

Ab initio Study on the Intermolecular Interaction and Thermodynamic Properties of Methyl Nitrate Dimer

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Three stable dimers of methyl nitrate have been obtained and their geometries have been fully optimized at the HF/6-31G* level. Binding energies have been calculated with correction for the basis set superposition error (BSSE) and zero point energy (ZPE). The cyclic overlap-type structure, the binding energy of which is 11.97 kJ/mol at the MP4SDTQ/6-31G* // HF/6-31G* level, is the most stable. No intermolecular hydrogen bond was found, and the charge transfer between two subsystems is minute. The thermodynamic properties of methyl nitrate and its dimers have been calculated based on the vibrational analysis and statistical thermodynamics.

Keyword Methyl nitrate dimer, intermolecular interaction, *ab initio*, thermodynamic properties

Introduction

Intermolecular forces are in general much weaker than intramolecular chemical bonds, and yet they play significant roles in a wide range of important fields in chemistry and biology.¹⁻³ In the past several decades, great progresses have been made⁴⁻⁷ in the investigation of intermolecular interaction with quantum chemical method. As the physical, chemical and explosive properties of energetic materials are concerned with the molecular aggregative state, the study of the intermolecular interactions of such materials has attracted wide attention.⁸⁻⁹ Recently, our group has applied the quantum chemical calculations to investigate the intermolecular interactions of energetic materials.¹⁰⁻¹⁶

Methyl nitrate, a prototypical energetic explosive

compound, is an important chemical agent. There are many theoretical studies on its properties and structures.¹⁷⁻²⁰ In this article, we report *ab initio* results of the geometries, electronic structures, and binding energies of methyl nitrate dimers and the changes in the thermodynamic properties from monomer to dimer.

Computational methods and details

Geometrical optimization and electronic structural calculations

The full geometrical optimization of a single methyl nitrate molecule was performed at the HF/6-31G* level with the Berny method.²¹ Then the possible structures of the dimers were constructed by chemical intuition and optimized at the same level. Three stable dimers were obtained. Natural population analysis²² and the vibrational frequency calculations on the optimized structures were subsequently carried out. Electronic correlation corrections were undertaken at the MP4SDTQ/6-31G* // HF/6-31G* level. All the optimized structures were found to be stable structures with no imaginary frequency.

Interaction energy calculations

For the *ab initio* calculation at the Hartree-Fork level, if the correlation interaction energy is calculated

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by the Møller-Plesset (MP) perturbation method,²³ the interaction energy (MP) of dimer is determined as follows:²⁴

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

where $\Delta E(\text{HF})$ is the HF interaction energy, ΔE^{MP} is the correlation interaction energy calculated by the MP method. When the basis set superposition error (BSSE) is corrected by the Boys-Bernardi "counterpoise method",²⁵ Eq. (1) can be written as:

$$\Delta E_{\text{C}}(\text{MP}) = \Delta E_{\text{C}}(\text{HF}) + \Delta E_{\text{C}}^{\text{MP}} \quad (2)$$

where $\Delta E_{\text{C}}(\text{MP})$, $\Delta E_{\text{C}}(\text{HF})$ and $\Delta E_{\text{C}}^{\text{MP}}$ are the total intermolecular interaction energy, the HF interaction energy and the MP correlation interaction energy corrected for BSSE, respectively.

All calculations were performed on a Pentium personal computer using the Gaussian 98 program.²⁶

Results and discussion

Optimized geometries and natural atomic charges

Fig. 1 shows the optimized structures of CH_3ONO_2 and $(\text{CH}_3\text{ONO}_2)_2$ obtained from HF/6-31G* calcula-

tions. Table 1 shows the geometrical parameters. Structure **3** is linear, while **2** and **4** are cyclic, and **2** is overlap-typed. As compared to the isolated molecule **1**, the r_{2-1} distances of **2**, **3** and **4** increase by 0.5, 0.3 and 0.5 pm, while the r_{3-2} distances of **2**, **3** and **4** decrease by 0.5, 0.6 and 0.5 pm, respectively, and other bond lengths have smaller changes. Thus the interaction between two CH_3ONO_2 molecules has only a slight effect on the chemical bonds. In most explosive molecules containing $-\text{NO}_2$, $-\text{XNO}_2$ ($\text{X} = \text{N}, \text{C}, \text{O}$) is thought to be the ignited bond of pyrolysis and priming.²⁷ As for this system, the decrease of O—N bond length shows that the intermolecular interaction has a passive effect on the bond O—N. Compared to the isolated molecule, the bond angles and dihedral angles of the three dimers change slightly, and the changes are below 3° . So the interaction between two CH_3ONO_2 molecules has little effect on bond angles and torsional angles. In the molecules of **2**, **3** and **4**, the shortest intermolecular distances ($\text{H}\cdots\text{O}$), as displayed in Fig. 1, are 0.2899, 0.2835 and 0.2913 nm, respectively. In addition, the distances of $\text{C}_1\cdots\text{O}_{12}$ in **2**, $\text{C}_9\cdots\text{O}_5$ in **3** and $\text{C}_1\cdots\text{O}_{13}$ in **4** are 0.3268, 0.3648 and 0.3383 nm, respectively. These distances are much longer than the normal H-bond length. So it can be seen that there exists no intermolecular hydrogen bond ($\text{C}-\text{H}\cdots\text{O}$) in these dimers and the interaction belongs to normal van der Waals force.

