

Supplementary Materials

Intermolecular Hydrogen Bonding in Alpha-Hydroxy Carboxylic Acids Crystals: Connectivity, Synthons, Supramolecular Motifs

Alexander A. Bredikhin*, Robert R. Fayzullin, Aidar T. Gubaidullin and Zemfira A.

Bredikhina

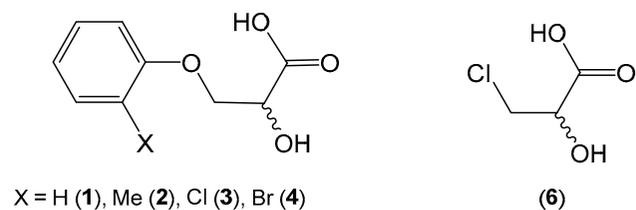
Arbuzov Institute of Organic and Physical Chemistry, FRC Kazan Scientific Center of RAS,
Arbuzov St., 8, Kazan 420088, Russian

*Corresponding Author: Alexander A. Bredikhin (baa@iopc.ru)

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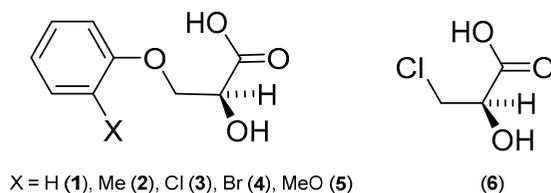
Table S1. Experimental crystallographic data for *rac*-2-hydroxy-3-aryloxypropanoic acids *rac*-**1-4** and *rac*-3-chloro-2-hydroxypropanoic acid *rac*-**6**



| Compound | <i>rac</i> - 1 | <i>rac</i> - 2 | <i>rac</i> - 3 | <i>rac</i> - 4 | <i>rac</i> - 6 |
|--|---|---|---|---|---|
| Empirical formula | C ₉ H ₁₀ O ₄ | C ₁₀ H ₁₂ O ₄ | C ₉ H ₉ ClO ₄ | C ₉ H ₉ BrO ₄ | C ₃ H ₅ ClO ₃ |
| Formula weight | 182.17 | 196.20 | 216.61 | 261.07 | 124.52 |
| Temperature (K) | 100(2) | 100(2) | 100(2) | 100(2) | 100(2) |
| Radiation, wavelength (Å) | Mo K α , 0.71073 | Mo K α , 0.71073 | Mo K α , 0.71073 | Mo K α , 0.71073 | Mo K α , 0.71073 |
| Crystal system | Monoclinic | Monoclinic | Orthorhombic | Orthorhombic | Monoclinic |
| Space group | <i>P</i> 2 ₁ / <i>c</i> (No. 14) | <i>P</i> 2 ₁ / <i>c</i> (No. 14) | <i>Pbca</i> (No. 61) | <i>Pbca</i> (No. 61) | <i>P</i> 2 ₁ / <i>c</i> (No. 14) |
| Unit cell dimensions (Å; deg) | <i>a</i> = 18.6821(17), <i>b</i> = 5.1437(5), <i>c</i> = 8.7181(10); β = 94.368(8) | <i>a</i> = 20.076(4), <i>b</i> = 10.714(2), <i>c</i> = 9.1002(8), β = 92.195(10) | <i>a</i> = 10.6314(6), <i>b</i> = 9.0254(5), <i>c</i> = 20.2379(11) | <i>a</i> = 10.6846(6), <i>b</i> = 9.0777(4), <i>c</i> = 20.2760(11) | <i>a</i> = 10.8508(5), <i>b</i> = 10.6566(4), <i>c</i> = 9.0318(4), β = 108.204(2) |
| Volume (Å ³) | 835.33(15) | 1956.0(7) | 1941.88(19) | 1966.60(18) | 992.10(7) |
| <i>Z</i> and <i>Z'</i> | 4 and 1 | 8 and 2 | 8 and 1 | 8 and 1 | 8 and 2 |
| Calculated density (g cm ⁻³) | 1.449 | 1.332 | 1.482 | 1.764 | 1.667 |
| Absorption coefficient (mm ⁻¹) | 0.115 | 0.103 | 0.378 | 4.165 | 0.656 |

| | | | | | |
|--|---|--|--|--|--|
| $F(000)$ | 384 | 832 | 896 | 1040 | 512 |
| Crystal size (mm ³) | 0.589 × 0.458 × 0.088 | 0.542 × 0.321 × 0.292 | 0.595 × 0.577 × 0.080 | 0.527 × 0.300 × 0.260 | 0.222 × 0.421 × 0.628 |
| θ range for data collection | 4.110° to 25.247° | 1.015° to 25.247° | 2.013° to 27.649° | 3.111° to 30.158° | 2.749° to 30.032° |
| Index ranges | $-22 \leq h \leq 22,$ $-6 \leq k \leq 6,$ $-9 \leq l \leq 10$ | $-23 \leq h \leq 24,$ $0 \leq k \leq 12,$ $0 \leq l \leq 10$ | $-13 \leq h \leq 13,$ $-11 \leq k \leq 11,$ $-26 \leq l \leq 26$ | $-15 \leq h \leq 15,$ $-12 \leq k \leq 12,$ $-28 \leq l \leq 28$ | $-15 \leq h \leq 15,$ $-14 \leq k \leq 15,$ $-12 \leq l \leq 12$ |
| Reflections collected | 8327 | 42926 | 30016 | 77333 | 13565 |
| Independent reflections | 1474 | 3546 | 2252 | 2909 | 2903 |
| R_{int} | 0.0533 | 0.0774 | 0.0452 | 0.0431 | 0.0307 |
| R_{σ} | 0.0430 | 0.0431 | 0.0231 | 0.0162 | 0.0259 |
| Observed Data [$I > 2\sigma(I)$] | 1158 | 3109 | 1864 | 2227 | 2526 |
| Completeness to θ_{max} (%) | 97.3 | 89.3 | 99.9 | 99.9 | 99.8 |
| Absorption correction | Numerical | Semi-empirical equivalents | from Numerical | Numerical | Multi-scan |
| Max. and min. transmission | 0.9705 and 0.8581 | 0.7460 and 0.6370 | 0.8910 and 0.7559 | 0.1395 and 0.0794 | 0.7473 and 0.5950 |
| Data / restraints / parameters | 1474 / 1 / 126 | 3546 / 4 / 269 | 2252 / 1 / 135 | 2909 / 1 / 135 | 2903 / 0 / 139 |
| Goodness-of-fit on F^2 | 1.052 | 1.154 | 1.053 | 1.047 | 1.032 |
| Final R indices [$I > 2\sigma(I)$] | $R1 = 0.0515,$ $wR2 = 0.1061$ | $R1 = 0.0690,$ $wR2 = 0.2065$ | $R1 = 0.0344,$ $wR2 = 0.0800$ | $R1 = 0.0255,$ $wR2 = 0.0577$ | $R1 = 0.0267,$ $wR2 = 0.0616$ |
| R indices (all data) | $R1 = 0.0700,$ $wR2 = 0.1158$ | $R1 = 0.0861,$ $wR2 = 0.2355$ | $R1 = 0.0466,$ $wR2 = 0.0868$ | $R1 = 0.0401,$ $wR2 = 0.0629$ | $R1 = 0.0338,$ $wR2 = 0.0644$ |
| Extinction coefficient | n/a | 0.053(8) | n/a | n/a | - |
| Largest diff. peak and hole (e Å ⁻³) | 0.262 and -0.331 | 0.580 and -0.716 | 0.402 and -0.284 | 0.335 and -0.652 | 0.413 and -0.284 |

