Theoretical Study on Intermolecular Interactions and Thermodynamic Properties of Difluoroamine Complex

JU, Xue-Hai(居学海) XIAO, He-Ming*(肖鹤鸣) XIA, Qi-Ying(夏其英)
Department of Chemistry, Nanjing University of Science and Technology, Nanjing, Jiangsu 210094, China

***Ab initio* calculations were carried out for difluoroamine complexes at the HF and MP2 levels with different basis sets. The BSSE correction was included with counterpoise procedure. The dimer, trimer and tetramer were all found to exhibit two minima. The corrected binding energies are −8.87, −19.19 and −33.81 kJ·mol^{-1} at the MP2/6-311G**//HF/6-311G** level for the more stable dimer, trimer and tetramer, respectively. At the G2 level, the binding energy for the cyclic dimer is −10.86 kJ·mol^{-1}. There are two types of complexes: cyclic and chain. The contribution of cooperative effect to the interaction energy is up to 12.9% of the binding energy in the cyclic complexes, but negligible in the chain ones. There exist weak hydrogen bonds which involve six and eight F···H contacts at *ca*. 0.23—0.24 nm in the cyclic trimer and cyclic tetramer, respectively. The intermolecular interaction is an exothermic process under 400.0 K accompanied by a decrease in the probability.**

Keywords difluoroamine complex, intermolecular interaction, *ab initio*, thermodynamic property

Introduction

Applications of *ab initio* calculations to intermolecular interactions including either weak van der Waals or stronger hydrogen bonding have drawn much attention in the past decades because they are important in a wide range of physical, chemical and biological fields.[1-5] In recent years, we have applied the intermolecular interactions to energetic systems and obtained some meaningful information that is valuable for the study of energetic materials.[6-14] The behavior of molecular complexes is usually between two extremes: the gas phase and the crystal solid phase. Consequently, one can obtain valuable knowledge about the transition of these extremes by examining the properties of complexes of large size. Complexes containing more than two molecules behave cooperative effects,[2,15,16] which is reflected in changes of some properties with increase in complex size such as the interaction intensity increase and the frequency shift. Properly characterizing these phenomena is thus crucial to understanding the behavior of complex.

Difluoroamines are energetic compounds that form another category of explosives when the nitro groups of nitro compounds are substituted with difluoramine group.[17] The previous investigations have limited to its monomer.[18,19] Difluoroamine is the simplest model for this kind of compounds, and properties such as the diffusion, the aggregation and the detonation are all related to the intermolecular forces. The detailed structural information and the characteristics of the interaction among difluoroamine complexes could be derived by theoretical methods, since no experimental measurements are available. The aim of this paper is to investigate theoretically the structures, the binding energies and the cooperative effects in complexes containing more than two molecules, and the changes of thermodynamic properties on going from the monomer to the complexes.

Methods

Difluoroamine monomer and its possible stable complexes obtained from Chem3D software are fully optimized by the Berny method at the HF/6-311G** level.[20-22] The Møller-Plesset (MP2) calculations are performed on the structures obtained by the HF optimizations.

The interaction energy of complex is evaluated as the sum of the SCF interaction energy and the correlation interaction energy. When the latter term is determined by the Møller-Plesset perturbation theory,[23-25] the interaction energy is as follows,

$$\Delta E(\mathrm{MP}) = \Delta E(\mathrm{HF}) + \Delta E^{\mathrm{MP}}$$

where $\Delta E(\mathrm{HF})$ is the HF interaction energy, ΔE^{MP} is the correlation interaction energy given by the MP method. The basis sets commonly used to calculate the energies in the above equation are far from being saturated and, hence in any complex each subsystem will tend to lower its energy by using the basis functions of the other subsystem. The energies obtained at the equilibrium geometry of the com-

* E-mail: xiao@mail.njust.edu.cn
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plex for each subsystem are lower than those calculated at the same geometry with the basis functions of the respective subsystem alone. This energy difference is the so-called BSSE that can be checked by the Boys and Bernardi's counterpoise procedure (CP).[26-28]

