Characterising supramolecular architectures in crystals featuring I···Br halogen-bonding: Persistence of X···X′ secondary-bonding in their congeners

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***** SUPPLEMENTARY MATERIAL *****

Table S1. Details of composition, images and geometric details in crystals featuring I···Br interactions in **1**-**41**.

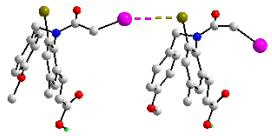
Table S2. Details of composition, images, unit-cell details and geometric details in congener crystals featuring putative X···X interactions.

Table S1. Details of composition, images and geometric details in crystals featuring I···Br interactions in **1**-**41**.

Zero-dimensional aggregates

1. OJACUY (P)-3-(3-bromo-2-((iodoacetyl)(4-methoxybenzyl)amino)-5-methylphenyl)acrylic acid

Guthrie, D.B.; Geib, S.J.; Curran, D.P. Synthesis of highly enantioenriched 3,4-dihydroquinolin-2-ones by 6-exo-trig radical cyclizations of axially chiral α-halo-ortho-alkenyl anilides. J. Am. Chem. Soc. 2009, 131, 15492-15500. doi: 10.1021/ja9066282.



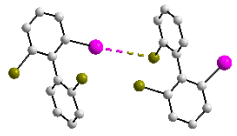
Four independent molecules with two being connected via one interaction; the second pair are connected similarly but, beyond the van der Waals radii [3.9125(11) Å].

d(I···Br) = 3.6830(11) Å; C–I···Br = 161.3(2)° & C–Br···I = 102.6(2)°

d(I···Br) = 3.9125(11) Å; C–I···Br = 116.2(2)° & C–Br···I = 154.8(2)°

2. RECROI 2,2'-dibromo-6-iodobiphenyl

Leroux, F.R.; Berthelot, A.; Bonnafoux, L.; Panossian, A.; Colobert, F. Transition-metal-free atropo-selective synthesis of biaryl compounds based on arynes. Chem.-Eur. J. 2012, 18, 14232-14236. doi: 10.1002/chem.201202739.



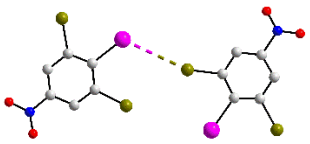
Two independent molecules connected via one interaction – supporting Br···Br contact at 3.6861(10) Å.

d(I···Br) = 3.7397(9) Å; C–I···Br = 172.38(19)° & C–Br···I = 85.37(16)°

d(Br···Br) = 3.6861(10) Å; C–Br···Br = 170.8(2)° & C–Br···Br = 86.91(16)°

3. DUPNIN 1,3-dibromo-2-iodo-5-nitrobenzene

Romero, J.A.; Aguirre Hernández, G.; Bernès, S. Anomalous halogen bonds in the crystal structures of 1,2,3-tri-bromo-5-nitro-benzene and 1,3-di-bromo-2-iodo-5-nitro-benzene. Acta Crystallogr., Sect. E: Cryst. Commun. 2015, 71, 960-965. doi: 10.1107/S2056989015013377.

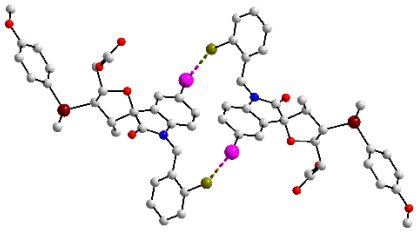


Two independent molecules connected via one interaction; the non-bonded I···Br contact within the dimer = 4.737(3) Å

d(I···Br) = 3.813(3) Å; C–I···Br = 117.2(5)° & C–Br···I = 161.2(5)°

4. NEYSUG methyl (1'-(2-bromobenzyl)-5'-iodo-4-(4-methoxyphenyl(dimethyl)silyl)-3-methyl-2'-oxo-1',2',4,5-tetrahydro-3H-spiro(furan-2,3'-indol)-5-yl)acetate

Franz, A.K.; Dreyfuss, P.D.; Schreiber, S.L. Synthesis and cellular profiling of diverse organosilicon small molecules. J. Am. Chem. Soc. 2007, 129, 1020-1021. doi: 10.1021/ja067552n.

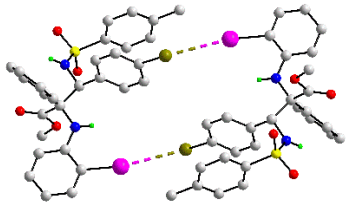


Two independent molecules, one self-associates into a centrosymmetric dimer. No other I···Br contacts less than the sum of the van der Waals radii

d(I···Br) = 3.5640(3) Å; C–I···Br = 73.4(3)° & C–Br···I = 159.70(4)°

5. LOBHOB methyl 4-bromo-N-(2-iodophenyl)-b-(((4-methylphenyl)sulfonyl)amino)-α-phenylphenylalaninate

Qiu, L.; Wang, D.; Lv, F.; Guo, X.; Hu, W.; Yang, L.; Liu, S. Three-component reactions based on trapping ammonium ylides with N-sulfonyl aldimines via cooperative catalysis of squaramides and $Rh_2(OAc)_4$. Tetrahedron 2014, 70, 1471-1477. doi: 10.1016/j.tet.2013.12.082.

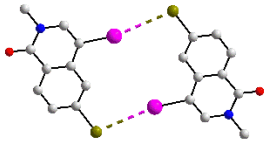


Centrosymmetric dimer

d(I···Br) = 3.6449(9) Å; C–I···Br = 160.07(13)° & C–Br···I = 124.72(15)°

6. SIZTED 6-bromo-4-iodo-2-methylisoquinolin-1(2H)-one

Fang, Z.; Wang, Y.; Wang, Y. Synthesis of 4-iodoisoquinolin-1(2H)-ones by a dirhodium(II)-catalyzed 1,4-bisfunctionalization of isoquinolinium iodide salts. Org. Lett. 2019, 21, 434-438. doi: 10.1021/acs.orglett.8b03614.



Two independent molecules; one self-assembles into a centrosymmetric dimer

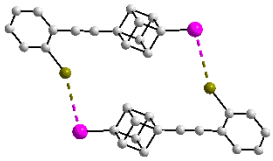
d(I···Br) = 3.7068(13) Å; C–I···Br = 168.8(2)° & C–Br···I = 102.8(3)°

The other independent molecule also assembles into a centrosymmetric dimer via Br···Br contacts

d(I···Br) = 3.7068(13) Å; C–I···Br = 168.8(2)° & C–Br···I = 102.8(3)°

7. QOCSUZ 1-((2-bromophenyl)ethynyl)-4-iodocubane

Flanagan, K.; Bernhard, S.S.R.; Plunkett, S.; Senge, M.O. Not Your Usual bioisosteres: Solid state study of 3D interactions in cubanes. Chem.-Eur. J. 2019, 25, 6941-6954. doi: 10.1002/chem.201806432.



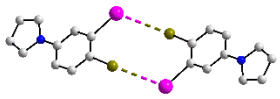
Centrosymmetric dimer

d(I···Br) = 3.7556(4) Å; C–I···Br = 93.01(5)° & C–Br···I = 155.75(6)°

8. KAGQUH 1-(4-bromo-3-iodophenyl)-1H-pyrrole

Messaoud, M.Y.A.; Bentabed-Ababsa, G.; Hedidi, M.; Derdour, A.; Chevallier, F.; Halauko, Y.S.; Ivashkevich, O.A.; Matulis, V.E.; Picot, L.; Thiéry, V.; Roisnel, T.; Dorcet, V.; Mongin, F.

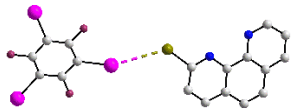
Deproto-metallation of N-arylated pyrroles and indoles using a mixed lithium–zinc base and regioselectivity-computed CH acidity relationship. Beilstein J. Org. Chem. 2015, 11, 1475-1485. doi: 10.3762/bjoc.11.160.


Centrosymmetric dimer

d(I···Br) = 3.8122(5) Å; C–I···Br = 117.83(10)° & C–Br···I = 166.26(12)°

9. VIXWIL 2-bromo-1,10-phenanthroline 1,3,5-trifluoro-2,4,6-triiodobenzene

Zhang, Y.; Wang, J.-G.; Wang, W. Noncovalent interactions between 1,3,5-trifluoro-2,4,6-triiodobenzene and a series of 1,10-phenanthroline derivatives: A combined theoretical and experimental study. Crystals 2019, 9, 140. doi: 10.3390/cryst9030140.



