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Nucleophilicity of diatomic Lewis bases MA in hydrogen-bonded complexes MA...HX: influence of the group and row of M in the periodic table†

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Nucleophilicities N_{MA} of diatomic Lewis bases MA acting as hydrogen-bond acceptors in complexes MA...HX are reported. The molecules MA were chosen so that the atom M adjacent to the atoms A directly involved in the hydrogen bonds belongs to Groups 13, 14, 15, 16 and 17 of the periodic table. The effects of changing atom M from rows 1 to 4 within a given group were also investigated. The hydrogen-bond donors HX involved in the complexes were HF, HCl, HBr, HI, HCCH, and HCP. Nucleophilicities N_{MA} were determined from dissociation energies D_e for the process MA...HX = MA + HX by using $D_e = cN_{MA}E_{HX} + d$, where E_{HX} are electrophilicities of the Lewis acids HX, and c and d are constants. The order of N_{MA} values was found to be Row 4 > Row 3 ~ Row 2 >> Row 1 in each of the Groups 13, 15, 16 and 17. The effect of adding an H atom to MA to give linear triatomic molecules HMA were considered. The reduced nucleophilicities $I_{MA} = N_{MA}/\sigma_{min}$ (σ_{min} is the minimum value of the molecular electrostatic surface potential of MA) as a function of the group and row of atom M were also discussed for diatomic molecules MA.

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1. Introduction

In a recent article,¹ we discussed how the gas-phase nucleophilicity of atoms A in hydrides H_nA involved in hydrogen-bonded complexes $H_nA...HX$ (X = F, Cl, Br, I CCH, CP) varied with the group and row of atom A in the periodic table. Atoms A considered spanned Groups 13, 14, 15, 16 and 17 of the Table. Within a given group, the hydrides H_nA from Rows 1, 2, 3 and 4 were investigated. It was discovered that the nucleophilicity of atom A (which is adjacent to the hydrogen atom of HX and therefore directly involved in the hydrogen bond) varied in the order Row 1 >> Row 2 > Row 3 > Row 4 in each of the Groups 13, 15, 16 and 17, with a large decrease from Row 1 to Row 2 but with only small decreases from Rows 2 to 3 to 4.

Here we focus attention again on the effect of changing the group and row of atoms in the periodic table on the nucleophilicity, but now the atom of interest (generically labelled M) in the Lewis base is not the atom A directly involved in a hydrogen bond. Instead, it is the atom M adjacent to atom A, herein after referred to as the adjacent atom. For simplicity, we

shall focus our attention mainly on diatomic Lewis bases, denoted as MA, and their participation in hydrogen-bonded complexes MA...HX. Atoms M belonging to Rows 1 to 4 of Groups 13 to 17 and Rows 1–4 of the periodic table will be considered. An investigation of the effect of substituting the Lewis base by linear triatomic molecules HMA is also presented.

A brief history of the term ‘nucleophilicity’ and scales of nucleophilicity is available in ref. 1, with reference to contributions of Ingold,² Swain and Scott,³ Ritchie,⁴ and Mayr.^{5,6} Here, we employ the gas-phase nucleophilicity N_{MA} (or N_{HMA}). The compound adjective gas-phase signifies that this quantity applies to an interacting pair of Lewis base and Lewis acid molecules in isolation. N_{MA} is defined in terms of the equilibrium dissociation energy D_e for the process MA...HX = MA + HX and the electrophilicity E_{HX} of the Lewis acid by means of eqn (1):

$$D_e = cN_{MA}E_{HX} + d \quad (1)$$

The evolution of eqn (1) from an initial proposal⁷ is described in ref. 1. When, as here, D_e values are calculated in units of kJ mol^{-1} it is convenient to define the constant $c = 1 \text{ kJ mol}^{-1}$. Then, N_{MA} and E_{HX} can be taken as dimensionless. In many cases investigated so far⁸ (but not always), d is zero within experimental error. The values of D_e employed here were calculated *ab initio* at the CCSD(T)(F12c)/cc-pVDZ-F12 level of theory. In the following sections, we discuss the variation of nucleophilicities N_{MA} (and of their relatives N_{HMA}) as a function of the group and row in the periodic table of atom M. Systematic variations within sets of

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† Dedicated to Professor Resnati, celebrating a career in fluorine and noncovalent chemistry on the occasion of his 70th birthday.



hydrogen bonds in $\text{MA} \cdots \text{HX}$ (or $\text{HMA} \cdots \text{HX}$) will be sought. The nucleophilicities are obtained from the gradients N_{MA} (or N_{HMA}) of straight-line graphs of D_e/c versus E_{HX} . The values of E_{HX} used (6.75, 4.35, 2.16 and 2.02, when $\text{X} = \text{F}$, Cl , CCH and CP , respectively) were obtained from a least-squares fitting procedure, as set out in ref. 9. The values $E_{\text{HBr}} = 3.94$ and $E_{\text{HI}} = 2.77$ employed are recent revisions quoted in ref. 10.