The effects of cooperativity in the interaction could be estimated from various parameters such as structural changes undergone by complexing and the shifts in some vibrational frequencies. The more direct evaluation of the contributions of cooperativity in this paper is obtained by comparing the interaction energy of the complex with the pairwise interaction energies calculated with the whole basis sets for the complex in order to exclude BSSE.[1,2,16] Thus, for trimer the cooperativity contribution is,

$$E_{\text{nopair}} = \Delta E_{\text{ABC}}(\text{ABC}) - \Delta E_{\text{AB}}(\text{ABC}) - \Delta E_{\text{AC}}(\text{ABC}) - \Delta E_{\text{BC}}(\text{ABC})$$

where terms in brackets mean that the whole basis sets for the complex are used in calculations.

For this type of study, one should choose an appropriate basis set. Usually a substantial size of basis set is required for an accurate description of the structures and energies of complexes. However, the size of the complexes studied in this work excluded the use of very large sets, and hence we employed the triple-zeta-quality 6-311G** basis set, which had been proved valid for interaction study.[29] To ensure the adequate of this basis set, we also provided the interaction energies with the 6-311+G** basis set. As shown below, the results obtained from both basis sets are quite similar except for some slight differences. Further more, the difluoroamine dimers were optimized by the full G2 method[30] for computing very accurate energies and for verifying the suitability of the basis set used.

All quantum chemical calculations were performed with the GAUSSIAN 98 suite of programs[31] at Compaq Alpha600 Workstation in our laboratory.

Results and discussion

Optimized geometries

A total of six stable structures of difluoroamine complexes, formed by two, three and four difluoroamine molecules, were obtained (Fig. 1). After stationary points were located, vibrational frequencies were calculated in order to ascertain that each structure found corresponds to a minimum on the potential energy surfaces (no imaginary frequencies for all structures in Fig. 1). There are two types of complexes: cycle-like and chain-like. The former (series a) contains only the H···F interaction, whereas the latter (series b) contains both the H···F and H···N interactions. A five or six numbered ring is formed in the dimers and in the chain complexes. A nine or twelve numbered ring is formed in cyclic trimer **3a** or tetramer **4a** respectively. The intermolecular distances decrease as the cyclic complex size increases, but this situation does not hold true for the chain complex in which only the H···N distances of the tetramer **4b** decrease slightly as compared to those of **2b**. Thus only the cyclic complexes exhibit a so-called cooperative effect, which is further convinced by discussion below. **4a** involves eight H···F contacts, all at quite shorter distances as compared to other complexes, from which it can be speculated that the intensities of interactions in **4a** may be the strongest. In general, the H···F contacts distances in cyclic complexes are close to or somewhat shorter than that of van der Waals distances, *i.e.* 0.2428 nm for H···F. Hence, there exists a weak hydrogen bonding in the cyclic complexes **3a** and **4a** judged by intermolecular distances. Although **2a**'s H(2)···F(7) distance is also *ca.* 0.24 nm, its F(7)—H(2)···N(1) angle (117.7°) is too deviated from 180° to facilitate the formation of hydrogen bonding. As can be seen from the selected optimization geometries (Table 1), the lengths of N—F bonds in **4a** increase by 0.5—0.6 pm, indicating a slightly stronger interaction in **4a**, whereas all the other bond lengths in all complexes remain nearly the same as those of monomer with exception of **2a**'s N(5)—F(7). All the bond angles are changed in the range of −1.1° to 0.6° as compared with those of monomer. Hence the molecular interaction hardly affects the geometries of the submolecules except for cyclic **4a**, in which the geometrical changes in the complexing processes are basically in the form of lengthened N—F distances.

NBO *charges and charge transfer*

Table 2 lists the NBO charges. As compared to the monomer, all hydrogen atoms in the complexes lose 0.0116—0.0309e. **4b**'s H(10), H(6) and **3b**'s H(6) lose much electron due to three interaction contacts by each atom. Fluorine atoms that contact with adjacent submolecules acquire 0.0003—0.0237e. **2a**'s F(7) acquires the most electrons instead of fluorine atoms in **4a**, though the latter contact with hydrogen atoms by the shortest distances, which is apparently owing to the electrons obtained from the hydrogen atom being shared by two fluorine atoms in **4a**. All the nitrogen atoms that contact with other submolecule acquire electrons. For complexes with similar shape, charge transfer increases as the complex becomes larger, *viz.* hydrogen atoms in **4a** lose more electrons whereas fluorine and nitrogen atoms of **4a** acquire more electrons than those of **3a**. This trend holds true for chain complex as its size enlarged. The dipole moments of the complexes are 1.1, 0.3, 0.0, 2.3, 0.0 and 1.5 D for **2a**, **2b**, **3a**, **3b**, **4a** and **4b** respectively, as compared to 2.2 D of monomer.