1:1 co-crystal

d(I···Br) = 3.6927(7) Å; C–I···Br = 156.68(11)° & C–Br···I = 130.84(14)°

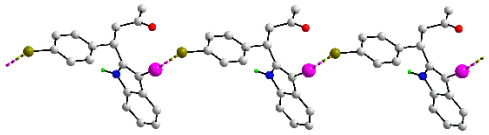
Also present but just beyond the van der Waals radii are type-I I···F interactions which connected the aggregates into a helical chain

d(I···F) = 3.452(3) Å; C–I···F = 154.09(11)° & C–Br···I = 146.5(2)°

Linear chains

10. MUJKUY (R)-4-(4-bromophenyl)-4-(3-iodo-1H-indol-2-yl)butan-2-one

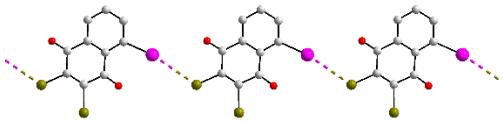
Hong, L.; Sun, W.; Liu, C.; Wang, L.; Wong, K.; Wang, R. Enantioselective Friedel–Crafts alkylation of 4,7-dihydroindoles with enones catalyzed by primary–secondary diamines. Chem.-Eur. J. 2009, 15, 11105-11108. doi: 10.1002/chem.200901635.



d(I···Br) = 3.5402(4) Å; C–I···Br = 169.74(9)° & C–Br···I = 121.58(9)°

11. MAMFIS 2,3-dibromo-5-iodo-1,4-naphthoquinone

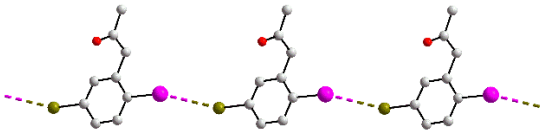
Jardim, G.A.M.; da Silva Júnior, E.N.; Bower, J.F. Overcoming naphthoquinone deactivation: Rhodium-catalyzed C-5 selective C–H iodination as a gateway to functionalized derivatives. Chem. Sci. 2016, 7, 3780-3784. doi: 10.1039/C6SC00302H.



d(I···Br) = 3.540(2) Å; C–I···Br = 173.67(16)° & C–Br···I = 91.44(19)°

12. SUWKUT 1-(5-bromo-2-iodophenyl)propan-2-one

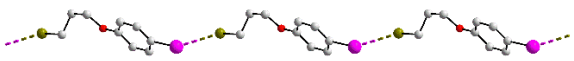
Bian, H.-L.; Tang, S.-Z.; Chen, M.-E.; Zhang, X.-M.; Lv, J.-W.; Chen, X.-W.; Qi, F.-M.; Chen, S.-W.; Zhang, F.-M. Transition-metal-free site-selective γ-C(sp^2)–H monoiodination of arenes directed by an aliphatic keto group. Org. Lett. 2020, 22, 5314-5319. doi: 10.1021/acs.orglett.0c01466.



d(I···Br) = 3.6421(9) Å; C–I···Br = 161.23(11)° & C–Br···I = 160.90(13)°

13. CIQMEV 1-(3-bromopropoxy)-4-iodobenzene

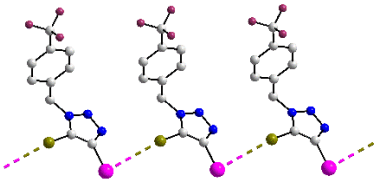
Wu, Z.; Liu, X.; Shen, P.; Jiang, S. 1-(3-Bromopropoxy)-4-iodobenzene. Acta Crystallogr., Sect. E: Struct. Rep. Online 2007, 63, o4760. doi: 10.1107/S1600536807058801.



d(I···Br) = 3.6623(10) Å; C–I···Br = 155.87(8)° & C–Br···I = 160.15(9)°

14. CORZER 5-bromo-4-iodo-1-{[4-(trifluoromethyl)phenyl]methyl}-1H-1,2,3-triazole

Rheingold, A.L. Private Communication to the Cambridge Structural Database (2019), Refcode CORZER.



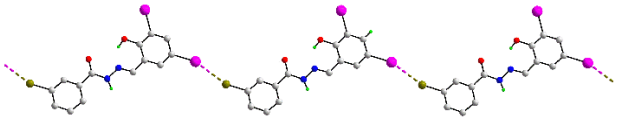
d(I···Br) = 3.7163(11) Å; C–I···Br = 84.5(3)° & C–Br···I = 148.8(3)°

Br···F interactions just above the van der Waals radii connect chains into a supramolecular tube

d(Br···F) = 3.322(9) Å; C–Br···F = 75.8(3)° & C–F···Br = 133.1(7)°

15. VOQQIC 3-bromo-N'-(2-hydroxy-3,5-diiodobenzylidene)benzohydrazide monohydrate

Ning, J.-H.; Xu, X.-W. 3-Bromo-N'-(2-hydroxy-3,5-diiodobenzylidene)benzohydrazide monohydrate. Acta Crystallogr., Sect. E: Struct. Rep. Online 2009, 65, o905-o906. doi: 10.1107/S1600536809010964.

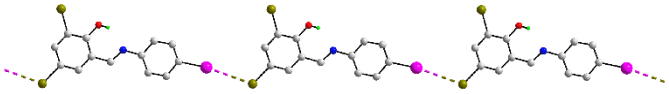


I···O interactions of 2.930(5) Å link chains into a double-layer

d(I···Br) = 3.7169(12) Å; C–I···Br = 149.09(17)° & C–Br···I = 140.37(19)°

16. HIRHUM 2,4-dibromo-6-(4-iodophenyliminomethyl)phenol

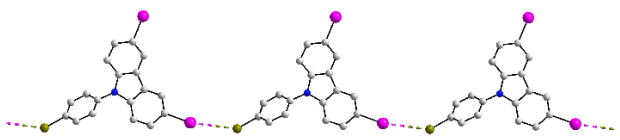
Guo, M.-L.; Nong, X.-R.; Yin, H. 2,4-Dibromo-6-(4-iodo-phenyl-imino-methyl)phenol. Acta Crystallogr., Sect. E: Struct. Rep. Online 2007, 63, o4640. doi: 10.1107/S1600536807055675.



d(I···Br) = 3.7226(16) Å; C–I···Br = 166.3(3)° & C–Br···I = 112.8(3)°

17. QAPQAC 9-(4-bromophenyl)-3,6-diiodo-9H-carbazole

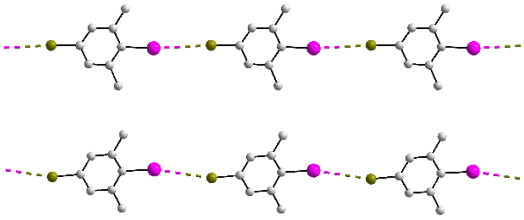
Tang, G.-M.; Chi, R.-H.; Wan, W.-Z.; Wang, Y.-T.; Cui, Y.-Z.; Ng, S.W. Synthesis, crystal structures, and nonlinear optic and thermal properties of two diiodocarbazole derivatives. J. Chem. Res. 2017, 41, 79-81. doi: 10.3184/174751917X14839766277297.



d(I···Br) = 3.7228(12) Å; C–I···Br = 158.5(2)° & C–Br···I = 135.2(2)°

18. YIRTOJ 5-bromo-2-iodo-1,3-dimethylbenzene

Liu, R.; Li, Y.-H.; Luo, W ; Liu, S.; Zhu, H.-J. 5-Bromo-2-iodo-1,3-dimethylbenzene. Acta Crystallogr., Sect. E: Struct. Rep. Online 2008, 64, o219. doi: 10.1107/S1600536807064537.



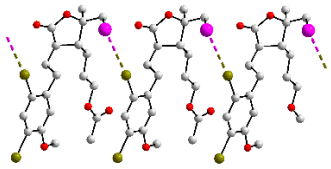
Three independent molecules: two self-associate into linear chains. The iodide and bromide atoms in the third molecule do not form a halogen bonding interaction < 4.0Å

d(I···Br) = 3.6869(15) Å; C–I···Br = 162.8(2)° & C–Br···I = 161.1(3)° {top view}

d(I···Br) = 3.7413(15) Å; C–I···Br = 159.8(3)° & C–Br···I = 156.0(3)°

19. CABCAM (R,R,R)-3-(4-(2-(2,4-dibromo-5-methoxyphenyl)ethyl)-2-(iodomethyl)-2-methyl-5-oxotetrahydrofuran-3-yl)propyl acetate

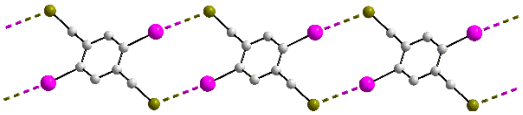
Kaluza, N.M.; Schollmeyer, D.; Nubbemeyer, U. Total synthesis of (–)-C/D-cis-de-hydro-3-O-methyl-estradiols. Eur. J. Org. Chem. 2016, 2016, 357-366. doi: 10.1002/ejoc.201501341.



d(I···Br) = 3.7558(13) Å; C–I···Br = 84.5(3)° & C–Br···I = 171.2(4)°

20. MESMED 2,5-diiodo-1,4-bis(bromomethyl)benzene

Gaefke, G.; Enkelmann, V.; Höger, S. A practical synthesis of 1,4-diiodo-2,5-bis(chloromethyl)benzene and 1,4-diiodo-2,5-bis(bromomethyl)benzene. Synthesis 2006, 2971-2973. doi: 10.1055/s-2006-942534.



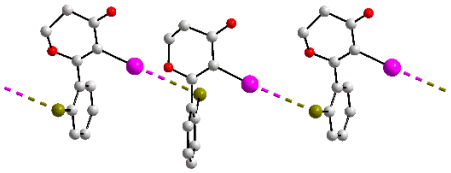
Molecule is centrosymmetric

d(I···Br) = 3.6271(4) Å; C–I···Br = 166.66(7)° & C–Br···I = 97.45(10)°

Zig-zag chains

21. YIZFUL 6-(2-bromophenyl)-5-iodo-2,3-dihydro-4H-pyran-4-one

Gholap, S.P; Jangid, D.; Fernandes, R.A. Metal-free Brønsted acid-catalyzed rearrangement of δ-hydroxyalkynones to 2,3-dihydro-4H-pyran-4-ones: Total synthesis of obolactone and a catechol pyran isolated from *Plectranthus sylvestris*. J. Org. Chem. 2019, 84, 3537-3551. doi: 10.1021/acs.joc.8b03141.

