Table 1'. Some observed and calculated properties of halogen-bonded complexes B···$X_2$ involving non-polar dihalogen molecules $X_2$ (including CABS singles in calculating BSSE corrections for B···$Br_2$)[a]

| Lewis base B | Dihalogen molecules $X_2$ | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Difluorine $F_2$ | | | | Dichlorine $Cl_2$ | | | | Dibromine $Br_2$ | | | |
| | $k_\sigma$/(N m $^{-1}$) | Ref. | $D_\sigma$/kJ mol$^{-1}$ | $r$(Z···$X_i$)/Å | $k_\sigma$/(N m $^{-1}$) | Ref. | $D_\sigma$/kJ mol$^{-1}$ | $r$(Z···$X_i$)/Å | $k_\sigma$/(N m $^{-1}$) | Ref. | $D_\sigma$/kJ mol$^{-1}$ | $r$(Z···$X_i$)/Å |
| | | | | | | | | | | | | |
| OC | - | - | - | - | 3.68(1) | 12 | 5.19 | 3.145 | 5.03(2) | 20 | 7.50 | 3.111 |
| $C_2H_2$ | - | - | - | - | 5.61(1) | 13 | 7.45 | 3.146 | 7.80(3) | 21 | 11.05 | 3.106 |
| $C_2H_4$ | - | - | - | - | 5.88(2) | 14 | 8.61 | 3.092 | 8.8(2) | 22 | 13.49 | 3.004 |
| $H_2S$ | 2.34(1) | 7 | 3.43 | 3.143 | 6.23(2) | 15 | 8.53 | 3.246 | 9.8(2) | 23 | 13.83 | 3.131 |
| $H_3P$ | - | - | - | - | 5.58(2) | 16 | 8.34 | 3.222 | 9.79(3) | 24 | 15.35 | 3.013 |
| HCN | 2.62(1) | 8 | 4.15 | 2.811 | 6.55(2) | 17 | 9.71 | 2.921 | - | - | - | - |
| $H_2O$ | 3.66(1) | 9,10 | 4.63 | 2.696 | 7.98(3) | 18 | 10.66 | 2.808 | 9.9(2) | 25 | 14.96 | 2.804 |
| $H_3N$ | 4.61(1) | 11 | 6.59 | 2.679 | 12.73(2) | 19 | 17.85 | 2.681 | 18.5(4) | 26 | 28.17 | 2.601 |

[a]Values of $k_\sigma$ are either taken directly from the reference having the number indicated in columns 3,7 or 11 , as appropriate, or are recalculated from the centrifugal distortion constant $D_J$ or $\Delta_J$ given therein by using eq.(1) or (2). The quoted error is that transmitted by the error in the distortion constant. $D_\sigma$ and $r$(Z···$X_i$) are equilibrium values calculated *ab initio* at the CCSD(T)(F12c)/cc-pVDZ-F12 level of theory (see text). $r$(Z···$X_i$) is the distance from the acceptor atom/centre Z in the Lewis base B to the inner halogen atom $X_i$

Table 2'. Some observed and calculated properties of halogen-bonded complexes B···XY involving polar dihalogen molecules XY (including CABS singles in calculating BSSE corrections for Br- and I- containing species)[a]

| Lewis base B | Dihalogen molecules XY | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Chlorine monofluoride ClF | | | | Bromine monochloride BrCl | | | | Iodine monochloride ICl | | | |
| | $k_\sigma$/(N m $^{-1}$) | Ref. | $D_\sigma$/kJ mol$^{-1}$ | $r$(Z···X)/ Å | $k_\sigma$/(N m $^{-1}$) | Ref. | $D_\sigma$/kJ mol$^{-1}$ | $r$(Z···X)/Å | $k_\sigma$/(N m $^{-1}$) | Ref. | $D_\sigma$/kJ mol$^{-1}$ | $r$(Z···X)/ Å |
| | | | | | | | | | | | | |
| $N_2$ | 5.00(3) | 27 | 6.28 | 2.918 | 4.40(2) | 35 | 5.75 | 3.106 | 5.37(2) | 44 | 7.22 | 3.187 |
| OC | 7.04(2) | 28 | 10.56 | 2.772 | 6.27(5) | 36 | 9.38 | 3.006 | 8.00(3) | 45 | 12.99 | 3.003 |
| $C_2H_2$ | 10.01(2) | 29 | 13.68 | 2.859 | 9.48(6) | 37 | 13.16 | 3.038 | 12.12(8) | 46 | 17.52 | 3.112 |
| $C_2H_4$ | 11.01(3) | 30 | 17.01 | 2.730 | 10.54(1) | 38 | 16.11 | 2.927 | 14.0(1) | 47 | 21.99 | 2.958 |
| $H_2S$ | 13.40(3) | 31 | 18.13 | 2.835 | 12.07(10) | 39 | 16.71 | 3.057 | 16.55(5) | 48 | 22.73 | 3.120 |
| $H_3P$ | - | - | - | - | 11.56(7) | 40 | 19.45 | 2.878 | 20.7(1) | 49 | 29.13 | 2.898 |
| HCN | 12.33(5) | 32 | 18.42 | 2.639 | 11.09(10) | 41 | 17.13 | 2.826 | 14.5(1) | 50 | 24.08 | 2.840 |
| $H_2O$ | 14.24(3) | 33 | 20.14 | 2.554 | 12.08(2) | 42 | 18.29 | 2.735 | 15.9(2) | 51 | 24.93 | 2.776 |
| $H_3N$ | 34.3(5) | 34 | 40.43 | 2.304 | 26.7(3) | 43 | 34.58 | 2.532 | 30.4(3) | 52 | 47.40 | 2.599 |

