015469	-0.002469	-0.004429	0.000077
H1c6c	0.021237	0.016756	0.016893	-0.005703	-0.003456	0.001003
H2c6c	0.021237	0.016756	0.016893	-0.005703	-0.003456	0.001003
H1c7c	0.019933	0.01958	0.017128	-0.012759	-0.007146	0.003412
H2c7c	0.019933	0.01958	0.017128	-0.012759	-0.007146	0.003412
H1c9c	0.034186	0.048428	0.018444	-0.025573	-0.002507	-0.003286
H2c9c	0.034186	0.048428	0.018444	-0.025573	-0.002507	-0.003286
H3c9c	0.034186	0.048428	0.018444	-0.025573	-0.002507	-0.003286

Table S3. Coordinates, isotropic displacement parameters and Fourier amplitudes of the displacive modulation function of cimetidine form *C* polytype 6M obtained with the (3+1)D superspace model for a single molecule. The waves are sorted by the term s for sinus, c for cosines and order n. The molecule shift parameters: 0.00021(3), 0.00871(8) and -0.00069(2) along *x*, *y* and *z*, respectively.

Atom	Wave	*x*	*y*	*z*	Ueq
S1		0.0181	0.4483	-0.8897	0.0156(2)
	s,1	0.00(3)	0.01(7)	-0.003(19)	
	c,1	0.00352(5)	0.01(5)	0.00186(4)	
N1		-0.2799	0.3297	-0.7126	0.0166(6)
	s,1	-0.01(4)	-0.02(8)	-0.01(2)	
	c,1	0.003(4)	-0.02(6)	0.003(4)	
C3		-0.1958	0.1912	-0.7524	0.0144(7)
	s,1	-0.01(4)	-0.02(8)	-0.01(2)	
	c,1	0.005(4)	-0.01(6)	0.002(3)	
N2		-0.2455	0.5011	-0.8258	0.0166(6)
	s,1	0.00(4)	0.02(8)	-0.01(2)	
	c,1	0.0020(5)	0.00(6)	0.005(4)	
C5		-0.0896	0.2248	-0.886	0.0155(7)
	s,1	0.00(3)	0.02(7)	-0.01(2)	
	c,1	0.0035(18)	0.01(5)	0.001(2)	
C2		-0.1752	0.2988	-0.822	0.0144(7)
	s,1	0.00(3)	0.01(8)	-0.01(2)	
	c,1	0.0034(17)	0.00(6)	0.003(3)	
C1		-0.3063	0.5113	-0.7586	0.0182(8)
	s,1	0.00(4)	0.00(8)	-0.01(2)	
	c,1	0.002(2)	-0.01(6)	0.005(5)	
N5		0.3384	0.0141	-0.9459	0.0172(6)
	s,1	0.00(3)	0.04(6)	0.000(19)	
	c,1	0.002(4)	0.00(5)	-0.004(6)	
N3		0.2873	0.2628	-1.0329	0.0156(6)
	s,1	0.00(3)	0.02(6)	-0.003(18)	
	c,1	0.002(3)	0.01(5)	-0.002(4)	
C6		0.1109	0.2645	-0.9607	0.0150(7)
	s,1	0.00(3)	0.02(7)	-0.004(19)	
	c,1	0.002(2)	0.01(5)	-0.0007(17)	
C10		0.3934	-0.1861	-0.9298	0.0171(7)
	s,1	0.00(3)	0.04(6)	0.003(19)	
	c,1	0.002(6)	-0.01(5)	-0.006(8)	
C7		0.2121	0.4082	-0.976	0.0156(7)
	s,1	0.00(3)	0.03(7)	-0.005(19)	
	c,1	0.0024(15)	0.01(5)	0.000(3)	
C8		0.3458	0.066	-1.0179	0.0137(7)
	s,1	0.00(3)	0.03(6)	0.000(19)	
	c,1	0.001(3)	0.00(5)	-0.004(6)	
C4		-0.1436	-0.0224	-0.7193	0.0189(9)
	s,1	-0.01(4)	-0.03(8)	-0.01(2)	
	c,1	0.007(6)	-0.01(6)	0.000(3)	
N6		0.4366	-0.3584	-0.9087	0.0245(7)
	s,1	0.00(3)	0.05(6)	0.008(19)	
	c,1	0.003(7)	-0.02(5)	-0.009(9)	
N4		0.4069	-0.0734	-1.0731	0.0170(6)
	s,1	0.00(3)	0.02(6)	0.002(19)	
	c,1	0.000(5)	0.01(5)	-0.005(7)	
C9		0.42	-0.0085	-1.1503	0.0220(8)
	s,1	0.00(3)	0.00(6)	0.000(19)	
	c,1	0.000(6)	0.02(5)	-0.004(6)	

H1c1		-0.3628	0.6336	-0.7439	0.021867
	s,1	-0.003	0.0031	-0.0109	
	c,1	-0.0004	-0.017	0.002	
H1n1		-0.3106	0.3049	-0.6663	0.019871
	s,1	-0.0117	-0.0276	-0.0139	
	c,1	-0.001	-0.0362	-0.0017	
H1c4		-0.0937	0.0636	-0.7	0.022723
	s,1	-0.0141	-0.0364	-0.0082	
	c,1	0.0065	-0.0153	-0.0021	
H2c4		-0.1915	-0.1147	-0.6802	0.022723
	s,1	-0.0136	-0.0393	-0.0182	
	c,1	0.006	-0.0226	-0.0044	
H3c4		-0.1118	-0.1535	-0.7565	0.022723
	s,1	-0.0056	-0.0158	-0.0161	
	c,1	0.006	-0.0092	-0.0038	
H1c5		-0.1095	0.2438	-0.9308	0.018623
	s,1	0.0043	0.0357	-0.0108	
	c,1	0.0033	0.0204	0.0004	
H2c5		-0.0709	0.0367	-0.8815	0.018623
	s,1	0.0003	0.0184	-0.0134	
	c,1	0.004	0.0114	-0.0022	
H1c6		0.117	0.0793	-0.9444	0.018034
	s,1	0.005	0.022	-0.0061	
	c,1	0.0008	0.0061	-0.0017	
H2c6		0.0896	0.2581	-1.0053	0.018034
	s,1	0.0029	0.0255	-0.0042	
	c,1	0.0008	0.0168	0	
H1c7		0.2058	0.5938	-0.9919	0.018747
	s,1	0.0034	0.0261	-0.0057	
	c,1	0.0023	0.0035	0.0024	
H2c7		0.2332	0.4154	-0.9313	0.018747
	s,1	0.0034	0.0311	-0.0044	
	c,1	0.0024	-0.0076	0.0004	
H1n3		0.2943	0.3067	-1.079	0.018712
	s,1	0.0043	0.0212	-0.004	
	c,1	-0.0001	0.0081	-0.0006	
H1n4		0.4408	-0.2106	-1.0622	0.020361
	s,1	0.0036	0.0262	0.0006	
	c,1	-0.0032	-0.0104	-0.0071	
H2c9		0.3569	-0.0239	-1.1617	0.026358
	s,1	0.0018	0.0188	0.0003	
	c,1	-0.0021	0.0448	-0.0033	
H1c9		0.467	-0.1338	-1.1804	0.026358
	s,1	-0.002	-0.0032	-0.0004	
	c,1	-0.0066	0.0085	-0.0062	
H3c9		0.4448	0.1752	-1.1599	0.026358
	s,1	0.0087	0.0039	-0.0045	
	c,1	0.0063	0.0102	-0.0021	

