

## Supplementary Materials

The following additional materials are available online.

1. Figure S1: The X-ray powder diffraction pattern of the Erdmann's salt of cocaine (**3**).
2. Figure S2: The X-ray powder diffraction pattern of the Erdmann's salt of methamphetamine (**4**).
3. Figure S3: The X-ray powder diffraction pattern of the Erdmann's salt of methylone (**5**).
4. Figure S4: ORTEP of Potassium Erdmann's Salt (**1**): Ellipsoids are drawn at 30% probability level.
5. Figure S5: ORTEP of Ammonium Erdmann's Salt (**2**): Ellipsoids are drawn at 30% probability level.
6. Figure S6: ORTEP of Erdmann's Salt of Cocaine (**3**): Ellipsoids are drawn at 30% probability level.
7. Figure S7: ORTEP of Erdmann's Salt of Methamphetamine (**4**): Ellipsoids are drawn at 30% probability level.
8. Figure S8: ORTEP of Erdmann's Salt of Methylone (**5**): Ellipsoids are drawn at 30% probability level.

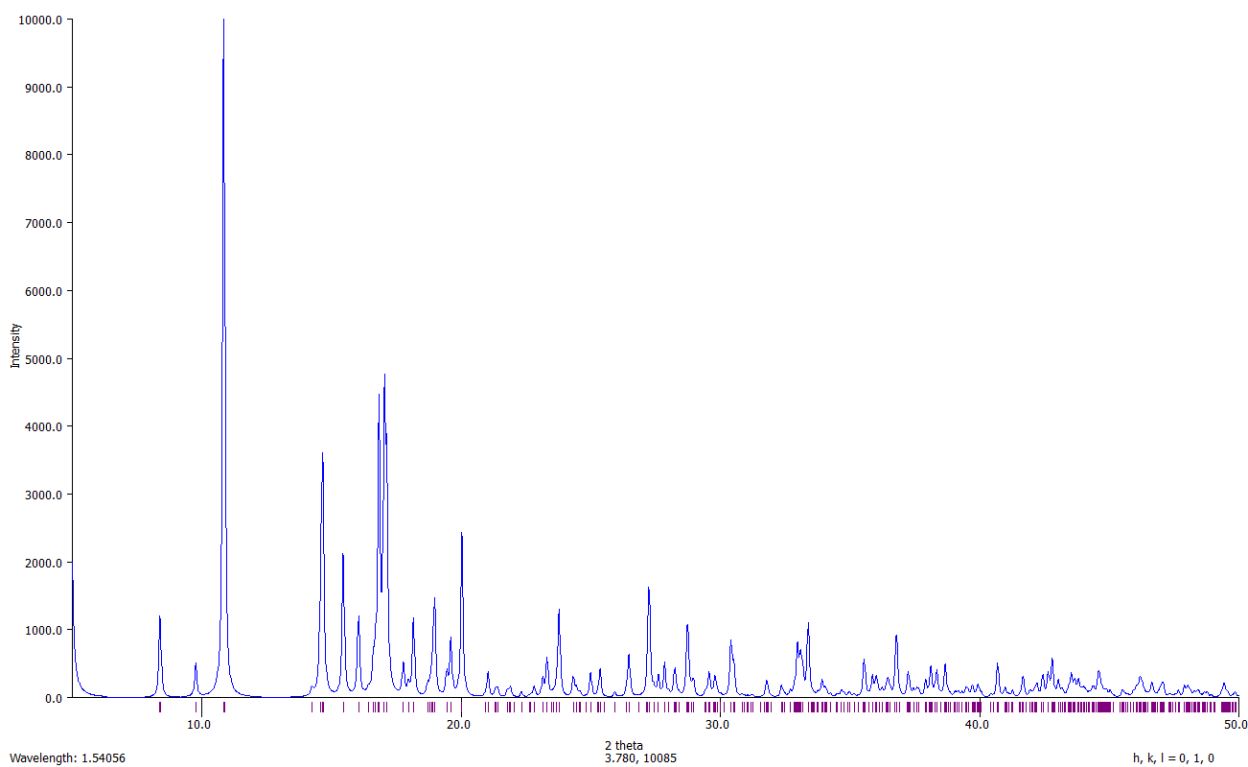


Figure S1: The X-ray powder diffraction pattern of the Erdmann's salt of cocaine (**3**).