2. Computational methods

The geometries of both monomeric and complex species were optimized by employing the CCSD(T)-F12c level of theory in combination with the cc-pVDZ-F12 basis set.^{11–13} For these calculations, the frozen-core approximation was applied across all systems. In those cases, 10(Sn), 13(Ga) and 13(In) electrons were included in the correlation treatment—rather than the standard 4, 3 and 3, respectively—to mitigate interference between core and valence orbitals.

To account for basis set superposition errors (BSSE), the full counterpoise correction technique developed by Boys and Bernardi¹⁴ was implemented. All quantum chemical computations were performed using the MOLPRO software suite.¹⁵ Molecular electrostatic potentials (MESP) were evaluated on the 0.001 au electron density iso-surface for isolated monomers MA. These calculations were executed at the MP2/aug-cc-pVTZ level¹⁶ of theory *via* Gaussian-16.¹⁷ Post-processing and analysis of the MESP data were carried out using the Multiwfn package.¹⁸

3. Results

3.1 The hydrogen bond acceptor is a diatomic Lewis base

3.1.1 The adjacent atom in the diatomic Lewis base belongs to Group 13. The Group 13 atoms $\text{M} = \text{B}$, Al , Ga , and In have the interesting property that their hydrides HM form hydrogen bonds of two types: $\text{H-M} \cdots \text{HX}$ and $\text{M-H} \cdots \text{HX}$.^{19,20} For a given M and HX , the latter are more strongly bound (according to the D_e criterion) than the corresponding more conventional hydrogen-bonded systems $\text{H-M} \cdots \text{HX}$, as discussed elsewhere in ref. 19 and 20. These Group 13 atoms can also form monofluorides²¹ M-F that can participate in hydrogen-bonded complexes $\text{M-F} \cdots \text{HX}$, because the axial region of the F atom is nucleophilic (see later). The complexes $\text{M-F} \cdots \text{HX}$ are of more relevance to this discussion than those of the monohydrides. Thus, graphs of D_e/c versus E_{HX} for the series $\text{M-F} \cdots \text{HX}$ are shown in Fig. 1.

Note from Fig. 1 that when the atom M adjacent to that directly involved in the hydrogen bond (the adjacent atom) belongs to Group 13 of the periodic table, the order of the gradients (and therefore of the nucleophilicities of the atoms F of MF) is $\text{In} > \text{Ga} > \text{Al} \gg \text{B}$. Thus, the nucleophilicity of the F atom increases with the row number of the adjacent atom. In fact, when the adjacent atom is boron, the complexes are barely bound.

3.1.2 The adjacent atom in the diatomic Lewis base belongs to Group 14 of the periodic table. There are two convenient groups of diatomic Lewis bases to be considered

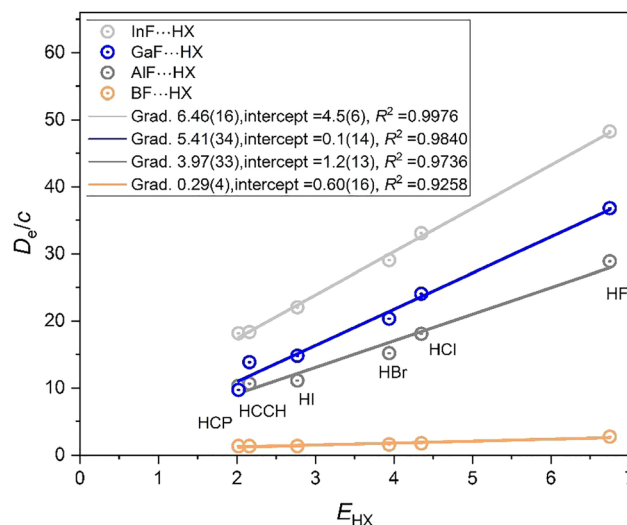


Fig. 1 Graphs of D_e/c for the four series of hydrogen-bonded complexes $\text{MF} \cdots \text{HX}$ ($\text{M} = \text{B}$, Al , Ga , In , and $\text{X} = \text{F}$, Cl , Br , I , CCH , CP). In each complex the atom M adjacent to that (F) directly involved in the hydrogen bond belongs to Group 13 of the periodic table.

here that form hydrogen-bonded complexes with molecules HX and in which the adjacent atom belongs to Group 14. These are MO and MS , where $\text{M} = \text{C}$, Si , Ge , or Sn . Fig. 2 and 3 show the graphs of D_e/c versus E_{HX} for the two series $\text{MO} \cdots \text{HX}$ and $\text{MS} \cdots \text{HX}$, respectively.

