Electronic Supplementary Information

Hirshfeld surface analysis of crystal packing in aza-aromatic picrate salts

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Table S1 Saturated base non-hydrogen geometries

Compound	**(pipH)(pic)·pip**		**(pipH)(pic)[21]**	**2[(morH)(pic)]·H_2O**		**(morH)(pic)[22a]**	
Entity	**pipH**	**pip**	**pipH**	**morH 1**	**morH 2**	**morH 1**	**morH 2**
Distances (Å)							
N-C(α)	1.472(2)	1.486(2)	1.494(3)	1.493(2)	1.497(2)	1.496(2)	1.497(2)
	1.475(2)	1.483(2)	1.488(3)	1.491(2)	1.490(2)	1.491(2)	1.491(2)
C(α)-C(β)	1.517(2)	1.513(2)	1.502(3)	1.516(2)	1.504(3)	1.513(2)	1.511(2)
	1.517(2)	1.515(2)	1.499(3)	1.516(2)	1.513(2)	1.515(2)	1.513(2)
C(β)-C(γ)/O	1.523(2)	1.524(2)	1.513(3)	1.423(2)	1.430(2)	1.434(2)	1.438(2)
	1.525(2)	1.524(2)	1.513(3)	1.423(2)	1.409(2)	1.436(2)	1.433(2)
Angles (deg.)							
C(α)-N-C(α)	111.67(9)	112.82(9)	112.51(2)	111.00(12)	110.10(13)	110.29(10)	110.35(10)
N-C(α)-C(β)	112.70(10)	111.75(9)	110.7(2)	108.51(12)	109.93(14)	108.48(11)	108.76(11)
	113.15(10)	111.14(10)	110.0(2)	108.17(12)	109.04(14)	108.92(10)	109.01(10)
C(α)-C(β)-C(γ)/O	110.87(10)	111.28(10)	112.2(2)	111.39(12)	111.27(17)	110.48(11)	110.24(11)
	110.11(11)	111.02(10)	110.9(2)	111.46(12)	112.09(14)	110.50(11)	110.54(10)
C(β)-C(γ)/O-C(β)	110.75(10)	110.51(10)	109.8(2)	110.90(11)	109.00(12)	110.98(10)	111.02(10)
Torsion angles (deg.)							
C(α)-N-C(α)-C(β)	54.26(13)	–54.78(13)	–54.9(2)	56.3(2)	–54.0(2)	57.62(14)	–57.23(14)
	–55.00(13)	55.50(12)	57.4(2)	–56.6(2)	53.6(2)	–57.29(14)	56.75(17)
N-C(α)-C(β)-C(γ)/O	–54.32(14)	53.89(13)	53.5(3)	–57.3(2)	57.9(2)	–58.84(14)	58.66(14)
	55.13(14)	–55.58(14)	–58.3(2)	58.0(2)	–58.8(2)	57.97(14)	–57.89(14)
C(α)-C(β)-Cγ)/O-C(β)	54.22(14)	–54.29(15)	–54.7(2)	59.9(2)	–61.4(2)	60.91(14)	–61.09(14)
	–54.27(14)	55.19(15)	56.9(2)	–60.4(2)	62.1(2)	–60.32(14)	60.61(14)

Atoms are denoted α, β, γ with respect to the nitrogen atom.

Table S2 Pyridine ring non-hydrogen geometries

Base (ring)	**2mp (1,2)**	**bpy (1,2)**	**dpa (1,2)***	**tpy (1,2,3)**	**py****
Distances (Å)					
N(1)-C(2)	1.346(3), 1.353(3)	1.357(3), 1.353(3)	1.353(2), 1.335(2)	1.3470(12), 1.3439(12), 1.3559(11)	1.3400
N(1)-C(6)	1.352(3), 1.343(3)	1.351(3), 1.344(3)	1.370(2), 1.348(2)	1.3407(13), 1.3477(11), 1.3428(12)	1.3384
C(2)-C(3)	1.387(3), 1.388(3)	1.394(3), 1.397(3)	1.405(2), 1.401(2)	1.3971(13), 1.4011(12), 1.3897(15)	1.3824
C(6)-C(5)	1.364(4), 1.376(3)	1.382(4), 1.400(4)	1.366(2), 1.377(3)	1.3894(15), 1.3956(12), 1.3785(16)	1.3822
C(3)-C(4)	1.379(4), 1.381(4)	1.401(4), 1.396(4)	1.372(2), 1.379(2)	1.3902(16), 1.3860(16), 1.3879(13)	1.3908
C(4)-C(5)	1.392(4), 1.384(4)	1.394(4), 1.385(4)	1.403(2), 1.393(3)	1.3847(14), 1.3925(14), 1.3899(13)	1.3915
C(2)-C(2')/N(O)	1.491(4), 1.489(4)	1.492(3), -	1.357(2), 1.393(2)	1.4896(15), - , 1.4796(12)	–
Angles (degrees)					
C(2)-N(1)-C(6)	123.2(2), 123.4(2)	123.6(2), 117.3(2)	122.19(12), 117.64(13)	117.42(9), 118.00(8), 123.90(8)	122.58
N(1)-C(2)-C(3)	117.8(2), 117.4(2)	118.4(2), 123.6(2)	118.86(12), 123.46(14)	122.93(9), 121.98(9), 118.20(8)	120.00
N(1)-C(6)-C(5)	120.1(2), 120.2(2)	119.5(2), 123.1(2)	120.48(13), 123.19(16)	123.72(10), 123.84(8), 119.31(8)	119.85
C(2)-C(3)-C(4)	120.3(2), 120.4(2)	119.2(2), 117.8(2)	119.31(13), 117.53(15)	118.23(9), 119.18(9), 119.00(8)	118.78
C(6)-C(5)-C(4)	118.7(2), 118.4(3)	118.8(2), 118.6(3)	118.69(14), 118.28(15)	118.13(9), 117.41(8), 118.70(9)	118.95
C(3)-C(4)-C(5)	119.9(2), 120.2(2)	120.4(2), 119.5(3)	120.47(14), 119.89(15)	119.49(9), 119.56(9), 120.85(8)	119.84
N(1)-C(2)-C(2')/N(O)	117.7(2), 117.4(2)	115.9(2), 114.0(2)	120.17(12), 117.84(12)	115.70(8), 117.23(8)†, 116.67(8)	-
C(3)-C(2)-C(2')/N(O)	124.5(2), 125.3(2)	125.7(2), 122.4(2)	120.97(12), 118.69(13)	121.34(8), 120.74(8)†, 125.10(8)	-

Where protonation is unsymmetrical, values for the protonated ring are given first; where rings are linked, C(2) carries the linker. The common ad hoc numbering scheme employed in this Table is shown in the pictogram.

*The angle at the central nitrogen atom is 127.98(12)º. †C(3),N-C(6)-C(2') 114.59(7), 121.55(8)º; ring 3 is '*anti*'.

**Theoretical (for (pyH)(pic)) (see text).

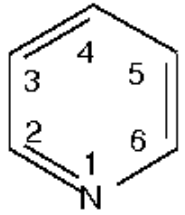


Table S3 Phenanthroline non-hydrogen geometries ((phenH)(pic) and (dmpH)(pic))

Base (ring)	**phen (1,2)**	**dmp (1,2)**
Distances (Å)		
N(1)-C(2)	1.387(2), 1.384(2)	1.366(2), 1.353(2)
N(1)-C(6)	1.352(3), 1.348(3)	1.338(2), 1.325(2)
C(2)-C(3)	1.430(3), 1.439(3)	1.400(2), 1.409(2)
C(6)-C(5)	1.425(3), 1.435(3)	1.403(2), 1.408(3)
C(3)-C(4)	1.437(3), 1.442(3)	1.410(3), 1.406(3)
C(4)-C(5)	1.405(3), 1.392(3)	1.353(3), 1.362(3)
C(2)-C(2')	1.465(3), -	1.436(2), -
C(3)-C(3')	1.466(3), 1.472(3)	1.426(3), 1.422(3)
C(6)-C(61)	- -	1.478(3), 1.499(3)
C(3')-C(3')	1.832(3), -	1.351(3), -
Angles (degrees)		
C(2)-N(1)-C(6)	122.95(17), 116.7(2)	123.41(15), 117.46(17)
N(1)-C(2)-C(3)	119.43(17), 124.6(2)	119.19(15), 124.15(16)
N(1)-C(6)-C(5)	120.05(19), 123.6(2)	118.13(17), 122.48(17)
C(2)-C(3)-C(4)	117.85(18), 116.1(2)	117.92(16), 116.59(16)
C(6)-C(5)-C(4)	119.1(2), 119.3(2)	120.83(17), 120.01(18)
C(3)-C(4)-C(5)	120.6(2), 119.6(2)	120.51(17), 119.29(18)
N(1)-C(2)-C(2')	118.92(17), 117.1(2)	119.83(15), 118.43(16)
C(3)-C(2)-C(2')	121.60(17), 118.3(2)	120.98(16), 117.39(15)
C(2)-C(3)-C(3')	118.37(18), 119.6(2)	119.32(16), 120.87(16)
C(4)-C(3)-C3')	123.78(19), 124.3(2)	122.75(16), 122.52(17)
C(3)-C(3')-C(3')	121.1(2), 121.0(2)	120.62(17), 120.81(18)
N(1)-C(6)-C(61)	-	119.37(17), 118.13(18)
C(5)-C(6)-C(61)	-	122.48(17), 119.37(17)

Values for the protonated ring are given first; the common *ad-hoc* numbering scheme employed in this Table is as follows:

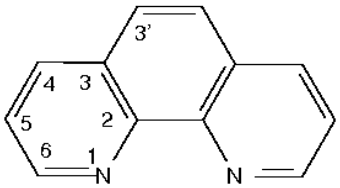


Table S4 (a) Comparative geometries of quinoline-derived arrays (ox = oxinate = 8-quinolinolate)

Base	**quinH** [a]	**iqH** [b]	**2mqH** [c]	**ohqH** [d]	**ohq** [e]	**ox**$^-$ [f]	**ox**$^-$ **(chelated)**[g]				
							Al	**Fe**	**Co**	**m1**[h]	**m2**[h]
Distances /Å											
X(1)-X(2)	1.312(3)	1.314(6)	1.325(4)	1.318(2)	1.3209(15)	1.313(4)	1.33_6	1.31_9	1.32_5	1.337(3)	1.306(8)
X(1)-C(9)	1.373(2)	1.412(6)	1.367(5)	1.361(2)	1.3648(14)	1.372(6)	1.35_8	1.36_3	1.36_9	1.337(3)	1.371(7)
C(2)-C(3)	1.387(3)	1.362(5)	1.387(4)	1.385(5)	1.4095(16)	1.392(3)	1.39_7	1.40_3	1.41_2	1.384(4)	1.410(9)
C(3)-C(4)	1.365(3)	1.343(6)	1.346(6)	1.356(3)	1.3702(16)	1.324(6)	1.36_1	1.34_9	1.36_6	1.369(4)	1.353(9)
C(4)-C(10)	1.406(3)	1.403(6)	1.407(5)	1.408(3)	1.4141(16)	1.402(5)	1.41_4	1.41_8	1.42_0	1.392(4)	1.401(9)
C(5)-C(6)	1.350(3)	1.368(6)	1.340(6)	1.354(3)	1.3684(16)	1.346(4)	1.36_7	1.35_9	1.37_7		1.356(9)
C(5)-C(10)	1.417(3)	1.419(6)	1.402(6)	1.406(3)	1.4179(14)	1.409(6)	1.42_1	1.40_5	1.41_6		1.425(8)
C(6)-C(7)	1.404(3)	1.407(6)	1.398(5)	1.402(3)	1.4105(16)	1.388(3)	1.40_9	1.40_8	1.41_1		1.407(8)
C(7)-C(8)	1.363(3)	1.355(7)	1.352(7)	1.374(2)	1.3773(16)	1.369(6)	1.37_6	1.38_2	1.39_1		1.364(8)
C(8)-O(8)	–	–	–	1.340(2)	1.3527(14)	1.329(2)	1.33_1	1.33_3	1.32_3		1.413(7)
C(8)-C(9)	1.404(2)	1.410(6)	1.382(5)	1.407(2)	1.4272(16)	1.439(4)	1.43_1	1.42_5	1.42_5		1.402(8)
C(9)-C(10)	1.412(2)	1.414(5)	1.396(4)	1.410(2)	1.4221(15)	1.406(3)	1.41_0	1.41_7	1.41_4	1.372(4)	1.426(8)
Angles /degrees											
X(2)-X(1)-C(9)	122.6(2)	121.3(3)	124.1(3)	123.24(15)	117.75(9)	116.6(3)	$118._6$	$119._0$	$119._7$	124.3(2)	116.7(5)
X(1)-X(2)-C(3)	121.1(2)	121.8(3)	118.7(4)	119.9(2)	123.80(10)	125.0(2)	$122._2$	$122._4$	$121._2$	119.0(2)	125.3(6)
X(2)-C(3)-C(4)	119.1(2)	120.8(4)	120.4(3)	118.8(2)	118.95(10)	118.2(1)	$119._7$	$119._4$	$120._1$	118.2(3)	118.1(6)
C(3)-C(4)-C(10)	120.6(2)	119.8(4)	120.6(3)	121.04(17)	119.51(10)	121.2(3)	$120._4$	$120._8$	$120._0$	121.2(3)	120.3(6)
C(6)-C(5)-C(10)	120.5(2)	119.6(4)	120.6(3)	119.64(16)	119.72(10)	119.0(2)	$119._0$	$119._6$	$119._1$		120.4(6)
C(5)-C(6)-C(7)	120.7(2)	120.7(4)	120.8(4)	122.09(8)	121.25(10)	122.6(2)	$122._9$	$122._6$	$122._8$		120.8(6)
C(6)-C(7)-C(8)	121.3(2)	121.4(4)	120.5(4)	120.3(2)	120.48(10)	121.5(1)	$120._1$	$120._1$	$119._9$		119.5(6)
C(7)-C(8)-O(8)	–	–	–	126.6(2)	119.26(10)	123.2(1)	$125._8$	$123._6$	$125._0$		115.9(5)
C(7)-C(8)-C(9)	118.6(2)	119.0(4)	118.9(3)	117.96(15)	119.72(10)	117.1(3)	$117._8$	$117._8$	$117._5$		122.5(5)
O(8)-C(8)-C(9)	–	–	–	115.42(14)	121.02(9)	119.7(2)	$116._4$	$118._6$	$117._5$		121.5(8)
N(1)-C(9)-C(8)	120.5(2)	122.4(4)	120.43)	119.34(14)	118.12(9)	117.2(3)	$114._7$	$115._8$	$114._8$	109.4(2)	120.0(5)
N(1)-C(9)-C(10)	118.4(2)	116.9(3)	117.8(3)	118.81(15)	122.72(10)	122.2(1)	$123._2$	$122._5$	$122._1$	118.6(3)	122.5(5)
C(8)-C(9)-C(10)	121.1(2)	120.6(4)	121.8(4)	121.82(15)	119.15(9)	120.5(2)	$122._0$	$122._6$	$122._8$	119.0(2)	117.6(5)
C(4)-C(10)-C(5)	123.9(2)	122.0(8)	124.2(3)	124.51(16)	123.10(10)	123.9(2)	$125._8$	$125._7$	$125._5$		123.6(5)
C(4)-C(10)-C(9)	118.2(2)	119.4(4)	118.4(4)	117.33(17)	117.24(9)	116.8(2)	$116._1$	$115._9$	$116._3$	118.7(3)	117.2(5)
C(5)-C(10)-C(9)	117.9(2)	118.6(3)	117.4(3)	118.14(16)	119.66(10)	119.3(1)	$118._1$	$118._4$	$118._2$		119.3(5)

[a]Ref.[8]; [b]ref.[28]; [c]ref.[29]; [d]this work; C_6(Ar)/CNO_2 interplanar dihedral angles are 34.44(7), 4.80(10), 9.08(14)^o; [e]ref.[51d] (100K); [f]in 'potassium quinolin-8-olate bis(quinolin-8-ol)', ref.[52] (room-temperature); [g]mean values of the three distances for the three ligands in each of the isomorphous $P2_1/n$ (Z = 4) complexes *mer*-[Mox_3]·MeOH (M = Al (HQUALA01), Fe

(high-spin) MEQDES), Co (low-spin) (AJUJIY03). (Details for the individual ligands, metal-ligand distances and references are summarized in Table S5.); [h]ref.[30] (room-temperature); m1,2 are the 8-hydroxyquinoline picrate proto-Meisenheimer and the 2-hydroxymethylpyridine picrate Meisenheimer complexes.

The common *ad-hoc* numbering scheme is as follows:

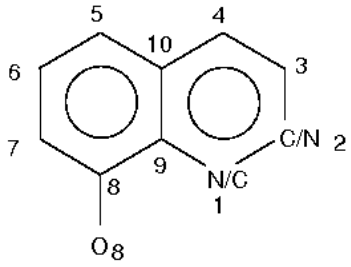


Table S4 (b) Chelated oxinate ligand geometries (ligands 1-3, <>) in isomorphous $P2_1/n$ *mer*-$[Mox_3]$·MeOH (M = Al, Fe, Co)*

M	Al[a] (HQUALA01)	< >	Fe[b] (MEQDES)	< >	Co[c] (AJUJIY03)	< >
O-M[†]	1.850(2), 1.881(2), **1.841(3)**	1.85_7	1.921(2), 1.908(2), **1.915(2)**	1.91_5	1.907(1), 1.900(1), **1.899(1)**	1.90_2
N-M[†]	**2.074(3)**, 2.026(3), 2.048(3)	2.05_6	2.237(2), **2.054(2)**, 2.272(2)	2.18_8	1.920(1), **1.928(1)**, 1.930(1)	1.92_6
N-2	1.330(5), 1.329(5), 1.331(5)	1.33_0	1.313(4), 1.324(3), 1.319(3)	1.31_9	1.322(2), 1.328(2), 1.326(2)	1.32_5
N-9	1.354(5), 1.364(6), 1.357(5)	1.35_8	1.358(4), 1.368(3), 1.363(3)	1.36_3	1.365(2), 1.372(2), 1.370(2)	1.36_9
2-3	1.396(6), 1.396(5), 1.399(5)	1.39_7	1.402(5), 1.401(4), 1.403(4)	1.40_2	1.413(2), 1.412(2), 1.410(2)	1.41_2
3-4	1.357(6), 1.366(7), 1.359(5)	1.36_1	1.331(7), 1.362(5), 1.354(5)	1.34_9	1.366(2), 1.372(3), 1.370(2)	1.36_6
4-10	1.423(6), 1.403(6) 1.417(5)	1.41_4	1.418(6), 1.417(4), 1.420(5)	1.41_8	1.420(3), 1.422(2), 1.418(2)	1.42_0
5-6	1.373(6), 1.361(6), 1.367(5)	1.36_7	1.362(7), 1.357(4), 1.359(5)	1.35_9	1.377(3), 1.378(2), 1.377(2)	1.37_7
5-10	1.408(6), 1.433(7), 1.422(5)	1.42_1	1.404(2), 1.407(4), 1.403(5)	1.40_5	1.415(2), 1.415(2), 1.419(2)	1.41_6
6-7	1.414(6), 1.405(6), 1.407(5)	1.40_9	1.409(6), 1.405(4), 1.411(4)	1.40_8	1.412(2), 1.410(2), 1.410(2)	1.41_1
7-8	1.371(5), 1.378(6), 1.380(5)	1.37_6	1.377(4), 1.380(3), 1.389(4)	1.38_2	1.388(2), 1.392(2), 1.393(2)	1.39_1
8-O	1.330(5), 1.330(4), 1.332(4)	1.33_1	1.334(3), 1.333(3), 1.322(3)	1.33_3	1.327(2), 1.322(2), 1.320(2)	1.32_3
8-9	1.433(5), 1.427(5), 1.433(5)	1.43_1	1.431(4), 1.415(3), 1.430(4)	1.42_5	1.426(2), 1.425(2), 1.425(2)	1.42_5
9-10	1.421(5), 1.405(5), 1.405(5)	1.41_0	1.418(4), 1.412(3), 1.422(4)	1.41_7	1.412(2), 1.413(2), 1.417(2)	1.41_4
2-N-9	118.3(3) 118.8(3), 118.6(3)	$118._6$	119.3(2), 118.9(2), 118.8(2)	$119._0$	120.1(1), 119.5(1), 119.4(1)	$119._7$
N-2-3	122.5(3), 122.1(4), 122.0(4)	$122._2$	122.5(3), 121.8(2), 122.8(2)	$122._4$	120.9(1), 121.1(2), 121.6(1)	$121._2$
2-3-4	119.7(4), 119.5(4), 119.8(4)	$119._7$	119.1(3), 119.9(3), 119.3(3)	$119._4$	120.0(2), 120.3(1), 120.0(1)	$120._1$
3-4-10	120.8(4), 120.3(3), 120.0(3)	$120._4$	121.5(3), 120.5(2), 120.6(3)	$120._8$	120.2(1), 120.0(1), 119.9(1)	$120._0$
6-5-10	118.8(4), 119.0(4), 119.3(3)	$119._0$	119.5(4), 119.7(2), 119.5(3)	$119._6$	119.2(1), 119.1(1), 119.0(1)	$119._1$
5-6-7	123.0(4), 123.0(4), 122.6(4)	$122._9$	123.0(4), 122.5(2), 122.3(3)	$122._6$	122.7(2), 122.7(2), 122.9(1)	$122._8$
6-7-8	119.9(4), 120.3(4), 120.1(3)	$120._1$	119.7(3), 120.1(2), 120.5(3)	$120._1$	119.8(2), 120.0(1), 120.0(1)	$119._9$
7-8-O	126.0(3), 126.0(3), 125.4(3)	$125._8$	123.5(2), 124.7(2), 122.8(2)	$123._6$	125.2(2), 125.0(1), 124.8(1)	$125._0$
7-8-9	118.1(3), 117.4(3), 117.9(3)	$117._8$	118.0(2), 117.7(2), 117.5(2)	$117._7$	117.2(2), 117.3(1), 117.5(1)	$117._5$
O-8-9	115.9(3), 116.5(3), 116.7(3)	$116._4$	118.6(2), 117.6(2), 119.7(2)	$118._6$	117.1(2), 117.7(1), 117.8(1)	$117._5$
N-9-8	114.6(3), 114.7(3), 114.9(3)	$114._7$	116.4(2), 114.8(2), 116.3(2)	$115._8$	115.0(1), 114.4(1), 115.0(1)	$114._8$
N-9-10	123.9(3), 122.6(4), 123.2(4)	$123._2$	122.0(3), 123.0(2), 122.5(2)	$122._5$	122.5(2), 122.9(1), 122.5(1)	$122._6$
8-9-10	121.5(3), 122.7(4), 121.9(3)	$122._0$	121.6(3), 122.2(2), 121.1(2)	$122._6$	122.5(2), 122.7(1), 122.5(1)	$122._6$
4-10-5	126.4(4), 125.6(4), 125.4(3)	$125._8$	126.1(3), 126.2(2), 124.9(3)	$125._7$	125.6(1), 125.6(1), 125.2(2)	$125._5$
4-10-9	115.0(4), 116.8(4), 116.4(3)	$116._1$	115.7(4), 115.9(2), 116.0(2)	$115._9$	116.2(1), 116.2(1), 116.6(1)	$116._3$
5-10-9	118.6(4), 117.6(4), 118.2(3)	$118._1$	118.2(3), 117.9(2), 119.0(3)	$118._4$	118.2(2), 118.1(1), 118.2(1)	$118._2$
8-O-M	117.6(2), 115.4(2), 115.6(2)	$116._2$	117.8(1), 115.0(2), 117.8(2)	$116._9$	111.4(1), 111.6(1), 111.0(1)	$111._3$
2-N-M	131.9(3), 130.9(3), 132.6(2)	$131._8$	133.1(2), 130.8(2), 134.6(2)	$132._8$	129.2(1), 129.9(1), 131.0(1)	$130._0$
9-N-M	109.8(2), 110.3(2), 108.8(2)	$110._7$	107.7(2), 110.3(2), 106.4(2)	$108._1$	110.6(1), 110.5(1), 109.7(1)	$109._3$

*The methanol OH hydrogen approaches the oxygen atom of ligand 2 (M = Al), ligand 1 (Fe, Co) at *ca* 1.9Å. The iron(III) and cobalt(III) complexes are high-and low-spin respectively. [†]The central distance of each meridian is shown in **bold**. The numbering schemes in the various determinations differ; that applied globally here is that of Table S4(a).

[a] H. Schmidbaur, J. Lettenbauer, P. L. Wilkinson, O. Muller, O. Kumberger, *Z. Naturforsch., Teil B*, 1991, **46**, 901 (**HQUALA01**, 233 K).

[b] G. Chen, *Acta Crystallogr.*, 2006, **E62**, m3383 (**MEQDES**, '283-303' K).

[c] D. Mandal, M. Mikuriya, H.-K. Fun and D. Ray, *Inorg. Chem. Comm.*, 2007, **10**, 657 (**AJUJIY03**, '283-303' K).

Table S5 Non-hydrogen atom picrate and picric acid geometries (this work, except picH)

Compound	**picH (1,2)***	**pip**	**mor (1,2)**	**2mp (1,2)**	**bpy**	**phen**	**dmp**	**ohq**	**dpa**	**tpy**
Distances (Å)										
C(1)-O(1)	1.318(2), 1.338(2)	1.2395(12)	1.261(2), 1.261(2)	1.256(3), 1.257(3)	1.246(3)	1.271(2)	1.239(2)	1.231(2)	1.247(2)	1.2360(11)
C(1)-C(2)	1.418(2), 1.412(3)	1.4535(14)	1.452(2), 1.437(2)	1.448(3), 1.453(3)	1.463(3)	1.488(3)	1.452(3)	1.449(2)	1.454(2)	1.4658(13)
C(1)-C(6)	1.416(3), 1.402(3)	1.4551(14)	1.447(2), 1.438(2)	1.458(3), 1.455(3)	1.463(3)	1.488(3)	1.452(3)	1.447(2)	1.455(2)	1.4640(13)
C(2)-C(3)	1.386(3), 1.384(3)	1.3700(14)	1.377(2), 1.373(2)	1.380(3), 1.379(3)	1.391(3)	1.397(3)	1.371(3)	1.361(2)	1.374(2)	1.3810(12)
C(5)-C(6)	1.379(3), 1.373(3)	1.3722(14)	1.380(2), 1.370(2)	1.373(3), 1.367(3)	1.374(3)	1.412(3)	1.368(2)	1.368(2)	1.374(2)	1.3660(12)
C(3)-C(4)	1.373(3), 1.380(3)	1.3909(15)	1.380(2), 1.384(2)	1.385(3), 1.379(3)	1.388(4)	1.426(3)	1.383(3)	1.384(2)	1.388(2)	1.3895(2)
C(4)-C(5)	1.384(3), 1.381(3)	1.3885(15)	1.388(2), 1.392(2)	1.402(3) 1.399(3)	1.402(4)	1.408(3)	1.381(3)	1.377(2)	1.387(2)	1.3967(12)
C(2)-N(2)	1.461(2), 1.459(3)	1.4511(13)	1.458(2), 1.458(2)	1.459(3), 1.453(3)	1.453(3)	1.492(2)	1.447(7)	1.452(2)	1.456(2)	1.4487(11)
C(6)-N(6)	1.471(2), 1.482(3)	1.4495(13)	1.461(2), 1.464(2)	1.468(3), 1.472(3)	1.469(3)	1.481(3)	1.450(2)	1.450(2)	1.456(2)	1.4577(12)
C(4)-N(4)	1.469(2), 1.464(2)	1.4355(13)	1.451(2), 1.442(2)	1.444(3), 1.445(3)	1.454(3)	1.471(2)	1.438(3)	1.441(2)	1.446(2)	1.4362(11)
N(2)-O(21)	1.238(2), 1.239(3)	1.2284(13)	1.217(2), 1.229(2)	1.235(2), 1.205(2)	1.239(3)	1.250(2)	1.227(2)	1.212(2)	1.228(2)	1.2306(14)
N(6)-O(61)	1.222(2), 1.204(3)	1.2263(13)	1.228(2), 1.220(2)	1.230(3), 1.226(3)	1.231(3)	1.252(2)	1.223(2)	1.201(2)	1.219(2)	1.2275(12)
N(2)-O(22)	1.213(2). 1.219(3)	1.2326(13)	1.229(8), 1.225(2)	1.238(3), 1.221(3)	1.235(3)	1.260(2)	1.225(2)	1.229(2)	1.234(2)	1.2381(10)
N(6)-O(62)	1.232(2), 1.216(3)	1.2363(13)	1.228(2), 1.221(2)	1.230(3), 1.226(3)	1.228(3)	1.266(2)	1.229(2)	1.210(3)	1.228(2)	1.2310(12)
N(4)-O(41)	1.220(2), 1.222(2)	1.2329(15)	1.219(2), 1.219(2)	1.241(3), 1.234(3)	1.239(4)	1.254(2)	1.228(2)	1.223(2)	1.234(2)	1.2446(10)
N(4)-O(42)	1.232(2), 1.232(2)	1.2379(14)	1.223(2), 1.228(2)	1.235(2), 1.237(3)	1.236(4)	1.267(2)	1.231(2)	1.226(2)	1.236(2)	1.2352(12)
O(1)...O(21)	2.563(2), 2.579(3)	2.7540(13)	2.702(2), 2.736(2)	2.755(3), 2.707(3)	2.733(3)	2.898(2)	2.701(2)	2.666(2)	2.684(2)	2.6348(11)
O(1)...O(61)	2.586(2), 2.599(3)	2.7361(12)	2.722(2), 2.718(3)	2.860(3), 2.826(3)	2.861(3)	2.748(2)	2.659(2)	2.638(2)	2.652(3)	2.7014(12)

Angles (deg.)

O(1)-C(1)-C(2)	124.1(2), 125.0(2)	124.30(9)	125.21(12), 122.93(15)	127.2(2), 126.8(2)	125.4(2)	122.7(2)	125.2(2)	122.13(15)	124.13(12)	125.47(9)
O(1)-C(1)-C(6)	120.9(2), 119.3(2)	124.72(9)	123.11(12), 124.59(14)	121.6(2), 121.7(2)	123.1(2)	125.9(2)	123.2(2)	126.10(15)	124.28(12)	122.97(9)
C(2)-C(1)-C(6)	115.0(4), 115.8(2)	110.99(8)	111.64(11), 112.35(12)	111.2(2), 111.4(2)	111.3(2)	111.5(2)	111.5(2)	111.74(14)	111.57(11)	111.47(7)
C(1)-C(2)-C(3)	123.4(2), 122.7(2)	125.13(9)	123.88(12), 124.70(13)	124.2(2), 123.2(2)	123.6(2)	125.9(2)	124.3(2)	124.83(15)	124.68(12)	123.77(8)
C(1)-C(6)-C(5)	122.8(2), 123.1(2)	124.88(9)	125.06(12), 124.39(12)	125.9(2), 125.8(2)	125.7(2)	123.1(2)	124.0(2)	123.67(15)	124.25(12)	124.74(8)
C(2)-C(3)-C(4)	117.7(2), 117.8(2)	118.71(9)	119.52(12), 118.28(12)	119.7(2), 120.4(2)	119.7(2)	117.8(2)	119.0(2)	118.78(15)	118.80(12)	119.41(8)
C(4)-C(5)-C(6)	118.4(2), 118.2(2)	118.87(9)	118.10(12), 118.54(13)	117.7(2), 117.9(2)	118.1(2)	120.3(2)	119.4(2)	119.82(15)	119.27(13)	118.91(8)
C(3)-C(4)-C(5)	122.7(2), 122.5(2)	121.28(9)	121.57(12), 121.69(12)	121.3(2), 121.0(2)	121.5(2)	121.4(2)	121.3(2)	121.07(15)	121.29(12)	121.29(8)
C(1)-C(2)-N(2)	119.9(2), 120.3(2)	118.26(8)	120.43(11), 118.96(12)	120.0(2), 120.4(2)	119.6(2)	117.8(2)	119.3(2)	118.25(14)	119.23(11)	119.93(7)
C(1)-C(6)-N(6)	120.6(2), 121.6(2)	118.43(8)	119.32(11), 118.98(14)	116.8(2), 116.9(2)	117.0(2)	120.9(2)	119.4(2)	119.66(14)	119.84(12)	118.81(7)
C(3)-C(2)-N(2)	116.9(2), 117.0(2)	116.60(9)	115.67(11), 116.29(13)	115.8(2), 116.3(2)	116.7(2)	116.3(2)	116.4(2)	116.79(15)	116.05(12)	116.24(8)
C(5)-C(6)-N(6)	116.6(2), 115.3(2)	116.66(9)	115.57(11), 116.58(14)	117.3(2), 117.2(2)	117.2(2)	115.9(2)	116.6(2)	116.62(14)	115.89(12)	116.44(8)
C(3)-C(4)-N(4)	119.0(2), 119.0(2)	119.28(10)	119.22(12), 118.91(12)	119.2(2), 119.4(2)	119.4(2)	119.5(2)	119.6(2)	119.32(15)	119.17(12)	119.96(8)
C(5)-C(4)-N(4)	118.3(2), 118.6(2)	119.43(10)	119.21(12), 119.40(12)	119.6(2), 119.5(2)	119.2(2)	119.0(2)	119.1(2)	119.54(15)	119.52(12)	118.75(8)
C(2)-N(2)-O(21)	118.6(2), 118.4(2)	118.38(9)	120.02(12), 118.70(16)	119.3(2), 120.3(2)	119.4(2)	118.5(2)	118.5(2)	120.09(15)	119.29(14)	119.52(3)
C(6)-N(6)-O(61)	119.7(2), 119.8(2)	119.03(9)	119.52(12), 118.40(7)	118.0(2), 118.7(2)	117.6(2)	119.8(2)	118.7(2)	119.99(15)	118.21(16	118.45(8)
C(2)-N(2)-O(22)	118.8(2), 119.1(2)	118.00(9)	117.69(12), 117.73(15)	118.2(2), 118.7(2)	118.7(2)	117.5(2)	118.5(2)	116.90(14)	117.76(13)	118.59(9)
C(6)-N(6)-O(62)	117.0(2), 117.5(2)	117.43(9)	117.36(12), 117.75(15)	117.7(2), 117.1(2)	118.3(2)	118.1(2)	118.7(2)	118.81(15)	118.79(12)	118.21(8)
C(4)-N(4)-O(41)	117.8(2), 117.9(2)	118.37(10)	118.51(13), 119.01(12)	118.9(2), 118.8(2)	118.7(2)	118.8(2)	118.5(1)	118.07(15)	118.27(11)	119.22(8)
C(4)-N(4)-O(42)	117.9(2), 117.6(2)	118.43(11)	118.68(13), 118.13(12)	118.4(2), 118.6(2)	118.3(2)	118.1(2)	118.4(2)	118.76(16)	118.10(13)	118.08(7)
O(21)-N(2)-O(22)	122.6(2), 122.5(2)	123.61(10)	122.26(13), 123.57(17)	122.5(2), 121.0(2	122.0(2)	124.0(2)	123.0(2)	123.00(15)	122.94(13)	121.88(9)
O(61)-N(6)-O(62)	124.2(2), 122.7(2)	123.53(10)	123.12(12), 123.85(19)	124.3(2), 124.2(2)	124.0(3)	122.0(2)	122.6(2)	121.20(17)	122.84(14)	123.33(8)
O(41)-N(4)-O(42)	123.3(2), 124.5(2)	123.20(10)	122.75(13), 122.86(12)	122.7(2), 122.6(2)	123.0(2)	123.1(2)	123.2(2)	123.16(16)	123.62(12)	122.69(9)

Interplanar dihedral angles (º)

$C_6/NO_2(2)$	9.63(7), 3.33(9)	40.58(5)	33.10(9), 36.22(7)	55.01(1), 54.8(1)	26.8(1)	51.84(8)	23.0(1)	34.98(3)	27.36(6)	0.86(4)
$C_6/NO_2(6)$	1.1(2), 5.12(8)	35.82(5)	33.18(8), 21.98(8)	23.2(1), 12.9(1)	51.8(1)	12.62(8)	21.33(8)	9.42(9)	21.64(8)	29.39(4)
$C_6/NO_2(4)$	19.05(8), 18.91(11)	4.05(5)	4.16(7), 16.27(8)	13.7(1), 2.4(1)	5.1(1)	7.98(8)	3.44(8)	4.52(7)	5.20(6)	9.24(4)
C_6/cation	-	4.05(5)	4.16(7), 16.27(8)	13.7(1), 2.4(1)	5.1(1)	7.98(8)	3.44(8)	4.52(7)	5.20(6)	9.24(4)

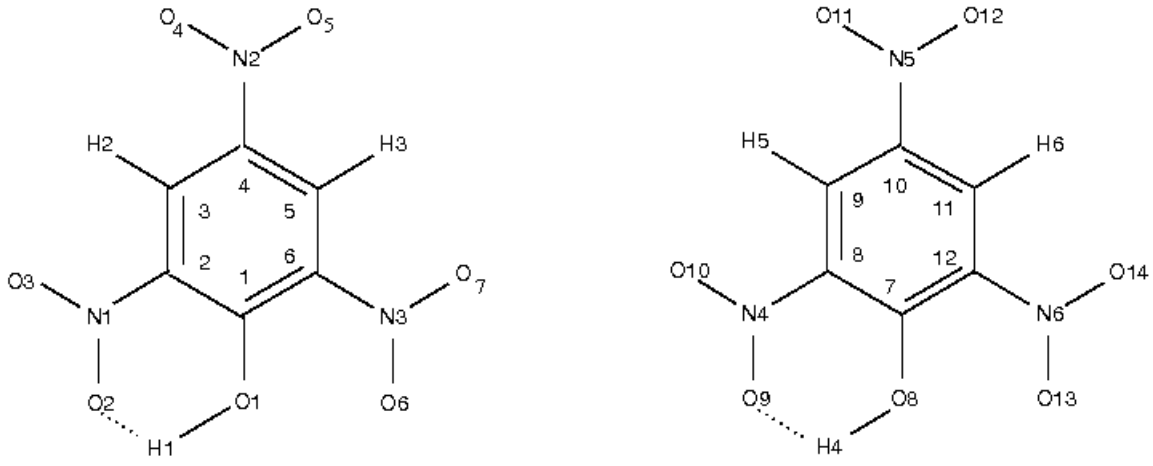
Values are given for the compounds experimentally determined in this work, together with those of the parent picric acid **(picH)**[1g].

* Calculated from the data of **PICRAC13** (two molecules)[1g]. The *ad-hoc* numbering scheme can be found in Table 3.

Table S6 Interspecies approaches (Å) in the compounds of Table 1

Interspecies interactions, corroborated by the fingerprint plots, denoted $(\overline{R})$, $(\overline{L})$, $(\overline{M})$ for the right, left, and middle spike, $(\overline{C})$ for the central marker, $(\overline{P}_{R,\ L})$ for lateral peripheral spikes, parenthetically ( ), [ ] for any second component of an asymmetric unit ($\bar{}$ denoting the inverse symmetry of the fingerprint plot assignment); see also main text. In the salts, cation…cation approaches do not feature in the fingerprint plots (which are of the picrate entity) and therefore carry no assignment. For the present determinations refined protonic hydrogen atom locations are included, as well as those, refined or not, for the other associated structures.

(α) **(picH) (*Pna*2$_1$) (PICRAC13[1g])** (Fig. 1)



Picric acid (picH) (x2)

There are two independent molecules in the asymmetric unit, forming largely independent arrays within the crystal, linked by a small number of CH...*O*(nitro) and other approaches, as given below.

(A) Protonating hydrogen atom approaches/distances within each of the individual molecules of the asymmetric unit; here and elsewhere, the O(phenolic)...O(*o*-nitro) pairs of distances are also given, any pair 'chelating' a protonating (cationic or solvent) hydrogen atom being shown **bold**.

H(1)...O(1,2)	0.78(3), 1.84(3)	H(4)...O(8,9)	0.85, 1.82(4)
O(1)...O(2,6)	**2.563(2)**, 2.586(2)	O(8)...O(9,13)	**2.579(3)**, 2.599(3)

(B) Other approaches/overlaps (<3.6 Å)

Screw-related approaches

Molecule 1...*molecule 1'* approaches			Molecule 2...*molecule 2'* approaches		
	(1–*x*, $\bar{y}$, ½+*z*)			(2–*x*, 1–*y*, ½+*z*)	
O(5)... *N(3)*	3.194(2)	(C, $\bar{C}$)	C(8)...*O(14)*	3.260(3)	[C, $\bar{C}$]
O(6)	3.285(2)	(C, $\bar{C}$)	C(9)...*O(14)*	3.075(3)	[C, $\bar{C}$]
O(7)	3.346(2)	(C, $\bar{C}$)	C(10)...*O(13)*	3.496(3)	[C, $\bar{C}$]
N(2)... *O(6)*	3.229(2)	(C, $\bar{C}$)	*O(14)*	3.129(3)	[C, $\bar{C}$]
C(4)... *O(6)*	3.355(2)	(C, $\bar{C}$)	C(11)...*O(14)*	3.404(3)	[C, $\bar{C}$]
H(3),C(5)... *O(1)*	2.73(2), 3.166(2)	(L, $\bar{R}$)			
O(7)...*H,O(1)*	2.42(2), 2.910(2)	(R, $\bar{L}$)			
O(2)	2.841(2)	(C, $\bar{C}$)			

n-Glide-related approaches

	($^3/_2$–*x*, *y*, *z*–½)			($^3/_2$–*x*, *y*, *z*–½)	
C(1)... *O(5)*	3.323(2)	(C, $\bar{C}$)	O(8)...*N(4)*	3.221(3)	[C, $\bar{C}$]
C(6)... *O(5)*	3.069(2)	(C, $\bar{C}$)	*O(10)*	3.122(3)	[C, $\bar{C}$]
N(3)... *O(5)*	3.249(2)	(C, $\bar{C}$)	O(13)...*C(7)*	3.168(3)	[C, $\bar{C}$]
O(6)...*H(3),C(5)*	2.35(2), 3.287(2)	(R, $\bar{L}$)	*C(8)*	3.229(3)	[C, $\bar{C}$]
O(5)	3.257(2)	(C, $\bar{C}$)	*N(4)*	3.247(3)	[C, $\bar{C}$]
O(7)	3.014(2)	(C, $\bar{C}$)	*O(8)*	3.089(3)	[C, $\bar{C}$]
			O(9)	3.093(3)	[C, $\bar{C}$]
	(½–*x*, *y*, ½+ *z*)			($^5/_2$–*x*, *y*, *z*–½)	
H(2),C(3)...*O(2)*	2.92(3), 3.314(2)	(L, $\bar{R}$)	C(11)...*O(11)*	2.913(2)	[C, $\bar{C}$]
O(4)...*N(1)*	3.349(2)	(C, $\bar{C}$)	C(12)...*O(11)*	3.156(2)	[C, $\bar{C}$]
O(2)	3.381(2)	(C, $\bar{C}$)	N(6)... *O(11)*	3.291(2)	[C, $\bar{C}$]
O(3)	3.139(3)	(C, $\bar{C}$)	*O(12)*	3.326(3)	[C, $\bar{C}$]
			O(14)...*O(12)*	3.122(3)	[C, $\bar{C}$]

a-Glide-related approaches

Molecule 1...*molecule 1'* approaches

(x–½, $\bar{y}$, z)

C(1)...*O(6)*	3.226(2)	(**C**, $\bar{C}$)
O(7)	3.468(3)	(**C**, $\bar{C}$)
C(2)...*O(6)*	3.447(2)	(**C**, $\bar{C}$)
O(7)	3.185(2)	(**C**, $\bar{C}$)
C(3)...*O(7)*	3.276(3)	(**C**, $\bar{C}$)
O(1)...*O(6)*	3.132(2)	(**C**, $\bar{C}$)
O(2)...*O(6)*	3.271(2)	(**C**, $\bar{C}$)

Molecule 2...*molecule 2'* approaches

(x–½, 1–y, z)

C(12)...*O(12)*	3.273(3)	[**C**, $\bar{C}$]
N(6)...*O(12)*	3.149(3)	[**C**, $\bar{C}$]
O(8)...*O(14)*	3.179(3)	[**C**, $\bar{C}$]
O(13)...*O(14)*	2.807(3)	[**C**, $\bar{C}$]
O(14)...*O(12)*	3.100(3)	[**C**, $\bar{C}$]
H(6),C(11)...O(13)	2.54(3), 3.590(3)	[**L**, $\bar{R}$]

Translation-related approaches

Molecule 1...*molecule 2'* approaches

($^3/_2$–x, y, z–½)

C(2)...*O(10)*	3.447(3)	***(C)***, [$\bar{C}$]
N(1)...*O(10)*	2.978(2)	***(C)***, [$\bar{C}$]
O(2)...*H(5),C(9)*	2.64(2), 3.459(2)	***(R)***, [$\bar{L}$]
O(10)	3.027(2)	***(C)***, [$\bar{C}$]
O(3)...*O(10)*	3.292(2)	***(C)***, [$\bar{C}$]
O(11)	3.326(2)	***(C)***, [$\bar{C}$]
H(5),C(9)	2.62(2), 3.518(3)	***(R)***, [$\bar{L}$]

($^3/_2$–x, y, ½+z)

O(4)...*C(8)*	3.266(3)
C(9)	3.329(3)

Molecule 1...*molecule 2'* approaches

(x–1, y, z)

H(2),C(3)...*O(9)*	2.77(3), 2.986(3)	***(L)***, [$\bar{R}$]
O(11)	2.53(2), 3.465(2)	***(L)***, [$\bar{R}$]
O(3)...*C(10)*	3.115(2)	***(C)***, [$\bar{C}$]
N(5)	2.771(2)	***(C)***, [$\bar{C}$]
O(11)	3.015(2)	***(C)***, [$\bar{C}$]
O(12)	3.055(1)	***(C)***, [$\bar{C}$]

(x, y, z)

C(4)...*O(9)*	3.427(3)	***(C)***, [$\bar{C}$]

Molecule 2...*molecule 2'* approaches

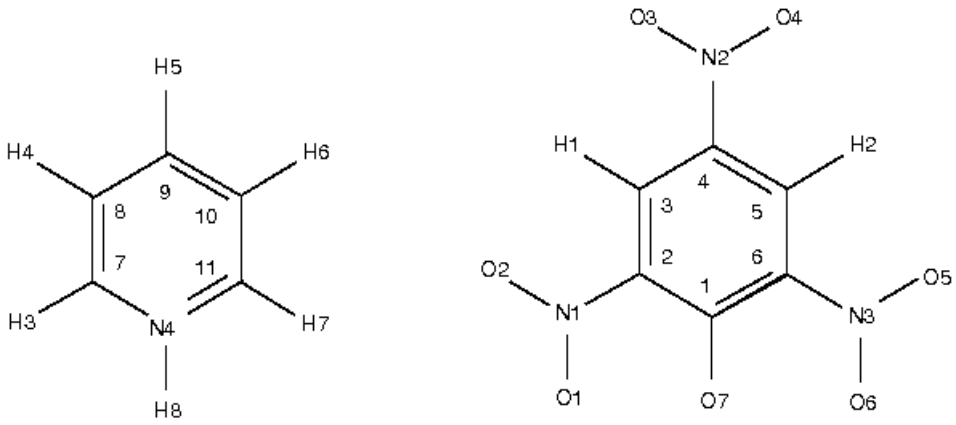
(x–1, y, z)

H(4),O(8)...*O(12)*	2.64(4), 3.083(2)	[**L**, $\bar{R}$]
O(9)...*O(11)*	3.216(2)	[**C**, $\bar{C}$]

($^3/_2$–x, y, ½+ z)

N(4)...*O(8)*	3.221(3)	[**C**, $\bar{C}$]
O(13)	3.247(3)	[**C**, $\bar{C}$]

(β)(i) **(pyH)(pic) (monoclinic) (*P*2$_1$/*c*) (PYRPIC02**[11c]**)** (Fig. S1(β)(i))



Pyridinium picrate (monoclinic)

(A) Hydrogen atom approaches/distances within the ion-pair of the asymmetric unit (also evident in Fig. S1(β)(i))

O(7)...H(8),N(4)	1.96(3), 2.631(4)	***(R)***	O(7)...H(3),C(7)	2.49(3), 2.964(4)	***(R)***
O(1)...H(8),N(4)	2.28(3), 2.927(4)	***(R)***	O(1)...H(7),C(11)	2.66(3), 3.179(4)	***(R)***
N(4)-H(8)	0.82(3)		O(7)... O(1,6)	**2.675(3)**, 2.724(3)	

(B) Other approaches/overlaps (< 3.6 Å)

Approaches within the *b*-translation-related stacks of anions and cations.