Molecular structure and geometry

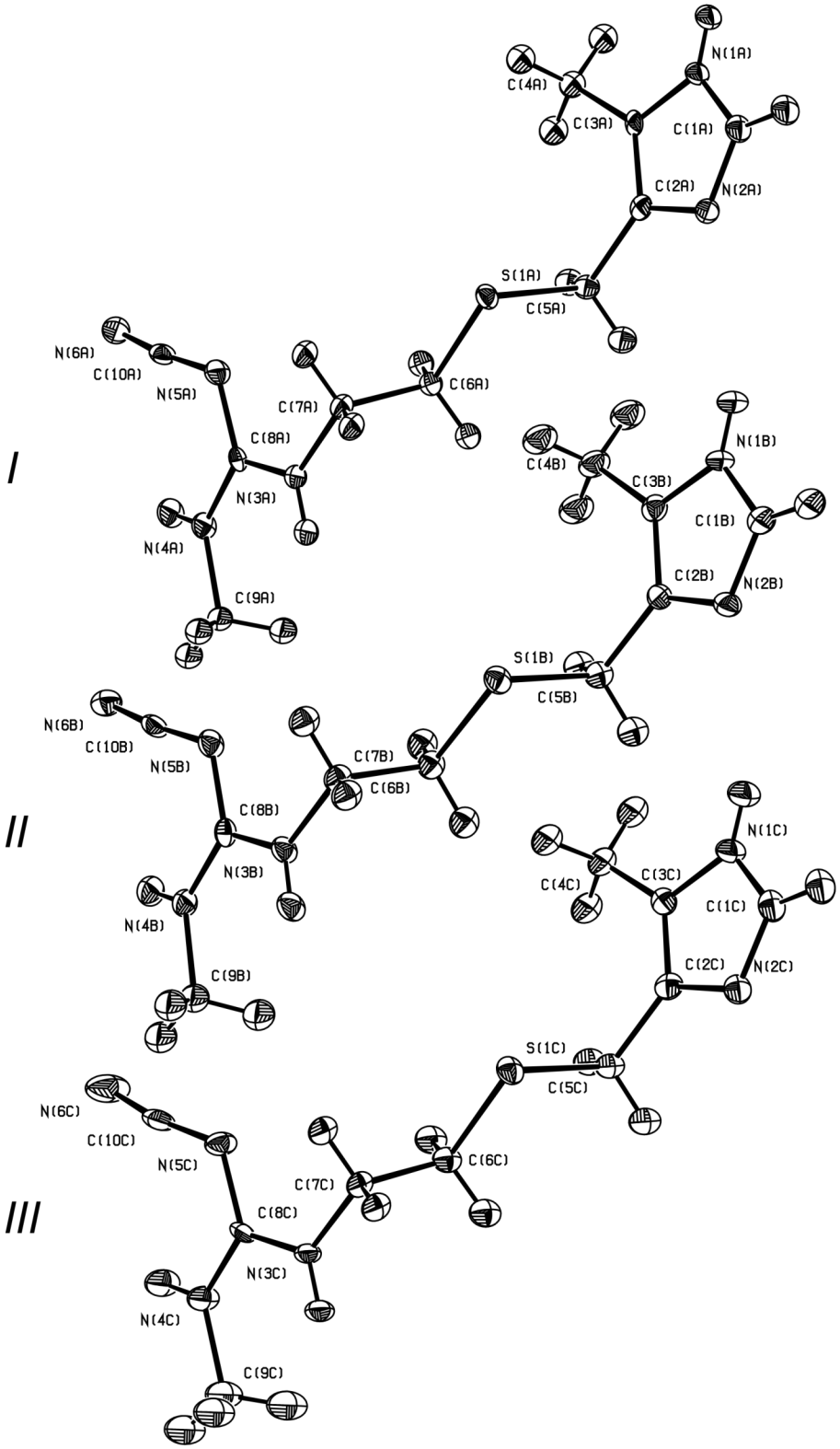

Figure S1. ORTEP plots of three similar molecules.

Table S4. Selected interatomic distances (Å) in three molecules

Atom - Atom	Molecule *I*	Molecule *II*	Molecule *III*
S1 – C5	1.822(4)	1.830(4)	1.831(4)
S1 – C6	1.820(3)	1.807(3)	1.809(3)
N1 – C3	1.376(4)	1.372(4)	1.380(4)
N1 – C1	1.349(5)	1.347(5)	1.352(5)
C3 – C2	1.368(5)	1.362(5)	1.366(5)
C3 – C4	1.499(5)	1.490(6)	1.488(6)
N2 – C2	1.396(5)	1.394(5)	1.399(5)
N2 – C1	1.318(4)	1.321(4)	1.317(4)
C5 – C2	1.491(4)	1.489(4)	1.484(4)
N5 – C10	1.321(5)	1.319(5)	1.323(5)
N5 – C8	1.357(5)	1.348(5)	1.340(5)
N3 – C7	1.465(4)	1.459(4)	1.452(4)
N3 – C8	1.327(5)	1.331(5)	1.333(5)
C6 – C7	1.515(5)	1.514(5)	1.526(5)
C10 – N6	1.169(5)	1.166(5)	1.148(6)
C8 – N4	1.329(4)	1.338(4)	1.329(4)
N4 – C9	1.444(5)	1.447(5)	1.448(5)

Table S5. Angles (°) in three molecules

Atom – Atom – Atom	Molecule *I*	Molecule *II*	Molecule *III*
C5-S1-C6	97.67(15)	98.74(16)	98.27(16)
C3-N1-C1	107.5(3)	107.8(3)	107.8(3)
C3-N1-H1n1	126.25	126.1	126.09
C1-N1-H1n1	126.26	126.09	126.09
N1-C3-C2	105.1(3)	105.5(3)	104.9(3)
N1-C3-C4	123.4(3)	123.0(3)	122.7(3)
C2-C3-C4	131.4(3)	131.6(3)	132.3(3)
C2-N2-C1	104.0(3)	104.6(3)	104.3(3)
S1-C5-C2	111.2(3)	109.6(3)	110.8(3)
S1-C5-H1c5	109.47	109.47	109.47
S1-C5-H2c5	109.47	109.47	109.47
C2-C5-H1c5	109.47	109.47	109.47
C2-C5-H2c5	109.47	109.47	109.47
H1c5-C5-H2c5	107.65	109.32	108.07
C3-C2-N2	110.7(3)	110.2(3)	110.8(3)
C3-C2-C5	127.0(3)	126.6(3)	126.5(3)
N2-C2-C5	122.3(3)	123.1(3)	122.7(3)
N1-C1-N2	112.7(3)	111.9(3)	112.2(3)
N1-C1-H1c1	123.65	124.06	123.88
N2-C1-H1c1	123.65	124.06	123.88
N2-C1-H1n1	133.33	132.58	132.89
C10-N5-C8	117.8(3)	118.1(3)	119.2(3)
C7-N3-C8	122.8(3)	123.4(3)	122.5(3)
C7-N3-H1n3	118.58	118.28	118.77
C8-N3-H1n3	118.58	118.27	118.77
S1-C6-C7	110.3(2)	110.0(3)	110.9(2)
S1-C6-H1c6	109.47	109.47	109.47
S1-C6-H2c6	109.47	109.47	109.47
C7-C6-H1c6	109.47	109.47	109.47
C7-C6-H2c6	109.47	109.47	109.47
H1c6-C6-H2c6	108.67	108.95	108
N5-C10-N6	174.1(3)	174.5(3)	171.7(4)
N3-C7-C6	111.1(3)	111.2(3)	110.5(3)
N3-C7-H1c7	109.47	109.47	109.47
N3-C7-H2c7	109.47	109.47	109.47
C6-C7-H1c7	109.47	109.47	109.47
C6-C7-H2c7	109.47	109.48	109.47

H1c7-C7-H2c7	107.83	107.64	108.38
N5-C8-N3	117.5(3)	117.7(3)	117.5(3)
N5-C8-N4	122.9(3)	123.0(3)	123.1(3)
N3-C8-N4	119.6(3)	119.3(3)	119.4(3)
C3-C4-H1c4	109.47	109.47	109.47
C3-C4-H2c4	109.47	109.47	109.47
C3-C4-H3c4	109.48	109.47	109.47
H1c4-C4-H2c4	109.47	109.47	109.47
H1c4-C4-H3c4	109.47	109.47	109.47
H2c4-C4-H3c4	109.47	109.48	109.47
C8-N4-C9	123.0(3)	123.3(3)	124.1(3)
C8-N4-H1n4	118.51	118.35	117.95
C9-N4-H1n4	118.51	118.35	117.95
N4-C9-H2c9	109.47	109.47	109.47
N4-C9-H1c9	109.47	109.47	109.47
N4-C9-H3c9	109.47	109.47	109.47
H2c9-C9-H1c9	109.47	109.47	109.47
H2c9-C9-H3c9	109.47	109.47	109.47
H1c9-C9-H3c9	109.47	109.47	109.47

