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Electronic Supplementary Information (ESI)

Solid Solutions of Quasi-Isomorphous Diastereomeric Salts – Kinetics versus Thermodynamics

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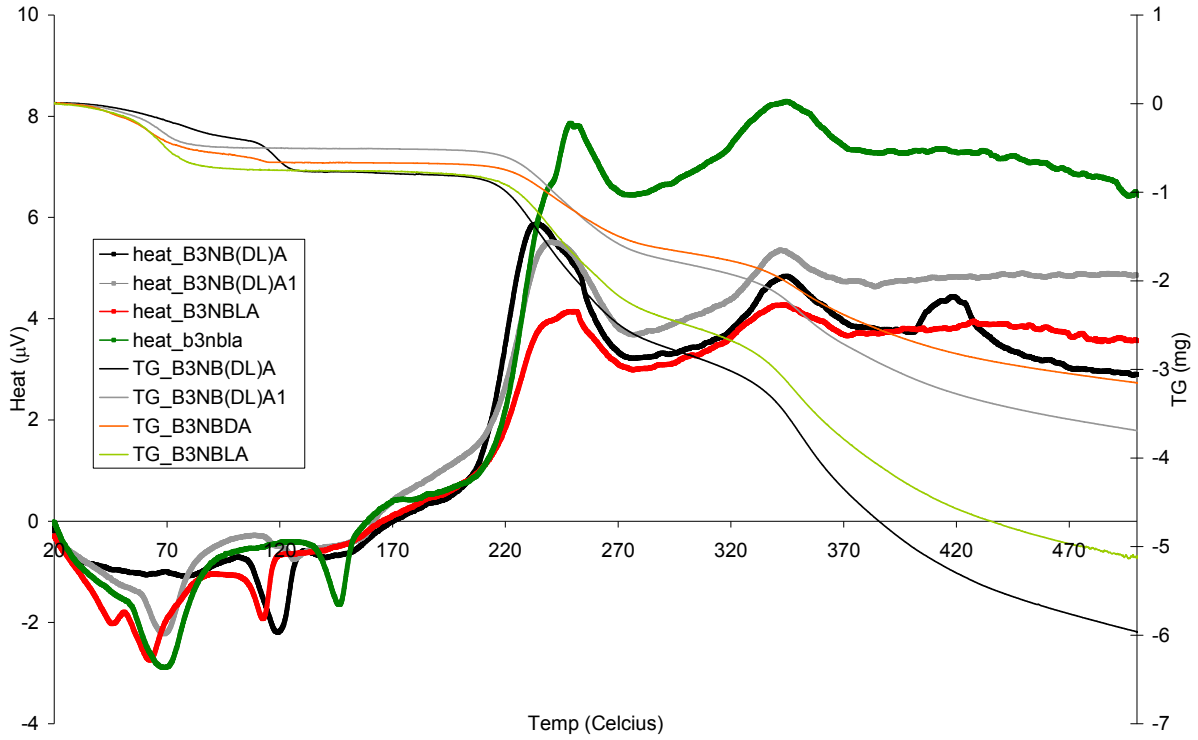

Figure S1. TG-DTA curves displaying a comparison of the stability of brucinium salt with *N*-(3-nitrobenzoyl)-D-, *N*-(3-nitrobenzoyl)-L- and *N*-(3-nitrobenzoyl)-(DL)-alanine (TG curves are marked as thin lines, and DTA curves are marked as thick lines).

