Electronic Supplementary Material (ESI) for CrystEngComm.

Halogen-bonded Liquid-crystalline Complexes Formed from 4-Alkoxyphenylpyridines with Iodine and with Interhalogens

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Supplementary Information

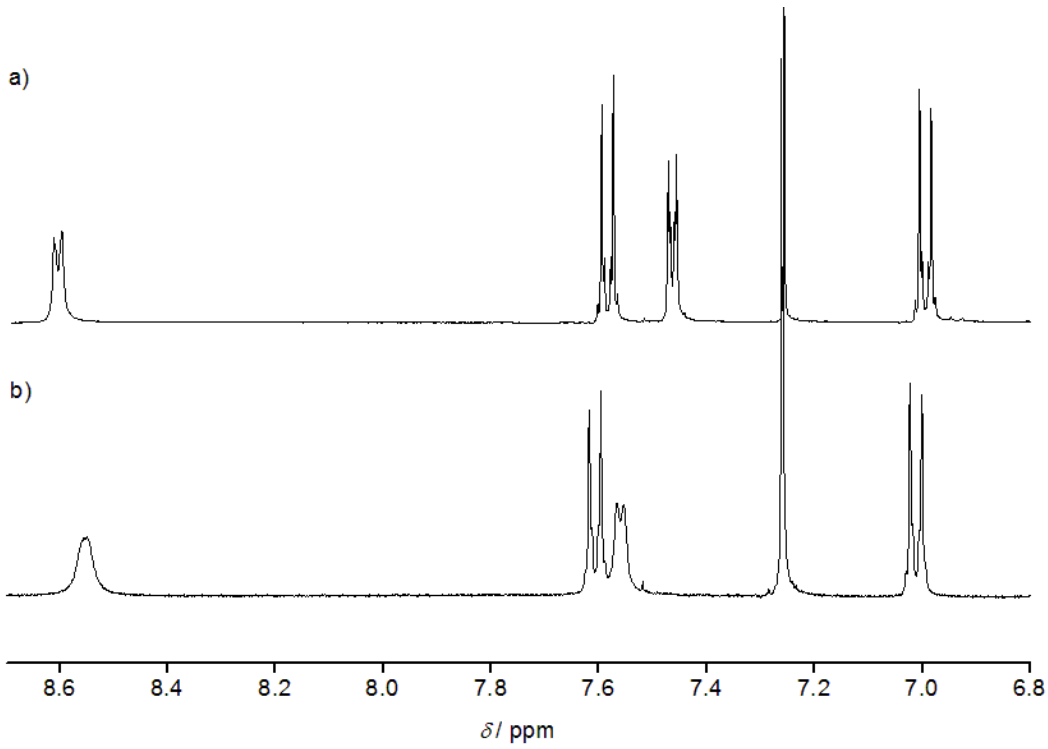
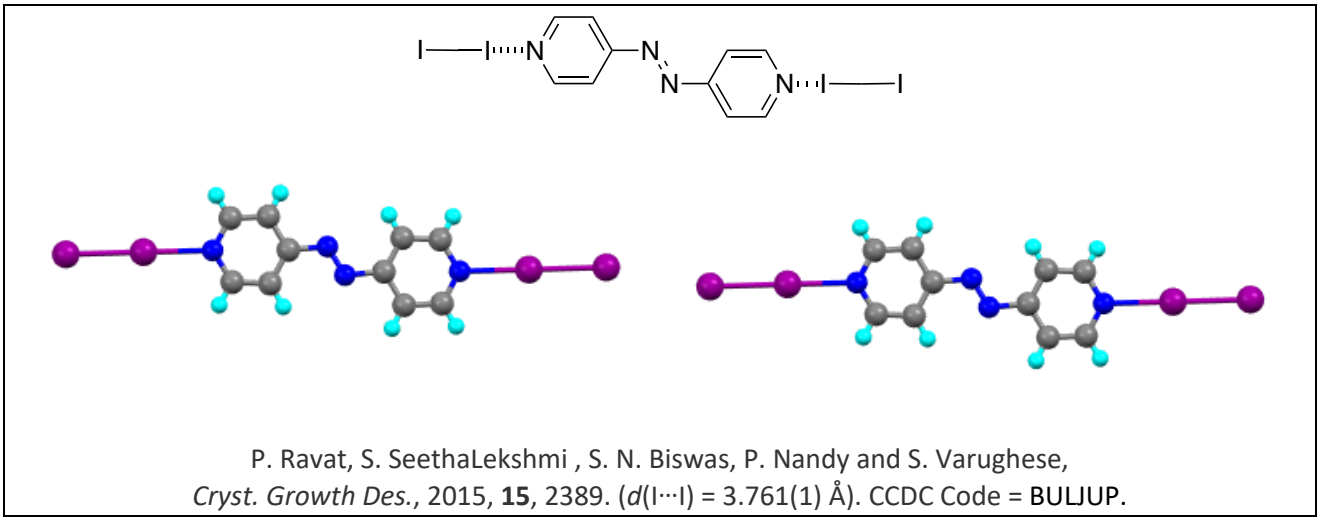
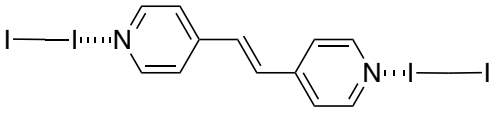


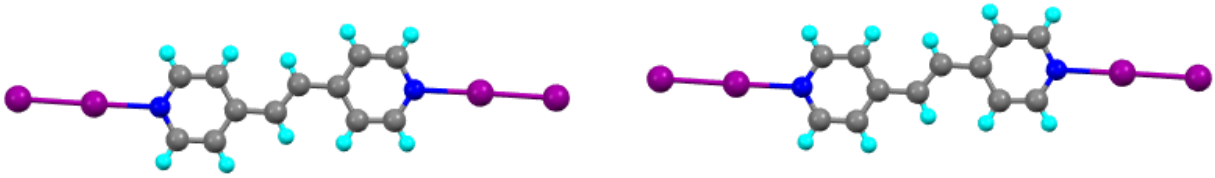
Figure **S1** The aromatic region of the ^{1}H NMR spectrum of a) dodecyloxyphenylpyridine (12-OPhPy) and b) its complex with bromine (12-OPhPy···Br_2).



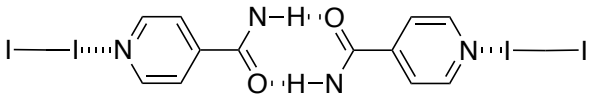
P. Ravat, S. SeethaLekshmi , S. N. Biswas, P. Nandy and S. Varughese,
Cryst. Growth Des., 2015, **15**, 2389. (*d*(I···I) = 3.761(1) Å). CCDC Code = BULJUP.



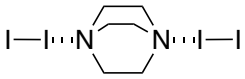
YIPKEG

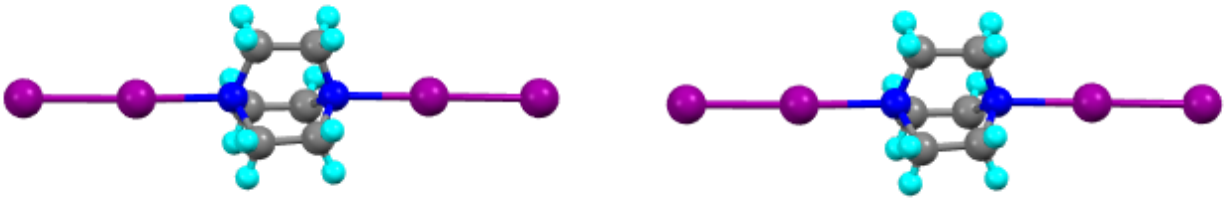


C. B. Aakeroy, J. Desper, B. A. Helfrich, P. Metrangolo, T. Pilati, G. Resnati and A. Stevenazzi, *Chem. Commun.*, 2007, 4236. (*d*(I···I) = 3.8852(9) Å). CCDC Code =YIPKEG.

