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# Intermolecular Interactions and Chiral Crystallization Effects in (1,5,3-Dithiazepan-3-yl)-alkanoic Acids

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## *Supporting information*

**Table 1** Common occurrence of N–OH and amino acid fragments in the compounds according to found results in Cambridge Structural Database

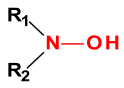
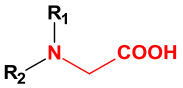
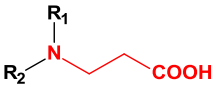
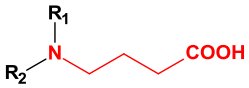
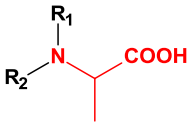
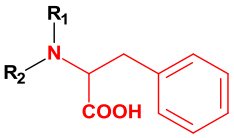
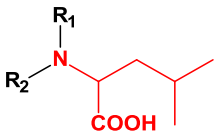
| | | | | |
|---|---|---|---|---|
| Structural fragment |  |  |  |  |
| Number of compounds | 1856 | 398 | 99 | 24 |
| Structural fragment |  |  |  | |
| Number of compounds | 81 | 70 | 34 | |

**Table 2** Some bond, Å

| | 1 | 2a | 2b | 3 | 4 | 5 | 6 | 7 | 8 |
|---|---|---|---|---|---|---|---|---|---|
| S1-mean plane | 1.139(4) | 1.110(3) | -0.710(4) | 0.867(4) | 0.717(5) | -1.114(3) | 1.110 (6) (-1.087(5)) | -1.118(3) (1.098(4)) | 1.126(17) |
| S5-mean plane | -1.084(3) | -1.105(2) | -0.836(3) | 0.815(2) | 0.842(6) | 1.107(5) | -1.108(4) (1.124(5)) | 1.126(3) (-1.138(5)) | -1.112(16) |

**Table 3** Some bonds, Å

| | 1 | 2a | 2b | 3 | 4 | 5 | 6 | 7 | 8 |
|---|---|---|---|---|---|---|---|---|---|
| **C(2)–N(3)** | 1.461(18) | 1.513(16) | 1.435(19) | 1.437(3) | 1.426(2) | 1.469(3) | 1.519(4) | 1.460(4) | 1.467(2) |
| **C(4)–N(3)** | 1.469(2) | 1.498(2) | 1.433(17) | 1.429(3) | 1.430(2) | 1.482(3) | 1.508(6) | 1.482(4) | 1.476(2) |
| **C(4)–S(5)** | 1.794(2) | 1.788(5) | 1.836(15) | 1.816(3) | 1.846(18) | 1.802(2) | 1.786(4) | 1.806(3) | 1.796(16) |
| **C(2)–S(1)** | 1.814(14) | 1.788(17) | 1.842(14) | 1.829(3) | 1.845(16) | 1.824(19) | 1.794(4) | 1.815(3) | 1.818(19) |
| **N(3)–C(8)** | – | 1.493(2) | 1.442(17) | 1.463(4) | 1.461(2) | 1.496(2) | 1.517(4) | 1.487(4) | 1.491(2) |

**Table 4** Hydrogen bonds and diverse intermolecular contacts

| Compound | D–H···A | *d*(D–H) | *d*(H···A) | *d*(D···A) | (D–H···A) | Symmetry code |
|---|---|---|---|---|---|---|
| **1** | O1–H1···H1 | 0.870(6) | 2.192(2) | 2.656(2) | 113.05(6) | 1–x, 1–y, –z |
| | C4–H4B···S1 | 0.952(6) | 2.947(2) | 3.654(3) | 132.11(5) | –1+x, y, z |
| | O1–H1···O1 | 0.870(6) | 2.656(2) | 3.289(3) | 130.59(4) | 1–x, 1–y, –z |
| | C7–H7A···O1 | 0.982(9) | 2.509(2) | 3.283(3) | 135.62(4) | x, –1+y, z |
| | O1–H1···N3 | 0.870(3) | 2.006(4) | 2.850(3) | 163.30(2) | 1–x, 1–y, –z |
| **2a** | C2–H2A···O1 | 0.920(4) | 2.706(2) | 3.448(2) | 138.30(2) | –2–x, –0.5+y, –2–z |
| | C8–H8B···O1 | 1.092(5) | 2.154(5) | 3.212(2) | 162.67(4) | –2–x, –0.5+y, –2–z |
| | O3–H3B···O2 | 0.850(4) | 1.869(9) | 2.701(1) | 165.75(9) | x, y, z |
| | O2–H2···O3 | 0.820(3) | 2.087(8) | 2.703(9) | 131.81(2) | –3–x, –0.5+y, –2–z |