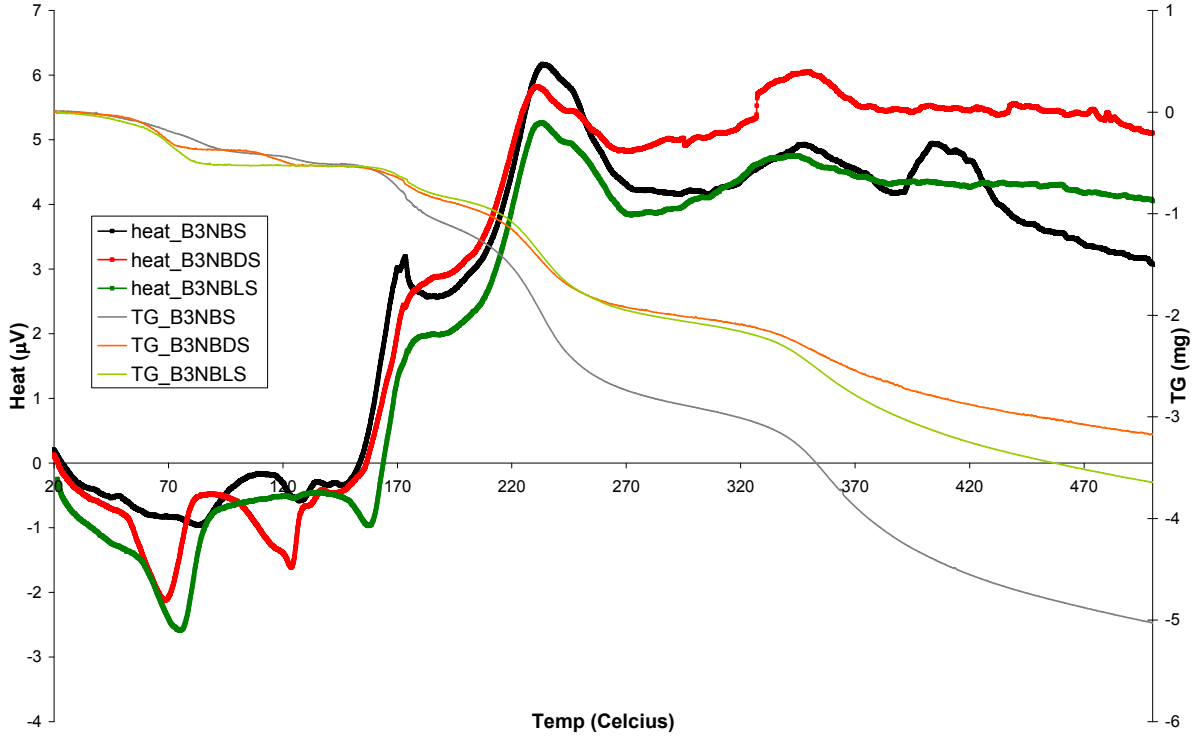

Figure S2. TG-DTA curves displaying a comparison of the stability of brucinium salt with *N*-(3-nitrobenzoyl)-D-, *N*-(3-nitrobenzoyl)-L- and *N*-(3-nitrobenzoyl)-(DL)-serine (TG curves are marked as thin lines, and DTA curves are marked as thick lines).

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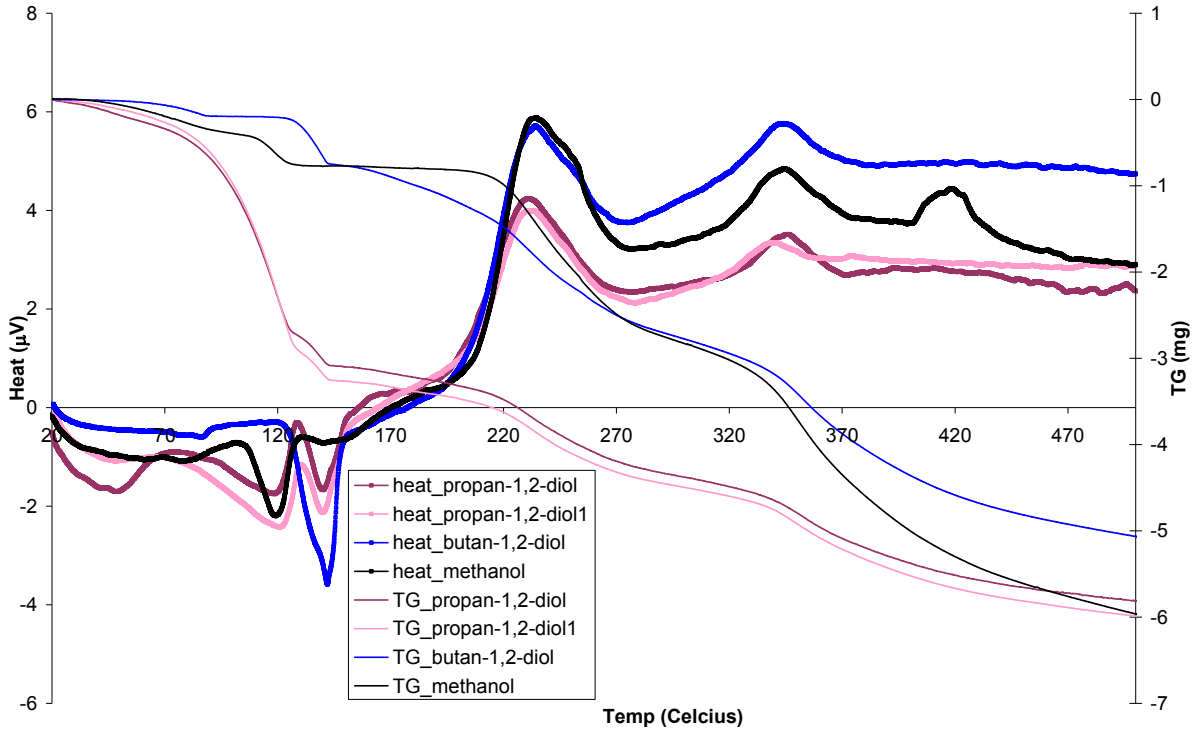

Figure S3. TG-DTA curves displaying a comparison of the stability of the solid solutions of brucinium *N*-(3-nitrobenzoyl)-(DL)-alaninate precipitated from methanol, propan-1,2-diol and from butan-1,2-diol (TG curves are marked as thin lines, and DTA curves are marked as thick lines).

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Table S1. Crystallographic data for brucinium *N*-(3-nitrobenzoyl)-D-alaninate methanol 1.61-solvate (B3NBDA), brucinium *N*-(3-nitrobenzoyl)-L-alaninate methanol disolvate (B3NBLA), brucinium *N*-(3-nitrobenzoyl)-(DL)-alaninate methanol disolvate (B3NB(DL)A') and brucinium *N*-(3-nitrobenzoyl)-(DL)-alaninate propan-1-ol solvate (B3NB(DL)A/propan-1-ol).