Anion...*anion'* approaches (Fig. S2(β)(i))			Anion...*cation'* approaches		
C(1)...*C(2)*	3.533(5)	***(C ,$\bar{C}$)***	O(1)...*N(4)*	3.271(4)	***(C)***
C(2)...*O(2)*	3.314(3)	***(C ,$\bar{C}$)***	O(7)...*C(7)*	3.416(4)	***(C)***
C(5)...*C(4)*	3.538(3)	***(C ,$\bar{C}$)***	O(1)...*C(11)*	3.473(4)	***(C)***
N(1)...*O(2)*	3.173(3)	***(C ,$\bar{C}$)***			
O(1)...*O(2)*	3.131(3)	***(C ,$\bar{C}$)***	Cation...*cation'* approaches		
N(2)...*O(3)*	3.324(3)	***(C ,$\bar{C}$)***	C(8)...*C(7)*	3.515(4)	
O(4)...*O(3)*	3.187(4)	***(C ,$\bar{C}$)***	C(9)...*C(10)*	3.565(4)	
O(6)...*C(1)*	3.238(3)	***(C ,$\bar{C}$)***	C(9)...*C(11)*	3.551(4)	
C(6)	3.183(3)	***(C ,$\bar{C}$)***	C(10)...*C(11)*	3.513(4)	
N(3)	3.171(3)	***(C ,$\bar{C}$)***			
O(5)	3.240(4)	***(C ,$\bar{C}$)***			
O(7)	3.255(3)	***(C ,$\bar{C}$)***			

Approaches between anion and cation columns

Anion...*anion'* approaches (screw-related)

	($\bar{x}$, *y*–½, ½–*z*)	
O(3)...*H(1),C(3)*	2.76(3), 3.204(4)	***(R , L)***
O(3)...*O(3)*	3.188(3)	***(C , C)***

Anion...*anion'* approaches (glide-related)

	(1–*x*, ½+*y*, ½–*z*)	
O(5)...*H(2),C(5)*	2.70(3), 3.291(4)	***(R , L)***

Anion...*cation'* approaches (glide-related)

	(*x*, ³/₂–*y*, ½+*z*)	
O(4)...*C(9)*	3.491(4)	***(C)***
O(4)...*H(6),C(10)*	2.82(3), 3.243(3)	***(R)***

	(*x*, ½–*y*, ½+*z*)	
O(4)...*H(5),C(9)*	2.39(3), 3.124(4)	***(R)***
C(10)	3.397(4)	***(C)***

Anion...*cation'* approaches (inversion-related)

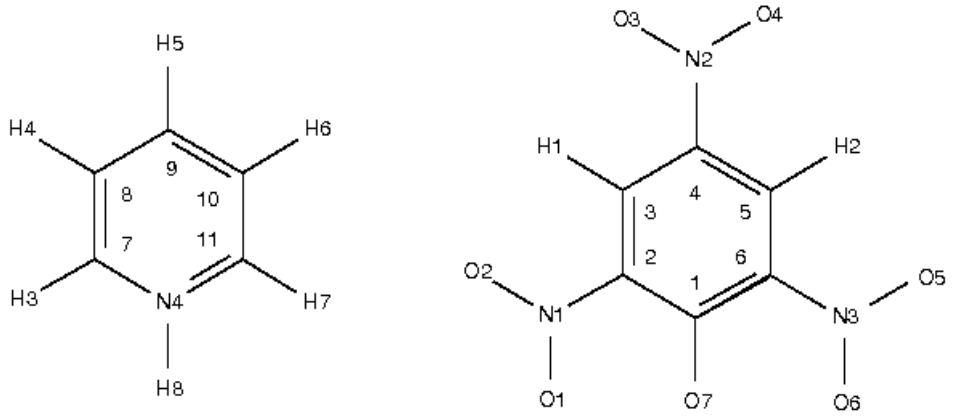
	($\bar{x}$, 1–*y*, $\bar{z}$)	
O(2)...*H(6),C(10)*	2.80(3), 3.362(3)	***(R)***
H(7),C(11)	2.63(3), 3.224(3)	***(R)***

	(1–*x*, 2–*y*, $\bar{z}$)	
O(6)...*H(4),C(8)*	2.92(3), 3.212(4)	***(R)***
C(9)	3.3412(3)	***(C)***

	($\bar{x}$, 2–*y*, $\bar{z}$)	
O(2)...*H(6),C(10)*	2.83(3), 3.347(2)	***(R)***

NO_2/C_6 interplanar dihedral angles: 20.45(12), 12.04(12), 37.00(12)º.

(β)(ii) **(pyH)(pic) (triclinic) ($P\bar{1}$) (PYRPIC03**[11c]**)** (Fig. S1(β)(ii))



Pyridinium picrate (triclinic)

(A) Hydrogen atom approaches/distances within the ion-pair of the asymmetric unit

O(7)...H(8),N(4)	1.82(5), 2.666(5) ***(R)***	O(7)...H(3),C(7)	2.64(4), 3.061(6) ***(R)***
O(1)...H(8),N(4)	2.21(5), 2.875(6) ***(R)***	O(1)...H(7),C(11)	2.55(5), 3.089(6) ***(R)***
N(4)-H(8)	0.95(5)	O(7)...O(1,6)	**2.700(5)**, 2.771(6)

(B) Other approaches/overlaps (< 3.6 Å)

Inversion-related approaches

Anion...*anion'* approaches (Fig. S2(β)(ii))			Anion...*cation'* approaches		
	(1–*x*, $\bar{y}$, 1–*z*)			(1–*x*, $\bar{y}$, $\bar{z}$)	
C(2)...*C(6)*	3.501(7)	***(C ,C)***	C(3)...*C(7)*	3.252(8)	***(C)***
H(1),C(3)...*O(6)*	2.96(5) 3.288(8)	***(L ,R)***	C(4)...*N(4)*	3.496(7)	***(C)***
C(4)...*O(7)*	3.494(6)	***(C ,C)***	*C(7)*	3.442(8)	***(C)***
C(5)...*O(1)*	3.500(7)	***(C ,C)***	C(5)...*C(11)*	3.535(9)	***(C)***
C(1)...*O(7)*	3.301(7)	***(C ,C)***			
C(2)...*O(7)*	3.236(6)	***(C ,C)***		(1–*x*, $\bar{y}$, 1–*z*)	
N(1)...*O(7)*	3.169(6)	***(C ,C)***	N(2)...*N(4)*	3.338(6)	***(C)***
O(7)...*O(7)*	3.354(5)	***(C ,C)***	*C(7)*	3.460(7)	***(C)***
			O(3)...*C(7)*	3.333(8)	***(C)***
			O(4)...*N(4)*	3.214(7)	***(C)***
	(1–*x*, $\bar{y}$ –1, 1–*z*)		*C(11)*	3.277(8)	**(C)**
H(2),C(5)...*O(5)*	2.64(5), 3.491(6)	***(L, R)***			

O(5)...*O(5)* 3.365(6) ***(C ,C)***

(2–*x*, $\bar{y}$, $\bar{z}$)

($\bar{x}$, $\bar{y}$, 1–*z*)

O(3)...*O(3)* 3.195(6) ***(C ,C)***

H(1),C(3) 2.74(5), 3.517(6) ***(R ,L)***

(1–*x*, 1–*y*, $\bar{z}$)

Cation...*cation*' approaches

(2–*x*, $\bar{y}$, $\bar{z}$)

H(3)...*H(4)* 2.54(8)

O(6)...*H(4),C(8)* 2.55(6), 3.195(6) ***(R)***

H(5),C(9) 2.60(5), 3.233(7) ***(R)***

O(2)...*H(6),C(10)* 2.44(5), 3.207(7) ***(R)***

Translation-related approaches

Anion...*anion'* approaches

(*x*, 1+*y*, *z*)

O(1)...*O(5)* 3.203(6) ***(C ,C)***

Anion...*cation'* approaches

(*x*, *y*–1, *z*)

O(5)...*H(7),C(11)* 2.69(5), 3.484(7) ***(R)***

Anion...*cation'* approaches

(*x*–1, *y*, 1+*z*)

O(3)...*H(4),C(8)* 2.64(6), 3.265(7) ***(R)***

C(7) 3.475(7) ***(C)***

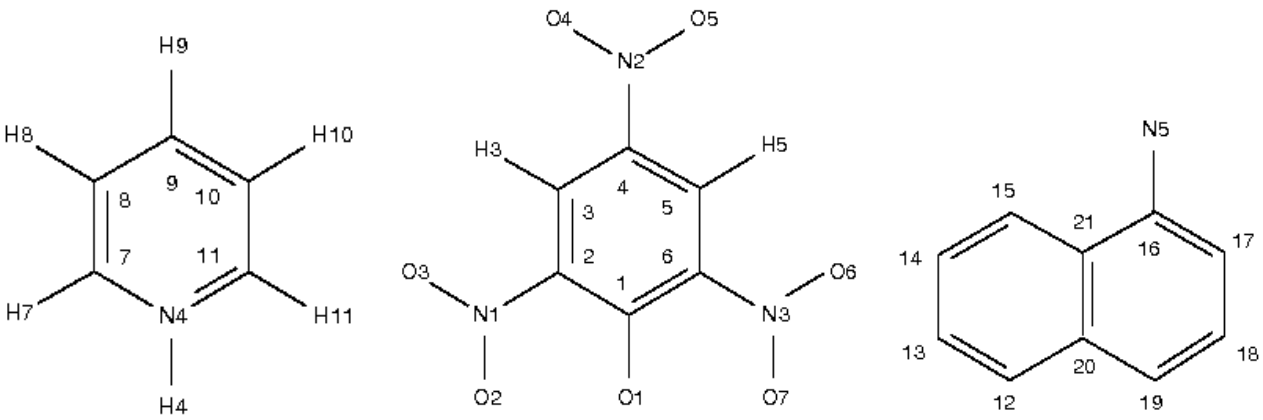
(*x*–1, *y*–1, 1+*z*)

O(4)...*H(5),C(9)* 2.41(5), 3.144(6) ***(R)***

H(6),C(10) 2.84(5), 3.334(7) ***(R)***

NO_2/C_6 interplanar dihedral angles: 20.9(3), 6.1(5), 41.4(3)º.

(β)(iii) **(pyH)(pic) (·naph) (*P*2$_1$/*a*) (PYNPCR[20])** (Fig. S1(β)(iii))



Pyridinium picrate : 1-naphthylamine (major component)

Contacts related only by the ionic components of this structure are tabulated. There are very few associated with the 1-naphthylamine component (the NH_2 residue excepted*), in keeping with its disordered nature. In this and a number of other structures obtained from the literature (and/or CCDC), the basic ion-pair component of the asymmetric unit may be generated by a symmetry transformation. This is noted as a footnote where relevant.*

(A) Hydrogen atom approaches/distances within the fundamental anion...cation pair (cation at (½–*x*, *y*+½, $\bar{z}$)) *

O(1)...H,N(4)	1.8_7, 2.694(7) ***(R)***	N(4)-H(4)	0.8_6
O(7)...H,N(4)	2.2_9, 2.811(7) ***(R)***	O(1)...O(2,7)	2.800(8), **2.684(7)**

(B) Other approaches/overlaps (< 3.6 Å)

Inversion-related approaches

Anion...*anion'* approaches (Fig. S2(β)(iii))

(1–*x*, 2–*y*, $\bar{z}$)

C(1)...*C(4)*	3.437(9)	***(C ,C̄)***
C(2)...*C(5)*	3.483(10)	***(C ,C̄)***
C(3)...*C(6)*	3.483(10)	***(C ,C̄)***
C(4)...*C(6)*	3.572(10)	***(C ,C̄)***
N(2)...*O(1)*	3.318(9)	***(C ,C̄)***
O(1)...O(5)	3.373(9)	***(C ,C̄)***

Screw-related approaches

Anion...*cation'* approaches

(½–*x*, ½+*y*, $\bar{z}$)

O(1)...*C(7)*	3.478(8)	
O(7)...*H,C(11)*	2.7_9, 3.082(9)	***(R)***

(½–*x*, ½+*y*, 1–*z*)

O(2)...*C(8)*	3.446(9)	***(C)***

	(1–*x*, 2–*y*, 1–*z*)		
N(1)...*O(4)*	3.216(9)	***(C, $\bar{C}$)***	
O(2)...*O(4)*	3.389(9)	***(C ,$\bar{C}$)***	
O(3)...*O(4)*	3.207(11)	***(C ,$\bar{C}$)***	

Anion...*cation'* approaches

	(1–*x*, 2–*y*, 1–*z*)		
O(5)...*H,C(10)*	2.7_7, 3.325(10)	***(R)***	

Translation-related approaches

Anion...*cation'* approaches

	(*x*, 1+*y*, *z*)		
O(2)...*H,C(11)*	2.6_8, 3.460(8)	***(R)***	
O(3)...*H,C(10)*	2.6_6, 3.395(10)	***(R)***	
	(*x*, *y*, *z*–1)		
O(7)...*H,C(8)*	2.5_9, 3.444(9)	***(R)***	

Glide-related approaches

Anion...*cation'* approaches

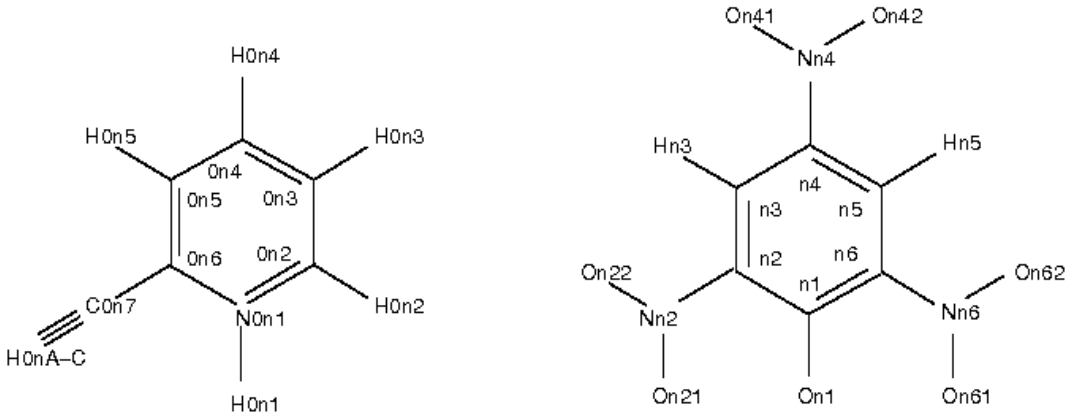
	(½+*x*, $^3/_2$–*y*, *z*)		
O(4)...*H,C(7)*	2.6_1, 3.230(9)	***(R)***	

NO_2/C_6 interplanar dihedral angles: 43.6(5), 1.14(8), 1.26(3)°.

*The CIF for this compound has the asymmetric unit cation related to the anion of the pair by the transformation (½–*x*, *y*+½, $\bar{z}$). The CCDC CIF has discarded the su's given in the original paper; these have been restored for the non-hydrogen atoms for the present calculations. Hydrogen atoms were not included in the available records and have been generated here provisionally for the ionic components. The closest approach to the naphthylamine N(5) as presented is from O(6) (*x*, *y*, 1+*z*) 3.24(2) Å.

The literature numbering scheme has been adapted for present purposes as shown above.

(β)(iv) **[(2mpH)(pic)]** (x2) ($P\bar{1}$) (this work) (Fig. S1(β)(iv))



2-Methylpyridinium picrate (n = 1,2)

(A) Hydrogen atom approaches/distances within the two independent ion-pairs of the asymmetric unit (Fig. 2(a))

O(n1)...H,N(0n1):	n = 1	1.80(3), 2.685(2)	***(R)***	O(n21)...H,N(0n1):	n = 1	2.25(3), 2.770(3)	***(R)***
	n = 2	1.84(3), 2.664(2)	***[R]***		n = 2	2.24(4), 2.756(3)	***[R]***
O(n1)...H(0nx),C(0n7):	n = 1	2.67(3), 3.531(3)	***(R)***	O(n21)...H,C(0n2):	n = 1	2.78(3), 3.102(3)	***(R)***
	n = 2	2.59(3), 3.352(3)	***[R]***		n = 2	(3.23(3)),3.341(3)	***[R]***
O(n1)…O(n21,n61)	n = 1	**2.755(3)**, 2.880(3)		N(0n1,2)-H(0n1,2)		0.92(3), 0.87(3)	
	n = 2	**2.707(3)**, 2.826(3)					

(B) Other approaches/overlaps

Anion...*anion'* approaches

Inversion-related approaches

	(2–*x*, 1–*y*, $\bar{z}$)	
N(12)...*N(12)*	3.343(3)	***(C ,C̄)***
O(121)	3.019(3)	***(C ,C̄)***
O(121)...*O(121)*	3.179(3)	***(C ,C̄)***
O(122)	3.081(3)	***(C ,C̄)***

(1–*x*, 1–*y*, $\bar{z}$) (Fig. S2(β)(iv))

O(141)...*O(161)*	3.178(3)	***(C ,C̄)***
O(161)...*C(13)*	3.332(3)	***(C ,C̄)***
C(14)	3.291(3)	***(C ,C̄)***
N(14)	3.110(3)	***(C ,C̄)***
O(122)...*H,C(15)*	2.40(2), 3.357(3)	***(R ,L̄)***
O(142)	3.145(3)	***(C ,C̄)***

Anion...*cation'* approaches

Inversion-related approaches

	(1–*x*, 1–*y*, $\bar{z}$)	
O(142)...*H,C(012)*	2.47(3), 3.146(3)	***(R)***

	(2–*x*, 1–*y*, $\bar{z}$)	
O(141)...*H,C(013)*	2.77(3), 3.213(3)	***(R)***
O(122)...*H,C(012)*	2.61(2), 3.446(3)	***(R)***

	(2–*x*, $\bar{y}$, $\bar{z}$)	
O(161)...*H,C(014)*	2.58(2), 3.333(3)	***(R)***

	(1–*x*, 1–*y*, 1–*z*)	
O(141)… *H,C(022)*	2.95(3), 3.475(3)	***(R)***
H,C(023)	2.71(3), 3.409(3)	***(R)***

(1–*x*, 1–*y*, 1–*z*)

N(22)... *N(22)*	3.291(3)	[C, $\bar{C}$]
O(221)	3.109(4)	[C, $\bar{C}$]
O(221)...*O(221)*	3.377(4)	[C, $\bar{C}$]
O(222)	3.030(4)	[C, $\bar{C}$]

($\bar{x}$, 1–*y*, 1–*z*) (Fig. S2(β)(iv))

O(241)...*O(261)*	3.153(3)	[C, $\bar{C}$]
N(24)...*O(261)*	3.377(3)	[C, $\bar{C}$]
O(261)...*H,C(23)*	3.00(2), 3.210(3)	[R, $\bar{L}$]
C(24)	3.373(3)	[C, $\bar{C}$]

Translation-related approaches

(1+*x*, *y*, *z*)

O(121)...*N(16)*	3.333(3)	(C, $\bar{C}$)
O(162)	3.054(3)	(C, $\bar{C}$)
O(221)...*N(26)*	3.283(3)	[C, $\bar{C}$]
O(262)	3.078(3)	[C, $\bar{C}$]
O(222)...*H,C(25)*	2.49(2), 3.385(3)	[R, $\bar{L}$]
O(242)	3.177(3)	[C, $\bar{C}$]

Anion...*other anion* approaches

(*x*, *y*, *z*) (Fig. S2(β)(iv)

C(13)...*O(222)*	3.216(4)	**(C)**, [$\bar{C}$]
C(14)...*O(222)*	3.291(3)	**(C)**, [$\bar{C}$]
N(14)...*H,C(23)*	3.00(2), 3.393(3)	**(R)**, [$\bar{L}$]
O(142)...*C(23)*	3.362(3)	**(C)**, [$\bar{C}$]
C(24)	3.451(3)	**(C)**, [$\bar{C}$]
N(24)	3.320(3)	**(C)**, [$\bar{C}$]
O(241)	3.077(3)	**(C)**, [$\bar{C}$]

(1–*x*, 1–*y*, 1–*z*)

O(222)...*H,C(022)*	2.50(2), 3.283(3)	**[R]**
O(241)...*H,C(023)*	2.87(3), 3.196(3)	**[R]**

(*x*–1, 1–*y*, *z*)

O(241)...*H,C(025)*	2.40(3), 3.346(7)	**[R]**

($\bar{x}$,1–*y*,1–*z*)

O(242)...*H,C(022)*	2.44(2), 3.208(3)	**[R]**

(1–*x*, $\bar{y}$, 1–*z*)

O(261)...*H,C(024)*	2.58(2), 3.475(3)	**[R]**

Translation-related approaches

(*x*–1, *y*, *z*)

O(161)...*C(012)*	3.474(3)	**(C)**
C(013)	3.460(4)	**(C)**
C(014)	3.475(3)	**(C)**
C(015)	3.492(3)	**(C)**
O(162)...*C(016)*	3.460(3)	**(C)**
H(01A),C(017)	2.80(4), 3.459(4)	**(R)**
O(261)...*C(022)*	3.474(3)	**[C]**
C(023)	3.479(3)	**[C]**
C(024)	3.440(3)	**[C]**
C(025)	3.397(3)	**[C]**
C(026)	3.400(3)	**[C]**
O(262)...*H(02C),C(027)*	2.83(4), 3.482(4)	**[R]**

(*x*, *y*, *z*)

O(21)...*N(021)*	2.664(2)	**[C]**
H(02A),C(027)	2.59(3), 3.352(3)	**[R]**

Anion...*other anion* approaches (translation-related)

		(*x*, *y*, *z*)	
O(142)...	*C(23)*	3.302(3)	***(C)***, $[\overline{C}]$
	C(24)	3.451(3)	***(C)***, $[\overline{C}]$
	N(24)	3.320(3)	***(C)***, $[\overline{C}]$
	O(241)	3.077(3)	***(C)***, $[\overline{C}]$
		(1+*x*, *y*, *z*)	
O(11)...	*O(262)*	3.211(3)	***(C)***, $[\overline{C}]$
C(11)...	*O(262)*	3.339(3)	***(C)***, $[\overline{C}]$
C(12)...	*O(262)*	3.338(3)	***(C)***, $[\overline{C}]$
	H,C(25)	2.95(2),2.938(3)	$\boldsymbol{(P_L),[\overline{P_R}]}$
O(122)...	*C(24)*	3.160(3)	***(C)***, $[\overline{C}]$
	H,C(25)	2.95(2), 3.446(3)	$\boldsymbol{(R)}$, $[\overline{L}]$
N(12)...	*O(262)*	3.243(3)	***(C)***, $[\overline{C}]$
		(*x*, *y*, *z*)	
N(14)...	*H,C(23)*	3.00(2), 3.393(3)	$\boldsymbol{(R)}$, $[\overline{L}]$

NO_2/C_6 interplanar dihedral angles:

22.44(9), 12.81(9), 54.93(9) º (picrate 1);

12.79(15), 2.3(2), 125.45(10)º (picrate 2).

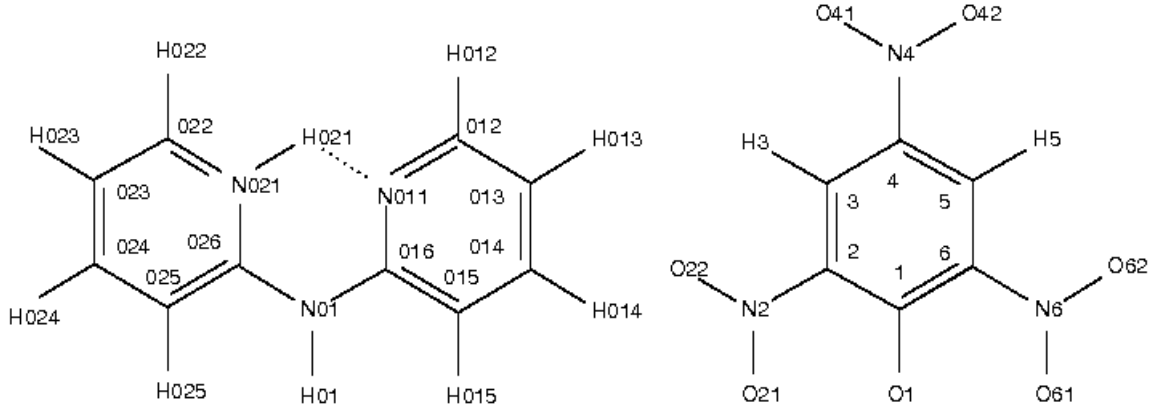
Anion...*other cation* approaches (inversion-related)

		(1–*x*, 1–*y*, 1–*z*)	
O(141)...	*H,C(022)*	2.95(3), 3.475(3)	***(R)***
	H,C(023)	2.71(3), 3.409(3)	***(R)***
		(1–*x*, 1–*y*, $\overline{z}$)	
O(242)...	*H,C(013)*	2.55(3), 3.388(3)	***[R]***
O(262)...	*C(017)*	3.482(4)	***[C]***

Cation...*cation'* approaches (inversion-related)

		(1–*x*, $\overline{y}$, 1–*z*)	
C(023)...	*C(027)*	3.530(4)	
N(021)...	*C(025)*	3.442(3)	

(β)(v) **(dpaH)(pic) (*P*2$_1$/*c*)** (this work) (Fig. S1(β)(v)



(2-Pyridinium)(2-pyridyl)amine picrate

(A) Hydrogen atom approaches/distances within the ion-pair of the asymmetric unit (Fig. 2(b))

O(1)...H,N(01)	2.92(2), 2.755(2) ***(R)***	O(21)...H,C(025)	2.69(2), 3.448(2) ***(R)***
O(21)...H,N(01)	2.44(2), 3.121(2) ***(R)***	O(61)...H,C(015)	2.68(2), 3.161(2) ***(R)***
N(011)...H,N(021)	1.81(2), 2.617(2)	O(1)...H,C(015)	2.83(2), 3.424(2) ***(R)***
N(01)-H(01),N(021)-H(021)	0.91(2), 0.93(3)	O(1)...O(21,61)	**2.684(2)**, 2.652(3)

(B) Other approaches/overlaps (< 3.6 Å)

Anion...*anion'* approaches

Inversion related approaches

(1–*x*, $\bar{y}$, 1–*z*) (Fig. 2(β)(v) (right))

O(1)...*C(4)*	3.460(2)	***(C ,$\bar{C}$)***
C(1)...*C(3)*	3.335(2)	***(C ,$\bar{C}$)***
C(4)	3.533(2)	***(C ,$\bar{C}$)***
C(2)...*C(5)*	3.587(2)	***(C ,$\bar{C}$)***
C(6)	3.470(2)	***(C ,$\bar{C}$)***
C(3)...*C(6)*	3.520(2)	***(C ,$\bar{C}$)***
C(5)...*N(2)*	3.407(2)	***(C ,$\bar{C}$)***
O(22)	3.325(2)	***(C ,$\bar{C}$)***
C(6)...*O(22)*	3.218(2)	***(C ,$\bar{C}$)***
N(6)...*O(22)*	2.988(2)	***(C ,$\bar{C}$)***
O(61)...*O(22)*	3.218(3)	***(C ,$\bar{C}$)***

Anion...*cation'* approaches

Screw-axis related approaches

(*x*, ½–*y*, ½+*z*) (Fig. S2(β)(v) (left))

C(3)...*N(011)*	3.396(2)	***(C)***
C(016)	3.337(2)	***(C)***
N(2)...*N(021)*	3.188(2)	***(C)***
C(022)	3.497(2)	***(C)***
O(21)...*N(021)*	3.343(2)	***(C)***
C(022)	3.325(2)	***(C)***
O(22)...*N(021)*	3.027(2)	***(C)***
C(022)	3.243(2)	***(C)***
C(026)	3.163(2)	***(C)***
O(41)...*C(015)*	3.300(2)	***(C)***

O(62)...*O(22)*	3.248(2)	(**C**, $\bar{C}$)
	(2–*x*, $\bar{y}$, 1–*z*)	
N(6)...*O(62)*	3.045(2)	(**C**, $\bar{C}$)
C(6)...*O(62)*	3.112(2)	(**C**, $\bar{C}$)
O(62)...*O(62)*	3.077(2)	(**C**, $\bar{C}$)
	(1–*x*, $\bar{y}$, 1–*z*)	
O(22)...*O(62)*	3.248(2)	(**C**, $\bar{C}$)

Screw-related approaches

	(*x*, ½–*y*, ½+*z*)	
O(41)...*O(21)*	3.278(2)	(**C**, $\bar{C}$)

Cation...*cation* approaches (inversion-related)

(1–*x*, $\bar{y}$, $\bar{z}$)	
C(016)...*C(023)*	3.446(2)
N(021)...*C(026)*	3.404(2)
C(022)...*N(01)*	3.417(2)
C(022)...*C(026)*	3.411(2)
C(023)...*N(01)*	3.496(2)

NO_2/C_6 interplanar dihedral angles: 26.82(7), 4.26(8), 22.81(14)º.

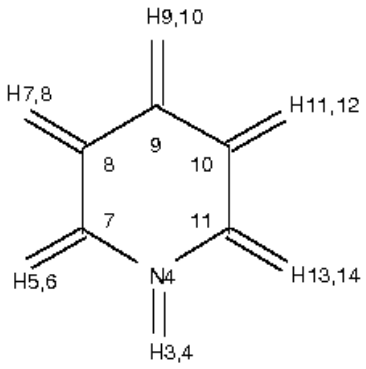
Translation-related approaches

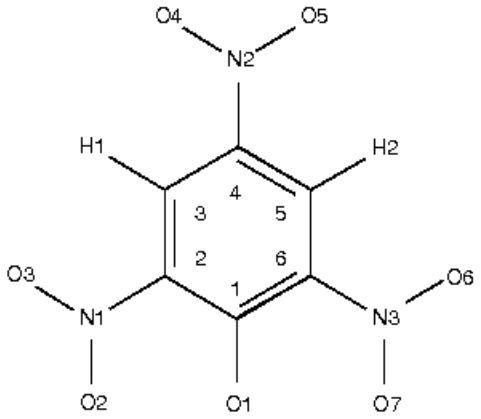
	(*x*–1, *y*, *z*)	
O(22)...*H,C(014)*	2.47(2), 3.355(2)	**(R)**
O(42)...*H,C(025)*	2.66(2), 3.246(2)	**(R)**
	(*x*, *y*, 1+*z*)	
O(41)... *N(011)*	3.264(2)	**(C)**
H,N(021)	2.53(2), 3.073(2)	**(R)**
H,C(022)	2.55(2), 3.196(2)	**(R)**
	(1+*x*, *y*, 1+*z*)	
O(42)...*H,C(023)*	2.76(2), 3.321(6)	**(R)**
H,C(024)	2.57(2), 3.237(2)	**(R)**
O(1)...*H,C(022)*	2.57(2), 3.224(2)	**(R)**

Inversion-related approaches

	(1–*x*, 1–*y*, 1–*z*)	
O(42)...*H,C(024)*	2.89(2), 3.365(2)	**(R)**
	(2–*x*, $\bar{y}$ –1, *z*)	
O(61)...*H,C(013)*	2.53(3), 3.247(3)	**(R)**
O(62)...*H,C(014)*	2.81(3), 3.261(2)	**(R)**
H,C(015)	2.68(2), 3.161(2)	**(R)**
	(1–*x*, $\bar{y}$, $\bar{z}$)	
O(61)...*H,C(022)*	2.42(2), 3.076(2)	**(R)**
H,C(023)	2.86(2), 3.331(3)	**(R)**
O(1)... *H,C(022)*	2.57(2), 3.224(2)	**(R)**
	(1–*x*, $\bar{y}$, 1–*z*)	
O(42)...*H,C(025)*	2.66(2), 3.246(2)	**(R)**

(γ)(i) **(pipH)(pic)** ($P\bar{1}$) **(VAZJAI**[21]**)** (Fig. S1(γ)(i))





Piperidinium picrate

(A) Hydrogen atom approaches/distances within the ion-pair of the asymmetric unit

O(1)...H(3),N(4)	1.82(3), 2.767(2)	***(R)***	N(4)-H(3,4)	0.95(3), 0.86(2)	
O(2)...H(3),N(4)	2.50(2), 2.996(3)	***(R)***	O(1)...O(2,7)	**2.702(2)**, 2.796(3)	
O(2)...H(5),C(7)	2.90, 3.437(3)	***(R)***			

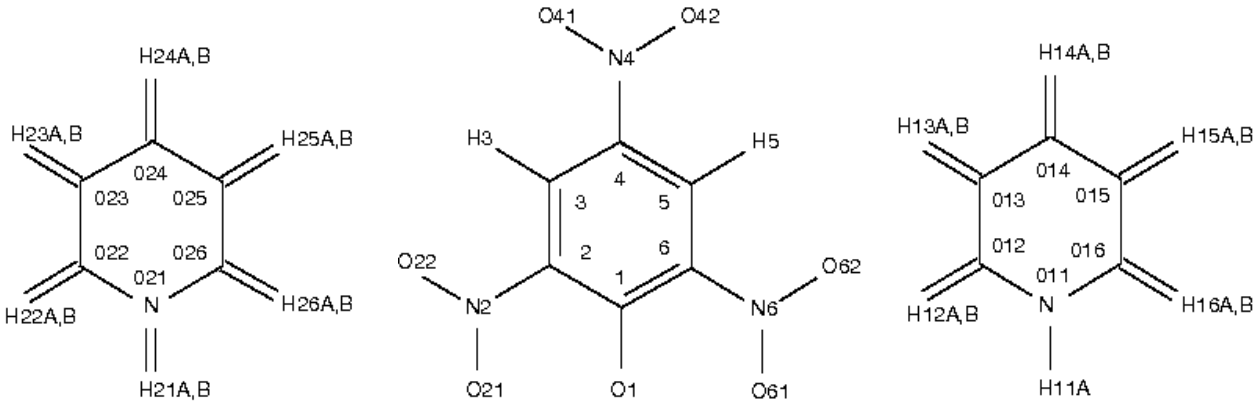
(B) Other approaches/overlaps (< 3.6 Å) (Fig. S2(γ)(i))

Anion...*anion'* approaches (inversion-related)			Anion...*cation'* approaches		
(1–*x*, 2–*y*, $\bar{z}$) (Fig. S2(γ)(i))			Inversion-related approaches		
O(2)...*O(5)*	3.342(3)	***(C ,C)***		($\bar{x}$, 1–*y*, $\bar{z}$)	
N(2)	3.188(3)	***(C ,C)***	O(3)...*H,N(4)*	2.28(2), 2.971(2)	***(R)***
C(4)	3.299(3)	***(C ,C)***	O(3)...*H(5),C(7)*	2.85, 3.060(2)	***(R)***
C(5)	3.437(3)	***(C ,C)***	*H(6)*	2.87	***(R)***
N(1)...*C(4)*	3.424(3)	***(C ,C)***			
C(5)	3.354(3)	***(C ,C)***		(1–*x*, 2–*y*, $\bar{z}$)	
C(1)...*C(3)*	3.517(3)	***(C ,C)***	O(4)...*H(7),C(8)*	2.58, 3.399(3)	***(R)***
C(2)...*C(3)*	3.460(3)	***(C ,C)***			
C(4)	3.493(3)	***(C ,C)***		(1–*x*, 2–*y*, 1–*z*)	
			O(6)...*H(10),C(9)*	2.90, 3.451(4)	***(R)***

	($\bar{x}$, 1–*y*, $\bar{z}$)				
O(2)...*O(2)*	3.247(2)	***(C*** ,$\bar{C}$***)***			
O(3)	3.292(2)	***(C*** ,$\bar{C}$***)***		($\bar{x}$, 2–*y*, 1–*z*)	
			O(7)...*H(11),C(10)*	2.53, 3.290(3)	***(R)***
	($\bar{x}$, 2–*y*, $\bar{z}$)		*C(11)*	3.475(3)	***(R)***
C(2)...*C(4)*	3.489(3)	***(C*** ,$\bar{C}$***)***			
C(1)...*C(3)*	3.590(3)	***(C*** ,$\bar{C}$***)***		($\bar{x}$, 2–*y*, $\bar{z}$)	
C(1)...*C(4)*	3.589(3)	***(C*** ,$\bar{C}$***)***	O(4)...*H(14),C(11)*	2.45, 3.361(4)	***(R)***
C(3)...*C(6)*	3.597(3)	***(C*** ,$\bar{C}$***)***	O(5)...*H(4),N(4)*	2.74(3), 3.288(3)	***(R)***
	(1–*x*, 3–*y*, $\bar{z}$)		Translation-related approaches		
O(5)...H(2),C(5)	2.67, 3.545(3)	***(R***, $\bar{L}$ ***)***		(*x*, 1+*y*, *z*)	
			O(6)...*H(5),C(7)*	2.92, 3.402(4)	***(R)***
			O(7)...*H(6),C(7)*	2.74, 3.452(4)	***(R)***
				(*x*, *y*, *z*–1)	
			O(4)...*H(9),C(9)*	2.87, 3.463(3)	***(R)***
			H(11),C(10)	2.70, 3.300(2)	***(R)***
			O(6)...*H(13),C(11)*	2.63, 3.274(2)	***(R)***

NO_2/C_6 interplanar dihedral angles: 15.96(13), 8.69(11), 50.43(9)°.

(γ)(ii) **(pipH)(pic)(·pip) ($P2_1/n$)** (this work) (Fig. 7)



Piperidinium picrate: piperidine

(A) Hydrogen atom approaches/distances within the asymmetric unit (Fig. 2(c))

O(1)...H(11A),N(011)	2.565(15), 3.0507(13) ***(R)***	O(1) ...H(21A),N(021)	2.245(16), 2.8143(12) ***(R)***
O(61)...H(11A),N(011)	2.585(15), 3.3027(13) ***(R)***	O(21)...H(21A),N(021)	2.602(15), 3.3525(13) ***(R)***
O(61)...H(12B),C(012)	2.99(2), 3.389(2) ***(R)***	O(21)...H(25B),C(025)	2.61(2), 3.395(2) ***(R)***
H(11A)-N(011);N(021)-H(21A,B)	0.87(2); 0.91(1), 0.88(1)	N(011)...H(21B),N(021)	1.81(2), 2.6895(14)
		O(1)...O(21,61)	**2.7540(13)**, **2.7361(12)**

(B) Other approaches/overlaps (< 3.6 Å)

Anion...*anion'* approaches (inversion-related)

($\bar{x}$, $\bar{y}$, $\bar{z}$) (Fig. S2(γ)(ii))			(1–*x*, $\bar{y}$, $\bar{z}$)		
O(1)...*N(4)*	3.2656(14)	***(C ,$\bar{C}$)***	O(1)...*C(4)*	3.4039(14)	***(C ,$\bar{C}$)***
C(1)...*C(4)*	3.2978(14)	***(C ,$\bar{C}$)***	O(1)...*N(4)*	3.3513(13)	***(C ,$\bar{C}$)***
C(5)	3.4298(14)	***(C ,$\bar{C}$)***	C(1)...*C(3)*	3.4039(15)	***(C ,$\bar{C}$)***
C(2)...*C(5)*	3.2642(14)	***(C ,$\bar{C}$)***	*C(4)*	3.2956(14)	***(C ,$\bar{C}$)***
C(6)	3.5788(13)	***(C ,$\bar{C}$)***	C(2)...*C(5)*	3.3428(14)	***(C ,$\bar{C}$)***
C(3)...*C(5)*	3.5712(15)	***(C ,$\bar{C}$)***	*C(6)*	3.3869(15)	***(C ,$\bar{C}$)***
C(6)	3.3394(14)	***(C ,$\bar{C}$)***	H,C(3)...*C(6)*	2.77(1), 3.2694(14)	***(L ,$\bar{C}$)***
N(6)	3.4843(14)	***(C ,$\bar{C}$)***	*O(61)*	2.77(1), 3.2750(14)	***(L ,$\bar{R}$)***
H,C(3)...*O(62)*	2.87(1), 3.2087(15)	***(L ,$\bar{R}$)***	C(5)...*N(2)*	3.4916(15)	***(C ,$\bar{C}$)***
C(4)...*C(6)*	3.4227(15)	***(C ,$\bar{C}$)***	H,C(5)...*O(22)*	3.01(1), 3.3037(15)	***(L ,$\bar{R}$)***
			C(6)...*O(22)*	3.4382(15)	***(C ,$\bar{C}$)***
			O(22)...*N(6)*	3.1875(14)	***(C ,$\bar{C}$)***

Cation...*cation'* approaches (H...H < 2.6 Å)

Glide-related approaches

	(½+*x*, ½–*y*, ½–*z*)	
H(13A)...*H(25B)*	2.46(3)	
H(14A)...*H(23A)*	2.46(2)	
H(25B)	2.57(3)	
	(½+*x*, ½–*y*, ½+*z*)	
H(15A)...*H(24B)*	2.47(3)	

Translation-related approaches

	(1+*x*, *y*, *z*)	
H(16A)...*H(22A)*	2.44(2)	

Anion...*cation'* approaches

Inversion-related approaches

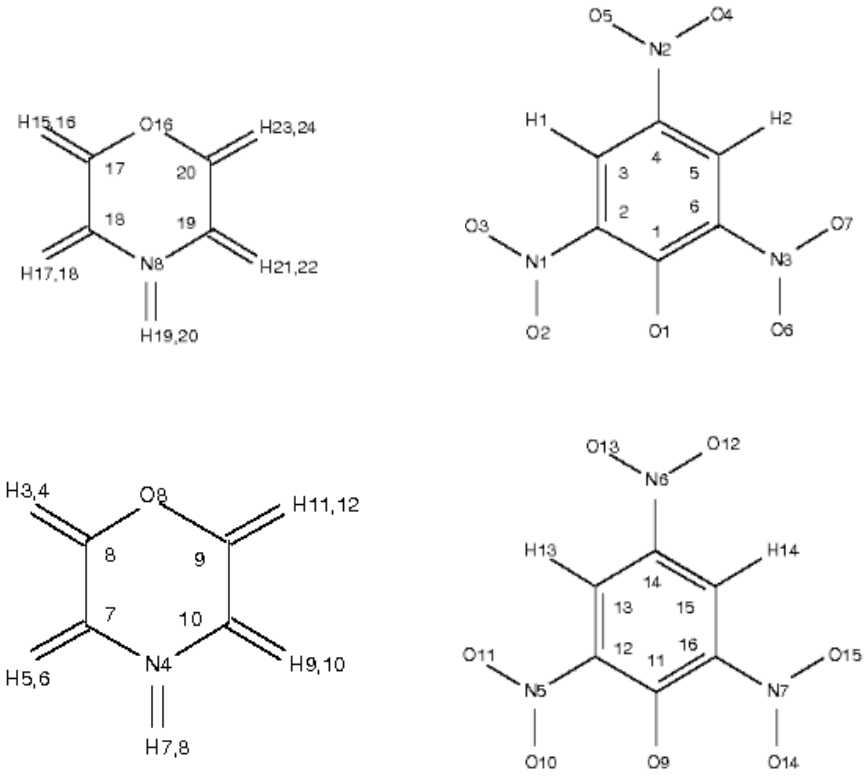
	(1–*x*, $\bar{y}$, $\bar{z}$)	
O(41)...*H(15A),C(015)*	2.78(2), 3.447(2)	***(R)***
H(16A),C(016)	2.70(2), 3.2147(2)	***(R)***
H(11A),N(011)	2.614(14), 3.2637(16)	***(R)***
O(42)...*H(21A),N(021)*	2.544(13), 3.2247(13)	***(R)***
H(22A),C(022)	2.747(15), 3.2409(15)	***(R)***
H(23A),C(023)	2.859(17), 3.4961(16)	***(R)***
	($\bar{x}$, $\bar{y}$, $\bar{z}$)	
O(41)...*H(12B),C(012)*	2.71(2), 3.631(2)	***(R)***
O(42)...*H(26B),C(025)*	2.633(15), 3.504(2)	***(R)***
	($\bar{x}$, $\bar{y}$ –1, $\bar{z}$)	
O(22)...*H(22A),C(022)*	2.90(2), 3.2393(15)	***(R)***
H(22B)	2.74(2)	***(R)***
	(1–*x*, $\bar{y}$ –1, $\bar{z}$)	
O(22)... *C(016)*	3.324(2)	***(C)***

Glide-related approaches

	(*x*–½, ½–*y*, *z*–½)	
O(62)...*H(16B),C(016)*	2.62(2), 3.422(2)	***(R)***
H(22B),C(022)	2.45(1), 3.366(2)	***(R)***

NO_2/C_6 interplanar dihedral angles: 40.32(5), 4.98(6), 35.57(5)º.

(γ)(iii) **[(morH)(pic)]** (x2) ($P\bar{1}$) **(KOMTUC**[22a]**)** (Fig. S1(γ)(iii))



Morpholinium picrate (x2)

(A) Hydrogen atom approaches/distances within the 'fundamental cluster' (two ion-pairs)*

Cation related by (2–*x*, 1–*y*, 1–*z*)

O(9)...H(5),C(8)	2.96(1), 3.280(2)	***[R]***
O(9)...H(8),N(4)	1.89(2), 2.684(14)	***[R]***
O(14)...H(8),N(4)	2.23(2), 2.923(2)	***[R]***
H(9),C(9)	2.69(1), 3.131(2)	***[R]***
N(4)…H(7,8)	0.90(2), 0.93(2)	
O(1)...O(2,6)	**2.7736(13)**, 2.8190(14)	

Cation related by (2–*x*, $\bar{y}$, $\bar{z}$)

O(1)...H(19),N(8)	1.92(2), 2.691(2)	***(R)***
H(17),C(18)	2.95(2), 3.278(2)	***(R)***
O(2)...H(19),N(8)	2.52(2), 2.9248(13)	***(R)***
H(22),C(19)	2.67(2), 3.131(2)	***(R)***
O(9)...O(10,14)	**2.8386(15)**, **2.7607(16)**	
N(8)-H(19,20)	0.89(2), 0.93(1)	

(B) Other approaches/overlaps

Anion...*anion'* approaches

Inversion-related approaches

(2–*x*, 1–*y*, $\bar{z}$) (Fig. S2(γ)(iii)(lower))

C(1)...*C(5)*	3.519(2)	***(C ,$\bar{C}$)***
C(3)...*O(6)*	3.113(2)	***(C ,$\bar{C}$)***
C(4)...*C(6)*	3.534(2)	***(C ,$\bar{C}$)***

Anion... *cation'* approaches

Inversion-related approaches

(2–*x*, 1–*y*, $\bar{z}$)

C(3)...*H(23),C(20)*	2.97(2), 3.395(2)	***(P_R)***

O(6)	3.175(2)	(**C** , $\bar{C}$)
O(1)...*O(4)*	3.2783(13)	(**C** , $\bar{C}$)
N(2)...*O(6)*	3.065(2)	(**C** , $\bar{C}$)
O(5)...*O(6)*	3.0952(14)	(**C** , $\bar{C}$)
	(2–*x*, 2–*y*, $\bar{z}$)	
N(2)...*O(4)*	3.079(2)	(**C** , $\bar{C}$)
O(4)...*O(4)*	2.9767(13)	(**C** , $\bar{C}$)
O(4)...*O(5)*	3.1933(15)	(**C** , $\bar{C}$)
	(2–*x*, 1–*y*, 1–*z*) (Fig. 2(γ)(iii)(upper))	
C(11)...*C(13)*	3.520(2)	[**C** , $\bar{C}$]
C(12)...*C(14)*	3.548(2)	[**C** , $\bar{C}$]
C(14)...*O(10)*	3.241(2)	[**C** , $\bar{C}$]
C(15)...*O(10)*	3.161(2)	[**C** , $\bar{C}$]
O(10)...*N(6)*	3.145(2)	[**C** , $\bar{C}$]
O(10)...*O(12)*	2.9937(13)	[**C** , $\bar{C}$]
O(6)...*H(1),C(3)*	2.98(2), 3.113(2)	(**R**, $\bar{L}$)
	(2–*x*, 2–*y*, $\bar{z}$)	
N(5)...*O(11)*	3.2372(14)	[**C** , $\bar{C}$]
O(10)...*O(11)*	3.2777(13)	[**C** , $\bar{C}$]
O(11)...*O(11)*	3.0611(12)	[**C** , $\bar{C}$]
Translation-related approaches		
	(*x*–1, *y*, *z*)	
N(5)...*O(14)*	3.3909(15)	[**C** , $\bar{C}$]
O(11)...*O(14)*	3.1133(14)	[**C** , $\bar{C}$]
O(15)	3.2441(12)	[**C** , $\bar{C}$]
H,C(13)...*O(15)*	2.49(2), 3.439(2)	[$\bar{L}$, $\bar{R}$]
	(2–*x*, $\bar{y}$, $\bar{z}$)	
O(4)...*H(20),N(8)*	2.53(2), 2.869(2)	**(R)**
H(19)	2.69(2)	**(R)**
H(21),C(19)	2.52(2), 3.121(2)	**(R)**
O(5)...*H(24),C(20)*	2.610(15), 3.432(2)	**(R)**
O(6)...*H(22),C(19)*	2.46(2), 3.368(2)	**(R)**
	(2–*x*, 1–*y*, 1–*z*)	
O(10)...*H(15),C(17)*	2.56(1), 3.3078(14)	**[R]**
	(1–*x*, 1–*y*, 1–*z*)	
O(10)...*H(9),C(9)*	2.50(2), 3.414(2)	**[R]**
	(1–*x*, 1–*y*, $\bar{z}$)	
O(15)...*H,C(18)*	2.71(2), 3.259(2)	**[R]**
Translation-related approaches		
	(*x*, *y*, *z*)	
O(13)...*H(10),C(9)*	2.48(2), 3.149(2)	**[R]**
O(12)...*H(23),C(20)*	2.529(14), 3.3427(14)	**[R]**
O(16)...*H(7),N(4)*	1.94(2), 2.801(2)	**[R]**
	(1+*x*, 1+*y*, *z*)	
H(1)... *H(22),C(19)*	2.37(2), 2.9299(15)	**(M)**
C(11)...*H(5),C(8)*	2.97(2), 3.400(2)	**[P_R]**
O(9)... *H(5),C(8)*	2.99(2), 3.467(2)	**[R]**
	(1+*x*, *y*, *z*)	
H(14)...*H(9),C(9)*	2.33(2), 2.94(2)	**[M]**
O(12)...*H(11),C(10)*	2.62(2), 3.381(2)	**[R]**

	(1+*x*, *y*, *z*)	
O(3)...*H(2),C(5)*	2.49(2), 3.444(2)	***(R*, [L] *)***
O(7)	3.286(2)	***(C*, [C]*)***
O(2)...*N(3)*	3.369(2)	***(C*, [C]*)***
O(7)	3.027(2)	***(C*, [C]*)***

Anion...*other anion'* approaches

Inversion-related approaches

	(2–*x*, 1–*y*, [z])	
C(1)...*N(6)*	3.235(2)	***(C)***, [C]
O(12)	2.972(2)	***(C)***, [C]
O(1)...*N(6)*	3.0012(14)	***(C)***, [C]
C(2)...*O(12)*	3.488(2)	***(C)***, [C]
C(6)...*O(12)*	3.065(2)	***(C)***, [C]
O(1)...*C(14)*	3.3911(15)	***(C)***, [C]
O(12)	3.1833(13)	***(C)***, [C]
O(13)	3.2554(13)	***(C)***, [C]
O(7)...*H(14),C(15)*	2.73(2), 3.464(2)	***(R)***, [L]
O(12)	3.3528(14)	***(C)***, [C]

Cation...*cation'* approaches

Translation-related approaches

	(*x*–1, *y*, *z*)	
O(8)...*H(20),N(8)*	1.94(2), 2.8183(12)	***(R)***
	(1+*x*, *y*, *z*)	
H(15),C(17)...*O(8)*	2.67(2), 3.321(2)	
H(17),C(18)...*O(8)*	2.97(2), 3.204(2)	

Anion...*other cation'* approaches

Inversion-related approaches

	(1–*x*, [y], [z])	
O(6)...*H(3),C(7)*	2.47(2), 3.263(2)	***(R)***
	(1–*x*, 1–*y*, *z*)	
O(7)...*H(10),C(9)*	2.47(2), 3.127(2)	***(R)***
H(11),C(10)	2.75(2) 3.273(2)	***(R)***

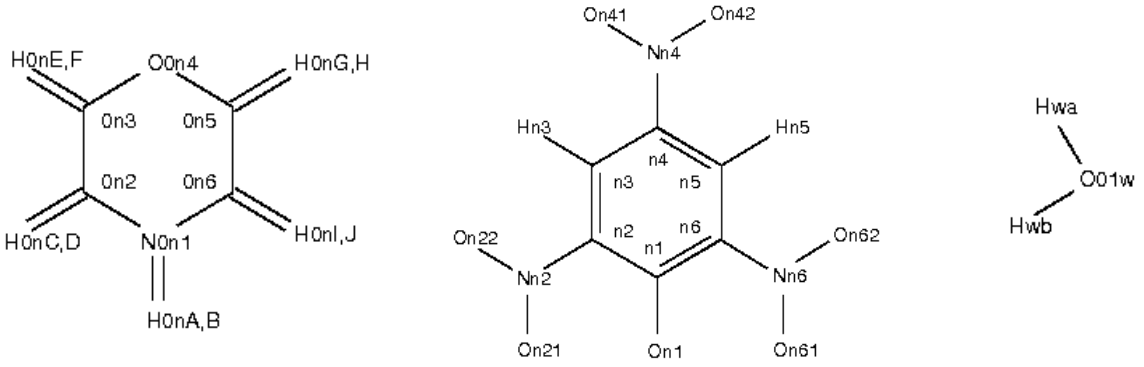
Translation-related approaches

	(*x*, 1+*y*, *z*)	
O(11)...*H(16),C(17)*	2.57(2), 3.153(2)	***[R]***
H(17),C(18)	2.90(2), 3.408(2)	***[R]***
H(13)...*H(18)*	2.49(2)	***[M]***
H(14)...*H,C(9)*	2.32(2), 2.94(2)	***[M]***
	(*x*+1, *y*+1, *z*)	
O(5)...*H(12),C(10)*	2.60(2), 3.392(2)	***(R)***

NO_2C_6 interplanar dihedral angles:

32.00(5), 12.23(6), 51.83(5) (picrate 1); 51.90(5), 4.15(10), 32.78(5)° (picrate 2)

(γ)(iv) 2**[(morH)(pic)] (·H_2O) (*C*2/*c*)** (this work) (Fig. S1(γ)(iv))



Morpholinium picrate (n = 1,2) : hydrate

(A) Hydrogen approaches/distances (Fig. 2(d)) within the fundamental cluster (two ion-pairs plus water)

O(11)...H(01A),N(011)	1.97(2), 2.808(2) ***(R)***	O(11)...H(0wa),O(01w)	2.23(3), 3.018(2) ***(R)***
O(21)...H(01B),N(011)	1.88(3), 2.705(2) ***[R]***	O(121)...H(0wa),O(01w)	2.11(3), 2.936(2) ***(R)***
O(01w)...H(02A),N(021)	2.00(2), 2.810(2)	O(21)...H(0wb),O(01w)	1.84(3), 2.763(2) ***[R]***
O(121)...H(02F),C(023)	2.63(2), 3.554(3) ***(R)***	O(21)...O(221,261)	**2.736(2)**, 2.718(3)
O(11)...O(121,161)	2.702(2), 2.722(2)		

N(011)-H(01A,B) 0.85(2) (x2); N(021)-H(02A,B) 0.84(2), 0.90(3); O(01w)-H(0wa,b) 0.96(3), 0.95(3).

