

Theoretical Study on Intermolecular Interactions and Thermodynamic Properties of Nitroamine Dimers

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Ab initio self-consistent field (SCF) and Møller-Plesset correlation correction methods employing 6-31G** basis set have been applied to the optimizations of nitroamine dimers. The binding energies have been corrected for the basis set superposition error (BSSE) and the zero-point energy. Three optimized dimers have been obtained. The BSSE corrected binding energy of the most stable dimer is predicted to be -31.85 kJ/mol at the MP4/6-31G**//MP2/6-31G** level. The energy barriers of the Walden conversion for $-NH_2$ group are 19.7 kJ/mol and 18.3 kJ/mol for monomer and the most stable dimer, respectively. The molecular interaction makes the internal rotation around $N_1 - N_2$ even more difficult. The thermodynamic properties of nitroamine and its dimers at different temperatures have been calculated on the basis of vibrational analyses. The change of the Gibbs free energy for the aggregation from monomer to the most stable dimer at standard pressure and 298.2 K is predicted to be 14.05 kJ/mol.

Keywords nitroamine dimer, intermolecular interaction, *ab initio*, thermodynamic properties

Introduction

The binding energies of intermolecular interaction are much less than those of chemical bonding, and yet play significant roles in a wide range of physical, chemical and biological fields. Researches on the weak interactions began with hydrogen bonds. Scheiner summarized in details the *ab initio* investigations on hydrogen bonding.¹ On the basis of the basis set improving and the basis set superposition error (BSSE) correcting, the Møller-Plesset perturbation theory could predict super-

molecular structures and binding energies not only for H-bonded systems but also for other systems.²⁻⁷ In the recent years, we have applied the intermolecular interactions to energetic systems and obtained some meaningful information.⁸⁻¹¹

Nitroamine is the simplest model for nitramine energetic compound that is especially used as explosives. Researches already done are focused only on its monomer.¹²⁻¹⁵ The intermolecular forces control diverse phenomena such as the diffusion, the aggregation and the detonation. The aim of the present paper is to investigate theoretically the structures, the binding energies, the effect of methyl internal rotation and Walden conversion of $-NH_2$ on the interaction and the thermodynamic properties of nitroamine dimers. We also perform natural bond orbital (NBO) analyses to probe the origin of the interaction.

Computational methods

Nitroamine monomer and all its possible stable dimers obtained from Chem3D software are fully optimized at the MP2/6-31G** level by the Bery method.^{16,17} NBO analyses and frequency calculations were performed on each optimized structure. Thermodynamic properties and their changes in the aggregation are derived from thermodynamic statistics based on the frequencies. The interaction energy of complex is evaluated as the sum of the self-consistent field (SCF) interaction energy and the correlation interaction energy. On condi-

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Received April 29, 2001; revised October 8, 2001; accepted November 11, 2001.

Project supported by the National Natural Science Foundation of China (No. 20173028) and the Postdoctoral Foundation of Chinese Educational Ministry.

tion that the latter term is determined by the Møller-Plesset perturbation theory,¹⁸⁻²⁰ the interaction energy is calculated as

$$\Delta E(\text{MP}) = \Delta E^{\text{HF}} + \Delta E^{\text{MP}} \quad (1)$$

where ΔE^{HF} is the HF interaction energy, ΔE^{MP} is the correlation interaction energy given by the MP calculation. 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 complex 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 so-called BSSE which can be checked by Boys and Bernardi's counterpoise procedure (CP).²¹⁻²³ For complex of two submolecules the BSSE is

$$\begin{aligned} \text{BSSE} &= \text{BSSE}(\text{A}) + \text{BSSE}(\text{B}) \\ &= \{E(\text{A}) - E(\text{A}[\text{B}])\} + \{E(\text{B}) - E(\text{B}[\text{A}])\} \quad (2) \end{aligned}$$

where the $E(\text{A}[\text{B}])$ and $E(\text{B}[\text{A}])$ are the energies of A and B respectively when the other subsystem's basis sets are added. Then the corrected interaction energy is

$$\Delta E(\text{MP})_{\text{C}} = \Delta E_{\text{C}}^{\text{HF}} + \Delta E_{\text{C}}^{\text{MP}} = \Delta E(\text{MP}) + \text{BSSE} \quad (3)$$

All calculations are performed with Gaussian98 program²⁴ at Compaq Alpha600 Workstation in our laboratory.

