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A New Empirical Potential Function and Its Application to Hydrogen Bonding

Young Kee Kang and Mu Shik Jhon

Department of Chemistry, Korea Advanced Institute of Science, P. O. Box 150, Cheong Ryang Ri, Seoul 131, Korea (Received December 9, 1980)

A new potential function based on spectroscopic results for diatomic molecules is presented and applied to the hydrogen bonding systems. The potential energy of interaction is supposed to have electrostatic, polarization, dispersion, repulsion and effective charge-transfer contributions. Estimates of the effective charge-transfer quantity have been made based on the average charge of the proton donor and the acceptor atoms. For dimers such as water, methanol, acetic acid and formic acid, the vibrational stretching frequencies and dimerization energies are calculated and discussed in connection with Badger-Bauer rule.

Introduction

There is a great deal of works about the hydrogen bonding because of its significant role in determining the structure and properties of molecular systems of importance to chemistry and biology. The phenomenon of the hydrogen bonding has been investigated extensively by a variety of spectroscopic and other physical methods and by theoretical considerations¹⁻⁸.

In early theoretical works, it had been suggested by Coulson *et al.*^{9,10} and independently by Tsubomura¹¹ that the significant nature of the hydrogen bonding is brought about by a complicated superposition of the following four contributions which are of similar magnitude; (a) electrostatic energy, (b) exchange repulsion, (c) polarization energy, (d) dispersion energy and (e) charge transfer energy or covalent contribution.

They thought that the success of the electrostatic models in the calculation of the hydrogen bonding energies in certain systems is possibly due to the fact that the other contributions are not significant, which met exactly other

calculations.^{12,13}

On the basis of these interpretations, first we will propose a new empirical potential function for diatomic molecules, and next calculate the vibrational frequencies and the interaction energies for several dimers by using this function.

Potential Energy Function

In earlier papers¹⁴⁻¹⁸, a number of authors have examined various potential functions for diatomic molecules with the spectroscopic measurements, but there are few simple forms to satisfy fairly well those results.

In the present work, we suggest a new function;

$$U(r) = D_e \left\{ 1 - \left(\frac{r}{r_e} \right)^n e^{-a(r-r_e)} \right\}^2 \quad (1)$$

where r is the internuclear distance, r_e is the equilibrium internuclear distance and D_e is the dissociation energy. Here two constants n and a are obtained from the following relationship;

$$ar_e = n + \Delta^{1/2} \quad (2)$$

$$E_{\text{cct}} = -\frac{K}{R} \quad (12)$$

where K is a constant obtained from the following relation;

$$k = b_0 + b\delta_{\text{ave}} \quad (13)$$

Here we used b_0 and b as $-85.93 \text{ kcal}\cdot\text{\AA}/\text{mole}$ and $-329.2 \text{ kcal}\cdot\text{\AA}/\text{e.c.u. mole}$, respectively, and δ_{ave} denotes the average charge of the hydrogen acceptor and the donor atoms.

Results and Discussion

We have obtained constants in eqs. 4 and 5 as follows; D_e and r_e are taken from the experimental values of water molecule²⁶, and n and a are known from these values and with the following condition and eq. 2.

$$(\partial U / \partial r)_{\text{eq}} = 0 \quad (14)$$

Now it is assumed that r_e^* is equal to r_e due to no available information. n^* , a^* and D_e^* are obtained from the experimental data of water dimer^{27,28} and the eq. 14. All constants used in this work are illustrated in Table 2.

