

Theoretical Study of the Cyclo Addition reactions of the Weakly Bound Molecular Trimers

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ABSTRACT

Minima on the potential energy surfaces of $(C_2H_2)_3$, $(HCN)_3$ and $(FCN)_3$ have been located by various type of the DFT, ab initio and semi-empirical MO methods. With the various theoretical methods, the cyclo-addition type isomerization reaction between these weakly bound trimers and their related aromatic six-membered ring type of molecules were also studied. All of these cyclization type reactions belong to the exothermic ones in nature. By checking the calculated and the observed ΔH° and ΔG° between benzene and 3 moles of C_2H_2 , and ΔH° between 1,3,5-triazine and 3 moles HCN, it was found that DFT method with B3LYP/6-311++G(3df,2pd) type basis gives the best results. The transition states of the above mentioned reactions have been all found by the selected methods. From various computational results, it proves that all the transition states between the monomers and the aromatic molecules are exactly identical to the transition states between the related weakly bound trimers and the same aromatic molecules. By comparison the potential curves of the above mentioned reactions, it shows that $3FCN = (FCN)_3 = C_3F_3N_3$ requires the lowest activation energy and $3C_2H_2 = (C_2H_2)_3 = C_6H_6$ requires the highest activation energy.

Keywords: weakly bound complexes $(C_2H_2)_3$, $(HCN)_3$ and $(FCN)_3$ trimers, cyclo-addition reactions, B3LYP/6-311+G(2d,p), B3LYP/6-311++G(3df,2pd)

弱結合三聚體分子環化加成反應之理論研究

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摘要

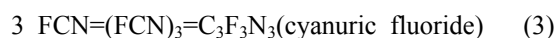
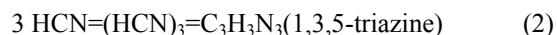
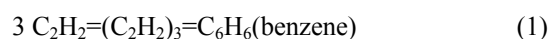
本研究以多種 DFT、ab initio 及半經驗分子軌域理論模擬獲得 $(C_2H_2)_3$ 、 $(HCN)_3$ 及 $(FCN)_3$ 等分子的穩定態極小值位能。藉由這些理論計算方法，同時探討前述弱結合三聚體(weakly bound trimer)及其相關芳香六環型分子環化加成聚合之反應機構。吾人檢視計算與實驗所獲數值，發覺 DFT 理論 B3LYP 型含 6-311++G(3df,2pd) 基底函數的方法對 3 分子 C_2H_2 聚合形成苯之 ΔH° 、 ΔG° 及 3 分子 HCN 聚合形成 1,3,5-三氮井(1,3,5-triazine)之 ΔH° 的計算結果最接近實驗值。從所有的計算結果中，均證實不論由分子單體聚合形成芳香環型分子抑或由弱結合三聚體轉變形成芳香環型分子，兩種途徑之過渡狀態相當近似。比較上述反應之位能曲線，反應由 $3FCN = (FCN)_3 = C_3F_3N_3$ 所需活化能最低，而反應由 $3C_2H_2 = (C_2H_2)_3 = C_6H_6$ 所需活化能最高。

關鍵詞: 弱結合三聚體、環化加成反應、B3LYP 型 6-311++G(3df,2pd) 基底函數

I. INTRODUCTION

To explore the structure and properties of weakly bound complexes is one of the interesting research subjects from both the spectroscopic and theoretical points of view. Within these complexes, van der Waals type of complexes are significantly weaker than the hydrogen-bonded type of complexes. In this work, we select the well known $(C_2H_2)_3$ [1,2] as well as $(HCN)_3$ and $(FCN)_3$ trimeric type of weakly bound complexes as our research targets and undergo the study by the most advanced quantum chemistry methodology.

Taking into account that trimerization leading to aromatic s-triazines (e.g. $3CICN \rightarrow C_3N_3Cl_3$) is a well-known and characteristic reaction for cyanides[3-6], it is logical to envision the cyclic aromatic trimers of HCN and FCN. It was heard from the recent well-known report which showed that ' C_2H_2 and benzene can be possibly found together in the out-space for the biological evolution, similar to the cyanides series we think that $3C_2H_2 \rightarrow C_6H_6$ reaction proceed in a special environment is quite probable. With these assumptions, three sets of reaction paths will be assumed in the following theoretical study. Since the optimized structures of the weakly bound trimers are all in the planar form with C_{3h} point group, it looks that changing the C_{3h} planar to the D_{3h} or D_{6h} planar aromatic stable molecules by the variation of their bond angles and distances is not very difficult. The cyclo addition type reactions of the related aromatic molecules as the following three reaction paths have been suggested:



The suggestion of above paths is made according to three reasons. (1) From chemical kinetics point of view the probability of three body collision of three monomers in the molecular system is very small and direct formation of aromatic molecule from monomers is very improbable. (2) The potential barrier between monomers and weakly bound trimers are very low and formation of these trimers is thermodynamically dependent. The temperature dependent effect of thermal distribution of them will be evaluated and discussed in this work. (3) From both theoretical and spectroscopic points of view the most structure and properties of these trimer-clusters have similar behaviors to a single molecule. The reactions between these trimers and their related aromatic molecules are quite similar to the uni-molecular type isomerization reaction. Under these reasons and assumptions, to find out the potential barriers of the reaction coordinates, as second part of the above mentioned paths, is the most important job and will be shown in the following sections.

II. METHODS OF CALCULATION

Several semiempirical, ab initio and density functional methods[7-21] in the Gaussian 98 program package[22], including PM3, MP2/6-31G(d,p), CBS/QB3, B3LYP/6-31G(d,p), B3LYP/6-311+G(2d,p) and B3LYP/6-311++(3df,2dp) methods were chosen to resolve the thermochemistry and chemical kinetics related theoretical problems of the above mentioned

topics. PM3 is one of the best semiempirical MO methods for thermochemical calculation whose calculated result sometimes better than the obtained ab initio ones. The Møller-Plesset second-order(MP2) procedure is a good perturbation type quantum mechanical method with considering suitable electron correlation effects. Limit to the computer memory space and it takes too much computational time in the frequencies calculation of (FCN)₃, we only select MP2/6-31G(d,p) basis set method for calculation. Recently, density functional theory (DFT) methods have gained steadily in popularity and have achieved greater accuracy than Hartree-Fock methods have done in many theoretical calculation researches. Especially, the hybrid functionals type Becke's three-parameter formulation with Lee-Yang-Parr correlation functional method (B3LYP) have proven to be superior to the traditional methods. From our former computational experience, we found that B3LYP is not only a reliable but also is a more efficient quantum mechanical method than MP2 type calculation. Since the dispersion correlation effect is very important, increasing sizes of basis set and adding the diffused type functions are particularly chosen for our project. Under this consideration three levels of basis including 6-31G(d,p), 6-311+G(2d,p) and 6-311++G(3df,2pd) were applied together for comparative study in the following sections. Among the ab initio methods, the CBS[16-21] complete basis set extrapolation-type energy calculation is one of the best newly developed effective way of quantum mechanical calculation in Gaussian 98 package. Within this composite type calculation most of the

high level electron correlation treatments such as MP4SDQ, CCSD(T), CISD etc. are included in this method. CBS-QB3[16] was thus selected for calculation in this work.

