Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Electronic Supplementary Information

Interplay between halogen bonds and π-π stacking interactions: CSD search and theoretical study

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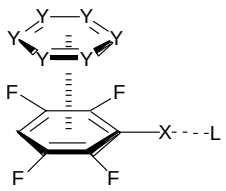
1. The search criteria for halogen bonds and stacking interactions.

The Cambridge Structural Database (CSD version 5.32, updates November 2010) was surveyed with the search criteria as follows: (1) the intermolecular X···L distances (X = Cl, Br, I and L = N, O, S) are shorter than the sums of van der Waals radii of the atoms involved; the C−X···L angles are larger than 120°. (2) the distances between the centroid of two six-membered aromatic rings ($R_{\pi\text{-}\pi}$) are less than 4.0 Å. Only crystal structures with no disorder and errors as well as the *R*-factor less than 0.1 were considered.

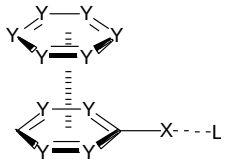
2. The results of the survey of the CSD.

Motif 1:



Hits 7: COWHUS, COWJEE, COWJII, JERHEU, KAVFIX, QOSCOR, WEFLAV

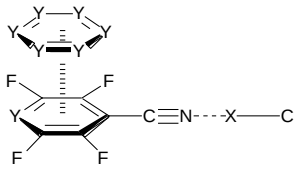
Motif 2:



Hits 211: ADUHUC, AJAKUR, AKIYUO, ATEQOF, AXOQIN, AZOKOP, BEFQIN, BOGVEZ, BPPRTO, CEWGAN, CIYDAQ, CIYDEU, CIYTEK, CLPCPN, COCZUQ, COKBEK, COSREI, COWHUS, COWJEE, COWJII, COWJOO, COXZOF, CPTZTR, CUZZUS, CYMEBF20, DADRIK, DADRIK01, DELYEZ, DERSUO10, DIYFAS, DOKWAC, DOPYAI, DOPYAI10, DUBKOB, DUNJUS, EBEZIU, ECUPAU, EDOMEP, EDUZUZ, EQONIH, ETIQED, ETIXUA, EVINIG, EZENEC, FEQTAW, FETYIN, FINKIX, FOFBOS, FOQLAZ, FUBRUP, GALMEM, GAWLUM, GAXLEW01, GEDCAU, GEDCEY, GIVQUX, GIZDAV, GOFTEB, GUZZUW, HEGYEX, HETHEU, HIGDEH, HOFTEB, HOFZOS, HUHQUW, IBUPIE, IHAPIR, IJEPOC, IOBNIT01, IROREM, IZILEI, JARHUG, JAWBIT, JEGBED, JEKZOP, JERHEU, JIYWEU, JIYWIY, JOXTAR, KARDEN, KARDOX, KAVFIX, KEFRIX, KEGBUT, KERFAP, KIKKEV, KOBFAI, KOBFOX, KOFGAO, KOHKAU, KUSSUN, LALNUH, LIJLIA, LORWEV, LORWOF, LOTZUP, MAJZIH, MBODZO10, MEHGIQ, MEHKIU, MEMZOU, MEQNUS, MEVYER, MIGVOO, MISPAG, MIYLEL, MOCCEM, MPODZO10, MXBTCP, NEKXOR, NESCIY, NEYBOJ, NIGFAK, NOKDAS, NOKDEW, NOQYUO, NULDAA, NUVVAB, OFIHUH, OGEHAK, PAFLAJ, PANHES, PAPDUG, PLENOL10, PONWAR, PUDFAW, PUTMUM, QAFTUM, QAFVEY, QAMZEJ, QAPROP, QAQKIC, QARDOC, QARDUI, QERYOC, QOSBIK, QOSCOR, RALPAV, REWDAZ, REXSAP, RIGWIO, RIWTOG, RIYCEH, ROGGUQ, RUDZUM, SEBJAK,

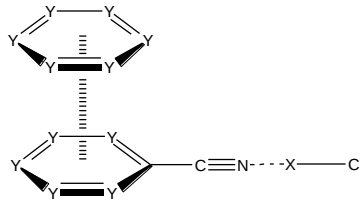
SEBPAQ, SENLED, SERHUT, SEZGUA, SIKWOY, SIMTEO, SIMZOE, SINGAY, SOGFIE, SOLMIQ, SUQDAJ, TAHCEK, TATDEX, TAVJAC, TCANTQ, TECDOV, TESPAJ, TIQDAY, TIZSIF, TUTYEM, ULAREE, VEBQEZ, VEKCUK, VOLFAE, VOMSEW06, VOPXON, VUFDUW, VUYWOC, WAMNOO, WEDJEV, WEFLAV, WEJCAQ, WILYAS, WIZTEF, XATMIP, XEQFAA, XESTIZ, XEZDEM, XIBGEV, XIZBOY, XOXLIG, YEPKAG, YERWUO, YESDAB, YIBXIR, YILGOP, YIQFEK, YITHOZ, YIVPUO, YODHAB, YOMNEU, YOQBEM, YOQCAJ, YUPPUV, ZEBZAH, ZEBZAH01, ZOGRUI, ZONYOQ, ZUPJEZ, DURPOW, PUNXAY, QUXCOC, SABHUA, YUQJEA, YUQNOO