Mulliken populations on intermolecular bonds

To elucidate the essential of the intermolecular interactions, Table 3 lists the Mulliken populations on the intermolecular N···H and F···H contacts. The Mulliken

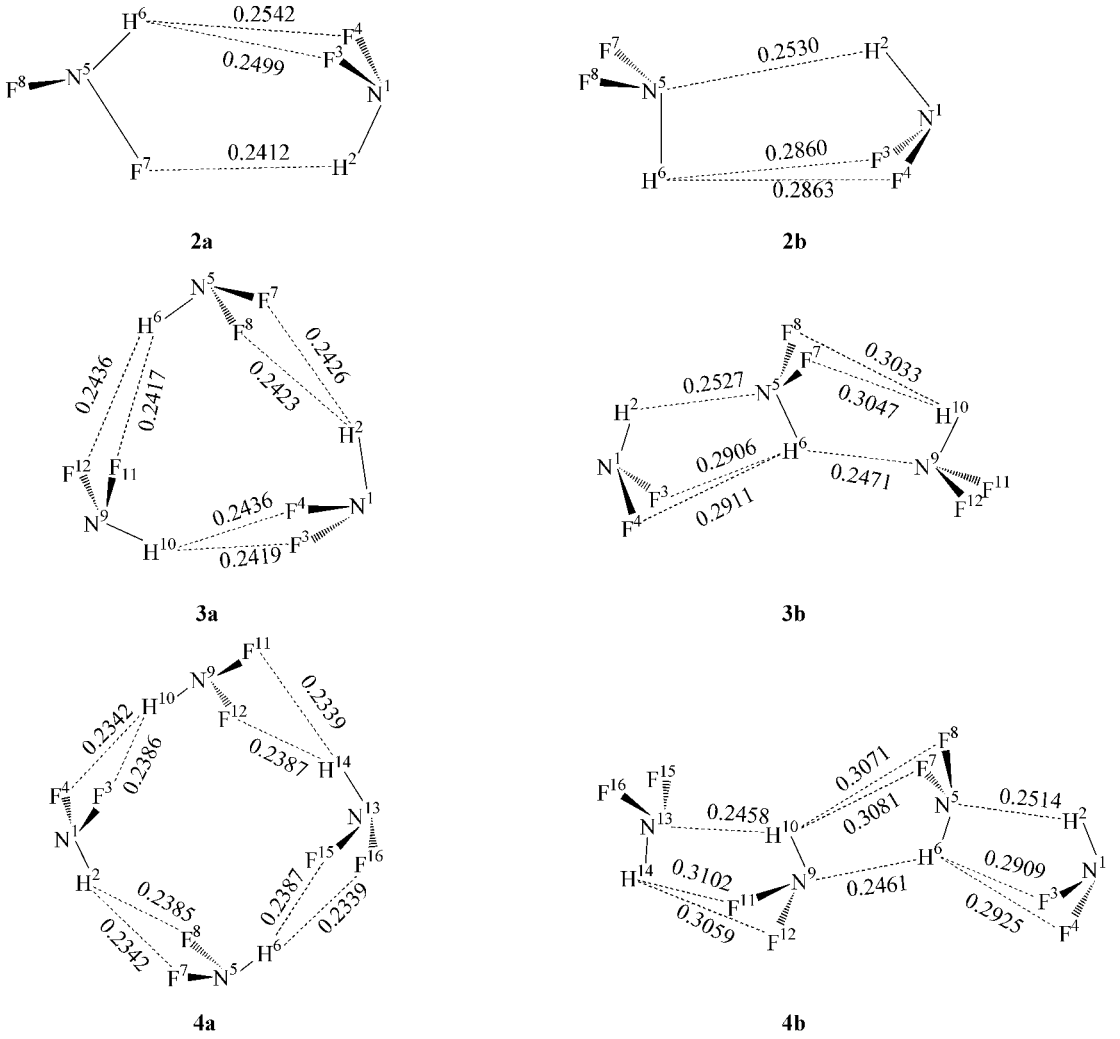

Fig. 1 Optimized structures, intermolecular distances (nm) at the HF/6-311G * * level and atomic numbering of difluoroamine complexes.