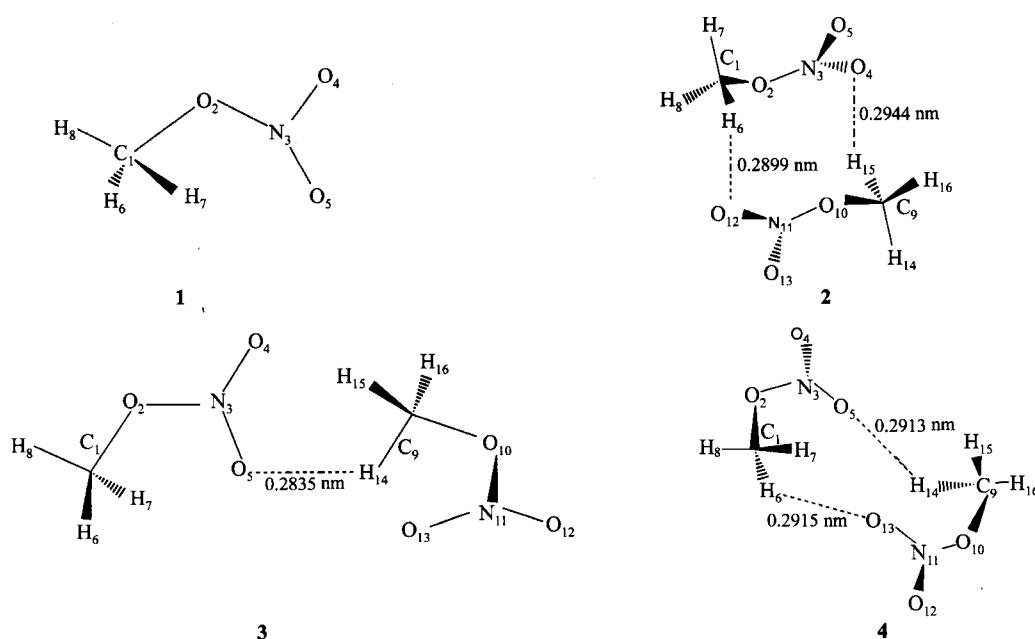


Fig. 1 Atomic numbering and optimized structures of CH_3ONO_2 and $(\text{CH}_3\text{ONO}_2)_2$.

Table 1 Optimized geometrical parameters of CH_3ONO_2 and $(\text{CH}_3\text{ONO}_2)_2$ at the HF/6-31G* level (bond length in nm, bond angle and dihedral angle in degree)