Table S6. Optimal planes and deviations (Å) of individual atoms in three molecules

Coefficients $m1$, $m2$, $m3$ and d in equations of the best planes expressed by $m1x + m2y + m3z + d = 0$			
Plane	Molecule *I*	Molecule *II*	Molecule *III*
I Imidazole ring	55.8136; -3.3305; 8.3632; -31.2817	57.0636; -3.4329; 6.3541; -21.1106	54.5410; -3.3023; 9.1453; -40.1964
II C2-C5-S	40.8443; 3.2623; 12.468; -28.3229	42.8839; 2.9089; 13.647; -23.2002	41.4522; 3.2255; 12.552; -35.1599
III S-C6-C7-N3	35.1488; 2.8349; 14.643; -26.7632	34.5608; -2.6874; 15.126; -21.2699	39.5916; 2.5882; 15.026; -35.4205
IV Guanidine group	63.2626; -3.1328; 3.4701; -35.4584	62.8674; -3.1613; 3.6652; -24.9131	58.0650; -3.4533; 2.6449; -42.1468
Deviations (Å) from the best plane			
	Molecule *I*	Molecule *II*	Molecule *III*
I Imidazole ring			
C1*	0.0007(45)	0.0016(47)	0.0052(47)
C2*	-0.0006(43)	0.0014(43)	0.0021(45)
C3*	0.0009(42)	-0.0007(43)	0.0005(44)
N1*	-0.0006(37)	-0.0002(38)	-0.0023(39)
N2*	0.0000(37)	-0.0012(38)	-0.0029(39)
C4	0.0420(63)	0.0084(65)	0.0481(67)
C5	0.0185(63)	0.0746(64)	0.0342(66)
H1c1	0.0020	0.0046	0.0152
H1n1	-0.0021	-0.0010	-0.0078
II C2-C5-S			
C2*	0.0000(52)	0.0000(53)	0.0000(54)
C5*	0.0000(51)	0.0000(53)	0.0000(53)
S1*	0.0000(10)	0.0000(11)	0.0000(11)
C7	0.3957(78)	0.4333(76)	0.2576(81)
N3	0.6567(129)	0.6088(126)	0.5474(133)
C6	0.3226(82)	0.2928(82)	0.2944(84)
III S-C6-C7-N3			
S1*	0.0000(10)	-0.0014(11)	0.0012(11)
C6*	-0.0005(47)	0.0203(49)	-0.0180(50)
C7*	-0.0007(46)	0.0268(47)	-0.0224(48)
N3*	0.0005(40)	-0.0185(41)	0.0158(41)
C5	0.0183(81)	0.1134(83)	-0.1161(84)

IV Guanidine group			
C8*	0.0061(35)	0.0054(35)	0.0059(36)
N3*	-0.0014(38)	-0.0012(38)	-0.0014(39)
N4*	-0.0016(38)	-0.0013(39)	-0.0017(42)
N5*	-0.0015(39)	-0.0013(39)	-0.0015(40)
C7	-0.1158(57) 0.1142(58)	-0.1070(57)	-0.1243(58)
C9	-0.0438(56)	0.1064(59)	0.0354(65)
C10	-0.1017(70)	-0.0271(56)	-0.0416(61)
N6	0.0643	-0.0582(71)	-0.0989(77)
H1n3	-0.0799	0.0609	0.0701
H1n4		-0.074	-0.0308
Dihedral angles (°) between the best planes in each molecule			
Plane-Plane	Molecule *I*	Molecule *II*	Molecule *III*
I – II	88.8(2)	88.4(2)	86.9(2)
I – III	85.8(3)	89.5(3)	79.9(3)
I – IV	17.95(15)	10.95(15)	21.64(15)
II – III	10.3(3)	8.9(2)	11.2(3)
II – IV	85.96(17)	89.74(18)	81.31(17)
III – IV	86.0(3)	87.0(3)	85.4(3)
Dihedral angles (°) between identical planes of *I*, *II* and *III* molecules at the similar orientations			
Plane-Plane	*I– II*	*I– III*	*II – III*
I – I	6.78(15)	2.89(15)	9.64(15)
II – II	5.5(4)	0.6(3)	5.0(4)
III – III	2.4(3)	4.2(4)	3.9(2)
IV – IV	0.82(15)	5.46(15)	5.31(15)

* Atoms with asterisks define the atomic plane

Molecule packing

Table S7. Inter-molecular H-bonds

Donor[a]	H atom[a]	Acceptor[a]	D-H (Å)	H...A (Å)	D-A (Å)	A-H...D (°)
H-bonds between *L*-layer						
N4a	H1n4a	N6b	0.87	2.18	2.986(4)	153.05
N4b	H1n4b	N6a	0.87	2.19	2.996(4)	153.47
N4c	H1n4c	N6c’	0.87	2.08	2.853(5)	148.44
H-bonds in *L*-layer						
N3a	H1n3a	N2a’	0.87	2.25	3.060(5)	155.36
N3b	H1n3b	N2c	0.87	2.23	3.036(5)	153.91
N3c	H1n3c	N2b	0.87	2.17	2.975(5)	154.63
N1a	H1n1a	N5a’	0.87	2.57	3.335(4)	147.48
N1b	H1n1b	N5c	0.87	2.12	2.937(4)	156.69
N1c	H1n1c	N5b	0.87	2.87	3.613(5)	145.10

[a] *a*, *b* and *c* letters presenting in labels of atoms indicate property of molecule *I*, *II* and *III*, respectively.

Generation of possible polytypes of cimetidine form *C* using the (3+1)D superspace model

Modeled polytype 1M of cimetidine form C

Table S8. Atomic coordinates of modelled polytype 1M (space group *P*2/*c*; the lattice constants at 295 K: a = 13.827, b = 4.887, c = 19.132 Å, β = 73.749)

Atom	x	x	z
S1	0.0166	0.4535	0.1096
N1	0.7156	0.3229	0.2869
C3	0.801	0.19	0.2463
N2	0.7517	0.5096	0.1746
C5	0.9077	0.2375	0.1125
C2	0.822	0.3062	0.1773
C1	0.6902	0.5102	0.2419
N5	0.333	0.9975	0.0505
N3	0.2837	0.256	0.9639
C6	0.1072	0.2678	0.037
C10	0.3863	0.7899	0.0654
C7	0.2096	0.4031	0.0219
C8	0.3405	0.0535	0.9785
C4	0.8543	0.9722	0.2778
N6	0.4286	0.6096	0.085
N4	0.4	0.9128	0.9228
C9	0.4143	0.9835	0.8459
H1	0.6321	0.6313	0.255
H2	0.6799	0.2809	0.3296
H3	0.9014	0.052	0.298
H4	0.8033	0.8644	0.313
H5	0.8861	0.8437	0.2377
H6	0.8878	0.2655	0.0669
H7	0.9254	0.048	0.1141
H8	0.1117	0.0796	0.0525
H9	0.0853	0.2677	0.9927
H10	0.2049	0.5894	0.0077
H11	0.2311	0.4015	0.067
H12	0.2908	0.3033	0.9184
H13	0.432	0.7676	0.9309
H14	0.3517	0.985	0.8331
H15	0.4604	0.8657	0.8132
H16	0.4427	0.1745	0.8374