Results and discussion

Optimized geometries

Three stable structures of nitroamine dimers are shown in Fig. 1. The optimized geometrical parameters at MP2/6-31G** level for monomer and three dimers are listed in Table 1. The monomer has C_s symmetry with N—NO₂ coplanar and the hydrogen atoms H₅ and H₆ out of the plane, which is in agreement with experiment.¹⁵ An eight-membered ring between two submolecules is formed in each dimer. The minimal intermolecular distances are in the order: **2**(0.2089 nm) \approx **3**(0.2046 nm) > **4**(0.1945 nm), from which it can be deduced that the magnitudes of interactions may be **2,3** < **4**. As compared with the geometry of monomer, for structure **4**, both the lengths of N₁—N₂ and the N₇—N₈ decrease by 2.4 pm, whereas those of N₁—O₄ and N₇—O₁₀ increase by 1.1 pm. The changes of bond lengths of **2** and **3** are less than those of **4**, the N₁—N₂ and N₇—N₈ bonds shorten by 1.2—1.5 pm, whereas the N₁—O₄ and N₇—O₁₀ bonds, which are in the eight-membered intermolecular rings, lengthen by 0.5—0.8 pm. The X—NO₂ (X = N, C, O) bond in nitro explosives usually refers as a detonation trigger.^{13,25} The amino group of one submolecule interacts with X—NO₂ of another submolecule to cause the shortening of the N₁—N₂ and N₇—N₈ bonds for all three dimers, especially for structure **4**. It can be speculated that the interaction may lower the sensitivity in a certain degree. The bond angles of all three dimers and the dihedral angles of **3** change slightly

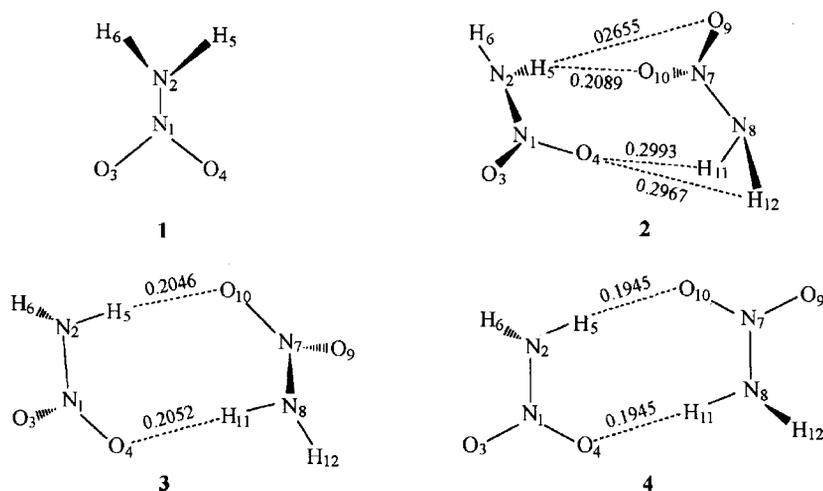


Fig. 1 Optimized structures, intermolecular distances (nm) and atomic numbering of nitroamine and its dimers

Table 1 Optimized geometries of nitroamine and its dimers at MP2/6-31G** level (bond length in nm, bond angle and dihedral angle in degree)

