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**Nucleophilicities  $N_{R-B}$  of molecules R-B (R = F, Cl, Br, I, CN, NC, CH<sub>3</sub>, SiH<sub>3</sub>, CF<sub>3</sub>, H) are determined from the equilibrium dissociation energies  $D_e$  of 70 hydrogen-bonded complexes R-B···HX (X = F, Cl, Br, I, HCN, HCCH, HCP). The change in  $N_{R-B}$  relative to  $N_{H-B}$  of H-B allows a quantitative measure of the inductive effect  $I_R$  of each group R because only the group R affects the electron density associated with the axial non-bonding electron pair carried by the boron in R-B. An alternative definition of  $I_R$ , suggested by the strong correlation of the  $N_{R-B}$  values with the minimum value  $\sigma_{\min}$  of the molecular electrostatic surface potential on the 0.001 e Bohr<sup>-3</sup> iso-surface along the R-B axis leads to excellent agreement between the two definitions.**

The molecule fluoroborylene F-B has a  $^1\Sigma^+$  electronic ground state, is isoelectronic with both CO and N<sub>2</sub>, and has been characterized experimentally<sup>1-3</sup> including *via* its millimeter wave spectrum.<sup>4</sup> It differs from its two isoelectronic analogues both in its chemical stability and in its considerably lower bond order. A generalized valence bond investigation<sup>5</sup> concludes that the predominant contribution to the valence-bond description of the molecule is from the Lewis structure that has a single covalent bond, 3 equivalent non-bonding electron pairs on F and one non-bonding pair on the axis at B. The negative end of the electric dipole moment<sup>3</sup> is at the B atom, indicating that B is the nucleophilic region of BF. In this article, we report *ab initio* calculations of the geometries and dissociation energies  $D_e$  of the 70 hydrogen-bonded complexes R-B···HX, where R is as listed above and X = F, Cl, Br, I, CN, CP or CCH.

The molecules CO and N<sub>2</sub> have featured centrally in the identification and characterization of both hydrogen-bonded interactions with Lewis acids<sup>6,7</sup> such as HX (X = F, Cl, Br, I, CN,

## Nucleophilicity of the boron atom in compounds R-B, (R = F, Cl, Br, I, CN, NC, CH<sub>3</sub>, SiH<sub>3</sub>, CF<sub>3</sub>, H): a new look at the inductive effects of the group R†

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CCH) and of halogen-bonded complexes with Lewis acids such as XY = ClF, Cl<sub>2</sub>, BrCl, Br<sub>2</sub> and ICl.<sup>8</sup> The electronic structure of B-F, especially the axial non-bonding pair at B, suggests that B-F, like N<sub>2</sub> and CO, will form linear hydrogen-bonded complexes of the type F-B···HX.<sup>9</sup> Moreover, given that the predominant valence-bond structure of F-B has a single bond, it should be possible to replace F in F-B by other monovalent atoms/groups R, for example, R = H, CH<sub>3</sub>, SiH<sub>3</sub>, CF<sub>3</sub>, Cl, Br, I, CN, NC.

Herein, we examine the effect of the group R on  $D_e$  of the R-B···HX complexes and from this determine the nucleophilicity of the boron atom in the various molecules R-B. It has been established elsewhere<sup>10-12</sup> that the equilibrium dissociation energy  $D_e$  of a complex formed by a Lewis base with a Lewis acid *via* a non-covalent interaction (such as a hydrogen bond, a halogen bond, *etc.*) can be written in terms of the nucleophilicity  $N_{\text{base}}$  of the Lewis base and the electrophilicity  $E_{\text{acid}}$  of the Lewis acid according to the expression

