Electronic Supplementary Material (ESI) for CrystEngComm.


# Structural characterization of form I of anhydrous rifampicin

*Amanda Laura Ibiapino,* [a] *Rafael Cardoso Seiceira,* [b] *Altivo Pitaluga Jr.,* [c] *Antonio Carlos Trindade* [d] *and Fabio Furlan Ferreira* [a*]

[a]Center of Natural and Human Sciences (CCNH), Federal University of ABC (UFABC), Av. dos Estados, 5001, Santo André, SP, 09210-580, Brazil

[b]Laboratory of Solid State Studies (LEES), Farmanguinhos, FIOCRUZ, Av. Comandante Guaranys, 447, Rio de Janeiro, RJ, 22775-903, Brazil

[c]Real Time Process and Chemical Analysis Development Center (NQTR), Chemistry Institute, Federal University of Rio de Janeiro (UFRJ), Rua Hélio de Almeida, 40, Rio de Janeiro, RJ, 21941-614, Brazil

[d]Federal Institute of São Paulo (IFSP), Av. Mogi das Cruzes, 1501, Suzano, SP, 08673-010, Brazil

[*] To whom correspondence should be addressed: e-mail: fabio.furlan@ufabc.edu.br. Tel.: +55 11 4996-8370; Fax: +55 11 4996-0090.

# Supporting Information

**Table S1 - Final coordinates and equivalent isotropic displacement parameters ($U_{iso} = B_{iso}/8\pi^2$) for all atoms in the polymorph I of anhydrous rifampicin crystal structure.**

