

Density Functional Theory Studies on Intermolecular Interactions of 4-Amino-3,5-dinitropyrazole with NH₃ and H₂O

Guo-Zheng Zhao and Ming Lu*

School of Chemical Engineering, Nanjing University of Science & Technology, Nanjing 210094, P. R. China

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Density functional theory (DFT) method with 6-311++G** basis set was applied to study intermolecular interactions of 4-amino-3,5-dinitropyrazole (LLM-116)/NH₃ and LLM-116/H₂O supermolecules. Four optimized stable supermolecules were found on the potential energy surface. The intermolecular interaction energy was calculated with basis set superposition error (BSSE) correction and zero point energy (ZPE) correction. The greatest corrected intermolecular interaction energies of LLM-116/NH₃ and LLM-116/H₂O supermolecules are -42.75 and -19.09 kJ·mol⁻¹ respectively, indicating that the intensity of interaction between LLM-116 and NH₃ is stronger than that of LLM-116/H₂O. The intermolecular interaction is an exothermic process accompanied by a decrease in the probability of supermolecules formation, and the interactions become weak as temperature increase. Natural bond orbital (NBO) analysis was performed to reveal the origin of interaction. The IR spectra were obtained and assigned by vibrational analysis. Based on vibrational analysis, the changes of thermodynamic properties from LLM-116 to supermolecules with temperature ranging from 200.0 to 400.0 K were obtained using statistical thermodynamic method.

Keywords: 4-Amino-3,5-dinitropyrazole; Ammonia; Water; Intermolecular interaction; Density functional theory.

INTRODUCTION

Intermolecular interactions, such as hydrogen bonding or van der Waals interactions, become more and more important in modern research.¹⁻⁴ These interactions are becoming an active field in condensed matter physics as well as in biology or chemistry.⁵⁻⁷ The importance of intermolecular interactions in biology and chemistry has promoted chemists to explore the nature of such interactions. The strongest interactions are hydrogen-bonding interactions, which play an important role in determining molecular conformation, crystal packing and structure of biological systems. A great deal of efforts were devoted to theoretically characterize these bonds using different computational techniques.⁸⁻¹⁰ Theoretical investigations on these intermolecular hydrogen bonding interactions can provide many important facts for revealing the essence of interaction for the complexes. A sound knowledge of hydrogen bond is fundamental to understand chemical structures, material properties, self-assembly phenomena, and functions of molecular and biological devices and ma-

chines.¹¹⁻¹³ Therefore, considerable amount of theoretical researches has been conducted concerning the structural and energetic issues of diverse hydrogen bonds.

Quantum chemistry method has become a powerful tool for disclosing molecular electronic structures including intermolecular interaction and essence of hydrogen bond.¹⁴⁻¹⁷ It is generally accepted that *ab initio* HF method neglected the electronic correlation energy, thus leading to large errors during structural optimization and energy calculation. MP2 method is not a cost-effective approach for the computation of complicate complexes even with a medium-size basis set.^{18,19} Because DFT method considers electron correlation, its calculation reliability is much higher than HF method. Recently, the B3LYP method of density functional theory has been applied to large H-bonded complexes.²⁰⁻²³ It is accepted that for H-bonded complexes, the B3LYP approach yields relatively reliable structures and interaction energies.²⁴⁻²⁶ Therefore, DFT method is an ideal tool for discovering intermolecular weak interactions, which has been proved by the previous