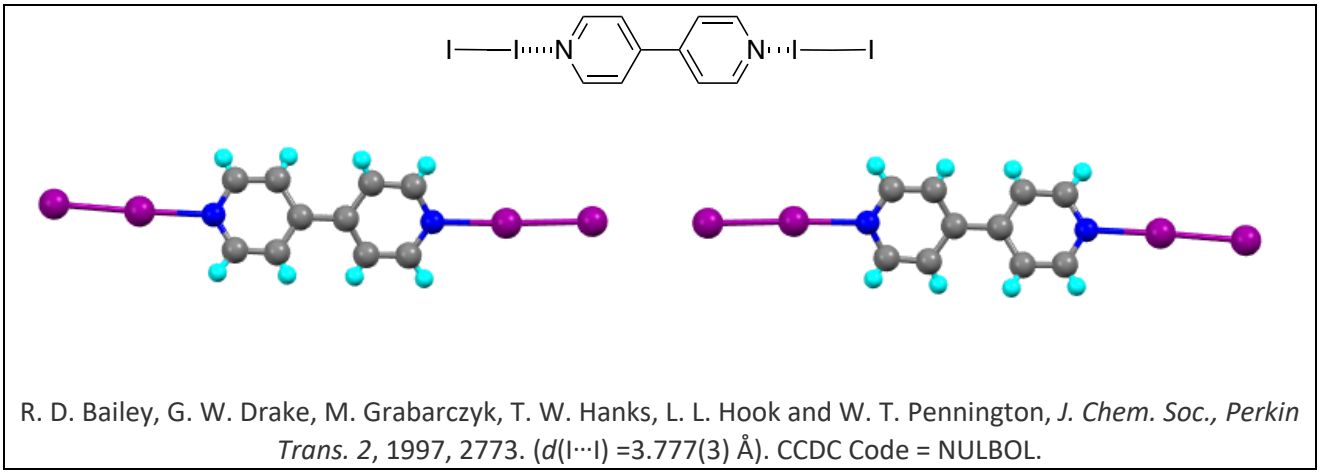


R. B. Walsh, C. W. Padgett, P. Metrangolo, G. Resnati, T. W. Hanks and W. T. Pennington, *Cryst. Growth Des.*, 2001, **1**, 165. (*d*(I···I) =3.6314(6) Å). CCDC Code = QIHBOY.





A. Peuronen, A. Valkonen, M. Kortelainen, K. Rissanen and M. Lahtinen, *Cryst. Growth Des.*, 2012, **12**, 4157. (*d*(I···I) =3.682(3) Å). CCDC Code = HEKZOO.



R. D. Bailey, G. W. Drake, M. Grabarczyk, T. W. Hanks, L. L. Hook and W. T. Pennington, *J. Chem. Soc., Perkin Trans. 2*, 1997, 2773. (*d*(I···I) =3.777(3) Å). CCDC Code = NULBOL.

Figure S2 Crystal structures of the five complexes found in the CSD with a Type I I···I motif.

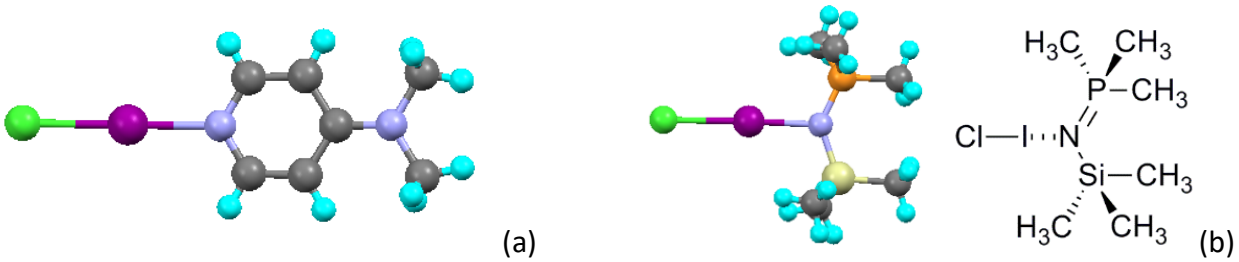


Figure S3 The molecular structures of complexes between ICl and a) DMAP and b) trimethylsilyl-trimethylphosphoranimine.

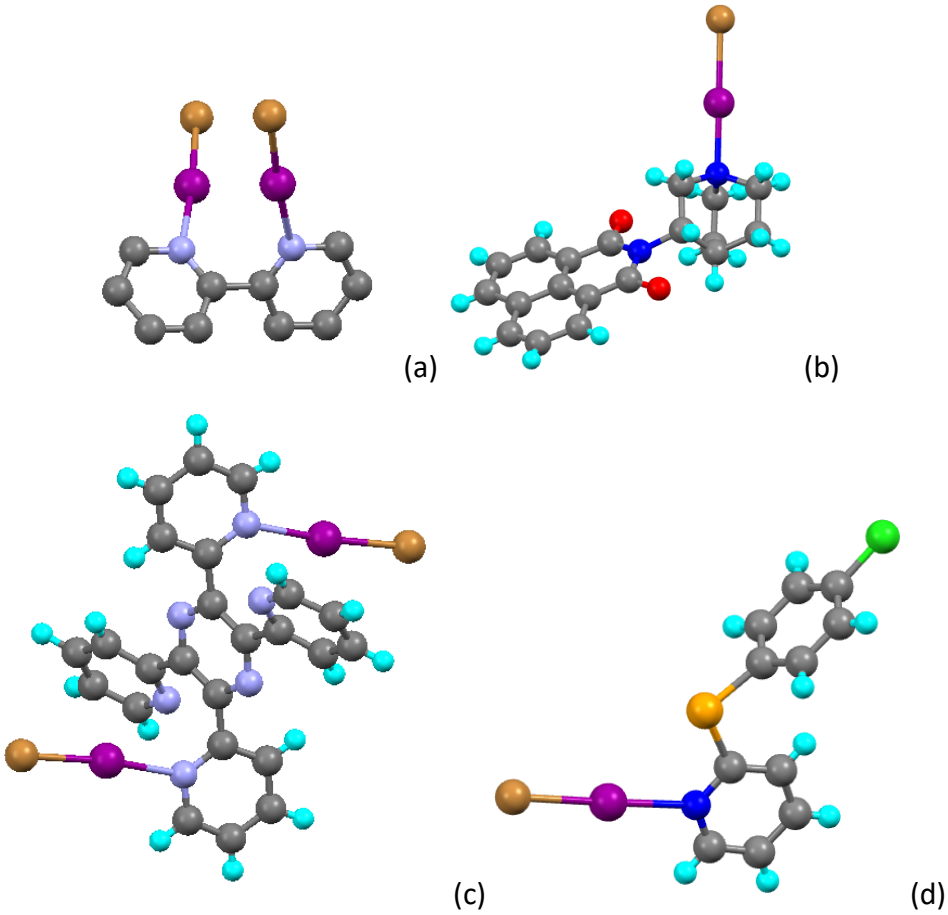


Figure S4 The molecular structures of complexes between IBr and a) 2,2'-bipyridine and b) a DABCO derivative (c) tetra-2-pyridyl-pyrazine and (d) a 2-(phenylseleno)pyridine. Hydrogen atoms in the structure with 2,2'-bipyridine have not been included.

