research papers

Halogen-bond geometry: a crystallographic database investigation of dihalogen complexes

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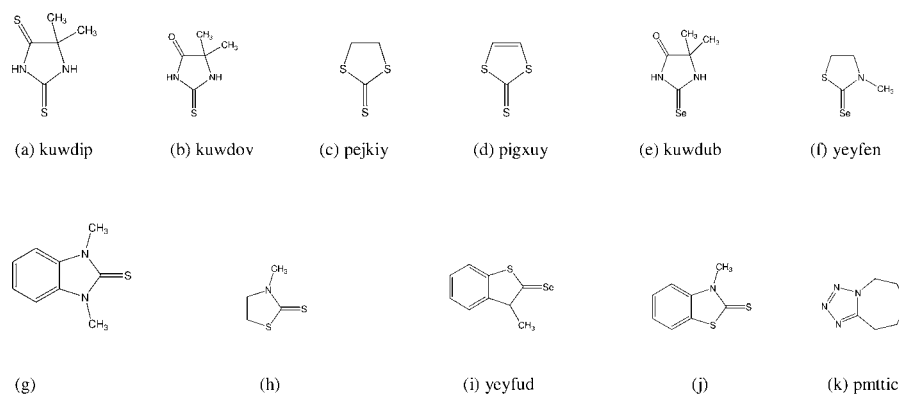laurence@chimie.univ-nantes.fr

X-ray crystal structures of 141 halogen-bonded complexes $Y—X\cdots B$ formed between homo- and heteronuclear dihalogens Cl_2, Br_2, I_2, IBr and ICl with O, S, Se, N, P and As Lewis bases show remarkable and constant geometrical features. The metrics of the halogen bond found in the gas phase for simple complexes [Legon (1999a). *Angew Chem. Int. Ed. Eng.* **38**, 2686–2714] is supported (i) in the solid state, (ii) for new Lewis acids (I_2 and IBr), (iii) for new basic centers (Se, As and $=N—$) and (iv) for more complicated bases. The $Y—X\cdots B$ arrangement is more linear than the corresponding $Y—H\cdots B$ hydrogen bond and the axis of the $Y—X$ molecule lies in the plane of the B lone pair(s), with a preference for the putative lone-pair direction within that plane. However, exceptions to this lone-pair rule are found for sterically hindered thiocarbonyl and selenocarbonyl bases. A bond-order model of the halogen bond correctly predicts the observed correlation between the shortening of the $X\cdots B$ distance and the lengthening, $\Delta d(Y—X)$, of the $Y—X$ bond. The expectation that the solid-state geometric parameters $d(X\cdots B)$ and $\Delta d(Y—X)$ reflect the strength of the interaction is supported by their significant relationships with the solution thermodynamic parameters of Lewis acidity and basicity strength, such as the Gibbs energy of 1:1 complexation of Lewis bases with diiodine. This analysis of halogen-bonded complexes in the solid state reinforces the similarities already known to exist between hydrogen and halogen bonding.

1. Introduction

Molecular interactions find their origin in the dispersion, polarization, electrostatic, charge-transfer and exchange forces (Rigby *et al.*, 1986; Buckingham, 1993). They give rise to quite diverse molecular complexes, ranging from van der Waals to strongly bound complexes (Mulliken & Person, 1969; Scheiner, 1997a). A particular blend of these forces occurs in the hydrogen-bonded complexes $Y—H\cdots B$ when an H atom covalently bonded to an electronegative atom Y is able to approach another electronegative atom B (Pimentel & McClellan, 1960; Joesten & Schaad, 1974; Scheiner, 1997b). A molecular interaction also occurs in the system $Y—X\cdots B$ when a halogen atom X approaches a Lewis base B. These complexes have been much studied since the discovery of the diiodine–benzene complex (Benesi & Hildebrand, 1948, 1949), their theoretical description in the framework of charge-transfer resonance theory (Mulliken, 1952), and the first X-ray crystallographic investigation devoted to the dibromine–dioxane complex (Hassel & Hvoslef, 1954). These studies have been described in several books (*e.g.* Foster, 1969; Mulliken & Person, 1969).

Table 1
Radial (Å) and angular (°) geometry of selected complexes of Cl_2, Br_2, I_2, IBr and ICl with Lewis bases.

| (a) kuwdip | (b) kuwdov | (c) pejkiy | (d) pigxuy | (e) kuwdub | (f) yeyfen |

| (g) | (h) | (i) yeyfud | (j) | (k) pmttic |

Site	Base	Refcode	$d(X\cdots B)$	$d(YX)$	$\alpha(XY\cdots B)$	θ	φ
Cl_2 complexes							
$C(\pi)$	Benzene		3.28	1.99			
O	1,4-Dioxane		2.67	2.02	178		
Br_2 complexes							
$C(\pi)$	Benzene	BENZBR	3.36	2.28			
O	Acetone	ACETBR	2.818	2.282	178	15.3	126.5
	1,4-Dioxane	DOXABR	2.723	2.303	178	0.0	142.3
$-S-$	Dimethylsulfide	RORNIV	2.299	2.717	175	0.5	105.3
	Tetrahydrothiophene	THINBR	2.321	2.724	178		
Nsp	Acetonitrile	ACTNBM	2.837	2.327	179	0.0	171.6
Nsp^2	1,3,5-Triazine	TEYPES	2.515	2.338	175	7.8	173.9
P	Triphenylphosphine	JOMSEJ	2.181	3.123	177	1.0	123.9
As	Trimethylarsine	TMASBR01	2.275	3.363	180	0.0	118.7
I_2 complexes							
O	1,4-Dioxane		2.81				
$-S-$	Benzylsulfide	BENZSI	2.779	2.819	178.9	0.0	105.4
	1,4-Dithiane	ISBCLS	2.717	2.818	178.6	1.3	106.5
	1,3,5-Trithiacyclohexane	RUQPIC	3.169	2.754	169.0	16.0	118.3
$C\!=\!S$	2-Imidazolidinethione	CEWNAT	2.588	2.986	178.2	0.0	101.2
	5,5-Dimethylimidazolidine-2,4-dithione (a)	KUWDIP	2.738	2.849	177.9	11.7	100.5
	5,5-Dimethyl-2-thioxoimidazolid-4-one (b)	KUWDOV	2.773	2.802	176.1	1.3	104.5
	1,3-Dithiolan-2-thione (c)	PEJKIY	2.715	2.823	176.5	1.6	103.7
	1,3-Dithiole-2-thione (d)	PIGXUY	2.715	2.843	176.7	2.3	102.0
	N-Methylthiocaprolactam	TCAPLI	2.687	2.879	176.2	0.9	110.0
	Thiourea	LOPQEM	2.503	3.054	176.0	7.0	104.9
PS	Triphenylphosphine sulfide	TPHPSI10	2.729	2.837	175.2		
$-Se-$	1,4-Diselenane	DSEIOD	2.830	2.870	178.7	0.4	107.5
	Diphenyldiselenide	GIHZIG	2.992	2.774	174.2	2.8	94.0
	1,4-Oxaselenane	OXSELI	2.755	2.955	174.8	4.0	110.3
	Dimethylselenide	RIZMES	2.768	2.915	174.3	2.0	99.6
	1,3,5-Triselenacyclohexane	RUPQOI	2.734	2.944	179.3	2.7	103.2
	Tetrahydroselenophene	THSELI01	2.765	2.913	179.1	7.4	108.6
$C\!=\!Se$	(e)	KUWDUB	2.699	2.962	173.8	9.5	100.2
	N,N'-Dimethylimidazolidine-2-selenone	REBNER	2.683	3.025	175.5	72.8	97.9
	(f)	YEYFEN	2.725	2.983	177.5	7.7	98.9
PSe	Tris(tert-butyl)phosphine selenide		2.760	2.915	171.7		
	Triphenylphosphine selenide	PAQKAT	2.802	2.881	173.7		
	Tris(dimethylamino)phosphine selenide	PAQKEX	2.711	2.960	177.3		
Nsp^3	Hexamethylenetetramine	HXMTDI	2.439	2.830	173.1	3.2	124.8
	Trimethylamine	TMEAMI	2.271	2.830	178.3	4.3	126.9
Nsp^2	2,2'-Bipyridine	CECZAL	2.604	2.746	179.4	11.2	177.8
	4-Cyanopyridine	NULBIF	2.554	2.750	175.5	5.0	177.9
	4,4'-Bipyridine	NULBOL	2.407	2.796	177.8	0.6	176.0
	Quinoxaline	NULBUR	2.918	2.724	175.8	1.1	178.7
	Phenazine	PHNAZI01	2.986	2.726	180.0	0.0	180.0
	4-Picoline	PICOLI	2.322	2.823	175.5	2.8	165.3
	Pyrazine	VUKDIO	2.817	2.733	175.2	0.0	169.6
	Tetramethylpyrazine	VUKDOU01	3.075	2.721	177.7	1.1	176.4
P	Triphenylphosphine	JITSIO	2.480	3.161	178.0	0.8	125.8

Table 1 (continued)