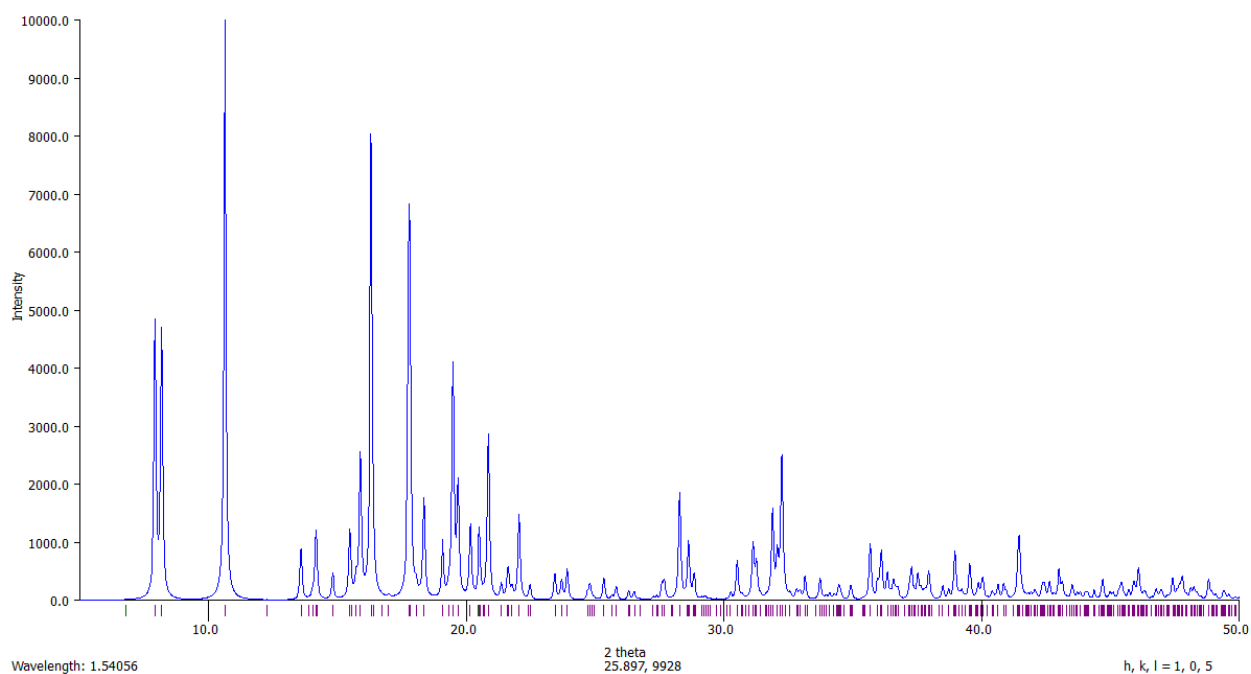


Figure S2: The X-ray powder diffraction pattern of the Erdmann's salt of methamphetamine (**4**).

