Theoretical insight to intermolecular hydrogen bond interactions between methyl N-(2-pyridyl) carbamate and acetic acid: substituent effects, cooperativity and energy decomposition analysis

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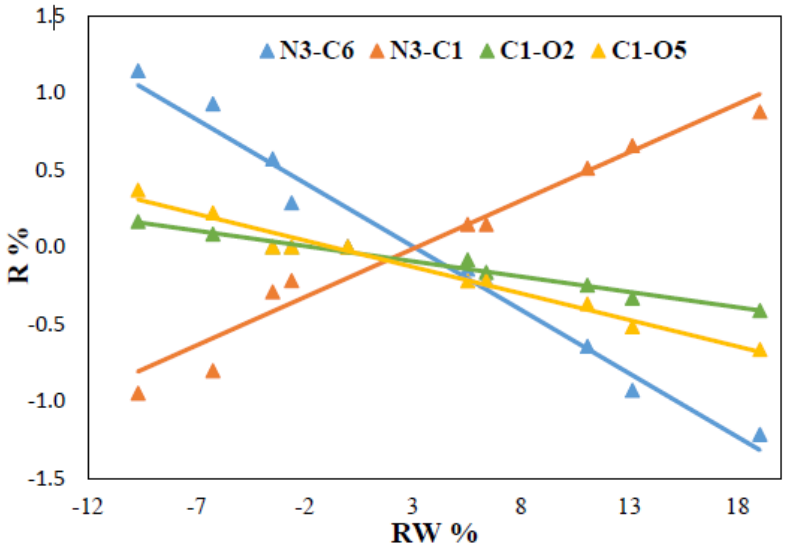

Fig. S1. Correlation between changes in the the Resonance Weight (RW %) of structures D and changes in the most important bond lengths (R %) shown in scheme 3. $\left[\mathrm{RW\%} = \left(\frac{\mathrm{RW_X - RW_H}}{\mathrm{RW_H}}\right) \times 100\right]$, $\left[\mathrm{R\%} = \left(\frac{\mathrm{R_X - R_H}}{\mathrm{R_H}}\right) \times 100\right]$

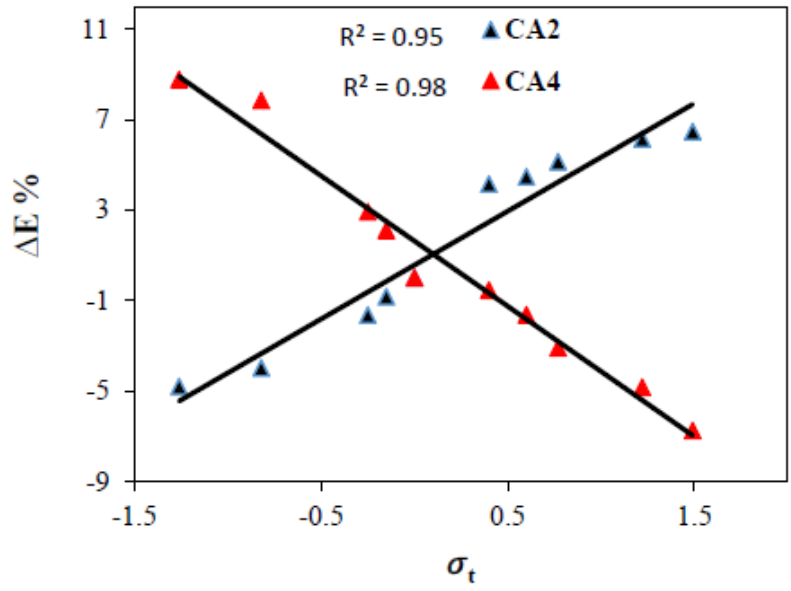

Fig. S2. Correlation between the change in the binding energies (ΔE %) and the Hammett constants σ_{tot} of substituents for the complexes **CA2** and **CA4**. $\left[\Delta\mathrm{E\%} = \left(\frac{\Delta\mathrm{E_X - \Delta E_H}}{\Delta\mathrm{E_H}}\right) \times 100\right]$

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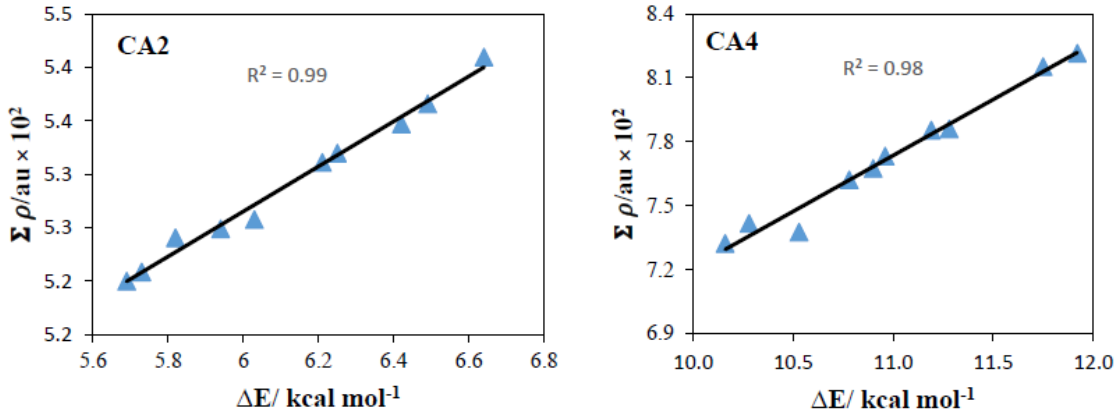

Fig. S3. Linear relationship between the sums of electron densities ∑ρ calculated at HBCPs and the binding energies (−ΔE in kcal mol^{-1}) in the complexes **CA2** and **CA4**.