| Atom | *x* | *y* | *z* | $U_{iso}$ (Å$^2$) |
|---|---|---|---|---|
| O(2) | 0.2744(9) | 0.300(2) | 1.0773(19) | 0.069(1) |
| O(6) | 0.1354(12) | 0.0768(2) | 0.841(2) | 0.069(1) |
| O(9) | 0.0525(11) | 0.175(3) | 0.791(2) | 0.069(1) |
| O(14) | 0.0264(10) | 0.503(3) | 0.7699(18) | 0.069(1) |
| O(17) | 0.0571(11) | 0.595(3) | 0.6599(19) | 0.069(1) |
| O(21) | 0.0707(11) | 0.724(3) | 0.590(2) | 0.069(1) |
| O(30) | 0.3302(10) | 0.670(2) | 0.801(2) | 0.069(1) |
| O(34) | 0.3881(9) | 0.535(2) | 0.9642(18) | 0.069(1) |
| O(38) | 0.3664(12) | 0.289(3) | 0.968(2) | 0.069(1) |
| O(41) | 0.4371(11) | 0.366(2) | 1.119(2) | 0.069(1) |
| O(55) | 0.1095(10) | 0.271(3) | 0.5205(19) | 0.069(1) |
| O(59) | 0.1020(10) | 0.128(2) | 0.611(2) | 0.069(1) |
| N(19) | 0.0944(13) | 0.609(3) | 0.507(3) | 0.069(1) |
| N(46) | 0.1348(13) | 0.511(3) | 0.403(3) | 0.069(1) |
| N(47) | 0.1595(13) | 0.504(4) | 0.340(3) | 0.069(1) |
| N(50) | 0.1512(15) | 0.478(3) | 0.138(3) | 0.069(1) |
| C(1) | 0.3105(11) | 0.250(3) | 1.174(2) | 0.069(1) |
| C(3) | 0.261(2) | 0.250(3) | 0.982(3) | 0.069(1) |
| C(4) | 0.2025(18) | 0.198(4) | 0.938(3) | 0.069(1) |
| C(5) | 0.1891(19) | 0.125(3) | 0.875(3) | 0.069(1) |
| C(7) | 0.078(2) | 0.111(4) | 0.747(4) | 0.069(1) |
| C(8) | 0.0363(11) | 0.027(3) | 0.693(2) | 0.069(1) |
| C(10) | 0.0513(18) | 0.261(5) | 0.749(6) | 0.069(1) |
| C(11) | 0.0365(17) | 0.341(6) | 0.784(4) | 0.069(1) |
| C(12) | 0.0133(13) | 0.339(3) | 0.860(3) | 0.069(1) |
| C(13) | 0.0386(19) | 0.424(5) | 0.735(5) | 0.069(1) |
| C(15) | 0.063(2) | 0.429(6) | 0.665(4) | 0.069(1) |
| C(16) | 0.0676(18) | 0.517(4) | 0.621(4) | 0.069(1) |
| C(18) | 0.0951(17) | 0.522(4) | 0.559(4) | 0.069(1) |
| C(20) | 0.0967(17) | 0.699(4) | 0.543(4) | 0.069(1) |
| C(22) | 0.1122(17) | 0.771(4) | 0.486(4) | 0.069(1) |
| C(23) | 0.0597(12) | 0.834(3) | 0.405(3) | 0.069(1) |
| C(24) | 0.1661(14) | 0.771(3) | 0.494(3) | 0.069(1) |
| C(25) | 0.2143(16) | 0.702(3) | 0.547(3) | 0.069(1) |
| C(26) | 0.2693(17) | 0.712(3) | 0.563(3) | 0.069(1) |
| C(27) | 0.3237(17) | 0.648(4) | 0.628(4) | 0.069(1) |
| C(28) | 0.3283(10) | 0.576(3) | 0.551(3) | 0.069(1) |
| C(29) | 0.3266(16) | 0.599(4) | 0.727(3) | 0.069(1) |
| C(31) | 0.3792(17) | 0.532(4) | 0.788(3) | 0.069(1) |
| C(32) | 0.4411(11) | 0.582(3) | 0.842(2) | 0.069(1) |
| C(33) | 0.3773(18) | 0.475(4) | 0.878(3) | 0.069(1) |
| C(35) | 0.3194(19) | 0.416(4) | 0.837(3) | 0.069(1) |
| C(36) | 0.3052(11) | 0.351(3) | 0.741(2) | 0.069(1) |
| C(37) | 0.3209(16) | 0.362(4) | 0.931(3) | 0.069(1) |
| C(39) | 0.4238(19) | 0.303(3) | 1.058(3) | 0.069(1) |
| C(40) | 0.4580(13) | 0.212(3) | 1.094(3) | 0.069(1) |
| C(42) | 0.2598(15) | 0.314(3) | 0.894(3) | 0.069(1) |
| C(43) | 0.2095(11) | 0.388(3) | 0.855(2) | 0.069(1) |
| C(44) | 0.1080(18) | 0.438(5) | 0.522(4) | 0.069(1) |
| C(45) | 0.1283(16) | 0.436(3) | 0.445(4) | 0.069(1) |