	B3NBDA	**B3NBLA**	**B3NB(DL)A'**	**B3NB(DL)A/ /propan-1-ol**
Chemical formula*	$B^+A^-\cdot 1.61CH_3OH$	$B^+A^-\cdot 2CH_3OH$	$B^+A^-\cdot 2CH_3OH$	$B^+A^-\cdot C_3H_8O$
diastereomeric excess	100%	100%	9% of **B3NBDA**	46% of **B3NBDA**
Chemical formula weight	684.33	696.74	696.74	692.75
temperature (K)	100	100	100	100
Cell setting, space group	orthorhombic, $P2_12_12_1$	orthorhombic, $P2_12_12_1$	monoclinic, $P2_1$	orthorhombic, $P2_12_12_1$
a, b, c (Å)	7.880(3), 12.092(2), 34.308(6)	7.919(2), 12.266(3), 34.420(5)	12.144(3), 7.893(2), 34.093(5)	7.826(2), 12.048(3), 35.119(6)
β (°)	90.00	90.00	90.63(3)	90.00
V (Å^3)	3269.0(15)	3343.4(13)	3267.7(13)	3311.3(13)
Z	4	4	4	4
D_c (Mg m^{-3})	1.390	1.384	1.416	1.390
Crystal form, colour	plate, pale-yellow	block, pale-yellow	plate, pale-yellow	plate, colorless
Data/parameter ratio (Rint)	12.85 (0.077)	16.00 (0.058)	9.41 (0.079)	10.17 (0.081)
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.048, 0.097, 1.040	0.071, 0.158, 1.140	0.083, 0.202, 1.167	0.068, 0.172, 1.052
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.340, -0.279	0.353, -0.271	0.370, -0.793	0.331, -0.278
CCDC no.	930484	930485	930486	930487

B3NBDA and B3NBLA were obtained from 10 mL of methanol solution containing 100 mg of brucine and equimolar amount of suitable D or L enantiomer of the alanine derivative. The specific optical rotation power (º cm^3 g^{-1} dm^{-1}) of B3NBDA and B3NBLA in ethanol solution are equal to $[\alpha]_D^{20}$ = -32.85 (c = 0.4, EtOH) and $[\alpha]_D^{20}$ = -7.20 (c = 0.4, EtOH), respectively. (B3NB(DL)A') was selected from a fraction crystallizing in the second minute ($[\alpha]_D^{20}$ = -19.25 (c = 0.4, EtOH)), after removing the fraction crystallizing (from 2 mL of methanol solution containing 100 mg of brucine and equimolar amount of *N*-(3-nitrobenzoyl)-DL-alanine) in the first minute ($[\alpha]_D^{20}$ = -24.55 (c = 0.4, EtOH)). B3NB(DL)A/propan-1-ol was selected from a first crystalline fraction precipitating from 5 mL of propan-1-ol solution containing 100 mg of brucine and equimolar amount of *N*-(3-nitrobenzoyl)-DL-alanine

* $B^+ = C_{23}H_{27}N_2O_4^+ \cdot A^- = C_{10}H_9NO_5^-$

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Table S2. Crystallographic data form brucinium *N*-(3-nitrobenzoyl)-(DL)-alaninate solvates (diols).

	B3NB(DL)A/ /propan-1,2-diol	**B3NB(DL)A/ /propan-1,3-diol**	**B3NB(DL)A/ /butan-1,2-diol**	**B3NB(DL)A/ /butan-1,4-diol**
Chemical formula*	$B^+A^-\cdot C_3H_8O_2$	$B^+A^-\cdot C_3H_8O_2$	$B^+A^-\cdot 0.82C_4H_{10}O_2\cdot 0.27H_2O$	$B^+A^-\cdot C_4H_{10}O_2$
diastereomeric excess of **B3NBDA** (%)	54	2	64	14
Chemical formula weight	708.75	708.75	711.46	722.78
temperature (K)	100	293	293	100
Cell setting, space group	orthorhombic, $P2_12_12_1$	orthorhombic, $P2_12_12_1$	orthorhombic, $P2_12_12_1$	orthorhombic, $P2_12_12_1$
a, b, c (Å)	7.798(2), 12.117(3), 35.287(5)	7.882(2), 12.211(3), 35.713(6)	7.922(2), 12.252(3), 35.746(6)	7.906(2), 12.047(3), 35.802(4)
β (°)	90.00	90.00	90.00	90.00
V (Å^3)	3334.2(13)	3437.3(13)	3469.5(14)	3409.9(13)
Z	4	4	4	4
D_c (Mg m^{-3})	1.412	1.370	1.362	1.408
Crystal form, colour	plate, colorless	needle, colorless	plate, colorless	plate, colorless
Data/parameter ratio (Rint)	14.73 (0.150)	5.96 (0.107)	6.86 (0.067)	5.86 (0.210)
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.077, 0.173, 1.021	0.0704, 0.165, 0.904	0.066, 0.137, 1.016	0.044, 0.060, 0.717
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.578, -0.360	0.197, -0.221	0.193, -0.174	0.186, -0.181
CCDC no.	930488	930489	930490	930492

Crystals were selected from a first crystalline fraction precipitating from 2 mL of propan-1,2-diol, propan-1,3-diol, butan-1,2-diol or butan-1,4-diol containing 100 mg of brucine and equimolar amount of *N*-(3-nitrobenzoyl)-DL-alanine.