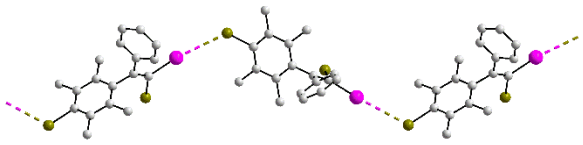


Glide symmetry

d(I···Br) = 3.6011(6) Å; C–I···Br = 175.22(11)° & C–Br···I = 103.29(13)°

22. JIPTEK 1-bromo-4-(2-bromo-2-iodo-1-phenylethenyl)-2,3,5,6-tetramethylbenzene

Maji, B.; Bhattacharya, A.; Hazra, S. Halogen-induced Friedel-Crafts alkenylation reactions with haloalkynes: Direct access to gem-1, 1-dihaloalkenes. Chem. Sel. 2017, 2, 10375-10378. doi: 10.1002/slct.201702265.

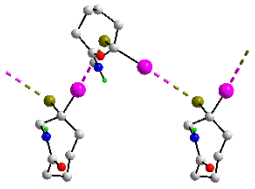


Glide symmetry

d(I···Br) = 3.640(1) Å; C–I···Br = 168.25(17)° & C–Br···I = 118.41(17)°

23. SELYOY 7-bromo-7-iodo-perhydro-1-azocin-2-one

Hu, T.; Shen, M.; Chen, Q.; Li, C. Pushing radical cyclization from regioselective to regiospecific: Cyclization of amidyl radicals controlled by vinylic halogen substitution. Org. Lett. 2006, 8, 2647-2650. doi: 10.1021/ol060983q.

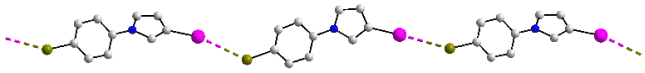


Glide symmetry

d(I···Br) = 3.6666(12) Å; C–I···Br = 175.7(2)° & C–Br···I = 115.3(2)°

24. JINJUO 1-(4-bromophenyl)-3-iodo-1H-pyrrole

Wang, F.; Zhang, X.; He, Y.; Fan, X. Selective synthesis of pyrrolidin-2-ones and 3-iodopyrroles via the ring contraction and deformylative functionalization of piperidine derivatives. Org. Biomol. Chem. 2019, 17, 156-164. doi: 10.1039/C8OB02640H.

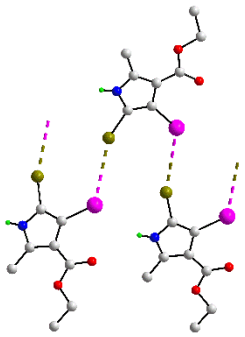


Glide symmetry

d(I···Br) = 3.691(3) Å; C–I···Br = 151.5(4)° & C–Br···I = 126.0(5)°

25. MOZTED ethyl 5-bromo-4-iodo-2-methyl-1H-pyrrole-3-carboxylate

Pandeeti, O.; Bijigiri, S.K.; Panda, P.K. One-pot synthesis of benzotripyrrole derivatives from 1H-pyrroles. New J. Chem. 2019, 43, 18437-18841. doi: 10.1039/C9NJ04700J.



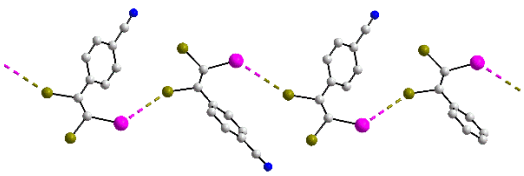
Two independent molecules associate and the two-molecule aggregates are connected into a zig-zag chain (glide symmetry)

d(I···Br) = 3.7380(17) Å; C–I···Br = 127.2(3)° & C–Br···I = 151.3(4)°

d(I···Br) = 3.7905(14) Å; C–I···Br = 126.8(3)° & C–Br···I = 158.3(4)°

26. BULZIU 4-(1,2-dibromo-2-iodoethenyl)benzonitrile

Zeng, X.; Liu, S.; Yang, Y.; Yang, Y.; Hammond, G.B.; Xu, B. Regio- and stereoselective synthesis of 1,2-dihaloalkenes using in-situ-generated ICl, IBr, BrCl, I_2, and Br_2. Cell Press: Chem. 2020, 6, 1018-1031. doi: 10.1016/j.chempr.2020.03.011.



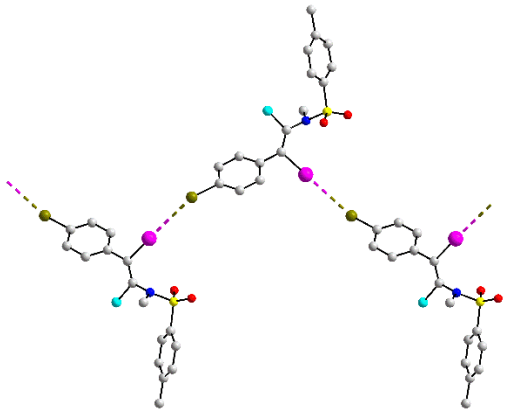
Glide symmetry

d(I···Br) = 3.8025(5) Å; C–I···Br = 127.28(11)° & C–Br···I = 152.94(12)°

Helical chains

27. BUNBAQ N-[2-(4-bromophenyl)-1-chloro-2-iodoethenyl]-N,4-dimethylbenzene-1-sulfonamide

Zeng, X.; Liu, S.; Yang, Y.; Yang, Y.; Hammond, G.B.; Xu, B. Regio- and stereoselective synthesis of 1,2-dihaloalkenes using in-situ-generated ICl, IBr, BrCl, I_2, and Br_2. Cell Press: Chem. 2020, 6, 1018-1031. doi: 10.1016/j.chempr.2020.03.011.



2_1-screw symmetry

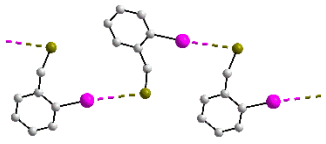
d(I···Br) = 3.6889(8) Å; C–I···Br = 169.87(9)° & C–Br···I = 138.90(11)°

Extra I···Br interactions [3.8353(6) Å] longer the van der Waals radii link chains into a layer

d(I···Br) = 3.8353(6) Å; C–I···Br = 72.94(10)° & C–Br···I = 157.93(11)°

28. CIQLEU 1-bromomethyl-2-iodobenzene

Betz, R.; Klüfers, P. 1-Bromomethyl-2-iodobenzene. Acta Crystallogr., Sect. E: Struct. Rep. Online 2007, 63, o4753. doi: 10.1107/S1600536807058151.

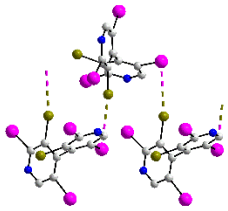


2_1-screw symmetry

d(I···Br) = 3.6943(4) Å; C–I···Br = 170.95(7)° & C–Br···I = 90.81(11)°

29. IMURAL 3,3'-dibromo-2,2',5,5'-tetraiodo-4,4'-bipyridine

Mamane, V.; Peluso, P.; Aubert, E.; Cossu, S.; Pale, P. Chiral hexahalogenated 4,4′-bipyridines. J. Org. Chem. 2016, 81, 4576-4587. doi: 10.1021/acs.joc.6b00413.

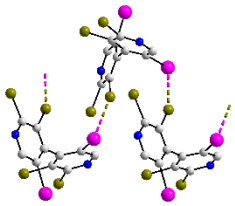


2_1-screw symmetry

d(I···Br) = 3.7136(15) Å; C–I···Br = 78.41(9)° & C–Br···I = 170.13(11)°

30. INADIM 2,2',3,3'-tetrabromo-5,5'-diiodo-4,4'-bipyridine

Mamane, V.; Peluso, P.; Aubert, E.; Cossu, S.; Pale, P. Chiral hexahalogenated 4,4'-bipyridines. J. Org. Chem. 2016, 81, 4576-4587. doi: 10.1021/acs.joc.6b00413.

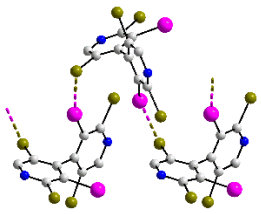


2_1-screw symmetry

d(I···Br) = 3.7281(18) Å; C–I···Br = 71.91(14)° & C–Br···I = 161.19(15)°

31. IMUQOY 2,2',5,5'-tetrabromo-3,3'-diiodo-4,4'-bipyridine

Mamane, V.; Peluso, P.; Aubert, E.; Cossu, S.; Pale, P. Chiral hexahalogenated 4,4'-bipyridines. J. Org. Chem. 2016, 81, 4576-4587. doi: 10.1021/acs.joc.6b00413.

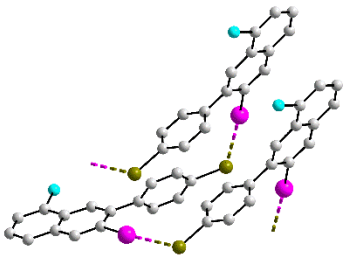


2_1-screw symmetry

d(I···Br) = 3.7330(7) Å; C–I···Br = 162.62(7)° & C–Br···I = 81.66(7)°

32. FABWIR 7-(4-bromophenyl)-1-chloro-6-iodonaphthalene

Lehnherr, D.; Alzola, J.M.; Lobkovsky, E.B.; Dichtel, W.R. Regioselective synthesis of polyheterohalogenated naphthalenes via the benzannulation of haloalkynes. Chem.-Eur. J. 2015, 21, 18122-18127. doi: 10.1002/chem.201503418.

