

Supporting information

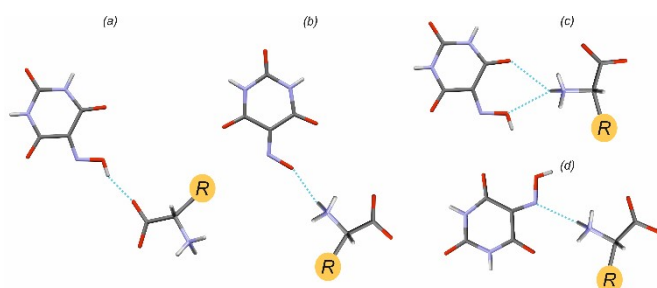
Deciphering colour mechanisms in co-crystals and salts containing violuric acid and chosen L-amino acids†

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Crystal Engineering

In order to design multi-component chromic materials composed of VA and AA, we started with a search in the Crystal Structural Database (CSD). We focused on crystal structures containing VA molecule or its anion to study hydrogen-bond motifs which are formed between VA and other components (including solvents). Based on these results (see SI), we design possible synthons which could occur between VA oxime group and AA, considering mainly ammonium and carboxylate groups (zwitterion form; Fig. S1). The carboxylate group can interact, e.g. with –OH oxime group (Fig. S1a), and ammonium group can form hydrogen bonds with either nitrogen and oxygen oxime atom (Fig. S2b, d). Bifurcated hydrogen bonds can be observed for VA as well for its anion, and could be formed via ammonium group of AA (Fig. 2c). The additional functional groups attached to the AA side chain, i.e. –OH, –NH₂, imidazole or guanidine group can replace some interactions described above, or be engaged in hydrogen bonds with secondary amine and carbonyl group of VA instead of formation of $R_2^2(8)$ dimers.



A CSD database search was narrowed to organic, not polymeric single crystals, with R_1 parameter less than 10%. We have also included into the analysis two polymorphic forms of VA ($P2_1/n^{31}$ and $Cmc2_1^{32}$). One of the crystal structures (refcode KEDYOI³³) was excluded from the final analysis due to severe disorder, making impossible to study hydrogen bonds involving VA oxime group. This analysis allowed us to identify the most frequent synthons (M1-M10) in materials containing VA or its deprotonated form (Fig. S2). The first assumption is, that VA molecules/anions likely form $R_2^2(8)$ dimers (M1 motif observed in 89% of studied phases) which together extend into the tapes,

Figure S1 Possible synthons which can be formed between VA molecule or anion and chosen AA (R denotes side chain of AA).

decreasing the number of possible donor and acceptor sites in VA. Thus, we can expect that this motif could also be present in our multicomponent crystal structures with selected AA. Because of that, further analysis was especially focused on hydrogen-bond preferences of the nitrogen and oxygen atoms in the oxime group. Single hydrogen bond of N-H...N (M6) and O-H...O type (M10) involving nitrogen oxime atom as an acceptor and oxygen oxime atom as a donor, respectively, are observed in 29% of the searched structures. Also, in the salt phases, the anion of VA frequently participates in the O-H...O interaction (M7; 24%). Carbonyl groups located in the vicinity of the oxime group enable formation of bifurcated hydrogen bonds either via N-H (M4, M9) or O-H (M3) donors (24, 19, 24%, respectively). Table S1 shows a summarized data for crystal structures included in the analysis.

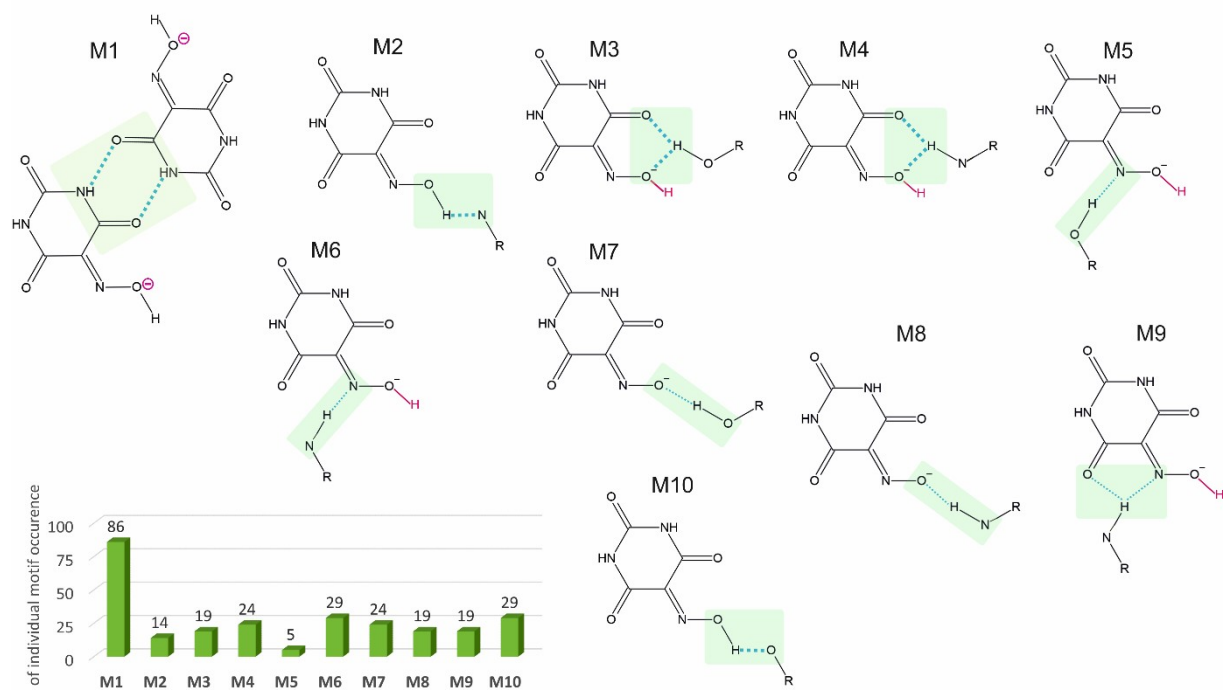


Fig. S2 Structural synthons found in the phases containing VA from our CSD search. On the bottom, the graph with percentage population of each motif found in those structures is presented. H-atoms and anion form of VA (⁻) shown in magenta means that a motif is observed for VA as well for its anion.

Table S1 The summarized data for the crystal structures included in the search. MX denotes a particular motif, and R_1 means the R-factor from the final refinement. Motifs including bifurcated hydrogen bonds, i.e. M3, M4 and M9 were taken into account if the difference in H...A distance between two hydrogen bonds was not greater than 0.2 Å. O denotes that motif is observed, X denotes that motif is absent.

	M1	M2	M3	M4	M5	M6	M7	M8	M9	M10	R_1
BENPIW ¹	O	O	X	O	X	X	X	X	X	O	7.5%
DAYHIV ²	O	X	X	X	X	X	X	X	X	O	4.1%
FIYXUJ ³	O	X	O	X	X	X	O	X	O	O	6.2%
FIYYAQ ³	X	X	X	X	X	O	X	O	X	O	5.6%
FIYYEU ³	X	X	X	X	X	X	X	X	X	O	5.3%
FUFPIG ^{*4}	X	X	X	X	X	O	X	X	O	O	6.3%
FUFPOM ⁴	X	X	O	X	X	O	X	X	X	O	3.7%
FUFPUS ^{*4}	X	X	X	X	X	O	X	X	O	O	8.8%
FUFQAZ ⁴	O	X	X	X	X	X	O	X	X	O	3.2%
JEFSUL ¹	X	X	X	X	X	O	O	O	X	O	7.1%
JEFTAS ¹	X	X	X	O	X	O	X	X	X	O	8.1%
MUYTAC ⁵	X	O	O	X	X	X	X	X	X	O	5.4%
MUYVOS ^{*5}	X	O	X	X	X	X	X	X	X	X	5.2%
PUQTIF ⁶	X	X	X	X	X	X	X	O	X	X	4.9%

WURCUJ* ⁷	X	X	X	X	X	X	X	X	X	O	
XIMKUA ⁸	X	X	X	X	X	X	X	O	X	O	5.3%
KOBNAT ⁹	X	X	X	O	X	X	O	X	X	O	4.0%
KOBNIB01 ⁹	X	X	X	O	O	X	X	X	X	O	8.1%
KOBNIB ⁹	X	X	X	O	X	X	O	X	X	O	6.7%
VIOLME03 ¹⁰	O	X	O	X	X	X	X	X	X	O	2.8%
VIOLME04 ¹¹	O	X	X	X	X	X	X	X	O	X	4.5%

* water molecules without hydrogens in a crystal structure

Table S2. Crystal data and details of structure refinement for the studied crystal structures.

	VASer	VATyr	VATrp*	VATrp	VALys	VAHis
Empirical formula	C ₇ H ₁₄ N ₄ O ₉	C ₁₃ H ₂₀ N ₄ O ₁₀	C ₁₅ H ₁₉ N ₅ O ₈	C ₁₅ H ₁₅ N ₅ O ₆	C ₂₀ H ₃₈ N ₁₀ O ₁₄	C ₂₀ H ₂₈ N ₁₂ O ₁₄
Formula weight [g/mol]	298.22	392.33	397.35	361.32	642.60	660.54
Temperature [K]	298(2)	100(2)	130(2)	298(2)	100(2)	293(2)
Wavelength [Å]	0.71073	0.71073	1.54184	1.54184	1.54184	1.54184
Crystal system	Orthorhombic	Orthorhombic	Monoclinic	Orthorhombic	Triclinic	Monoclinic
Space group	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>P</i> 2 ₁	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>P</i> 1	<i>P</i> 2 ₁
Unit cell dimensions [Å, °]	a = 6.2773(2) b = 12.2828(3) c = 15.5226(3) α = 90 β = 90 γ = 90	a = 6.7731(2) b = 14.3180(3) c = 17.8700(4) α = 90 β = 90 γ = 90	a = 7.2300(6) b = 16.1009(8) c = 8.0712(6) α = 90 β = 108.353(8) γ = 90	a = 5.5711(1) b = 7.6596(1) c = 35.1063(4) α = 90 β = 90 γ = 90	a = 5.0347(1) b = 10.3457(2) c = 14.3529(2) α = 108.720(2) β = 93.029(2) γ = 97.024(2)	a = 5.0921(1) b = 36.4707(4) c = 7.54320(10) α = 90 β = 109.463(1) γ = 90
Volume [Å ³]	1196.84(5)	1732.98(7)	891.77(12)	1498.07(4)	699.37(2)	1320.82(4)
Z/Z'	4/1	4/1	2/1	4/1	1/2	2/2
Density [g/cm ³]	1.655	1.504	1.480	1.602	1.526	1.661
Absorption coefficient [mm ⁻¹]	0.154	0.130	1.045	1.081	1.117	1.234
F(000)	624	824	416	752	340	688
Crystal size [mm]	0.40 x 0.20 x 0.20	0.17 x 0.02 x 0.01	0.05 x 0.05 x 0.010	0.10 x 0.04 x 0.02	0.22 x 0.08 x 0.02	0.13 x 0.05 x 0.01
Theta range for data collection [°]	3.105 to 27.497	1.823 to 27.498	5.495 to 66.965	2.517 to 69.949	3.267 to 71.963	2.423 to 69.000
Index ranges	-8<=h<=8 -15<=k<=15 -20<=l<=20	-8<=h<=8 -18<=k<=18 -23<=l<=23	-8<=h<=8 -19<=k<=18 -9<=l<=9	-6<=h<=6 -7<=k<=9 -42<=l<=42	-5<=h<=6 -12<=k<=12 -17<=l<=17	-6<=h<=6 -44<=k<=44 -8<=l<=9
Reflections collected	58263	63253	30224	14377	55829	34683
Independent reflections	2733 [R(int) = 0.0627]	3981 [R(int) = 0.0712]	3136 [R(int) = 0.3044]	2841 [R(int) = 0.0262]	5297 [R(int) = 0.0427]	4856 [R(int) = 0.0431]