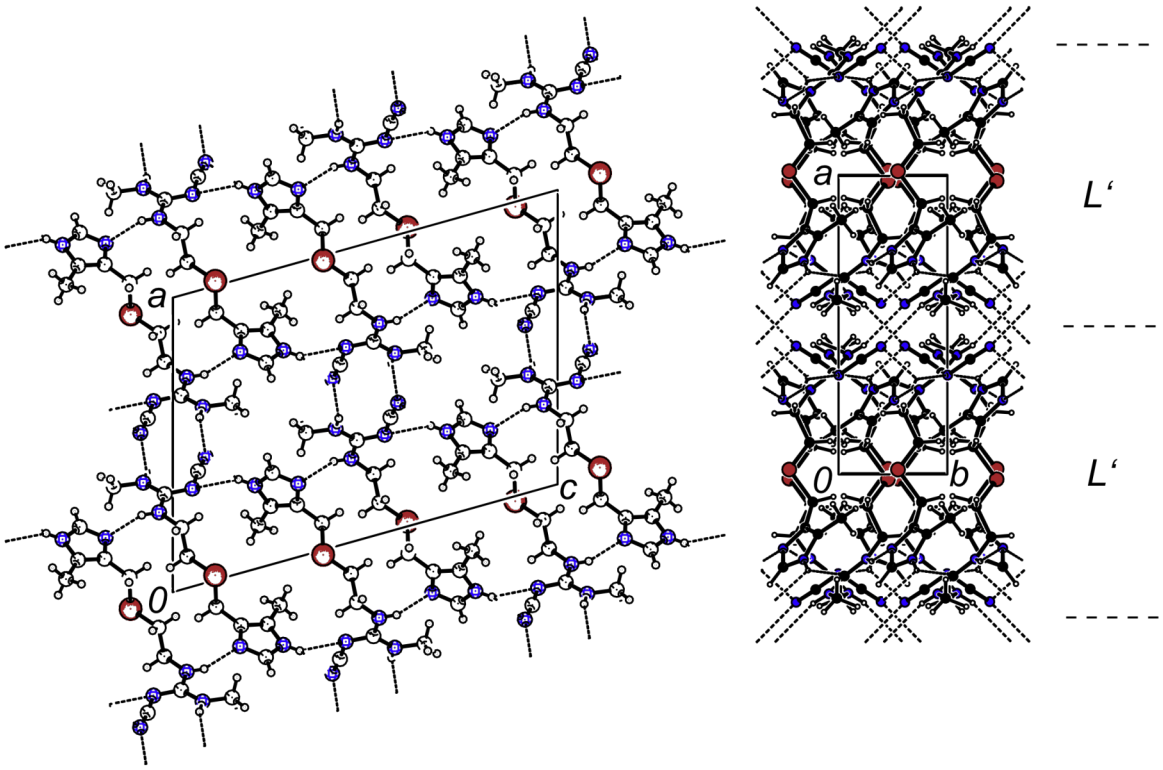

Figure S2. Packing of molecules in cimetidine form *C* modelled polytype 1M. The *ac* (left) and *ab* (right) structure projections are shown. Broun circles indicate S1 atoms, which are associated with centres of molecules. *L*' indicate the layer with $y \approx 0.5$ for centres of the molecules. Only one *L* layer consisting of identical molecule is associated with the *a* lattice constant.

Modeled polytype 2M of cimetidine form C

Table S9. Atomic coordinates of modelled polytype 2M (space group *C*2/*c*; the lattice constants at 295 K: a = 27.654, b = 4.887, c = 19.132 Å, β = 73.749)

Atom	x	y	z
S1	0.0087	0.4504	0.11
N1	0.8584	0.3225	0.2876
C3	0.901	0.189	0.247
N2	0.8763	0.5076	0.1751
C5	0.9542	0.2345	0.1131
C2	0.9114	0.3042	0.178
C1	0.8456	0.5092	0.2425
N5	0.1667	0.991	0.0507
N3	0.1422	0.2508	0.9643
C6	0.054	0.2637	0.0375
C10	0.1934	0.7827	0.0655
C7	0.1052	0.3981	0.0223
C8	0.1705	0.0476	0.9788
C4	0.9277	0.9715	0.2787
N6	0.2145	0.6017	0.085
N4	0.2002	0.9069	0.9231
C9	0.2075	0.9787	0.8461
Hc1	0.8166	0.63	0.2555
Hn1	0.8405	0.2804	0.3303
H1c4	0.9515	0.051	0.2982
H2c4	0.9022	0.865	0.3142
H3c4	0.9432	0.8413	0.2387
H1c5	0.9443	0.2622	0.0675
H2c5	0.963	0.0451	0.1148
H1c6	0.0561	0.0754	0.053
H2c6	0.043	0.2637	0.9931
H1c7	0.103	0.5845	0.0083
H2c7	0.116	0.3959	0.0675
Hn3	0.1458	0.2984	0.9189
Hn4	0.2161	0.7611	0.9311
H2c9	0.176	0.9864	0.8337
H1c9	0.2297	0.8573	0.8134
H3c9	0.2227	0.1677	0.8375

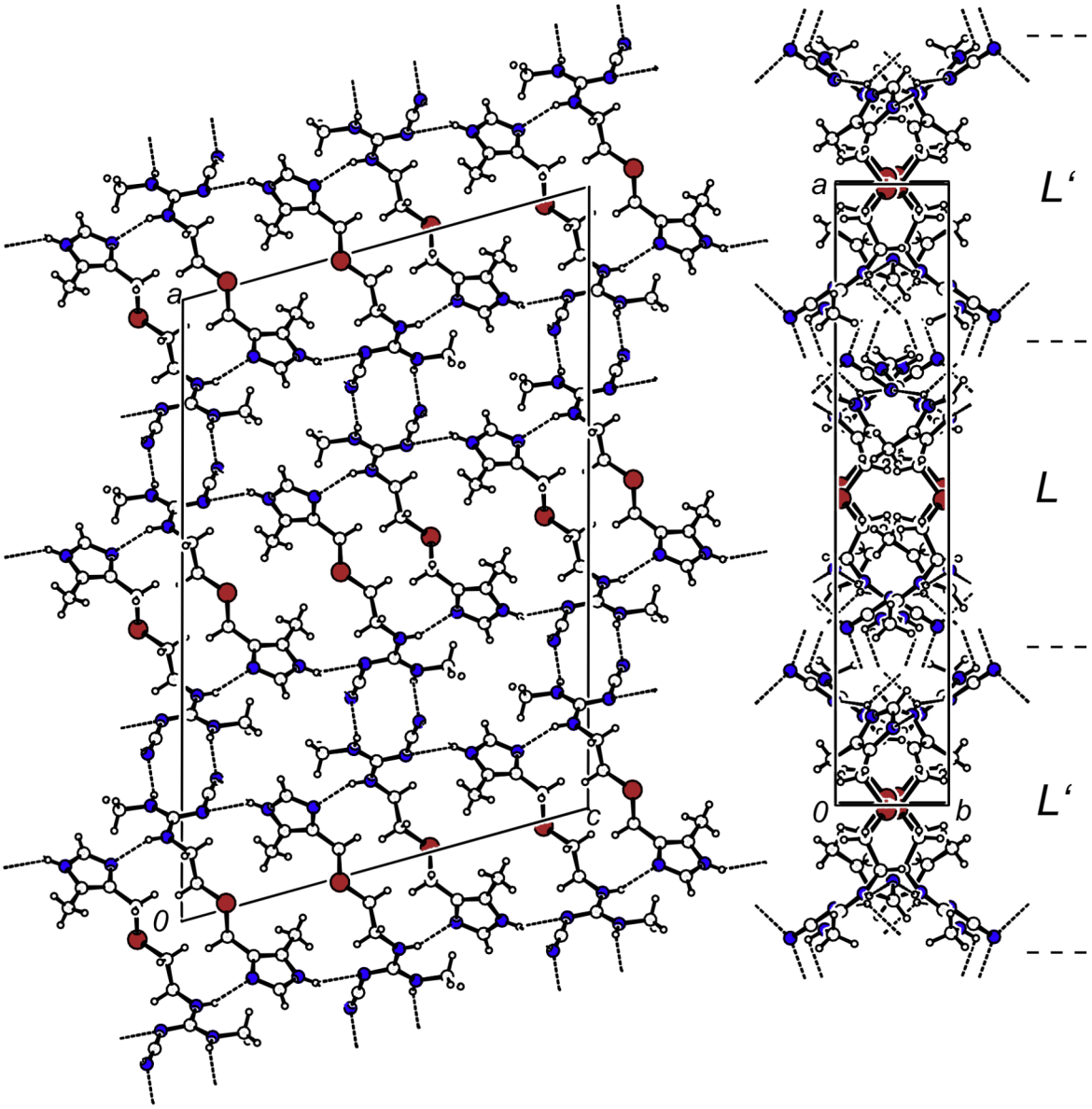

Figure S3. Packing of molecules in cimetidine form *C* modelled polytype 2M. The *ac* (left) and *ab* (right) structure projections are shown. Broun circles indicate S atoms, which are associated with centres of molecules. *L* and *L*' indicate the layers with $y \approx 0$ and $y \approx 0.5$, respectively for centres of the molecules. Two *L* layers, (*L'L*), consisting of identical molecule are associated with the *a* lattice constant.

