A theoretical study on the intermolecular interaction of energetic system—Nitromethane dimer

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Three optimized geometries of nitromethane dimer have been obtained at the HF/6-31G* level. Dimer binding energies have been corrected for the basis set superposition error (BSSE) and the zero point energy. Computed results indicate that the cyclic structure of $(CH_3NO_2)_2$ is the most stable of three optimized geometries, whose corrected binding energyis 17.29 kJ·mol^{-1} at the MP4SDTQ/6-31G*//HF/6-31G* level. In the optimized structures of nitromethane dimer, the intermolecular hydrogen bond has not been found; and the charge-transfer interaction between CH_3NO_2 subsystems is weak; and the correlation interaction energy makes a little contribution to the intermolecular interaction energy of the dimer.

Keywords Nitromethane dimer, intermolecular interaction, *ab initio*

Introduction

Intermolecular forces are in general much weaker than intramolecular chemical bonds , and yet they are ubiquitous and play significant roles in a wide range of important fields in chemistry and biology.[1-3] In the past several decades, great advances in molecular beam electric resonance, Fourier transform microwave spectroscopy, and other experimental techniques have led to an explosive growth in our knowledge of the accurate structures of van der Waals molecules;[4-6] and enormous progresses have been made in the investigation on intermolecular interaction with quantum-chemical methods.[7-18]

The study of intermolecular interaction of energetic materials has attracted wide attention.[19-21] Cumming *et al*. has calculated the interaction of HMX (cyclotetramethylene tetranitramine) with PNMMO (homopolymer of 3-nitrate-3-methyl oxetane) by the molecular dynamical method.[22] Recently we have applied the quantum chemical calculations of intermolecular interaction to energetic systems, and have obtained some meaningful results that will be useful for the development of energetic materials.[23-25]

Nitromethane, a prototypical energetic compound, is an important liquid explosive and a chemical agent. There are many theoretical studies on its properties and structures.[26-31] On the basis of the experiment results, Trevino *et al*. has suggested that the rotation motion of the methyl group be dominated by the interaction between nitromethane molecules in condensed phase.[32] However, no theoretical reports on the interaction between nitromethane molecules from survey. In order to assist in understanding the properties (such as intermolecular force) of nitromethane, *ab initio* calculations have been performed on the nitromethane dimer in this paper.

Computational method and details

Geometrical optimizations and electronic structural calculations

The full geometrical optimization of single nitromethane molecule was performed at the HF/6-31G* level with the Berny method.[33] Then at the same level,

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Received April 10, 2000; accepted June 1, 2000.

Project supported by the Foundation of China Academy of Engineering Physics (No. 99050330, 20000552).

the three optimized dimer geometries were obtained by the full geometrical optimization of possible stable geometries of nitromethane dimer created with the Chem3D software. The natural population analysis[34] and the vibrational frequency calculation on the optimized structures were carried out at the level of HF/6-31G* . Electronic correlation corrections were carried out at the MP4SDTQ/6-31G*//HF/6-31G* level. The vibrational analysis shows that **I**, **II** and **III** are stable structures and that **IV** is one saddle point of potential surface of nitromethane dimer (structures **I**, **II** and **III** have no imaginary vibrational frequency, but **IV** has one sole imaginary vibrational frequency, see Table 1). Further calculations demonstrate that **IV** is practically one of saddle points of the conversion between **II** and **III** (see Fig.1).

Table 1 Total energies ($kJ \cdot mol^{-1}$), zero point energy correction (ZPEC, $kJ \cdot mol^{-1}$), number of imaginary frequencies (N_i) and interaction energies ($kJ \cdot mol^{-1}$)

