Nucleophilicities of Lewis Bases B and Electrophilicities of Lewis Acids A Determined from the Dissociation Energies of Complexes B· · · A Involving Hydrogen Bonds, Tetrel Bonds, Pnictogen Bonds, Chalcogen Bonds and Halogen Bonds

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Abstract: It is shown that the dissociation energy D_e for the process B· · · A = B + A for 250 complexes B· · · A composed of 11 Lewis bases B (N_2, CO, HC≡CH, CH_2=CH_2, C_3H_6, PH_3, H_2S, HCN, H_2O, H_2CO and NH_3) and 23 Lewis acids (HF, HCl, HBr, HC≡CH, HCN, H_2O, F_2, Cl_2, Br_2, ClF, BrCl, H_3SiF, H_3GeF, F_2CO, CO_2, N_2O, NO_2F, PH_2F, AsH_2F, SO_2, SeO_2, SF_2, and SeF_2) can be represented to good approximation by means of the equation $D_e = c'N_B E_A$, in which N_B is a numerical nucleophilicity assigned to B, E_A is a numerical electrophilicity assigned to A, and c' is a constant, conveniently chosen to have the value 1.00 kJ mol^{-1} here. The 250 complexes were chosen to cover a wide range of non-covalent interaction types, namely: (1) the hydrogen bond; (2) the halogen bond; (3) the tetrel bond; (4) the pnictogen bond; and (5) the chalcogen bond. Since there is no evidence that one group of non-covalent interaction was fitted any better than the others, it appears the equation is equally valid for all the interactions considered and that the values of N_B and E_A so determined define properties of the individual molecules. The values of N_B and E_A can be used to predict the dissociation energies of a wide range of binary complexes B· · · A with reasonable accuracy.

Keywords: noncovalent bonds; binary complexes; dissociation energies; nucleophilicity; electrophilicity; *ab initio* calculations; geometry

1. Introduction

The best known, earliest identified non-covalent interaction is the hydrogen bond, although the halogen bond was discovered (but not so called) as long ago as 1869 through the reaction of iodine with ammonia [1]. The pioneering experiments of Hassel and co-workers in the late 1950s and early 1960s [2] led to the recognition of the halogen bridge (the term used by Hassel for the halogen bond). This was followed by a lull in experimental work until the mid-1990s when there was a very rapid growth of interest [3,4] in what then became known as the halogen bond. In the last 10 years, several new types of non-covalent interaction have been named, including the tetrel bond [5], the pnictogen bond [6] and the chalcogen bond [7], although it has been pointed out [8,9] that these types of interaction were known for at least 30 years before they were assigned their current names.

Each non-covalent bond can be described [9,10] in terms of the interaction of an electrophilic region of one molecule with a nucleophilic region of another molecule (or even the same molecule). In this article, we shall concentrate on the pairwise interaction B· · · A of a Lewis base molecule B (the provider of the nucleophilic site, usually a non-bonding (n) or a π-bonding electron pair) and

a Lewis acid A molecule (the provider of the electrophilic site). The electrophilic site in A can be identified variously as associated with a hydrogen atom (Group 1 of the Periodic Table), a tetrel atom (Group 14), a pnictogen atom (Group 15), a chalcogen atom (Group 16) or a halogen atom (Group 17); hence, the names assigned to the different types of non-covalent interaction. The electrophilic regions associated with halogen atoms in Lewis acids A were identified as positive regions on the molecular electrostatic surface potentials (MESP) by Clark, Murray and Politzer [11], who named the regions as σ-holes. Subsequently, σ-holes were similarly identified at or near Group 16 [12], 15 [13] and 14 [14] atoms in various Lewis acid molecules A.

An important aim in attempting to obtain a deeper understanding of non-covalent interactions in complexes B· · ·A is to be able to predict the strength of the interaction in terms of the properties of the individual molecules B and A. Two measures of interaction strength have been recognized, namely the intermolecular stretching force constant k_σ and the dissociation energy D_e for the process B· · ·A = B + A. The former is a measure of the energy $\frac{1}{2}k_\sigma$ required for a unit infinitesimal extension of the intermolecular bond from its equilibrium length, while the latter is the energy required for infinite extension of that bond. It was recognized some time ago [15] that experimental k_σ. values (determined, for example, by rotational spectroscopy [16] from centrifugal distortion constants) of weak hydrogen-bonded complexes B· · ·HX (X = F, Cl, Br, CCH or CN) could be described by the following expression:

$$k_\sigma = cN_B E_A \qquad (1)$$

in which c = 2.5 N m^{-1} (a conveniently chosen constant) and N_B and E_A are the numerical nucleophilicity and electrophilicity of the Lewis base B and the Lewis acid A, respectively. It was shown later [3,17] that Equation 1 also applied to halogen-bonded complexes B· · ·XY, where XY is a homo- or hetero-dihalogen molecule. A subsequent analysis [18] established that, for many hydrogen-bonded and halogen-bonded complexes B· · ·HX and B· · ·XY, the property D_e (not generally available from experiment, but readily calculated *ab initio*) is directly proportional to the property k_σ to a good level of accuracy and therefore that Equation 1 can be rewritten as

$$D_e = c'N_B E_A \qquad (2)$$

where c' is another constant.

If the various types of non-covalent interaction referred to earlier can all be described through the interaction of a nucleophilic region of B with an electrophilic region of A, it should be possible to use Equation (2) to define a scale of nucleophilicities and electrophilicities for a wide range of Lewis bases B and Lewis acids A, whether held together in the complex B· · ·A by a hydrogen bond, a tetrel bond, a pnictogen bond, a chalcogen bond or a halogen bond. In this article, we test this hypothesis for 11 Lewis bases and 23 Lewis acids. Thus, the values of D_e for 250 complexes B· · ·A covering the whole range of interaction types have been calculated *ab initio* at a high level of theory and fitted to Equation (2) (with the convenient choice $c' = 1.00$ kJ mol^{-1}) to yield N_B and E_A values for the individual molecules. It is concluded that Equation (2) does indeed lead to a reliable scale of nucleophilicities and electrophilicities for the specified Lewis bases and acids.