Table S2. Experimental crystallographic data for (*S*)-2-hydroxy-3-aryloxypropanoic acids (*S*)-**1-5** and (*R*)-3-chloro-2-hydroxypropanoic acid (*R*)-**6**.



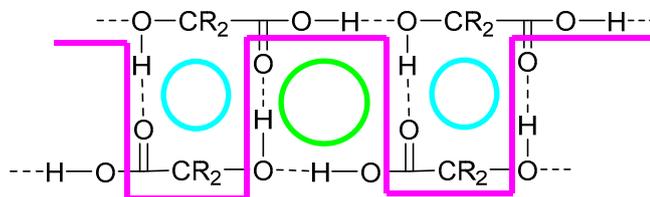
| Compound | (<i>S</i>)- 1 | (<i>S</i>)- 2 | (<i>S</i>)- 3 | (<i>S</i>)- 4 | (<i>S</i>)- 5 | (<i>R</i>)- 6 |
|--|---|---|--|--|--|---|
| Empirical formula | C ₉ H ₁₀ O ₄ | C ₁₀ H ₁₂ O ₄ | C ₉ H ₉ ClO ₄ | C ₉ H ₉ BrO ₄ | C ₁₀ H ₁₂ O ₅ | C ₃ H ₅ ClO ₃ |
| Formula weight | 182.17 | 196.20 | 216.61 | 261.07 | 212.20 | 124.52 |
| Temperature (K) | 120(2) | 120(2) | 120(2) | 100(2) | 100(2) | 100(2) |
| Radiation, wavelength (Å) | CuKα, 1.54178 | CuKα, 1.54178 | CuKα, 1.54178 | MoKα, 0.71073 | Synchrotron, 0.79312 | Mo Kα, 0.71073 |
| Crystal system | Monoclinic | Orthorhombic | Orthorhombic | Orthorhombic | Orthorhombic | Monoclinic |
| Space group | <i>P</i> 2 ₁ (No. 4) | <i>P</i> 2 ₁ 2 ₁ 2 ₁ (No. 19) | <i>P</i> 2 ₁ 2 ₁ 2 ₁ (No. 19) | <i>P</i> 2 ₁ 2 ₁ 2 ₁ (No. 19) | <i>P</i> 2 ₁ 2 ₁ 2 ₁ (No. 19) | <i>C</i> 2(No. 5) |
| Unit cell dimensions (Å; deg) | <i>a</i> = 8.2250(2), <i>b</i> = 5.18250(10), <i>c</i> = 9.9850(3); <i>β</i> = 92.6523(11) | <i>a</i> = 5.17224(8), <i>b</i> = 18.7560(3), <i>c</i> = 29.4481(4) | <i>a</i> = 5.2419(3), <i>b</i> = 9.2250(6), <i>c</i> = 19.9409(15) | <i>a</i> = 4.7812(3), <i>b</i> = 9.9333(9), <i>c</i> = 20.5217(17) | <i>a</i> = 5.2900(11), <i>b</i> = 9.6700(19), <i>c</i> = 19.566(4) | <i>a</i> = 8.448(5), <i>b</i> = 5.804(5), <i>c</i> = 10.426(9), <i>β</i> = 102.67(4) |
| Volume (Å ³) | 425.165(18) | 2856.77(7) | 964.27(11) | 974.64(13) | 1000.9(3) | 498.8(7) |
| <i>Z</i> and <i>Z'</i> | 2 and 1 | 12 and 3 | 4 and 1 | 4 and 1 | 4 and 1 | 4 and 1 |
| Calculated density (g cm ⁻³) | 1.423 | 1.368 | 1.492 | 1.779 | 1.408 | 1.658 |
| Absorption coefficient (mm ⁻¹) | 0.956 | 0.892 | 3.431 | 4.202 | 0.149 | 0.652 |
| <i>F</i> (000) | 192 | 1248 | 448 | 520 | 448 | 256 |

