Crystal engineering with iodoethynylnitrobenzenes: A group of highly effective halogen-bond donors

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Supplementary Information

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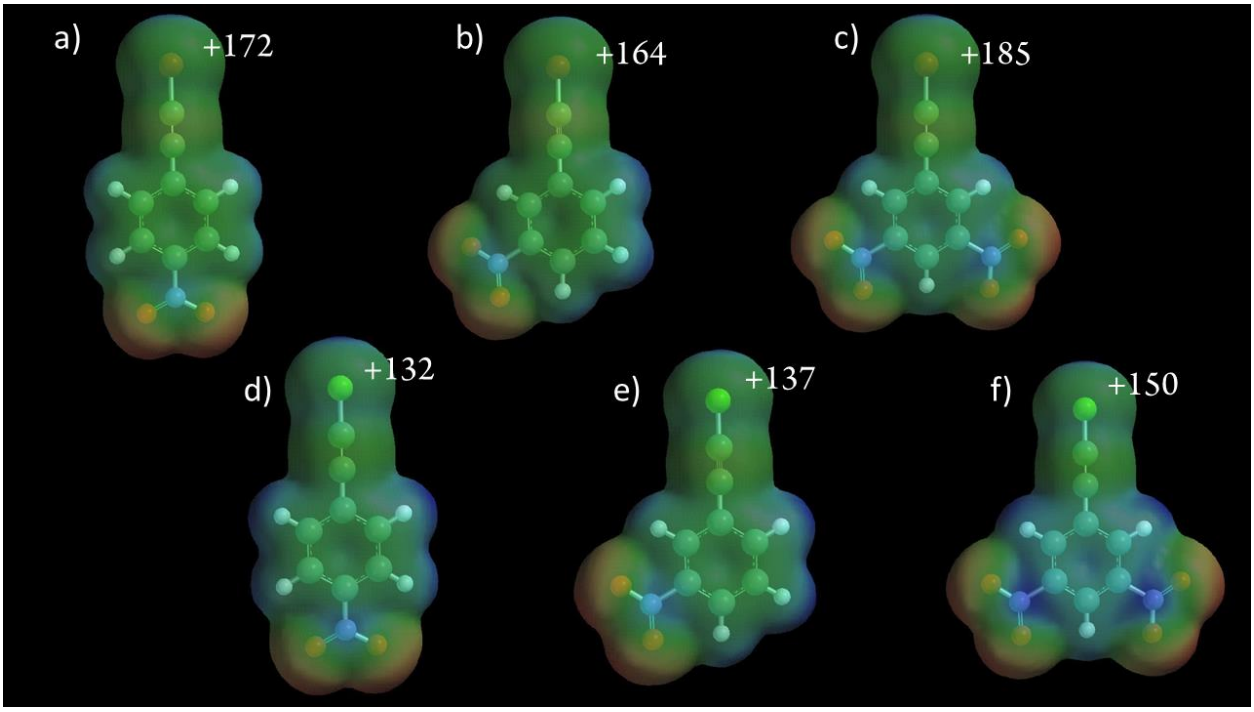
1. **Electrostatic potential surfaces for bromo- and chloro- compounds (in kJ/mol)**



a) 4N-Br b) 3N-Br c) 3,5DN-Br d) 4N-Cl e) 3N-Cl f) 3,5-DN-Cl

2. Experimental and IR data - iodoethynylnitrobenzenes

Code	Combined stoichiometry	IR results (wave numbers cm^{-1})		Shifts $\Delta(cm^{-1})$	Result	Crystal formation from solution
		Halogen bond donor	Co-crystal			
4N-I:A1	2:1	2165 (triple bond) 1498 (nitro asy.) 1335 (nitro sym.)	2170 1503 1340	+5 +5 +5	Co-crystal	Y
4N-I:A2	2:1	2165 (triple bond) 1498 (nitro asy.) 1335 (nitro sym.)	2168 1500 1338	+3 +2 +3	Co-crystal	Y
4N-I:A3	2:1	2165 (triple bond) 1498 (nitro asy.) 1335 (nitro sym.)	2151 1511 1338	-14 +13 +3	Co-crystal	Y
4N-I:A4	2:1	2165 (triple bond) 1498 (nitro asy.) 1335 (nitro sym.)	2152 1510 1338	-13 +12 +3	Co-crystal	Y
4N-I:A5	2:1	2165 (triple bond) 1498 (nitro asy.) 1335 (nitro sym.)	2155 1504 1339	-10 +6 +4	Co-crystal	Powder
4N-I:A6	2:1	2165 (triple bond) 1498 (nitro asy.) 1335 (nitro sym.)	2152 1508 1339	-13 +8 +4	Co-crystal	Y
4N-I:A7	2:1	2165 (triple bond) 1498 (nitro asy.) 1335 (nitro sym.)	2152 1510 1336	-13 +12 +1	Co-crystal	Y
4N-I:A8	2:1	2165 (triple bond) 1498 (nitro asy.) 1335 (nitro sym.)	2169 1499 1338	+4 +1 +3	Co-crystal	Y
4N-I:A9	2:1	2165 (triple bond) 1498 (nitro asy.) 1335 (nitro sym.)	2170 1500 1337	+5 +2 +2	Co-crystal	Y
4N-I:A10	2:1	2165 (triple bond) 1498 (nitro asy.) 1335 (nitro sym.)	2168 1487 1342	+3 -12 +7	Co-crystal	Y
4N-I:A11	1:1	2165 (triple bond) 1498 (nitro asy.) 1335 (nitro sym.)	2152 1508 1338	-13 +10 +3	Co-crystal	Y
4N-I:A12	1:1	2165 (triple bond) 1498 (nitro asy.) 1335 (nitro sym.)	2156 1501 1337	-9 +3 +2	Co-crystal	Y
4N-I:A13	2:1	2165 (triple bond) 1498 (nitro asy.) 1335 (nitro sym.)	2168 1495 1334	+3 +3 -1	Co-crystal	Y
4N-I:A14	2:1	2165 (triple bond) 1498 (nitro asy.) 1335 (nitro sym.)	2169 1499 1338	+4 +1 +3	Co-crystal	Y
4N-I:A15	2:1	2165 (triple bond) 1498 (nitro asy.) 1335 (nitro sym.)	2177 1509 1341	+15 +11 +6	Co-crystal	Powder
3N-I:A1	2:1	2172 (triple bond) 1514 (nitro asy.)	2151 1502	-21 -12	Co-crystal	Y