Table 1 The selected geometric parameters for difluoroamine and its complexes at the HF/6-311G * * level (bond lengths in nm, bond angles in degree) [a]

Parameters	1 [b]	2a	2b	3a	3b	4a	4b
N(1)—F(3)	0.1343	0.1346	0.1346	0.1348	0.1346	0.1348	0.1346
N(1)—H(2)	0.1004	0.1004	0.1004	0.1004	0.1004	0.1004	0.1004
N(5)—F(7)	(0.1343)	0.1352	0.1340	0.1348	0.1343	0.1349	0.1343
N(5)—H(6)	(0.1004)	0.1004	0.1004	0.1004	0.1005	0.1004	0.1005
N(9)—F(11)	(0.1343)			0.1348	0.1340	0.1349	0.1342
N(9)—H(10)	(0.1004)			0.1004	0.1004	0.1004	0.1005
N(13)—F(15)	(0.1343)					0.1348	0.1340
N(13)—H(14)	(0.1004)					0.1004	0.1004
F(3)-N(1)-F(4)	104.0	103.2	103.4	102.9	103.4	102.9	103.4
F(3)-N(1)-H(2)	102.3	102.1	101.9	102.3	101.9	102.2	101.9
F(7)-N(5)-F(8)	(104.0)	103.6	104.2	102.9	103.6	102.9	103.7
F(7)-N(5)-H(6)	(102.3)	101.9	102.9	102.3	102.4	102.4	102.4
F(11)-N(9)-F(12)	(104.0)					102.9	103.7
F(11)-N(9)-H(10)	(102.3)					102.4	102.3

[a] Values in parentheses are also the parameters of monomer. [b] Monomer.

Table 2 Natural charges of difluoroamine monomer and complexes at the HF/6-311G * * level [a]

Atom	**1** [b]	**2a**	**2b**	**3a**	**3b**	**4a**	**4b**
N(1)	0.2646	0.2719	0.2676	0.2711	0.2666	0.2716	0.2663
H(2)	0.3012	0.3165	0.3185	0.3216	0.3177	0.3257	0.3184
F(3)	−0.2829	−0.2934	−0.2925	−0.2967	−0.2917	−0.2972	−0.2917
F(4)	−0.2829	−0.2927	−0.2926	−0.2961	−0.2916	−0.3001	−0.2920
N(5)	(0.2646)	0.2700	0.2368	0.2712	0.2382	0.2716	0.2369
H(6)	(0.3012)	0.3128	0.3146	0.3216	0.3321	0.3257	0.3318
F(7)	(−0.2829)	−0.3066	−0.2762	−0.2963	−0.2856	−0.3001	−0.2848
F(8)	(−0.2829)	−0.2786	−0.2762	−0.2964	−0.2859	−0.2972	−0.2849
N(9)	(0.2646)			0.2712	0.2350	0.2716	0.2354
H(10)	(0.3012)			0.3216	0.3136	0.3257	0.3317
F(11)	(−0.2829)			−0.2968	−0.2743	−0.3002	−0.2832
F(12)	(−0.2829)			−0.2960	−0.2743	−0.2971	−0.2841
N(13)	(0.2646)					0.2716	0.2337
H(14)	(0.3012)					0.3257	0.3144
F(15)	(−0.2829)					−0.2971	−0.2739
F(16)	(−0.2829)					−0.3002	−0.2738

[a] Charges in parentheses are of monomer. [b] Monomer.

Table 3 Mulliken populations on intermolecular H···F or H···N (a.u.)