Site	Base	Refcode	$d(X\cdots B)$	$d(YX)$	$\alpha(XY\cdots B)$	θ	φ
	Dimethylphenylphosphine	ZEKMOR	2.410	3.408	177.0	0.3	124.5
As	Triphenylarsine	FESKAP01	2.653	3.005	174.3	3.5	128.8
IBr complexes							
—S—	1,4-Dithiane	DTHIBR10	2.687	2.646	178.2	3.1	107.8
C=S	N,N'-Dimethylbenzimidazole-2(3H)-thione (g)		2.607	2.751	173.3		
	N-Methyl-1,3-thiazolidine-2(3H)thione (h)		2.588	2.749	177.0		
PS	Triphenylphosphine sulfide	ZZZHUE01	2.665	2.668	175.0		
—Se—	Diphenylselenide	NOWLOA	2.808	2.641	177.3	4.8	106.0
	Dimethylselenide	NOWLUG	2.664	2.797	175.8	5.9	99.0
C=Se	(f)	YEYFIR	2.689	2.908	177.0	9.6	99.3
	(i)	YEYFUD	2.564	3.129	174.3	7.6	97.8
Nsp^2	2,2'-Bipyridine		2.460	2.577	175.9		
P	Triphenylphosphine	PESJOM	2.461	3.062	178.0		
As	Triphenylarsine	CUXCON	2.590	2.855	174.8		
ICl complexes							
O	1,4-Dioxane		2.57	2.33	linear		
PS	Triphenylphosphine sulfide	SIBJOC	2.641	2.586	175.0		
C=S	N-Methylbenzothiazole-2(3H)-thione (j)	LIFXIH	2.556	2.604	180		
—Se—	1-Oxa-4-selenacyclohexane	OXSEIC	2.630	2.731	175.8	3.20	107.0
C=Se	(i)		2.626	2.691	178.9		
Nsp^3	Trimethylamine	TMEICL	2.303	2.524	176.9	2.0	121.2
Nsp^2	2-Chloroquinoline	CLQUIC	2.432	2.446	180.0	0.4	177.1
	Pentamethylenetetrazole (k)	PMTTIC	2.374	2.446	176.1	1.9	178.5
	Pyridine	PYRIIC10	2.290	2.510	178.7	0.4	177.6
	2,2'-Bipyridine		2.336	2.479	179.6		

The interaction which has been previously termed 'charge transfer' or 'electron–donor–acceptor' is now generally called 'halogen bonding' (Dumas *et al.*, 1983, 1984; Blackstock *et al.*, 1987; Murray *et al.*, 1994; Legon, 1999*a*; Metrangolo & Resnati, 2001) to stress its similarities with hydrogen bonding (Bent, 1968, 1976; Huyskens, 1986; Legon, 1998*b,c*, 1999*a*).
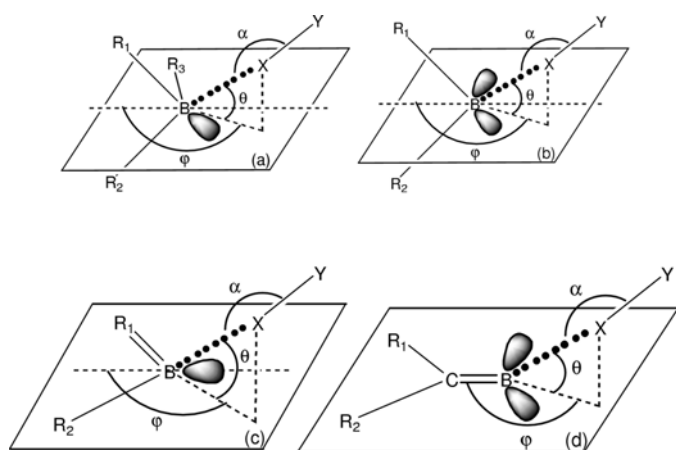

Figure 1
Definition of angular parameters describing the geometry of halogen bonding. B is (*a*) an sp^3 hybridized atom of group 15 (N, P, As), (*b*) an sp^3 hybridized atom of group 16 (O, S, Se), (*c*) an sp^2 hybridized atom of group 15 (N) or (*d*) an sp^2 hybridized atom of group 16 (O, S, Se). α is the halogen-bond angle $Y-X\cdots B$, and θ and φ are the pseudo-polar angles describing the position of X with respect to the electron donor B. The putative lone-pair direction corresponds to $\theta = 0$ and $\varphi = 125.5°$ (*a, b*), 180° (*c*) and 120° (*d*).

Even if charge transfer is more important in the $Y-X\cdots B$ interaction than in the $Y-H\cdots B$ interaction (Alkorta *et al.*, 1998), it is in fact not the dominant contribution to the interaction energy (Singh & Kollman, 1983). As with the hydrogen bond (Buckingham, 1997), the halogen bond seems mainly electrostatic in origin, with some contribution from dihalogen polarization upon complex formation (Hanna, 1968; Bloemink *et al.*, 1994; Legon *et al.*, 1994; Bloemink & Legon, 1995; Hinds *et al.*, 1996; Waclawik *et al.*, 1999).

The geometry of halogen bonding has been studied using theoretical calculations, rotational spectroscopy and X-ray crystal diffraction. *Ab initio* and density functional theory
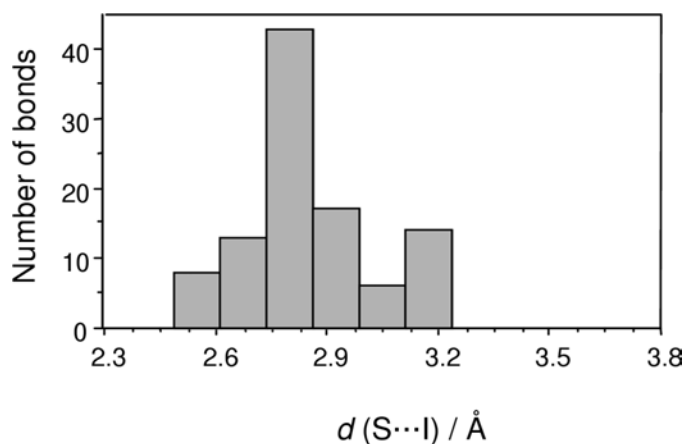

Figure 2
Histogram of the distribution of distances $S\cdots I$ for the complexes of diiodine with sulfur bases.

calculations are becoming increasingly used, but because of the number of electrons on heavy halogens, they are still limited to small complexes, *e.g.* acetone-I_2 (Setokuchi & Shimizu, 1993), Et_2O-I_2, Et_2S-I_2 (Ammal *et al.*, 1996), NH_3-Cl_2 (Latajka & Berski, 1996), C_2H_4-I_2, NH_3-X_2 (Ruiz *et al.*, 1996), pyridine-I_2 (Reiling *et al.*, 1997) and benzene-I_2 (Su & Zewail, 1998). The gas-phase structures of *ca* 60 complexes of F_2, Cl_2, Br_2, BrCl, ClF and ICl with Lewis bases have been determined by rotational spectroscopy by the Legon group (Legon, 1995, 1998*b*,*c*, 1999*a*,*b*) and important generalizations about the angular and radial geometries in these complexes have been drawn. In particular, Legon's work demonstrates:

(i) that the angular geometries of $Y-X{\cdots}B$ are isostructural with those of $Y-H{\cdots}B$ for a given B,

(ii) that these angular geometries can be understood in terms of the halogen X aligning with the direction of the axis of the non-bonding electron pair or π-electron cloud on B and

(iii) that the significant non-linearity of hydrogen bonds is absent in halogen bonds.

Unfortunately the two important Lewis acids IBr and I_2 are lacking in the YX Legon series, and rotational spectroscopy is limited to simple Lewis bases so that with very few exceptions (Page *et al.*, 1999; Waclawik *et al.*, 1998) important functionalities (*e.g.* C=S, C=Se, PS, PSe, $-Se-$, $=N-$ and As bases) as well as structural variations are lacking. Complexes of dihalogens with a much larger variety of Lewis bases have been studied by X-ray diffraction. Today the data accumulated include atomic centers B

(i) belonging to three periods and two columns of the periodic table and

(ii) substituted by very diversified groups.

These large structural variations of B should allow:

(i) a study to determine whether the rules established by Legon for isolated simple molecules in the gas phase are also valid for larger complexes in the solid state,

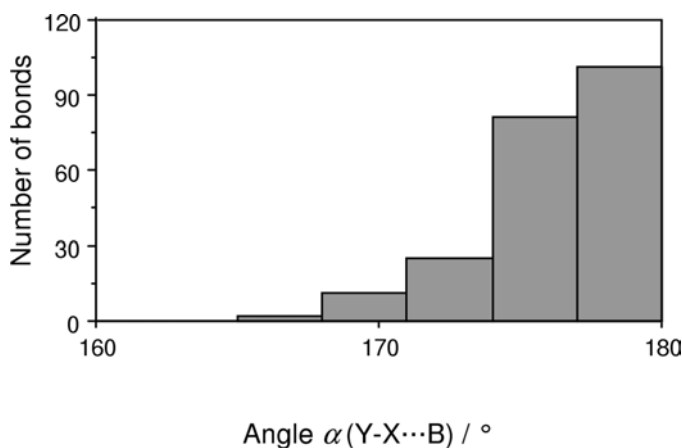(ii) study of the halogen-bond geometry for complexes of new basic centers (Se, As, $=N-$) and

(iii) a calculation of the mean geometrical parameters of halogen bonding through a statistical study of the enlarged database.

Another advantage of X-ray data is that many results refer to diiodine complexes for which many thermodynamical properties (complexation constants, enthalpies of complexation) have already been determined in solution (*e.g.* Aragoni, Arca, Devillanova *et al.*, 1999). A sufficient body of data is therefore available to allow us to attempt the determination of the influence of intrinsic base strength, measured for 1:1 complexes in inert solvents, on the halogen bond length (*i.e.* another scale of strength). For hydrogen bonds, despite the huge body of geometrical and thermodynamical data, no quantitative correlation seems to have been established between the hydrogen bond length in the crystal and the thermodynamics of hydrogen bonding in solution. For molecular complexes the link we seek to establish for halogen-bonded complexes between geometry and thermodynamics and/or solid state and solution seems to be missing.

