Ab Initio Study of the Interaction Hyperpolarizabilities of H-Bond Dimers between Two π-Systems

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The effects of intermolecular interaction on dipole moment (μ), the mean (α) and anisotropy ($\Delta\alpha$) of the polarizability, and the first and second hyperpolarizabilities (β and γ, respectively) for four hydrogen bond dimers between two π-systems (HCN···HCN, HNC···HCN, HCN···HNC, and HNC···HNC) have been calculated in the finite-field approach. The properties were calculated at the MP4/d-aug-cc-pVTZ level. Intermolecular interaction significantly increases the first hyperpolarizabilities of four dimers between two π-systems (177% for HCN···HCN, 47.9% for HNC···HCN, 65.3% for HCN···HNC, and 37.9% for HNC···HNC). Intermolecular interaction effects of the second hyperpolarizabilities are 3.0% for HCN···HCN, −3.1% for HNC···HCN, 5.4% for HCN···HNC, and −2.1% for HNC···HNC. For the four dimers, electron correlation effects are important to the total and interaction electric properties.

Introduction

Intermolecular interaction is a very active subject because of its important role in chemistry, physics, and biology.[1] Recently, several experimental works[2,3] have proved intermolecular interaction has important effects on electric hyperpolarizabilities which are related to the nonlinear optical (NLO) phenomena.[4] Consequently, interaction hyperpolarizability, which is an effect of intermolecular interaction on hyperpolarizability, has attracted increasing interest in recent years. Since it is difficult to experimentally determine the interaction hyperpolarizabilities, the ab initio method plays an important role in this field. The interaction hyperpolarizabilities have been calculated for a number of small van der Waals systems, such as He_2, Ne_2, He_3;[5] Ar_2, He_2;[6−8] H_2···H_2, Ne···Ne, Ar···Ar, Kr···Kr, Ne···HF, Ne···FH,[9] and Ar···HF.[10] In addition, some theoretical calculations on the effects of hydrogen bonding on hyperpolarizabilities have also been reported.[11−13]

Great deals of studies showed an enhancement in the first hyperpolarizabilities with an increase in π-conjugation length in a molecule.[14] It should be examined whether this rule about molecular hyperpolarizabilities is proper to the interaction hyperpolarizabilities of complexes. But in high level ab initio studies of interaction hyperpolarizabilities, much attention had been paid to the complexes[5−11] without π-electrons. In a quite recent paper,[15] the interaction hyperpolarizabilities of the dimers containing one π-subsystem (HCN···HF and HNC···HF) are calculated and large interaction hyperpolarizabilities are predicted. It seems to be reasonable to expect that larger interaction hyperpolarizabilities will be obtained in the dimers composed of two π-subsystems (HCN···HCN, HNC···HCN, HCN···HNC, and HNC···HNC).

The four dimers between HCN and HNC (HCN···HCN, HNC···HCN, HCN···HNC, and HNC···HNC) are typical H-bond complexes. The HCN···HCN dimer has alreadybeen already extensively studied both experimentally[16−19] and computationally.[20−22] In a recent paper of Heikkilä and Lundell,[23] the equilibrium structures, interaction energies, and harmonic vibrational frequencies for the four dimers have been calculated, and the results about HCN···HCN are in reasonable agreement with experimental data. To search new effect factors of hyperpolarizabilities for hydrogen bond complexes, we calculated the interaction electric properties (dipole moment μ, polarizability α, the first hyperpolarizability β, and the second hyperpolarizability γ) of the four dimers in the finite-field approach.