Fig. 2 indicates clearly that the gradients (and therefore the nucleophilicities of the atom O directly involved in the hydrogen bond) lie in the order $\text{SnO} > \text{GeO} \sim \text{SiO} \gg \text{CO}$, that is N_{MO} is greatest when the adjacent atom belongs to Row 4 of the periodic table, and the values decrease as the row in the table decreases.

This pattern is repeated in Fig. 3. The order of nucleophilicities N_{MS} is again $\text{SnS} > \text{GeS} \sim \text{SiS} \gg \text{CS}$ and in fact

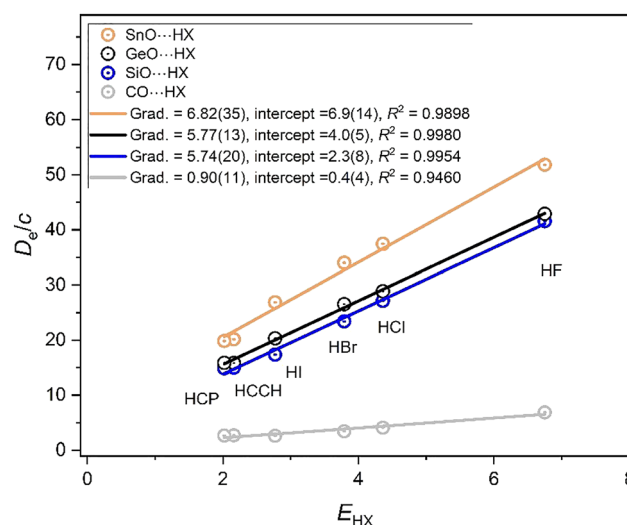


Fig. 2 Graphs of D_e/c versus E_{HX} for the four series $\text{MO} \cdots \text{HX}$ ($\text{M} = \text{C}$, Si , Ge and Sn , and $\text{X} = \text{F}$, Cl , Br , I , CCH , and CP), in which the atom M adjacent to that (O) directly involved in the hydrogen bond belongs to Group 14.



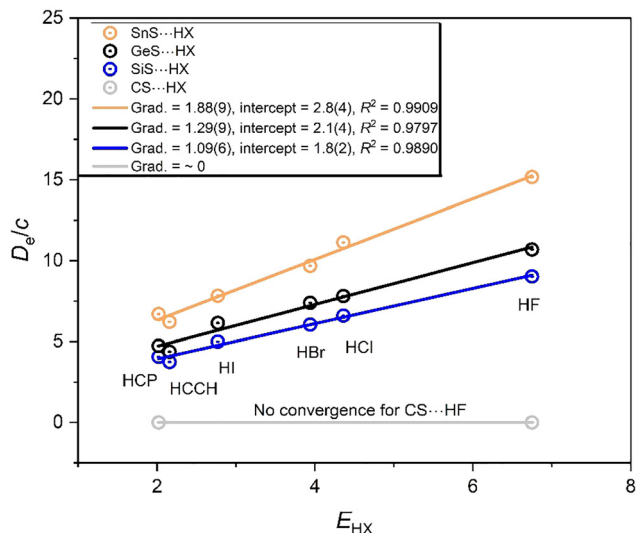


Fig. 3 Graphs of D_e/c for the four series $MS \cdots HX$ ($M = C, Si, Ge, Sn$, and $X = F, Cl, Br, I, CCH, CP$), in which the atom M adjacent to that (S) directly involved in the hydrogen bond belongs to Group 14.

complexes $CS \cdots HX$ are essentially unbound, indicating that the nucleophilicity of the S atom in this context is effectively zero. The patterns of the straight lines in Fig. 1–3 are very similar.

3.1.3 The adjacent atom in the diatomic Lewis base belongs to group 15 of the periodic table. The complexes in which the adjacent atom is from Group 15 of the periodic table were chosen as the set $MN \cdots HX$, in which $M = N, P, As$ or Sb and $X = F, Cl, Br, I, CCH, CP$. The corresponding graphs of D_e/c versus E_{HX} are in Fig. 4. It is clear from Fig. 4 that the gradients of the straight-line graphs are again in the order of the atoms in the rows 4, 3, 2, 1 in Group 15, that is $Sb > As \sim P \gg N$. Evidently, the nucleophilicity of the atom involved directly in the hydrogen bond is greatly enhanced when the adjacent atom is from Row 4 relative to that from Row 1. The enhancement is less (but nearly equal) when the adjacent atoms are from Rows 2 and 3.