| | | | | | | |
|--|--|--|--|--|--|--|
| Crystal size (mm ³) | 0.360×0.260×0.069 | 0.480×0.098×0.060 | 0.243×0.234×0.084 | 0.544×0.116×0.110 | 0.240×0.012×0.008 | 0.032×0.195×0.642 |
| θ range for data collection | 4.433 to 67.431° | 3.001 to 67.773° | 4.434 to 67.609° | 3.616° to 27.525° | 2.323° to 29.673° | 4.295° to 29.151° |
| Index ranges | $-9 \leq h \leq 9,$ $-6 \leq k \leq 6,$ $-11 \leq l \leq 11$ | $-5 \leq h \leq 6,$ $-20 \leq k \leq 22,$ $-35 \leq l \leq 34$ | $-6 \leq h \leq 6,$ $-10 \leq k \leq 10,$ $-23 \leq l \leq 19$ | $-6 \leq h \leq 5,$ $-11 \leq k \leq 12,$ $-25 \leq l \leq 16$ | $-6 \leq h \leq 5,$ $-12 \leq k \leq 12,$ $-24 \leq l \leq 24$ | $-11 \leq h \leq 11,$ $-7 \leq k \leq 7,$ $-14 \leq l \leq 14$ |
| Reflections collected | 6555 | 36747 | 6559 | 18489 | 6854 | 2599 |
| Independent reflections | 1451 | 5044 | 1710 | 2241 | 2019 | 1292 |
| R_{int} | 0.0212 | 0.0349 | 0.0300 | 0.0522 | 0.0603 | 0.0613 |
| R_{σ} | 0.0200 | 0.0206 | 0.0294 | 0.0391 | 0.0530 | 0.0874 |
| Observed Data [$I > 2\sigma(I)$] | 1450 | 4834 | 1670 | 1999 | 1819 | 967 |
| Completeness to θ_{max} (%) | 97.1 | 98.2 | 99.0 | 99.8 | 99.3 | 98.1 |
| Absorption correction | Semi-empirical from equivalents | Semi-empirical from equivalents | Semi-empirical from equivalents | Numerical | Semi-empirical from equivalents | Multi-scan |
| Max. and min. transmission | 0.8642 and 0.6960 | 0.9153 and 0.8502 | 0.5988 and 0.4184 | 0.3617 and 0.1552 | 0.942 and 0.983 | 0.7458 and 0.5534 |
| Data / restraints / parameters | 1451 / 1 / 127 | 5044 / 3 / 406 | 1710 / 285 / 199 | 2241 / 2 / 135 | 2019 / 2 / 145 | 1292 / 2 / 72 |
| Goodness-of-fit on F^2 | 1.100 | 1.071 | 1.056 | 1.055 | 1.062 | 0.951 |
| Final R indices [$I > 2\sigma(I)$] | $R1 = 0.0239,$ $wR2 = 0.0602$ | $R1 = 0.0257,$ $wR2 = 0.0621$ | $R1 = 0.0260,$ $wR2 = 0.0695$ | $R1 = 0.0267,$ $wR2 = 0.0503$ | $R1 = 0.0394,$ $wR2 = 0.0916$ | $R1 = 0.0454,$ $wR2 = 0.0849$ |
| R indices (all data) | $R1 = 0.0239,$ $wR2 = 0.0602$ | $R1 = 0.0274,$ $wR2 = 0.0632$ | $R1 = 0.0266,$ $wR2 = 0.0698$ | $R1 = 0.0348,$ $wR2 = 0.0529$ | $R1 = 0.0461,$ $wR2 = 0.0953$ | $R1 = 0.0729,$ $wR2 = 0.0935$ |
| Flack parameter | 0.00(9) | 0.00(5) | -0.007(8) | -0.009(6) | -0.4(7) | -0.07(10) |
| Extinction coefficient | 0.035(3) | n/a | n/a | n/a | n/a | - |
| Largest diff. peak and hole (e Å ⁻³) | 0.154 and -0.149 | 0.146 and -0.191 | 0.248 and -0.200 | 0.439 and -0.475 | 0.166 and -0.208 | 0.295 and -0.329 |

Connectivity diagrams in crystals of the studied compounds.

Motif: $C_3^3(11):23/23/12$; $R_2^2(10):23/23$; $R_4^4(12):12/23/12/23$.

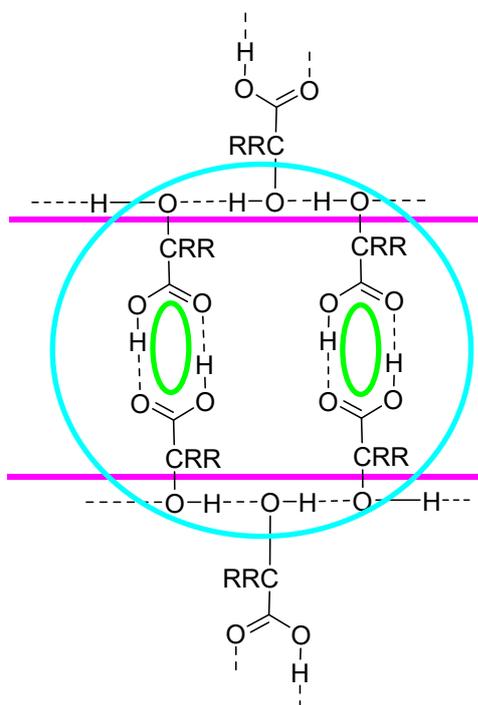
Representatives: NIQSUC, HXIBAC, WULJAQ



Scheme S1. Connectivity diagram in NIQSUC crystals. The purple broken line corresponds to the continuous chain $C_3^3(11):23/23/12$, the colored circles visualize the rings $R_2^2(10):23/23$ (blue) and $R_4^4(12):12/23/12/23$ (green).

Motif: $C_1^1(2):22$; $R_2^2(8):13/13$; $R_6^6(24):22/22/13/22/22/13$.

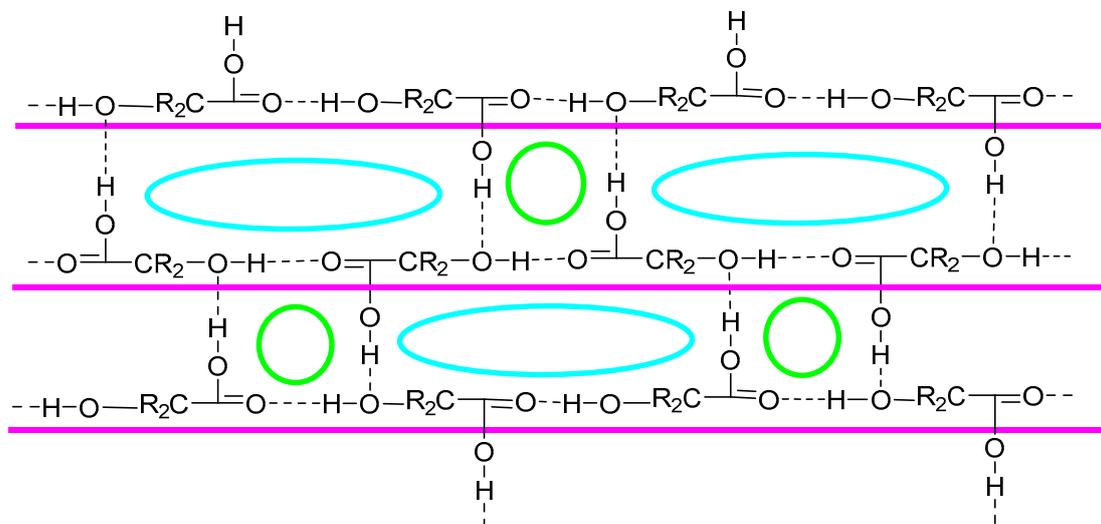
Representatives: AFEVIR.