(B) Other approaches/overlaps (< 3.6 Å)

Anion...*anion'* approaches			Anion...*other anion'* approaches		
Screw-related approaches			Glide-related approaches		
	(½–*x*, ½+*y*, ½–*z*)			(*x*–½, ½–*y*, *z*–½) (Fig. S2(γ)(iv))	
N(12)...*O(162)*	3.299(2)	***(C ,$\bar{C}$)***	C(11)...*N(24)*	3.265(2)	***(C)***, ***[$\bar{C}$]***
O(122)...*N(16)*	3.100(2)	***(C ,$\bar{C}$)***	*O(241)*	3.394(2)	***(C)***, ***[$\bar{C}$]***
O(161)	3.269(2)	***(C ,$\bar{C}$)***	*O(242)*	3.338(2)	***(C)***, ***[$\bar{C}$]***
O(162)	3.051(2)	***(C ,$\bar{C}$)***	C(12)...*N(24)*	3.497(2)	***(C)***, ***[$\bar{C}$]***
H,C(13)...*O(161)*	**2.76(2)**, 3.593(2)	***(L ,$\bar{R}$)***	*O(241)*	3.350(2)	***(C)***, ***[$\bar{C}$]***
			C(13)...*C(23)*	3.390(2)	***(C)***, ***[$\bar{C}$]***
Glide-related approaches			C(14)...*C(23)*	3.463(2)	***(C)***, ***[$\bar{C}$]***
	(1–*x*, *y*, ½–*z*)		*C(24)*	3.436(2)	***(C)***, ***[$\bar{C}$]***
C(21)...*N(24)*	3.326(2)	***[C ,$\bar{C}$]***	C(15)...*C(24)*	3.529(2)	***(C)***, ***[$\bar{C}$]***
O(241)	3.405(2)	***[C ,$\bar{C}$]***	*C(25)*	3.461(2)	***(C)***, ***[$\bar{C}$]***
C(23)...*C(23)*	3.426(2)	***[C ,$\bar{C}$]***	C(16)...*N(24)*	3.491(2)	***(C)***, ***[$\bar{C}$]***
C(24)...*C(24)*	3.476(2)	***[C ,$\bar{C}$]***	*O(242)*	3.359(2)	***(C)***, ***[$\bar{C}$]***

C(25)	3.451(2)	[C ,$\bar{C}$]
C(26)	3.554(2)	[C ,$\bar{C}$]
C(25)...*C(25)*	3.185(2)	[C ,$\bar{C}$]
C(26)...*N(24)*	3.405(2)	[C ,$\bar{C}$]
O(242)	3.370(2)	[C ,$\bar{C}$]
O(242)...*N(26)*	3.308(2)	[C ,$\bar{C}$]
O(262)	3.239(2)	[C ,$\bar{C}$]

Inversion-related approaches

(1–*x*, 1–*y*, 1–*z*)

O(261)...*O(261)*	3.201(3)	[C ,$\bar{C}$]

Anion...*cation'* approaches

Translation-related approaches

(*x*, *y*, *z*)

O(11)...*C(016)*	3.458(2)	**(C)**

Glide-related approaches

(*x*–½, ½–*y*, *z*–½)

O(142)...*H(01C),C(012)*	2.61(2), 3.426(2)	**(R)**

(½+*x*, ½–*y*, ½+*z*)

O(241)...*H(02G),C(025)*	2.31(2), 3.080(2)	**[R]**

Inversion-related approaches

(½–*x*, ½–*y*, 1–*z*)

O(222)...*H(02H),C(025)*	2.63(2), 3.549(2)	**[R]**

($^5/_2$–*x*,½–*y*, $\bar{z}$)

O(221)...*H(02J),C(026)*	2.90(3), 3.300(2)	**[R]**

($^3/_2$–*x*, ½–*y*, 1–*z*)

O(242)...*H(02D),C(022)*	2.33(3), 2.983(2)	**[R]**
N(14)...*C(21)*	3.449(2)	**(C)**, [C ,$\bar{C}$]
C(22)	3.400(2)	**(C)**, [C ,$\bar{C}$]
O(141)...*O(221)*	3.261(3)	**(C)**, [C ,$\bar{C}$]
O(142)...*C(21)*	3.122(2)	**(C)**, [C ,$\bar{C}$]
C(26)	3.245(2)	**(C)**, [C ,$\bar{C}$]
O(161)...*O(242)*	3.303(2)	**(C)**, [C ,$\bar{C}$]

Inversion-related approaches

(1–*x*, 1–*y*, 1–*z*)

O(122)...*H,C(25)*	2.69(2),3.478(2)	**(R)** ,[$\bar{L}$]
O(262)	3.357(2)	**(C)**, [C ,$\bar{C}$]

(1–*x*, $\bar{y}$,1–*z*)

N(16)...*O(222)*	3.395(2)	**(C)**, [C ,$\bar{C}$]
O(161)...*O(222)*	3.270(2)	**(C)**, [C ,$\bar{C}$]
O(162)...*O(222)*	3.241(2)	**(C)**, [C ,$\bar{C}$]
H,C(23)	2.53(2), 3.393(2)	**(R)** ,[$\bar{L}$]

Anion...*other cation'* approaches

Screw-related approaches

(½–*x*, *y*–½, ½–*z*)

H,C(15)...	*O(024)*	2.54(3), 3.299(2)	**(L)**
O(141)...*H(02C),C(022)*		2.36(3), 3.206(3)	**(R)**
	C(023)	3.403(3)	**(C)**
	O(024)	3.239(2)	**(C)**
O(142)...*H(02E),C(023)*		2.27(3), 3.089(2)	**(R)**
	O(024)	3.163(2)	**(C)**
O(162)...*H(02H),C(025)*		2.98(3), 3.334(2)	**(R)**

Inversion-related approaches

(½–*x*, ½–*y*, 1–*z*)

O(11)...*H(02B),N(021)*	2.32(2), 3.145(2)	**(R)**
O(161)...*H(02B),N(021)*	2.34(2), 2.964(2)	**(R)**
H(02C),C(022)	2.51(3), 3.082(3)	**(R)**

Screw-related approaches

The oxygen atom of morpholinium 1

approaches the centre of the aromatic ring of anion 1, thus:

O(014)...*C(11-16)* (1–*x*, *y*, ½–*z*)

3.418(2), 3.243(2), 3.162(2), 3.190(2), 3.253(2), 3.319(2) (all ***(C)***)

(1–*x*, *y*, $^{3}/_{2}$–*z*)

O(242)...*H(02A),N(021)* 2.85(2), 2.913(2) ***[R]***

H(02B) 2.51(2) ***[R]***

Cation...*cation'* approaches (screw-related)

(1–*x*, *y*, ½–*z*)

C(013)...*H(01E),C(013)* 2.94(2), 3.496(2)

NO_2C_6 interplanar dihedral angles:

21.57(8), 16.60(8), 35.67(6) (picrate 1);

37.21(8), 3.74(7), 32.69(9)º (picrate 2)

(1–*x*, $\bar{y}$, 1–*z*)

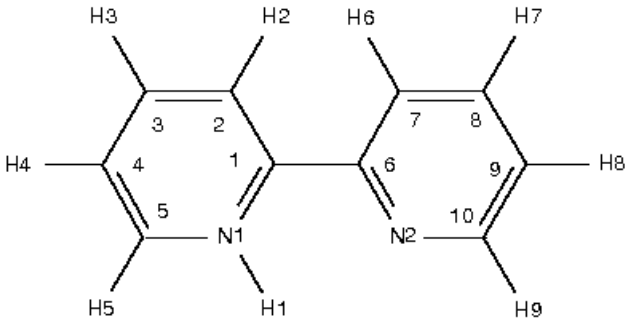
O(222)...*H(01G),C(015)* 2.81(2), 3.124(2) ***[R]***

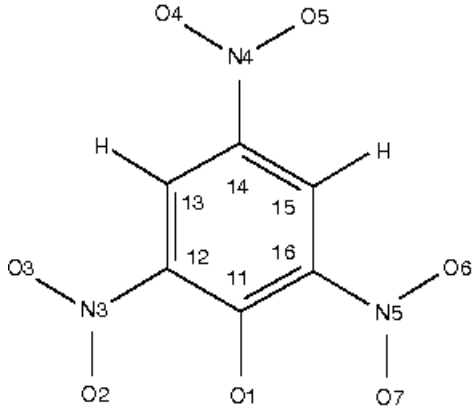
H(01I),C(016) 2.79(2), 3.354(2) ***[R]***

O(262)...*H(01D),C(012)* 2.80(2), 3.321(2) ***[R]***

H(01F),C(013) 2.63(2), 3.190(2) ***[R]***

(δ)(i) **(bpyH)(pic)** ($P\bar{1}$) **(UCOFUO[23])** (Fig. S1(δ)(i))





2,2'-Bipyridinium picrate

(A) Hydrogen atom approaches/distances within the ion-pair of the asymmetric unit

N(2)...H,N(1)	2.21, 2.613(3)		O(4)...H,C(5)	2.36, 3.284(3)	***(R)***
O(5)...H,N(1)	2.55, 3.204(2)	***(R)***	O(1)...O(2,7)	2.805(3), 2.691(3)	
N(1)-H(1)	0.88				

(B) Other approaches/overlaps (< 3.6 Å)

Anion...*anion'* approaches

Inversion-related approaches

(2–*x*, 1–*y*, 1–*z*) (Fig. S2(δ)(i) (left))

O(1)…*O(5)*	3.207(2)	***(C ,$\bar{C}$)***
C(11)...*O(5)*	3.204(2)	***(C ,$\bar{C}$)***
C(12)...*O(5)*	3.475(2)	***(C ,$\bar{C}$)***
H(10),C(13)...*C(15)*	3.52, 3.276(3)	***(P_L ,$\bar{P}_R$)***
O(6)	2.98, 3.485(3)	***(L ,$\bar{R}$)***
C(14)...*C(14)*	3.502(3)	***(C ,$\bar{C}$)***
C(15)	3.304(3)	***(C ,$\bar{C}$)***
C(16)	3.369(3)	***(C ,$\bar{C}$)***
N(4)...*C(11)*	3.221(2)	***(C ,$\bar{C}$)***
C(16)	3.235(3)	***(C ,$\bar{C}$)***
O(4)...*C(16)*	3.287(2)	***(C ,$\bar{C}$)***
N(5)	3.081(2)	***(C ,$\bar{C}$)***

Anion...*cation'* approaches

Transition-related approaches

(1+*x*, 1+*y*, *z*–1)

O(1)...*H,C(2)*	2.37, 3.279(2)	***(R)***
H(6),C(7)	2.42, 3.325(2)	***(R)***
O(2)...*H,C(2)*	2.63, 3.147(2)	***(R)***
H,C(3)	2.38, 3.028(2)	***(R)***
O(7)...*H(6),C(7)*	2.65, 3.282(2)	***(R)***
H(7),C(8)	2.72, 3.323(2)	***(R)***

(1+*x*, *y*, *z*–1)

O(7)...*H,C(4)*	2.68, 3.319(2)	***(R)***
O(6)...*H,C(3)*	2.75, 3.403(2)	***(R)***

	O(6)	3.281(2)	***(C ,$\bar{C}$)***
O(5)...	*C(11)*	3.204(2)	***(C ,$\bar{C}$)***
		(2–*x*, 2–*y*, 1–*z*)	
N(3)...	*N(3)*	3.377(3)	***(C ,$\bar{C}$)***
	O(3)	3.124(2)	***(C ,$\bar{C}$)***
O(2)...	*O(3)*	3.214(2)	***(C ,$\bar{C}$)***
	H(10),C(13)	2.61, 3.488(3)	***($\bar{L}$,R)***
O(3)...	*O(3)*	3.339(2)	***(C ,$\bar{C}$)***
	H(10),C(13)	3.01, 3.461(3)	***($\bar{L}$,R)***
		(1–*x*, 1–*y*, 1–*z*)	
O(5)...	*O(5)*	3.366(2)	***(C ,$\bar{C}$)***
O(5)…*H(11),C(15)*		2.48,3.204(3)	***(R ,$\bar{L}$)***

Cation...*cation'* approaches

Inversion-related approaches

	(1–*x*, $\bar{y}$, 2–*z*)	
C(1)...*C(1)*	3.457(3)	
C(2)	3.499(3)	
C(2)...*C(6)*	3.390(3)	
	($\bar{x}$, $\bar{y}$, 2–*z*)	
C(2)...*H(7),C(8)*	3.19, 3.468(3)	
C(3)... *C(6)*	3.594(3)	

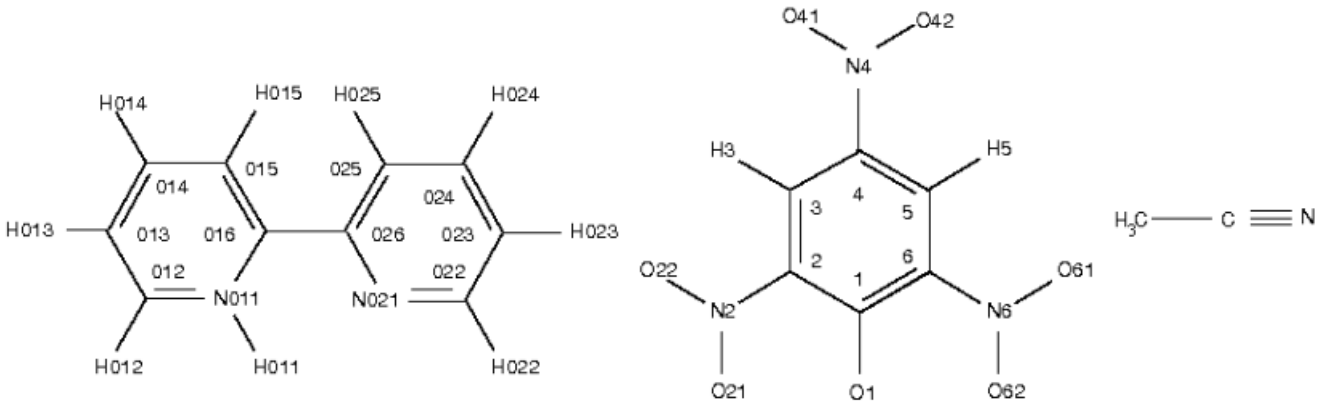
NO_2C_6 interplanar dihedral angles: 46.34(8), 5.8(2), 20.38(9)°;
the dihedral angle between the pair of pyridyl planes is 8.44(8)°.

	(1+*x*, 1+*y*, *z*)	
O(3)...*H(8),C(9)*	2.64, 3.303(7)	***(R)***
	(*x*, 1+*y*, *z*)	
O(4)...*H(8),C(9)*	2.89, 3.123(3)	***(R)***

Inversion-related approaches

	(1–*x*, 1–*y*, 1–*z*) (Fig. S2(δ)(i) (right))	
O(2)...*C(9)*	3.459(3)	***(C)***
C(16)...*N(2)*	3.416(2)	***(C)***
N(5)...*N(1)*	3.165(2)	***(C)***
C(1)	3.496(2)	***(C)***
C(5)	3.399(3)	***(C)***
O(6)...*C(5)*	3.275(3)	***(C)***
O(7)...*N(1)*	3.171(2)	***(C)***
C(1)	3.096(2)	***(C)***
C(2)	3.293(2)	***(C)***
C(3)	3.490(2)	***(C)***
C(5)	3.392(3)	***(C)***
	(1–*x*, 1–*y*, 2–*z*)	
O(4)...*H,C(3)*	2.79, 3.401(3)	***(R)***
H,C(4)	2.94, 3.461(3)	***(R)***
	(1–*x*, $\bar{y}$, 1–*z*)	
O(6)...*H(7),C(8)*	2.79, 3.368(4)	***(R)***
H(8),C(9)	2.64, 3.292(4)	***(R)***
	(2–*x*, 1–*y*, 1–*z*)	
O(1)...*H,N(1)*	2.52, 2.922(3)	***(R)***
O(1)... *C(5)*	3.271(3)	***(C)***
O(2)... *N(2)*	3.280(2)	***(C)***
C(10)	3.432(2)	***(C)***

(δ)(ii) **(bpyH)(pic)(·MeCN)** ($P\bar{1}$) (this work) (Fig. S1(δ)(ii))



2,2'-Bipyridinium picrate : acetonitrile

(A) Hydrogen atom approaches within the ion-pair of the asymmetric unit (Fig. 2(e))

O(1)...H,N(011)	2.18(4), 2.781(3)	***(R)***	O(1)...H,C(012)	2.50(3), 2.980(3)	***(R)***
N(021)...H,N(011)	2.22(4), 2.638(3)		O(21)...H,C(012)	2.67(3), 3.452(3)	***(R)***
N(011)-H(011)	0.85(3)		O(62)...H,C(022)	2.67(3), 3.271(4)	***(R)***
O(1)...O(21,62)	2.733(3), 2.861(3)				

(B) Other approaches/overlaps (< 3.6 Å)

a-Translation-related approaches (1+*x*, *y*, *z*)

Anion...*anion'* approaches			Cation...*cation'* approaches	
C(1)...*O(1)*	3.330(3)	(**C** ,$\bar{C}$)	C(012)...*C(013)*	3.366(4)
C(3)...*C(2)*	3.427(4)	(**C** ,$\bar{C}$)	C(015)...*C(014)*	3.571(4)
C(3)...*O(22)*	3.380(4)	(**C** ,$\bar{C}$)	C(016)...*C(014)*	3.526(4)
C(4)...*C(2)*	3.522(4)	(**C** ,$\bar{C}$)	C(016)...*C(015)*	3.394(4)
C(3)	3.534(4)	(**C** ,$\bar{C}$)	N(021)...*C(026)*	3.335(3)
C(5)...*C(1)*	3.549(4)	(**C** ,$\bar{C}$)	C(022)...*C(025)*	3.527(4)
C(6)	3.417(4)	(**C** ,$\bar{C}$)	*C(026)*	3.428(4)
C(6)...*O(1)*	3.413(3)	(**C** ,$\bar{C}$)	C(023)...*C(024)*	3.356(4)
C(1)	3.509(4)	(**C** ,$\bar{C}$)	*C(025)*	3.478(4)
N(4)...*C(4)*	3.366(4)	(**C** ,$\bar{C}$)	C(024)...*C(025)*	3.560(4)
C(3)	3.472(4)	(**C** ,$\bar{C}$)	N(021)...*C(016)*	3.411(3)
O(42)...*C(4)*	3.320(4)	(**C** ,$\bar{C}$)	C(026)...*C(015)*	3.579(4)

C(5)	3.488(4)	***(C ,C)***	*C(016)*	3.551(3)	
N(6)...*O(61)*	3.364(4)	***(C ,C)***			
O(62)...*O(61)*	3.353(3)	***(C ,C)***	Anion...*cation'* approaches		
			O(1)...*N(011)*	3.344(3)	***(C)***
			C(012)	3.107(3)	***(C)***
			O(21)...*C(012)*	3.304(4)	***(C)***
			O(62)...*N(021)*	3.165(3)	***(C)***

Other translation-related approaches (anion...*cation*')

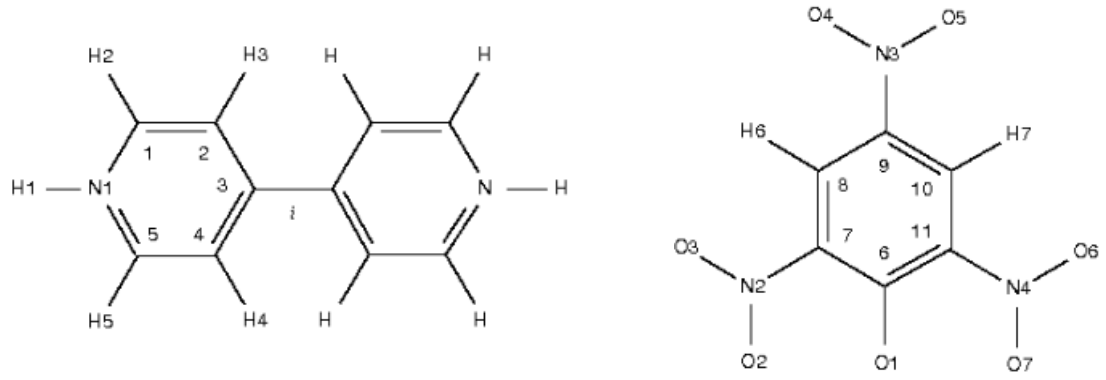
	(2+*x*, 1+*y* , *z*)			(1+*x*, 1+*y*, *z*)	
O(41)...*H,C(015)*	2.45(4), 3.318(4)	***(R)***	O(42)...*H,C(025)*	2.99(3), 3.331(3)	***(R)***
O(42)...*H,C(025)*	2.59(3), 3.467(3)	***(R)***			

Inversion-related approaches (anion...*cation*')

	(, 1–*y*,)			(1–*x*, 1–*y*, 1–*z*)	
O(22)...*H,C(013)*	2.89(3), 3.428(3)	***(R)***	O(61)...*H,C(023)*	2.91(3), 3.463(4)	***(R)***
H,C(014)	2.64(3), 3.295(3)	***(R)***	*H,C(024)*	2.82(4), 3.356(4)	***(R)***
	(1–*x*, 1–*y*,)				
O(21)...*H,C(013)*	2.86(3), 3.441(4)	***(R)***			

NO_2/C_6 interplanar dihedral angles: 25.89(11), 6.0(2), 50.60(12)º;
the dihedral angle between the pair of pyridyl planes is 5.84(9)º.

(δ)(iii) **[bpy'H$_2$)(pic)$_2$]** (x0.5) ($P\bar{1}$) **(KAMPIY[24])** (Fig. S1(δ)(iii))



4,4-BipyridylH$_2^{2+}$ bis(picrate)

(A) Hydrogen atom approaches/distances within the asymmetric unit

O(1)...H,N(1)	1.86, 2.647(2) ***(R)***	O(1)...H,C(5)	2.88, 3.162(2) ***(R)***
O(7)...H,N(1)	2.49, 3.097(3) ***(R)***	O(2)...H,C(5)	2.53, 3.414(2) ***(R)***
N(1)-H(1)	0.86	O(7)...H(2),C(1)	2.989(2), 3.372(3) ***(R)***
O(1)...O(2,7)	2.726(2), **2.687(2)**		

(B) Other approaches/overlaps (< 3.6 Å)

Anion...*anion'* approaches

Inversion-related approaches

($2-x, \bar{y}, \bar{z}$) (Fig. S2(δ)(iii) (lower))

O(2)...	*O(4)*	2.976(2)	***(M, $\bar{M}$)***
	N(3)	3.012(3)	***(M, $\bar{M}$)***
	H(6),C(8)	2.96, 3.129(3)	***(R, $\bar{L}$)***
	C(9)	3.165(3)	***(C, $\bar{C}$)***
N(2)...	*C(8)*	3.380(3)	***(C, $\bar{C}$)***

($2-x, 2-y, \bar{z}$)

O(4)...	*O(6)*	3.155(3)	***(C, $\bar{C}$)***
O(5)...	*C(9)*	3.468(3)	***(C, $\bar{C}$)***
	H(7),C(10)	3.01, 3.140(3)	***(R, $\bar{L}$)***

Anion...*cation'* approaches

Inversion-related approaches

($1-x, 1-y, \bar{z}$)

O(1)...	*H(2),C(1)*	2.53, 3.363(3)	***(R)***
N(4)...	*H,N(1)*	2.90, 3.243(3)	***(R)***
	C(1)	3.308(3)	***(C)***
N(1)...	*O(7)*	3.243(3)	***(C)***

($1-x, 1-y, 1-z$)

O(5)...	*H,C(4)*	3.08, 3.486(3)	***(R)***
O(4)...	*H,C(5)*	2.40, 3.059(3)	***(R)***
	H,C(4)	2.68, 3.196(3)	***(R)***

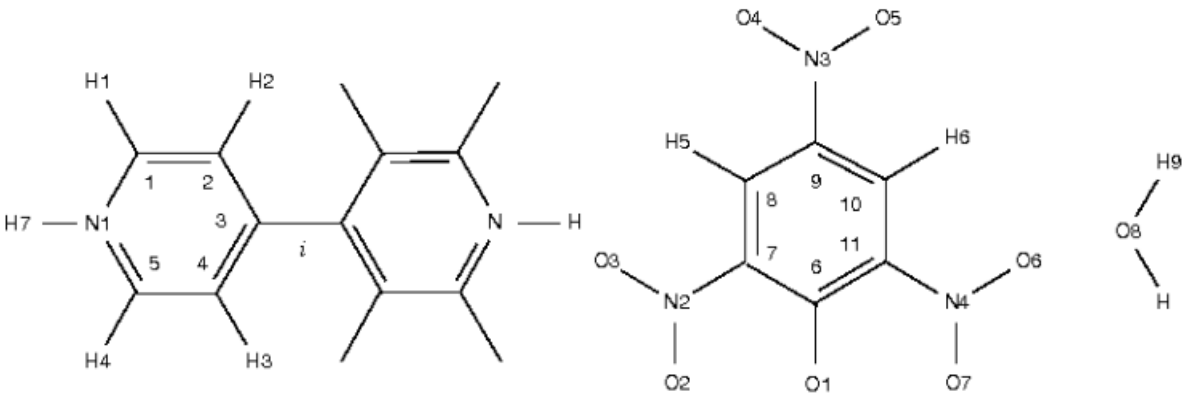
				($\bar{x}$, 1–*y*, *z*)	
	(1–*x*, 2–*y*, 1–*z*)		O(6)...*H(3),C(2)*	2.38, 3.271(3)	***(R)***
O(5)...*O(6)*	3.018(3)	***(M , M)***			

Translation-related approaches

	(1–*x*, 1–*y*, $\bar{z}$)			(1+*x*, *y*, *z*)	
O(1)...*O(7)*	3.326(2)	***(C , C)***	O(1)...*H(2),C(1)*	3.08, 3.364(3)	***(R)***
			O(2)... *N(1)*	3.100(2)	***(C)***
Translation-related approaches			*C(1)*	3.255(3)	***(C)***
(*x*–1, *y*, *z*) (Fig. S3(δ)(iii) (upper))			*C(2)*	3.474(3)	***(C)***
O(1)...*O(3)*	3.381(2)	***(C , C)***	*C(4)*	3.320(2)	***(C)***
O(7)...*O(1)*	3.334(2)	***(C , C)***	*C(5)*	3.119(2)	***(C)***
O(3)	3.318(3)	***(C , C)***	O(3)... *N(1)*	3.259(3)	***(C)***
N(2)	3.292(3)	***(C , C)***	*C(5)*	3.267(2)	***(C)***
C(6)	3.340(2)	***(C , C)***	N(2)... *N(1)*	3.278(2)	***(C)***
C(7)	3.230(3)	***(C , C)***	*C(5)*	3.473(3)	***(C)***
N(4)...*C(7)*	3.403(3)	***(C , C)***			
C(6)...O*(3)*	3.039(3)	***(C , C)***	Cation...*cation'* approaches (inversion-related)		
C(11)...*O(3)*	3.097(3)	***(C , C)***		(1–*x*, $\bar{y}$, $\bar{z}$)	
			C(4)... *C(4)*	3.450(3)	

NO_2C_6 interplanar dihedral angles: 36.58(8), 10.43(8), 19.92(9)º

(δ)(iv) **(bpy'H_2)(pic)$_2$(·H_2O) (*C*2/*c*) (UJOQUF[25])** (Fig. S1(δ)(iv))



4,4-BipyridylH$_2^{2+}$ bis(picrate) : hydrate

(A) Hydrogen atom approaches/distances within the asymmetric unit

O(1)...H(7),N(1)	1.90(4), 2.708(3)	***(R)***	O(1)...H(9),O(8)	2.8(3), 3.034(3)	***(R)***
O(7)...H(7),N(1)	2.28(3), 2.769(3)	***(R)***	O(2)...H(9),O(8)	2.2(3), 2.802(2)	***(R)***
N(1)…H(7)	0.85(4)		O(1)...O(2,7)	**2.646(3)**, **2.688(3)**	

(B) Other approaches/overlaps (<3.6 Å)

Anion...*anion'* approaches

Translation-related approaches

	(*x*, *y*–1, *z*)	
O(1)...*O(6)*	3.128(3)	***(C ,$\bar{C}$)***
O(2)...*N(4)*	3.253(4)	***(C ,$\bar{C}$)***
C(6)	3.309(3)	***(C ,$\bar{C}$)***
C(11)	3.080(4)	***(C ,$\bar{C}$)***
C(6)...*O(6)*	3.011(4)	***(C ,$\bar{C}$)***
C(7)...*O(6)*	3.303(4)	***(C ,$\bar{C}$)***
N(2)...*C(10)*	3.405(4)	***(C ,$\bar{C}$)***
C(11)	3.403(4)	***(C ,$\bar{C}$)***

Screw-related approaches

	($^5/_2$–*x*, *y*–½, $^3/_2$–*z*)	
O(4)...*O(5)*	3.084(4)	***(C ,$\bar{C}$)***
N(3)	3.121(4)	***(C ,$\bar{C}$)***
O(3)...*O(4)*	3.189(2)	***(C ,$\bar{C}$)***

Anion...*cation'* approaches

Translation-related approaches

	(*x*, 1+*y*, *z*)	
O(7)...*H(1),C(1)*	2.54, 3.408(3)	***(R)***

Screw-related approaches

	(2–*x*, *y*, ½–*z*) (Fig. S2(δ)(iv) (upper))	
O(1)...*H(4),C(5)*	2.93, 3.179(4)	***(R)***
O(3)... *C(3)*	3.238(3)	***(C)***
N(2)... *C(3)*	3.365(4)	***(C)***
H(3),C(4)	2.93, 3.341(3)	***(R)***
C(4)... *C(7)*	3.530(4)	***(C)***

	(2–*x*, *y*–1, ½–*z*) (Fig. S2(δ)(iv) (upper))	
O(2)...*H(3),C(4)*	2.50, 3.192(4)	***(R)***
H(4),C(5)	2.67, 3.259(3)	***(R)***

		($^5/_2$–*x*, ½+*y*, $^3/_2$–*z*)	
O(4)...*H(5),C(8)*	2.54, 3.485(4)	***(R* , $\bar{L}$ *)***	
O(4)	3.361(4)	***(C* , $\bar{C}$ *)***	

		($^5/_2$–*x*, $^3/_2$–*y*, 1–*z*)	
O(6)... *O(6)*	3.002(2)	***(C* , $\bar{C}$ *)***	
H(6),C(10)	2.64(3), 3.553(4)	***(R* , $\bar{L}$ *)***	

		($^5/_2$–*x*, *y*–½, $^3/_2$–*z*)	
O(5)... *N(1)*	3.353(4)	***(C)***	
H(1),C(1)	2.65, 2.951(3)	***(R)***	

		(*x* , $\bar{y}$, ½+*z*)	
O(3)...*H,C(2)*	2.55(4), 3.483(4)	***(R)***	
C(3)	3.156(4)	***(C)***	

		(*x*, *y*–1, *z*)	
O(8)…*H(4),C(5)*	2.36, 3.306(4)		

		(*x*, *y*, *z*)	
H(9),O(8)… *N(1)*	2.97, 3.240(3)		

Inversion-related approaches

Glide-related approaches

Cation...solvent approaches

Translation-related approaches

($^5/_2$–*x*, ½–*y*, 1–*z*) (Fig. S2(δ)(iv) (over))

O(5)...*O(7)* 3.118(4) ***(C* , $\bar{C}$ *)***

O(7)...*N(3)* 3.092(4) ***(C* , $\bar{C}$ *)***

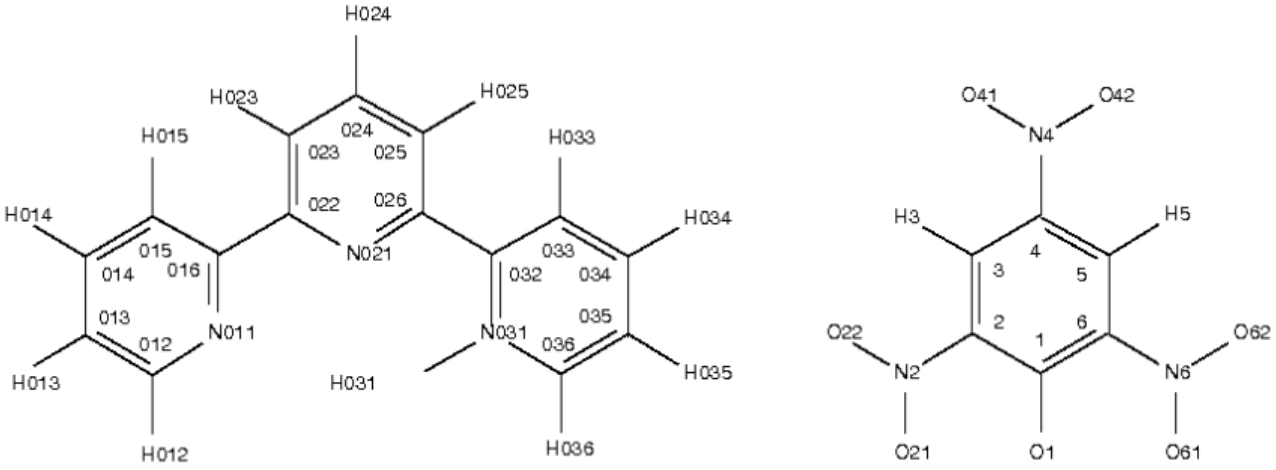
C(9) 3.385(4) ***(C* , $\bar{C}$ *)***

C(10) 3.455(3) ***(C* , $\bar{C}$ *)***

N(4)...*C(10)* 3.347(4) ***(C* , $\bar{C}$ *)***

NO_2/C_6 interplanar dihedral angles: 17.61(11), 14.15(12), 20.58(13)°.

(δ)(v) **(tpyH)(pic)** ($P\bar{1}$) (this work) (Fig. S1(δ)(v))



2,2':6',2"-Terpyridinium picrate

(A) Hydrogen atom approaches/distances within the asymmetric unit (Fig. 2(f))

O(41)...H,N(031)	2.34(2), 3.1083(13) ***(R)***	O(42)...H,C(036)	2.29(2), 3.1666(14) ***(R)***
N(031)-H(031)	0.89(2)	O(41)...H,C(015)	2.52(2), 3.3374(11) ***(R)***
O(1)...O(21,61)	2.6348(11), 2.7014(12)	O(22)...H,C(014)	2.38(2), 3.2974(14) ***(R)***
N(021)...H,N(031)	2.25(2), 2.6535(11)	H(3)...H,C(014)	2.36(2), 3.087(13) ***(L)***
H(025)…H(033)	2.24(2)		

(B) Other approaches/overlaps (< 3.6 Å)

Anion...*anion'* approaches		Anion...*cation'* approaches	
Inversion-related approaches		Inversion-related approaches	
($\bar{x}$, 1–*y*, 1–*z*) (Fig. S2(δ)(v))		(1–*x*, 1–*y*,1 –*z*)	
C(1)...*C(3)*	3.3341(14) ***(C ,C)***	C(1)...*N(021)*	3.4323(13) ***(C)***
C(2)...*C(2)*	3.4604(13) ***(C ,C)***	C(2)...*N(021)*	3.4996(12) ***(C)***
C(3)	3.3879(13) ***(C ,C)***	C(4)...*C(014)*	3.5414(16) ***(C)***
C(4)	3.5106(14) ***(C ,C)***	*C(015)*	3.5886(14) ***(C)***
C(4)...*N(2)*	3.3376(12) ***(C ,C)***	C(5)...*N(011)*	3.4543(13) ***(C)***
O(21)	3.3760(13) ***(C ,C)***	*C(012)*	3.4247(15) ***(C)***
C(5)...*N(2)*	3.2798(13) ***(C ,C)***	*C(013)*	3.5406(17) ***(C)***
O(22)	3.3121(14) ***(C ,C)***	*C(016)*	3.5253(13) ***(C)***
C(6)...*O(22)*	3.4166(13) ***(C ,C)***	C(6)...*N(011)*	3.3801(14) ***(C)***

O(21)...*N(4)*	3.3307(13)	(***c*** ,$\bar{\boldsymbol{c}}$)
O(42)	3.2826(14)	(***c*** ,$\bar{\boldsymbol{c}}$)
	($\bar{x}$, 2–*y*, 1–*z*)	
O(42)...*O(62)*	3.0072(13)	(***c*** ,$\bar{\boldsymbol{c}}$)

Cation...*cation* approaches

Inversion-related approaches

	(1–*x*, 1–*y*, 2–*z*)	
N(021)...*C(032)*	3.3964(12)	
C(023)...*C(036)*	3.4046(13)	
C(024)...*C(036)*	3.4546(15)	
C(025)...*N(031)*	3.4676(14)	
C(026)...*N(031)*	3.4673(13)	
C(032)	3.5996(14)	
N(031)...*C(025)*	3.4676(14)	
C(026)	3.4673(13)	
	(2–*x*, 1–*y*, 2–*z*)	
C(024)...*C(033)*	3.5318(15)	

Translation-related approaches

	(*x*, *y*–1, *z*)	
C(012)...*H,C(035)*	3.00(2), 3.275(2)	
C(013)...*H,C(035)*	2.98(2), 3.487(2)	

Cation H...*cation' (H)* approaches (inversion-related)

H(023)...*H(023)*	(2–*x*, $\bar{y}$, *z*)	2.22(2)
H(024)...*H,C(012)*	(2–*x*, $\bar{y}$, 2–*z*)	2.34(2), 3.011(15)
H(034)...*H(035)*	(2–*x*, $\bar{y}$, 2–*z*)	2.49(2)

	C(016)	3.4060(14)	***(C)***
N(6)...	*N(011)*	3.2362(14)	***(C)***
	H,C(014)	2.98(2), 3.400(2)	***(R)***
N(2)...	*N(031)*	3.0887(11)	***(C)***
	C(036)	3.3784(12)	***(C)***
O(21)...	*N(031)*	3.0833(12)	***(C)***
	C(032)	3.0924(13)	***(C)***
	C(033)	3.3883(13)	***(C)***
	C(036)	3.3700(12)	***(C)***
	C(036)	3.0736(12)	***(C)***
O(22)...	*N(031)*	3.2091(12)	***(C)***
	H,C(036)	2.99(1), 3.0736(12)	***(R)***
O(61)...	*N(011)*	3.3634(14	***(C)***
	C(023)	3.2911(13)	***(C)***
		(1–*x*, $\bar{y}$, 1–*z*)	
O(21)...*H,C(012)*		2.68(2), 3.4933(13)	***(R)***
		(1–*x*, 1–*y*, 2–*z*)	
O(42)...*H,C(024)*		2.79(2), 3.3312(13)	***(R)***
		($\bar{x}$, 2–*y*,1–*z*)	
O(61)...*H,C(035)*		2.61(1), 3.3798(12)	***(R)***
O(62)...*H,C(036)*		2.63(1), 3.3344(11)	***(R)***
		($\bar{x}$, 1–*y*, 1–*z*)	
O(62)...*H,C(014)*		2.93(2), 3.318(2)	***(R)***
N(6)...	*H,C(014)*	2.98(2), 3.400(2)	***(R)***

Translation-related approaches

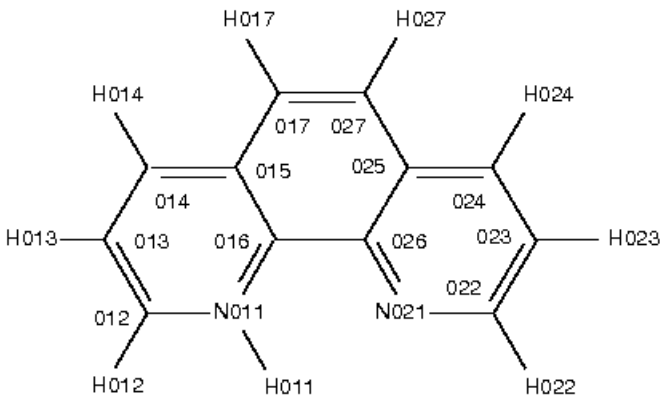
		(*x*–1, 1+*y*, *z*)	
O(62)...*H,C(013)*		2.69(2), 3.529(2)	***(R)***
		(*x*–1, *y*, *z*–1)	
O(1)...	*H,C(033)*	2.27(2), 3.1885(13)	***(R)***
	H,C(025)	2.30(2), 3.2477(15)	***(R)***

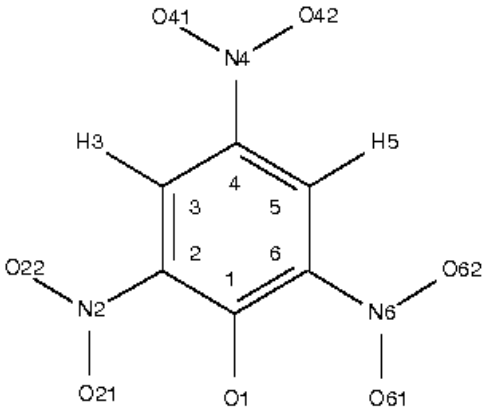
O(21)...*H,C(024)*	2.69(2), 3.2924(16)	***(R)***
H,C(025)	2.68(2), 3.2766(13)	***(R)***
O(61)...*H,C(033)*	2.67(2), 3.2291(14)	***(R)***
H,C(034)	2.44(2), 3.1099(14)	***(R)***

NO_2/C_6 interplanar dihedral angles: 0.80(11), 7.88(5), 150.85(5);

interpyridyl dihedral angles within the cation: 1/2 23.54(4); 1/3 28.86(6); 2/3 9.41(4)º.

(ε)(i) **(phenH)(pic) (*P*2$_1$/*c*)** (this work) (Fig. S1(ε)(i))





1,10-Phenanthrolinium picrate

(A) Hydrogen atom approaches/distances within the asymmetric unit (Fig. 2(g))

O(1)...N,H(011)	1.92(2), 2.706(2)	***(R)***	O(1)...H,C(012)	2.65(2), 3.083(3) ***(R)***
N(021)...N,H(011)	2.39(3), 2.767(3)		O(61)...H,C(012)	2.33(2), 3.324(3) ***(R)***
N(011)-H(011)	0.93(2)		O(1)...O(21,61)	2.898(2), 2.748(2)

(B) Approaches/overlaps (< 3.6 Å) within the screw-related stack of alternating anions and cations (Figs. S2(ε)(i)).

(i) Anion...*cation* approaches (see Fig. S2(ε)(i) (upper and lower))

Cation' at (1–*x*, ½+*y*, ½–*z*) (upper)			*Cation'* at (1–*x*, *y*–½, ½–*z*) (lower)		
C(2)...	*C(012)*	3.566(3) ***(C)***	C(4)...	*C(015)*	3.473(3) ***(C)***
C(3)...	*C(012)*	3.243(3) ***(C)***	C(5)...	*C(026)*	3.532(3) ***(C)***
	C(013)	3.549(3) ***(C)***	C(6)...	*C(026)*	3.495(3) ***(C)***
C(4)...	*N(011)*	3.407(3) ***(C)***		*C(015)*	3.5886(14) ***(C)***
	C(016)	3.464(3) ***(C)***	O(21)...	*H,C(012)*	2.81(2), 3.162(3) ***(R)***
O(22)...	*H,C(012)*	2.85(2), 3.495(3) ***(R)***	N(4)...	*C(017)*	3.426(3) ***(C)***
	O(61)	2.935(2) ***(C)***	N(6)...	*N(021)*	3.372(2) ***(C)***
C(5)...	C*(016)*	3.581(3) ***(C)***		*C(022)*	3.478(2) ***(C)***
N(4)...	*C(015)*	3.381(3) ***(C)***	O(61)...	*N(021)*	3.349(2) ***(C)***
O(41)...	*C(014)*	3.442(3) ***(C)***		*C(022)*	3.366(3) ***(C)***
O(42)...	*C(015)*	3.414(3) ***(C)***	O(62)...	*C(022)*	3.393(3) ***(C)***
	C(017)	3.416(3) ***(C)***			

(ii) Anion...*anion'* approaches

		(1–*x*, ½+*y*, ½–*z*)	
C(1)...	*O(1)*	3.416(3)	***(C ,C)***
O(22)...	*O(61)*	2.935(2)	***(C ,C)***

		(1–*x*, *y*–½, *z*–½)	
O(21)...	*N(6)*	3.146(2)	***(C ,C)***
	O(61)	3.011(2)	***(C ,C)***

(C) Other approaches

Anion...*anion'* approaches (inversion-related)

		(1–*x*, 1–*y*, –*z*)	
O(22)...	*H,C(3)*	2.58(2), 3.426(3)	***(R, L)***
	N(2)	3.261(3)	***(C ,C)***
	O(22)	2.961(2)	***(C ,C)***

Anion...*cation'* approaches (translation-related)

		(*x*–1, *y*, *z*)	
H(5)...	*H(024)*	2.41(3)	***(M)***
O(42)...	*H,C(023)*	2.50(2), 3.385(3)	***(R)***
O(62)...	*H,C(024)*	2.75(2), 3.577(3)	***(R)***

Anion...*cation'* approaches (inversion-related)

		(1–*x*, 1–*y*, –*z*)	
O(41)...	*H,C(023)*	2.83(2), 3.401(3)	***(R)***
	H,C(022)	2.63(3), 3.272(3)	***(R)***

		(1–*x*, 1–*y*, 1–*z*)	
O(61)...	*H,C(013)*	2.46(2), 3.263(3)	***(R)***
	H,C(014)	2.96(2), 3.442(3)	***(R)***

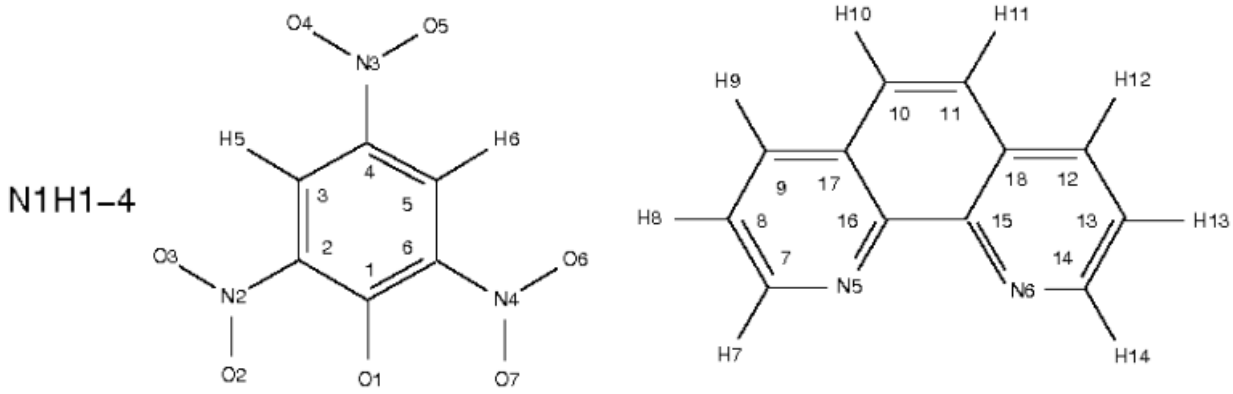
		(1–*x*, –*y* , –*z*)	
C(5)...	*C(026)*	3.532(3)	***(C)***
C(6)...	*C(026)*	3.495(3)	***(C)***

Anion...*cation'* approaches (glide-related)

		(*x*–1, ½–*y*, *z*–½)	
O(42)...	H,C(017)	2.52(2), 3.403(3)	***(R)***

NO_2/C_6 interplanar dihedral angles: 51.88(8), 7.38(8), 12.28(8)°.