Parameters	1	2	3	4
R ₁₋₂	0.1400	0.1388	0.1386	0.1376
R ₁₋₃	0.1234	0.1234	0.1233	0.1233
R ₁₋₄	0.1234	0.1239	0.1242	0.1245
R ₂₋₅	0.1012	0.1017	0.1016	0.1019
R ₂₋₆	0.1012	0.1012	0.1013	0.1011
R ₇₋₈	0.1400 ^a	0.1385	0.1386	0.1376
R ₇₋₉	0.1234 ^a	0.1234	0.1233	0.1233
R ₇₋₁₀	0.1234 ^a	0.1240	0.1242	0.1245
R ₈₋₁₁	0.1012 ^a	0.1013	0.1016	0.1018
R ₈₋₁₂	0.1012 ^a	0.1013	0.1013	0.1011
θ ₂₋₁₋₃	116.08	116.80	117.34	117.35
θ ₂₋₁₋₄	116.08	116.51	116.41	116.73
θ ₁₋₂₋₅	108.13	109.30	107.96	110.92
θ ₁₋₂₋₆	108.13	107.97	107.79	109.15
θ ₅₋₂₋₆	114.37	114.68	113.77	116.98
θ ₈₋₇₋₉	116.08 ^a	117.08	117.33	117.35
θ ₈₋₇₋₁₀	116.08 ^a	116.43	116.42	116.73
θ ₇₋₈₋₁₁	108.13 ^a	107.66	107.91	110.93
θ ₇₋₈₋₁₂	108.13 ^a	107.65	107.75	109.15
θ ₁₁₋₈₋₁₂	114.37 ^a	113.57	113.65	116.98
φ ₃₋₁₋₂₋₅	153.92	152.85	-147.57	-155.24
φ ₃₋₁₋₂₋₆	29.59	27.49	-24.27	-24.93
φ ₄₋₁₋₂₋₅	-29.59	-30.95	36.31	28.81
φ ₄₋₁₋₂₋₆	-153.92	-156.32	159.61	159.11
φ ₉₋₇₋₈₋₁₁	153.92 ^a	152.42	-147.44	155.22
φ ₉₋₇₋₈₋₁₂	29.59 ^a	29.63	-24.34	24.91

^a Data are also the parameters of the monomer.

from monomer, whereas the dihedral angles of **2** and **4** alter at the range of 66° which implies that the interaction makes the Walden conversion of -NH₂ or the internal rotation around N—N bond taking place (see below).

Atomic charges and charge transfer

Table 2 lists the atomic charges. The charge redistribution mainly occurs on the adjacent O···H atoms between submolecules. Atoms O₄ and O₁₀ of the dimers acquire 0.0277—0.0690 e, whereas H₅ and H₁₁ lose 0.0117—0.0557 e, and the closer the interacting atoms between submolecules are, the more the charge transfer is. The net result of charge transfer for **2** is that a submolecule acquires 0.0167 e, whereas there are no net charge transfer for **3** and **4** due to the distances of their

Table 2 Atomic charges of nitroamine monomer and dimers

Atom	1	2	3	4
N ₁	0.6867	0.7006	0.7043	0.7094
N ₂	-0.4419	-0.4538	-0.4474	-0.4682
O ₃	-0.4572	-0.4545	-0.4429	-0.4451
O ₄	-0.4572	-0.5134	-0.5221	-0.5262
H ₅	0.3348	0.3686	0.3694	0.3905
H ₆	0.3348	0.3356	0.3383	0.3397
N ₇	0.6867 ^a	0.6882	0.7042	0.7094
N ₈	-0.4419 ^a	-0.4213	-0.4461	-0.4683
O ₉	-0.4572 ^a	-0.4586	-0.4425	-0.4451
O ₁₀	-0.4572 ^a	-0.4850	-0.5219	-0.5263
H ₁₁	0.3348 ^a	0.3465	0.3682	0.3905
H ₁₂	0.3348 ^a	0.3469	0.3384	0.3397

^a Charges are of the monomer.

two O...H being approximately the same or equal to each other. The dipole moments of the dimers, 1.95, 1.71 and 0.00 Debye for **2**, **3** and **4** respectively, are much less than the monomer's 4.20 Debye, because the dipoles in submolecules array oppositely.

Total energies and interaction energies

Table 3 gives the HF energies, MP energies, corrected interaction energies at MP4/6-31G**/MP2/6-31G** and at MP4/6-31G**/HF/6-31G* levels. There are no imaginary frequencies for all structures in Table 3, which convicts that all the structures in Fig. 1 correspond to the minimal points on their potential energy surfaces. The HF energies, MP energies and interaction energies after being corrected for BSSE and for zero-point energy (ZPE) consistently demonstrate that the stability order for the three dimers is **2**—**3** < **4**.