Structure	Contact	Population	Structure	Contact	Population
2a	H(6)···F(3)	0.0073	**4a**	H(2)···F(7)	0.0103
	H(6)···F(4)	0.0064		H(2)···F(8)	0.0081
	H(7)···F(2)	0.0065		H(6)···F(15)	0.0081
2b	H(6)···F(3)	0.0029		H(6)···F(16)	0.0103
	H(6)···F(4)	0.0029		H(14)···F(11)	0.0103
	H(2)···N(5)	0.0094		H(14)···F(12)	0.0081
3a	H(10)···F(3)	0.0086		H(10)···F(3)	0.0081
	H(10)···F(4)	0.0084		H(10)···F(4)	0.0103
	H(6)···F(11)	0.0086	**4b**	H(2)···N(5)	0.0092
	H(6)···F(12)	0.0084		H(6)···F(3)	0.0036
	H(2)···F(7)	0.0085		H(6)···F(4)	0.0037
	H(2)···F(8)	0.0085		H(6)···N(9)	0.0090
3b	H(10)···F(7)	0.0020		H(10)···F(7)	0.0029
	H(10)···F(8)	0.0020		H(10)···F(8)	0.0029
	H(6)···F(3)	0.0036		H(10)···N(13)	0.0092
	H(6)···F(4)	0.0036		H(14)···F(11)	0.0020
	H(6)···N(9)	0.0091		H(14)···N(12)	0.0021
	H(2)···N(5)	0.0091			

populations on intermolecular F···H increase in the sequence of **2a**, **3a** and **4a**, but approximately the same for **2b**, **3b** and **4b**. The largest population on F···H of **4a** is 0.0103 a.u., whereas all the other intermolecular populations are under or much less than this value. Associated with the intermolecular distance, it then could be predicted that there exists a weak hydrogen bond in **4a**, but the dispersion and electrostatic forces are dominant in all the other complexes.

Total energies, binding energies and cooperative effects

Table 4 gives the HF energies, MP2 energies, corrected binding energies and the contributions of cooperativity with 6-311G * * basis set. The contribution of correlation energy to the overall binding energy, $[\Delta E(\mathrm{MP2}) - \Delta E(\mathrm{HF})]/\Delta E(\mathrm{MP2})$, is at least 26.6%, indicating the necessity of including the electron correlation into the binding energy. The uncorrected HF and MP2 binding energies are both in the order: **a** > **b**. The order of the corrected binding energies for trimer and tetramer is also **a** >

Table 4 Total energies, ZPE, binding energies and cooperative energies for the $(NHF_2)_n$, $n = 1-4$, complexes (MP2/6-311G**//HF/6-311G**) and G2 binding energy for the dimers (in kJ·mol^{-1})[a]

Energy[b]	**1**[c]	**2a**	**2b**	**3a**	**3b**	**4a**	**4b**
HF	−666401.13	−1332819.61	−1332816.82	−1999243.83	−1999231.77	−2665665.83	−2665646.79
MP2	−667936.95	−1335897.55	−1335895.13	−2003867.10	−2003852.93	−2671831.39	−2671810.78
ZPE	58.77	120.69	120.58	182.34	182.05	242.82	243.55
ΔE(HF)		−17.35	−14.56	−40.44	−28.38	−61.31	−42.27
ΔE(MP2)		−23.64 (26.6)	−21.22 (31.4)	−56.25 (28.1)	−42.08 (32.6)	−83.58 (26.6)	−62.97 (32.9)
$\Delta E(HF)_C$		−9.49	−9.56	−21.59	−18.58	−36.03	−27.83
$\Delta E(MP2)_C$		−10.34	−11.91	−25.22	−23.85	−41.55	−36.14
$\Delta E(MP2)_{C,ZPE}$		−7.19	−8.87	−19.19	−18.11	−33.81	−27.67
ΔE(G2)		−7.57	−10.86				
$\Delta E(HF)_C$[d]		−9.45	−9.90	−19.76	−18.87	−33.80	−28.45
$\Delta E(MP2)_C$[d]		−11.29	−12.94	−25.12	−25.47	−41.75	−38.69
$E(MP2)_{nopair}$				−2.10	−0.45	−4.36	−0.98