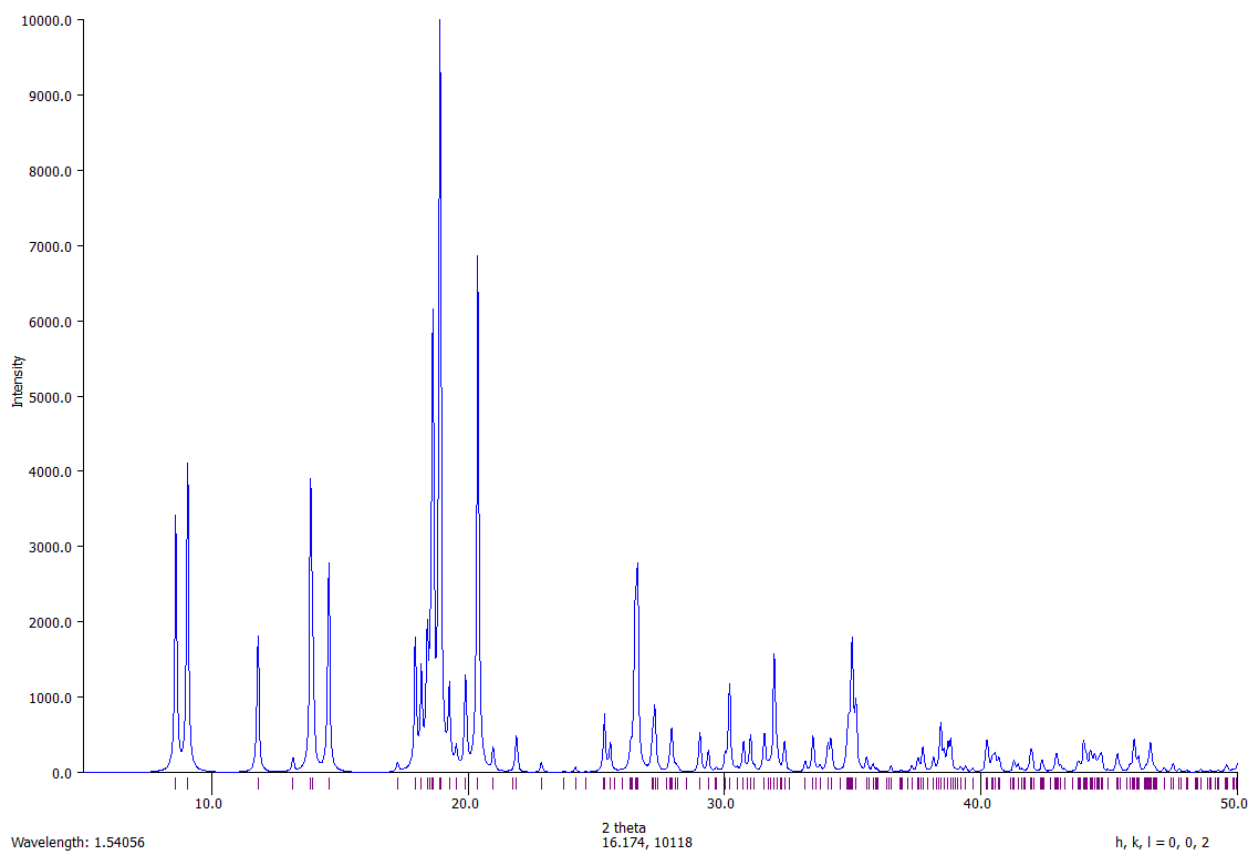


Figure S3: The X-ray powder diffraction pattern of the Erdmann's salt of methylene (**5**).

ORTEP DIAGRAMS FOR (1), (2), (3), (4), (5). All were plotted using 30% ellipsoids.

Figure S4: Potassium Erdmann's salt (1):

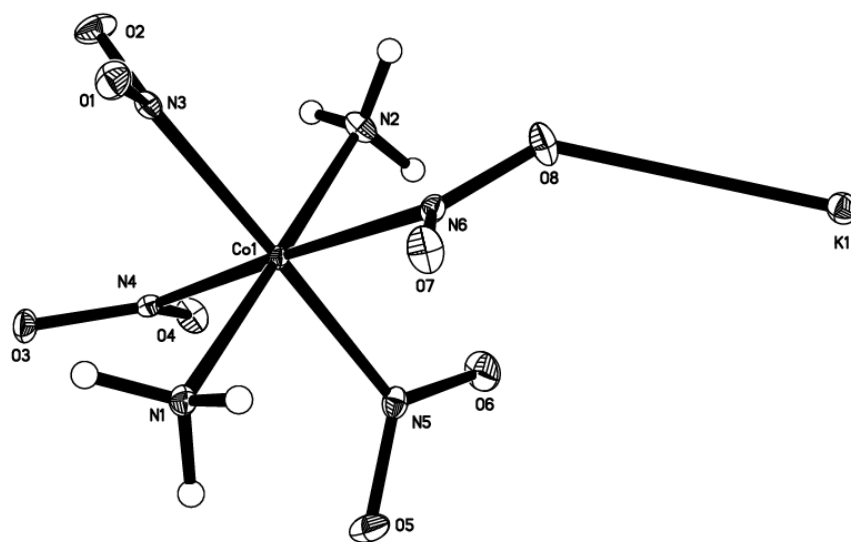


Figure S5: Ammonium Erdmann's salt (**2**):