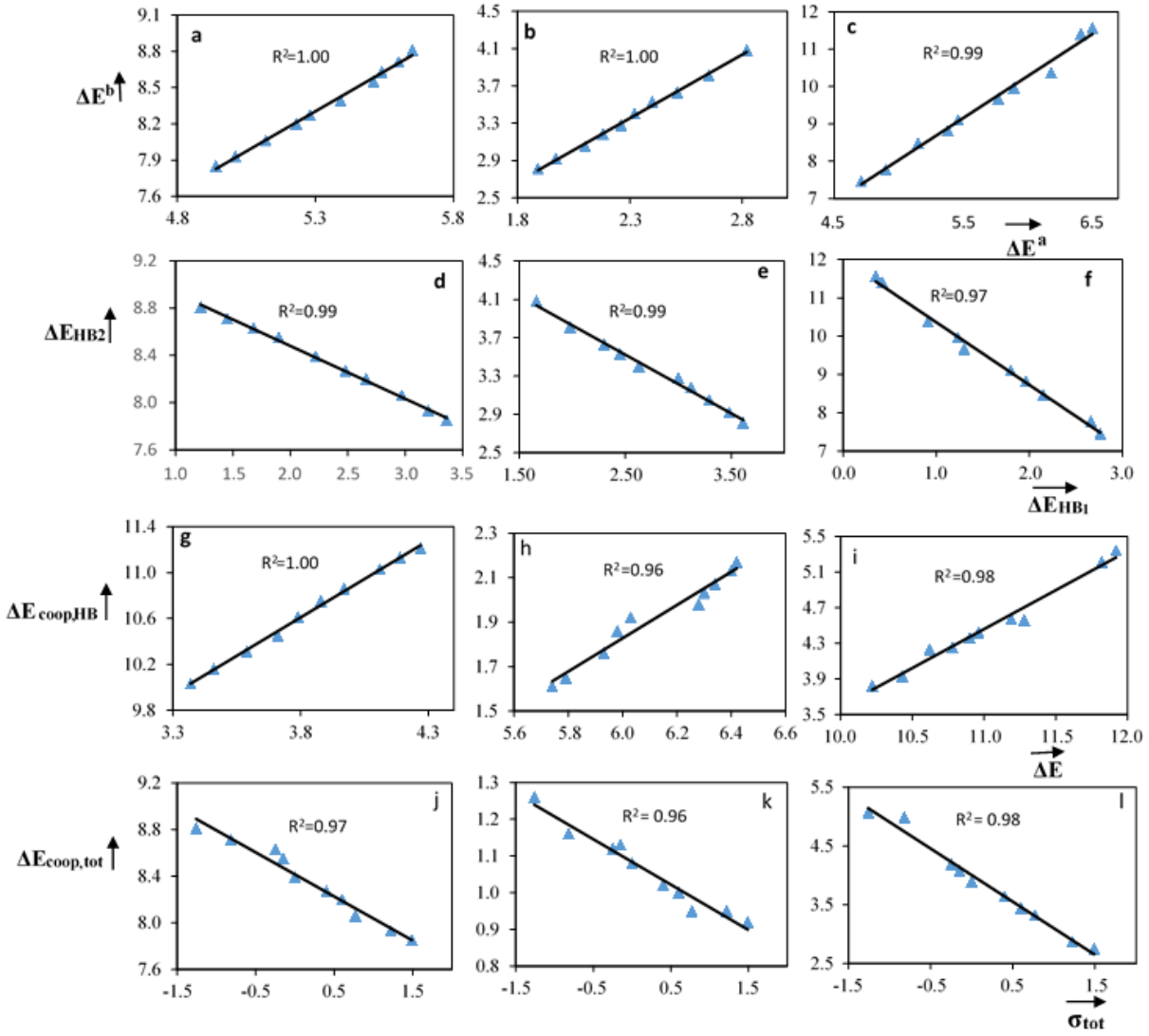

Fig. S4. (a)-(c) Correlation between the individual HB energies estimated using the SHB structures, ΔE^{a}_{HB} and the ρ values of the DHB complexes, ΔE^{b}_{HB} for HB2 interaction (d)-(f) Correlation between the ΔE^{b}_{HB1} and ΔE^{b}_{HB2} (g)-(i) Correlation between the cooperativity of total HB interaction ($-\Delta E_{coop,\ tot}$) and the binding energy (−ΔE) and (i)-(l) Correlation between ΔE_{coop} for HB2 interaction ($-\Delta E_{coop,\ HB1}$) and the Hammett constants (σ_{tot}), in the complexes **CA1**, **CA2** and **CA4**, respectively. The HB1 and HB2 correspond to the NH···O and N…OH interactions, respectively. All energies were given in kcal mol^{-1}.