The transition state of each reaction by using synchronous transit-guided quasi-Newton (STQN) type calculation[23,24] were proceeded hereafter. An effective way of the counterpoise (CP) type correction[25] was set up to reduce the basis-set superposition error (BSSE) from the B3LYP/6-311+G(2d,p) and B3LYP/6-311++G(3df,2pd) methods in order to increase the reliability of their results for the following calculation.

In addition to quantum mechanical calculations of the related molecules and transition states, the thermal chemical and thermal distribution type calculation among various weakly bound isomers and their related monomer were also discussed in the following sections.

III.RESULTS AND DISCUSSION

A.Monomers and aromatics

First of all, both optimization and frequency types calculation of the above mentioned methods were applied to C₂H₂, HCN and FCN monomers as well as their related aromatic molecules, benzene, 1,3,5-triazine and cyanuric fluoride in order to find out the local minima and thermochemical data of them. By means of checking the reliability of the above mentioned method, ΔH° and ΔG° between each aromatic molecule and the related monomers was calculated and listed in Table 1 for comparison. In this Table, the observed values of ΔH° and ΔG° are calculated by the experimental data of the

enthalpy of formation and Gibbs free energy of formation of the related aromatic and monomer[26-28]. Unfortunately, due to run out of computational memory space of our computer, the CBS/QB3 calculations of (FCN)₃ and C₃N₃F₃ could not be completed in this work. The error was calculated by the observed value minus the calculated value and then divided by the observed value to obtain the absolute value of the error (ARE%). Looking through the results of Table 1, it is easily found that result of B3LYP/6-311++G(3df,2pd) is the best one which calculated values are very closed to the related observed values. All the calculated ARE are less than or closed to 1%. B3LYP/6-311+(2d,p) is the second best method with ARE around 1%. The semiempirical type PM3 method is an underestimated calculation. Both MP2/6-31G(d,p) and B3LYP/6-31G(d,p) are overestimated calculations. In the cases of CBS/QB3 calculation as shown in Table 1, only the result of ΔH° of 3C₂H₂ = C₆H₆ is good, but both the results of ΔH° of 3HCN = C₃N₃H₃ and ΔG° of 3C₂H₂ = C₆H₆ are not as good as we expect. For the reasons of these unsuccessful results and the incomplete

calculation of (FCN)₃ and C₃N₃F₃ as we mentioned in this work, we ignore the most parts of CBS type computation and interpretation in the following thermodynamics and kinetics study.

B. Weakly bound trimers

Local minima, vibration frequencies and thermochemical properties of the weakly bound complex trimers including (C₂H₂)₃, (HCN)₃ and (FCN)₃ were successfully calculated by above mentioned methods. All the structures of these trimers are in the planar type with C_{3h} point group as shown in Figs. 1 to 3. Vibration frequencies of them are real positive for all the cases. The calculated harmonic frequencies of them and their related monomers by B3LYP/6-311++G(3df,2pd) were particularly listed in Table 2 for comparison. After compare the strongest IR active CH stretching frequencies of C₂H₂ and (C₂H₂)₃, and their frequency shift, 3288.8-3265.5=23.3 cm⁻¹, we may clearly find out that these calculated frequencies and their difference are very closed to the former experimental result of Prichard et al.[2]. As shown in Table 2 the inter-monomer type of frequencies of these

Table1. ΔH° and ΔG° between the Aromatics and Their Related Monomers (in kJ/mol) at 25°C.

Items Reaction	Energy	Obs.	PM3	MP2/ 6-31G(d,p)	B3LYP /6-31G(d,p)	B3LYP/ 6-311+ G(2d,p)	B3LYP/ 6-311++ G(3df,2pd)	CBS-QB3
3(C ₂ H ₂) →C ₆ H ₆	^b ΔH°	-597.26 ^a	-512.59	-644.258	-672.635	-605.503	-601.834	-601.20
	ARE%	—	-14.18%	7.87%	12.62%	1.38%	0.77%	0.66%
	^b ΔG°	-497.88 ^a	-416.45	-539.31	-570.14	-504.45	-503.08	-547.46
	ARE%	—	-16.36%	8.32%	14.51%	1.32%	1.04%	9.96%
3HCN →C ₃ H ₃ N ₃	^b ΔH°	-179.90 ^c	-104.93	-162.11	-233.55	-180.34	-181.76	-137.35
	ARE%	—	-41.67%	-9.89%	29.82%	0.24%	1.03%	-23.65%
	^b ΔG°	—	-203.11	-31.65	-122.05	-78.99	-82.09	-95.49
3FCN →C ₃ F ₃ N ₃	^b ΔH°	—	-425.03	-423.42	-506.93	-476.33	-473.65	—
	^b ΔG°	—	-324.52	-319.28	-402.09	-373.65	-371.06	—

^a Observed values selected from Ref.'s 26 and 28.

^b Except PM3 and CBS-QB3 methods, all include BSSE correction energy.

^c Observed value selected from Ref.'s 17 and 18.

three trimers are the weak skeletal type of motions. All of these frequencies are less than 140 cm^{-1} . The intra-monomer bending type frequencies of the trimers are all larger than the related frequencies of their monomers. This result indicates that the cluster complex formation usually constructing a more rigid skeletal framework for the trimer than the rigidity of its original monomer. However, the intra-monomer stretching type frequencies of the different trimers are quite different. Without hydrogen atom or hydrogen bonding in the pure van der Waals type of $(\text{FCN})_3$, the intra-monomer type frequencies are all larger than the related frequencies of FCN molecules. On the other hand, all the intra-monomer

stretching type frequencies of $(\text{C}_2\text{H}_2)_3$ and $(\text{HCN})_3$ are smaller than the frequencies of their related monomers. Especially, this interesting frequency shift is prominently happened in the cases of the strongest IR active CH stretching motions. In the $3\text{HCN} = (\text{HCN})_3$ case, this shift is $3316.7-3281.1=35.6\text{ cm}^{-1}$ which is significantly larger than 23.3 cm^{-1} shift of the $3\text{C}_2\text{H}_2=(\text{C}_2\text{H}_2)_3$ complex formation case as mentioned above. From the geometric structure point of view, the inter-monomers N-H distance is over 2.5 \AA for $(\text{HCN})_3$ and the inter-monomers C-H distance is over 3.0 \AA for $(\text{C}_2\text{H}_2)_3$ which are not the significant hydrogen bonded type of clusters in nature. However, from the frequency shift point