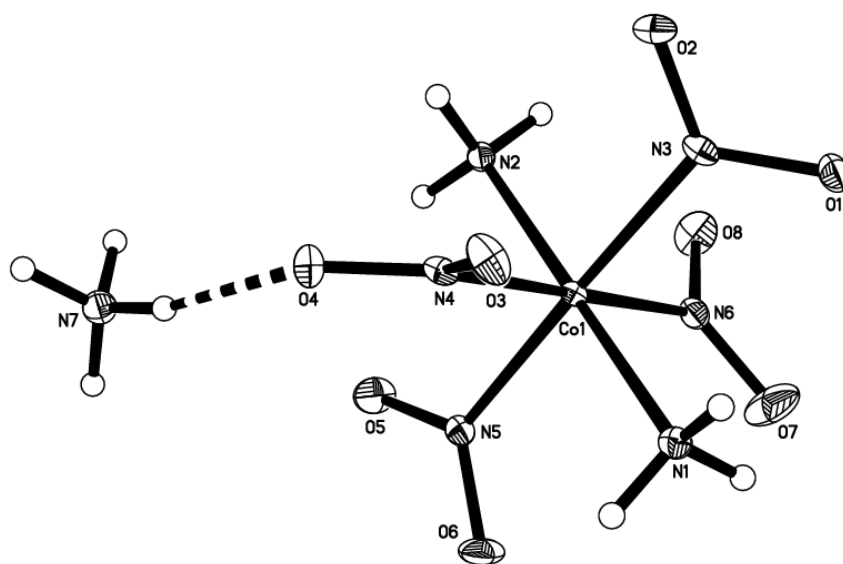


Figure S6: Erdmann's salt of cocaine (3):

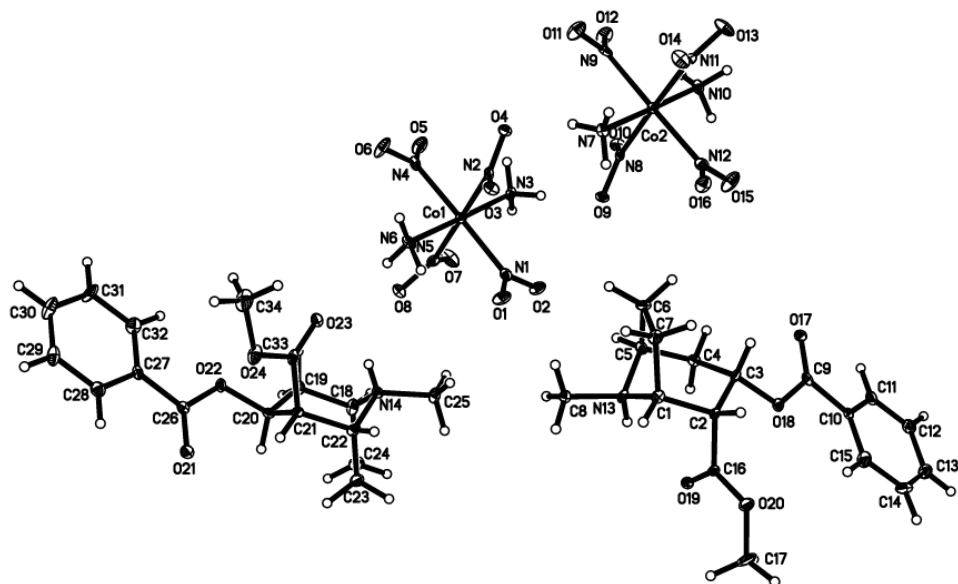


Figure S7: Erdmann's salt of methamphetamine (**4**):

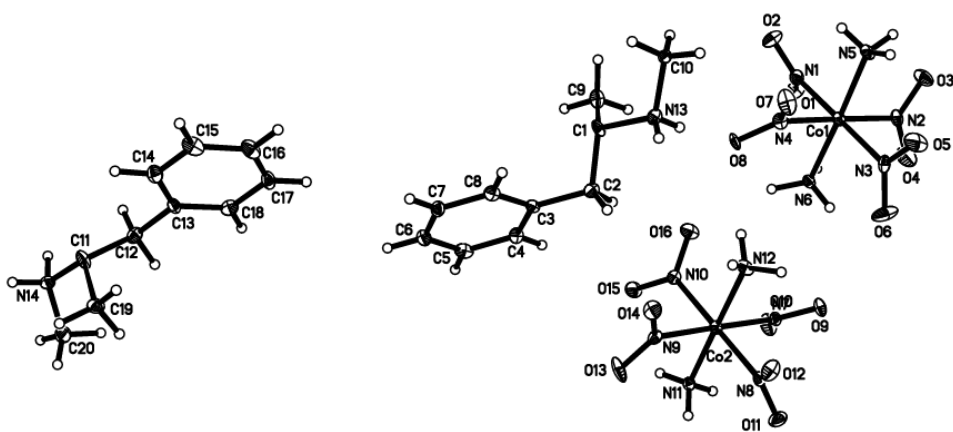
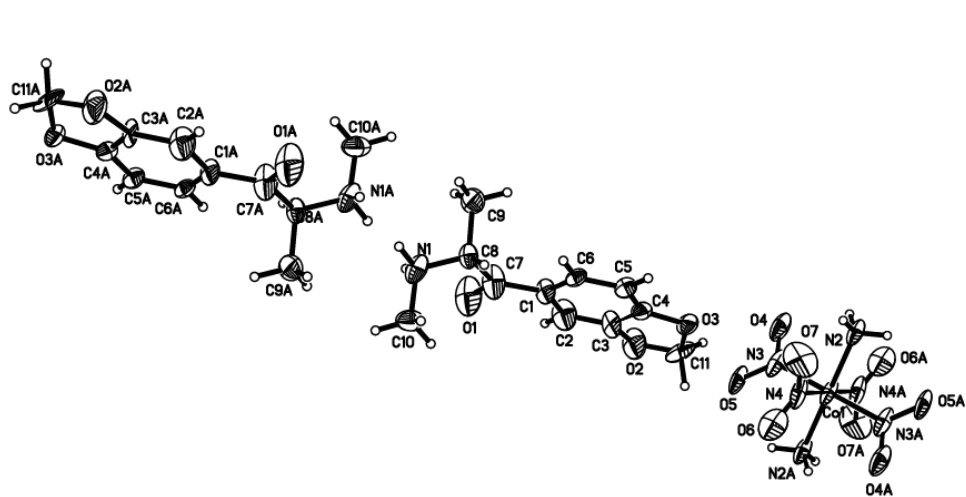