2. Computational Methods

The geometries of the isolated monomers and complexes have been optimized at the MP2/aug-cc-pVTZ computational level [19–21] with the Gaussian-09 program [22]. Frequency calculations at the same level have been carried out to confirm that the resulting geometry corresponds to an energy minimum. Using these geometries, a series of calculations have been performed to derive the complete basis set (CBS) extrapolation at MP2 level. In addition, CCSD(T)/aug-cc-pVTZ calculations [23] have been carried out with the MOLPRO program [24] to derive the CCSD(T)/CBS energy. The extrapolation scheme is divided in the three parts. The first one corresponds to the Hartree–Fock (HF) contribution that is obtained using the aug-cc-pVTZ (AVTZ, X = 3) in

Equations (3)–(6), aug-cc-pVQZ (AVQZ, X = 4) and aug-ccV5Z (AV5Z, X = 5) and Equations 1,2 [25]. In the second part, the MP2 correlation contribution is derived from the results obtained with MP2/aug-cc-pVTZ and MP2/aug-cc-pVQZ calculations and applying Equations (5)–(7) [26]. In the third part, higher order contributions are obtained as the difference of the CCSD(T)/aug-cc-pVTZ and MP2/aug-cc-pVTZ energies (Equation (6)) [27,28]. Finally, a CCSD(T)/CBS quality energy is generated by adding the E_{CBS}^{HF}, $E_{CBS}^{MP2corr}$ and $\Delta E_{AVTZ}^{CCSD(T)}$ (Equation (9)). The latter energy has been obtained for all systems and used to calculate the dissociation energy, D_e, of the complexes as the difference of the energy of the complex and the sum of the isolated monomers in their minimum geometry.

$$E_X^{HF} = E_{CBS}^{HF} + Ae^{-BX} \tag{3}$$

$$E_{CBS}^{HF} = E_{AVTZ}^{HF} - \frac{\left(E_{AVTZ}^{HF} - E_{AVQZ}^{HF}\right)^2}{\left(E_{AVTZ}^{HF} - 2E_{AVQZ}^{HF} + E_{AV5Z}^{HF}\right)} \tag{4}$$

$$E_X^{MP2corr} = E_X^{MP2} - E_X^{HF} \tag{5}$$

$$E_X^{MP2corr} = E_{CBS}^{MP2corr} + AX^{-3} \tag{6}$$

$$E_{CBS}^{MP2corr} = \frac{4^3 E_{AVQZ}^{MP2corr} - 3^3 E_{AVTZ}^{MP2corr}}{4^3 - 3^3} \tag{7}$$

$$\Delta E_{AVTZ}^{CCSD(T)} = E_{AVTZ}^{CCSD(T)} - E_{AVTZ}^{MP2} \tag{8}$$

$$E_{CBS}^{CCSD(T)} = E_{CBS}^{HF} + E_{CBS}^{MP2corr} + E_{AVTZ}^{CCSD(T)} \tag{9}$$

The D_e energies of all the complexes have been used to fit simultaneously the nucleophilicities and electrophilicities of the Lewis bases and Lewis acids studied by means of Equation (10).

$$D_e = \left(\sum_{i=1}^{\text{Lewis bases}} x_i \times N_{Bi}\right) \times \left(\sum_{j=1}^{\text{Lewis acids}} x_j \times E_{Aj}\right) \tag{10}$$

The values of x_i and x_j are 1.0 when the corresponding Lewis base or Lewis acid is present in the complex, and 0.0 if it is absent.

The molecular electrostatic surface potentials (MESP) of the isolated Lewis bases and Lewis acids in their minimum-energy configurations have been calculated at the MP2/aug-cc-pVTZ computational level and analyzed with the Multiwfn [29,30] and DAMQT [31] programs. In the Lewis acids, the maximum value on the 0.001 au electron density isosurface associated with the interaction, $V_{S,max}$, has been characterized. For the Lewis bases, two different values have been obtained. The first one, in analogy with the Lewis acids, is the minimum on the 0.001 au electron density isosurface, $V_{S,min}$. The second value avoids the arbitrariness of the isosurface value by evaluation of the real minimum, V_{min}.

3. Results

Table 1 displays values of N_B for 11 Lewis bases and E_A for 23 Lewis acids obtained from a least-squares fit of D_e values calculated *ab initio* for 250 binary complexes B···A by using Equation (10). We actually carried out calculations of D_e for the all of the 264 possible complexes that can be formed from the following 11 molecules B acting as Lewis bases: N_2, CO, HC≡CH, $CH_2=CH_2$, C_3H_6 (cyclopropane), PH_3, H_2S, HCN, H_2O, H_2CO and NH_3; and the following 24 molecules acting as Lewis acids: HF, HCl, HBr, HC≡CH, HCN, and H_2O (constituting the hydrogen-bonded group); F_2, Cl_2, Br_2, ClF, and BrCl (the halogen-bonded group); H_3SiF, H_3GeF, F_2CO, and CO_2 (the tetrel-bonded group); N_2O, NO_2F, PH_2F, and AsH_2F (the pnictogen-bonded group); and SO_2, SO_3, SeO_2, SF_2, and SeF_2 (the chalcogen-bonded group). The resulting D_e values are given in Tables 2–6, respectively, for these various classes of non-covalent interaction. The reasons that 14 values were excluded from the global

fit were as follows: (1) The complex $H_3P \cdots ClF$ is known [32] to have significant ion-pair character $[H_3PCl]^+ \cdots Cl^-$ with an enhanced D_e as a consequence and was excluded; (2) It was clear that several of the 11 complexes containing SO_3 as a Lewis acid considerably worsened the fit. We noted that each $B \cdots SO_3$ complex had much a larger D_e value than any of its $B \cdots A$ counterparts, possibly a sign of significant ionic character and accordingly these too were excluded from the fit; (3) The complexes $H_3P \cdots AsH_2F$ and $H_3P \cdots PH_2F$ were significant outliers when included in the fit, perhaps because in these complexes each molecule can act simultaneously as a Lewis acid and a Lewis base [6,33], in contrast to the rest of the complexes where each molecule has only a single role. The values in Table 1 indicate that the order of nucleophilicities of the Lewis bases is:

$N_2 < CO < HC{\equiv}CH \sim PH_3 < CH_2{=}CH_2 \sim C_3H_6 \sim H_2S < HCN < H_2O < H_2CO < NH_3$
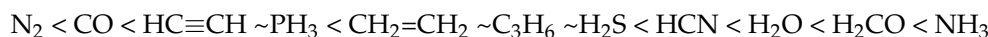
For the hydrogen-bonded complexes, the order of the electrophilicities of the Lewis acids is:

$HF < HBr \sim HCl < HCN \sim H_2O < HC{\equiv}CH$

The order among the halogen-bonded systems is:

$ClF > BrCl \sim Br_2 > Cl_2 > F_2$

Table 1. Values of nucleophilicities N_B of 11 Lewis bases B and electrophilicities E_A of 23 Lewis acids A obtained by fitting the dissociation energies D_e of 250 complexes $B \cdots A$ to Equation (10).

