

## A Theoretical Study of Correlation between Hydrogen-Bond Stability and *J*-Coupling through a Hydrogen Bond

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*trans*-Hydrogen-bond hyperfine splitting *via* magnetic interaction, which is observed as *J*-coupling in NMR experiments, was theoretically studied. *trans*-Hydrogen-bond hyperfine splitting should be closely related to the orbital interaction between the lone-pair orbital of the H-bond acceptor and the antibond orbital of the H-bond donor. A linear relationship was observed between magnetic interaction hyperfine splitting through a H-bond and the H-bond strength. The relationship was dependent on the type of the nucleus forming the H-bond; linear correlation was observed in N–H···O/N type or O–H···N type H-bonded complexes, but not in O–H···O type H-bonded complexes.

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**Introduction.** – The H-bond is a most important molecular interaction, and it has been widely studied [1–6]. H-Bond stabilization is attributable mainly to electrostatic interaction [4–6]; nevertheless, poor correlation was observed between the H-bond energy and atomic charges of the H-bond-forming atoms [7–10]<sup>1</sup>). Recently, *Dingley* and *Grzesiek* found *trans*-H-bond *J*-coupling (<sup>2h</sup>*J*<sub>NN</sub>) in nucleic acid base pairs [11]. With this finding, *trans*-H-bond *J*-coupling has attracted much attention [11–27]. Although many theoretical studies regarding *trans*-H-bond *J*-coupling have been reported [16–27], there are few systematic studies on the relationship between the *trans*-H-bond *J*-coupling and the H-bond strength. We report herein a theoretical study of natural-bond-orbital (NBO) [28] analysis of *trans*-H-bond *J*-coupling, and the relationship between the *J*-coupling and the H-bond strength in model complex systems containing a single H-bond.

**Computational Methods.** – *Fermi*-contact (FC) contributions are the most important ones for the theoretical evaluation of the *J*-coupling value, and the other contributions are negligible in most of the cases [21]. *Del Bene et al.* reported theoretically estimated total and FC coupling constants for some H-bond complexes, and total coupling constants were almost completely reproduced by the FC contribution [18]. Herein, only FC contributions were calculated by the finite perturbation theory [29][30]. The *J*-coupling and reduced coupling constants (*K*) evaluated according to *Eqns. 1* and *2* [31][32].

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<sup>1</sup>) *Platts* reported simple and good methods to estimate H-bond-donor ability ( $\alpha$ ) [8] and H-bond acceptability ( $\beta$ ) [9]. However, the values of  $\alpha$  and  $\beta$  cannot be compared directly.

$$J_{XY} = (\mu_0/4\pi)^2 \cdot (h/2\pi) \cdot (8\pi\beta/3)^2 \cdot a_0^{-6} \cdot \gamma_X \cdot \gamma_Y \cdot \Delta/\lambda$$

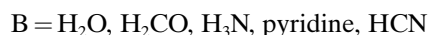
$$= 1.05828 \times 10^{-14} \cdot \gamma_X \cdot \gamma_Y \cdot \Delta/\lambda \text{ [Hz]} \quad (1)$$

$$K = 1.05828 \times 10^{-14} \cdot \Delta/\lambda \quad (2)$$

where  $\gamma_X$  and  $\gamma_Y$  [rad/T·s] are gyromagnetic ratios for nuclei X and Y,  $\lambda$  is an applied spin-density perturbation, and  $\Delta$  is the production of unpaired electron spin density (= FC term, [au]). The  $\Delta$  value is in proportion to the  $\lambda$  value; thus, hyperfine splitting,  $\Delta/\lambda$ , is independent of the strength of the perturbation. All coupling calculations were performed with FC perturbation ( $\lambda$ ) of 0.01 au.

The  $J$ -coupling depends on the gyromagnetic ratios of the nuclei; thus, the  $J$ -coupling cannot be a direct indicator of the strength of magnetic interaction for different nucleus combinations. On the other hand, hyperfine splitting ( $\Delta/\lambda$  in Eqn. 1) and reduced coupling constants ( $K$ ) are magnetic-interaction-independent of the gyromagnetic ratio. Hereafter, we discuss the interaction intensity by use of  $\Delta/\lambda$  instead of  $J$ -coupling, to compare the magnitude of magnetic interactions between the different nucleus combinations.