Completeness [%]	99.1	99.8	99.9	99.8	99.8	99.4
Data / restraints / parameters	2733 / 7 / 223	3981 / 10 / 274	3136 / 9 / 254	2841 / 3 / 269	5297 / 26 / 476	4856 / 14 / 470
Goodness-of-fit on F^2	1.066	1.025	1.031	1.084	1.066	1.090
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0315 wR2 = 0.0767	R1 = 0.0309 wR2 = 0.0771	R1 = 0.0742 wR2 = 0.1530	R1 = 0.0300 wR2 = 0.0760	R1 = 0.0294 wR2 = 0.0808	R1 = 0.0362 wR2 = 0.0922
R indices (all data)	R1 = 0.0367 wR2 = 0.0805	R1 = 0.0352 wR2 = 0.0792	R1 = 0.1504 wR2 = 0.1966	R1 = 0.0311 wR2 = 0.0770	R1 = 0.0300 wR2 = 0.0813	R1 = 0.0377 wR2 = 0.0932
Absolute structure parameter	0.1(5)	-0.5(4)	0.0(5)	-0.11(6)	-0.01(7)	-0.05(7)
Largest diff. peak and hole [$e/\text{\AA}^{-3}$]	0.175 and -0.166 rms 0.044	0.320 and -0.188 rms 0.042	0.529 and -0.250	0.158 and -0.230 rms 0.037	0.343 and -0.256 rms 0.042	0.451 and -0.172 rms 0.039

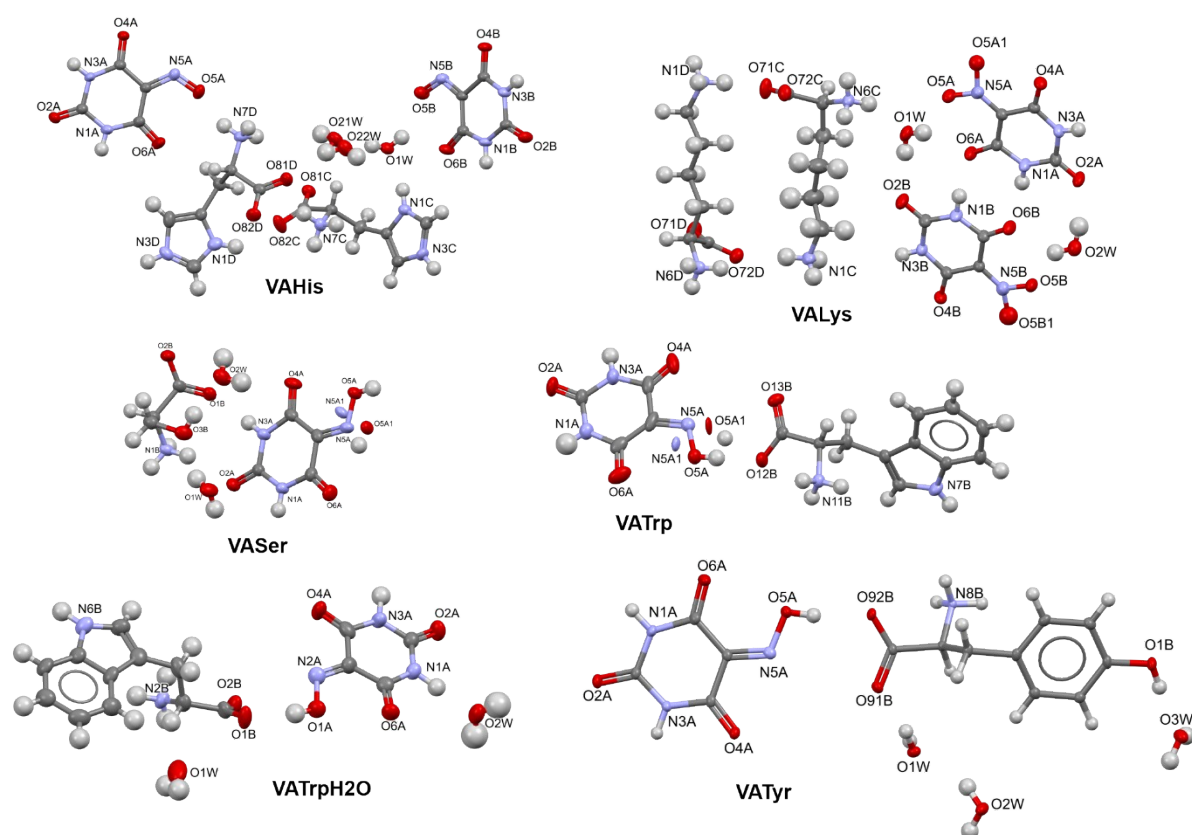


Fig. S3 Asymmetric units of the violurate salts with amino acids. Atomic electron density is represented by ellipsoids at 50% probability. Labels are provided for the non-carbon and non-hydrogen atoms.

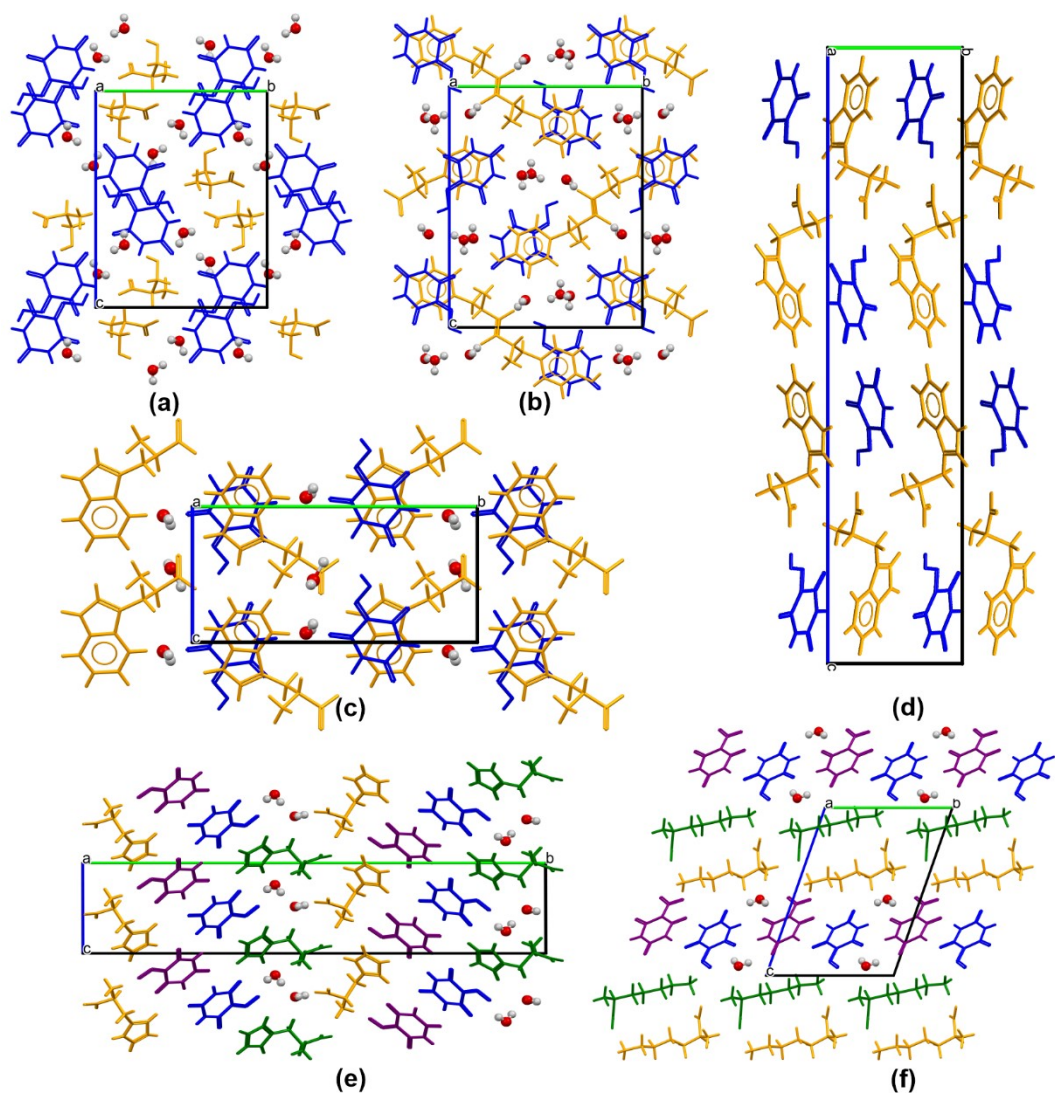


Fig. S4 Packing of the structural components viewed along [100] direction in a) VASer, b) VATyr, (c) VATrp, (d) VATrp*, (e) VAHis and (f) VALys. Symmetry equivalent molecules/ions were marked in the same colour.