At MP4/6-31G**/MP2/6-31G** level, the differences between $\Delta E(\text{MP4SDTQ})_C$ and $\Delta E(\text{MP2})_C$ are 1.16, 0.99 and 2.28 kJ/mol for **2**, **3** and **4** respective-

ly, which are merely 4.9, 3.7 and 7.2 percents of their corresponding $\Delta E(\text{MP4SDTQ})_C$. So MP2 is also a preferable choice for correction of interaction calculations on larger systems. It could also be seen that shorter or more intermolecular contacts, as in the case of dimer **4** and **2** respectively, result in larger energy differences between $\Delta E(\text{MP4SDTQ})_C$ and $\Delta E(\text{MP2})_C$. The proportion of correlated interaction energies (ΔE^{MP4}) to their total interaction energies $\Delta E(\text{MP4SDTQ})$ for all dimers is at least 9.5%, so it is imperative to include the electron correlation energies into the interaction energies. The discrepancies between $\Delta E(\text{MP4SDTQ})_C$ and $\Delta E(\text{MP4SDTQ})$ are 18.2, 15.1 and 15.6 kJ/mol for **2**, **3** and **4** respectively, indicating that it is also necessary to correct the BSSE. The ZPE corrections for the interaction energies are much less than those of BSSE. The BSSE corrected binding energy for the most stable dimer is -31.85 kJ/mol at the MP4/6-31G**/MP2/6-31G** level, and this value becomes -24.67 kJ/mol after the ZPE correction.

Table 3 Total energies, ZPE and interaction energies (kJ/mol)

Levels	Energies	1	2	3	4
MP4//MP2/ 6-31G**	$E(\text{HF})$	-681680.47	-1363393.77	-1363395.81	-1363403.88
	$E(\text{MP2})$	-683570.40	-1367183.30	-1367183.04	-1367189.32
	$E(\text{MP4SDTQ})$	-683670.24	-1367382.56	-1367382.51	-1367387.93
	ZPE	109.68	227.69	228.30	227.43
	$\Delta E(\text{HF})$		-32.83	-34.87	-42.94
	$\Delta E(\text{MP2})$		-42.50	-42.24	-48.53
	$\Delta E(\text{MP4SDTQ})$		-42.07(21.7) ^a	-42.02(17.0) ^a	-47.44(9.5) ^a
	$\Delta E(\text{HF})_C$		-23.26	-28.14	-36.99
	$\Delta E(\text{MP2})_C$		-25.06	-27.92	-34.13
	$\Delta E(\text{MP4SDTQ})_C$		-23.90	-26.93	-31.85
	$\Delta E(\text{MP4SDTQ})_{C,ZPEC}$		-16.49	-18.98	-24.67
MP4//HF/ 6-31G*	$E(\text{HF})$	-681683.19	-1363399.46	-1363400.05	-1363407.24
	$E(\text{MP2})$	-683500.87	-1367043.74	-1367045.07	-1367051.56
	$E(\text{MP4SDTQ})$	-683593.24	-1367228.45	-1367230.29	-1367235.92
	ZPE	114.62	233.83	232.93	233.21
	$\Delta E(\text{HF})$		-33.07	-33.66	-40.85
	$\Delta E(\text{MP2})$		-42.00	-43.33	-49.82
	$\Delta E(\text{MP4SDTQ})$		-41.97(22.2) ^a	-43.81(23.2) ^a	-49.44(17.4) ^a
	$\Delta E(\text{HF})_C$		-26.11	-27.13	-35.43
	$\Delta E(\text{MP2})_C$		-29.10	-30.01	-36.89
	$\Delta E(\text{MP4SDTQ})_C$		-28.59	-29.91	-35.52
	$\Delta E(\text{MP4SDTQ})_{C,ZPEC}$		-24.90	-25.32	-31.56

^a Values in parentheses represent $[\Delta E(\text{MP4SDTQ})/(\Delta E(\text{MP4SDTQ}) + \Delta E(\text{HF}))] \times 100$.