We refer to a H-bond donor molecule and a H-bond acceptor molecule as A–H and B, respectively. Meanwhile, X and Y represent a H-bond-donor heavy atom and a H-bond acceptor heavy atom, respectively. For the HO–H⋯pyridine complex, X and Y are the O-atom in the H<sub>2</sub>O molecule and the N-atom in the pyridine molecule, respectively. A–H and B in this study are listed below.



The structures of the H-bond donors, the acceptors, and the complexes were optimized with calculations at the B3LYP/6-311G\*\* level [33]. The following properties were evaluated by using the B3LYP/6-311G\*\*-level-optimized structures: The H-bond energies ( $-\delta E$  [kcal/mol]; the larger value of  $-\delta E$  indicates the stronger H-bond) were evaluated at the B3LYP/6-311+G\*\*-level calculations. The basis-set super-position error (BSSE) was not corrected, because the BSSE at this calculation level is very small<sup>2)</sup>. Moreover, the error, which originates from the incompleteness of the basis set employed, should be comparable for all of the H-bonded complexes examined in the present study. The NMR shielding tensors were calculated at the HF/6-311+G\*\* level, based on the gauge-including atomic orbitals (GIAO) [31]. The FC perturbations were calculated at the UB3LYP/6-311+G\*\* level, based on the finite perturbation theory [29][30]. The  $\lambda$  value was recommended for 0.001 [34]; however, the  $\Delta$  value is in proportion to the  $\lambda$  value, and  $\Delta/\lambda$  is independent of the  $\lambda$  value. When the  $\Delta$  value is small, the numerical accuracy becomes low; therefore, we used a  $\lambda$  value of 0.01 for the calculations.

<sup>2)</sup> For example, BSSE-corrected H-bond energy of cytosine–pyrimidin-6-one at this level calculation was –18.66 kcal/mol, while only 0.68 kcal/mol BSSE was observed in the system (unpublished result).

NBO Analysis was carried out to investigate orbital interaction for *trans*-H-bond hyperfine splitting [26] [35–38] at the B3LYP/6-311G\*\* and UB3LYP/6-311G\*\* level calculations without and with FC perturbations, respectively. The molecular-interaction stabilization energies ( $E^2$  [kcal/mol]) described by donor–acceptor NBO interaction was calculated by the second-order perturbation-energy analysis with the NBO basis, in the B3LYP/6-311G\*\* level calculations. The secondary orbital interactions, which have 0.03 kcal/mol or larger stabilization, were considered. Stabilization energy,  $E^2(\text{BD}^*(\text{X-H}) \leftarrow \text{LP}(\text{:Y}))$ , resulting from charge transfer from the lone pair (LP) of the H-bond acceptor {LP(:Y)} to the two-center antibond orbital (BD\*) of the H-bond donor [BD\*(X-H)] was calculated. Moreover, the ratio of  $E^2(\text{BD}^*(\text{X-H}) \leftarrow \text{LP}(\text{:Y}))$  to the sum of all the  $E^2$  values { $\Sigma(\text{A-B})$ } was also considered.  $\Sigma(\text{A-B})$  includes orbital interactions in both  $\text{A-H} \leftarrow \text{B}$  and  $\text{A-H} \rightarrow \text{B}$  interactions (the arrow shows the electron donor–acceptor direction).

Upon applying perturbation ( $\lambda = 0.01$ ) in the UB3LYP/6-311G\*\* level calculations, natural localized molecular orbitals (NLMO) were utilized to express the following properties. 1) The sum of the differences in the occupation of the  $\alpha$  and the  $\beta$  spin electron in each orbital, which corresponds to the total spin density on the X and Y atoms. 2) The ratio of the spin density of LP of the Y atom to the total spin density of Y atom (LP/Y). 3) The ratio of the spin density of X–H antibonding orbital BD\*(X–H) to the total spin density of the X atom (X\*H/X). The calculations were carried out with the GAUSSIAN 94 program [39].

