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Electron Density Characteristics in *Bond Critical Point* (QTAIM) vs. Interaction Energy Components (SAPT) – the Case of Charge-assisted Hydrogen Bonding

by

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S1. Motivation for using SAPT

In terms of the supermolecular approach, the interactions energy (E_{int}), e. g. the intermolecular hydrogen bond energy as in our case, is generally defined as the difference between the total energy of the complex (E_{AB}) and the energies of the isolated monomers (E_A and E_B)[S1]. The interaction energy of a stable complex assumes its negative value.

Eq. S1 $$E_{int} = E_{AB} - (E_A + E_B)$$

Nevertheless, the interaction energy obtained by means of eq. S1 does not give us many possibilities to interpret. By contrast, the SAPT approach defines E_{int} as a sum of energy correction terms with well-defined physical interpretation. For the purpose of calculating the E_{int} components and their further analysis, we have decided to apply the SAPT approach.

S2. Details of the SAPT calculations

The first stage of the SAPT calculations involved computing integrals between one-electron basis functions, and the SCF orbitals and orbital energies for the monomers. This stage was performed using the GAMESS package[S2,S3] that was interfaced to the SAPT2008.2 code[S4]. In all the SAPT calculations we made use of the aug-cc-pVTZ basis set, mostly for the purpose of being consistent with the methodology applied in the previous study.[S5] The dimer-centered basis set (DCBS) approach[S4] was employed, as it is a close relation to the supermolecular approach with the basis set superposition error (BSSE) correction. The latter was employed in ref. S5, although the authors omitted there the BSSE correction. In the post-SCF stage of the SAPT calculations, all orbitals were used for electron excitations.

S3. Motivation for the application of SAPT for CAHB(+/-)

SAPT has been intended for weak noncovalent intermolecular interactions and its use in this work for the CAHB(+), CAHB(-), and non-CAHB systems requires no justification. All the three CAHBs(+/-) systems exhibited, however, the interaction energies more exoenergetic than -95 kcal/mol for $d_{H...A} < 2.5$ Å and, in fact, they correspond to complexes with very strong bonds dominated by electrostatic interaction between ions. In consequence, the application of SAPT for such systems is questionable. We are fully aware of this fact, but our aim was to compare various CAHBs within the same computational approach. In order to support the reason to use SAPT in our comparative study, we first compared the interaction energies obtained by means of SAPT and MP2 (the latter was taken from ref. S5). For $d_{H...Cl}$ = 1.75 Å in the H_3N^+-H...Cl^- complex, the SAPT/aug-cc-pVTZ interaction energy is equal to -122.92 kcal/mol, while the MP2/aug-cc-pVTZ one amounts to -123.06 kcal/mol. Even though the latter may be slightly inaccurate, as the BSSE correction was not taken into account in ref. S5, the difference between these SAPT and MP2 values is small.

S4. Tables of results

Table S1. QTAIM and SAPT properties for the investigated range of H...Cl distances in the N-H...Cl bridge of the CAHB(+) type. All symbols are explained in the manuscript.

$d_{H...Cl}$ [Å]	ρ_{BCP} [a.u.]	$\nabla^2\rho_{BCP}$ [a.u.]	V_{BCP} [a.u.]	G_{BCP} [a.u.]	H_{BCP} [a.u.]	DI(A,B) [a.u.]	E_{elst} [kcal/mol]	E_{ind} [kcal/mol]	E_{disp} [kcal/mol]	E_{exch} [kcal/mol]	$\delta E^{HF}_{int,resp}$ [kcal/mol]	E^{SAPT}_{int} [kcal/mol]
2.209	2.560E-02	5.690E-02	-1.950E-02	1.680E-02	-2.620E-03	9.760E-02	-6.437E+00	-9.049E+00	-2.890E+00	1.215E+01	-1.967E+00	-8.194E+00
2.300	2.090E-02	5.100E-02	-1.490E-02	1.380E-02	-1.060E-03	8.510E-02	-5.716E+00	-7.457E+00	-2.385E+00	8.981E+00	-1.515E+00	-8.091E+00
2.400	1.680E-02	4.420E-02	-1.100E-02	1.100E-02	2.020E-07	7.340E-02	-5.067E+00	-6.101E+00	-1.934E+00	6.421E+00	-1.144E+00	-7.823E+00
2.500	1.341E-02	3.757E-02	-8.225E-03	8.809E-03	5.840E-04	6.346E-02	-4.537E+00	-5.051E+00	-1.571E+00	4.578E+00	-8.703E-01	-7.451E+00
2.600	1.070E-02	3.150E-02	-6.140E-03	7.000E-03	8.610E-04	5.450E-02	-4.100E+00	-4.229E+00	-1.279E+00	3.256E+00	-6.680E-01	-7.021E+00
2.800	6.870E-03	2.130E-02	-3.470E-03	4.400E-03	9.310E-04	3.980E-02	-3.432E+00	-3.056E+00	-8.552E-01	1.635E+00	-4.045E-01	-6.112E+00
3.000	4.410E-03	1.410E-02	-1.990E-03	2.750E-03	7.630E-04	2.860E-02	-2.947E+00	-2.288E+00	-5.799E-01	8.169E-01	-2.542E-01	-5.253E+00
3.500	1.440E-03	4.890E-03	-5.440E-04	8.830E-04	3.390E-04	1.150E-02	-2.183E+00	-1.244E+00	-2.351E-01	1.381E-01	-8.843E-02	-3.612E+00
4.000	4.699E-04	1.729E-03	-1.568E-04	2.945E-04	1.378E-04	4.245E-03	-1.731E+00	-7.570E-01	-1.071E-01	2.244E-02	-3.422E-02	-2.607E+00
4.500	1.510E-04	5.908E-04	-4.074E-05	9.423E-05	5.348E-05	1.539E-03	-1.427E+00	-4.938E-01	-5.412E-02	3.511E-03	-1.398E-02	-1.985E+00
5.000	4.728E-05	1.886E-04	-9.709E-06	2.843E-05	1.872E-05	5.611E-04	-1.208E+00	-3.380E-01	-2.968E-02	5.237E-04	-5.884E-03	-1.581E+00
5.500	1.481E-05	5.452E-05	-2.308E-06	7.969E-06	5.661E-06	2.104E-04	-1.043E+00	-2.402E-01	-1.735E-02	7.361E-05	-2.549E-03	-1.303E+00
6.000	4.603E-06	1.508E-05	-6.017E-07	2.186E-06	1.584E-06	7.662E-05	-9.162E-01	-1.762E-01	-1.069E-02	9.500E-06	-1.179E-03	-1.104E+00
6.500	1.437E-06	4.555E-06	-2.299E-07	6.843E-07	4.544E-07	2.572E-05	-8.170E-01	-1.327E-01	-6.866E-03	9.400E-07	-5.888E-04	-9.572E-01

Table S2. QTAIM and SAPT properties for the investigated range of H...Cl distances in the N-H...Cl bridge of the CAHB(-) type. All symbols are explained in the manuscript.

$d_{H...Cl}$ [Å]	ρ_{BCP} [a.u.]	$\nabla^2\rho_{BCP}$ [a.u.]	V_{BCP} [a.u.]	G_{BCP} [a.u.]	H_{BCP} [a.u.]	DI(A,B) [a.u.]	E_{elst} [kcal/mol]	E_{ind} [kcal/mol]	E_{disp} [kcal/mol]	E_{exch} [kcal/mol]	$\delta E^{HF}_{int,resp}$ [kcal/mol]	E^{SAPT}_{int} [kcal/mol]
2.325	2.080E-02	5.310E-02	-1.450E-02	1.390E-02	-6.150E-04	1.000E-01	-1.128E+01	-8.657E+00	-4.887E+00	1.735E+01	-1.642E+00	-9.114E+00
2.400	1.790E-02	4.730E-02	-1.170E-02	1.180E-02	4.490E-05	9.110E-02	-1.017E+01	-7.362E+00	-4.267E+00	1.408E+01	-1.327E+00	-9.048E+00
2.500	1.460E-02	4.010E-02	-8.900E-03	9.460E-03	5.580E-04	8.140E-02	-8.939E+00	-6.000E+00	-3.564E+00	1.067E+01	-9.940E-01	-8.827E+00
2.600	1.200E-02	3.350E-02	-6.790E-03	7.580E-03	7.920E-04	7.270E-02	-7.933E+00	-4.951E+00	-2.980E+00	8.101E+00	-7.419E-01	-8.506E+00
2.800	8.090E-03	2.290E-02	-4.040E-03	4.880E-03	8.350E-04	5.680E-02	-6.421E+00	-3.483E+00	-2.093E+00	4.695E+00	-4.100E-01	-7.713E+00
3.000	5.530E-03	1.540E-02	-2.480E-03	3.170E-03	6.850E-04	4.490E-02	-5.356E+00	-2.542E+00	-1.480E+00	2.742E+00	-2.237E-01	-6.859E+00
3.200	3.810E-03	1.040E-02	-1.570E-03	2.090E-03	5.210E-04	3.470E-02	-4.574E+00	-1.912E+00	-1.053E+00	1.613E+00	-1.203E-01	-6.046E+00
3.400	2.650E-03	7.160E-03	-1.010E-03	1.400E-03	3.900E-04	2.690E-02	-3.984E+00	-1.475E+00	-7.561E-01	9.546E-01	-6.346E-02	-5.324E+00
5.000	1.640E-04	4.350E-04	-2.830E-05	6.850E-05	4.020E-05	3.400E-03	-1.840E+00	-3.245E-01	-7.618E-02	1.759E-02	2.002E-03	-2.221E+00
6.000	3.470E-05	7.110E-05	-4.730E-06	1.130E-05	6.520E-06	9.660E-04	-1.303E+00	-1.657E-01	-2.484E-02	1.604E-03	1.117E-03	-1.491E+00
8.000	2.300E-06	4.290E-06	-3.580E-07	7.150E-07	3.570E-07	7.230E-05	-7.574E-01	-5.768E-02	-4.647E-03	1.575E-05	2.408E-04	-8.195E-01

Table S3. QTAIM and SAPT properties for the investigated range of H...Cl distances in the N-H...Cl bridge of the CAHB(+/-) type. All symbols are explained in the manuscript.