* Corresponding author. E-mail: lumingchem@163.com

work.²⁷⁻³⁰

Research into the field of energetic materials is nowadays directed towards the synthesis and properties of compounds with high energy, high density and low sensitivity to impact and friction. As a pyrazole based compound, 4-amino-3,5-dinitropyrazole (LLM-116) was synthesized in Lawrence Livermore National Laboratory (LLNL) for the first time. It is reported that, LLM-116 exhibits a density of 1.90 g/cm³ that is the highest in the five-membered heterocyclic compounds containing nitro and amino which have been known, relatively insensitive energetic material (Dh₅₀ = 167.5 cm) with 81-90% the energy of 1,3,5,7-tetranitro-1,3,5,7-tetrazocane (HMX).³¹⁻³⁴ The energy content, power and thermal stability of LLM-116 make it very promising for several applications, including insensitive boosters, oxidizers and possibly main charges in specialty munitions. But research already done has focused mainly on its monomer.^{35,36} Water and ammonia are common solvents for the preparation of LLM-116. Solvent molecules have a great impact on the crystal structure of LLM-116, thus affect the detonation performance. The detailed structural information and characteristics of interactions among LLM-116/NH₃ and LLM-116/H₂O supermolecules could be derived by theoretical methods, which will provide theoretical guide for the relationship between structure and property of LLM-116. In this work, we study LLM-116/NH₃ and LLM-116/H₂O supermolecules using density functional theory method at B3LYP/6-311++G** and B3PW91/6-311++G** level and obtain some meaningful information that is valuable for further study of energetic materials.

COMPUTATIONAL METHODS

Computations were performed with Gaussian 03 package at B3LYP³⁷⁻³⁹ and B3PW91^{40,41} method with 6-311++G** basis set.⁴² The geometric parameters were allowed to be optimized, and no constraints were imposed on molecular structure during optimization process. All of optimized structures were characterized to be true local energy minima on potential energy surfaces without imaginary frequencies. Vibration analyses were performed at B3LYP/6-311++G** level. Based on frequencies, thermodynamic data and expected changes upon dimerizing were derived using statistical thermodynamics. The natural bond orbital analyses were performed at the same computational level.

Interaction energy of supermolecules was evaluated

from energy difference between supermolecules and LLM-116. The basis sets commonly used to calculate energies are far from being saturated. As a result, each sub-system in any complex will tend to lower its energy depending on the use of basis set functions of the other sub-system. The energies obtained at equilibrium geometry of complex for each sub-system are lower than those calculated at the same geometry with basis set functions of respective sub-system alone. This energy difference is so-called basis set superposition error that can be checked using Boys and Bernardi's counterpoise procedure (CP).⁴³⁻⁴⁵

RESULTS AND DISCUSSION

Optimized geometries

Four stable structures of LLM-116/NH₃ and LLM-116/H₂O supermolecules were obtained (Fig. 1). Table 1 lists the optimized geometric parameters. Supermolecules II-V possess the same C₁ symmetries. In supermolecules IV and V, the O atom of one nitro group and one H atom of one amino group of LLM-116 act as H-bond acceptor and donor for the water. In supermolecules II and III, the H atom of LLM-116 acts as H-bond donor for the ammonia. Some geometrical changes at B3LYP/6-311++G** level on going from LLM-116 to supermolecules are collected in Table 1. The LLM-116 and supermolecules differ in the following respects: (a) the N6-H8 length in supermolecule II have increased by 2.0 pm with respect to LLM-116; (b) the

Table 1. Fully optimized geometries of LLM-116, LLM-116/NH₃ and LLM-116/H₂O at B3LYP/6-311++G** level^a

Geometry	I	II	III	IV	V
C1-C2	0.1429	0.1437	0.1425	0.1434	0.1435
C3-N4	0.1371	0.1374	0.1372	0.1371	0.1374
N4-H5	0.1011	0.1011	0.1057	0.1011	0.1011
C1-N9	0.1438	0.1436	0.1433	0.1435	0.1437
C2-N6	0.1339	0.1333	0.1341	0.1335	0.1334
N6-H7	0.1009	0.1010	0.1008	0.1018	0.1010
N6-H8	0.1009	0.1029	0.1009	0.1010	0.1019
C3-N12	0.1405	0.1401	0.1403	0.1402	0.1401
N16-H17	(0.1015) ^b	0.1016	0.1016		
N16-H18	(0.1015) ^b	0.1016	0.1017		
N16-H19	(0.1015) ^b	0.1017	0.1016		
O16-H17	(0.0962)			0.0962	0.0962
O16-H18	(0.0962)			0.0965	0.0965

^a Bond lengths are in nm and values in parentheses are data of NH₃ and H₂O.