Theory and Computational Strategy

In the presence of a weak and static electric field, the energy of a molecule is a function of the field strength. The energy of the perturbed system is described by the expansion[24]

$$E = E^{\circ} - \mu_i F_i - (^1/_2!)\alpha_{ij}F_iF_j - (^1/_3!)\beta_{ijk}F_iF_jF_k - (^1/_4!)\gamma_{ijkl}F_iF_jF_kF_l + ... \quad (1)$$

where μ_i, α_{ij}, β_{ijk}, and γ_{ijkl} are the components of the dipole moment, the polarizability, the first hyperpolarizability, and the second hyperpolarizability, respectively. For a system of linear symmetry, the static electric properties (μ, α, β, and γ) may be calculated by the following formulas:

$$\alpha_0 = (2\alpha_{xx} + \alpha_{zz})/3 \quad (2)$$

$$\Delta\alpha = \alpha_{zz} - \alpha_{xx} \quad (3)$$

$$\beta_0 = {}^3/_5(2\beta_{xxz} + \beta_{zzz}) \quad (4)$$

$$\gamma_0 = (8\gamma_{xxxx} + 3\gamma_{zzzz} + 12\gamma_{xxzz})/15 \quad (5)$$

The components of the electric properties (μ_z, α_{xx}, α_{zz}, β_{xxz}, β_{zzz}, γ_{xxxx}, γ_{zzzz}, and γ_{xxzz}) are calculated in a finite-field approach.[25,26] A detail description about the parameters and

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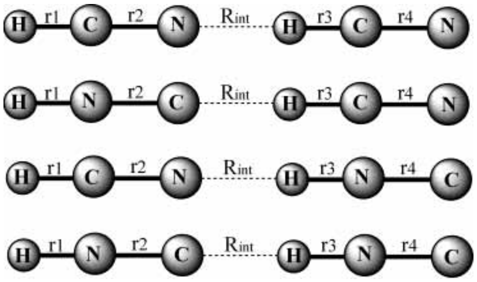

Figure 1. Geometrical structures of the four dimers between HCN and HNC (HCN···HCN, HNC···HCN, HCN···HNC, and HNC···HNC).

TABLE 1: Geometrical Parameters (in Å) and Intermolecular Interactions (in kJ/mol) of the Four Dimers between HCN and HNC (HCN···HCN, HNC···HCN, HCN···HNC, and HNC···HNC)[a]

	r_1	r_2	r_3	r_4	R_{int}	E_{int}
HCN···HCN	1.064	1.165	1.070	1.167	2.207	−17.947
HNC···HCN	0.997	1.173	1.071	1.167	2.339	−17.898
HCN···HNC	1.064	1.163	1.010	1.176	1.946	−27.650
HNC···HNC	0.997	1.171	1.013	1.176	2.053	−28.566

[a] All data in this table are from ref 23.

formulas of the finite-field approach used in this paper is presented in our early papers.[10,15]

In the computation of the interaction static electric properties, the counterpoise (CP) correction[27] is employed to eliminate basis set superposition errors (BSSE). Thus, the interaction property P_{int} can be defined by the following equation:

$$P_{int} = P(A-B) - P(A-X) - P(X-B) \tag{6}$$

$P(A-X)$ is the calculated value of property P for subsystem A in the presence of the ghost orbitals of subsystem B, and $P(X-B)$ is the calculated value of property P for subsystem B in the presence of the ghost orbitals of subsystem A.

All static electric properties in this paper are calculated in self-consistent field (SCF) and Møller−Plesset perturbation theory (MP2, MP3, and MP4). The aug-cc-pVTZ and d-aug-cc-pVTZ basis sets[28−32] are used in the calculations of the electric properties. All calculations were performed with *Gaussian 98* program package.[33]

Results and Discussion

A. Geometries of the Four Dimers. The HCN dimer has been studied extensively both experimentally and computationally, and all data indicate a linear, hydrogen-bonded complexation between the two HCN monomers. Recently, Heikkilä and Lundell[23] reported an ab initio study on the four bimolecular complexes of HCN and HNC (HCN···HCN, HNC···HCN, HCN···HNC, and HNC···HNC). We adopt the geometrical structures obtained by Heikkilä and Lundell. The geometries of the complexes are shown in Figure 1, and the parameters of the structures are listed in Table 1.