$d_{H...Cl}$ [Å]	ρ_{BCP} [a.u.]	$\nabla^2\rho_{BCP}$ [a.u.]	V_{BCP} [a.u.]	G_{BCP} [a.u.]	H_{BCP} [a.u.]	DI(A,B) [a.u.]	E_{elst} [kcal/mol]	E_{ind} [kcal/mol]	E_{disp} [kcal/mol]	E_{exch} [kcal/mol]	$\delta E^{HF}_{int,resp}$ [kcal/mol]	E^{SAPT}_{int} [kcal/mol]
1.750	7.560E-02	3.810E-02	-7.900E-02	4.430E-02	-3.470E-02	2.100E-01	-1.320E+02	-5.055E+01	-1.058E+01	8.125E+01	-1.108E+01	-1.229E+02
1.800	6.790E-02	4.330E-02	-6.790E-02	3.940E-02	-2.850E-02	2.000E-01	-1.288E+02	-4.549E+01	-9.592E+00	7.135E+01	-1.012E+01	-1.226E+02
1.900	5.480E-02	4.890E-02	-5.040E-02	3.130E-02	-1.910E-02	1.820E-01	-1.229E+02	-3.720E+01	-7.887E+00	5.508E+01	-8.336E+00	-1.212E+02
2.000	4.450E-02	5.010E-02	-3.760E-02	2.500E-02	-1.250E-02	1.660E-01	-1.177E+02	-3.078E+01	-6.497E+00	4.263E+01	-6.792E+00	-1.191E+02
2.300	2.440E-02	4.080E-02	-1.580E-02	1.300E-02	-2.810E-03	1.270E-01	-1.047E+02	-1.836E+01	-3.663E+00	1.994E+01	-3.646E+00	-1.104E+02
2.500	1.650E-02	3.110E-02	-9.080E-03	8.430E-03	-6.540E-04	1.060E-01	-9.783E+01	-1.342E+01	-2.520E+00	1.209E+01	-2.466E+00	-1.041E+02
2.700	1.130E-02	2.210E-02	-5.360E-03	5.450E-03	8.390E-05	8.850E-02	-9.194E+01	-1.000E+01	-1.746E+00	7.363E+00	-1.725E+00	-9.805E+01
3.000	6.590E-03	1.250E-02	-2.560E-03	2.840E-03	2.870E-04	6.710E-02	-8.446E+01	-6.648E+00	-1.021E+00	3.519E+00	-1.080E+00	-8.969E+01
4.000	1.200E-03	2.180E-03	-2.710E-04	4.080E-04	1.370E-04	2.450E-02	-6.686E+01	-2.148E+00	-2.011E-01	3.151E-01	-3.178E-01	-6.922E+01
6.000	4.380E-05	5.540E-05	-4.520E-06	9.190E-06	4.670E-06	2.440E-03	-4.748E+01	-4.378E-01	-1.718E-02	2.972E-03	-2.807E-02	-4.796E+01
8.000	2.060E-06	2.440E-06	-2.050E-07	4.080E-07	2.030E-07	1.820E-04	-3.688E+01	-1.472E-01	-3.277E-03	3.235E-05	-2.905E-03	-3.703E+01

Table S4. QTAIM and SAPT properties for the investigated range of H...Cl distances in the N-H...Cl bridge of the non-CAHB type. All symbols are explained in the manuscript.

$d_{H...Cl}$ [Å]	ρ_{BCP} [a.u.]	$\nabla^2\rho_{BCP}$ [a.u.]	V_{BCP} [a.u.]	G_{BCP} [a.u.]	H_{BCP} [a.u.]	DI(A,B) [a.u.]	E_{elst} [kcal/mol]	E_{ind} [kcal/mol]	E_{disp} [kcal/mol]	E_{exch} [kcal/mol]	$\delta E^{HF}_{int,resp}$ [kcal/mol]	E^{SAPT}_{int} [kcal/mol]
2.746	7.600E-03	2.640E-02	-4.200E-03	5.400E-03	1.250E-03	3.960E-02	-1.034E+00	-5.824E-01	-1.331E+00	2.269E+00	-1.522E-01	-8.308E-01
2.800	6.770E-03	2.360E-02	-3.620E-03	4.760E-03	1.600E-03	3.650E-02	-9.195E-01	-4.820E-01	-1.200E+00	1.885E+00	-1.260E-01	-8.426E-01
2.900	5.480E-03	1.920E-02	-2.770E-03	3.780E-03	1.650E-03	3.140E-02	-7.476E-01	-3.427E-01	-9.940E-01	1.341E+00	-8.889E-02	-8.323E-01
3.000	4.440E-03	1.550E-02	-2.130E-03	3.000E-03	1.720E-03	2.690E-02	-6.159E-01	-2.465E-01	-8.262E-01	9.563E-01	-6.277E-02	-7.951E-01
3.200	2.940E-03	1.020E-02	-1.280E-03	1.920E-03	1.120E-03	1.960E-02	-4.350E-01	-1.327E-01	-5.794E-01	4.935E-01	-3.149E-02	-6.852E-01
3.600	1.310E-03	4.530E-03	-5.010E-04	8.170E-04	5.010E-04	9.960E-03	-2.415E-01	-4.200E-02	-2.968E-01	1.294E-01	-7.908E-03	-4.587E-01
4.000	5.870E-04	2.050E-03	-1.990E-04	3.550E-04	2.960E-04	4.880E-03	-1.470E-01	-1.568E-02	-1.597E-01	3.235E-02	-2.021E-03	-2.921E-01
5.000	8.040E-05	2.810E-04	-1.810E-05	4.410E-05	3.800E-05	8.550E-04	-5.118E-02	-2.889E-03	-4.372E-02	1.006E-03	-9.516E-05	-9.688E-02
6.000	1.150E-05	3.740E-05	-2.170E-06	5.760E-06	4.980E-06	1.670E-04	-1.865E-02	-9.243E-04	-1.553E-02	3.062E-05	-1.013E-05	-3.508E-02
7.000	1.710E-06	5.710E-06	-2.760E-07	8.520E-07	6.280E-07	3.400E-05	-6.063E-03	-3.768E-04	-6.562E-03	5.700E-07	-2.060E-06	-1.300E-02

Table S5. QTAIM and SAPT properties for the investigated range of H...Cl distances in the P-H...Cl bridge of the CAHB(+) type. All symbols are explained in the manuscript.

$d_{H...Cl}$ [Å]	ρ_{BCP} [a.u.]	$\nabla^2\rho_{BCP}$ [a.u.]	V_{BCP} [a.u.]	G_{BCP} [a.u.]	H_{BCP} [a.u.]	DI(A,B) [a.u.]	E_{elst} [kcal/mol]	E_{ind} [kcal/mol]	E_{disp} [kcal/mol]	E_{exch} [kcal/mol]	$\delta E^{HF}_{int,resp}$ [kcal/mol]	E^{SAPT}_{int} [kcal/mol]
2.428	1.708E-02	1.708E-02	-1.058E-02	1.114E-02	5.596E-04	1.043E-01	-4.661E+00	-4.743E+00	-2.549E+00	8.146E+00	-1.403E+00	-5.210E+00
2.500	1.464E-02	4.131E-02	-8.640E-03	9.483E-03	8.435E-04	9.341E-02	-4.222E+00	-4.043E+00	-2.208E+00	6.406E+00	-1.126E+00	-5.192E+00
2.600	1.184E-02	3.434E-02	-6.557E-03	7.571E-03	1.014E-03	8.001E-02	-3.728E+00	-3.288E+00	-1.811E+00	4.581E+00	-8.317E-01	-5.077E+00
2.800	7.742E-03	2.315E-02	-3.846E-03	4.817E-03	9.705E-04	5.810E-02	-3.021E+00	-2.280E+00	-1.226E+00	2.326E+00	-4.565E-01	-4.658E+00
3.000	5.069E-03	1.539E-02	-2.301E-03	3.075E-03	7.733E-04	4.169E-02	-2.555E+00	-1.672E+00	-8.390E-01	1.173E+00	-2.573E-01	-4.150E+00
3.500	1.773E-03	5.693E-03	-6.789E-04	1.051E-03	3.722E-04	1.748E-02	-1.874E+00	-9.144E-01	-3.495E-01	2.114E-01	-7.262E-02	-2.999E+00
4.000	6.139E-04	2.145E-03	-2.017E-04	3.690E-04	1.673E-04	6.830E-03	-1.503E+00	-5.703E-01	-1.611E-01	3.610E-02	-2.492E-02	-2.223E+00
4.500	2.005E-04	7.596E-04	-5.265E-05	1.213E-04	6.863E-05	1.213E-04	-1.268E+00	-3.803E-01	-8.148E-02	5.517E-03	-9.545E-03	-1.734E+00
5.000	6.862E-05	2.645E-04	-1.415E-05	4.014E-05	2.599E-05	9.955E-04	-1.079E+00	-2.678E-01	-4.556E-02	9.438E-04	-4.437E-03	-1.395E+00
6.000	6.279E-06	2.434E-05	-1.053E-06	3.569E-06	2.517E-06	1.176E-04	-8.444E-01	-1.441E-01	-1.655E-02	1.586E-05	-8.725E-04	-1.006E+00

Table S6. QTAIM and SAPT properties for the investigated range of H...Cl distances in the P-H...Cl bridge of the CAHB(-) type. All symbols are explained in the manuscript.

$d_{H...Cl}$ [Å]	ρ_{BCP} [a.u.]	$\nabla^2\rho_{BCP}$ [a.u.]	V_{BCP} [a.u.]	G_{BCP} [a.u.]	H_{BCP} [a.u.]	DI(A,B) [a.u.]	E_{elst} [kcal/mol]	E_{ind} [kcal/mol]	E_{disp} [kcal/mol]	E_{exch} [kcal/mol]	$\delta E^{HF}_{int,resp}$ [kcal/mol]	E^{SAPT}_{int} [kcal/mol]
2.315	2.310E-02	5.487E-02	-1.518E-02	1.445E-02	-7.304E-04	1.621E-01	-8.896E+00	-1.271E+01	-6.343E+00	2.395E+01	-3.110E+00	-7.103E+00
2.400	1.950E-02	4.853E-02	-1.205E-02	-1.205E-02	-2.410E-02	1.460E-01	-7.466E+00	-1.058E+01	-5.478E+00	1.896E+01	-2.458E+00	-7.027E+00
2.500	1.601E-02	4.126E-02	-9.238E-03	9.776E-03	5.381E-04	1.291E-01	-6.120E+00	-8.651E+00	-4.610E+00	1.440E+01	-1.851E+00	-6.835E+00
2.600	1.319E-02	3.461E-02	-7.138E-03	7.896E-03	7.573E-04	1.141E-01	-5.069E+00	-7.175E+00	-3.883E+00	1.095E+01	-1.386E+00	-6.565E+00
2.800	9.022E-03	2.381E-02	-4.361E-03	5.157E-03	7.961E-04	8.895E-02	-3.596E+00	-5.127E+00	-2.763E+00	6.357E+00	-7.665E-01	-5.896E+00
3.000	6.227E-03	1.627E-02	-2.735E-03	3.402E-03	6.666E-04	6.907E-02	-2.675E+00	-3.819E+00	-1.976E+00	3.718E+00	-4.141E-01	-5.165E+00
3.500	2.539E-03	6.598E-03	-9.160E-04	1.283E-03	3.668E-04	3.621E-02	-1.536E+00	-2.075E+00	-8.806E-01	1.000E+00	-7.590E-02	-3.567E+00
4.000	1.075E-03	2.839E-03	-3.172E-04	5.135E-04	1.963E-04	1.885E-02	-1.064E+00	-1.268E+00	-4.156E-01	2.811E-01	-4.590E-03	-2.472E+00
5.000	2.003E-04	5.168E-04	-3.500E-05	8.210E-05	4.710E-05	5.208E-03	-6.600E-01	-5.738E-01	-1.116E-01	2.436E-02	6.323E-03	-1.315E+00
6.000	4.179E-05	9.110E-05	-6.037E-06	1.441E-05	8.369E-06	1.424E-03	-4.658E-01	-3.027E-01	-3.749E-02	2.257E-03	2.821E-03	-8.010E-01
8.000	2.442E-06	5.357E-06	-3.477E-07	8.435E-07	4.958E-07	9.457E-05	-2.719E-01	-1.096E-01	-7.343E-03	2.219E-05	5.336E-04	-3.883E-01