		1343 (nitro sym.)	1336	-7		
3N-I:A2	2:1	2172 (triple bond) 1514 (nitro asy.) 1343 (nitro sym.)	2159 1499 1339	-13 -15 -4	Co-crystal	Y
3N-I:A3	2:1	2172 (triple bond) 1514 (nitro asy.) 1343 (nitro sym.)	2163 1519 1347	-9 +5 +4	Co-crystal	Y
3N-I:A4	2:1	2172 (triple bond) 1514 (nitro asy.) 1343 (nitro sym.)	2159 1522 1348	-13 +8 +5	Co-crystal	Y
3N-I:A5	2:1	2172 (triple bond) 1514 (nitro asy.) 1343 (nitro sym.)	2159 1520 1346	-13 +6 +3	Co-crystal	Y
3N-I:A6	2:1	2172 (triple bond) 1514 (nitro asy.) 1343 (nitro sym.)	2159 1522 1344	-13 +8 +1	Co-crystal	Y
3N-I:A7	2:1	2172 (triple bond) 1514 (nitro asy.) 1343 (nitro sym.)	2168 1519 1346	-4 +5 +3	Co-crystal	Y
3N-I:A8	2:1	2172 (triple bond) 1514 (nitro asy.) 1343 (nitro sym.)	2175 1519 1347	+3 +5 +4	Co-crystal	Powder
3N-I:A9	2:1	2172 (triple bond) 1514 (nitro asy.) 1343 (nitro sym.)	2168 1516 1346	-4 +2 +3	Co-crystal	Y
3N-I:A10	2:1	2172 (triple bond) 1514 (nitro asy.) 1343 (nitro sym.)	2156 1515 1346	-16 +1 +3	Co-crystal	Y
3N-I:A11	1:1	2172 (triple bond) 1514 (nitro asy.) 1343 (nitro sym.)	2159 1519 1345	-13 +5 +2	Co-crystal	Y
3N-I:A12	1:1	2172 (triple bond) 1514 (nitro asy.) 1343 (nitro sym.)	2177 1515 1346	+5 +1 +3	Co-crystal	Y
3N-I:A13	2:1	2172 (triple bond) 1514 (nitro asy.) 1343 (nitro sym.)	2176 1522 1352	+4 +8 +9	Co-crystal	Y
3N-I:A14	2:1	2172 (triple bond) 1514 (nitro asy.) 1343 (nitro sym.)	2151 1520 1348	-21 +6 +5	Co-crystal	Y
3N-I:A15	2:1	2172 (triple bond) 1514 (nitro asy.) 1343 (nitro sym.)	2169 1518 1350	+3 +4 +7	Co-crystal	Y
3,5DN-I:A1	2:1	2167 (triple bond) 1525 (nitro asy.) 1336 (nitro sym.)	2159 1533 1339	-8 +8 +3	Co-crystal	Powder
3,5DN-I:A2	2:1	2167 (triple bond) 1525 (nitro asy.) 1336 (nitro sym.)	2156 1529 1338	-11 +4 +2	Co-crystal	Y
3,5DN-I:A3	2:1	2167 (triple bond) 1525 (nitro asy.) 1336 (nitro sym.)	2154 1532 1346	-13 +7 +10	Co-crystal	Y
3,5DN-I:A4	2:1	2167 (triple bond) 1525 (nitro asy.) 1336 (nitro sym.)	2157 1532 1339	-10 +7 +3	Co-crystal	Y

3,5DN-I:A5	2:1	2167 (triple bond) 1525 (nitro asy.) 1336 (nitro sym.)	2158 1528 1339	-9 +3 +3	Co-crystal	Y
3,5DN-I:A6	2:1	2167 (triple bond) 1525 (nitro asy.) 1336 (nitro sym.)	2151 1532 1341	-16 +7 +5	Co-crystal	Y
3,5DN-I:A7	2:1	2167 (triple bond) 1525 (nitro asy.) 1336 (nitro sym.)	2150 1531 1343	-17 +6 +7	Co-crystal	Y
3,5DN-I:A8	2:1	2167 (triple bond) 1525 (nitro asy.) 1336 (nitro sym.)	2160 1533 1340	-7 +8 +4	Co-crystal	Y
3,5DN-I:A9	2:1	2167 (triple bond) 1525 (nitro asy.) 1336 (nitro sym.)	2160 1531 1342	-7 +6 +6	Co-crystal	Y
3,5DN-I:A10	2:1	2167 (triple bond) 1525 (nitro asy.) 1336 (nitro sym.)	2160 1533 1340	-7 +8 +4	Co-crystal	Y
3,5DN-I:A11	1:1	2167 (triple bond) 1525 (nitro asy.) 1336 (nitro sym.)	2177 1530 1340	+10 +5 +4	Co-crystal	Y
3,5DN-I:A12	1:1	2167 (triple bond) 1525 (nitro asy.) 1336 (nitro sym.)	2163 1526 1341	-4 +1 +5	Co-crystal	Y
3,5DN-I:A13	2:1	2167 (triple bond) 1525 (nitro asy.) 1336 (nitro sym.)	2171 1531 1341	+4 +6 +5	Co-crystal	Y
3,5DN-I:A14	2:1	2167 (triple bond) 1525 (nitro asy.) 1336 (nitro sym.)	2170 1531 1342	+3 +6 +6	Co-crystal	Y
3,5DN-I:A15	2:1	2167 (triple bond) 1525 (nitro asy.) 1336 (nitro sym.)	2150 1530 1341	-17 +5 +5	Co-crystal	Powder

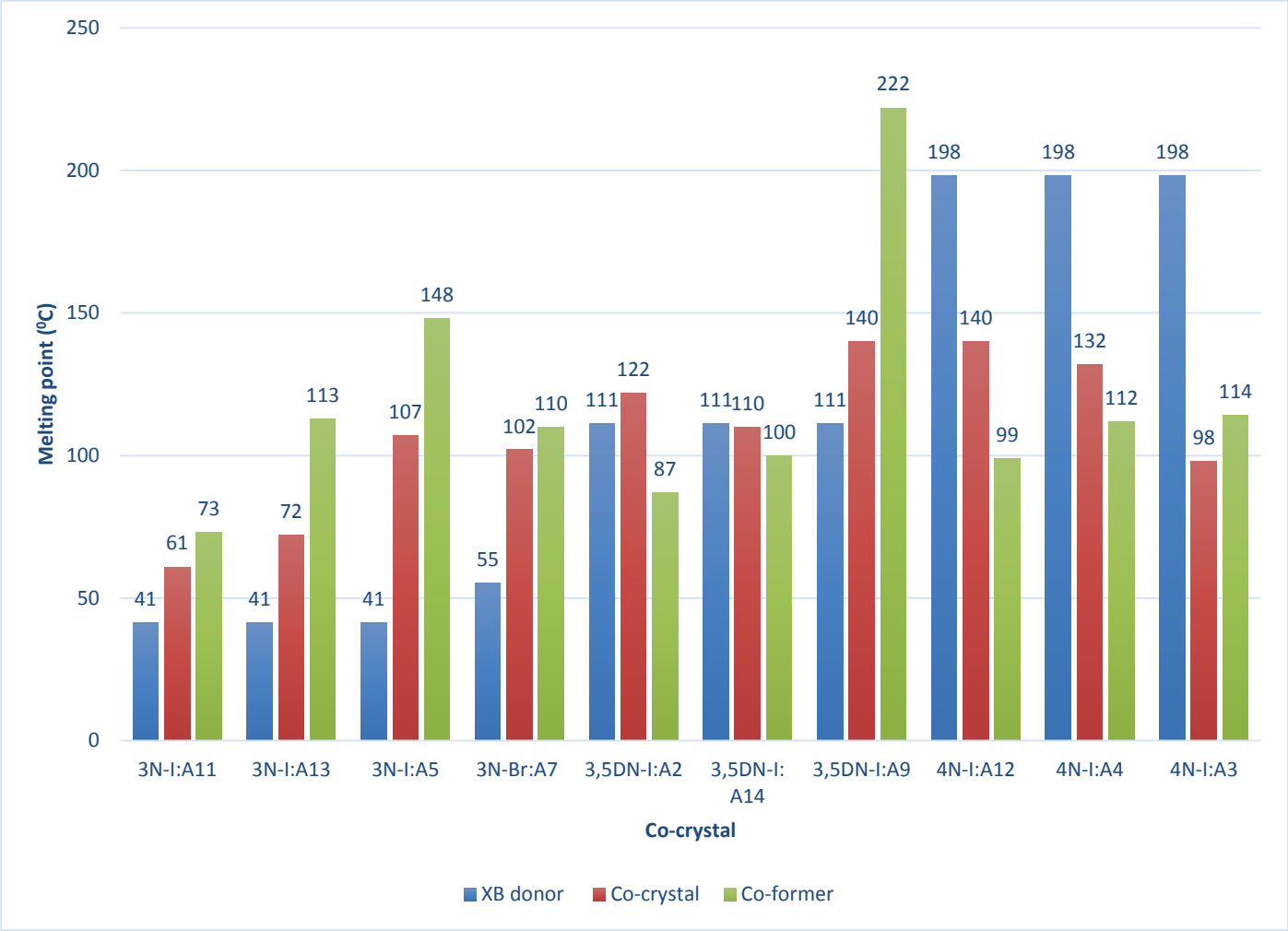
3. Experimental and IR data – bromoethynylnitrobenzenes