On the basis of eq. 3 and the following condition, we can calculate IR stretching vibrational frequencies and interaction energies for the dimers shown in Table 3, i.e.,

$$\nu_{\text{OH}} = (\partial^2 U / \partial r^2)_{\text{eq}} \quad (15)$$

It is assumed that the OH stretching is to be harmonic, and for the water dimer we obtained the value 3544 cm^{-1} compared with the experimental result 3547.5 cm^{-1} .²⁹ The results for the other dimers, methanol, acetic acid and formic acid, are 3135 , 3128 and 3117 cm^{-1} compared with the experimental values, 3245 , 3027 and 3110 cm^{-1} , respectively, within the error limits of the order of $\pm 100 \text{ cm}^{-1}$.³⁰⁻³²

For the structures of acetic and formic acids, we take the cyclic configuration from the microwave spectroscopy³³ and gas-phase electron diffraction.^{34,35}

TABLE 2: Constants Used in the Potential E_D and E_A .

Potential E_D		Potential E_A	
D_e	117.8 kcal/mole ^a	D_e^*	38.0 kcal/mole
n	-50.0	n^*	2.936
a	-47.625 \AA^{-1}	a^*	1.454 \AA^{-1}
r_e	0.96 \AA	r_e^*	0.96 \AA

^aData from ref 26.

TABLE 3: Energy Components and Vibrational Frequencies for dimers^a

Dimers	Energy components (kcal/mole)						E_{tot}	Vibrational frequencies (cm^{-1})
	E_A	E_D	E_{cct}	E_{pol}	E_{d-r}	E_{cct}		
Water	-7.00	0.00	45.64	-1.88	0.09	-41.85	-5.00(-5.0) ^b	3544 (3457.5) ^f
Methanol	-13.38	1.91	34.28	-2.81	0.98	-32.54	-11.56 (-6.1~-9.4) ^c	3135 (3245) ^e
Acetic acid	-25.39	3.82	35.34	-2.46	1.62	-28.94	-16.01 (-16.08±0.2) ^d	3128 (3027) ^h
Formic acid	-24.11	3.82	33.10	-2.24	1.42	-26.08	-14.09 (-15.08±0.3) ^e	3117 (3110) ⁱ

^aValues in parentheses in E_{tot} and ν_{OH} correspond to experimental ones. ^bRef 41, ^crefs 39 and 40, ^drefs 37 and 38, ^eref 33, ^fref 29, ^gref 30, ^href 31, ⁱref 32.

In case of methanol, the gas-phase dimer has not been observed experimentally, thus the linear configuration based on the crystal structure is taken.³⁶ Also for water dimer, the linear configuration found by the microwave spectroscopy is used.

The resulting energies for the intermolecular interaction including the hydrogen bonding are shown in Table 3. The calculated values of the dimerization energies give reasonable agreement with experimental results.