| | | | | | | |
|---|---|---|---|---|---|---|
| | O3–H3A···O1 | 0.850(3) | 2.636(1) | 3.339(2) | 140.93(2) | –2–x, –0.5+y, –2–z |
| | C7–H7A···S1 | 1.026(5) | 2.914(2) | 3.919(2) | 166.61(1) | –1–x, –0.5+y, –1–z |
| | C4–H4A···S5 | 0.934(3) | 2.917(1) | 3.547(2) | 125.93(2) | –2–x, –0.5+y, –1–z |
| **2b** | C1'–H1'B···S5 | 0.960(2) | 2.765(5) | 3.477(7) | 131.57(1) | 2–x, –0.5+y, 1.5–z |
| | C7–H7A···S5 | 0.935(3) | 2.945(8) | 3.773(1) | 149.27(1) | x, 1.5–y, –0.5+z |
| | C1'–H1'C···O1 | 0.960(3) | 2.448(5) | 3.282(7) | 145.17(7) | x, y, z |
| | O2–H2···O1' | 0.830(2) | 1.772(5) | 2.592(6) | 169.35(9) | x, y, z |
| | C6–H6B···O1 | 0.966(2) | 2.710(6) | 3.675(8) | 175.55(1) | 2–x, 1–y, 2–z |
| **3** | C2–H2B···H8B | 0.970(1) | 2.323(2) | 3.115(2) | 138.37(3) | –1+x, y, z |
| | C8–H8A···S5 | 0.970(5) | 2.969(2) | 3.899(2) | 160.92(1) | x, y, –1+z |
| | C7–H7A···S1 | 0.970(6) | 2.914(2) | 3.815(3) | 154.87(1) | –0.5+x, 0.5–y, –0.5+z |
| | C9–H9A···O2 | 0.970(5) | 2.489(2) | 3.453(2) | 172.83(3) | 1–x, 1–y, 2–z |
| | C9–H9B···O2 | 0.970(8) | 2.700(2) | 3.609(2) | 156.36(6) | –1+x, y, z |
| | O1–H1···O2 | 0.879(9) | 1.771(2) | 2.641(2) | 170.26(8) | –x, 1–y, 1–z |
| **4** | O2–H2C···O1 | 0.783(6) | 1.854(1) | 2.631(2) | 172.07(8) | –x, 3–y, –z |
| | C10–H10B···O2 | 0.991(5) | 2.544(1) | 3.442(2) | 150.55(3) | –x, 2–y, –z |
| | C9–H9A···O2 | 1.000(9) | 2.686(2) | 3.539(2) | 143.48(9) | –1+x, y, z |
| **5** | C9–H9A···S5 | 0.980(5) | 2.885(2) | 3.524(2) | 123.65(4) | –1+x, y, z |
| | C7–H7A···O2 | 0.888(5) | 2.704(2) | 3.424(2) | 138.93(3) | –x, –0.5+y, 1–z |
| | C7–H7A···O1 | 0.888(5) | 2.707(2) | 3.461(2) | 143.31(3) | x, y, –1+z |
| | C2–H2B···O1 | 0.971(7) | 2.701(1) | 3.211(2) | 113.36(5) | –x, –0.5+y, –z |
| | C9–H9B···O1 | 1.006(5) | 2.716(2) | 3.354(2) | 121.52(5) | –x, –0.5+y, –z |
| **6** | C11–H11B···H6A | 0.960(6) | 2.196(9) | 2.984(1) | 138.61(9) | –1.5–x, –1–y, –0.5+z |
| | C13–H13B···H6A | 0.960(6) | 2.263(9) | 3.035(1) | 136.91(2) | –1.5–x, –1–y, –0.5+z |