Table S7. QTAIM and SAPT properties for the investigated range of H...Cl distances in the P-H...Cl bridge of the CAHB(+/-) type. All symbols are explained in the manuscript.

$d_{H...Cl}$ [Å]	ρ_{BCP} [a.u.]	$\nabla^2\rho_{BCP}$ [a.u.]	V_{BCP} [a.u.]	G_{BCP} [a.u.]	H_{BCP} [a.u.]	DI(A,B) [a.u.]	E_{elst} [kcal/mol]	E_{ind} [kcal/mol]	E_{disp} [kcal/mol]	E_{exch} [kcal/mol]	$\delta E^{HF}_{int,resp}$ [kcal/mol]	E^{SAPT}_{int} [kcal/mol]
1.650	1.006E-01	-1.444E-02	-1.050E-01	5.071E-02	-5.432E-02	3.823E-01	-1.352E+02	-7.514E+01	-1.592E+01	1.307E+02	-2.531E+01	-1.208E+02
1.750	8.072E-02	1.884E-02	-7.746E-02	4.108E-02	-3.637E-02	3.503E-01	-1.266E+02	-5.829E+01	-1.324E+01	1.010E+02	-2.154E+01	-1.187E+02
1.800	7.249E-02	2.958E-02	-6.666E-02	3.703E-02	-2.963E-02	3.506E-01	-1.228E+02	-5.167E+01	-1.208E+01	8.880E+01	-1.967E+01	-1.174E+02
1.900	5.866E-02	4.311E-02	-4.950E-02	3.014E-02	-1.936E-02	3.192E-01	-1.159E+02	-4.108E+01	-1.006E+01	6.868E+01	-1.615E+01	-1.145E+02
2.000	4.769E-02	4.884E-02	-3.684E-02	2.452E-02	-1.231E-02	2.893E-01	-1.101E+02	-3.315E+01	-8.376E+00	5.315E+01	-1.314E+01	-1.116E+02
2.200	3.182E-02	4.741E-02	-2.054E-02	1.620E-02	-4.345E-03	2.359E-01	-1.005E+02	-2.241E+01	-5.828E+00	3.198E+01	-8.498E+00	-1.052E+02
2.500	1.770E-02	3.308E-02	-8.899E-03	8.584E-03	-3.149E-04	1.724E-01	-8.988E+01	-1.338E+01	-3.409E+00	1.508E+01	-4.387E+00	-9.597E+01
3.000	7.048E-03	1.339E-02	-2.623E-03	2.985E-03	3.620E-04	1.009E-01	-7.771E+01	-6.471E+00	-1.431E+00	4.405E+00	-1.561E+00	-8.277E+01
3.500	2.940E-03	5.579E-03	-8.842E-04	1.139E-03	2.553E-04	5.752E-02	-6.900E+01	-3.525E+00	-6.306E-01	1.313E+00	-6.325E-01	-7.248E+01
4.000	1.262E-03	2.560E-03	-3.061E-04	4.730E-04	1.670E-04	3.229E-02	-6.227E+01	-2.115E+00	-2.958E-01	4.001E-01	-2.925E-01	-6.458E+01
6.000	4.497E-05	7.169E-05	-4.108E-06	1.102E-05	6.908E-06	2.806E-03	-4.508E+01	-4.730E-01	-2.693E-02	3.940E-03	-2.278E-02	-4.560E+01
8.000	2.238E-06	4.069E-06	-2.821E-07	6.497E-07	3.676E-07	1.942E-04	-3.542E+01	-1.679E-01	-5.351E-03	4.366E-05	-2.912E-03	-3.559E+01

Table S8. QTAIM and SAPT properties for the investigated range of H...Br distances in the N-H...Br bridge of the CAHB(+) type. All symbols are explained in the manuscript.

$d_{H...Br}$ [Å]	ρ_{BCP} [a.u.]	$\nabla^2\rho_{BCP}$ [a.u.]	V_{BCP} [a.u.]	G_{BCP} [a.u.]	H_{BCP} [a.u.]	DI(A,B) [a.u.]	E_{elst} [kcal/mol]	E_{ind} [kcal/mol]	E_{disp} [kcal/mol]	E_{exch} [kcal/mol]	$\delta E^{HF}_{int,resp}$ [kcal/mol]	E^{SAPT}_{int} [kcal/mol]
2.312	2.605E-02	4.747E-02	-1.839E-02	1.513E-02	-3.261E-03	1.105E-01	-6.002E+00	-1.142E+01	-3.237E+00	1.484E+01	-2.371E+00	-8.188E+00
2.400	2.168E-02	4.339E-02	-1.448E-02	1.266E-02	-1.815E-03	9.855E-02	-5.329E+00	-9.522E+00	-2.710E+00	1.127E+01	-1.881E+00	-8.175E+00
2.500	1.759E-02	3.832E-02	-1.103E-02	1.031E-02	-7.276E-04	8.523E-02	-4.695E+00	-7.831E+00	-2.216E+00	8.215E+00	-1.452E+00	-7.979E+00
2.600	1.427E-02	3.324E-02	-8.408E-03	8.359E-03	-4.925E-05	7.395E-02	-4.173E+00	-6.514E+00	-1.815E+00	5.978E+00	-1.130E+00	-7.654E+00
2.800	9.377E-03	2.405E-02	-4.884E-03	5.449E-03	5.642E-04	5.567E-02	-3.381E+00	-4.647E+00	-1.225E+00	3.149E+00	-7.026E-01	-6.807E+00
3.000	6.148E-03	1.674E-02	-2.846E-03	3.516E-03	6.698E-04	4.144E-02	-2.817E+00	-3.436E+00	-8.346E-01	1.648E+00	-4.528E-01	-5.893E+00
3.500	2.115E-03	6.236E-03	-7.600E-04	1.160E-03	3.995E-04	1.859E-02	-1.951E+00	-1.823E+00	-3.388E-01	3.183E-01	-1.706E-01	-3.965E+00
4.000	7.215E-04	2.295E-03	-2.185E-04	3.962E-04	1.777E-04	7.529E-03	-1.469E+00	-1.092E+00	-1.523E-01	5.954E-02	-7.102E-02	-2.725E+00
5.000	8.615E-05	3.018E-04	-1.867E-05	4.707E-05	2.839E-05	1.091E-03	-9.463E-01	-4.824E-01	-4.120E-02	1.941E-03	-1.399E-02	-1.482E+00
6.000	1.061E-05	3.342E-05	-1.463E-06	4.909E-06	3.446E-06	1.783E-04	-6.679E-01	-2.505E-01	-1.470E-02	6.116E-05	-3.333E-03	-9.363E-01
7.000	1.331E-06	3.753E-06	-1.957E-07	5.670E-07	3.712E-07	2.930E-05	-4.955E-01	-1.442E-01	-6.242E-03	1.670E-06	-1.079E-03	-6.469E-01

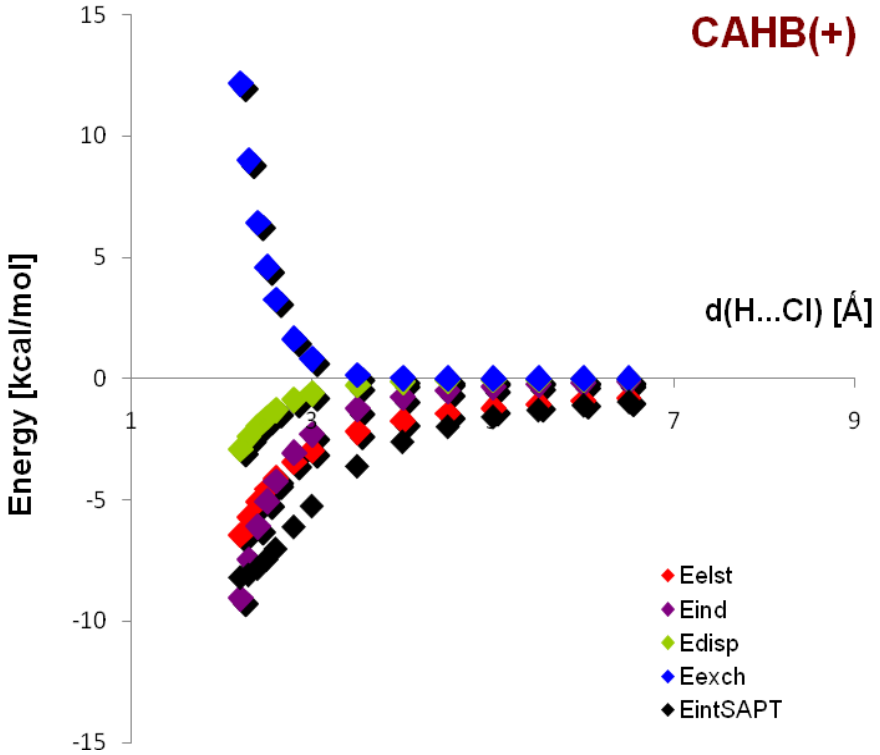
Table S9. QTAIM and SAPT properties for the investigated range of H...Br distances in the N-H...Br bridge of the CAHB(-) type. All symbols are explained in the manuscript.