B. Static Electric Properties. To discuss the effects of methods (theory levels) and basis sets on the calculated results, the static electric properties (the dipole moment μ_z, the mean of the polarizabilities α_0, the anisotropy of the polarizabilities $\Delta\alpha$, the first hyperpolarizabilities β_0, and the second hyperpolarizabilities γ_0) of the four dimers (HCN···HCN, HNC···HCN, HCN···HNC, and HNC···HNC) are calculated at SCF, MP2, and MP4 levels with the aug-cc-pVTZ and d-aug-cc-pVTZ basis sets and the results are listed in Table 2.

TABLE 2: Static Electric Properties (in au) of HCN···HCN, HNC···HCN, HCN···HNC, and HNC···HNC)

		HCN···HCN			HNC···HCN		
P	basis set	SCF	MP2	MP4	SCF	MP2	MP4
μ_z	aug-cc-pVTZ	2.9297	2.6895	2.6714	2.7213	2.7889	2.7346
	d-aug-cc-pVTZ	2.9295	2.6894	2.6712	2.7212	2.7892	2.7348
α_0	aug-cc-pVTZ	34.805	34.399	34.925	35.188	35.885	36.077
	d-aug-cc-pVTZ	34.899	34.501	35.021	35.295	36.011	36.194
$\Delta\alpha$	aug-cc-pVTZ	23.298	21.952	23.192	22.250	22.445	23.037
	d-aug-cc-pVTZ	23.181	21.849	23.092	22.083	22.277	22.879
β_0	aug-cc-pVTZ	-3.07	23.83	9.43	38.87	47.00	42.71
	d-aug-cc-pVTZ	0.62	27.53	13.04	38.96	47.08	42.91
γ_0	aug-cc-pVTZ	3397.2	3937.2	4039.6	3512.0	4476.7	4624.1
	d-aug-cc-pVTZ	4074.0	4631.1	4738.3	4178.7	5238.6	5361.7

		HCN···HNC			HNC···HNC		
P	basis set	SCF	MP2	MP4	SCF	MP2	MP4
μ_z	aug-cc-pVTZ	2.8728	2.9446	2.8901	2.6657	3.0515	2.9586
	d-aug-cc-pVTZ	2.8724	2.9443	2.8897	2.6655	3.0517	2.9588
α_0	aug-cc-pVTZ	35.608	36.345	36.528	35.962	37.828	37.673
	d-aug-cc-pVTZ	35.712	36.474	36.646	36.076	37.972	37.804
$\Delta\alpha$	aug-cc-pVTZ	23.294	23.254	23.867	22.419	24.120	24.052
	d-aug-cc-pVTZ	23.189	23.138	23.757	22.268	23.952	23.896
β_0	aug-cc-pVTZ	50.54	67.06	62.14	88.04	85.27	89.91
	d-aug-cc-pVTZ	50.07	66.75	61.86	84.66	81.69	86.58
γ_0	aug-cc-pVTZ	3727.8	4930.0	5089.4	3819.7	5426.5	5591.4
	d-aug-cc-pVTZ	4362.3	5746.4	5858.9	4411.2	6237.1	6371.2

For the basis set effect on the static electric properties of the four dimers, with the improvement of the basis set from aug-cc-pVTZ to d-aug-cc-pVTZ, the values of dipole moment and polarizabilities are very stable, but the first and second hyperpolarizabilities are significantly changed. For HCN···HCN, the value of β_0 significantly increased by 3.61 au (38.3%) with the improvement of the basis set. For HNC···HCN, the change of the basis set has a negligible effect on β_0. For HCN···HNC and HNC···HNC, the d-aug-cc-pVTZ results of β_0 are slightly lower than the aug-cc-pVTZ results. For all the four dimers, the improvement of basis set from aug-cc-pVTZ to d-aug-cc-pVTZ increases the values of γ_0. For the MP4 results, the increases of γ_0 are 14.7% for HCN···HCN, 13.8% for HNC···HCN, 13.1% for HCN···HNC, and 12.2% for HNC···HNC.