*$B^+ = C_{23}H_{27}N_2O_4^+\cdot A^- = C_{10}H_9NO_5^-$

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Table S3. Crystallographic data for brucinium *N*-(3-nitrobenzoyl)-D-serinate trihydrate (B3NBDS*) and brucinium *N*-(3-nitrobenzoyl)-L-serinate methanol solvate hydrate (B3NBLS).

	B3NBDS*	**B3NBLS**
Chemical formula*	$B^+S^-\cdot 3H_2O$	$B^+S^-\cdot CH_4O\cdot H_2O$
Chemical formula weight	702.71	698.72
Cell setting, space group	orthorhombic, $P2_12_12_1$	orthorhombic, $P2_12_12_1$
temperature (K)	100	100
a, b, c (Å)	7.944(2), 12.520(3), 33.073(4)	7.835(2), 12.067(3), 34.634(6)
β (°)	90.00	90.00
V (Å^3)	3289.4(12)	3274.5(13)
Z	4	4
D_c (Mg m^{-3})	1.419	1.417
Crystal form, colour	plate, colorless	plate, colorless
Data/parameter ratio (Rint)	14.58 (0.031)	6.70 (0.108)
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.035, 0.072, 0.940	0.048, 0.082, 0.890
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.235, -0.189	0.252, -0.202
CCDC no.	930493	930494

B3NBDS* and B3NBLS were obtained from 100 mL and10 mL, respectively, of methanol solution containing 100 mg of brucine and equimolar amount of suitable D or L enantiomer of the serine derivative.

* $B^+ = C_{23}H_{27}N_2O_4^+\cdot S^- = C_{10}H_9NO_6^-$

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Table S4. Geometry of hydrogen bonds in B3NB(DL)A, B3NBDA and B3NBLA (atom labels are presented in figure below; O100-H100, O110-H110, O120-H120, O200-H200, O210-H210 – hydroxyl group of methanol molecules, hydroxyl group of disordered solvent molecules are marked by the same first (like O**1**00, O**1**10 and O**1**21) digit and various third (and sometimes forth) (like O2**00** and O2**10**) digits of the labels)

B3NB(DL)A_at 80 K	D...A	DHA	B3NBDA	D...A	DHA	B3NBLA	D...A	DHA
N2-H2A...O5	2.734(9)	155	N2-H2A...O5	2.647(3)	162	N2-H2A...O51	2.589(13)	168
N2-H2A...O51	2.588(10)	170	N3-H3...O6^{iv}	2.797(3)	159	N2-H2A...O5	2.695(10)	167
N31-H31A...O61^{i}	2.776(14)	152	O100-H100...O5	2.916(15)	140	N3-H3...O61^{vi}	2.743(9)	145
N3-H3...O6^{ii}	2.813(11)	158	O110-H110...O5	2.593(8)	171	N3-H3...O6^{vi}	2.884(9)	160
O100-H100...O51	2.861(13)	148	O120-H120...O5	2.801(8)	129	O100-H100...O5	2.722(9)	143
O100-H100...O5	2.698(9)	173	O200-H200...O4^{v}	2.740(4)	151	O110-H110...O51	2.67(2)	168
O200-H200...O4^{iii}	2.756(6)	170				O200-H200...O4^{vii}	2.739(6)	160
						O210-H210...O4^{vii}	2.87(5)	168

B3NB(DL)A: (*i*) x-1/2, -y-1/2, -z; (*ii*) x+1/2, -y-1/2, -z; (*iii*) -x+1, y-1/2, -z+1/2
B3NBDA: (*iv*) x+1/2, -y+1/2, -z+2; (*v*) -x+1, y+1/2, -z+3/2
B3NBLA: (*vi*) x+1/2, -y+3/2, -z+1; (*vii*) -x+1, y-1/2, -z+1/2