Lewis Base		Lewis Acid		Lewis Acid	
B	N_B	**A**	E_A	**A**	E_A
N_2	1.50	HF	6.75	SeO_2	5.76
$C{\equiv}O$	2.12	HBr	4.59	SeF_2	6.69
$HC{\equiv}CH$	3.13	HCl	4.36	SF_2	3.75
$H_2C{=}CH_2$	3.44	$HC{\equiv}N$	3.71	SO_2	2.92
C_3H_6	3.39	H_2O	3.74	AsH_2F	5.04
PH_3	3.12	$HC{\equiv}CH$	2.16	PH_2F	3.88
H_2S	3.43	ClF	5.18	NO_2F	2.55
$HC{\equiv}N$	4.27	BrCl	4.77	N_2O	1.80
$H_2C{=}O$	5.48	Br_2	4.40	GeH_3F	4.63
H_2O	4.89	Cl_2	2.71	SiH_3F	3.45
NH_3	7.52	F_2	1.13	$F_2C{=}O$	3.30
				CO_2	2.15

Table 2. Values of $D_e/(\text{kJ mol}^{-1})$ for 66 hydrogen-bonded complexes calculated *ab initio*.

Lewis Base	Lewis Acid					
	HF	**HBr**	**HCl**	**HC≡N**	**H₂O**	**HC≡CH**
N_2	10.34	6.21	5.81	5.37	5.43	3.40
CO	15.09	8.39	8.44	7.28	7.68	4.45
$HC{\equiv}CH$	18.84	13.07	12.22	10.30	10.83	6.22
$H_2C{=}CH_2$	19.15	14.34	12.56	9.93	10.64	5.96
C_3H_6	19.57	18.39	14.00	11.63	11.31	7.62
PH_3	20.15	12.90	12.97	10.10	10.13	5.51
H_2S	21.29	13.63	14.06	10.92	12.03	6.30
$HC{\equiv}N$	31.99	20.06	19.60	20.09	16.92	10.56
$H_2C{=}O$	35.38	24.57	23.46	19.87	23.01	13.42
H_2O	36.91	22.33	22.65	21.72	21.06	12.05
NH_3	52.81	36.69	34.75	27.28	27.07	15.15

Table 3. Values of $D_e/(\text{kJ mol}^{-1})$ for 55 halogen-bonded complexes calculated *ab initio*.

Lewis Base	Lewis Acid				
	ClF	**BrCl**	**Br$_2$**	**Cl$_2$**	**F$_2$**
N$_2$	7.35	7.98	7.93	4.20	2.33
CO	12.25	11.06	10.35	6.08	2.80
HC≡CH	15.96	16.23	15.38	8.99	3.89
H$_2$C=CH$_2$	18.79	19.14	18.33	10.16	4.31
C$_3$H$_6$	14.46	18.16	18.36	10.18	4.92
PH$_3$	38.56	19.35	17.85	10.28	3.54
H$_2$S	21.36	18.56	16.58	10.63	4.02
HC≡N	20.28	18.87	17.56	10.93	4.82
H$_2$C=O	24.70	22.76	21.02	13.69	6.16
H$_2$O	22.11	19.95	18.06	11.97	5.20
NH$_3$	43.96	35.37	31.63	19.98	7.57

Table 4. Values of $D_e/(\text{kJ mol}^{-1})$ for 44 tetrel-bonded complexes calculated *ab initio*.

Lewis Base	Lewis Acid			
	GeH$_3$F	**SiH$_3$F**	**F$_2$C=O**	**CO$_2$**
N$_2$	8.02	5.36	6.11	4.11
CO	10.23	7.59	7.57	4.97
HC≡CH	13.97	9.66	10.65	9.16
H$_2$C=CH$_2$	16.36	10.96	10.41	7.51
C$_3$H$_6$	17.05	9.88	11.47	8.99
PH$_3$	13.86	11.53	8.90	5.26
H$_2$S	13.93	11.48	10.41	6.80
HC≡N	22.05	14.92	14.72	9.27
H$_2$C=O	25.09	18.87	21.49	12.96
H$_2$O	22.04	16.41	17.67	12.38
NH$_3$	34.42	27.67	21.74	12.90

Table 5. Values of $D_e/(\text{kJ mol}^{-1})$ for 44 pnictogen-bonded complexes calculated *ab initio*.

Lewis Base	Lewis Acid			
	AsH$_2$F	**PH$_2$F**	**NO$_2$F**	**N$_2$O**
N$_2$	8.11	6.33	5.93	4.06
CO	12.41	10.00	7.19	4.77
HC≡CH	17.54	13.73	8.31	8.33
H$_2$C=CH$_2$	20.62	14.88	10.33	7.04
C$_3$H$_6$	17.23	11.44	10.75	8.35
PH$_3$	27.79	20.90	7.00	4.05
H$_2$S	17.50	14.55	8.02	5.88
HC≡N	22.76	16.69	12.51	8.11
H$_2$C=O	26.28	21.81	15.15	9.76
H$_2$O	22.84	18.02	11.83	9.86
NH$_3$	36.37	27.53	15.79	10.37

Table 6. Values of $D_e/(kJ\,mol^{-1})$ for 55 chalcogen-bonded complexes calculated *ab initio*.

Lewis Base	Lewis Acid				
	SO_3	SeF_2	SeO_2	SF_2	SO_2
N_2	6.30	8.95	7.21	5.24	0.92
CO	12.56	12.81	9.53	7.26	2.36
HC≡CH	19.92	22.08	17.21	12.14	8.17
$H_2C=CH_2$	23.30	26.21	18.31	13.03	7.97
C_3H_6	17.11	21.27	22.21	11.54	9.03
PH_3	43.73	23.27	14.86	11.72	8.71
H_2S	31.71	23.42	19.94	13.23	11.23
HC≡N	28.48	25.16	21.40	14.82	10.86
$H_2C=O$	43.80	36.64	37.14	21.95	19.53
H_2O	37.89	31.55	28.78	18.63	16.07
NH_3	99.23	51.06	42.70	28.14	22.20

The electrophilicity of the molecules forming chalcogen bonds via Se atoms are significantly larger than those involving S. Likewise, the AsH_2F molecule has a larger electrophilicity and forms stronger pnictogen bonds than its P analogue, and the same order obtains for the propensity to form of tetrel bonds in H_3GeF and H_3SiF containing complexes.