The present study uses geometrical data on halogen-bonded complexes $Y-X{\cdots}B$ calculated from crystal structures retrieved from the Cambridge Structural Database (CSD: Allen, 2002). The mean values of the geometrical parameters are used to quantify the linearity (angle $Y-X{\cdots}B$) and the directionality (spatial orientation of the $X{\cdots}B$ vector) of the halogen bond in the solid state. Then we focus on the lengthening (weakening) of the $Y-X$ bond when the $X{\cdots}B$ interaction shortens (strengthens), since the weakening of a chemical bond of the electron-acceptor partner constitutes an important characteristic of specific intermolecular bonds (Zeegers-Huyskens & Huyskens, 1991). This is exemplified by the well known $Y-H$ bond weakening in $Y-H{\cdots}B$ hydrogen-bonded complexes (Steiner, 1998). Finally we study the existence of relationships between halogen bond length (*i.e.* strength) and the Lewis basicity and acidity strengths of B and XY, respectively. Scales of Lewis acid strength for mole-
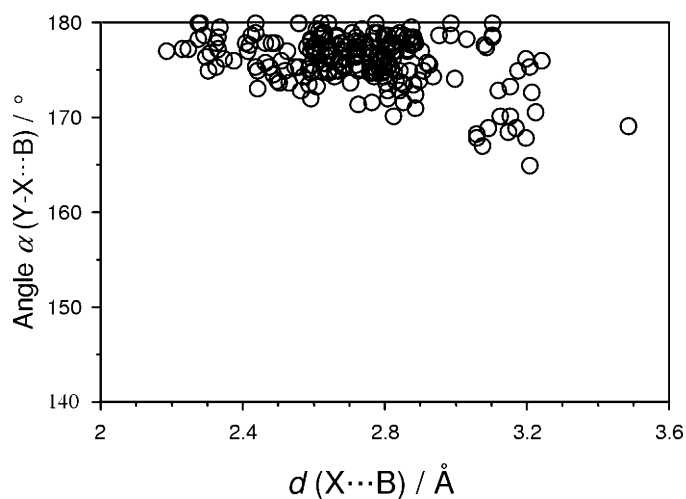

Figure 3
Linearity of the halogen bond: histogram of the distribution of $Y-X{\cdots}B$ angles.

Figure 4
Quasi-independence of linearity *versus* length (strength): $\alpha(Y-X{\cdots}B)$/$d(X{\cdots}B)$ scatterplot.

cules *XY* have been established from enthalpies and constants of complexation (Foster, 1969), and from intermolecular force constants (Legon, 1999*a*), but, according to the theory of hard and soft acids and bases (Pearson, 1963), there is no general scale of acidity and reversals can occur when the character (hard or soft) of the base is varied. Using bases (from oxygen to arsenic ones) with very diverse hard or soft character and a different criterion of strength (the bond length), we want here to see if a universal order of strength exists for the acids *XY*. With regard to basicity, we have assembled a diiodine basicity scale from the complexation constants of diiodine with Lewis bases and looked at relationships not only with the halogen bond length but also with the lengthening of the *X*—*Y* bond upon complexation, in order to point out similarities with relationships existing between thermodynamic and spectroscopic properties in hydrogen-bonded complexes.

2. Results and discussion

2.1. Geometrical parameters of halogen-bonded complexes

Complexes of dihalogens were searched in the CSD (version 5.24, October 2002). We did not find any complex of IF (observed only in flames), BrF (the synthesis of pure BrF is difficult), ClF, BrCl, F_2 or Cl_2. However, approximate structures are available in the old literature for the complexes of Cl_2 with benzene (Hassel & Stromme, 1959*a*) and dioxane (Hassel & Stromme, 1959*b*). Surprisingly, two structures in the literature, namely 2,2'-bipyridine:2ICl and 2,2'-bipyridine:2IBr (Soled & Carpenter, 1974), could not be retrieved from the
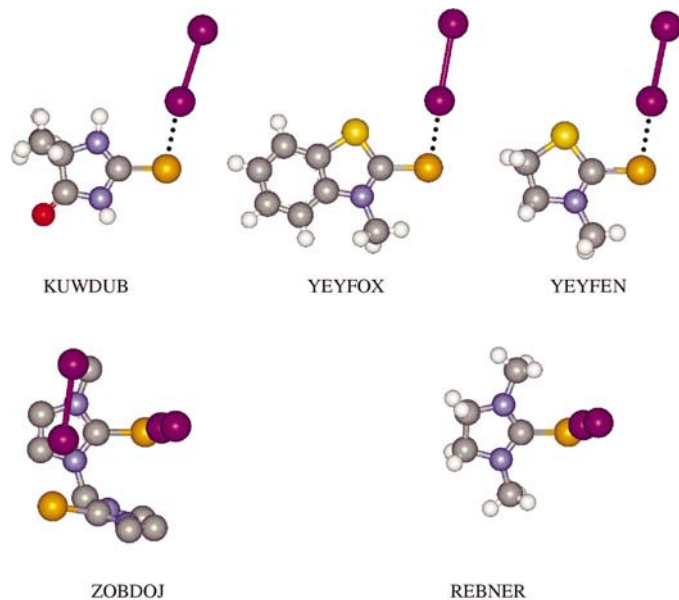
CSD. Our study refers to 141 complexes corresponding to 219 halogen bonds (the same complex could have been studied either independently by different authors or at different temperatures, or have several polymorphs, and several halogen bonds could be present in the asymmetric unit). These complexes refer mainly to the dihalogen I_2, but also to IBr, ICl, Br_2 and Cl_2, and to the *B* atomic centers C(π), O, S, (—S—, C=S, PS), Se (—Se—, C=Se, PSe), N (sp^3, sp^2, sp), P (sp^3) and As (sp^3).

The geometrical parameters retrieved from the CSD are the distances $d(X\cdots B)$ and $d(Y—X)$, and the angles $\alpha(Y—X\cdots B)$ (linearity), θ and φ (directionality), as defined in Fig. 1. Selected parameters are given in Table 1. All the data are taken into account in the calculation of the average parameters and for establishing the $d(X\cdots B)/\Delta d(XY)$ relationships. Where one or more structure determinations were reported for a particular compound, only the determination at the lowest temperature was generally considered for the correlations between distances and Gibbs energies of complexation.

In the analysis of results which follows, it is useful to recognize the major differences between solid-state structures and individual complexes in solution or in the gas phase. First, the 1:1 stoichiometry in the asymmetric unit may correspond equally well to crystals built up from well defined 1:1 units as to structures consisting of chains (*e.g.* 1,4-dioxane:Br_2; Hassel & Hvoslef, 1954) or sheets (*e.g.* acetone:Br_2; Hassel & Stromme, 1959*c*) in which Br_2 and *B* molecules alternate in a regular way (*n:n* complexes). Secondly, bases with several halogen-bond acceptor sites may give complexes with the stoichiometries 1:1, 1:2, 1:3 *etc*. For example, hexamethylenetetramine forms 1:1 (HXMTDI), 1:2 (HXMIOD; Pritzkow, 1975) and 1:3 (YUYNUB; Tebbe & Nagel, 1995) complexes with I_2. Lastly, diiodine chains of varying lengths may be attached to *B* (*e.g.* ethylenethiourea·$2I_2$, CEWMIA; Herbstein

Figure 5
X-ray structures of the diiodine complexes of selenourea (amides). Planar diiodine complexes are observed with the selenourea unhindered on both Se sides (KUWDUB) and the selenoamides unhindered on one Se side (YEYFEN and YEYFOX), while selenoureas hindered on both selenium sides give quasi-perpendicular complexes (torsion angle NCSe···I *ca* 90°) (REBNER and ZOBDOJ).
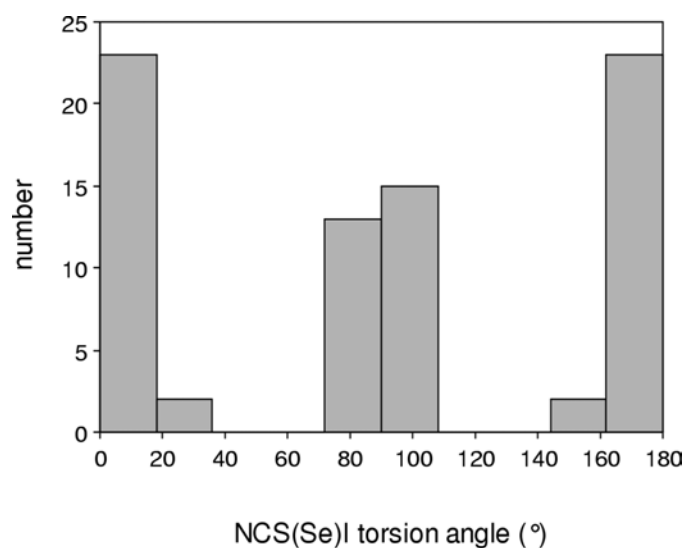

Figure 6
Histogram of the distribution of NCSI and NCSeI torsion angles for diiodine complexes of thiocarbonyl and selenocarbonyl bases.

Table 2
Comparison of the linearity α (°) of halogen bonds I—I$\cdots B$ and hydrogen bonds O—H$\cdots B$ for various families of bases B.

O—H$\cdots B$: NH$\cdots B$ for Se bases; n: number of data; $\Delta\alpha = |\alpha(\text{I—I}\cdots B) - \alpha(\text{O—H}\cdots B)|$.

Bases	Hydrogen bond			Halogen bond[a]		
	n	α	Reference	n	α	Δd
Oxygen sp^2, sp^3	†	165	(b)	3	175.2	10.2
Sulfur —S—	31	137	(c)	63	174.8	37.8
Sulfur C=S	119	157	(d)	31	176.6	19.6
Selenium C=Se	17	153	(e)	11	176.0	23
Selenium P=Se	4	158	(e)	8	175.1	17.1
Nitrogen sp^3	437	164	(f)	6	175.4	11.4
Nitrogen sp^2	304	163	(g)	24	177.1	14.1
Phosphorus sp^3	1	151	(e)	4	175.8	24.8

† Very large number of data.   References: (a) this work; (b) Lommerse et al. (1997); (c) Allen et al. (1997a); (d) Allen et al. (1997b); (e) Desiraju & Steiner (1999); (f) J. Graton, private communication; (g) Llamas-Saiz et al. (1992).