^b The calculated values are taken from ref. ²⁸

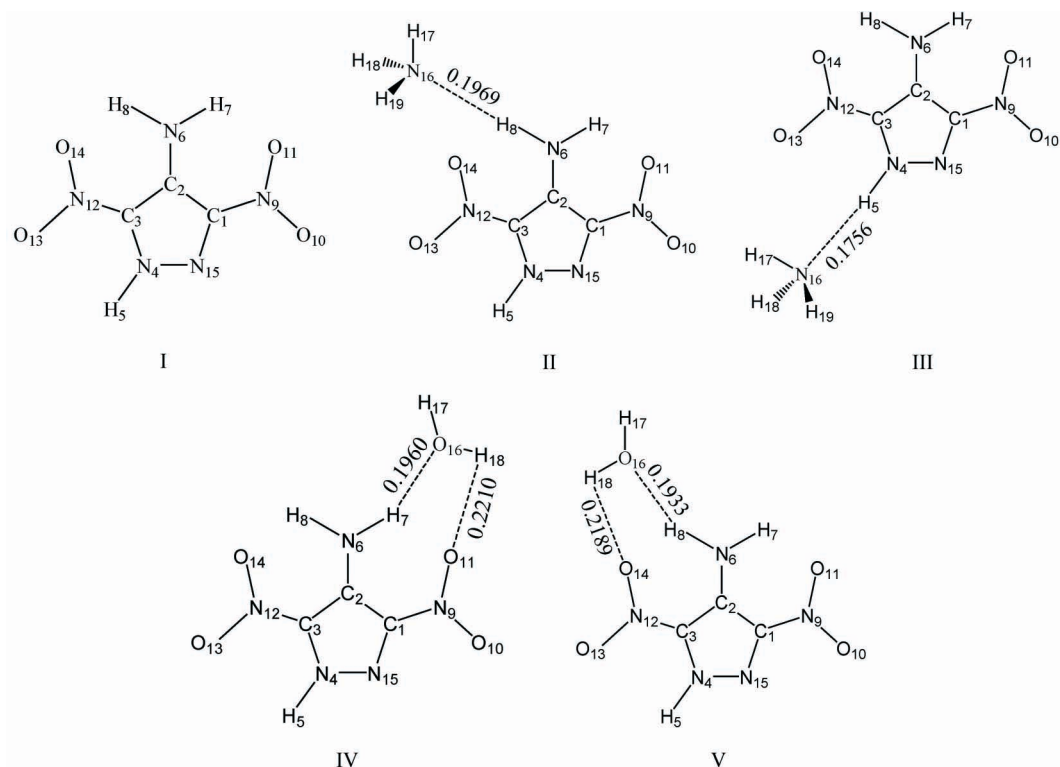


Fig. 1. Optimized geometries, atomic numbering of LLM-116, LLM-116/ NH_3 and LLM-116/ H_2O and intermolecular distance (nm) at B3LYP/6-311++G** level.

N4–H5 length in supermolecule III is 4.6 pm greater, and O16–H18 lengths in supermolecules IV and V are 0.3 pm greater; (c) the N6–H7 and C1–C2 lengths of IV are longer than that of LLM-116; (d) the C2–N6 and C3–N12 lengths of V are smaller than that of LLM-116. The influence of supermolecule interaction on bond bending or internal rotation is small, since the bond angles of all supermolecules are changed only slightly with respect to LLM-116. This also applies to the dihedral angles. The interaction energies depend not only on the hydrogen bond lengths when the intermolecular contacts are similar, but also on the damage of conjugated system and directivity of optimized structures. Therefore, it can be speculated that the intensities of interactions may be in the order of III > II > V > IV.

Interaction energies

Table 2 shows both the uncorrected and corrected interaction energies based on B3LYP/6-311++G** level. There are no imaginary frequencies for any structures in Table 2, indicating that the structures in Fig. 1 indeed represent the minima on their potential energy surfaces. It is imperative to correct both the BSSE and ZPE. Hydrogen bond