In early work,[10,15] we had investigated the dependencies of the hyperpolarizabilities on the basis set for Ar···HF,[10] HCN···HF, and HNC···HF.[15] Those results showed that aug-cc-pVTZ is the suitable basis set for calculations of dipole moments and polarizabilities, but the values of hyperpolarizabilities are more sensitive to basis set and the more flexible basis set d-aug-cc-pVTZ is suitable. For the four dimers investigated in this paper, the aug-cc-pVTZ basis set is also suitable for the calculations of dipole moments and polarizabilities but d-aug-cc-pVTZ is necessary for the calculations of the first and second hyperpolarizabilities.

For HCN···HCN, the results of the static electric properties calculated at the MP4/d-aug-cc-pVTZ level are $\mu_z = 2.6712$ au, $\alpha_0 = 35.021$ au, $\Delta\alpha = 23.092$ au, $\beta_0 = 13.04$ au, and $\gamma_0 = 4738.3$ au. For μ_z, the MP2 result is very close to the MP4 result. For polarizabilities (α_0 and $\Delta\alpha$), the MP2 results are slightly lower than the MP4 results and the SCF results are closer to the MP4 results. The value of β_0 is strongly dependent on the level of the method. The SCF result ($\beta_0 = 0.62$ au) is significantly lower than the MP4 result, and the MP2 result ($\beta_0 = 27.53$ au) is significantly higher than the MP4 result. For γ_0, the MP2 result ($\gamma_0 = 4631.1$ au) is in good agreement with the MP4 result and the SCF result is lower.

For HNC···HCN, the results of the static electric properties calculated at the MP4/d-aug-cc-pVTZ level are $\mu_z = 2.7348$ au, $\alpha_0 = 36.194$ au, $\Delta\alpha = 22.879$ au, $\beta_0 = 42.91$ au, and $\gamma_0 =$

TABLE 3: Interaction Static Electric Properties (in au) of HCN···HCN, HNC···HCN, HCN···HNC, and HNC···HNC Calculated with d-aug-cc-pVTZ

		$(\mu_z)_{\text{int}}$	$(\alpha_0)_{\text{int}}$	$(\Delta\alpha)_{\text{int}}$	$(\beta_0)_{\text{int}}$	$(\gamma_0)_{\text{int}}$
HCN···HCN	SCF	0.3307	0.847	5.549	16.37	7.3
	MP2	0.3072	0.857	5.591	24.59	105.7
	MP4	0.3142	0.918	5.816	23.14	144.4
HNC···HCN	SCF	0.2960	0.697	5.795	16.66	−108.6
	MP2	0.3100	0.711	6.235	18.66	−229.5
	MP4	0.3097	0.769	6.361	20.55	−168.4
HCN···HNC	SCF	0.4456	1.105	6.828	28.04	79.8
	MP2	0.4602	1.138	6.987	39.46	266.2
	MP4	0.4608	1.195	7.143	40.37	314.6
HNC···HNC	SCF	0.4055	0.900	7.226	24.62	−112.6
	MP2	0.4667	0.966	7.999	28.91	−207.0
	MP4	0.4576	1.009	8.010	32.80	−135.7

5361.7 au. For μ_z, the MP2 result is slightly larger than the MP4 result and the SCF result is closer to the MP4 result. For polarizabilities (α_0 and $\Delta\alpha$), the MP2 results agree well with the MP4 results. For β_0, the SCF result ($\beta_0 = 38.96$ au) is lower by 9.2% than the MP4 result and the MP2 result ($\beta_0 = 47.08$ au) is higher by 9.7% than the MP4 result. For γ_0, the MP2 result ($\gamma_0 = 5238.6$ au) is in good agreement with the MP4 result and the SCF result is significantly lower.