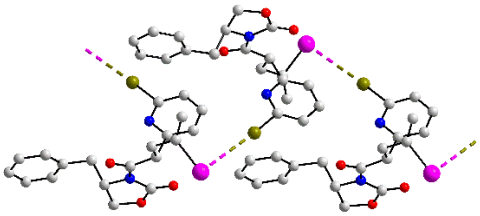


Two independent molecules – one self-associates into a helical chain (2_1-screw symmetry). No I···Br < 4.0 Å for the second molecule and no X···X less than the sum of the van der Waals radii. d(I···Br) = 3.7592(4) Å; C–I···Br = 173.40(6)° & C–Br···I = 104.68(8)°

Br···Cl contacts beyond the van der Waals radii (shortest = 3.6511(8) Å) link both independent molecules into a 2-D array.

33. ZIMLIT (R)-4-benzyl-3-((S)-2-(6-bromopyridin-2-yl)-4-iodopent-4-enoyl)oxazolidin-2-one

Barát, V.; Csókás, D.; Bates, R.W. Synthesis of (−)-cytisine using a 6-endo aza-Michael addition. J. Org. Chem. 2018, 83, 9088-9095. doi: 10.1021/acs.joc.8b01156.

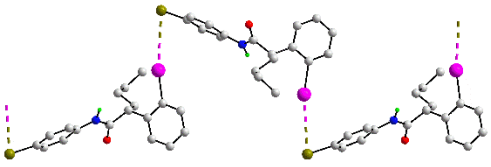


2_1-screw symmetry

d(I···Br) = 3.7631(7) Å; C–I···Br = 87.09(15)° & C–Br···I = 168.75(18)°

34. WUJYUY (R)-N-(4-bromophenyl)-2-(2-iodophenyl)hexanamide

Tian, J.; Luo, F.; Zhang, Q.; Liang, Y.; Li, D.; Zhan, Y.; Kong, L.; Wang, Z.-X.; Peng, B. Asymmetric iodonio-[3,3]-sigmatropic rearrangement to access chiral α-aryl carbonyl compounds. J. Am. Chem. Soc. 2020, 142, 6884-6890. doi: 10.1021/jacs.0c00783.

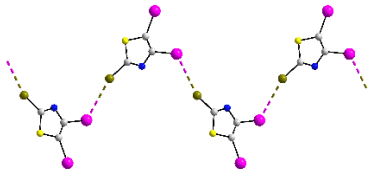


Two independent molecules: only one forms I···Br interactions (2_1-screw symmetry). For the second molecule, no X···X interactions < 4.0 Å are apparent. The independent molecules are connected into a supramolecular chain via amide-N–H···O(carbonyl) hydrogen-bonds, also having 2_1-screw symmetry (different direction)

d(I···Br) = 3.7724(9) Å; C–I···Br = 167.18(16)° & C–Br···I = 76.25(18)°

35. IKUZAR 2-bromo-4,5-diiodo-1,3-thiazole

Shi, Q.; Zhang, S.; Zhang, J.; Oswald, V.F.; Amassian, A.; Marder, S.R.; Blakey, S.B. KO^{t}Bu-initiated aryl C–H iodination: A powerful tool for the synthesis of high electron affinity compounds. J. Am. Chem. Soc. 2016, 138, 3946-3949. doi: 10.1021/jacs.5b12259.

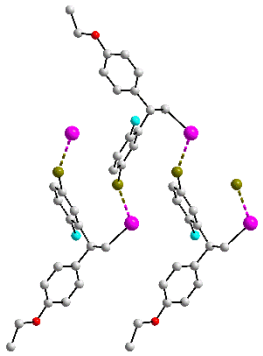


2_1-screw symmetry

d(I···Br) = 3.7966(13) Å; C–I···Br = 107.0(3)° & C–Br···I = 160.7(3)°

36. GUMMEI 4-bromo-1-chloro-2-(1-(4-ethoxyphenyl)-2-iodoethyl)benzene

Zhang, S.; Wang, W.; Li, C.; Liu, P.; Xu, W.; Tang, L.; Wang, J.; Zhao, G. Facile synthesis of enantiomerically pure 1-(5-bromo-2-chlorophenyl)-1-(4-ethoxyphenyl)ethane. Chem. Res. Chin. Univ. 2014, 30, 250-256. doi: 10.1007/s40242-014-3257-1.

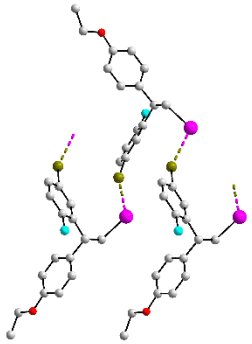


2_1-screw symmetry

d(I···Br) = 3.7973(9) Å; C–I···Br = 103.12(13)° & C–Br···I = 159.62(14)°

37. GUMLUX 4-bromo-1-chloro-2-(1-(4-ethoxyphenyl)-2-iodoethyl)benzene

Zhang, S.; Wang, W.; Li, C.; Liu, P.; Xu, W.; Tang, L.; Wang, J.; Zhao, G. Facile synthesis of enantiomerically pure 1-(5-bromo-2-chlorophenyl)-1-(4-ethoxyphenyl)ethane. Chem. Res. Chin. Univ. 2014, 30, 250-256. doi: 10.1007/s40242-014-3257-1.

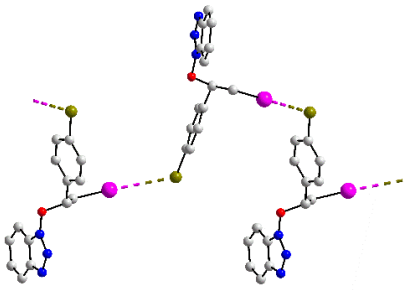


2_1-screw symmetry

d(I···Br) = 3.8053(7) Å; C–I···Br = 103.40(10)° & C–Br···I = 159.58(11)°

38. VEXDAG 1-[1-(4-bromophenyl)-2-iodoethoxy]-1H-benzotriazole

Sun, K.; Zhang, S.; Liu, Z.; Lv, Y. Eco-friendly C–I and C–O bond formation of simple alkenes: Direct access to β-iodo oxyamines. Chem. Sel. 2018, 3, 5766-5768. doi: 10.1002/slct.201800878.

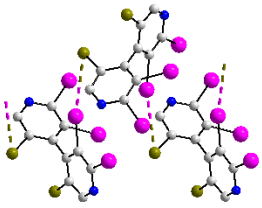


2_1-screw symmetry

d(I···Br) = 3.8001(10) Å; C–I···Br = 165.44(11)° & C–Br···I = 121.92(14)°

39. IMURUF 5,5'-dibromo-2,2',3,3'-tetraiodo-4,4'-bipyridine

Mamane, V.; Peluso, P.; Aubert, E.; Cossu, S.; Pale, P. Chiral hexahalogenated 4,4′-bipyridines. J. Org. Chem. 2016, 81, 4576-4587. doi: 10.1021/acs.joc.6b00413.



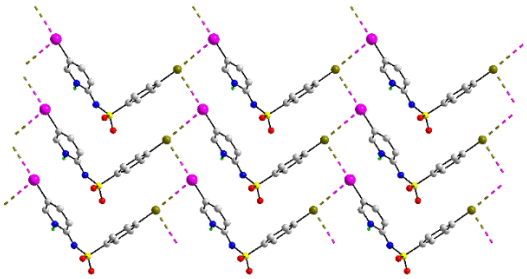
2_1-screw symmetry

d(I···Br) = 3.8140(9) Å; C–I···Br = 169.03(7)° & C–Br···I = 77.36(8)°

Two-dimensional array

40. VEGSOR (5-iodopyridinium-2-yl)([4-bromophenyl]sulfonyl)azanide

Gelbrich, T.; Threlfall, T.L.; Hursthouse, M.B. XPac dissimilarity parameters as quantitative descriptors of isostructurality: The case of fourteen 4,5′-substituted benzenesulfonamido-2-pyridines obtained by substituent interchange involving CF_3/I/Br/Cl/F/Me/H. CrystEngComm 2012, 14, 5454-5464. doi: 10.1039/c2ce25508a.



Flat topology

d(I···Br) = 3.7436(5) Å; C–I···Br = 158.64(11)°; C–Br···I = 87.49(12)°

d(I···Br) = 3.7465(6) Å; C–I···Br = 80.73(11)°; C–Br···I = 172.51(12)°

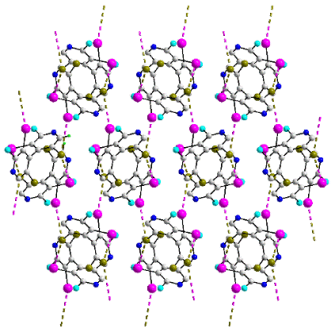
{Evidence for a S=O···π(arene) contact within the pictured array with the O…Cg(arene) separation being 3.137(3) Å and angle at O being 127.86(16)°. This separation shorter than the assumed van der Waals radius of O (1.52 Å) and half a phenyl ring (1.80 Å)

C. Janiak, J. Chem. Soc., Dalton Trans., 2000, 3885–3896. doi: 10.1039/B003010O}

Three-dimensional architecture

41. INADOS 5,5'-dibromo-2,2'-dichloro-3,3'-diiodo-4,4'-bipyridine

Mamane, V.; Peluso, P.; Aubert, E.; Cossu, S.; Pale, P. Chiral hexahalogenated 4,4′-bipyridines. J. Org. Chem. 2016, 81, 4576-4587. doi: 10.1021/acs.joc.6b00413.