| | | | | |
|---|---|---|---|---|
| C(48) | 0.1581(16) | 0.411(3) | 0.297(3) | 0.069(1) |
| C(49) | 0.1849(14) | 0.411(3) | 0.227(3) | 0.069(1) |
| C(51) | 0.1720(13) | 0.475(3) | 0.061(3) | 0.069(1) |
| C(52) | 0.1613(16) | 0.571(3) | 0.187(3) | 0.069(1) |
| C(53) | 0.1350(14) | 0.578(4) | 0.258(3) | 0.069(1) |
| C(54) | 0.1005(17) | 0.351(4) | 0.560(4) | 0.069(1) |
| C(56) | 0.080(2) | 0.345(6) | 0.634(5) | 0.069(1) |
| C(57) | 0.071(2) | 0.259(4) | 0.673(5) | 0.069(1) |
| C(58) | 0.0830(18) | 0.167(5) | 0.662(4) | 0.069(1) |
| H(60) | 0.2158(19) | 0.105(3) | 0.853(3) | 0.082(1) |
| H(61) | 0.0299(11) | -0.003(3) | 0.746(2) | 0.082(1) |
| H(62) | -0.0024(11) | 0.046(3) | 0.629(2) | 0.082(1) |
| H(63) | 0.0550(11) | -0.017(3) | 0.668(2) | 0.082(1) |
| H(64) | 0.1736(18) | 0.219(4) | 0.956(3) | 0.082(1) |
| H(65) | 0.293(2) | 0.205(3) | 1.005(3) | 0.082(1) |
| H(66) | 0.2487(15) | 0.276(3) | 0.830(3) | 0.082(1) |
| H(67) | 0.0433(13) | 0.311(3) | 0.929(3) | 0.082(1) |
| H(68) | 0.0053(13) | 0.402(3) | 0.873(3) | 0.082(1) |
| H(69) | -0.0245(13) | 0.304(3) | 0.825(3) | 0.082(1) |
| H(70) | 0.3319(16) | 0.404(4) | 0.991(3) | 0.082(1) |
| H(71) | 0.2174(11) | 0.425(3) | 0.917(2) | 0.082(1) |
| H(72) | 0.2088(11) | 0.428(3) | 0.799(2) | 0.082(1) |
| H(73) | 0.1704(11) | 0.358(3) | 0.823(2) | 0.082(1) |
| H(74) | 0.3481(11) | 0.239(3) | 1.178(2) | 0.082(1) |
| H(75) | 0.3197(11) | 0.287(3) | 1.237(2) | 0.082(1) |
| H(76) | 0.2946(11) | 0.189(3) | 1.176(2) | 0.082(1) |
| H(77) | 0.1045(10) | 0.209(3) | 0.5475(19) | 0.082(1) |
| H(78) | 0.0277(10) | 0.564(3) | 0.7369(18) | 0.082(1) |
| H(79) | 0.2857(19) | 0.460(4) | 0.808(3) | 0.082(1) |
| H(80) | 0.1369(16) | 0.377(3) | 0.425(4) | 0.082(1) |
| H(81) | 0.0239(11) | 0.639(3) | 0.6091(19) | 0.082(1) |
| H(82) | 0.4117(18) | 0.432(4) | 0.911(3) | 0.082(1) |
| H(83) | 0.2653(11) | 0.324(3) | 0.710(2) | 0.082(1) |
| H(84) | 0.3049(11) | 0.388(3) | 0.684(2) | 0.082(1) |
| H(85) | 0.3365(11) | 0.305(3) | 0.766(2) | 0.082(1) |
| H(86) | 0.0907(13) | 0.604(3) | 0.442(3) | 0.082(1) |
| H(87) | 0.3763(17) | 0.488(4) | 0.734(3) | 0.082(1) |
| H(88) | 0.3885(9) | 0.510(2) | 1.0293(18) | 0.082(1) |
| H(89) | 0.4603(13) | 0.189(3) | 1.033(3) | 0.082(1) |
| H(90) | 0.5000(13) | 0.224(3) | 1.154(3) | 0.082(1) |
| H(91) | 0.4379(13) | 0.166(3) | 1.112(3) | 0.082(1) |
| H(92) | 0.2890(16) | 0.564(4) | 0.697(3) | 0.082(1) |
| H(93) | 0.4740(11) | 0.537(3) | 0.875(2) | 0.082(1) |
| H(94) | 0.4420(11) | 0.618(3) | 0.786(2) | 0.082(1) |
| H(95) | 0.4460(11) | 0.625(3) | 0.899(2) | 0.082(1) |
| H(96) | 0.1453(14) | 0.638(4) | 0.293(3) | 0.082(1) |
| H(97) | 0.0909(14) | 0.571(4) | 0.209(3) | 0.082(1) |
| H(98) | 0.1164(16) | 0.389(3) | 0.251(3) | 0.082(1) |
| H(99) | 0.1822(16) | 0.368(3) | 0.358(3) | 0.082(1) |
| H(100) | 0.3595(17) | 0.687(4) | 0.660(4) | 0.082(1) |
| H(101) | 0.3322(10) | 0.649(2) | 0.869(2) | 0.082(1) |
| H(102) | 0.1740(14) | 0.823(3) | 0.461(3) | 0.082(1) |
| H(103) | 0.0448(12) | 0.867(3) | 0.444(3) | 0.082(1) |
| H(104) | 0.0738(12) | 0.880(3) | 0.375(3) | 0.082(1) |
| H(105) | 0.0266(12) | 0.798(3) | 0.347(3) | 0.082(1) |
| H(106) | 0.2046(16) | 0.584(3) | 0.231(3) | 0.082(1) |
| H(107) | 0.1421(16) | 0.616(3) | 0.128(3) | 0.082(1) |
| H(108) | 0.1827(14) | 0.351(3) | 0.197(3) | 0.082(1) |