& Schwotzer, 1984). More generally, secondary interactions occur extensively in the solid-state complexes of dihalogens: they have been thoroughly analysed for the diiodine complexes of sulfur and selenium bases (Rudd et al., 1997).

2.2. Halogen bond length

The $d(X\cdots B)$ distances found are intermediate in length between van der Waals contacts and normal covalent $X—B$ bonds. This property of dihalogen complexes is well known (Mulliken & Person, 1969; Foster, 1969; Hassel, 1970; Bent, 1968) and we have only illustrated it in Fig. 2 by showing, for the complexes of diiodine with sulfur bases, that the distribution of S$\cdots$I distances lies closer to the sum of covalent radii (2.37 Å) than to the sum of van der Waals radii (3.79 Å).

2.3. Linearity of halogen bonds

Fig. 3 shows the distribution of $Y—X\cdots B$ angles observed for 219 contacts between Cl_2, Br_2, I_2, IBr or ICl and oxygen, sulfur, selenium, nitrogen, phosphorus and arsenic bases. The mean of the distribution is 176.1 (0.2)°. The average geometry thus corresponds to a quasi-linear halogen bond. Only five complexes have angles less than 170°. They correspond to complexes of I_2 with a diselenide (KIGKEL; Du Mont et al., 1990), a cyclodextrin (CDEXTI10; McMullan et al., 1973) and three thiocrown ethers: PELXUZ (Blake et al., 1993), RUKKAJ (Blake et al., 1997) and RUQPIC (Arca et al., 1997). In the former, the steric effect of two bulky ^{i}Pr substituents ortho to selenium clearly prevents the Se atom from aligning with the I—I axis.

In the solid state, the halogen bond appears to be much more linear than the hydrogen bond. A comparison of I—I$\cdots B$ halogen bonds and O—H$\cdots B$ hydrogen bonds for various families of bases (B) shows (Table 2) that in the solid state halogen bonds are always more linear. The propensity to a greater linearity amounts to 10–38°, depending on the family of bases involved. Moreover, while long hydrogen bonds tend to be less linear than short ones (Desiraju & Steiner, 1999; Taylor & Kennard, 1984) the linearity of the halogen bond

seems less affected by the XB distance. Fig. 4 illustrates this poor correlation: the XB distances and the $Y—X\cdots B$ angles of 219 halogen bonds are found to have a correlation coefficient of −0.39. This correlation coefficient is lower than those reported between H$\cdots B$ distances and $Y—H\cdots B$ angles of hydrogen bonds: $r = -0.52$ for 1357 NH$\cdots$O=C bonds (Taylor & Kennard, 1984), $r = -0.55$ for 86 OH$\cdots$S< and NH$\cdots$S< bonds (Allen et al., 1997a) and $r = -0.72$ for 649 OH$\cdots$S=C and NH$\cdots$S=C bonds (Allen et al., 1997b).

The halogen bonds studied in this work appear to be generally stronger than the corresponding O—H$\cdots B$ hydrogen bonds (Table 3). An explanation of the differences in linearity might thus be that it is less blurred by crystal packing forces in stronger halogen bonds than in weaker hydrogen bonds. However, Legon and co-workers (Bloemink et al., 1996; Cooke et al., 1997, 1998; Legon & Lister, 1999) have previously shown that in the gas phase the halogen bonds lie closer to linearity than hydrogen bonds. The quasi-strict linearity of the halogen bond can therefore be regarded as an intrinsic feature of this molecular interaction in the solid state as well as in the gas phase.

2.4. Lone-pair directionality of halogen bonds

Another important question about angular halogen-bond geometry is whether halogen bonds tend to form along lone-pair directions. In order to answer this question we have carried out a geometrical analysis of $Y—X\cdots B$ contacts using the directional parameters θ and φ defined in Fig. 1. These parameters have profitably been exploited in studies of hydrogen-bond directionality in the solid state (Taylor & Kennard, 1984; Lommerse et al., 1997; Taylor et al., 1983; Allen et al., 1997b). They are calculated with respect to the plane that is perpendicular to the R_1BR_2 plane and contains the bisector of the R_1BR_2 angle (Figs. 1a and b) or that is defined by R_1BR_2 (Fig. 1c) or $R_1R_2C=B$ (Fig. 1d). θ measures the angle of elevation of the $B\cdots X$ vector from that plane, while φ represents the angle of rotation, from the bisector of the R_1BR_2 angle (Figs. 1a–c) or from the C=B bond (Fig. 1d), of the projection of the $B\cdots X$ vector onto that plane. Assuming local tetrahedral sp^3 (Figs. 1a and b) or trigonal sp^2 (Figs. 1c and d) geometry at B, the B lone pair(s) lie(s) in that plane, and angles of $|\theta| \simeq 0$, $|\varphi| \simeq 125.5$ (Figs. 1a and b), 180 (Fig. 1c) or 120° (Fig. 1d) would indicate the colinearity of the B lone pairs and $B\cdots X$ vectors.

Mean values of the halogen-bond directionality parameters, $|\theta|$ and $|\varphi|$, are collected in Table 4. The overall mean $|\theta|$ value for 152 halogen bonds is 3.9°, i.e. not statistically different from the $|\theta|$ of ca 0° that corresponds to X approaching B in the lone-pair plane. Thus, upon halogen bonding dihalogens exhibit a strong tendency to lie in the plane of the lone pair (Fig. 1) of amines, phosphines, arsines, pyridines, thioethers, selenoethers and of most (see below) thiocarbonyl and selenocarbonyl compounds. In the case of the chair conformer of six-membered cyclic ethers, thioethers and selenoethers, an equatorial orientation of $Y—X$ is observed for ethers (DOXABR; Hassel & Hvoslef, 1954) and 1,4-dioxane:I_2
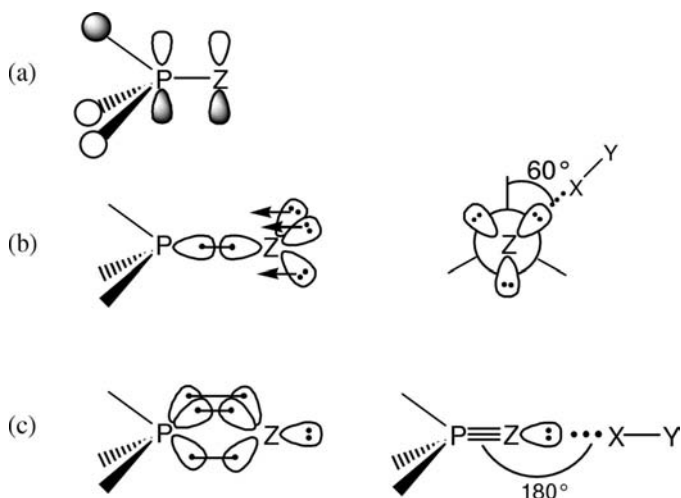
Table 3
Comparison of the strength of halogen and hydrogen bonds: enthalpy, $\Delta H°$ (kJ mol^{-1}), of halogen- and hydrogen-bonding complexation (in CCl$_4$, cyclohexane or heptane).

Family	Base	$-\Delta H°$ (I$_2$···B)	Reference	$-\Delta H°$ (ArOH···B)	Reference
Oxygen sp^3	Et$_2$O	18.0	(a)	20.1	(e)
Oxygen sp^2	Me$_2$CO	15.3	(b)	13.8	(e)
Sulfur —S—	Et$_2$S	37.2	(a)	15.1	(e)
Sulfur C=S	MeCSNMe$_2$	39.7	(c)	16.7	(e)
Sulfur PS	Ph$_3$PS	30.5	(d)	13.1	(f)
Selenium —Se—	Me$_2$Se	35.6	(a)	15.4	(e)
Selenium PSe	Ph$_3$PSe	38.5	(d)	13.1	(f)
Nitrogen sp^3	Et$_3$N	50.2	(a)	37.3	(e)
Nitrogen sp^2	Pyridine	32.6	(a)	30.1	(e)

References: (a) Mulliken & Pearson (1969); (b) Laurence et al. (1979); (c) Niedzielski et al. (1964); (d) Giera et al. (1980); (e) Joesten & Schaad (1974); (f) Rostueso et al. (1987).

(Hassel, 1965), and thioethers [DTHINI (Chao & McCullough, 1960), RUQPIC (Arca et al., 1997), ISBCLS (Kiel, 1981) and DTHIBR10 (Knobler et al., 1971)], while for selenoethers the iodine is bonded to selenium either in the axial [OXSEIC (Knobler & McCullough, 1968), OXSELI (Maddox & McCullough, 1966) and DSEIOD (Chao & McCullough, 1961)] or the equatorial position [RUQPOI, 1,4-selenothiane: I$_2$ (Hope & McCullough, 1962)].

Not all diiodine complexes of thiocarbonyl and selenocarbonyl compounds are planar. Laurence et al. (1998) previously performed a CSD search of I$_2$:thioamide (urea) complexes and showed, from the analysis of the torsion angles N—C=S···I around C=S, that two groups of complexes are found. In the first of these, at least one sulfur lone pair is unhindered and the torsion angles of ca 0 and ±180° (corre-

sponding to θ ca 0°) indicate that the diiodine is not much displaced from the NCS plane. These complexes were termed planar. In the second series, both sulfur lone pairs are sterically crowded and the torsion angles of ca 90° (θ ca 80°) show that the diiodine lies quasi-perpendicular to the NCS plane. These complexes were termed perpendicular. We now find that the diiodine complexes of selenoamides (ureas) behave similarly. We see from Fig. 5 that perpendicular complexes are formed with hindered selenoureas [REBNER (Demartin et al., 1997) and ZOBDOJ (Bigoli et al., 1994)] while selenoamides (ureas) unhindered on one [YEYFEN (Cristiani et al., 1994) and YEYFOX (Cristiani et al., 1994)] or both (KUWDUB; Cristiani et al., 1992) selenium sides give planar complexes with diiodine situated on the unhindered selenium side. Fig. 6 summarizes the distribution of the torsion angles N—C=S(Se)···I for diiodine complexes of thiocarbonyl and selenocarbonyl compounds showing modes close to 0 or 180° for the planar complexes and close to 90° for the perpendicular ones.