$$D_e = c' N_{\text{base}} E_{\text{acid}} \quad (1)$$

For convenience, the constant  $c'$  is chosen to be the unit of energy 1.0 kJ mol<sup>-1</sup> so that  $N_{\text{base}}$  and  $E_{\text{acid}}$  will be dimensionless when  $D_e$  is measured in kJ mol<sup>-1</sup>. Through a least-squares analysis of *ab initio*-calculated  $D_e$  values of 250 complexes involving a range of types of non-covalent interaction, a set of  $N_{\text{base}}$  and  $E_{\text{acid}}$  values were determined<sup>12</sup> for 11 simple Lewis bases (N<sub>2</sub>, CO, HC ≡ CH, CH<sub>2</sub> = CH<sub>2</sub>, C<sub>3</sub>H<sub>6</sub>, PH<sub>3</sub>, H<sub>2</sub>S, HCN, H<sub>2</sub>O, H<sub>2</sub>CO and NH<sub>3</sub>) and 24 Lewis acids (including most of the series of interest here, namely HF, HCl, HBr, HC ≡ CH, HCN, HCP). The values of  $E_{\text{HX}}$  for these Lewis acids are set out in Table 1. Note that the value  $E_{\text{HBr}} = 3.94$  is corrected from the value 4.56 given in ref. 12. It was re-determined from the gradient of the linear regression fit of the  $D_e$  versus  $N_{\text{base}}$  plot for the series of complexes base···HBr, where base = N<sub>2</sub>, CO, HC ≡ CH, CH<sub>2</sub> = CH<sub>2</sub>, PH<sub>3</sub>, H<sub>2</sub>S, HCN, H<sub>2</sub>O and NH<sub>3</sub>. This graph is available as Fig. S1 of the ESI.† The previously undetermined value  $E_{\text{HI}} = 2.77$  was similarly obtained from the linear

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† Electronic supplementary information (ESI) available: Optimised geometries and energies, Molecular electrostatic potential diagrams of molecules R-B. See DOI: <https://doi.org/10.1039/d2cp01565j>



**Table 1** Electrophilicities  $E_{HX}$  of Lewis acids HX and equilibrium dissociation energies  $D_e/(kJ \text{ mol}^{-1})$  for the process  $\text{R-B}\cdots\text{HX} = \text{R-B} + \text{HX}$  calculated at the CCSD(T)(F12c)/cc-pVDZ-F12 level, with counterpoise correction

Lewis acid HX	$E_{HX}$	$\text{H}_3\text{C-B}$	$\text{H}_3\text{Si-B}$	$\text{H-B}$	$\text{F-B}$	$\text{Cl-B}$	$\text{Br-B}$	$\text{I-B}$	$\text{NC-B}$	$\text{CN-B}$	$\text{F}_3\text{C-B}$
HF	6.75	40.46	35.82	33.39	21.52	25.59	24.10	23.19	23.07	24.82	21.50
HCl	4.36	26.26	22.92	20.52	12.81	15.73	14.90	14.51	13.49	14.85	12.58
HBr	3.94	23.80	20.79	18.00	10.93	13.72	13.11	12.67	11.57	12.80	10.77
HI	2.77	17.28	14.62	12.59	7.67	9.79	9.31	9.46	8.02	8.99	7.50
HCN	3.71	22.26	18.40	17.28	11.43	13.91	13.03	12.45	10.99	12.81	10.17
HCCH	2.16	11.34	9.54	9.01	6.13	7.24	6.80	6.49	6.22	6.93	5.79
HCP	2.02	11.39	9.60	8.94	6.08	7.28	6.88	6.64	6.13	6.89	5.73

regression fit of the corresponding graph for the base- $\cdots\text{HI}$  series, also shown in Fig. S1 (ESI $\ddagger$ ).

The main aim of this report is to measure the nucleophilicity of the molecule R-B as a function of the group R when acting as a hydrogen-bond acceptor at boron. According to eqn (1), if  $D_e/(kJ \text{ mol}^{-1})$  is plotted on the ordinate against  $E_{HX}$  along the abscissa for each of the series of hydrogen-bonded complexes R-B- $\cdots$ HX (X = F, Cl, Br, I, CN, CCH, CP), the result for a given R should be a straight line through the origin. The gradient of each such graph yields  $N_{R-B}$  (given that  $c' = 1.0 \text{ kJ mol}^{-1}$ ). The change in  $N_{R-B}$  with group R is a measure of the change in electron density at the non-bonding pair carried by the B atom and is presumably caused by the differing inductive effects of groups R. Some quantitative definitions of the inductive effects of the groups R based on this work are presented.