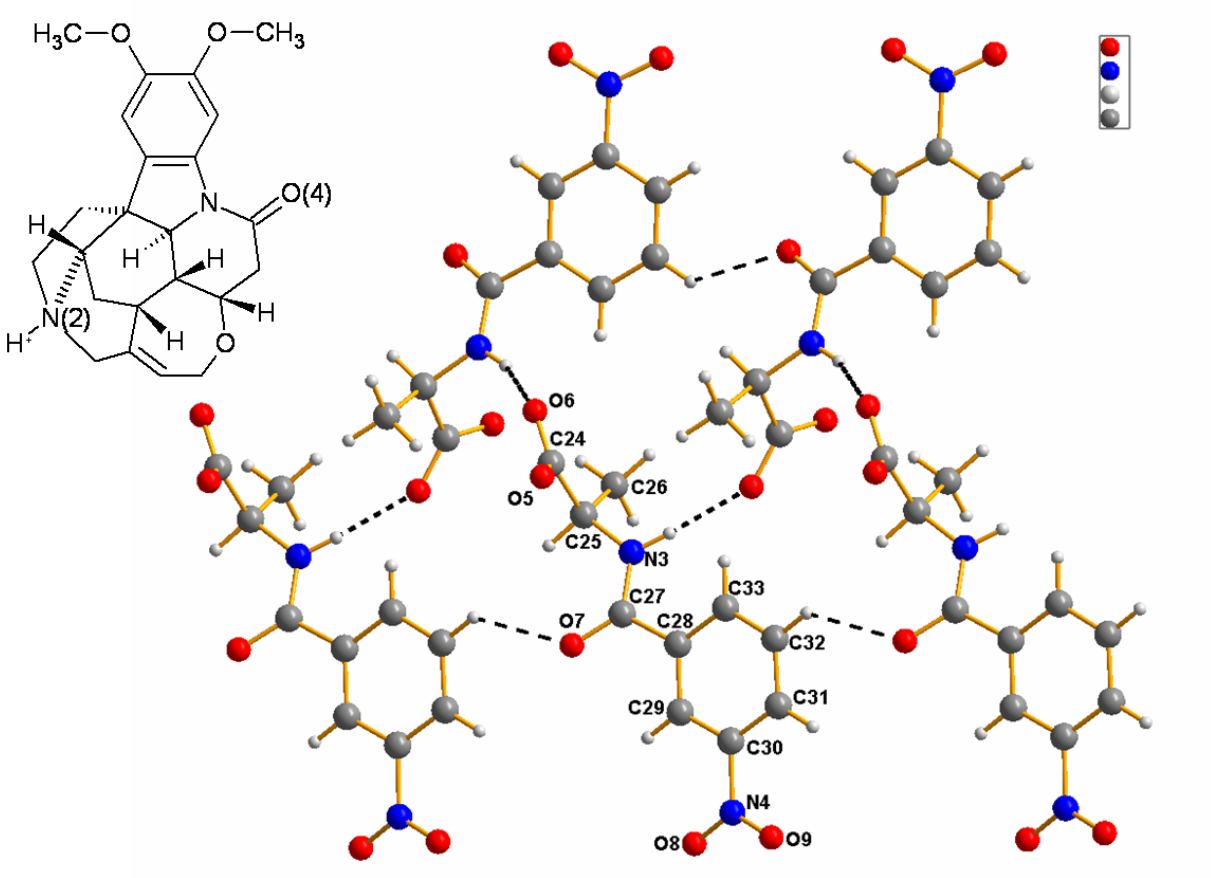

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Table S4a. Geometry of hydrogen bonds in B3NB(DL)A', B3NB(DL)A/propan-1-ol and B3NB(DL)A/propan-1,3-diol (numbering scheme similar like presented in figure below Table S4)

B3NB(DL)A'	D...A	DHA	B3NB(DL)A /propan-1-ol	D...A	DHA	B3NB(DL)A /propan-1,3-diol	D...A	DHA
N2-H2A...O5	2.621(6)	167	N2-H2A...O51	2.595(13)	168	N2-H2A...O51^{viii}	2.640(12)	172
N2-H2A...O51	2.78(2)	154	N2-H2A...O5	2.658(5)	159	N2-H2A...O5^{viii}	2.712(13)	156
N3-H3...O6^{i}	2.49(4)	165	N3-H3A...O6^{vi}	2.897(6)	146	O101-H101...O5^{ix}	2.93(4)	138
N31-H31...O61^{ii}	2.662(6)	160	N31-H31A..O61^{vii}	2.882(19)	156	O111-H111...O51^{ix}	3.17(3)	147
O100-H100...O5	2.804(7)	148	O110-H11D...O5	2.801(5)	178	O113-H113...O51	3.29(4)	156
O110-H110...O51	2.77(2)	160	O112-H112...O51	2.83(4)	146	O121-H121...O7^{ix}	2.86(3)	133
N2A-H2AA...O5B	2.798(6)	158				O123-H123...O4	2.77(3)	168
N2A-H2AA...O5A	2.896(16)	136				O131-H131...O4	3.28(6)	154
N3A-H3A...O6A^{iii}	2.816(8)	167						
O200-H200...O4A^{iv}	2.59(3)	157						
O210-H210...O4A^{iv}	2.61(3)	164						
O300-H300...O5A	2.589(13)	161						
O400-H400...O4^{v}	2.801(16)	170						
O410-H410...O4^{v}	2.718(14)	154						

B3NB(DL)A': (*i*) -x+2, y-1/2, -z+1; (*ii*) -x+2, y+1/2, -z+1; (*iii*) -x+1, y-1/2, -z+2; (*iv*) x+1, y, z; (*v*) x, y-1, z

B3NB(DL)A/propan-1-ol: (*vi*) x+1/2, -y+3/2, -z; (*vii*) x-1/2, -y+3/2, -z

B3NB(DL)A/propan-1,3-diol: (*viii*) -x+1, y+1/2, -z+1/2; (*ix*) x+1, y, z

Table S4b. Geometry of hydrogen bonds in B3NB(DL)A/propan-1,2-diol, B3NB(DL)A/butan-1,2-diol and B3NB(DL)A/butan-1,4-diol (numbering scheme similar like presented in figure below Table S4)