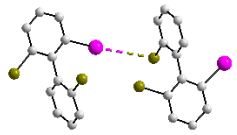
d(I···Br) = 3.6944(7) Å; C–I···Br = 161.40(5)° & C–Br···I = 83.20(5)°

d(I···Br) = 3.7405(5) Å; C–I···Br = 95.99(5)° & C–Br···I = 155.52(5)°

Table S2. Details of composition, images, unit-cell details and geometric details in congener crystals featuring putative X···X interactions.

2. RECROI 2,2'-dibromo-6-iodobiphenyl

Leroux, F.R.; Berthelot, A.; Bonnafoux, L.; Panossian, A.; Colobert, F. Transition-metal-free atropo-selective synthesis of biaryl compounds based on arynes. Chem.-Eur. J. 2012, 18, 14232-14236. doi: 10.1002/chem.201202739.



Two independent molecules connected via one interaction

orthorhombic $P2_12_12$, Z′ = 2; a = 16.7820(4), b = 18.8039(5), c = 7.9459(2) Å, β = 91.429(3)°

d(I···Br) = 3.7397(9) Å; C–I···Br = 172.38(19)° & C–Br···I = 85.37(16)°

RECSAV 2'-bromo-2-chloro-6-iodobiphenyl

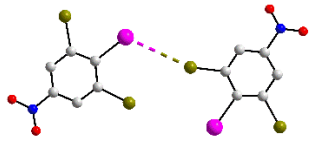
monoclinic C2, Z′ = 2; a = 21.2611(10), b = 7.9582(2), c = 16.1680(8) Å, β = 114.519(2)°

d(I···Br) = 3.8303(9) Å; C–I···Br = 167.5(2)° & C–Br···I = 90.87(18)°

{the Br substituted by a Cl in the disubstituted ring, leaving one each of I and Br; not isostructural; interaction persists but at the van der Waals limit}

3. DUPNIN 1,3-dibromo-2-iodo-5-nitrobenzene

Romero, J.A.; Aguirre Hernández, G.; Bernès, S. Anomalous halogen bonds in the crystal structures of 1,2,3-tri-bromo-5-nitro-benzene and 1,3-di-bromo-2-iodo-5-nitro-benzene. Acta Crystallogr., Sect. E: Cryst. Commun. 2015, 71, 960-965. doi: 10.1107/S2056989015013377.



Two independent molecules connected via one interaction; the non-bonded contact within the dimer = 4.737(3) Å

monoclinic $P2_1/c$, Z′ = 2; a = 13.548(3), b = 20.037(3), c = 9.123(2) Å, β = 130.37(2)°

d(I···Br) = 3.813(3) Å; C–I···Br = 117.2(5)° & C–Br···I = 161.2(5)°

DUPNEJ 1,2,3-tribromo-5-nitrobenzene

Triclinic $P\bar{1}$, Z' = 2; a = 7.641(5), b = 8.040(5), c = 14.917(6) Å, α = 83.91(3), β = 79.86(4), γ = 81.94(4)°

d(Br···Br) = 3.642(3) Å; C–Br···Br = 165.2(4)° & C–Br···Br = 82.2(5)°

{the I substituted by a Br; not isostructural; is with HIBWIY; Br···Br involving equivalent atoms}

HIBWIY 3,4,5-trichloronitrobenzene

Bhar, A.; Aune, J.P.; Benali-Cherif, N.; Benmenni, L.; Giorgi, M. Three polychloromononitrobenzenes: $C_6H_3Cl_2NO_2$, $C_6H_2Cl_3NO_2$ and $C_6HCl_4NO_2$. Acta Crystallogr., Sect. C: Cryst. Struct. Commun. 51 (1995) 256-260. doi: 10.1107/S0108270194002957

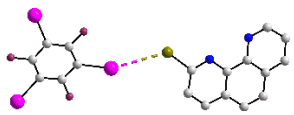
Triclinic $P\bar{1}$, Z' = 2; a = 7.842(2), b = 14.450(5), c = 7.548(2) Å, α = 101.08(2), β = 98.10(2), γ = 84.38(3)°

d(Cl···Cl) = 3.571(3) Å; C–Cl···Cl = 168.1(2)° & C–Cl···Cl = 82.5(2)°

{all X substituted by a Cl; not isostructural; is isostructural with DUPNEJ; Cl···Cl involving equivalent atoms}

9. VIXWIL 2-bromo-1,10-phenanthroline 1,3,5-trifluoro-2,4,6-triiodobenzene

Zhang, Y.; Wang, J.-G.; Wang, W. Noncovalent interactions between 1,3,5-trifluoro-2,4,6-triiodobenzene and a series of 1,10-phenanthroline derivatives: A combined theoretical and experimental study. Crystals 2019, 9, 140. doi: 10.3390/cryst9030140.



1:1 co-crystal

Monoclinic $P2_1/c$, Z' = 1 (pair); a = 14.2515(4), b = 18.2923(6), c = 7.6939(3) Å, β = 90.725(3)°

d(I···Br) = 3.6927(7) Å; C–I···Br = 156.68(11)° & C–Br···I = 130.84(14)°

VIXWUX 2-chloro-1,10-phenanthroline 1,3,5-trifluoro-2,4,6-triiodobenzene

Monoclinic $P2_1/c$, Z' = 1; a = 14.2733(5), b = 18.2696(6), c = 7.6371(4) Å, β = 91.662(3)°

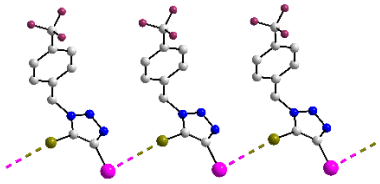
d(I···Cl) = 3.6748(15) Å; C–I···Cl = 158.55(11)° & C–Cl···I = 133.47(16)°

d(I···F) = 3.436(3) Å; C–I···F = 154.15(11)° & C–F···I = 146.6(2)°

{Phen-Br now a Cl; isostructural; I···Cl involving equivalent atoms; type I I···F also noted, just below the some of the van der Waals radii}

14. CORZER 5-bromo-4-iodo-1-{[4-(trifluoromethyl)phenyl]methyl}-1H-1,2,3-triazole

Rheingold, A.L. Private Communication to the Cambridge Structural Database (2019), Refcode CORZER.



d(I···Br) = 3.7163(11) Å; C–I···Br = 84.5(3)° & C–Br···I = 148.8(3)°

Orthorhombic Pbca, Z′ = 1; a = 6.7102(5), b = 14.0870(11), c = 25.650(2) Å

COMJUM 4-bromo-5-iodo-1-{[4-(trifluoromethyl)phenyl]methyl}-1H-1,2,3-triazole

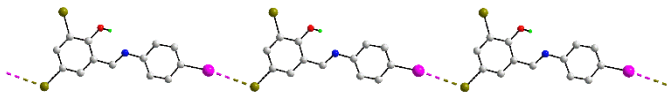
Rheingold, A.L. Private Communication to the Cambridge Structural Database (2019), Refcode COMJUM.

Monoclinic $P2_1/c$, Z′ = 1; a = 12.880(4), b = 7.414(2), c = 13.948(4) Å, β = 106.247(3)°

{Isomer: the positions of the I and Br atoms have been interchanged; not isostructural; I···Br contacts are noted but at 3.88(1) Å, beyond the van der Waals radii; the topology of the chain is zig-zag (glide symmetry)}

16. HIRHUM 2,4-dibromo-6-(4-iodophenyliminomethyl)phenol

Guo, M.-L.; Nong, X.-R.; Yin, H. 2,4-Dibromo-6-(4-iodo-phenyl-imino-methyl)phenol. Acta Crystallogr., Sect. E: Struct. Rep. Online 2007, 63, o4640. doi: 10.1107/S1600536807055675.



Triclinic $P\bar{1}$, Z′ = 1; a = 8.0213(17), b = 8.5936(18), c = 11.290(2) Å, α = 87.066(3), β = 76.541(4), γ = 66.203(3)°

d(I···Br) = 3.7226(16) Å; C–I···Br = 166.3(3)° & C–Br···I = 112.8(3)°

CIQBUA 2,4-dibromo-6-(4-bromophenyliminomethyl)phenol

Guo, M.-L.; Zhang, L. 2,4-Dibromo-6-(4-bromophenyliminomethyl)phenol. Acta Crystallogr., Sect. E: Struct. Rep. Online 63 (2007) o4558 doi: 10.1107/S1600536807054335.