Parameter	1	2	3	4
Within subsystem				
r_{2-1}	0.1428	0.1433	0.1431	0.1433
r_{3-2}	0.1331	0.1326	0.1325	0.1326
r_{4-3}	0.1177	0.1182	0.1180	0.1176
r_{5-3}	0.1187	0.1184	0.1187	0.1190
r_{6-1}	0.1078	0.1076	0.1078	0.1077
r_{7-1}	0.1078	0.1078	0.1078	0.1077
r_{8-1}	0.1077	0.1077	0.1077	0.1077
r_{10-9}		0.1433	0.1433	0.1433
r_{11-10}		0.1326	0.1327	0.1326
r_{12-11}		0.1182	0.1179	0.1176
r_{13-11}		0.1184	0.1187	0.1190
r_{14-9}		0.1078	0.1076	0.1077
r_{15-9}		0.1077	0.1077	0.1077
r_{16-9}		0.1076	0.1077	0.1077
θ_{3-2-1}	115.78	115.87	115.87	116.04
θ_{4-3-2}	113.91	113.91	114.05	114.18
θ_{5-3-2}	117.89	118.28	118.18	118.07
θ_{6-1-2}	110.50	110.17	110.37	110.53
θ_{7-1-2}	110.50	110.11	110.36	110.54
θ_{8-1-2}	103.26	103.13	103.14	103.07
$\theta_{11-10-9}$		115.89	115.94	116.04
$\theta_{12-11-10}$		113.91	114.02	114.18
$\theta_{13-11-10}$		118.28	118.09	118.06
$\theta_{14-9-10}$		110.10	110.59	110.54
$\theta_{15-9-10}$		110.17	110.43	110.53
$\theta_{16-9-10}$		103.14	103.27	103.07
$\varphi_{4-3-2-1}$	180.00	177.94	-179.63	-179.96
$\varphi_{5-3-2-1}$	359.99	-2.36	0.40	0.04
$\varphi_{6-1-2-3}$	298.67	-60.44	-61.54	-61.27
$\varphi_{7-1-2-3}$	61.34	62.57	61.13	61.26
$\varphi_{8-1-2-3}$	180.00	-178.62	179.79	-179.99
$\varphi_{12-11-10-9}$		-177.69	179.69	-179.97
$\varphi_{13-11-10-9}$		2.59	-0.35	0.04
$\varphi_{14-9-10-11}$		-62.26	-61.50	-61.24
$\varphi_{15-9-10-11}$		60.26	61.37	61.29
$\varphi_{16-9-10-11}$		178.42	179.84	-179.98
Between two subsystems				
r_{9-1}		0.4994	0.6001	0.4527
θ_{9-1-2}		36.32	43.93	106.16
θ_{10-9-1}		35.91	155.36	106.14
$\varphi_{9-1-2-3}$		-90.23	7.98	0.04
$\varphi_{10-9-1-2}$		179.29	177.43	179.87
$\varphi_{11-10-9-1}$		92.49	-58.12	-0.58

The computed natural atomic charges are listed in Table 2. Compared to those in the isolated molecule **1**, O(4) and O(12) in **2** both acquire 0.029 e, while H(6), H(15), O(5) and O(13) lose 0.010 e, 0.009 e, 0.012 e and 0.012 e, respectively. This shows that the charge on one O atom of $-\text{NO}_2$ increases, while that on the other O atom decreases. Also the charge densities between two molecules increase. As the distance between H(6)—O(12) and H(15)—O(4) becomes shorter, the charge transfer counteracts, and the charge transfer between two methyl nitrate subsystems goes to zero. For **3**, O(4) acquires 0.015 e, while N(3) and O(2) lose 0.004 e and 0.007 e, respectively, and the net result is that this subsystem acquires 0.004 e. For **4**, O(5) acquires 0.021 e, while N(3), O(4) and O(2) lose 0.004 e, 0.004 e and 0.002 e, respectively, with the amount of charge transfer being zero. It can be seen that the charge on the O atom of $-\text{NO}_2$ changes greatly when two molecules interact, but the charge transfer between two subsystems is very weak. From HF/6-31G* calculated charges, the dipole moments of **1**, **2**, **3** and **4** are 3.83, 0.07, 7.24 and 0.03 Debye, respectively.

Table 2 Atomic charges (e) of CH_3ONO_2 and $(\text{CH}_3\text{ONO}_2)_2$

Atom	1	2	3	4
C(1)	-0.249	-0.248	-0.249	-0.246
O(2)	-0.438	-0.438	-0.431	-0.436
N(3)	0.931	0.937	0.935	0.935
O(4)	-0.423	-0.452	-0.438	-0.419
O(5)	-0.472	-0.460	-0.472	-0.493
H(6)	0.214	0.224	0.216	0.218
H(7)	0.214	0.210	0.217	0.218
H(8)	0.223	0.227	0.226	0.223
C(9)		-0.247	-0.248	-0.246
O(10)		-0.439	-0.440	-0.436
N(11)		0.936	0.932	0.935
O(12)		-0.452	-0.432	-0.419
O(13)		-0.460	-0.475	-0.493
H(14)		0.210	0.220	0.218
H(15)		0.223	0.215	0.218
H(16)		0.229	0.224	0.223

Energy

Table 3 reports the total energies [$E(\text{MP2})$, $E(\text{MP4SDTQ})$] and intermolecular interaction energies calculated at the MP4SDTQ/6-31G* // HF/6-31G* level, where $\Delta E_C^{\text{ZPEC}}(\text{MP4SDTQ})$ is the correction for the