B3NB(DL)A/ /propan-1,2-diol	D...A	DHA	**B3NB(DL)A/** /butan-1,2-diol	D...A	DHA	**B3NB(DL)A/** /butan-1,4-diol	D...A	DHA
N2-H2A...O51	2.652(11)	169	N2-H2A...O51	2.65(2)	162	N2-H2A...O51	2.660(10)	168
N2-H2A...O5	2.665(4)	161	N2-H2A...O5	2.671(7)	162	N2-H2A...O5	2.688(8)	160
N3-H3A...O6^{i}	2.914(5)	146	N3-H3A...O6^{iv}	2.976(9)	145	N3-H3...O6^{vii}	2.867(10)	152
N31-H31C...O61^{ii}	2.863(16)	161	N31-H31B..O61^{v}	2.86(4)	157	N31-H31A...O61^{viii}	2.846(12)	145
O101-H101...O5	2.799(6)	137	O101-H101...O5	2.832(8)	178	O101-H101...O5^{ix}	2.88(3)	143
O102-H102...O4^{iii}	2.824(4)	173	O102-H102..O4^{vi}	2.821(6)	164	O104-H104...O7	2.830(18)	140
O111-H111...O51	2.88(3)	154				O111-H111...O4^{x}	2.691(12)	160
O112-H112...O4^{iii}	2.716(17)	138				O114-H114...O51	2.895(16)	160
						O121-H121...O124^{ix}	2.83(3)	154

B3NB(DL)A/propan-1,2-diol: (*i*) x-1/2, -y+3/2, -z; (*ii*) x+1/2, -y+3/2, -z; (*iii*) -x, y+1/2, -z+1/2

B3NB(DL)A/butan-1,2-diol: (*iv*) x+1/2, -y+3/2, -z+1; (*v*) x-1/2, -y+3/2, -z+1; (*vi*) $3 -x+1, y-1/2, -z+3/2

B3NB(DL)A/butan-1,4-diol: (*vii*) x+1/2, -y+3/2, -z; (*viii*) x-1/2, -y+3/2, -z; (*ix*) x-1, y, z; (*x*) -x+1, y-1/2, -z+1/2

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Table S5. Geometry of hydrogen bonds in B3NB(DL)S, B3NBLS and B3NBDS* (atom labels are presented in figure below; the hydroxyl group of methanol molecules are labeled as O100, O110, O120, O200, O210, O220 – disorder of methanol molecules are marked in the same way like for crystal structures of brucinium salts with the alanine analogue; water molecules are marked by 'W' as the last sign of a given label – in B3NBLS O1W and O11W mean one disordered over two positions water molecule)

B3NB(DL)S	D...A	DHA	B3NBLS	D...A	DHA	B3NBDS*	D...A	DHA
N2-H2A...O51^{i}	2.570(12)	173	N2-H2A...O5	2.604(5)	177	N2-H2A...O5^{x}	2.5877(19)	170
N2-H2A...O6	2.762(12)	142	O7-H7A...O6^{vi}	2.723(5)	171	O7-H7A...O2W^{xi}	2.704(2)	177
O7-H7...O5^{ii}	2.50(2)	160	O100-H100...O7^{vii}	2.798(7)	134	O71-H71A...O2W^{xi}	2.99(2)	180
O71-H71...O61^{iii}	2.64(2)	170	O110-H110..O11W	2.86(5)	147	O1W-H11W...O6^{xii}	2.804(2)	151
O100-H100...O7^{iii}	2.71(3)	173	O120 -H120...O4^{viii}	2.87(5)	131	O1W-H12W...O4^{xiii}	2.8478(17)	165
O110-H110...O71^{iv}	3.00(3)	160	O1W -H11W...O5	3.105(6)	179	O2W-H21W...O3W	2.755(2)	165
O120-H120...O4^{v}	2.69(2)	153	O1W -H12W...O4^{ix}	2.900(6)	179	O2W-H22W...O7^{xii}	2.967(3)	167
O200-H200...O6	2.85(3)	143	O11W -H13W...O5	3.34(3)	148	O2W-H22W...O61^{xii}	2.77(3)	115
O210-H210...O4^{v}	2.963(12)	137	O11W-H14W...O4^{ix}	2.95(3)	156	O3W-H31W...O1W	2.7898(18)	159
O220-H220...O4^{v}	2.96(3)	142				O3W-H32W...O5^{xiv}	2.774(2)	176

B3NB(DL)S: (*i*) x+1, y, z; (*ii*) x-1/2, -y+3/2, -z; (*iii*) x+1/2, -y+3/2, -z; (*iv*) x+3/2, -y+3/2, -z; (*v*) -x+1, y+1/2, -z+1/2

B3NBLS: (*vi*) x-1/2, -y+3/2, -z; (*vii*) x+1/2, -y+3/2, -z; (*viii*) -x+2, y-1/2, -z+1/2; (*ix*) -x+1, y-1/2, -z+1/2