3.1.4 The adjacent atom in the diatomic Lewis base belongs to Group 16 of the periodic table. Here an appropriate choice of the diatomic Lewis bases is the series MC , in which the adjacent atom $M = O, S, Se$ or Te . The four graphs of D_e/c versus E_{HX} are set out in Fig. 5. The order of the nucleophilicities of the atoms M in the diatomic molecules MC with respect to hydrogen bond formation are again $M = Te > Se \sim S \gg O$. This appears to be a property common to all the adjacent atoms M in diatomic Lewis bases MA so far investigated, namely that the atom from Row 4 leads to the largest enhancement of the nucleophilicity relative to that of the Row 1 atom, while the Row 2 and 3 atoms lead to lesser but nearly equal increase.

3.1.5 The adjacent atom in the diatomic Lewis base belongs to Group 17 of the periodic table. Although the most common valency of the atoms in Group 13 is three, it turns out that, for example, $F-B$ is a known compound that has been investigated both theoretically and spectroscopically.^{21,22} It is therefore possible to examine the boron mono-halides $M-B$ ($M = F, Cl, Br, I$) as an appropriate series of diatomic molecules

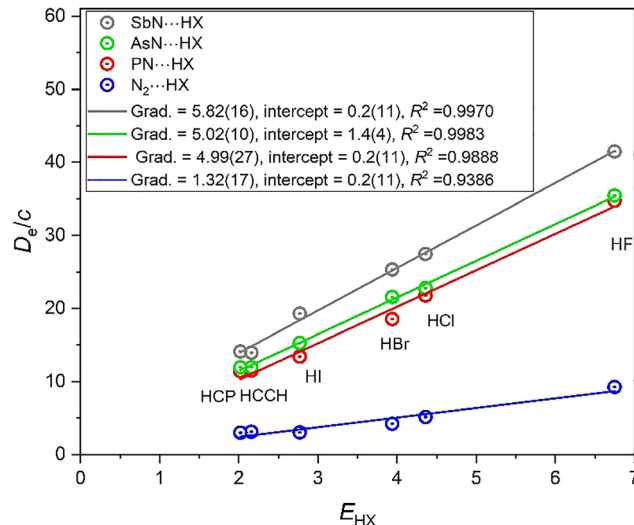


Fig. 4 Graphs of D_e/c for the four series $MN \cdots HX$ ($M = N, P, As, Sb$, and $X = F, Cl, Br, I, CCH, CP$) in which the atom M adjacent to that (N) directly involved in the hydrogen bond belongs to Group 15.

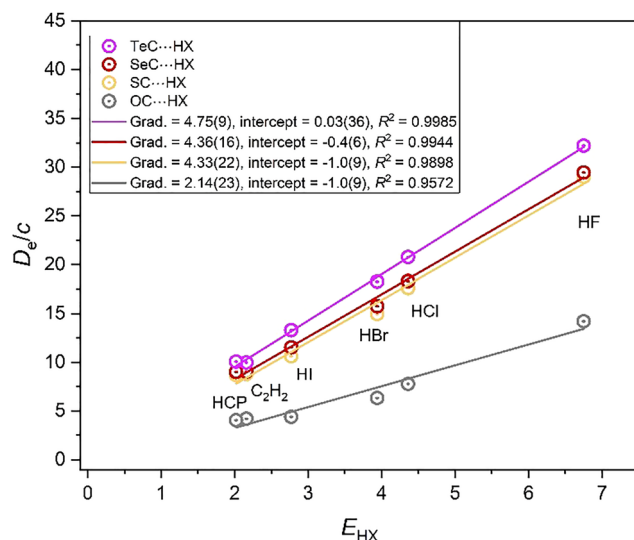


Fig. 5 Graphs of D_e/c for the four series $MC \cdots HX$ ($M = O, S, Se, Te$, and $X = F, Cl, Br, I, CCH, CP$) in which the atom M adjacent to that (C) directly involved in the hydrogen bond belongs to group 16.

to form hydrogen-bonded complexes of the type $M-B \cdots HX$ and therefore that in which the adjacent atom M is from Group 17 of the periodic table. Graphs of D_e/c versus E_{HX} for this series are displayed in Fig. 6. Two observations can be made about Fig. 6. First, the spread of gradients is much smaller than observed in Fig. 1–5. Secondly, the order of the gradients when the adjacent atom M is a halogen is different from those noted previously. No longer does the Row 4 adjacent atom I confer the largest enhancement of nucleophilicity on the boron atom. Cl now fulfils that role.