The IR spectroscopy of hydrogen bonding involves the

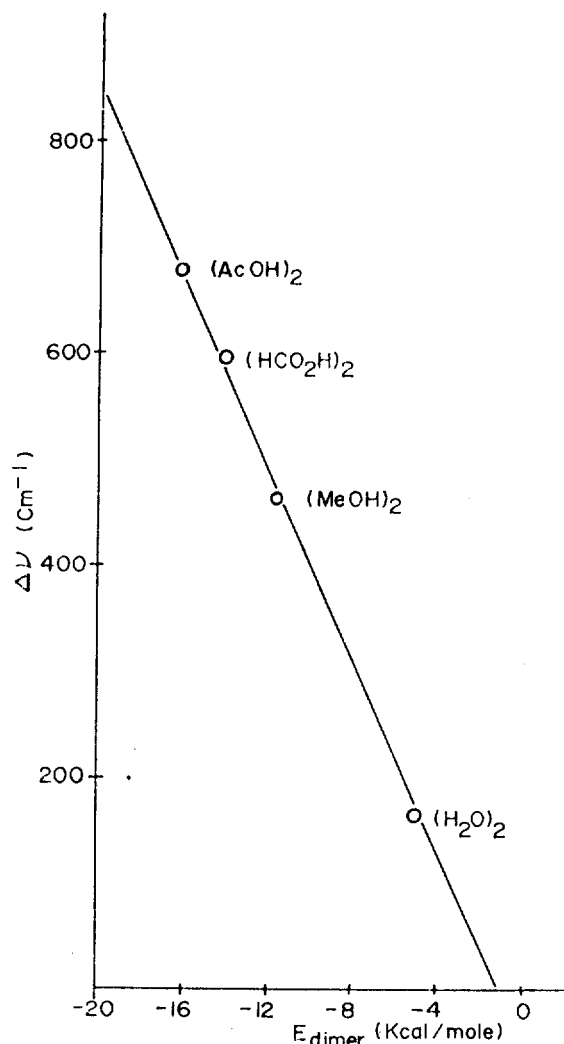


Figure 2. Plot of vibrational wave number shift $\Delta\nu$ against dimerization energy. $\Delta\nu$ is obtained from the difference between the vibration of free OH group (3707 cm^{-1}) and the hydrogen-bonded species.

Badger-Bauer rule; the wave number shift between the vibration of free OH group and the hydrogen-bonded ones is proportional to the hydrogen bonding interaction energy.⁴² We plot the relationship between the experimental wave number shift and the dimerization energy in Figure 2, which consequently shows the validity of our calculations for hydrogen-bonded dimers.

Although the temperature dependence of the vibrational frequencies has not been considered, we obtain reasonable results by using the appropriate conditions. The calculated vibrational frequencies and interaction energies for dimers are in reasonable agreement with the experimental ones. This supports that our simplified considerations based on the molecular structure are likely to represent fairly the other hydrogen-bonded system.

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Alkyl and Alkenyl Substituent Effects on Nonbonded Interactions of Hexatriene

Ikchoon Lee and Keun Bae Rhyu

Department of Chemistry, Inha University, Incheon 160, Korea

Bon-Su Lee

Department of Chemical Engineering, Ajou University, Suwon 170, Korea (Received December 19, 1980)

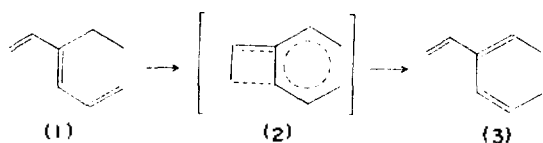
Alkyl and alkenyl substituent effects on nonbonded interactions of hexatriene were examined using CNDO/2 method. The results showed that: (1) rapid rate of thermal electrocyclization of 3-vinyl hexa-1,3,5-triene is due to increased overlap population between atom pair reacting resulting from strong electron repelling interaction of vinyl group on the triene moiety; (2) stability of a conformer is determined by additive effect of composite π structures; (3) a substituent on positions 2 and 3 increases the HOMO AO coefficient of sites 1 and 4 considerably and activates interactions with these sites.

Introduction

Recently Spangler and his co-workers¹ have reported effects of alkyl and alkenyl substitution on the rate of thermal electrocyclization of 1,3,5-hexatriene (HTE) to cyclohexa-1,3-diene.

Their study showed the extremely fast thermal electrocyclization of 3-vinyl substituted HTE, which was over 30 times faster than the rate of ring closure of the ethyl substituted HTE.

They have attributed the accelerative effect of the 3-vinyl substituted to anchimeric π -bond participation of the vinyl group in the electrocyclization transition state, (2).



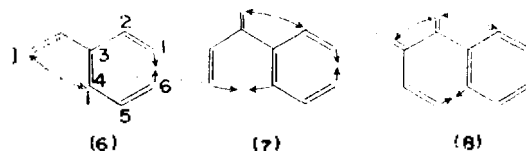
However they found no such π -bond anchimeric rate enhancement with 3-allyl substituent for which homoallylic π -bond participation², (4), may be expected; electrocyclization rate and activation parameters for 3-allyl and 3-propyl



analogues were very nearly the same although in the latter, (5), homoallylic π -bond participation is not possible (see Table 1). Thus anchimeric π -bond participation does not offer a completely satisfactory explanation of the extraordinary rate enhancement of the 3-vinyl substituent.