A plot of D_e from the *ab initio* calculations for the 250 complexes versus D_e values generated from Equation (10) by using the N_B and E_A values given in Table 1 is shown in Figure 1. The correlation coefficient is 0.959 and indicates strongly that Equation (10) represents a good approximation for the 250 complexes included in the fit, a group that includes the sub-classes of complex in which the non-covalent interaction is a hydrogen bond, a halogen bond, a tetrel bond, a pnictogen bond and a chalcogen bond. Thus, it appears that Equation (2) (and therefore Equation (10)) provides a method of assigning nucleophilicities and electrophilicities to Lewis bases and Lewis acids, respectively, when involved in a wide range of non-covalent interactions. Conversely, the N_B and E_A values provide a method of predicting D_e for a given complex B⋯A.
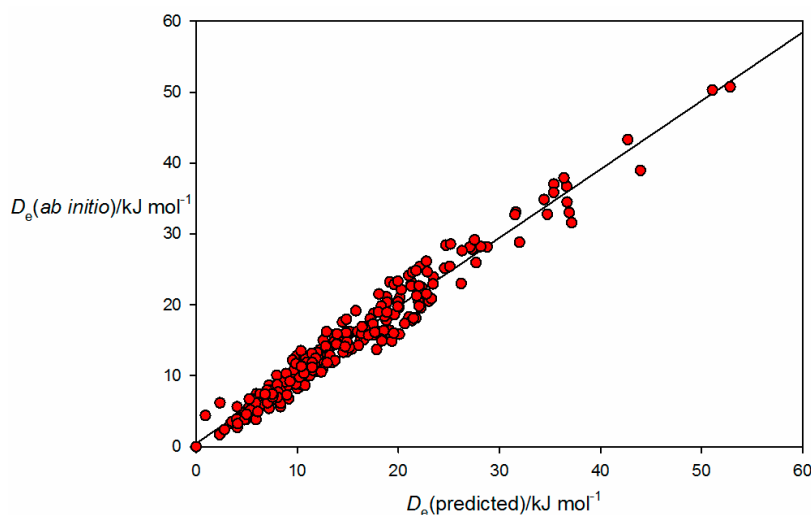
Figure 1. A graph of D_e values of 250 complexes B⋯A calculated *ab initio* versus values of D_e predicted from the nucleophilicities N_B and electrophilicites E_A of the 11 Lewis bases and the 24 Lewis acids, respectively (see Table 1), involved in the complexes.

It is instructive to discuss the behavior of the *ab initio* calculated D_e values of the B⋯A within a given non-covalent interaction type with the N_B values determined by the least-squares fit (see Table 1). This discussion will refer to the *ab initio* geometries of the six selected complexes shown in Figure 2.