Scheme S2. Connectivity diagram in AFEVIR crystals. The purple line corresponds to the continuous chain $C_1^1(2):22$, the colored circles visualize the centrosymmetric rings $R_2^2(8):13/13$ (green) and $R_6^6(24):22/22/13/22/22/13$ (blue).

Motif: $C_1^1(5):23$; $R_4^4(12):23/12/23/12$; $R_4^4(20):\{23\}\{12\}\{23\}\{12\}$.

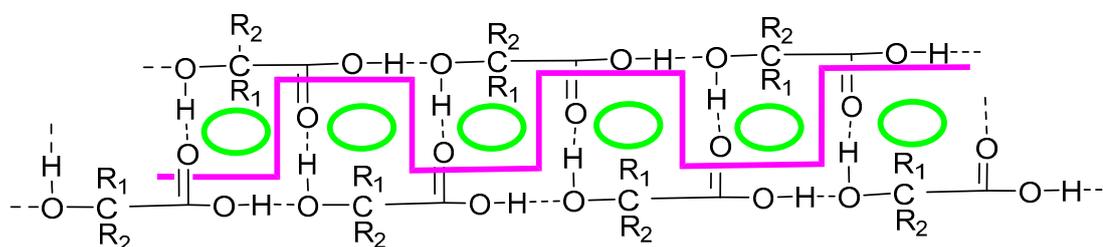
Representatives: SIMCEX; *rac*-3-Iodolactic acid *rac*-8 (CCDC ref. 2102493).



Scheme S3. Connectivity diagram in SIMCEX crystals.

Motif: $C_2^2(6):12/23$; $R_3^3(11):12/23/23$.

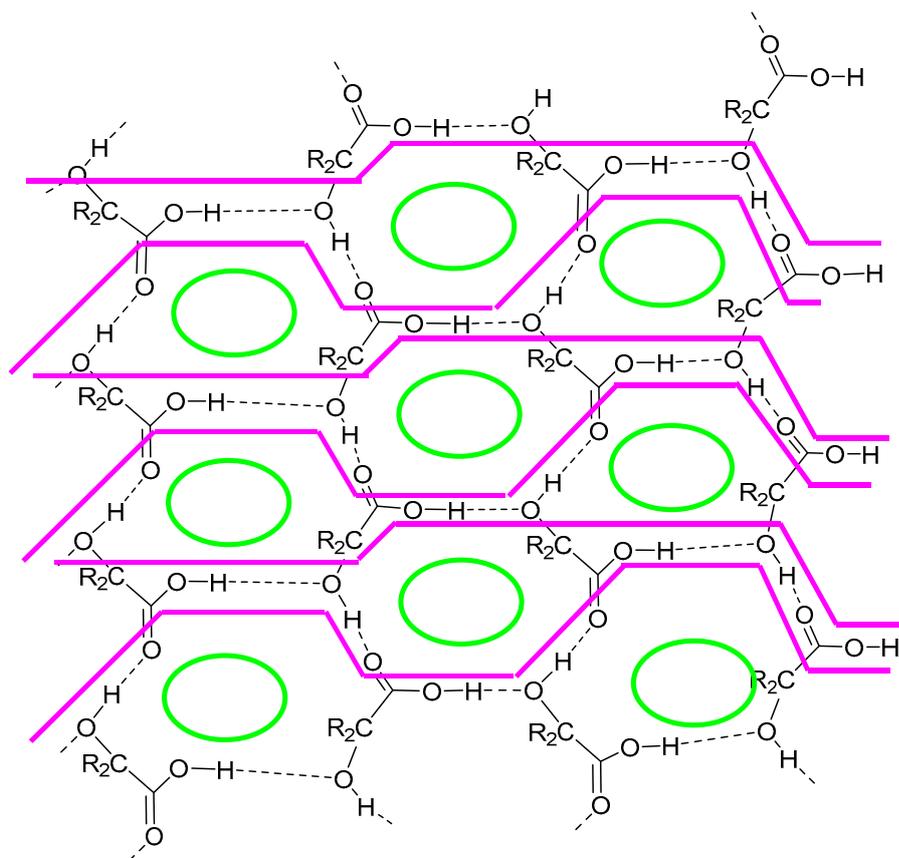
Representatives: MEWZOF; KEYYUJ; WERHEJ; (*S*)-PANRIG; (*R*)-6; (*S*)-OBEKAK; *scal*-PLACTA01.



Scheme S4. Connectivity diagram in MEWZOF crystals.

Motif: $C_2^2(6):12/23$; $R_4^4(16):\{23/12/23\}\{12\}$.

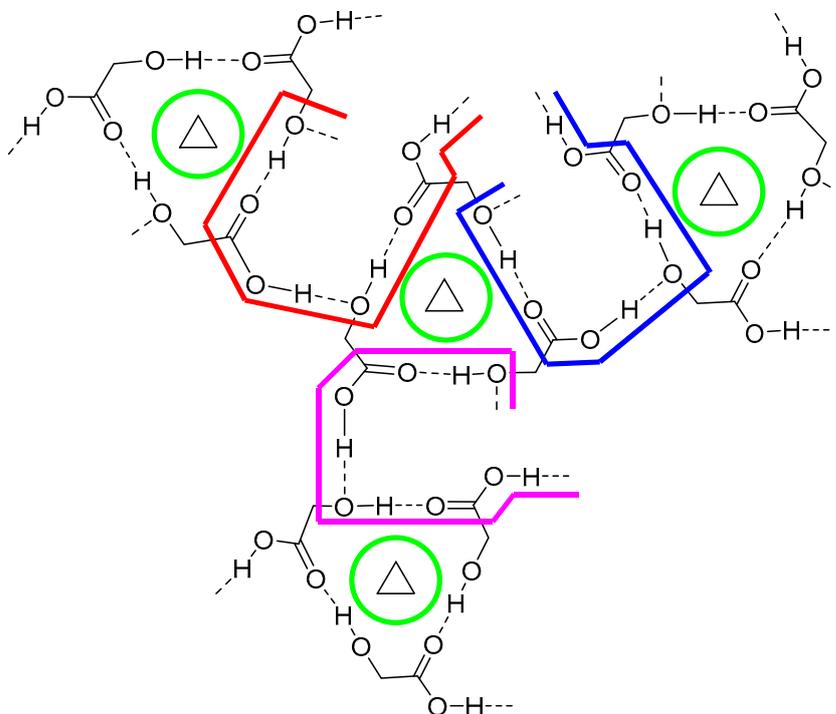
Representatives: TOWGEU.