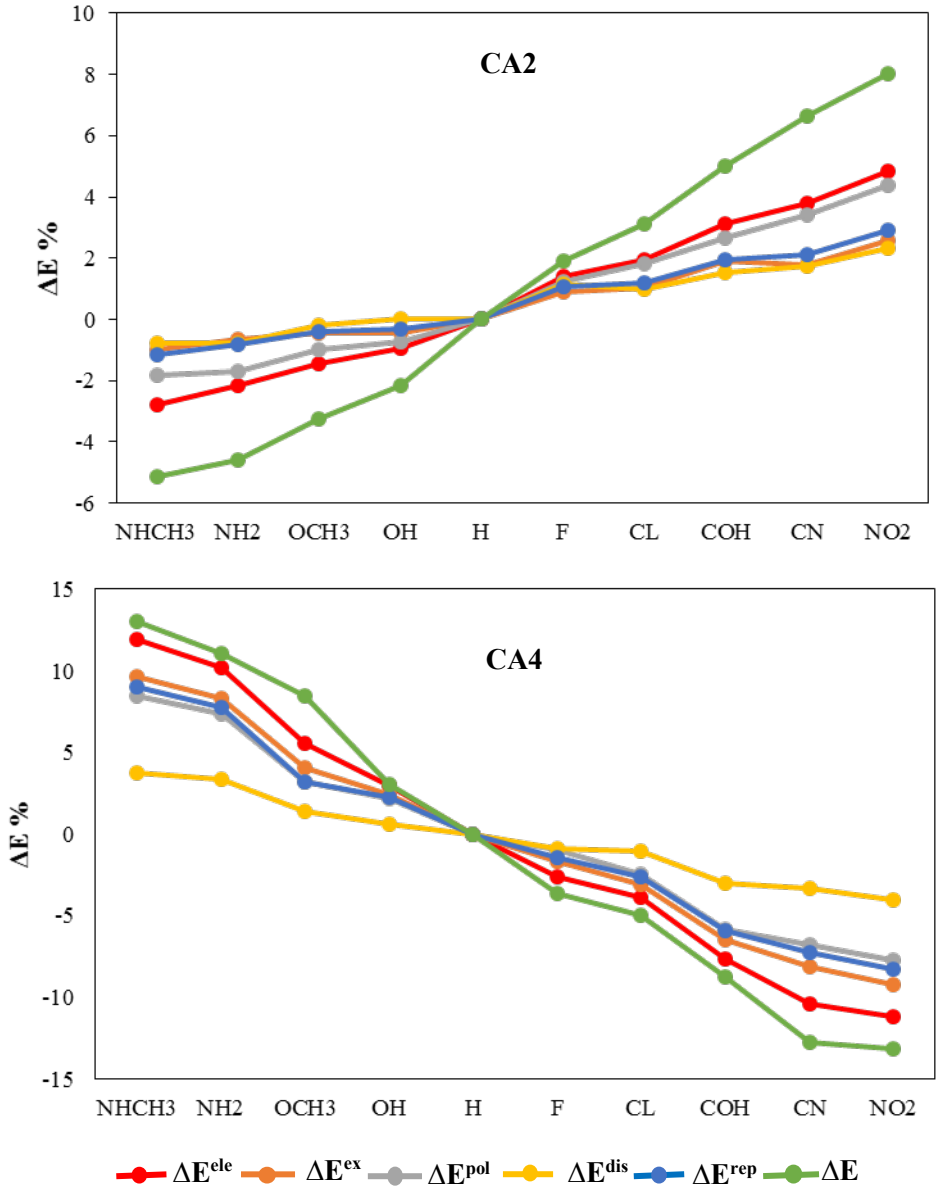

Fig. S5. The changes in energy terms (ΔE %) obtained using the LMO-EDA scheme for the complexes **CA2** and **CA4**. $\left[\Delta E\% = \left(\frac{\Delta E_X - \Delta E_H}{\Delta E_H}\right) \times 100\right]$

Table S1. The values of -ΔE (kcal mol^{-1}) of complexes calculated using several methods in conjunction with the 6-311++G(d,p) basis set.