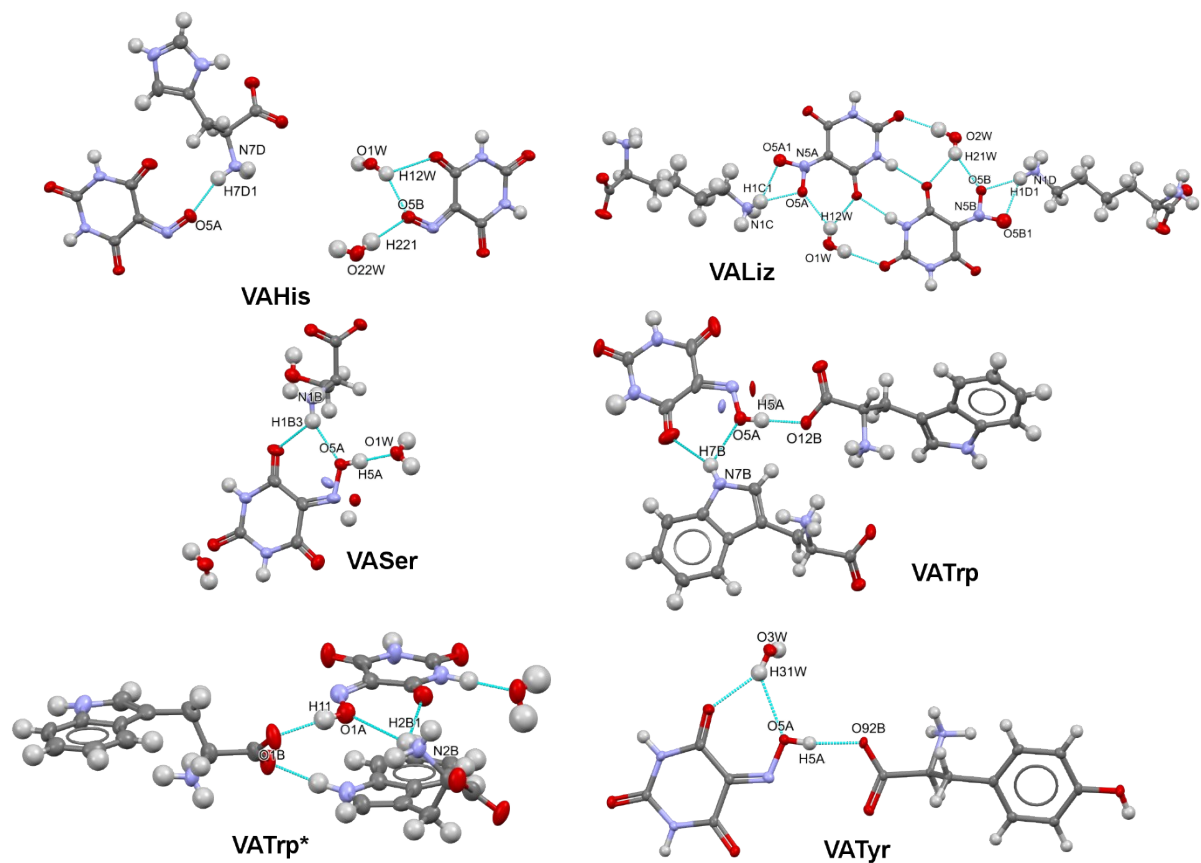


Fig. S5 Hydrogen bonds around each oxime group in the studied crystals.

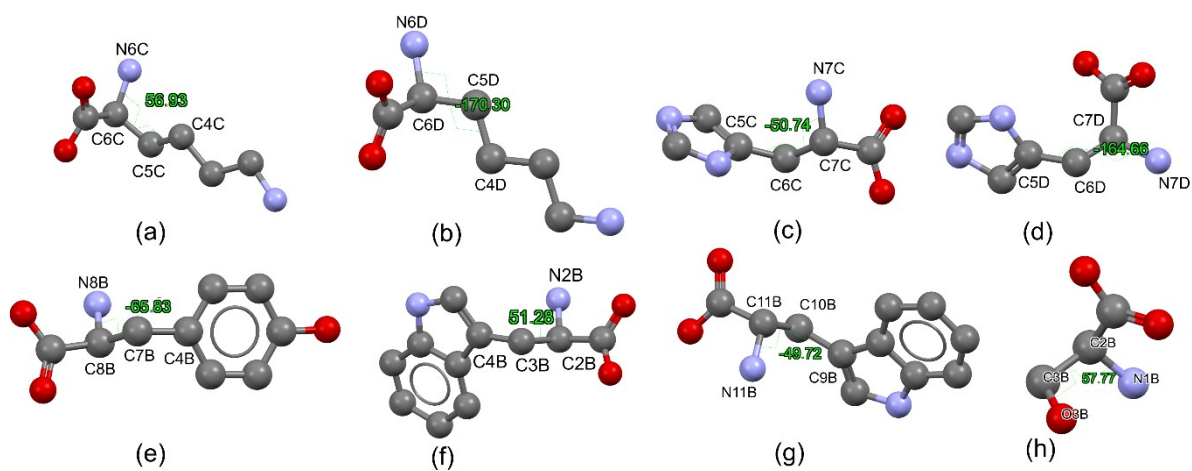


Fig. S6 Conformations of a) C-cation of L-Lys in VALys; b) D-cation of L-Lys in VALys; c) C-cation of L-His in VAHis; d) D-cation of L-His in VAHis; e) L-Tyr in VATyr; f) L-Trp in VATrp*; and g) L-Trp in VATrp h) L-Ser in VASer crystal structures.

Table S3 Geometry of hydrogen bonds found in VASer, VATyr, VATrp, VALys and VAHis crystal structures.

	D-H [Å]	H...A [Å]	D...A [Å]	D-H...A [°]
VATyr, T=100K				
N1A-H1A...O2W ⁽ⁱ⁾	0.88(1)	2.02(2)	2.819(2)	151(2)
N3A-H3A...O1W ⁽ⁱⁱ⁾	0.88(1)	1.92(1)	2.796(2)	172(2)
O5A-H5A...O92B	0.84(1)	1.78(2)	2.615(2)	171(3)
O1B-H1B...O3W	0.84(1)	1.82(1)	2.653(2)	175(3)
C2B-H2B...O6A ⁽ⁱⁱⁱ⁾	0.95	2.50	3.428(2)	166
C8B-H8B...N5A ^(iv)	1.00	2.69	3.396(3)	128
N8B-H8B1...O91B ^(iv)	0.91	2.00	2.815(2)	148
N8B-H8B2...O1B ^(v)	0.91	2.09	2.940(2)	154
N8B-H8B3...O4A ^(iv)	0.91	1.94	2.829(2)	165
O1W-H11W...O91B	0.84(1)	1.88(1)	2.705(2)	169(3)
O1W-H12W...O92B ^(iv)	0.83(1)	2.04(1)	2.849(2)	166(3)
O2W-H21W...O2A ⁽ⁱⁱⁱ⁾	0.84(1)	2.48(3)	2.986(2)	120(2)
O2W-H21W...O4A ^(vi)	0.84(1)	2.11(2)	2.912(2)	158(3)
O2W-H22W...O1W	0.84(1)	2.00(2)	2.801(2)	158(3)
O3W-H31W...O5A ⁽ⁱⁱⁱ⁾	0.83(1)	2.35(2)	2.993(2)	135(2)
O3W-H31W...O6A ⁽ⁱⁱⁱ⁾	0.83(1)	2.05(2)	2.803(2)	150(3)
O3W-H32W...O2W ^(vii)	0.83(1)	2.02(1)	2.850(3)	173(3)
(i) x, y+1, z; (ii) -x+1, y+1/2, -z+1/2; (iii) x, y-1, z; (iv) x+1/2, -y+3/2, -z+1; (v) -x+1, y+1/2, -z+3/2; (vi) -x+1, y-1/2, -z+1/2; (vii) x+1/2, -y+1/2, -z+1				
VASer, T=298K				
N1A-H1A...O2B ⁽ⁱ⁾	0.86(1)	1.93(1)	2.788(2)	173(2)
N3A-H3A...O1B	0.86(1)	2.00(1)	2.851(2)	172(3)
O5A-H5A...O1W ⁽ⁱⁱ⁾	0.82	1.64	2.458(4)	175
O5A1-H5A1...O6A	0.82	2.18	2.841(4)	138
O5A1-H5A1...O2W ⁽ⁱⁱ⁾	0.82	2.29	2.912(5)	133
C2B-H2B...O1B ⁽ⁱⁱⁱ⁾	0.98	2.49	3.432(3)	162
N1B-H1B1...O2B ^(iv)	0.89	2.01	2.874(3)	162
N1B-H1B2...O2A	0.89	2.09	2.948(2)	161
N1B-H1B3...O4A ⁽ⁱ⁾	0.89	2.23	2.838(2)	125
N1B-H1B3...O6A ^(v)	0.89	2.61	3.041(3)	111
N1B-H1B3...O5A ⁽ⁱ⁾	0.89	2.04	2.842(4)	150

N1B-H1B3...N5A1 ⁽ⁱ⁾	0.89	2.51	3.386(8)	169
O3B-H7B...O2W	0.82(1)	1.86(1)	2.670(3)	173(3)
O1W-H11W...O1B ⁽ⁱ⁾	0.83(1)	1.98(2)	2.767(2)	158(3)
O1W-H12W...O4A ⁽ⁱ⁾	0.82(2)	2.65(3)	3.172(3)	123(3)
O1W-H12W...O3B	0.82(2)	2.01(2)	2.750(2)	150(3)
O2W-H21W...O2A ^(vi)	0.82(1)	2.14(1)	2.906(3)	157(3)
O2W-H22W...O6A ^(vii)	0.82(1)	2.10(2)	2.880(3)	159(3)
O2W-H22W...O5A1 ^(vii)	0.82(1)	2.40(3)	2.912(5)	121(3)

(i) $-x, y-1/2, -z+1/2$; (ii) $x+1/2, -y+1/2, -z+1$; (iii) $x-1/2, -y+1/2, -z$; (iv) $x+1/2, -y+1/2, -z$; (v) $-x+1/2, -y, z-1/2$; (vi) $-x, y+1/2, -z+1/2$; (vii) $x-1/2, -y+1/2, -z+1$