Thus, an unambiguous conclusion is not possible in this case.

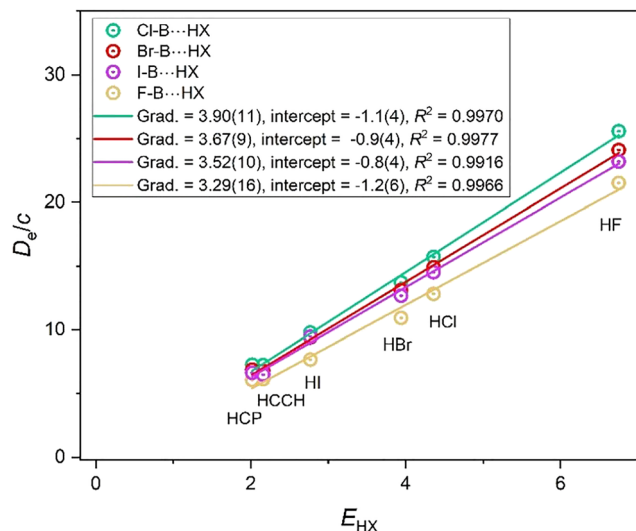


Fig. 6 Graphs of D_e/c for the four series $MB \cdots HX$ ($M = F, Cl, Br, I$, and $X = F, Cl, Br, I, CCH, CP$) in which the atom M adjacent to that directly involved in the hydrogen bond belongs to Group 17 of the periodic table.

3.2 The hydrogen-bond acceptor is a linear triatomic molecule HMA

The general conclusion from Section 3.1 is that the nucleophilicity of the atom A of a diatomic molecule MA directly involved in a hydrogen bond complex $MA \cdots HX$ formed with Lewis acids HX ($X = F, Cl, Br, I, CCH, CP$) varies in a systematic way with the group and row of M in the periodic table. Thus, when the adjacent atom M belongs to one of the Groups 13–17 of the periodic table, the nucleophilicity of atom A varies with rows according to $Row\ 4 > Row\ 3 \geq Row\ 2 \gg Row\ 1$, although the example when M is a Group 17 atom is possibly an exception. It is of interest to examine whether a similar pattern emerges when the hydrogen-bond acceptor molecule consists of a hydrogen atom added to MA to yield triatomic molecule HMA in which M is again the adjacent atom. We consider three cases: HMO (M is a Group 13 atom), HMN (M is a Group 14 atom) and HMC (M is a Group 15 atom). Hydrogen bonds with O of HMO were investigated recently,²³ while HNC and HCN as Lewis bases are well known.

3.2.1 The adjacent atom M resides in Group 13 of the periodic table. The example chosen in this category is $HMO \cdots HX$, with $M = B, Al, Ga$ or In and $A = O$. Fig. 7 shows the D_e/c versus E_{HX} graphs for the four series $HMO \cdots HX$ ($X = F, Cl, Br, I, CCH, CP$). The order of the nucleophilicity of the O atom in its direct involvement in a hydrogen bond is now $M = Al > Ga \sim In \gg B$. Recall that this order represents a change from that $In > Ga \sim Al \gg B$ given in Fig. 1 for the series $MF \cdots HX$. Row 4 (In) and Row 2 (Al) atoms are now interchanged.

3.2.2 The adjacent atom M resides in Group 14 of the periodic table. A convenient series of hydrogen-bonded complexes $HMA \cdots HX$ in which M is from Group 14 of the periodic table is $HMN \cdots HX$, where $M = C, Si, Ge$ or Sn . Thus, the HMN are analogues of hydrocyanic acid. The graphs of D_e/c versus E_{HX} for this series are set out in Fig. 8. HSiN now has the largest