Basis set		I	II	III	IV
6-31G*	E^{MP2}	-641473.34	-1282967.01	-1282979.05	-1282966.89
	$E^{MP4SDTQ}$	-641580.71	-1283182.30	-1283194.11	-1283182.14
	ZPEC		2.00	3.77	2.18
	N_i	0	0	0	1
	$\triangle E^{HF}$		-16.28	-24.70	-15.80
	$\triangle E$(MP2)		-20.33	-32.37	-20.21
	$\triangle E$(MP4SDTQ)		-20.88	-32.69	-20.72
	$\triangle E_C^{HF}$		-11.32	-17.98	-11.12
	$\triangle E_C$(MP2)		-11.02	-20.99	-11.53
	$\triangle E_C^{MP4SDTQ}$		0.06	-3.08	-0.59
	$\triangle E_C$(MP4SDTQ)		-11.26	-21.06	-11.71
	$\triangle E_C^{ZPEC}$(MP4SDTQ)		-9.26	-17.29	-9.53
6-311G**	E^{MP2}	-641828.88	-1283677.78	-1283690.01	-1283677.83
	$\triangle E$(MP2)		-20.02	-32.25	-20.07
	$\triangle E_C$(MP2)		-10.26	-19.80	-10.52
6-311++G**	E^{MP2}	-641865.64	-1283746.74	-1283762.52	-1283746.56
	$\triangle E$(MP2)		-15.46	-31.24	-15.28
	$\triangle E_C$(MP2)		-11.50	-21.81	-11.26

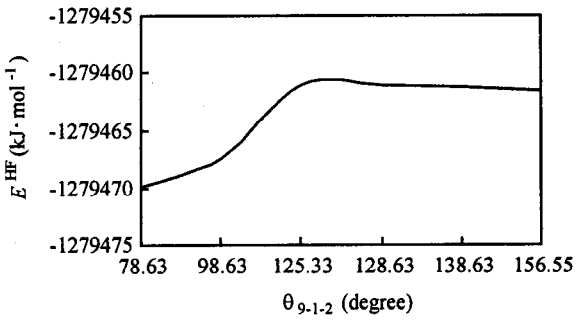

Fig. 1 Potential curve of $(CH_3NO_2)_2$ along $\theta_{9\text{-}1\text{-}2}$ coordinate calculated at the HF/6-31G* level.

Interaction energy calculations

For the *ab initio* calculation at the Hartree-Fock level, if the correlation interaction energy is calculated by the Moller-Plesset (MP) perturbation method,[35] the intermolecular interaction energy $\triangle E$(MP) of dimer is determined as[36]

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

where $\triangle E^{HF}$ is the HF interaction energy, $\triangle E^{MP}$ is the correlation interaction energy calculated by the MP method. When the basis set superposition error (BSSE)[37] is corrected by the Boys-Bernadi "counterpoise" method,[7] Eq. (1) can be written as

$$\triangle E_C(MP) = \triangle E_C^{HF} + \triangle E_C^{MP} \quad (2)$$

where $\triangle E_C$(MP), $\triangle E_C^{HF}$ and $\triangle E_C^{MP}$ are the total

intermolecular interaction energy, the HF interaction energy and the MP correlation interaction energy corrected for BSSE, respectively.

All calculations have been carried out with the Gauss94[38] program implemented on a Pentium personal microcomputer using the default Gaussian convergence criteria.

Results and discussions

Optimized geometries and natural atomic charges

Fig. 2 presents the optimized structures of CH_3NO_2 and of $(CH_3NO_2)_2$, whose geometrical parameters are listed in Table 2. As compared to the isolated molecule, for the linear structure **II** the $r_{6\text{-}1}$ decreases by 0.2 pm, other geometrical parameters have smaller changes, bond angles and dihedral angles also change very slightly; for the cyclic structure **III** the $r_{2\text{-}3}$ and the $r_{14\text{-}9}$ increase by 0.6 pm and 0.3 pm, respectively, but the $r_{7\text{-}2}$ decreases by 0.4 pm, dihedral angles $\theta_{4\text{-}1\text{-}2\text{-}3}$, $\theta_{5\text{-}1\text{-}2\text{-}3}$, $\theta_{6\text{-}1\text{-}2\text{-}3}$ and $\theta_{7\text{-}2\text{-}1\text{-}4}$ increase by 16.74°, 17.30°, 18.51° and 17.83°, respectively; for the structure **IV** all of changes of bond lengths are within 0.1 pm, while dihedral angles $\theta_{4\text{-}1\text{-}2\text{-}3}$, $\theta_{5\text{-}1\text{-}2\text{-}3}$, $\theta_{6\text{-}1\text{-}2\text{-}3}$ and $\theta_{7\text{-}2\text{-}1\text{-}4}$ increase by 7.76°, 8.13°, 8.75° and 8.00°, respectively. So it can be known that the internal rotation of $-CH_3$ group occurs in structures **III** and **IV**. For **II**, **III** and **IV**, the shortest intermolecular distances, displayed in Fig. 2, are 0.2677 nm, 0.2504 nm and 0.2574 nm, respectively, which demonstrates that there exists no intermolecular hydrogen bond (C—H···O) in these optimized dimers.