**Results and Discussion.** – A summary of the calculations is shown in the *Table*. As shown in the  $E^2(\text{BD}^*(\text{X-H}) \leftarrow \text{LP}(\text{:Y}))/\Sigma(\text{A-B})$  column of the *Table*, the orbital interaction between LP of the H-bond acceptor (:Y) and BD\* of the H-bond donor (X–H) has the largest contribution: over 80% of all the second-order perturbation molecular-interaction energies for most of the complexes. It is expected that total molecular-interaction energy ( $\delta E$ ) correlates well with the LP(:Y)  $\rightarrow$  BD\*(X–H) interaction energy [ $E^2(\text{BD}^*(\text{X-H}) \leftarrow \text{LP}(\text{:Y}))$ , kcal/mol]. As shown in *Fig. 1*, the  $-\delta E$  correlates with  $E^2(\text{BD}^*(\text{X-H}) \leftarrow \text{LP}(\text{:Y}))$ . The relationship was not influenced by the difference in combination of the types of heavy atoms forming the H-bond.

We examined the spin density of BD\*(X–H) orbital and LP(:Y) orbital (LP:Y). In the *Table*, BD\*/X represents the ratio of the spin density of BD\*(X–H) orbital to the total spin density of the X atom. LP/Y represents the ratio of the spin density of LP(:Y) orbital to the total spin density of the Y atom. In almost all of the cases, more than 80% contribution of the spin density to these two orbitals was observed<sup>3)</sup>. *Wilkins et al.*, reported the NBO analysis of the *trans*-H-bond *J*-coupling of DNA A-T base pair [26]. Based on their report, the delocalized LP(:Y)  $\rightarrow$  BD\*(X–H) interaction has about half contribution of the whole *J*-coupling, and interaction of the localized NBOs, LP(:Y), and BD(X–H), which corresponds to the steric effect, has the other half contribution of the *J*-coupling. Our results do not conflict with their results for the importance of the contribution of the LP(:Y)  $\rightarrow$  BD\*(X–H) interaction.

<sup>3)</sup> The spin density in the s-orbital component of the molecular orbitals is responsible for spin-spin coupling. The s-orbital component in the LP(:Y)  $\rightarrow$  BD\*(X–H) interaction has an important role in the *trans*-H-bond hyperfine splitting.