For complexes with amines, phosphines and arsines the mean $|\varphi|$ value of 125 (2)° is very close to the value $|\varphi| = 125.5°$ that corresponds to an alignment of the $Y—X$ axis with an idealized N, P or As sp^3 lone pair. For complexes with pyridines (Bailey et al., 1997), phosphazene (HMCPZI; Markila & Trotter, 1974), azole (PMTTIC; Baenziger et al., 1967), azoalkane (GAWXEH; Engel et al., 1998), and phosphanimines [WEKGIC (Nubhär et al., 1994), REWWUL (Grebe et al., 1996), ZAVDAB and ZAVDEF (Harms et al., 1995)], the mean $|\varphi|$ value of 173 (7)° indicates that $Y—X$ points almost directly at an N sp^2 lone pair (ideally $\varphi = 180°$). On the contrary, complexes of thioethers, planar thiocarbonyls, selenoethers and planar selenocarbonyls have mean $|\varphi|$ values of 15–21° below the $|\varphi| = 125.5°$ or $|\varphi| = 120°$ values that might be considered to correspond to the position of an idealized S (Se) sp^3 or sp^2 lone pair, respectively. This observation is consistent with the large size of the valence shell of elements of the third and subsequent periods, allowing lone pairs to repel each other more strongly than in the valence shell of oxygen (Gillespie & Hargittai, 1991). This might explain why the two S (Se) lone pairs make a greater angle than the oxygen lone pairs and therefore lower φ directional parameters (Fig. 1).

The directionality of halogen bonds formed by phosphine sulfides and selenides (R_3PZ) cannot be parametrized by the θ and φ angles since the nature of the PZ (Z = O, S, Se) bond in phosphine oxides, sulfides and selenides, and therefore of the lone pair(s) on the chalcogen, is a point of much discussion by theoreticians and experimenters (Gilheany, 1994). Rather than using θ and φ, we characterize the position of $Y—X$ relative to the PZ bond by the angle PZ···X and the minimum torsion angle $RPZ···X$ around the PZ bond. These angles should allow discrimination between the following three

Figure 7
Representation of the three alternative views of the PZ bonding in phosphine chalcogenides (left) and the consequence on the directionality of the halogen bond (right). Scheme (a) shows one of the $p_\pi(Z)$ lone pairs and one orbital of e symmetry on the phosphine moiety suitable for a π-type interaction (back-bonding).

Table 4
Mean values of the geometrical descriptors of directionality, θ (°) and φ (°) (Fig. 1) with e.s.d.'s in parentheses for halogen bonds to various basic centers in the solid state.

n is the number of data. Perpendicular complexes (see text) are not included for the last two basic centers in the table.

Basic center	Putative lone-pair directionality	θ	φ	n
$>$N, $>$P, $>$As	125.5 (if sp^3)	2 (2)	125 (4)	20
$>$N	180 (if sp^2)	3 (3)	173 (7)	30
$>$S	125.5 (if sp^3)	4 (4)	105 (8)	55
$>$Se	125.5 (if sp^3)	6 (6)	108 (14)	10
$>$C=S	120 (if sp^2)	5 (7)	105 (4)	23
$>$C=Se	120 (if sp^2)	6 (3)	100 (1)	9

alternative descriptions of the PZ bonding (Gilheany, 1994) presented in Fig. 7:

Scheme (*a*) one σ-bond and two π back-bonds (negative hyperconjugation; Reed & Schleyer, 1990),

Scheme (*b*) one σ-bond and three π back-bonds, and

Scheme (*c*) three 'banana bonds'.

In the 'banana bond' description, the chalcogen atom bears one lone pair pointing away from phosphorus along the PZ axis and halogen-bonded complexes must exhibit bond angles $PZ\cdots X$ at the chalcogen of *ca* 180°. In scheme (*b*) of Fig. 7 three chalcogen lone pairs are staggered with respect to the three substituents R on phosphorus and the torsion angle $RPZ\cdots X$ must approach 60°. This staggered conformation differs from the negative hyperconjugation description [scheme (*a*)] which would have an eclipsed conformation, *i.e.* an $RPZ\cdots X$ torsion angle of *ca* 0°. The results collected in Table 5 are clearly inconsistent with a linear geometry and an eclipsed conformation, and favor a staggered conformation as indicated by the average $PZ\cdots X$ and $RPZ\cdots X$ angles of 105 and 57°, respectively. Insofar as the halogen-bond geometry is governed by the Z lone-pair direction, these observations provide an experimental foundation for electron pairs on the chalcogen (at least S or Se) in a staggered distribution relative to the P-substituent bonds as in scheme (*b*). It is interesting that a recent application of the 'atoms in molecules' theory to H_3PS and Me_3PS also concludes (Dobado *et al.*, 1998) that there are three equivalent maxima of electron density around sulfur, symmetrically oriented and staggered with respect to the PH/PC bonds.

2.5. Lengthening of the $Y—X$ bond in halogen-bonded complexes

It is an inherent characteristic of hydrogen bonds that the $Y—H$ bond in hydrogen-bonded complexes $Y—H\cdots B$ is elongated compared to the free $Y—H$ group and that the $Y—$

(*a*)

(*b*)
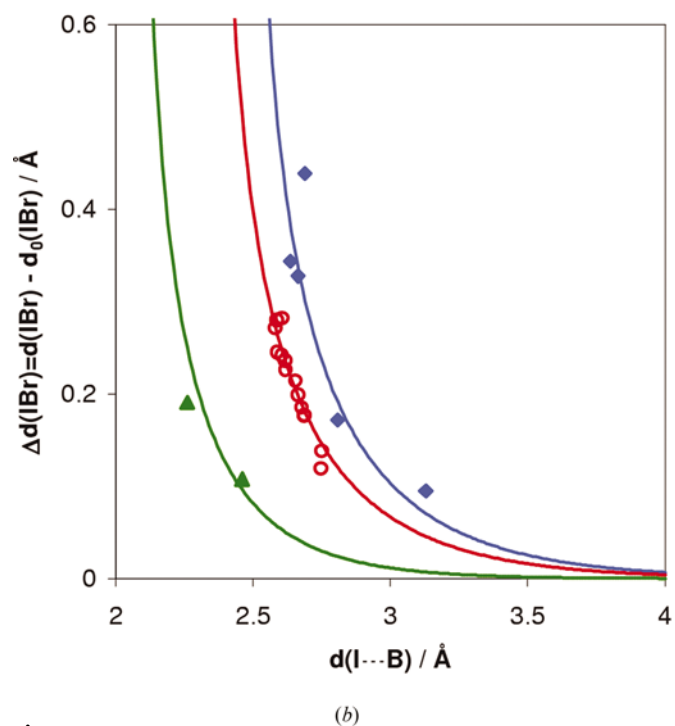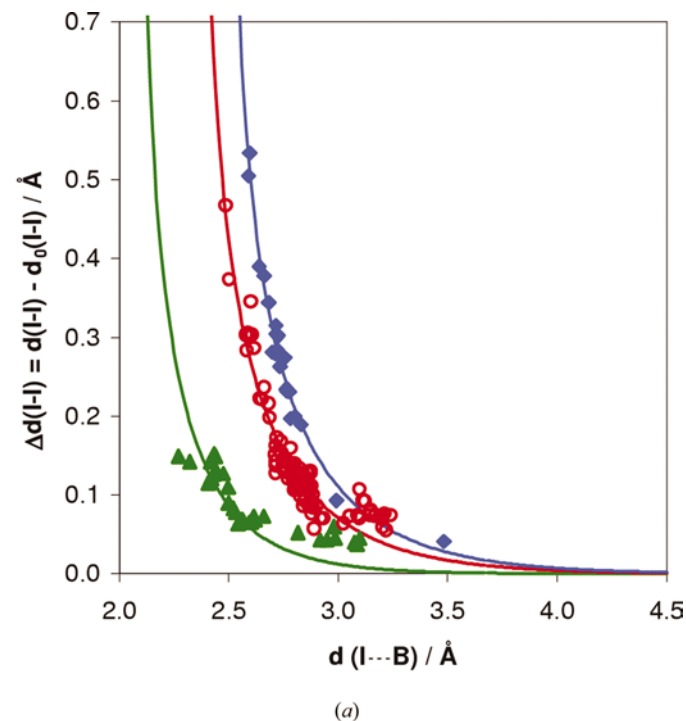
Figure 8
Lengthening (*a*) $\Delta d(I—I)$ and (*b*) $\Delta d(I—Br)$ of the I—X bond *versus* halogen bond length $d(I\cdots B)$ in halogen-bonded complexes with nitrogen bases (filled triangles), sulfur bases (open circles) and selenium bases (filled diamonds). The theoretical lines are fitted against the valence model of the halogen bond (3) with parameters given in Tables 6 and 7.

Table 5
Angles (°) $PZ \cdots I$ and $RPZ \cdots I$ in complexes $R_3PZ \cdots IY$.