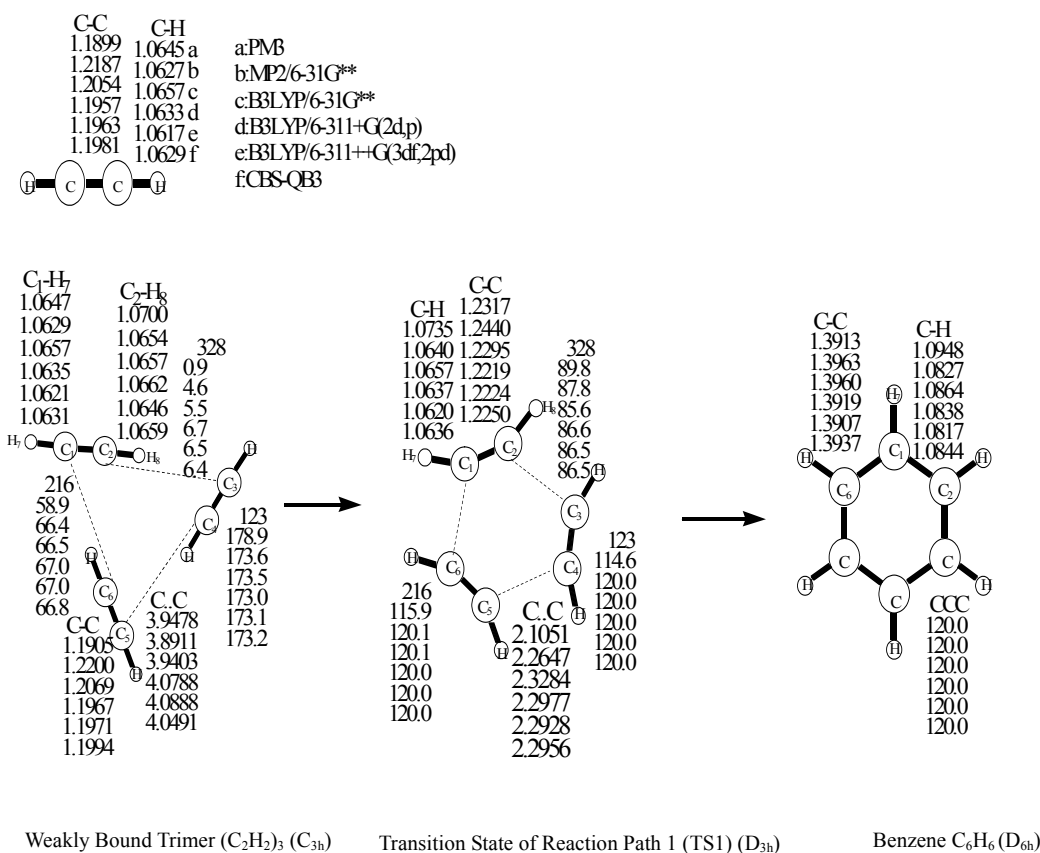


Fig.1. The optimized structures of the reaction path 1 (bond distance in \AA ;bond angle in degree).

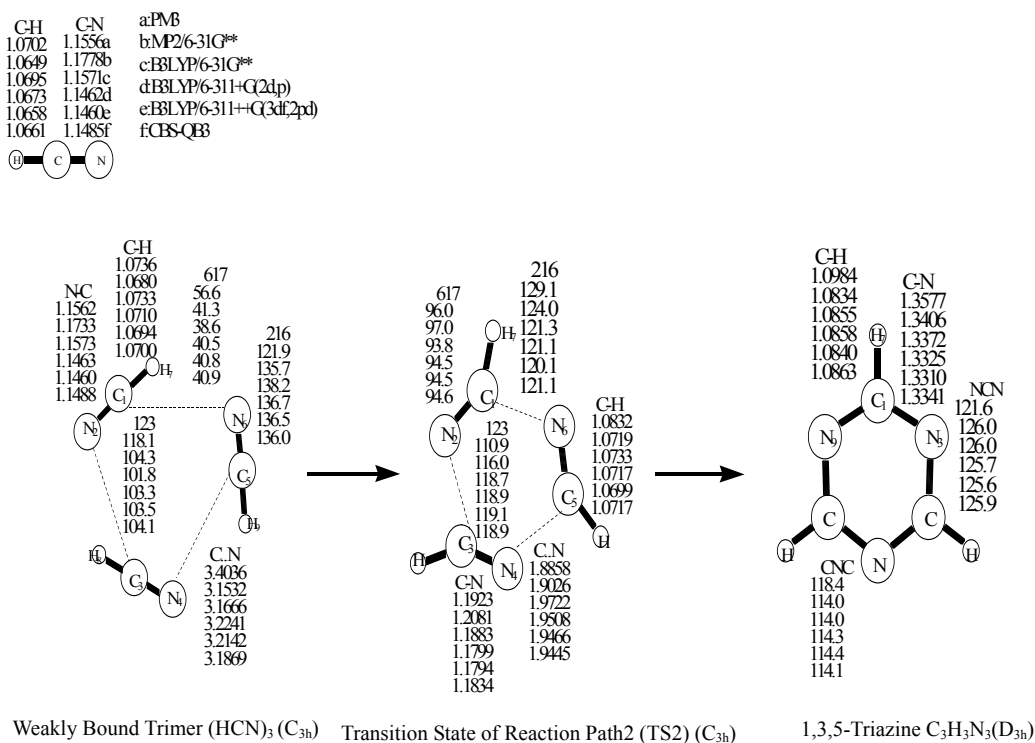


Fig.2. The optimized structures of the reaction path 2 (bond distance in Å ;bond angle in degree).

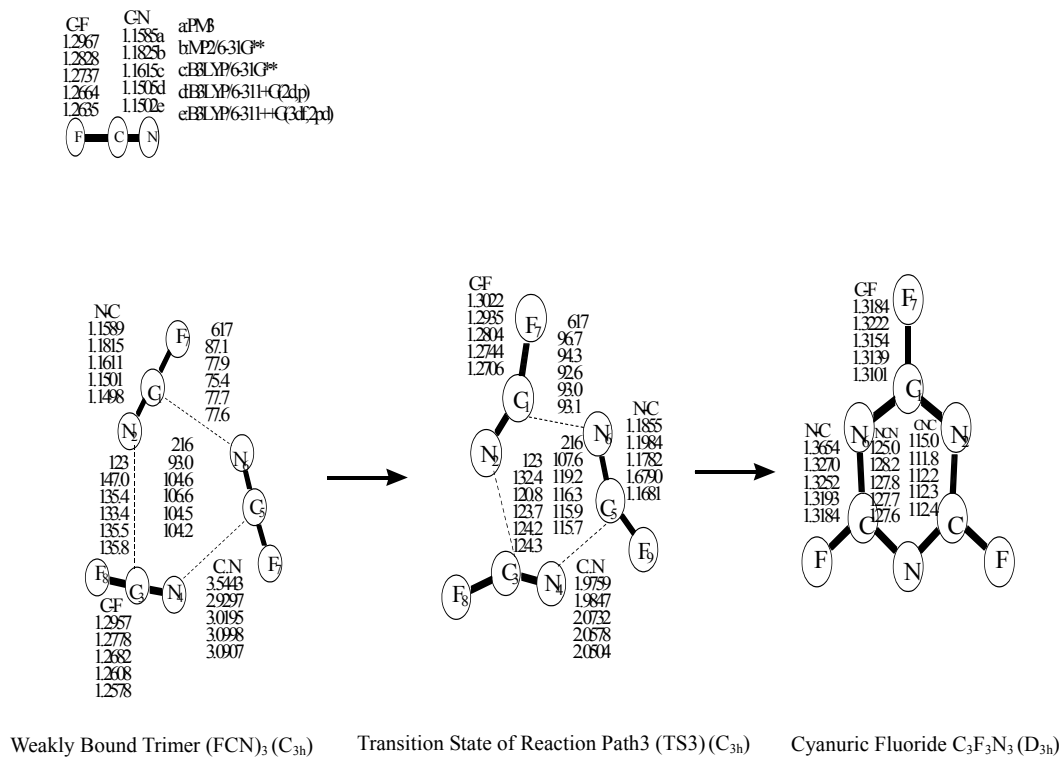


Fig. 3. The optimized structures of the reaction path 3 (bond distance in Å ;bond angle in degree).

