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시안화수소와 플루오르화수소와의 수소결합 삼합체들에 관한 *Ab Initio* 연구

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Ab Initio Studies on Hydrogen-Bonded Trimers Formed between Hydrogen Cyanide and Hydrogen Fluorides

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요 약. 한 분자의 시안화수소와 두 분자의 플루오르화수소 사이에 생성 가능한 다섯개의 수소결합 삼합체들에 대하여 TZ+P 수준의 기본조를 사용하여 *ab initio* 계산을 하였다. 이것들의 몇 가지 바닥상태 성질을 구하여 단위체와 이합체들의 대응하는 성질과 비교하였다. 앞으로 얻을 수 있게 될 실험 자료들을 보충하기 위하여 계산한 평형 기하구조, 안정화 에너지 및 쌍극자 모멘트를 나타냈다. 이 수준의 근사법에서는 분자내 결합거리는 항상 실험값보다 작게 계산되었지만, 분자간 거리와 쌍극자 모멘트는 크게 계산되었다. 다섯개의 삼합체중에서 $HCN(HF)_2$가 가장 안정하고, 또한, $(HCN)_2HF$보다도 더 안정한 것으로 나타났다. 분자간 상호작용의 비가감성에 대한 전형적인 특징은 $HCN(HF)_2$에서 비교적 강했다.

ABSTRACT. *Ab initio* SCF calculations have been carried out for the five conceivable trimers formed between one hydrogen cyanide and two hydrogen fluorides using a basis set of TZ+P quality. Several ground state properties of these trimeric complexes have been evaluated, and compared with those of isolated monomers and appropriate dimers. Computed equilibrium geometries, stabilization energies, and dipole moments are given in order to suppliment the available experimental data. At this level of approximation, intramolecular bond distances are consistently shorter than experimental ones. However, intermolecular distances upon complex formation, and dipole moments are overestimated compared with experimental ones. $HCN(HF)_2$ trimer appears to be the most favourable among the five kinds of trimer complex, and also more stable than $(HCN)_2HF$. The typical features of the non-additivity of intermolecular interaction are relatively strong in the $HCN(HF)_2$ trimer.

INTRODUCTION

In the last years a large number of works on hydrogen-bonded systems have been reported. On one hand due to their variety and the advent of large-scale computational facilities, on the other hand because of their importance in biological processes as well as in biochemical and chemical ones hydrogen-bonded aggregates give a continuous challenge to both the theorist and the spectroscopist nowadays. So a great deal of information on hydrogen bonding is now available from experimental and theoretical perspectives.[1~6] Both gas phase spectroscopic studies,[1,5,6] and detailed theoretical calculations[1~4] have immensely contributed to our current understanding of the structures and dynamics of dimeric hydrogen-bonded complexes. But, experimental results of similar precision on higher oligomers than trimers are quite rare so

far. While experimental studies on larger clusters are hampered because of the low concentration in the vapor phase, quantum-mechanical studies may give valuable information which is hardly accessible otherwise. In small oligomers, theoretical results are generally close to the experimental values. For the larger complexes, however, full geometry optimization is avoided and small basis sets are used. Because full geometry optimization is protracted, tedious job, intramolecular geometry of each subsystem is kept constant, and only intermolecular coordinates are optimized generally. In simple complexes, geometry changes of subsystem are negligible substantially. However, if the directions of polarity of subsystems are quite different from those of the complexes, severe geometry changes of subsystems in complexes may be found. So a necessary prerequisite for reliable predictions is the use of extended basis sets accompanied by extensive geometry optimization.

In the case of trimers, comparable experimental information derived from vapor phase investigations is only about to appear. In a recent conference abstract, Ruoff and coworkers[7] presented the first Fourier transform microwave investigations on a considerable number of hydrogen-bonded trimers. All of these trimers contained the linear $(HCN)_2$ unit, and the third partner molecule was either HF, HCl, HCF_3, NH_3, N_2, CO, C_2H_4, or C_3H_6. Chain-like trimers formed between hydrogen cyanide, and hydrogen fluorides have large dipole moments. Therefore, they seem to be particulary suitable candidates for vapor phase investigations. In a previous work,[8] Rhee and Karpfen have reported the structures and vibrational spectra of the trimers formed between linear $(HCN)_2$ dimer and HCN, HF, HCl, H_2O and NH_3. There we didn't consider that respective hydrorogen cyanide and hydrogen fluoride could act as both the hydrogen-bond acceptors and donors.