B3NBDS*: (*x*) x+1/2, -y+1/2, -z+1; (*xi*) -x+1, y-1/2, -z+3/2; (*xii*) -x+3/2, -y, z+1/2; (*xiii*) x, y-1, z; (*xiv*) -x+1/2, -y, z+1/2

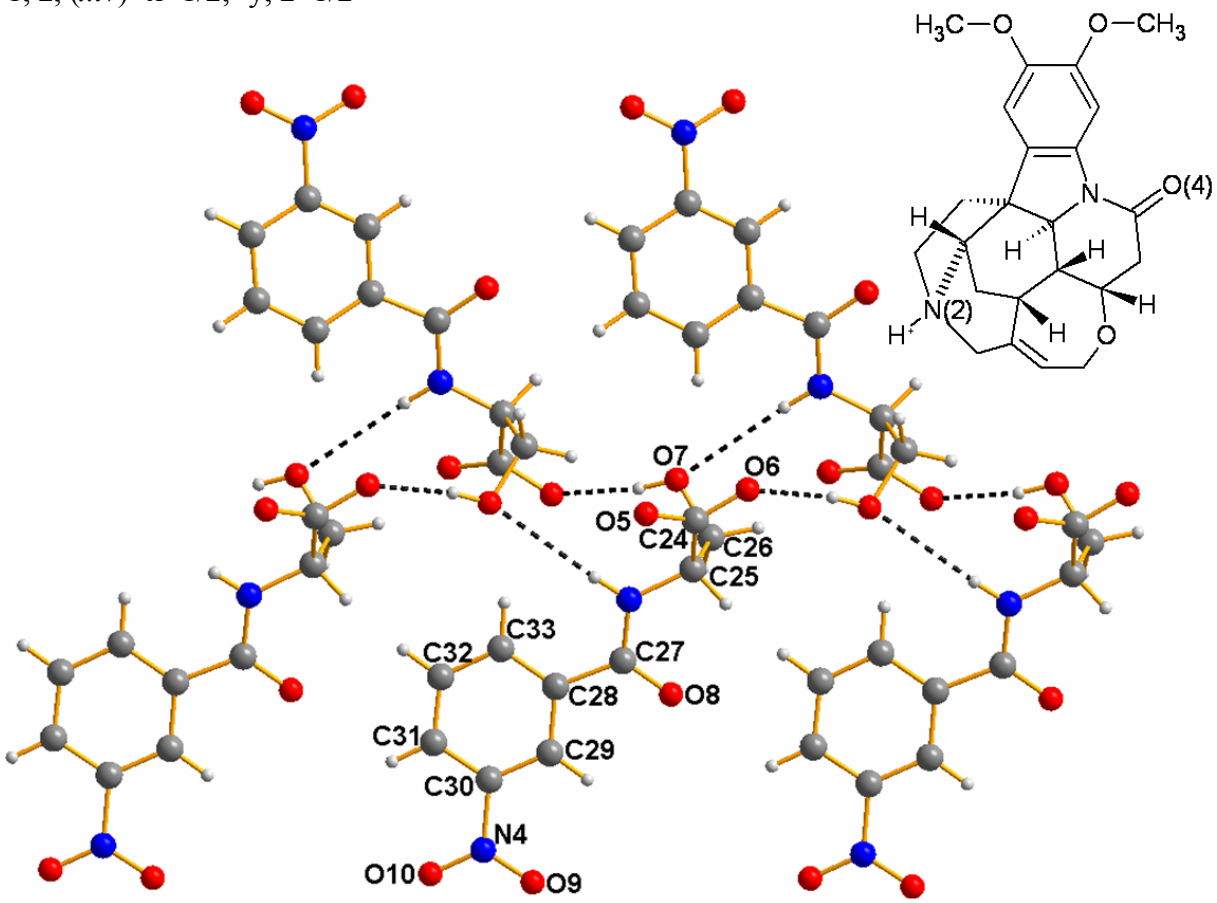

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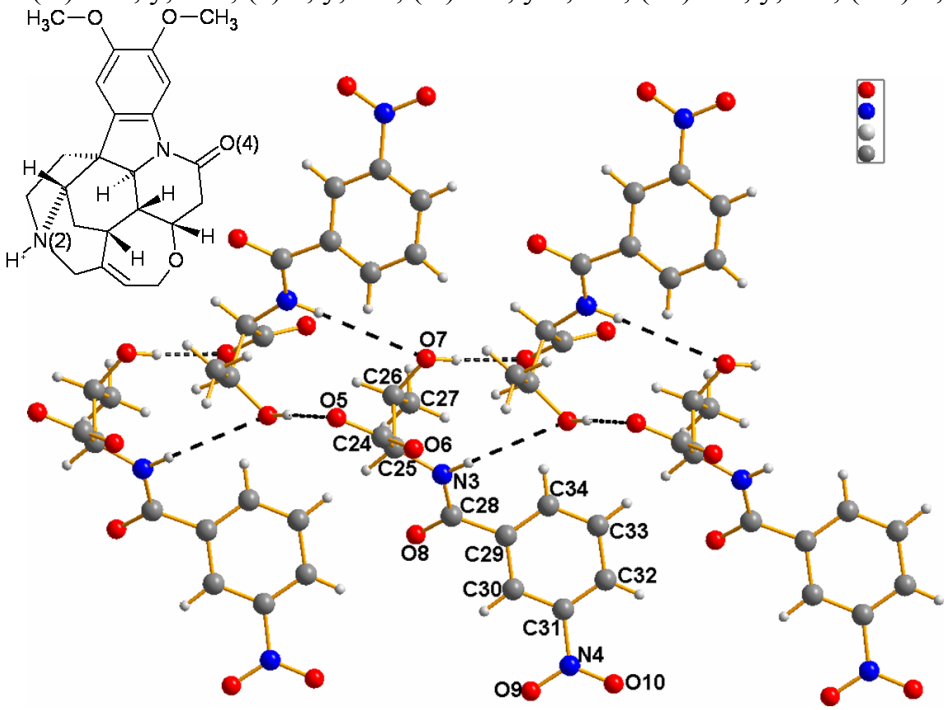
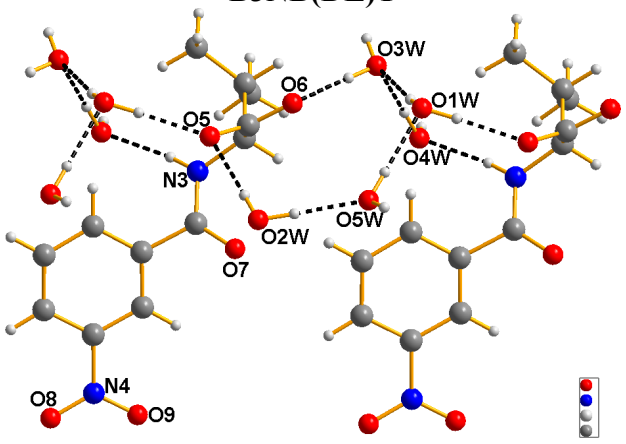
Table S6. Geometry of hydrogen bonds in B3NB(DL)T and B3NBLV (atom labels are presented in figure below; the hydroxyl group of disordered ethanol molecule is labeled as O100, O101, O121; water molecules are marked by 'W' as the last sign of a given label)

B3NB(DL)T	D...A	DHA	B3NBLV	D...A	DHA
N2-H2A...O5	2.705(9)	162	N2-H2...O6	2.648(4)	165
N2-H2A...O51	2.73(4)	170	N3-H3...O4W^{iv}	3.109(5)	171
O7-H7A...O5^{i}	2.749(9)	175	O3W-H31W...N2A	2.820(5)	152
O71-H71...O61^{ii}	2.80(5)	151	O3W-H32W...O6^{v}	2.686(4)	180
O100-H100...O4^{iii}	2.74(3)	171	O5W-H51W...O4A^{vi}	2.827(4)	178
O101-H101...O4^{iii}	2.80(2)	168	O5W-H52W...O1W	2.828(5)	180
O121-H121...O4^{iii}	3.06(4)	144	O4W-H41W...O3W	2.816(4)	166
O1W-H12W...O101	2.57(5)	175	O4W-H42W...O4	2.874(4)	154
			O1W-H11W...O3W	2.840(4)	168
			O1W-H12W...O5^{vii}	2.736(4)	178
			O2W-H21W...O5^{v}	2.991(4)	179
			O2W-H22W...O5W	2.810(5)	179