Table. Calculated NMR and Energy Properties

H-Bond type	Complex <sup>a)</sup>	2nd-Order perturbative energy		Spin density ratio		Hyperfine splitting	H-Bond energy	H-Bond length	Chemical shift
		Ratio <sup>b)</sup>	Energy <sup>c)</sup> [kcal/mol]	BD*/X <sup>d)</sup>	LP/Y <sup>e)</sup>	$\Delta/\lambda^f)$	$-\delta E$ [kcal/mol]	$R_{\text{HB}}$ [Å]	$\delta H^g)$ [ppm]
O–H···O (● in the Figs.)	MeOH-OH <sub>2</sub>	0.90	10.66	0.88	0.97	0.014	5.37	2.86	3.83
	HOH-OH <sub>2</sub>	0.89	9.48	0.90	0.93	–0.007	5.55	2.89	4.35
	HOH-fa	0.77	4.06	0.87	0.78	0.042	4.70	2.85	4.09
	PhOH-HOH	0.88	13.73	0.91	0.93	0.120	7.12	2.80	8.36
	PhOH-fa	0.91	6.88	0.90	0.84	0.063	5.59	2.87	7.95
	FA-OH <sub>2</sub>	0.91	16.68	0.96	0.95	0.102	8.99	2.75	10.14
	FA-fa	0.92	9.33	0.99	0.86	0.050	7.33	2.82	9.78
O–H···N (○ in the Figs.)	MeOH-NH <sub>3</sub>	0.89	15.24	0.90	0.96	0.302	7.16	2.90	5.53
	MeOH-NCH	0.88	4.05	0.89	0.91	0.075	3.64	3.08	1.84
	MeOH-Py	0.69	10.65	0.87	1.07	0.333	6.51	2.92	5.71
	HOH-NH <sub>3</sub>	0.90	13.18	0.90	0.97	0.231	7.30	2.93	5.84
	HOH-Py	0.77	7.75	0.89	0.95	0.210	5.99	2.89	9.45
	HOH-NCH	0.66	3.13	0.88	1.41	0.018	3.72	3.11	2.4
	PhOH-NH <sub>3</sub>	0.88	20.57	0.94	0.96	0.496	9.01	2.83	10.41
	PhOH-Py	0.88	17.88	0.92	0.91	0.549	8.84	2.83	11.14
	PhOH-NCH	0.74	6.39	0.91	0.94	0.210	4.82	3.02	6.16
	FA-NH <sub>3</sub>	0.90	25.92	0.98	0.97	0.460	11.79	2.79	12.45
N–H···O (+ in the Figs.)	FA-Py	0.90	22.12	0.96	0.92	0.577	11.31	2.78	13.07
	FA-NCH	0.77	8.83	0.97	0.94	0.180	6.81	2.96	7.81
	H <sub>2</sub> NH-fa	0.66	1.76	0.72	1.44	–0.008	0.86	3.25	2.15
	AN-OH <sub>2</sub>	0.81	6.95	0.92	0.98	0.318	3.88	3.03	6.54
	AN-fa	0.81	2.11	0.87	0.94	0.223	2.90	3.12	6.28
	Pr-OH <sub>2</sub>	0.92	9.26	0.89	0.91	0.441	5.37	2.95	10.61
N–H···N (× in the Figs.)	Pr-fa	0.92	2.39	0.90	0.97	0.259	3.91	3.07	10.24
	Fa-OH <sub>2</sub>	0.91	8.53	0.94	0.97	0.372	5.37	2.96	7.82
	Fa-fa	0.92	2.97	0.92	0.64	0.208	4.01	3.09	7.44
	H <sub>2</sub> NH-Py	0.77	3.10	0.86	1.02	0.136	2.27	3.25	9.07
	H <sub>2</sub> NH-NCH	0.63	1.17	0.84	4.67	0.029	1.51	3.44	1.17
	AN-NH <sub>3</sub>	0.87	10.88	0.92	0.96	0.564	5.27	3.09	7.95
	AN-Py	0.88	8.03	0.90	0.87	0.557	5.09	3.09	8.21
	AN-NCH	0.71	3.18	0.90	0.94	0.295	2.89	3.27	4.90
	Pr-NH <sub>3</sub>	0.88	13.85	0.93	0.99	0.643	6.88	3.25	12.04
	Pr-Py	0.86	10.93	0.89	0.88	0.653	6.68	3.02	12.41
N–H···N (× in the Figs.)	Pr-NCH	0.71	4.66	0.90	0.94	0.371	3.91	3.19	8.82
	Fa-NH <sub>3</sub>	0.89	12.77	0.94	0.98	0.555	6.86	3.04	9.26
	Fa-Py	0.90	8.77	0.93	0.90	0.544	6.07	3.08	9.19
	Fa-NCH	0.72	4.28	0.94	1.02	0.317	4.11	3.20	6.02

<sup>a)</sup> Abbreviations: Py = pyridine, fa = formaldehyde, FA = formic acid, Fa = formamide, AN = aniline, and Pr = pyrrole. <sup>b)</sup>  $E^2(\text{BD}^*(\text{X}-\text{H}) \leftarrow \text{LP}(\text{:Y})) / \Sigma(\text{A}-\text{B})$ ; an energetic ratio of  $\text{BD}^*(\text{X}-\text{H}) \leftarrow \text{LP}(\text{:Y})$  interaction for all molecular interaction estimated in second-order perturbation-energy analysis. <sup>c)</sup>  $E^2(\text{BD}^*(\text{X}-\text{H}) \leftarrow \text{LP}(\text{:Y}))$ ; stabilization energy in the second-order perturbative estimation of lone pair of H-bond acceptor and two-center antibond of H-bond donor. <sup>d)</sup> Ratio of a spin density on  $\text{BD}^*(\text{X}-\text{H})$  orbital in total spin density on atom X. <sup>e)</sup> Ratio of a spin density on  $\text{LP}(\text{:Y})$  orbital ( $\text{LP}/\text{Y}$ ) in total spin density on atom Y. <sup>f)</sup> *trans*-H-bond hyperfine splitting. <sup>g)</sup> Chemical shift of H-bond-forming proton (proton of TMS as a standard).