In this work we present the results of *ab initio* calculations carried out within the framework of the Hartree-Fock (SCF) approximation on the conceivable hydrogen-bonded trimers. $HCN(HF)_2$, $NCH(FH)_2$ (upward and downward forms) and FH-NCH-FH (linear and bent forms), which are formed between one hydrogen cyanide and two hydrogen fluoride, are considerd.

METHOD OF CALCULATION

The same standard *ab initio* SCF method was applied to the monomers, dimers, and trimers. The COLUMBUS program[9,10] was used. It contains SCF and analytic gradient programs written by Pitzer based on HONDO routines.[11,12] 10s6p1d basis set was chosen for C, N and F, respectively, and 6s1p for H. All s and p basis sets were taken from Huzinaga's compilation.[13,14] As exponents of the polarization functions we chose 1.0, 0.95, 1.6 and 0.75 on C, N, F and H, respectively. These basis sets were contracted into [6,4,1] for C, N and F, respectively, and to [4,1] for H.

Equilibrium geometries were obtained with gradient optimization,[15] and with full geometry optimization. In the geometry optimizations, $C_{\infty v}$ symmetry was retained for the linear complexes, and C_s symmetry for nonlinear ones. For the stabilization energy evaluations, we don't considered the basis set superposition errors because at this level of calculation they are erroneous compared to experimental results.

RESULTS AND DISCUSSION

MONOMERS

Computed ground state properties of the monomers, HCN and HF, are listed in *Table* 1, and confronted with experimental data[16~20] in order to assess the methodological errors, and the basis set limitations coming from our SCF calculations at this point.

Table 1. Ground state properties of monomers

	HCN		HF	
	SCF	exp.	SCF	exp.
r(HX)(Å)	1.0587	1.065	0.8990	0.917
r(CN)(Å)	1.1242	1.153	–	–
μ(debye)	3.25	2.99	2.03	1.803
E(hartree)	−92.90675	–	−100.06099	–

The performance of such SCF calculations is generally well documented. At this level of approximation, bond distances are consistently shorter than experimental ones. Thus, we found already that corresponding bond stretching frequencies were too high, and rotational constant too large.[8] Similarly, dipole moments are uniformly overestimated. Evidently, these errors will persist in the SCF results for dimers, and trimers formed from these monomers.

DIMERS

The conceivable dimeric structures which are parts of the trimers built up from one molecule of hydrogen cyanide, and two molecules of hydrogen fluoride, are only considered. Since hydrogen-bond donors, and acceptors can exchange their roles, there will be four possible configurations. In the case of FH-NCH, linear orientation was confirmed experimentally,[21] therefore bent form is not considered. Geometries, and numbering of internal coordinates are shown in *Fig.* 1.

FH-NCH. The complex between hydrogen cyanide acting as hydrogen-bond acceptor, and hydrogen fluoride acting as hydrogen-bond donor is the by far studied hetero-dimer. We have reported its ground state properties in the previous work[8] in detail. Therefore we reproduce some of them in *Table* 2. Here, we compare computed equilibrium geometry, stabilization energy (or hydrogen bonding energy), and dipole moment of the complex with the experimental results.[21,22~24]

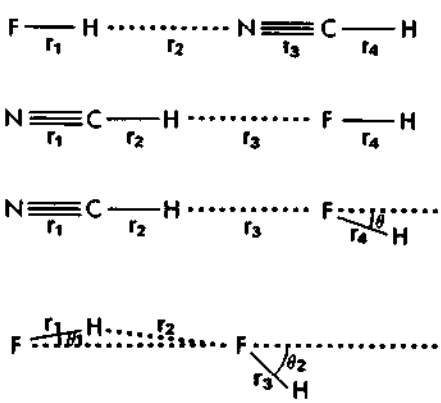

Fig. 1. Structures, and internal coordinates of dimers.