The geometries of the 70 complexes were optimized at the CCSD(T) (F12c) computational level<sup>13,14</sup> with the cc-pVDZ-F12 basis set<sup>15</sup> using the frozen-core approximation and were constrained to have  $C_{\infty v}$  or  $C_{3v}$  symmetry, as appropriate. The cartesian coordinates of the optimized geometries are available in Table S1 of the ESI. $\ddagger$  The dissociation energies  $D_e$  were corrected for basis set superposition error (BSSE) using the full counterpoise method of Boys and Bernadi.<sup>16</sup> The calculation were executed with the MOLPRO program.<sup>17</sup> The molecular electrostatic surface potentials (MESP) of the isolated R-B molecules were calculated at the MP2/aug-cc-pVTZ level with the GAUSSIAN program<sup>18</sup> and analyzed on the 0.001 e Bohr<sup>-3</sup> electron density iso-surface with the multiwfn program.<sup>19</sup> MESP diagrams for all R-B molecules are available in Table S2 ESI. $\ddagger$

The dissociation energies  $D_e$  calculated at the CCSD(T)(F12c)/cc-pVTZ-F12 level of theory (after counterpoise correction) for the 10 series of hydrogen-bonded complexes R-B- $\cdots$ HX having R = H, CH<sub>3</sub>, SiH<sub>3</sub>, CF<sub>3</sub>, F, Cl, Br, I, CN, NC, where X is one of F, Cl, Br, CN, I, CCH and CP for each R, are included in Table 1.

Graphs of  $D_e$  plotted against the electrophilicity  $E_{HX}$  of the HX molecule (from Table 1) are set out in three separate figures, for clarity, while each contains the line for H-B- $\cdots$ HX, recognizing that H is the usual reference when the inductive effects of different groups R are compared. Included in Fig. 1 are the plots for R = H, F, Cl, Br, I, while those R = H, H<sub>3</sub>C and H<sub>3</sub>Si are in Fig. 2, and those for R = H, CN, NC, F<sub>3</sub>C are in Fig. S2 (ESI $\ddagger$ ). The gradients and the values of  $R^2$  from linear regression fits of the points for each group are shown in the inset of

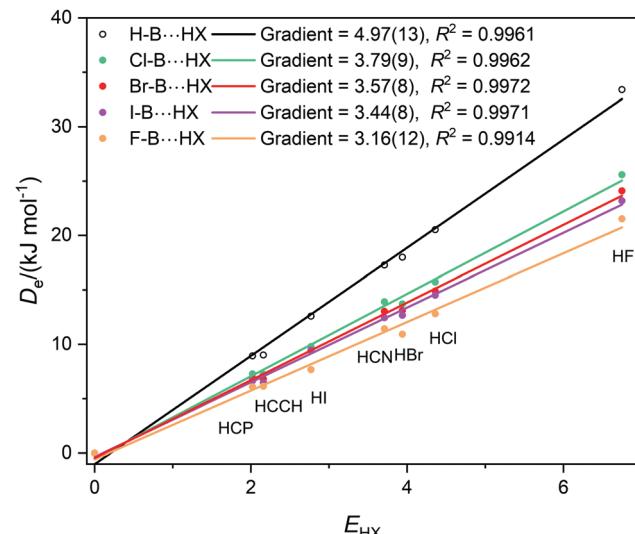


Fig. 1 Graphs of dissociation energy  $D_e$  of complexes R-B- $\cdots$ HX versus the electrophilicity  $E_{HX}$  of the Lewis acid HX for R = H-, F-, Cl-, Br- and I-.

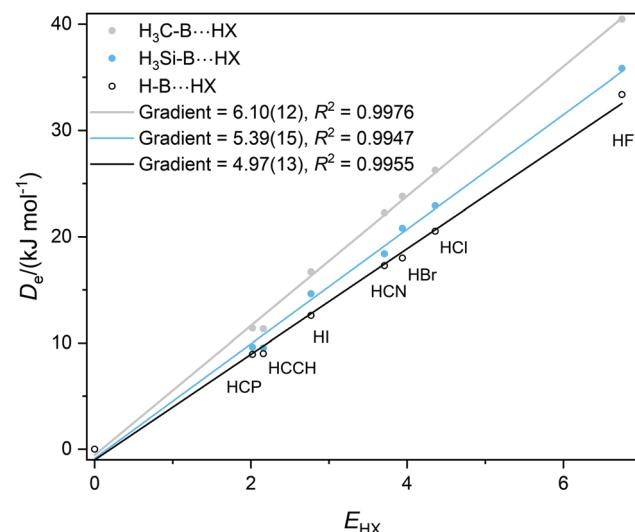


Fig. 2 Graphs of dissociation energy  $D_e$  of complexes R-B- $\cdots$ HX versus the electrophilicity  $E_{HX}$  of the Lewis acids HX for R = H-, H<sub>3</sub>C- and H<sub>3</sub>Si-.

each figure. The quality of the fit for each group R is excellent (as indicated by  $R^2 > 0.99$  in all but one case).