[a]Values of $k_\sigma$ are either taken directly from the reference having the number indicated in columns 3, 7 or 11 , as appropriate, or are recalculated from the centrifugal distortion constant $D_J$ or $\Delta_J$ given therein by using eq.(1) or (2). The quoted error is that transmitted by the error in the distortion constant. $D_\sigma$ and $r$(Z···X$_i$) are equilibrium values calculated *ab initio* at the CCSD(T)(F12c)/cc-pVDZ-F12 level of theory (see text). $r$(Z···X) is the distance from the acceptor atom/centre Z in the Lewis base B to the inner halogen atom X.

Table 3'. Some observed and calculated properties of hydrogen-bonded complexes B···HX (including CABS singles in calculating BSSE corrections for Br and I containing species)[a]

| Lewis base B | Hydrogen halide molecules HX | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Hydrogen fluoride HF | | | | Hydrogen chloride HCl | | | |
| | $k_\sigma$/(N m $^{-1}$) | Ref. | $D_\sigma$/kJ mol$^{-1}$ | $r$(Z···H)/Å | $k_\sigma$/(N m $^{-1}$) | Ref. | $D_\sigma$/kJ mol$^{-1}$ | $r$(Z···H)/Å |
| | | | | | | | | |
| $N_2$ | 5.13(3) | 53 | 9.26 | 2.099 | 2.55(1) | 62,63 | 5.12 | 2.400 |
| OC | 8.48(9) | 54 | 14.21 | 2.103 | 3.88(1) | 64 | 7.78 | 2.393 |
| $C_2H_2$ | - | - | - | - | 6.4(3) | 65 | 11.03 | 2.378 |
| $C_2H_4$ | - | - | - | - | 5.88(16) | 66 | 11.32 | 2.396 |
| $H_2S$ | 12.0(2) | 55,56 | 20.36 | 2.284 | 6.81(1) | 67 | 12.73 | 2.480 |
| $H_3P$ | 10.94(4) | 57 | 19.38 | 2.354 | 6.01(2) | 68 | 11.89 | 2.569 |
| HCN | 18.26(5) | 58 | 30.33 | 1.859 | 9.25(4) | 69 | 18.33 | 2.092 |
| $H_2O$ | 24.51(2) | 59,60 | 35.34 | 1.721 | 12.72(12) | 70 | 21.34 | 1.912 |
| $H_3N$ | 32.8 | 61 | 50.98 | 1.703 | 18.2(3) | 71 | 32.72 | 1.820 |
| | Hydrogen bromide HBr | | | | Hydrogen iodide HI | | | |
| | $k_\sigma$/(N m $^{-1}$) | Ref. | $D_\sigma$/kJ mol$^{-1}$ | $r$(Z···H)/Å | $k_\sigma$/(N m $^{-1}$) | Ref. | $D_\sigma$/kJ mol$^{-1}$ | $r$(Z···H)/Å |
| | | | | | | | | |
| $N_2$ | 1.92(1) | 72 | 4.19 | 2.503 | - | - | - | - |
| OC | 2.99(1) | 73 | 6.33 | 2.489 | 1.713(1) | 81 | 4.38 | 2.675 |
| $C_2H_2$ | 5.39(2) | 74 | 9.54 | 2.440 | - | - | - | - |
| $C_2H_4$ | 5.21(2) | 75 | 9.94 | 2.456 | - | - | - | - |
| $H_2S$ | 5.86(2) | 76 | 11.12 | 2.526 | 4.02(1) | 82 | 8.04 | 2.670 |
| $H_3P$ | 5.05(1) | 77 | 10.35 | 2.618 | 3.409(2) | 83 | 7.48 | 2.778 |
| HCN | 7.64(2) | 78 | 15.28 | 2.161 | 4.44(1) | 84 | 10.93 | 2.319 |
| $H_2O$ | 10.06(15) | 79 | 17.85 | 1.969 | 6.64(1) | 85 | 12.52 | 2.117 |
| $H_3N$ | 13.4(3) | 80 | 29.05 | 1.800 | 7.18(6) | 86 | 20.45 | 1.926 |

[a]Values of $k_\sigma$ are either taken directly from the reference having the number indicated in columns 3 or 7 , as appropriate, or are recalculated from the centrifugal distortion constant $D_J$ or $\Delta_J$ given therein by using eq.(1) or (2). The quoted error is that transmitted by the error in the distortion constant. $D_\sigma$ and $r$(Z···H) are equilibrium values calculated *ab initio* at the CCSD(T)(F12c)/cc-pVDZ-F12 level of theory (see text). $r$(Z···H) is the distance from the acceptor atom/centre Z of the Lewis base B to the hydrogen atom H.