Scheme S5. Connectivity diagram in TOWGEU crystals.

Motif: $C_2^2(6):12/23$; $R_3^3(15):23/23/23$.

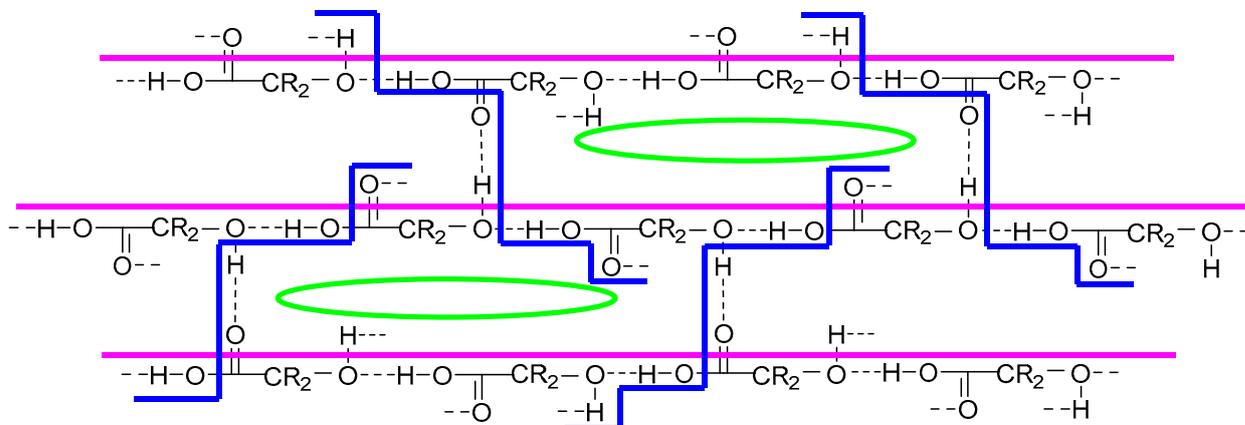
Representatives: HILMEV.



Scheme S6. Connectivity diagram in HILMEV crystals.

Motif: $C_1^1(5):12$; $C_2^2(6):12/23$; $R_6^6(26):\{23/12/12\}\{12/12/23\}$.

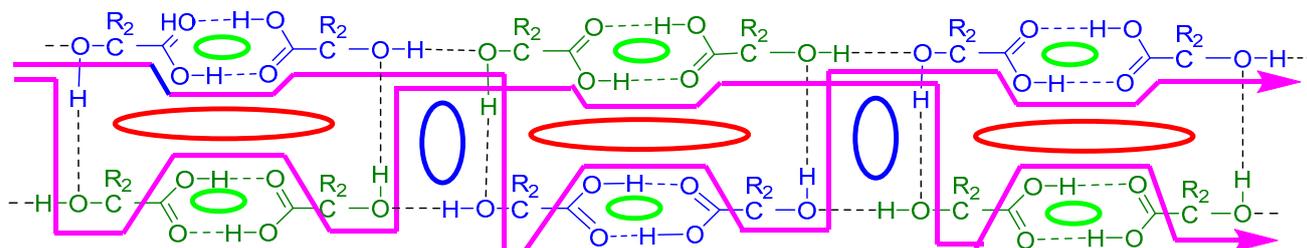
Representatives: GLICAC01.



Scheme S7. Connectivity diagram in GLICAC01 crystals. Purple segments denote chains $C_1^1(5):12$, blue broken lines denote fragments of chains $C_2^2(6):12/23$, green ovals denote cycles $R_6^6(26):\{23/12/12\}\{12/12/23\}$.

Motif: $C_3^3(12):22/22/13$; $R_2^2(8):13/13$; $R_4^4(8):22/22/22/22$; $R_4^4(20):\{13/22/13\}\{22\}$.

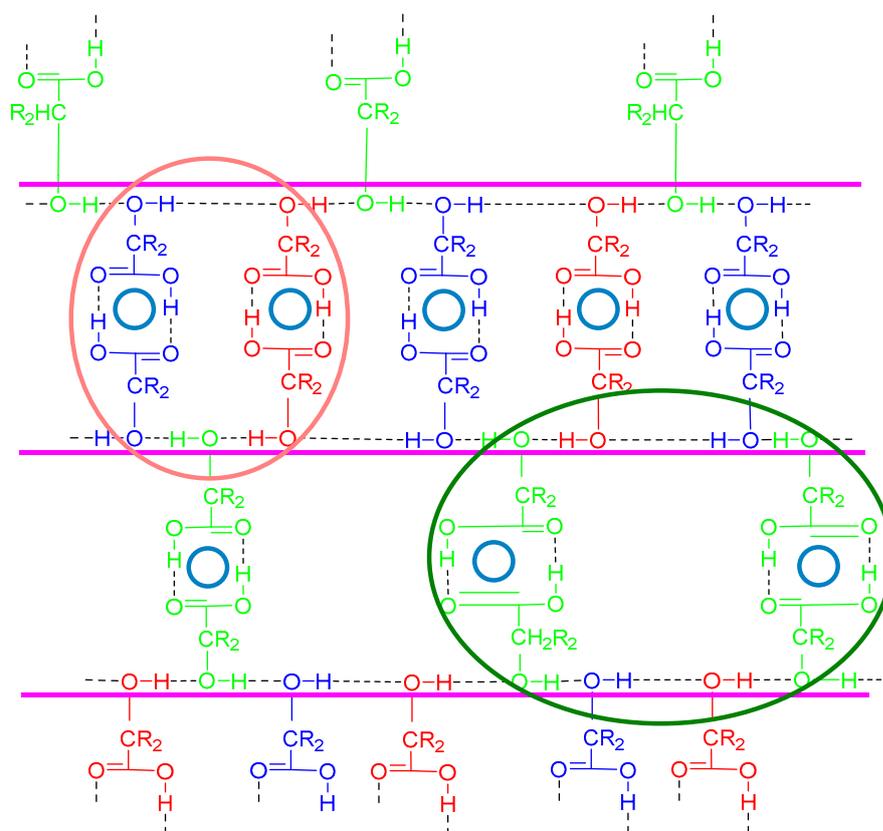
Representatives: SOYQIG01.