Figure 3 shows the plot of D_e versus N_A for 44 hydrogen bonded complexes B· · · HX formed from the 11 Lewis bases with HF, HCl, HBr and HC≡CH. The geometry determined for cyclopropane· · · HCl is shown in Figure 2a, where it is seen that the HCl molecules lies along a median of the cyclopropane equilateral triangle and therefore the electrophilic H atom of HCl samples one of the pseudo-π bonds of cyclopropane, in agreement with experiment [34]. Complexes involving HCN and H_2O as the hydrogen donors are treated separately in Figure 4 because the points for the B· · · HCN and B· · · HOH complexes would be almost coincident with those associated with B· · · HCl and B· · · HBr if they were included in Figure 3. The individual straight lines represent the least-squares fit of the points for each B· · · HX series. The slope of each straight line is a measure of the electrophilicity of the given HX and corresponds approximately to the E_A value obtained in the global fit shown in Figure 1, as seen in Table 1.
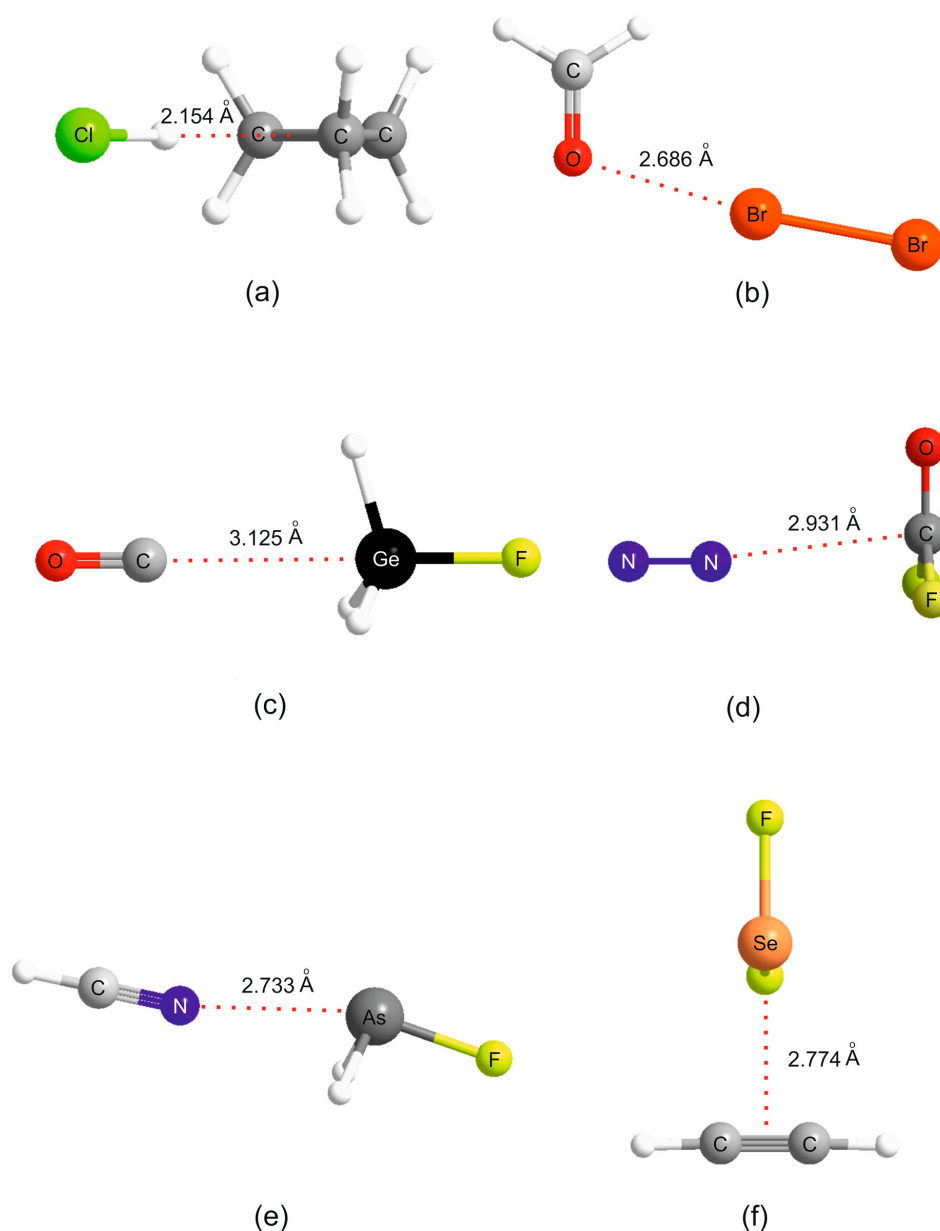
Figure 2. The geometries of selected complexes calculated *ab initio*. They provides examples of the following classes of non-covalent bonds: (**a**) a hydrogen-bond; (**b**) a halogen-bond; (**c,d**) different types of tetrel bond; (**e**) a pnictogen bond; and (**f**) a chalcogen bond. These examples are cited in the text when Figures 3–8 are discussed.
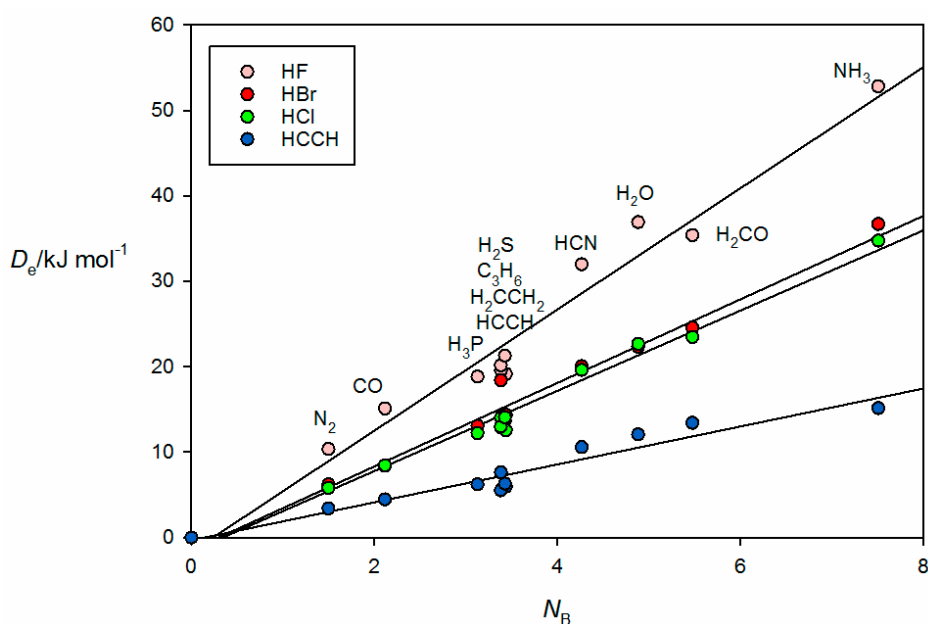
Figure 3. D_e versus N_B for the series of hydrogen-bonded complexes B···HF,B···HCl, B···HBr and B···HC≡CH (see Table 1 for N_B of the indicated Lewis bases B).
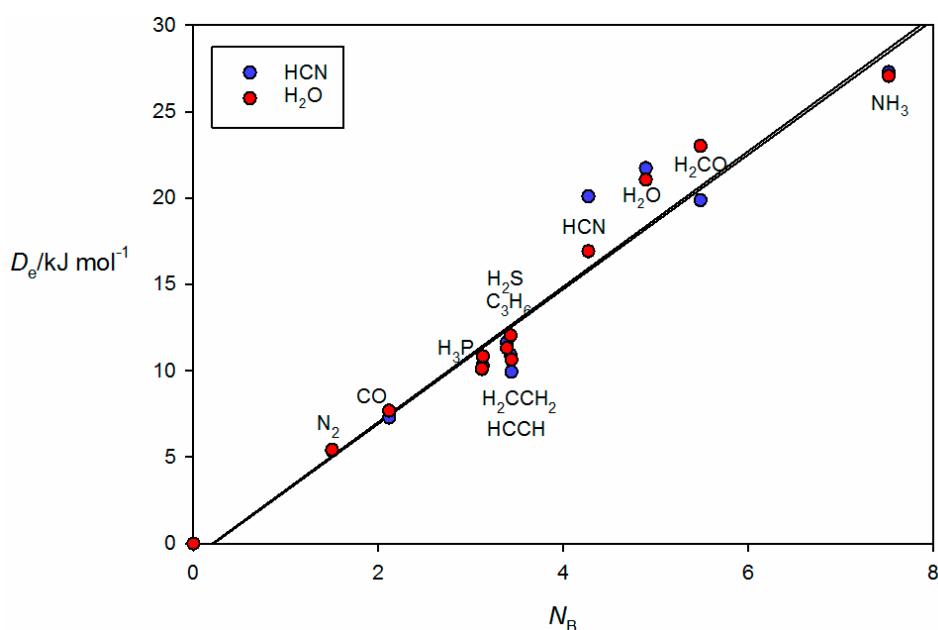

Figure 4. D_e versus N_B for the series of hydrogen-bonded complexes B···HCN and B···HOH (see Table 1 for N_B of the indicated Lewis bases B).

We note that, in Figures 3 and 4, there is a bunching of the points for B···HX, when B = PH$_3$, H$_2$S, HC≡CH, C$_3$H$_6$ and CH$_2$=CH$_2$ for each HX. The bunching is clearly systematic and independent of the HX molecule. Further, it is clear that the scatter of points from the appropriate straight line increases with the electrophilicity of HX.