Figure S8: Erdmann's salt of methylone (**5**):





## Tables T1-T5: Hydrogen-Bonding Interactions

Table T1: H-bonding interactions in K Erdmann's salt (**1**)K+ Erdmann's salt [**B**]: H-bond geometry (Å) and angle (°)

D-H...A	D-H	H...A	D...A	D-H...A
N1-H1...O3 <sup>iii</sup>	0.91(3)	2.46(3)	3.268(3)	149(3)
N1-H1...O7	0.91(3)	2.10(3)	2.789(3)	132(3)
N1-H2...O2 <sup>iii</sup>	0.96(3)	2.53(3)	3.009(3)	111(2)
N1-H2...O5	0.96(3)	2.15(3)	2.754(3)	120(3)
N2-H6...O5 <sup>i</sup>	0.83(4)	2.25(4)	2.962(4)	145(3)
N2-H4...O6	0.87(4)	2.16(3)	2.754(3)	124(3)
N2-H5...O2 <sup>ii</sup>	0.85(4)	2.17(4)	2.984(3)	162(4)
N1-H3...O6 <sup>iv</sup>	0.89(4)	2.12(4)	2.996(3)	167(3)

Symmetry: i = [-x+1,y+1/2,-z+1/2]; ii = [x+1/2,-y+3/2,-z+1]; iii = [-x,y-1/2,-z+1/2]; iv = [x-1,y,z]

Table T2: H-bonding interactions in NH<sub>4</sub> Erdmann's salt (**2**)NH<sub>4</sub><sup>+</sup> Erdmann's salt [**A**]: H-bond geometry (Å) and angle (°)

D-H...A	D-H	H...A	D...A	D-H...A
N1-H1...O8 <sup>i</sup>	0.9896(14)	2.15(2)	2.987(3)	141(2)
N1-H2...O7	0.9896(14)	2.15(3)	2.752(3)	118(2)
N1-H3...O3 <sup>ii</sup>	0.9896(14)	2.087(13)	3.027(3)	158(3)
N2-H4...O5	0.81(3)	2.16(3)	2.763(3)	166(3)
N2-H6...O7 <sup>iii</sup>	0.93(3)	2.04(3)	2.960(4)	169(3)
N7-H7...O1 <sup>iv</sup>	0.8800(14)	2.121(8)	2.986(3)	167(3)
N7-H8...O4	0.8800(14)	2.038(8)	2.900(3)	166(3)
N7-H9...O6 <sup>iii</sup>	0.8800(14)	2.157(19)	2.913(4)	144(3)
N7-H10...O1 <sup>v</sup>	0.8800(14)	2.183(5)	3.058(3)	173(3)

Symmetry: [i = -x,y-1/2,-z+1/2]; [ii = x-1/2,-y+1/2,-z+1]; [iii = 1+x,y,z]; [iv = 1-x,1/2+y,1/2-z]; [v = 1/2-x,1-y,1/2+z]

Table T3: H-bonding interactions in the Cocaine Erdmann's salt (**3**)

H-bond geometry (Å) and angle (°)

D-H...A	D-H	H...A	D...A	D-H...A
N3-H3...O1 <sup>i</sup>	0.87	2.35(7)	3.140(7)	150(6)
N6-H4...O5 <sup>ii</sup>	0.91	2.37(6)	3.044(7)	131(6)
N3-H2...O3 <sup>i</sup>	0.88	2.36(7)	3.024(8)	132(4)
N3-H1...O9	0.88	2.30(2)	3.126(7)	156(5)
N3-H1...O10	0.88	2.47(4)	3.183(7)	139(5)
N6-H5...O7 <sup>ii</sup>	0.88	2.48(6)	3.286(8)	153(5)
N6-H6...O23	0.92	2.43(6)	3.103(7)	130(5)
N7-H7...O12 <sup>ii</sup>	0.94(6)	2.25(6)	3.072(7)	146(6)