Triclinic $P\bar{1}$, $Z' = 1$; a = 7.985(3), b = 8.594(3), c = 11.020(4) Å, α = 87.801(6), β = 76.688(7), γ = 65.180(5)°

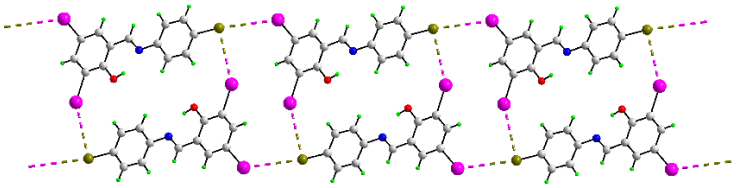
d(Br···Br) = 3.669(2) Å; C–Br···Br = 167.3(3)° & C–Br···Br = 116.5(3)°

{The I has been replaced by a Br; isostructural; same linear chain mediated by Br···Br contacts}

LAPTIH 2-(((4-bromophenyl)imino)methyl)-4,6-diiodophenol

Ji, H.; Ma, H.-P.; Yang, Y.-A.; Zhu, H.-L. 2-[(4-Brom-phenylimino)methyl]-4,6-diiodophenol. Acta Crystallogr., Sect. E: Struct. Rep. Online 68 (2012) o788. doi: 10.1107/S160053681200551X

Triclinic $P\bar{1}$, $Z' = 1$; a = 7.9870(13), b = 8.9811(14), c = 11.3907(18) Å, α = 91.093(2), β = 99.873(2), γ = 114.570(2)° {apply transformation [1 0 0 0 -1 0 0 0 -1]}



{Interchange of I with Br throughout; two independent type-II I···Br interaction occur at beyond the van der Waals radii, that is, 3.9394(10), to give a dimer, and 3.9489(9) Å, to connect the dimers, link molecules into a tape}

RAHWUU 2-bromo-6-(((4-bromophenyl)imino)methyl)-4-chlorophenol

Zhang, X.-L.; Guo, Y.-N. Crystal structure of 2-bromo-4-chloro-6-[(4-bromophenylimino) methyl]phenol, $C_{13}H_8Br_2ClNO$. Z. Kristallogr. - New Cryst. Struct. 226 (2011) 521-522. doi: 10.1524/ncrs.2011.0231.

Triclinic $P\bar{1}$, $Z' = 1$; a = 7.941(5), b = 8.486(6), c = 11.024(8), Å, α = 86.83(3), β = 75.39(3), γ = 64.50(2)°

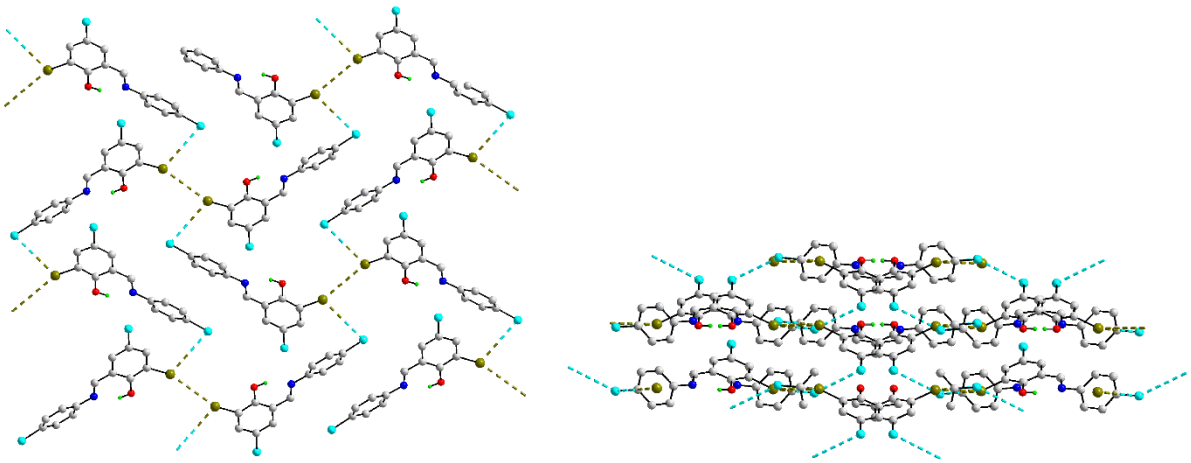
{The Br away from the OH group is now a Cl and the terminal I is now a Br; isostructural; independent type-II Br···Br and Br···Cl interactions occur at beyond the van der Waals radii,

that is, 3.815(3) and 3.660(3) Å, respectively, link molecules into a tape as for LAPTIH; the Br···Br interaction lead to the dimer}

RAJCEM 2-bromo-4-chloro-6-(((4-chlorophenyl)imino)methyl)phenol

Zhang, X.-L. Z. Crystal structure of 2-bromo-4-chloro-6-[(4-chlorophenylimino) methyl]phenol, $C_{13}H_8BrCl_2NO$. Kristallogr. - New Cryst. Struct. 226 (2011) 567-568. doi: 10.1524/ncrs.2011.0253.

Monoclinic $P2_1/c$, Z′ = 1; a = 7.712(2), b = 21.437(5), c = 8.541(2) Å, β = 113.138(3)°



{The Br away from the OH group is now a Cl and the terminal I is now a Cl; independent type-II Br···Br and Br···Cl interactions occur at beyond the van der Waals radii, that is, 3.8365(8) and 3.9614(10), respectively, and link molecules into a 2-D array. Type-II Cl···Cl interactions of 3.6009(12) Å, again beyond the van der Waals radii occur between layers to form the 3D assembly}

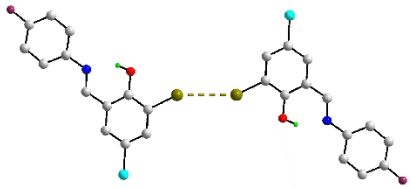
JOFFOA 2-bromo-4-chloro-6-(4-fluorophenyliminomethyl)phenol

Puthilibai, G.; Vasudhevan, S.; Rajagopal, G. 2-Bromo-4-chloro-6-(4-fluorophenyliminomethyl)phenol. Acta Crystallogr., Sect. E: Struct. Rep. Online 64 (2008) o1333. doi: 10.1107/S1600536808017443.

Triclinic $P\bar{1}$, Z′ = 1; a = 8.2274(3), b = 8.6566(3), c = 10.8880(4) Å, α = 69.545(2), β = 70.820(2), γ = 62.341(2)°

d(Br···Br) = 3.5526(9) Å; C–Br···Br = 140.32(10)° & C–Br···Br = 140.32(10)°

{The I atom has been replaced by a F and one of the Br by a Cl; a type-I Br···Br contact over a centre of inversion leads to a two-molecule aggregate}



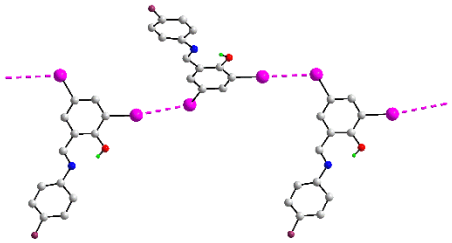
TESBUQ 2-(((4-fluorophenyl)imino)methyl)-4,6-diiodophenol

Yang, Z.-M.; Zhu, H.; Zhu, H.-L. Crystal structure of 2[(4-fluorophenylimino)methyl]-4,6-diiodophenol, $C_{13}H_8FI_2NO$. Z. Kristallogr. - New Cryst. Struct. 227 (2012) 447-448. doi: 10.1524/ncrs.2012.0202.

Monoclinic Cc, Z′ = 2; a = 4.5485(13), b = 35.025(2), c = 17.307(1) Å, β = 95.255(2)°

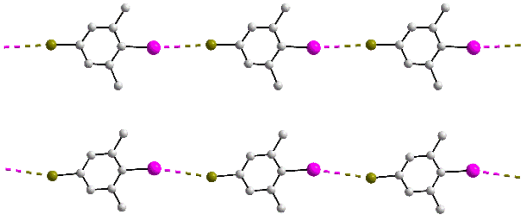
d(I···I) = 3.7476(15) Å; C–I···I = 161.58(4)° & C–I···I = 109.34(4)°

{Both positions in the di-substituted ring are I and the terminal position is now F; two independent molecules, one self-associates into a chain via I···I contacts}



18. YIRTOJ 5-bromo-2-iodo-1,3-dimethylbenzene

Liu, R.; Li, Y.-H.; Luo, W ; Liu, S.; Zhu, H.-J. 5-Bromo-2-iodo-1,3-dimethylbenzene. Acta Crystallogr., Sect. E: Struct. Rep. Online 2008, 64, o219. doi: 10.1107/S1600536807064537.



Three independent molecules: two self-associate into linear chains. The iodide and bromide atoms in the third molecule do not form a halogen bonding interaction < 4.0Å

d(I···Br) = 3.6869(15) Å; C–I···Br = 162.8(2)° & C–Br···I = 161.1(3)° {top view}

d(I···Br) = 3.7413(15) Å; C–I···Br = 159.8(3)° & C–Br···I = 156.0(3)°

Triclinic $P\bar{1}$, Z′ = 3; a = 10.282(2), b = 11.314(2), c = 12.951(3) Å, α = 69.27(3), β = 89.11(3), γ = 83.70(3)°

XISQIA 2-bromo-5-iodo-1,3-dimethylbenzene

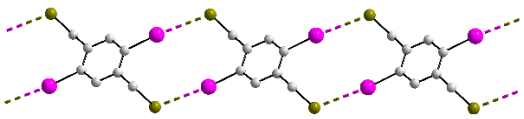
Liu, R.; Wu, W.-Y.; Li, Y.-H.; Deng, S.-P.; Zhu, H.-J. Acta Crystallogr., Sect. E: Struct. Rep. Online 64 (2008) o280. doi: 10.1107/S1600536807065415.

Orthorhombic Pnma, Z′ = 1; a = 16.686(3), b = 7.0640(14), c = 8.2130(16) Å

{Isomer; molecule has mirror symmetry with the ring in the plane; closest X···X contact is a type-II I···Br contact of 3.9941(13) Å}

20. MESMED 2,5-diiodo-1,4-bis(bromomethyl)benzene

Gaefke, G.; Enkelmann, V.; Höger, S. A practical synthesis of 1,4-diiodo-2,5-bis(chloromethyl)benzene and 1,4-diiodo-2,5-bis(bromomethyl)benzene. Synthesis 2006, 2971-2973. doi: 10.1055/s-2006-942534.