Motif 3:



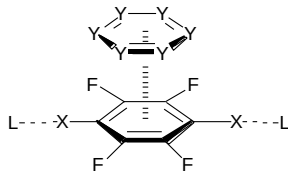
Hit 1: QOSBIK

Motif 4:



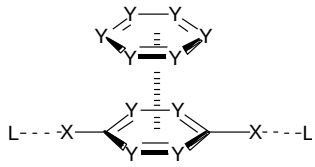
Hits 13: GEDCEY, HUMLOQ, IOBNIT01, LALMEQ, LALNUH, NELSOM, NUGRAJ, QOSBIK, QOSCOR, TIQDAY, VONNOC, WEFLAV, WEVSEW

Motif 5:



Hits 16: EDAGIZ, FEQVON, HUMLOQ, IHUMUT, IHUNUU, JEFFOQ, JEFFUW, QIHCAL, QIHCAL01, QIHCAL02, QIHCAL03, QIHCAL04, QIHCAL05, QIHCAL06, TOJBIE, TOJCAX

Motif 6:



Hits 25: BBZSUL, EDAGIZ, FEQVON, HUMLOQ, IHUMUT, IHUNUU, JEFFOQ, JEFFUW, MIQQUZ, MIQQUZ01, NACKUY, QIHCAL, QIHCAL01, QIHCAL02, QIHCAL03, QIHCAL04, QIHCAL05, QIHCAL06, TOJBIE, TOJCAX, ULALUO01, YESZEB, BUNJEA, BUNJOK, DUTTES

Table S1 Calculated interaction energies without BSSE corrections for the dimers **13**-**40** and the trimers **41**-**56**[a]

	ΔE		ΔE		ΔE	E_{coop}	E_{syn}
13(**1**-ph)	-17.88	**25**(**1**-2NH_3)	-14.71	**41**(**1**-ph-2NH_3)	-32.11	0.67	0.48
14(**2**-ph)	-16.89	**26**(**2**-2NH_3)	-9.84	**42**(**2**-ph-2NH_3)	-26.32	0.64	0.40
15(**3**-ph)	-12.81	**27**(**3**-2NH_3)	-9.85	**43**(**3**-ph-2NH_3)	-22.49	0.34	0.17
16(**4**-ph)	-11.50	**28**(**4**-2NH_3)	-6.06	**44**(**4**-ph-2NH_3)	-17.53	0.24	0.03
17(**5**-ph)	-17.36	**29**(**5**-2NH_3)	-16.98	**45**(**5**-ph-2NH_3)	-34.31	0.13	0.03
18(**6**-ph)	-16.88	**30**(**6**-2NH_3)	-11.69	**46**(**6**-ph-2NH_3)	-28.56	0.12	0.01
19(**7**-ph)	-12.07	**31**(**7**-2NH_3)	-15.23	**47**(**7**-ph-2NH_3)	-27.43	-0.03	-0.13
20(**8**-ph)	-11.64	**32**(**8**-2NH_3)	-10.27	**48**(**8**-ph-2NH_3)	-21.99	0.02	-0.08
21(**9**-ph)	-13.21	**33**(**9**-2FCl)	-12.02	**49**(**9**-ph-2FCl)	-29.98	-1.45	-4.75
22(**10**-ph)	-7.44	**34**(**9**-2FBr)	-18.13	**50**(**9**-ph-2FBr)	-38.04	-2.06	-6.71
23(**11**-ph)	-16.89	**35**(**10**-2FCl)	-29.53	**51**(**10**-ph-2FCl)	-44.83	-4.38	-7.85
24(**12**-ph)	-11.11	**36**(**10**-2FBr)	-39.32	**52**(**10**-ph-2FBr)	-55.16	-3.68	-8.39
		37(**11**-2FCl)	-11.61	**53**(**11**-ph-2FCl)	-29.48	-0.51	-0.98
		38(**11**-2FBr)	-17.44	**54**(**11**-ph-2FBr)	-36.00	-0.92	-1.67
		39(**12**-2FCl)	-13.50	**55**(**12**-ph-2FCl)	-25.45	-0.39	-0.85
		40(**12**-2FBr)	-20.29	**56**(**12**-ph-2FBr)	-32.91	-0.77	-1.50

[a] All values are given in kilocalories per mole.