In addition, Table 3 shows the HF energies, MP energies, corrected interaction energies at the MP4/6-31G**//HF/6-31G* level. Although the total HF or MP energies are much lower than those at the MP4/6-31G**//MP2/6-31G** level, the differences of $\Delta E(\text{HF})$ between these two level for the same dimer are only -0.24 , 1.21 and 2.09 kJ/mol for **2**, **3** and **4** respectively, whereas those of $\Delta E(\text{MP4SDTQ})$ are 0.10 , -1.79 and -2.00 kJ/mol. Therefore, the binding energy is insensitive to the polarized basis set of hydrogen and/or electronic correlation correction. Also, the basis sets affect ΔE^{MP2} more than they affect ΔE^{HF} for calculations from monomer to dimers. The ZPE corrections are very sensitive to the basis sets or electronic correlation, partly due to the approximation of harmonic calculations for the soft intermolecular vibration. Actually, interaction energies at MP2 level are in good agreement with experiments for typical hydrogen bonding dimers even though ZPE corrections are not considered,²⁶ as the over-corrected feature of BSSE in the MP methods partly compensate for the lack of ZPE correction.²⁷

Walden conversion and internal rotation

Fig. 2 shows the projection on $\text{N}_1\text{—N}_2$ during Walden conversion. Fig. 3 and Fig. 4 show the energy changes at HF/6-31G* level in the processes of the Walden conversion of amino group on N_2 and of the internal rotation around $\text{N}_1\text{—N}_2$, respectively, for monomer and the most stable dimer **4**. The energy barriers of the Walden conversion are 19.7 kJ/mol and 18.3 kJ/mol for **1** and **4**, respectively. The actual energy barrier is expected to be less than 18.3 kJ/mol owing to the interaction between atoms H_5 and O_{10} , which means that the Walden conversion takes place more freely within **4**. The energy barriers of internal rotation around $\text{N}_1\text{—N}_2$ are 103.23 kJ/mol and 70.47 kJ/mol for **1** and **4**, respectively, so it can not occur at room temperature and the molecular interaction makes the rotation even more difficult. It could then be speculated that the great changes

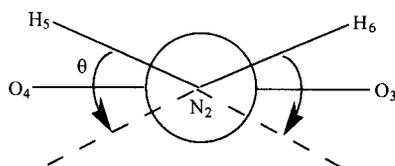


Fig. 2 Projection on $\text{N}_1\text{—N}_2$ during Walden conversion

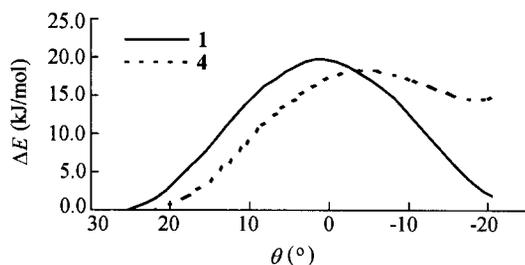


Fig. 3 Energy changes vs. θ during Walden conversion.

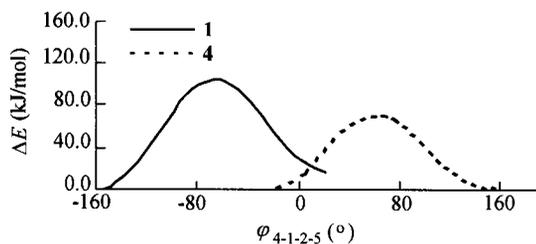


Fig. 4 Energy changes vs. φ during the internal rotation around $\text{N}_1\text{—N}_2$.

of dihedral angles from **2** to **4** are caused by the Walden conversion.

Natural bond orbital and Mulliken populations

The natural bond orbital occupancies are collected in Table 4. Considering the contributions of bonding and anti-bonding to NBO, the $\text{N}_1\text{—O}_3$ and $\text{N}_7\text{—O}_9$ bonds are strengthened for all dimers as compared with monomer. Whereas the $\text{N}_1\text{—O}_4$ bonds of **2** and **3**, and the $\text{N}_7\text{—O}_{10}$ bond of **3** are weakened. The $\text{N}_7\text{—O}_{10}$ bond for **2** is strengthened instead of weakening, which is probably due to its different interacting structure from that of **3**. The interaction in **4** is so large that the π electrons on $\text{N}_1\text{—O}_4$ and $\text{N}_7\text{—O}_{10}$ convert to lone pairs on the oxygen atom. The changes of NBO occupancies for the dimers as compared with those of monomer demonstrate that charge transfer and redistribution occurs in the interacting process, and there is a dipole-dipole interaction besides the dispersion force.