Fig. 1 shows clearly that the nucleophilicities  $N_{R-B}$  of the R-B molecules [see eqn (1)] are in the order  $R = H > Cl > Br \sim I > F$ . If the inductive effect  $I_R$  of a group R relative to H is defined by eqn (2):

$$I_R = (N_{R-B} - N_{H-B}) \quad (2)$$

Then  $I_H = 0$ ,  $I_{Cl} = -1.18(22)$ ,  $I_{Br} = -1.40(21)$ ,  $I_I = -1.53(21)$ , and  $I_F = -1.81(25)$ . This definition is consistent with the sign of the inductive effect chosen by Ingold,<sup>20</sup> who assigned electron attracting groups, such as halogen atoms, to have a negative inductive effect  $-I$ .

It is immediately obvious from Fig. 2 that the gradients of the  $D_e$  versus  $E_{HX}$  graphs for the  $H_3C-B \cdots HX$  and  $H_3Si-B \cdots HX$  series are greater than that for the  $H-B \cdots HX$  series. This indicates that substitution of H by a methyl or a silyl group pushes electron density onto B relative to H. According to the definition given in eqn (2) the inductive effect  $I_R$  of the group  $H_3C$  is  $I_{H_3C} = +1.13(25)$  and that of  $H_3Si$  is  $I_{H_3Si} = +0.42(28)$ . Thus, both groups exhibit a positive inductive effect, although the range of each value transmitted from the errors in the gradients is larger than ideal.

The corresponding graphs of  $D_e$  versus  $E_{HX}$  for the series  $R-B \cdots HX$  when  $R-$  is  $H-$ ,  $CN-$  (isocyanide),  $NC-$  (cyanide), and  $F_3C-$  (trifluoromethyl) are available in the ESI† as Fig. S2. The last three groups R are electron-withdrawing relative to H. In fact, the gradients of the graphs for  $R = F_3C-$  (Fig. 3) and  $R = F-$  (Fig. 1) are the same. Given the definition  $I_R = N_{R-B} - N_{H-B}$  in eqn (2) the inductive effects are  $I_{F_3C} = -1.82(27)$ ,  $I_{NC} = -1.32(25)$  and  $I_{CN} = -1.56(26)$ . Thus, the electron-withdrawing effects of the  $CF_3$  group and the F atom are identical, while the cyanide group is a better electron-withdrawing group than isocyanide and has a value  $I_{CN}$  comparable with that of Br or I. Unfortunately, the errors in the fitted  $D_e$  versus the  $E_{HX}$  straight lines are

sufficient that more precise values of the inductive effects  $I_R$  of the groups R cannot be obtained by the present approach.

In conclusion, we have shown that by calculating the equilibrium dissociation energies  $D_e$  for the series of hydrogen-bonded complexes  $R-B \cdots HX$ , where  $X = F, Cl, Br, I, HCN, HCCH$  and  $HCP$ , it is possible to determine the nucleophilicity  $N_{R-B}$  of the axially symmetric molecules R-B. Repeating this procedure for each group in the series  $R = H_3C, H_3Si-, H-, F-, Cl-, Br-, I-, CN-, NC-,$  and  $F_3C-$  shows that, relative to  $H-$ , the groups  $H_3C-$  and  $H_3Si-$  increase the nucleophilicity of the B atom in forming hydrogen bonds with  $HX$ , while the halogen atoms, the pseudo-halogens  $CN-$  and  $NC-$ , and the fully fluorinated methyl group, withdraw electronic charge from the non-bonding electron pair carried by boron. The change  $N_{R-B} - N_{H-B}$  in the nucleophilicity of the axial, non-bonding electron pair on B in molecules R-B relative to H-B thus, in principle, provides a clean method of assessing the inductive effect  $I_R$  of the group R. This approach has the advantage that the molecular complexes R-B  $\cdots$  HX are isolated from solvent effects, that the group R is directly attached to the boron atom and the changes in the  $D_e$  values when R is changed result directly from the changes in electron density in the non-bonding pair carried by B.

Politzer and co-workers<sup>21,22</sup> showed some time ago that electrostatic potentials can also be related to nucleophilic processes. A useful, recent general discussion<sup>23</sup> of molecular electrostatic surface potentials (MESP) is available from the same group. We now examine the relationship between MESP and the inductive effect.