Concerning intramolecular equilibrium distances we observe the similar errors as in the monomers. The relative changes of these structural parameters accompanying complex formation are, however, well described, and agree closely with SCF, and more importantly also with electron correction studies.[25] At our SCF level the intermolecular distance is overestimated by about 0.1 Å. Stabilization energy ΔE is in reasonable agreement with the experimental result. To a certain extent this is a result of error cancellation. Compared to −6.05 kcal/mol in ref. [25] where a near valence shell Hartree-Fock limit basis set was used, our stabilization energy is too large about 0.6 kcal/mol. About this amount of energy is gained back by incorporating electron correlation at the CEPA level.[25] The basis set superposition error(BSSE) on the stabilization energy of this dimer calculated with the counterpoise correction was investigated by Leclercq, Allavena and Bouteiller.[26] Their stabilization energy value using 10s6p basis set at SCF level, −7.2 kcal/mol is overestimated by about 0.6 and 1.0 kcal/mol, respectively, compared to ours without counterpoise correction, and the experimental one.

The computed dipole moment of the complex

Table 2. Ground state properties of FH-NCH dimer. Distances in Å, total energy in hartree, stabilization energies in kcal/mol, and dipole moments in debye (For numbering of internal coordinates see *Fig.* 1)

	r_1	Δr_1	r_2	r_3	Δr_3	r_4	Δr_4
SCF	0.9070	0.0080	1.9701	1.1221	−0.0021	1.0596	0.0009
exp.	0.931	0.014	1.887	–	–	–	
	E	ΔE	μ	$\Delta\mu$			
SCF	−192.978292	−6.61	6.07	0.79			
exp.	–	−6.24± 0.38	5.59	0.78			

is too large by about 0.5 debye as a consequence of the overestimated monomer moments. The non-additive behavior of the dipole moment is satisfactorily reproduced. The induced dipole moment agrees closely with experimental one.

Linear, and bent NCH-FH. For the dimers in which hydrogen cyanide acts as a hydrogen-bond donor, and hydrogen fluoride as a hydrogen-bond acceptor experimental results have not yet been reported. Therefore, we compile only the calculated ground state properties in *Table* 3.

Because of the weaker hydrogen bond (see ΔE), all intramolecular geometry relaxations are smaller in NCH-FH dimers than in FH-NCH dimer. The intermolecular distances in these two complexes are repectively 0.140, and 0.135 Å, larger than that in FH-NCH complex. Stabilization energies for these complexes are 3.05, and 3.06 kcal/mol compared to 6.61 kcal/mol for FH-NCH complex. Therefore, we can conclude that FH-NCH complex is more favorable, and stable than NCH-FH complexes. In these two dimers the bent structure is slightly stable compared to linear one. This fact is also reflected in the increased intermolecular distance of the linear structure compared to bent one.

Dipole moment of the bent structure is smaller than that of the linear one, and related to the distorted direction of polarity in the dimer. Again values of the complexes show the non-additive behavior of dipole moment in chain-like oligomers.

HF-HF. Ground state properties of $(HF)_2$ are listed in *Table* 4 and compared to CEPA,[27] and experimental[28] results. It reveals the commonly expected features of an ordinary hydrogen bond: the complex is planar, and exhibits Cs-symmetry. A small elongation of the HF bond in the proton donor molecule relative to the bond in free HF, is found. Our SCF results are similar to CPEA ones. For this dimer Loushin, Liu and Dykstra[29] had performed both the counterpoise and the polarization counterpoise corrections for the BSSE

Table 3. Ground state properties of (1) linear, and (2) bent NCH-FH dimers. Distances in Å, angles in degree, total energies in hartree, stabilization energies in kcal/mol, and dipole moments in debye (For numbering of internal coordinates see *Fig.* 1)

	r_1	Δr_1	r_2	Δr_2	r_3	r_4	Δr_4
(1)	1.1246	0.0004	1.0609	0.0021	2.2099	0.9007	0.0017
(2)	1.1246	0.0004	1.0611	0.0023	2.2052	0.9008	0.0018
	E	ΔE	μ	Δμ	θ		
(1)	−192.972613	−3.05	5.63	0.35	−		
(2)	−192.972637	−0.06	5.48	0.20	24.09		