| | C4–H4B···H2' | 0.939(5) | 2.328(9) | 2.523(1) | 90.84(5) | –0.5+x, –1.5–y,–1–z |
| | C2'–H2'A···S5 | 0.998(5) | 2.970(1) | 3.755(2) | 136.33(4) | x, y, z |
| | C13–H13C···S5' | 0.960(6) | 2.973(2) | 3.900(2) | 162.60(2) | –0.5+x, –0.5–y, –1–z |
| | C8–H8···O1' | 0.986(5) | 2.691(2) | 3.594(2) | 152.35(6) | x, y z |
| | C4–H4A···O1' | 0.904(4) | 2.353(1) | 3.257(1) | 178.65(4) | x, y, z |
| | C2–H2A···O1' | 0.970(5) | 2.677(2) | 3.198(2) | 114.04(2) | –0.5+x, –1.5–y, –1–z |
| | C2'–H2'B···O2 | 0.989(6) | 2.603(1) | 3.299(2) | 127.41(5) | –0.5+x, –0.5–y, –1–z |
| | C4'–H4'B···O2 | 0.970(4) | 2.319(1) | 3.164(5) | 145.16(9) | –1+x, y, z |
| **7** | C2–H2A···H2' | 0.977(2) | 2.398(3) | 2.768(5) | 102.09(1) | x, y, z |
| | C4–H4B···O3 | 0.917(9) | 2.645(4) | 3.170(4) | 117.19(8) | –1+x, y, z |
| | C6–H6A···O1 | 0.970(2) | 2.624(3) | 3.593(5) | 176.72(9) | –1+x, y, 1+z |
| | C7–H7A···O3 | 1.037(1) | 2.642(3) | 3.398(4) | 129.55(9) | –1+x, y, 1+z |
| | O1–H1A···O3 | 0.686(1) | 1.977(3) | 2.640(4) | 162.72(3) | x, –1+y, z |
| | C7–H7A···O3' | 1.037(2) | 2.399(3) | 3.184(4) | 131.62(9) | x, –1+y, 1+z |
| | O2'–H2'···O2 | 0.820(1) | 2.593(3) | 3.141(4) | 125.55(1) | x, y, z |
| | O1'–H1'···O3' | 0.820(1) | 2.025(4) | 2.674(5) | 135.72(9) | 1+x, y, z |
| | C6'–H6'B···O3' | 0.970(2) | 2.396(5) | 3.228(7) | 143.60(9) | –1+x, y, 1+z |
| | C9–H9B···S1' | 0.970(2) | 2.950(4) | 3.618(6) | 127.02(1) | x,–1+y, 1+z |
| | C9'–H9'B···S5' | 1.083(1) | 2.638(3) | 3.659(5) | 156.90(4) | x, y, z |
| **8** | C4–H4B···H7A | 1.006(3) | 2.373(6) | 2.745(7) | 100.77(1) | –0.5+x, y, 1.5–z |
| | C13–H13···S1 | 0.977(3) | 2.942(8) | 3.775(9) | 143.90(3) | –0.5+x, 0.5–y, 1–z |
| | O1–H1···C8 | 0.910(3) | 2.639(8) | 3.404(1) | 142.14(2) | 1.5–x, –0.5+y, z |
| | O1–H1···C4 | 0.910(3) | 2.493(6) | 3.257(8) | 141.70(1) | 1.5–x, –0.5+y, z |
| | O1–H1···C2 | 0.910(3) | 2.641(7) | 3.487(1) | 154.97(9) | 1.5–x, –0.5+y, z |
| | C7–H7A···C4 | 0.979(2) | 2.745(7) | 3.524(9) | 136.87(1) | –0.5+x, y, 1.5–z |