energy with high precision exhibits the same magnitude order with BSSE energy. In addition, the relative errors are often among 10%-40%. As revealed by Table 2, the BSSE correction energies of four complexes are 4.22, 4.93, 3.36 and 3.18 $\text{kJ}\cdot\text{mol}^{-1}$. The $E_{\text{BSSE}}/\Delta E_{\text{C}, \text{ZPEC}}$ can amount to a maximum of 19.40%, which also indicates the necessity of BSSE correction. The $E_{\text{ZPEC}}/\Delta E_{\text{C}, \text{ZPEC}}$ is up to a maximum of 42.51%, which is larger than that of BSSE correction. Thereby, ZPE correction is also essential at this calculation level. The corrected interaction energies for IV and V are generally similar to each other. The $\Delta E_{\text{C}, \text{ZPEC}}$ value of III is $-42.75 \text{ kJ}\cdot\text{mol}^{-1}$ at B3LYP/6-311++G**, being larger than those of other structures. From the values of interaction energies, it can be deduced that a large proportion of III might be produced in LLM-116/ NH_3 supermolecules. Ratio of IV and V is almost equal in LLM-116/ H_2O supermolecules. The corrected interaction energies indicate that the stability of supermolecules is in the order: III > II > V > IV. This order is almost consistent with proposed order based on mean intermolecular distances. Furthermore, to confirm the reliability of calculated results and access the performance of B3LYP/6-311++G**, we also choose

Table 2. Total energy, zero-point energy and interaction energy at B3LYP/6-311++G** and B3PW91/6-311++G** level (kJ·mol⁻¹)

	Energy	II	III	IV	V
B3LYP/ 6-311++G**	<i>E</i>	-1962189	-1962209	-2014368	-2014369
	ΔE	-33.11	-53.87	-28.10	-29.74
	ZPEC	7.14	6.19	7.38	7.47
	BSSE	4.22	4.93	3.36	3.18
	$\Delta E_{C,ZPEC}$	-21.75	-42.75	-17.36	-19.09
B3PW91/ 6-311++G**	<i>E</i>	-1961426	-1961449	-2013584	-2013585
	ΔE	-31.04	-53.29	-25.45	-26.15
	ZPEC	7.09	6.09	7.27	7.41
	BSSE	4.18	4.87	3.31	3.09
	$\Delta E_{C,ZPEC}$	-19.77	-42.33	-14.87	-15.65

B3PW91/6-311++G** level to study the intermolecular interactions of LLM-116 with NH₃ and H₂O. The differences of values of $\Delta E_{C,ZPEC}$ caused by using two methods are almost within 3.44 kJ·mol⁻¹, suggesting the energies are also close to the method limit. The corrected interaction energies based on B3PW91/6-311++G** level indicate that the stability of supermolecules is in the order: III > II > V > IV. This order is consistent with the order based on B3LYP/6-311++G**.

Atomic charge and charge transfer

Table 3 summarizes the changes of Mulliken charges resulting from the dimerization at B3LYP/6-311++G** level. Compared with LLM-116, atomic charges on all supermolecules change largely, and the change mainly oc-

curs on the adjacent N–H···N, N–H···O and O–H···O atoms of supermolecules between submolecules and on nitrogen/oxygen atoms located on pyrazole ring. Hydrogen atoms that act as H–bond donors, such as II's H(8), III's H(5), IV's H(7), V's H(8), lose 0.011–0.270e. Nitrogen and oxygen atoms that act as H–bond acceptors acquire 1.028–1.623e. The net result of charge transfer is that a submolecule acquires 1.843, 1.867, 1.064 and 1.052e for II, III, IV and V respectively. It can be observed that, due to complexation, hydrogen atoms involving in hydrogen bonding gain more positive charges, the nitrogen and oxygen atoms which are acting as hydrogen acceptor, gain more negative charges. One can attribute hydrogen–bonding strength to charge densities on atoms. Dipole moment is the first derivative of energy with respect to an applied electric field and is the measure of the asymmetry in molecular charge distribution. Because of asymmetrical structure of supermolecules II–V, their dipole moments increase. The dipole moments of supermolecules are 3.9922, 4.2142, 1.9457, and 3.4925 D for II, III, IV, and V, respectively, compared with 1.3429 D at LLM-116.