Modeled polytype 3M of cimetidine form C

Table S10. Atomic coordinates of modelled polytype 3M (space group *P*2/*c*; the lattice constants at 295 K: *a* = 41.481, *b* = 4.887, *c* = 19.132 Å, *β* = 73.749)

Atom	x	y	z
Molecule *I*			
S1a	0.0059	0.4493	0.1101
N1a	0.9057	0.3224	0.2878
C3a	0.9341	0.1887	0.2473
N2a	0.9176	0.507	0.1753
C5a	0.9696	0.2335	0.1133
C2a	0.941	0.3035	0.1782
C1a	0.8972	0.5089	0.2427
N5a	0.1112	0.9889	0.0509
N3a	0.0949	0.2491	0.9645
C6a	0.0361	0.2623	0.0376
C10a	0.129	0.7804	0.0656
C7a	0.0702	0.3965	0.0225
C8a	0.1138	0.0457	0.9789
C4a	0.9519	0.9712	0.279
N6a	0.1431	0.5992	0.085
N4a	0.1335	0.9051	0.9231
C9a	0.1384	0.9772	0.8462
H1	0.8778	0.6296	0.2557
H2	0.8938	0.2803	0.3306
H3	0.9678	0.0508	0.2985
H4	0.9349	0.8648	0.3145
H5	0.9623	0.8409	0.239
H6	0.9629	0.2611	0.0677
H7	0.9754	0.0441	0.1151
H8	0.0374	0.0741	0.0532
H9	0.0288	0.2624	0.9933
H10	0.0688	0.583	0.0085
H11	0.0774	0.3942	0.0676
H12	0.0973	0.2968	0.9191
H13	0.1441	0.759	0.9312
H14	0.1174	0.9854	0.8338
H15	0.1531	0.8555	0.8135
H16	0.1486	0.166	0.8377
Molecule *II*			
S1b	0.3445	0.9086	0.1152
N1b	0.2474	0.8443	0.2981
C3b	0.2743	0.6915	0.2594
N2b	0.2573	0.9781	0.1816
C5b	0.3082	0.6839	0.1242
C2b	0.2804	0.7763	0.1877
C1b	0.2381	0.0116	0.2496
N5b	0.4503	0.4374	0.0603
N3b	0.4339	0.6999	0.9747
C6b	0.3751	0.7118	0.0468
C10b	0.4684	0.2323	0.0748
C7b	0.4091	0.847	0.0321

C8b	0.4529	0.4969	0.9887
C4b	0.2915	0.4855	0.295
N6b	0.4831	0.0541	0.0937
N4b	0.4731	0.359	0.9324
C9b	0.4779	0.4352	0.8557
H17	0.2195	0.1291	0.2644
H19	0.2383	0.8309	0.347
H21	0.3089	0.5775	0.3128
H23	0.2763	0.4016	0.337
H25	0.3021	0.3472	0.2601
H27	0.3011	0.6903	0.0799
H29	0.3142	0.4968	0.1326
H31	0.3763	0.528	0.0648
H33	0.3684	0.7038	0.0017
H35	0.4076	0.0351	0.0166
H37	0.4161	0.8519	0.0769
H39	0.4366	0.7471	0.9291
H41	0.484	0.2181	0.9449
H43	0.4565	0.4246	0.8458
H45	0.4928	0.2981	0.8268
H47	0.4868	0.6095	0.848
Molecule *III*			
S1c	0.6673	0.019	0.1027
N1c	0.5664	0.8488	0.2726
C3c	0.5954	0.7214	0.2323
N2c	0.5791	0.0486	0.1624
C5c	0.6323	0.7893	0.1013
C2c	0.603	0.847	0.1648
C1c	0.5579	0.0413	0.2287
N5c	0.7766	0.6535	0.0483
N3c	0.7583	0.875	0.9591
C6c	0.6995	0.8538	0.0306
C10c	0.7957	0.4671	0.0677
C7c	0.7323	0.0153	0.0147
C8c	0.7788	0.6913	0.9762
C4c	0.6126	0.5042	0.2644
N6c	0.8102	0.3097	0.0933
N4c	0.8001	0.5522	0.9226
C9c	0.8034	0.5942	0.8445
H18	0.5395	0.1706	0.245
H20	0.5566	0.8297	0.32
H22	0.6288	0.5925	0.2866
H24	0.5967	0.4132	0.3035
H26	0.624	0.383	0.227
H28	0.6262	0.8132	0.0564
H30	0.6392	0.601	0.104
H32	0.7031	0.6697	0.0454
H34	0.6921	0.8426	0.9862
H36	0.7289	0.1979	0.9969
H38	0.7392	0.0347	0.0588
H40	0.7604	0.9129	0.9119
H42	0.8127	0.4296	0.9348
H44	0.783	0.5324	0.8322
H46	0.8222	0.4873	0.8156
H48	0.807	0.789	0.8318