(ε)(ii) **(NH_4)(pic)(·phen) ($P2_1/c$) (AMPCPL[26a])** (Fig. S1(ε)(ii))



Ammonium picrate : phenanthroline

(A) The ammonium environment

O(1)...H(2),N(1)	2.23, 2.834(3)	***(R)***	N(5)...H(1),N(1)	1.89, 2.840(3)
O(1)...H(2)*,N(1)*	2.33, 2.991(3)	***(R)***	N(6)...H(1),N(1)	2.36, 3.044(4)
O(7)...H(2)*,N(1)*	2.35, 3.080(4)	***(R)***	N(1)–H(1-4)	1.03, 0.87, 0.91, 0.87
O(1)...H(3),N(1)	1.99, 2.834(2)	***(R)***		
O(2)...H(3),N(1)	2.20, 2.851(4)	***(R)***	Also:	
O(6)...H(4),N(1) †	2.19, 3.013(3)	***(R)***	O(1)...O(2,7)	**2.675(3)**, **2.644(3)**
			O(7)...H(7),C(7)	2.47, 3.354(3)

*(1–*x*, $\bar{y}$, $\bar{z}$), †(*x*, $\bar{y}$ –½, z–½)

(B) Other approaches/overlaps (< 3.6 Å)

Inversion-related approaches

Anion...*anion'* approaches (1–*x*, $\bar{y}$ –1, $\bar{z}$) (Fig. S2(ε)(ii))			Anion...*phen'* approaches (1–*x*, $\bar{y}$, 1–*z*)		
C(1)...*O(2)*	3.204(4)	***(C, $\bar{C}$)***	O(3)...*H,C(7)*	2.85, 3.333(4)	***(R)***
O(6)...*O(2)*	3.299(3)	***(C, $\bar{C}$)***	N(3)...*C(14)*	3.425(4)	***(C)***
O(1)...*N(2)*	3.386(3)	***(C, $\bar{C}$)***	O(4)...*C(15)*	3.211(3)	***(C)***
O(2)	3.352(3)	***(C, $\bar{C}$)***	*C(16)*	3.479(3)	***(C)***
O(2)...*C(6)*	3.299(3)	***(C, $\bar{C}$)***	O(5)...*C(14)*	3.159(4)	***(C)***
			N(3)...*N(6)*	3.114(3)	***(C)***

phen...*phen'* approaches

(2–*x*, $\bar{y}$, $\bar{z}$)

C(8)...*C(11)* 3.576(5)

C(9)...*C(10)* 3.481(4)

Screw-related approaches

(1–*x*, ½+*y*, *z*–½)

O(7)...*O(6)* 3.274(4) ***(C,C)***

O(7)...*H(6),C(5)* 2.83, 3.605(4) ***(R, $\bar{L}$)***

Anion...*phen'* approaches (cont.)

Glide-related approaches

(*x*–1, $\bar{y}$ –½, *z*–½)

O(4)...*H,C(12)* 2.73, 3.443(4) ***(R)***

Translation-related approaches

(*x*–1, *y*–1, *z*)

O(4)...*H,C(9)* 2.37, 3.342(4) ***(R)***

H(5)...*H(10)* 2.52 ***(M)***

O(4)...*N(6)* 3.170(3) ***(C)***

O(5)...*N(6)* 3.344(3) ***(C)***

(1–*x*, $\bar{y}$, $\bar{z}$) (Fig. S2(ε)(ii))

C(2)...*C(16)* 3.442(3) ***(C)***

C(3)...*C(11)* 3.597(4) ***(C)***

C(4)...*C(18)* 3.387(3) ***(C)***

C(6)...*N(6)* 3.397(3) ***(C)***

O(3)...*C(9)* 3.457(4) ***(C)***

O(4)...*C(11)* 3.488(4) ***(C)***

C(15) 3.211(3) ***(C)***

C(16) 3.479(3) ***(C)***

(1–*x*, $\bar{y}$ –1, $\bar{z}$)

H(5),C(3)...*N(5)* 2.95, 3.380(3) ***(L)***

O(3)...*H,C(7)* 2.85, 3.333(4) ***(R)***

Screw-related approaches

(1–*x*, *y*–½, ½–*z*)

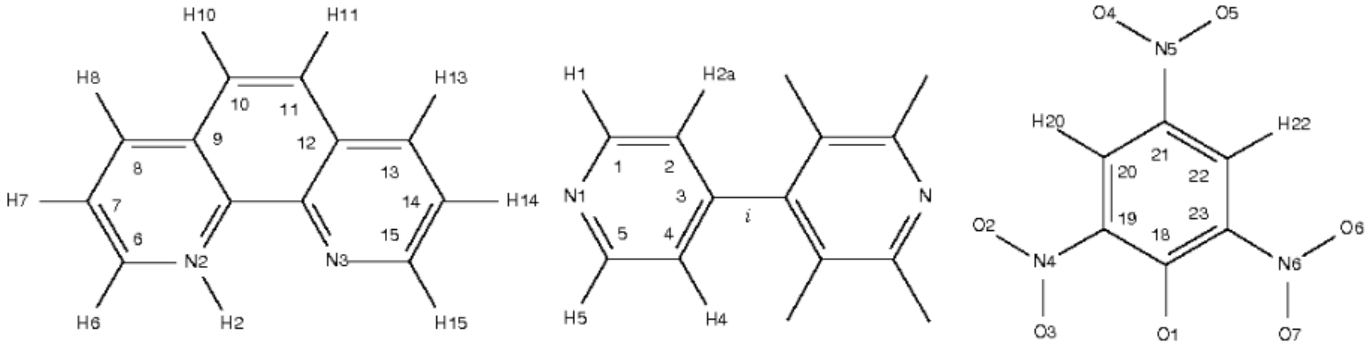
O(3)...*H,C(13)* 2.65, 3.458(3) ***(R)***

(1–*x*, *y*–½, $\bar{z}$ –½)

O(5)...*H,C(8)* 2.35, 3.369(3) ***(R)***

NO_2/C_6 interplanar dihedral angles: 14.8(9), 5.4(3), 5.62(12)º.

(ε)(iii) **'[(phenH)(bpy'H)(phen)](pic)$_2$'** (x 0.5) **(*P* $\bar{1}$) * (INOSUZ[27])** (Fig. S1(ε)(iii))



1,10-Phenanthrolinium 1,10-phenanthroline 4,4'-bipyridinium bis(picrate)

(A) Hydrogen atom approaches/distances within the asymmetric unit

N(1)...H,N(2)	1.87 , 2.716(4)	H(2)-N(2,3)	0.86, 2.40
N(3)...N(1,2)	3.063(2), 2.725(4)	O(1)...O(3,7)	2.943(4), 2.703(4)

(B) Other approaches/overlaps (< 3.6 Å)

Anion...*anion'* approaches

Inversion-related approaches

($\bar{x}$, 2–*y*, 1–*z*)

O(2)...*O(2)*	3.251(5)	(***C***, $\bar{\boldsymbol{C}}$)
N(4)	3.221(5)	(***C***, $\bar{\boldsymbol{C}}$)
H,C(20)	2.66, 3.399(4)	(***R***, $\bar{\boldsymbol{L}}$)

(1–*x*, 2–*y*, 1–*z*) (Fig. S2(ε)(iii))

O(4)...*C(18)*	3.432(5)	(***C***, $\bar{\boldsymbol{C}}$)
C(19)	3.496(5)	(***C***, $\bar{\boldsymbol{C}}$)
O(5)...*O(2)*	2.919(4)	(***C***, $\bar{\boldsymbol{C}}$)
N(5)...*O(2)*	3.078(5)	(***C***, $\bar{\boldsymbol{C}}$)
C(20)...*C(20)*	3.523(5)	(***C***, $\bar{\boldsymbol{C}}$)
C(21)	3.453(5)	(***C***, $\bar{\boldsymbol{C}}$)

Anion...*bpy'H*$^+$*cation'* approaches

Inversion-related approaches

(1–*x*, 1–*y*, 1–*z*) (Fig. S2(ε)(iii))

O(1)...*C(5)*	3.341(4)	***(C)***
O(6)...*C(1)*	3.360(5)	***(C)***
C(18)...*C(4)*	3.394(5)	***(C)***
C(5)	3.292(5)	***(C)***
C(19)...*C(4)*	3.403(5)	***(C)***
C(21)...*C(3)*	3.480(5)	***(C)***
C(22)...*C(2)*	3.513(5)	***(C)***
C(3)	3.480(5)	***(C)***
C(23)...*C(5)*	3.567(5)	***(C)***

(2–*x*, 1–*y*, 1–*z*)

O(6)...*H,C(4)*	2.73, 3.267(4)	***(R)***

Translation-related approaches

(x–1, y, z)

O(3)...*O(6)*	3.040(5)	*(C ,C̄)*
N(6)	3.097(6)	*(C ,C̄)*
O(3)...*H,C(22)*	3.01, 3.317(5)	***(R**, L̄)*
C(23)	3.413(5)	*(C ,C̄)*

phenH$^+$cation...*phenH$^+$cation'* approaches

Inversion-related approaches

($\bar{x}$, 1–y, 2–z)

C(12)...*C(17)*	3.567(5)

(1–x, 1–y, 1–z)

C(17)...*C(17)*	3.596(5)

H,C(5)	2.57, 3.194(4)	***(R)***
H(22)...*H(4)*	2.82	***(M)***

Translation-related approaches (1+x,y,z)

O(5)...*H,C(1)*	2.67, 3.279(4)	***(R)***
H(2a),C(2)	2.74, 3.308(4)	***(R)***
H(22)...*H(2a)*	2.89	***(M)***

Anion...*phenH$^+$cation'* approaches

Translation-related approaches

(x, 1+y, z–1)

O(1)...*H,C(8)*	2.61, 3.296(4)	***(R)***
O(7)...*H,C(7)*	2.62, 3.360(4)	***(R)***

(1+x, y, z–1)

O(6)...*H,C(11)*	2.42, 3.327(5)	***(R)***
O(7)...*H,C(13)*	2.90, 3.734(3)	***(R)***

Inversion-related approaches

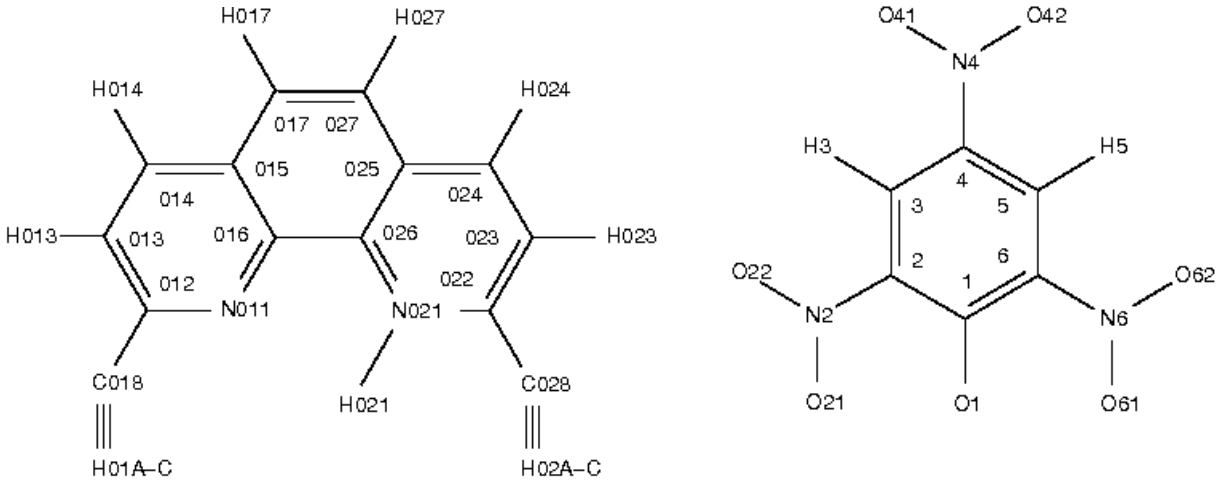
($\bar{x}$, 2–y, 1–z)

O(1)...*H,C(14)*	2.82, 3.396(4)	***(R)***
O(1)...*H,C(8)*	2.61, 3.296(4)	***(R)***

NO_2/C_6 interplanar dihedral angles: 66.9(2), 11.8(2), 18.73(14)º.

*****'[(phenH)(4,4'-bpyH)(phen)](pic)$_2$', recorded as such in ref.[27], is presented therein in triclinic space group $P\bar{1}$ with one such 'centrosymmetric supramolecular unit' comprising the cell contents. Although 'hydrogen atoms of the ligands were generated geometrically', the coordinate file we have obtained has none. Consideration of the non-hydrogen atom geometries obtained from the set of nicely precise coordinates supplied shows angles at the nitrogen atoms to be 119.2(3)º at the bpy nitrogen atom (N(1)), and 120.4(3), 116.4(3)º at those of the phen (N(2,3)), suggesting that the latter (N(3)) has no protonic association. For the purpose of the present exercise, we have located the hydrogen atom required to satisfy the stoichiometry on N(2), positioned so as to bridge to the bpy as described in ref.[27], all others being reasonably readily calculable.

(ε)(iv) **(dmpH)(pic)** ($P\bar{1}$) (this work) (Fig. S1(ε)(iv))



2,9-Dimethyl-1,10-phenanthrolinium picrate

(A) Hydrogen atom approaches/distances within the asymmetric unit (Fig. 2(h))

O(1)...H,N(021)	1.81(2), 2.718(2)	***(R)***	O(1)...H(02A),C(028)	2.32(3), 3.058(3)	***(R)***
O(21)...H,N(021)	2.58(3), 3.034(3)	***(R)***	C(2)...H(01A),C(018)	2.88(3), 3.398(3)	***(P_R)***
N(011)...H,N(021)	2.44(2), 2.760(2)		Also:		
N(021)-H(021)	0.94(2)		O(1)...O(21,61)	2.701(2), 2.659(2)	

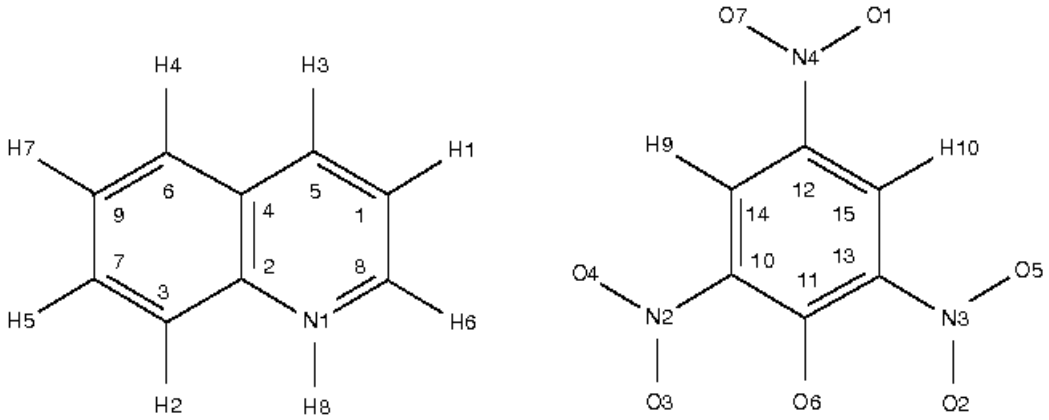
(B) Other approaches/overlaps (< 3.6 Å)

Anion...*anion'* approaches (inversion-related) (1–*x*, 2–*y*, 1–*z*) (Fig. S2(ε)(iv))			Anion...*cation'* approaches Inversion-related approaches (1–*x*, 1–*y*, 1–*z*)		
C(1)...*C(3)*	3.549(3)	***(C ,$\bar{C}$)***			
C(2)...*C(5)*	3.539(3)	***(C ,$\bar{C}$)***	O(22)...*H,C(013)*	2.77(2), 3.339(3)	***(R)***
C(6)	3.500(3)	***(C ,$\bar{C}$)***	O(41)...*H,C(014)*	2.70(3), 3.113(2)	***(R)***
C(3)...*C(6)*	3.533(3)	***(C ,$\bar{C}$)***			
C(5)...*N(2)*	3.412(3)	***(C ,$\bar{C}$)***		($\bar{x}$, 1–*y*, $\bar{z}$)	
H(5),C(5)...*O(21)*	2.93(3), 3.168(3)	***(L , $\bar{R}$)***	O(21)...*H,C(024)*	2.53(2), 3.361(2)	***(R)***
			H,C(027)	2.44(2), 3.270(2)	***(R)***

	(2–*x*, 2–*y*, 1–*z*)				
C(4)...*O(62)*	3.109(3)	***(C ,C)***		(2–*x*, 2–*y*, 1–*z*)	
C(5)...*C(5)*	3.469(3)	***(C ,C)***	O(62)...*C(018)*	3.245(2)	***(C)***
O(62)	3.474(3)	***(C ,C)***			
N(4)...*O(62)*	2.929(3)	***(C ,C)***		(1–*x*, 2–*y*, –*z*)	
O(41)...*O(62)*	3.345(2)	***(C ,C)***	O(61)...*C(022)*	3.445(3)	***(C)***
O(42)...*N(6)*	3.189(3)	***(C ,C)***	*C(023)*	3.429(3)	***(C)***
O(42)...*O(62)*	3.109(2)	***(C ,C)***	*H(02C),C(028)*	2.57(4), 3.318(3)	***(R)***
			O(41)...*H(02B),C(028)*	2.75(3), 3.357(3)	***(R)***
Cation...*cation'* approaches					
Inversion-related approaches				(*x*, *y*–1, *z*)	
	(1–*x*, 1–*y*, –*z*)		O(41)...*H,C(023)*	2.62(3), 3.455(3)	***(R)***
N(011)...*C(027)*	3.447(3)				
C(012)...*C(024)*	3.591(3)		Translation-related approaches		
C(025)	3.376(3)			(1+*x*,1+*y*,1+*z*)	
C(027)	3.468(3)		O(42)...*H,C(017)*	2.59(2), 3.198(2)	***(R)***
C(013)...*C(023)*	3.555(3)		*H,C(027)*	2.59(2), 3.207(2)	***(R)***
C(024)	3.374(3)				
C(025)	3.484(3)			(*x*, 1+*y*, *z*)	
C(014)...*N(021)*	3.471(3)		O(61)...*H,C(013)*	2.62(2), 3.170(3)	***(R)***
C(026)	3.572(8)		*H,C(014)*	2.42(2), 3.086(3)	***(R)***
C(015)...*C(026)*	3.506(3)				
C(016)...*C(016)*	3.504(2)				
N(021)...*C(014)*	3.471(3)				
	(–*x* , 1–*y*, –*z*)				
C(017)...*C(023)*	3.485(3)				
C(022)...*C(027)*	3.438(3)				
C(023)...*C(027)*	3.487(3)				
C(024)...*C(025)*	3.485(3)				
C(026)	3.445(3)				
C(025)...*C(025)*	3.445(3)				

NO_2/C_6 interplanar dihedral angles: 23.03(9), 4.0(2), 21.39(10)º.

(ζ)(i) **(quinH)(pic) (*P*2$_1$/*c*) (UBEGAL[8])** (Fig. S1(ζ)(i))



Quinolinium picrate

(A) Hydrogen atom approaches/distances within the fundamental ion-pair (cation at (1–*x*, ½+*y*, ½–*z*))*

O(6)...H(8),N(1)	1.82(2), 2.685(2)	***(R)***	N(1)-H(8)	0.88(2)
O(2)...H(8),N(1)	2.52, 3.075(2)	***(R)***		
H(6),C(8)	2.48, 3.081(2)	***(R)***		
O(3)...H(2),C(3)	2.39, 3.278(2)	***(R)***		
O(6)...H(2),C(3)	2.45, 3.147(2)	***(R)***	Also:	
(O(6)...C(2)	3.338(2)	***(C))***	O(6)...O(2,3)	**2.655(2)**, **2.693(2)**

(B) Other approaches/overlaps (< 3.6 Å)

Anion...*anion'* approaches (Fig. S2(ζ)(i))

Inversion-related approaches

	(2–*x*, 2–*y*, 1–*z*)	
O(1)...*N(2)*	3.339(2)	***(C ,$\bar{C}$)***
C(14)	3.456(2)	***(C ,$\bar{C}$)***
O(7)...*C(10)*	3.443(2)	***(C ,$\bar{C}$)***
C(14)	3.391(2)	***(C ,$\bar{C}$)***
N(4)...*C(14)*	3.213(2)	***(C ,$\bar{C}$)***
C(12)...*C(14)*	3.562(2)	***(C ,$\bar{C}$)***
	(2–*x*, 1–*y*, 1–*z*)	
O(1)...*O(4)*	3.145(2)	***(C ,$\bar{C}$)***
O(4)...*C(12)*	3.215(2)	***(C ,$\bar{C}$)***

Anion...*cation'* approaches

Inversion-related approaches

	(1–*x*, 1–*y*, 1–*z*)	
O(3)...*H,C(1)*	**2.55, 3.237(3)**	***(R)***
H(6),C(8)	3.06, 3.495(3)	***(R)***
O(4)...*H(6),C(8)*	2.76, 3.440(3)	***(R)***
O(1)...*H(1),C(1)*	2.61, 3.090(2)	***(R)***
	(2–*x*, 1–*y*, 1–*z*)	
O(7)...*H(3),C(5)*	2.66, 3.477(2)	***(R)***
H(4),C(6)	2.57, 3.400(2)	***(R)***

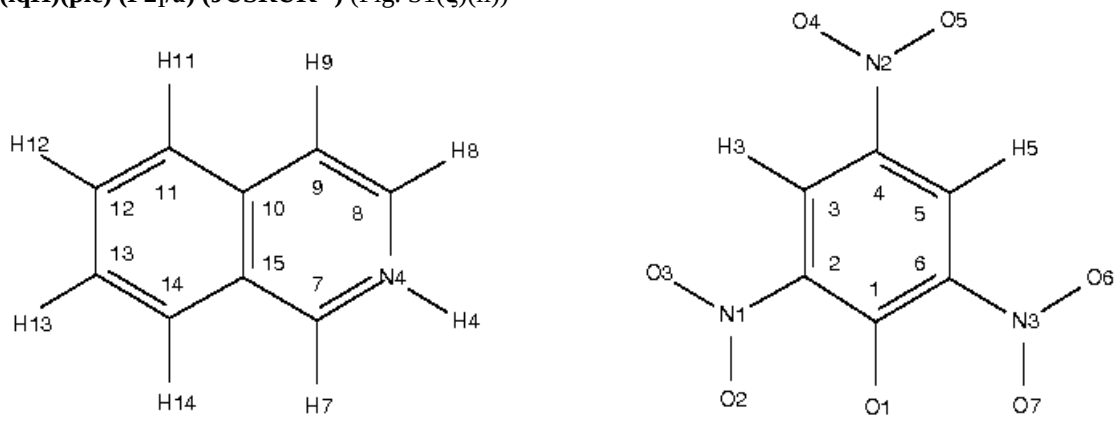
N(4)	2.936(2)	(***C*** ,$\bar{\boldsymbol{C}}$)
O(7)	3.262(2)	(***C*** ,$\bar{\boldsymbol{C}}$)
C(10)...*O(7)*	3.360(2)	(***C*** ,$\bar{\boldsymbol{C}}$)
C(12)...*O(4)*	3.215(2)	(***C*** ,$\bar{\boldsymbol{C}}$)
C(14)...*C(14)*	3.354(2)	(***C*** ,$\bar{\boldsymbol{C}}$)
N(2)...*O(7)*	3.325(2)	(***C*** ,$\bar{\boldsymbol{C}}$)
Glide-related approaches		
	(x, $^3/_2$–y, z–½)	
O(2)...*O(4)*	3.293(2)	(***C*** ,$\bar{\boldsymbol{C}}$)
Screw-related approaches		
	(2–x, ½+y, ½–z)	
O(5)...*N(3)*	3.343(3)	(***C*** ,$\bar{\boldsymbol{C}}$)
C(13)	3.395(3)	(***C*** ,$\bar{\boldsymbol{C}}$)
	(2–x, y–½, ½–z)	
O(2)...*H(10),C(15)*	2.84, 3.559(3)	(***R***, $\bar{\boldsymbol{L}}$)

Translation-related approaches		
	(1+x, 1+y, z)	
O(1)...*H(6),C(8)*	2.60, 3.317(3)	***(R)***
O(2)...*H(7),C(9)*	3.09, 3.458(3)	***(R)***
Glide-related approaches		
	(x, ½–y, ½+z)	
O(4)...*H(5),C(7)*	2.82, 3.391(3)	***(R)***
H(7),C(9)	2.86, 3.410(3)	***(R)***
Screw-related approaches		
	(2–x, ½+y, ½–z)	
H(10),C(15)…H(7)	2.43, 3.058(2)	***(M)***
Cation...*cation'* approaches (screw-related)		
	(1–x, ½+y, ½–z)	
N(1)...*C(7)*	3.482(3)	
C(2)...*C(2)*	3.427(2)	
C(3)	3.522(3)	
C(4)...*C(3)*	3.582(3)	
C(7)...*C(8)*	3.507(3)	
	(1–x, y–½, ½–z)	
C(2)...*C(3)*	3.560(3)	
C(3)...*C(4)*	3.582(3)	
C(7)...*C(8)*	3.336(3)	

NO_2/C_6 interplanar dihedral angles: 32.98(9), 9.0(2), 6.66(8)º.

*The two components of the asymmetric unit as presented in the CCDC CIF do not constitute the ion-pair without appropriate transformation, the cation being displaced to (1–x, ½+y, ½–z) relative to that of the CIF file.

(ζ)(ii) **(iqH)(pic) (*P*2$_1$/*a*) (JUSRUK[28])** (Fig. S1(ζ)(ii))



iso-Quinolinium picrate

(A) Hydrogen atom approaches/distances within the fundamental ion-pair (all generated by cation at (1–*x*, 1–*y*, $\bar{z}$)*)

O(1)...H,N(4)	1.76, 2.590(4)	***(R)***	N(4)-H(4)	0.86
O(7)...H,N(4)	2.52, 3.086(5)	***(R)***	O(1)...O(2,7)	2.704(4), **2.635(5)**
H,C(8)	2.47, 3.077(6)	***(R)***		

(B) Other approaches/overlaps (< 3.6 Å)

Anion...*anion'* approaches

Inversion-related approaches

(1–*x*, $\bar{y}$, 1–*z*)

O(3)...*O(4)*	3.230(5)	***(C ,$\bar{C}$)***
O(4)...*H,C(3)*	2.69, 3.365(4)	***(R, $\bar{1}$)***

Glide-related approaches

(½+*x*, ½–*y*, *z*)

O(2)...*O(6)*	3.209(6)	***(C ,$\bar{C}$)***
C(5)	3.449(4)	***(C ,$\bar{C}$)***

Screw-related approaches

(½–*x*, *y*–½, $\bar{z}$)

O(6)...*O(7)*	3.220(5)	***(C ,$\bar{C}$)***

Anion...*cation'* approaches

Translation-related approaches

(*x*, *y*–1, *z*) (Fig. S2(ζ)(ii))

N(2)...*C(12)*	3.403(6)	***(C)***
C(2)...*C(9)*	3.456(6)	***(C)***
C(3)...*C(10)*	3.543(5)	***(C)***
C(4)...*C(10)*	3.560(5)	***(C)***
C(11)	3.496(6)	***(C)***
C(5)...*C(15)*	3.566(5)	***(C)***
O(2)...*C(8)*	3.174(7)	***(C)***
O(5)...*C(12)*	3.279(5)	***(C)***
C(13)	3.470(6)	***(C)***

Inversion-related approaches

(1–*x*, 1–*y*, 1–*z*)

O(4)...*H,C(9)*	2.65, 3.400(5)	***(R)***
H(3)...*H(11)*	2.55	***(M)***

Anion...*cation'* approaches (cont.)

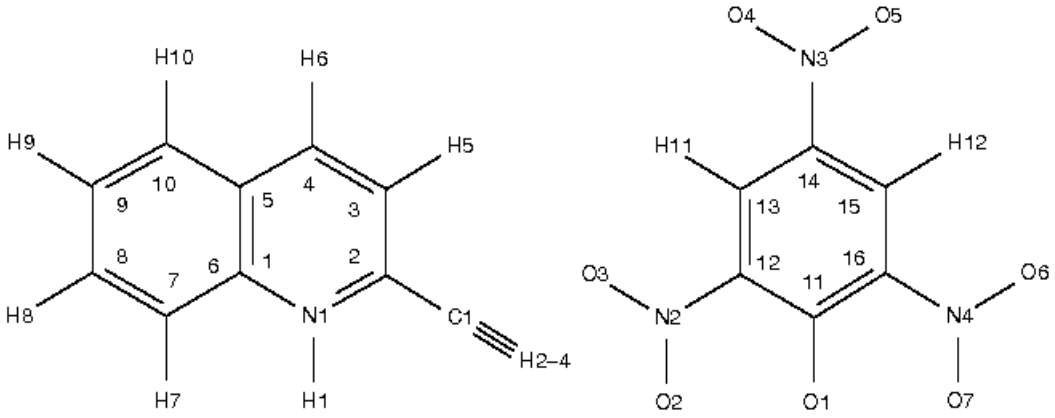
Glide-related approaches

	(x–½, ½–y, z)		Screw-related approaches		
				(½–x, y–½, 1–z)	
O(6)...*N(4)*	3.392(6)	***(C)***			
C(8)	2.87, 3.161(7)	***(C)***	O(5)...*H,C(12)*	2.52, 3.342(5)	***(R)***
O(5)...*H,C(9)*	2.80, 3.551(6)	***(R)***			
	(½+x, ½–y, 1+z)				
O(2)...*H,C(13)*	2.72, 3.412(6)	***(R)***			

NO_2/C_6 interplanar dihedral angles: 34.2(2), 10.6(2), 1.1(4)°.

*The two components of the asymmetric unit as presented in the CCDC CIF do not constitute the ion-pair without appropriate transformation, the cation being displaced to (1–x, 1–y, $\bar{z}$) relative to that of the CIF file.

(ζ)(iii) **(2mqH)(pic)** (***P*** $\bar{1}$) **(VATTER**[29]**)** (Fig. S1(ζ)(iii))



2-Methylquinolinium picrate

(A) Hydrogen atom approaches/distances within the fundamental ion-pair (all generated by cation at (x, 1+y, z)*)

O(1)...H,N(1)	1.93, 2.749(3) ***(R)***	O(1)...H(2),C(1)	2.68, 3.443(4) ***(R)***
O(2)...H,N(1)	2.29, 2.857(3) ***(R)***	O(1)...O(2,7)	**2.680(4)**, 2.948(4)
N(1)-H(1)	0.86		

(B) Other approaches/overlaps (< 3.6 Å)

Anion...*anion'* approaches

Translation-related approaches

(1+x, y, z)

O(2)...*N(4)*	3.218(3)	***(C ,$\bar{C}$)***
O(6)	3.173(4)	***(C ,$\bar{C}$)***
O(7)	3.229(4)	***(C ,$\bar{C}$)***
O(3)...*H(12),C(15)*	2.46, 3.339(4)	***(R, $\bar{L}$)***

Inversion-related approaches

(1–x, 2–y, 2–z)

O(2)...*N(2)*	3.372(5)	***(C ,$\bar{C}$)***
O(3)	3.167(4)	***(C ,$\bar{C}$)***
O(3)...*N(2)*	3.264(5)	***(C ,$\bar{C}$)***

Anion...*cation'* approaches

Translation-related approaches

(x–1, y, 1+z)

O(4)...*H(5),C(3)*	2.64, 3.345(4)	***(R)***
H(6),C(4)	2.92, 3.482(4)	***(R)***

(x–1, 1+y, z)

O(6)...*H(3),C(1)*	2.72, 3.327(5)	***(R)***
C(2)	3.439(5)	***(C)***
N(1)	3.398(4)	***(C)***
C(6)	3.449(4)	***(C)***
O(7)... *N(1)*	3.398(4)	***(C)***

(x, 1–y, z)

O(7)... *C(6)*	3.449(4)	***(C)***

($\bar{x}$, 1–*y*, 2–*z*)

O(4)...*O(5)*	3.398(4)	(*C*,$\bar{C}$)
O(5)...*N(3)*	3.160(5)	(*C*,$\bar{C}$)
O(5)	3.357(4)	(*C*,$\bar{C}$)

($\bar{x}$, 2–*y*, 2–*z*) (Fig. S2(ζ)(iii))

O(7)...*O(4)*	3.188(5)	(*C*,$\bar{C}$)
N(3)	3.369(6)	(*C*,$\bar{C}$)
C(13)	3.459(5)	(*C*,$\bar{C}$)
C(14)	3.487(6)	(*C*,$\bar{C}$)

Cation...*cation'* approaches (inversion-related)

(1–*x*, 2–*y*, 2–*z*)

N(2)...*N(2)*	3.240(5)

(2–*x*, 1–*y*, 1–*z*)

C(4)...*C(4)*	3.447(5)

(1–*x*, $\bar{y}$, 1–*z*)

C(1)...*C(1)*	3.556(5)

(1–*x*, 1–*y*, 1–*z*)

C(3)...*C(7)*	3.553(5)

Inversion-related approaches

(1–*x*, 1–*y*, 2–*z*)

O(3)...*H,C(7)*	2.78, 3.463(4)	***(R)***
O(4)... *C(8)*	3.292(5)	***(R)***
C(9)	3.131(5)	***(R)***
C(10)	3.408(4)	***(R)***

($\bar{x}$,1–*y*, 2–*z*)

O(5)...*H,C(7)*	2.53, 3.168(4)	***(R)***
C(8)	3.427(5)	***(C)***

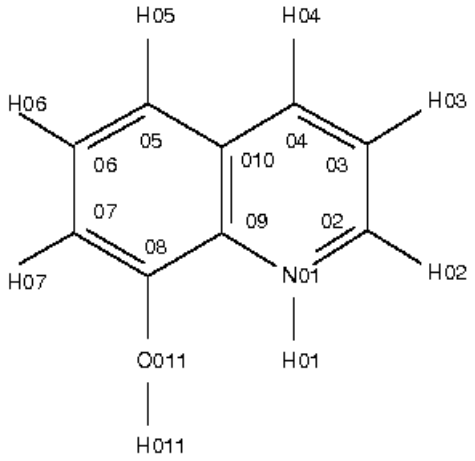
(1–*x*, 2–*y*, 1–*z*)

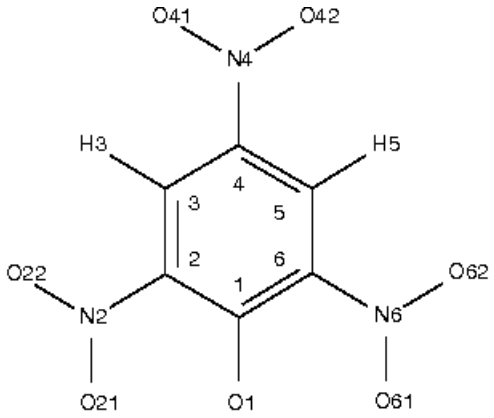
O(7)...*H(6),C(4)*	2.39, 3.302(4)	***(R)***
O(1)... *C(4)*	3.496(4)	***(C)***

NO_2/C_6 interplanar dihedral angles: 10.3(2), 0.9(1), 64.6(2)º.

*The two components of the asymmetric unit as presented in the CCDC CIF do not constitute the ion-pair without appropriate transformation, the cation being displaced to (*x*, 1+*y*, *z*) relative to that of the CIF file.

(ζ)(iv) **(ohqH)(pic)** (***P*2$_1$/*c***) (this work) (Fig. S1(ζ)(iv))





8-Hydroxyquinolinium picrate

(A) Hydrogen atom approaches/distances within the asymmetric unit (Fig. 2(i))

O(21)...	H,C(07)	2.49(2), 3.413(2) ***(R)***	O(61)...H,O(011)	2.44(2), 2.926(2) ***(R)***
O(1)…	H,C(07)	2.41(2), 3.081(2)	O(1)... H,O(011)	1.75(3), 2.594(2) ***(R)***
O(011)...H,N(01)		2.30(2), 2.649(2)	N(01)-H(01), O(011)-H(011)	0.86(2), 0.86(3)
O(1)...	O(21,61)	2.666(2), **2.638(2)**		

(B) Other approaches/overlaps (< 3.6 Å)

Anion...*anion'* approaches (inversion-related)

(2–*x*, 1–*y*, 1–*z*)

O(1)...*C(5)*	3.431(2)	***(C ,$\bar{C}$)***
C(1)...*C(6)*	3.431(2)	***(C ,$\bar{C}$)***
N(6)	3.459(2)	***(C ,$\bar{C}$)***
C(3)...*O(61)*	3.414(2)	***(C ,$\bar{C}$)***
C(4)...*O(61)*	3.412(3)	***(C ,$\bar{C}$)***
C(6)...*C(6)*	3.378(2)	***(C ,$\bar{C}$)***

(2–*x*, 2–*y*, $\bar{z}$)

O(41)...*N(2)*	2.930(2)	***(C ,$\bar{C}$)***
O(21)	3.101(2)	***(C ,$\bar{C}$)***
O(22)	2.931(2)	***(C ,$\bar{C}$)***

Anion...*cation'* approaches

Inversion-related approaches

(1–*x*, 1–*y*, 1–*z*) (Fig. S2(ζ)(iv))

C(1)...*C(07)*	3.567(2)	***(C)***
C(08)	3.359(2)	***(C)***
O(011)	3.473(2)	***(C)***
C(2)...*C(08)*	3.461(2)	***(C)***
C(09)	3.527(2)	***(C)***
O(011)	3.413(2)	***(C)***
C(3)...*N(01)*	3.322(3)	***(C)***
C(02)	3.579(3)	***(C)***
C(09)	3.420(2)	***(C)***
C(4)...*C(09)*	3.587(2)	***(C)***
C(010)	3.471(2)	***(C)***

	(1–*x*, 2–*y*, 1–*z*)	
O(22)...*O(22)*	2.796(2)	***(C ,C̄)***

Cation...*cation'* approaches (screw-related)

	(1–*x*, *y*–½, ½–*z*)	
C(02)...*C(06)*	3.597(3)	
C(03)...*C(06)*	3.586(3)	

Anion...*cation'* approaches (cont.)

Translation-related approaches

	(*x*, 1+*y*, *z*)	
O(21)...*H,N(01)*	2.94(2), 3.392(2)	***(R)***
H,C(02)	2.67(2), 3.284(2)	***(R)***
O(22)... *C(02)*	3.486(2)	***(C)***
O(011)	3.199(2)	***(C)***
H,N(01)	2.06(2), 2.890(2)	***(R)***
N(4)... *O(011)*	3.239(2)	***(C)***

Screw-related approaches

	(1–*x*, ½+*y*, ½–*z*)	
O(21)...*H,C(05)*	2.91(2), 3.430(2)	***(R)***

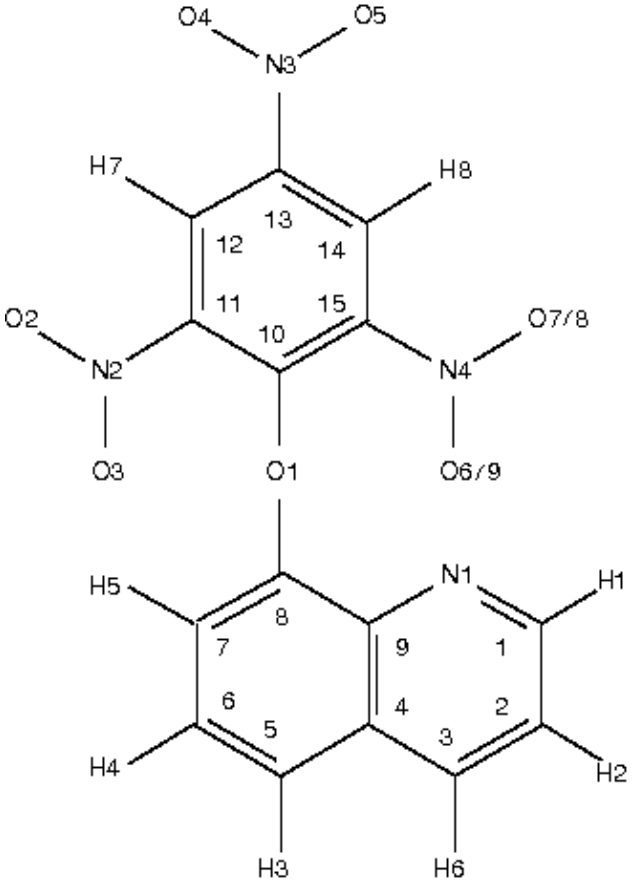
C(5)...*C(05)*	3.565(3)	***(C)***
C(010)	3.568(2)	***(C)***
C(6)... *C(06)*	3.594(3)	***(C)***
C(07)	3.465(2)	***(C)***
N(2)... *O(011)*	3.333(2)	***(C)***
O(22)...*H,N(01)*	2.73, 3.217(2)	***(R)***
O(011)	3.370(2)	***(C)***
N(4)... *C(04)*	3.384(2)	***(C)***
O(41)...*C(03)*	3.354(3)	***(C)***
O(62)...*C(06)*	3.500(3)	***(C)***
	(2–*x*, 1–*y*, 1–*z*)	
O(42)...*C(08)*	3.215(2)	***(C)***
O(011)	3.164(2)	***(C)***
	(1–*x*, *ȳ* , 1–*z*)	
O(61)...*H,C(02)*	2.67(2), 3.391(3)	***(R)***

Glide-related approaches

	(1+*x*, ³/₂–*y*, ½+*z*)	
O(41)...*H,C(05)*	2.58(2), 3.453(2)	***(R)***
O(42)...*H,C(06)*	2.71(2), 3.455(2)	***(R)***
	(1+*x*, ½–*y*, ½+*z*)	
O(42)...*H,C(03)*	2.54(2), 3.350(3)	***(R)***
O(62)...*H,C(04)*	2.44(2), 3.397(3)	***(R)***

NO_2/C_6 interplanar dihedral angles: 34.44(7), 4.80(10), 9.08(14)°.

(ζ)(v) **(oqpic)** (*proto*-Meisenheimer Complex) **(*C*2/*c*) (JOKTOS[30])** (Fig. S1(ζ)(v))



8-Hydroxyquinoline-picrate, proto-Meisenheimer Complex

Screw-related approaches

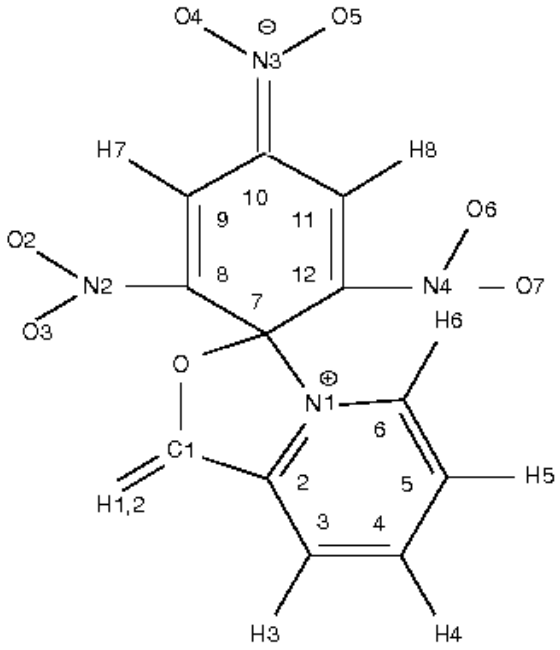
	(1–*x*, *y*, ³/₂–*z*)			(½–*x*, ½+*y*, ½–*z*)	
C(3)...*C(3)*	3.538(9)		O(2)...*O(5)*	3.076(9)	(***C*** ,$\bar{C}$)
C(4)...*C(5)*	3.482(9)		O(4)...*C(10)*	3.075(7)	(***C*** ,$\bar{C}$)
			C(11)	3.438(7)	(***C*** ,$\bar{C}$)
			C(14)	3.482(8)	(***C*** ,$\bar{C}$)
Inversion-related approaches			*C(15)*	3.022(8)	(***C*** ,$\bar{C}$)
	(½–*x*, $\bar{y}$ –½, 1–*z*)		C(1)...*O(4)*	3.287(7)	(***C*** ,$\bar{C}$)
O(8)...*O(8)*	2.48(2)*				
			Glide-related approaches		
	(½–*x* ,½–*y*, 1–*z*)			(*x*, 1–*y*, *z*–½)	
O(5)...*O(6)*	2.912(15)	(***C*** ,$\bar{C}$)	O(2)...*C(1)*	3.298(9)	(***C*** ,$\bar{C}$)
N(1)	3.331(9)	***(C)***	*C(2)*	3.423(10)	(***C*** ,$\bar{C}$)
O(6)...*N(3)*	3.010(15)	(***C*** ,$\bar{C}$)			

C(13)	3.458(15)	(***C*** ,$\bar{C}$)		(x, $\bar{y}$, ½+z)	
O(8)...*H(1)*	2.66*		O(6)...*N(2)*	3.183(13)	(***C*** ,$\bar{C}$)
			O(3)	3.220(12)	(***C*** ,$\bar{C}$)
	(1–x, 1–y, 1–z)		*C(11)*	3.373(15)	(***C*** ,$\bar{C}$)
O(2)...*H(3)(,C(5))*	2.63, 3.581(8)	***(R)***	*C(12)*	3.312(16)	(***C*** ,$\bar{C}$)
C(3)...*C(5)*	3.546(10)		O(8)...*H(7),C(12)*	2.54,3.282(18)	($\bar{L}$)
			O(4)	3.370(20)	(***C*** ,$\bar{C}$)
	(1–x, y, 1–z)				
O(3)...*H(4),C(6)*	2.59, 3.340(8)	***(R)***		(½–x, y–½, ½–z)	
			C(1)...*O(4)*	3.289(7)	($\bar{C}$)
Translation related approaches					
	Nil			(x–½, ½–y, z–½)	
			O(5)...*H(3),C(5)*	2.76(5), 3.273(7)	***(R)***
Intramolecular distances			*H(4),C(6)*	2.61(5), 3.298(7)	***(R)***
O(1)...*O(3,6)*	2.898(7), 2.607(16)				
O(3)...*C(8)*	2.783(8)				
N(1)…C(10)	2.792(7)				

NO_2/C_6 interplanar dihedral angles: 38.9(3), 3.7(5), 42.1(8)/31.7(3)º.

*O(8) is a disordered component of O(7), removed in production of the fingerprint plot.

(ζ)(vi) **(omppic)** (Meisenheimer Complex) **($P2_1/n$) (JOKTIM[30])** (Fig. S1(ζ)(vi)



2-Hydroxymethylpyridine picrate, Meisenheimer Complex

Inversion-related approaches	(1–*x*, 1–*y*, 1–*z*)		Glide-related approaches	(½+*x*, ½–*y*, ½+*z*)	
O(2)...*O(5)*	3.352(3)	***(C ,$\bar{C}$)***	O(1)...*H,C(5)*	2.76(2), 3.491(3)	***(R)***
O(3)...*O(4)*	3.308(3)	***(C ,$\bar{C}$)***	O(2)...*C(4)*	3.179(4)	***(C)***
O(5)	3.218(3)	***(C ,$\bar{C}$)***	*C(5)*	3.189(3)	***(C)***
N(3)	3.092(3)	***(C ,$\bar{C}$)***	O(3)...*O(6)*	2.835(3)	***(C ,$\bar{C}$)***
O(5)...*N(2)*	3.026(3)	***(C ,$\bar{C}$)***	*N(4)*	3.155(3)	***(C ,$\bar{C}$)***
H,C(6)	2.77(3), 3.139(3)	***(R)***	*C(5)*	3.484(4)	***(C)***
C(8)	3.310(3)	***(C ,$\bar{C}$)***	*C(6)*	3.427(3)	***(C)***
N(2)...*N(3)*	3.379(3)	***(C ,$\bar{C}$)***	N(2)...*C(5)*	3.301(3)	***(C)***
C(9)...*H(7),C(9)*	3.00(3), 3.443(4)	***(P_R ,$\bar{P}_L$)***			
	(1–*x*, $\bar{y}$, 1–*z*)			(*x*–½, ½–*y*, ½+*z*)	
O(1)...*H(8),C(11)*	2.73(2), 3.176(4)	***(R, $\bar{L}$)***	O(2)...*O(4)*	3.239(4)	***(C ,$\bar{C}$)***
O(4)...*O(1)*	3.159(3)	***(C ,$\bar{C}$)***	H(1),C(1)...*O(4)*	2.74, 3.448(4)	***($\bar{R}$)***
H(2),C(1)	2.48(3), 3.194(3)	***(R)***	C(2)...*O(4)*	3.351(4)	***($\bar{C}$)***
O(6)...*N(3)*	3.304(3)	***(C ,$\bar{C}$)***	H,C(3)...*O(4)*	2.84, 3.133(2)	***($\bar{R}$)***

C(10)	3.422(3)	(***C*** , $\overline{\boldsymbol{C}}$)
O(7)...*C(9)*	3.482(4)	(***C*** , $\overline{\boldsymbol{C}}$)
N(3)...*O(6)*	3.304(3)	(***C*** , $\overline{\boldsymbol{C}}$)
N(4)...*C(10)*	3.449(4)	(***C*** , $\overline{\boldsymbol{C}}$)
C(11)...*C(12)*	3.545(4)	
	($\overline{x}$, $\overline{y}$, 1–*z*)	
O(6)...*H,C(3)*	2.69(2), 3.397(4)	***(R)***

Intramolecular distances

O(1)...*O(2,6)*	2.782(3), 2.751(2)	
O(2)...*H(1),C(1)*	2.63(2), 2.921(3)	***(R)***
O(6)...*H(2),C(1)*	2.59(3), 2.911(4)	***(R)***

Translation-related approaches

	(*x*+1, *y*, *z*)	
O(5)...*H,C(4)*	2.48(4), 3.417(4)	($\overline{\boldsymbol{R}}$)

Screw-related approaches

	(½–*x*, ½+*y*, $^3/_2$–*z*)	
O(2)...*H(1),C(1)*	2.83(2), 3.070(4)	***(R)***
H(2)	2.52(3)	***(R)***
	(½–*x*, ½+*y*, ½–*z*)	
H,C(6)...*O(7)*	2.42(3), 3.147(4)	($\overline{\boldsymbol{R}}$)

NO_2/C_6 interplanar dihedral angles: 7.94(11), 3.5 (2), 5.9(2)°.