**Table 5** S···S contacts vs conformation of dithiazepane cycle

| | 1 | 2a | 2b | 3 | 4 | 5 | 6 | 7 | 8 |
|---|---|---|---|---|---|---|---|---|---|
| *d*(S···S), Å | 3.598(5) | – | – | – | – | 3.380(4) | – | 3.596(7) | 3.568(8) |
| Conformation | chair | chair | boat | boat | boat | chair | chair | chair | chair |

**Table 6** Crystal data and structure refinement for compounds **1–8**

| | **1** | **2a** | **2b** | **3** |
|---|---|---|---|---|
| **l formula** | $C_4H_9N_1O_1S_2$ | $C_6H_{11}NO_2S_2,H_2O$ | $C_6H_{11}NO_2S_2$, $C_2H_6OS$ | $C_7H_{13}NO_2S_2$ |
| **Formula weight** | 151.24 | 211.29 | 271.41 | 206.30 |
| **Crystal** | triclinic | monoclinic | monoclinic | monoclinic |

| **system** | | | | |
|---|---|---|---|---|
| **Space group** | P-1 | $P2_1$ | $P2_1/c$ | $P2_1/n$ |
| **a,Å** | 6.5256(4) | 6.6882(3)Å | 6.58182(17) | 4.9212(5) |
| **b,Å** | 6.9753(5) | 8.6039(4) | 16.4019(4) | 30.519(2) |
| **c, Å** | 8.1848(5) | 8.0793(4) | 11.5843(4) | 6.7336(4) |
| **α,°** | 110.266(6) | 90.00° | 90.00° | 90 |
| **β,°** | 96.816(5) | 94.507(5) | 98.923(3) | 103.709(8) |
| **γ,°** | 94.924(5) | 90.00° | 90.00° | 90 |
| **V, Å$^3$** | 343.79(4) | 463.48(4) | 1235.44(6) | 982.53(14) |
| **Z** | 2 | 2 | 4 | 4 |
| **$D_{calc}$g/cm$^3$** | 1.461 | 1.514 | 1.459 | 1.395 |
| **F(000)** | 160 | 224 | 576.0 | 436 |
| **$2\Theta_{max,}$ °** | 62.34° | 62.378 | 62.2 | 62.42 |
| **Reflections collected** | 2975 | 2436 | 6313 | 3485 |
| **Independent reflections ($R_{int}$)** | 1957[R(int) = 0.0115] | 2054 ($R_{int}$ = 0.0084) | 3538 ($R_{int}$ = 0.0137) | 2291 ($R_{int}$ = 0.0168) |
| **S** | 0.857 | 0.853 | 1.067 | 1.057 |
| $R_1$ **[I>=2σ (I)]** | 0.0274 | 0.0303 | 0.0318 | 0.0536 |
| $wR_2$ | 0.1031 | 0.0888 | 0.0762 | 0.1448 |
| **Largest diff. peak/hole, e Å$^{-3}$** | 0.34/-0.22 | 0.44/-0.50 | 0.30/-0.27 | 0.50/-0.63 |
| **Flack parameter** | n/a | -0.13(7) | n/a | n/a |

| | **4** | **5** | **6** | **7** | **8** |
|---|---|---|---|---|---|
| **Empirical formula** | $C_8H_{15}NO_2S_2$ | $C_7H_{13}NO_2S_2$ | $C_7H_{13}NO_3S_2$ | $C_{10}H_{19}NO_2S_2$ | $C_{13}H_{17}NO_2S_2$ |
| **Formula weight** | 221.33 | 207.30 | 223.30 | 249.38 | 283.4 |
| **Crystal system** | triclinic | monoclinic | triclinic | orthorhombic | orthorhombic |
| **Space group** | P-1 | $P2_1$ | P1 | $P2_12_12_1$ | Pbca |
| **a,Å** | 5.0968(3) | 6.4993(6) | 6.8616(11) | 10.6926(6) | 10.5874(4) |
| **b,Å** | 6.7869(3) | 8.6630(6) | 8.8688(8) | 10.9871(7) | 10.2833(3) |
| **c, Å** | 16.6360(10) | 8.5034(5) | 8.9458(10) | 21.4364(15) | 25.2185(10) |
| **α,°** | 78.801(5) | 90 | 66.923(10) | 90 | 90 |