Code	Combined stoichiometry	IR results (wave numbers cm^{-1})		Shifts Δcm^{-1}	Result	Crystal formation from solution
		Halogen bond donor	Co-crystal			
4N-Br:A3	2:1	2190 (triple bond) 1502 (nitro asy.) 1341 (nitro sym.)	2194 1505 1340	+4 +3 -1	Co-crystal	Flimsy crystals
4N-Br:A4	2:1	2190 (triple bond) 1502 (nitro asy.) 1341 (nitro sym.)	2194 1503 1340	+4 -2 -1	Co-crystal	Powder
4N-Br:A7	2:1	2190 (triple bond) 1502 (nitro asy.) 1341 (nitro sym.)	2188 1502 1341	-2 0 0	Not a co-crystal	NA
4N-Br:A11	1:1	2190 (triple bond) 1502 (nitro asy.) 1341 (nitro sym.)	2193 1503 1343	+3 +1 +2	Co-crystal	Flimsy crystals
4N-Br:A13	2:1	2190 (triple bond) 1502 (nitro asy.) 1341 (nitro sym.)	2190 1503 1340	0 +1 -1	Not a co-crystal	Flimsy crystals
3N-Br:A3	2:1	2198 (triple bond) 1518 (nitro asy.) 1344 (nitro sym.)	2193 1523 1346	-5 +5 +2	Co-crystal	Powder
3N-Br:A4	2:1	2198 (triple bond) 1518 (nitro asy.) 1344 (nitro sym.)	2199 1519 1344	+1 +1 0	Not a co-crystal	NA
3N-Br:A7	2:1	2198 (triple bond) 1518 (nitro asy.) 1344 (nitro sym.)	2190 1521 1343	-8 +3 -1	Co-crystal	Flimsy crystals
3N-Br:A11	1:1	2198 (triple bond) 1518 (nitro asy.) 1344 (nitro sym.)	2201 1521 1347	+3 +3 +3	Co-crystal	Powder
3N-Br:A13	2:1	2198 (triple bond) 1518 (nitro asy.) 1344 (nitro sym.)	2194 1523 1344	-4 +5 0	Co-crystal	Gel
3,5DN-Br:A3	2:1	2193 (triple bond) 1532 (nitro asy.) 1339 (nitro sym.)	2196 1531 1342	+3 -1 +3	Co-crystal	Powder
3,5DN-Br:A4	2:1	2193 (triple bond) 1532 (nitro asy.) 1339 (nitro sym.)	2193 1533 1340	0 +1 +1	Not a co-crystal	NA
3,5DN-Br:A7	2:1	2193 (triple bond) 1532 (nitro asy.) 1339 (nitro sym.)	2197 1534 1341	+4 +2 +2	Co-crystal	Flimsy crystals
3,5DN-Br:A11	1:1	2193 (triple bond) 1532 (nitro asy.) 1339 (nitro sym.)	2193 1532 1341	0 0 +2	Not a co-crystal	NA
3,5DN-Br:A13	2:1	2193 (triple bond) 1532 (nitro asy.) 1339 (nitro sym.)	2193 1532 1339	0 0 0	Not a co-crystal	NA

4. Experimental and IR data – chloroethynylnitrobenzenes

Code	Combined stoichiometry	IR results (wave numbers cm^{-1})		Shifts Δcm^{-1}	Co-crystal or not	Crystal formation from solution
		Halogen bond donor	Co-crystal			
4N-Cl:A3	2:1	2208 (triple bond) 1505 (nitro asy.) 1343 (nitro sym.)	2210 1507 1341	+2 +2 -2	Not a co-crystal	NA
4N-Cl :A4	2:1	2208 (triple bond) 1505 (nitro asy.) 1343 (nitro sym.)	2209 1503 1341	+1 -2 -2	Not a co-crystal	NA
4N-Cl :A7	2:1	2208 (triple bond) 1505 (nitro asy.) 1343 (nitro sym.)	2210 1505 1342	+2 0 -1	Not a co-crystal	NA
4N-Cl :A11	1:1	2208 (triple bond) 1505 (nitro asy.) 1343 (nitro sym.)	2209 1507 1343	+1 +2 0	Not a co-crystal	NA
4N-Cl:A13	2:1	2208 (triple bond) 1505 (nitro asy.) 1343 (nitro sym.)	2210 1503 1343	+2 -2 0	Not a co-crystal	NA
3N-Cl:A3	2:1	2221 (triple bond) 1524 (nitro asy.) 1337 (nitro sym.)	2221 1526 1339	0 +2 +1	Not a co-crystal	NA
3N-Cl:A4	2:1	2221 (triple bond) 1524 (nitro asy.) 1337 (nitro sym.)	2222 1523 1338	+1 -1 +1	Not a co-crystal	NA
3N-Cl:A7	2:1	2221 (triple bond) 1524 (nitro asy.) 1337 (nitro sym.)	2219 1522 1338	-2 -2 +1	Not a co-crystal	NA
3N-Cl:A11	1:1	2221 (triple bond) 1524 (nitro asy.) 1337 (nitro sym.)	2221 1523 1338	0 -1 +1	Not a co-crystal	NA
3N-Cl:A13	2:1	2221 (triple bond) 1524 (nitro asy.) 1337 (nitro sym.)	2222 1525 1338	+1 +1 +1	Not a co-crystal	NA
3,5DN-Cl:A3	2:1	2213 (triple bond) 1536 (nitro asy.) 1340 (nitro sym.)	2215 1534 1338	+2 -2 -2	Not a co-crystal	NA
3,5DN-Cl:A4	2:1	2213 (triple bond) 1536 (nitro asy.) 1340 (nitro sym.)	2214 1535 1340	+1 -1 0	Not a co-crystal	NA
3,5DN-Cl:A7	2:1	2213 (triple bond) 1536 (nitro asy.) 1340 (nitro sym.)	2215 1535 1340	+2 -1 0	Not a co-crystal	NA
3,5DN-Cl:A11	1:1	2213 (triple bond) 1536 (nitro asy.) 1340 (nitro sym.)	2211 1534 1340	-2 -2 0	Not a co-crystal	NA
3,5DN-Cl:A13	2:1	2213 (triple bond) 1536 (nitro asy.) 1340 (nitro sym.)	2214 1537 1339	+1 +1 -1	Not a co-crystal	NA

5. Melting point data



6. X-ray experimental data

The samples were analyzed with a Bruker APEX II system using MoKα radiation. Data collection was carried out using APEX2 software.[1] Initial cell constants were found by small widely separated "matrix" runs. Data collection strategies were determined using COSMO.[2] Scan speed and scan widths were chosen based on scattering power and peak rocking curves. All datasets were collected at -153 °C using an Oxford Croystream low-temperature device.

Unit cell constants and orientation matrix were improved by least-squares refinement of reflections thresholded from the entire dataset. Integration was performed with SAINT,[3] using this improved unit cell as a starting point. Precise unit cell constants were calculated in SAINT from the final merged dataset. Lorenz and polarization corrections were applied. Multi-scan absorption corrections were performed with SADABS[4] unless otherwise indicated.

Data were reduced with SHELXTL.[5] The structure was solved by direct methods without incident. All hydrogen atoms were located in idealized positions and were treated with a riding model. Unless otherwise noted, non-hydrogen atoms were assigned anisotropic thermal parameters. Refinements continued to convergence, using the recommended weighting schemes.

Dataset for **3,5DN-I:A9** was collected on an Oxford Diffraction Xcalibur four-circle kappa geometry single-crystal diffractometer with Sapphire 3 CCD detector, using a graphite monochromated MoKα (λ = 0.71073 Å) radiation, and applying the CrysAlisPro Software system[6] at 296 K. The crystal–detector distance was 45 mm.

Data reduction, including Lorentz and polarization corrections as well as absorption correction, was done by CrysAlis RED program.[6] The structure was solved by direct methods implemented in the SHELXS-2013 program.[7] The coordinates and the anisotropic displacement parameters for all non-hydrogen atoms were refined by full-matrix least-squares methods based on F^2 using the SHELXL-2013 program.[7]

All hydrogen atoms were placed in geometrically idealized positions and constrained to ride on their carbon atom at distances of 0.93 or 0.96 Å for aromatic or methyl hydrogen atoms, respectively, and with $U_{iso}(H) = 1.2U_{eq}(C)$ (for aromatic H) and $U_{iso}(H) = 1.5U_{eq}(C)$ (for methyl group).