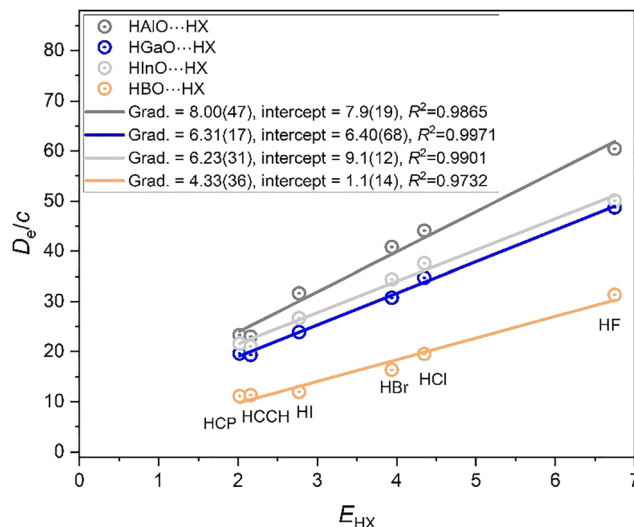


Fig. 7 Graphs of D_e/c for the four series $HMO \cdots HX$ ($M = B, Al, Ga, In$, and $X = F, Cl, Br, I, CCH, CP$) in which the adjacent atom M directly involved in the hydrogen bond belongs to Group 13.

gradient and nucleophilicity, while those associated with HGeN, HSnN and HCN are equal within the standard errors of the fit but smaller than that of HSiN. The order is thus different from that observed in Section 3.1 for the various series $MA \cdots HX$.

3.2.3 The adjacent atom resides in Group 15 of the periodic table. An example of a group of triatomic molecules capable of forming hydrogen bonds in which the atom adjacent to that directly involved in a hydrogen bond to HX resides in Group 15 of the periodic table are those related to HNC, namely HMC, where $M = N, P, As, Sb$. Fig. 9 carries the D_e/c versus E_{HX} graphs for the four series $HNC \cdots HX$ ($M = N, P, As, Sb$). The gradients are in the order $Row\ 1 > Row\ 2 > Row\ 3 > Row\ 4$. This order is reversed from that ($Row\ 4 > Row\ 3 \sim Row\ 2 \gg Row\ 1$) found in

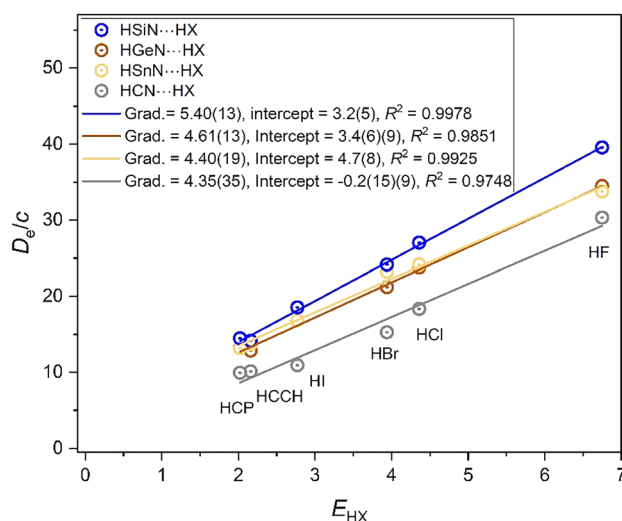


Fig. 8 Graphs of D_e/c versus E_{HX} for the four series $HMN \cdots HX$ ($M = C, Si, Ge, Sn$, ($X = F, Cl, Br, I, CCH, CP$) in which the atom M adjacent to that directly involved in the hydrogen bond belongs to Group 14.



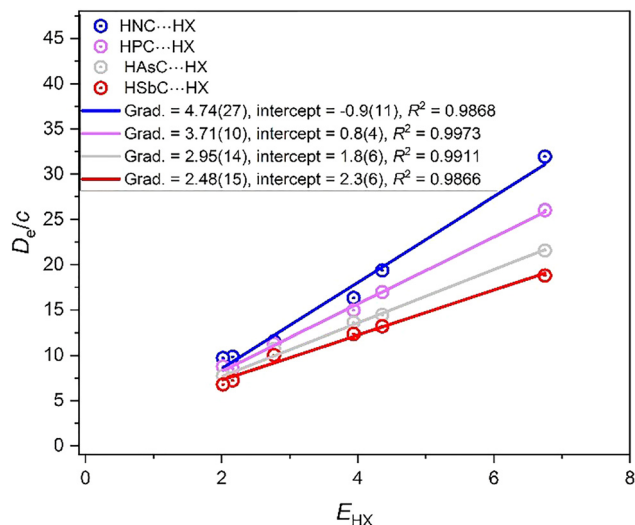


Fig. 9 Graphs of D_e/c versus E_{HX} for the four series HMC...HX ($M = N, P, As, Sb$), ($X = F, Cl, Br, I, CCH, CP$) in which the atoms M are adjacent to that (C) directly involved in the hydrogen bond belongs to group 15.