[a] Data in parentheses represent $[\Delta E(MP2) - \Delta E(HF)]/\Delta E(MP2) \times 100\%$, *i.e.*, the contribution of correlation energy. [b] Binding energy with a subscript of C denotes the BSSE correction. [c] Monomer. [d] Data are from the 6-311+G** basis set.

b, but a reverse order for dimer, that is **2a** < **2b**. Since the difference of binding energy between dimers is so small that the effect of BSSE changes the actual stability sequence of dimers. The BSSE of **2a** is much greater than that of **2b**, which is apparently derived from its shorter F(7)···F(3) and F(7)···F(4) distances (*ca.* 0.29 nm) in **2a** and thus a larger basis set superposition. As a consequence, larger repulsion energy is produced. This shorter F···F distance also provides the reason why the dimer with all its four fluorine atoms contacting with hydrogen atoms is not located as a stable structure, *viz.* F(8) of **2a** does not take part in the interaction. The BSSEs are in the range of 5.00—25.28 kJ·mol^{-1} and 9.31—42.03 kJ·mol^{-1} for HF and MP2 methods respectively, indicating the necessity of BSSE correction. The BSSEs from cyclic complexes are much greater than those of chain ones for the same reason of F···F repulsion mentioned above. The MP2 method produces much larger BSSE than the HF method, partially due to its BSSE overcorrect feature.[4] The ZPE correction is also needed though it is less or much less than that of BSSE. After corrected for the BSSE and ZPE, the binding energies are −8.87, −19.19 and −33.81 kJ·mol^{-1} for the more stable dimer, trimer and tetramer respectively. Based on the changes of binding energies upon addition of a new molecule to a complex, the transition from the trimer to the tetramer involves larger stabilization than that from the dimer to trimer. Judged by the contributions of cooperativity, the cyclic complexes display a cooperative effect (it accounts as much as 10.9%—12.9% of the overall corrected binding energies), and this effect increases from trimer to tetramer. However, the cooperativity in chain complexes is negligible.

The corrected binding energies given by both HF and MP2 method with 6-311+G** basis set are generally close to those obtained with 6-311G** basis set. The use of a larger basis set has no significant influence on the binding energies, which exhibits that the 6-311G** is suitable for complexes studied here.

The discrepancies of binding energies obtained from the MP2/6-311G**//HF/6-311G** level and from the G2 level for the dimers are within 2 kJ·mol^{-1}. This demonstrates further that the 6-311G** basis set is adequate. Judged by values of binding energies at the G2 level, it could be predicted that the hydrogen bonding is so weak that the dispersion force is dominant in the dimer, which is in good agreement with the experimental fact that the boiling point of difluoroamine (−23 ℃) is only 10 ℃ higher than that of ammonia, although the molecular weight of difluoroamine is three times as larger as that of ammonia.

Thermodynamic properties

On the basis of vibrational analysis and statistical thermodynamics, the standard thermodynamic functions, heat capacities ($C_p^{\ominus}$), entropies ($S_m^{\ominus}$) and enthalpies ($H_m^{\ominus}$), were obtained and listed in Table 5. The magnitudes of $C_p^{\ominus}$ for the complexes with the same number of molecules (n) are approximately the same at each temperature, and larger than $n \times C_p$ (**1**) by 14.7—16.2, 29.4—32.4 and 45.2—49.0 J·mol^{-1}·K^{-1} for n = 2, 3 and 4, respectively. In the courses of **1**→**2**, **3** and **4**, both the ΔS_T and ΔH_T values are minus at 200.0—400.0 K. The values of ΔS_T and ΔH_T increase as temperature increases. The intermolecular interaction is therefore an exothermic process under 400.0 K accompanied by a decrease in the probability, and the interactions become weak as temperature increases. It is interesting to note that ΔS_T in transition of **1**→**3a** is much less than that in **1**→**3b** but the same trend does not appear in process of **1**→**4**. This phenomenon is caused by the fact that the cyclic trimer owns lower probability than the chain trimer, with six interaction contacts for both trimers. Both the ΔH_T and

Table 5 Thermodynamic properties of difluoroamine monomer and its complexes at different temperatures [a]