$d_{H...Br}$ [Å]	ρ_{BCP} [a.u.]	$\nabla^2\rho_{BCP}$ [a.u.]	V_{BCP} [a.u.]	G_{BCP} [a.u.]	H_{BCP} [a.u.]	DI(A,B) [a.u.]	E_{elst} [kcal/mol]	E_{ind} [kcal/mol]	E_{disp} [kcal/mol]	E_{exch} [kcal/mol]	$\delta E^{HF}_{int,resp}$ [kcal/mol]	E^{SAPT}_{int} [kcal/mol]
2.483	1.848E-02	4.330E-02	-1.185E-02	1.134E-02	-5.097E-04	1.003E-01	-1.017E+01	-8.865E+00	-4.825E+00	1.764E+01	-1.480E+00	-7.707E+00
2.500	1.789E-02	4.223E-02	-1.133E-02	1.095E-02	-3.891E-04	9.721E-02	-9.943E+00	-8.519E+00	-4.685E+00	1.684E+01	-1.417E+00	-7.726E+00
2.600	1.474E-02	3.615E-02	-8.746E-03	8.892E-03	1.458E-04	8.643E-02	-8.726E+00	-6.788E+00	-3.937E+00	1.282E+01	-1.090E+00	-7.719E+00
2.800	1.217E-02	3.066E-02	-6.772E-03	7.219E-03	4.470E-04	7.738E-02	-7.731E+00	-5.485E+00	-3.312E+00	9.787E+00	-8.343E-01	-7.575E+00
3.000	6.922E-03	1.803E-02	-3.220E-03	3.864E-03	6.434E-04	5.447E-02	-5.668E+00	-3.115E+00	-1.986E+00	4.413E+00	-3.673E-01	-6.723E+00
3.500	2.781E-03	7.202E-03	-1.011E-03	1.406E-03	3.949E-04	2.979E-02	-3.845E+00	-1.465E+00	-8.730E-01	1.217E+00	-8.995E-02	-5.055E+00
4.000	1.159E-03	2.997E-03	-3.455E-04	5.473E-04	2.019E-04	1.589E-02	-2.879E+00	-8.105E-01	-4.045E-01	3.492E-01	-2.069E-02	-3.765E+00
5.000	2.205E-04	5.532E-04	-4.214E-05	9.022E-05	4.808E-05	4.310E-03	-1.859E+00	-3.316E-01	-1.045E-01	3.169E-02	1.974E-04	-2.263E+00
6.000	4.583E-05	9.805E-05	-6.186E-06	1.535E-05	9.163E-06	1.255E-03	-1.316E+00	-1.672E-01	-3.391E-02	3.096E-03	7.915E-04	-1.513E+00
8.000	2.992E-06	5.119E-06	-4.312E-07	8.554E-07	4.243E-07	1.047E-04	-7.662E-01	-5.790E-02	-6.249E-03	3.533E-05	2.133E-04	-8.301E-01

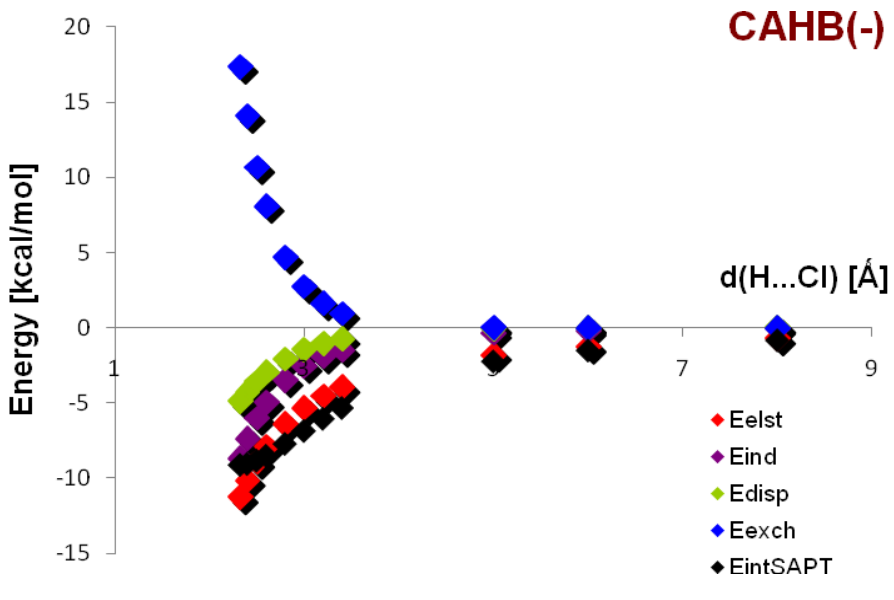
Table S10. QTAIM and SAPT properties for the investigated range of H...Br distances in the N-H...Br bridge of the CAHB(+/-) type. All symbols are explained in the manuscript.

$d_{H...Br}$ [Å]	ρ_{BCP} [a.u.]	$\nabla^2\rho_{BCP}$ [a.u.]	V_{BCP} [a.u.]	G_{BCP} [a.u.]	H_{BCP} [a.u.]	DI(A,B) [a.u.]	E_{elst} [kcal/mol]	E_{ind} [kcal/mol]	E_{disp} [kcal/mol]	E_{exch} [kcal/mol]	$\delta E^{HF}_{int,resp}$ [kcal/mol]	E^{SAPT}_{int} [kcal/mol]
1.940	6.012E-02	3.184E-02	-5.423E-02	3.110E-02	-2.314E-02	2.098E-01	-1.215E+02	-4.851E+01	-9.420E+00	7.277E+01	-9.199E+00	-1.158E+02
2.000	5.299E-02	3.676E-02	-4.525E-02	2.722E-02	-1.803E-02	2.001E-01	-1.182E+02	-4.280E+01	-8.381E+00	6.225E+01	-8.282E+00	-1.154E+02
2.250	3.251E-02	3.951E-02	-2.260E-02	1.624E-02	-6.360E-03	1.659E-01	-1.070E+02	-2.714E+01	-5.272E+00	3.363E+01	-5.217E+00	-1.110E+02
2.500	2.037E-02	3.114E-02	-1.170E-02	9.742E-03	-1.958E-03	1.238E-01	-9.805E+01	-1.812E+01	-3.342E+00	1.837E+01	-3.267E+00	-1.044E+02
2.750	1.295E-02	2.180E-02	-6.199E-03	5.824E-03	-3.747E-04	1.022E-01	-9.071E+01	-1.253E+01	-2.135E+00	1.011E+01	-2.128E+00	-9.740E+01
3.000	8.344E-03	1.429E-02	-3.361E-03	3.467E-03	1.057E-04	8.167E-02	-8.454E+01	-8.908E+00	-1.378E+00	5.591E+00	-1.463E+00	-9.069E+01
3.500	3.574E-03	5.777E-03	-1.050E-03	1.247E-03	1.972E-04	5.284E-02	-7.460E+01	-4.835E+00	-5.952E-01	1.730E+00	-7.943E-01	-7.909E+01
4.000	1.581E-03	2.509E-03	-3.540E-04	4.906E-04	1.366E-04	3.319E-02	-6.687E+01	-2.848E+00	-2.739E-01	5.429E-01	-4.705E-01	-6.992E+01
6.000	6.594E-05	7.908E-05	-6.616E-06	1.319E-05	6.577E-06	4.045E-03	-4.749E+01	-5.826E-01	-2.323E-02	5.930E-03	-5.033E-02	-4.814E+01
8.000	3.117E-06	3.127E-06	-2.559E-07	5.188E-07	2.629E-07	3.020E-04	-3.688E+01	-1.965E-01	-4.361E-03	7.483E-05	-5.421E-03	-3.709E+01

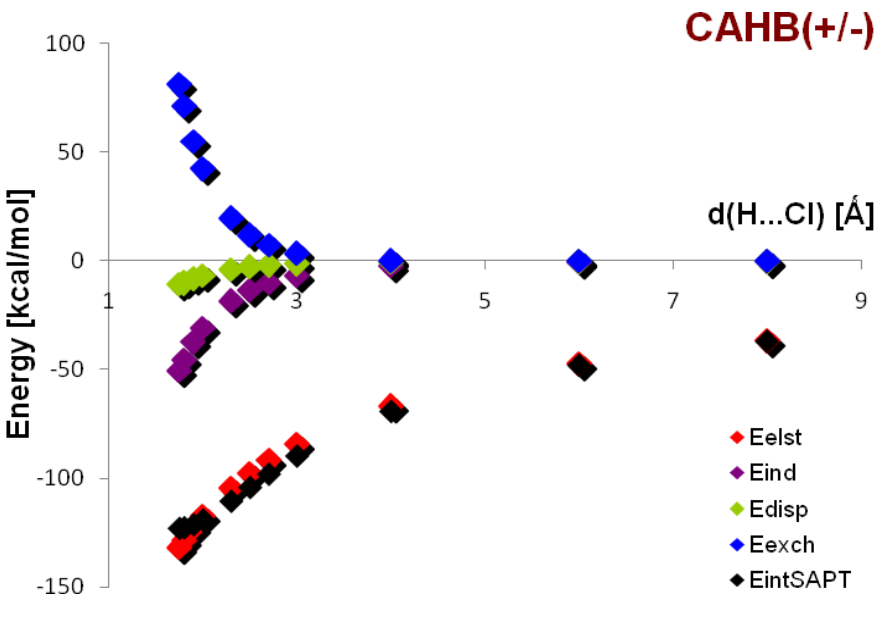
S5. Figures for the subsection "The influence of atom types in H-bridge on energy and QTAIM parameters of CAHBs in question"



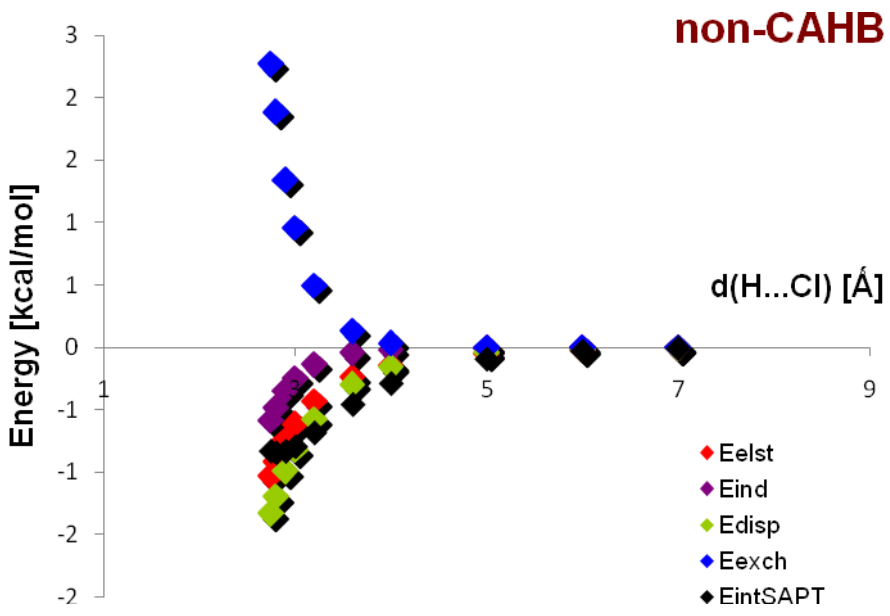
(a)