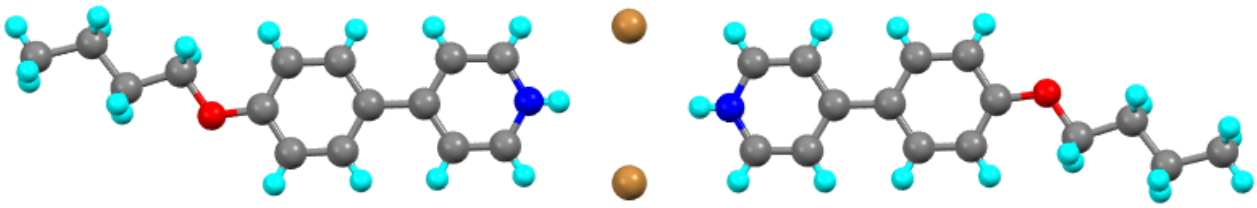


Figure S5 Hydrogen-bonded, dimeric arrangement for $[4\text{-OPhPyH}]^{+}Br^{-}$

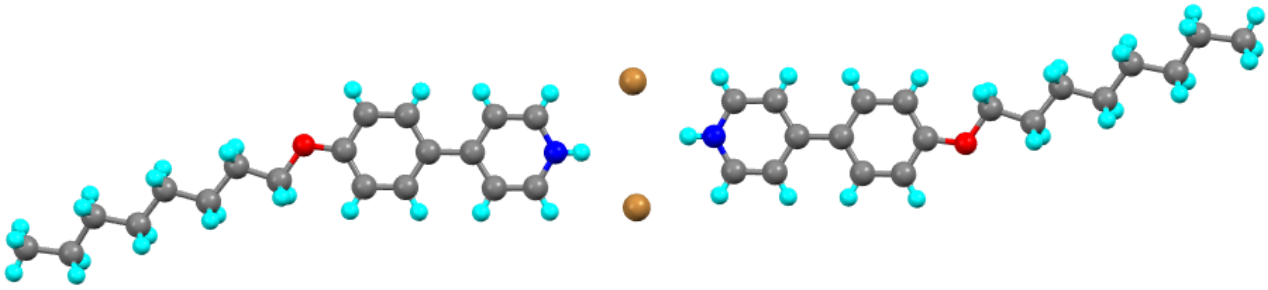


Figure S6 Hydrogen-bonded, dimeric arrangement for $[8\text{-OPhPyH}]^{+}Br^{-}$

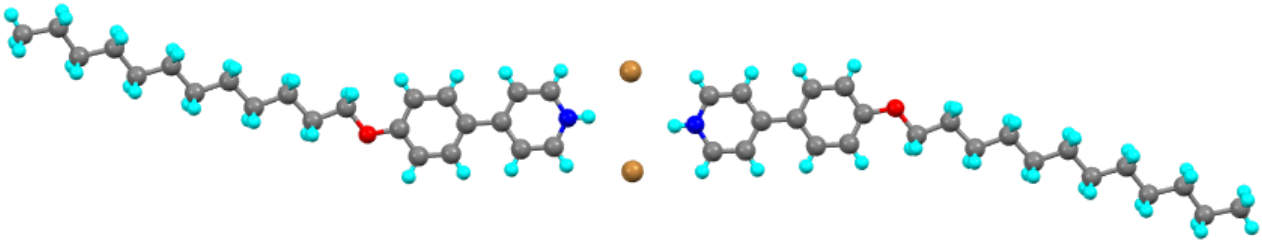


Figure S7 Hydrogen-bonded, dimeric arrangement for [12-OPhPyH]$^{+}$Br^{-}

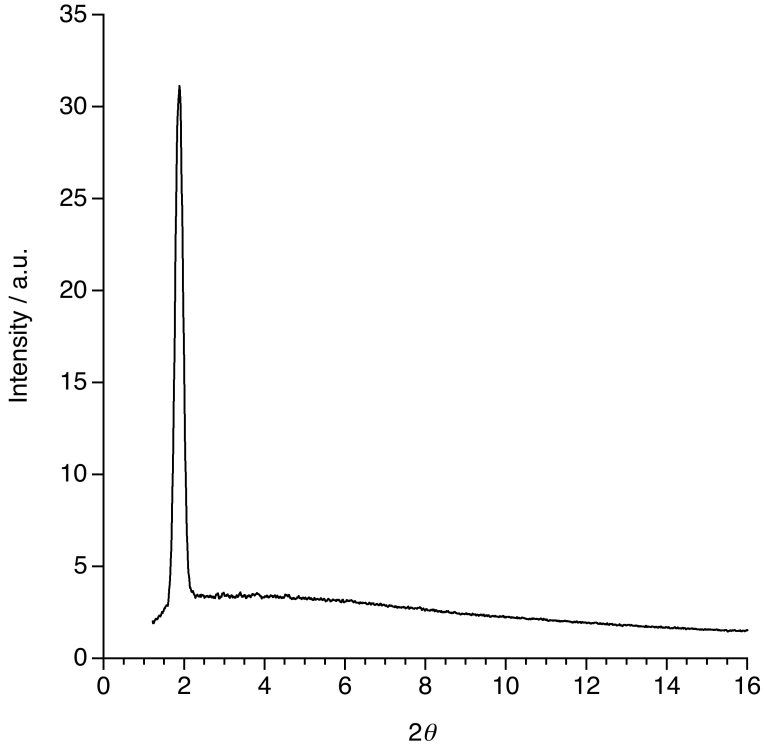


Figure S8 Small-angle diffraction pattern for 12-OPhPy···ICl at 135 °C.

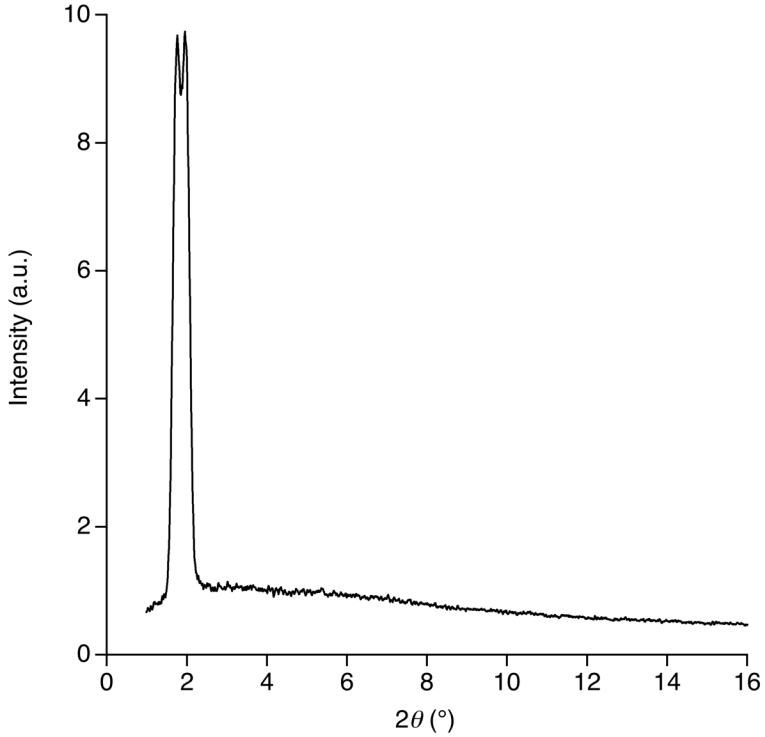


Figure S9 Small-angle diffraction pattern for 12-OPhPy···I_2 at 110 °C showing the two small-angle reflections.

Experimental

Table S1 Crystallographic parameters of (inter)halogen complexes.