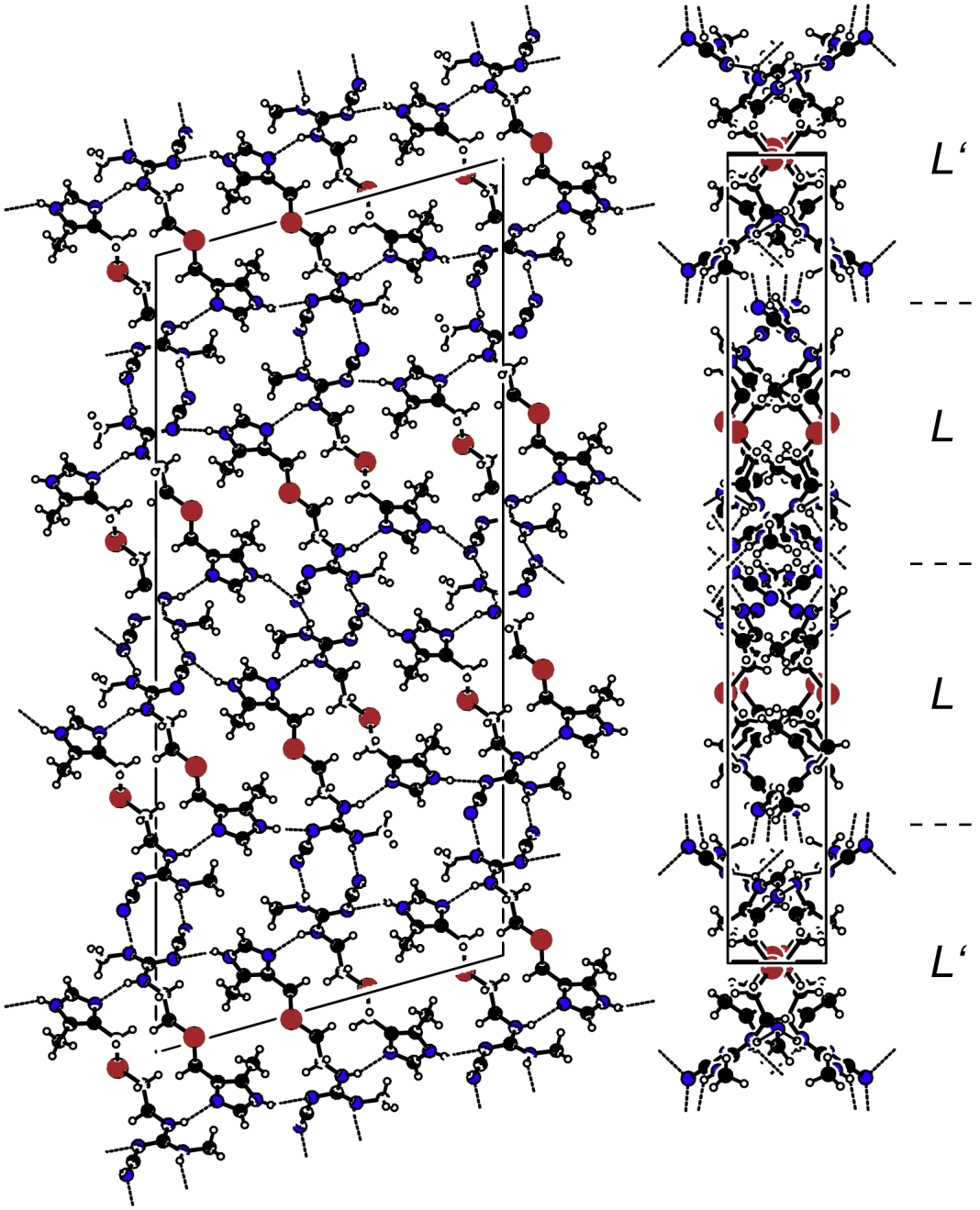

Figure S4. Packing of molecules in cimetidine form *C* modelled polytype 3M. The *ac* (left) and *ab* (right) structure projections are shown. Broun circles indicate S atoms, which are associated with centres of molecules. *L* and *L*’ indicate the layers with $y \approx 0$ and $y \approx 0.5$, respectively for centres of the molecules. Three *L* layers, (*L’LL*), consisting of 3 similar molecules are associated with the *a* lattice constant.

Modeled polytype 4M of cimetidine form C

Table S11. Atomic coordinates of modelled polytype 4M (space group *C*2/*c*; the lattice constants at 295 K: *a* = 55.308, *b* = 4.887, *c* = 19.132 Å, β = 73.749)

Atom	x	y	z
Molecule *I*			
S1a	0.1265	0.5	0.1047
N1a	0.0509	0.3403	0.2767
C3a	0.0725	0.2117	0.2363
N2a	0.0603	0.5374	0.166
C5a	0.1	0.2747	0.1045
C2a	0.0781	0.3352	0.1684
C1a	0.0446	0.5317	0.2325
N5a	0.2076	0.1069	0.0487
N3a	0.1943	0.3397	-0.0397
C6a	0.1502	0.3287	0.0324
C10a	0.2216	0.9139	0.0667
C7a	0.1751	0.4821	0.0167
C8a	0.2093	0.1503	-0.0233
C4a	0.0856	0.9941	0.2681
N6a	0.2324	0.7495	0.0905
N4a	0.2249	0.0106	-0.0776
C9a	0.2277	0.0613	-0.1553
H1	0.0305	0.6586	0.2479
H3	0.043	0.3134	0.3226
H5	0.0976	0.0794	0.2896
H7	0.0734	0.8978	0.3059
H9	0.0939	0.8704	0.2298
H11	0.0953	0.3003	0.0593
H13	0.1049	0.086	0.1067
H15	0.1524	0.1432	0.0473
H17	0.1447	0.3211	0.988
H19	0.173	0.6658	0
H21	0.1804	0.4949	0.0611
H23	0.1959	0.3806	-0.0864
H25	0.2339	0.8809	-0.0667
H27	0.2123	0.0207	-0.1678
H29	0.241	0.9506	-0.1855
H31	0.2319	0.2548	-0.1668
Molecule *II*			
S1b	0.8825	0.417	0.114
N1b	0.8089	0.3367	0.2959
C3b	0.8294	0.1891	0.2566
N2b	0.8168	0.4844	0.1804
C5b	0.8551	0.1955	0.1216
C2b	0.8341	0.282	0.1856
C1b	0.8021	0.5092	0.2483
N5b	0.9615	0.9443	0.0577
N3b	0.9493	0.2081	-0.028
C6b	0.9052	0.222	0.0445
C10b	0.975	0.7371	0.072
C7b	0.9308	0.3556	0.0297
C8b	0.9635	0.0039	-0.0141
C4b	0.8425	0.9798	0.2911
N6b	0.9859	0.5569	0.0907
N4b	0.9785	0.8652	-0.0703

C9b	0.9821	0.9417	-0.147
H2	0.788	0.6273	0.2624
H4	0.8014	0.3139	0.3428
H6	0.8552	0.0678	0.3093
H8	0.8307	0.8886	0.331
H10	0.8503	0.8433	0.2546
H12	0.8499	0.2082	0.0769
H14	0.8596	0.0077	0.1281
H16	0.9061	0.0367	0.0618
H18	0.9001	0.2169	-0.0004
H20	0.9298	0.5434	0.0148
H22	0.9361	0.3573	0.0746
H24	0.9513	0.2558	-0.0735
H26	0.9865	0.7216	-0.0592
H28	0.9662	0.9399	-0.1576
H30	0.9931	0.8083	-0.1771
H32	0.9894	0.1198	-0.1547

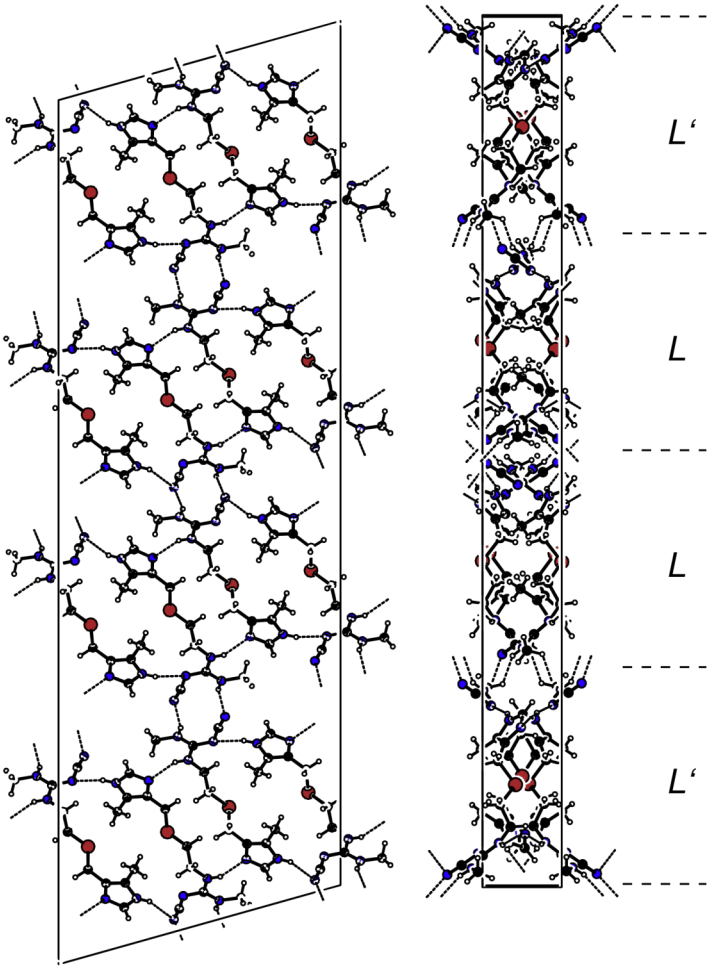

Figure S5. Packing of molecules in cimetidine form *C* modelled polytype 4M. The *ac* (left) and *ab* (right) structure projections are shown. Broun circles indicate S atoms, which are associated with centres of molecules. *L* and *L*’ indicate the layers with $y \approx 0$ and $y \approx 0.5$, respectively for centres of the molecules. Four *L* layers, (*L’L’LL*), consisting of 2 similar molecules are associated with the *a* lattice constant.