	CA1				CA2			
	B3LYP	M06-2X	MP2	B3LYP-D3	B3LYP	M06-2X	MP2	B3LYP-D3
$NHCH_3$	**11.33**	12.54, **13.03**	12.74, **12.98**	13.99, **14.25**	**6.30**	9.01,**9.41**	9.41, **9.56**	9.48, **9.63**
NH_2	**11.33**	12.84, **13.14**	12.98, **13.26**	13.94, **14.24**	**6.33**	9.06,**9.49**	9.42, **9.57**	9.52, **9.68**
OCH_3	**11.49**	13.01,**13.35**	13.04, **13.32**	14.25, **14.56**	**6.48**	9.17,**9.57**	9.44, **9.59**	9.62, **9.78**
OH	**11.65**	13.13, **13.47**	13.19, **13.47**	14.20, **14.50**	**6.54**	9.28,**9.70**	9.55, **9.70**	9.74, **9.89**
H	**11.65**	13.34, **13.64**	13.38, **13.65**	14.29, **14.58**	**6.67**	9.40,**9.84**	9.60, **9.73**	9.85, **9.98**
F	**11.81**	13.51, **13.81**	13.59, **13.86**	14.39, **14.68**	**6.94**	9.52,**9.96**	9.76, **9.89**	10.06, **10.19**
Cl	**11.93**	13.65, **13.87**	13.64, **13.92**	14.42, **14.71**	**6.97**	9.59,**9.96**	9.63, **9.76**	10.07, **10.21**
COH	**12.11**	13.77, **14.11**	13.87, **14.15**	14.62, **14.92**	**7.01**	9.76,**10.16**	9.95, **10.08**	10.27, **10.41**
CN	**12.02**	13.89, **14.25**	13.99, **14.33**	14.63, **14.99**	**7.21**	9.87,**10.22**	9.89, **9.96**	10.43, **10.50**
NO_2	**12.14**	14.08, **14.38**	14.19, **14.53**	14.76, **15.11**	**7.33**	10.02,**10.40**	9.93, **10.00**	10.56, **10.63**
	CA3				**CA4**			
	B3LYP	M06-2X	MP2	B3LYP-D3	B3LYP	M06-2X	MP2	B3LYP-D3
$NHCH_3$	**14.70**	15.74, **16.49**	16.16, **16.67**	17.96, **18.52**	**13.13**	14.59,**14.97**	14.82,**15.17**	16.52, **16.90**
NH_2	**14.53**	15.57, **16.28**	15.96, **16.49**	17.76, **18.34**	**12.95**	14.36,**14.75**	14.61,**14.98**	16.31, **16.72**
OCH_3	**14.32**	15.56, **16.08**	15.70, **16.22**	17.57, **18.15**	**12.36**	14.19,**14.25**	14.13,**14.49**	13.32, **13.65**
OH	**13.80**	15.16, **15.61**	15.30, **15.80**	16.07, **16.61**	**12.26**	13.98,**14.20**	14.09,**14.44**	15.71, **16.11**
H	**13.57**	15.02, **15.31**	15.09, **15.58**	16.78, **17.33**	**12.13**	13.81,**13.88**	13.88,**14.21**	15.48, **15.85**
F	**13.50**	14.90, **15.22**	15.01, **15.50**	16.74, **17.29**	**12.06**	13.75,**13.85**	13.86,**14.19**	15.43, **15.80**
Cl	**13.37**	14.82, **15.14**	14.83, **15.31**	16.61, **17.16**	**11.93**	13.56,**13.67**	13.69,**14.01**	15.30, **15.66**
COH	**12.86**	14.31, **14.55**	14.32, **14.79**	16.04, **16.57**	**11.75**	13.09,**13.20**	13.30,**13.61**	14.77, **15.12**
CN	**12.88**	14.21, **14.54**	14.33, **14.84**	16.05, **16.62**	**11.46**	13.02,**13.13**	13.20,**13.56**	14.76, **15.16**
NO_2	**12.75**	14.17, **14.47**	14.35, **14.85**	15.93, **16.49**	**11.34**	12.95,**13.08**	13.23,**13.57**	14.66, **15.04**

The bold data belong to the values calculated with the aug-cc-pVTZ basis set.

Table S2. The binding energies (-ΔE_{HB} in kcal mol^{-1}) of complexes studied at the B3LYP/6 311++G(d,p) computational level in PCM−Water Phase.

	CA1	CA2	CA3	CA4
$NHCH_3$	8.22	5.06	11.28	10.94
NH_2	8.28	5.04	11.06	10.77
OCH_3	8.31	5.08	10.86	10.21
OH	8.36	5.11	10.23	9.93
H	8.38	5.14	10.10	9.86
F	8.39	5.16	9.94	9.60
Cl	8.41	5.19	10.03	9.44
COH	8.45	5.22	9.65	9.31
CN	8.50	5.26	9.33	9.07
NO_2	8.54	5.29	9.20	8.90

Table S3. The bond lengths optimized at the B3LYP/6-311++G(d,p) level (in A^{-1}), Partial Charges on the oxygen atom of carbonyl and alkoxy groups (in au) in syn rotamer of methyl N-(2-pyridyl) carbamate

	Bond Length			Partial Charges	Resonance Weight			
	N_3-C_6	N_3-C_1	C_1-O_2(C_1-O_5)	O_2(O_5)	A	B	C	D
$NHCH_3$	1.417	1.358	1.213(1.361)	-0.6466(-0.5671)	22.44	11.24	7.68	5.02
NH_2	1.414	1.360	1.212(1.359)	-0.6448(-0.5665)	23.83	11.17	8.05	5.22
OCH_3	1.409	1.367	1.211(1.356)	-0.6454(-0.5647)	28.55	10.89	8.15	5.58
OH	1.405	1.368	1.211(1.356)	-0.6360(-0.5656)	30.28	10.96	8.20	5.63
H	1.401	1.371	1.211(1.356)	-0.6393(-0.5653)	30.83	10.75	8.23	5.78
F	1.398	1.373	1.209(1.353)	-0.6354(-0.5628)	30.14	10.43	8.52	6.15
Cl	1.399	1.373	1.210(1.353)	-0.6353(-0.5628)	30.02	10.40	8.36	6.10
COH	1.392	1.378	1.208(1.351)	-0.6287(-0.5636)	29.41	10.01	8.55	6.42
CN	1.388	1.380	1.207(1.349)	-0.6320(-0.5604)	27.10	9.91	8.71	6.54
NO_2	1.384	1.383	1.206(1.347)	-0.6278(-0.5602)	25.24	9.76	8.98	6.88

Resonance Weight calculated from natural resonance theory (NTR) within the NBO methodology for resonance structures A-C shown in scheme 3.