4N-I:A3 - The crystal was a non-merohedral twin, and data were processed with TWINABS.[8] The asymmetric unit contains a half-iodo compound (located on a mirror plane), a quarter-diamine compound (located on a 2/m special position) and a solvent site (straddling a 2/m special position).

Solvent was assigned as 10% ethyl acetate and 15% water. No attempt was made to locate the hydrogen atoms on the water. All solvent atoms shared the same isotropic thermal parameter. The ethyl acetate was constrained to an idealized geometry and refined as a rigid body.

4N-I:A4 - The asymmetric unit contains an iodo compound and a half-diamine compound (located on an inversion center).

4N-I:A12 - The asymmetric unit contains a single iodo compound and a single amine compound.

3N-I:A5 - The asymmetric unit contains an iodo compound and a half-diamine compound (located on an inversion center).

3N-I:A11 - The asymmetric unit contains two iodo compound / amine compound pairs. Each pair was assigned to a SHELXL RESIdue.

3N-I:A13 - The asymmetric unit contains an iodo compound and an amine / amine oxide compound. The nitro group was disordered over two closely related positions, representing wobble around the C-NO_2 bond. Geometries of the two species were restrained with the SAME command, and thermal parameters were pairwise constrained using EADP commands.

3,5DN-I:A2 - The asymmetric unit contains an iodo compound and a half-diamine compound (located on an inversion center).

3,5DN-I:A14 - The asymmetric unit contains an iodo compound and a half-amine / amine oxide compound. The latter compound straddles a crystallographic inversion center and was assigned 50% occupancy. Thermal parameters for closely located atoms were pairwise constrained using the EADP command.

3N-Br:A7 - The asymmetric unit contains a bromo compound and a half-diamine compound (located on an inversion center).

7. Crystallographic data

Code	**4N-I:A3**	**4N-I:A4**	**4N-I:A12**	**3N-I:A5**	**3N-I:A11**
Systematic name	4-(iodoethynyl)-nitrobenzene, 4,4'-bipyridyl	[4-(iodo-ethynyl)-nitro-benzene]$_2$, 1,2-bis(4-pyridyl)ethane	4-(iodoethynyl)-nitrobenzene, (4-pyridyl)-N=N-(phenyl)	[3-(iodo-ethynyl)-nitro-benzene]$_2$, 1,2-bis(4-pyridyl)ethylene	3-(iodoethynyl)-nitrobenzene, 4-phenyl-pyridine
Formula moiety	$(C_8H_4INO_2)$ $(C_{10}H_8N_2)_1$ $(C_4H_8O_2)_{0.4}$ $(O)_{0.6}$	$(C_8H_4INO_2)$ $(C_{12}H_{12}N_2)$	$(C_8H_4INO_2)$ $(C_{11}H_9N_3)$	$(C_8H_4INO_2)_2$ $(C_{12}H_{10}N_2)$	$(C_8H_4INO_2)$ $(C_{11}H_9N)$
Empirical formula	$C_{27.60}H_{19.20}I_2N_4O_{5.40}$	$C_{28}H_{20}I_2N_4O_4$	$C_{19}H_{13}IN_4O_2$	$C_{28}H_{18}I_2N_4O_4$	$C_{19}H_{13}IN_2O_2$
Molecular weight	747.07	730.28	456.23	728.26	428.21
Color, Habit	yellow plate	bronze plate	orange plate	orange plate	bronze prism
Crystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic	Triclinic
Space group, Z	C2/m, 2	C2/c, 4	P -1, 2	C2/c, 4	P -1, 4
a, Å^3	37.367(9)	27.050(4)	6.9150(16)	30.735(4)	10.8063(11)
b, Å^3	9.281(2)	6.5379(9)	7.4716(17)	4.1717(5)	11.8386(12)
c, Å^3	3.9389(10)	15.045(2)	17.015(4)	24.404(3)	14.1068(15)
α, °	90.00	90.00	81.600(6)	90.00	75.741(3)
β, °	93.504(13)	90.353(3)	86.083(5)	122.674(2)	74.494(3)
γ, °	90.00	90.00	88.809(5)	90.00	77.324(3)
Volume, Å^3	1363.5(5)	2660.7(6)	867.6(3)	2633.9(5)	1662.5(3)
Density, g/cm^3	1.820	1.823	1.746	1.837	1.711
Temp, °K	120(2)	120(2)	120(2)	120(2)	120(2)
Crystal size, min x mid x max	0.06 x 0.20 x 0.34	0.18 x 0.42 x 0.44	0.240 x 0.380 x 0.500	0.08 x 0.28 x 0.42	0.220 x 0.300 x 0.420
X-ray wavelength, Å	0.71073	0.71073	0.71073	0.71073	0.71073
μ, mm^{-1}	2.353	2.406	1.867	2.430	1.939
Absorption corr	multi-scan	multi-scan	multi-scan	multi-scan	multi-scan
Trans min / max	0.5017 / 0.8717	0.4174 / 0.6713	0.518 / 0.663	0.4284 / 0.8293	0.596 / 0.675
θ_{min}, °	1.09	1.51	2.425	1.57	1.529
θ_{max}, °	30.70	31.75	32.067	31.62	32.384
Reflections					
collected	10251	23927	24441	18477	77079
independent	10251	4226	5375	4178	11385
observed	9111	3947	4820	3862	10260
Threshold expression	>2σ(I)	>2σ(I)	>2σ(I)	>2σ(I)	>2σ(I)
R_1 (observed)	0.0663	0.0184	0.0386	0.0201	0.0240
wR_2 (all)	0.1853	0.0492	0.1262	0.0582	0.0610
Goodness of fit (all)	1.061	0.959	1.211	1.095	1.035
Δρ max / min	3.267 / -2.547	0.600 / -0.420	1.594 / -1.417	0.503 / -0.583	1.043 / -0.677
2θ limit	30.00	30.00	30.000	30.00	31.500
Completeness to 2θ limit	0.957	0.989	0.972	0.996	0.982