| | | | | |
|---|---|---|---|---|
| H(109) | 0.2274(14) | 0.431(3) | 0.273(3) | 0.082(1) |
| H(110) | 0.2744(17) | 0.763(3) | 0.526(3) | 0.082(1) |
| H(111) | 0.2947(10) | 0.532(3) | 0.522(3) | 0.082(1) |
| H(112) | 0.3263(10) | 0.610(3) | 0.493(3) | 0.082(1) |
| H(113) | 0.3674(10) | 0.544(3) | 0.595(3) | 0.082(1) |
| H(114) | 0.2062(16) | 0.646(3) | 0.574(3) | 0.082(1) |
| H(115) | 0.2154(13) | 0.490(3) | 0.102(3) | 0.082(1) |
| H(116) | 0.1656(13) | 0.414(3) | 0.030(3) | 0.082(1) |
| H(117) | 0.1494(13) | 0.520(3) | 0.002(3) | 0.082(1) |

**Table S2 Some selected H-bonds in the structure of form I of anhydrous RMP. Intermolecular bonds are denoted by superscripts.**

| D–H···A | D–H (Å) | H···A (Å) | D···A (Å) | D–H···A (°) |
|---|---|---|---|---|
| O(55)–H(77)···O(59) | 1.00(6) | 1.49(5) | 2.48(5) | 167(3) |
| O(14)–H(78)···O(17) | 1.00(6) | 1.70(4) | 2.49(5) | 132(4) |
| O(17)–H(81)···N(19)[a] | 0.99(5) | 2.60(5) | 3.31(5) | 128(4) |
| N(19)–H(86)···N(46) | 0.88(5) | 2.02(6) | 2.64(6) | 126(4) |
| O(34)–H(88)···O(41) | 0.99(3) | 2.39(4) | 3.05(4) | 123(3) |
| O(34)–H(88)···O(6)[b] | 0.99(3) | 2.44(4) | 3.21(4) | 134(3) |
| O(30)–H(101)···O(34) | 0.99(4) | 2.11(4) | 2.76(4) | 121(3) |
| C(3)–H(65)···O(38) | 0.96(7) | 2.54(6) | 2.90(7) | 103(4) |
| C(12)–H(68)···O(14) | 0.97(6) | 2.33(5) | 2.78(6) | 108(4) |
| C(37)–H(70)···O(34) | 0.95(6) | 2.53(6) | 2.91(6) | 104(4) |
| C(37)–H(70)···O(41) | 0.95(6) | 2.37(5) | 2.73(5) | 102(5) |
| C(45)–H(80)···O(55) | 0.96(6) | 2.39(6) | 2.75(6) | 102(5) |
| C(25)–H(114)···N(19) | 0.96(6) | 2.56(6) | 3.13(6) | 118(4) |

[a] Symmetry: -x, y, 1-z; [b] Symmetry: ½-x, ½+y, 2-z.

**Table S3 - Some selected bond distances for the polymorph I of anhydrous rifampicin.**

| Bonds | Lengths (Å) |
|---|---|
| O(2)-C(1) | 1.37(4) |
| O(2)-C(3) | 1.40(5) |
| O(6)-C(5) | 1.38(6) |
| O(6)-C(7) | 1.44(6) |
| O(9)-C(7) | 1.46(7) |
| O(9)-C(10) | 1.36(8) |
| O(14)-C(13) | 1.34(8) |
| O(17)-C(16) | 1.34(7) |
| O(21)-C(20) | 1.23(6) |
| O(30)-C(29) | 1.43(6) |
| O(34)-C(33) | 1.40(5) |