Table2. Calculated Harmonic frequencies(in cm^{-1}) of trimers and monomers at the B3LYP/6-311++G(3df,2pd) level.

Bonding type	Monomer C_2H_2	Trimer $(\text{C}_2\text{H}_2)_3$	Monomer HCN	Trimer $(\text{HCN})_3$	Monomer FCN	Trimer $(\text{FCN})_3$
Inter- monomer Type frequencies		E' 43.4(2)		E' 52.6(2)		E'' 23.6(2)
		E'' 51.4(2)		E'' 77.2(2)		A'' 36.9
		A'' 61.0		A' 98.4		E' 54.6(2)
		A' 62.5		E' 117.8(2)		A' 68.1
		E' 78.1(2)		A'' 130.6		E' 70.6(2)
		A' 127.5		A' 133.8		A' 86.7
Intra- monomer bending type frequencies	Π_g 628.1(2)	A'' 639.5	Π 727.6(2)	E' 746.8(2)	Π 473.9(2)	E' 477.3(2)
		E'' 639.5(2)		A' 749.3		A' 477.6
		E' 649.0(2)		E'' 774.0(2)		E'' 484.3(2)
		A' 658.3		A'' 778.3		A'' 486.0
	Π_u 734.6(2)	E'' 746.6(2)				
		E' 759.5(2)				
		A'' 760.4				
		A' 769.6				
Intra- monomer stretching type frequencies	Σ_g 1991.3	A' 1983.1	Σ 2120.2	E' 2118.7(2)	Σ 1055.9	A' 1069.7
		E' 1986.1(2)		A' 2120.1		E' 1071.9(2)
	Σ_u 3288.8 (s)	A' 3263.6	Σ 3316.7 (s)	A' 3276.4	Σ 2321.9 (s)	E' 2327.6(2) (s)
		E' 3265.5(2)(s)		E' 3281.1(2) (s)		A' 2329.2
	Σ_g 3384.5	A' 3367.1				
		E' 3368.2(2)				

Scale factor = 0.9638 which calibrated by the most strong IR active stretching frequencies of C_2H_2 and $(\text{C}_2\text{H}_2)_3$
 (s) means the most strong IR active stretching frequencies.

of view, the trace amount of hydrogen bonding effect in $(\text{HCN})_3$ and $(\text{C}_2\text{H}_2)_3$ can not be ignored. The similar type of frequency red shift problem has been shown in several of our recent works which related to the intra-molecular hydrogen bonding problems[29-31].

C. Trimerization reaction

Since the binding energies of these weakly bound trimers are small and the geometrical structure of the monomer parts inside the trimers as shown in Fig.1 are quite similar to the related structure of the original monomers. It is very difficult to find out the transition state of the trimerization reactions. Without any significant height of the potential energy barrier, the yield of

this kind of reaction may be assumed to be the purely thermodynamics dependent in nature. Under room temperature (25°C) ΔH° and ΔG° were calculated and listed in Table 3. In this Table, although $\Delta H^\circ < 0$ which means this type of reaction is exothermic in nature, but all ΔG° are the large positive value due to the entropy effect. With this large ΔG° the probability of finding trimers under this condition is very small. Under the concept of thermochemistry, there are two ways to increase the yield of trimers. According to Le Chatelier principle either lowering temperature or increasing pressure of the reaction system will increase the yield. By means demonstrate this thermodynamics effect, we taking the $3 \text{C}_2\text{H}_2 = (\text{C}_2\text{H}_2)_3$ reaction as an example to show its temperature dependent effect by

Table 3. ΔH° and ΔG° (in kJ/mol) between the Weakly Bound Trimers and Their Related Monomers at 25°C.

Reaction	Items	Energy	PM3	MP2/ 6-31G(d,p)	B3LYP/ 6-31G(d,p)	B3LYP/ 6-311+G (2d,p)	B3LYP /6-311++G (3df,2pd)	CBS-QB3
$3\text{CH}\equiv\text{CH}\rightarrow(\text{CH}\equiv\text{CH})_3$	ΔH°	-4.68	-17.37	-14.01	-3.99	-3.90	-12.93	
	ΔG°	41.49	34.87	35.88	40.57	40.18	32.23	
$3\text{HCN}\rightarrow(\text{HCN})_3$	ΔH°	-10.98	-39.29	-36.07	-28.87	-28.66	-38.65	
	ΔG°	30.25	19.03	23.55	28.47	28.78	16.92	
$3\text{FCN}\rightarrow(\text{FCN})_3$	ΔH°	-3.27	-31.48	-23.07	-15.05	-15.88	—	
	ΔG°	40.69	28.64	32.61	39.32	39.47	—	

1 au = 2625.5 k/mol

using B3LYP/6-311++G(3df,2pd) and B3LYP/6-311+(2d,p) as shown in Table 4. It is clearly indicated in this table that both ΔH° and ΔG° of this reaction are less than zero and the yield of $(\text{C}_2\text{H}_2)_3$ will be prominently increased whenever temperature lower than 40 K.

thermal population of the various weakly bound isomers, in addition to proceed the trimers and monomers calculation we better to select the other relative stable weakly bound isomers for comparison. With above mentioned calculation

Table 4. ΔG° , ΔH° and ΔS° of $3\text{HC}\equiv\text{CH}\rightarrow(\text{HC}\equiv\text{CH})_3$ (ΔG° , ΔH° in kJ/mol and ΔS° in J/mol K) at various temperatures.

Methods Temperature(K)	B3LYP/6-311+(2d,p)			B3LYP/6-311++(3df,2dp)		
	ΔG°	ΔH°	ΔS°	ΔG°	ΔH°	ΔS°
0	-6.3681	-6.3681	0	-6.3862	-6.3862	0
5	-6.1975	-6.6412	-87.9	-6.2182	-6.5700	-87.8
10	-5.6540	-6.9064	-125.1	-5.6747	-6.9271	-125.0
20	-4.2178	-7.3606	-157.2	-4.2333	-7.3682	-156.8
30	-2.6583	-7.5496	-162.9	-2.6055	-7.6386	-167.9
40	-0.8703	-7.7728	-172.5	-0.9042	-7.7646	-171.6
45	-0.1877	-7.6468	-165.8	-0.0378	-7.7961	-172.2
50	0.8599	-7.8043	-173.4	0.8234	-7.7988	-172.4
55	1.7289	-7.8017	-173.2	1.6793	-7.7856	-172.2
60	2.5953	-7.7807	-172.9	2.5405	-7.7699	-171.8
70	4.3177	-7.7124	-171.9	4.2523	-7.6990	-170.7
100	9.4137	-7.3606	-167.8	9.3169	-7.3367	-166.5
200	25.5790	-5.7118	-156.5	25.3377	-5.6590	-155.0
300	40.8489	-3.9605	-149.4	40.4526	-3.8658	-147.7
400	55.5097	-2.1463	-144.2	54.9586	-2.0332	-142.5
500	69.7110	-0.2665	-140.0	68.9840	-0.1349	-138.2