Table 4. Ground state properties of HF-HF dimer. Distances in Å, angles in degree, total energy in hartree, stabilization energies in kcal/mol, and dipole moments in debye (For numbering of internal coordinates see *Fig.* 1)

	r_1	Δr_1	r_2	r_3	Δr_3	r_{FF}	θ_1	θ_2
SCF	0.9029	0.0039	1.9195	0.9017	0.0027	2.8145	5.60	53.57
CEPA	0.904	−	−	0.902	−	2.83	6.0	56.8
exp.	−	−	−	−	−	2.789	−	60~70
	E	ΔE	μ	Δμ				
SCF	−200.128930	−4.36	3.82	−0.24				
CEPA		−4.18						
exp.		−4.52						

using several different basis sets. Their stabilization energies using 6-311G** were −4.59, −3.66, and −3.33 kcal/mole without the correction, with the counterpoise correction, and with the polarization counterpoise correction, respectively. The corrected values show more larger deviation from the experimental one. Therefore, it seems reasonable not to consider the BSSE in our calculation. Intermolecular distance rFF is overestimated by about 0.026 compared to experimental one. This distance (rFF~3 Å) is considered to be characteristic of ordinary hydrogen bonds between neutral molecules.[4]

TRIMERS

Structures of the conceivable five trimers formed between one hydrogen cyanide, and two hydrogen fluorides are considerd, and depicted in *Fig.* 2.

Structures. Equilibrium geometries of the five trimers are compiled in *Table* 5, 6, and 7. Intramolecular geometry relaxations compared to monomers, and corresponding dimers are included. Intermolecular geometry relaxations compared to corresponding dimers also are included.

As we see in the *Table* 5, 6, and 7, intramolecular bond relaxations upon complex formations with three monomers, or with one monomer and one dimer, are relatively small compared to the corresponding monomers, and dimers. $HCN(HF)_2$ in which HCN acts as hydrogen-bond acceptor, and $(HF)_2$ donor shows largest values (in the *Table* 5 Δr_4 are about 0.015 Å with respect to monomer, HF, and about 0.013 Å with repect to homo-dimer, $(HF)_2$). But these values do not exceed 0.009 Å in the other four cases. Viewing the trimer structure as a superposition of two dimers, intramolecular bond relaxations also are relatively small in all five cases. Intermolecular distances are, however, significantly contracted. For $HCN(HF)_2$ trimer the sum of the two intermolecular distances is reduced by about 0.2 Å compared to isolated dimers, HCN-HF, and $(HF)_2$ (in the *Table* 5 the sum of ΔR_3 with respect to heteo-dimer, HCN-HF, and Δr_5 with respect to homo-dimer, $(HF)_2$). For the other four trimers those are reduced by about 0.1 Å, respectively. In the $(HCN)_3$ homo-trimer,[30,31] and $(HCN)_2HF$, $(HCN)_2HCl$, $(NCH)_2OH_2$, and $(NCH)_2NH_3$ hetero-trimers[8] exactly the same reduction was observed. In this open chain HCN $(HF)_2$ hetro-trimer, and $(HF)_3$ homo-trimer[32] significantly larger contractions have been computed indicating that non-additivity plays a more important role in HF clusters than in HCN clusters. Because of the overestimation of intermolecular distances in the dimers we expect that the computed sum of intermolecular distances in the trimers

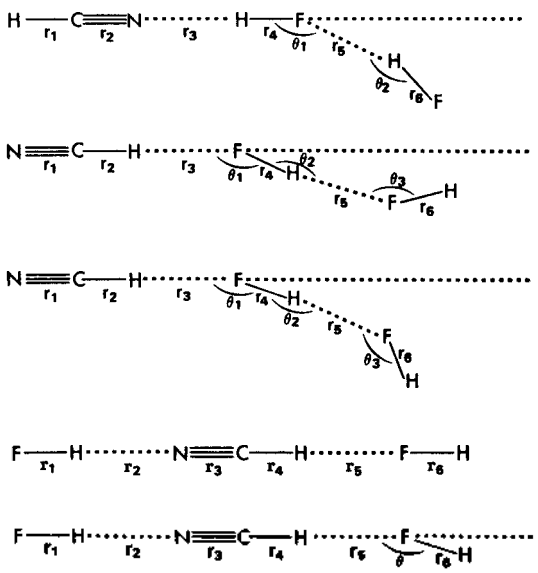

Fig. 2. Structures, and internal coordinates of trimers.