| | | | | | |
|---|---|---|---|---|---|
| **β,°** | 87.344(5) | 104.738(7) | 70.122(13) | 90 | 90 |
| **γ,°** | 69.141(5) | 90 | 85.373(10) | 90 | 90 |
| **V, Å$^3$** | 527.34(5) | 463.01(6) | 470.11(11) | 2518.3(3) | 2745.64(17) |
| **Z** | 2 | 2 | 2 | 8 | 8 |
| **$D_{calc}$g/cm$^3$** | 1.394 | 1.487 | 1.577 | 1.316 | 1.371 |
| **F(000)** | 236 | 220.0 | 236.0 | 1072.0 | 1200 |
| **2Θ$_{max,}$ °** | 62.12 | 62.494 | 61.838 | 62.24 | 62.22 |
| **Reflections collected** | 4589 | 2474 | 4183 | 8525 | 9252 |
| **Independent reflections ($R_{int}$)** | 3000 ($R_{int}$ = 0.0162) | 2052 ($R_{int}$ = 0.0178) | 3248 ($R_{int}$ = 0.0782) | 6260 ($R_{int}$ = 0.0762) | 3986 ($R_{int}$ = 0.0181) |
| **S** | 0.943 | 1.108 | 0.864 | 1.012 | 1.110 |
| $R_1$ **[I>=2σ (I)]** | 0.0384 | 0.0381 | 0.0467 | 0.0602 | 0.0464 |
| $wR_2$ | 0.1328 | 0.1108 | 0.1182 | 0.1211 | 0.1176 |
| **Largest diff. peak/hole, e Å$^{-3}$** | 0.74/-0.43 | 0.42/-0.61 | 0.43/-0.29 | 0.75/-0.47 | 0.32/-0.32 |
| **Flack parameter** | n/a | -0.02(12) | -0.12(9) | -0.11(9) | n/a |

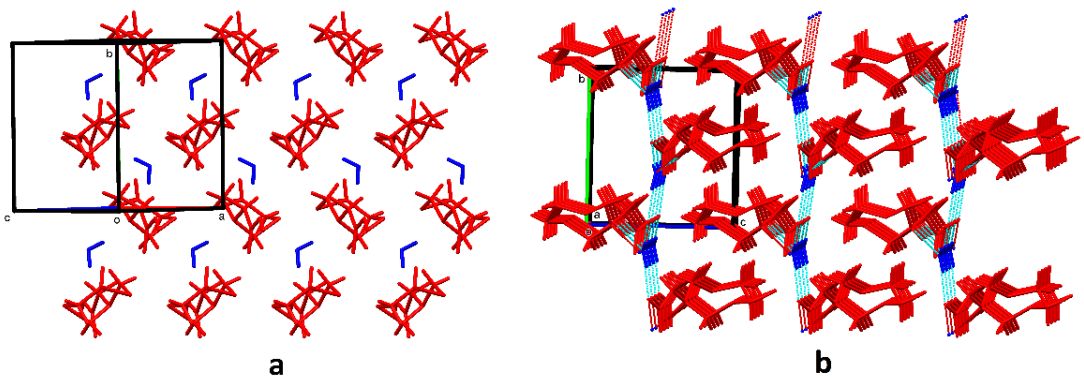



Fig. 1. Projections of clathrate **2a**: (a) along *a* axis and (b) along *b* axis. The molecules of the main compound are painted with red colour and water molecules are with blue colour.

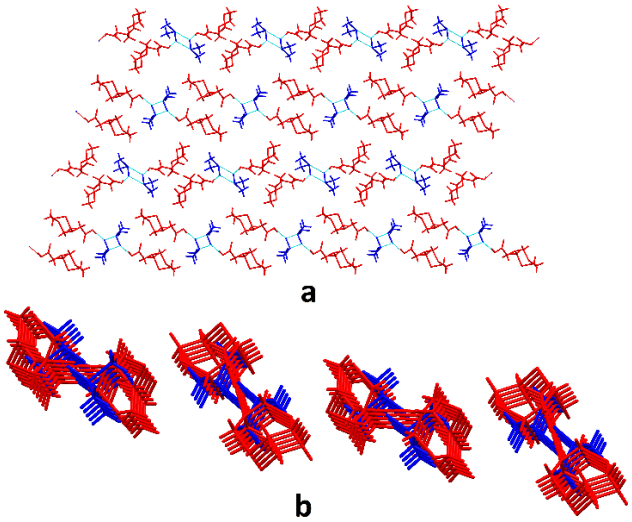



**Fig. 2.** Projections of tetrameric associates **2b** along two orthogonal axes. The molecules of the main compound are in red, whereas DMSO are in blue.