XY	R_3PZ	Refcode	$PZ \cdots I$	$RPZ \cdots I$
I_2	Ph_3PS	NOFKOI	109	59
I_2	Ph_3PS	TPHPSI10	107	56
I_2	Ph_3PS	BAQTOC	106	65
I_2	$Ph_2PSCH_2PSPh_2$	NENRON	113	72
I_2	$Ph_2PSCH_2PSPh_2$	NENRON	104	70
I_2	$Ph_2PS(CH_2)_2PS\,Ph_2$	NENRUT	102	69
IBr	Ph_3PS	ZZZHUE01	108	60
IBr	Ph_3PS	ZZZHUE02	108	60
ICl	Ph_3PS	SIBJOC	108	60
I_2	$(^tBu)_2IPSe$	HECMOR	105	38
I_2	Ph_3PSe	PAQKAT	106	60
I_2	$(NMe_2)_3PSe$	PAQKEX	100	74
I_2	$(NMe_2)_3PSe$	PAQKEX	101	43
I_2	$(NEt_2)_3PSe$	PAQKIB	106	48
I_2	$(NMe_2)_3PSe$	RIJQAC	101	37
I_2	$(C_4H_8ON)_3PSe$	RIJQEG	98	48

H bond lengthening correlates with the $H \cdots B$ hydrogen-bond distance (Pimentel & McClellan, 1960; Joesten & Schaad, 1974; Scheiner, 1997b; Zeegers-Huyskens & Huyskens, 1991). A simplistic valence model (*see below*) of the hydrogen bond provides theoretical curves $\Delta d(Y-H)$ versus $d(H \cdots B)$, which satisfactorily fit the experimental data (Steiner, 1998).

This reciprocal relationship, whereby the lengthening of an intramolecular bond is concomitant with a shortening of an intermolecular distance, also occurs for halogen bonds $Y-X \cdots B$. It was first graphically presented by Herbstein & Schwotzer (1984) for diiodine:thione complexes. Subsequent papers (Blake *et al.*, 1997, 1998; Cristiani *et al.*, 1994; Bock *et al.*, 1996, 1997; Bigoli *et al.*, 1996; Arca *et al.*, 1998) have extended this observation to the complexes of diiodine with thioethers, selenones and to further thiones, but only Rudd *et al.* (1997) have given an analytical formula to represent the graphical correlations $\Delta d(I-I)$ versus $d(I \cdots S(Se))$. They used a valence (bond-order) model of the halogen bond, using
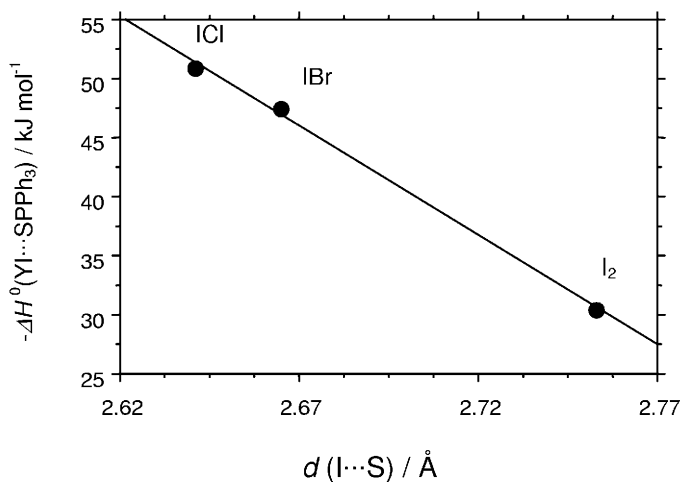

Figure 9
The same acid strength order, ICl > IBr > I_2, is found from their enthalpies of complexation with Ph_3PS in CCl_4 and the distance $I \cdots S$ in the solid state.

Table 6
Numerical values of the constants $b(YX)$ in (3) for various linear $[YXY]^-$ symmetrical fragments.

$d_0(Y-X)$: Mogadoc database (gas phase) (Vogt *et al.*, 1999); n: number of linear symmetrical $[YXY]^-$ fragments retrieved from the CSD; $b(YX) = [d_0(Y-X) - d(Y \cdots X)]/\ln 0.5$.

$[Y \cdots X \cdots Y]^-$	$d_0(Y-X)$ (Å)	$d(Y \cdots X)$ (Å)	n	$b(YX)$ (Å)
$[I \cdots I \cdots I]^-$	2.681	2.921	75	0.346
$[Br \cdots I \cdots Br]^-$	2.469	2.695	6	0.326
$[Cl \cdots I \cdots Cl]^-$	2.321	2.557	4	0.340
$[Br \cdots Br \cdots Br]^-$	2.280	2.540	8	0.375

a valence of halogen which is assumed to be shared between the bonds it forms, so that for the $Y-X \cdots B$ complex

$$n(YX) + n(X \cdots B) = 1, \tag{1}$$

where n is the valence (bond order). For many types of bonds n has been found to correlate inversely with the bond length d according to some empirical relation such as:

$$n = \exp[(d_0 - d)/b], \tag{2}$$

which was originally proposed by Pauling (1947), where d_0 is the bond length of a single bond ($n = 1$) and b is an empirical constant characteristic of each bond. Equations (1) and (2) lead to an expression for the dependence of the $Y-X$ on the $X \cdots B$ bond distance:

$$d(YX) = d_0(YX) - b(YX) \ln\{1 - \exp[(d_0(XB) \\ - d(X \cdots B))/b(XB)]\}. \tag{3}$$

Before fitting (3) against 48 $I-I \cdots S$ and 12 $I-I \cdots Se$ experimental data, $d_0(I-I) = 2.67$ Å (the gas-phase value for the $I-I$ single bond length) was chosen. We have found that a more recent value of 2.681 Å (Buentempo *et al.*, 1997) gives a better fit (*see below*). They also assumed $d_0(IS)$ and $d_0(ISe)$ to be the sum of Pauling's covalent radii for the $I-S$ (2.37 Å) and $I-Se$ (2.50 Å) single bonds, respectively. We prefer either to fit the parameter $d_0(XB)$ to (3) or to take the average of the experimental $X-B$ distances retrieved from the CSD (*see below*). Lastly, $b(II) = b(IS)$ for the $I-I \cdots S$ interaction was assumed, but $b(II) = b(ISe)$ for the $I-I \cdots Se$ interaction and so calculated $b(II) = b(IS) = 0.362$ and $b(II) = b(ISe) = 0.357$. These assumptions seem valid for the two halogen bonds ($I \cdots S$ and $I \cdots Se$) studied, but generally it might be more correct to start the fit using separate b values for each bond.

In this work we have searched for a strategy which allows the fitting of (3) to all the halogen bonds for which experimental data currently exist. The best compromise between statistical quality, chemical intuition and paucity of experimental data, depends on the three following points.

Firstly, we have performed a non-linear least-squares curve fitting (Harris, 1998) by minimizing the quantity Σ[experimental $d(YX)$ − calculated $d(YX)$]^2 and not the same quantity for $d(X \cdots B)$ instead of $d(YX)$. The accuracy is generally better for the halogen–halogen YX than for the halogen–base $X \cdots B$ distance, because it is easier to locate the heavier halogen atoms.

Table 7
Comparison between $d_0(X-B)$ values obtained from the CSD and fitted values, and $b(X\cdots B)$ fitted coefficients in (3).

n: number of $X-B$ distances retrieved from the CSD.

	Values from CSD		Fitted values	
$Y-X\cdots B$	n	$d_0(X-B)$	$d_0(X-B)$	$b(X\cdots B)$
I—I$\cdots$N	13	2.091	†	0.271‡
Cl—I$\cdots$N	13	2.091	†	0.271‡
I—I$\cdots$S	2	2.396	2.370	0.373
I—I$\cdots$Se	1	2.528	2.495	0.389
Br—Br$\cdots$N	4	1.860	‡	§
Br—Br$\cdots$S	4	2.193	†	§

† Insufficient and/or insufficiently diversified experimental data. ‡ See text. § Only three experimental data. See text for the choice of $b = 0.37$.

Table 8
Halogen-bond distances, $d(B\cdots X)$ (Å), of various $B\cdots XY$ complexes.

Comparison of the strength of the Lewis acids XY.

	XY			
B	ICl	IBr	I$_2$	Br$_2$
1,4-Dioxane	2.57	–	2.81	2.72
1,4-Dithiane	–	2.69	2.87	–
Ph$_3$PS	2.64	2.67	2.75	–
	–	2.58	2.77	–
Me$_2$Se	–	2.66	2.77	–
1,4-Oxaselenane	2.63	–	2.76	–
Hexamethylenetetramine	–	–	2.44	2.16
2,2′-Bipyridine	2.34	2.46	2.60	–
Ph$_3$P=N—SiMe$_3$	2.33	–	2.43	–
Ph$_3$P	–	2.46	2.48	2.18
Me$_3$As	–	–	2.27	2.28
Ph$_3$As	–	2.59	2.64	

Secondly, we have calculated (and not fitted) the b constant characteristic of the $Y-X$ bond from the linear symmetrical $[Y\cdots X\cdots Y]^-$ fragments. In these anions the halogen X is equally bonded to both atoms Y, thus $n = 0.5$, and $b = (d_0 - d)/\ln 0.5$ from (2): d_0 is the gas-phase value and d the average of the $X\cdots Y$ distances describing linear symmetrical I_3^-, ICl_2^-, IBr_2^- and Br_3^- anions retrieved from the CSD. The b parameters are listed in Table 6. The b values of I$_2$, IBr and ICl appear to be very similar. From (3) one can therefore predict that, within experimental error, I$_2$, IBr and ICl must have very similar curves of $\Delta d(IY) = d(IY) - d_0(IY)$ versus $d(I\cdots B)$ for the same atom B. This finding has already been reported for a restricted set of data (Aragoni, Arca, Demartin et al., 1999; Blake et al., 1999). A referee suggests that 'considering the parameter $\Delta d(IY)$ (Y = I, Br, Cl), the charge transfer interaction between N-, S- or Se-containing donors and halogens or interhalogens is independent of the nature of the latter, and strictly determined by the nature of the donor atom'.