The molecular electrostatic surface potential (MESP) calculated at the MP2/aug-cc-pVTZ level on the  $0.001 \text{ e Bohr}^{-3}$  iso-surface (in particular, the value  $\sigma_{\min}$  on the R-B molecular axis near to the boron atom) provides a measure of the change in electrostatic potential at the non-bonding electron pair carried by B when the group R is changed.

The values of  $\sigma_{\min}$  for the 10 compounds R-B ( $R = H_3C-, H_3Si-, H-, F-, Cl-, Br-, I-, CN-, NC-,$  and  $F_3C-$ ) are collected in Table 2. Fig. 3 displays a graph of  $N_{R-B}$  versus  $\sigma_{\min}$ . It is clear from Fig. 3 that there is a strong correlation between the two last-named quantities. Indeed, this suggests another way to express the inductive effect  $I'_R$  of group R, namely by the equation:

$$I'_R = \{\sigma_{\min}(R-B) - \sigma_{\min}(H-B)\} / \{\sigma_{\min}(H-B)\} \quad (3)$$

where division by  $\sigma_{\min}(H-B)$  ensures a dimensionless quantity that is normalised with respect to the value for H-B. The  $I'_R$  so calculated from the  $\sigma_{\min}(R-B)$  are included in Table 2.

The values determined from the nucleophilicities ( $N_{R-B} - N_{H-B}$ ), but normalised according to the value of  $N_{HB}$ , to give

$$I_R^{\text{norm}} = (N_{R-B} - N_{H-B}) / N_{H-B} \quad (4)$$

are included in Table 2 and allow a more strict comparison. The conclusion of interest from Table 2 is that whichever of the two definitions of the inductive effect presented here is used, the values in the two scales are very similar. The linear correlation

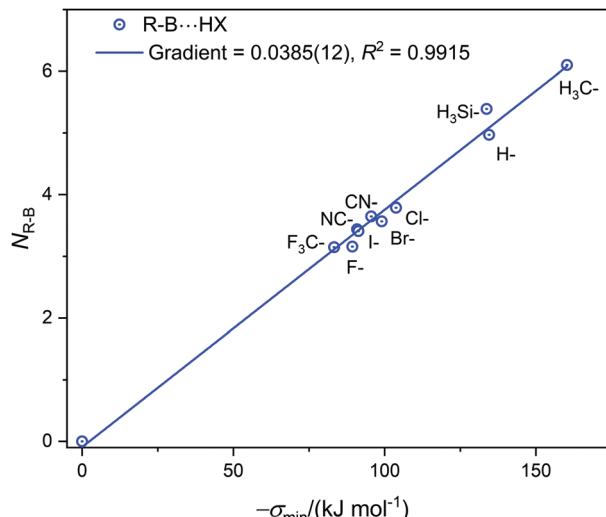


Fig. 3 The nucleophilicities  $N_{R-B}$  of molecules R-B (determined from the gradient of the  $D_e$  versus  $E_{HX}$  graphs in Fig. 1, 2 and Fig. S2, ESI†) plotted against  $\sigma_{\min}$  (the minimum value of the electrostatic potential on the  $0.001 \text{ e Bohr}^{-3}$  iso-surface of R-B on the molecular axis at the boron atom).



**Table 2** Comparison of three methods of measuring the inductive effect of monovalent groups R

Group R	$\sigma_{\min}$ (R–B) <sup>a</sup> kJ mol <sup>-1</sup>	Inductive effect $I_R^{\text{norm}}$ <sup>b</sup>	Inductive effect $I_R'$ <sup>c</sup>	Hammett $\sigma$ constant <sup>d</sup>
H <sub>3</sub> C–	−160.3	0.23	0.19	−0.17
H <sub>3</sub> Si–	−133.7	0.08	−0.01	0.10
H–	−134.5	0.00	0.00	0.00
F–	−89.3	−0.36	−0.34	0.06
Cl–	−103.7	−0.24	−0.23	0.23
Br–	−99.0	−0.28	−0.26	0.23
I–	−90.9	−0.31	−0.32	0.18
NC–	−91.4	−0.31	−0.32	0.66
CN–	−95.5	−0.27	−0.29	0.49
F <sub>3</sub> C–	−83.3	−0.37	−0.38	0.54

<sup>a</sup> Value of the MESP on the 0.001 e Bohr<sup>−3</sup> iso-surface on the R–B molecular axis at boron. <sup>b</sup> As defined in eqn (4). <sup>c</sup> As defined by eqn (3).