N7-H8...O10 <sup>ii</sup>	0.88(6)	2.36(6)	3.110(7)	143(5)
N7-H9...O3	0.88	2.60(5)	3.165(7)	123(5)
N7-H9...O4	0.88	2.29(2)	3.146(7)	163(6)
N10-H11...O16 <sup>i</sup>	0.90 (6)	2.55(6)	3.023(7)	113(5)
N10-H11...O14 <sup>i</sup>	0.90 (6)	2.51(6)	3.185(8)	134(5)
N10-H10...O19 <sup>iv</sup>	0.88	2.23(3)	3.059(7)	157(6)
N13-H13...O14 <sup>iii</sup>	0.83(6)	2.36(5)	3.019(7)	134(5)
N13-H13...O19	0.86(6)	2.19(6)	2.838(7)	132(5)
N14-H14...O8	0.82(6)	2.62(6)	3.052(7)	114(5)
N14-H14...O23	0.82(6)	2.07(6)	2.805(7)	148(6)

Symmetry: [i = x-1,y,z]; [ii = x+1,y,z]; [iii = x,y+1,z]; [iv = x-1,y-1,z]

Table T4: H-bonding interactions in the Methamphetamine Erdmann's salt (4)

H-bond geometry (Å) and angle (°)

D-H...A	D-H	H...A	D...A	D-H...A
N12-H11...O8	0.92(7)	2.32(7)	3.215(9)	164(6)
N6-H6...O16	1.02(6)	2.33(6)	3.313(8)	161(5)
N6-H4...O9	0.89(7)	2.60(8)	3.302(9)	137(5)
N13-H14...O8	0.90(6)	2.01(6)	2.883(8)	164(7)
N13-H14...O7	0.95(7)	2.58(6)	3.207(8)	127(6)
N14-H16...O6 <sup>i</sup>	0.28(7)	2.45(7)	3.182(9)	136(6)
N14-H16...O5 <sup>i</sup>	0.92(7)	2.02(7)	2.921(8)	165(6)
N14-H15...O9 <sup>iv</sup>	0.88	1.99(2)	2.851(8)	164(6)
N11-H7...O12 <sup>ii</sup>	0.89(6)	1.74(6)	2.550(9)	149(6)
N11-H9...O14 <sup>ii</sup>	0.88(6)	1.53(7)	2.320(8)	147(7)
N12-H10...O10 <sup>iii</sup>	0.84(7)	2.54(8)	3.070(8)	122(6)

Symmetry: [i = x-1,y,z-1]; [ii = x-1,y,z]; [iii = x+1,y,z]; [iv = x,y,z-1]

Table T5: H-bonding interactions in the Methylone Erdmann's salt (5)

H-bond geometry (Å) and angle (°)

D-H...A	D-H	H...A	D...A	D-H...A
N2-H3...O4	0.91	2.32	2.82(1)	114
N2-H4...O3 <sup>i</sup>	0.91	2.51	3.28(1)	141
N2-H4...O5 <sup>ii</sup>	0.91	2.24	2.83(1)	122
N2-H2...O7	0.91	2.14	2.75()	123
N2-H2...O7 <sup>i</sup>	0.91	2.33	3.15(1)	149
N1-H1...N1 <sup>iii</sup>	0.88	2.40	2.90(1)	117
N1-H1...O4 <sup>iv</sup>	0.88	2.40	3.16(1)	145

Symmetry: [i = -x+1,-y+2,-z]; [ii = -x,-y+2,-z]; [iii = -x+2, -y,-z+1]; [iv = -x+1,-y+1,-z+1]

