ON INTRAMOLECULAR NON-BONDED INTERACTION OF 1,1-DIFLUOROETHANE AND 1,2-DIFLUOROETHANE

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An *ab initio* PD/LSF and (exp-6-1) model has been used to deal with intramolecular non-bonded interaction of 1,1-difluoroethane and 1,2-difluoroethane. It is concluded that the energy difference of isomers comes from intramolecular non-bonded interaction between the atoms. This model provides a useful, simple and easily understood approximation to intramolecular non-bonded interaction.

Keywords: Intramolecular non-bonded interaction, *Ab initio* calculation, PD/LSF charge, (exp-6-1) model, Difluoroethane

Introduction

In *ab initio* calculations the intermolecular non-bonded interaction energy is defined as the total energy difference between an entire system and its isolated subsystems. Several methods separating the interaction energy into electrostatic, polarization, exchange and charge transfer energy terms have been proposed. The Hartree-Fock matrix scheme proposed by Morokuma is one of the most extensively used procedures^[1], but a serious limitation of this approach is its inability to account for dispersion forces^[2]. A more complete understanding of non-bonded interaction can be achieved through the application of perturbation theory^[3]. On the other hand the effects of exchange, polarization and charge transfer on the shape of a given system (such as dimer) are found to be compensative approximately. These suggest that it should be possible to construct a simple physical model, involving electrostatic interaction and short range repulsion interaction to predict non-bonded interaction energy^[3-5]. Such a model has been proposed by Buckingham and Fowler^[6], but this simple model excludes the mutual distortion of the interacting molecules, and therefore lacks the attractive induction and dispersion contributions. In molecular packing

analysis, the intermolecular non-bonded energy in crystals is described by the PD/LSF and (exp-6-1) model^[6]. This model has enjoyed considerable success in modelling the structure of molecular clusters and crystals^[6,7]. The model is also more easily understood and makes the calculations less time-consuming than the perturbation method.

In this paper, the *ab initio* PD/LSF & (exp-6-1) model is extended to describe the intramolecular non-bonded interactions.

Computational methods

The intermolecular energy in crystals is assumed to be a summation of the repulsion, dispersion and coulombic components, and each component is further assumed to be an atompairwise summation^[6]. The corresponding pairwise terms are given by

$$V_{jk}(\text{exp-6-1}) = B \exp(-Cr_{jk}) - Ar_{jk}^{-6} + q_j q_k r_{jk}^{-1}$$

where r_{jk} is a non-bonded atom-atom distance, q_j is an atomic charge, and A , B and C are adjustable parameters. The atomic charges $\{q_j\}$ are given by potential-derived point-charge least-squares fitting (PD/LSF) and the quantum mechanical potentials are calculated analytically from *ab initio* SCF wavefunctions^[6]. The *ab initio* SCF calculations and electric potential calculations are performed by using G80USF program^[8] at 6-31G basis level^[9].

The intramolecular atom-atom interactions can be divided into bonded interaction, called chemical bond, and non-bonded interaction. We divide the intramolecular non-bonded interaction into 1-3 interaction and 1-4 interaction, etc. In the 1-3 interaction, the two interacting atoms are directly attached to a common central atom by chemical bonds, and in the 1-4 interaction, the two interacting atoms are separated by two chemical bonds.

The experimentally determined geometries of 1,1-difluoroethane(A) and 1,2-difluoroethane(B)^[10,11], shown in Fig.1, are used in calculations. The staggered conformer of isomer A and the gauche conformer of isomer B are of different energies^[12] and then considered here.

Results and discussion

Fig.1 The geometries of 1,1-difluoroethane (A) and 1,2-difluoroethane (B)

The Hartree-Fock SCF energies and dipole moments are listed in Table 1 together with the experimental enthalpies and dipole moments^[13]. The relative SCF total energy agrees well with the relative experimental enthalpy. The other numerous calculations have demonstrated that

in this case only the relationships between the chemical bonds are altered, the electronic correlation corrections are unimportant, and the single-determinant Hartree-

Table 1 Energies and components of 1,1-difluoroethane (A) and 1,2-difluoroethane (B) (kcal·mol⁻¹)

Molecule	ΔH_f^0	E_{SCF}	Non-bonded interaction energy				Dipole moment (Debye)	
			Total	Repulsion	Dispersion	Coulomb	calcd.	obsd.
A	-119.7	-173729.9	3.7	17.1	-4.5	-8.9	2.94	2.30
B	-106.6	-173717.9	16.4	14.7	-4.1	5.8	3.66	2.67
Relative	13.1	12.0	12.7	-2.4	0.4	14.7	—	—

Fock SCF theory can provide an adequate description of the system^[14]. From Table 1 isomer A is much more stable than isomer B, even though the number and type of chemical bonds is conserved in the two molecules if the different environment of the bonds is neglected. This difference might arise from the non-bonded interaction, which will be discussed later.