B3NB(DL)T: (*i*) x-1/2, -y+1/2, -z+1; (*ii*) x+1/2, -y+1/2, -z+1; (*iii*) $3 -x+1, y+1/2, -z+3/2
B3NBLV: (*iv*) x+1, y, z+1; (*v*) x, y, z-1; (*vi*) x-1, y-1, z-1; (*vii*) x-1, y, z-1; (*viii*) x, y+1, z



B3NB(DL)T



B3NBLV

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Table S7. Crystallographic data for brucine propan-1,2-diol solvate 0.19-hydrate (**B12pr**) and brucine butan-1,2-diol 0.84-solvate 0.16-hydrate (**B12bu**).

	B12pr	**B12bu**
Chemical formula*	$C_{23}H_{26}N_2O_4 \cdot C_3H_8O_2$ $0.19H_2O$	$C_{23}H_{26}N_2O_4 \cdot 0.84C_4H_{10}O_2$ $0.16H_2O$
Chemical formula weight	473.93	473.23
Temperature (K)	293	100
Cell setting, space group	orthorhombic, $P2_12_12_1$	orthorhombic, $P2_12_12_1$
a, b, c (Å)	12.470(3), 13.622(3), 14.178(4)	12.481(2), 13.650(2), 13.981(3)
β (°)	90.00	90.00
V (Å^3)	2408.4(10)	2381.9(7)
Z	4	4
D_c (Mg m^{-3})	1.307	1.320
Crystal form, colour	needle, colorless	plate, colorless
Data/parameter ratio (Rint)	6.73 (0.026)	13.20 (0.066)
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.059, 0.162, 0.976	0.055, 0.149, 1.050
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.321, -0.369	0.498, -0.268
CCDC no.	930495	930496