We have recently developed simple rules for predicting intramolecular nonbonded interactions based on the frontier orbital (FMO) theory³: (1) nonbonded interactions between end-to-end atoms are significant only in crowded forms; (2) nonbonded interactions become appreciable only in crowded π -conjugated (or π -isoconjugate) systems; (3) non-

bonded interactions can be assessed by the signs of the products of AO coefficients of two end atoms in the highest occupied (HOMO). The $4N+2$ π electron system has attractive, while $4N$ π electron system has repulsive interactions. Systems with $4N+1$ and $4N-1$ π electrons are attractive but stabilizing effects are smaller than that for $4N+2$ system. We have also pointed out that the interacting atom pair may be considered to form a loose center (or bond) which acts either as an electron source (donating) when there is a repulsive interaction, or as an electron sink (withdrawing) when the interaction is attractive. We have adopted a notation of $(n\pi/m)$ to represent $n\pi$ electrons delocalized over m atoms or centers, and have shown that the effect of stabilizing (attractive interaction) and destabilizing (repulsive interaction) composite π structures within a molecule is additive. According to these rules, 3-vinyl group on HTE⁶ forms a $(4\pi/4)$ repulsive center (triene moiety itself forms a $(6\pi/6)$ attractive center) which will act as an electron repelling center (shown by arrows as $\leftarrow\rightarrow$) at the interacting site i (which is position 4 in this case) and



hence will increase the overlap population, P_{16}^{π} , of the electrocyclization center. On the other hand 3-allyl, (7), and 3-propyl, (8), substituents, when isoconjugate π structures of methylene groups are taken into consideration, give a repulsive site at position 2 from a $(4\pi/4)$ structure and an attractive (shown by arrows as $\leftarrow\rightarrow$) site at position 4 from $(5\pi/5)$ and $(6\pi/6)$ respectively.

Attractive interaction leads to electron withdrawal from the main triene moiety and hence decreases overlap population, p_{16}^{π} , of the electrocyclization center.

Note that there is an extra $(4\pi/4)$ system in (8), which does not interact directly with the triene moiety; it will

TABLE 1: Average Percent Errors in Various Quantities

	This work	Varshni ^a	Lippincott ^b	Levine ^c
$ U-U_{\text{RKR}} /D_e$, average error	2.06	2.30	2.21	1.99
$ U-U_{\text{RKR}} /D_e$, standard deviation error	1.27	1.43	1.37	1.05
Vibration-rotation interaction constant, α_e^d	0.0	15.6	13.8	11.1
Anharmonicity constant, $\omega_e \chi_e^d$	16.3	14.6	12.2	14.5

^aData from ref 17, ^bdata from ref 16, ^cdata from ref 18.

^dSee refs 15 and 16 for the detailed explanation.

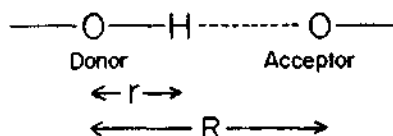


Figure 1. A scheme proposed for the hydrogen bonding.

where Δ means Sutherland parameter. With $n=0$, eq. 1 becomes the Mores type.

The relative accuracy of the potential may be determined by calculating the vibration-rotation interaction constant α_e and the anharmonicity constant $\omega_e \chi_e$ for molecules¹⁵ and by comparing them with the experimental results. Also the potential energies are compared with those obtained from the Rydberg-Klein-Rees (RKR) method based on the first-order Wentzel-Kramers-Brillouin (WKB) approximation for 19 states of diatomic molecules.^{17,18}

The average percent errors in $|U-U_{\text{RKR}}|/D_e$, α_e and $\omega_e \chi_e$ for them are listed in Table 1 and compared with other works.

We find that the function of eq. 1 gives an average error in $|U-U_{\text{RKR}}|/D_e$ for those states of 2.06% as compared with 2.21% for the Lippincott function¹⁶, 2.30% for the Varshni function¹⁷ and 1.99% for the Levine function¹⁸. Also in Table 1 we see that eq. 1 gives the best prediction of α_e , but the slightly larger values of $\omega_e \chi_e$ than other works. From this result we may judge the present function to be suitable for the various states of diatomic molecules (except for too small distance).