methods, all the related results of dimers can be easily calculated and most of them are closed to the ab initio results[32,33]. Since the relative stronger hydrogen bonding effect between the HCN molecules than the other two cases, in addition to linear dimer, there exist a set of linear type weakly bound $(\text{HCN})_n$ polymers (n from 2 to 7) which have been recently reported by Galabov et al.[34]. On the other hand, for FCN and C_2H_2 molecules, without effective hydrogen bonding and the limitation of spatial geometrical arrangement, the possibility of forming the relative stable polymer with the degree higher than three or forming the other forms of dimer or trimer is very seldom. Under this assumption, we are going to analyze the thermal population problems of the weakly bound isomers of FCN and C_2H_2 in this work only as following. The optimized local minima of $(\text{C}_2\text{H}_2)_2$ is in T shape and the local minima of $(\text{FCN})_2$ is formed with two parallel lines as shown in Fig.4. The calculated Gibbs energies of these weakly bound dimers were picked up together with the related values of monomer and trimer for the purpose of the thermal population analysis. Similar to the isomer groups thermal analysis treatment suggested by Professor Alberty[35]:

$$r_i = K_i / \sum_j K_j = \exp(-\Delta G_i^\circ / RT) / \sum_j \exp(-\Delta G_j^\circ / RT) \quad (4)$$

In Eq.(4) K_i and ΔG_i° are the equilibrium constant and Gibb's energy difference of the i th reaction within a set of parallel type of reactions, and r_i is the distribution fraction of this reaction among all the assigned reactions. In this work, for $(\text{C}_2\text{H}_2)_n$ and $(\text{FCN})_n$ with the cases of $n = 1, 2$ or 3 and to set the monomer as reference point, three

modeling reactions are assumed to be:

$$\text{Monomer} = \text{Monomer} \quad \Delta G_{\text{MM}}^\circ = G_{\text{M}}^\circ - G_{\text{M}}^\circ = 0 \quad (5a)$$

$$\text{Monomer} = (1/2)\text{Dimer} \quad \Delta G_{\text{MD}}^\circ = G_{\text{D}}^\circ / 2 - G_{\text{M}}^\circ \quad (5b)$$

$$\text{Monomer} = (1/3)\text{Trimer} \quad \Delta G_{\text{MT}}^\circ = G_{\text{T}}^\circ / 3 - G_{\text{M}}^\circ \quad (5c)$$

G_{M}° , G_{D}° and G_{T}° of the above equations are the Gibb's energies of the related monomer, dimer and trimer, which were directly picked up from the computer output of the different methods at the given temperature. According to the idea of Eq.(4), the fractions of the above reactions are the same as the fraction of the existence of related isomers under the equilibrium condition. With this assumption, the thermal distribution factors of monomer, dimer and trimer are defined to be:

$$r_{\text{M}} = 1 / [1 + \exp(-\Delta G_{\text{MD}}^\circ / RT) + \exp(-\Delta G_{\text{MT}}^\circ / RT)] \quad (6a)$$

$$r_{\text{D}} = \exp(-\Delta G_{\text{MD}}^\circ / RT) / [1 + \exp(-\Delta G_{\text{MD}}^\circ / RT) + \exp(-\Delta G_{\text{MT}}^\circ / RT)] \quad (6b)$$

$$r_{\text{T}} = \exp(-\Delta G_{\text{MT}}^\circ / RT) / [1 + \exp(-\Delta G_{\text{MD}}^\circ / RT) + \exp(-\Delta G_{\text{MT}}^\circ / RT)] \quad (6c)$$

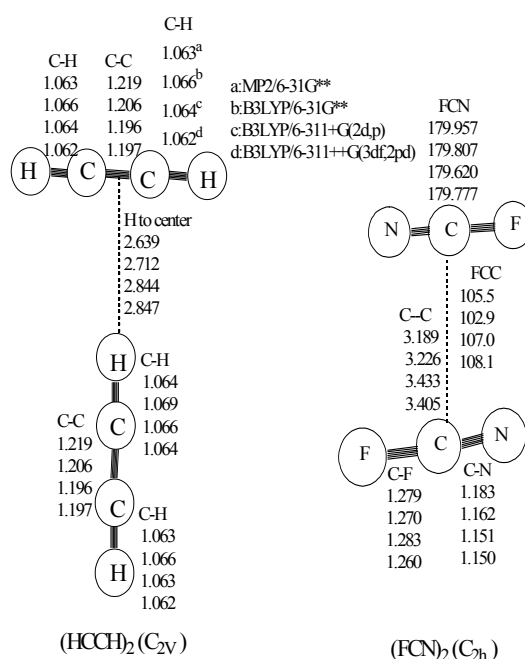


Fig.4. Optimizational Geometries of Weakly Bound Dimers (bond distance in Å; bond angle in degree)

To apply these three equations to the weakly bound isomers of C_2H_2 and FCN systems, all the thermal distribution factors at various temperatures were calculated and listed with the related Gibbs energy differences separately on Tables 5 and 6 for comparison. Plots of these thermal distribution factors of B3LYP/6-311++(3df,2dp) versus temperature are shown in Figs 5 and 6. Looking through these Tables and Figures, it is found that significant amount of $(C_2H_2)_3$ appeared when temperature is lower than 100 K, and $(FCN)_3$ is found lower than 150 K. r_T greater than r_M for $(C_2H_2)_3$ when temperature is lower than 40 K and for $(FCN)_3$ is lower than 90 K. The result of this analysis clearly tells us that $(FCN)_3$ is easier to form than $(C_2H_2)_3$ by the technique of decreasing temperature.

Table5. ΔG° 's and thermal distribution factor of various weakly bound isomers of C_2H_2 at various temperature.

Items Temperature(K)	ΔG°_{MD}	ΔG°_{MT}	r_M	r_D	r_T
5	-0.9443 ^a	-1.9149	0	0	1.0
	-0.9809 ^b	-1.9420	0	0	1.0
10	-0.8629	-1.7337	0	0	1.0
	-0.8995	-1.7608	0	0	1.0
20	-0.6226	-1.2532	0.0005	0.0220	0.9774
	-0.6632	-1.28212	0.0004	0.0236	0.9760
30	-0.3483	-0.7106	0.0448	0.1811	0.7741
	-0.4164	-0.7623	0.0363	0.1927	0.7710
40	-0.0634	-0.1435	0.2667	0.3227	0.4106
	-0.0987	-0.1663	0.2504	0.3369	0.4128
45	0.0902	0.1453	0.4058	0.3189	0.2752
	0.0667	0.0613	0.3723	0.3116	0.3161
50	0.2372	0.4323	0.5212	0.2946	0.1842
	0.1914	0.4105	0.4991	0.3150	0.1859
55	0.3816	0.7176	0.6089	0.2643	0.1268
	0.3384	0.7001	0.5905	0.2817	0.1277
60	0.5286	1.0047	0.6757	0.2342	0.0902
	0.4841	0.9889	0.6594	0.2498	0.0908
70	0.8122	1.5753	0.7608	0.1884	0.0508
	0.7729	1.5630	0.7501	0.1988	0.0511
100	1.6655	3.3423	0.8674	0.1170	0.0156
	1.6210	3.2617	0.8605	0.1225	0.0170
200	4.3291	8.6038	0.9262	0.0686	0.0052
	4.2806	8.6501	0.9245	0.0704	0.0051
300	6.8102	13.6421	0.9351	0.0610	0.0039
	6.7538	13.7401	0.9339	0.0623	0.0038
400	9.1665	18.4774	0.9369	0.0595	0.0036
	9.1037	18.6271	0.9360	0.0606	0.0035

^aResults of B3LYP/6-311++G(3df,2dp).