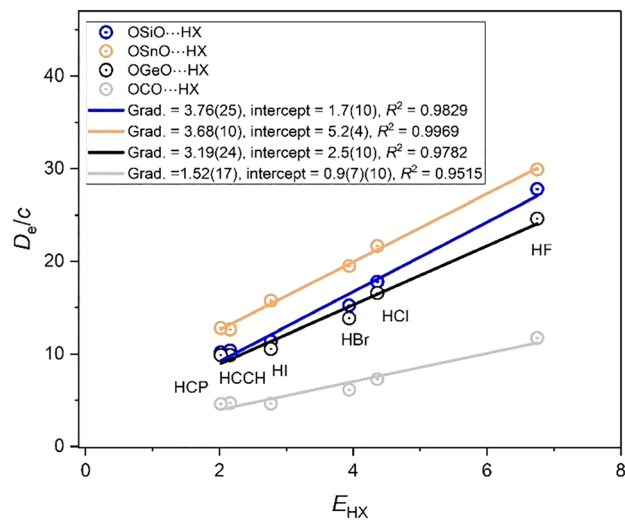


Fig. 10 Graphs of D_e/c versus E_{HX} for the four series OMO...HX ($M = C, Si, Ge, Sn$), ($X = F, Cl, Br, I, CCH, CP$) in which the atom M adjacent to the O atom directly involved in the hydrogen bond belongs to Group 14.

Fig. 4 for the series $MN \cdots HX$ in which the diatomic Lewis bases were N_2 , PN , AsN and SbN .

A more direct comparison of the effect on nucleophilicity of converting a diatomic Lewis base to a linear triatomic molecule is possible by comparing the series $OMO \cdots HX$ with that $MO \cdots HX$ ($M = C, Si, Ge, Sn$). The latter series was discussed with the aid of Fig. 2. The graphs of D_e/c versus E_{HX} for the series $OMO \cdots HX$ ($M = C, Si, Ge, Sn$) are in Fig. 10.

The gradients (and therefore the nucleophilicities of the O atom directly involved in the hydrogen bond) are in the order $Si \sim Sn \sim Ge \gg C$. The result from Fig. 2 for the $MO \cdots HX$ series is $Sn > Ge \sim Si \gg C$. Thus, the conversion of Lewis base MO to OMO appears to change the order of the nucleophilicities of the O atom involved in the hydrogen bond but these do involve quite large standard errors.

The general conclusion from considering hydrogen-bonded complexes $HMA \cdots HX$ formed from linear triatomic molecules HMA is that the systematic pattern observed for various series $MA \cdots HX$ considered in Section 3.1 is destroyed by attaching a hydrogen to the adjacent atom M .

3.3 Reduced nucleophilicities of diatomic Lewis bases MA

If hydrogen-bonded complexes can be described as having a significant electrostatic contribution to the H-bond interaction energy, an important property of an axially symmetric Lewis base molecule (such as those MA discussed in this article) involved is the so-called molecular electrostatic surface potential (MESP),²⁴ which is commonly defined as the value of the electrostatic potential energy of a proton at the 0.001 e bohr⁻³ electron-density iso-surface of the molecule. Such Lewis bases have a non-bonding electron pair on the symmetry axis that is associated with the atom directly involved in the hydrogen bond. The MESP on the molecular axis, near that atom, is usually the minimum (most negative) value associated with the molecule and is assigned the symbol σ_{min} . As discussed

elsewhere,^{9,10} it is possible to define, through eqn (2), a reduced nucleophilicity I_{MA} for a Lewis base MA as follows:

$$I_{MA} = cN_{MA}/\sigma_{min} \quad (2)$$

Eqn (2) was tested for several groups of simple, axially symmetric Lewis bases, each carrying a non-bonding electron pair on the symmetry axis.^{9,10} The terminal atom M of all members of a given group of complexes $MA \cdots HX$ was identical but was varied from group to group. Examples of groups were $(RC, R = O, S, Se)$, $(RCN, R = CH_3, H, F)$, $(RNC, R = CH_3, H, F)$, and so on. Within a given group, the quantity I obtained via eqn (2) was found to be invariant within the standard errors imposed on it by the scatter in the nucleophilicity values N and was therefore assigned the name 'reduced nucleophilicity'. Thus, I is clearly an intrinsic property of a given group. It is of interest to examine whether the notion of a reduced nucleophilicity can be extended to include the diatomic Lewis bases MA that were discussed in Section 3.1. In particular, how does I vary with the adjacent atom M ?