In Table 2 the PD/LSF atomic-charges are listed along with the Mulliken atomic charges. The PD/LSF atomic charges arising from molecular electric potentials have real quantum mechanical meaning, unlike the Mulliken charges arising from the population analysis^[15]. Although the charge on an atom in a molecule can be neither defined uniquely nor subjected to experimental measurement, the dipole moment, which is the principal experimental quantity related to the charges, is comparable with theoretical value. In order to characterize the molecular properties exactly, the PD/LSF atomic charges must be corrected by scaling. The scale factors ($D(\text{obsd})/D(\text{calcd})$) for isomer A and isomer B are 0.782 and 0.730, respectively.

Table 2 PD/LSF charges and Mulliken charges of 1,1-difluoroethane (A) and 1,2-difluoroethane (B)

Molecule	Atom	PD/LSF charges ($ e $)	Mulliken charges ($ e $)
A	C ₁	0.8793	0.6450
	C ₂	-0.5080	-0.5277
	F ₁ , F ₂	-0.3875	-0.4302
	H ₁	-0.0225	0.1705
	H ₂ , H ₃	0.1285	0.1851
	H ₄	0.1692	0.2023
B	C ₁ , C ₂	0.3195	0.0934
	F ₁ , F ₂	-0.3572	-0.4446
	H ₁ , H ₂	0.0045	0.1665
	H ₃ , H ₄	0.0332	0.1848

Table 3 shows some of the atom-atom non-bonded interaction energies and their repulsion, dispersion, and electrostatic(coulombic) components, in which the potential

functions (exp-6-1) derived from crystal structures^[16] are used to calculate the interaction components.

Bond separation reactions, in which all bonds between heavy atoms (non-hydrogen) are separated into the simplest (two heavy-atom) fragments containing the same kinds of linkages, provide a useful means of viewing the interaction between groups that are not directly bonded, since the numbers and types of chemical bonds of each molecule and its fragment are conserved and only the relationships between the bonds are altered if the different environment of the bonds is neglected^[17]. For example, for the bond separation reaction $\text{CH}_3\text{CHF}_2 + \text{CH}_3\text{CH}_3 \longrightarrow 2\text{CH}_3\text{CH}_2\text{F}$, the reaction energy, i.e., bond separation energy, is $14.1 \text{ kcal}\cdot\text{mol}^{-1}$ ^[13], though the reactants and the products have the same numbers and types of chemical bonds^[14]. But the bond separation energy provides only the overall difference of atom-atom non-bonded interaction, not their various components, so all the previous research set the overall energy difference to heavy-atom-heavy-atom interaction, called as geminal interaction.

Table 3 Atom-atom non-bonded energies and their components of 1,1-difluoroethane (A) and 1,2-difluoroethane (B) ($\text{kcal}\cdot\text{mol}^{-1}$)

Molecule	Atom pair	Total energy	Repulsion energy	Dispersion energy	Coulomb energy
A	1-3 non-bonded	27.21	14.47	-3.07	15.81
	F ₁ -F ₂	22.29	10.33	-1.93	13.89
	H ₂ -H ₃	4.92	4.14	-1.14	1.92
	1-4 non-bonded	-23.50	2.62	-1.46	-24.67
	F ₁ -H ₂ , F ₂ -H ₃	-3.59	0.49	-0.25	-3.83
	F ₁ -H ₃ , F ₂ -H ₂	-3.11	0.04	-0.07	-3.08
	F ₁ -H ₄ , F ₂ -H ₄	-4.80	0.51	-0.25	-5.06
	H ₁ -H ₂ , H ₁ -H ₃	-0.12	0.26	-0.14	-0.24
	H ₁ -H ₄	-0.26	0.03	-0.04	-0.25
B	1-3 non-bonded	9.00	11.80	-2.52	-0.28
	F ₁ -H ₂ , F ₂ -H ₄	4.50	5.90	-1.26	-0.14
	1-4 non-bonded	7.37	2.91	-1.56	6.02
	F ₁ -F ₂	7.97	0.56	-0.37	7.78
	F ₁ -H ₄ , F ₂ -H ₂	-0.12	0.03	-0.06	-0.09
	F ₁ -H ₃ , F ₂ -H ₁	-0.40	0.75	-0.32	-0.83
	H ₂ -H ₄	0.16	0.31	-0.15	0.00
	H ₂ -H ₃ , H ₄ -H ₁	0.11	0.22	-0.12	0.01
	H ₁ -H ₃	0.06	0.04	-0.04	0.06