	4-OPhPy···ICl	**4-OPhPy···I_2**	**4-OPhPy···IBr**
CCDC Reference No.	2123967	2123968	2123969
Empirical formula	$C_{15}H_{17}NOICl$	$C_{15}H_{17}NOI_2$	$C_{15}H_{17}NOIBr$
Formula weight / g mol^{-1}	389.64	481.09	434.11
T / K	110.05(10)	110.05(10)	110.05(10)
Wavelength (Å)	0.7107	0.7107	0.7107
Crystal system	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
Colour	Colourless	Yellow	Colourless
Shape	Plate	Plate	Plate
Unit cell dimensions a /Å	7.8428(3)	8.7375(3)	10.0323(4)
b /Å	8.7456(4)	9.2799(4)	11.3017(4)
c /Å	11.7865(6)	10.6024(7)	15.5236(5)
α / °	81.274(4)	106.226(5)	106.418(3)
β / °	82.709(4)	98.182(4)	94.206(3)
γ / °	72.451(4)	100.729(4)	113.861(4)
Volume / Å^3	757.89(6)	793.61(7)	1508.27(11)
Z	2	2	4
ρ_{calc} / Mg m^{-3}	1.707	2.013	1.912
Absorption coefficient / mm^{-1}	2.281	3.955	4.764
F(000)	384	456	840
Crystal size / mm^3	0.23 × 0.11 × 0.03	0.23 × 0.11 × 0.01	0.16 × 0.08 × 0.01
θ range for data collection	2.84 to 28.16°	2.95 to 28.11°	2.80 to 28.03°
Index ranges	$-10 \le h \le 10$, $-11 \le k \le 11$, $-15 \le l \le 14$	$-11 \le h \le 10$, $-12 \le k \le 11$, $-13 \le l \le 13$	$-13 \le h \le 12$, $-10 \le k \le 14$, $-20 \le l \le 20$
Reflections collected	8707	9193	11341
Independent reflections	3180 $R_{(int)}$ = 0.0281	3348 $R_{(int)}$ = 0.0264	6069 $R_{(int)}$ = 0.0274
Completeness	99.8% to θ = 25.24°	99.8% to θ = 25.24°	99.7% to θ = 25.21°
Max. and min. transmission	0.936 and 0.744	0.944 and 0.664	0.933 and 0.620
Data/restraints/ parameters	3180 / 0 / 173	3348 / 20 / 208	6069 / 0 / 345
Goodness-of-fit on F^2	1.041	1.087	1.046
Final R indices [$I > 2\sigma$(I)]	R_1 = 0.0235 wR_2 = 0.0434	R_1 = 0.0242 wR_2 = 0.0489	R_1 = 0.0285 wR_2 = 0.0481
R indices (all data)	R_1 = 0.0280 wR_2 = 0.0456	R_1 = 0.0355 wR_2 = 0.0429	R_1 = 0.0395 wR_2 = 0.0517
Largest diff. peak and hole	0.45 and −0.46	0.69 and −0.68	0.59 and −0.58

Table S2 Crystallographic parameters of alkoxyphenylpyridinium salts.

	[10-OPhPyH]Br_3	**[12-OPhPyH]$_2Br_3$**	**[4-OPhPyH]Br**	**[6-OPhPyH]Br**	**[8-OPhPyH]Br**	**[12-OPhPyH]Br**
CCDC Reference No.	2123970	2123971	2123972	2123966	2123973	2123974
Empirical formula	$C_{21}H_{30}Br_3NO$	$C_{46}H_{67}Br_3N_2O_2$	$C_{15}H_{18}BrNO$	$C_{17}H_{22}NOBr$	$C_{19}H_{26}BrNO$	$C_{23}H_{34}BrNO$
Formula weight / g mol^{-1}	552.19	919.75	308.21	336.26	364.32	420.42
T / K	110.05(10)	110.05(10)	110.05(10)	110.05(10)	110.05(10)	110.05(10)
Wavelength (Å)	0.7107	0.7107	0.7107	0.7107	0.7107	0.7107
Crystal system	monoclinic	monoclinic	triclinic	Triclinic	triclinic	triclinic
Space group	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
Colour	Yellow	Yellow	light yellow	Yellow	colourless	yellow
Shape	Irregular	Irregular	plate	Plate	plate	needle
Unit cell dimensions a /Å	4.63873(14)	28.1904(12)	6.6716(3)	6.7843(3)	6.7554(3)	6.7504(3)
b /Å	56.6665(12)	9.1296(2)	8.3651(4)	8.3585(3)	8.4116(3)	8.3652(4)
c /Å	8.4248(2)	17.0705(6)	13.0803(6)	15.1607(7)	16.8284(7)	20.1363(10)
α / °	90.00	90.00	86.724(4)	97.295(3)	97.564(3)	81.710(4)
β / °	95.637(2)	98.313(4)	86.237(4)	93.314(4)	96.503(4)	86.632(4)
γ / °	90.00	90.00	70.833(4)	111.978(4)	110.294(4)	70.675(4)
Volume / Å^3	2203.83(10)	4347.2(3)	687.56(6)	785.58(6)	876.00(6)	1061.71(9)
Z	4	4	2	2	2	2
ρ_{calc} / Mg m^{-3}	1.664	1.405	1.489	1.422	1.381	1.315
Absorption coefficient / mm^{-1}	5.502	2.822	2.977	2.612	2.349	1.947
F(000)	1104.0	1912.0	316.0	348	380.0	444.0
Crystal size / mm^3	0.3087 × 0.1563 × 0.1294	0.227 × 0.157 × 0.046	0.278 × 0.077 × 0.031	0.3226 × 0.1893 × 0.0387	0.303 × 0.169 × 0.034	0.2183 × 0.0703 × 0.0616
θ range for data collection	3.02 to 30.03°	2.84 to 25.09°	2.96 to 30.03°	3.18 to 30.05°	3.1 to 30.08°	2.92 to 29.32°
Index ranges	–6 ≤ h ≤ 6, –79 ≤ k ≤ 59, –6 ≤ l ≤ 11	–21 ≤ h ≤ 33, –10 ≤ k ≤ 8, –20 ≤ l ≤ 19	–9 ≤ h ≤ 9, –11 ≤ k ≤ 7, –18 ≤ l ≤ 16	–9 ≤ h ≤ 7, –11 ≤ k ≤ 11, –18 ≤ l ≤ 21	–6 ≤ h ≤ 9, –10 ≤ k ≤ 11, –23 ≤ l ≤ 23	–9 ≤ h ≤ 8, –10 ≤ k ≤ 11, –15 ≤ l ≤ 27
Reflections collected	10718	15250	6296	6843	7701	7571
Independent reflections	6356 [R_{int} = 0.0302]	7698 [R_{int} = 0.0257]	4001 [R_{int} = 0.0273]	4465 [$R_{(int)}$ = 0.0256]	5098 [R_{int} = 0.0245]	4902 [R_{int} = 0.0256]
Completeness	98.9% to θ = 25.24°	99.7% to θ = 25.09°	99.3% to θ = 26.00°	97.10% to θ = 25.24°	99.2% to θ = 26.00°	99.2 to θ = 25.0°
Max. and min. transmission	0.567 and 0.365	0.883 and 0.657	0.912 and 0.724	0.906 and 0.486	0.924 and 0.591	0.942 and 0.869
Data/restraints/parameters	6356/0/240	7698/0/481	4001/0/168	4465 / 0 / 186	5098/0/204	4902/0/240
Goodness-of-fit on F^2	1.190	1.053	1.063	1.076	1.051	1.059
Final R indices [$I > 2\sigma$(I)]	R_1 = 0.0586, wR_2 = 0.0960	R_1 = 0.0393, wR_2 = 0.0798	R_1 = 0.0373, wR_2 = 0.0735	R_1 = 0.0367 wR_2 = 0.0832	R_1 = 0.0353, wR_2 = 0.0728	R_1 = 0.0351, wR_2 = 0.0744
R indices (all data)	R_1 = 0.0742, wR_2 = 0.1021	R_1 = 0.0715, wR_2 = 0.0919	R_1 = 0.0458, wR_2 = 0.0779	R_1 = 0.0460 wR_2 = 0.0890	R_1 = 0.0453, wR_2 = 0.0772	R_1 = 0.0439, wR_2 = 0.0787
Largest diff. peak and hole	0.68 and –1.87	0.63 and –0.44	0.71/–0.68	0.80 and –1.18	0.52/–0.34	0.53/–0.32

Instrumentation

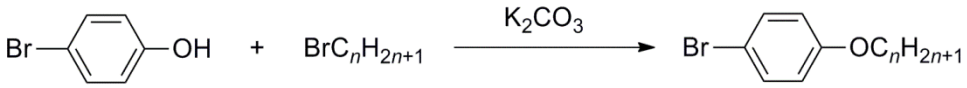
NMR spectra were obtained using either a Jeol ECS400 400 MHz, which operates at 400 MHz for ^{1}H spectroscopy or a Bruker AV500 500 MHz spectrometer, which operates at 500 MHz for ^{1}H spectroscopy. All spectra were obtained at ambient temperature using $CDCl_3$ as the solvent and as the internal standard for ^{1}H and ^{13}C spectra. All chemical shifts are given in ppm.