VATrp, T=298K

N1A-H1A...O2A ⁽ⁱ⁾	0.86(1)	2.02(1)	2.881(3)	174(3)
O5A-H5A...O12B	0.82	1.72	2.543(4)	177
O5A1-H5A1...O12B	0.82	1.69	2.504(8)	173
O5A1-H5A1...O13B	0.82	2.44	2.854(8)	112
N7B-H7B...O5A ⁽ⁱⁱ⁾	0.86(1)	2.37(2)	2.966(3)	127(2)
N7B-H7B...N5A19 ⁽ⁱⁱ⁾	0.86(1)	2.57(2)	3.324(9)	146(2)
N7B-H7B...O6A ⁽ⁱⁱ⁾	0.86(1)	2.13(2)	2.923(3)	153(2)
C8B-H8B...O5A ⁽ⁱⁱ⁾	0.99(3)	2.62(3)	3.153(4)	114(2)
C8B-H8B...O12B ⁽ⁱⁱ⁾	0.99(3)	2.44(3)	3.429(3)	174(2)
C10B-H10B...O5A ⁽ⁱⁱⁱ⁾	0.97	2.62	3.272(3)	125
C11B-H11B...O5A1 ^(iv)	0.98	2.57	3.131(5)	117
N11B-H11D...O4A ^(iv)	0.89	2.00	2.880(2)	168
N11B-H11A...O13B ^(iv)	0.89	2.06	2.944(2)	172
N11B-H11C...O13B ^(v)	0.89	2.13	2.938(2)	151

(i) $x+1/2, -y+1/2, -z+1$; (ii) $-x+2, y+1/2, -z+3/2$; (iii) $-x+1, y+1/2, -z+3/2$; (iv) $-x+1, y-1/2, -z+3/2$; (v) $x+1, y, z$

VALys, T=100K

N1A-H1A...O6B	0.87(1)	1.95(1)	2.817(3)	177(3)
N3A-H3A...O4B ⁽ⁱ⁾	0.87(1)	1.98(1)	2.849(2)	175(3)
N1B-H1B...O6A	0.87(1)	1.95(2)	2.816(2)	173(3)
N3B-H3B...O4A ⁽ⁱⁱ⁾	0.87(1)	1.98(1)	2.843(3)	176(3)
N1C-H1C1...N5A ⁽ⁱⁱⁱ⁾	0.90(1)	2.61(2)	3.416(3)	149(3)
N1C-H1C1...O5A ⁽ⁱⁱⁱ⁾	0.90(1)	1.98(2)	2.802(3)	152(3)
N1C-H1C1...O5A' ⁽ⁱⁱⁱ⁾	0.90(1)	2.14(3)	2.789(13)	128(3)

N1C-H1C2...O72D	0.89(1)	2.00(2)	2.870(3)	164(3)
N1C-H1C2...O71D ^(iv)	0.89(1)	2.44(3)	2.876(3)	110(2)
N1C-H1C3...O4A ⁽ⁱⁱ⁾	0.90(1)	2.20(2)	2.874(2)	131(2)
N1C-H1C3...N5A ⁽ⁱⁱ⁾	0.90(1)	2.34(2)	3.160(3)	151(3)
N1C-H1C3...O5A' ⁽ⁱⁱ⁾	0.90(1)	2.13(2)	2.938(14)	148(3)
C2C-H2C1...O5A' ⁽ⁱⁱⁱ⁾	0.99	2.37	2.957(10)	118
C2C'-H2C4...O72D	0.99	2.61	3.21(2)	119
C6C-H6C...O5A ^(v)	1.00	2.53	3.392(3)	144
N6C-H6C1...O71C ^(iv)	0.90(1)	1.90(2)	2.791(3)	172(3)
N6C-H6C2...O1W	0.90(1)	1.84(2)	2.736(2)	171(3)
N6C-H6C3...O72D ^(vi)	0.90(1)	1.95(2)	2.803(2)	157(3)
N1D-H1D1...N5B ^(vii)	0.90(1)	2.66(2)	3.494(3)	155(2)
N1D-H1D1...O5B ^(vii)	0.90(1)	1.90(2)	2.789(3)	170(3)
N1D-H1D2...O4B ^(viii)	0.92(1)	2.45(3)	2.952(2)	115(2)
N1D-H1D2...N5B ^(viii)	0.92(1)	2.18(2)	3.042(3)	156(3)
N1D-H1D3...O71C	0.92(1)	1.88(2)	2.763(2)	161(3)
C2D-H2D2...O2A ^(ix)	0.99	2.60	3.496(3)	150
N6D-H6D1...O72C ⁽ⁱⁱⁱ⁾	0.91(1)	1.92(2)	2.804(2)	164(3)
N6D-H6D2...O71D ^(iv)	0.91(1)	1.83(2)	2.735(3)	171(3)
N6D-H6D3...O5B ^(x)	0.92(1)	2.60(3)	3.044(2)	110(2)
N6D-H6D3...O2W ^(x)	0.92(1)	1.89(2)	2.802(3)	173(3)
O1W-H1W1...O5A	0.85(1)	2.19(2)	2.869(3)	137(3)
O1W-H1W1...O6A	0.85(1)	2.03(2)	2.758(2)	144(3)
O1W-H1W2...O2B	0.84(1)	2.03(2)	2.870(2)	175(3)
O2W-H2W1...O5B	0.84(1)	2.27(3)	2.836(2)	125(3)
O2W-H2W1...O6B	0.84(1)	1.99(2)	2.776(2)	156(3)
O2W-H2W2...O2A	0.84(1)	2.06(2)	2.900(2)	177(3)

(i) x-1, y+1, z; (ii) x+1, y-1, z; (iii) x, y-1, z; (iv) x-1, y, z; (v) x+1, y, z; (vi) x, y+1, z; (vii) x+2, y, z-1; (viii) x+1, y, z-1; (ix) x+2, y-1, z-1; (x) x+1, y-1, z-1

VAHis, T=293K

N1A-H1A...O2B ⁽ⁱ⁾	0.86(2)	2.05(2)	2.912(4)	175(4)
N3A-H3A...O4B ⁽ⁱⁱ⁾	0.86(2)	2.01(2)	2.859(4)	171(4)
N1B-H1B...O2A ⁽ⁱⁱⁱ⁾	0.86(2)	2.06(1)	2.916(4)	177(4)
N1C-H1C...O6B	0.86(2)	2.64(4)	3.158(4)	120(3)
N1C-H1C...O1W	0.86(2)	1.93(2)	2.769(4)	165(4)

C2C-H2C...O2A ⁽ⁱⁱⁱ⁾	0.93	2.39	3.240(4)	152
N3C-H3C...O4B ^(iv)	0.86(2)	1.99(2)	2.851(4)	171(4)
N3C-H3C...N5B ^(iv)	0.86(2)	2.55(4)	3.050(4)	118(4)
C4C-H4C...N5B ^(iv)	0.93	2.52	3.031(5)	115
C4C-H4C...O5B ^(iv)	0.93	2.55	3.348(4)	144
C4C-H4C...O22W ^(v)	0.93	2.38	3.188(14)	146
C6C-H6C1...O21W ^(v)	0.97	2.37	3.296(8)	161
C7C-H7C...O21W	1.01(4)	2.56(4)	3.508(7)	155(3)
C7C-H7C...O22W	1.01(4)	2.67(4)	3.547(12)	145(3)
N7C-H7C3...O1W ^(vi)	0.89	2.04	2.870(4)	155
N7C-H7C1...O81D	0.89	1.94	2.755(4)	151
N7C-H7C2...O81C ^(vi)	0.89	2.05	2.803(4)	142
N1D-H1D...O81C ^(vi)	0.87(2)	2.14(3)	2.938(4)	153(4)
C2D-H2D...N5A ^(iv)	0.93	2.36	2.906(5)	117
C2D-H2D...O5A ^(iv)	0.93	2.32	3.152(5)	148
C2D-H2D...O82C ^(vi)	0.93	2.65	3.193(5)	118
N3D-H3D...O4A ^(iv)	0.86(2)	2.11(2)	2.972(4)	178(5)
C4D-H4D...O6A	0.93	2.58	3.235(5)	128
C6D-H6D1...O6A	0.97	2.34	3.090(5)	134
C6D-H6D2...O82C	0.97	2.66	3.559(5)	155
C7D-H7D...O5A ^(vi)	0.94(4)	2.41(4)	3.337(4)	167(3)
N7D-H7D1...O5A	0.89	1.98	2.830(4)	160.3
N7D-H7D2...O81C ^(vii)	0.89	1.90	2.790(4)	174
N7D-H7D3...O82D ^(viii)	0.89	1.89	2.768(4)	171
O1W-H11W...O21W	0.88(5)	1.86(5)	2.733(8)	171(5)
O1W-H11W...O22W	0.88(5)	1.88(5)	2.734(13)	165(5)
O1W-H12W...O5B	0.78(4)	2.06(5)	2.763(4)	150(5)
O1W-H12W...O6B	0.78(4)	2.27(5)	2.833(4)	129(4)
O21W-H211...O81D ^(viii)	0.83(2)	2.70(7)	3.323(18)	133(8)
O21W-H211...O82D ^(viii)	0.83(2)	1.97(3)	2.787(18)	171(10)
O22W-H221...O5B ^(vi)	0.91(2)	1.94(2)	2.81(3)	159(14)
O21W-H222...O81D	0.82(2)	2.03(2)	2.762(7)	149(3)
O22W-H222...O81D	0.82(2)	2.03(2)	2.805(11)	156(3)

(i) $-x+1, y+1/2, -z+1$; (ii) $-x+3, y+1/2, -z+2$; (iii) $-x+1, y-1/2, -z+1$; (iv) $x-2, y, z-1$; (v) $x-1, y, z-1$; (vi) $x-1, y, z$; (vii) $x, y, z+1$; (viii)

Table S4 Geometry of $\pi\cdots\pi$ and $LP\cdots\pi$ in VATyr, VATrp and VAHis crystal structures.