^bResults of B3LYP/6-311+G(2d,p)

Table6. ΔG° 's and thermal distribution factor of various weakly bound isomers of FCN at various temperature.

Items Temperature(K)	ΔG°_{MD}	ΔG°_{MT}	r_M	r_D	r_T
30	-2.1411 ^a	-4.5930	0.0000	0.0000	1.0000
	-2.1595 ^b	-4.3566	0.0000	0.0001	0.9999
50	-1.3154	-3.1691	0.0005	0.0114	0.9881
	-1.3364	-2.9493	0.0008	0.0202	0.9790
60	-0.9045	-2.4584	0.0069	0.0422	0.9509
	-0.9281	-2.2483	0.0102	0.0655	0.9243
70	-0.5002	-1.7548	0.0421	0.0994	0.8585
	-0.5212	-1.5508	0.0561	0.1375	0.8064
80	-0.0958	-1.0538	0.1422	0.1643	0.6935
	-0.1221	-0.8620	0.1708	0.2052	0.6241
90	0.3046	-0.3607	0.3044	0.2026	0.4929
	0.2770	-0.1768	0.3382	0.2335	0.4283
100	0.6984	0.3281	0.4749	0.2050	0.3201
	0.6695	0.5015	0.5015	0.2242	0.2744
110	1.0922	1.0107	0.6120	0.1854	0.2027
	1.0594	1.1736	0.6285	0.1973	0.1742
150	2.6321	3.2617	0.8373	0.1015	0.0612
	2.5901	3.8175	0.8531	0.1069	0.0400
298	8.0458	13.1545	0.9580	0.0372	0.0047
	7.9671	13.1161	0.9568	0.0384	0.0048
450	13.2890	22.3307	0.9697	0.0278	0.0025
	13.1524	22.1268	0.9686	0.0288	0.0026

^aResults of B3LYP/6-311++G(3df,2dp).

^bResults of B3LYP/6-311+G(2d,p)

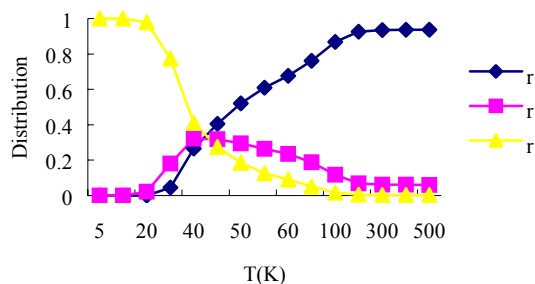


Fig5. r_M , r_D and r_T of C_2H_2 isomers predicted by B3LYP/6-311++G(3df,2dp) (see Table 5).

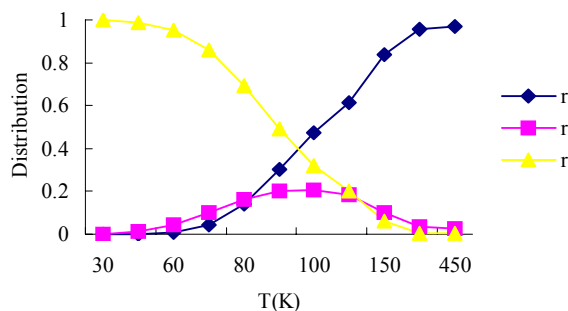


Fig6. r_M , r_D and r_T of FCN isomers predicted by B3LYP/6-311++G(3df,2dp) (see Table 6).

D. Transition state calculation

There are transition states of two types of chemical reactions that will be found and discussed in the following section. The first type of reaction is defined by the three disconnected monomers as the reactants and the related synthesized aromatic molecule as the product. The second type of reaction is the isomerization reaction between the weakly bound trimer and its related aromatic molecular product. The synchronous transit-guided quasi-Newton (STQN) type methods with QST3 option[23,24] were applied to both first and second types of reactions for each reaction path. It is very interesting that the identical transition state of the above mentioned two types reactions was reached in all the assigned paths with various levels of calculation. This result clearly tells us that no matter start with three disconnected monomers as the reactants or start with the weakly bound trimers as the reactant, the transition state of the cyclo addition reaction of an aromatic ring compound is a sole structure in each case. The transition states of the assigned three paths in the various calculation levels of this work were found to possess the C_{3h} or D_{3h} type planar structures with only one imaginary frequency in each structure without any exception. All the optimized transition states accompanied with their related structures of monomer, trimer and aromatic molecules were listed in Figs 1-3. The zero point corrected transition state energies accompanied with all the related energies were tabulated in Table 7 for the activation energy calculation. In this Table the energy differences are defined as: $\Delta E^0 = \text{energy of aromatic molecule} - 3 \times \text{energy of}$

monomers. $\Delta E^{TM} = \text{energy of trimer} - 3 \times \text{energy of monomers}$. $\Delta E^{TS1} = \text{energy of transition state} - 3 \times \text{energy of monomers}$. $\Delta E^{TS2} = \text{energy of transition state} - \text{energy of trimer}$. $\Delta E^{TSb} = \text{energy of transition state} - \text{energy of aromatic molecule}$. By means of making a simplified and clarified analysis for these activation energy calculation, we selected the result of B3LYP/6-311++G(3df,2pd) method and using the BSSE corrected energy of three monomers as the reference point to draw an energy barrier diagram on Fig.7 for our comparative study of the various reaction paths .

E. Comparison of reaction paths

Theoretically speaking the three reaction paths assigned in this work are all in the same pattern. First step is the combination of three monomers into weakly bound trimer. This step is depending on the thermodynamics conditions. Temperature and pressure are the most important dependent variables of this step. Second step of this cyclo-addition reaction is how to attain the transition state either by activation of the weakly bound trimer with variation of molecular structure or by three body collision type activation of monomers. From the geometrical point of view especially in the cases of paths 2 and 3, the trimer and transition state structures are quite similar with the same point group C_{3h} . We could do just by changing a little bit of bond angles and bond distances and lead the trimer change to the transition state. If this assumption is correct, one may predict that directly changing trimer to transition state could be easier than the three monomers type combination in this step. However, the activation energy of a reaction is one of the

most important quantities for the chemical kinetics study. Since the transition states of this work are the identical transition state for steps of both three monomers to aromatics and one trimer to the same aromatics in each path, there are two activation energies including ΔE^{TSf1} and ΔE^{TSf2} for the forward direction of reaction which were listed in Table 7 or Fig.7 for comparison.