Table S4. The electron density ($\rho \times 10^2$) values (in au) calculated at the HBCPs and the bond lengths optimized at the B3LYP/6-311++G(d,p) level (in Å)

	CA1		CA2		CA3		CA4	
	ρ_{HB1}	ρ_{HB2}	ρ_{HB1}	ρ_{HB2}	ρ_{HB1}	ρ_{HB2}	ρ_{HB1}	ρ_{HB2}
$NHCH_3$	2.31(1.969)	4.14(1.709)	2.06(2.017)	3.14(1.824)	2.84(1.895)	5.60(1.677)	2.72(1.908)	5.50(1.693)
NH_2	2.35(1.962)	4.11(1.711)	2.10(2.008)	3.10(1.828)	2.83(1.891)	5.63(1.684)	2.75(1.903)	5.41(1.700)
OCH_3	2.39(1.954)	4.08(1.712)	2.17(1.994)	3.07(1.833)	2.86(1.889)	5.43(1.699)	2.70(1.909)	5.16(1.718)
OH	2.42(1.943)	4.07(1.718)	2.21(1.987)	3.04(1.837)	2.86(1.892)	5.46(1.709)	2.74(1.903)	5.11(1.722)
H	2.48(1.939)	4.01(1.720)	2.19(1.992)	3.07(1.832)	2.81(1.893)	5.13(1.723)	2.74(1.904)	4.99(1.733)
F	2.55(1.924)	3.97(1.724)	2.29(1.971)	3.02(1.839)	2.90(1.880)	5.02(1.731)	2.82(1.890)	4.85(1.743)
Cl	2.56(1.926)	3.98(1.725)	2.30(1.970)	3.02(1.839)	2.89(1.881)	4.98(1.734)	2.82(1.891)	4.80(1.748)
COH	2.55(1.921)	4.04(1.723)	2.31(1.969)	3.04(1.836)	2.82(1.891)	4.83(1.747)	2.75(1.901)	4.66(1.760)
CN	2.67(1.906)	3.91(1.731)	2.40(1.951)	2.96(1.847)	2.93(1.874)	4.68(1.759)	2.86(1.884)	4.51(1.773)
NO_2	2.71(1.900)	3.89(1.733)	2.95(1.943)	2.95(1.848)	2.94(1.873)	4.60(1.766)	2.87(1.883)	4.45(1.778)

The data in the parentheses correspond to the bond lengths.
The HB1 and HB2 correspond to the O (N) ···H and NH···O hydrogen bonds, respectively.

Table S5. The estimated values of individual hydrogen bond energies ($-\Delta E_{HB}$ in kcal mol^{-1}) and the cooperativity energy ($-\Delta E_{COOP}$ in kcal mol^{-1}) in the complexes **CA2** and **CA4**

	ΔE^{a}_{HB1}	ΔE^{a}_{HB2}	ΔE^{b}_{HB1}	ΔE^{b}_{HB2}	$\Delta E_{COOP(HB1)}$	$\Delta E_{COOP(HB2)}$	$\Delta E_{COOP(T)}$
CA1(CA2)							
$NHCH_3$	1.01(1.31)	5.65(2.82)	1.22(1.66)	8.81(4.08)	0.21(0.35)	3.16(1.26)	3.37(1.61)
NH_2	1.10(1.49)	5.60(2.65)	1.45(1.98)	8.71(3.81)	0.35(0.49)	3.11(1.16)	3.46(1.65)
OCH_3	1.18(1.66)	5.54(2.51)	1.68(2.30)	8.63(3.63)	0.50(0.64)	3.09(1.12)	3.59(1.76)
OH	1.23(1.72)	5.51(2.40)	1.90(2.45)	8.55(3.53)	0.67(0.73)	3.04(1.13)	3.71(1.86)
F	1.59(2.04)	5.28(2.26)	2.48(3.00)	8.27(3.28)	0.89(0.96)	2.99(1.02)	3.88(1.98)
Cl	1.66(2.09)	5.23(2.18)	2.66(3.12)	8.20(3.18)	1.00(1.03)	2.97(1.00)	3.97(2.03)
COH	1.80(2.17)	5.12(2.10)	2.97(3.29)	8.06(3.05)	1.17(1.12)	3.94(0.95)	4.11(2.07)
CN	1.93(2.30)	5.01(1.97)	3.20(3.48)	7.93(2.92)	1.27(1.18)	2.92(0.95)	4.19(2.13)
NO_2	2.00(2.36)	4.94(1.89)	3.36(3.61)	7.85(2.81)	1.30(1.25)	2.91(0.92)	4.27(2.17)
CA3(CA4)							
$NHCH_3$	0.18(0.18)	7.01(6.50)	0.27(0.45)	13.13(11.57)	0.09(0.27)	6.12(5.07)	6.21(5.34)
NH_2	0.25(0.20)	6.89(6.41)	0.30(0.42)	12.92(11.40)	0.09(0.22)	6.03(4.99)	6.12(5.21)
OCH_3	0.50(0.54)	6.59(6.18)	0.92(0.91)	12.02(10.37)	0.42(0.37)	5.43(4.19)	5.85(4.56)
OH	0.74(0.73)	6.47(5.89)	1.30(1.23)	11.17(9.96)	0.56(0.50)	4.70(4.07)	5.26(4.57)
F	1.16(1.08)	5.87(5.46)	2.01(1.80)	10.14(9.10)	0.86(0.73)	4.27(3.64)	5.12(4.36)
Cl	1.22(1.15)	5.79(5.38)	2.11(1.96)	9.92(8.82)	0.89(0.81)	4.13(3.44)	5.02(4.25)
COH	1.31(1.24)	5.47(5.15)	2.22(2.15)	9.35(8.47)	0.92(0.91)	3.88(3.32)	4.80(4.23)
CN	1.63(1.60)	5.17(4.90)	2.77(2.66)	8.71(7.77)	1.14(1.06)	3.54(2.87)	4.68(3.93)
NO_2	1.78(1.69)	5.04(4.71)	2.98(2.76)	8.39(7.46)	1.20(1.07)	3.35(2.75)	4.55(3.82)

The data in the parenthesis correspond to complex **CA2**.