Apart from the NBO analyses, the Mulliken populations of intermolecular $\text{O}\cdots\text{H}$ are particularly relevant to reveal the essential of intermolecular interaction. The Mulliken populations of $\text{O}_{10}\cdots\text{H}_5$ are 0.0212 , 0.0188 and 0.0274 , and those of $\text{O}_4\cdots\text{H}_{11}$ are 0.0011 , 0.0185 and 0.0274 for **2**, **3** and **4**, respectively, which reveals

Table 4 Natural bond orbital occupancies (a. u.)

Bond or LP	1	2	3	4
N ₁ —N ₂	1.9948	1.9953	1.9953	1.9956
N ₁ —O ₃	1.8629	1.8724	1.8761	1.9852
N ₁ —O ₃	1.7947	1.7965	1.7971	1.9831
N ₁ —O ₄	1.8629	1.8495	1.8277	1.9960
N ₁ —O ₄ π	1.7947	1.8013	1.8107	
N ₂ —H ₅	1.9861	1.9848	1.9825	1.9842
N ₂ —H ₆	1.9861	1.9850	1.9854	1.9849
O ₄ LP(1)	1.9806	1.9805	1.9760	1.9734
O ₄ LP(2)	1.9191	1.9245	1.9229	1.9195(1.6088) ^b
N ₁ —N ₂ [*]	0.0835	0.0762	0.0745	0.0725
N ₁ —O ₃ [*]	0.1692	0.1597	0.1584	0.2380
N ₁ —O ₃ [*] π	0.2676	0.2655	0.2596	0.3559
N ₁ —O ₄ [*]	0.1692	0.1895	0.2207	0.0475
N ₁ —O ₄ [*] π	0.2676	0.2750	0.2594	
N ₂ —H ₅ [*]	0.0061	0.0186	0.0178	0.0257
N ₂ —H ₆ [*]	0.0061	0.0062	0.0061	0.0065
N ₇ —N ₈	1.9948 ^a	1.9945	1.9953	1.9956
N ₇ —O ₉	1.8629 ^a	1.8623	1.8759	1.9852
N ₇ —O ₉ π	1.7947 ^a	1.7890	1.7967	1.9831
N ₇ —O ₁₀	1.8629 ^a	1.9106	1.8321	1.9960
N ₇ —O ₁₀ π	1.7947 ^a	1.7923	1.8084	
N ₈ —H ₁₁	1.9861 ^a	1.9837	1.9825	1.9842
N ₈ —H ₁₂	1.9861 ^a	1.9838	1.9854	1.9849
O ₁₀ LP(1)	1.9806 ^a	1.9767	1.9758	1.9734
O ₁₀ LP(2)	1.9191 ^a	1.9208	1.9229	1.9195(1.6088) ^b
N ₇ —N ₈ [*]	0.0835 ^a	0.0761	0.0746	0.0725
N ₇ —O ₉ [*]	0.1692 ^a	0.1640	0.1584	0.2380
N ₇ —O ₉ [*] π	0.2676 ^a	0.2603	0.2591	0.3558
N ₇ —O ₁₀ [*]	0.1692 ^a	0.1211	0.2136	0.0475
N ₇ —O ₁₀ [*] π	0.2676 ^a	0.3048	0.2652	
N ₈ —H ₁₁ [*]	0.0061 ^a	0.0061	0.0175	0.0257
N ₈ —H ₁₂ [*]	0.0061 ^a	0.0061	0.0061	0.0065

* Antibond. ^a values of the monomer. ^b LP(3) of O(4) or O(10), LP means lone pair.

that there exist weak H-bonds in nitroamine dimers, and the O₁₀···H₅ and O₄···H₁₁ of **4** are slightly stronger.