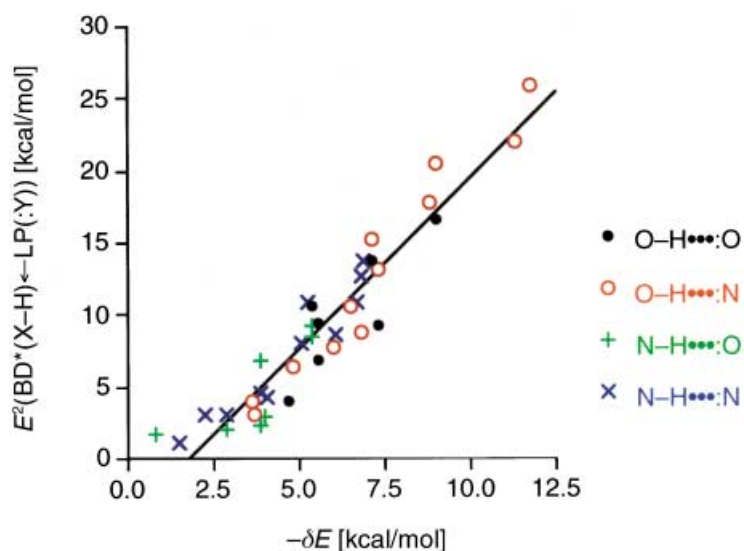


Fig. 1. Relationship between the  $-\delta E$  and  $E^2(\text{BD}^*(\text{X}-\text{H}) \leftarrow \text{LP}(:\text{Y}))$  [kcal/mol]

Fig. 2 shows the relationship between the hyperfine splitting,  $\Delta/\lambda$ , and the H-bond length ( $R_{\text{HB}}$  [Å]). As expected from previous findings reported [19][23–27][32], larger  $\Delta/\lambda$  values were observed in complexes with shorter H-bonds. Our results

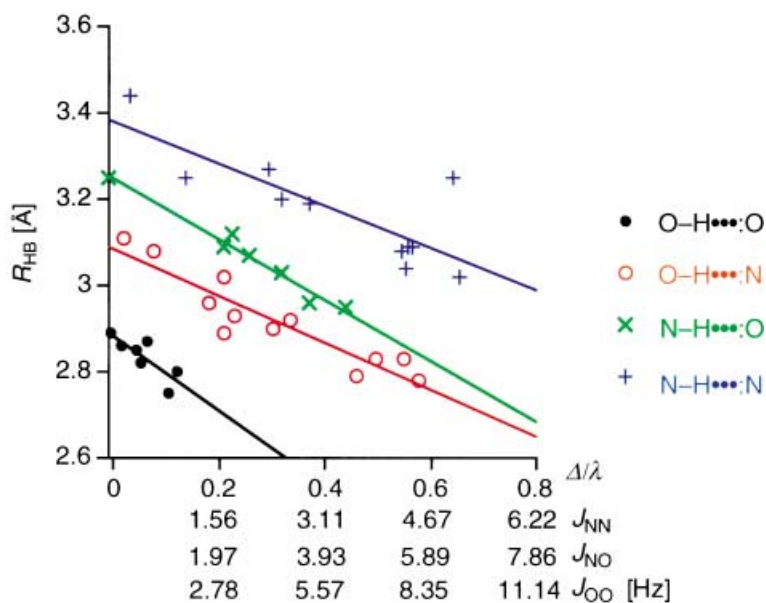


Fig. 2. Relationship between the  $\Delta/\lambda$  and the H-bond strength ( $-\delta E$  [kcal/mol]), including the H-bonded complex