Table S7 Analysis of contact types in the picrate compounds of Table 1

	N...N	N...H	N...C	N...O	H...H	H...C	H...O	C...C	C...O	O...O
(picH) (PICRAC13[1g]) (mol.1)	0	0.1	0.6	12.1	0.7	0	35.1	0	26.15	25.1
(mol.2)	0	1.9	0	10.7	0.8	0.3	33.7	0	26.1	26.4
(pyH)(pic) (PYRPIC02[11c])	0	2.3	1.8	6.3	1.0	4.3	59.4	8.1	6.1	10.7
(PYRPIC03[11c])	1.2	0.7	2.3	5.7	3.7	4.2	56.0	5.8	9.7	10.7
(pyH)(pic)(·naph) (PYNPCR[20])	n/a	-	-	-	-	-	-	-	-	-
(2mpH)(pic) (units 1) (this work)	0	1.8	1.5	7.2	2.7	6.2	51.1	4.6	11.9	12.9
(units 2)	0.1	2.2	1.4	7.9	2.2	5.3	49.7	5.6	11.7	14.4
(dpaH)(pic) (this work)	0.2	4.4	3.8	5.3	5.1	4.7	55.9	6.8	9.3	4.5
(pipH)(pic) (VAZJAI[21])	0.1	2.5	2.9	4.0	4.0	4.8	59.0	8.3	2.8	11.1
(pipH)(pic)(·pip) (this work)	0	2.9	0.7	6.6	5.5	1.0	66.2	11.8	2.4	2.9
(morH)(pic) (units 1) (KOMTUC[22a])	0	1.2	0.6	8.0	7.5	6.8	52.5	4.4	5.0	13.9
(units 2)	0	1.9	0.6	7.4	5.1	8.7	55.0	4.5	4.5	12.2
2[(morH)(pic)](·H_2O) (units 1) (this work)	0	1.8	4.1	2.5	2.7	3.2	61.7	6.5	7.0	10.5
(units 2)	0	3.1	2.1	4.7	6.0	5.8	57.9	2.9	7.4	10.1
(bpyH)(pic) (UCOFUO[23])	0.8	2.1	4.2	5.6	3.7	5.5	61.4	5.0	7.6	4.2
(bpyH)(pic)(·MeCN) (this work)	0.6	1.0	3.9	6.1	8.5	2.7	59.7	7.9	5.9	3.8
(bpy'H_2)$(pic)_2$ (KAMPIY[24])	0.4	2.8	4.0	4.5	4.7	6.0	44.2	0.1	19.9	13.5
(bpy'H_2)$(pic)_2$(·H_2O) (UJOQUF[25])	0	1.1	4.3	6.3	1.6	8.0	48.8	0.3	16.8	12.9
(tpyH)(pic) (this work)	1.4	2.9	4.9	3.2	7.6	4.8	54.4	6.9	8.4	5.6
(phenH)(pic) (this work)	1.0	0.9	5.1	5.8	6.3	7.5	50.3	6.7	8.9	8.4
(NH_4)(pic)(·phen) (AMPCPL[26a])	1.4	3.6	3.3	3.3	5.9	7.6	57.1	5.1	8.5	4.1
'[(phenH)(bpy'H)(phen)]$(pic)_2$' (INOSUZ[27])	0.7	0.5	1.9	5.2	5.4	6.3	58.0	6.5	7.9	7.5
(dmpH)(pic) (this work)	1.5	2.2	1.1	6.1	7.6	7.7	60.1	5.3	5.9	2.5

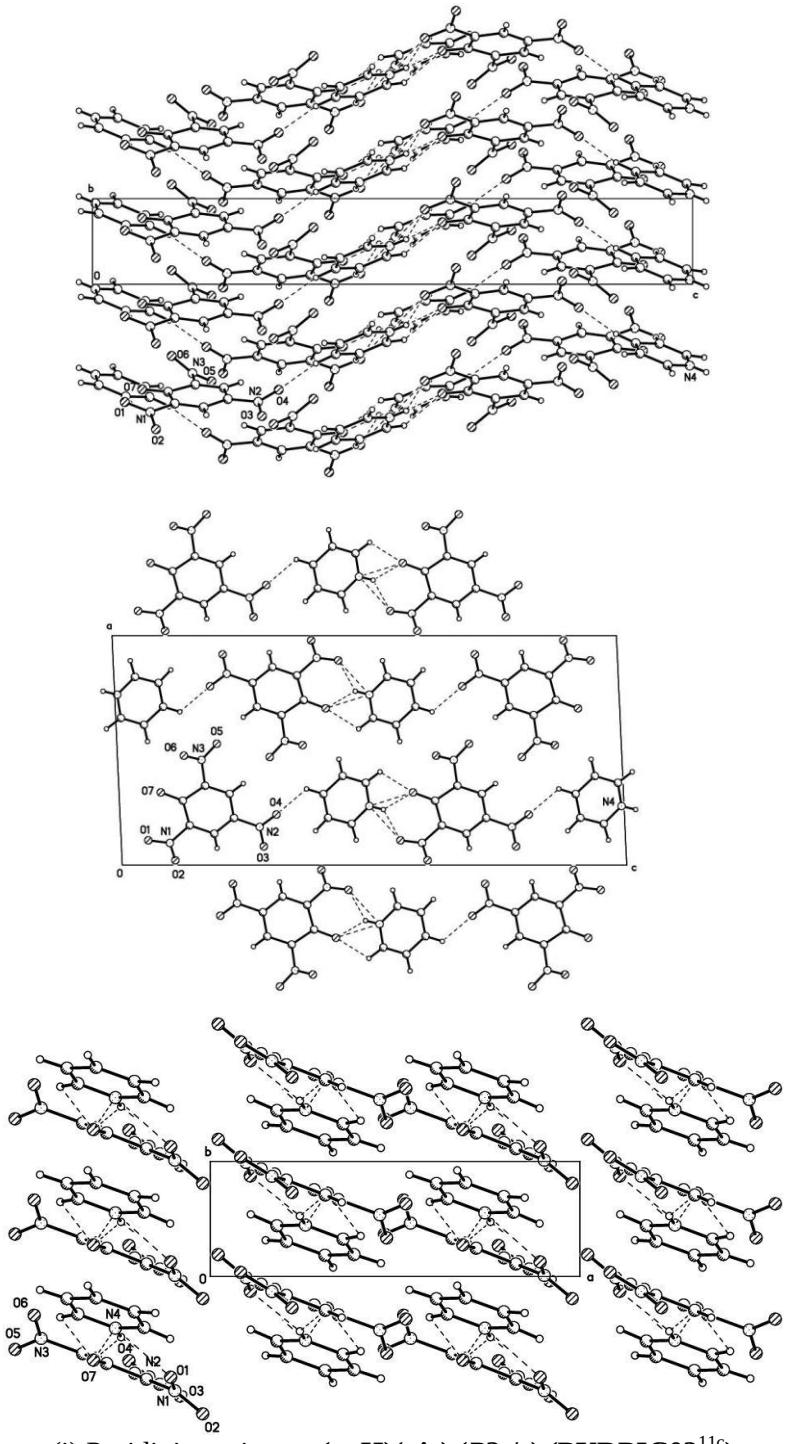
(quinH)(pic) (UBEGAL[8])	0	2.6	1.5	6.6	3.6	8.5	57.0	0.6	13.3	6.4
(iqH)(pic) (JUSRUK[28])	0	3.5	2.4	2.0	6.3	4.5	52.4	10.1	5.2	13.4
(2mqH)(pic) (VATTER[29])	0.4	1.7	0.2	6.5	4.6	8.9	55.7	3.7	8.4	9.7
(ohqH)(pic) (this work)	0	1.4	4.1	3.6	8.0	2.8	50.8	7.1	9.7	12.4
(oqpic) (Meisenheimer precursor) **(JOKTOS[30])**	n/a	-	-	-	-	-	-	-	-	-
(omppic) (Meisenheimer compound) **(JOKTIM[30])**	n/a	-	-	-	-	-	-	-	-	-

Proportions of contacts (%) of particular type as evidenced from Hirshfeld surface calculations.

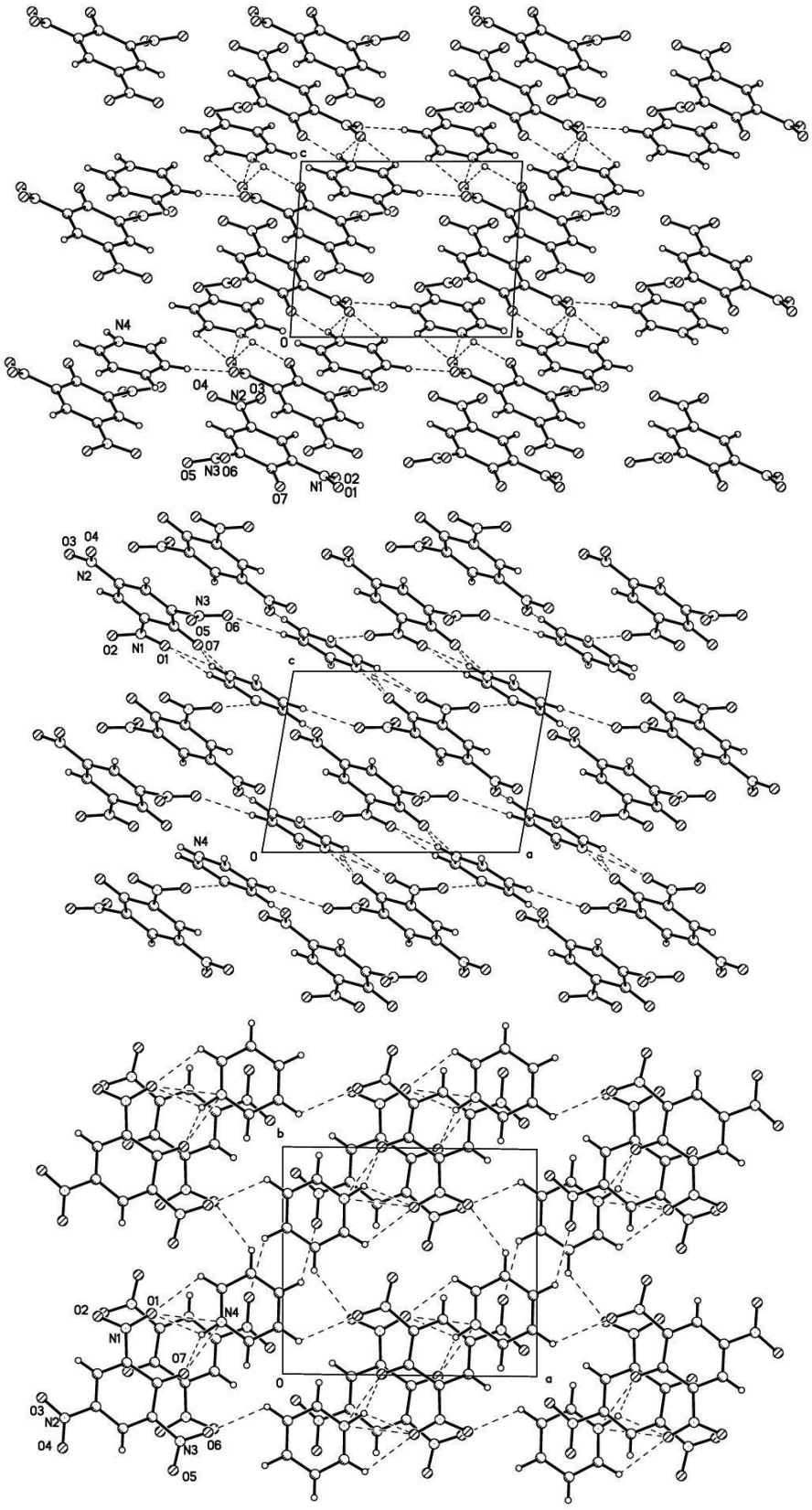
Fig. S1 Unit cell projections for the compounds of Table 1 (projections down *a*, *b*, *c*, respectively)

(α) Picric acid – see main text

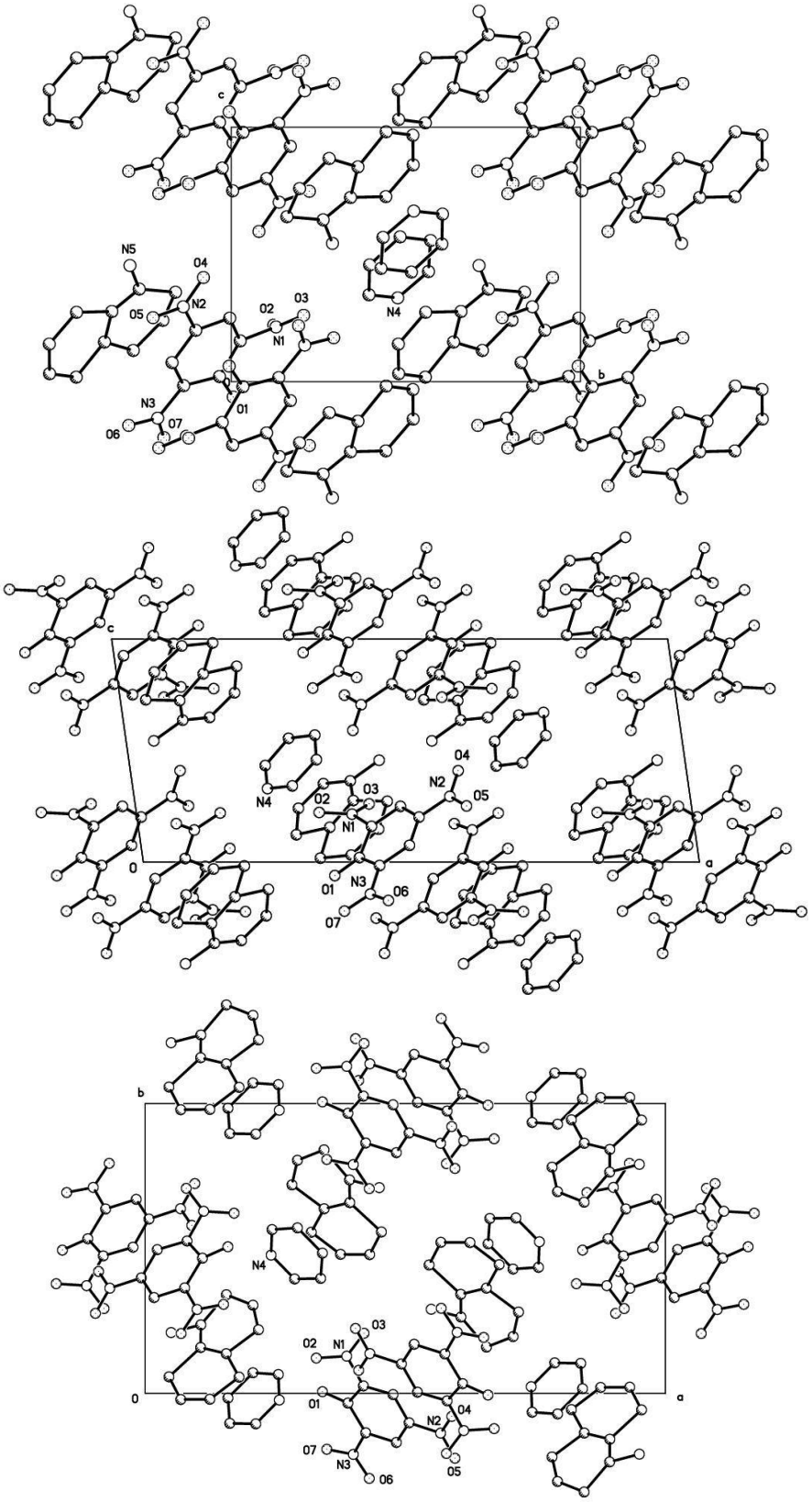
(β) Pyridinium and 2-substituted pyridinium (substituents other than pyridyl) picrates

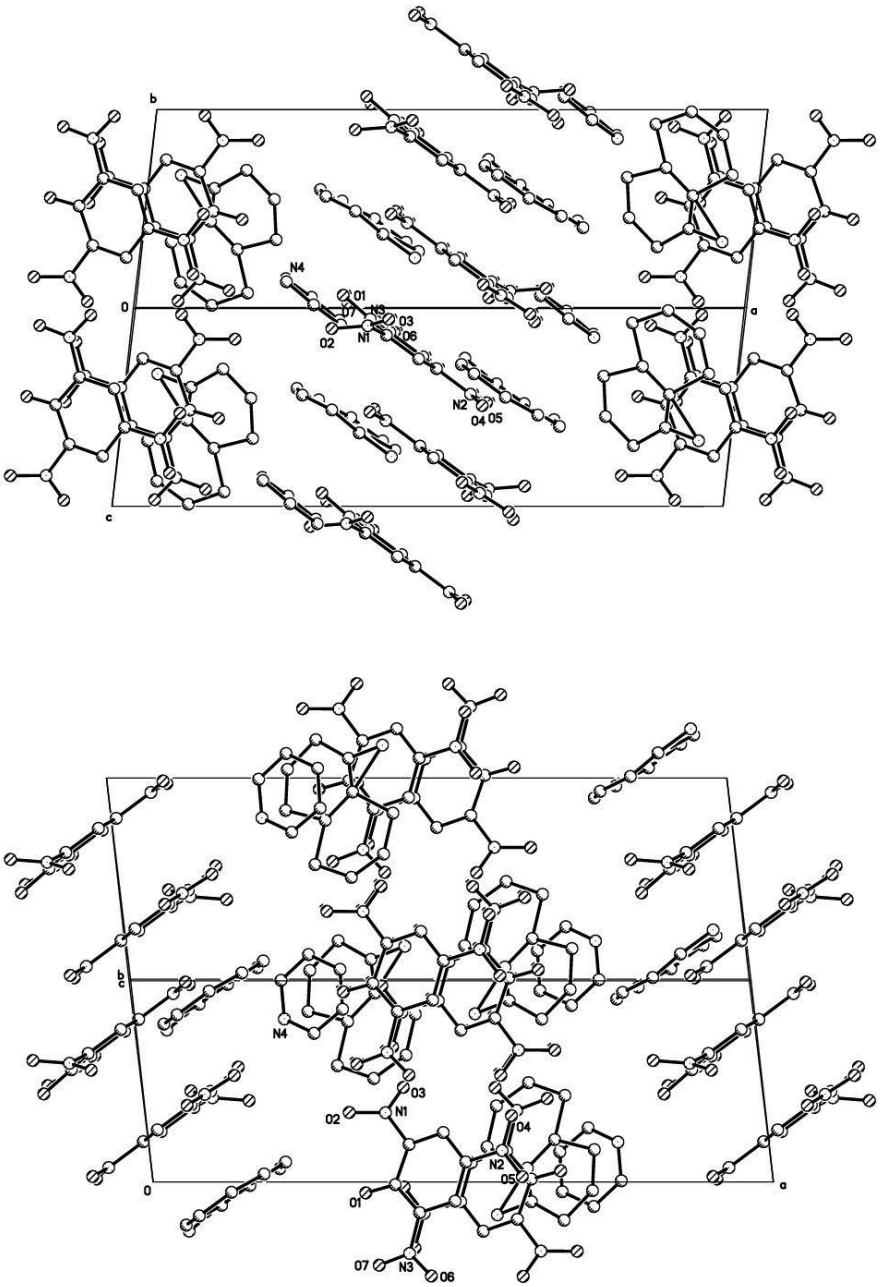


(i) Pyridinium picrate, **(pyH)(pic) (*P*2$_1$/*c*) (PYRPIC02**[11c]**)**

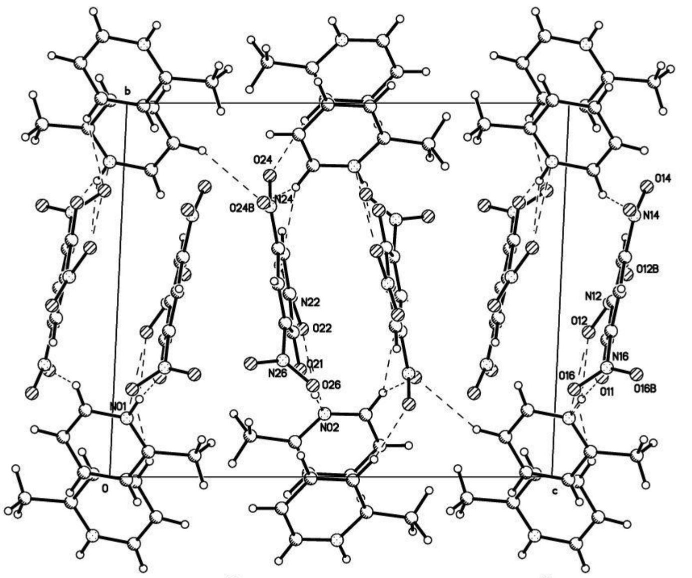


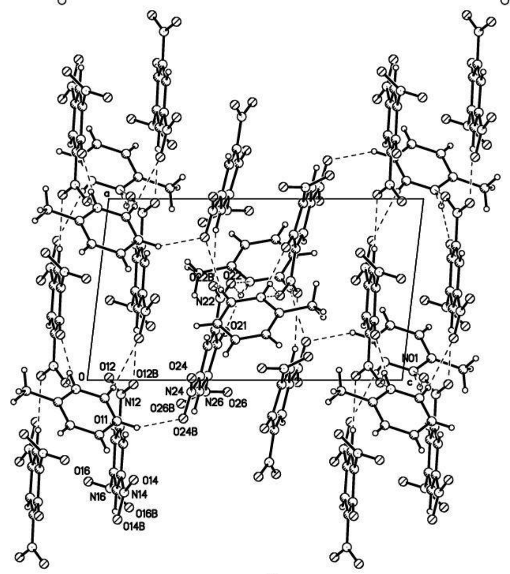
(ii) Pyridinium picrate, **(pyH)(pic)** ($P\bar{1}$) **(PYRPIC03**[11c]**)**

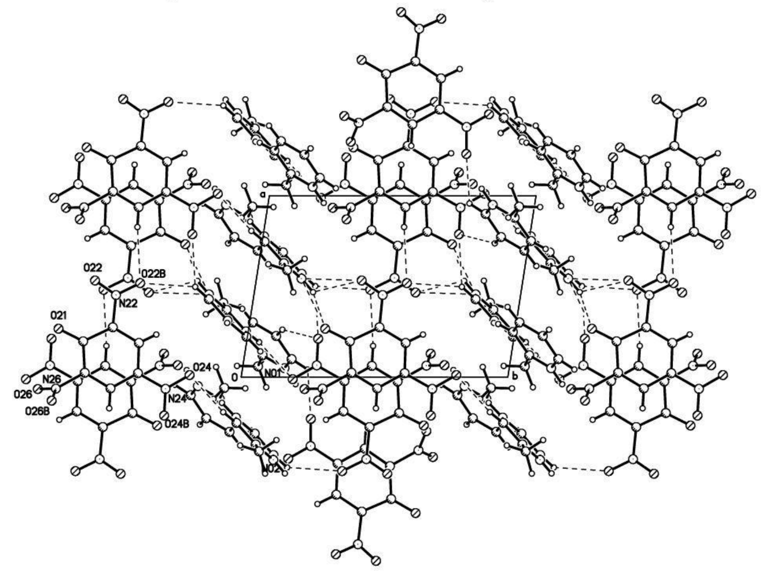

c
N5
04
N2
05
02
03
N1
N4
b
N3
01
07
06
c
N4
02
03
04
N2
05
N1
0
01
N3
06
07
a
b
N4
02
N1
03
0
01
N2
04
07
N3
06
05
a

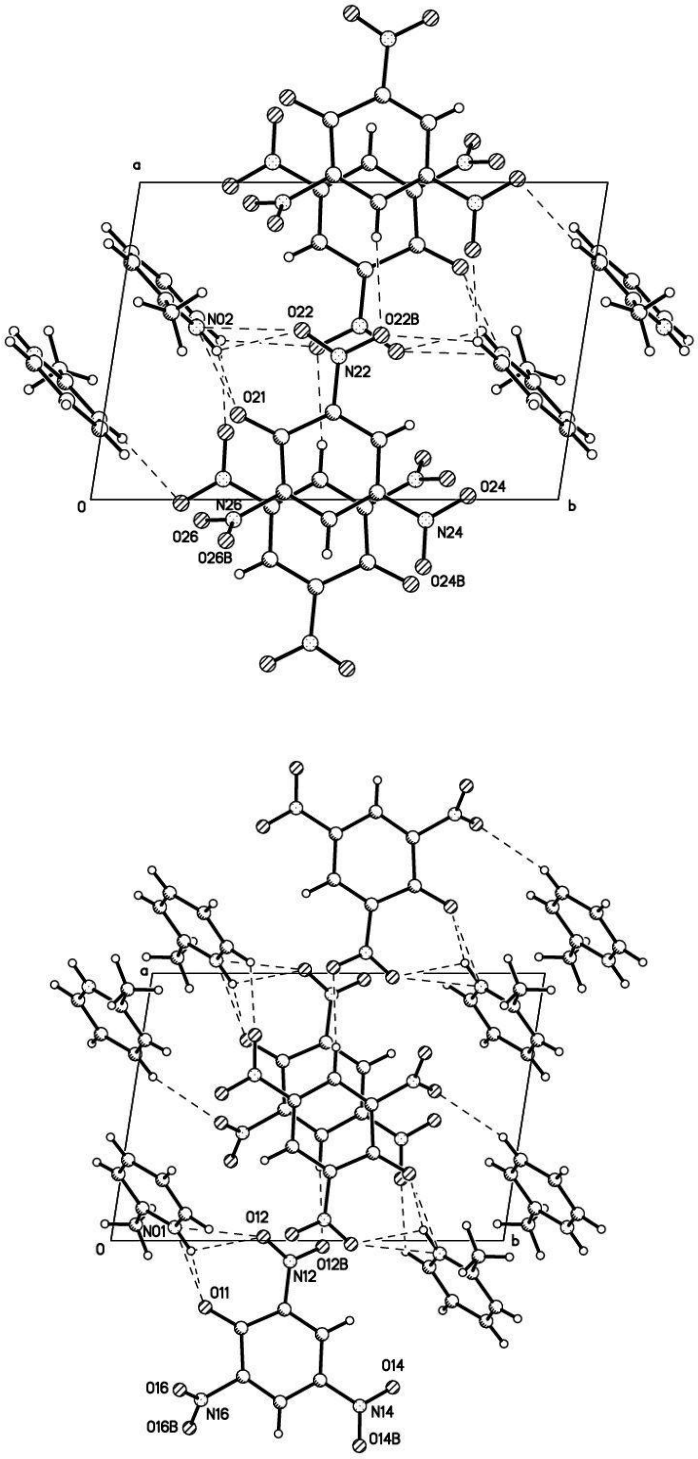


(iii) Pyridinium picrate : 1-naphthylamine (1:1), **(pyH)(pic)(·naph) (*P*2$_1$/*a*) (PYNPCR[20])**; additional projections are shown down (011) and (01$\bar{1}$), showing the parallel packing of the planar entities

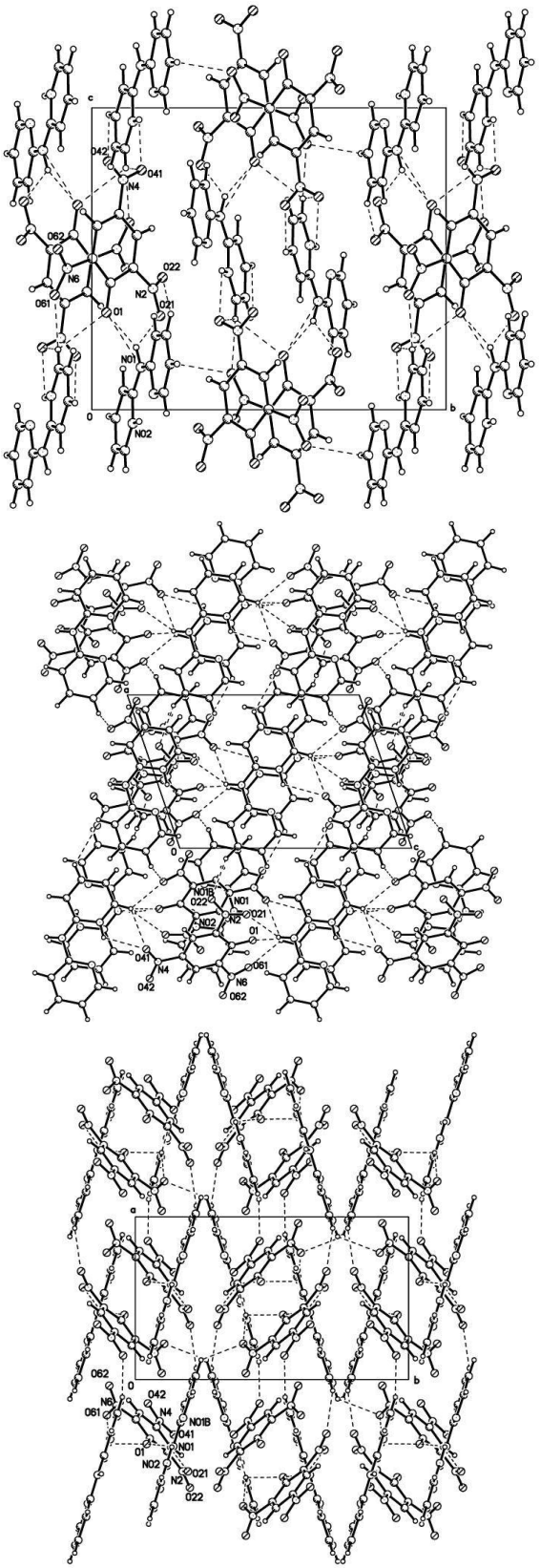

b
O24
O24B
N24
O14
N14
O12B
N12
O12
N22
O22
O21
N26
O26
N16
O16
O11
O16B
N01
N02
0
c


O22B
N22
O21
O12
O12B
O24
N24
N26
O26
O26B
O24B
N12
O11
O16
N16
O14
N14
O16B
O14B
N01
0
c


O22
O22B
N22
O21
N26
O26
O26B
O24
N24
O24B
N01
0
b

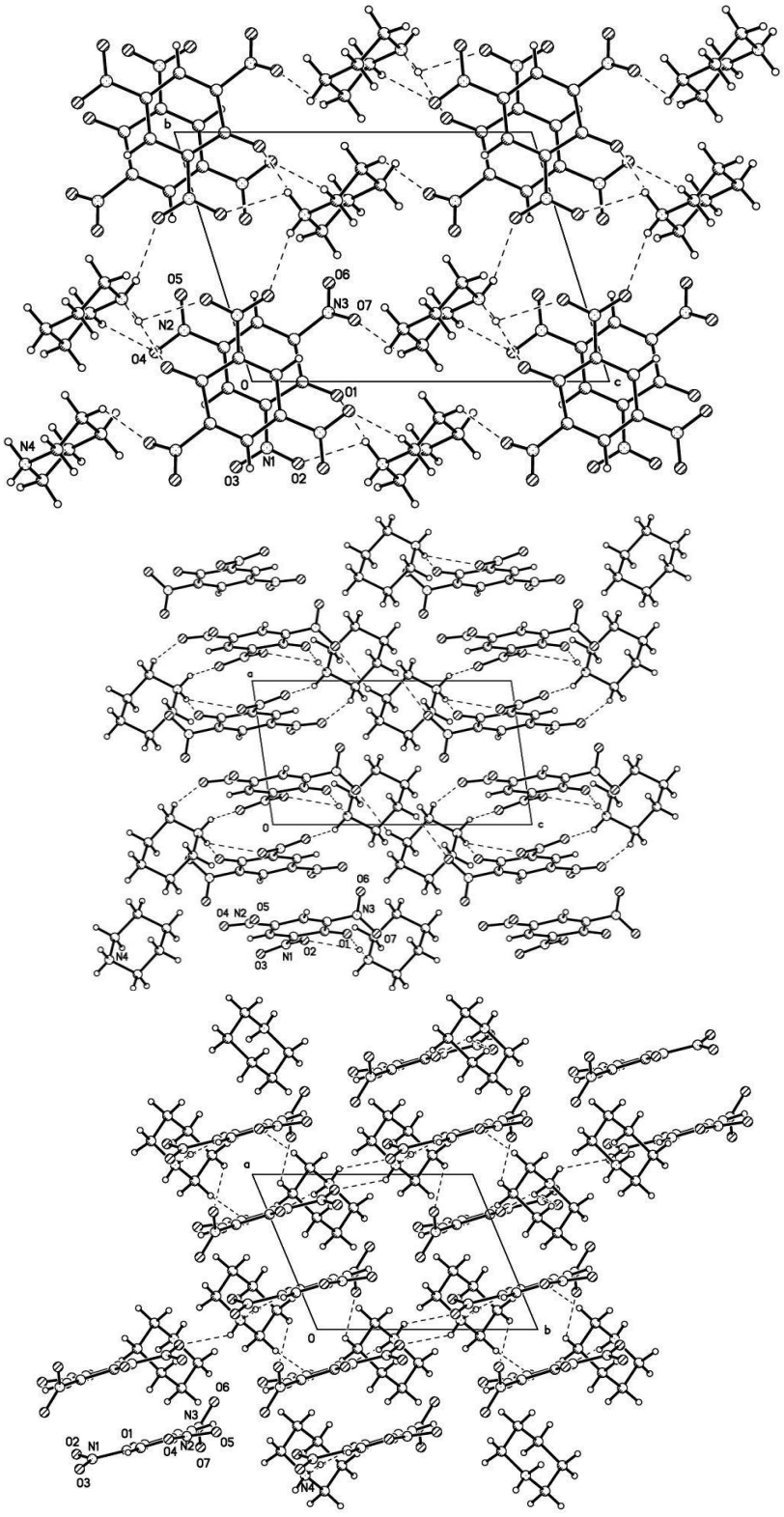


(iv) 2-Methylpyridinium picrate, **(2mpH)(pic)** (x2) ($P\bar{1}$) (this work); additional projections are shown down *c*, for the sections of the unit cell bounded by *z* = –0.25-0.75 and 0.25-0.75, made up of molecules 1 and 2, respectively

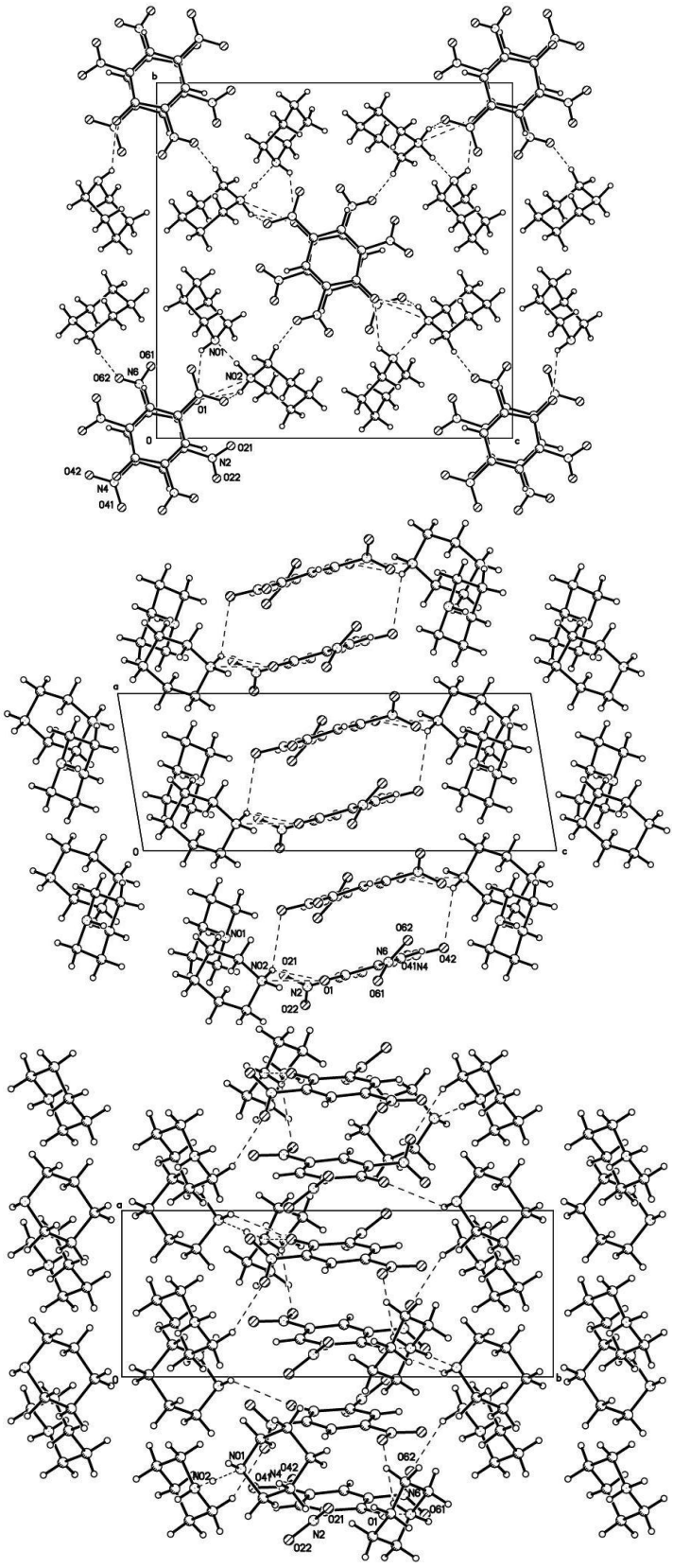


(v) (2-Pyridinium)(2-pyridyl)amine picrate, **(dpaH)(pic) (*P*2$_1$/*c*)** (this work)

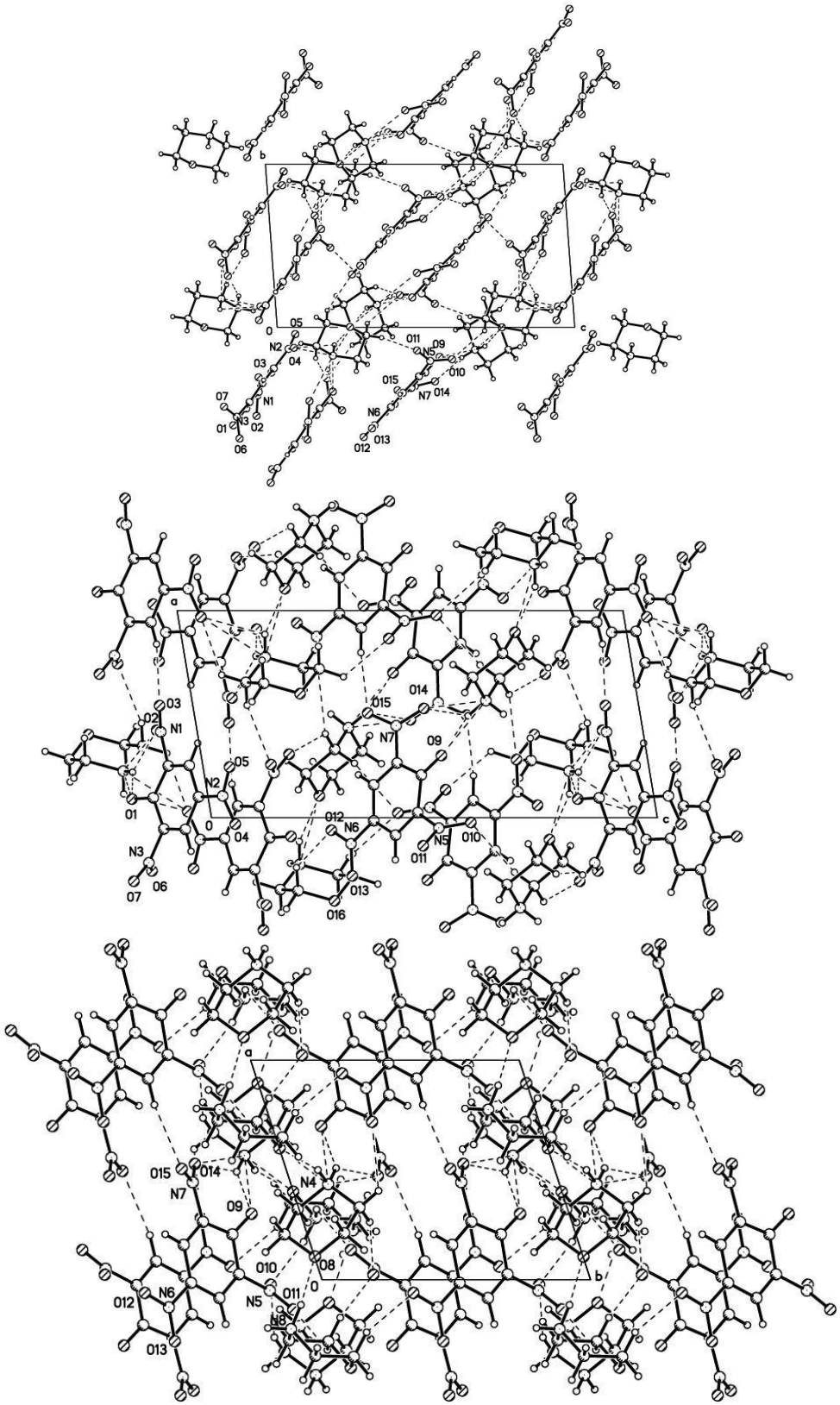
(γ) Aza-alicyclic base salts – Saturated derivatives of pyridinium picrate



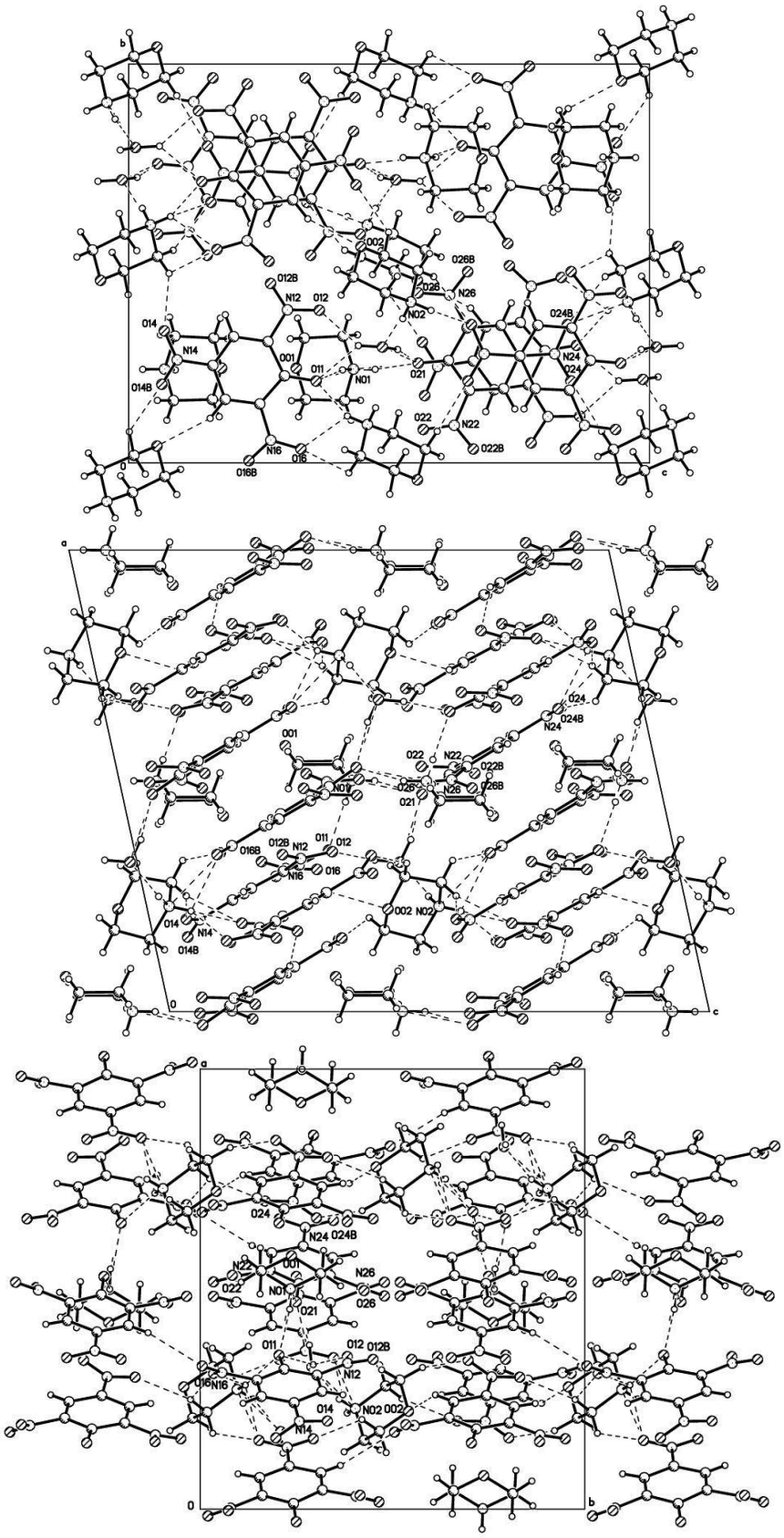
(i) Piperidinium picrate, **(pipH)(pic)** ($P\bar{1}$) **(VAZJAI**[21]**)**



(ii) Piperidinium picrate monopiperidine solvate, **(pipH)(pic)(·pip) (*P*2$_1$/*n*)** (this work)

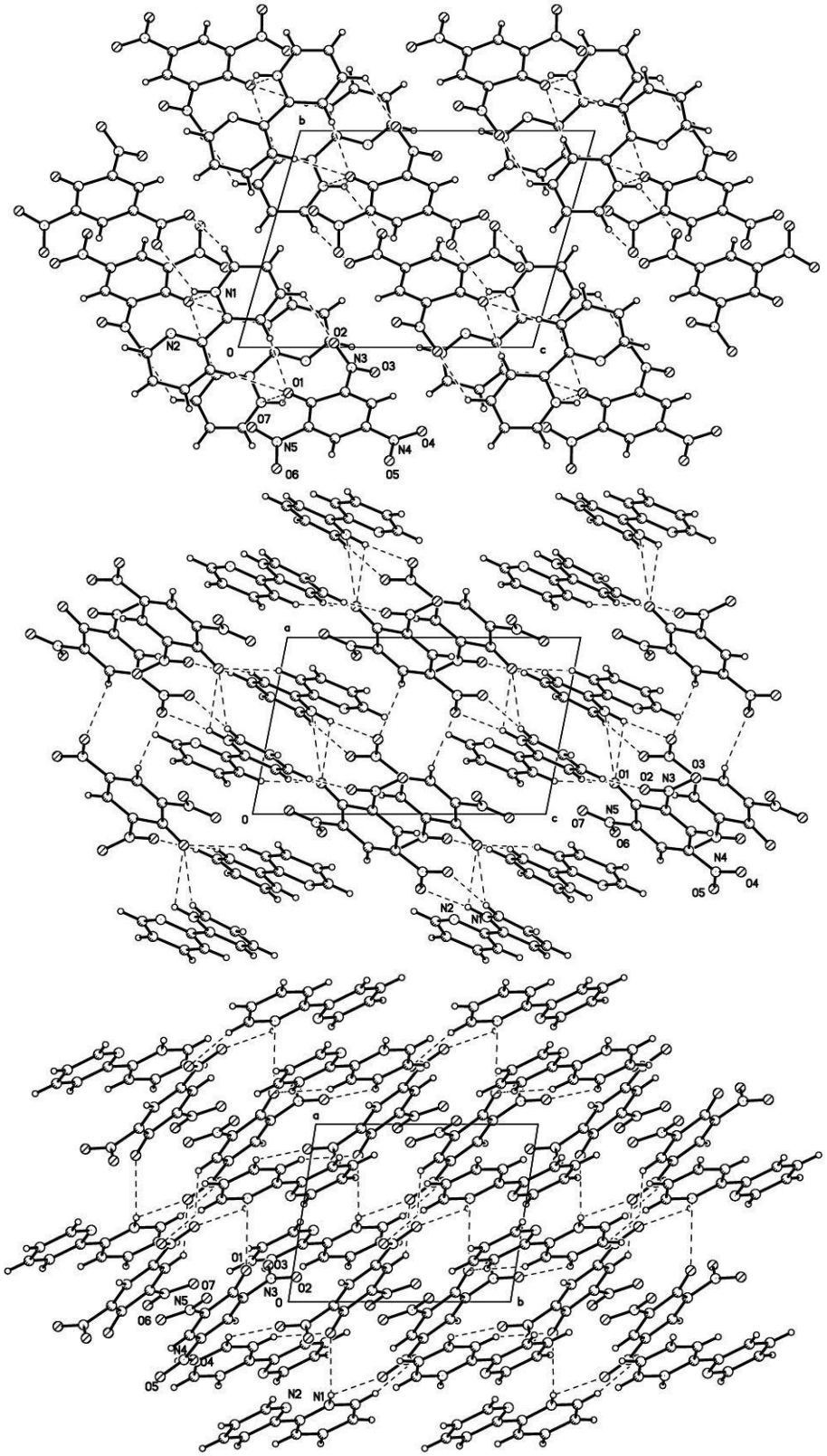


(iii) Morpholinium picrate, **(morH)(pic)** (x2) ($P\bar{1}$) **(KOMTUC**[22a]**)**