The computed natural atomic charges are displayed in Table 3. As compared to the isolated CH_3NO_2 (see **I** in Table 3), for structures **II**, **III** and **IV**, the natural atomic charges change slightly. With respect to the corresponding atomic charges of isolated CH_3NO_2, for structure **II**, H(6) loses 0.011e, while O(14) acquires 0.012e, other atomic charges have smaller changes; for structure **III**, O(3) and O(14) acquire 0.045e and 0.022e, respectively, where as H(6), O(7) and H(13) lose 0.017e, 0.021e and 0.019e, respectively. From Table 3, it can be gotten that the quantities of charge transfer between nitromethane subsystemsfor structures **II**, **III** and **IV** are 0.006e, 0.003e and 0.008e, respectively, which are the same as the NBO[9] analysis's results, and show that the charge-transfer interaction between CH_3NO_2 subsystems is very weak.

Table 2 Optimized geometrical parameters of CH_3NO_2 and of $(CH_3NO_2)_2$ at the HF/6-31G* level (Data in parentheses are also the geometrical parameters of CH_3NO_2, bond length in nm, bond angle and dihedral angle in degree)

	I	II	III	IV
$r_{2\text{-}1}$	0.1478	0.1478	0.1479	0.1478
$r_{3\text{-}2}$	0.1192	0.1193	0.1198	0.1193
$r_{4\text{-}1}$	0.1076	0.1076	0.1075	0.1076
$r_{5\text{-}1}$	0.1076	0.1076	0.1078	0.1077
$r_{6\text{-}1}$	0.1080	0.1078	0.1079	0.1079
$r_{7\text{-}2}$	0.1192	0.1193	0.1188	0.1192
$r_{9\text{-}8}$	(0.1478)	0.1479	0.1477	0.1479
$r_{10\text{-}9}$	(0.1192)	0.1191	0.1191	0.1192
$r_{11\text{-}8}$	(0.1076)	0.1077	0.1077	0.1076
$r_{12\text{-}8}$	(0.1076)	0.1076	0.1076	0.1076
$r_{13\text{-}8}$	(0.1080)	0.1080	0.1079	0.1080
$r_{14\text{-}9}$	(0.1192)	0.1193	0.1195	0.1192
$\theta_{3\text{-}2\text{-}1}$	117.10	117.31	116.81	116.97
$\theta_{4\text{-}1\text{-}2}$	107.97	108.00	107.96	107.95
$\theta_{5\text{-}1\text{-}2}$	107.97	108.02	107.26	107.67
$\theta_{6\text{-}1\text{-}2}$	106.55	107.12	106.64	107.08
$\theta_{7\text{-}2\text{-}1}$	117.10	117.28	118.07	117.59
$\theta_{9\text{-}1\text{-}2}$		156.55	78.63	125.33
$\theta_{4\text{-}1\text{-}2\text{-}3}$	152.04	151.55	168.78	159.80
$\theta_{5\text{-}1\text{-}2\text{-}3}$	29.73	29.47	47.03	37.86
$\theta_{6\text{-}1\text{-}2\text{-}3}$	-89.12	-89.52	-70.61	-80.37
$\theta_{7\text{-}2\text{-}1\text{-}4}$	-29.77	-30.24	-11.94	-21.77