Scheme S8. Connectivity diagram in SOYQIG01 crystals. Broken purple lines indicate chains $C_3^3(12):22/22/13$, green, blue and red ellipses correspond to rings $R_2^2(8):13/13$, $R_4^4(8):22/22/22/22$ and $R_4^4(20):\{13/22/13\}\{22\}$ respectively.

Motif: $C_1^1(2):22$; $R_2^2(8):13/13$; $R_5^5(22):22/13/22/22/13$; $R_8^8(28):22/22/22/13/22/22/22/13$.

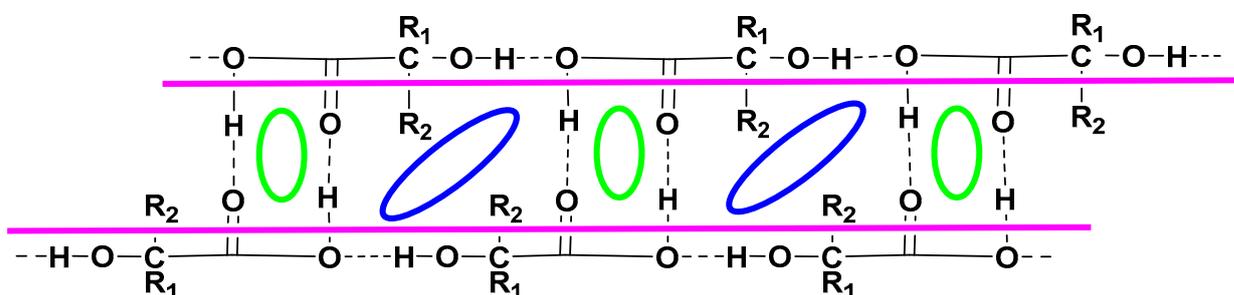
Representatives: SILDIB.



Scheme S9. Connectivity diagram in SILDIB crystals. Purple straight lines represent $C_1^1(2):22$ chains, emerald circles represent $R_2^2(8):13/13$ rings. The pink ring marks the unidirectional cycle $R_5^5(22):22/13/22/22/13$. The unidirectional cycle $R_8^8(28):22/22/22/13/22/22/22/13$ is highlighted in green.

Motif: $C_1^1(5):21$; $R_2^2(8):13/13$; $R_4^4(14):21/13/21/13$.

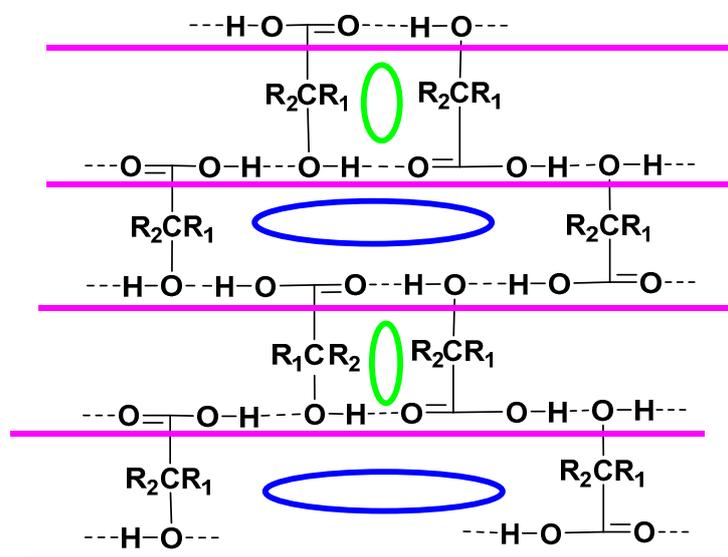
Representatives: *rac*-DLHTDA10.



Scheme S10. Connectivity diagram in *rac*-DLHTDA10 crystals.

Motif: $C_2^2(6):12/23$; $R_2^2(10):23/23$; $R_6^6(22):12/23/12/12/23/12$.

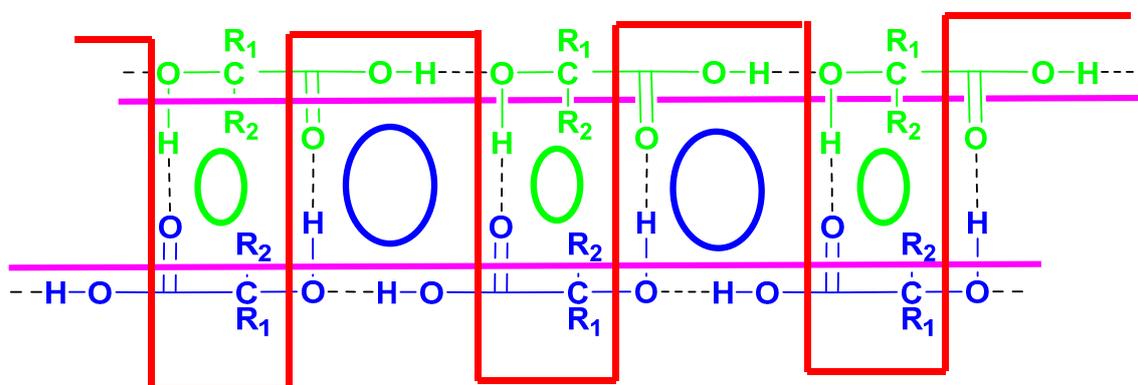
Representatives: *rac*-1; *rac*-AVIMEY; *rac*-2; *rac*-3; *rac*-4.



Scheme S11. Connectivity diagram in *rac*-1 crystals.

Motif: $C_1^1(5):12$; $C_3^3(11):12/23/23$; $R_2^2(10):23/23$; $R_4^4(12):12/23/12/23$.