Modeled polytype 5M of cimetidine form C

Table S12. Atomic coordinates of modelled polytype 5M (space group *P*2/*c*; the lattice constants at 295 K: *a* = 69.135, *b* = 4.887, *c* = 19.132 Å, β = 73.749)

Atom	x	y	z
Molecule *I*			
S1a	0.0036	0.4485	0.1102
N1a	0.9435	0.3224	0.288
C3a	0.9605	0.1884	0.2475
N2a	0.9506	0.5064	0.1755
C5a	0.9818	0.2328	0.1135
C2a	0.9647	0.303	0.1784
C1a	0.9384	0.5086	0.2428
N5a	0.0668	0.9873	0.0509
N3a	0.057	0.2478	0.9646
C6a	0.0217	0.2613	0.0377
C10a	0.0774	0.7786	0.0656
C7a	0.0422	0.3953	0.0226
C8a	0.0683	0.0443	0.979
C4a	0.9712	0.9711	0.2792
N6a	0.0859	0.5973	0.085
N4a	0.0801	0.9036	0.9232
C9a	0.0831	0.976	0.8463
H1	0.9268	0.6292	0.2558
H4	0.9364	0.2803	0.3308
H7	0.9807	0.0507	0.2987
H10	0.961	0.8647	0.3147
H13	0.9774	0.8406	0.2393
H16	0.9778	0.2602	0.0679
H19	0.9853	0.0434	0.1153
H22	0.0225	0.073	0.0533
H25	0.0173	0.2614	0.9934
H28	0.0413	0.5818	0.0086
H31	0.0465	0.3928	0.0678
H34	0.0584	0.2956	0.9192
H37	0.0865	0.7575	0.9312
H40	0.0704	0.9846	0.8339
H43	0.0919	0.8541	0.8136
H46	0.0892	0.1647	0.8378
Molecule *II*			
S1b	0.1998	0.5318	0.1014
N1b	0.1392	0.3534	0.2698
C3b	0.1566	0.2272	0.2295
N2b	0.1469	0.5562	0.16
C5b	0.179	0.2996	0.0991
C2b	0.1612	0.3549	0.1624
C1b	0.1341	0.5471	0.2261
N5b	0.2658	0.1832	0.0478
N3b	0.2546	0.3978	0.958
C6b	0.2193	0.3705	0.0293
C10b	0.2774	0.0008	0.068
C7b	0.2389	0.5368	0.0133
C8b	0.2671	0.2177	0.9757
C4b	0.1669	0.01	0.2616
N6b	0.2862	0.8477	0.0947
N4b	0.28	0.0788	0.9224
C9b	0.2818	0.1155	0.8441
H2	0.1231	0.678	0.2431
H5	0.1335	0.3382	0.318

H8	0.1766	0.0998	0.2844
H11	0.1574	0.9217	0.3013
H14	0.1738	0.8904	0.2247
H17	0.1753	0.3229	0.0543
H20	0.1832	0.1115	0.1019
H23	0.2217	0.1871	0.0439
H26	0.2149	0.3573	0.9849
H29	0.2366	0.7188	0.9947
H32	0.243	0.5601	0.0572
H35	0.2558	0.434	0.9105
H38	0.2878	0.9604	0.9354
H41	0.2696	0.0412	0.8318
H44	0.2936	0.0113	0.8158
H47	0.2833	0.3113	0.8307
Molecule *III*			
S1c	0.8074	0.4003	0.1162
N1c	0.7495	0.3497	0.3002
C3c	0.7655	0.1927	0.262
N2c	0.7552	0.4721	0.1829
C5c	0.7856	0.1733	0.1265
C2c	0.769	0.2706	0.1897
C1c	0.7438	0.5126	0.251
N5c	0.871	0.928	0.0624
N3c	0.8611	0.1904	0.9769
C6c	0.8258	0.2015	0.0488
C10c	0.8819	0.7239	0.0769
C7c	0.8462	0.3374	0.0342
C8c	0.8725	0.9878	0.9908
C4c	0.7757	0.9892	0.2985
N6c	0.8908	0.5467	0.0958
N4c	0.8847	0.8505	0.9345
C9c	0.8875	0.9273	0.8579
H3	0.7328	0.6296	0.2663
H6	0.7445	0.3431	0.3506
H9	0.7863	0.0842	0.316
H12	0.7668	0.9107	0.342
H15	0.7821	0.8492	0.2648
H18	0.7813	0.1748	0.0825
H21	0.7892	0.9868	0.1364
H24	0.8266	0.0189	0.0674
H27	0.8219	0.1915	0.0035
H30	0.8453	0.5258	0.0183
H33	0.8503	0.3442	0.0789
H36	0.8627	0.2373	0.9313
H39	0.8913	0.7111	0.9481
H42	0.8747	0.9113	0.8485
H45	0.8966	0.7868	0.8299
H48	0.8927	0.0983	0.8503
Molecule *IV*			
S1d	0.4055	0.922	0.1134
N1d	0.3464	0.8321	0.2945
C3d	0.3629	0.6877	0.2549
N2d	0.3528	0.9882	0.1797
C5d	0.3836	0.7025	0.1201
C2d	0.3668	0.7855	0.1843
C1d	0.341	0.0078	0.2475
N5d	0.4687	0.4484	0.0561
N3d	0.4589	0.7129	0.9704
C6d	0.4236	0.7281	0.0431
C10d	0.4793	0.24	0.0703
C7d	0.4441	0.8607	0.0283

C8d	0.4702	0.5081	0.9843
C4d	0.3734	0.4763	0.2887
N6d	0.488	0.0585	0.089
N4d	0.4821	0.3689	0.9281
C9d	0.4851	0.4455	0.8514
H49	0.3296	0.1261	0.2612
H51	0.3401	0.8036	0.3402
H53	0.3834	0.5619	0.3071
H55	0.3638	0.3807	0.3274
H57	0.3797	0.341	0.2513
H59	0.3795	0.719	0.0751
H61	0.3871	0.5143	0.1254
H63	0.4243	0.5419	0.06
H65	0.4195	0.7247	0.9983
H67	0.4433	0.0483	0.0138
H69	0.4484	0.8605	0.0733
H71	0.4605	0.7611	0.925
H73	0.4885	0.2237	0.9383
H75	0.4723	0.4491	0.8404
H77	0.4938	0.3144	0.8205
H79	0.4911	0.6261	0.8437
Molecule *V*			
S1e	0.6017	0.9884	0.1059
N1e	0.5413	0.8349	0.2792
C3e	0.5585	0.7056	0.2387
N2e	0.5487	0.0305	0.1682
C5e	0.5803	0.7658	0.1063
C2e	0.5629	0.828	0.1706
C1e	0.5362	0.0257	0.2349
N5e	0.6661	0.5784	0.049
N3e	0.6557	0.8181	0.961
C6e	0.6204	0.8134	0.0334
C10e	0.6772	0.3812	0.0661
C7e	0.6405	0.9618	0.0178
C8e	0.6675	0.6251	0.9769
C4e	0.569	0.4877	0.2703
N6e	0.6858	0.2124	0.0888
N4e	0.6799	0.485	0.9223
C9e	0.6823	0.5411	0.8447
H50	0.5248	0.1511	0.2496
H52	0.5347	0.8031	0.324
H54	0.5786	0.5711	0.2914
H56	0.5591	0.388	0.3073
H58	0.5756	0.3626	0.2314
H60	0.5765	0.7927	0.061
H62	0.5841	0.5769	0.1082
H64	0.6219	0.627	0.0484
H66	0.616	0.808	0.9891
H68	0.639	0.1462	0.0019
H70	0.6447	0.9705	0.0625
H72	0.657	0.8607	0.9147
H74	0.6868	0.351	0.9322
H76	0.6699	0.5138	0.8322
H78	0.6924	0.4282	0.8138
H80	0.6864	0.7339	0.834