Single crystal X-ray diffraction data were collected at 110 K on a Brucker Smart Apex diffractometer with Mo*K*α radiation (λ = 0.71073 Å) using a SMART CCD camera.

Small angle X-ray scattering was performed using a Bruker D8 Discover equipped with a bespoke temperature-controlled, bored graphite rod furnace, custom built at the University of York. The radiation used was copper K_α (λ = 0.154056 nm) from a 1 µS microfocus source. Diffraction patterns were recorded on a 2048 x 2048 pixel Bruker VANTEC 500 area detector set at a distance of 121 mm from the sample. Samples were filled into 0.9 mm capillary tubes.

Optical microscopy was performed using an Olympus BX50 microscope at X100 magnification. Temperature was controlled using a Linkam Scientific LTS 350 heating stage.

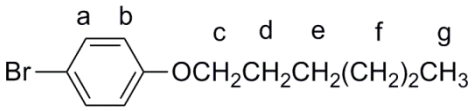
General Procedure for the Preparation of 4-Alkoxybromobenzene



4-Bromophenol (3.46 g, 20 mmol) and potassium carbonate (13.82 g, 100 mmol) were added to acetone (160 cm^3) in a round-bottomed flask and the mixture was stirred for 10 min. A flow of nitrogen was passed through the equipment. The flask was heated under reflux at 60 °C. Once reflux was achieved 1-bromoalkane (26 mmol) was added dropwise to the flask. The reaction mixture was heated under reflux for 16 h whilst stirring. The mixture was filtered and the filtrate

was concentrated *in vacuo*. The crude product was purified by column chromatography on silica gel eluted with 100:1 petroleum ether (40 – 60 °C): acetone.

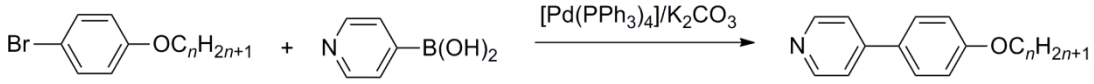
4-Hexyloxybromobenzene



Yield: 71%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.35 (2H, Ha, AA'XX', *J* = 9.0 Hz), 6.77 (2H, Hb, AA'XX', *J* = 8.9 Hz), 3.91 (2H, Hc, t, *J* = 6.6 Hz), 1.76 (2H, Hd, m), 1.44 (2H, He, m), 1.33 (4H, Hf, m), 0.90 (3H, Hg, t, *J* = 7.1 Hz).

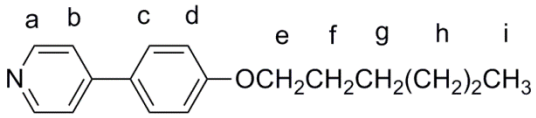
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 158.07, 132.00, 116.11, 112.36, 68.08, 31.39, 28.96, 25.50, 22.42, 13.86. Spectra for other homologues are essentially the same with a different integration in the ^{1}H NMR spectra for the peak at δ = 1.33 ppm and additional peaks in the high field region of the ^{13}C NMR spectra corresponding to the alkyl chain.

General Procedure for the Synthesis of 4-Alkoxyphenylpyridines (*n*-OPhPy)



Potassium carbonate (7.7 g, 56 mmol) was dissolved in a mixture of water (20 cm^3) and THF (40 cm^3). This solution was added to 4-alkoxybromobenzene (14 mmol) in a round-bottomed flask under nitrogen. Tetrakis(triphenylphosphine)palladium(0) (0.485 g, 0.42 mmol) was added to the flask, which was then heated to 60 °C. A suspension of 4-pyridineboronic acid (2.46 g , 20 mmol) in THF (40 cm^3) was added to the flask and the reaction mixture heated under reflux at 80 °C whilst stirring for 16 hours. The mixture was extracted with diethyl ether (100 cm^3) and washed with NaOH solution (10% w/v, 50 cm^3) and water (100 cm^3). The organic layer was dried over anhydrous magnesium sulfate and, after filtration, the solvent was removed using a rotary evaporator. The crude product was purified by column chromatography on silica gel, eluting with 1:1 petroleum ether (40 – 60 °C): acetone (1% triethylamine). The product was crystallised from hot petroleum ether (40 – 60 °C) to give a colourless solid.

4-Hexyloxyphenylpyridine (6-OPhPy)



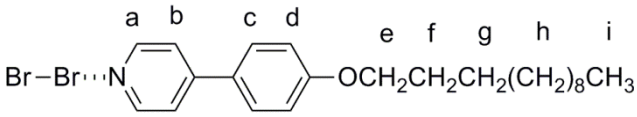
Yield: 28%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.61 (2H, Ha, AA'XX', *J* = 6.2 Hz), 7.59 (2H, Hc, AA'XX', *J* = 8.8 Hz), 7.47 (2H, Hb, AA'XX', *J* = 6.2 Hz), 7.00 (2H, Hd, AA'XX', *J* = 8.8 Hz), 4.01 (2H, He, t, *J* = 6.6 Hz), 1.81 (2H, Hf, m), 1.48 (2H, Hg, m), 1.35 (4H, Hh, m), 0.91 (3H, Hi, t, *J* = 7.0 Hz). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 159.96, 150.02, 147.68, 129.92, 127.93, 120.85, 114.90, 68.00, 31.41, 29.02, 25.55, 22.44, 13.88. Spectra of other homologues are essentially identical with different integration for the peak at δ = 1.35 ppm in the ^{1}H NMR spectra and additional peaks in the high field region of the ^{13}C NMR spectra corresponding to atoms in the alkoxy chain.

Table **S3** Yields and elemental analysis of alkoxyphenylpyridines (*n*-OPhPy)

Complex	Yield / %	Anal. Calcd. / %			Found / %		
		C	H	N	C	H	N
4-OPhPy	23	79.3	7.5	6.2	78.9	7.5	6.0
6-OPhPy	28	80.0	8.3	5.5	79.0	8.2	5.4
8-OPhPy	24	80.5	8.9	4.9	79.5	8.9	4.7
10-OPhPy	52	81.0	9.4	4.5	80.6	9.4	4.5
12-OPhPy	59	81.4	9.8	4.1	81.3	9.8	4.0

Halogen-Bonded Complexes between 4-Dodecyloxyphenylpyridine and Bromine

Bromine (0.0064 cm^3, 0.125 mmol) was added to a solution of 4-decyloxyphenylpyridine (0.0425 g, 0.125 mmol) in hexane (20 cm^3) in a round-bottomed flask. The reaction mixture was stirred at room temperature for 2 h. The precipitate was filtered, washed with hexane and dried under vacuum.



Yield: 52%

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.55 (2H, Ha, AA'XX', *J* = 4.3 Hz), 7.61 (2H, Hc, AA'XX', *J* = 8.8 Hz), 7.56 (2H, Hb, AA'XX', *J* = 5.0 Hz), 7.01 (2H, Hd, AA'XX', *J* = 8.8 Hz), 4.02 (2H, He, t, *J* = 6.6 Hz), 1.81 (2H, Hf, m), 1.47 (2H, Hg, m), 1.26 (16H, Hh, m), 0.88 (3H, Hi, t, *J* = 6.8 Hz).

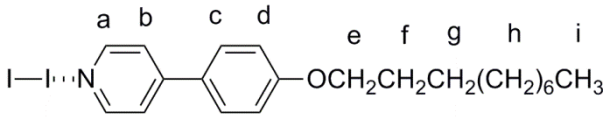
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ = 193.72, 164.45, 128.71, 115.63, 104.60, 101.22, 99.23, 68.58, 40.77, 32.22, 29.96, 29.94, 29.87, 29.68, 29.66, 29.46, 26.31, 23.00, 14.44.

Anal. Calcd. For $C_{23}H_{33}NOBr_2$: C, 55.3; H, 6.7; N, 2.8%. Found: C, 55.5; H, 6.7; N, 2.8%.