(b)

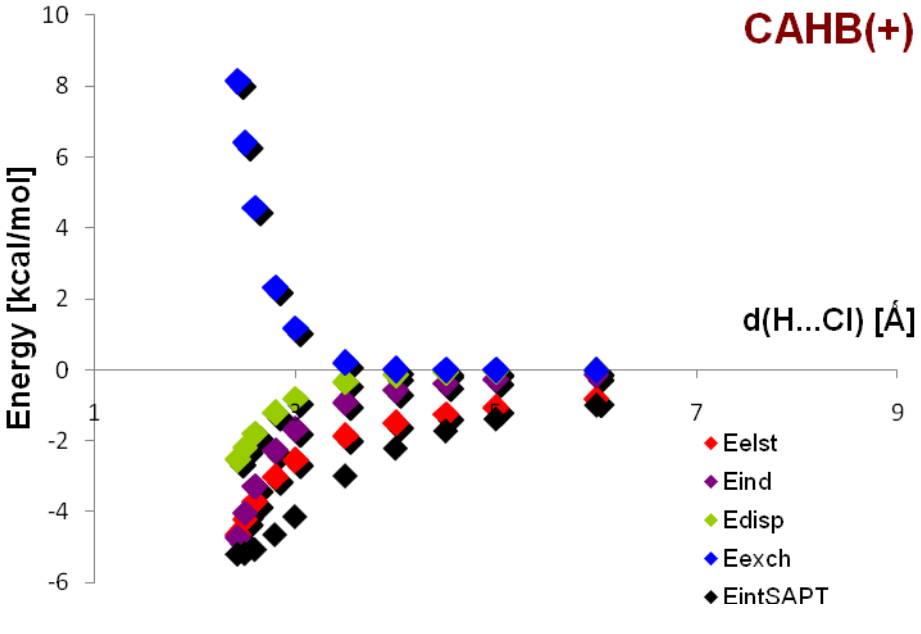


(c)

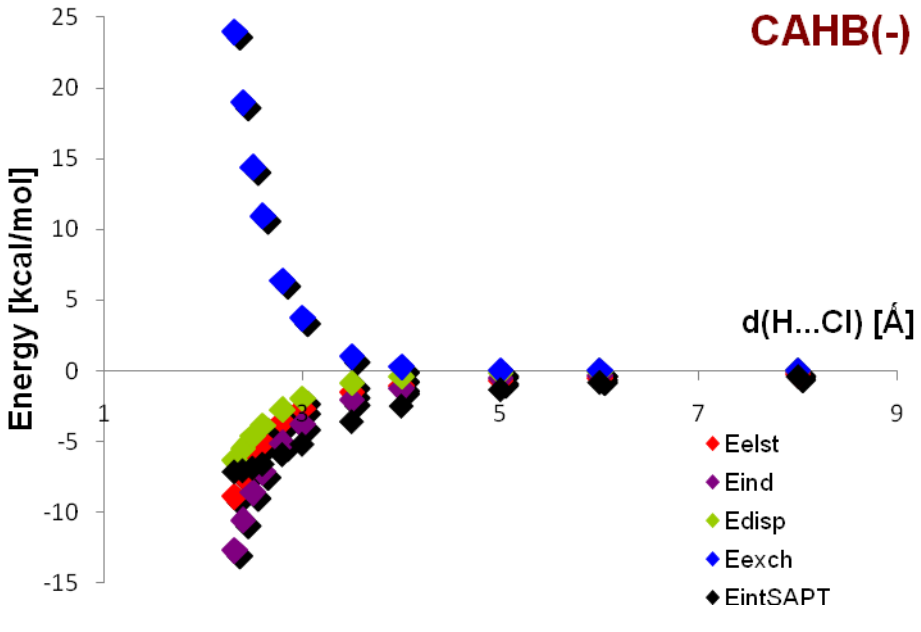


(d)

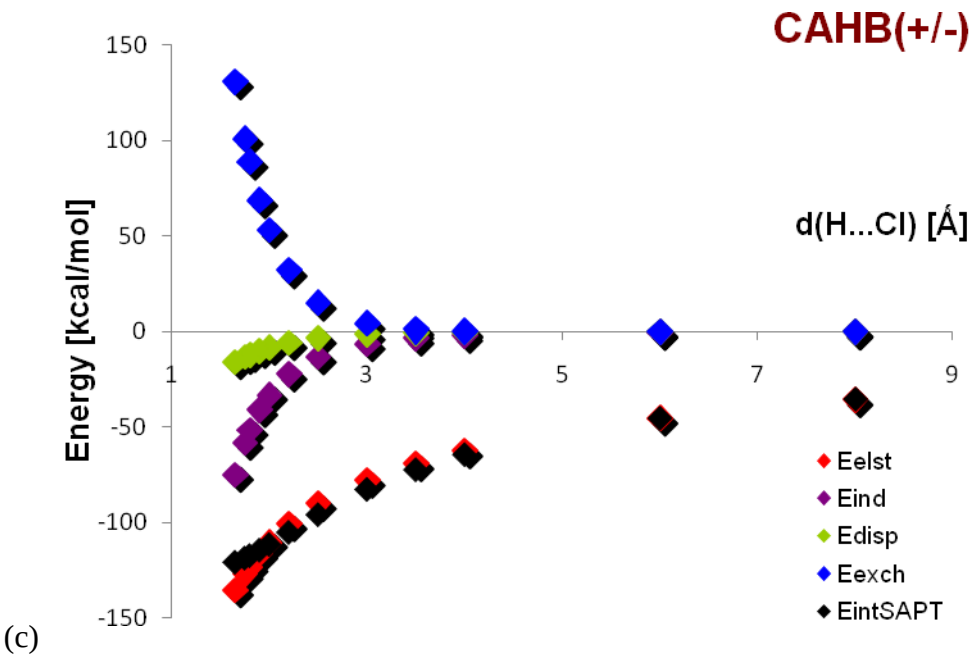
Fig. S1. SAPT energy components and SAPT interaction energy as a function of H-bond length for (a) N-H...Cl^+, (b) N-H...Cl^-, (c) N^+-H...Cl^-, and (d) N-H...Cl bridges.


CAHB(+)
Energy [kcal/mol]
d(H...Cl) [Å]
Eelst
Eind
Edisp
Eexch
EintSAPT

(a)

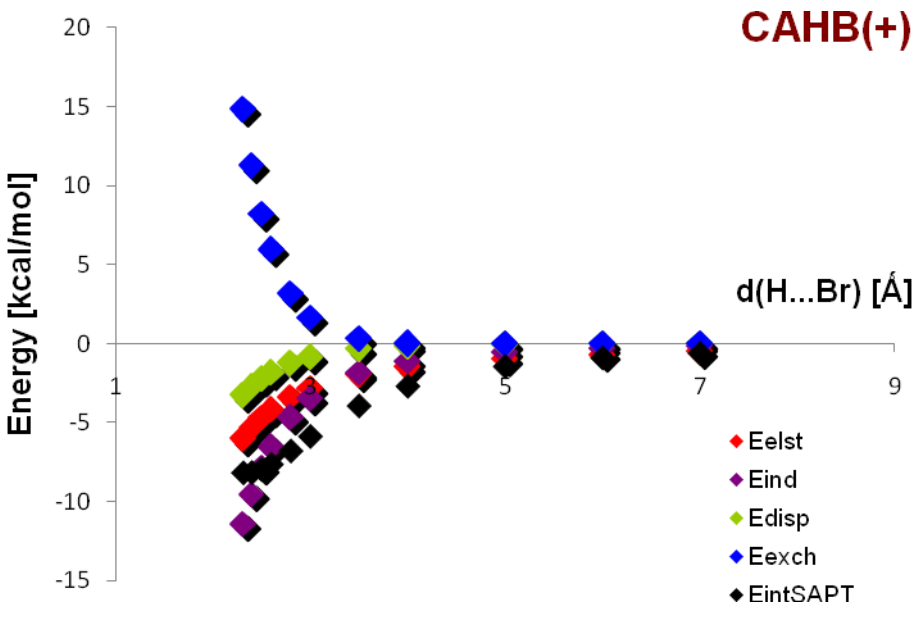

CAHB(-)
Energy [kcal/mol]
d(H...Cl) [Å]
Eelst
Eind
Edisp
Eexch
EintSAPT

(b)

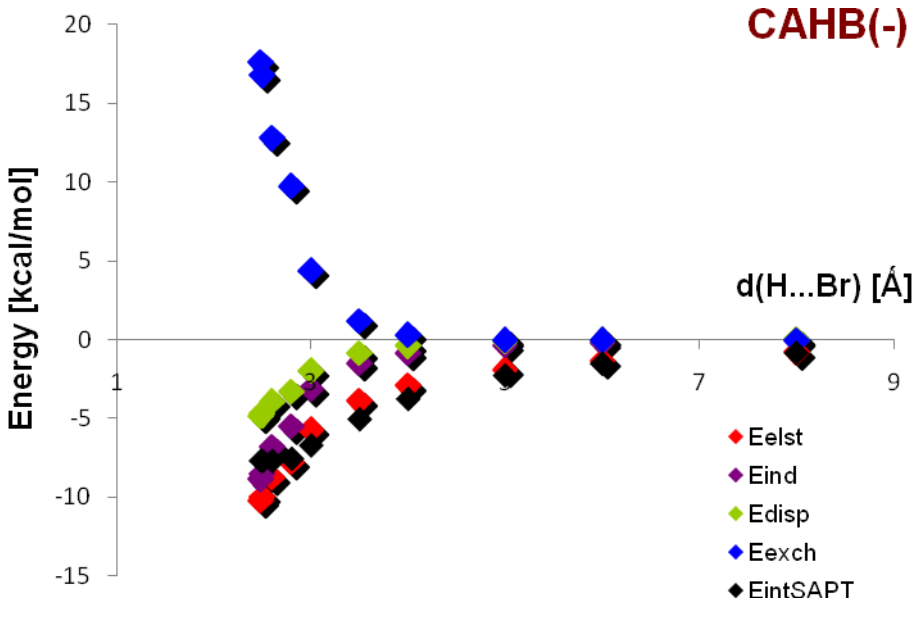


(c)