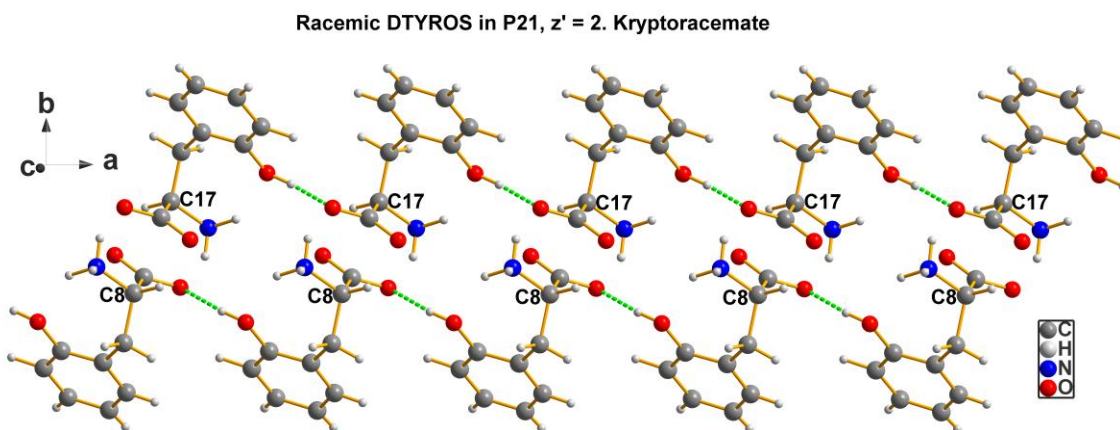
## Supplementary Material – Part 2

When the earliest observations on what became labeled as Racemic Mimics occurred (*ca.* 1950-1975; see refs. 14-17 in the text above), the phenomenon of kryptoracemic crystallization had not been noted and published. The initial announcement, and the coining of the word, did not come until 1995, when it was revealed (ref. 12 above.) Consequently, the authors of paper (ref. 17) labeled the crystals of (+/-)-o-tyrosine as racemic. The fact is that they really constitute a kryptoracemic pair, as demonstrated below.

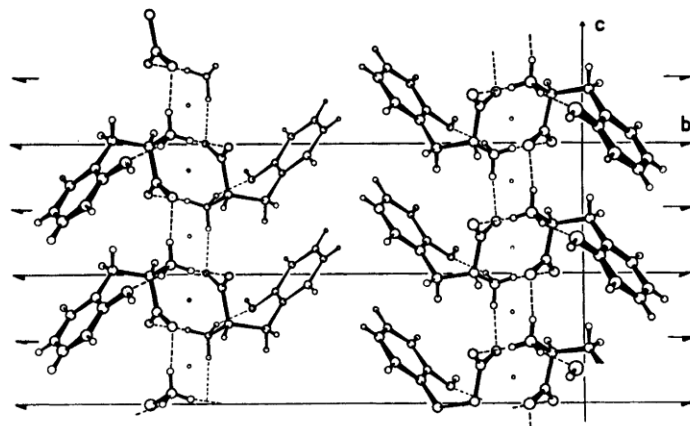
### Racemates in Chiral Lattices

#### 1. (+/-)-o-Tyrosine. Space group = $P2_1$ . DTYROS

Structure ordered,  $Z = 4$ ; therefore, it has a racemic pair of ordered enantiomers as the asymmetric unit. See: A. Mostad, C. Rømming and L. Tressum, *Acta Chem. Scand.*, **1975**, B29, 171-176. Therefore, this is a case of *kryptoracemic crystallization*. The pure enantiomer packs almost identically to this one.



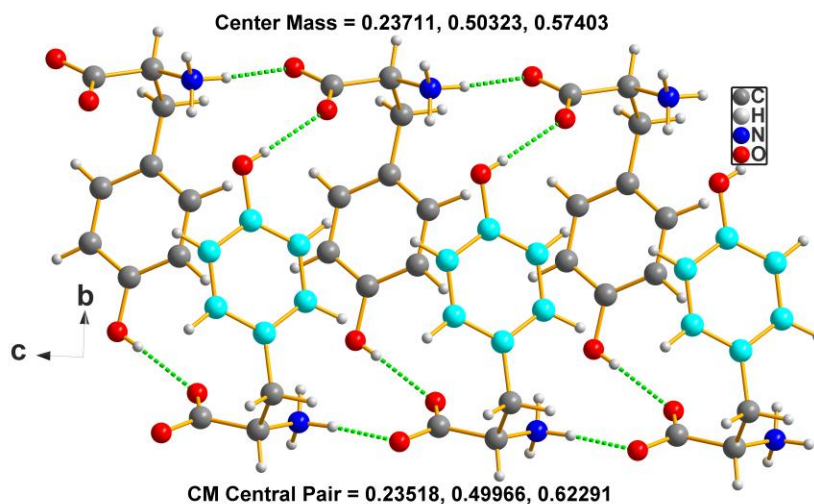
Note the pseudo-inversion center between the carboxylates. Also note that C8 and C17 are enantiomers. Additional, examples of such behavior are given below. Please compare that kryptoracemic packing (of the racemate) with the structure published by Mostad, Rømming and Tressum, noted above. The packing is identical for both; also note the pseudo-inversion centers in the pure chiral form displayed below.