Interaction	Cg...Cg distance [\AA] ^[a]	γ angle [$^\circ$] ^[b]
$\pi(\text{double bond})\cdots\pi$		
VATyr		
Cg(C4A=O4A) \cdots Cg(1)	3.236	6.63
Cg(1) [C1B-C2B-C3B-C4B-C5B-C6B]		
VATrp		
Cg(C6A=O6A) \cdots Cg(1)	3.293	11.90
Cg(C4A=O4A) \cdots Cg(3)	3.546	26.05
Cg(C5A=N5A) \cdots Cg(3)	3.399	12.90
Cg(1) [C1B-C2B-C3B-C4B-C5B-C6B]		
Cg(3) [C5B-C6B-N7B-C8B-C9B]		
VATrp*		
Cg(C2A=O2A) \cdots Cg(1)	3.385	5.78
Cg(1) [C7B-C8B-C9B-C10B-C11B-C12B]		
VAHis		
Cg(C5A=N5A) \cdots Cg(3)	3.370	8.80
Cg(C5B=N5B) \cdots Cg(4)	3.451	7.62
LP(O1W) \cdots Cg(4)	3.386	89.95
Cg(1) [N1A-C2A-N3A-C4A-C5A-C6A]		
Cg(2) [N1B-C2B-N3B-C4B-C5B-C6B]		
Cg(3) [N1D-C2D-N3D-C4D-C5D]		
Cg(4) [N1C-C2C-N3C-C4C-C5C]		
[a] perpendicular distance of Cg(x) to the Cg(y) ring best plane;		
[b] the angle between the Cg(x) \cdots Cg(y) vector and normal to Cg(x) ring best plane		

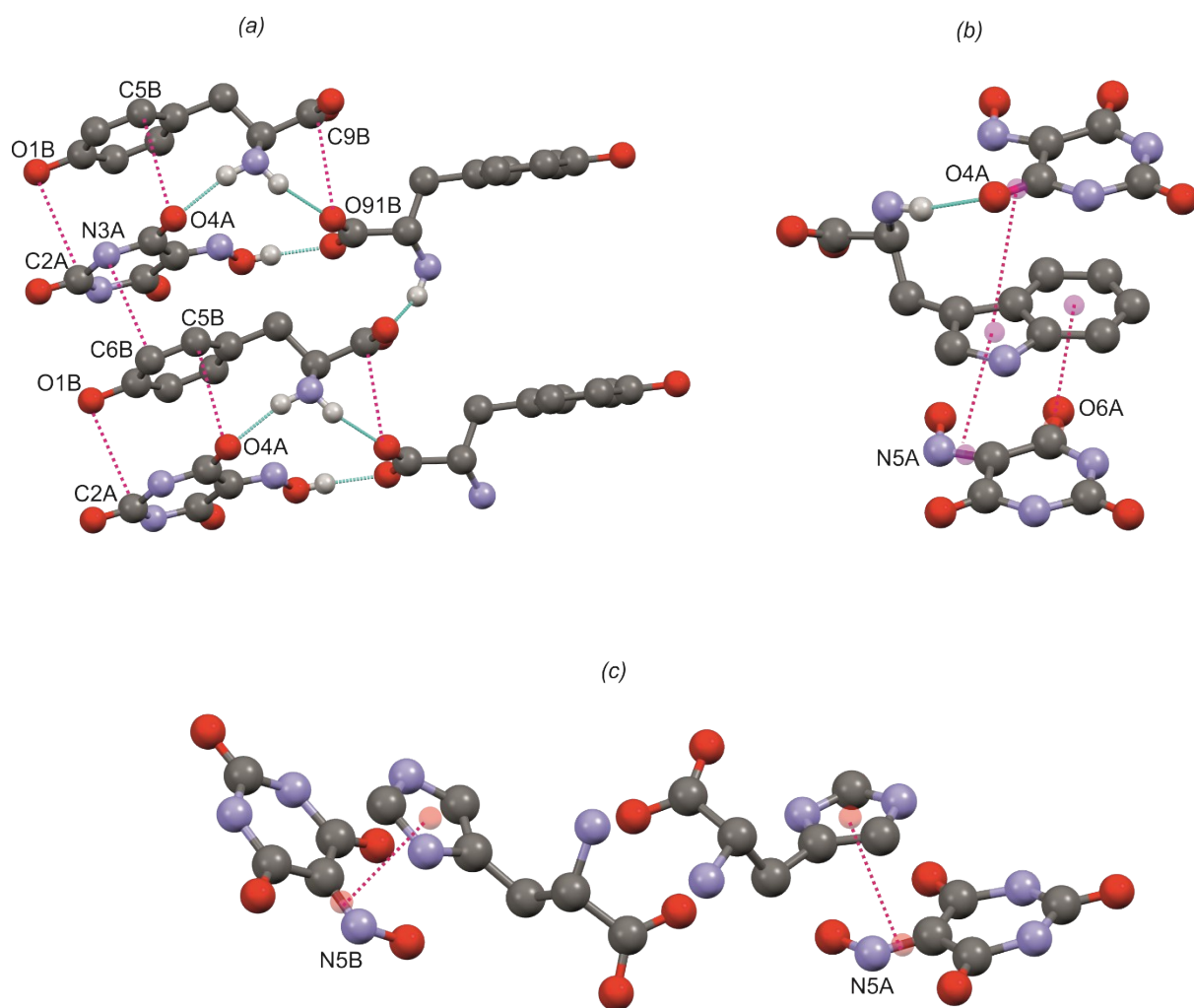


Fig. S7 Visualization of $\pi \cdots \pi$ interactions in a) VATyr, b) VATrp and c) VAHis crystal structures. Hydrogen atoms which do not participate in intermolecular interactions were omitted for clarity.

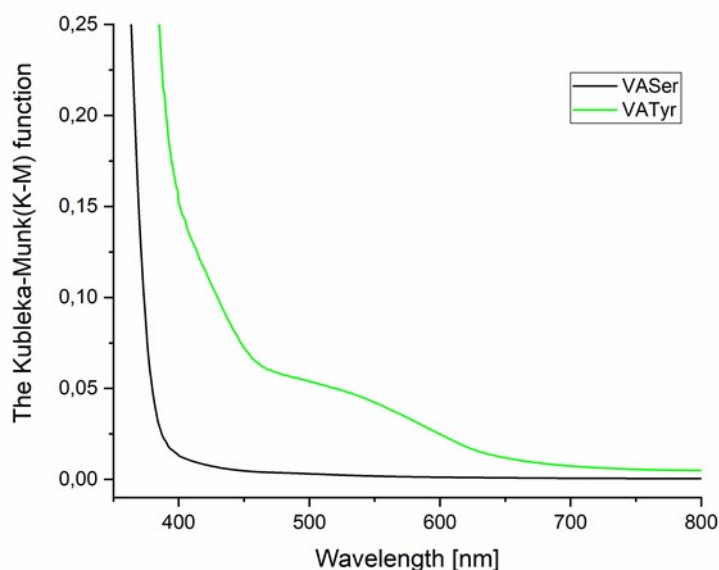


Fig. S8 UV-Vis spectra for VATyr crystals (scale factor x5) compared with colorless VASer crystals.

¹H NMR spectroscopy:

For a mixture of L-His and VA and for the salt V(L-His) in D₂O, a decrease in the population with antiperiplanar conformation (*trans* for imidazole and carboxylic anion groups with dihedral angle $\theta=180^\circ$) was observed¹². At the same time an increase in the population with antiperiplanar conformation was observed (*trans* for imidazole and ammonium groups with dihedral angle $\theta=180^\circ$). The ¹H NMR data for L-Arg in D₂O indicated the presence of two set of signals with overlapping triplets of H_a (3.25 ppm), H_a' (3.24 ppm) and H_e (3.117 ppm), H_e' (3.113 ppm). Origin of these two sets may be connected with the occurrence of two tautomeric forms of guanidine group in solution^{13,14} or two rotamers induced via formation of intramolecular hydrogen bond with guanidine nitrogen atom as donor and carboxylic oxygen atom as acceptor of proton¹⁵. The comparison of vicinal coupling constants ³J for diastereotopic and H_a protons with the data available in the literature confirmed the contribution of gauche conformation in L-Ser for mixture with VA and V(L-Ser) co-crystals dissolved in D₂O¹⁶. Also the main population of amino acids rotamers with bulky side-chain group is that with antiperiplanar conformation (*trans* for aryl or hetaryl and carboxylic anion groups with dihedral angle $\theta=180^\circ$) in mixtures VA with L-Trp or L-Tyr and dissolved co-crystal V(L-Trp)^{17,18}. The values of coupling constant *J* are consistent with the data available in the literature.¹⁹

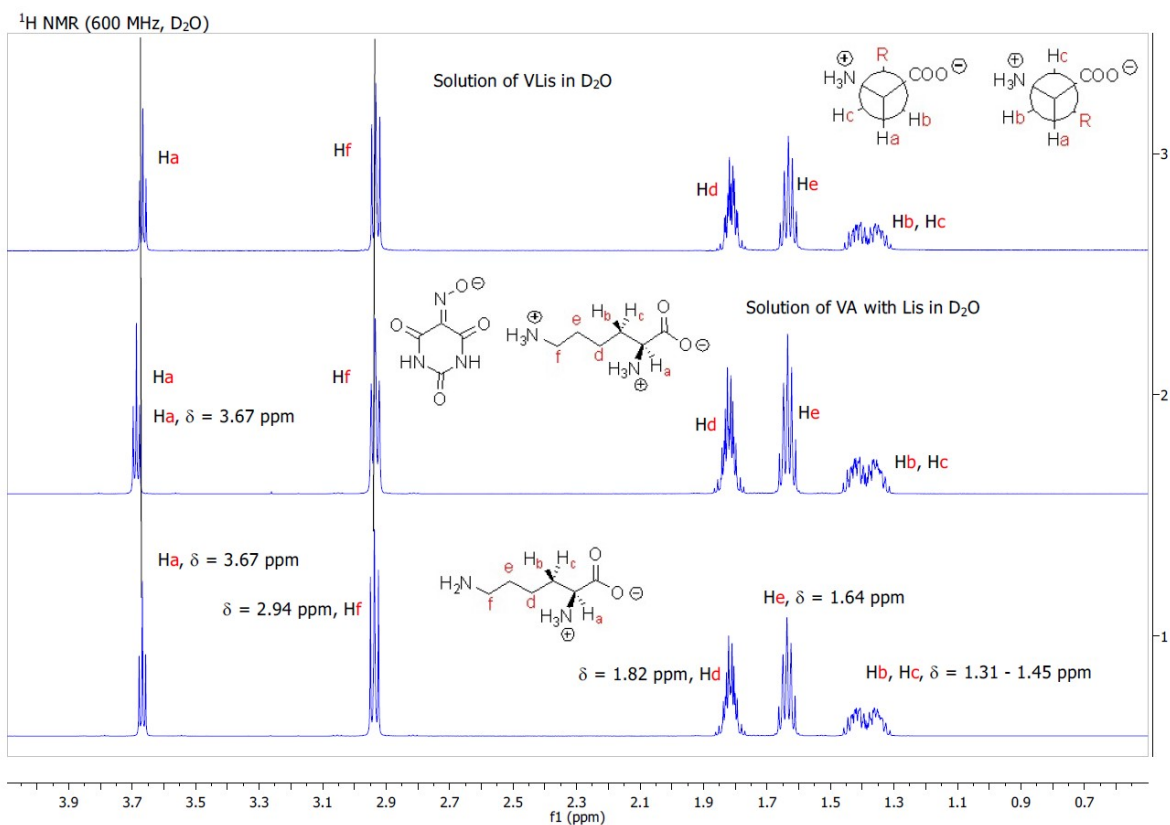


Fig. S9 ¹H NMR spectra in D₂O for VALys, a mixture of VA and L-Lys and for L-Lys.