For HNC···HCN, the results of the static electric properties calculated at the MP4/d-aug-cc-pVTZ level are $\mu_z = 2.8897$ au, $\alpha_0 = 36.646$ au, $\Delta\alpha = 23.757$ au, $\beta_0 = 61.86$ au, and $\gamma_0 = 5858.9$ au. For μ_z, like HNC···HCN, the MP2 result is slightly larger than the MP4 result and the SCF result is closer to the MP4 result. For α_0 the MP2 result is quite close to the MP4 result, and for $\Delta\alpha$ the SCF and MP2 results are slightly lower than the MP4 result. For β_0, the SCF result ($\beta_0 = 50.07$ au) is lower by 19.1% than the MP4 result and the MP2 result ($\beta_0 = 66.75$ au) is higher by 7.9% than the MP4 result. For γ_0, like HCN···HCN and HNC···HCN, the MP2 result ($\gamma_0 = 5746.4$ au) is in good agreement with the MP4 result and the SCF result is significantly lower.

For HNC···HCN, the results of the static electric properties calculated at the MP4/d-aug-cc-pVTZ level are $\mu_z = 2.9588$ au, $\alpha_0 = 37.804$ au, $\Delta\alpha = 23.896$ au, $\beta_0 = 86.58$ au, and $\gamma_0 = 6371.2$ au. For μ_z, the MP2 result is very close to the MP4 result and the SCF result is slightly lower. For polarizabilities (α_0 and $\Delta\alpha$), the MP2 results agree well with the MP4 results. For β_0, the SCF and MP2 results are lower (by 2.2% for SCF and 5.6% for MP2) than the MP4 results. For γ_0, like the cases of other three dimers, the MP2 result ($\gamma_0 = 4411.2$ au) is in good agreement with the MP4 result and the SCF result is significantly lower.

C. Interaction Static Electric Properties. The interaction static electric properties [$(\mu_z)_{\text{int}}$, $(\alpha_0)_{\text{int}}$, $(\Delta\alpha)_{\text{int}}$, $(\beta_0)_{\text{int}}$, and $(\gamma_0)_{\text{int}}$] of the four dimers (HCN···HCN, HNC···HCN, HCN···HNC, and HNC···HNC) are calculated at the SCF, MP2, and MP4 levels with the aug-cc-pVTZ basis set, and the results are listed in Table 3.

For HCN···HCN, the results of the interaction static electric properties calculated at the MP4/d-aug-cc-pVTZ level are $(\mu_z)_{\text{int}} = 0.3142$ au, $(\alpha_0)_{\text{int}} = 0.918$ au, $(\Delta\alpha)_{\text{int}} = 5.816$ au, $(\beta_0)_{\text{int}} = 23.14$ au, and $(\gamma_0)_{\text{int}} = 144.4$ au. Compared with the MP4 results, the MP2 result of $(\mu_z)_{\text{int}}$ is agreement with the MP4 result, but the SCF and MP2 results of polarizabilities [$(\alpha_0)_{\text{int}}$ and $(\Delta\alpha)_{\text{int}}$] are slightly lower than the MP4 results. For $(\beta_0)_{\text{int}}$ and $(\gamma_0)_{\text{int}}$, the SCF results are significantly lower than the MP4 results. The MP2 result for $(\beta_0)_{\text{int}}$ (24.59 au) is larger by 6.3% than the MP4 result, and the MP2 result for $(\gamma_0)_{\text{int}}$ (105.7 au) is smaller by 26.8% than the MP4 result.

For HNC···HCN, the results of the interaction static electric properties calculated at the MP4/d-aug-cc-pVTZ level are $(\mu_z)_{\text{int}} = 0.3097$ au, $(\alpha_0)_{\text{int}} = 0.769$ au, $(\Delta\alpha)_{\text{int}} = 6.361$ au, $(\beta_0)_{\text{int}} = 20.55$ au, and $(\gamma_0)_{\text{int}} = -168.4$ au. For $(\mu_z)_{\text{int}}$, the SCF and MP2 results are close to the MP4 results. The MP2 results of polarizabilities [$(\alpha_0)_{\text{int}}$ and $(\Delta\alpha)_{\text{int}}$] are slightly lower than the MP4 results. For $(\beta_0)_{\text{int}}$, the SCF result is lower by 18.9% than the MP4 result and the MP2 result is lower by 9.2% than the MP4 result. For an absolute value of $(\gamma_0)_{\text{int}}$, the SCF result is lower by 35.5% than the MP4 result and the MP2 result is significantly larger (by 36.3%) than the MP4 result.