The corresponding graph for the halogen-bonded complexes B···ClF, B···BrCl, B···Br$_2$, B···Cl$_2$ and B···F$_2$ is displayed in Figure 5. Note that, for reasons already given, the result for H$_3$P···ClF is omitted. The systematic bunching of complexes involving B = PH$_3$, H$_2$S, HC≡CH, C$_3$H$_6$ and CH$_2$=CH$_2$ for each XY and the increased scatter as the electrophilicity of the Lewis acid increases are

again apparent for the B$\cdots$XY. The geometry determined for H$_2$CO$\cdots$Br$_2$ (see Figure 2b) suggests that the axial σ hole at each Br atom in the Br$_2$ molecule lies along the direction of a nonbonding electron pair (n pair) on O, as conventionally envisaged. A similar geometry has been determined experimentally for H$_2$CO$\cdots$ClF [35]. Such interpretations led to sets of simple rules for predicting the geometries of hydrogen- and halogen-bonded complexes [3,36].
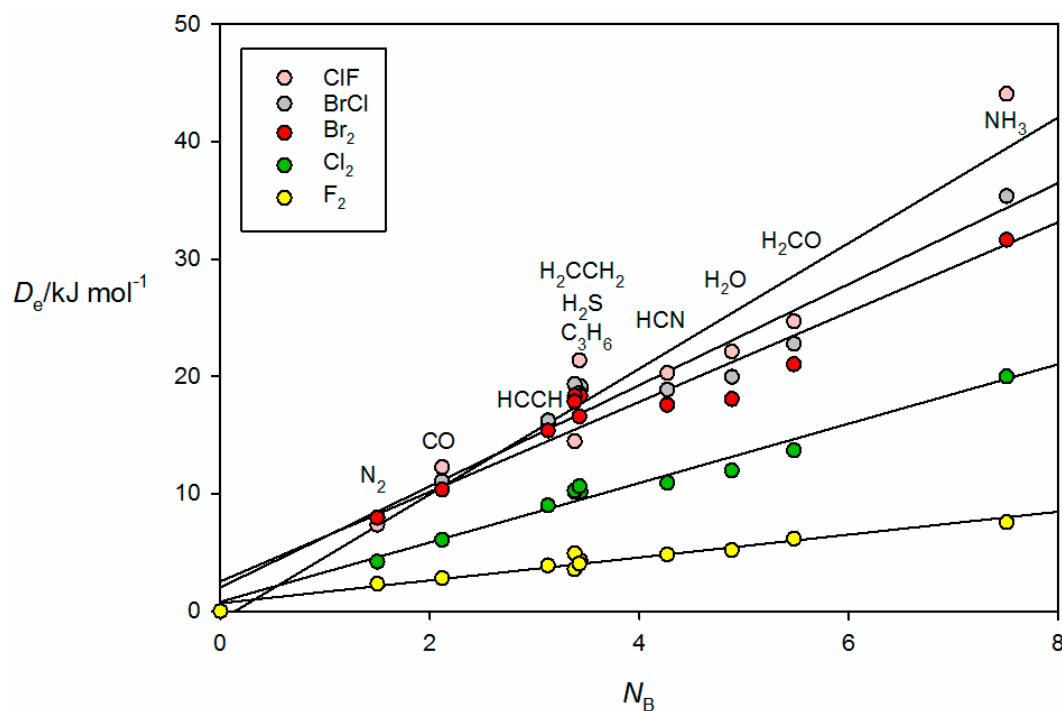

Figure 5. D_e versus N_B for the series of halogen-bonded complexes B$\cdots$XY, where XY = F$_2$, Cl$_2$, Br$_2$, BrCl and ClF (see Table 1 for the N_B values of the indicated Lewis bases B).

Figure 6 gives the results for tetrel-bonded complexes B$\cdots$CO$_2$, B$\cdots$H$_3$SiF, B$\cdots$H$_3$GeF and B$\cdots$F$_2$C=O when their *ab initio* values of D_e are plotted against N_B of the 11 Lewis bases B. For the B$\cdots$H$_3$SiF and B$\cdots$H$_3$GeF complexes, the tetrel bond involves the n- or π-electron pairs of the Lewis base interacting with a σ hole that lies near the Si or Ge atom on the C_3 axis, as can be clearly seen in the *ab initio* geometry determined for OC$\cdots$H$_3$GeF.shown in Figure 2c. The n-pair on the C atom of OC clearly interacts with the σ hole at Ge. F$_2$CO forms tetrel bonds of a different type. This planar molecule has a π-hole at the carbon atom which is perpendicular to the molecular plane and the n- or π-pair of electrons of a Lewis base can interact with this, as is evident from the geometry determined for N$_2\cdots$F$_2$CO complex displayed in Figure 2d. A π-hole at C is also involved in the tetrel bond in B$\cdots$CO$_2$. The systematic features identified for hydrogen- and halogen-bonded complexes in Figures 3–5 may also be seen in Figure 6.
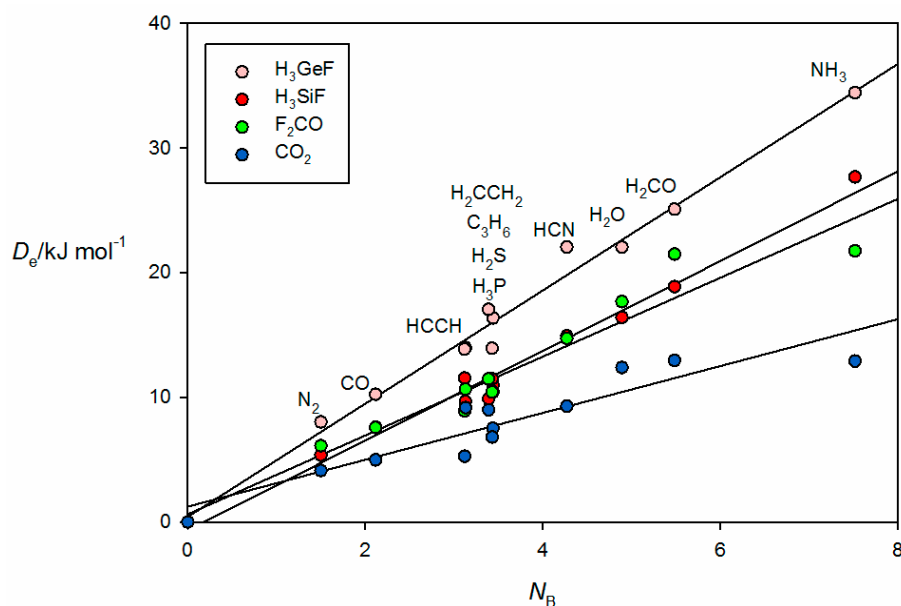
Figure 6. D_e versus N_B for the series of tetrel-bonded complexes B$\cdots$CO$_2$, B$\cdots$H$_3$SiF, B$\cdots$H$_3$GeF and B$\cdots$F$_2$C=O (see Table 1 for the N_B values of the indicated Lewis bases B).