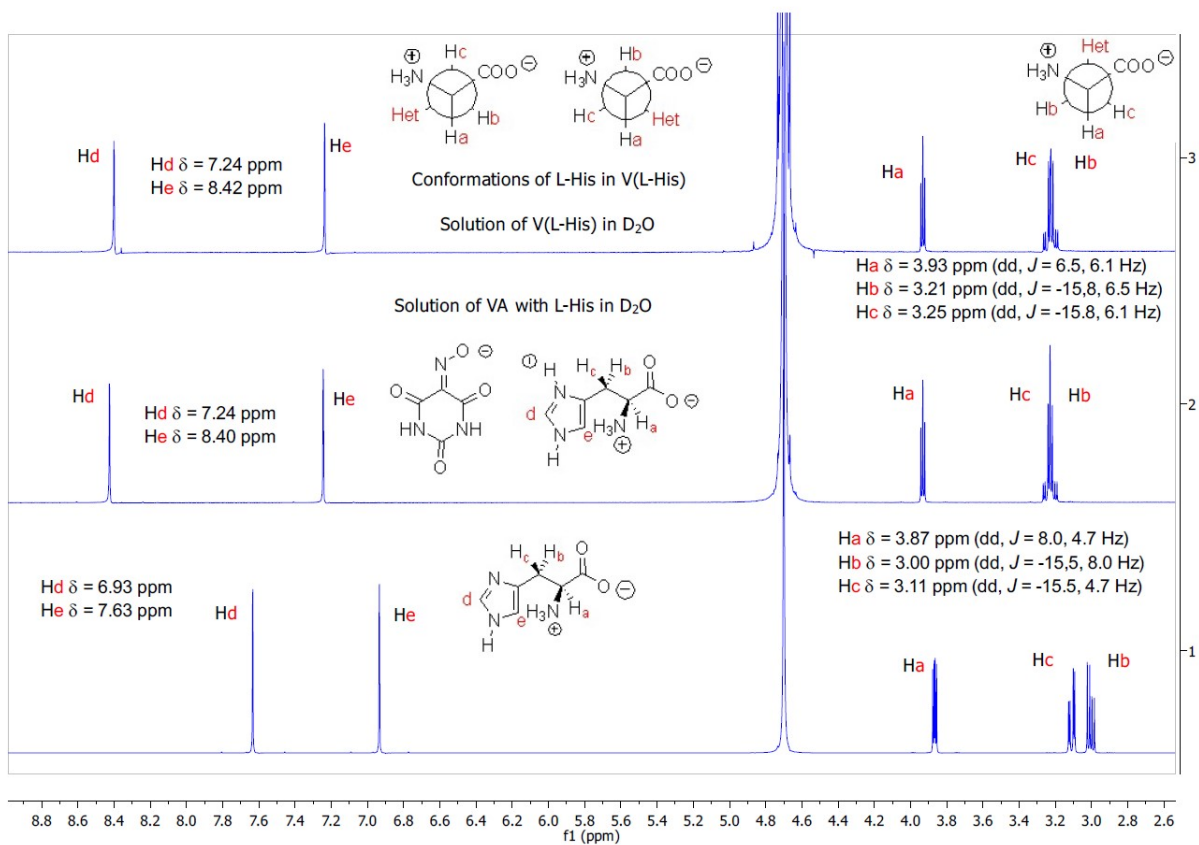


Fig. S10 ¹H NMR spectra in D₂O for VAHis, a mixture of VA and L-His and for L-His.

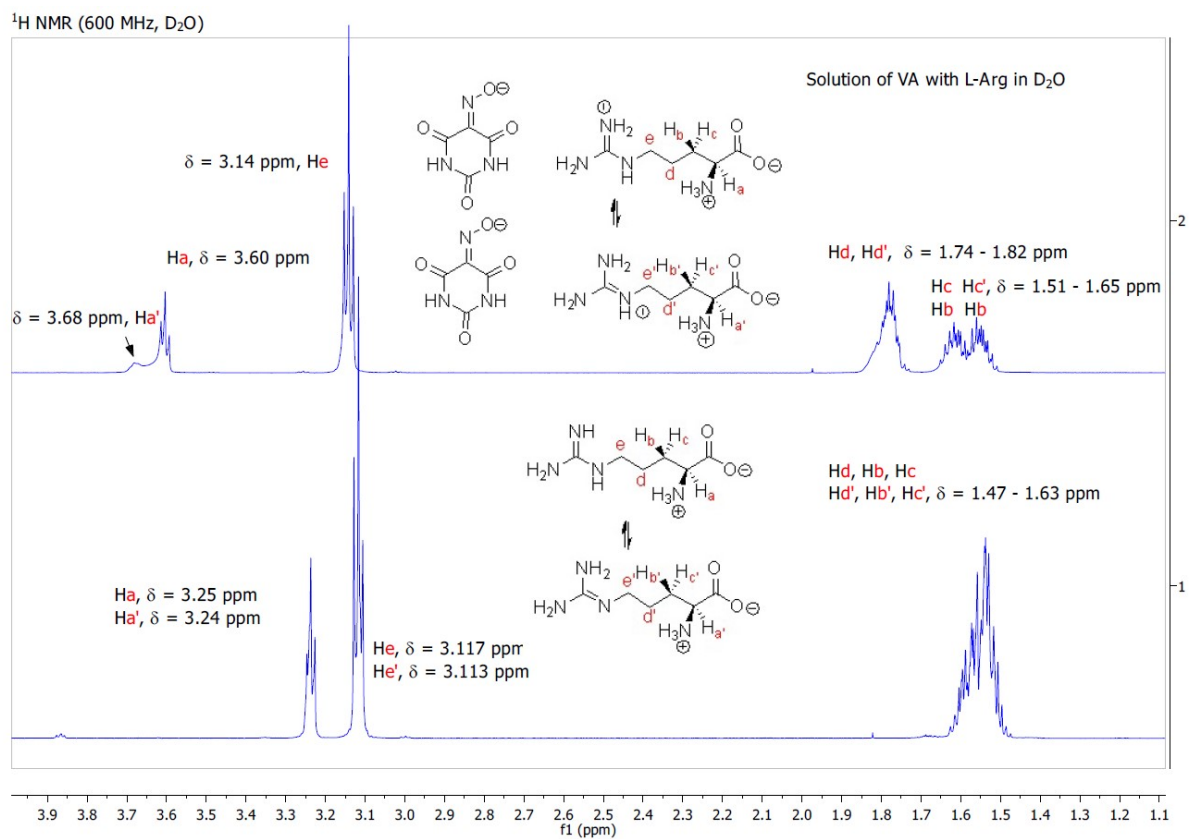


Fig. S11 ¹H NMR spectra in D₂O for a mixture of VA with L-Arg and for L-Arg.

^1H NMR (600 MHz, D_2O)

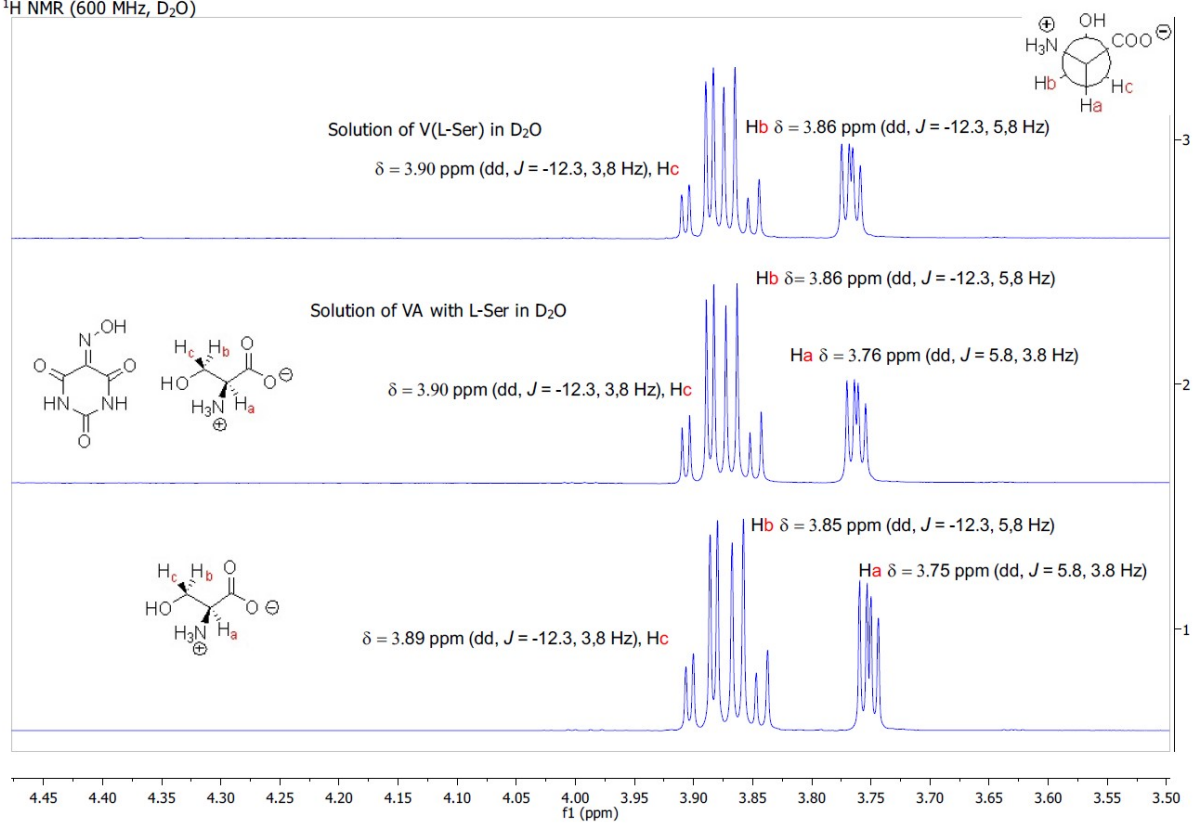


Fig. S12 ^1H NMR spectra in D_2O for: VASer, a mixture of VA and L-Ser and for L-Ser.