For HCN···HNC, the results of the interaction static electric properties calculated at the MP4/d-aug-cc-pVTZ level are $(\mu_z)_{\text{int}} = 0.4608$ au, $(\alpha_0)_{\text{int}} = 1.195$ au, $(\Delta\alpha)_{\text{int}} = 7.143$ au, $(\beta_0)_{\text{int}} = 40.37$ au, and $(\gamma_0)_{\text{int}} = 314.6$ au. For $(\mu_z)_{\text{int}}$, the MP2 result is very close to the MP4 result. For polarizabilities [$(\alpha_0)_{\text{int}}$ and $(\Delta\alpha)_{\text{int}}$], the MP2 results are slightly lower than the MP4 results. For $(\beta_0)_{\text{int}}$ and $(\gamma_0)_{\text{int}}$, the SCF results are significantly lower than the MP4 results. The MP2 result of $(\beta_0)_{\text{int}}$ is only lower by 2.3% than the MP4 result, but the MP2 result of $(\gamma_0)_{\text{int}}$ is lower by 15.4% than the MP4 result.

For HNC···HNC, the results of the interaction static electric properties calculated at the MP4/d-aug-cc-pVTZ level are $(\mu_z)_{\text{int}} = 0.4576$ au, $(\alpha_0)_{\text{int}} = 1.009$ au, $(\Delta\alpha)_{\text{int}} = 8.010$ au, $(\beta_0)_{\text{int}} = 32.80$ au, and $(\gamma_0)_{\text{int}} = -135.7$ au. For $(\mu_z)_{\text{int}}$, the MP2 result is slightly larger than the MP4 result. The MP2 result of $(\alpha_0)_{\text{int}}$ is slightly lower than the MP4 result, and the MP2 result of $(\Delta\alpha)_{\text{int}}$ is very close to the MP4 result. For $(\beta_0)_{\text{int}}$, like the case of HNC···HCN, the SCF result is lower by 24.9% than the MP4 result and the MP2 result is lower by 11.9% than the MP4 result. For an absolute value of $(\gamma_0)_{\text{int}}$, like the case of HNC···HCN, the SCF result is lower by 17.0% than the MP4 result but the MP2 result is significantly larger (by 52.5%) than the MP4 result.

D. Electron Correlation Effects. Electron correlation effects on the total and interaction electric properties calculated with the basis set d-aug-cc-pVTZ are listed in Table 4. The electron correlation effects on μ_z are significant for the homodimers (HCN···HCN and HNC···HNC) and are very small for the heterodimers (HNC···HCN and HCN···HNC). The electron correlation effects on polarizabilities (α_0 and $\Delta\alpha$) for the four dimers are small. The contribution of electron correlation effect to the first hyperpolarizability of HCN···HCN is 95.2%, which is very large. For the first hyperpolarizability of HNC···HCN and HCN···HNC, electron correlation effects (9.2% and 19.1%) are also important. But for HNC···HNC, the electron correlation effect (2.2%) on β_0 is small. Electron correlation effects have important contributions (from 14.0% to 30.8%) to the values of the second hyperpolarizabilities of the four dimers.

For the electron electron correlation effects on the interaction electric properties, the electron correlation contributions to $(\mu_z)_{\text{int}}$ are −5.3% for HCN···HCN, 4.4% for HNC···HCN, 3.3% for HCN···HNC, and larger, 11.4%, for HNC···HNC. Electron correlation effects have obvious contributions (from 7.5% to 10.8%) to the values of the interaction polarizabilities $(\alpha_0)_{\text{int}}$ of the four dimers. The electron correlation effects on the interaction first and second hyperpolarizabilities are more significant than those on the interaction dipole moment and polarizabilities. For $(\beta_0)_{\text{int}}$, the electron correlation contributions are 29.3% for HCN···HCN, 18.9% for HNC···HCN, 30.5% for HCN···HNC, and 24.9% for HNC···HNC. For $(\gamma_0)_{\text{int}}$, the electron correlation contributions are 94.9% for HCN···HCN, 35.5% for HNC···HCN, 74.6% for HCN···HNC, and 17.0% for HNC···HNC.