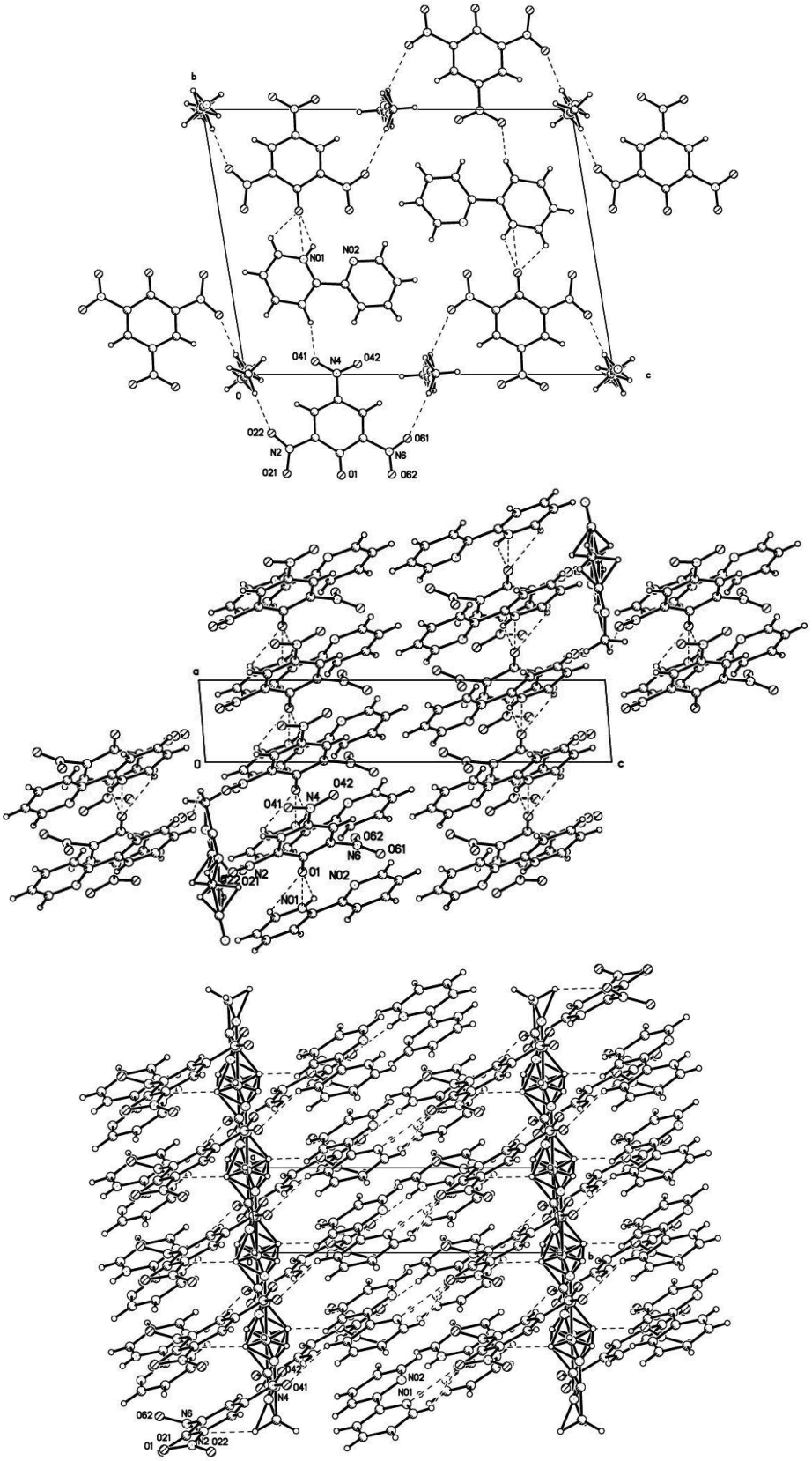


(iv) Morpholinium picrate hemihydrate, **2[(morH)(pic)](·H_2O) (*C*2/*c*)** (this work)

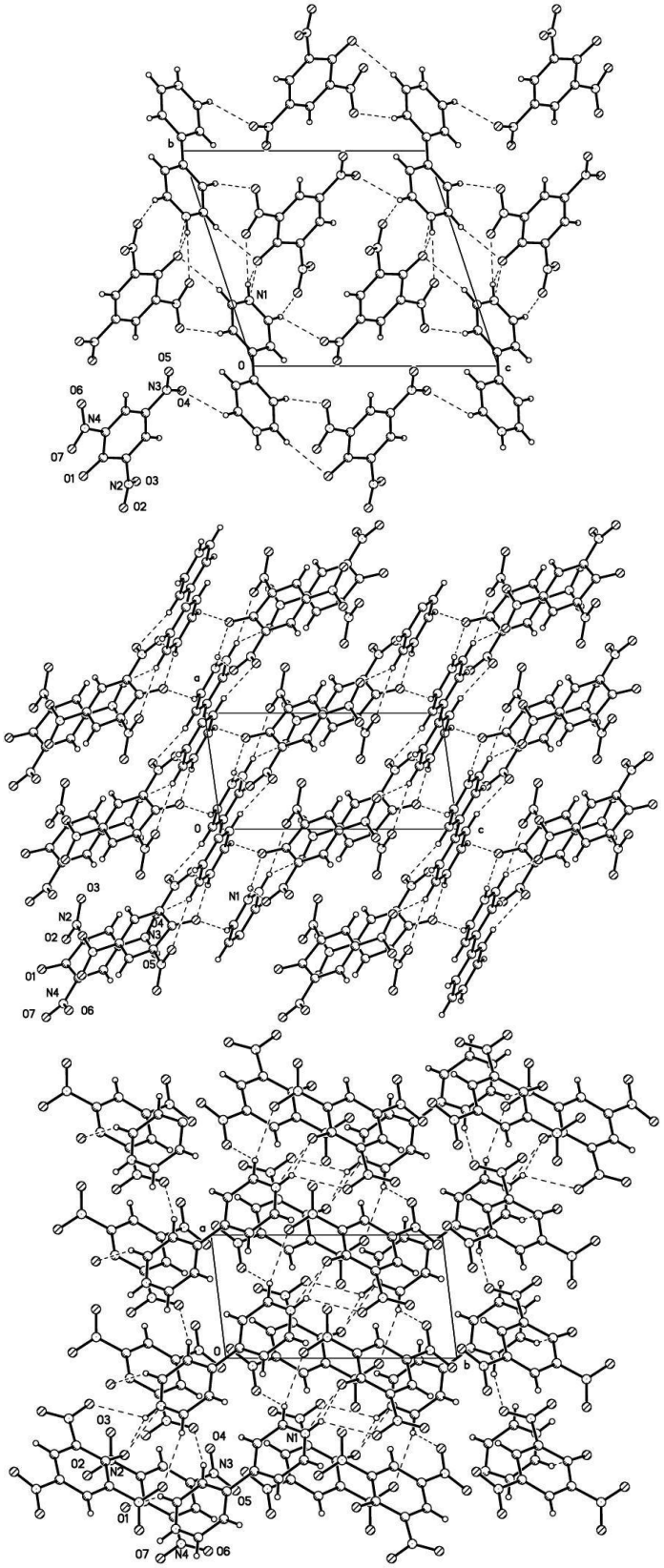
(δ) Bipyridinium picrates and derivative systems



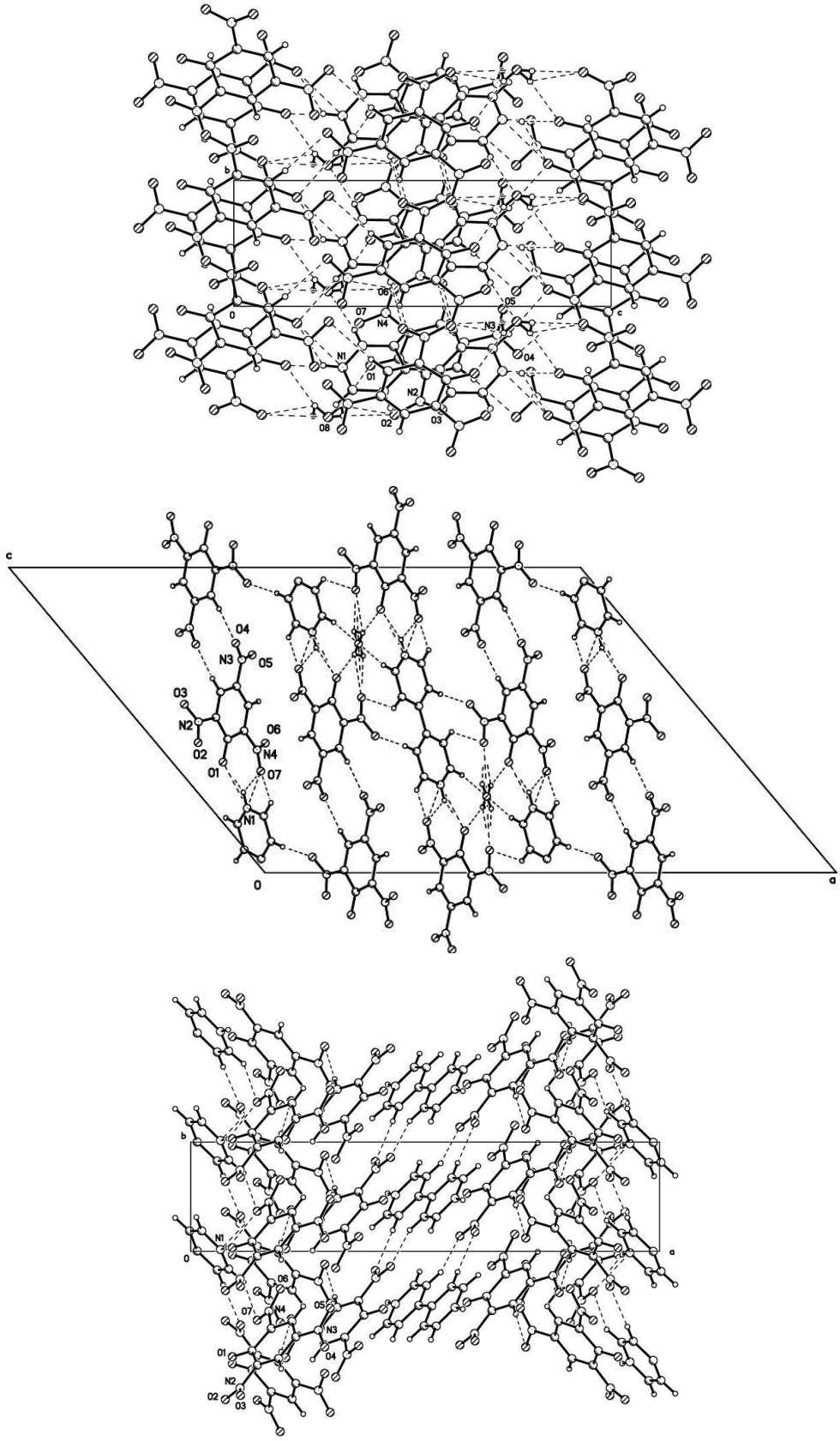
(i) 2,2'-BipyridylH^{+} picrate, **(bpyH)(pic)** **(** $P\bar{1}$ **)** **(UCOFUO[23])**



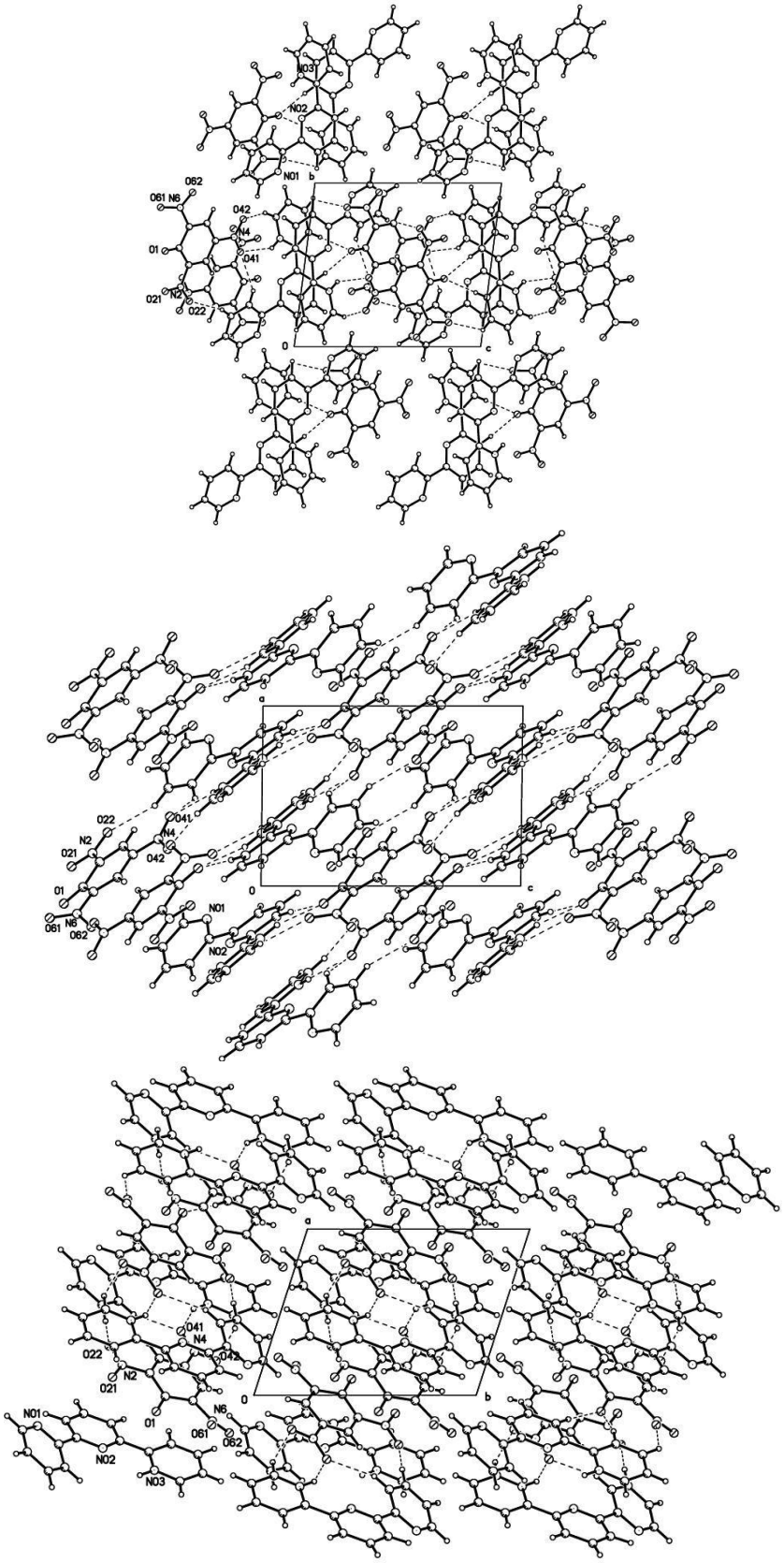
(ii) 2,2'-BipyridylH^{+} picrate acetonitrile monosolvate, **(bpyH)(pic)(·MeCN)** (x2) **(*P* $\bar{1}$)** (this work)



(iii) 4,4'-Bipyridyl H_2^{2+} bis(picrate), **(bpy'H$_2$)(pic)$_2$** (x0.5) **(*P* $\bar{1}$)** **(KAMPIY[24])**

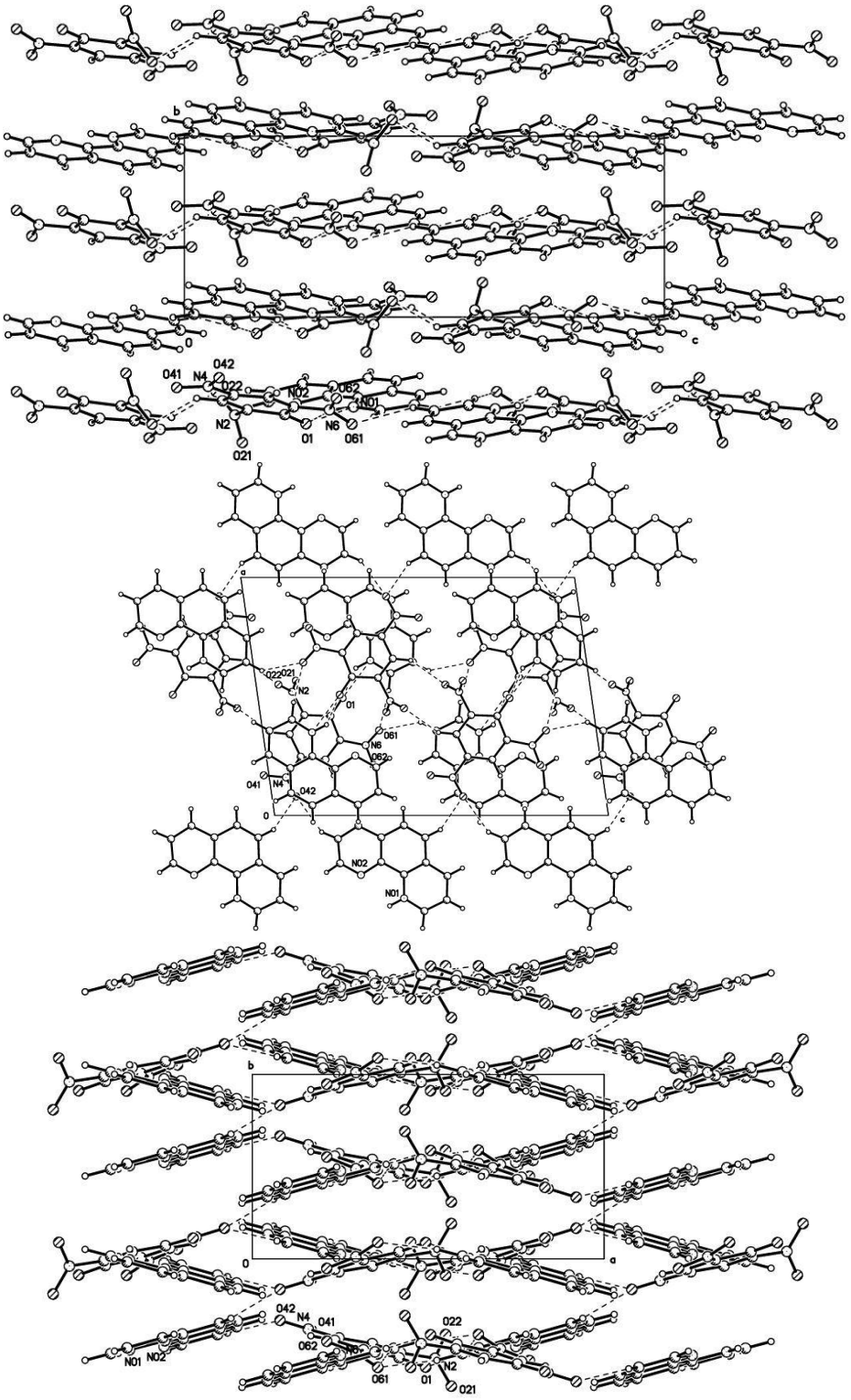


(iv) 4,4'-Bipyridyl H_2^{2+} bis(picrate) monohydrate, **(bpy'H_2)(pic)$_2$(·H_2O) (*C*2/*c*) (UJOQUF[25])**

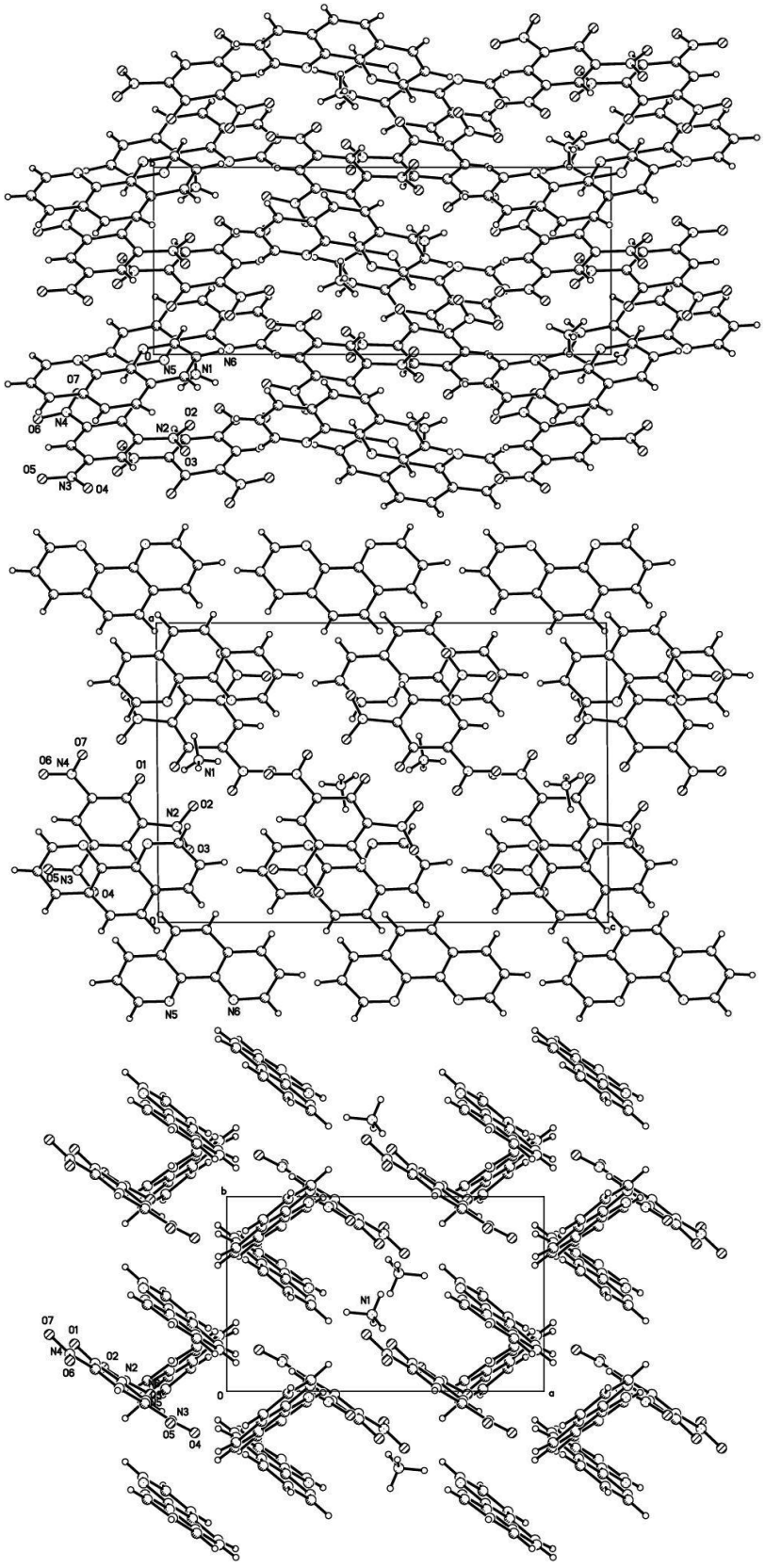


(v) 2,2':6',2''-Terpyridinium picrate, **(tpyH)(pic)** ($P\bar{1}$) (this work)

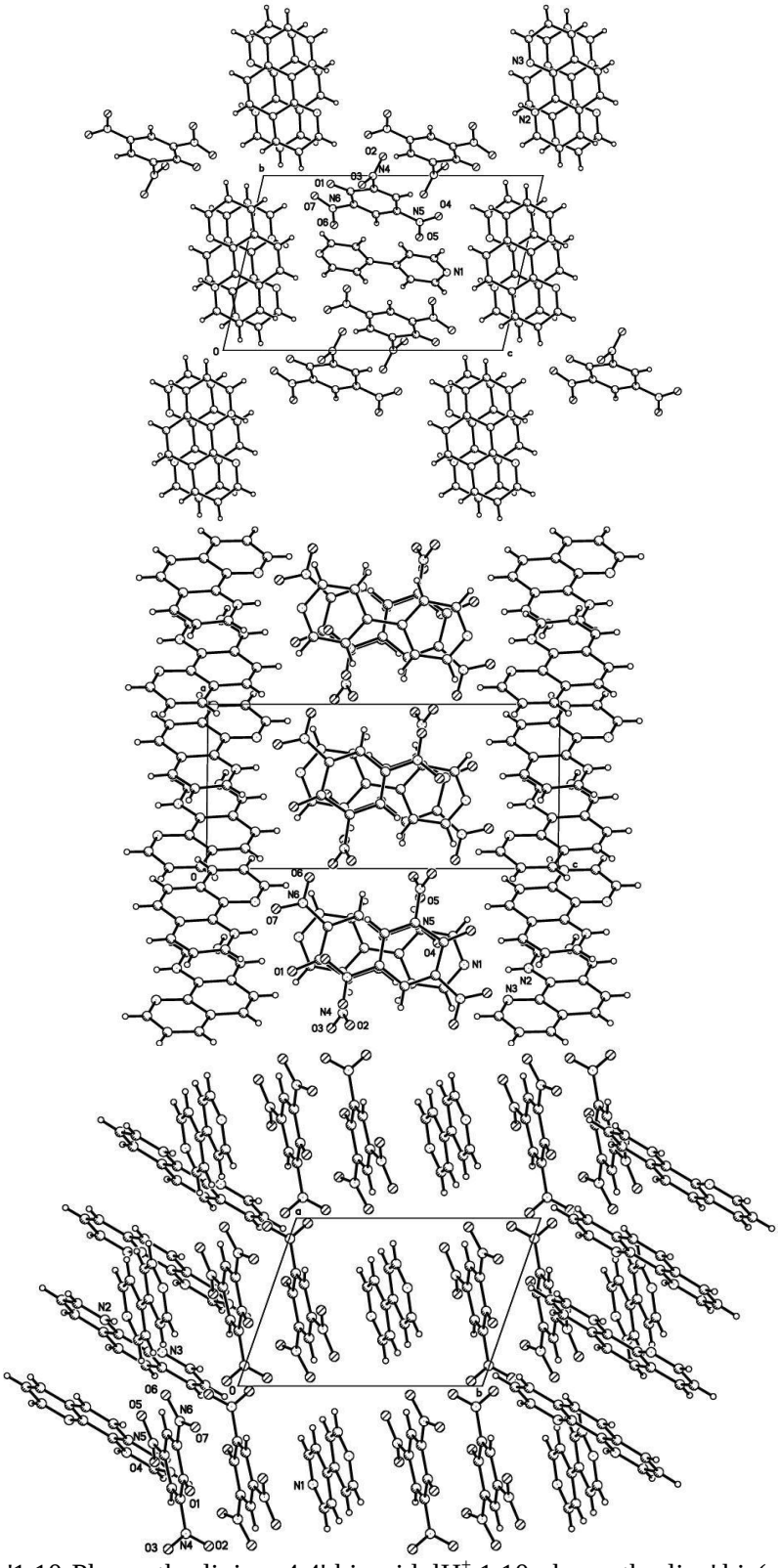
(ε) 1,10-Phenanthrolinium picrate and derivative systems



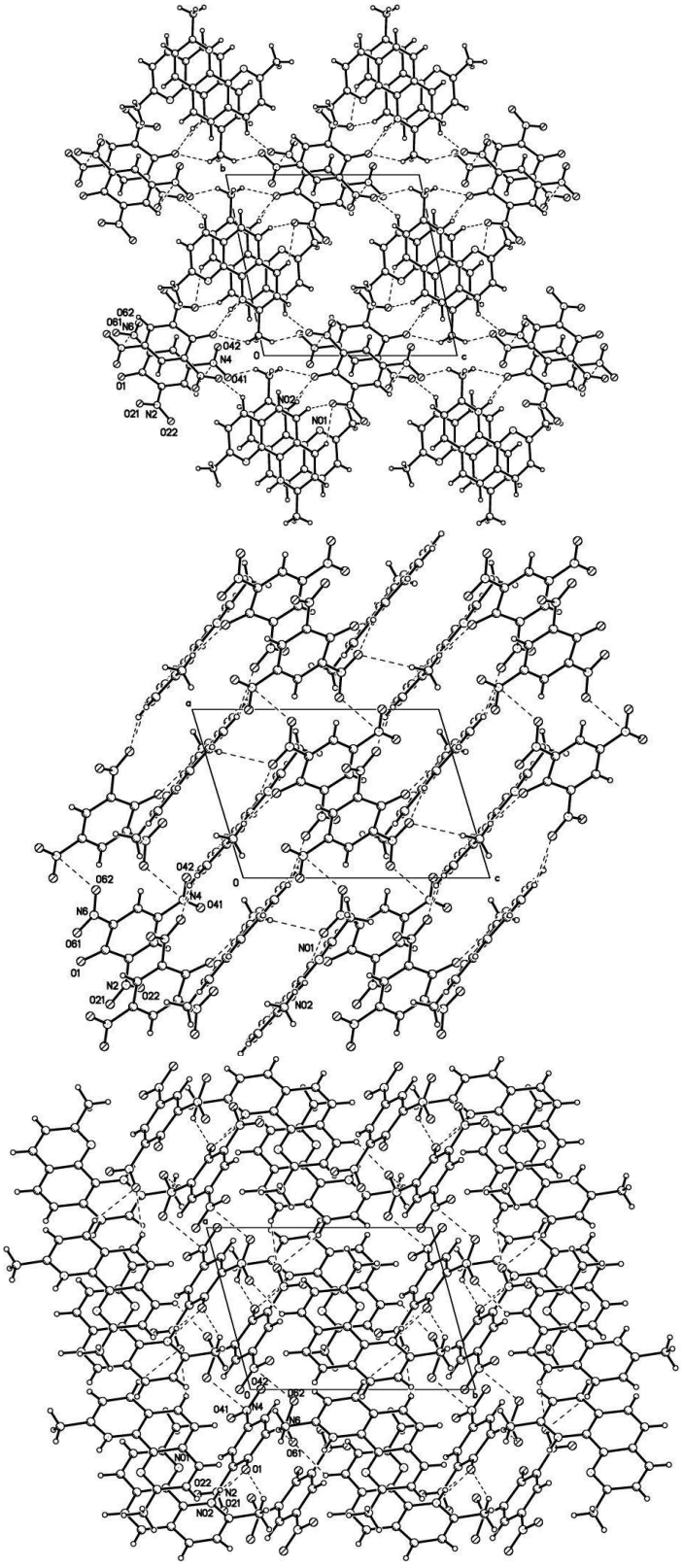
(i) 1,10-Phenanthrolinium picrate, **(phenH)(pic) (*P*2$_1$/*c*)** (this work)



(ii) Ammonium picrate : 1,10-phenanthroline (1:1), **(NH_4)(pic)(·phen) (*P*2_1/*c*) (AMPCPL**[26a]**)**

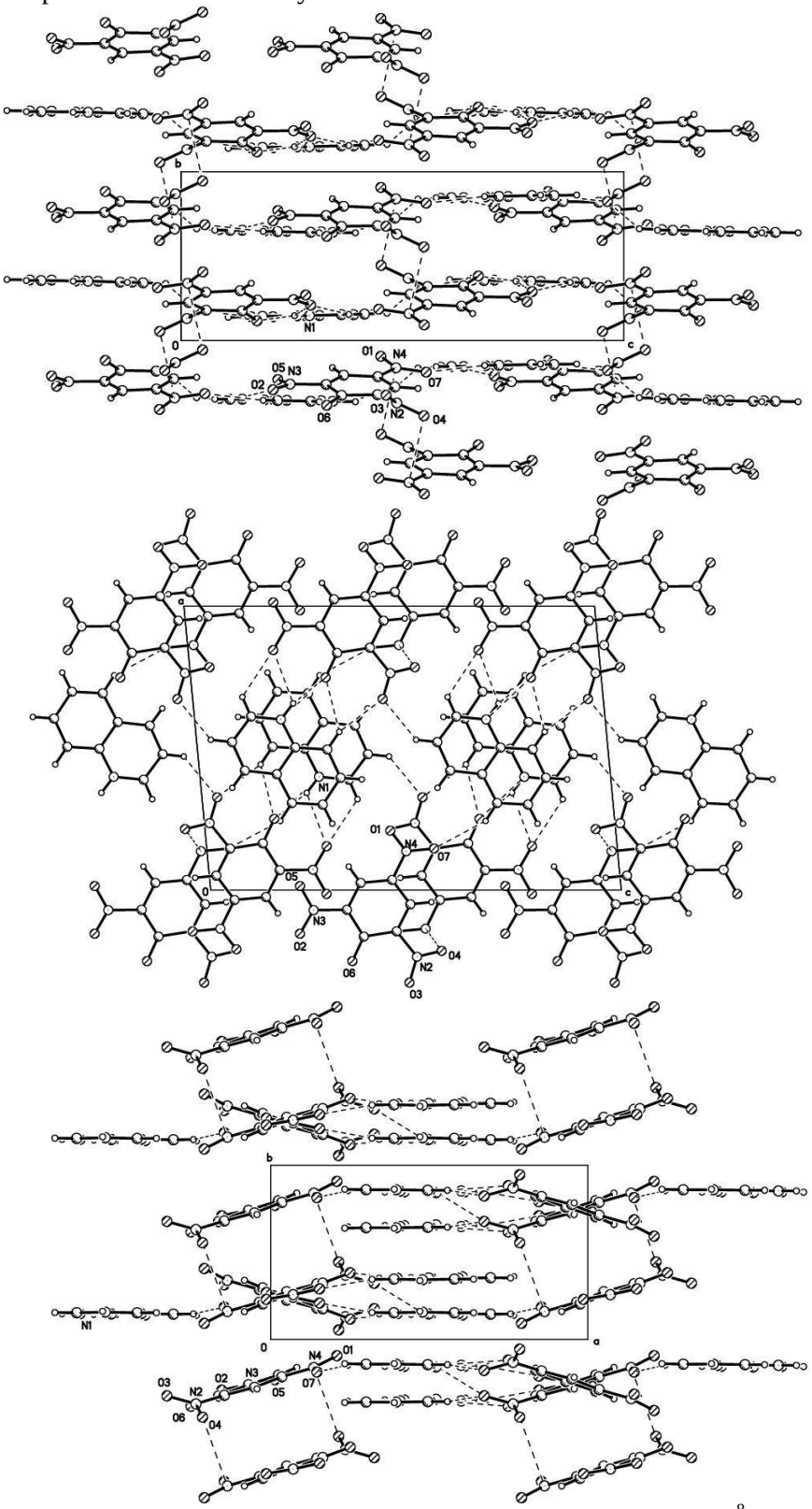


(iii) '1,10-Phenanthrolinium 4,4'-bipyridylH$^+$ 1,10-phenanthroline' bis(picrate), '**[(phenH)(bpy'H)(phen)](pic)$_2$**' (x0.5) **(*P* $\bar{1}$) (INOSUZ[27])**

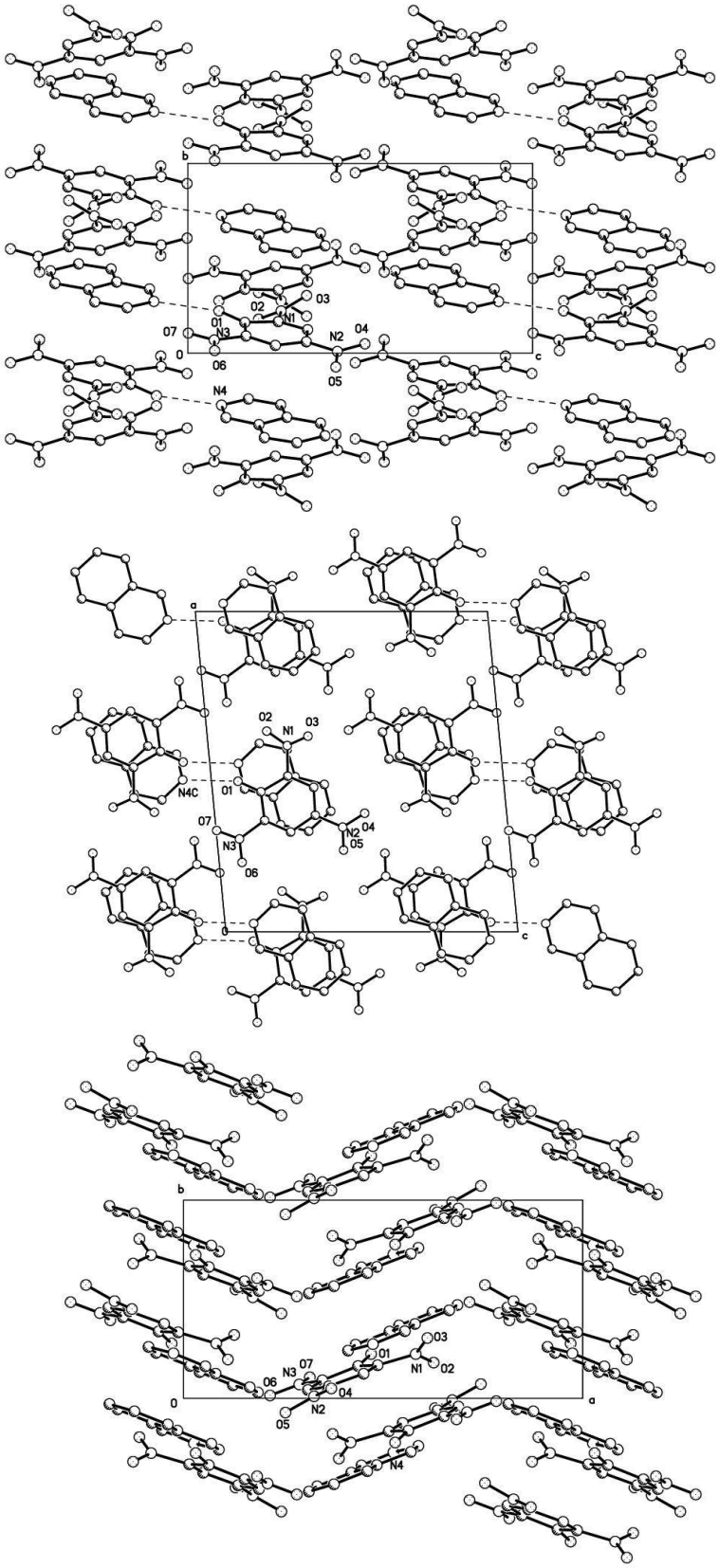


(iv) 2,9-Dimethyl-1,10-phenanthrolinium picrate, **(dmpH)(pic)** ($P\bar{1}$) (this work)

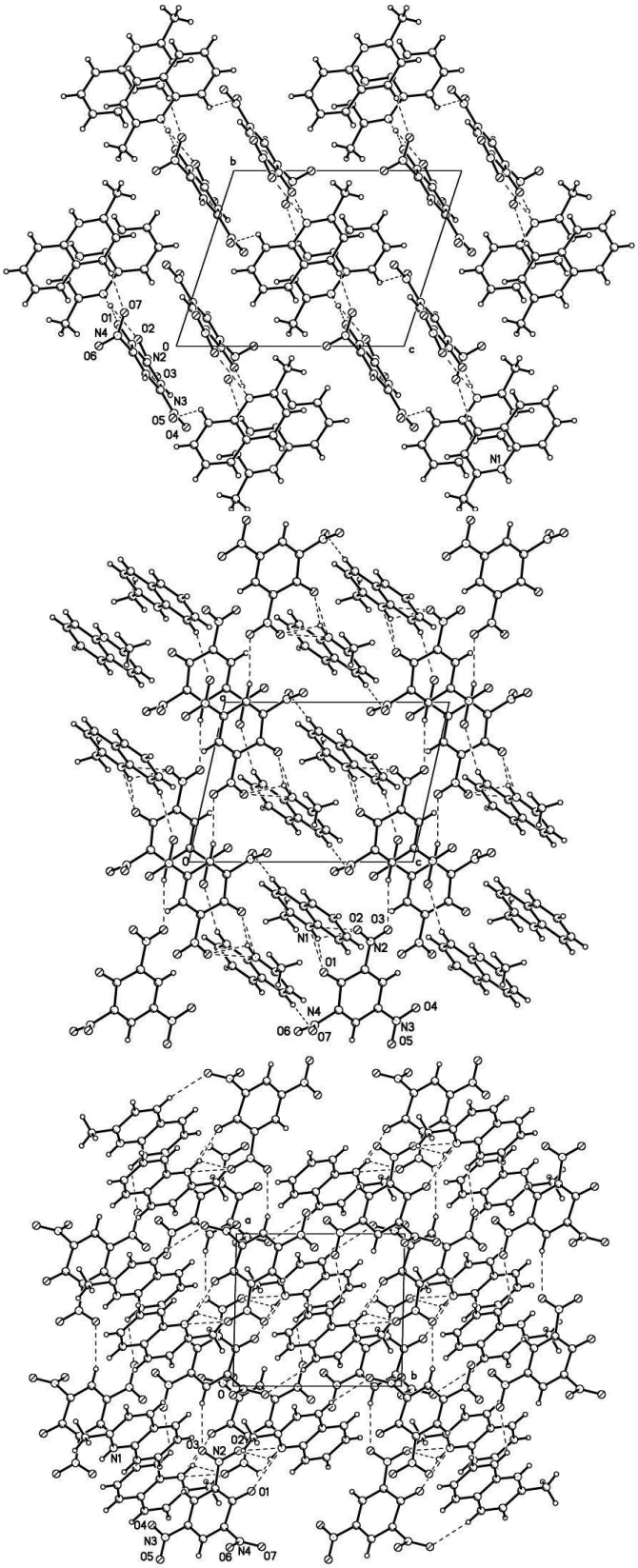
(ζ) Quinolinium picrate and derivative systems



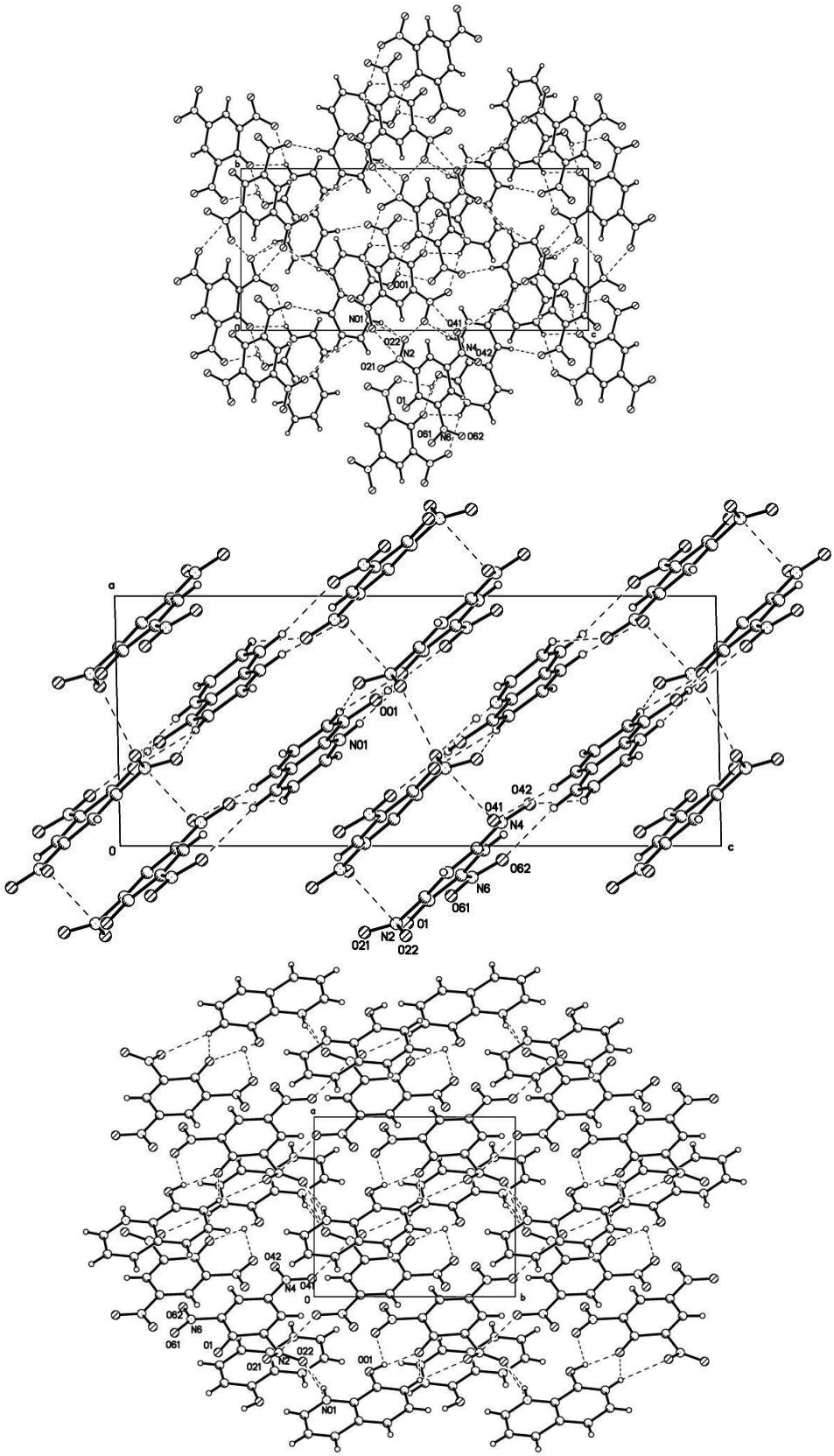
(i) Quinolinium picrate, **(quinH)(pic) (*P*2$_1$/*c*) (UBEGAL**[8]**)**



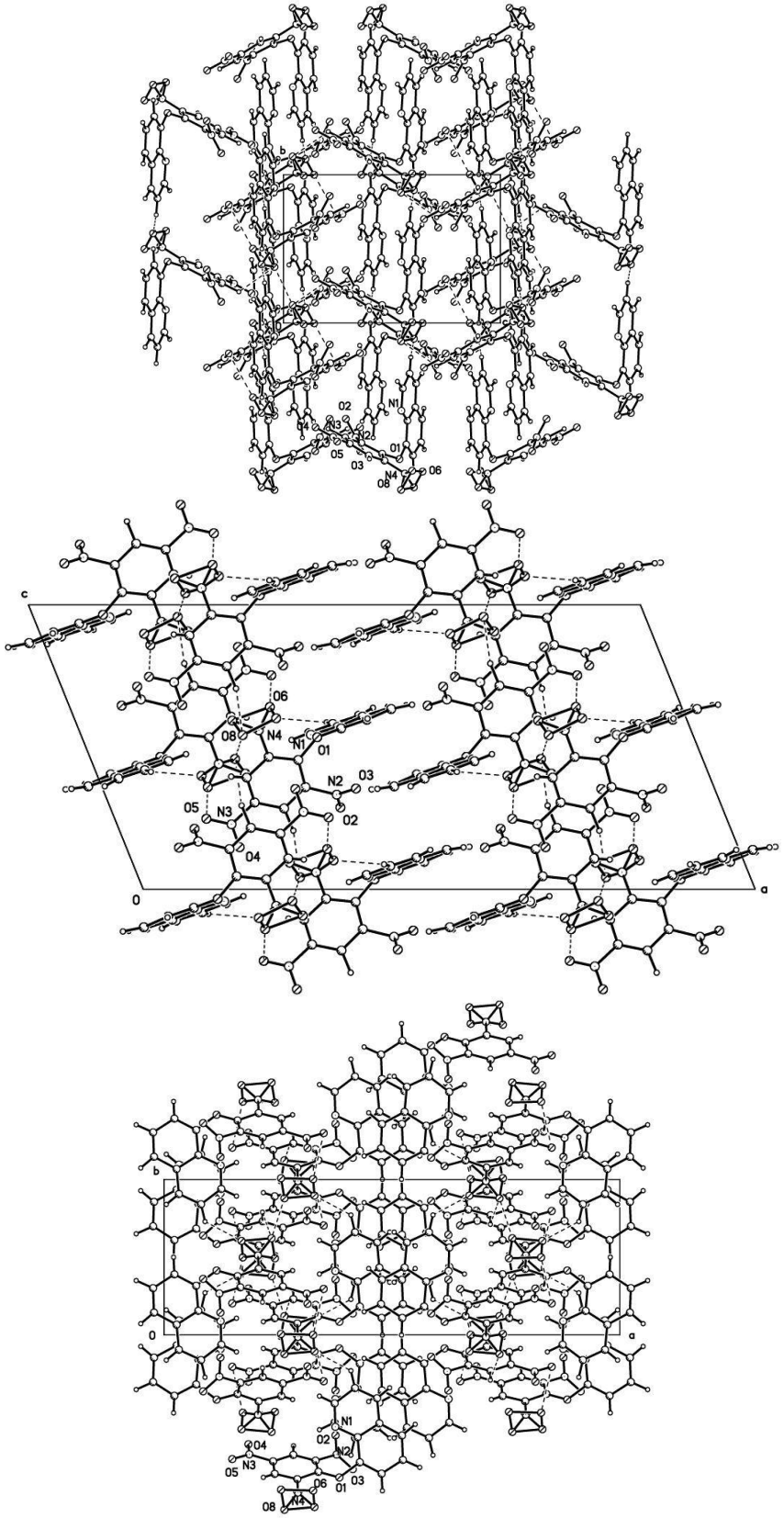
(ii) iso-Quinolinium picrate, **(iqH)(pic) (*P*2$_1$/*a*) (JUSRUK**[28]**)**



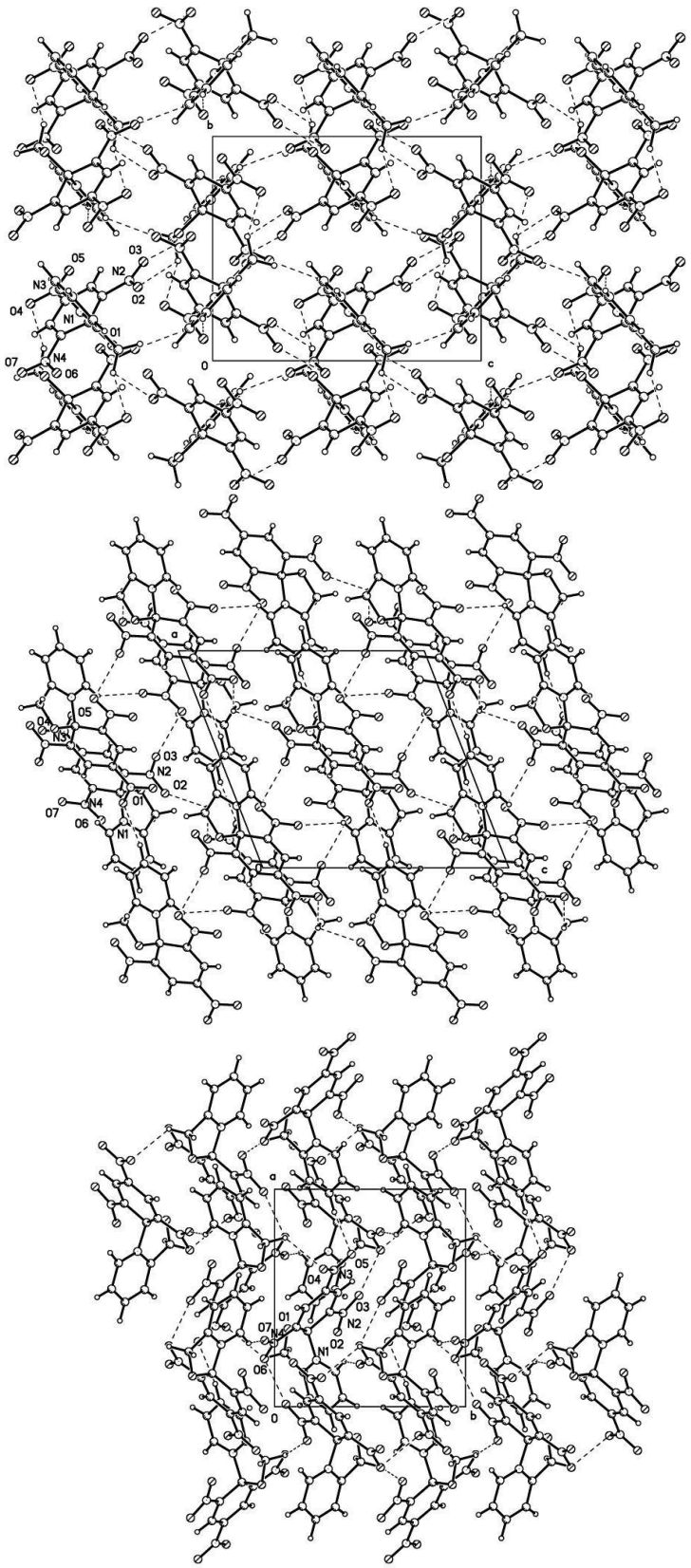
(iii) 2-Methylquinolinium picrate, **(2mqH)(pic)** ($P\bar{1}$) **(VATTER**[29]**)**



(iv) 8-Hydroxyquinolinium picrate, **(ohqH)(pic) (*P*2$_1$/*c*)** (this work)



(v) 8-Hydroxyquinolinium picrate 'Meisenheimer Salt' precursor, **(oqpic) (*C*2/*c*) (JOKTOS[30])**

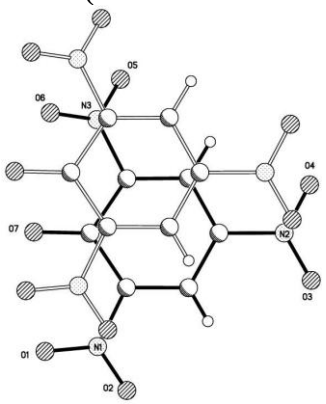


(vi) 2-Hydroxymethylpyridine 'Meisenheimer Salt', **(omppic) (*P*2$_1$/*n*) (JOKTIM**[30]**)**

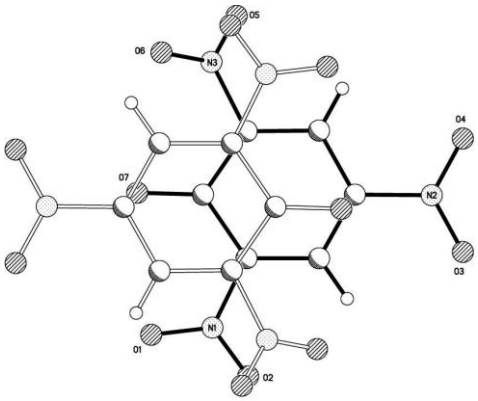
Fig. S2 Aromatic overlap projections for the compounds of Table 1
All overlaps involve at least one picrate anion and are shown in projection normal to the plane of that (solid bonds).