Structures	Temp. (K)	$C_p^{\ominus}$ (J·mol^{-1}·K^{-1})	$S_m^{\ominus}$ (J·mol^{-1}·K^{-1})	$H_m^{\ominus}$ (kJ·mol^{-1})	ΔS_T (J·mol^{-1}·K^{-1})	ΔH_T (kJ·mol^{-1})	ΔG_T (kJ·mol^{-1})
1 [b]	200.00	35.66	235.07	6.76			
	273.15	38.69	246.61	9.47			
	298.15	39.91	250.05	10.45			
	400.00	45.31	262.52	14.79			
2a	200.00	85.98	355.99	14.19	−114.15	−6.52	16.31
	273.15	92.99	383.80	20.73	−109.42	−5.40	24.49
	298.15	95.61	392.05	23.09	−108.05	−5.00	27.22
	400.00	106.85	421.71	33.40	−103.33	−3.37	37.96
2b	200.00	86.05	361.59	14.36	−108.55	−8.03	13.68
	273.15	92.94	389.40	20.90	−103.82	−6.91	21.45
	298.15	95.53	397.65	23.26	−102.45	−6.51	24.04
	400.00	106.70	427.27	33.55	−97.77	−4.90	34.21
3a	200.00	136.41	465.71	22.03	−239.50	−19.00	28.90
	273.15	147.24	509.79	32.40	−230.04	−16.76	46.08
	298.15	151.24	522.86	36.13	−227.29	−15.97	51.80
	400.00	168.29	569.67	52.40	−217.89	−12.72	74.44
3b	200.00	136.53	490.45	22.39	−214.76	−17.56	25.39
	273.15	147.20	534.55	32.76	−205.28	−15.32	40.75
	298.15	151.15	547.60	36.49	−202.55	−14.53	45.86
	400.00	168.05	594.37	52.74	−193.19	−11.30	65.98
4a	200.00	187.83	624.72	30.81	−315.56	−32.12	30.99
	273.15	202.16	685.33	45.07	−301.11	−28.70	53.55
	298.15	207.49	703.26	50.19	−296.94	−27.50	61.03
	400.00	230.21	767.39	72.47	−282.69	−22.58	90.50
4b	200.00	186.97	619.51	30.43	−320.77	−26.20	37.95
	273.15	201.43	679.89	44.63	−306.55	−22.84	60.89
	298.15	206.74	697.76	49.73	−302.44	−21.66	68.51
	400.00	229.37	761.65	71.93	−288.43	−16.82	98.55

[a] $\Delta S_T = (S_m^{\ominus})_i - n(S_m^{\ominus})_i$, $\Delta H_T = (H_m^{\ominus} + E_{(MP2)C} + ZPE)_i - n(H_m^{\ominus} + E_{(MP2)C} + ZPE)_i$ (i = **2**, **3**, **4** with n = 2, 3, 4 respectively), $\Delta G_T = \Delta H_T - T\Delta S_T$, and no scaling factor for frequencies is imposed. [b] Monomer.

ΔG_T imply that the stability sequences are: **2b** > **2a** and **4a** > **4b**, which are in consistent with results from the corrected binding energy. As for trimer, ΔH_T establishes the stability sequence **3a** > **3b**, but ΔG_T gives a reverse order. Since the difference of ΔH_T between two trimers is small, the effect of entropy changes the actual stability sequence.

Conclusions

(1) Our calculations predict that the difluoroamine dimer, trimer and tetramer all possess two minima that belong to two structural types: cyclic and chain. Both the structural changes and charge transfers are generally small in the complexing processes. (2) The binding energy of the cyclic complex is larger than that of chain one. Also, cyclic complexes display a cooperative effect, however this effect becomes negligible in chain complex. (3) There exist weak hydrogen bonds in the cyclic complexes. (4) The BSSE correction is needed in all cases. When the energy differences among complexes are very small, the effect of BSSE may alter the actual stability order. (5) Both the values of ΔH_T and ΔG_T establish the same stability sequence as the corrected binding energy, with the exception that ΔG_T gives a reverse order for the trimer, which is caused by the effect of entropy.