Table 5. Equilibrium geometry of $HCN(HF)_2$ trimer. Bond distances in Å, and bond angles in degree (For numbering of internal coordinates see *Fig.* 2)

	r or θ	Δr_{mon}[a]	Δr_{het}[b]	Δr_{hom}[c]
r_1	1.0601	0.0014	0.0005	–
r_2	1.1215	−0.0027	−0.0006	–
r_3	1.8666	–	−0.1035	–
r_4	0.9143	0.0153	0.0073	0.0126
r_5	1.8220	–	-	−0.0975
r_6	0.9060	0.0070	-	0.0031
θ_1	152.88	–	–	–
θ_2	174.95	–	–	–

[a]Bond length changes with respect to monomers. [b]Bond length changes with respect to hetero-dimer. [c]Bond length changes with respect to homo-dimer.

Table 6. Equilibrium geometries of $NCH(FH)_2$ trimers. (1) Upward form. (2) Downward form. Bond distances in Å, and bond angles in degree (For numbering of internal coordinates see *Fig.* 2)

	(1)				(2)			
	r or θ	Δr_{mon}[a]	Δr_{het}[b]	Δr_{hom}[c]	r or θ	Δr_{mon}[a]	Δr_{het}[b]	Δr_{hom}[c]
r_1	1.1248	0.0006	0.0002	–	1.1248	0.0006	0.0002	–
r_2	1.0621	0.0027	−0.0006	–	1.0621	0.0034	0.0010	–
r_3	2.1372	–	−0.0680	–	2.1371	–	−0.0681	–
r_4	0.9058	0.0068	0.0050	0.0031	0.9057	0.0067	0.0049	0.0030
r_5	1.8596	–	–	−0.0599	1.8634	–	–	−0.0561
r_6	0.9024	0.0034	–	−0.0005	0.9023	0.0033	–	−0.0006
θ_1	152.84	–	–	–	158.97	–	–	–
θ_2	175.07	–	–	–	175.81	–	–	–
θ_3	133.53	–	–	–	135.88	–	–	

[a]Bond length changes with respect to monomers. [b]Bond length changes with respect to hetero-dimer. [c]Bond length changes with respect to homo-dimer.

Table 7. Equilibrium geometries of FH-NCH-FH trimers. (1) Linear form. (2) Bent form. Bond distances in Å, and bond angles in degree (For numbering of internal coordinates see *Fig.* 2)

	(1)				(2)			
	r or θ	Δr_{mon}[a]	Δr_{het}[b]	Δr_{hom}[c]	r or θ	Δr_{mon}[a]	Δr_{het}[b]	Δr_{hom}[c]
r_1	0.9082	0.0092	0.0012	–	0.9082	0.0092	0.0012	–
r_2	1.9462	–	−0.0239	–	1.0621	–	−0.0241	–
r_3	1.1226	−0.0016	0.0005	−0.0020	1.1226	0.0005	−0.0020	–
r_4	1.0621	0.0034	0.0025	0.0012	1.0622	0.0035	0.0026	0.0011
r_5	2.1529	–	–	−0.0523	2.1512	–	–	−0.0540
r_6	0.9012	0.0022	–	0.0005	0.9012	0.0022	–	0.0004
θ	–	–	–	–	160.17	–	–	

[a]Bond length changes with respect to monomers. [b]Bond length changes with respect to hetero-dimer, FH-NCH. [c]Bond length changes with respect to corresponding hetro-dimers, NCH-FH(linear), and NCH-FH(bent).

is too large by about 0.1 to 0.20 Å[8].

Energetics and dipole moments. Total energies, stabilization energies, dipole moments and induced dipole moments of these trimers are compiled in *Table* 8.