(α) Overlaps in the structure of picric acid **(picH) (PICRAC13**[1g]**)** are peripheral and are not shown.

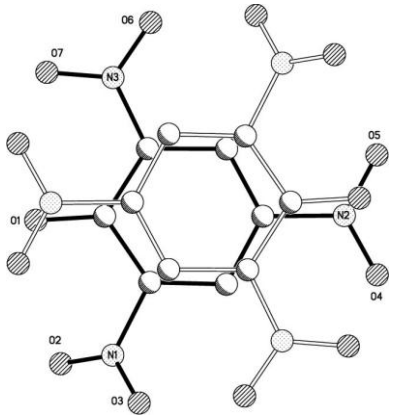
(β) Pyridinium and 2-substituted pyridinium (substituents other than pyridyl) salts



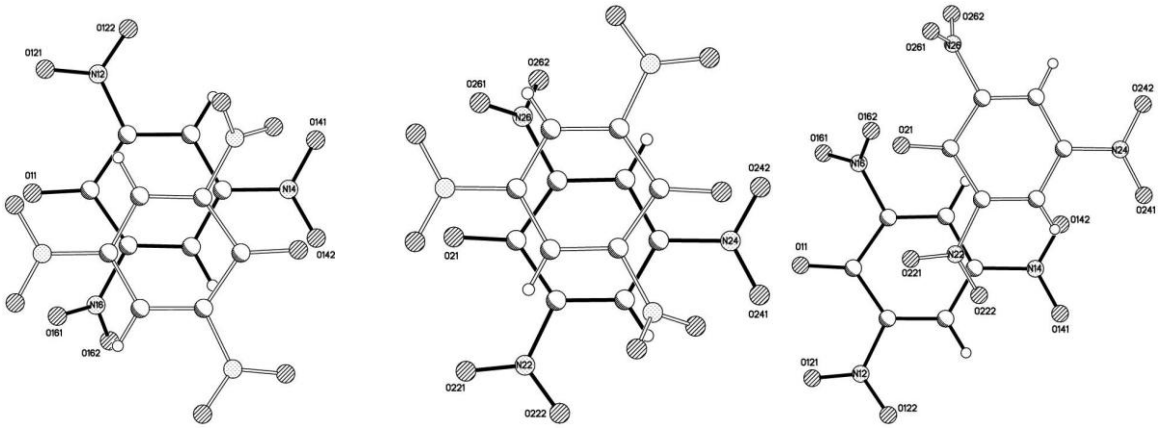
(i) Pyridinium picrate, **(pyH)(pic) (*P*2$_1$/*c*) (PYRPIC02**[11c]**)**, anion (*x*, *y*, 1–*z*) on anion (Table S6(β)(i))



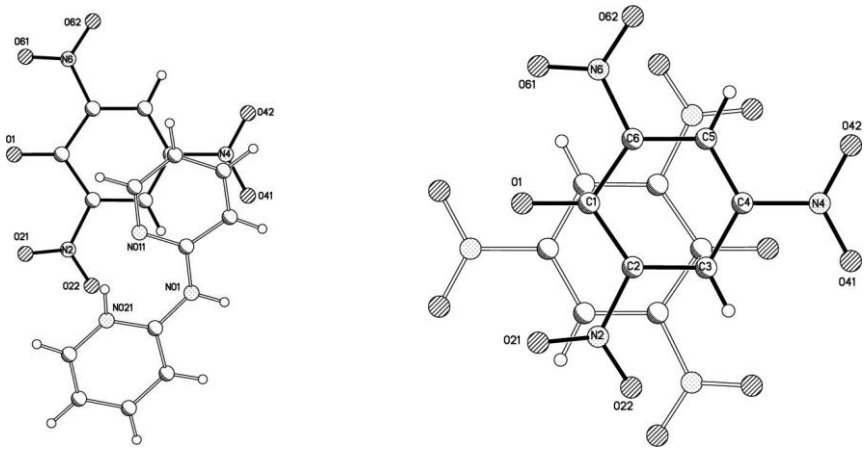
(ii) Pyridinium picrate, **(pyH)(pic) ($P\bar{1}$) (PYRPIC03**[11c]**)**, anion (*x*, 1+*y*, *z*) on anion (Table S6(β)(ii))



(iii) Pyridinium picrate : 1-naphthylamine (1:1), **(pyH)(pic)(·naph)(*P*2$_1$/*a*) (PYNPCR**[20]**)**, anion (1–*x*, 2–*y*, $\bar{z}$) on anion (Table S6(β)(iii))

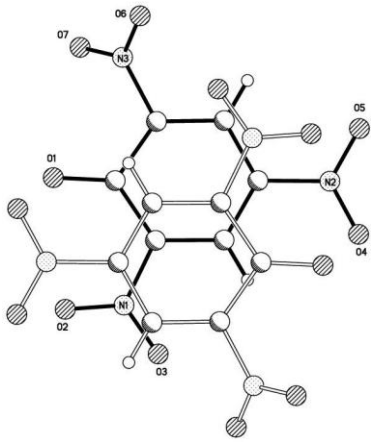


(iv) 2-Methylpyridinium picrate, **(2mpH)(pic)** (x2) (***P*** $\bar{1}$) (this work), all anion on anion: left ($\bar{x}$, 1–*y*, 1–*z*) (anions 1); middle (1–*x*, 1–*y*, $\bar{z}$) (anions 2); right: anion 2 (*x*, *y*, *z*) on anion 1 (Table S6(β)(iv))

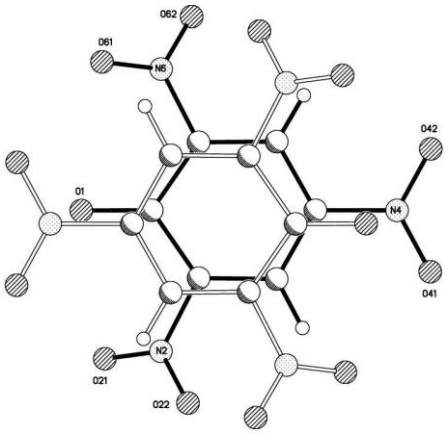


(v) (2-Pyridinium)(2-pyridyl)amine picrate, **(dpaH)(pic)** (***P*2$_1$/*c*)** (this work), left: cation (*x*, ½–*y*, ½+*z*) on anion, right: anion (1–*x*, $\bar{y}$, 1–*z*) on anion (Table S6(β)(v))

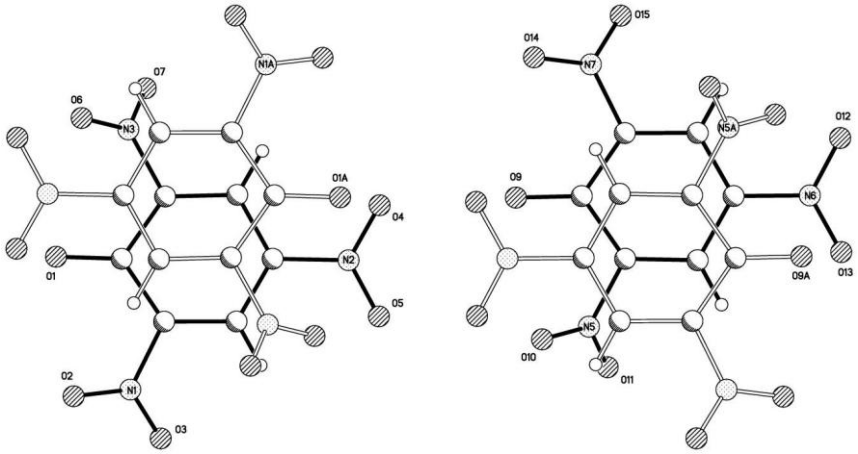
(γ) Aza-alicyclic base salts – Saturated derivatives of pyridinium picrate



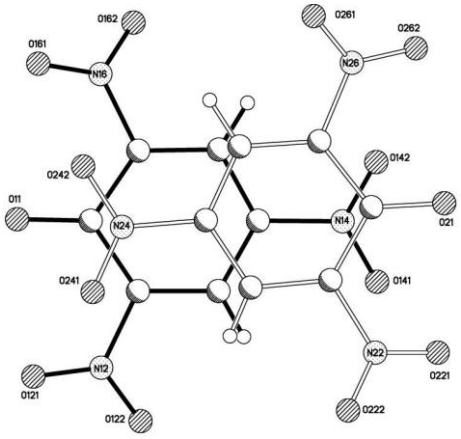
(i) Piperidinium picrate, **(pipH)(pic)** (***P*** $\bar{1}$) **(VAZJAI[21]),** anion (1–*x*, 2–*y*, $\bar{z}$) on anion (Table S6(γ)(i))



(ii) Piperidinium picrate monopiperidine solvate, **(pipH)(pic)(·pip) (*P*2$_1$/*n*)** (this work), anion ($\bar{x}$, $\bar{y}$, $\bar{z}$) on anion (Table S6(γ)(ii))

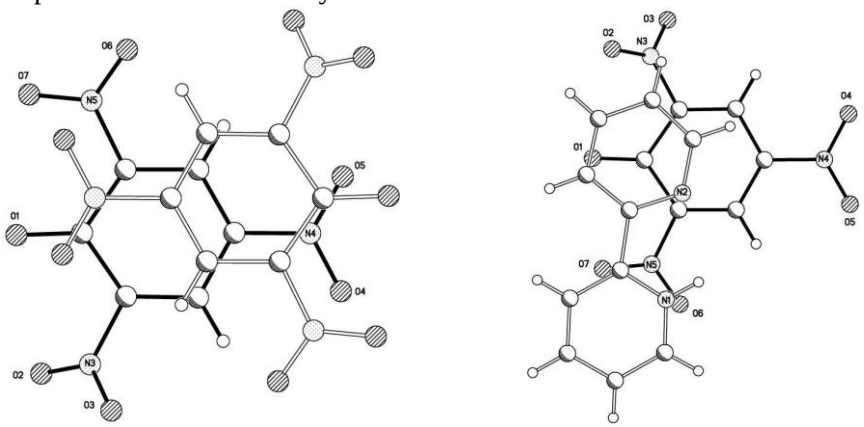


(iii) Morpholinium picrate, **(morH)(pic)** (x2) (***P*** $\bar{1}$) **(KOMTUC[22a])**, left: anion 1 (2–*x*, 1–*y*, $\bar{z}$) on anion 1, right: anion 2 (2–*x*, 1–*y*, $\bar{z}$) on anion 2 (Table S6(γ)(iii))

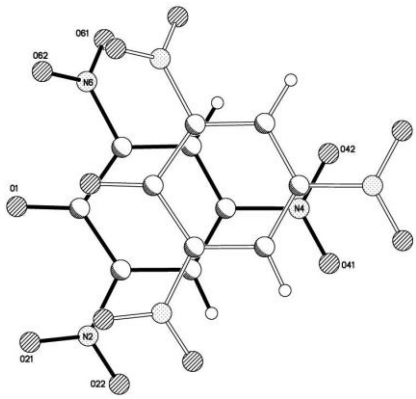


(iv) Morpholinium picrate hemihydrate, **2[(morH)(pic)](·H_2O) (*C*2/*c*)** (this work), anion 2 (*x*–½, ½–*y*, *z*–½) on anion 1 (Table S6(γ)(iv))

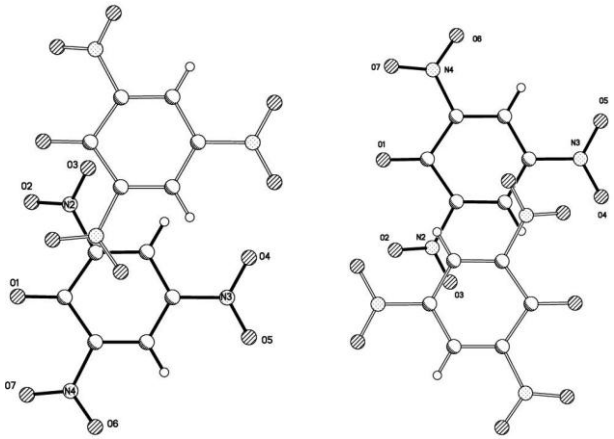
(δ) Bipyridinium picrates and derivative systems



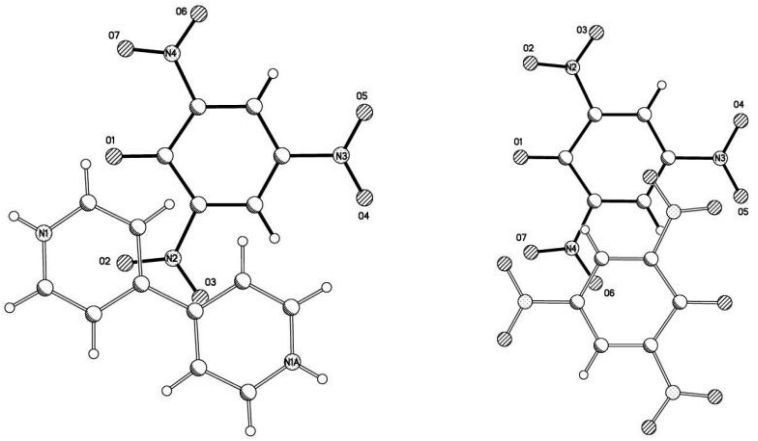
(i) 2,2'-BipyridylH$^+$ picrate, **(bpyH)(pic)** ($P\bar{1}$) **(UCOFUO[23])**, left: anion (2–*x*, 1–*y*, 1–$\bar{z}$) on anion, right: cation (1–*x*, 1–*y*, 1–*z*) on anion (Table S6(δ)(i))



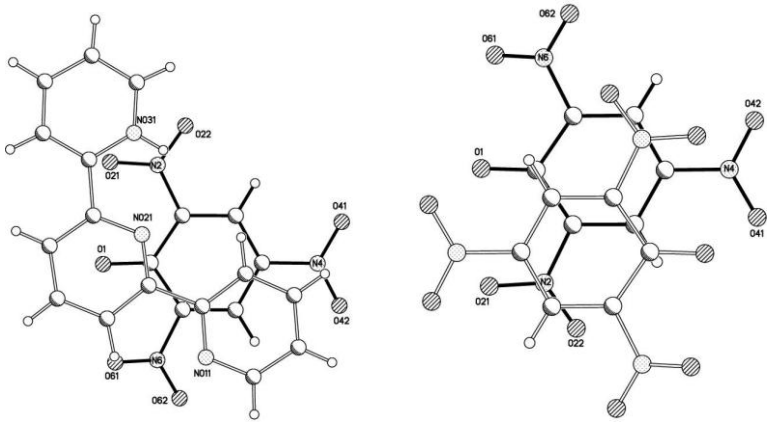
(ii) 2,2'-BipyridylH$^+$ picrate acetonitrile monosolvate, **(bpyH)(pic)(·MeCN)** (x2) ($P\bar{1}$) (this work), anion (1–*x*, $\bar{y}$, $\bar{z}$) on anion (Table S6(δ)(ii))



(iii) 4,4'-Bipyridyl H_2^{2+} bis(picrate), **(bpy'H$_2$)(pic)$_2$** (x0.5) ($P\bar{1}$) **(KAMPIY[24])**, left: anion (*x*–1, *y*, *z*) on anion, right: anion (2–*x*, $\bar{y}$, $\bar{z}$) on anion (Table S6(δ)(iii))

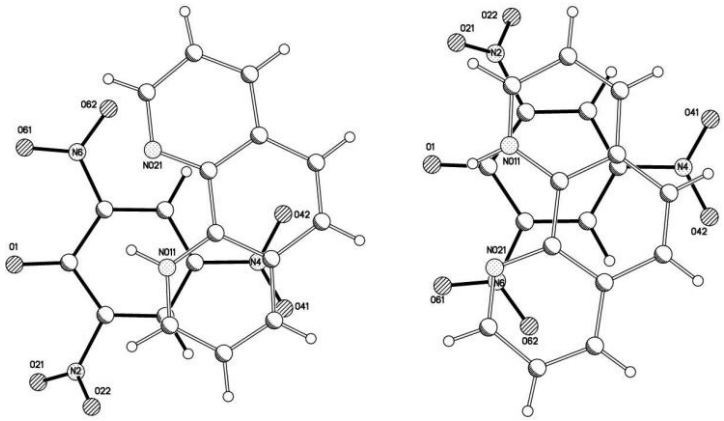


(iv) 4,4'-Bipyridyl H_2^{2+} bis(picrate) monohydrate, **(bpy'H$_2$)(pic)$_2$(·H$_2$O)(*C*2/*c*) (UJOQUF[25])**, left: cation (2–*x*, *y*, ½–*z*) on anion, right: anion ($^5/_2$–*x*, ½–*y*, 1–*z*) on anion (Table S6(δ)(iv))

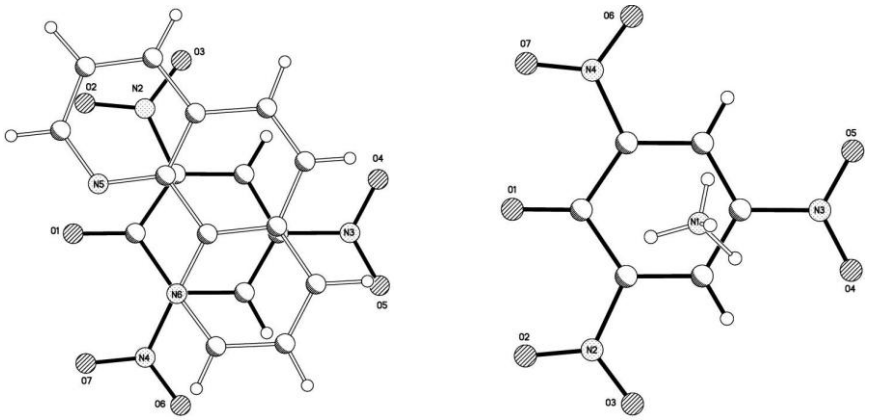


(v) 2,2':6',2''-Terpyridinium picrate, **(tpyH)(pic)** (***P*** $\bar{1}$) (this work), left: cation (1–*x*, 1–*y*, 1–*z*) on anion, right: anion (*x* , 1–*y*, 1–*z*) on anion (Table S6(δ)(v))

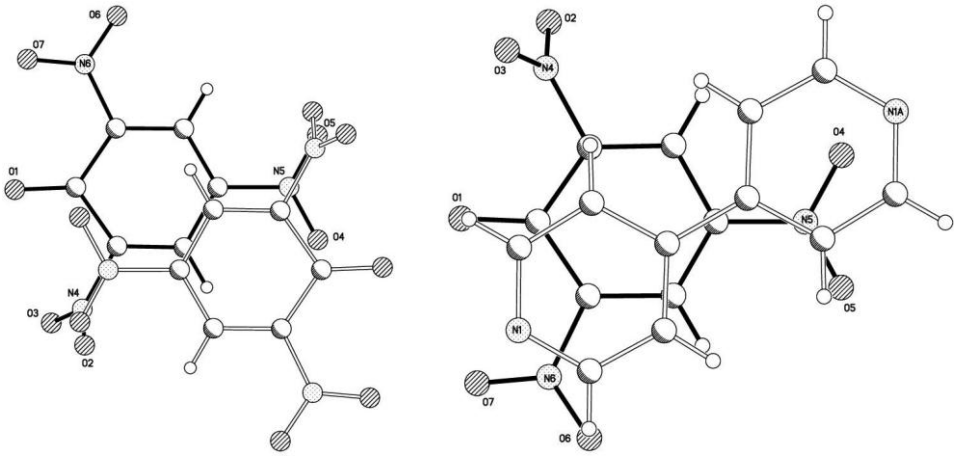
(ε) 1,10-Phenanthrolinium picrate and derivative systems



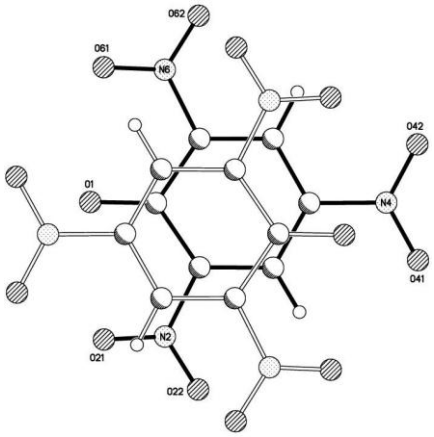
(i) 1,10-Phenanthrolinium picrate, **(phenH)(pic) (*P*2$_1$/*c*)** (this work), left: cation (1–*x*, ½+*y*, ½–*z*) on anion, right: cation (1–*x*, *y*–½, ½–*z*) on anion (Table S6(ε)(i))



(ii) Ammonium picrate : 1,10-phenanthroline (1:1), **(NH_4)(pic)(·phen) ($P2_1/c$) (AMPCPL[26a])**, left: phenanthroline (1–*x*, $\bar{y}$, 1–*z*) on anion, right: cation on anion (Table S6(ε)(ii))

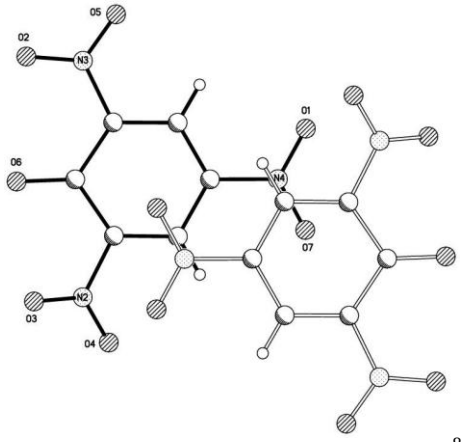


(iii) '1,10-Phenanthrolinium 4,4'-bipyridylH^+ 1,10-phenanthroline bis(picrate)', **'[(phenH)(bpy'H)(phen)](pic)$_2$'** (x0.5) **($P\bar{1}$) (INOSUZ[27])**, left: anion (1–*x*, 2–*y*, 1–*z*) on anion, right: 4,4'-bipyridylH^+ (1–*x*, 1–*y*, 1–*z*) on anion (Table S6(ε)(iii))

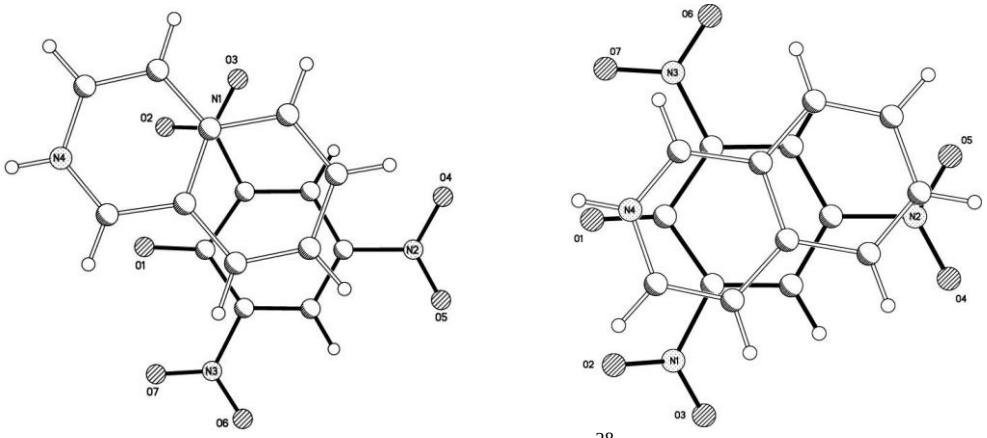


(iv) 2,9-Dimethyl-1,10-phenanthrolinium picrate, **(dmpH)(pic) ($P\bar{1}$)** (this work), anion (1–*x*, 2–*y*, 1–*z*) on anion (Table S6(ε)(iv))

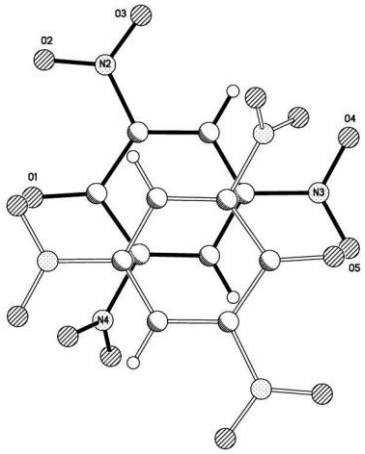
(ζ) Quinolinium picrate and derivative systems



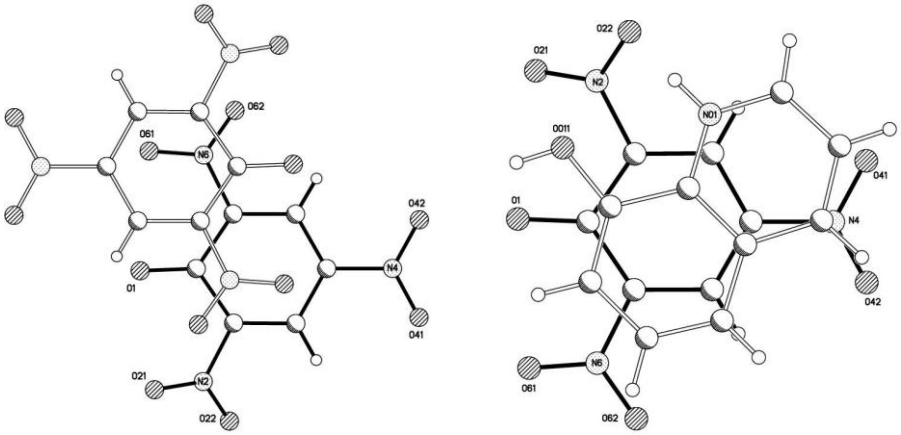
(i) Quinolinium picrate, **(quinH)(pic) (*P*2$_1$/*c*) (UBEGAL[8])** has no significant overlaps; Figure shows approach of anion (2–*x*, 2–*y*, 1–*z*) to anion (*x*, *y*, *z*) (Table S6(ζ)(i))



(ii) iso-Quinolinium picrate, **(iqH)(pic) (*P*2$_1$/*a*) (JUSRUK[28])**, left: cation (*x*, *y*–1, *z*) on anion, right: cation (1–*x*, 1–*y*, $\bar{z}$) on anion (Table S6(ζ)(ii))



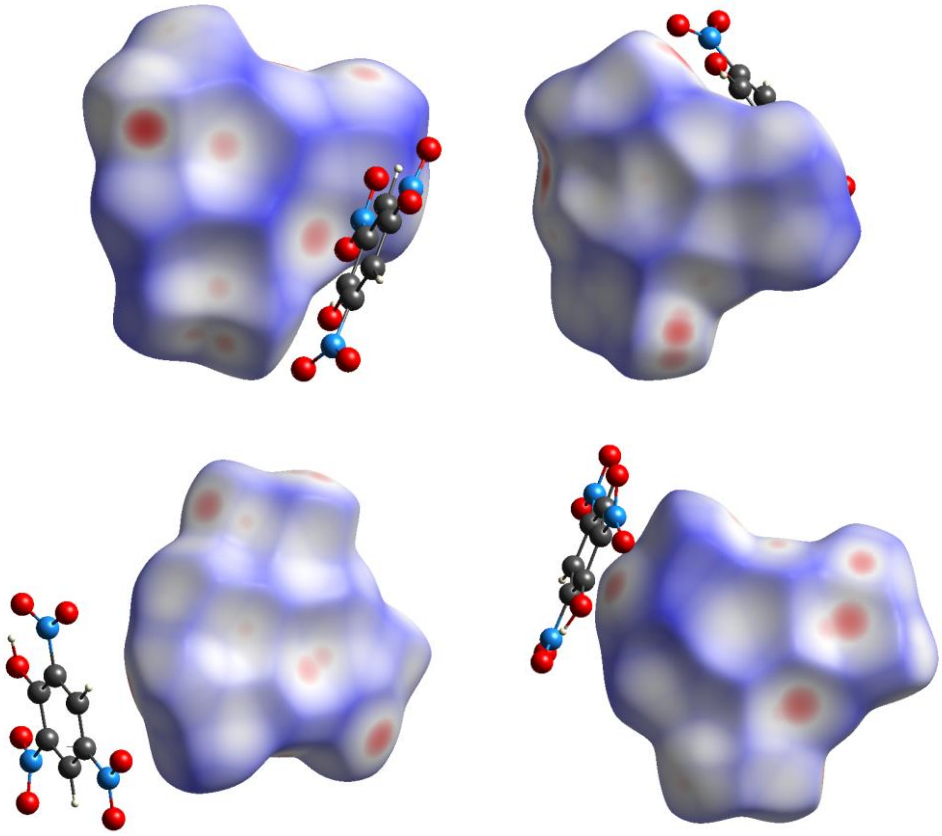
(iii) 2-Methylquinolinium picrate, **(2mqH)(pic)** ($P\bar{1}$) **(VATTER[29])**, anion ($\bar{x}$, 2–*y*, 2–*z*) on anion (Table S6(ζ)(iii))



(iv) 8-Hydroxyquinolinium picrate, **(ohqH)(pic) (*P*2$_1$/*c*)** (this work), left: anion (2–*x*, 1–*y*, 1–*z*) on anion, right: cation (1–*x*, 1–*y*, 1–*z*) on anion (Table S6(ζ)(iv))

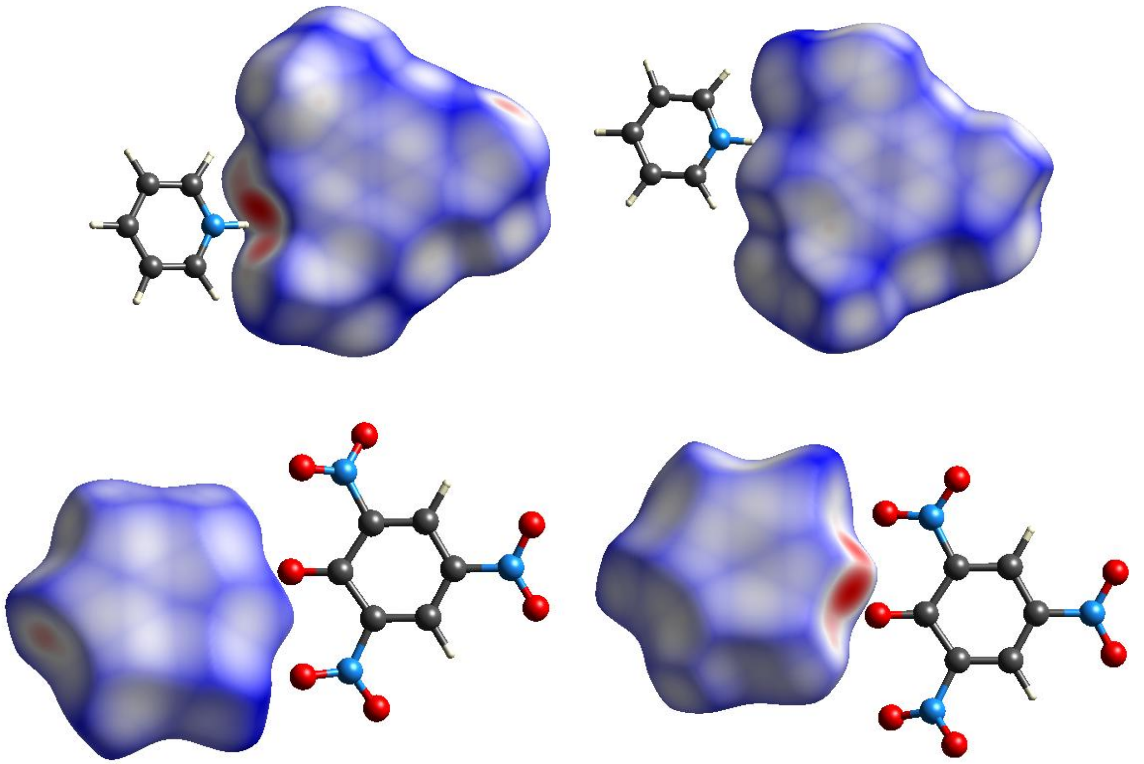
Fig. S3 Hirshfeld surfaces for the anionic and cationic components of the compounds of Table 1

These are shown for the anion (upper) and cation (lower) (projections normal to the associated picrate). Property d_{norm} mapped, range –0.42 (red) to 1.6 Å (blue) (see more details in the text).

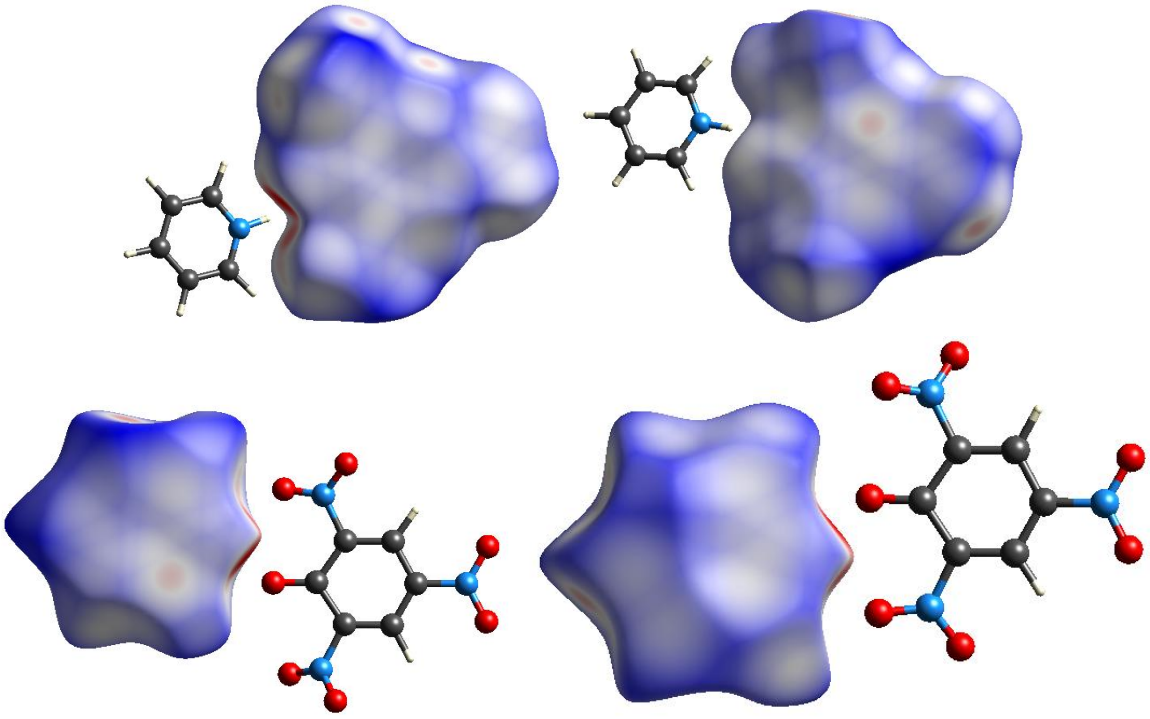


(α) The parent picric acid **(picH) (*Pna*2$_1$) (PICRAC13**[1g]**)**, two independent molecules (upper, lower), full asymmetric unit shown

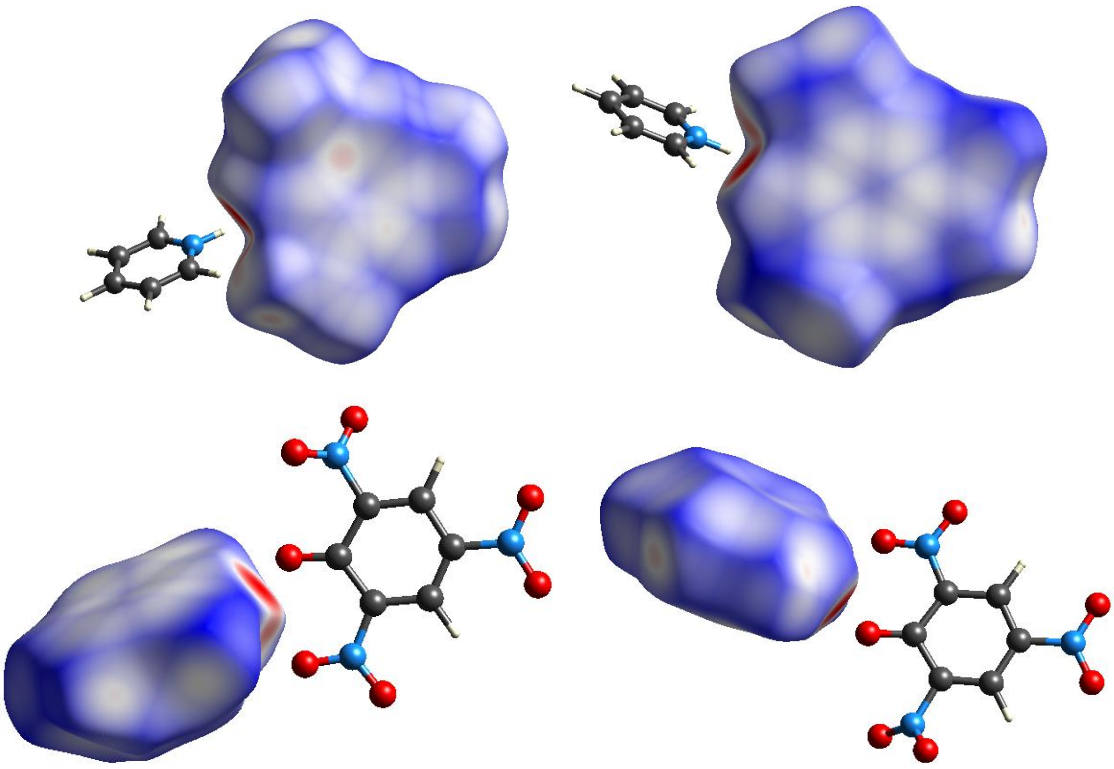
(β) Pyridinium and 2-substituted pyridinium (substituents other than pyridyl) picrates



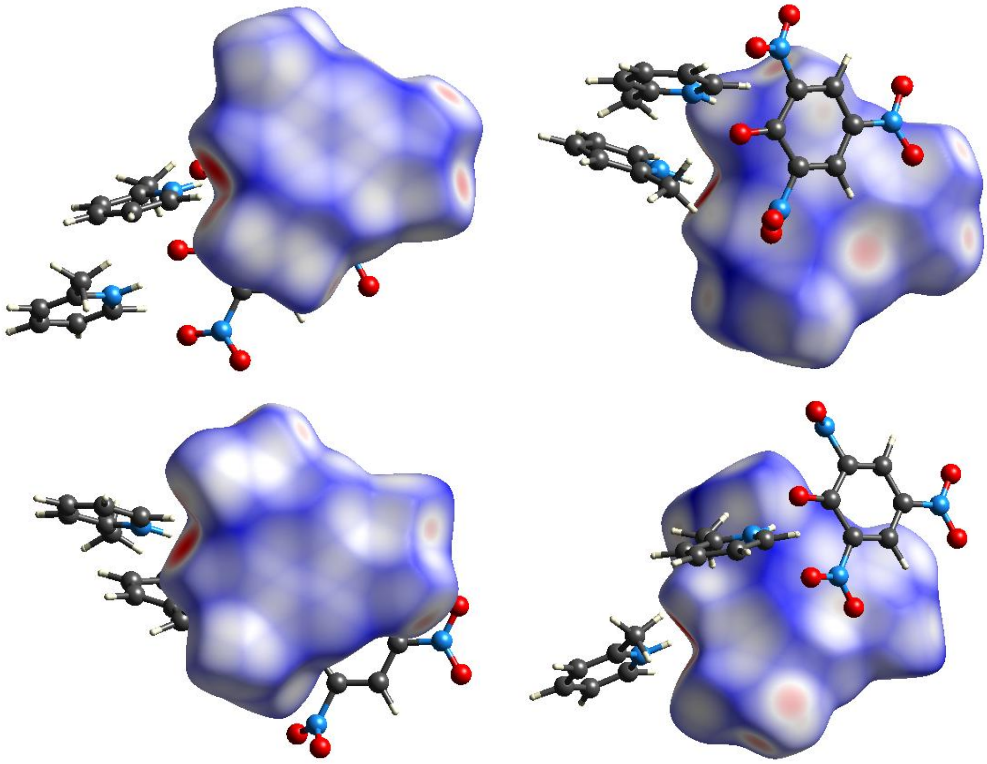
(i) Pyridinium picrate, **(pyH)(pic) (*P*2$_1$/*c* (PYRPIC02**[11c]**)**



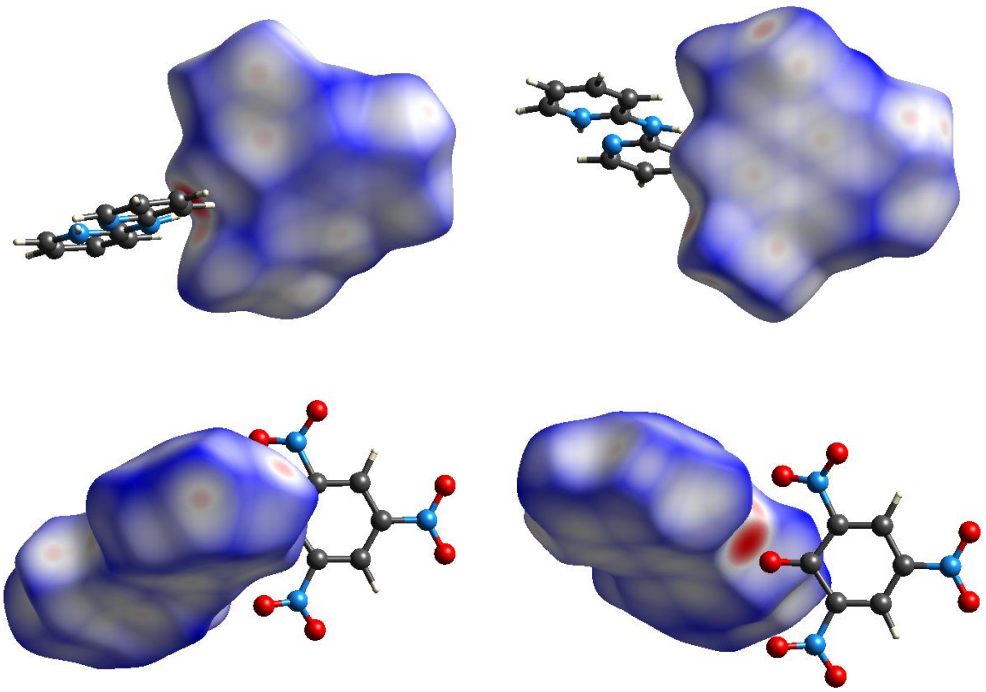
(ii) Pyridinium picrate, **(pyH)(pic) (*P* $\bar{1}$) (PYRPIC03**[11c]**)**



(iii) Pyridinium picrate : 1-naphthylamine (1:1), **(pyH)(pic)(·naph)** (***P*2$_1$/*a***) **(PYNPCR**[20]**)**

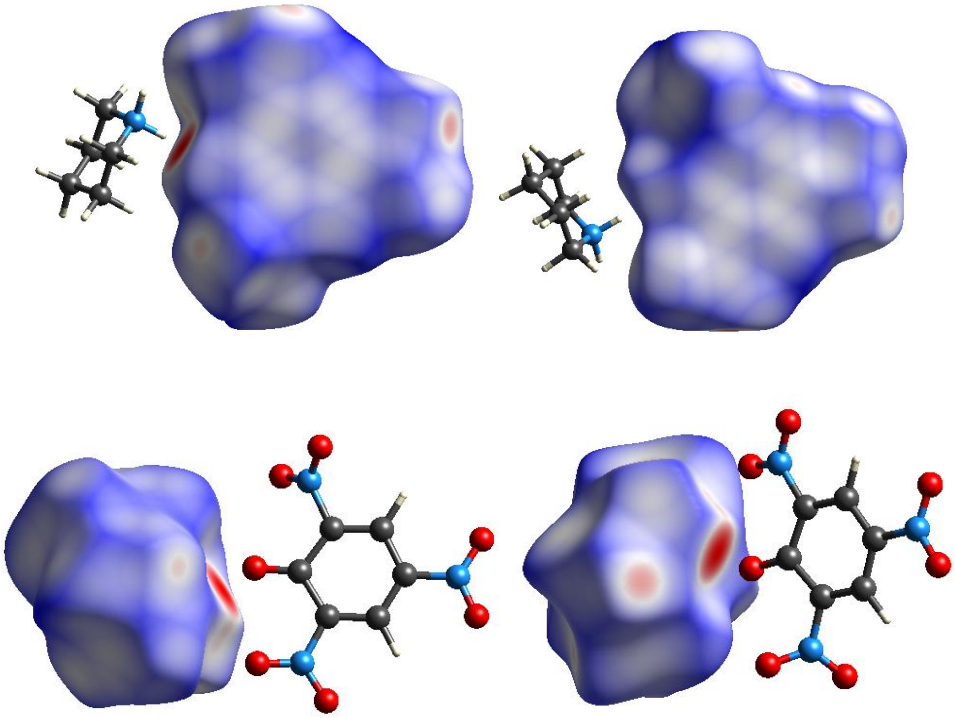


(iv) 2-Methylpyridinium picrate, **(2mpH)(pic)** (x2) ($P\bar{1}$) (this work)