Among the atom-atom non-bonded interaction components, the absolute value of the repulsion interaction energy varies with the atom-atom distance most dramatically

because of the exponential expression of the repulsion interaction. It is obvious from Table 3 that the 1-3 non-bonded interaction energies have larger magnitude than the 1-4 non-bonded interaction energies. Since most of the 1-3 non-bonded interactions are the same in the two isomers and then can be cancelled each other. The only two 1-3 non-bonded interactions treated with (exp-6-1) functions are those existing in one of the two isomers and not being cancelled each other.

From Table 3 the energy difference of 1-3 non-bonded interaction between 1,1-difluoroethane and 1,2-difluoroethane is $-18.2 \text{ kcal}\cdot\text{mol}^{-1}$, and the corresponding energy difference of 1-4 non-bonded interaction is $30.9 \text{ kcal}\cdot\text{mol}^{-1}$, so the total energy difference of non-bonded interaction between them is $12.7 \text{ kcal}\cdot\text{mol}^{-1}$. These are fairly agreeable to the relative SCF energy ($12.0 \text{ kcal}\cdot\text{mol}^{-1}$) and the experimental enthalpy ($13.1 \text{ kcal}\cdot\text{mol}^{-1}$). A similar conclusion has been followed in the calculation of *o*-, *m*-, & *p*-difluorobenzene^[18]. From Table 3, the F-F non-bonded interaction energy for 1,1-difluoroethane and 1,2-difluoroethane are 22.3 and $8.0 \text{ kcal}\cdot\text{mol}^{-1}$, respectively, i.e., the F-F non-bonded interaction destabilizes 1,1-difluoroethane more than 1,2-difluoroethane. Since 1,1-difluoroethane is more stable than 1,2-difluoroethane, this means that although the F-F non-bonded interaction destabilizes 1,1-difluoroethane more than 1,2-difluoroethane, the H-F and the H-H non-bonded interactions stabilize 1,1-difluoroethane much more than 1,2-difluoroethane.

It is demonstrated from Table 1 that the total energy difference between 1,1-difluoroethane and 1,2-difluoroethane mainly comes from the difference of coulombic energy. The similar conclusion had been made from perturbation theory method^[3,6], and this is why the hard sphere electrostatic model^[4] can deal with non-bonded interaction correctly in most cases.

Conclusion

We have shown that the *ab initio* PD/LSF and (exp-6-1) model incorporating repulsion, dispersion and electrostatic interactions has considerable success in describing the non-bonded energy contributions to the energy difference between 1,1-difluoroethane and 1,2-difluoroethane. The energy difference of non-bonded interaction between 1,1-difluoroethane and 1,2-difluoroethane shows that although the F-F non-bonded interaction destabilizes 1,1-difluoroethane more than 1,2-difluoroethane, the H-F and the H-H non-bonded interactions stabilize 1,1-difluoroethane much more than 1,2-difluoroethane. We conclude that the *ab initio* PD/LSF and (exp-6-1) model provides a useful approximation to the non-bonded interaction and reveals the contributions from the non-bonded interaction to the total molecular energy and molecular structures.

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1,1-二氟乙烷和1,2-二氟乙烷分子内

原子间非键相互作用

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摘要 用从头算势诱导极小二乘拟合(PD/LSF)和(exp-6-1)函数研究了1,1-二氟乙烷和1,2-二氟乙烷分子内非键原子间的相互作用。计算结果表明,同分异构体的能量稳定性差,在于分子内非键原子间的相互作用。该模式提供了一种简单、实用的研究分子内非键相互作用的方法。

关键词: 分子内非键相互作用 从头计算 PD/LSF电荷 (exp-6-1)模式 二氟乙烷