The corresponding plots of D_e against N_B for the pnictogen-bonded complexes B$\cdots$PFH$_2$, B$\cdots$AsFH$_2$, B$\cdots$NO$_2$F and B$\cdots$N$_2$O are given in Figure 7. The first two groups of pnictogen-bonded complexes utilize a σ hole near P or As along the P–F or As–F bond direction to form the non-covalent bond, while for the last two groups a π hole at the central N atom fulfills the role. The *ab initio* geometry of HCN$\cdots$AsH$_2$F in Figure 2e provides evidence of the σ-hole type of interaction. The pattern displayed by the D_e values of the pnictogen-bonded complexes in Figure 7 is similar to that seen in Figure 6 for the tetrel-bonded systems and again involves the characteristic bunching of points for the complexes in which B = PH$_3$, H$_2$S, HC≡CH, C$_3$H$_6$ and CH$_2$=CH$_2$. Recall that, for reasons given earlier, complexes H$_3$P$\cdots$PFH$_2$ and H$_3$P$\cdots$AsFH$_2$ were excluded from the global fit in Figure 1 and therefore from Figure 7.
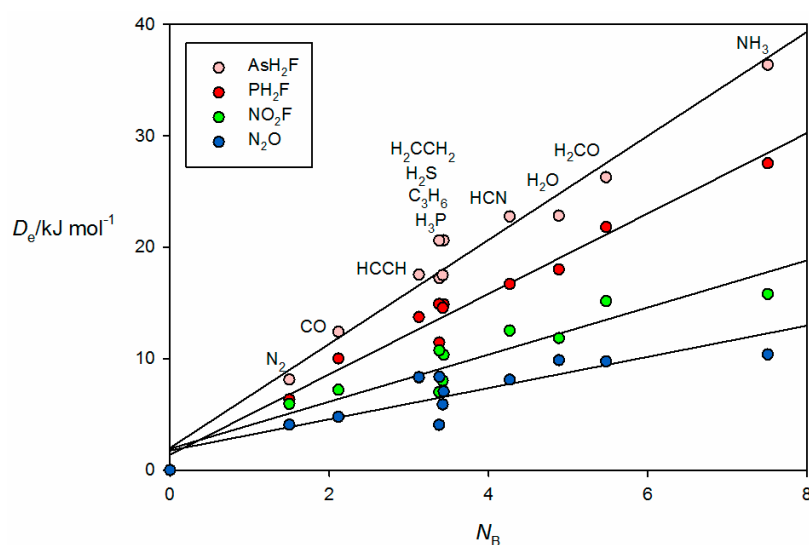

Figure 7. D_e versus N_B for the series of pnictogen-bonded complexes B$\cdots$PFH$_2$, B$\cdots$AsFH$_2$, B$\cdots$NO$_2$F and B$\cdots$N$_2$O (see Table 1 for the N_B values of the indicated Lewis bases B).

The familiar bunching pattern is again observed in Figure 8, in which the *ab initio* calculated values of D_e for complexes of the 11 Lewis bases B with each of the four Lewis acids SF_2, SeF_2, SO_2 and SeO_2 are plotted as a function of the N_B values of the various B. The complexes here all involve chalcogen bonds. In the B$\cdots SO_2$ and B$\cdots SeO_2$, the chalcogen bond is between a π hole at S or Se that is perpendicular to the plane containing the SO_2 or SeO_2 nuclei, but for B$\cdots SF_2$ and B$\cdots SeF_2$ a σ hole near S or Se at the termination of a S–F or Se–F bond is involved, as seen from the *ab initio* geometry of the complex formed by the interaction of π electrons of acetylene with the Se atom of SeF_2 shown in Figure 2f.
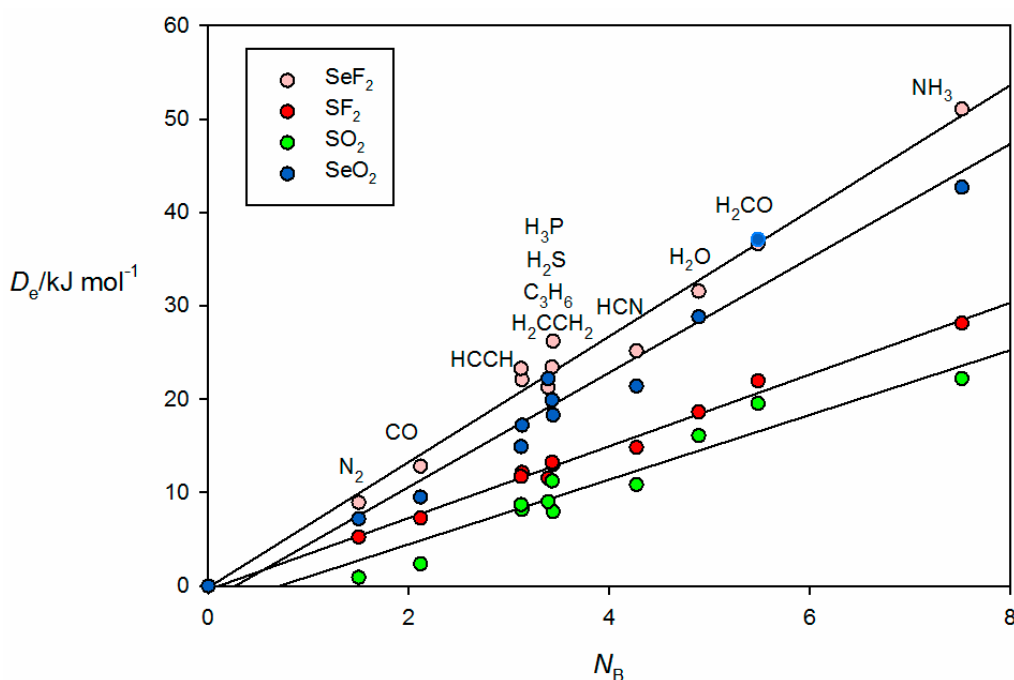

Figure 8. D_e versus N_B for the series of chalcogen-bonded complexes B$\cdots SeF_2$, B$\cdots SF_2$, B$\cdots SO_2$ and B$\cdots SeO_2$ (see Table 1 for the N_B values of the indicated Lewis bases B).