The HB1 and HB2 correspond to the NH···O and O (N) ···H hydrogen bonds, respectively.

a and b correspond to the individual HB energies estimated using the SHB structures and estimated from the ρ values calculated at the HBCPs of DHB complexes, respectively.

Table S6. The LMO-EDA results of **CA1** complex at the B3LYP/6-311++G(d,p) computational level(kcal mol^{-1})

	ΔE^{ele}	ΔE^{ex}	ΔE^{pol}	ΔE^{disp}	ΔE^{rep}	ΔE
$NHCH_3$	-23.73, *-6.88,* **-15.78**(-1.07**)**	-12.55, *-4.01*,**-8.59**(0.05)	-12.50, *-3.35*, **-8.34**(-0.81)	-5.76, *-2.56*, **-3.69**(0.49)	42.44, *14.80*, **29.03**(-1.39)	-12.10, *-2.00*, **-7.37**(-2.73)
NH_2	-24.00, *-7.38,* **-15.55**(-1.07)	-12.57, *-4.10*,**-8.52**(0.05)	-12.63, *-3.46*, **-8.26**(-0.91)	-5.77, *-2.77*, **-3.69**(0.69)	42.77, *15.56*, **28.70**(-1.49)	-12.20, *-2.15*, **-7.32**(-2.73)
OCH_3	-24.11, *-7.57,* **-15.48**(-1.06)	-12.60, *-4.36*,**-8.27**(0.03)	-12.65, *-3.58*, **-8.25**(-0.82)	-5.78, *-2.80*, **-3.66**(0.68)	42.85, *15.91*, **28.58**(-1.64)	-12.29, *-2.40*, **-7.08**(-2.81)
OH	-24.26*, -7.77,* **-15.29**(-1.20)	-12.63, *-4.50*, **-8.19**(0.06)	-12.66, *-3.69*, **-8.01**(-0.96)	-5.78, *-2.85*, **-3.63**(0.70)	42.87, *16.35*, **28.11**(-1.59)	-12.46, *-2.46*, **-7.01**(-2.99)
F	-24.40, *-8.39,* **-14.78**(-1.23)	-12.69, *-4.69*, **-8.00**(0.00)	-12.70, *-3.95*, **-7.73**(-1.02)	-5.78, *-2.92*, **-3.59**(0.73)	42.95, *17.05*, **27.55**(-1.65)	-12.62, *-2.90*, **-6.74**(-3.17)
Cl	-24.52, *-8.49,* **-14.75**(-1.28)	-12.71, *-4.71*, **-8.04**(0.04)	-12.78, *-4.02*, **-7.69**(-1.07)	-5.78, *-2.92*, **-3.61**(0.75)	43.09, *17.15*, **27.59**(-1.65)	-12.70, *-2.99*, **-6.55**(-3.21)
COH	-24.68, *-8.56,* **-14.83**(-1.29)	-12.72, *-4.78*, **-8.01**(0.07)	-12.81, *-4.05*, **-7.70**(-1.06)	-5.79, *-3.94*, **-3.61**(0.79)	43.16, *17.34*, **27.70**(-1.88)	-12.84, *-2.99*, **-6.45**(-3.40)
CN	-24.74, *-9.01,***-14.41**(-1.32)	-12.74, *-4.95*, **-7.88**(0.09)	-12.85, *-4.31*, **-7.45**(-1.09)	-5.80, *-3.00*, **-3.57**(0.77)	43.26, *17.97*, **27.15**(-1.86)	-12.87, *-3.30*, **-6.16**(-3.41)
NO_2	-24.83, *-9.19,* **-14.32**(-1.32)	-12.79, *-5.04*, **-7.83**(0.08)	-12.90, *-4.40*, **-7.38**(-1.12)	-5.81, *-3.05*, **-3.56**(0.80)	43.38, *18.28*,**27.01**(-1.91)	-12.95, *-3.40*, **-6.08**(-3.47)

The first column corresponds to DHB complexes, the second column corresponds to NH…O hydrogen bond (Italic data), the third column corresponds to O…HO hydrogen bond (bold data) and the forth column corresponds to ΔΔEX that was estimated from Eqs. (7) – (10) (data in parentheses)

Table S7. The LMO-EDA results of **CA2** complex at the B3LYP/6-311++G(d,p) computational level(kcal mol^{-1})