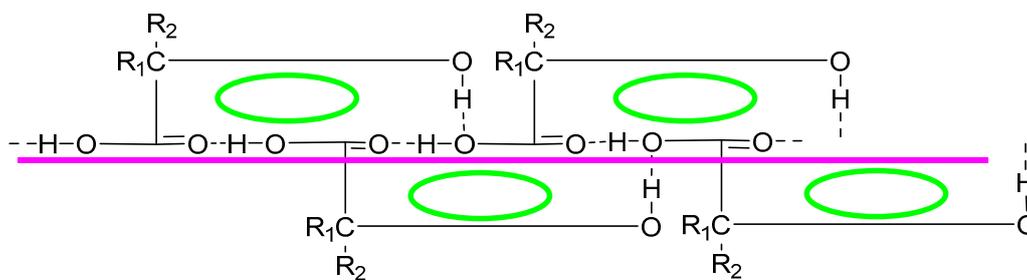
Representatives: *rac*-AVIMEY01.



Scheme S12. Connectivity diagram in *rac*-AVIMEY01 crystals.

Motif: $C_1^1(4):13$; $R_3^3(11):13/13/21$.

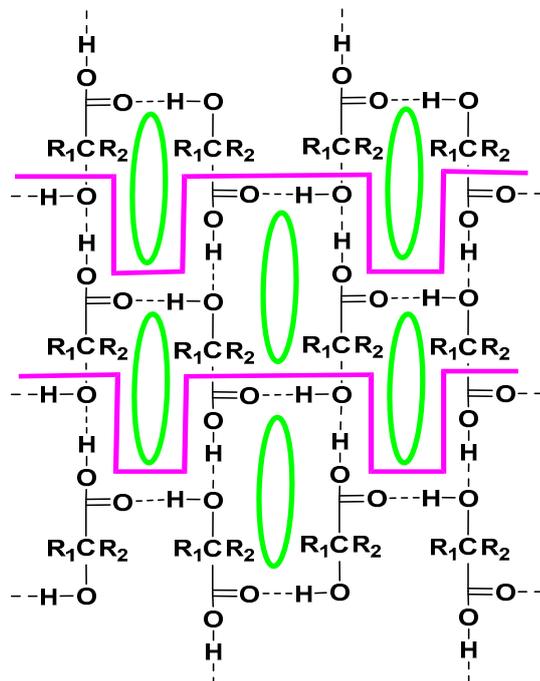
Representatives: (*S*)-1.



Scheme S13. Connectivity diagram in (*S*)-1 crystals.

Motif: $C_2^2(6):12/23; R_4^4(16):\{12/23/12\}\{23\}$.

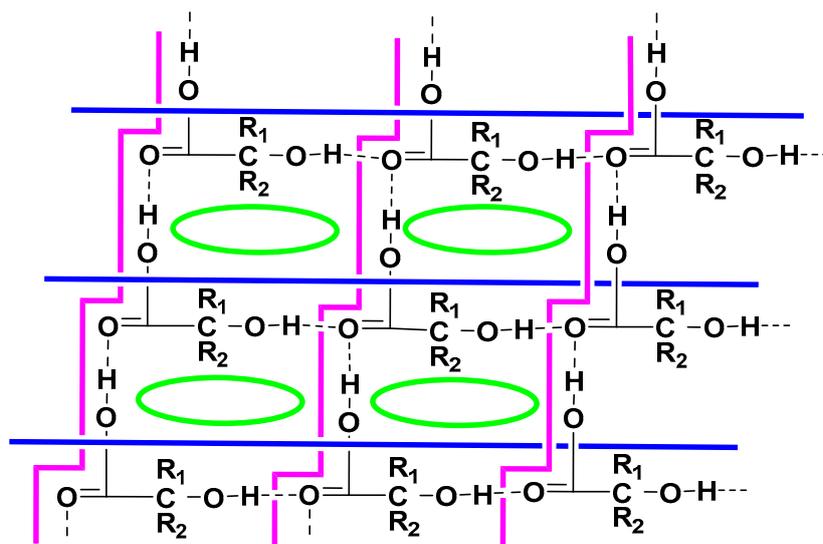
Representatives: (S)-3; (S)-5.



Scheme S14. Connectivity diagram in (S)-3 and (S)-5 crystals.

Motif: $C_1^1(4):13; C_1^1(5):23; R_4^4(16):\{13/23/13\}\{23\}$.

Representatives: (S)-4.

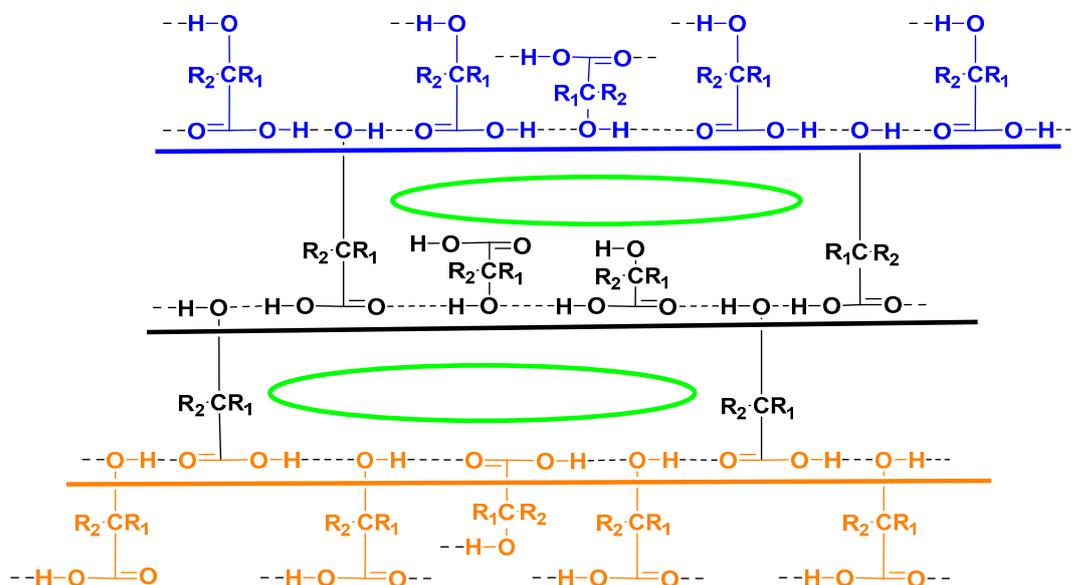


Scheme S15. Connectivity diagram in (S)-4 crystals.