ZPE. From $E(\text{MP4SDTQ})$ in Table 3, it can be seen that the total energy of the structure **2** is 10.98 kJ/mol lower than that of the structure **3**, and 12.42 kJ/mol lower than that of the structure **4**, so that the structure **2** is the most stable among the three optimized structures. Though $E(\text{MP4SDTQ})$ is lower than $E(\text{MP2})$, for **2**, **3** and **4**, $\Delta E_C(\text{MP2})$ is nearly equal to $\Delta E_C(\text{MP4SDTQ})$ and $\Delta E(\text{MP2})$ is also close to $\Delta E(\text{MP4SDTQ})$. This indicates that the MP2 interaction energy is very close to the MP4SDTQ interaction energy for methyl nitrate dimer, which is in agreement with earlier reports.¹⁰⁻¹⁵ For structures **2**, **3** and **4**, the $\Delta E_C^{\text{MP4SDTQ}}/\Delta E_C(\text{MP4SDTQ})$ values are 28.6%, 0.1% and 1.3%, respectively, which indicates that the correlation energy makes more contribution to the interaction energy in structure **2** than to that of **3** or **4**. From Table 3, it can also be seen that the BSSE of all the dimers is large. For the MP4SDTQ method, after BSSE correction, the binding energies of **2**, **3** and **4** decrease 11.49, 7.05 and 4.58 kJ/mol, respectively. The data in Table 3 show that the largest corrected binding energy $\Delta E_C^{\text{ZPEC}}(\text{MP4SDTQ})$ of methyl nitrate dimer is 11.97 kJ/mol.

In order to check the quality of the 6-31G* basis set, the calculations were carried out at the MP2/6-311G** // HF/6-31G* and MP2/6-311++G** // HF/6-31G* levels. The results are listed in Table 3 too. It can be seen that for the structures **2**, **3** and **4**, the intermolecular interaction energies $\Delta E_C(\text{MP2})$ calculated at the MP2/6-31G* // HF/6-31G* level are very close to those at the MP2/6-311G** // HF/6-31G* and MP2/6-311++G** // HF/6-31G* levels, respectively. This shows that the 6-31G* basis set may be a suitable choice for the calculation of the binding energy of the methyl nitrate dimer.

Thermodynamic properties

Based on the vibrational analysis, the standard thermodynamic functions have been derived from the scaled frequencies (the scale factor is 0.89²⁸) using the statistical thermodynamic method. The results are shown in Table 4. It can be seen that the values of the calculated functions of all structures increase with the increasing temperature. At the same temperature, the heat capacities (C_p) of all dimers are twice as large as the heat capacity of monomer, and the difference is about 16.0

Table 3 Total energies (kJ/mol), zero point energy correction [ΔE (ZPEC), kJ/mol] and interaction energies (kJ/mol)

Basis set		1	2	3	4
6-31G*	$E(\text{HF})$	-836152.34	-1672321.67	-1672316.29	-1672315.67
	$E(\text{MP2})$	-838355.50	-1676737.08	-1676725.76	-1676724.17
	$E(\text{MP4SDTQ})$	-838480.08	-1676986.16	-1676975.18	-1676973.73
	$\Delta E(\text{ZPEC})$		2.54	1.45	1.24
	$\Delta E(\text{HF})$		-16.99	-11.62	-10.99
	$\Delta E(\text{MP2})$		-26.08	-14.75	-13.17
	$\Delta E(\text{MP4SDTQ})$		-26.00	-15.02	-13.58
	$\Delta E_{\text{C}}(\text{HF})$		-10.36	-7.98	-8.91
	$\Delta E_{\text{C}}^{\text{MP2}}$		-4.42	0.07	0.12
	$\Delta E_{\text{C}}(\text{MP2})$		-14.78	-7.91	-8.79
	$\Delta E_{\text{C}}^{\text{MP4SDTQ}}$		-4.15	0.01	0.12
	$\Delta E_{\text{C}}^{\text{MP4SDTQ}}$		-14.51	-7.97	-9.00
	$\Delta E_{\text{C}}^{\text{ZPEC}}(\text{MP4SDTQ})$		-11.97	-6.52	-7.76
6-311G**	$E(\text{MP2})$	-838810.48	-1677647.68	-1677635.49	-1677634.22
	$\Delta E(\text{MP2})$		-26.72	-14.53	-13.26
	$\Delta E_{\text{C}}(\text{MP2})$		-14.13	-7.26	-8.75
6-311++G**	$E(\text{MP2})$	-838852.07	-1677735.13	-1677716.76	-1677718.93
	$\Delta E(\text{MP2})$		-30.99	-12.61	-14.78
	$\Delta E_{\text{C}}(\text{MP2})$		-17.37	-8.07	-9.89