From total energies and stabilization energies we find that the order of relative stability is following: $HCN(HF)_2$>FH-NCH-FH(linear)~FH-NCH-FH(bent)>$NCH(FH)_2$(upward)~$NCH(FH)_2$(downward). We observe that the most stable trimer is obtained when HCN acts as a hydrogen bond acceptor, and $(HF)_2$ as a hydrogen bond donor, the medium stable trimer when repective HCN, and HF do as both donors, and acceptors, and the least stable trimer when HCN does as a donor, and $(HF)_2$ as a acceptor. Although the difference of stabilization energies of the upward, and downward $NCH(FH)_2$ trimers is very small, the former is slightly stable than the latter. In the case of FH-NCH-FH trimer, the linear form actually has the same stability as bent one.

For the trimers considered here non-additive effects of stabilization energies are relatively small. In order to elucidate this behavior we introduce the following energy differences of the trimers by viewing the trimer structure as a superposition of two dimers, and one monomer and one dimer: for the $HCN(HF)_2$,

$$\Delta E_1 = \Delta E(\text{trimer}) - \Delta E(\text{HCN-HF}) - \Delta E((HF)_2) \quad (1)$$

$$\Delta E_2 = \Delta E(\text{trimer}) - \Delta E(\text{HCN-HF}) \quad (2)$$

Table 8. Total energies (hartree), stabilization energies and stabilization energy differences (kcal/mol), and dipole moments and induced dipole moments (debye) of trimers

Trimers	E	ΔE	ΔE_1	ΔE_2	ΔE_3
$HCN(HF)_2$	−293.050087	−13.39	−2.42	−9.03	−6.78
$NCH(FH)_2$(upward)	−293.042252	−8.48	−1.06	−5.42	−5.12
$NCH(FH)_2$(downward)	−293.042213	−8.45	−1.03	−5.39	−4.09
FH-NCH-FH(linear)	−293.045393	−10.45	−0.79	−3.84	−7.40
FH-NCH-FH(bent)	−293.045392	−10.45	−0.78	−3.84	−7.39

Trimers	μ	$\Delta\mu_1$	$\Delta\mu_2$	$\Delta\mu_3$
$HCN(HF)_2$	7.91	0.60	−0.19	0.84
$NCH(FH)_2$(upward)	7.71	0.40	0.20	0.64
$NCH(FH)_2$(downward)	7.07	−0.24	−0.44	0.00
FH-NCH-FH(linear)	8.54	1.23	0.88	0.44
FH-NCH-FH(bent)	8.41	1.10	0.90	0.31

$$\Delta E_3 = \Delta E(\text{trimer}) - \Delta E((HF)_2) \quad (3)$$

for the upward and downward $NCH(FH)_2$,

$$\Delta E_1 = \Delta E(\text{trimer}) - \Delta E(\text{NCH-FH}) - \Delta E((FH)_2) \quad (4)$$

$$\Delta E_2 = \Delta E(\text{trimer}) - \Delta E(\text{NCH-FH}) \quad (5)$$

$$\Delta E_3 = \Delta E(\text{trimer}) - \Delta E((FH)_2) \quad (6)$$

for the corresponding linear and bent FH-NCH-FH,

$$\Delta E_1 = \Delta E(\text{trimer}) - \Delta E(\text{FH-NCH})) - \Delta E(\text{NCH-FH}) \quad (7)$$