Table 3. The calculated natural atomic charges of LLM-116, LLM-116/NH₃ and LLM-116/H₂O supermolecules at B3LYP/6-311++G** level^a

Atom	LLM-116	II	III	IV	V
C(1)	-0.186	-10.072	-7.897	-8.962	-8.792
H(5)	0.306	0.290	0.036	0.291	0.291
N(6)	-0.665	0.553	0.616	0.605	0.586
H(7)	0.305	0.334	0.335	0.191	0.333
H(8)	0.261	0.123	0.337	0.332	0.185
N(9)	1.337	-0.063	0.037	-0.148	-0.065
O(11)	-0.657	-0.158	-0.160	-0.226	-0.162
N(12)	1.463	-0.397	-0.385	-0.221	-0.426
O(14)	-0.653	-0.134	-0.108	-0.074	-0.132
N(16)[O(16)]	-0.672(-0.502)	0.951	0.945	0.536	0.526
H(17)[H(17)]	0.224 (0.251)	0.298	0.302	0.265	0.264
H(18)[H(18)]	0.224 (0.251)	0.298	0.319	0.263	0.262
H(19)	0.224	0.296	0.301		

^a Values in parentheses are data of H₂O.

Natural bond orbital analysis

Table 4 lists the second-order perturbative estimates for “donor-acceptor” (bond–antibond) interactions in the NBO basis for all the supermolecules. It was carried out by examining all possible interactions between “filled” (donor) Lewis-type NBOs and “empty” (acceptor) non-Lewis NBOs, and estimating their stabilization energy by second-order perturbation theory.⁴⁶ In typical stable complex, the stabilization energy *E* is defined as the interaction between orbital *I* of electronic donor and orbital *j* of elec-

Table 4. Significant donor–acceptor NBO interaction in supermolecules and second-order perturbation stabilization energies E , calculated at B3LYP/6-311++G** level^a

Structure	Donor NBO (i)	Acceptor NBO (j)	$E/(\text{kJ}\cdot\text{mol}^{-1})$
II	BD(1) N(16)–H(19)	BD*(1) N(6)–H(8)	3.14
	LP (1) N16	BD*(1) N(6)–H(8)	69.00
III	BD(1) N(16)–H(19)	BD*(1) N(4)–H(5)	81.80
	LP (1) N16	BD*(1) N(4)–H(5)	1150.04
IV	BD(1) O(16)–H(18)	BD*(1) N(6)–H(7)	1.71
	LP (2) O16	BD*(1) N(6)–H(7)	38.01
V	BD(1) O(16)–H(18)	BD*(1) N(6)–H(8)	1.80
	LP (2) O16	BD*(1) N(6)–H(8)	42.22

^a BD represents bonding orbital, BD* represents antibonding orbital, LP represents lone-pair. For BD and BD*: (1) and (2) represents σ orbital and π orbital, respectively. For LP: (1) and (2) represents the first and the second lone pair electron, respectively.

tronic acceptor. The larger E indicates stronger interaction between i and j , i.e., higher electronic transfer tendency from i to j . The stabilization energies E are proportional to NBO interaction intensities. It is the intermolecular NBO interaction that reveals the origin of intermolecular interactions.

The analysis of NBO data show that supermolecule III possesses a strong hydrogen bond, and their second-order perturbation energies for interaction are in range of 19.90–1150.04 $\text{kJ}\cdot\text{mol}^{-1}$. In supermolecule II, lone pair electrons on N(16) transfer to σ^* anti-orbital of N(6)–H(8) with stabilization energy of 69.00 $\text{kJ}\cdot\text{mol}^{-1}$. In supermolecule IV, lone pair electrons on O(16) transfer to σ^* anti-orbital of N(6)–H(7) with stabilization energy of 38.01 $\text{kJ}\cdot\text{mol}^{-1}$. In supermolecule V, lone pair electrons on O(16) transmit to σ^* anti-orbital of N(6)–H(8) with stabilization energy of 42.22 $\text{kJ}\cdot\text{mol}^{-1}$. As can be seen from the intermolecular NBO interaction in Table 4, the main NBO interacting in supermolecules are that the lone pair on nitrogen (oxygen) of one submolecular acts as donor and that the N–H antibond of another submolecular as acceptor. Two lone pairs of each nitrogen (oxygen) interact with N–H antibonds in supermolecules II, III, IV and V, and the total stabilization energies of these two NBO interactions are over 35 $\text{kJ}\cdot\text{mol}^{-1}$, forming a strong hydrogen bond. These results are consistent with the above structure and energy analyses. So stabilization energy order of four supermolecules is: III > II > V > IV, which is in agreement with intermolecular interaction energy order.