Code	**3N-I:A13**	**3,5DN-I:A2**	**3,5DN-I:A9**	**3,5DN-I:A14**	**3N-Br:A7**
Systematic name	3-(iodoethynyl)-nitrobenzene, pyrazine 1-oxide	[5-(iodo-ethynyl)-1,3-dinitro-benzene]$_2$, 2,3,5,6-Me$_4$-pyrazine	1-(iodoethynyl)-2,5dinitrobenze 2,3,5,6-tetramethylpyrazine 1,4-dioxide	[5-(iodo-ethynyl)-1,3-dinitro-benzene]$_2$, 2,3,5,6-Me$_4$-pyrazine-1-oxide	[3-(bromo-ethynyl)-nitro-benzene]$_2$, (4-pyridyl)-N=N-(4-pyridyl)
Formula moiety	$(C_8H_4INO_2)$ $(C_4H_4N_2O)$	$(C_8H_3IN_2O_4)_2$ $(C_8H_{12}N_2)$	$(C_8H_3IN_2O_4)$ $0.5(C_8H_{12}N_2O_2)$	$(C_8H_3IN_2O_4)_2$ $(C_8H_{12}N_2O_2)$	$(C_8H_4INO_2)$ $(C_{10}H_8N_4)$
Empirical formula	$C_{12}H_8IN_3O_3$	$C_{24}H_{18}I_2N_6O_8$	$C_{12}H_9IN_3O_5$	$C_{24}H_{18}I_2N_6O_9$	$C_{26}H_{16}Br_2N_6O_4$
Molecular weight	369.11	772.24	402.12	788.24	636.27
Color, Habit	bronze rod	bronze prism	colourless block	red block	bronze prism
Crystal system	Triclinic	Triclinic	Monoclinic	Monoclinic	Triclinic
Space group, Z	P-1, 2	P-1, 1	C2/c, 8	C 2/c, 4	P -1, 1
a, Å^3	4.0966(5)	8.1864(10)	15.4144(6)	15.1898(10)	3.8963(5)
b, Å^3	11.8038(16)	8.5567(11)	8.2857(3)	8.2587(5)	11.7174(15)
c, Å^3	13.4460(18)	11.0361(14)	22.9469(7)	22.1641(14)	14.7266(18)
α, °	98.083(4)	70.225(3)	90.00	90	70.319(3)
β, °	97.777(3)	72.603(3)	95.327(3)	93.6905(17)	82.570(4)
γ, °	94.731(3)	68.891(3)	90.00	90	87.838(4)
Volume, Å^3	634.38(14)	664.70(14)	2918.1(2)	2774.7(3)	627.73(14)
Density, g/cm^3	1.932	1.929	1.831	1.887	1.683
Temp, °K	120(2)	120(2)	296(2)	120(2)	120(2)
Crystal size, min x mid x max	0.08 x 0.12 x 0.38	0.28 x 0.42 x 0.44	0.26 x 0.37 x 0.43	0.240 x 0.280 x 0.300	0.200 x 0.360 x 0.480
X-ray wavelength, Å	0.71073	0.71073	0.71073	0.71073	0.71073
μ, mm^{-1}	2.531	2.426	2.219	2.329	3.275
Absorption corr	multi-scan	multi-scan	multi-scan	multi-scan	multi-scan
Trans min / max	0.4463 / 0.8231	0.4149 / 0.5499	0.426 / 0.573	0.473 / 0.605	0.432 / 0.560
θ_{min}, °	1.75	2.00	4.60	1.841	1.846
θ_{max}, °	31.49	32.03	30.84	32.597	32.591
Reflections					
collected	16750	14426	7862	17959	18433
independent	4002	4337	4245	4749	4237
observed	3747	3996	3437	4565	3954
Threshold expression	>2σ(I)	>2σ(I)	>2σ(I)	>2σ(I)	>2σ(I)
R_1 (observed)	0.0278	0.0399	0.0331	0.0292	0.0298
wR_2 (all)	0.0728	0.1139	0.0775	0.0822	0.0795
Goodness of fit (all)	1.061	1.082	0.971	1.175	1.014
Δρ max / min	2.040 / -1.079	2.328 / -2.282	0.446 / -0.543	0.633 / -0.959	1.303 / -0.504
2θ limit	31.49	30.00	30.00	30.000	30.000
Completeness to 2θ limit	0.955	0.994	0.995	0.987	0.994