Halogen-Bonded Complexes between 4-Alkoxyphenylpyridines and Iodine

Iodine (0.0635 g, 0.25 mmol) in hexane (5 cm^3) was added to a solution of 4-alkoxyphenylpyridine (0.25 mmol) in chloroform (5 cm^3) in a round-bottomed flask. The reaction mixture was stirred at room temperature for 2 h. The precipitate was filtered, washed with hexane and dried under vacuum.

Iodine···4-Decyloxyphenylpyridine



Yield: 30%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.57 (2H, Ha, AA'XX', *J* = 5.8 Hz), 7.59 (2H, Hc, AA'XX', *J* = 8.8 Hz), 7.49 (2H, Hb, AA'XX', *J* = 6.2 Hz), 7.00 (2H, Hd, AA'XX', *J* = 8.9 Hz), 4.01 (2H, He, t, *J* = 6.6 Hz), 1.81 (2H, Hf, m), 1.47 (2H, Hg, m), 1.28 (12H, Hh, m), 0.88 (3H, Hi, t, *J* = 6.8 Hz). Spectra for other homologues were effectively identical save for the integration of the signal at δ = 1.28.

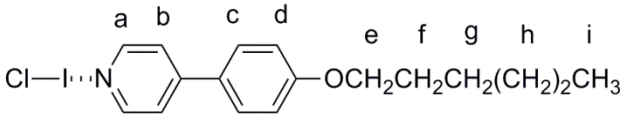
Table S4 Yields and elemental analysis for complexes of iodine with alkoxyphenylpyridines (7-*n*).

Complex	Yield / %	Anal. Calcd. / %			Found / %		
		C	H	N	C	H	N
4-OPhPy···I_2	29	37.5	3.6	2.9	37.8	3.5	2.9
6-OPhPy···I_2	46	40.1	4.2	2.8	39.8	4.3	2.8
8-OPhPy···I_2	45	42.5	4.7	2.6	42.8	4.7	2.6
10-OPhPy···I_2	30	44.6	5.2	2.5	44.0	5.1	2.4
12-OPhPy···I_2	24	46.6	5.6	2.4	46.4	5.5	2.3

Halogen-Bonded Complexes between Alkoxyphenylpyridines and Iodine Monochloride

Iodine monochloride (25 μL, 0.5 mmol) in dry hexane (5 cm^3) was added to a solution of alkoxyphenylpyridine (0.5 mmol) in chloroform (5 cm^3) in a round-bottomed flask under a nitrogen atmosphere. The mixture was stirred at room temperature for 2 h. The precipitate was filtered, washed with dry hexane and dried under vacuum.

Iodine Monochloride···4-Hexyloxyphenylpyridine



Yield: 79%.^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.57 (2H, Ha, AA'XX', *J* = 5.0 Hz), 7.59 (2H, Hc, AA'XX', *J* = 8.8 Hz), 7.56 (2H, Hb, AA'XX', *J* = 5.8 Hz), 7.01 (2H, Hd, AA'XX', *J* = 8.8 Hz), 4.01 (2H, He, t, *J* = 6.6 Hz), 1.80 (2H, Hf, m), 1.46 (2H, Hg, m), 1.34 (4H, Hh, m), 0.90 (3H, Hi, t, *J* = 7.1 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ = 161.52, 148.28, 128.50, 123.22, 115.51, 100.89, 98.91, 68.34, 31.52, 29.06, 25.65, 22.58, 14.02. Spectra of other homologues are essentially identical with different integration of the peak at δ = 1.34 ppm in the ^{1}H NMR spectra and additional peaks in the high field region of the ^{13}C NMR spectra corresponding to carbons in the alkoxy chain. Table shows the yields and results of elemental analysis for these complexes.

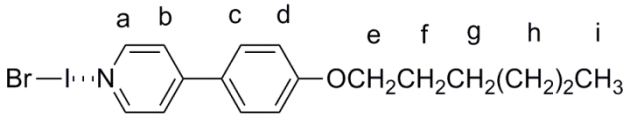
Table S5 Yields and elemental analysis for complexes of iodine monochloride with 4-alkoxyphenylpyridines (8-*n*).

Complex	Yield / %	Anal. Calcd. / %			Found / %		
		C	H	N	C	H	N
4-OPhPy···ICl	66	46.2	4.4	3.6	45.7	4.3	3.5
6-OPhPy···ICl	79	48.9	5.1	3.4	48.6	4.9	3.2
8-OPhPy···ICl	56	51.2	5.7	3.1	51.1	5.6	3.1
10-OPhPy···ICl	64	53.2	6.2	3.0	52.9	6.0	2.8
12-OPhPy···ICl	57	55.0	6.6	2.8	54.4	6.6	2.8

Halogen bonded complexes between 4-alkoxyphenylpyridines and iodine monobromide

Iodine monobromide (0.1034 g, 0.5 mmol) in dry hexane (5 cm^3) was added to a solution of 4-alkoxyphenylpyridine (0.5 mmol) in chloroform (5 cm^3) in a round-bottomed flask under a nitrogen atmosphere. The reaction mixture was stirred at room temperature for 2 h. The precipitate was filtered, washed with dry hexane and dried under vacuum.

Iodine Monobromide···4-Hexyloxyphenylpyridine



Yield: 64%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.56 (2H, Ha, AA'XX', *J* = 6.5 Hz), 7.60 (2H, Hc, AA'XX', *J* = 8.8 Hz), 7.56 (2H, Hb, AA'XX', *J* = 6.5 Hz), 7.02 (2H, Hd, AA'XX', *J* = 8.8 Hz), 4.02 (2H, He, t, *J* = 6.6 Hz), 1.81 (2H, Hf, m), 1.48 (2H, Hg, m), 1.35 (4H, Hh, m), 0.91 (3H, Hi, t, *J* = 7.1 Hz).
^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ = 161.35, 151.31, 147.93, 128.44, 123.07, 115.46, 106.05, 68.31, 31.52, 29.07, 25.65, 22.57, 14.02. Spectra for other homologues were essentially identical with different integration of the peak at δ = 1.35 ppm in the ^{1}H NMR spectra and additional peaks in the high field region of the ^{13}C NMR spectra corresponding to carbon atoms in the alkoxy chain.

Table S6 Yields and elemental analysis for complexes of iodine monobromide with 4-alkoxyphenylpyridine.

Complex	Yield / %	Anal. Calcd. / %			Found / %		
		C	H	N	C	H	N
4-OPhPy···IBr	58	41.5	4.0	3.2	41.1	3.9	3.2
6-OPhPy···IBr	64	44.2	4.6	3.0	43.8	4.5	2.9
8-OPhPy···IBr	63	46.6	5.1	2.9	46.2	4.9	2.5
10-OPhPy···IBr	76	48.7	5.6	2.7	48.2	5.5	2.6
12-OPhPy···IBr	74	50.6	6.1	2.6	50.4	5.8	2.4

Computational Details

All calculations reported in this paper were carried out using GAUSSIAN.[S1] The geometries of the monomers and complexes between I_2, ICl, IBr and Br_2 and methoxyphenylpyridine were optimised at the MP2 and M06-2X levels of theory. The geometries of the complexes between I_2, ICl, IBr and Br_2 and pyridine were optimised at the M06-2X level of theory. For iodine, in all calculations use was made of the aug-cc-pVDZ-PP basis set with effective core potentials (ECPs). In the M06-2X calculations all other atoms were assigned aug-cc-pVDZ basis sets. To reduce computational effort without a significant decrease in accuracy, in the MP2 calculations aug-cc-pVDZ basis sets were used for the dihalogen (except iodine, see above) and the pyridyl ring, while smaller cc-pVDZ basis sets were used for atoms from the phenyl ring and the methoxy substituent, which are not directly involved in the interaction. The MP2(Full) keyword was employed to include correlation effects for all electrons. The M06-2X functional was chosen because it was found to produce geometries for the halogen-bonded complexes which are in close agreement with those obtained at the MP2 level of theory.