Infrared spectra

The vibrational spectroscopy is one of the most useful experimental tools for the study of supermolecules, so the information on calculated harmonic vibrational frequencies can be useful. Fig. 2 provides calculated IR spectra of LLM-116/ NH_3 , LLM-116/ H_2O and LLM-116 obtained at B3LYP/6-311++G** level. Due to the complexity of vibrational modes, it is difficult to assign all bands. Therefore, only some typical vibrational modes were analyzed and discussed. On the basis of optimized geometry, vibrational modes and frequencies of the supermolecules and LLM-116 have been assigned. Since frequency shifts are relatively stable with respect to theoretical methods, one can estimate the IR spectrum for the supermolecule by combining observed fundamental vibrational frequency and frequency shift. For the isolated LLM-116 molecule, the asymmetric N6–H7 and N6–H8 stretches appear at 3702.5 cm^{-1} , the symmetric C2–N6 and C3–N12 stretches appear at 1680.0, 1347.4 cm^{-1} , and symmetric N4–H5 stretches appear at 3620.9 cm^{-1} , while the N12–O13 stretch

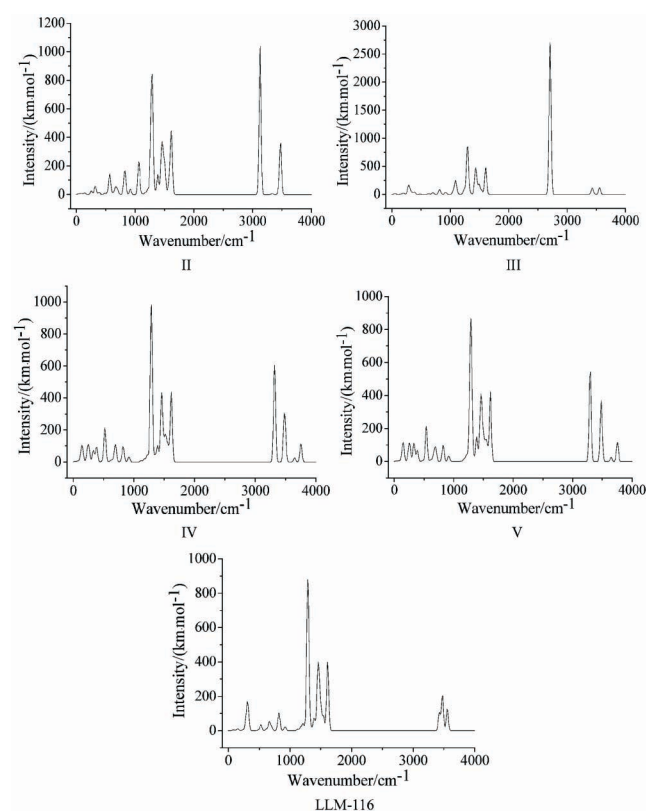


Fig. 2. Calculated infrared spectra of LLM-116/ NH_3 , LLM-116/ H_2O and LLM-116 at B3LYP/6-311++G** level.

is at 1512.7 cm^{-1} . The N6–H7 and N6–H8 stretching frequency is found to decrease for all structures considered here. From II to V, the frequency shifts are 82.55, 85.24, 62.74 and 67.23 cm^{-1} , respectively. This is in consistent with the intermolecular interaction energy order, implying that the formation of supermolecules weaken the N–H bond. It is obtained the symmetric stretching mode of C–N is red shifted during the formation of supermolecules. And with strengthen of interaction between subsystems, the frequency shifts and IR intensities tend to increase.