8. IR spectra

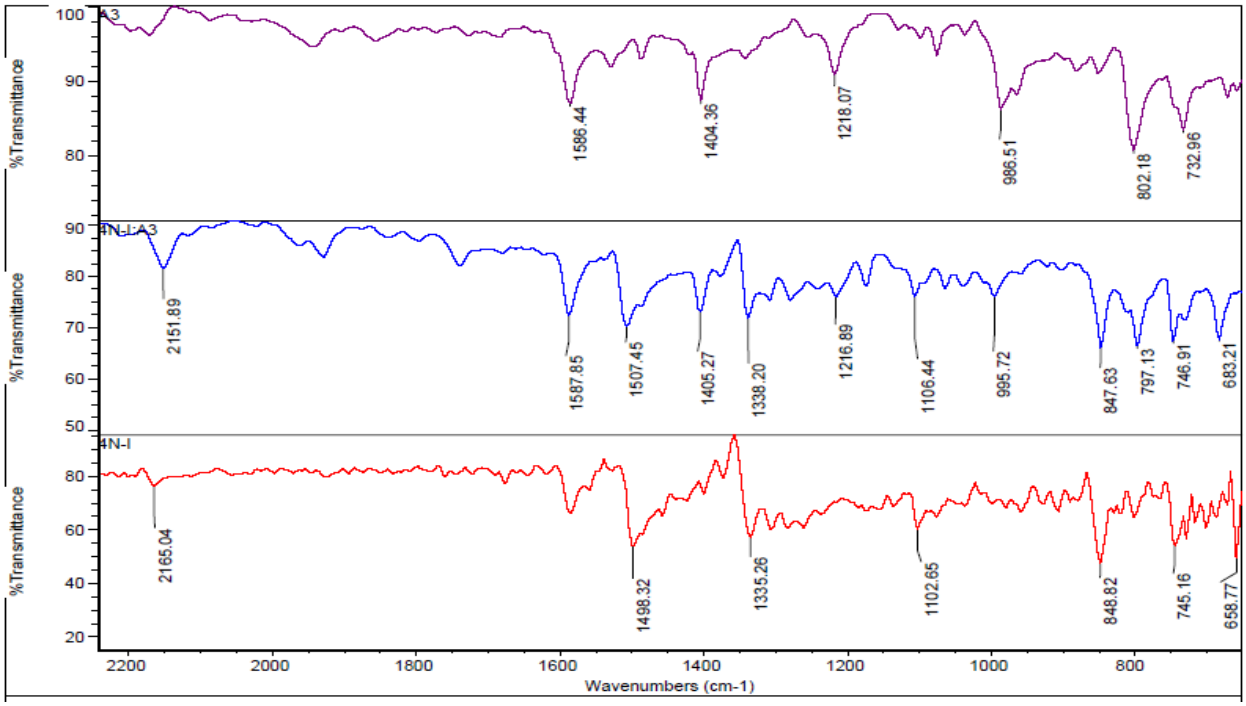


Fig. S1: IR spectra comparison for **4N-I:A3** co-crystal

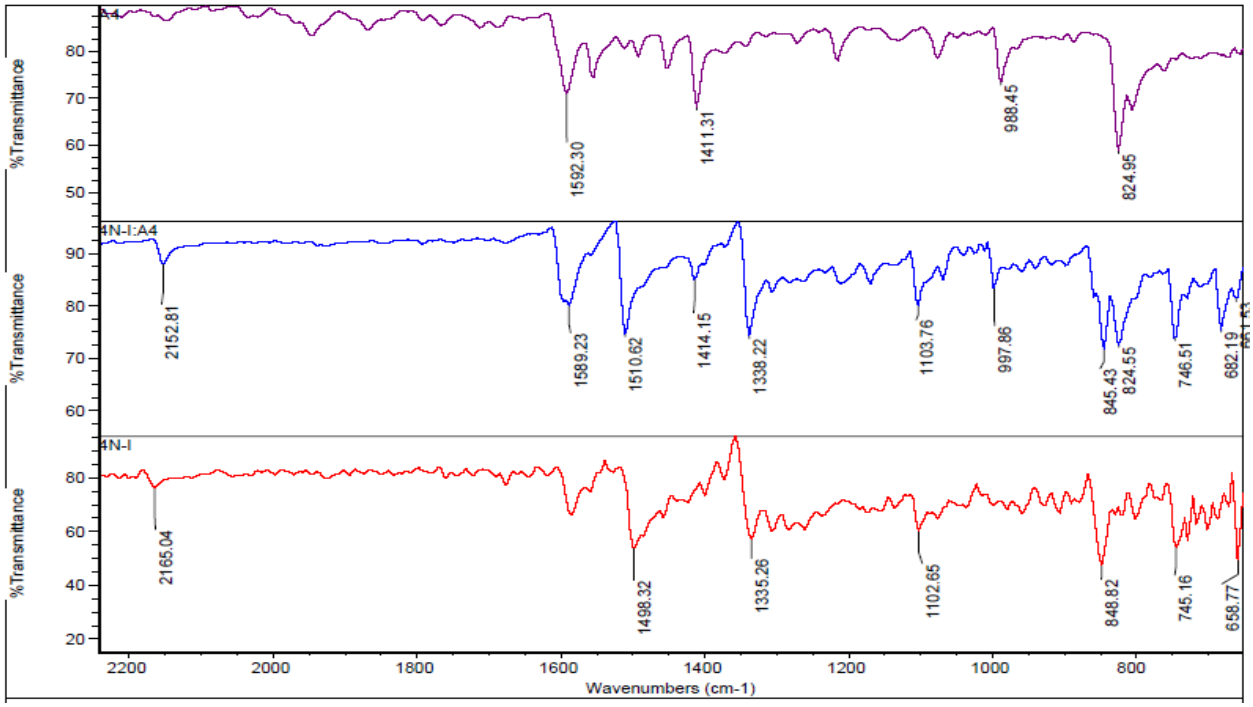


Fig. S2: IR spectra comparison for **4N-I:A4** co-crystal

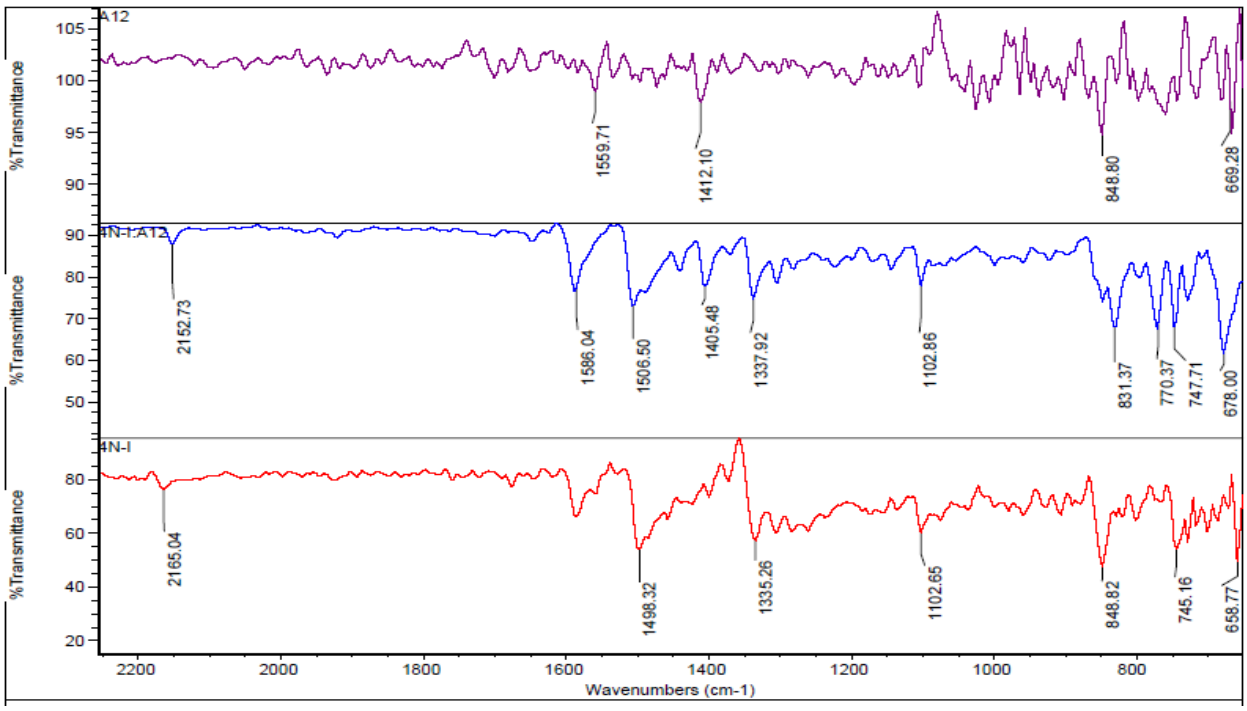


Fig. S3: IR spectra comparison for **4N-I:A12** co-crystal

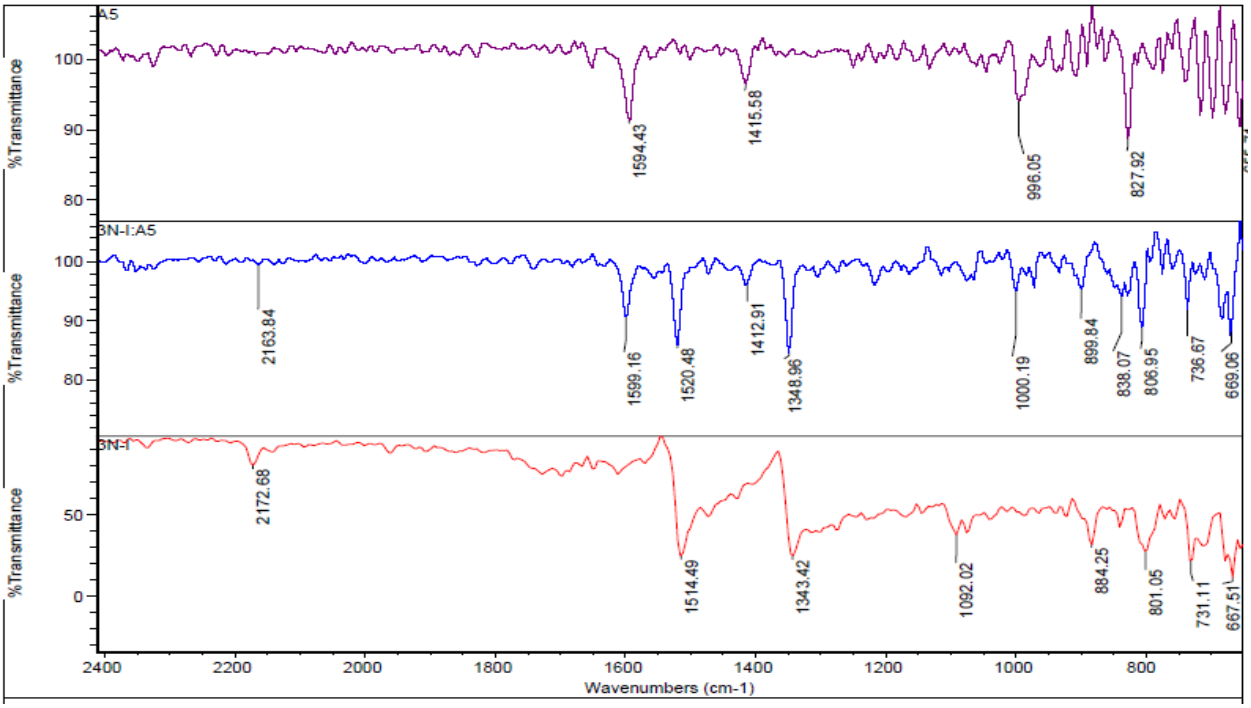