Model Based on a Potential Function

The potential function eq. 1 is applicable to a model of hydrogen bonding provided that it be modified suitably, which is illustrated in Figure 1 for OH...O bonding as shown in Lippincott *et al.*⁷ and Reid.⁸

The potential energy for this model consists of the sum of three contributions

$$U = E_D + E_A + E_0 \quad (3)$$

where E_D and E_A are the potential energies for the hydrogen donor and the acceptor bonds, respectively, based on eq. 1 as follows;

$$E_D = D_e \left\{ 1 - \left(\frac{r}{r_e} \right)^n e^{-\sigma(r-r_e)} \right\}^2 \quad (4)$$

and

$$E_A = D_e^* \left\{ 1 - \left(\frac{R-r}{r_e^*} \right)^{n^*} e^{-\sigma^*(R-r-r_e^*)} \right\}^2 - D_e^* \quad (5)$$

where D_e and D_e^* denote the dissociation energies for the hydrogen donor and the acceptor bonds, respectively; r and R , bond distances for those bonds; r_e and r_e^* , their equilibrium distances; n , σ , n^* and σ^* are constants.

And E_0 denotes the interaction energy between the hydrogen-bonded molecules without considering the interactions between the atoms which directly form the hydrogen bonding. For the sake of an efficient calculation, we assume E_0 only to be the interaction energy between the hydrogen donor and the acceptor atoms, since their charges and polarizabilities represent different aspects of the electronic environment in hydrogen-bonded molecules.

Accordingly, we have expressed E_0 by using the empirical potential functions¹⁹⁻²¹ and an additional term, E_{ect} , due to the effective charge-transfer through the hydrogen bonding;

$$E_0 = E_{\text{cou}} + E_{\text{pol}} + E_{d-r} + E_{\text{ect}} \quad (6)$$

where

$$E_{\text{cou}} = \frac{\delta_A \delta_D}{R} \quad (7)$$

$$E_{\text{pol}} = -\frac{1}{2} \{ \alpha_A (\vec{\epsilon}_D)^2 + \alpha_D (\vec{\epsilon}_A)^2 \}, \quad (8)$$

and

$$E_{d-r} = k_A k_D \left\{ -\frac{B}{Z^6} + \left(1 - \frac{\delta_A}{N_A} \right) \left(1 - \frac{\delta_D}{N_D} \right) \cdot C \cdot \exp(-\alpha Z) \right\} \quad (9)$$

Here δ_A and δ_D mean the net charges of the hydrogen acceptor and the donor atoms, respectively; α_A and α_D , the polarizabilities; $\vec{\epsilon}_A$ and $\vec{\epsilon}_D$, the electric fields.

In eq. 9, k_A and k_D are constants for the calibration of the potential depths, N_A and N_D are the number of valence electrons in the hydrogen acceptor and the donor atoms, and constants B , C and α are 0.214 kcal/mole, 4.7×10^4 kcal/mole and 12.35, respectively.

And Z value in eq. 9 is obtained from the following relations, *i.e.*,

$$Z = R/R_0 \quad (10)$$

and

$$R_0 = \sqrt{(2R_A)(2R_D)} \quad (11)$$

where R_A and R_D are the van der Waals radii of the hydrogen acceptor and the donor atoms, respectively.

Also the other specific property of hydrogen bonding is the charge transfer phenomenon. The dipole enhancement upon hydrogen-bond formation and the infrared O-H stretching intensity enhancement can be used to explain this specificity⁶, but since the amount of transferred charge in molecular associations can not be directly measured and hence usually semiempirical or *ab initio* calculations are applied^{6,22-26}. We consider the effective charge-transfer contribution as eq. 12, since it is roughly proportional to the square of molecular overlap and hence falls off very much more rapidly with increasing distance R ,