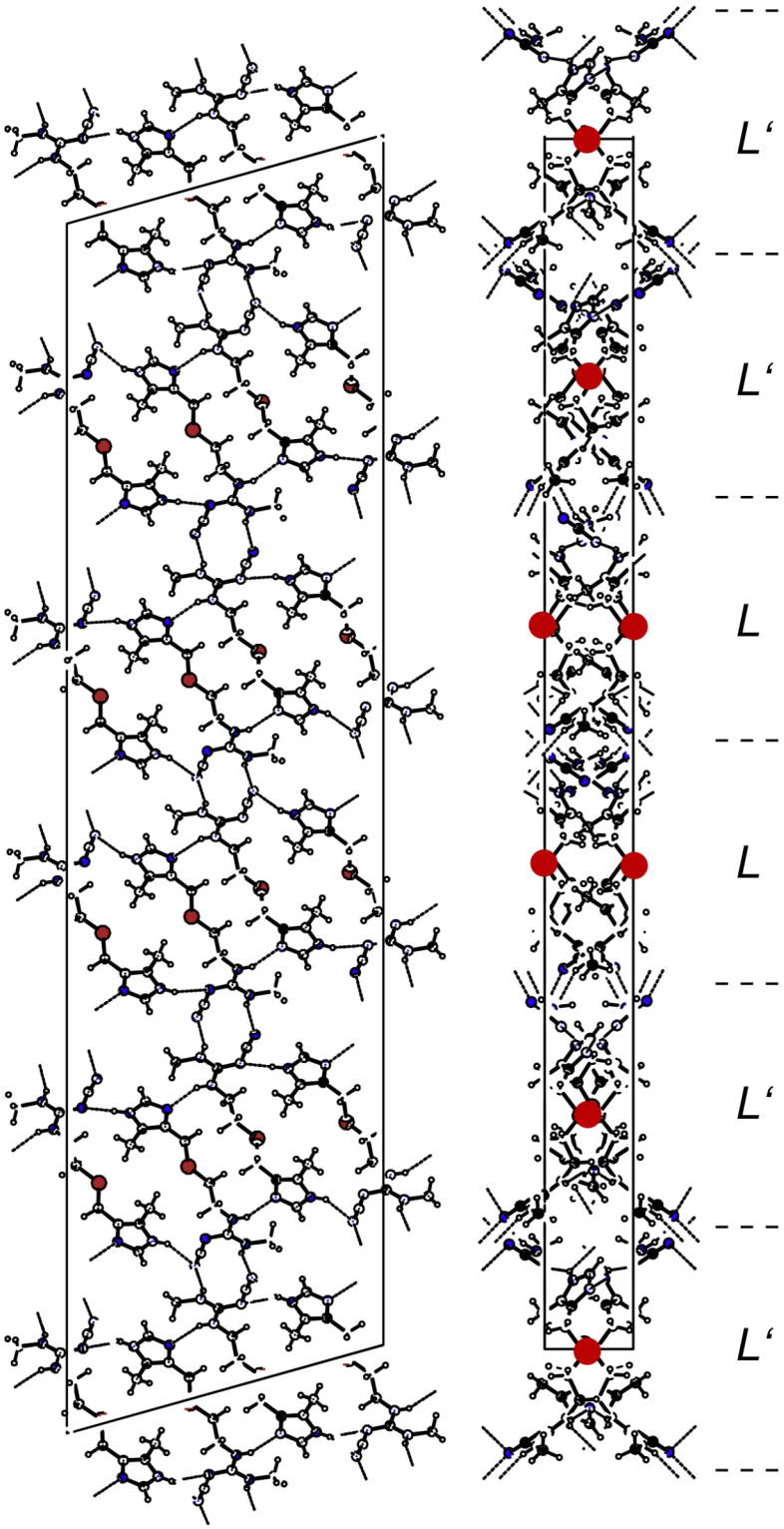

Figure S6. Packing of molecules in cimetidine form *C* modelled polytype 5M. The *ac* (left) and *ab* (right) structure projections are shown. Broun circles indicate S atoms, which are associated with centres of molecules. *L* and *L*’ indicate the layers with $y \approx 0$ and $y \approx 0.5$, respectively for centres of the molecules. Five *L* layers, (*L’L’L’LL*), consisting of 5 similar molecules are associated with the *a* lattice constant.

Analysis of XRD patters reported for cimetidine form *C*

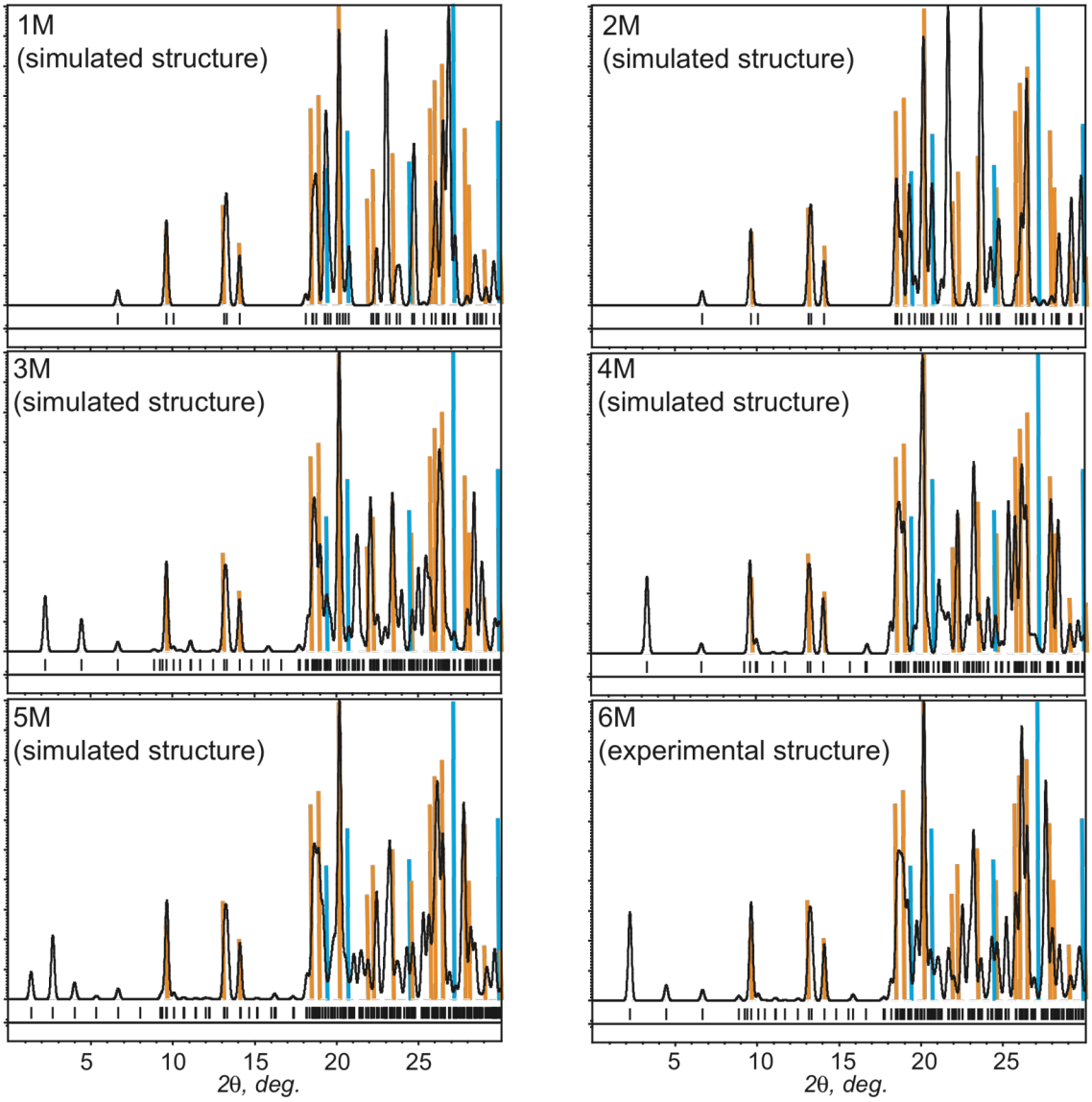

Figure S7. The powder XRD patterns simulated for the modelled 1M, 2M, 3M, 4M, 5M polytypes and for the experimental structure of 6M polytype. The XRD reference patterns 00-032-1586 and 00-036-1639 (CCD PDF2) are shown as orange and respectively blue vertical lines in each diagram.