It is of interest to ask whether there exists a linear relationship between the calculated D_e values and the intermolecular distances in the various complexes B$\cdots$A investigated. For this purpose, the intermolecular distances of the hydrogen-bonded complexes have been gathered in Table 7 while the intermolecular distances for the rest of the complexes are given in Tables S1–S4 (Supplementary Materials). (The full optimized geometries of all the systems are gathered in Table S5 of the Supplementary Materials). When seeking a linear relationship between the calculated D_e values (given in Table 2) and the intermolecular distances of all complexes a poor R^2 value of 0.68 results. A more detailed analysis considering the individual hydrogen-bonded donors with all the bases ($n = 11$ for each correlation) reveals values of R^2 between 0.80 and 0.53 (Table S6). Alternatively, looking to the correlation for a given base with the different HB donors ($n = 5$ for each correlation), leads to R^2 values between 0.94 and 0.53. Similar results are obtained for the rest of the interactions considered here (Table S6). Thus, it is clear that the D_e values and the intermolecular distances are poorly correlated for the systems considered and consequently cannot be used to predict each other.

Table 7. Intermolecular distances $r(B\cdots H)/\text{Å}$ between the atom of the B and the H atom of A involved in the hydrogen-bond interaction in 66 hydrogen-bonded complexes.

Lewis Base	Lewis Acid					
	HF	**HBr**	**HCl**	**HC≡N**	**H$_2$O**	**HC≡CH**
N$_2$	2.055	2.342	2.297	2.412	2.318	2.499
C≡O	2.057	2.355	2.301	2.490	2.337	2.600
HC≡CH	2.125	2.301	2.292	2.498	2.348	2.602
H$_2$C=CH$_2$	2.129	2.309	2.297	2.540	2.367	2.645
C$_3$H$_6$	2.024	2.158	2.154	2.314	2.421	2.249
PH$_3$	2.336	2.519	2.505	2.794	2.615	2.926
H$_2$S	2.268	2.434	2.416	2.670	2.513	2.795
HC≡N	1.835	2.052	2.015	2.186	2.089	2.321
H$_2$C=O	1.708	1.840	1.830	2.075	1.972	2.225
H$_2$O	1.704	1.893	1.863	2.044	1.945	2.188
NH$_3$	1.679	1.687	1.738	2.102	1.957	2.259

Parameters used in the literature to rationalize the D_e values are the molecular electrostatic potential values of the isolated bases ($V_{S,min}$ and V_{min}) or acids ($V_{S,max}$) (see Section 2. for the definitions of the various quantities V). The corresponding values have been gathered in Table S7. The comparison of the D_e values of the complexes of each Lewis acids with the $V_{S,min}$ or V_{min} of the Lewis bases ($n = 11$ for each correlation) provide R^2 values between 0.95 and 0.37 and between 0.97 and 0.43, respectively. Alternatively, the relationship of the $V_{S,max}$ of the Lewis acids with the corresponding D_e values for a single Lewis base ($n = 24$) show R^2 values between 0.75 and 0.25 (Table S8). Attempts to use simultaneously $V_{S,min}$ of the Lewis bases and $V_{S,max}$ of the Lewis acids in conjunction with the intermolecular distances for all the systems provide R^2 values smaller than 0.56. As in the case of the intermolecular distances, these parameters do not seem to be useful as predictive tool, save in closely related systems.

4. Conclusions

It has been shown that the dissociation energy D_e for the reaction $B\cdots A = B + A$ for 250 complexes $B\cdots A$ composed of 11 Lewis bases B and 23 Lewis acids can be represented to good approximation by means of the equation $D_e = c'N_B E_A$, in which N_B is a numerical nucleophilicity assigned to B, E_A is a numerical electrophilicity assigned to A, and c' is a constant, conveniently chosen to have the value 1.00 kJ mol^{-1} here. The 250 complexes were chosen to cover a wide range of non-covalent interaction types, namely: (1) the hydrogen bond; (2) the halogen bond; (3) the tetrel bond; (4) the pnictogen bond; and (5) the chalcogen bond. There was no evidence that one group of non-covalent interaction was fitted any better than the others. Therefore, the equation appears to be equally valid for all the interactions considered here and the values of N_B and E_A determined in the manner discussed appear to be valid properties of the individual molecules. The values of N_B and E_A can therefore be used from to predict the dissociation energies of a wide range of binary complexes $B\cdots A$ with reasonable accuracy.

If the weak interaction in the complexes $B\cdots A$ considered here is predominantly electrostatic in nature, it seems reasonable that the individual molecular properties N_B and E_A are related to the molecular electrostatic surface potentials in the regions of the molecules to which these properties apply. We attempted to test this by examining the product of the maximum positive surface potential (to represent the electrophilic region of molecule A) and the maximum negative surface potential (to represent the nucleophilic region of molecule B) but the correlation was poor.

$r(\text{B}\cdots\text{X})/\text{Å}$ between the atom of the B and the Z atom of A involved in the pnictogen-bond interaction in 44 pnictogen-bonded complexes, Table S4: Intermolecular distances $r(\text{B}\cdots\text{X})/\text{Å}$ between the atom of the B and the Y atom of A involved in the chalcogen-bond interaction in 55 chalcogen-bonded complexes, Table S5: Optimized geometries (Å, °) and energies (Hartree) at MP2/aug-cc-pVTZ computational level, Table S6: Linear correlations of D_e vs. the interatomic distance (R^2 coefficients), Table S7: $V_{S,min}$ and V_{min} of the Lewis Bases and $V_{S,max}$ of the Lewis acids. The 0.001 au electron density isosurface has been chosen to calculate $V_{S,min}$ and $V_{S,max}$, Table S8: Linear correlations of D_e vs. the MEP parameters ($V_{S,max}$ $V_{S,min}$ and V_{min}) (R^2 coefficients)

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