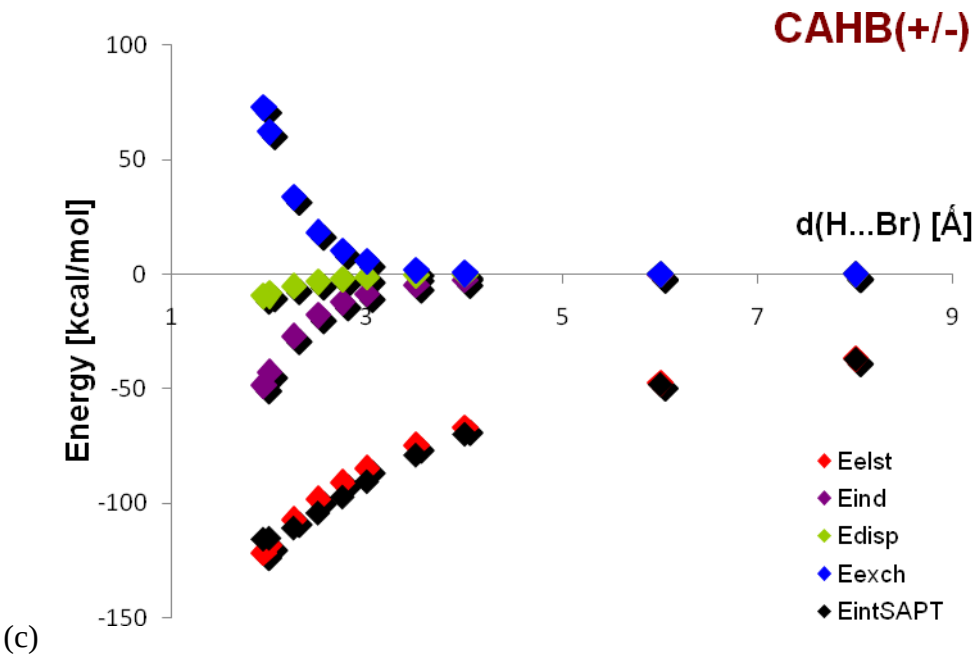
Fig. S2. SAPT energy components and SAPT interaction energy as a function of H-bond length for (a) P-H...Cl^+, (b) P-H...Cl^-, and (c) P^+-H...Cl^- bridges.


CAHB(+)
Energy [kcal/mol]
d(H...Br) [Å]
Eelst
Eind
Edisp
Eexch
EintSAPT

(a)


CAHB(-)
Energy [kcal/mol]
d(H...Br) [Å]
Eelst
Eind
Edisp
Eexch
EintSAPT

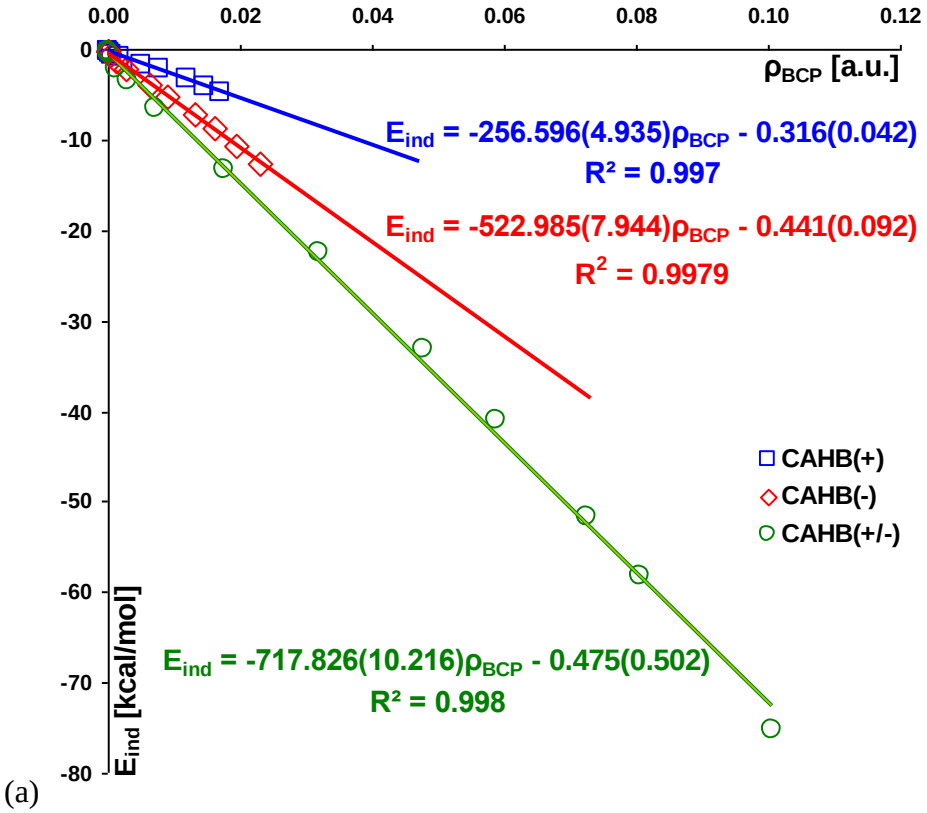
(b)



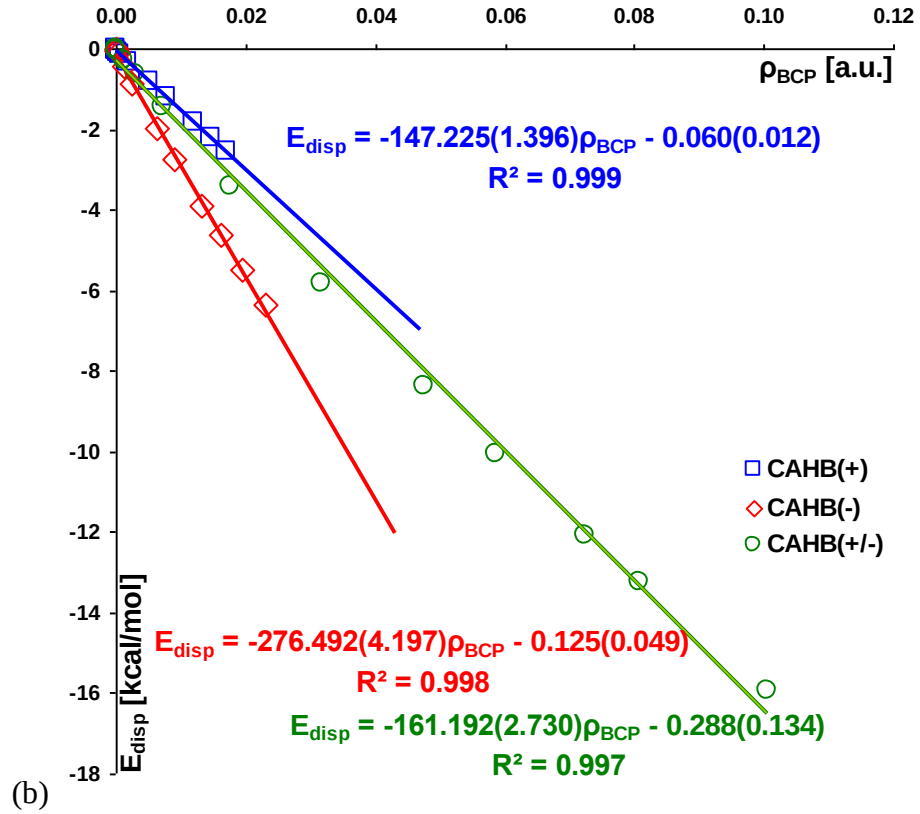
(c)

Fig. S3. SAPT energy components and SAPT interaction energy as a function of H-bond length for (a) N-H...Br^{+}, (b) N-H...Br^{-}, and (c) N^{+}-H...Br^{-} bridges.

S6. Figures for the subsection "QTAIM vs. SAPT"



(a)



(b)