Table 1 applies to the Lewis bases MA used in the discussion of Fig. 1–6. It includes σ_{min} values of each MA molecule calculated at the MP2/aug-cc-pVTZ level of theory, the nucleophilicities N_{MA} and, in the penultimate column, the reduced nucleophilicities I_{MA} , as calculated with eqn (2). The Lewis base MA for all systems in Table 1 carries an axial non-bonding electron pair that is involved in the H-bond interaction.

Table 1 reveals that the reduced nucleophilicities are close to being independent of the row and group of the atom A in the Periodic Table, given the magnitude of the standard errors in the values of N_{MA} from which they are determined. There is some indication that the Row 4 atoms do not fit the pattern, however. In the final column of Table 1 is recorded the mean value of I_{MA} for the Rows 1, 2 and 3 atoms M only. These values suggest (but do not prove) that there is not only little



Table 1 Values of nucleophilicities N_{MA} and reduced nucleophilicities I_{MA} of Lewis bases MA

Source of data	Lewis base MA	$\sigma_{\min}(MA)/$ kJ mol^{-1}	N_{MA}	$I_{MA} = cN_{MA}/$ σ_{\min}	I_{MA} (mean)
Fig. 1 ^a	BF	+10.1	0.29(4)	—	0.0343(23)
	AlF	−125.8	3.97(33)	−0.0315(28)	
	GaF	−146.4	5.41(34)	−0.0369(24)	
	InF	−187.7	6.46(16)	−0.0344(9)	
Fig. 2	CO	−17.2	0.90(11)	−0.052(9)	0.0374(8) ^b
	SiO	−157.4	5.74(20)	−0.0365(12)	
	GeO	−151.1	5.77(13)	−0.0382(8)	
	SnO	−171.0	6.82(35)	0.0399(20)	
Fig. 3	CS	−21.6	No value	—	0.0357(1)
	SiS	−30.6	1.09(6)	0.0356(20)	
	GeS	−36.0	1.29(9)	0.0358(25)	
	SnS	−66.4	1.88(9)	0.0283(14)	
Fig. 4	N ₂	−35.8	1.32(17)	0.0369(47)	0.0379(10)
	PN	−131.5	4.99(27)	0.0379(21)	
	AsN	−128.9	5.02(10)	0.0389(8)	
	SbN	−134.2	5.82(16)	0.0433(13)	
Fig. 5	OC	−58.5	2.14(23)	0.0369(36)	0.0359(11)
	SC	−119.7	4.33(22)	0.0362(18)	
	SeC	−125.6	4.36(16)	0.0347(13)	
	TeC	−140.9	4.75(9)	0.0337(6)	
Fig. 6	FB	−89.3	3.29(16)	0.0368(18)	0.0372(4)
	ClB	−103.7	3.90(11)	0.0376(11)	
	BrB	−99.0	3.67(9)	0.0371(9)	
	IB	−90.9	3.52(10)	0.0387(12)	

^a Data for the M–H···HX are included for completeness only. The M–H complexes acting as a Lewis base when M is a Group 13 atom do not involve a non-bonding electron pair on H and therefore the nature of the M–H···HX interaction must be different from that at play in the other systems considered here. ^b Very low value for CO (O as the acceptor atom) excluded from mean.

variation of I_{MA} with the row of M in the periodic table, but also with its group.

It has been shown elsewhere²⁵ that it is possible to use a parallel approach involving the maximum value σ_{\max} of the MESP of the Lewis acids HX to define the corresponding reduced electrophilicities $\Xi_{HX} = E_{HX}/\sigma_{\max}$ of the Lewis acids HX.

4. Conclusions

The conclusions from the investigations reported in this article may be summarised as follows:

(a) There is a pattern in the changes in the nucleophilicity N_{MA} of a diatomic Lewis base MA when involved in hydrogen-bonded complexes MA···HX. The pattern is brought about by changing the group and row of the atom M adjacent to the atom A directly involved in the hydrogen bond. The pattern is independent of the group of atom A (with the possible exception of Group 17) but has the order Row 4 > Row 3 ≥ Row 2 >> Row 1 for atom M.

(b) The reduced nucleophilicities I_{MA} for most diatomic Lewis bases MA investigated here are very similar and are close to being independent of the group and row of M in the periodic table, after obviously difficult cases are excluded.

(c) When a hydrogen atom is added to MA to give the linear triatomic Lewis base HMA, the pattern identified in (a) for the MA···HX systems is not reproduced for the HMA···HX systems.

Conflicts of interest

The authors declare no conflicts of interest.

Data availability

The data supporting this article have been included as part of the supplementary information (SI). Supplementary information: the optimised Cartesian coordinates of all H-bonded complexes. See DOI: <https://doi.org/10.1039/d5cp03257a>.

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