Fig. S4: IR spectra comparison for **3N-I:A5** co-crystal

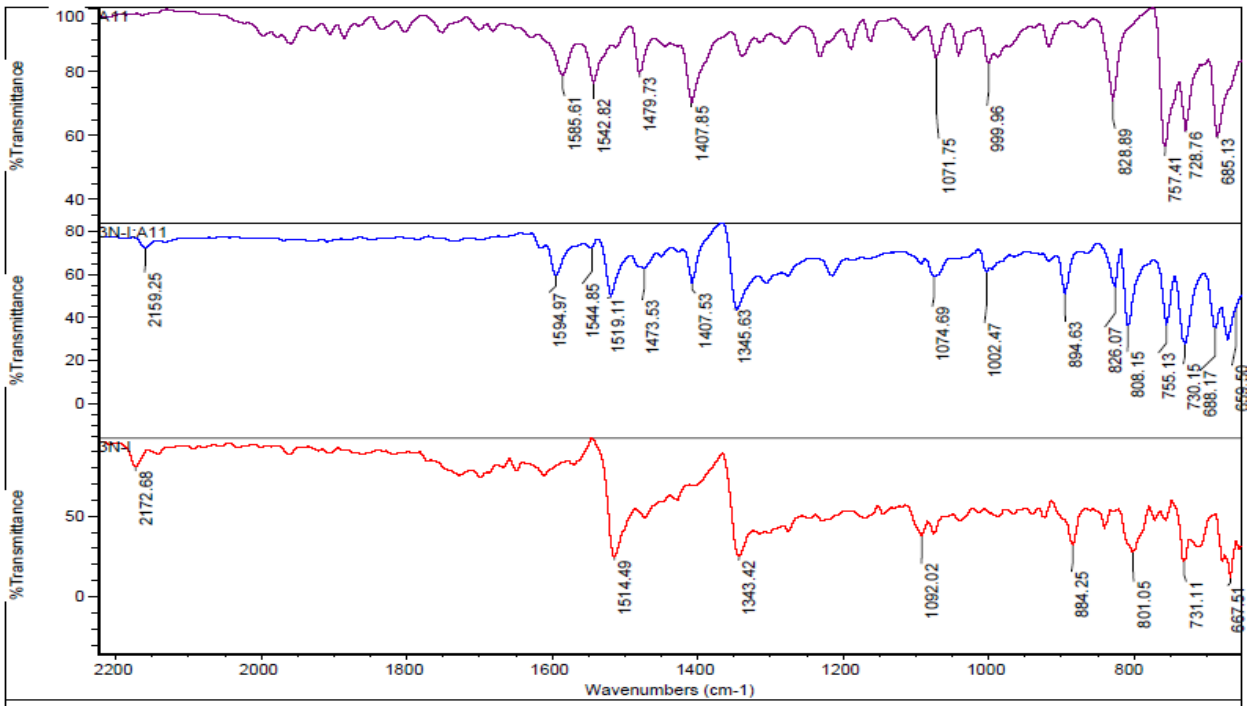


Fig. S5: IR spectra comparison for **3N-I:A11** co-crystal

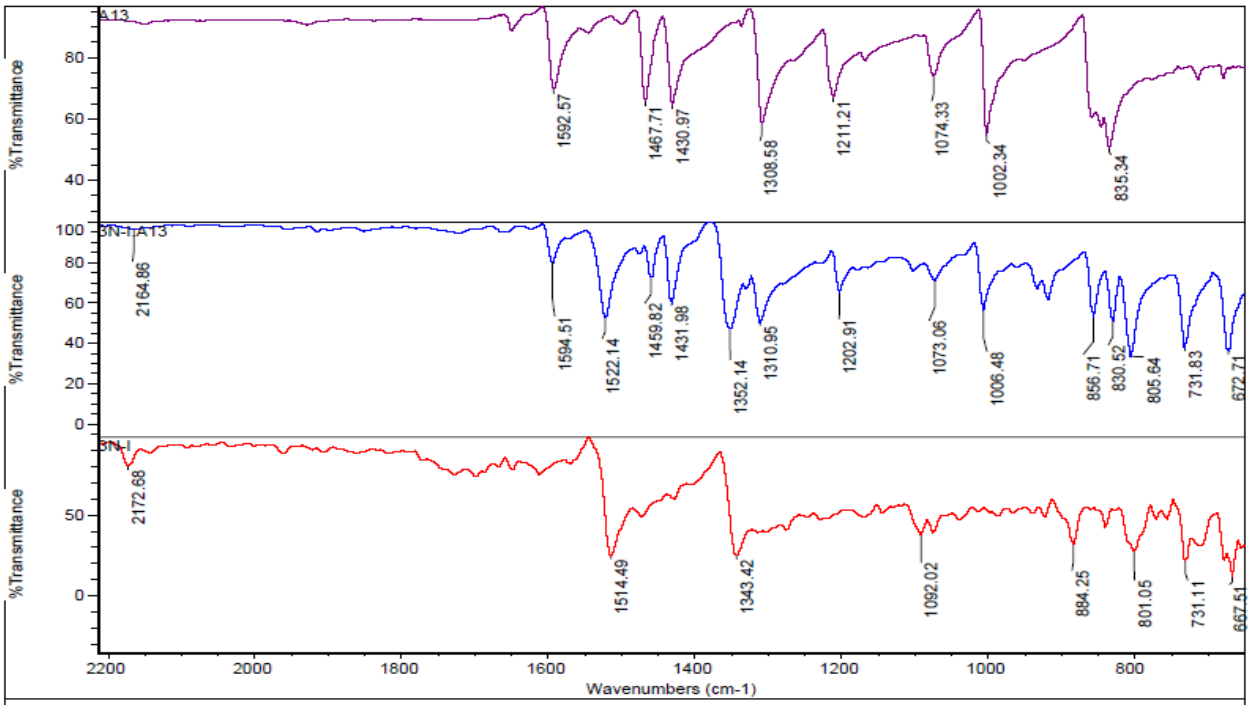


Fig. S6: IR spectra comparison for **3N-I:A13** co-crystal

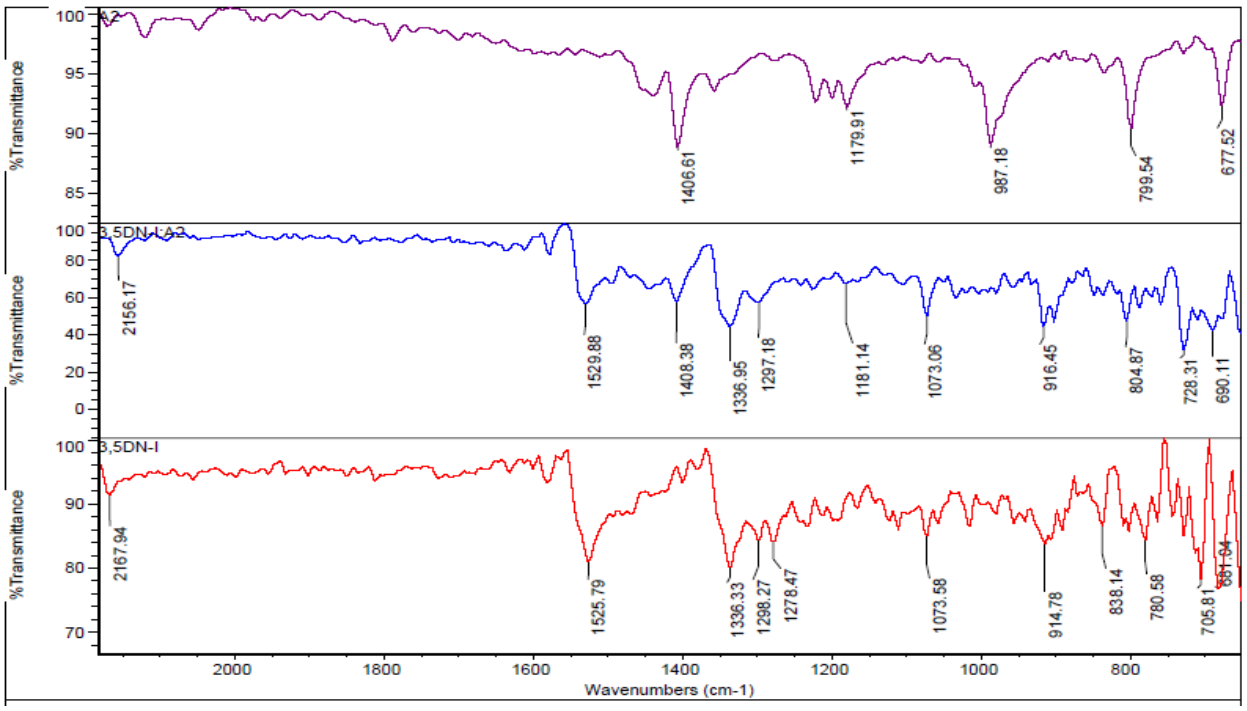


Fig. S7: IR spectra comparison for **3,5DN-I:A2** co-crystal