Thermodynamic properties

On the basis of vibrational analysis and statistical thermodynamic, the standard thermodynamic functions, heat capacities (C_p^0), entropies (S_m^0) and enthalpies (H_m^0), were obtained and listed in Table 5. The magnitudes of C_p^0 for **2**—**4** are approximately the same at each temperature, but are larger than $C_p^0 \times 2$ of **1** by 7.6—

15.4 J·mol⁻¹·K⁻¹. In the course of **1**→**2**, **3** and **4**, both the entropy and the enthalpy decrease at any temperature ranging from 200.0 K to 700.0 K. The intermolecular interaction is therefore an exothermic process accompanied by a decrease in the probability, and the interactions weaken as temperature increases. The order of $(\Delta H_T)_2 \approx (\Delta H_T)_3 > (\Delta H_T)_4$ demonstrates once again that the interacting order is **4** > **2**—**3**. From $\Delta G = \Delta H - T\Delta S$ equation, the change of Gibbs free energy (ΔG) in the process **1**→**4** is 14.05 kJ/mol at 298.2 K on the calculation model of ideal-gas, and the calculated equilibrium constant, based on the equation $\Delta G = -RT \ln K_p$, is

Table 5 Thermodynamic properties of nitroamine monomer and dimers at different temperatures^a

Structure	T (K)	C_p^0 (J·mol ⁻¹ ·K ⁻¹)	S_m^0 (J·mol ⁻¹ ·K ⁻¹)	H_m^0 (kJ/mol)	ΔS_T (J·mol ⁻¹ ·K ⁻¹)	ΔH_T (kJ/mol)	ΔG_T (kJ/mol)
1	200.00	42.96	247.52	7.09			
	273.15	53.01	262.38	10.60			
	298.15	56.44	267.17	11.96			
	500.00	9.41	302.18	25.84			
	700.00	93.68	331.35	43.26			
2	200.00	94.70	319.56	12.23	-175.48	-27.36	7.74
	273.15	117.75	352.52	20.01	-172.24	-26.60	20.45
	298.15	125.22	363.15	23.05	-171.19	-26.28	24.76
	500.00	173.39	440.22	53.56	-164.14	-23.53	58.54
	700.00	202.77	503.61	91.41	-159.09	-20.52	90.84
3	200.00	94.12	320.83	12.19	-174.21	-28.91	5.93
	273.15	117.08	353.59	19.92	-171.17	-28.20	18.56
	298.15	124.54	364.17	22.94	-170.17	-27.90	22.84
	500.00	172.81	440.90	53.32	-163.46	-25.28	56.45
	700.00	202.35	504.12	91.07	-158.58	-22.37	88.64
4	200.00	93.56	320.44	12.12	-174.60	-37.82	-2.90
	273.15	116.87	353.07	19.83	-171.69	-37.13	9.77
	298.15	124.46	363.64	22.84	-170.70	-36.84	14.05
	500.00	173.23	440.48	53.27	-163.88	-34.17	47.77
	700.00	202.78	503.85	91.11	-158.85	-31.17	80.03

^a $\Delta S_T = (S_m^0)_i - 2(S_m^0)_1$, $\Delta H_T = (H_m^0 + E^{HF} + ZPE)_i - 2(H_m^0 + E^{HF} + ZPE)_1$ ($i = 2, 3, 4$), $\Delta G_T = \Delta H_T - T\Delta S_T$, and the scale factor for frequencies is 0.89.²⁸

0.003. It reveals that the monomer is the main component at equilibrium under ordinary temperature if the related compounds are isolated molecules at 0 K. The proportions of dimers increase as temperature decreases. The ratio for **2**:**3**:**4** is equal to 1.0:2.2:74.4 at 298.2 K.

Conclusions

From the *ab initio* calculations in the paper, the following conclusions can be drawn:

(1) The most stable dimer of nitroamine is **4**, whose BSSE corrected binding energy is -31.85 kJ/mol at the MP4/6-31G**//MP2/6-31G** level, and this value becomes -24.67 kJ/mol after the ZPE correction.

(2) There exist weak H-bonds and dipole-dipole interaction between the submolecules of the dimers.

(3) The interaction is an exothermic process with

the probability decreasing, which is intensified as temperature decreases.

(4) Intermolecular interaction makes the Walden conversion for -NH₂ group easier but the internal rotation around N₁-N₂ even more difficult.

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(E0104293 SONG, J. P.; DONG, L. J.)