E. Intermolecular Interaction Effects. Intermolecular interaction electric properties calculated at the MP4/d-aug-cc-

TABLE 4: Electron Correlation Effects on the Total and Interaction Electric Properties Calculated with the Basis Set d-aug-cc-pVTZ[a]

	HCN⋯HCN	HNC⋯HCN	HCN⋯HNC	HNC⋯HNC
μ_z	−0.2583 (−9.7%)	0.0136 (0.5%)	0.0173 (0.6%)	0.2933 (9.9%)
α_0	0.122 (0.3%)	0.899 (2.5%)	0.934 (2.5%)	1.728 (4.6%)
$\Delta\alpha$	−0.089 (−0.4%)	0.796 (3.5%)	0.568 (2.4%)	1.628 (6.8%)
β_0	12.42 (95.2%)	3.95 (9.2%)	11.79 (19.1%)	1.92 (2.2%)
γ_0	664.3 (14.0%)	1183.0 (22.1%)	1496.6 (25.5%)	1960.0 (30.8%)
$(\mu_z)_{\mathrm{int}}$	-0.0165 (−5.3%)	0.0137 (4.4%)	0.0152 (3.3%)	0.0521 (11.4%)
$(\alpha_0)_{\mathrm{int}}$	0.071 (7.7%)	0.072 (9.4%)	0.090 (7.5%)	0.109 (10.8%)
$(\Delta\alpha)_{\mathrm{int}}$	0.267 (4.6%)	0.566 (8.9%)	0.315 (4.4%)	0.784 (9.8%)
$(\beta_0)_{\mathrm{int}}$	6.77 (29.3%)	3.89 (18.9%)	12.33 (30.5%)	8.18 (24.9%)
$(\gamma_0)_{\mathrm{int}}$	137.1 (94.9%)	−59.8 (35.5%)	234.8 (74.6%)	−23.1 (17.0%)

[a] The values in parentheses are calculated by the following formula: $(P_{\mathrm{MP4}} - P_{\mathrm{HF}})/P_{\mathrm{HF}}$.

TABLE 5: Intermolecular Interaction Effects on the Static Electric Properties Calculated at the MP4/d-aug-cc-pVTZ Level[a]

	HCN⋯HCN	HNC⋯HCN	HCN⋯HNC	HNC⋯HNC
$(\mu_z)_{\mathrm{int}}$	0.3142 (11.8%)	0.3097 (11.3%)	0.4608 (15.9%)	0.4576 (15.5%)
$(\alpha_0)_{\mathrm{int}}$	0.918 (2.6%)	0.769 (2.1%)	1.195 (3.3%)	1.009 (2.7%)
$(\Delta\alpha)_{\mathrm{int}}$	5.816 (25.2%)	6.361 (27.8%)	7.143 (30.1%)	8.010 (33.5%)
$(\beta_0)_{\mathrm{int}}$	23.14 (177%)	20.55 (47.9%)	40.37 (65.3%)	32.80 (37.9%)
$(\gamma_0)_{\mathrm{int}}$	144.4 (3.0%)	−168.4 (−3.1%)	314.6 (5.4%)	−135.7 (−2.1%)

[a] The values in parentheses are calculated by the following formula: P_{int}/P.

pVTZ level are listed in Table 5. For all the four dimers, the intermolecular interactions have important effects on the dipole moment μ_z, the anisotropy of the polarizabilities $\Delta\alpha$, and the first hyperpolarizabilities β_0, but they have rather small effects on the mean of the polarizabilities α_0 and the second hyperpolarizabilities γ_0.