| | |
|---|---|
| O(38)-C(37) | 1.44(6) |
| O(38)-C(39) | 1.35(5) |
| O(41)-C(39) | 1.17(5) |
| O(55)-C(54) | 1.35(7) |
| O(59)-C(58) | 1.21(7) |
| N(19)-C(18) | 1.44(7) |
| N(19)-C(20) | 1.38(7) |
| N(46)-N(47) | 1.36(6) |
| N(46)-C(45) | 1.28(6) |
| N(47)-C(53) | 1.44(7) |
| N(47)-C(48) | 1.46(7) |
| N(50)-C(51) | 1.47(6) |
| C(33)-C(35) | 1.53(7) |
| C(35)-C(37) | 1.53(6) |
| C(35)-C(36) | 1.53(6) |
| C(37)-C(42) | 1.53(7) |
| C(39)-C(40) | 1.50(6) |
| C(42)-C(43) | 1.53(6) |
| C(44)-C(45) | 1.45(7) |
| C(44)-C(54) | 1.41(9) |
| C(48)-C(49) | 1.50(6) |
| C(52)-C(53) | 1.50(6) |
| C(54)-C(56) | 1.42(8) |
| C(56)-C(57) | 1.42(10) |
| C(57)-C(58) | 1.38(9) |
| N(50)-C(52) | 1.46(6) |
| N(50)-C(49) | 1.45(6) |
| C(3)-C(4) | 1.49(7) |
| C(3)-C(42) | 1.54(6) |
| C(4)-C(5) | 1.30(7) |
| C(7)-C(8) | 1.52(7) |
| C(7)-C(58) | 1.52(8) |
| C(10)-C(57) | 1.43(9) |
| C(10)-C(11) | 1.38(10) |

| | |
|---|---|
| C(11)-C(12) | 1.50(7) |
| C(11)-C(13) | 1.39(10) |
| C(13)-C(15) | 1.45(8) |
| C(15)-C(56) | 1.43(11) |
| C(15)-C(16) | 1.44(10) |
| C(16)-C(18) | 1.41(8) |
| C(18)-C(44) | 1.42(9) |
| C(20)-C(22) | 1.50(8) |
| C(22)-C(23) | 1.51(7) |
| C(22)-C(24) | 1.34(7) |
| C(24)-C(25) | 1.44(6) |
| C(25)-C(26) | 1.32(7) |
| C(26)-C(27) | 1.50(7) |
| C(27)-C(29) | 1.54(7) |
| C(27)-C(28) | 1.56(7) |
| C(29)-C(31) | 1.50(7) |
| C(31)-C(33) | 1.55(7) |
| C(31)-C(32) | 1.53(6) |

**Table S4 - Some selected bond angles for the polymorph I of anhydrous rifampicin.**

| Bonds | Angles (°) |
|---|---|
| C(1)-O(2)-C(3) | 113(3) |
| C(5)-O(6)-C(7) | 119(3) |
| C(7)-O(9)-C(10) | 107(4) |
| C(37)-O(38)-C(39) | 120(4) |
| C(18)-N(19)-C(20) | 129(4) |
| N(47)-N(46)-C(45) | 118(5) |
| N(46)-N(47)-C(53) | 109(4) |
| C(48)-N(47)-C(53) | 115(3) |
| N(46)-N(47)-C(48) | 116(4) |
| C(49)-N(50)-C(52) | 109(3) |
| C(51)-N(50)-C(52) | 110(4) |
| C(49)-N(50)-C(51) | 110(4) |
| O(2)-C(3)-C(4) | 109(4) |