J/(mol·K). The total entropies of the system decrease as two monomers form a dimer and the extent decreases as the temperature increases. For the structure **2**, the entropy changes ΔS_{T} are the greatest, which indicates that **2** is in better order than **3** or **4**. The enthalpy changes ΔH_{T} of the dimers at various temperatures calculated with corrections for zero point energies are collected in Table 4. It can be seen that ΔH_{T} values are below zero since the aggregative process is exothermic. At the same temperature, the ΔH_{T} value of **2** is lower than that of **3** or **4**, which is consistent with the results of binding energy. The absolute values of ΔH_{T} decrease with the increasing temperature, which indicates that the interactions between molecules are becoming weaker. Using $\Delta G_{\text{T}} = \Delta H_{\text{T}} - T\Delta S_{\text{T}}$, the ΔG_{T} values were obtained at various temperatures. It can be seen that ΔG_{T} of **2** is smaller than that of **3** or **4** at the lower temperature, which also demonstrates that **2** is the most stable. But with the increasing temperature, ΔG_{T} of **2** becomes greater than that of **3** or **4**, which indicates that the aggregative process turns to be controlled by entropy

change. So the stability of **2** is lower than that of **3** or **4** with the increasing temperature. Obviously, these results are only applicable to systems in the gas phase at low pressure.

Conclusions

From *ab initio* calculations, the following conclusions can be drawn: (1) The intermolecular interactions have a slight effect on the geometries of the dimers, and there exists no intermolecular hydrogen bond in the optimized methyl nitrate dimers. (2) In methyl nitrate dimers, the charge transfer is very weak. (3) The cyclic overlap-type structure **2** is the most stable among the three optimized structures at the lower temperature, the corrected binding energy of which is 11.97 kJ/mol at the MP4SDTQ/6-31G* // HF/6-31G* level. (4) From monomer to dimer, ΔG_{T} of **2** is greater than the ΔG_{T} of **3** or **4** with the increasing temperature and the aggregative process turns to be controlled by entropy change.

Table 4 Thermodynamic properties of CH₃ONO₂ and (CH₃ONO₂)₂ at different temperatures

Structure	<i>T</i> (K)	<i>C_p</i> [J/(mol·K)]	<i>S_T⁰</i> [J/(mol·K)]	<i>H_T⁰</i> (kJ/mol)	ΔS_T [J/(mol·K)]	ΔH_T (kJ/mol)	ΔG_T (kJ/mol)
1	100.00	45.12	236.46	3.76			
	200.00	58.37	271.84	8.94			
	273.15	68.92	291.56	13.59			
	298.15	72.73	297.76	15.36			
	400.00	88.22	321.31	23.56			
	500.00	101.92	342.51	33.09			
	600.00	113.47	362.14	43.88			
2	100.00	104.24	348.76	7.60	-124.16	-14.37	-1.95
	200.00	132.31	429.58	19.42	-114.10	-12.91	9.91
	273.15	153.89	473.96	29.88	-109.16	-11.75	18.07
	298.15	161.61	487.77	33.82	-107.75	-11.35	20.77
	400.00	192.83	539.66	51.89	-102.96	-9.68	31.50
	500.00	220.33	585.72	72.58	-99.30	-8.05	41.60
	600.00	243.49	628.00	95.81	-96.28	-6.40	51.37
3	100.00	105.56	374.01	8.16	-98.91	-9.53	0.36
	200.00	132.99	455.77	20.11	-87.91	-7.94	9.64
	273.15	154.28	500.31	30.61	-82.81	-6.74	15.88
	298.15	161.96	514.15	34.56	-81.37	-6.33	17.93
	400.00	193.05	566.12	52.65	-76.50	-4.64	25.96
	500.00	220.50	612.23	73.37	-72.79	-2.98	33.41
	600.00	243.62	654.54	96.61	-69.74	-1.32	40.52
4	100.00	106.05	374.50	8.23	-98.42	-9.04	0.80
	200.00	133.26	456.51	20.22	-87.17	-7.41	10.02
	273.15	154.51	501.13	30.73	-81.99	-6.20	16.19
	298.15	162.18	514.99	34.69	-80.53	-5.78	18.23
	400.00	193.24	567.03	52.80	-75.59	-4.07	26.17
	500.00	220.65	613.17	73.53	-71.85	-2.40	33.52
	600.00	243.74	655.50	96.78	-68.78	-0.73	40.54

$$\Delta S_T = (S_T^0)_i - 2(S_T^0)_1, \Delta H_T = (H_T^0 + E(\text{HF}) + \text{ZPE})_i - 2(H_T^0 + E(\text{HF}) + \text{ZPE})_1, (i = 2, 3, 4).$$

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