References

1 Chalasinski, G.; Szczesniak, M. M. *Chem. Rev.* **1994**, *94*, 1723.

2 Elrod, M. J.; Saykally, R. J. *Chem. Rev.* **1994**, *94*, 1975.

3 Hobza, P.; Selzle, H. L.; Schlag, E. W. *Chem. Rev.* **1994**, *94*, 1767.

4 Sauer, J.; Ugliego, P.; Garrone, E.; Saunders, V. R.

Chem. Rev. **1994**, *94*, 2095.
5 Stone, A. J. *The Theory of Intermolecular Forces*, Clarendon Press, Oxford, **1996**.
6 Li, J. S.; Xiao, H. M.; Dong, H. S. *Int. J. Quantum Chem.* **2000**, *78*, 94.
7 Li, J. S.; Xiao, H. M.; Dong, H. S. *Chin. J. Chem.* **2000**, *18*, 815.
8 Xiao, H. M.; Li, J. S.; Dong, H. S. *Acta Chim. Sinica* **2000**, *58*, 297 (in Chinese).
9 Xiao, H. M.; Li, J. S.; Dong, H. S. *J. Phys. Org. Chem.* **2001**, *14*, 644.
10 Tan, J. Z.; Xiao, H. M.; Gong, X. D.; Li, J. S. *Chin. J. Chem.* **2001**, *19*, 931.
11 Ju, X. H.; Xiao, H. M.; Gong, X. D. *Chem. J. Chin. Univ.* **2002**, *23*, 440.
12 Ju, X. H.; Xiao, H. M. *Chin. J. Chem.* **2002**, *20*, 227.
13 Ju, X. H.; Xiao, H. M. *J. Mol. Struct.* (*THEOCHEM*) **2002**, *588*, 79.
14 Ju, X. H.; Xiao, J. J.; Xiao, H. M. *J. Mol. Struct.* (*THEOCHEM*) **2003**, *626*, 231.
15 Latajka, Z.; Scheiner, S. *J. Chem. Phys.* **1988**, *122*, 413.
16 Cabaleiro-Lago, E. M.; Rios, M. A. *J. Phys. Chem. A* **1999**, *103*, 6468.
17 Peter, P.; Pat, L. *Adv. Mol. Struct. Res.* **1997**, *3*, 269.
18 Grebennikov, V. N.; Manelis, G. B.; Nazin, G. M. *Int Annu Conf ICT*, 27 th edn, **1996**, 8.1.
19 Hillebrand, C.; Klessinger, M.; Eckert-Maksic, M.; Maksic, Z. B. *J. Phys. Chem.* **1996**, *100*, 9698.
20 Fletcher, R.; Powell, M. J. D. *Comput. J.* **1963**, *6*, 163.
21 Schlegel, H. B. *J. Comput. Chem.* **1982**, *3*, 214.
22 Peng, C.; Ayala, P. Y.; Schlegel, H. B.; Frisch, M. J. *J. Comput. Chem.* **1996**, *17*, 49.
23 Binkley, J. S.; Pople, J. A. *Int. J. Quantum Chem.* **1975**, *9*, 229.
24 McDouall, J. J.; Peasley, K.; Robb, M. A. *Chem. Phys. Lett.* **1988**, *148*, 183.
25 Raghavachari, K.; Pople, J. A.; Replogle, E. S.; Head-Gordon, M. *J. Phys. Chem.* **1990**, *94*, 5579.
26 Boys, S. F.; Bernardi, F. *Mol. Phys.* **1970**, *19*, 553.
27 Johnson, A.; Kollman, P.; Rothenberg, S. *Theor. Chem. Acta* **1973**, *29*, 167.
28 Chalasinski, G.; Szczesniak, M. M. *Mol. Phys.* **1988**, *63*, 205.
29 Paizs, B.; Suhai, S. *J. Comput. Chem.* **1998**, *19*, 575.
30 Curtiss, L. A.; Raghavachari, K.; Trucks, G. W.; Pople, J. A. *J. Chem. Phys.* **1991**, *94*, 7221.
31 Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, Revision A.7, Gaussian Inc, Pittsburgh PA, **1998**.

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