indicate a good correlation between  $\Delta/\lambda$  and the H-bond length in the same atom combination. For H-bond systems with comparable values of  $\Delta/\lambda$ , we can expect that the H-bond length will increase in the following order,  $\text{O}-\text{H}\cdots\text{O} < \text{O}-\text{H}\cdots\text{N} < \text{N}-\text{H}\cdots\text{O} < \text{N}-\text{H}\cdots\text{N}$ .

Fig. 3 shows the relationship between the  $\Delta/\lambda$  and the chemical shift of the H-bond proton. The relationship was extremely vague, and no remarkable trends were observed between the structure of the H-bonded complexes, and the chemical shift of the proton or  $\Delta/\lambda$ . Thus, the chemical shift of the proton in the H-bonded complexes would not be a good index of the H-bond strength, at least for our model complexes in the chemical-shift calculations in the HF level of theory.

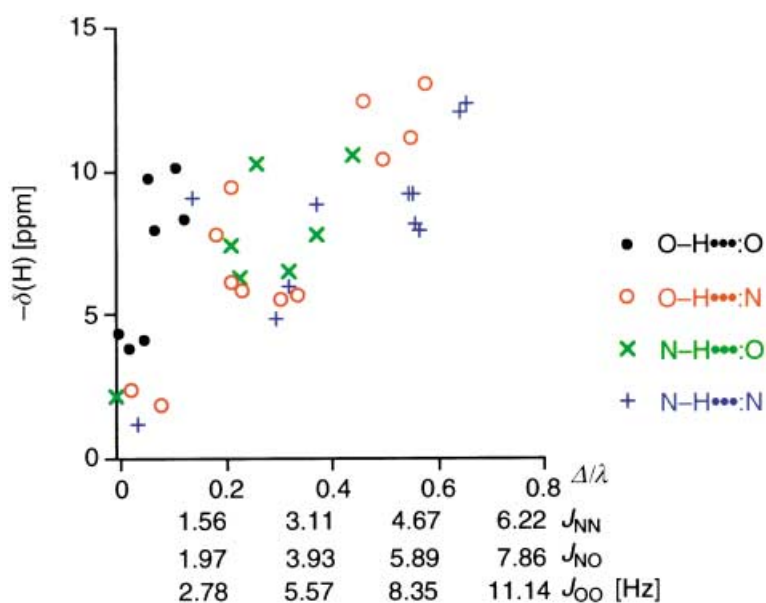


Fig. 3. Relationship between the  $\Delta/\lambda$  and the chemical shift of the H-bond proton [ppm]

Fig. 4 shows the relationship between the  $\Delta/\lambda$  value and the H-bond strength,  $-\delta E$ , of  $\text{A}-\text{H}\cdots\text{B}$  complexes. We found a good correlation between the  $\Delta/\lambda$  value and the  $-\delta E$  in the model systems in the  $\text{N}-\text{H}\cdots\text{Y}$  H-bond), (Eqn. 3), and  $\text{O}-\text{H}\cdots\text{N}$ -type H-bond (Eqn. 4).

$$-\delta E = 8.44 \cdot \Delta/\lambda - 1.29 \quad (r = 0.945) = 8.01 \times 10^{14} \cdot K - 1.29$$

(in kcal/mol, for  $\text{N}-\text{H}\cdots\text{N}$  or  $\text{O}$ )

(3)

$$-\delta E = 12.88 \cdot \Delta/\lambda - 3.34 \quad (r = 0.895) = 12.23 \times 10^{14} \cdot K - 3.34$$

(in kcal/mol, for  $\text{O}-\text{H}\cdots\text{N}$ )

(4)

However, for the  $\text{O}-\text{H}\cdots\text{O}$ -type H-bonded complex, such a good correlation was not observed between the  $\Delta/\lambda$  value and the H-bond strength,  $-\delta E$ .