For the various calculation levels, most of calculated order of both ΔE^{TSf1} and ΔE^{TSf2} are quite similar. In which the activation energies of path 1 are the highest and the activation energies of path 3 are lowest, except in the MP2/6-31G(d,p) level the activation energies of path 2 is a little higher than path 1. Under B3LYP/6-311+(2d,p) and B3LYP/6-311++(3df,2pd) levels,

Table 7. The BSSE-corrected optimized energies(in au) $^a\Delta E^\circ$ 、 $^b\Delta E^{\text{TM}}$ 、 $^c\Delta E^{\text{TSf1}}$ 、 $^d\Delta E^{\text{TSf2}}$ and $^e\Delta E^{\text{TSb}}$ (in kJ/mol) at 0 K.

Molecular status	Method	PM3	MP2/6-31 G(d,p)	B3LYP/6-31G(d,p)	B3LYP/6-311+ G(2d,p)	B3LYP/6-311++G (3df,2pd)	CBS QB3
Reaction Path 1	3C ₂ H ₂	0.3260130	-231.166580	-231.908530	-231.993853	-232.006440	-231.562677
	(C ₂ H ₂) ₃	0.3234930	-231.173489	-231.914410	-231.995855	-232.008329	-231.568480
	TS.1	0.4252770	-231.090950	-231.838183	-231.914746	-231.926511	-231.485635
	C ₆ H ₆	0.1359970	-231.404186	-232.157585	-232.217346	-232.229243	-231.790667
	ΔE°	-498.89	-623.83	-653.89	-586.77	-584.97	-598.59
	ΔE^{TM}	-6.61	-18.14	-15.43	-5.26	-4.96	-15.24
	ΔE^{TSf1}	260.62	198.57	184.70	207.70	209.85	202.27
	ΔE^{TSf2}	267.23	216.71	200.13	212.95	214.81	217.51
	ΔE^{TSb}	759.49	882.40	838.59	794.48	794.82	800.86
	Reaction Path 2	3HCN	0.207030	-279.450534	-280.224342	-280.320207	-280.333166
(HCN) ₃		0.2015940	-279.465811	-280.238317	-280.331322	-280.344134	-279.87794
TS.2		0.281276	-279.366634	-280.163576	-280.250756	-280.263173	-279.791043
C ₃ H ₃ N ₃		0.134733	-279.495185	-280.303306	-280.382449	-280.395872	-279.924557
ΔE°		-189.82	-117.23	-207.32	-163.42	-164.63	-161.99
ΔE^{TM}		-14.28	-40.11	-36.69	-29.18	-28.80	-39.59
ΔE^{TSf1}		194.93	220.28	159.54	182.34	183.77	188.56
ΔE^{TSf2}		209.21	260.39	196.23	211.53	212.56	228.15
ΔE^{TSb}		384.75	337.51	366.86	345.76	348.40	350.54
Reaction Path 3		3FCN	0.062868	-576.423435	-577.862571	-578.070098	-578.096548
	(FCN) ₃	0.060000	-576.436341	-577.872494	-578.076925	-578.103634	
	TS.3	0.105647	-576.382808	-577.836472	-578.036863	-578.062926	
	C ₃ F ₃ N ₃	-0.095120	-576.580058	-578.051219	-578.246989	-578.272424	
	ΔE°	-414.80	-411.21	-495.30	-464.43	-461.76	
	ΔE^{TM}	-7.53	-33.88	-26.06	-17.92	-18.60	
	ΔE^{TSf1}	112.32	106.67	68.52	87.26	88.24	
	ΔE^{TSf2}	119.85	140.55	94.58	105.18	106.88	
	ΔE^{TSb}	527.11	517.88	563.82	551.69	550.04	
	ΔE^{TSb}	527.11	517.88	563.82	551.69	550.04	

$^a\Delta E^\circ = \Delta H^\circ = \Delta U^\circ = \Delta G^\circ$ is the energy difference between aromatic molecule and related 3 monomers.

$^b\Delta E^{\text{TM}}$ is energy difference between trimer and 3 monomers.

$^c\Delta E^{\text{TSf1}}$ is activation energy of forward direction between transition state and 3 monomers.

$^d\Delta E^{\text{TSf2}}$ is activation energy of forward direction between transition state and trimer.

$^e\Delta E^{\text{TSb}}$ is activation energy of backward direction. 1 au = 2625.5 kJ/mol.