Vibrational frequencies were calculated to ensure that optimised geometries correspond to local minima on the potential energy surface. The M06-2X calculations were carried out using the pruned “UltraFine” integration grid. The geometries of all complexes were optimised using the

Boys-Bernardi counterpoise correction (CP)[S2] to reduce the basis set superposition error (BSSE), separating each complex into two fragments, one of which is the dihalogen. Binding energies were calculated by subtracting the sum of the energies of the monomers from the energy of the complex.

M06-2X Energies and Optimized Geometries of All Complexes

All geometries are in the respective standard orientations used by GAUSSIAN,[S2] all coordinates in Å.

1-OPhPy…Br_2

```
CP corrected energy: -5742.0562 Ha
 C    1.736688    0.100853   -0.036492
 C    0.985257    1.208512    0.377299
 C   -0.402998    1.136536    0.367219
 N   -1.063122    0.044399   -0.021585
 C   -0.363664   -1.020003   -0.418594
 C    1.026024   -1.035625   -0.444304
 C    3.215761    0.130229   -0.041478
 C    3.912987    1.307501   -0.360918
 C    5.297065    1.338305   -0.368299
 C    6.027528    0.185928   -0.045360
 C    5.352566   -0.994857    0.279200
 C    3.957854   -1.009842    0.273416
 H    1.473875    2.114014    0.731533
 H   -1.015651    1.979217    0.689269
 H   -0.945386   -1.886733   -0.734116
 H    1.547049   -1.920052   -0.805499
 H    3.360951    2.205298   -0.636144
 H    5.842231    2.243202   -0.628670
 H    5.893273   -1.898880    0.543826
 H    3.443052   -1.928771    0.551430
 O    7.376495    0.314215   -0.074484
 C    8.147939   -0.830812    0.241194
 H    9.191859   -0.521425    0.158123
 H    7.946992   -1.646743   -0.467231
 H    7.944195   -1.170841    1.266260
Br   -3.521921   -0.017431    0.003261
Br   -5.895524   -0.082374    0.029335
```

4-OPhPy…Br_2

```
CP corrected energy: -5859.9527 Ha
 C  0.362139  0.254571 -0.070845
 C -0.432901  1.304334  0.407937
 C -1.816581  1.171549  0.405952
```

N	-2.432352	0.073185	-0.034738
C	-1.691328	-0.936788	-0.493792
C	-0.302719	-0.889196	-0.532339
C	1.838074	0.350199	-0.087144
C	2.479204	1.573117	-0.346379
C	3.860412	1.666146	-0.364258
C	4.646094	0.532050	-0.112161
C	4.026251	-0.693855	0.151882
C	2.633887	-0.771043	0.157173
H	0.019346	2.210550	0.805840
H	-2.462147	1.968050	0.777533
H	-2.237944	-1.810659	-0.849717
H	0.252634	-1.729296	-0.944560
H	1.885080	2.459178	-0.566901
H	4.361290	2.607874	-0.578901
H	4.609453	-1.585640	0.361068
H	2.163526	-1.725999	0.388151
O	5.986451	0.721941	-0.145697
C	6.824834	-0.401952	0.096343
H	6.615640	-1.184075	-0.650600
H	6.613719	-0.809376	1.097722
C	8.264375	0.058742	-0.000213
H	8.428950	0.861043	0.731843
H	8.432221	0.489655	-0.996644
C	9.243084	-1.086194	0.247603
H	9.055923	-1.518002	1.241485
H	9.059837	-1.887751	-0.482584
C	10.696736	-0.631818	0.153396
H	10.908272	0.150309	0.893884
H	10.911735	-0.220672	-0.841385
H	11.386510	-1.464518	0.332804
Br	-4.881707	-0.092359	0.015792
Br	-7.251394	-0.253288	0.070230

1-OPhPy…I_2

CP corrected energy: -1184.9684 Ha (ECP basis on I)

C	2.739419	0.116043	-0.058475
C	1.992182	1.227150	0.353860
C	0.604085	1.165347	0.333334
N	-0.064006	0.079755	-0.065036
C	0.633883	-0.987484	-0.462117
C	2.022995	-1.012762	-0.477545
C	4.218244	0.133538	-0.049260
C	4.928149	1.307777	-0.351711
C	6.312333	1.327210	-0.344614
C	7.030027	0.166223	-0.023338
C	6.342165	-1.011674	0.284524

C	4.947661	-1.015274	0.263916
H	2.483795	2.127686	0.716321
H	-0.002792	2.012047	0.655939
H	0.050453	-1.850050	-0.786016
H	2.539590	-1.899633	-0.838909
H	4.386496	2.212375	-0.625297
H	6.867568	2.229614	-0.591924
H	6.872757	-1.922092	0.547636
H	4.422771	-1.932185	0.529375
O	8.379835	0.283689	-0.037108
C	9.139031	-0.869961	0.277692
H	10.186092	-0.568099	0.207972
H	8.939165	-1.678635	-0.439252
H	8.921791	-1.216149	1.297884
I	-2.658725	0.011742	-0.018391
I	-5.411452	-0.080034	0.048595

4-OPhPy…I_2

CP corrected energy: -1302.8649 Ha (ECP basis on I)

C	1.475953	0.282729	-0.091459
C	0.686105	1.334040	0.392660
C	-0.697936	1.211787	0.384132
N	-1.323305	0.121833	-0.068215
C	-0.584815	-0.889256	-0.533134
C	0.803720	-0.851595	-0.565612
C	2.952217	0.367063	-0.099588
C	3.603963	1.588338	-0.339896
C	4.985788	1.670909	-0.349093
C	5.761432	0.527704	-0.106623
C	5.130813	-0.696763	0.138466
C	3.738023	-0.763390	0.134846
H	1.142638	2.233590	0.800499
H	-1.336994	2.011196	0.760855
H	-1.134213	-1.757218	-0.899270
H	1.353676	-1.692670	-0.982884
H	3.018042	2.481716	-0.552649
H	5.495044	2.611338	-0.549130
H	5.706099	-1.595440	0.339835
H	3.259349	-1.717585	0.351401
O	7.102935	0.707842	-0.129856
C	7.931976	-0.424966	0.104018
H	7.722122	-1.196398	-0.653740
H	7.711338	-0.842742	1.099026
C	9.375230	0.026833	0.022440
H	9.540425	0.819106	0.765198
H	9.552653	0.468479	-0.967600
C	10.344345	-1.127798	0.262930
H	10.160601	-1.919187	-0.478140
H	10.147549	-1.570234	1.250247
C	11.801650	-0.682295	0.183979
H	12.013473	0.089295	0.935353

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H   12.484471   -1.521858    0.357853
H   12.026176   -0.260621   -0.804257
I   -3.910706   -0.035423   -0.007665
I   -6.660494   -0.202245    0.073992
```

1-OPhPy…IBr

```
CP corrected energy: -3463.5223 Ha (ECP basis on I)
 C    2.134781    0.098011   -0.032326
 C    1.382120    1.207598    0.375348
 C   -0.004733    1.136643    0.367496
 N   -0.665030    0.039824   -0.014850
 C    0.035426   -1.028482   -0.406515
 C    1.423710   -1.041474   -0.432358
 C    3.612773    0.128780   -0.039378
 C    4.308010    1.308082   -0.356616
 C    5.691705    1.340104   -0.366289
 C    6.423879    0.187383   -0.047161
 C    5.750582   -0.995206    0.275533
 C    4.356237   -1.011837    0.271284
 H    1.869269    2.115855    0.723872
 H   -0.617874    1.980382    0.684838
 H   -0.546120   -1.896931   -0.716612
 H    1.943857   -1.928058   -0.788890
 H    3.755236    2.206180   -0.629273
 H    6.235662    2.246023   -0.625458
 H    6.292751   -1.899111    0.537382
 H    3.843342   -1.932166    0.548128
 O    7.771565    0.317169   -0.077902
 C    8.546074   -0.827500    0.233746
 H    9.589052   -0.515516    0.149589
 H    8.345405   -1.641706   -0.476598
 H    8.344610   -1.170020    1.258337
 I   -3.161137   -0.014944    0.003532
Br   -5.742731   -0.074333    0.023373
```

4-OPhPy…IBr