	ΔE^{ele}	ΔE^{ex}	ΔE^{pol}	ΔE^{disp}	ΔE^{rep}	ΔE
$NHCH_3$	-16.14, *-6.40*, **-9.61,** (-0.13)	-8.84, *-3.41,* **-5.75,** (0.32)	-8.08, *-2.96,* **-5.01,** (-0.11)	-5.13, *-2.55,***-3.39,**(0.81)	31.20, *13.09,* **20.46,** (-2.35)	-6.98, *-2.23,* **-3.30,** (-1.46)
NH_2	-16.24, *-6.70,* **-9.41,** (-0.13)	-8.87, *-3.61,* **-5.69,** (0.43)	-8.09, *-3.02,* **-4.94,** (-0.13)	-5.13, *-2.56,***-3.38,**(0.81)	31.30, *13.51,* **20.24,** (-2.45)	-7.04, *-2.38,* **-3.19,** (-1.46)
OCH_3	-16.36, *-7.00,* **-9.28,** (-0.08)	-8.89, *-3.73,* **-5.53,** (0.37)	-8.15, *-3.19,* **-4.84,** (-0.12)	-5.16, *-2.57,***-3.36,**(0.77)	31.43, *13.96,* **19.88,** (-2.41)	-7.13, *-2.53,* **-3.12,** (-1.48)
OH	-16.44, *-7.15,* **-9.28,** (-0.01)	-8.89, *-3.76,* **-5.47,** (0.34)	-8.17, *-3.20,* **-4.79,** (-0.18)	-5.17, *-2.59,***-3.27,**(0.69)	31.46, *14.00,* **19.80,** (-2.34)	-7.21, *-2.70,* **-3.02,** (-1.49)
F	-16.83, *-7.75,* **-8.97,** (-0.11)	-9.01, *-4.01,* **-5.35,** (0.35)	-8.33, *-3.46,* **-4.63,** (-0.24)	-5.23, *-2.72,***-3.29,**(0.78)	31.89, *14.83,* **19.43,** (-2.37)	-7.51, *-3.11,* **-2.81,** (-1.59)
Cl	-16.92, *-7.82,* **-8.95,** (-0.15)	-9.02, *-4.02,* **-5.37,** (0.37)	-8.38, *-3.52,* **-4.60,** (-0.26)	-5.22, *-2.71,***-3.31,**(0.80)	31.94, *14.88,* **19.45,** (-2.39)	-7.60, *-3.19,* **-2.78,** (-1.63)
COH	-17.12, *-8.05,* **-8.91,** (-0.16)	-9.10, *-4.14,* **-5.30,** (0.34)	-8.45, *-3.65,* **-4.56,** (-0.24)	-5.25, *-2.75,***-3.29,**(0.79)	32.18, *15.25,* **19.33,** (-2.40)	-7.74, *-3.34,* **-2.73,** (-1.67)
CN	-17.23, *-8.31,***-8.74,** (-0.18)	-9.09, *-4.24,* **-5.27,** (0.42)	-8.51, *-3.78,* **-4.46,** (-0.27)	-5.26, *-2.79,***-3.27,**(0.80)	32.23, *15.64,* **18.14,** (-2.55)	-7.86, *-3.48,* **-2.60,** (-1.78)
NO_2	-17.40,*-8.55,* **-8.69** (-0.17)	-9.16, *-4.36,* **-5.23,** (0.43)	-8.59, *-3.89,* **-4.42,** (-0.29)	-5.29, *-2.87,***-3.26,**(0.84)	32.48, *16.08,* **18.04,** (-2.65)	-7.96, *-3.58,* **-2.56,** (-1.83)

The first column corresponds to DHB complexes, the second column corresponds to NH…O hydrogen bond (Italic data), the third column corresponds to O…HO hydrogen bond (bold data) and the forth column corresponds to ΔΔEX that was estimated from Eqs. (7) – (10) (data in parentheses)

Table S8. The LMO-EDA results of **CA3** complex at the B3LYP/6-311++G(d,p) computational level(kcal mol^{-1})

	ΔE^{ele}	ΔE^{ex}	ΔE^{pol}	ΔE^{disp}	ΔE^{rep}	ΔE
$NHCH_3$	-35.63,*-9.20,***-24.57,**(-1.86)	-20.40,*-5.60,***-15.65,**(0.85)	-19.71,*-4.50,***-14.24,**(-0.97)	-7.07,*-3.17,***-4.96,**(1.06)	65.66,*19.90,***49.99,**(-4.23)	-17.15,*-2.57,***-9.43,**(-5.15)
NH_2	-34.99,*-9.33,***-23.84,**(-1.82)	-20.10,*-5.65,***-15.27,**(0.82)	-19.47,*-4.55,***-14.04,**(-0.88)	-7.02,*-3.20,***-4.90,**(1.08)	64.76,*20.12,***48.79,**(-4.15)	-16.82,*-2.61,***-9.26,**(-4.95)
OCH_3	-33.71,*-9.46,***-22.46,**(-1.79)	-19.44,*-5.71,***-14.58,**(0.85)	-18.98,*-4.60,***-13.62,**(-0.76)	-6.92,*-3.23,***-4.86,**(1.17)	62.82,*20.37,***46.50,**(-4.05)	-16.23,*-2.63,***-9.03,**(-4.57)
OH	-32.48,*-9.54,***-21.22,**(-1.72)	-18.92,*-5.73,***-13.94,**(0.75)	-18.47,*-4.66,***-13.18,**(-0.63)	-6.83,*-3.25,***-4.70,**(1.12)	61.18,*20.52,***44.68,**(-4.02)	-15.52,*-2.66,***-8.36,**(-4.50)
F	-30.86,*-10.00,***-19.73,**(-1.13)	-18.12,*-5.84,***-12.99,**(0.71)	-17.87,*-4.85,***-12.26,**(-0.76)	-6.71,*-3.28,***-4.58,**(1.15)	58.82,*21.17,***41.58,**(-3.93)	-14.74,*-2.80,***-7.98,**(-3.96)
Cl	-30.30,*-10.02,***-19.25,**(-1.03)	-17.89,*-5.87,***-12.60,**(0.58)	-17.63,*-4.90,***-12.02,**(-0.71)	-6.70,*-3.30,***-4.52,**(1.12)	58.2,*21.25,***40.73,**(-3.78)	-14.32,*-2.84,***-7.66,**(-3.82)
COH	-28.96,*-10.17,***-17.79,**(-1.00)	-17.24,*-5.90,***-12.05,**(0.71)	-17.01,*-4.94,***-11.39,**(-0.68)	-6.57,*-3.30,***-4.38,**(1.11)	56.13,*21.35,***38.64,**(-3.86)	-13.65,*-2.96,***-6.97,**(-3.72)
CN	-28.46,*-10.27,***-17.32,**(-0.87)	-16.97,*-5.96,***-11.52,**(0.51)	-16.86,*-5.01,***-11.09,**(-0.76)	-6.56,*-3.32,***-4.30,**(1.06)	55.47,*21.53,***37.54,**(-3.60)	-13.38,*-3.03,***-6.69,**(-3.66)
NO_2	-28.08,*-10.38,***-16.94,**(-0.76)	-16.70,*-6.03,***-11.15,**(0.48)	-16.65,*-5.04,***-10.85,**(-0.76)	-6.49,*-3.33,***-4.15,**(0.99)	54.65,*21.71,***36.50,**(-3.56)	-13.27,*-3.07,***-6.59,**(-3.61)