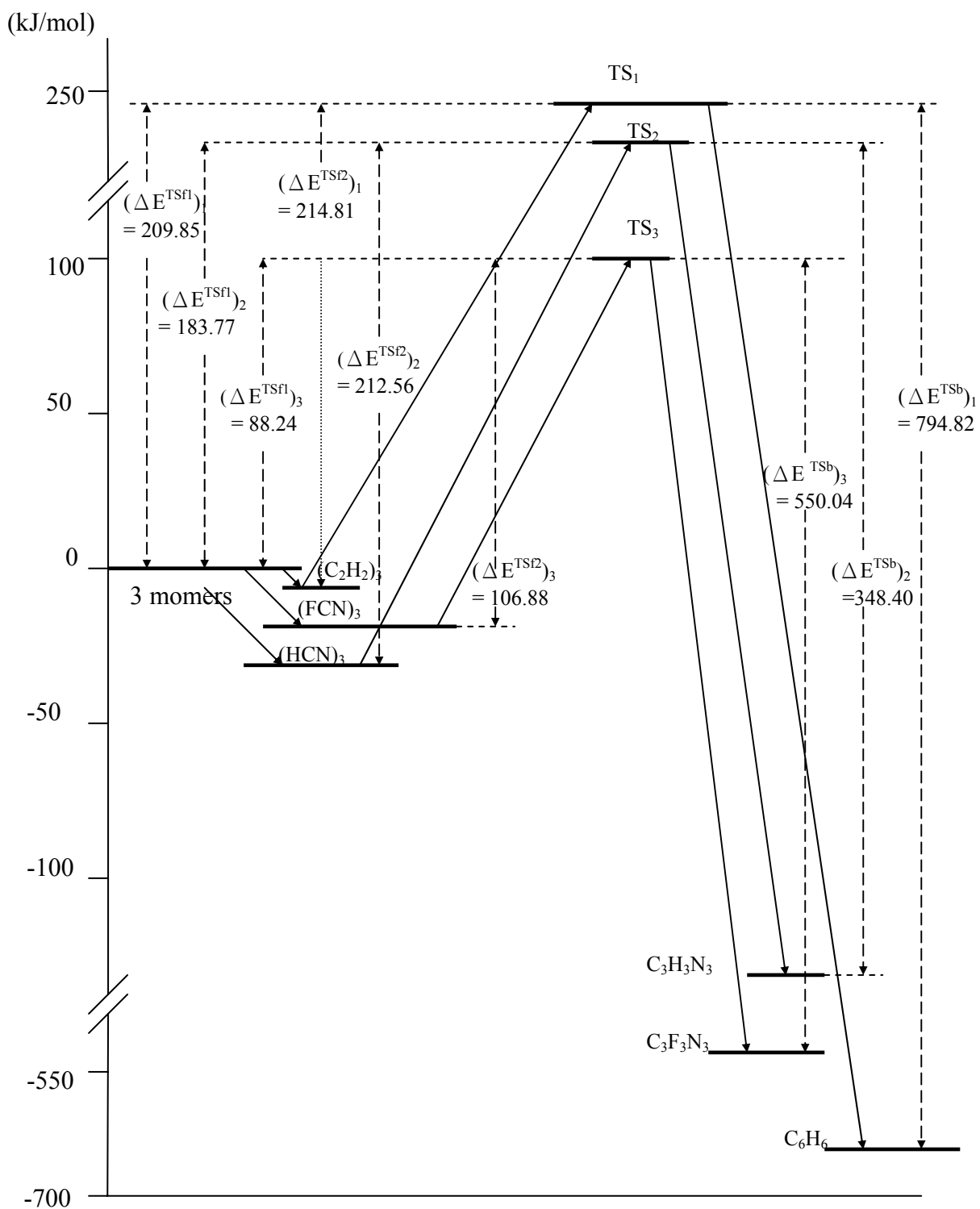


Fig. 7. Energy barriers of reaction paths at B3LYP/6-311++G(3df,2dp) level. (see Table 7)

both $(\Delta E^{\text{TSf1}})_1 > (\Delta E^{\text{TSf1}})_2 > (\Delta E^{\text{TSf1}})_3$ and $(\Delta E^{\text{TSf2}})_1 > (\Delta E^{\text{TSf2}})_2 > (\Delta E^{\text{TSf2}})_3$ are in the same pattern with no exception. According to lowest activation energies, closely similarity structures between trimer and transition state and $(\text{FCN})_3$ is easier prepared than $(\text{C}_2\text{H}_2)_3$ by lowering temperature, one may undoubtedly believe that the cyclo-addition of $\text{C}_3\text{F}_3\text{N}_3$ is the easiest case among the cyclo-addition of various aromatic molecules in this work. All the ΔE^{TSb} shown in Table 7 and Fig.7 are large positive value for all the paths. The overall reactions of all the three reaction paths are exothermic type in nature from thermodynamics point view. Whether this type of reaction can be proceeding properly, it will depend on how to control the conditions of temperature and pressure, how to supply energy, and how to select the special type of catalyst to conquer the activation energy barrier of the related reaction path.

IV.CONCLUSION

From the result of the thermochemical calculation of the overall reactions between monomers and aromatic molecule and the result of the frequency shift of the IR active CH stretching band of weakly bound complex $(\text{C}_2\text{H}_2)_3$, most of the evidences indicate that B3LYP type density function method with triple zeta and diffuse functions type basis levels, 6-311+G(2d,p) and 6-311++G(3df,2pd) are quantitatively reliable methods. The results of B3LYP/6-311++G(3df,2pd) are significantly better than the results of B3LYP/6-311+G(2d,p) which indicate that adding diffuse functions to hydrogen can not be ignored. The results of MP2/6-31G(d,p), B3LPY/6-31G(d,p)

and the semiempirical type PM3 were also successfully obtained. But these results without high accuracy only supply their qualitative or semi-quantitative support shown in the related Table's and Fig.'s. Including the high levels electron correlation effect, CBS/QB3 is a effective quantum mechanical method[16] in Gaussian 98 package. In the case of ΔH° calculation of $3 \text{C}_2\text{H}_2 = \text{C}_6\text{H}_6$, it got the excellent result. Unfortunately, while in the cases of $(\text{FCN})_3$ and $\text{C}_3\text{H}_3\text{F}_3$ treatment, it happened to meet computational trouble of insufficient computer memory space.

With various calculation levels, the three assigned weakly bound complexes, $(\text{C}_2\text{H}_2)_3$, $(\text{HCN})_3$ and $(\text{FCN})_3$ are all proved to be the stable local minima with all positive real vibration frequencies. With B3LYP/6-311++G(3df,2pd) level calculation, the calculated frequency red shift of strong CH stretching of $(\text{C}_2\text{H}_2)_3$ is very close to the observed value of Ref.2, and the calculated value of this type frequency red shift for $(\text{HCN})_3$ is 35.6 cm^{-1} which is larger than the related value of $(\text{C}_2\text{H}_2)_3$. Both of this type of frequency shift in $(\text{HCN})_3$ and $(\text{C}_2\text{H}_2)_3$ indicate that the complex formation of these two trimers more or less closely related to hydrogen bonding effect. In the pure van der Waals type $(\text{FCN})_3$ case, all the intra-monomers type frequencies are larger than the related frequencies of FCN monomer which is quite different from the frequency shift effect of the other two weakly bound trimers. Since these trimers are weakly bonded with van der Waals force or weak hydrogen bonding, and the local intra-monomer structures of these trimers are very closed to their related monomer structures, the

energy of combination of this monomers (ΔE^{TM}) are very small. Therefore, activation energy of this combination step is negligible. Under this assumption, this combination step may be assumed to be depending on the thermodynamics conditions only. To decreasing temperature and increasing pressure are the better conditions for this combination process. The thermal distribution analysis of $(C_2H_2)_3$ and $(FCN)_3$ in this work for various temperature is the sound evidence to show this effect.

Within the transition state seeking procedure, we found an interesting result that is one unique transition state for each reaction path. The transition state between three monomers and aromatic product is identical to the transition state between the related weakly bound trimer and the same aromatic product. To attain this unique transition state may either by three body collision and conquer the activation energy ΔE^{TSf1} , or by simple uni-molecular type geometrical variation and conquer the activation energy ΔE^{TSf2} . Although ΔE^{TSf2} is a little higher than ΔE^{TSf1} , but from statistical point of view the probability of three body collision is less significant than the simple geometrical variation. Under this assumption, the cyclo-addition reaction path of this work may be suggested as: 3 Monomers \rightarrow Trimer \rightarrow Transition State \rightarrow Aromatic Product. With this suggestion, the reaction path is favored or not is not only depending on its activation energy but also depending on the geometrical similarity between the weakly bound trimer and its related structure of transition state. In the case 3 FCN = $(FCN)_3 = C_3F_3N_3$ of path 3, with the electron withdrawing effect of F atom (ΔE^{TSf2})₃, is the lowest

activation energy among the ΔE^{TSf2} 's of the three paths and structures of trimer and transition state are quite similar as shown in Fig.3. The temperature effect of path 3 is also more favored than such effect of path 1 according to the thermal analysis. With all the activation energy thermal distribution and geometrical effects, it may be clearly predicted that the cyclo-addition reaction of three FCN in path 3 is the easiest and most favored path among the three paths suggested in this work. In these reaction paths their ΔE^{TSf2} 's are all greater than the related energy differences of $-\Delta E^{TM}$, it seems that all these reactions are very difficult to be activated. However, if one control the reaction environment to suitable thermodynamics conditions for the purpose of weakly bound trimer preservation, and select the non-thermal type energy source for the initial step of activation procedure, this problem may not very difficult to be conquered for such exothermic type of reactions.

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