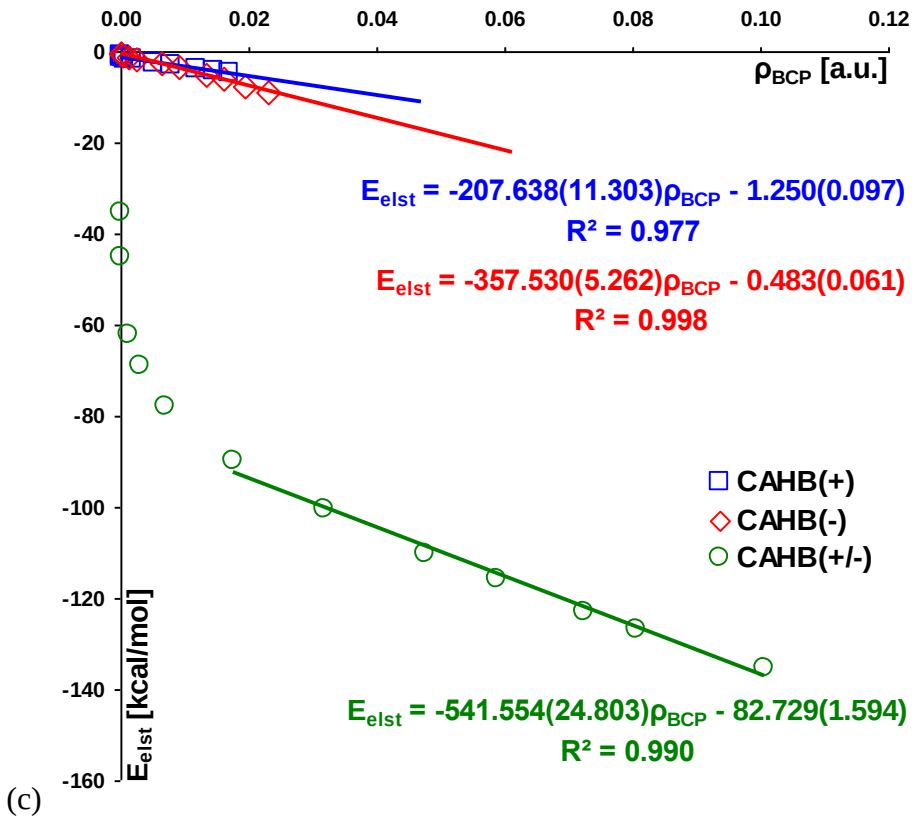
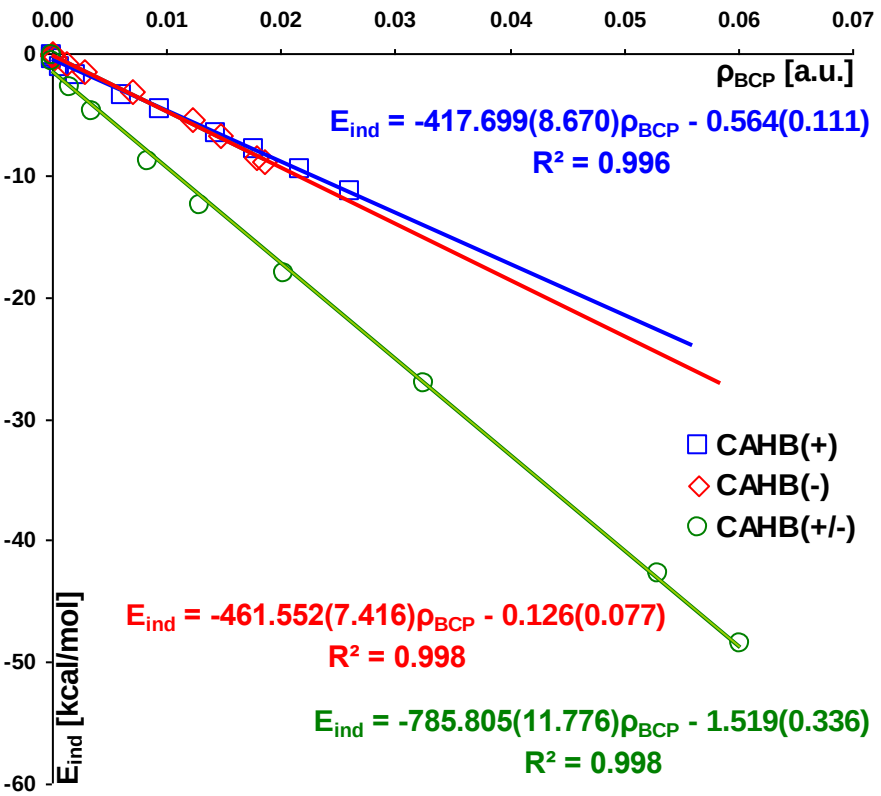
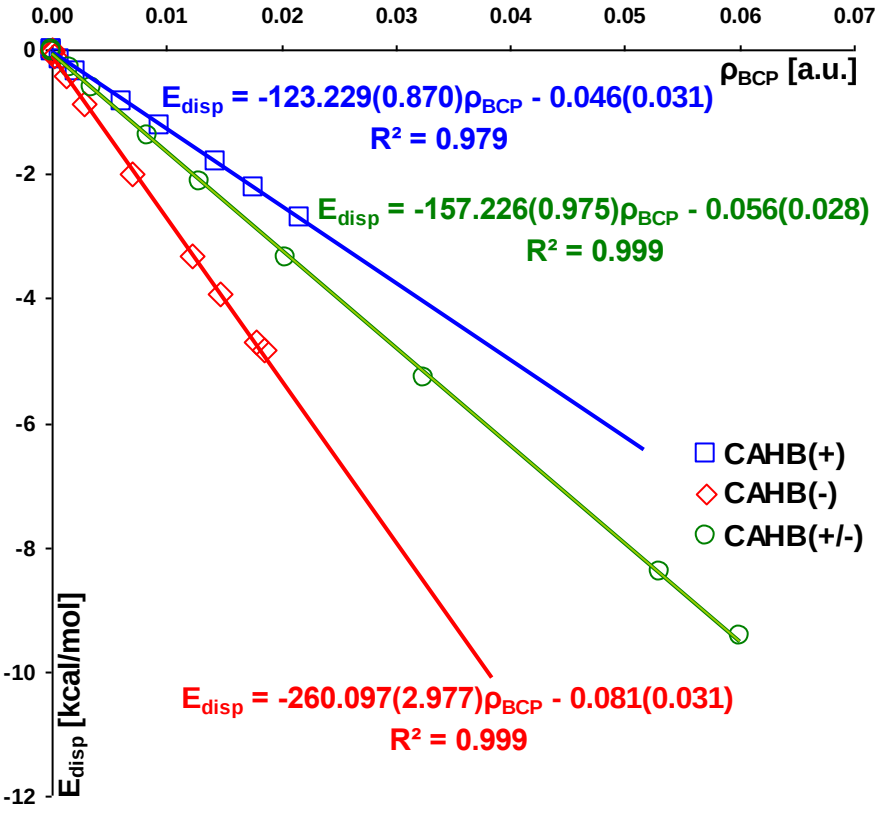


Fig. S4. Relation between the individual attractive components of E_{int}^{SAPT}: (a) E_{ind}; (b) E_{disp}; (c) E_{elst}; and the electron density calculated in H-BCP, ρ_{BCP}. Data obtained for H-bonds of P-H...Cl type. The equations determined using linear regression, the appropriate coefficients of determination, R^2, and e. s. d. s (in parentheses) are also shown. In the case of the relation between E_{elst} and ρ_{BCP} in the CAHB(+/-) bridge, the linear regression equation, R^2, and e.s.d.s (in parentheses) were calculated for E_{elst} and ρ_{BCP} that correspond to the distances $1.65 < d_{H...Cl} < 2.5$ Å.


0.00
0.01
0.02
0.03
0.04
0.05
0.06
0.07
0
-10
-20
-30
-40
-50
-60
ρBCP [a.u.]
Eind [kcal/mol]
Eind = -417.699(8.670)ρBCP - 0.564(0.111)
R² = 0.996
CAHB(+)
CAHB(-)
CAHB(+/-)
Eind = -461.552(7.416)ρBCP - 0.126(0.077)
R² = 0.998
Eind = -785.805(11.776)ρBCP - 1.519(0.336)
R² = 0.998

(a)


0.00
0.01
0.02
0.03
0.04
0.05
0.06
0.07
0
-2
-4
-6
-8
-10
-12
ρBCP [a.u.]
Edisp [kcal/mol]
Edisp = -123.229(0.870)ρBCP - 0.046(0.031)
R² = 0.979
Edisp = -157.226(0.975)ρBCP - 0.056(0.028)
R² = 0.999
CAHB(+)
CAHB(-)
CAHB(+/-)
Edisp = -260.097(2.977)ρBCP - 0.081(0.031)
R² = 0.999

(b)

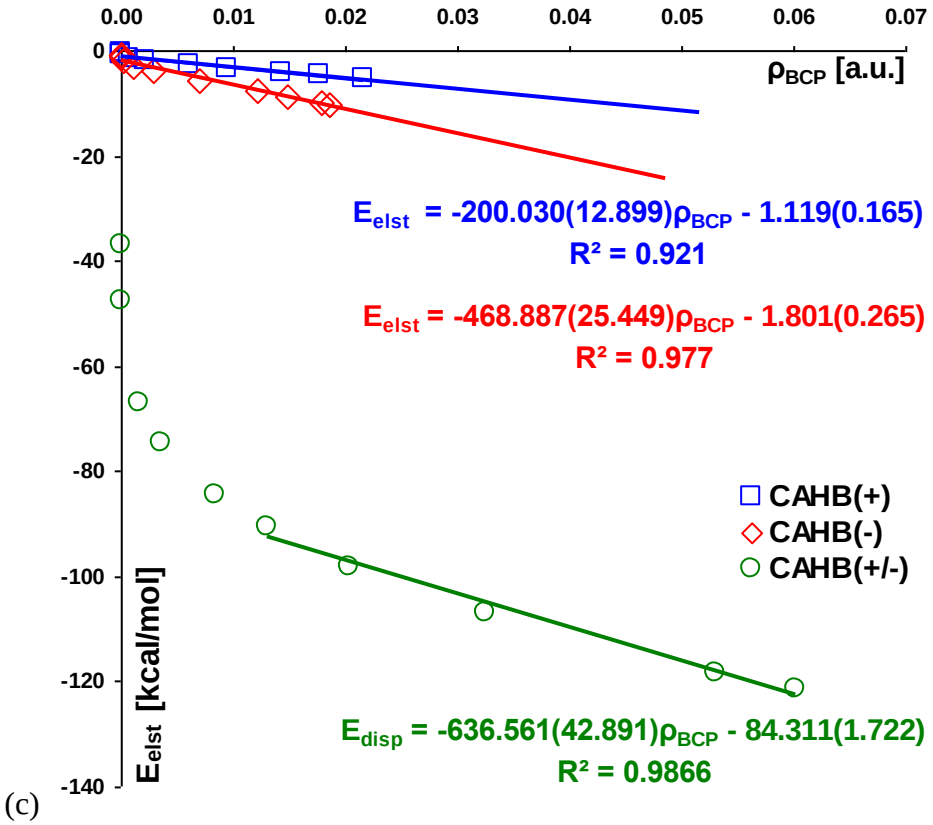


Fig. S5. Relation between the individual attractive components of E_{int}^{SAPT}: (a) E_{ind}; (b) E_{disp}; (c) E_{elst}; and the electron density calculated in H-BCP, ρ_{BCP}. Data obtained for H-bonds of N-H...Br type. The equations determined using linear regression, the appropriate coefficients of determination, R^2, and e. s. d.s (in parentheses) are also shown. In the case of the relation between E_{elst} and ρ_{BCP} in the CAHB(+/-) bridge, the linear regression equation, R^2, and e.s.d.s (in parentheses) were calculated for E_{elst} and ρ_{BCP} that correspond to the distances $1.94 < d_{H...Br} < 2.75$ Å.