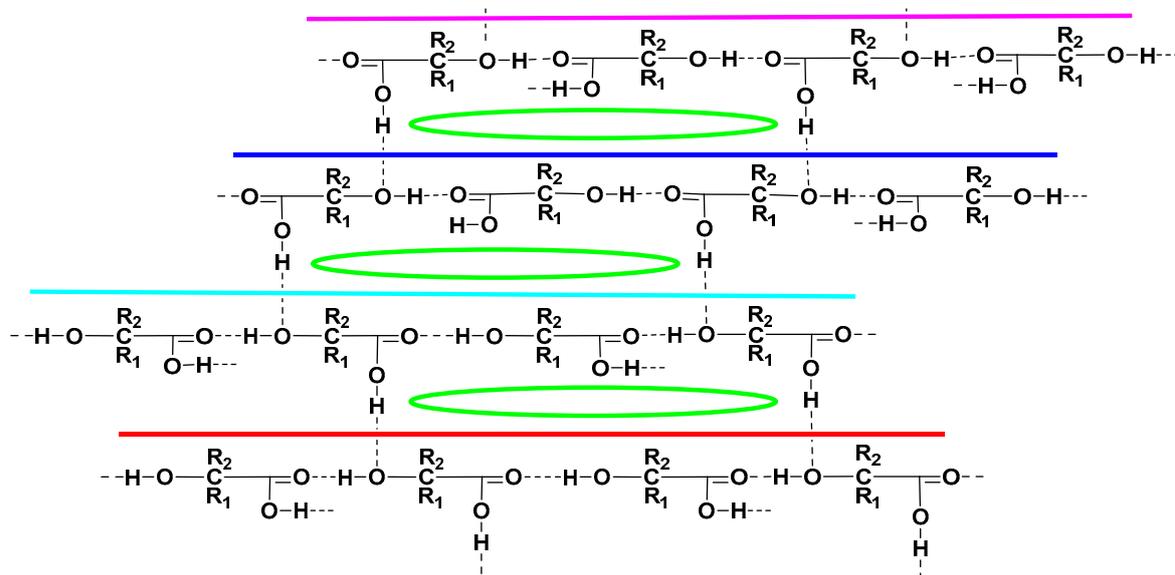
Motif: $C_1^1(6):23$; $C_2^2(6):12/23$; $R_6^6(26):\{12/23/23\}\{23/23/12\}$;

$R_8^8(28):(12/23/12/23/12/23/12/23)$.

Representatives: (*S*)-YILLAG.



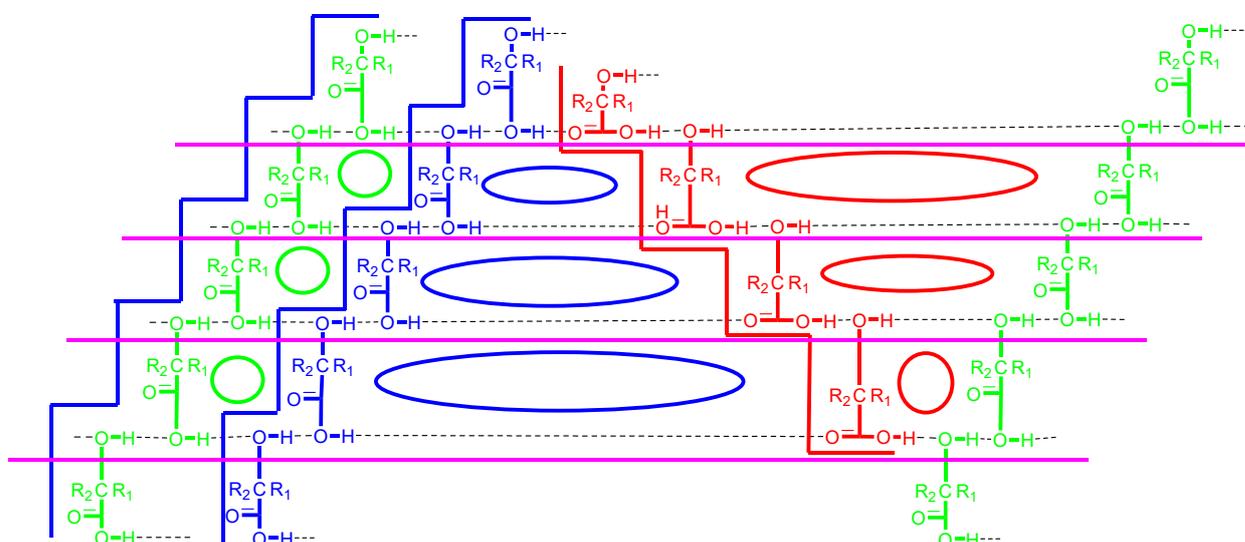
Scheme S16. $C_2^2(6):12/23$ chains, formed around screw axes 2_1 parallel to the $0b$ direction, and $R_8^8(28):(12/23/12/23/12/23/12/23)$ rings formed on their basis in (*S*)-YILLAG crystals.



Scheme S17. Chains $C_1^1(6):23$, formed around screw axes 2_1 parallel to $0a$ direction, and multidirectional rings $R_6^6(26):\{12/23/23\}\{23/23/12\}$ formed on their basis in (*S*)-YILLAG crystals.

Motif: $C_1^1(5):12$; $C_1^1(5):21$; $C_6^6(14):21/12/21/13/12/22$; $R_4^4(14):\{21/12\}\{12/21\}$;
 $R_4^4(14):\{22\}\{12/22/12\}$; $R_4^4(16):\{21/13/12\}\{13\}$.

Representatives: (S)-2.



Scheme S18. Connectivity diagram in crystals (S)-2; A molecules are shown in green, B molecules in blue, and C molecules in red. The red broken line corresponds to chains $C_1^1(5):12$, the blue broken lines correspond to chains $C_1^1(5):21$, and the purple straight lines correspond to chains $C_6^6(14):21/12/21/13/12/22$. The green ovals correspond to the rings $R_4^4(14):\{21/12\}\{12/21\}$, the red ones correspond to the rings $R_4^4(14):\{22\}\{12/22/12\}$, and the blue ones correspond to the rings $R_4^4(16):\{21/13/12\}\{13\}$.