Lastly, values for $d_0(X-B)$ and $b(X\cdots B)$ should be obtained by fitting (3) against experimental data. Unfortunately, it turns out that for most systems except I—I$\cdots$S and I—I$\cdots$Se, experimental data are not sufficiently numerous or diversified (i.e. do not contain both long and short halogen bonds) to give fitted $d_0(X-B)$ which agree with experimental $X-B$ distances retrieved from the CSD. For example, for I—

I$\cdots$N, I—I$\cdots$S and I—I$\cdots$Se complexes we find d_0 values of 1.733, 2.370 and 2.495 Å for the I—N, I—S and I—Se bonds, respectively. The two latter values agree within 0.04 Å with the experimental values $d(I-S) = 2.396$ Å, from the CSD structures GIGBED (Minkwitz et al., 1988) and JITQOS (Goto et al., 1998), and with $d(I-Se) = 2.528$ Å in the FOHNEV (Du Mont et al., 1987) structure. However, the first value departs severely from the value of 2.091 (35) Å for $d(I-N)$ obtained by averaging 13 N—I values [HINXEH, HINXIL, HINXOR (Grebe et al., 1999), HMTNTI (Pritzkow, 1974a), IFORAM (Pritzkow, 1974b), REWXAS (Grebe et al., 1996), ZZZVCQ01 (Padmanabhan et al., 1990) and PYDTIN (Hartl & Ullrich, 1974)]. Moreover, the fitted $b(IN)$ value of 0.558 Å lies too far from the average b value of 0.37 Å found for most chemical bonds (Brown & Altermatt, 1985). So, for this I—I$\cdots$N system and other $Y-X\cdots B$ systems with insufficient experimental data we have taken an average I—N $(X-B)$
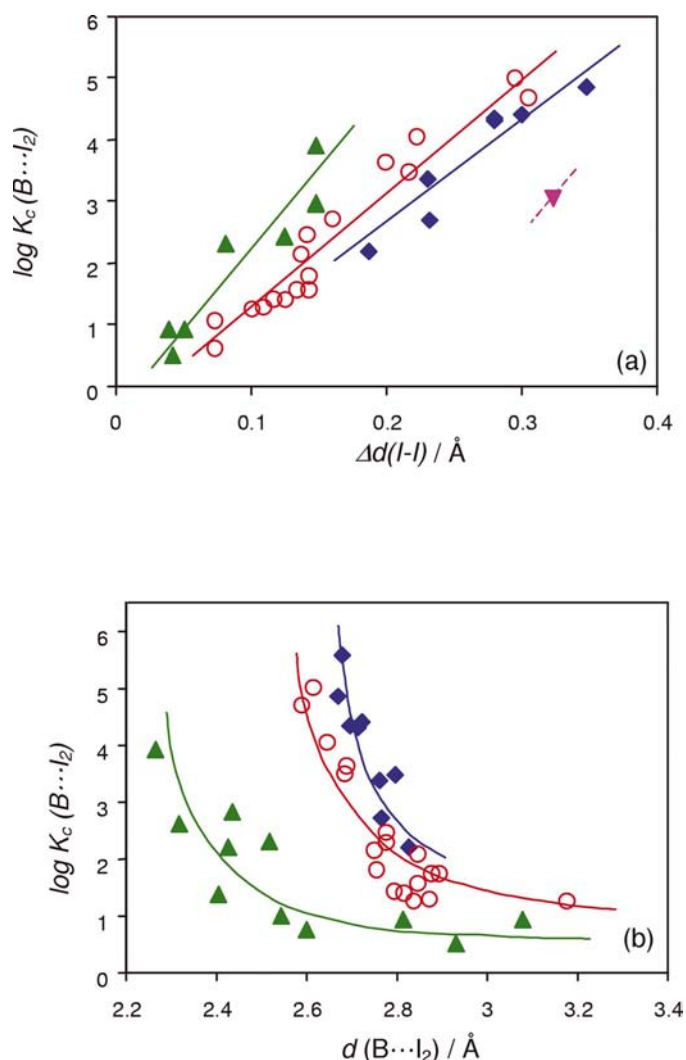

Figure 10
Family-dependent plots of log $K_c(B\cdots I_2)$ against (a) $\Delta d(I-I)$, the lengthening of the I—I bond, and (b) $d(I\cdots B)$, the halogen-bond length. (Filled triangles), nitrogen bases; (open circles) sulfur bases; (filled diamonds) selenium bases; (filled upturned triangle) Ph$_3$As. Data from Table 9. For the sake of clarity a number of points are omitted in each family.

Table 9
Selected equilibrium constants ($dm^3 mol^{-1}$) for the complexation of diiodine with Lewis bases in solution at 298 K; see (6) and (7); corresponding radial geometries (Å) of the complexes in the solid state.

The full list, with literature references and solvents (generally heptane, CCl_4 or CH_2Cl_2), is given in Ouvrard (2001).

GEGNUB   KUWDOV   ZEBQOM
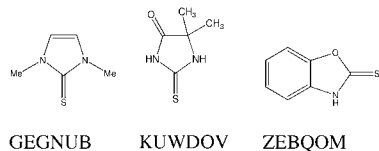
Refcode	Base	$\log K_c$	$\Delta d(I—I)$	$d(B\cdots X)$
Nitrogen bases				
TMEAMI	Me_3N	3.88	0.149	2.271
PICOLI	4-Picoline	2.57	0.142	2.322
GAWXEH	2,3-Diazabicyclo[2.2.2]oct-2-ene	2.18	0.126	2.431
NULBIF	4-Cyanopyridine	0.95	0.067	2.549
VUKDIO	Pyrazine	0.88†	0.052	2.817
NULBUR	Quinoxaline	0.47†	0.043	2.934
Sulfur bases				
GEGNUB	See above	5.03	0.295	2.612
TCAPLI	*N*-Methylthiocaprolactam	3.66	0.198	2.687
KUWDOV	See above	2.30	0.121	2.773
ZEBQOM	See above	1.77	0.088	2.873
RUQPIC	1,3,5-Trithiane	0.64†	0.073	3.169
Selenium bases				
YEYFOX	Fig. 5	4.82	0.349	2.674
YEYFEN	Fig. 5	4.37	0.302	2.725
PAQKEX	$(Me_2N)_3PSe$	4.27	0.282	2.716
THSELI01	Tetrahydroselenophene	3.34	0.232	2.765
RIZMES	Dimethylselenide	2.67	0.234	2.768
DSEIOD	1,4-Diselenane	2.15†	0.189	2.830
Arsenic base				
FESKAP	Triphenylarsine	3.03	0.325	2.641

† Statistically corrected by $\log n$, n being the number of (assumed) equivalent basic centers.

distance of 2.091 Å and have only adjusted the parameter $b(IN)$ *i.e.* $[b(XB)]$. We thus obtain $b(IN) = 0.277$ Å. This value for the I/N atom pair is not significantly different from that of 0.265 Å obtained from $Cl—I\cdots N$ complexes and we have retained the mean (0.271 Å) of these two values for our summary of results in Table 7. The d_0 and b values of Tables 6 and 7 are used in (3) to calculate the theoretical curves for the complexes of I_2 (Fig. 8a), IBr (Fig. 8b) and ICl (not shown) with nitrogen, sulfur and selenium bases. Fig. 8 shows that the experimental points are generally well fitted by the theoretical function $d(YX) = f[d(X\cdots B)]$ as given in (3).

For the Br_2 complexes with N and S bases, we already know $b(BrBr) = 0.375$ Å from the Br_3^- anion (Table 6) and were able to retrieve the mean values for the $d_0(Br—N)$ and $d_0(Br—S)$ distances from the CSD. However, the paucity of experimental data prevented the fitting of the $b(BrN)$ and $b(BrS)$ empirical parameters. Since a value of b close to 0.37 Å was found for many atom pairs [Brown & Altermatt, 1985; indeed, if we exclude $b(IN)$, we find b values ranging between 0.32 and 0.39 Å, see Tables 6 and 7], we have accepted this general

value of 0.37 Å for the $Br\cdots N$ and $Br\cdots S$ halogen bonds. Thus we were able to calculate the two theoretical curves for the complexes of Br_2 with nitrogen and sulfur bases and to confirm that the experimental points are satisfactorily located near these curves of (3).

In summary, as for the hydrogen bond, the experimental data support a valence model of the halogen bond, *i.e.* a model where the 'bond orders' or 'valences' fully characterize the dependence of the $Y—X$ lengthening on the $X\cdots B$ distance.

2.6. Crystallographic order of halogen-bond acidity

The strength of the halogen bonds $YX\cdots B$ depends both on the halogen-bond donor strength of I_2, Br_2, IBr, ICl *etc.* and on the halogen-bond acceptor strength of the base B. Structurally, donor (acceptor) strengths are reflected in $X\cdots B$ halogen-bond distances, which are shorter for the stronger donor (acceptor). However, a direct comparison can be made only when the same atoms interact, because an increase in halogen-bond strength can be compensated for by the effect of a larger halogen and/or basic-atom radius. The comparison of distances $I\cdots O$, N, S, Se, P and As in Table 8 shows that the acid strength always increases in the order $I_2 <$ IBr < ICl. This result might appear banal if we remember that this order of strength was indicated by the thermodynamic parameters (Gibbs energy and enthalpy of formation) for halogen-bonded complexes (Foster, 1969; see Fig. 9). However, thermodynamic data have been obtained mainly for oxygen and nitrogen bases [except Ph_3PS (Sieper & Paetzold, 1974)], which are hard or border-line in the hard and soft classification of bases (Pearson, 1963, 1985, 1987). With soft bases a reversal of the order $I_2 <$ IBr < ICl might occur if the interaction changes from one dominated by charge (dipole) effects (the dipole moments of I_2, IBr and ICl are 0, 0.73, and 1.24 D, respectively; Lide, 1998–1999) to one where orbital effects are the most important (the electron affinities of I_2, IBr and ICl are 1.72, 1.62, and 1.48 eV, respectively; Hubers *et al.*, 1976). Such a reversal of acid strength has already been observed (Laurence & Queignec-Cabanetos, 1981) between the soft I_2 and the harder $IC\equiv N$ Lewis acids; ICN complexes with (hard) oxo-bases are more stable than I_2 complexes, whereas the reverse occurs with (soft) sulfur bases. Thus, it is important to note that the

crystallographic acidity scale ICl > IBr > I_2 remains valid for selenoethers, phosphines and arsines, which are very soft bases (Pearson, 1963, 1985, 1987), indicating that the electrostatic energy component remains dominant in the halogen bonding of I_2, IBr and ICl with many (possibly all) types of bases (O, N, S, Se, P and As bases).