Thermodynamic properties

On the basis of vibrational analysis and statistical thermodynamic study, standard thermodynamic functions, heat capacities ($C_{p,m}^{\theta}$), entropies (S_m^{θ}) and enthalpies (H_m^{θ}), were obtained and listed in Table 5. The magnitudes of heat capacities for supermolecules are approximately the same at each temperature. Both entropy and enthalpy changes for LLM-116/NH₃ and LLM-116/H₂O supermolecules process are negative throughout the temperature range from 200.0 to 400.0 K. Both ΔS_T and ΔH_T increase as temperature increases. The process is therefore an exothermic process, and the interactions become weak as temperature increases. The values of (ΔH_T) for each supermolecule at the same

temperature give the same sequence $(\Delta H_T)\text{III} < (\Delta H_T)\text{II} < (\Delta H_T)\text{V} < (\Delta H_T)\text{IV}$. From equation $\Delta G_T = \Delta H_T - T\Delta S_T$, the change in Gibbs free energy (ΔG_T) in process was predicted according to ideal-gas model. The ΔG_T value increases as temperature increases for each supermolecule, thus the interactions weaken as temperature increases. The ΔG_T value gives a different stability below 400 K. The ΔG_T values of supermolecules II, IV and V are negative below 200 K. This indicates that these supermolecules can be spontaneously produced from isolated monomer below 200 K, while III can be produced at room temperature. Both ΔH_T and ΔG_T imply that stability sequence is: III > II > V > IV, which is consistent with the results from corrected bond energies.

CONCLUSIONS

In this study, we performed quantum chemical DFT calculations for the geometries and intermolecular interaction of LLM-116/NH₃ and LLM-116/H₂O supermolecules. Intermolecular hydrogen bonding, damage of conjugated system and directivity of optimized structures play an important role in the stabilization of supermolecules and lead to geometry and electronic structure change. The corrected intermolecular interaction energies were calculated and

Table 5. The thermodynamic properties of LLM-116, LLM-116/NH₃ and LLM-116/H₂O at different temperatures^{a,b}

Structure	T/K	$C_{p,m}^{\theta} /$ J·mol ⁻¹ ·K ⁻¹	$S_m^{\theta} /$ J·mol ⁻¹ ·K ⁻¹	$H_m^{\theta} /$ kJ·mol ⁻¹	$\Delta S_T /$ J·mol ⁻¹ ·K ⁻¹	$\Delta H_T /$ kJ·mol ⁻¹	$\Delta G_T /$ kJ·mol ⁻¹
LLM-116	200.0	123.83	318.90	15.23			
	298.2	164.81	376.20	29.45			
	400.0	200.25	429.76	48.10			
II	200.0	162.50	386.20	20.72	-120.54	-27.02	-2.92
	298.2	208.70	459.92	39.00	-117.84	-26.34	8.80
	400.0	249.39	527.12	62.39	-115.00	-25.35	20.65
III	200.0	163.08	387.00	20.74	-119.74	-48.70	-24.75
	298.2	208.34	460.78	39.03	-116.98	-48.01	-13.13
	400.0	248.41	527.77	62.34	-114.35	-47.10	-1.36
IV	200.0	162.91	380.04	20.42	-114.14	-23.04	-0.21
	298.2	208.39	453.86	38.72	-110.93	-22.24	10.84
	400.0	246.90	520.68	61.97	-107.62	-21.09	21.96
V	200.0	162.52	379.25	20.36	-114.93	-23.73	-0.74
	298.2	208.10	452.93	38.62	-111.86	-22.97	10.39
	400.0	246.70	519.68	61.85	-108.62	-21.84	21.61

^a $\Delta S_T = (S_T^{\theta})_i - (S_T^{\theta})_1 - (S_T^{\theta})_{ii}$, $\Delta H_T = (H_m^{\theta} + E(\text{HF}) + \text{ZPE})_i - (H_m^{\theta} + E(\text{HF}) + \text{ZPE})_1 - (H_m^{\theta} + E(\text{HF}) + \text{ZPE})_{ii}$ (I = II and III, ii = NH₃; I = IV, and V, ii = H₂O). $\Delta G_T = \Delta H_T - T\Delta S_T$.

^b The thermodynamic properties of NH₃ and H₂O are taken from ref.²⁸

corresponding interaction intensity sequence is III > II > V > IV. The results of NBO analysis indicate that intermolecular interaction in supermolecule III is stronger than those in II, IV, and V. Electrons in supermolecular systems transfer from NH₃ or H₂O to LLM-116. It was found that supermolecule III can be produced spontaneously from LLM-116 and NH₃ at room temperature, while structures IV and V can only be produced spontaneously from LLM-116 and H₂O at lower temperature.

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