Molecule is centrosymmetric

d(I···Br) = 3.6271(4) Å; C–I···Br = 166.66(7)° & C–Br···I = 97.45(10)°

Triclinic P$\bar{1}$, Z′ = 0.5; a = 4.3865(4), b = 7.4454(4), c = 9.0972(5) Å, α = 71.7302(13), β = 83.6831(12), γ = 84.8666(12)°

MESMIH 2,5-diiodo-1,4-bis(chloromethyl)benzene

Triclinic P$\bar{1}$, Z′ = 0.5; a = 4.3575(4), b = 7.2917(4), c = 8.9994(5) Å, α = 70.8917(13), β = 83.3779(12), γ = 84.9725(12)°

d(I···Cl) = 3.5373(9) Å; C–I···Cl = 166.82(10)° & C–Cl···I = 99.27(14)°

{Br replaced by Cl; isostructural; I···Cl interactions form}

AKEWIY 1,4-dibromo-2,5-bis(bromomethyl)benzene

Näther, C.; Jess, I.; Kuś, P.; Jones, P.G. Dimorphism of 1,4-dibromo-2,5-bis(bromomethyl)benzene: crystallographic and physicochemical investigations. CrystEngComm 18 (2016) 3142-3149. doi: 10.1039/C6CE00438E

Triclinic P$\bar{1}$, Z′ = 0.5; a = 4.3542(3), b = 7.3675(6), c = 8.7140(6) Å, α = 72.481(7), β = 83.722(6), γ = 84.917(6)°

d(Br···Br) = 3.5663(5) Å; C–Br···Br = 164.25(8)° & C–Br···Br = 91.88(7)°

{I replaced by Br; isostructural; Br···Br interactions form the chain. Weaker (3.7610(5) Å) Br···Br contacts link chains into a layer}

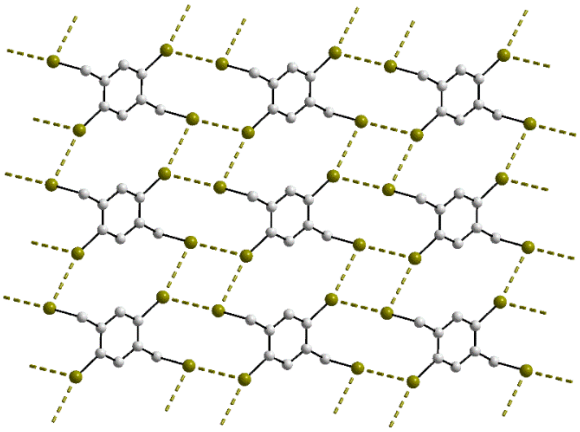
AKEWIY01 1,4-dibromo-2,5-bis(bromomethyl)benzene

Monoclinic $P2_1/c$, Z′ = 0.5; a = 6.6114(5), b = 8.7776(6), c = 9.1807(6) Å, β = 104.041(7)°

d(Br···Br) = 3.6617(6) Å; C–Br···Br = 171.60(10)° & C–Br···Br = 102.29(11)° - to form chain

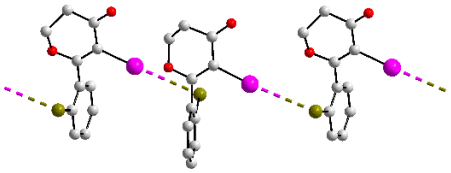
d(Br···Br) = 3.5231(6) Å; C–Br···Br = 161.48(11)° & C–Br···Br = 92.01(10)°

{Polymorph of AKEWIY; Br···Br interactions form the chain as for the other structures but this contact is longer than the inter-chain interactions which generate the layer}



21. YIZFUL 6-(2-bromophenyl)-5-iodo-2,3-dihydro-4H-pyran-4-one

Gholap, S.P; Jangid, D.; Fernandes, R.A. Metal-free Brønsted acid-catalyzed rearrangement of δ-hydroxyalkynones to 2,3-dihydro-4H-pyran-4-ones: Total synthesis of obolactone and a catechol pyran isolated from *Plectranthus sylvestris*. J. Org. Chem. 2019, 84, 3537-3551. doi: 10.1021/acs.joc.8b03141.



Glide symmetry

d(I···Br) = 3.6011(6) Å; C–I···Br = 175.22(11)° & C–Br···I = 103.29(13)°

Monoclinic $P2_1/c$, Z′ = 1; a = 10.7766(4), b = 7.8221(3), c = 13.4995(6) Å, β = 94.552(4)°

YIZFOF 5-bromo-6-(2-bromophenyl)-2,3-dihydro-4H-pyran-4-one

Monoclinic $P2_1/c$, Z′ = 1; a = 10.6794(5), b = 7.5795(3), c = 13.4516(6) Å, β = 92.023(4)°

d(Br···Br) = 3.5512(5) Å; C–Br···Br = 175.86(9)° & C–Br···Br = 100.68(9)°

{I replaced by Br; isostructural}

YIZFIZ 5-bromo-6-(2-chlorophenyl)-2,3-dihydro-4H-pyran-4-one

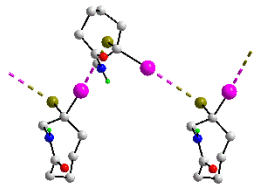
Monoclinic $P2_1/c$ Z′ = 1; a = 10.7391(4), b = 7.3560(3), c = 13.5262(4) Å, β = 90.473(3)°

d(Br···Cl) = 3.4969(6) Å; C–Br···Cl = 174.70(6)° & C–Cl···Br = 100.98(7)°

{I replaced by Br and Br replaced by Cl; isostructural}

23. SELYOY 7-bromo-7-iodo-perhydro-1-azocin-2-one

Hu, T.; Shen, M.; Chen, Q.; Li, C. Pushing radical cyclization from regioselective to regiospecific: Cyclization of amidyl radicals controlled by vinylic halogen substitution. Org. Lett. 2006, 8, 2647-2650. doi: 10.1021/ol060983q.



Glide symmetry

d(I···Br) = 3.6666(12) Å; C–I···Br = 175.7(2)° & C–Br···I = 115.3(2)°

Orthorhombic Pbca, Z′ = 1; a = 7.9917(13), b = 10.5745(18), c = 23.462(4) Å

SELYUE 7,7-Diiodo-perhydro-1-azocin-2-one

Orthorhombic Pbca, Z′ = 1; a = 8.0936(6), b = 10.7502(8), c = 23.5836(17) Å

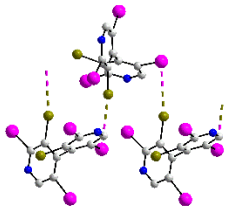
d(I···I) = 3.7541(7) Å; C–I···I = 173.90(16)° & C–I···I = 112.67(16)°

{Extra I; isostructural; zig-zag chain}

29. IMURAL 3,3'-dibromo-2,2',5,5'-tetraiodo-4,4'-bipyridine

d(I···Br) = 3.7136(15) Å; C–I···Br = 78.41(9)° & C–Br···I = 170.13(11)°

Orthorhombic $P2_12_12_1$, Z′ = 1; a = 7.985(3), b = 11.766(4), c = 17.716(7) Å



2_1-screw symmetry

{Chain along the a-axis; no I···I nor I···Br within van der Waals radii}

30. INADIM 2,2',3,3'-tetrabromo-5,5'-diiodo-4,4'-bipyridine

d(I···Br) = 3.7281(18) Å; C–I···Br = 71.91(14)° & C–Br···I = 161.19(15)°

Orthorhombic $P2_12_12_1$, Z′ = 1; a = 7.888(4), b = 12.138(5), c = 16.364(8) Å

{Chain along the a-axis; no I···I nor I···Br within van der Waals radii }

31. IMUQOY 2,2',5,5'-tetrabromo-3,3'-diiodo-4,4'-bipyridine

d(I···Br) = 3.7330(7) Å; C–I···Br = 162.62(7)° & C–Br···I = 81.66(7)°

Orthorhombic $P2_12_12_1$, Z′ = 1; a =7.997(2), b = 11.722(2), c = 16.948(3) Å

{Chain along the a-axis; no I···I nor I···Br within van der Waals radii}

39. IMURUF 5,5'-dibromo-2,2',3,3'-tetraiodo-4,4'-bipyridine

d(I···Br) = 3.8140(9) Å; C–I···Br = 169.03(7)° & C–Br···I = 77.36(8)°

Orthorhombic $P2_12_12_1$, Z′ = 1; a = 8.028(2), b = 11.128(2), c = 18.411(4) Å

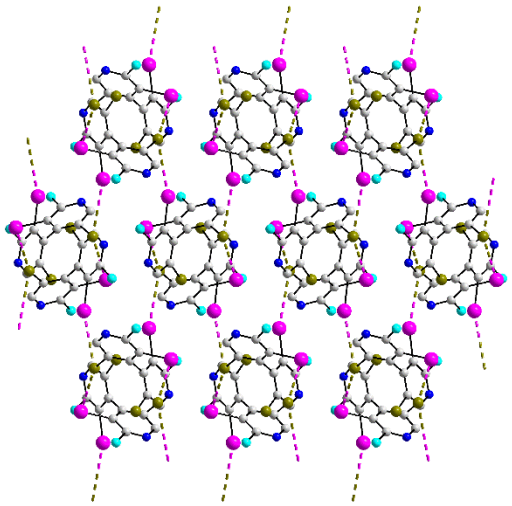
{Isostructural; chain along the a-axis; no I···I nor I···Br within van der Waals radii}