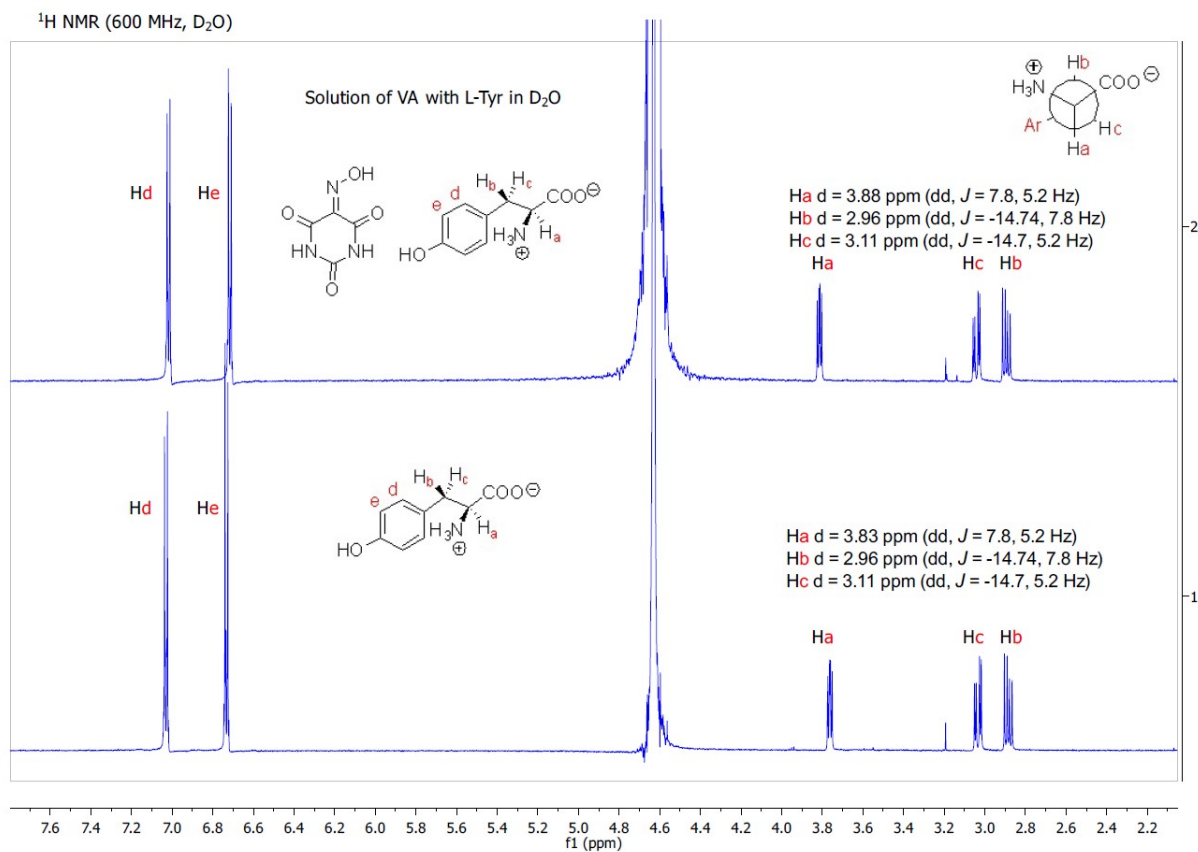


Fig. S13 ¹H NMR spectra in D₂O for a mixture of VA and L-Tyr and for L-Tyr.

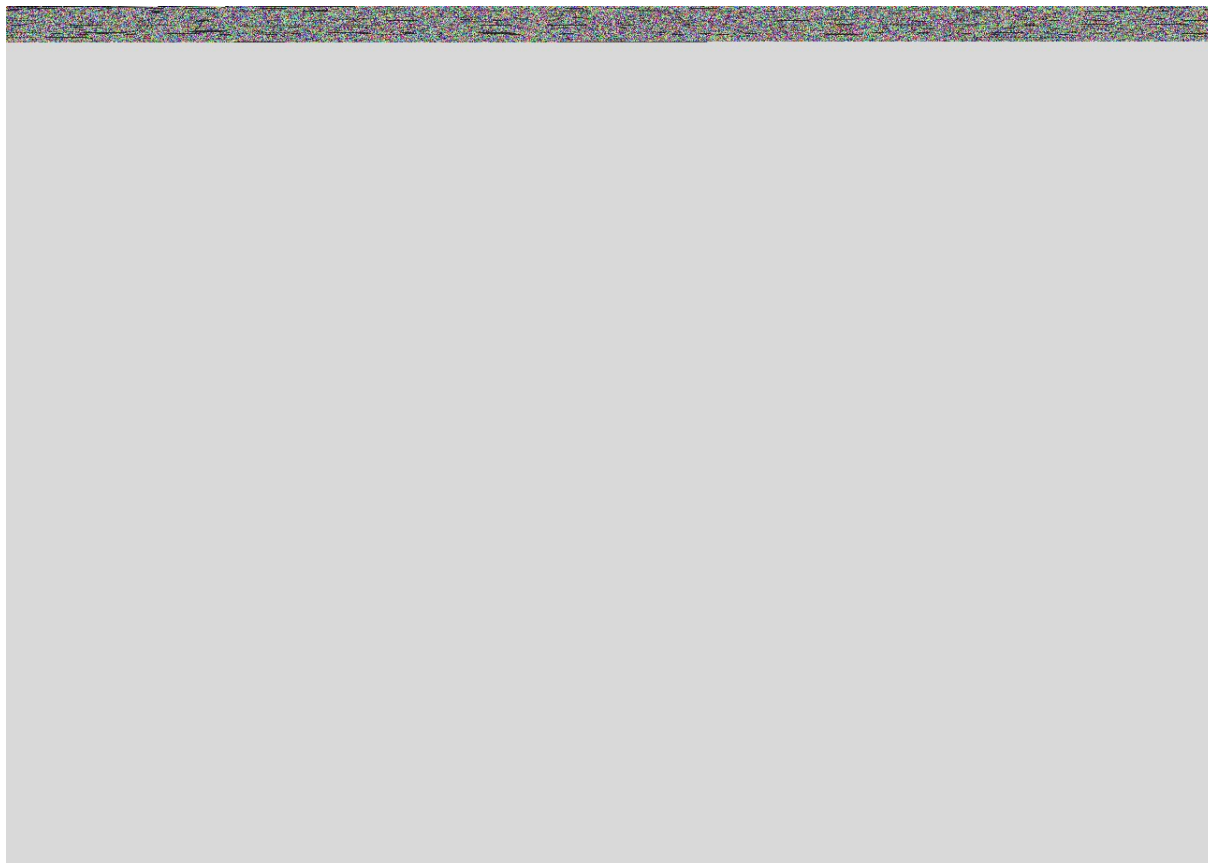


Fig. S14 ^1H NMR spectra in D_2O for: VATrp, a mixture of VA and L-Tryp and for L-Trp.

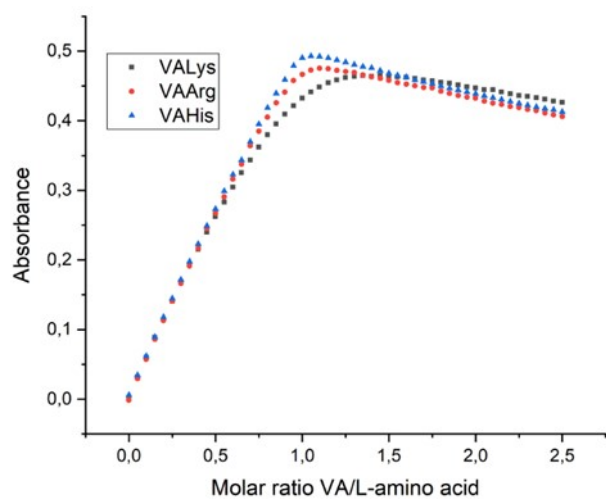


Fig. S15 The titration curves for VAArg, VAllys and VAHis. The titrations of 2ml of 0.01M VA amino acid solutions were carried out using 20 μL portions of 0.05M of VA.

Determination limit of detection (LoD):

The Limit of Detection (LoD) was determined using following equation (1)²⁰:

$$LoD = (3 \cdot S)/b \tag{1}$$

Where S is the sum of the square of the vertical deviations from each data point to the fitting regression line, and b is the slope of calibration curve. Fig. S10-S12 shows calibration curves in the linear range for VAHis, VALys and VAArg salts obtained from titration experiments.

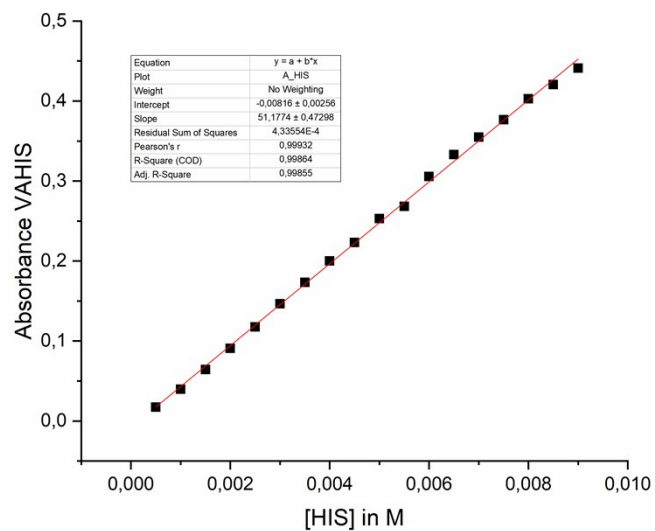


Fig. S16 Calibration curve for VAHis salt.