S7. Relation between the components of interaction energy and the electronic density in BCP

As it is discussed in the manuscript, some ranges of the linear relation between a given component of the interaction energy (E_{elst} defined by eq. 3, E_{ind} by eq. 4, and E_{disp} by eq. 5) and the electron density in H-BCP (ρ_{BCP}) can be found for all the CAHBs and one investigated non-CAHB. In order to check whether the character of this relation is influenced by the forms of induction and dispersion components, we have applied another grouping scheme for the energy correction terms from eq. 1:

Eq. S2 $$E_{int}^{SAPT} = E_{elst} + E_{ind}^{*} + E_{disp}^{*} + E_{exch}^{*}$$

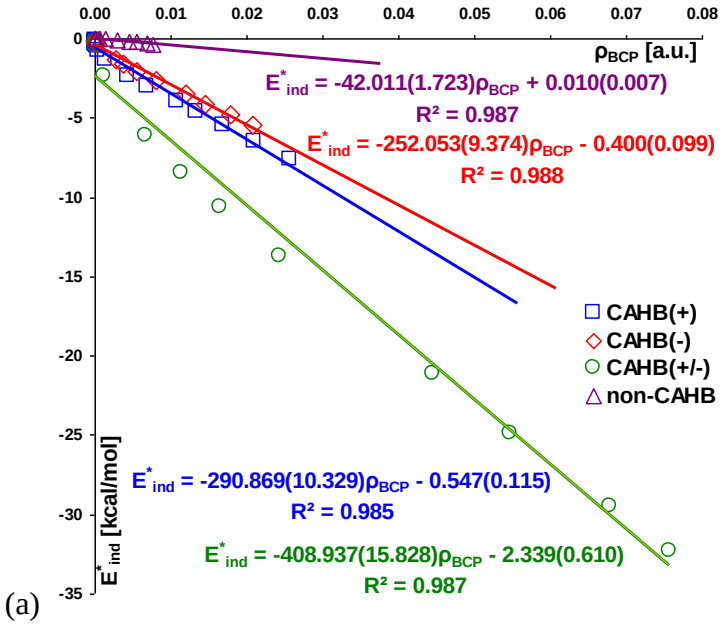
where E_{elst} is the same as in eq. 3, whereas the remaining components collect the following energy correction terms:

Eq. S3 $$E_{ind}^{*} = E_{ind,resp}^{(20)} + {}^{t}E_{ind}^{(22)} + E_{exch-ind,resp}^{(20)} + {}^{t}E_{exch-ind}^{(22)} + \delta E_{int,resp}^{HF}$$

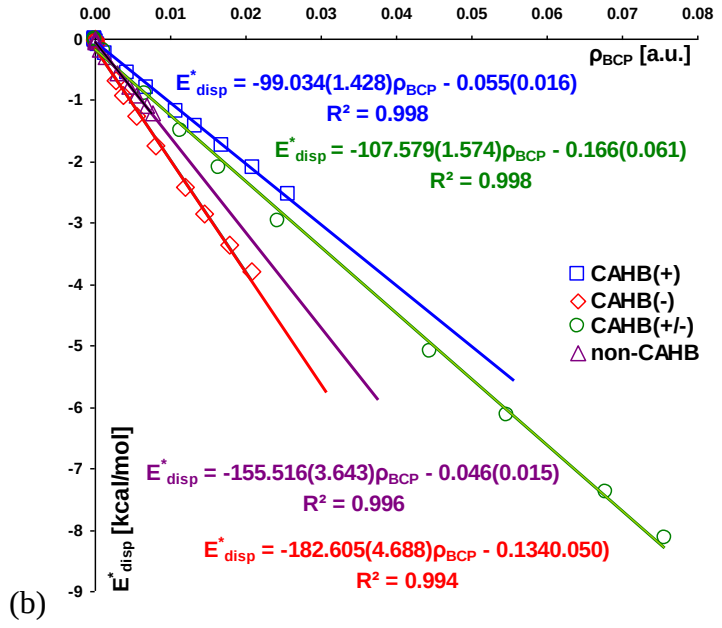
Eq. S4 $$E_{disp}^{*} = E_{disp}^{(20)} + \varepsilon_{disp}^{(2)}(2) + E_{exch-disp}^{(20)}$$

Eq. S5 $$E_{exch}^{*} = E_{exch}^{(10)} + \varepsilon_{exch}^{(1)}(CCSD).$$

This grouping scheme was previously proposed by Thanthiriwatte et al.[S6] The plots of the relation between E_{ind}^{*} or E_{disp}^{*} and ρ_{BCP} are shown in Figs. S6-S8. The ranges of the linear relation are also clearly evident for the grouping scheme in which the induction and dispersion energy correction terms are quenched by their exchange counterparts.

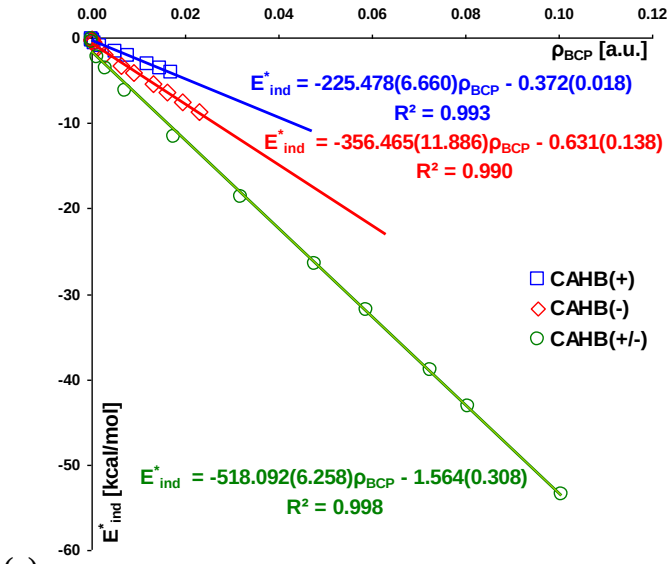


(a)

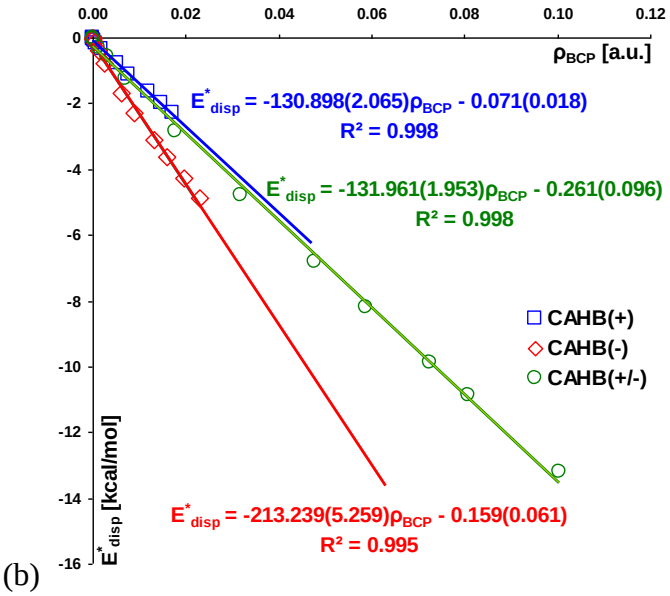


(b)

Fig. S6. Relation between a given component of E_{int}^{SAPT}: (a) E_{ind}^{*}; (b) E_{disp}^{*}; and the electron density calculated in H-BCP, ρ_{BCP}. Data obtained for H-bonds of N-H...Cl type. The E_{ind}^{*} and E_{disp}^{*} components are given by eqs. S3 and S4, respectively. The equations determined using linear regression, the appropriate coefficients of determination, R^2, and e.s.d.s (in parentheses) are also shown.

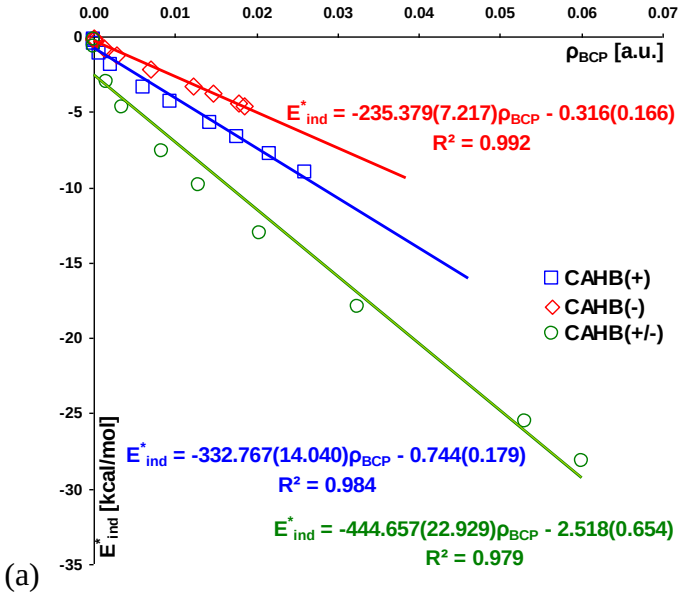


(a)

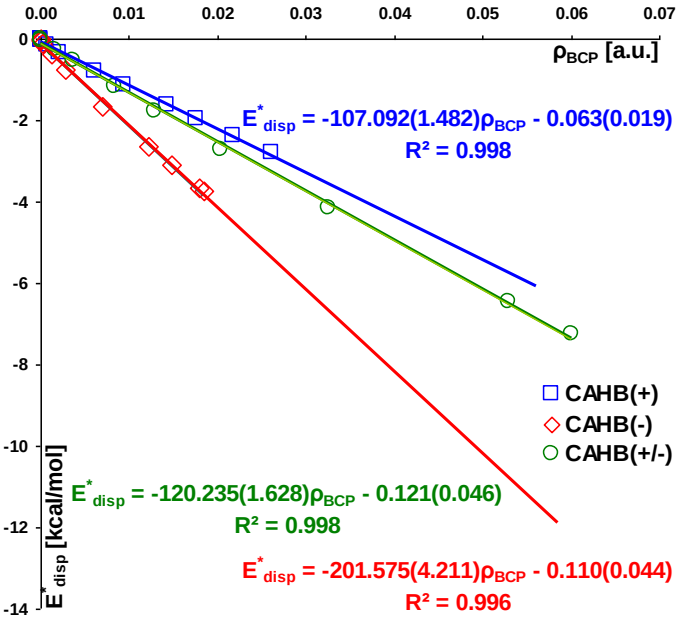


(b)

Fig. S7. Relation between a given component of E_{int}^{SAPT}: (a) E_{ind}^{*}; (b) E_{disp}^{*}; and the electron density calculated in H-BCP, ρ_{BCP}. Data obtained for H-bonds of P-H...Cl type. The E_{ind}^{*} and E_{disp}^{*} components are given by eqs. S3 and S4, respectively. The equations determined using linear regression, the appropriate coefficients of determination, R^2, and e.s.d.s (in parentheses) are also shown.



(a)



(b)

Fig. S8. Relation between a given component of E_{int}^{SAPT}: (a) E_{ind}^{*}; (b) E_{disp}^{*}; and the electron density calculated in H-BCP, ρ_{BCP}. Data obtained for H-bonds of N-H...Br type. The E_{ind}^{*} and E_{disp}^{*} components are given by eqs. S3 and S4, respectively. The equations determined using linear regression, the appropriate coefficients of determination, R^2, and e.s.d.s (in parentheses) are also shown.

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