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Common quantitative trends for the halogen, chalcogen, and pnictogen bonds

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In the focus of our study are the noncovalent bonds, B···E, in which E-atom = P, As, S, Se Cl, Br, delivers the electrophilic site, and the possible nucleophilic B-molecule = NH_3, H_2O, HCN. We aimed to disclose the quantitative common trends of electronic properties for noncovalent bonds B···E formed by the halogen, chalcogen, pnictogen atoms in molecular complexes. The values of potential, $v(\mathbf{r}_b)$, and kinetic, $g(\mathbf{r}_b)$, electronic energy densities at the bond critical points and the behavior of electrostatic potential, ESP(**r**), and potential acting on an electron in a molecule,[1,2] PAEM(**r**), along the bond lines were analyzed.

Parameters of relationships $E_{int} = a_0+a_1P(\mathbf{r}_b)$ with the best correlation coefficients between the local property $P(\mathbf{r}_b)$ and the binding energy $E_{bind}=E_{BE}–(E_E+E_B)$ (PBE0/aug-cc-pVDZ) for series of molecular complexes were compared. It was established that for fixed B-molecule, the highest R^2 are observed for E_{int} *vs* $ESP(\mathbf{r}_b)$ or E_{int} *vs* $PAEM(\mathbf{r}_b)$ relationships; for fixed E-atom the best models are E_{int} *vs* $V(\mathbf{r}_b)$ or E_{int} *vs* $G(\mathbf{r}_b)$. The results are summarized below.

	ESP	PAEM	G	V
P…B	R^2= 0.91 a_0= –0.80 a_1= –38	R^2= 0.96 a_0=7 a_1=19	R^2= 0.95 a_0=0.5 a_1= –390	R^2= 0.97 a_0= –0.5 a_1=305
As…B	R^2= 0.87 a_0=0.2 a_1= –46	R^2=94 a_0=9 a_1=24	R^2= 0.94 a_0=0.9 a_1= –485	R^2= 0.95 a_0= –0.4 a_1= 374
S…B	R^2= 0.90 a_0= –0.67 a_1= –42	R^2= 0.95 a_0=8 a_1=21	R^2= 0.98 a_0=0.8 a_1= –341	R^2= 0.97 a_0= –0.6 a_1=272
Se…B	R^2= 0.86 a_0=0.99 a_1= –50	R^2= 0.92 a_0=13 a_1=29	R^2= 0.95 a_0=2.2 a_1= –471	R^2= 0.97 a_0=0.1 a_1=358
Cl…B	R^2= 0.88 a_0=1.2 a_1= –56	R^2= 0.93 a_0=14 a_1=29	R^2= 0.96 a_0=2.7 a_1= –361	R^2= 0.99 a_0=0.5 a_1=282
Br…B	R^2= 0.80 a_0=2.7 a_1= –61	R^2= 0.88 a_0=19 a_1=36	R^2= 0.90 a_0=4.2 a_1= –493	R^2= 0.95 a_0=1.5 a_1=386

	ESP	PAEM	G	V
Ch…NH_3	R^2= 0.94 a_0=0.1 a_1= –54	R^2= 0.94 a_0=16 a_1=33	R^2= 0.85 a_0=0.8 a_1= –395	R^2= 0.89 a_0= –0.3 a_1=320
Ch…H_2O	R^2= 0.98 a_0= –0.8 a_1= –35	R^2= 0.95 a_0=8 a_1=20	R^2= 0.84 a_0= –0.2 a_1= –284	R^2= 0.91 a_0= –0.3 a_1=288
Ch…NCH	R^2= 0.99 a_0= –1.3 a_1= –27	R^2= 0.97 a_0=5 a_1=15	R^2= 0.91 a_0= –0.8 a_1= –235	R^2= 0.94 a_0= –1.1 a_1=240
Pn…NH	R^2= 0.94 a_0= –0.5 a_1= –55	R^2=89 a_0=14 a_1=30	R^2= 0.95 a_0= 10 a_1= –950	R^2= 0.65 a_0= 5 a_1= 649
Pn…H_2O	R^2= 0.93 a_0= –1.4 a_1= –42	R^2=97 a_0=8 a_1=21	R^2= 0.88 a_0= 4 a_1= –696	R^2= 0.83 a_0= 3 a_1= 644
Pn…NCH	R^2= 0.97 a_0= –1.5 a_1= –31	R^2=95 a_0=5 a_1=15	R^2= 0.77 a_0= 0.5 a_1= –441	R^2= 0.75 a_0= –0.5 a_1= 414

The electronic criterion [3] for categorizing the halogen, chalcogen, pnictogen bonds was formulated: *minimum of ESP(**r**) is always located at the side of atom that donates electrons; the minimum of ρ(**r**) is closer to the atom that delivers its electrophilic site and prescribes the name of bonding.*

References

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