In the four dimers, the interaction first hyperpolarizabilities $(\beta_0)_{\mathrm{int}}$ of HCN⋯HCN (23.14 au) and HNC⋯HCN (20.55 au) are smaller than those of HCN⋯HNC (40.37 au) and HNC⋯HNC (32.80 au). The intermolecular interactions slightly increase γ_0 of HCN⋯HCN and HCN⋯HNC, but they decrease γ_0 of HNC⋯HCN and HNC⋯HNC. The interaction first hyperpolarizabilities are 144.4 au (3.0%) for HCN⋯HCN, −168.4 au (−3.1%) for HNC⋯HCN, 314.6 au (5.4%) for HCN⋯HNC, and −135.7 au (−2.1%) for HNC⋯HNC.

Comparing the two homodimers (HCN⋯HCN and HNC⋯HNC), the HNC dimer has a larger interaction first hyperpolarizability than the HCN dimer. For the two heterodimers, although they consist of the same monomers, their interaction first hyperpolarizabilities are quite different with the change of hydrogen donors and acceptors. The HCN⋯HNC dimer has a significantly larger interaction first hyperpolarizability than the HNC⋯HCN dimer. As above, the dimers in which HNC acts as the hydrogen donor have larger $(\beta_0)_{\mathrm{int}}$ values; for example, the $(\beta_0)_{\mathrm{int}}$ values of HCN⋯HNC and HNC⋯HNC are larger than those of HCN⋯HCN and HNC⋯HCN. For the dimers with the same hydrogen donors, the dimers in which HCN acts as the hydrogen acceptor have larger $(\beta_0)_{\mathrm{int}}$ values; for example, $(\beta_0)_{\mathrm{int}}$ of HCN⋯HCN is large than that of HNC⋯HCN and $(\beta_0)_{\mathrm{int}}$ of HCN⋯HNC is larger than that of HNC⋯HNC. This rule is roughly related to the results of interaction energies that HCN⋯HCN and HNC⋯HCN have weaker intermolecular interactions than HCN⋯HNC and HNC⋯HNC (see Table 1).[23] In the four dimers, the dimer composed by a strong hydrogen donor (HNC) and a strong hydrogen acceptor (HCN) has a large interaction first hyperpolarizability. For the second hyperpolarizabilities, the intermolecular interaction increases the values of γ_0 for HCN⋯HCN and HCN⋯HNC and decreases the values of γ_0 for HNC⋯HCN and HNC⋯HNC.

In early work, we had calculated the interaction hyperpolarizabilities for the dimers with one π-system (HCN⋯HF and HNC⋯HF).[15] The values of $(\beta_0)_{\mathrm{int}}$ obtained at the MP4/d-aug-cc-pVTZ level are 5.07 au for HCN⋯HF and −7.46 au for HNC⋯HF. The interaction first hyperpolarizabilities of the four dimers (between two π-systems) investigated in this paper are significantly larger than those of HCN⋯HF and HNC⋯HF in absolute terms. It shows that the value of the interaction first hyperpolarizability increases with increase of the number of π-systems. However, this rule is not proper for the interaction second hyperpolarizabilities.

Conclusions

We have investigated intermolecular interaction effects on the static electric properties (μ_z, α_0, $\Delta\alpha$, β_0, and γ_0) by ab initio calculations for four dimers between two π-systems (HCN⋯HCN, HNC⋯HCN, HCN⋯HNC, and HNC⋯HNC). We found that electron correlation effects are quite important for the calculations of the static electric properties, particularly the first and second hyperpolarizabilities.

The contribution of intermolecular interaction first hyperpolarizability to the total first hyperpolarizability is large, but the interaction second hyperpolarizability is relatively small for the four dimers. The dimer composed of a strong hydrogen donor (HNC) and a strong hydrogen acceptor (HCN) has a large interaction first hyperpolarizability. Comparing the HCN⋯HF and HNC⋯HF dimers with one π-system, the intermolecular interaction first hyperpolarizabilities for these dimers between two π-systems are large. This shows that the intermolecular interaction first hyperpolarizability increases with increase of the number of π-system.

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