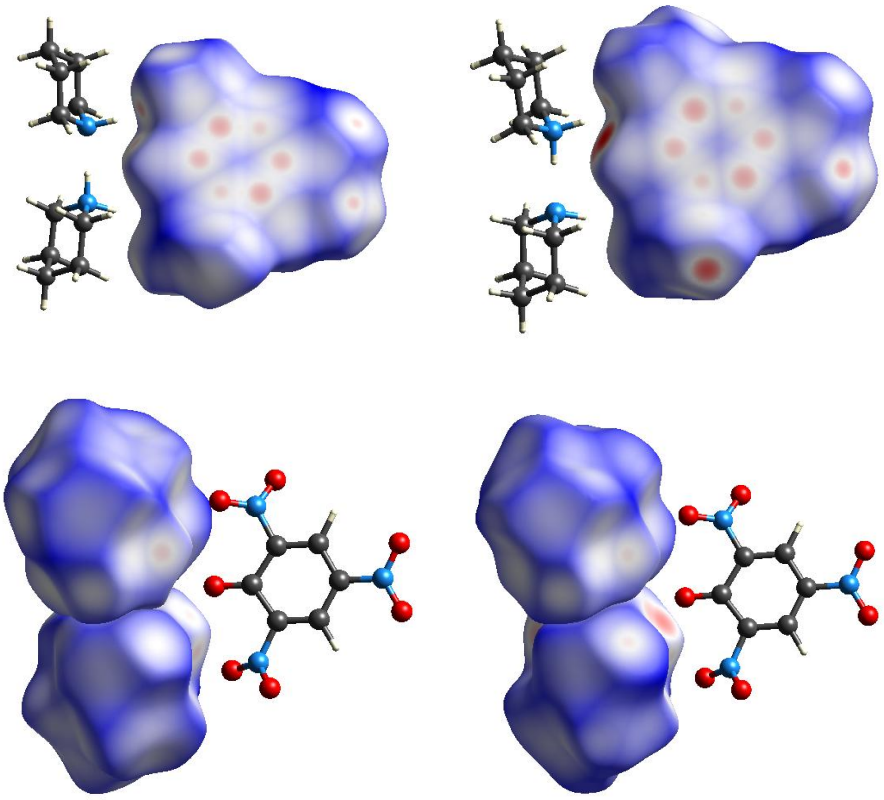


(v) (2-Pyridinium)(2-pyridyl)amine picrate, **(dpaH)(pic) (*P*2$_1$/*c*)** (this work)

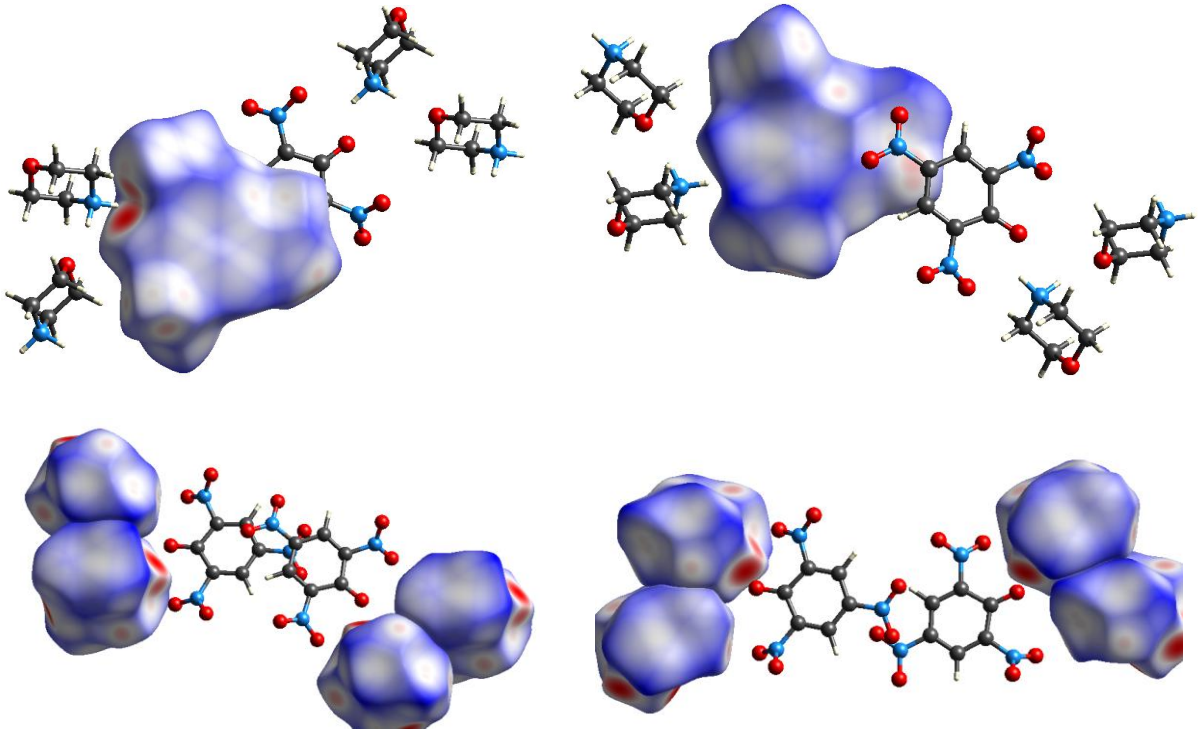
(γ) Aza-alicyclic base salts – Saturated derivatives of pyridinium picrate



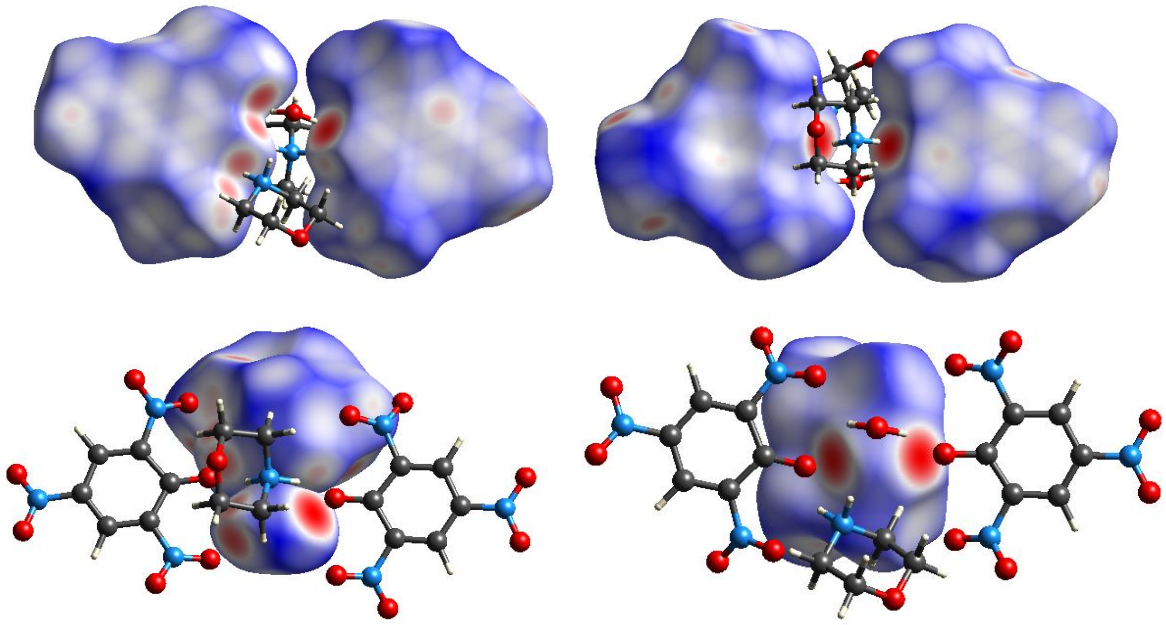
(i) Piperidinium picrate, **(pipH)(pic)** ($P\bar{1}$) **(VAZJAI**[21]**)**



(ii) Piperidinium picrate monopiperidine solvate, **(pipH)(pic)(·pip) (*P*2$_1$/*n*)** (this work)

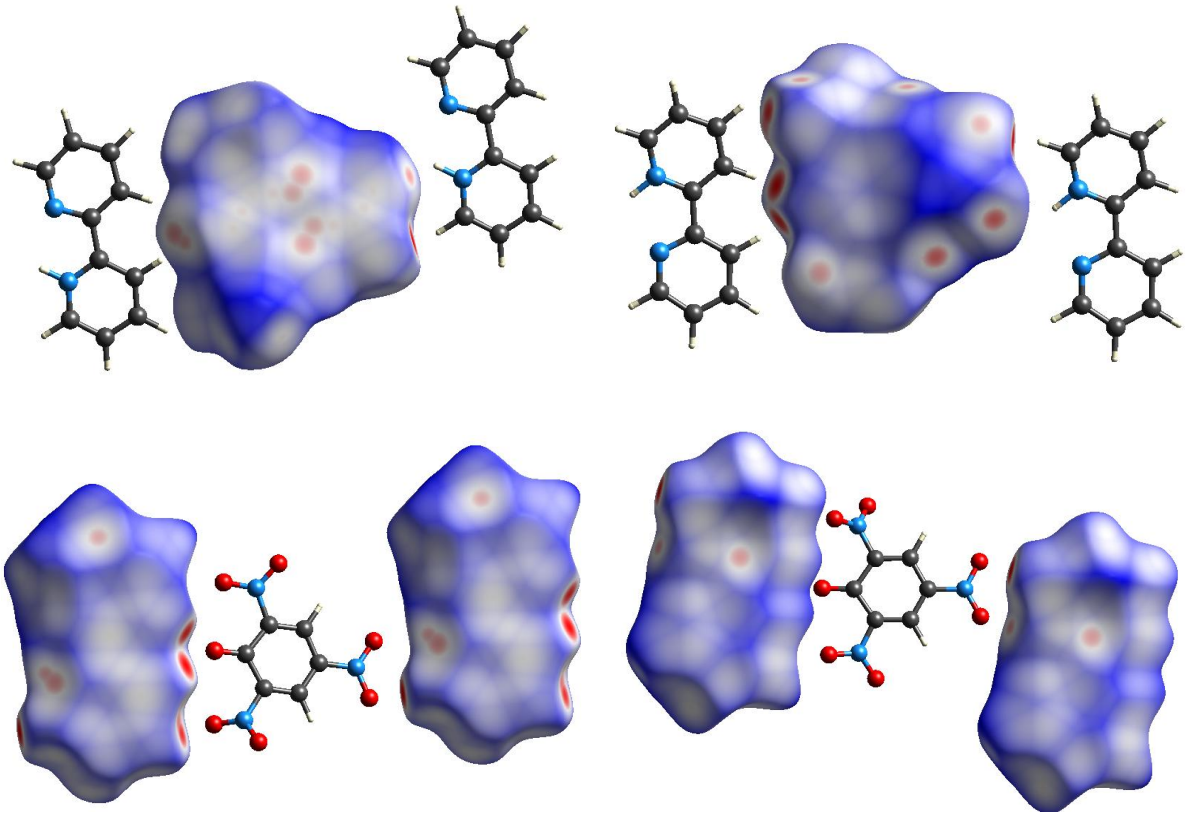


(iii) Morpholinium picrate, **(morH)(pic)** (x2) **(*P* $\bar{1}$) (KOMTUC[22a])**

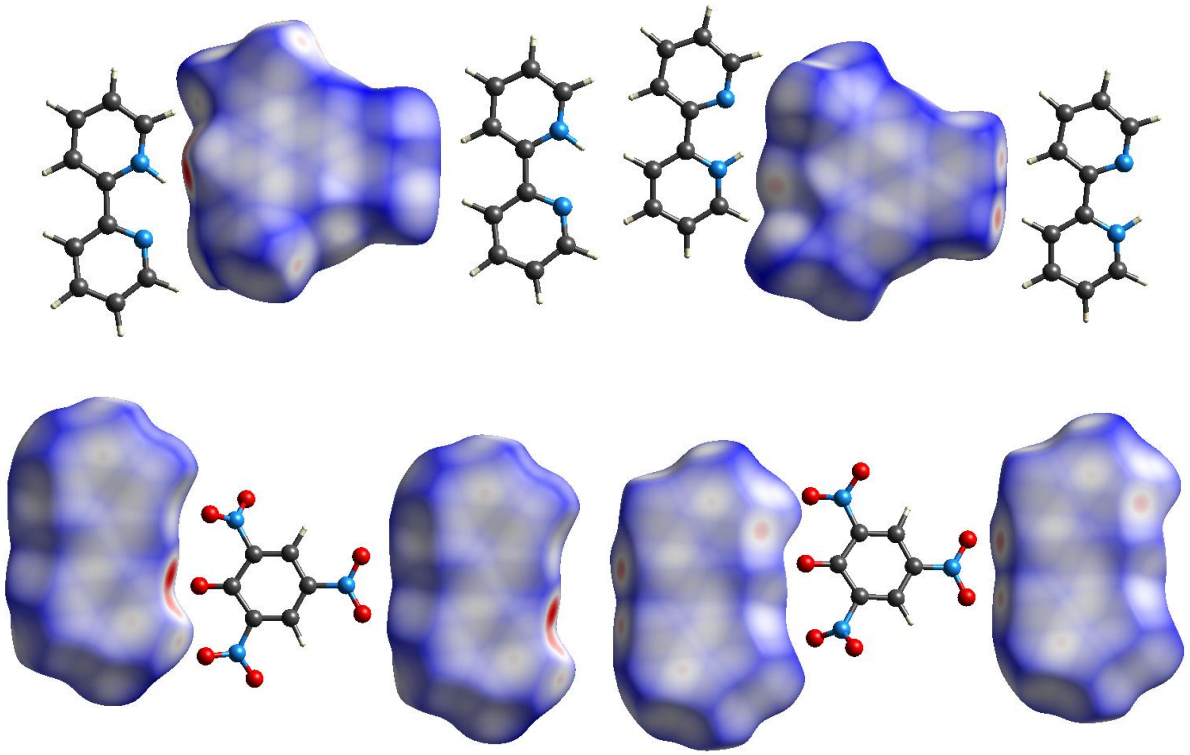


(iv) Morpholinium picrate hemihydrate, **2[(morH)(pic)](·H_2O) (*C*2/*c*)** (this work)

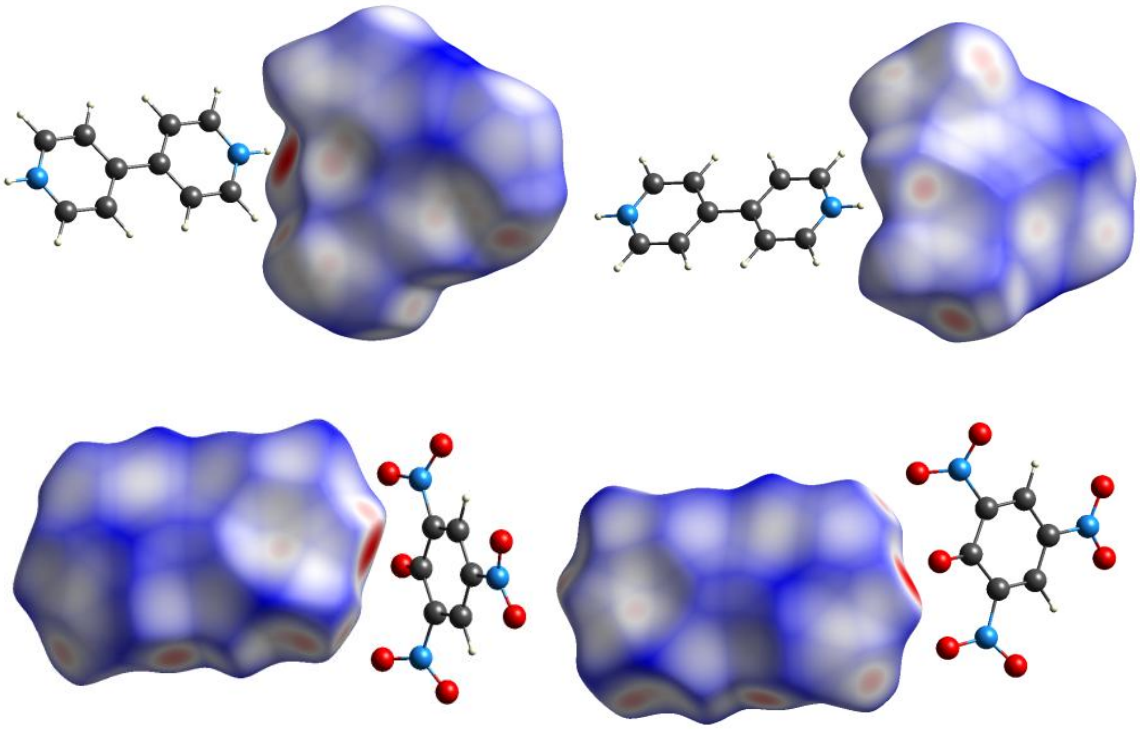
(δ) Bipyridinium picrates and derivative systems



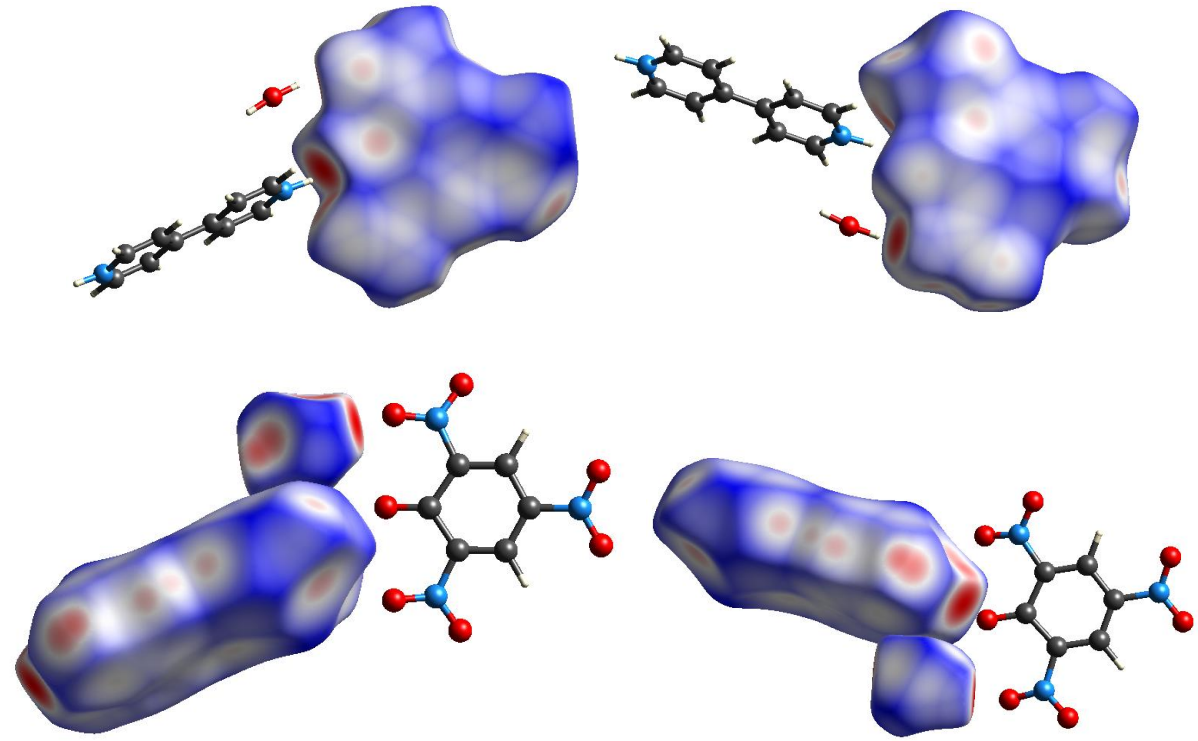
(i) 2,2'-BipyridylH$^+$ picrate, **(bpyH)(pic)** ($P\bar{1}$) **(UCOFUO[23])**



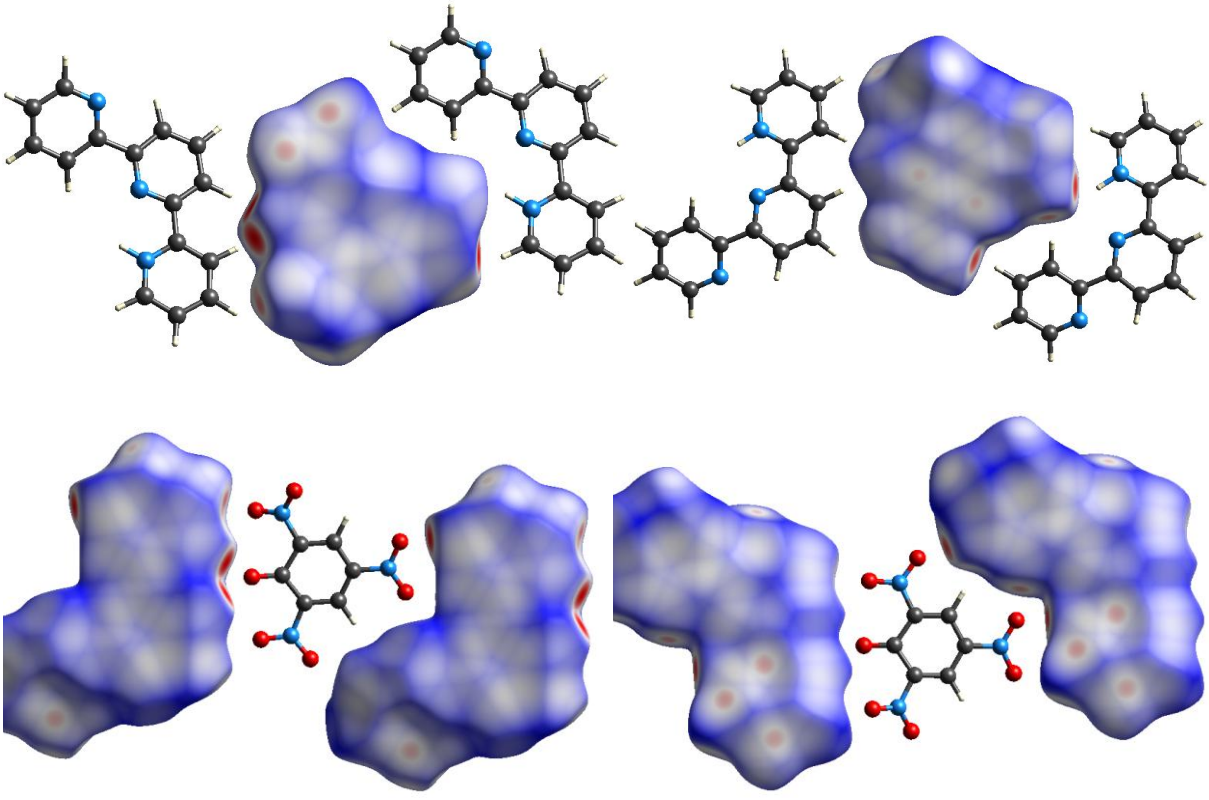
(ii) 2,2'-BipyridylH^{+} picrate acetonitrile monosolvate, **(bpyH)(pic) (·MeCN)** (x2) ($P\bar{1}$) (this work)



(iii) 4,4'-Bipyridyl H_2^{2+} bis(picrate), **(bpy'H$_2$)(pic)$_2$** (x0.5) ($P\bar{1}$) **(KAMPIY[24])**

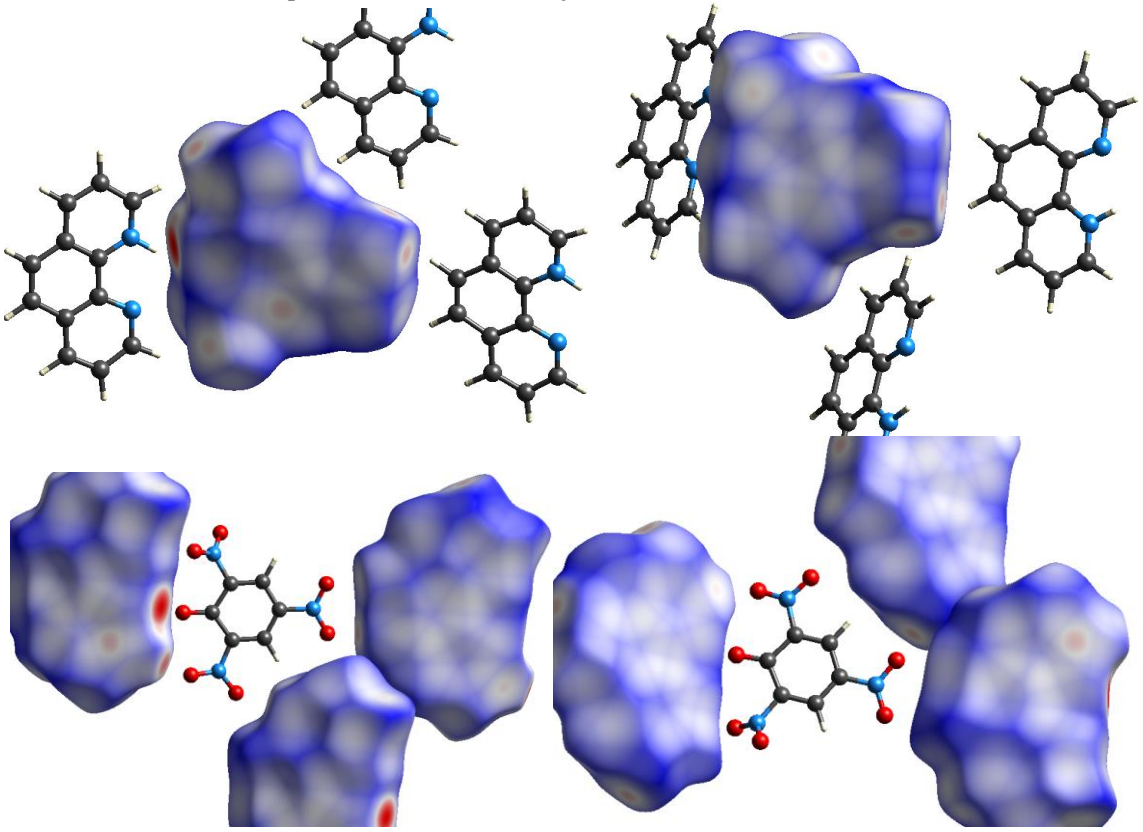


(iv) 4,4'-Bipyridyl H_2^{2+} bis(picrate) monohydrate, **(bpy'H_2)(pic)$_2$(·H_2O) (*C*2/*c*) (UJOQUF[25])**

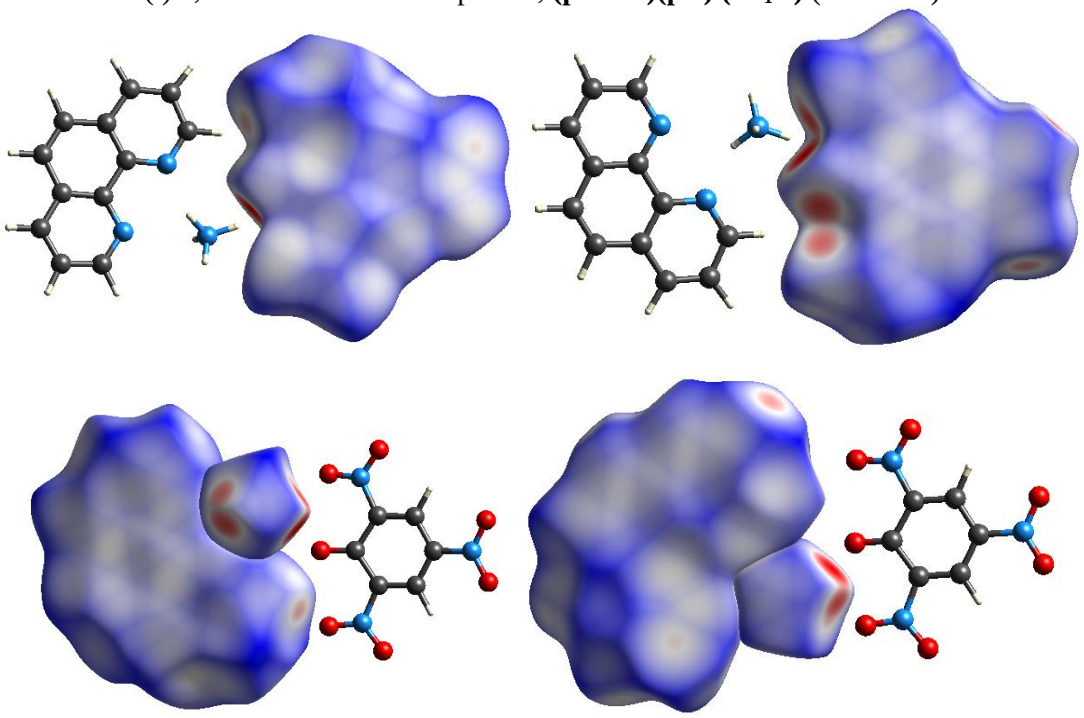


(v) 2,2':6',2''-Terpyridinium picrate, **(tpyH)(pic)** **(*P* $\bar{1}$)** (this work)

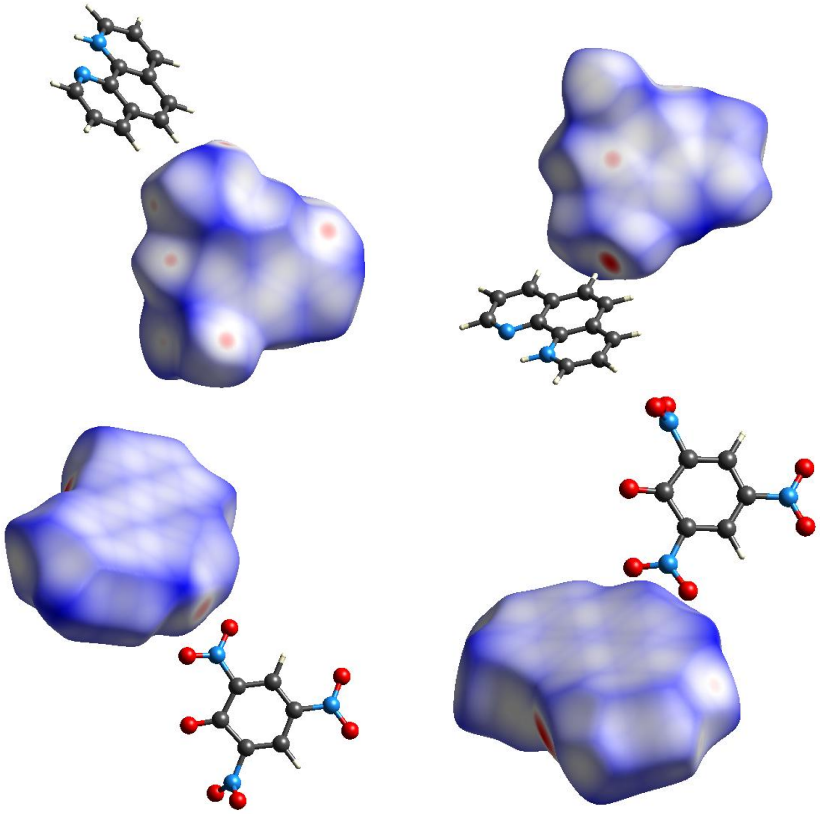
(ε) 1,10-Phenanthrolinium picrate and derivative systems



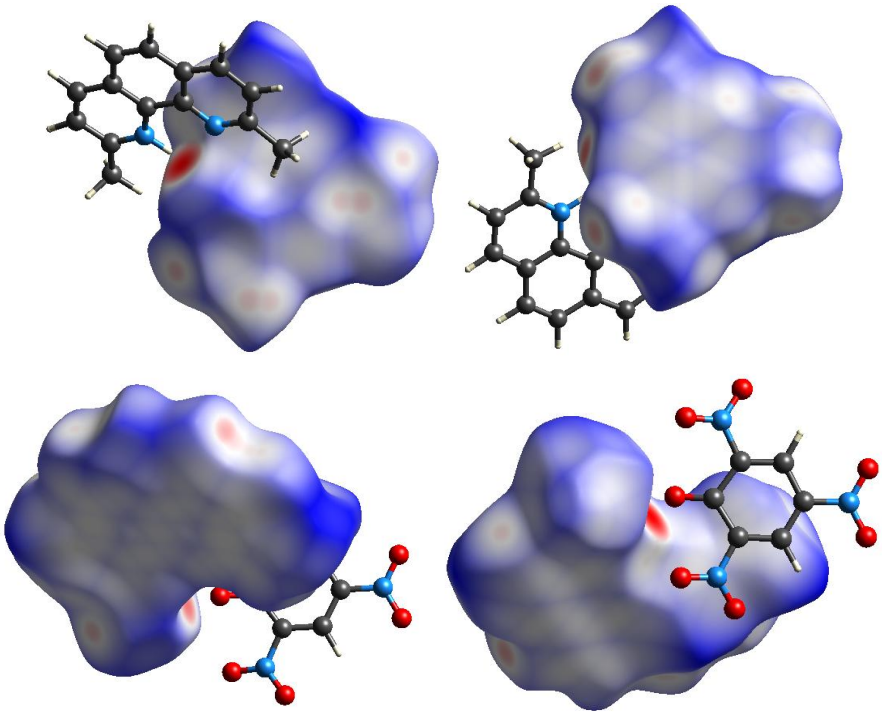
(i) 1,10-Phenanthrolinium picrate, **(phenH)(pic) (*P*2$_1$/*c*)** (this work)



(ii) Ammonium picrate : 1,10-phenanthroline (1:1), **(NH_4)(pic)(·phen) (*P*2$_1$/*c*) (AMPCPL[26a])**

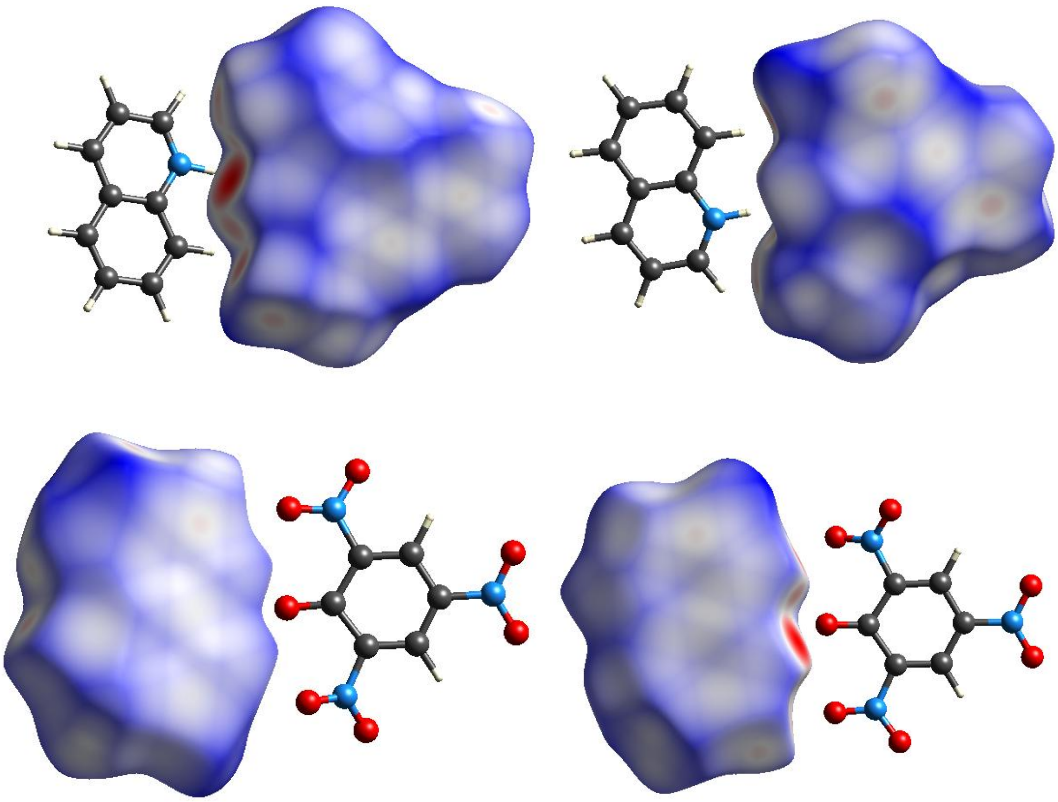


(iii) '1,10-Phenanthrolinium 4,4'-bipyridylH$^+$ 1,10-phenanthroline' bis(picrate), **'[(phenH)(bpy'H)(phen)](pic)$_2$'** (x0.5) **($P\bar{1}$) (INOSUZ[27])**

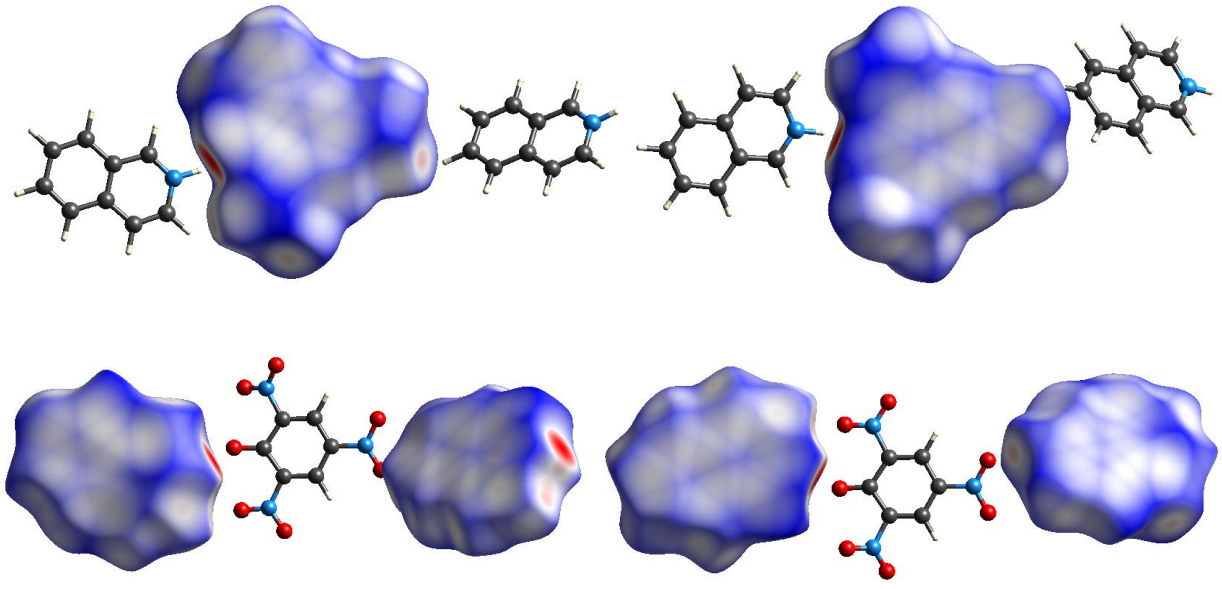


(iv) 2,9-Dimethyl-1,10-phenanthrolinium picrate, **(dmpH)(pic)** **($P\bar{1}$)** (this work)

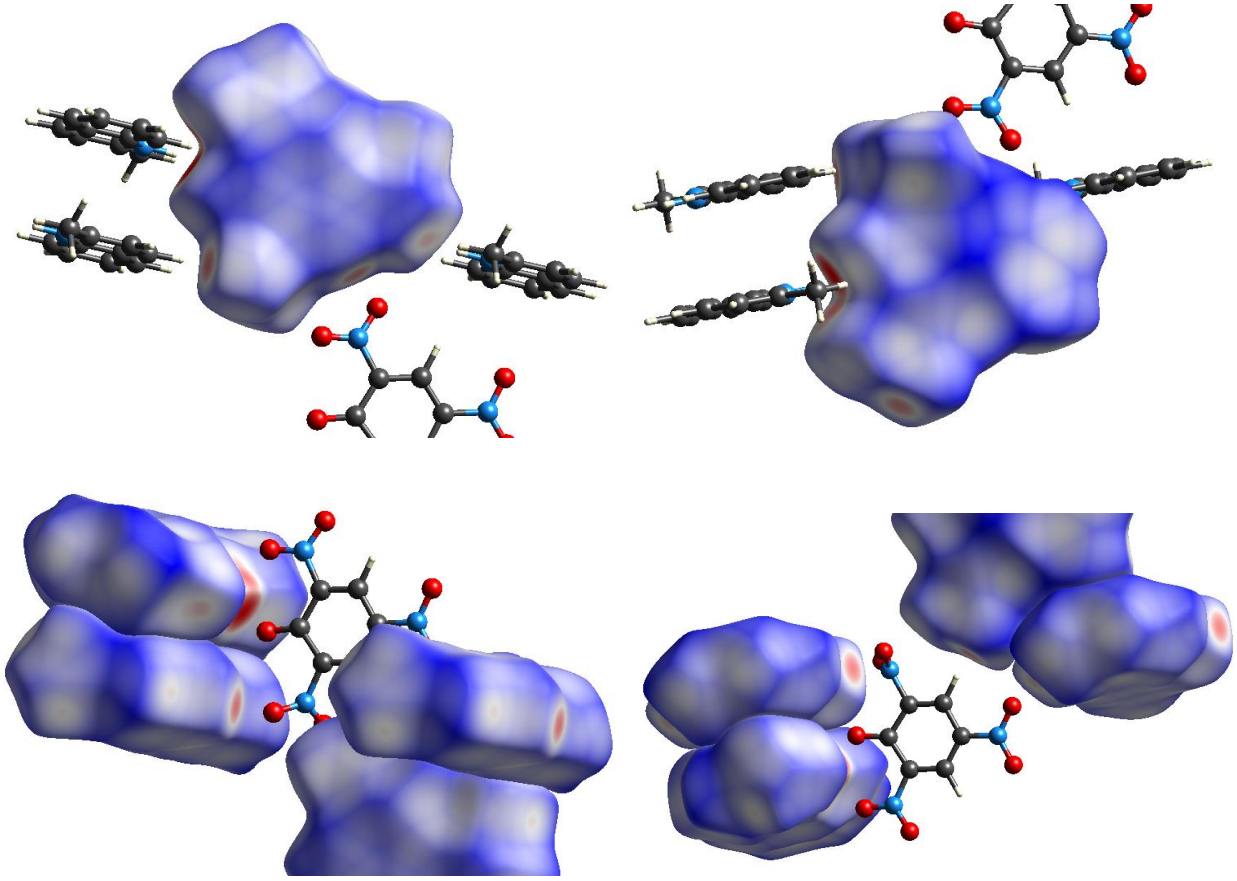
(ζ) Quinolinium picrate and derivative systems



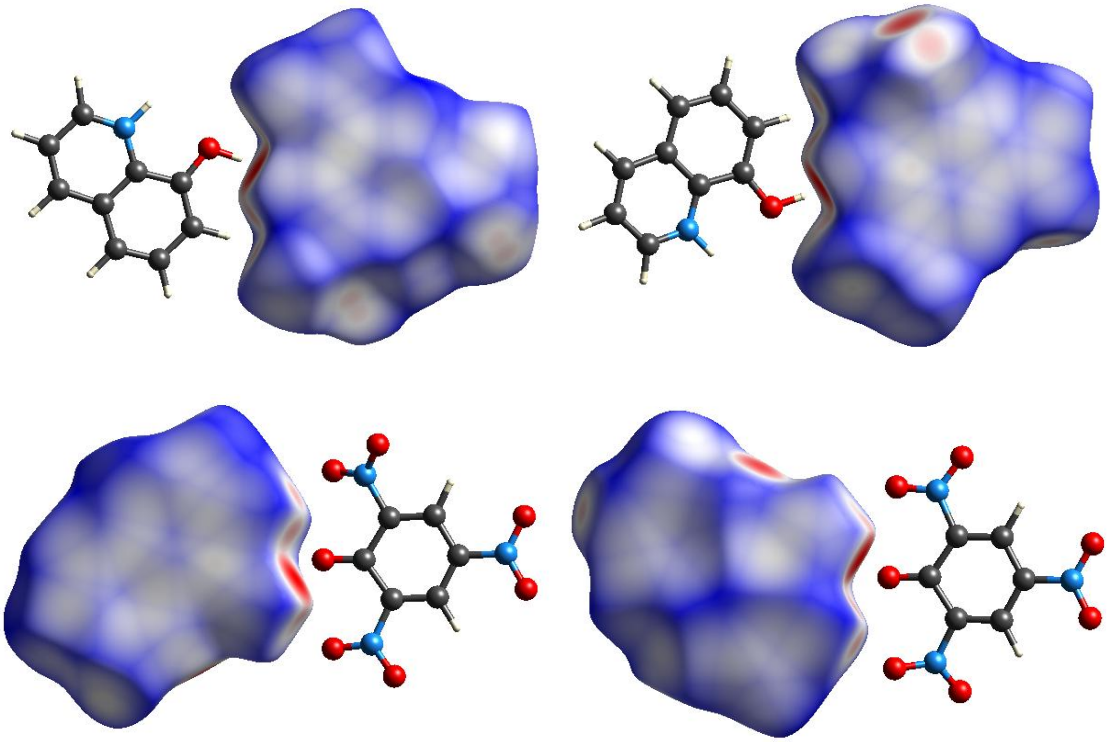
(i) Quinolinium picrate, **(quinH)(pic) (*P*2$_1$/*c*) (UBEGAL[8])**



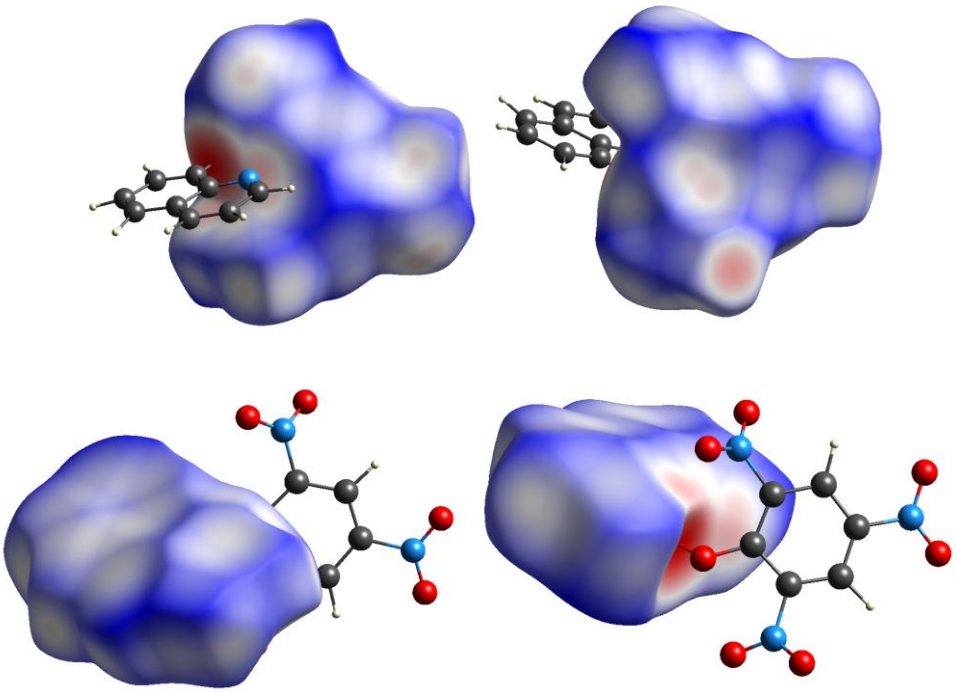
(ii) iso-Quinolinium picrate, **(iqH)(pic) (*P*2$_1$/*a*) (JUSRUK[28])**



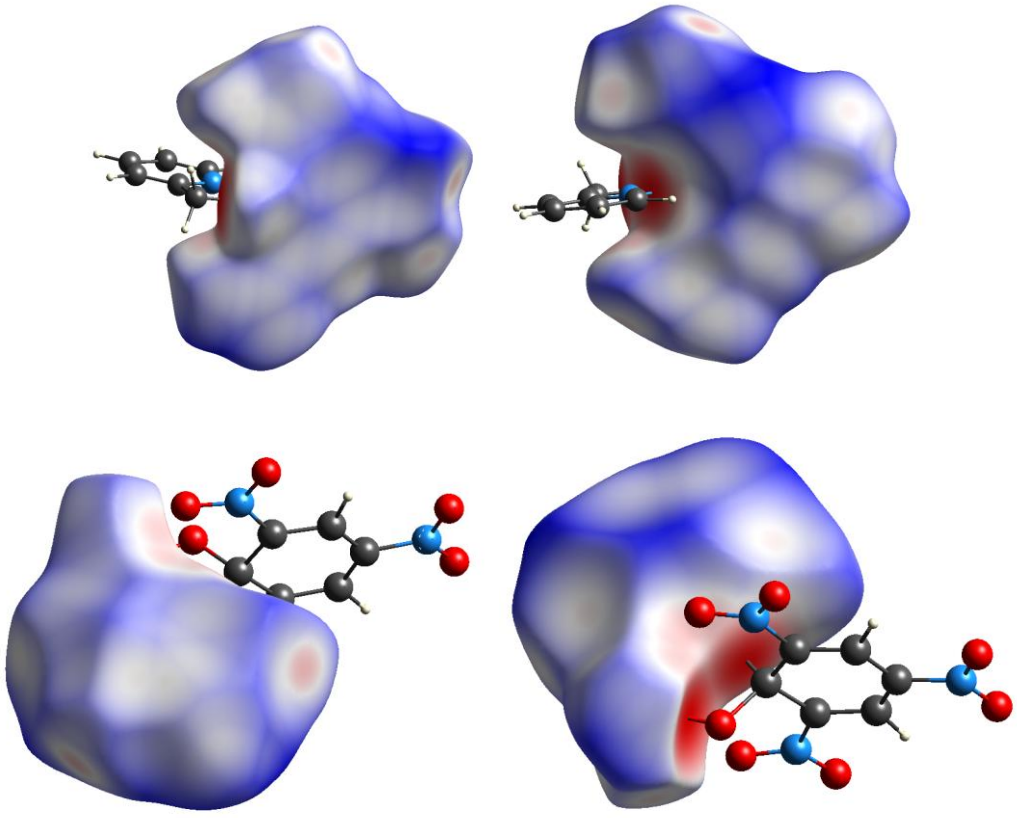
(iii) 2-Methylquinolinium picrate, **(2mqH)(pic)** ($P\bar{1}$) **(VATTER**[29]**)**



(iv) 8-Hydroxyquinolinium picrate, **(ohqH)(pic)** (***P*2$_1$/*c*) (this work)



(v) 8-Hydroxyquinolinium picrate Meisenheimer Salt 'precursor', **(oqpic) (*C*2/*c*) (JOKTOS[30])**



(vi) 2-Hydroxymethylpyridine 'Meisenheimer Salt', **(omppic) (*P*2$_1$/*n*) (JOKTIM[30])**