<sup>d</sup> The Hammett  $\sigma$  substituent constants for the para-position of benzoic acid [24]. They are positive for electron withdrawing groups and negative electron donating groups, relative to hydrogen.

between the two sets of parameters,  $I_R^{\text{norm}}$  and  $I_R'$ , has  $R^2 = 0.983$ , a slope close to one (0.90), and an intercept near to zero (−0.032). Finally, the Hammett  $\sigma$  substituent constant is commonly cited<sup>24</sup> as a measure of the relative inductive effects of groups R attached to, for example, benzoic acid and is based on how equilibrium constants for dissociation of the acid are affected by substituents R at the *para*- and *meta*-positions of the benzene ring. The values for the *para*-position are included in Table 2 and, after noting they are of opposite sign from the  $I_R$  proposed here, the magnitudes are in only fair agreement with those of the  $I_R$  introduced here, but the Hammett constant applies to equilibria/chemical reactions in solvents, and are therefore not strictly comparable.

## Conflicts of interest

There are no conflicts to declare.

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## Notes and references

- D. L. Hildenbrand and E. Murad, *J. Chem. Phys.*, 1965, **43**, 1400–1403.
- P. L. Timms, *J. Am. Chem. Soc.*, 1967, **89**, 1629–1632.
- D. Vidovic and S. Aldridge, *Chem. Sci.*, 2011, **2**, 601–608.
- G. Cazzoli, L. Cludi, C. Degli Esposti and L. Dore, *J. Mol. Spectrosc.*, 1989, **134**, 159–167.
- F. Fantuzzi, T. M. Cardozo and M. A. C. Nasimento, *J. Phys. Chem. A*, 2014, **119**, 5335–5343.
- A. C. Legon, P. D. Soper, M. R. Keenan, T. K. Minton, T. J. Balle and W. H. Flygare, *J. Chem. Phys.*, 1980, **73**, 583–584.
- P. D. Soper, A. C. Legon, W. G. Read and W. H. Flygare, *J. Chem. Phys.*, 1982, **76**, 292–300.
- A. C. Legon, *Angew. Chem., Int. Ed.*, 1999, **38**, 2686–2714.
- I. Rozas, I. Alkorta and J. Elguero, *J. Phys. Chem. A*, 1999, **103**, 8861–8869.
- A. C. Legon and D. J. Millen, *J. Am. Chem. Soc.*, 1987, **109**, 356–358.
- A. C. Legon, *Phys. Chem. Chem. Phys.*, 2014, **16**, 12415–12421, see Correction 2014, **16**, 25199–25199.
- I. Alkorta and A. C. Legon, *Molecules*, 2017, **22**, 1786–1799.
- C. Hättig, D. P. Tew and A. Köhn, *J. Chem. Phys.*, 2010, **132**, 231102.
- C. Hättig, W. Klopper, A. Köhn and D. P. Tew, *Chem. Rev.*, 2012, **112**, 4–74.
- J. G. Hill and K. A. Peterson, *J. Chem. Phys.*, 2014, **141**, 094106.
- S. F. Boys and F. Bernardi, *Mol. Phys.*, 1970, **19**, 553–566.
- H.-J. Werner, P. J. Knowles, G. Knizia, F. R. Manby and M. Schütz, *Wiley Interdiscip. Rev.: Comput. Mol. Sci.*, 2012, **2**, 242–253.
- M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson and H. Nakatsuji, *et al.*, *Gaussian 16; Revision A.03*, Gaussian, Inc.: Wallingford, CT, USA, 2016.
- T. Lu and F. Chen, *J. Comput. Chem.*, 2012, **33**, 580–592.
- C. K. Ingold, *Structure and Mechanism in Organic Chemistry*, Cornell University Press, Ithaca, New York, 1953, p. 71.
- J. S. Murray and P. Politzer, *Chem. Phys. Lett.*, 1988, **152**, 364–370.
- P. Sjöberg and P. Politzer, *J. Chem. Phys.*, 1990, **94**, 3959–3961.
- J. S. Murray and P. Politzer, *WIREs Comput. Mol. Sci.*, 2017, **7**, e1326.
- C. Hansch, A. Leo and R. W. Taft, *Chem. Rev.*, 1991, **91**, 165–195.