41. INADOS 5,5'-dibromo-2,2'-dichloro-3,3'-diiodo-4,4'-bipyridine -3D

d(I···Br) = 3.6944(7) Å; C–I···Br = 161.40(5)° & C–Br···I = 83.20(5)° - chain along a

d(I···Br) = 3.7405(5) Å; C–I···Br = 95.99(5)° & C–Br···I = 155.52(5)°

Orthorhombic $P2_12_12_1$, Z′ = 1; a = 8.034(2), b = 11.838(2), c = 16.278(3) Å



{Chain along the a-axis as observed for other structures but additional, slightly longer I···Br are noted leading to a 3-D architecture; no I···I, I···Cl, Br···Br, Br···Cl nor Cl···Cl within van der Waals radii}

IMURIT 5,5'-dichloro-2,2',3,3'-tetraiodo-4,4'-bipyridine

Orthorhombic $P2_12_12_1$, Z′ = 1; a = 7.957(3), b = 10.910(4), c = 18.607(7) Å

{isostructural; isolated molecule with no X···X less than 4.0 Å}

IMUQUE 3,3',5,5'-tetrabromo-2,2'-diiodo-4,4'-bipyridine

Orthorhombic $P2_12_12_1$, Z′ = 1; a = 7.800(3), b = 11.334(5), c = 18.031(7) Å

d(Br···Br) = 3.7441(15) Å; C–Br···Br = 171.66(10)° & C–Br···Br = 75.70(10)°

{isostructural; Br···Br, longer than van der Waals, sustain chain along the a-axis; no I···I nor I···Br within van der Waals radii}

INAFEK 2,2'-dibromo-3,3'-dichloro-5,5'-diiodo-4,4'-bipyridine

Orthorhombic $P2_12_12_1$, Z′ = 1; a = 7.779(4), b = 12.148(5), c = 16.057(7) Å

d(I···Cl) = 3.7327(17) Å; C–I···Cl = 79.93(6)° & C–Cl···I = 158.98(8)°

{Isostructural; chain along the a-axis via I···Cl; no additional X···X within van der Waals radii}

IMUROZ 3,3'-dichloro-2,2',5,5'-tetraiodo-4,4'-bipyridine

Orthorhombic $P2_12_12_1$, Z′ = 1; a = 7.906(3), b = 11.780(5), c = 17.605(7) Å

d(I···Cl) = 3.7163(16) Å; C–I···Cl = 77.10(7)° & C–Cl···I = 174.03(8)°

{Isostructural; chain along the a-axis via I···Cl; no additional I···I within van der Waals radii; long I···I [3.9750(12) Å] occur within chain}

INADAE 3,3',5,5'-tetrabromo-2,2'-dichloro-4,4'-bipyridine

Orthorhombic $P2_12_12_1$, Z′ = 1; a = 7.659(4), b = 11.921(6), c = 15.999(11) Å

d(Br···Br) = 3.600(2) Å; C–Br···Br = 162.48(6)° & C–Br···Br = 80.95(6)°

{isostructural; Br···Br sustain chain along the a-axis; no Br···Cl nor Cl···Cl within van der Waals radii}

INADEI 2,2',3,3',5,5'-hexabromo-4,4'-bipyridine

Orthorhombic $P2_12_12_1$, Z′ = 1; a = 7.6444(1), b = 11.7708(2), c = 16.6604(3) Å

d(Br···Br) = 3.6378(9) Å; C–Br···Br = 164.5(2)° & C–Br···Br = 79.3(2)°

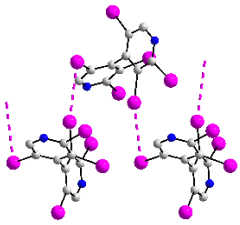
{isostructural; Br···Br sustain chain along the a-axis; no Br···Br within van der Waals radii}

IMUREP 2,2',3,3',5,5'-hexaiodo-4,4'-bipyridine

Orthorhombic $P2_12_12_1$, Z′ = 1; a = 8.219(3), b = 11.493(5), c = 18.059(7) Å

d(I···I) = 3.8016(15) Å; C–I···I = 166.46(8)° & C–I···I = 78.27(8)°

{Isostructural; chain along the a-axis via I···I; no additional I···I within van der Waals radii}



INAFAG 2,2'-dibromo-5,5'-dichloro-3,3'-diiodo-4,4'-bipyridine

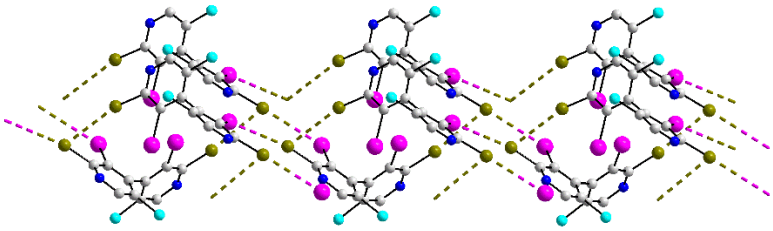
d(I···Br) = 3.749(2) Å; C–I···Br = 125.61(10)° & C–Br···I = 157.27(11)°

Orthorhombic $P2_12_12_1$, Z′ = 1; a = 7.913(5), b = 11.911(9), c = 15.781(12) Å

d(Br···Br) = 3.565(2) Å; C–Br···Br = 165.29(11)° & C–Br···Br = 73.51(11)°

d(I···Br) = 3.749(2) Å; C–I···Br = 125.61(10)° & C–Br···I = 157.27(11)°

{Chain along the a-axis via Br···Br interactions; these are linked into a 2-D array via I···Br interactions; one bromide connects to both I and Br and the other only forms Br···Br interactions}



INADUY 2,2'-dibromo-3,3',5,5'-tetraiodo-4,4'-bipyridine

Orthorhombic $P2_12_12_1$, Z′ = 1; a = 8.177(6), b = 12.152(8), c = 16.434(10) Å

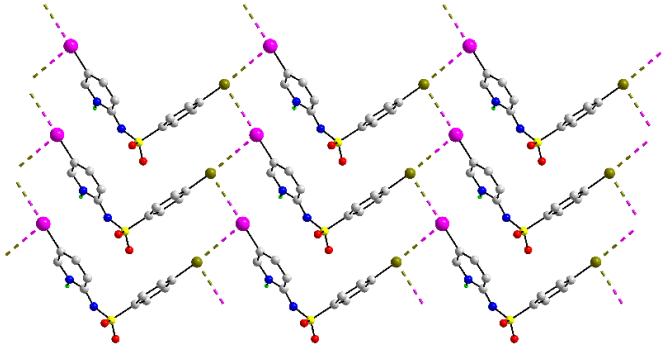
d(I···I) = 3.817(2) Å; C–I···I = 158.60(7)° & C–I···I = 80.62(6)° - chain along a

d(I···I) = 3.8534(17) Å; C–I···I = 92.23(6)° & C–I···I = 160.28(6)°

{Chain along the a-axis as observed for other structures but additional, slightly longer I···I are noted leading to a 3-D architecture; no Br···Br nor I···Br within van der Waals radii; same as INADOS; one I forms two contacts}

40. VEGSOR (5-iodopyridinium-2-yl)([4-bromophenyl]sulfonyl)azanide

Gelbrich, T.; Threlfall, T.L.; Hursthouse, M.B. XPac dissimilarity parameters as quantitative descriptors of isostructurality: The case of fourteen 4,5′-substituted benzenesulfonamido-2-pyridines obtained by substituent interchange involving CF_3/I/Br/Cl/F/Me/H. CrystEngComm 2012, 14, 5454-5464. doi: 10.1039/c2ce25508a.



Flat topology

d(I···Br) = 3.7436(5) Å; C–I···Br = 158.64(11)°; C–Br···I = 87.49(12)°

d(I···Br) = 3.7465(6) Å; C–I···Br = 80.73(11)°; C–Br···I = 172.51(12)°

Monoclinic, $P2_1/c$, Z′ = 1; a = 12.3761(5), b = 19.3231(7), c = 5.5652(2) Å, β = 98.824(1)°

VEGSIL (5-iodopyridinium-2-yl)([4-iodophenyl]sulfonyl)azanide

Monoclinic, $P2_1/c$, Z′ = 1; a = 12.7165(8), b = 19.5032(14), c = 5.6759(3) Å, β = 99.204(4)°

d(I···I) = 3.9277(8) Å; C–I···I = 160.50(19)°; C–I···I = 88.39(19)°

d(I···I) = 3.8761(9) Å; C–I···I = 83.8(2)°; C–I···I = 175.2(2)°

{Isostructural; I···I interactions}

VEGSUX (5-iodopyridinium-2-yl)([4-chlorophenyl]sulfonyl)azanide

Monoclinic, $P2_1/c$, Z′ = 1; a = 12.1910(5), b = 19.2471(7), c = 5.5793(2) Å, β = 98.441(1)°

d(I···Cl) = 3.6890(9) Å; C–I···Cl = 156.80(8)°; C–Cl···I = 87.45(12)°

d(I···Cl) = 3.7310(11) Å; C–I···Cl = 78.73(8)°; C–Cl···I = 169.42(13)°

{Isostructural; I···Cl interactions}

VEGTAE (5-iodopyridinium-2-yl)([4-fluorophenyl]sulfonyl)azanide

Monoclinic, $P2_1/c$, Z′ = 1; a = 11.2100(3), b = 18.4797(4), c = 6.0146(2) Å, β = 97.104(2)°

d(I···F) = 3.742(2) Å; C–I···F = 152.21(9)°; C–F···I = 80.44(16)°

d(I···F) = 3.512(3) Å; C–I···F = 69.70(9)°; C–F···I = 159.44(19)°

{Isostructural; I···F interactions}