The comparison of I_2 with Br_2 is not so straightforward, because of the different radii of these halogens. However, I_2 appears from the $d(I\cdots As)$ and $d(Br\cdots As)$ distances (Table 8) to be a stronger acid towards trimethylarsine than Br_2. This extends to a very soft base (Me_3As; Pearson, 1987) the thermodynamic order $I_2 > Br_2$, which was previously found in solution for the complexes with the hard and borderline bases benzene (Drepaul et al., 1996), nitriles (Klaboe, 1962), oxobases (Beggiato et al., 1974) and pyridines (Aloisi et al., 1970). Thus, the order $I_2 > Br_2$ appears to be independent of the hardness or softness of the base.

In summary, the crystallographic sequence of Lewis acid strength $Br_2 < I_2 < IBr < ICl$ matches and can therefore be merged with the order $F_2 < Cl_2 < Br_2 < BrCl < ClF < ICl$ established (Legon, 1998a, 1999b) from $X\cdots B$ force constants in the gas phase. This gives the order $F_2 < Cl_2 < Br_2 < I_2 < IBr < ICl$, which seems independent of the softness of the reference base. The position of ClF and BrCl in this sequence can only be resolved by studies of I_2 and IBr complexes in the gas phase.

2.7. Crystallographic and thermodynamic orders of halogen-bond basicity

We set out to establish the influence of base strength on the length of the halogen bond, a parameter which evidently must be shorter for the stronger bases, given a common halogen-bond donor YX. Owing to the relationship between $\Delta d(Y-X)$ and $d(X\cdots B)$ (see above), a stronger basicity also means greater lengthening of the $Y-X$ distance.

We have chosen the Gibbs energy of formation of 1:1 complexes of diiodine with Lewis bases (6) as a measure of base strength towards dihalogens, which is related to the complexation constant K_c (7) through (8), for the simple reason that the values of many complexation constants for equilibrium (6) are available in the literature.

$$I_2 + B \rightleftharpoons B\cdots I_2 \qquad (6)$$

$$K_c(\mathrm{dm^3\ mol^{-1}}) = [B\cdots I_2]/[I_2][B] \qquad (7)$$

$$\Delta G_{298}^0\ (\mathrm{kJ\ mol^{-1}}) = -5.709 \log K_c \qquad (8)$$

We have been able to collect 60 $\log K_c$ values for those bases whose dihalogen complexes have been structurally characterized. Selected values are given in Table 9. This diiodine basicity scale extends over 6.16 $\log K$ units (i.e. 35 kJ mol^{-1} on the Gibbs energy scale) from benzene, the weakest base, to the selenourea REBNER (Fig. 5), the strongest one.

We first studied the relationship between $\log K_c(B\cdots I_2)$ and $\Delta d(I-I)$. For 43 diiodine complexes of N, S, Se and As bases, the correlation coefficient of 0.878 between these two parameters is statistically significant. In spite of many extrinsic factors influencing the $I-I$ bond length in the solid state, this correlation indicates the intrinsic stability of diiodine complexes and vice versa. However, a closer examination of the $\log K_c(B\cdots I_2) - \Delta d(I-I)$ plot (Fig. 10a) shows that data points are not statistically distributed, but rather define family-dependent lines. The families of nitrogen, sulfur, selenium and arsenic bases are arranged from left to right, respectively. Depending on whether we adopt the Pearson (1963) HSAB theory, the electrostatic–covalent Drago (1980) description or the charge-transfer Mulliken theory (Mulliken & Person, 1969) of molecular complexes, we can say that for the same stability constant K_c the elongation of the $I-I$ bond is proportional to the softness of the base (Pearson), its covalency (Drago) or its ability to transfer electrons (Mulliken).

This behaviour is reminiscent of the linear family-dependent relationships often observed (Joesten & Schaad, 1974; Gramstad, 1963) for the hydrogen-bonded complexes $Y-H\cdots B$ between their thermodynamic parameters of complexation and their vibrational frequency shift upon hydrogen bonding, $\Delta\nu(Y-H)$, since stretching frequencies depend on bond distances, via the frequency–bond force constant and the force constant–bond length relationships.

As a consequence of the family-dependent linear $\log K_c(B\cdots I_2) - \Delta d(I-I)$ (Fig. 10a) and inverse $\Delta d(I-I) - d(I\cdots B)$ (Fig. 8) relationships, we observe in Fig. 10(b) roughly hyperbolic family-dependent relationships between $\log K_c(B\cdots I_2)$ and $d(I\cdots B)$.

Insofar as the $\log K_c$ values for ICl, IBr and Br_2 complexes are correlated to $\log K_c$ of diiodine complexes (with a possible family dependence), we are tempted to correlate $\log K_c(B\cdots I_2)$ with $\Delta d(I-Cl)$, $\Delta d(I-Br)$, $\Delta d(Br-Br)$, $d(ClI\cdots B)$, $d(BrI\cdots B)$ and $d(Br_2\cdots B)$. Indeed these correlations (not shown) for the ICl, IBr and Br_2 complexes are of the same kind as for the I_2 complexes, i.e. they are family dependent and, for the same stability constant, the degree of elongation of the $X-Y$ bond is greater if the base is softer, i.e. can better transfer electrons to the $\sigma^*(X-Y)$ molecular orbital. The statistics of the $\log K_c(B\cdots I_2) - \Delta d(Y-X)$ correlations are summarized for the four dihalogens (I_2, ICl, IBr and Br_2) in Table 10.

3. Conclusions

The halogen-bond geometry reported in the gas phase for simple complexes of dihalogens (Legon, 1999a) is found to be valid

(i) in the solid state,

(ii) for new important Lewis acids (I_2 and IBr) and

(iii) for new basic centers ($-Se-$, $C=Se$, PSe, $C=S$, PS, $=N-$ and As).

For 141 halogen-bonded complexes the following is found:

(i) The mean linearity is 176°; halogen bonds $I-I\cdots B$ are more linear by 11–38° (according to the family of B) than the corresponding $O-H\cdots B$ hydrogen bonds.

Table 10
Correlation between the Lewis base strength measured by $\log K_c$ $(B \cdots I_2)$, the complexation constant of diiodine complexes, and $\Delta d(Y-X)$, the lengthening of the $Y-X$ bond upon complex formation.

n: number of bases; r: correlation coefficient; s: standard deviation of the estimate.

Acid	Base	n	r	s
I_2	All (As, N, S, Se)	43	0.878	0.65
	Nitrogen bases	11	0.879	0.54
	Sulfur bases	21	0.934	0.44
	Selenium bases	10	0.787	0.75
Br_2	All (C, N, O, S)	10	0.792	0.80
IBr	All (N, S, Se)	10	0.898	0.55
ICl	All (O, N, S, Se)	10	0.747	1.15
	Nitrogen bases	5	0.921	0.68

(ii) The direction of the halogen bond (vector $X \cdots B$) is very close to the axis of the non-bonding electron pair of N (sp^3), P (sp^3), As (sp^3) and N (sp^2) bases.

(iii) For thio(seleno)ethers and thio(seleno)carbonyl bases the halogen bond is quasi-perpendicular (angles $\varphi = 99–108°$) to the $R_1S(Se)R_2$ plane (Fig. 1b) or to the plane bisector of the angle R_1CR_2 (Fig. 1d). However, for thio(seleno)amides (ureas), the torsion angle NCS(Se)$\cdots$I changes from ca 0 or 180° to ca 90° when bulky groups R_1 and R_2 hinder the S(Se) lone pairs (Figs. 1d and 5).

(iv) For thio(seleno)phosphoryl bases, the halogen-bond directionality indicates that non-bonding electron pairs on the chalcogen are staggered relative to the substituents on P (Fig. 7b).

(v) The lengthening of the $X-Y$ bond is explained by a bond-order model $[n(YX) + n(X \cdots B) = 1]$.

(vi) The crystallographic order of Lewis acid strength, $Br_2 < I_2 <$ IBr < ICl, appears to be independent of the softness of the base.

(vii) The lengthening $\Delta d(X-Y)$ and the halogen bond length $d(X \cdots B)$ are significantly related to the Lewis base strength. Relationships are family dependent and show (Fig. 10) that for complexes of the same stability, the elongation of the $X-Y$ bond depends on the degree to which the base can transfer electrons into the $\sigma^*(X-Y)$ molecular orbital.

This geometric description of halogen bonding in the solid state has been established from inorganic halogens. The principal source of knowledge about halogen bonds formed by organic halogens is the statistical study of $C-X \cdots B$ contacts in organic crystals (e.g. Lommerse et al., 1996). A study similar to ours for organic halogens would need a greater number of X-ray structures than are available today. Data on the halogen-bonded complexes of $IC \equiv N$, $IC \equiv CPh$, $IC \equiv CI$, CHI_3, $Br_2C \equiv CBr_2$, $ClC(O)C(O)Cl$, CBr_4, IC_6H_4I, diiodoperfluorocarbons etc. (see CSD for references) are still limited to a very restricted number and a variety of Lewis bases.

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