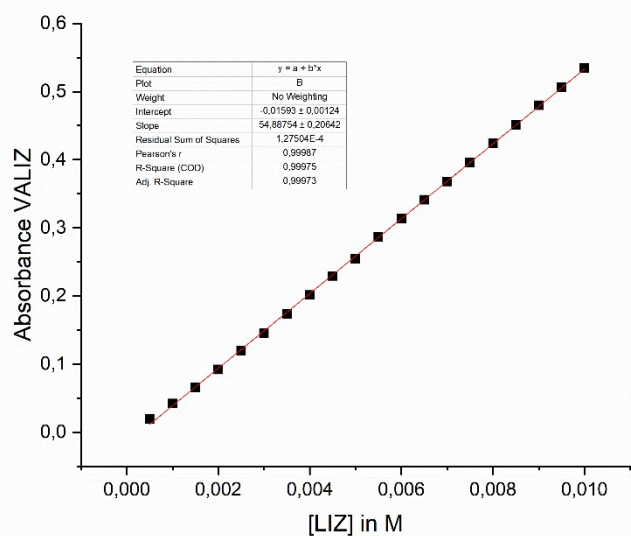


Fig. S17 Calibration curve for VALys salt.

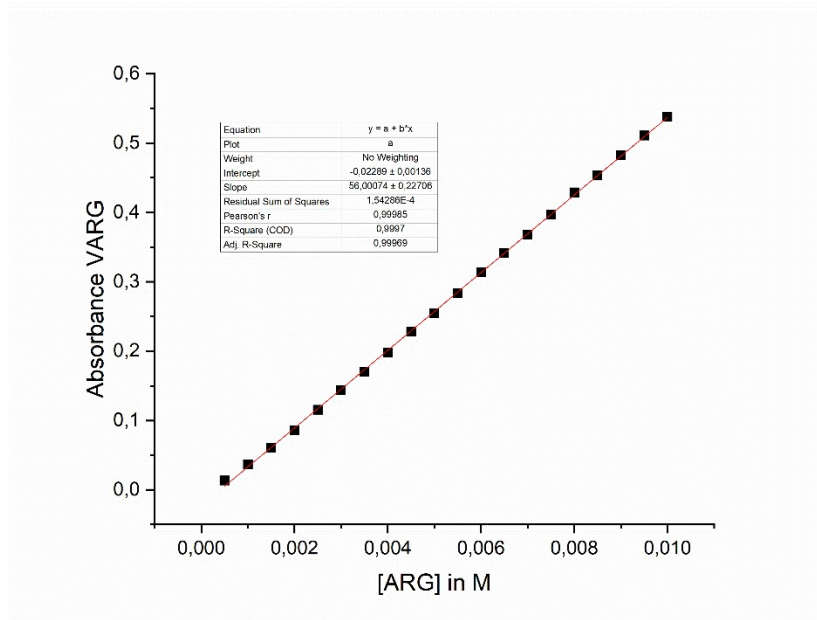


Fig. S18 Calibration curve for VArg salt.

Table S5 Topological analysis of BCPs for C-N and N-O bonds of oxime group in studied crystalline phases. $\rho(r)$ – charge density (a.u.); $\nabla^2\rho(r)$ – Laplacian of electron density (a.u.).

	C-N			N-O		
	Bond length [Å]	$\rho(r)$	$\nabla^2\rho(r)$	Bond length [Å]	$\rho(r)$	$\nabla^2\rho(r)$
VHis (A)	1.325	0.349	-1.078	1.287	0.381	-0.433
VHis (B)	1.336	0.343	-1.067	1.282	0.386	-0.440
VALys (A)	1.328	0.348	-1.080	1.291	0.373	-0.395
VALys (B)	1.328	0.347	-1.069	1.295	0.377	-0.407
VATrp_A	1.292	0.370	-0.977	1.338	0.338	-0.311
VATrp*	1.291	0.370	-0.965	1.336	0.339	-0.313
VATyr	1.285	0.375	-0.950	1.354	0.325	-0.266
VASer_A	1.289	0.372	-0.968	1.356	0.324	-0.262
VASer_B*	1.292	0.370	-0.967	1.339	0.337	-0.300

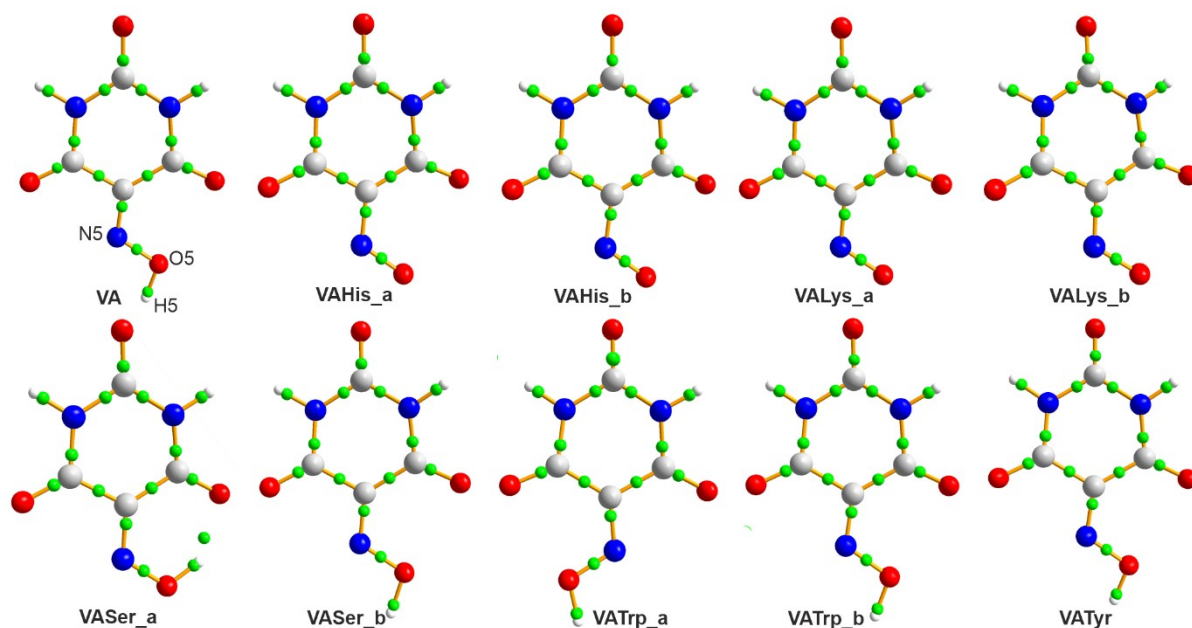


Fig. S19 Molecular graphs for VA molecules and ions in the crystal structures of VA monohydrate (VA) and the respective salts and co-crystals with amino acids. BCPs are marked in green colour. VATrp_b denotes VATrp* crystal structure.

Table S6 Selected hydrogen bonds involving oxime group in the examined structures. $\rho(r)$ – charge density (a.u.); $\nabla^2\rho(r)$ – Laplacian of electron density (a.u.); G, V– local kinetic, potential energy density (a.u.), E_{int} – interaction energy in kcal/mol estimated using Espinosa approximation.

		$\rho(r)$	$\nabla^2\rho(r)$	G	V	E_{int}
VASerA	H5A1...O6A	0.054	0.143	0.047	-0.058	-18.321
	H5A1...O2W ⁱ	0.017	0.078	0.016	-0.013	-4.194
VASerB	H1B3...O5A ⁱⁱ	0.021	0.088	0.019	-0.016	-4.935
	H5A...O1W ⁱ	0.127	0.050	0.089	-0.165	-51.788
VATrpA	H5A1...O12B	0.099	0.125	0.075	-0.118	-37.001
	H11D...N5A	0.013	0.064	0.013	-0.010	-3.214
VATrp*	H5A1...O12B	0.094	0.142	0.074	-0.112	-35.002
	H7B...O5A ⁱⁱⁱ	0.012	0.055	0.011	-0.008	-2.458
VATyr	H5A...O92B	0.064	0.147	0.053	-0.068	-21.435
	H8B...N5A ^v	0.019	0.081	0.017	-0.014	-4.498
	H7B2...N5A	0.008	0.027	0.005	-0.004	-1.327
VAHisA	H12W...O5B	0.029	0.105	0.025	-0.025	-7.764
	H4C...N5B ^v	0.013	0.053	0.011	-0.009	-2.937
	H3C...N5B ^v	0.012	0.047	0.010	-0.008	-2.476
VAHisB	H7D1...O5A ^{vi}	0.037	0.128	0.033	-0.034	-10.717
	H7D...O5A	0.014	0.052	0.011	-0.008	-2.630
	H2D...O5A ^v	0.020	0.084	0.018	-0.016	-4.946

VALysA	H1C1...N5A ^{vii}	0.013	0.047	0.010	-0.008	-2.410
	H1W1...O5A	0.019	0.081	0.017	-0.014	-4.498
	H1C1...O5A ^{vii}	0.040	0.114	0.033	-0.037	-11.500
VALysB	H1D2...N5B ^{viii}	0.029	0.081	0.020	-0.020	-6.371
	H1D1...O5B ^{ix}	0.039	0.114	0.031	-0.034	-10.782
	H2W1...O5B	0.018	0.077	0.016	-0.013	-4.122

Table S7 TDDFT calculations for model clusters constructed from VA and HIS ions, as derived from the VAHIS crystal structure and optimized. Cluster 1 consists of one VA anion, one HIS cation, and a water molecule (the VAHIS asymmetric unit). Cluster 2 contains one VA anion and one HIS cation.

	VAHis cluster 1	VAHis cluster 2
Position of the n- π^* absorption band	613.49nm	636.48nm
H...A bond length	1.804Å (H2O)H...O(oxime)	2.109 Å (NH2)H...O(oxime)

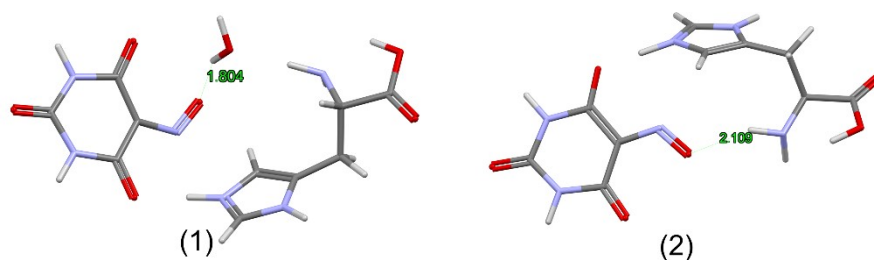


Fig. S20 Clusters selected for the calculations with marked hydrogen bonds.

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