$$\Delta E_2 = \Delta E(\text{trimer}) - \Delta E(\text{FH-NCH}) \quad (8)$$

$$\Delta E_3 = \Delta E(\text{trimer}) - \Delta E(\text{NCH-FH}) \quad (9)$$

ΔE_1 corresponds to ΔE^{COOP} of ref. [32], and presents a measure for the stability enhancement of a trimer with respect to initialy separated dimers. In a more strict sense the direct interaction between non-neighbouring molecules should be subtracted from ΔE_1 in oder to determine the correct non-additivity. Here we neglect this "1-3" interaction. ΔE_1 values exceed the sum of two dimer stabilization energies by about 2.4 kcal/mol in $HCN(HF)_2$, and 0.8~1.1 kcal/mol in the other three trimers. ΔE_2 represents the stabilization energy between a monomer and an already computed dimer, whereas the alternative route to build up a trimer from a monomer and a dimer is considered for ΔE_3. ΔE_2 and ΔE_3 values range from about −3.8 of the FH-NCH-FH(linear and bent) to −9.0 kcal/mol of the $HCN(HF)_2$. For reference, ΔE_1, ΔE_2 and ΔE_3 values of the $HCN(HF)_2$, −2.42, −9.03 and −6.78 kcal/mol are significantly large compared to those of the $(HCN)_2HF_8$, −1.21, −5.60 and −7.82, and to those of the $(HCN)_3$,[8] −1.06, −5.45 and −5.45 kcal/mol. Thus, the typical features of non-additivity of intermolecular interaction are significantly strong in the $HCN(HF)_2$ trimer in which $(HF)_2$ acts as a hydrogen bond donor, and comparatively weak in the other four trimers in which $(HF)_2$ as hydrogen bond acceptors, or HF as both hydrogen bond donors, and acceptors. Non-additive behavior of dipole moment is a well known phenomenon in hydrogen bonds. The polarities of AH bonds in hydrogen bond donors increase upon hydrogen bond formation, usually leading to larger dipole moment of the complexes than expected from vectorial addition of the components.[4] Considering the too large dipole moment, and the magnitude of the SCF error for the dipole moments of $(HCN)_3$,[7,30] and $(HCN)_2HF$, $(HCN)_2HCl$, $(HCN)_2OH_2$, and $(HCN)^2NH_3$[8] we can expect that all of the computed trimer dipole moments compiled in *Table* 8 are too large by about 1D. In order to characterize the induced dipole moments in the trimers we define the following quantities with an obvious physical meaning:

for all the trimers,

$$\Delta\mu_1 = \mu(\text{trimer}) - \mu(\text{HCN}) - 2\mu(\text{HF}) \quad (10)$$

for the $HCN(HF)_2$,

$$\Delta\mu_2 = (\text{trimer}) - \mu(\text{HF}) - \mu(\text{HCN-HF}) \quad (11)$$

for the upward and downward $NCH(FH)_2$, and the corresponding linear and bent FH-NCH-FH,

$$\Delta\mu_2 = \mu(\text{trimer}) - \mu(\text{HF}) - \mu(\text{NCH-FH}) \quad (12)$$

for the $HCN(HF)_2$, and the upward and downward $NCH(FH)_2$,

$$\Delta\mu_3 = \mu(\text{trimer}) - (\text{HCN}) - \mu((\text{HF})_2) \quad (13)$$

for the corresponding linear and bent FH-NCH-FH,

$$\Delta\mu_3 = \mu(\text{trimer}) - \mu(\text{HF}) - \mu(\text{FH-NCH}) \quad (14)$$

$\Delta\mu_1$ reprents dipole moment increase of monomers, $\Delta\mu_2$ that of a monomer and a dimer, and $\Delta\mu_3$ that of the alternative route upon trimer formation, respectively. $\Delta\mu_1$'s of FH-NCH-FH(linear) and FH-NCH-FH(bent) are 1.23, and 1.10, respectively, showing expected values. Smaller, and even negative values of the other trimers mean that their directions of polarities changed more severely on complex formations than on subunits, thus reflect their severely distorted structures. $\Delta\mu_2$ and $\Delta\mu_3$ show a similar behavior.

CONCLUSIONS

The conceivable five hydrogen-bonded trimers have been studied with the aid of conventional *ab initio* SCF techniques using a basis set of TZ+P quality. All monomers and dimers contained in these chain-like open trimers have been investigated at the same level of sophistication.

From a comparison of a variety of ground state properties of these complexes a coherent picture emerges. With this basis set, and at this level of approximation intramolecular distances are consistently shorter than experimental ones. However, intermolecular bond distances upon complex formation are consistently overestimated. The sum of the two intermolecular distances in the trimers is consistently smaller than the sum of the two dimer intermolecular separations by about 0.1 to 0.2 Å. Trimer stabilization energies exceed the sum of dimer stabilization energies by about 2.4 kcal/mol in the $HCN(HF)_2$, and 0.8 to 1.1 kcal/mol in the other four trimers. Thus the typical features of non-additivity of intermolecular interacton are comparatively strong in the $HCN(HF)_2$ trimer. Dipole moments of the trimers exceed the monomer dipole moments by about 0.4 to 1.2 D. The actually computed dipole moments are very probably too large by about 1 D due to the use of the SCF approximation.

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