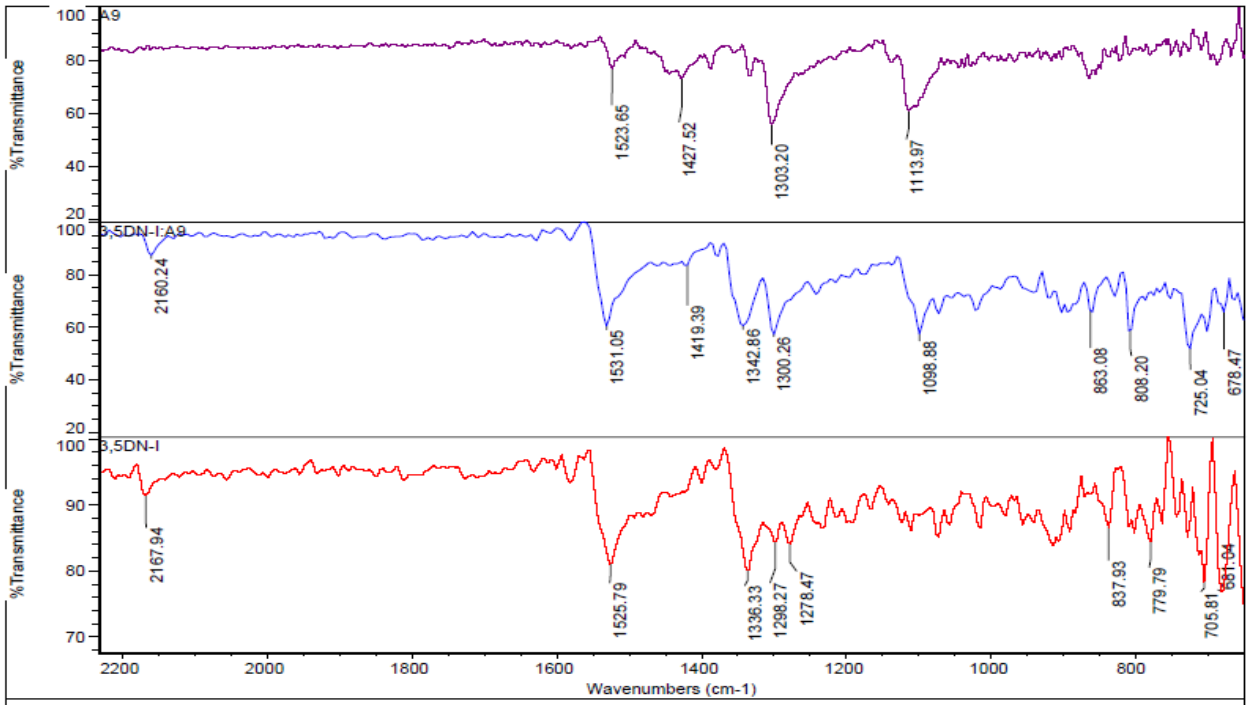


Fig. S8: IR spectra comparison for **3,5DN-I:A9** co-crystal

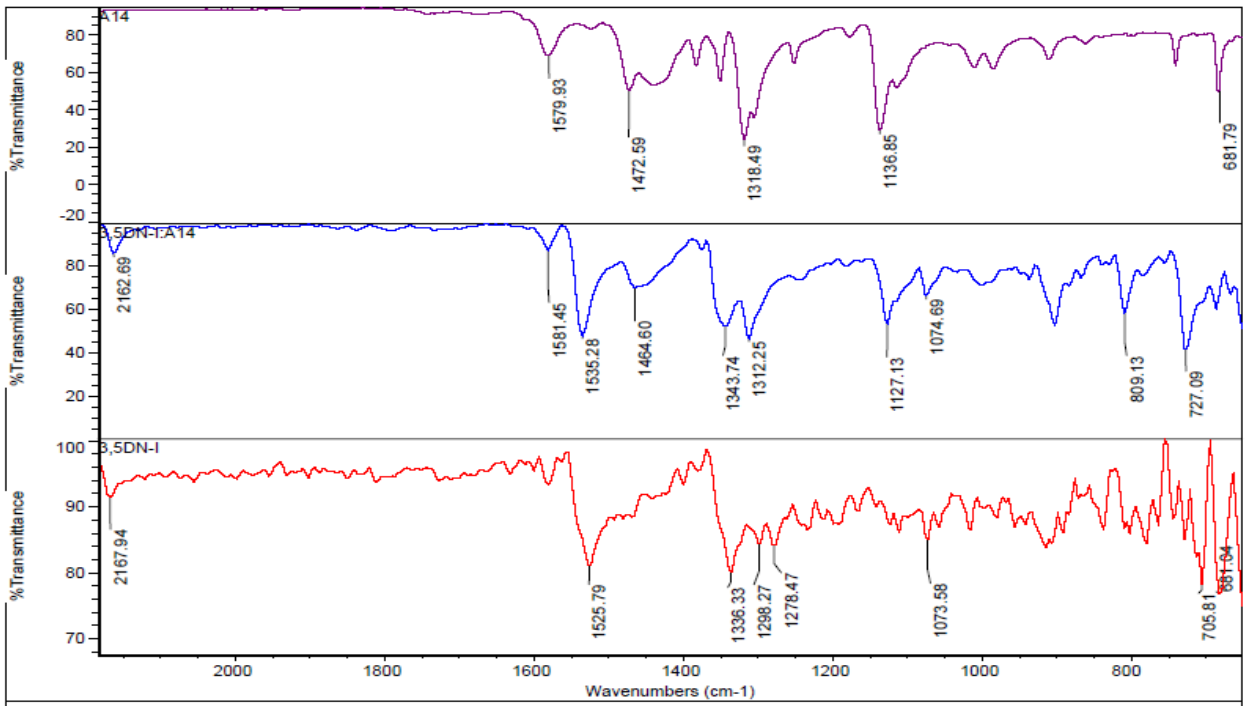


Fig. S9: IR spectra comparison for **3,5DN-I:A14** co-crystal

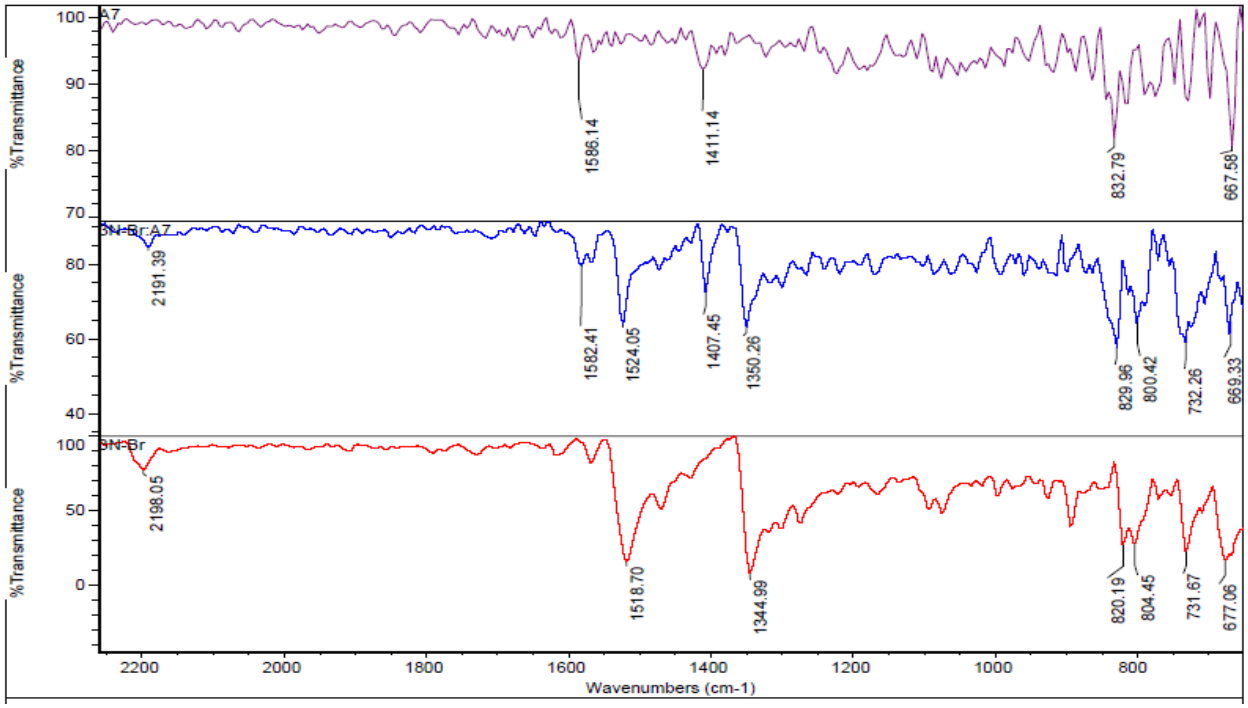


Fig. S10: IR spectra comparison for **3N-Br:A7** co-crystal

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