The first column corresponds to DHB complexes, the second column corresponds to NH…O hydrogen bond (Italic data), the third column corresponds to N…HO hydrogen bond (bold data) and the forth column corresponds to ΔΔEX that was estimated from Eqs. (7) – (10) (data in parentheses)

Table S9. The LMO-EDA results of **CA4** complex at the B3LYP/6-311++G(d,p) computational level(kcal mol^{-1})

	ΔE^{ele}	ΔE^{ex}	ΔE^{pol}	ΔE^{disp}	ΔE^{rep}	ΔE
$NHCH_3$	-32.93,*-8.62,***-23.11,**(-1.19)	-18.94,*-5.37,***-14.94,**(1.37)	-18.79,*-4.33,***-13.49,**(-0.98)	-6.88,*-3.11,***-4.99,**(1.22)	62.25,*19.08,***47.51,**(-4.34)	-15.29,*-2.35,***-9.03,**(-3.92)
NH_2	-32.42,*-8.83,***-22.46,**(-1.13)	-18.70,*-5.41,***-14.63,**(1.34)	-18.60,*-4.37,***-13.29,**(-0.93)	-6.85,*-3.13,***-4.92,**(1.20)	61.54,*19.25,***46.56,**(-4.28)	-15.03,*-2.49,***-8.74,**(-3.80)
OCH_3	-31.07,*-8.95,***-21.06,**(-1.06)	-17.97,*-5.47,***-13.57,**(1.27)	-17.87,*-4.40,***-12.50,**(-0.87)	-6.72,*-3.16,***-4.68,**(1.16)	58.95,*19.48,***43.68,**(-4.11)	-14.68,*-2.50,***-8.14,**(-3.94)
OH	-30.30,*-9.03,***-20.29,**(-0.98)	-17.68,*-5.49,***-13.47,**(1.28)	-17.70,*-4.47,***-12.38,**(-0.84)	-6.67,*-3.17,***-4.62,**(1.12)	58.41,*19.61,***42.84,**(-4.04)	-13.94,*-2.55,***-7.92,**(-3.47)
F	-28.65,*-9.51,***-18.77,**(-0.37)	-16.98,*-5.59,***-12.45,**(1.06)	-17.15,*-4.67,***-11.60,**(-0.88)	-6.57,*-3.20,***-4.52,**(1.15)	56.31,*20.32,***39.99,**(-4.00)	-13.04,*-2.65,***-7.36,**(-3.04)
Cl	-28.30,*-9.52,***-18.26,**(-0.52)	-16.74,*-5.62,***-12.18,**(0.93)	-16.90,*-4.72,***-11.35,**(-0.83)	-6.56,*-3.23,***-4.45,**(1.12)	55.64,*20.41,***39.05,**(-3.82)	-12.86,*-2.68,***-7.19,**(-2.99)
COH	-27.19,*-9.63,***-17.12,**(-044)	-16.15,*-5.65,***-11.53,**(1.02)	-16.31,*-4.74,***-10.77,**(-0.80)	-6.43,*-3.22,***-4.32,**(1.11)	53.73,*20.44,***37.10,**(-3.80)	-12.35,*-2.80,***-6.64,**(-2.91)
CN	-26.36,*-9.72,***-16.43,**(-0.21)	-15.87,*-5.70,***-11.01,**(0.84)	-16.14,*-4.81,***-10.46,**(-0.86)	-6.41,*-3.24,***-4.24,**(1.07)	52.98,*20.61,***35.89,**(-3.51)	-11.80,*-2.88,***-6.25,**(-2.67)
NO_2	-26.14,-9.80,***-16.18,**(-0.16)	-15.68,*-5.77,***-10.70,**(0.79)	-15.98,*-4.83,***-10.28,**(-0.86)	-6.36,*-3.25,***-4.10,**(0.99)	52.41,*20.74,***35.07,**(-3.40)	-11.75,*-2.91,***-6.19,**(-3.65)

The first column corresponds to DHB complexes, the second column corresponds to NH…O hydrogen bond (Italic data), the third column corresponds to N…HO hydrogen bond (bold data) and the forth column corresponds to ΔΔEX that was estimated from Eqs. (7) – (10) (data in parentheses)