```
CP corrected energy: -3581.4188 Ha (ECP basis on I)
  C    0.832991    0.257792   -0.061085
  C    0.038987    1.313775    0.406780
  C   -1.343612    1.185161    0.407656
  N   -1.962008    0.081172   -0.021460
  C   -1.221975   -0.936791   -0.470427
  C    0.165217   -0.890077   -0.509260
  C    2.307927    0.351589   -0.080349
  C    2.949489    1.573941   -0.342432
  C    4.330397    1.665286   -0.363694
  C    5.115545    0.530446   -0.111477
  C    4.494945   -0.694733    0.155805
  C    3.102881   -0.770628    0.163668
```

H	0.491662	2.223843	0.794702
H	-1.987810	1.986323	0.770606
H	-1.770268	-1.813067	-0.816883
H	0.717794	-1.735844	-0.912995
H	2.356419	2.460527	-0.563550
H	4.831909	2.605998	-0.581079
H	5.077814	-1.586602	0.365352
H	2.632602	-1.724934	0.397414
O	6.454847	0.718911	-0.148159
C	7.294207	-0.405157	0.093420
H	7.082784	-1.187883	-0.652142
H	7.085233	-0.810770	1.095893
C	8.733336	0.055640	-0.007400
H	8.898653	0.485083	-1.004865
H	8.899639	0.858947	0.723128
C	9.712674	-1.088966	0.239642
H	9.527702	-1.891562	-0.488956
H	9.528064	-1.519309	1.234628
C	11.165982	-0.634436	0.141102
H	11.856228	-1.466810	0.320000
H	11.378443	-0.224770	-0.854818
H	11.379284	0.148751	0.879939
I	-4.451615	-0.074533	0.014842
Br	-7.029406	-0.235835	0.053451

1-OPhPy…ICl

CP corrected energy: -1349.5260 Ha (ECP basis on I)

C	1.494365	0.097631	-0.035984
C	0.739412	1.205792	0.371443
C	-0.647125	1.132378	0.363870
N	-1.305232	0.033878	-0.018467
C	-0.602628	-1.033231	-0.410601
C	0.785442	-1.043103	-0.436399
C	2.972196	0.130707	-0.041901
C	3.666047	1.311309	-0.357399
C	5.049683	1.345249	-0.365646
C	5.783165	0.193273	-0.046685
C	5.111209	-0.990561	0.274326
C	3.716942	-1.009164	0.268569
H	1.224632	2.114998	0.720088
H	-1.262295	1.974416	0.681478
H	-1.182868	-1.902521	-0.720474
H	1.307211	-1.928664	-0.792992
H	3.112333	2.208889	-0.629851
H	5.592649	2.252136	-0.623490
H	5.654378	-1.893896	0.536052
H	3.205110	-1.930435	0.544226
O	7.130603	0.324968	-0.075844
C	7.906470	-0.818791	0.235993
H	8.949067	-0.505177	0.153291
H	7.707862	-1.632798	-0.475145

```
 H    7.704263   -1.162248    1.260116
 I   -3.776216   -0.032934    0.009164
Cl   -6.213658   -0.106767    0.039971
```

4-OPhPy…ICl

```
CP corrected energy: -1467.4225 Ha (ECP basis on I)
 C    0.150492    0.247012   -0.081038
 C   -0.648807    1.295408    0.394893
 C   -2.030534    1.159610    0.396475
 N   -2.643418    0.055186   -0.040285
 C   -1.898368   -0.955203   -0.498879
 C   -0.511741   -0.900349   -0.538735
 C    1.624949    0.346981   -0.096753
 C    2.262587    1.574075   -0.346002
 C    3.643196    1.670966   -0.361411
 C    4.431903    0.537090   -0.115795
 C    3.815141   -0.692876    0.138188
 C    2.423429   -0.774288    0.140186
 H   -0.200768    2.204697    0.789878
 H   -2.678949    1.953735    0.767006
 H   -2.442699   -1.831579   -0.850991
 H    0.044867   -1.740030   -0.949485
 H    1.666860    2.460304   -0.561366
 H    4.141784    2.615523   -0.568593
 H    4.400706   -1.584255    0.342176
 H    1.956129   -1.732399    0.364103
 O    5.770514    0.731082   -0.144954
 C    6.613123   -0.391394    0.093105
 H    6.409682   -1.169091   -0.659897
 H    6.399439   -0.805677    1.091020
 C    8.050978    0.075934    0.005290
 H    8.209290    0.874063    0.743234
 H    8.221185    0.513859   -0.987646
 C    9.033084   -1.066847    0.249884
 H    8.856419   -1.864152   -0.486543
 H    8.843160   -1.506048    1.239986
 C   10.485266   -0.605931    0.165430
 H   10.690298    0.171821    0.912304
 H   11.177438   -1.437143    0.342260
 H   10.703161   -0.187126   -0.825496
 I   -5.105848   -0.129556    0.029814
Cl   -7.536262   -0.319183    0.111206
```

Py…Br_2

```
CP corrected energy: -5396.5603 Ha
 N    0.000000    0.000000   -1.774816
 C    0.000000    1.150935   -2.448875
 C    0.000000   -1.150935   -2.448875
 C    0.000000   -1.199816   -3.841167
```

```
 C    0.000000   -0.000000   -4.548352
 C    0.000000    1.199816   -3.841167
 H    0.000000    2.060343   -1.846969
 H    0.000000   -2.060343   -1.846969
 H    0.000000   -2.160108   -4.352621
 H    0.000000    0.000000   -5.637588
 H    0.000000    2.160108   -4.352621
Br    0.000000    0.000000    3.086127
Br    0.000000    0.000000    0.720475
```

Py…I_2

```
CP corrected energy: -839.4726 Ha (ECP basis on I)
N    0.000000    0.000000   -2.467874
C    0.000000    1.151029   -3.144271
C    0.000000   -1.151029   -3.144271
C    0.000000   -1.199580   -4.536121
C    0.000000   -0.000000   -5.243610
C    0.000000    1.199580   -4.536121
H    0.000000    2.061553   -2.543976
H    0.000000   -2.061553   -2.543976
H    0.000000   -2.160090   -5.047044
H    0.000000    0.000000   -6.332814
H    0.000000    2.160090   -5.047044
I    0.000000    0.000000    2.905819
I    0.000000    0.000000    0.158640
```

Py…IBr

```
CP corrected energy: -3118.0259 Ha (ECP basis on I)
 N    0.000000    0.000000   -1.948119
 C    0.000000    1.153310   -2.621574
 C    0.000000   -1.153310   -2.621574
 C    0.000000   -1.199930   -4.012753
 C    0.000000    0.000000   -4.719706
 C    0.000000    1.199930   -4.012753
 H    0.000000    2.061794   -2.018833
 H    0.000000   -2.061794   -2.018833
 H    0.000000   -2.160292   -4.523686
 H    0.000000    0.000000   -5.808820
 H    0.000000    2.160292   -4.523686
Br    0.000000   -0.000000    3.146738
 I    0.000000   -0.000000    0.572170
```

Py…ICl

```
CP corrected energy: -1004.0294 Ha (ECP basis on I)
 N    0.000000    0.000000   -1.403321
 C    0.000000    1.153739   -2.076629
```

C	0.000000	-1.153739	-2.076629
C	0.000000	-1.199931	-3.467616
C	0.000000	-0.000000	-4.174551
C	0.000000	1.199931	-3.467616
H	0.000000	2.061783	-1.473404
H	0.000000	-2.061783	-1.473404
H	0.000000	-2.160295	-3.978473
H	0.000000	-0.000000	-5.263648
H	0.000000	2.160295	-3.978473
Cl	0.000000	0.000000	3.520840
I	0.000000	0.000000	1.088955

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S2 Gaussian 16, Revision A.03, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016; see http://www.gaussian.com/.