| | |
|---|---|
| O(2)-C(3)-C(42) | 112(3) |
| C(4)-C(3)-C(42) | 113(3) |
| C(3)-C(4)-C(5) | 122(5) |
| O(6)-C(5)-C(4) | 119(5) |
| C(8)-C(7)-C(58) | 111(4) |
| O(6)-C(7)-O(9) | 107(3) |
| O(6)-C(7)-C(8) | 107(4) |
| O(6)-C(7)-C(58) | 116(5) |
| C(25)-C(26)-C(27) | 127(4) |
| C(26)-C(27)-C(28) | 112(4) |
| C(26)-C(27)-C(29) | 114(4) |
| C(28)-C(27)-C(29) | 111(4) |
| C(27)-C(29)-C(31) | 114(4) |
| O(30)-C(29)-C(27) | 108(4) |
| O(30)-C(29)-C(31) | 111(3) |
| C(29)-C(31)-C(32) | 112(4) |
| C(29)-C(31)-C(33) | 113(4) |
| C(32)-C(31)-C(33) | 109(3) |
| O(34)-C(33)-C(31) | 109(4) |
| O(34)-C(33)-C(35) | 111(4) |
| C(31)-C(33)-C(35) | 116(3) |
| C(33)-C(35)-C(36) | 113(4) |
| C(36)-C(35)-C(37) | 111(4) |
| C(33)-C(35)-C(37) | 113(3) |
| O(38)-C(37)-C(35) | 108(4) |
| C(35)-C(37)-C(42) | 113(3) |
| O(38)-C(37)-C(42) | 107(4) |
| O(38)-C(39)-C(40) | 110(4) |
| O(41)-C(39)-C(40) | 122(4) |
| O(38)-C(39)-O(41) | 123(5) |
| C(3)-C(42)-C(37) | 115(3) |
| C(3)-C(42)-C(43) | 110(4) |
| C(37)-C(42)-C(43) | 109(4) |
| C(18)-C(44)-C(45) | 124(5) |

| | |
|---|---|
| C(18)-C(44)-C(54) | 119(5) |
| C(45)-C(44)-C(54) | 117(5) |
| O(9)-C(7)-C(8) | 111(4) |
| O(9)-C(7)-C(58) | 106(5) |
| O(9)-C(10)-C(11) | 122(6) |
| O(9)-C(10)-C(57) | 113(5) |
| C(11)-C(10)-C(57) | 125(6) |
| C(10)-C(11)-C(12) | 123(6) |
| C(10)-C(11)-C(13) | 115(5) |
| C(12)-C(11)-C(13) | 121(6) |
| O(14)-C(13)-C(11) | 117(5) |
| O(14)-C(13)-C(15) | 120(6) |
| C(11)-C(13)-C(15) | 123(6) |
| C(13)-C(15)-C(16) | 121(7) |
| C(13)-C(15)-C(56) | 120(7) |
| C(16)-C(15)-C(56) | 119(5) |
| O(17)-C(16)-C(18) | 120(5) |
| C(15)-C(16)-C(18) | 121(5) |
| O(17)-C(16)-C(15) | 118(5) |
| C(16)-C(18)-C(44) | 120(5) |
| N(19)-C(18)-C(44) | 118(4) |
| N(19)-C(18)-C(16) | 120(5) |
| O(21)-C(20)-N(19) | 123(5) |
| O(21)-C(20)-C(22) | 119(5) |
| N(19)-C(20)-C(22) | 114(4) |
| C(20)-C(22)-C(23) | 116(4) |
| C(20)-C(22)-C(24) | 122(5) |
| C(23)-C(22)-C(24) | 122(4) |
| C(22)-C(24)-C(25) | 128(4) |
| C(24)-C(25)-C(26) | 124(4) |
| N(46)-C(45)-C(44) | 122(5) |
| N(47)-C(48)-C(49) | 112(4) |
| N(50)-C(49)-C(48) | 108(4) |
| N(50)-C(52)-C(53) | 111(4) |

| | |
|---|---|
| N(47)-C(53)-C(52) | 110(4) |
| C(44)-C(54)-C(56) | 122(6) |
| O(55)-C(54)-C(44) | 120(5) |
| O(55)-C(54)-C(56) | 119(5) |
| C(15)-C(56)-C(57) | 118(6) |
| C(15)-C(56)-C(54) | 119(7) |
| C(54)-C(56)-C(57) | 124(7) |
| C(10)-C(57)-C(56) | 119(6) |
| C(10)-C(57)-C(58) | 108(5) |
| C(56)-C(57)-C(58) | 133(6) |
| O(59)-C(58)-C(7) | 119(6) |
| O(59)-C(58)-C(57) | 134(6) |
| C(7)-C(58)-C(57) | 107(5) |