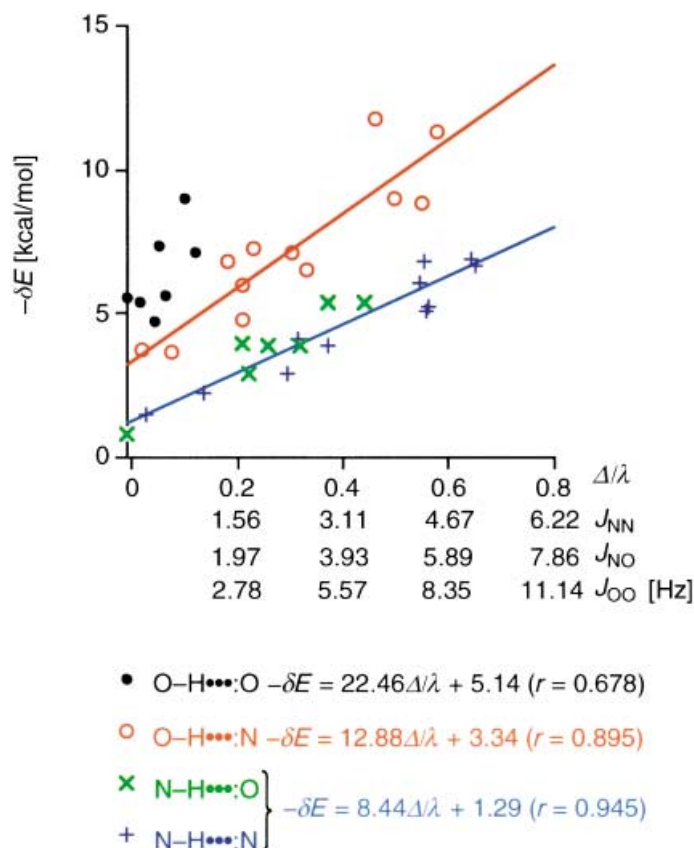


Fig. 4. Relationship between the  $\Delta/\lambda$  and the H-bond strength ( $-\delta E$  [kcal/mol])

Therefore,  $\Delta/\lambda$  is a good index of the H-bond strength in N–H...N and N–H...O systems. N–H...N and N–H...O H-bond strengths can be compared directly by using the  $\Delta/\lambda$  or  $K$  values instead of  $J$ -coupling values. The O–H...N H-bond strength can be compared with the N–H...N and N–H...O H-bond strengths, after the conversion from  $\Delta/\lambda$  to  $\delta E$  according to Eqns. 3 and 4.

Considering the results reported by Wilkens *et al.* [26] and the linear correlation between the  $\Delta/\lambda$  and the  $-\delta E$ , described here, the ratio of the contribution of the LP(:Y)  $\rightarrow$  BD\*(X–H) interaction and the contribution of the LP(:Y)  $\rightarrow$  BD(X–H) interaction for the hyperfine splitting should be almost constant for the H-bonded complexes in this study.

**Conclusions.** – From the results of natural-bond-orbital (NBO) analysis, the H-bond energy was correlated well with second-order perturbative stabilization energy of the lone pair of the H-bond acceptor and the antibond orbital of the H-bond donor. About 80% of the intermolecular stabilization energies (second-order perturbation energies) originated from these two orbital interactions, in most of the H-bonded

complexes. More than 80% of the total spin density was observed in these two orbitals of the H-bond-forming atoms. Therefore, *trans*-H-bond hyperfine splitting should be mainly described by interaction between these two orbitals.

The relationship between magnetic-interaction hyperfine splitting through a H-bond and H-bond strength was dependent on the types of nuclei forming the H-bond. A good linear correlation was observed in the N–H $\cdots$ O/N-type or the O–H $\cdots$ N type H-bonded complexes, but not in the O–H $\cdots$ O-type H-bonded complexes. Thus, the *trans*-H-bond hyperfine splittings between the different nucleus combinations can be compared as an index of the H-bond strength, except for the O–H $\cdots$ O-type H-bonded complexes.

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