*Fig. 3.* The crystal structure of *o*-tyrosine as viewed down the *a* axis. The non-crystallographic centres of symmetry are drawn as small circles.

*Acta Chem. Scand. B* 29 (1975) No. 2

A more modern view of the above packing is shown next:



The two racemic molecules are color-coded for emphasis.

Similar comments can be made on the structures below. However, this is not a proper forum for additional discussions, which can become quite elaborate. The brief remarks below may be helpful to the interested reader.

2. (+/-)-erythro-phenylglyceric acid. Space group =  $P2_1$ .

Structure ordered,  $Z = 4$ ; therefore, it has a pair of ordered enantiomers as the asymmetric unit. Also, see: (a) C. N. Riiber and E. Berner, Ber., **1917**, 50, 893; (b) S. Furberg and O. Hassel, Acta Chem. Scand., **1950**, 4, 1020; (c) M. Cesario, J. Guilhem, C. Pascard, A. Collet and J. Jacques, Nouv. J. Chim., **1978**, 2, 343. (*Another kryptoracemate.*)

3. (+/-)-carvoxime. Space group:  $P2_1$ .

Structure ordered,  $Z = 4$ ; therefore, it has a pair of ordered enantiomers as the asymmetric unit. See: Fulton, M., Baert, F., Fouret, Acta Cryst., **1979**, B35, 683. This species forms a series of continuous solid solutions with "unbalanced" amounts of enantiomers. The degree of disorder depends on the actual composition. That of the nearly (1:1) is almost ordered. The same is the case with carboximebenzene, Baert, F., Fouret, R., Oonk, N. A. J., Kroon, J., Acta Cryst., **1978**, B34, 222.

4. DL-methylsuccinic acid. Space group:  $P2_1$ .

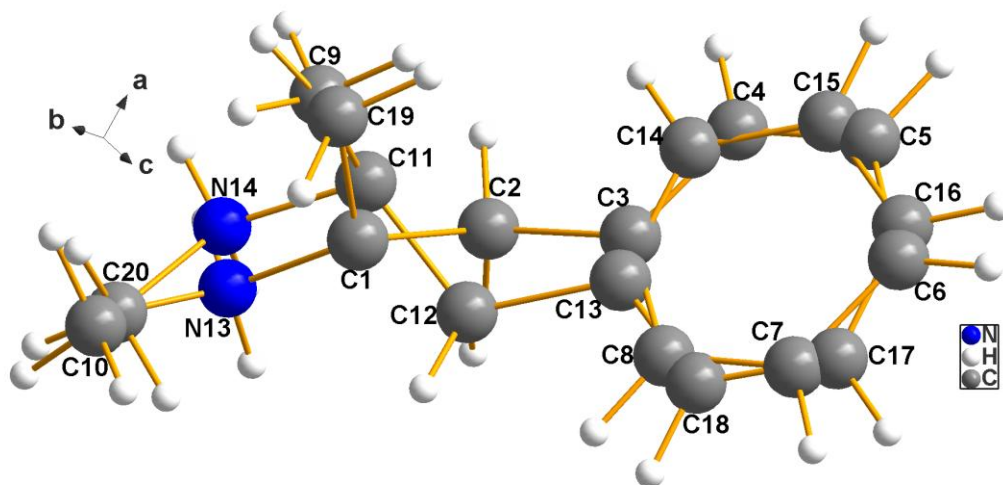
This structure has  $Z = 4$ ; it has a pair of ordered enantiomers as the asymmetric unit. See: Y. Schouwstra, Acta Cryst., **1973**, B29, 1636. *Therefore, it appears to be another kryptoracemate.*

There are many other examples of such behavior in the case of organic, metallo-organic and coordination compounds, all of which constitutes a gigantic area of investigation; many are old structures of possible unreliable information, such as space groups. Therefore, this constitutes an enormous area of research on its own – not a topic to be a side-line of a paper such as this.

*If the referee is really serious, please identify yourself and we can have a really long discussion of this topic. Maybe we can even publish some joint material on this subject.*

## Graphical Abstract

Overlay of the two independent molecules (racemic mimic) for the methamphetamine-Erdmann's complex.



Erdmann's anion crystallizes with methamphetamine in space group  $P2_1$ , with  $Z' = 2$ . An overlay of the two chirally-pure molecules by MERCURY (molecule2 was inverted, overlayed onto molecule 1, and the overlay optimized) produces the above result.