Table 3 Calculated natural atomic charges (e) at the HF/6-31G* level (Data in parentheses are also the natural atomic charges of CH_3NO_2)

Atom	I	II	III	IV
C(1)	-0.465	-0.464	-0.468	-0.467
N(2)	0.650	0.650	0.660	0.652
O(3)	-0.460	-0.467	-0.505	-0.471
H(4)	0.243	0.242	0.238	0.237
H(5)	0.243	0.242	0.246	0.241
H(6)	0.248	0.259	0.265	0.263
O(7)	-0.460	-0.468	-0.439	-0.463
C(8)	(-0.465)	-0.464	-0.465	-0.464
N(9)	(0.650)	0.654	0.661	0.655
O(10)	(-0.460)	-0.458	-0.460	-0.464
H(11)	(0.243)	0.248	0.242	0.247
H(12)	(0.243)	0.247	0.240	0.246
H(13)	(0.248)	0.251	0.267	0.252
O(14)	(-0.460)	-0.472	-0.482	-0.464

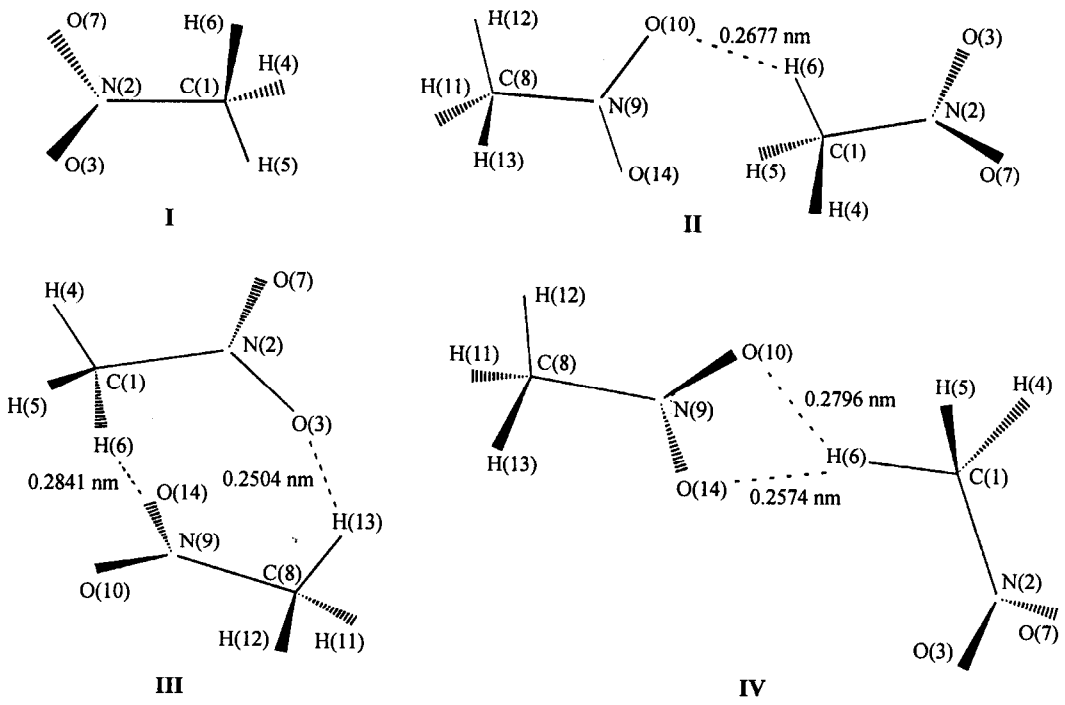

Fig. 2 Atomic numberings and optimized structures of CH_3NO_2 and of $(CH_3NO_2)_2$.

Energetics

Table 1 shows total energies (E^{MP2}, $E^{MP4SDTQ}$) and intermolecular interaction energies calculated at the MP4SDTQ/6-31G*//HF/6-31G*, where the $\triangle E_C^{ZPEC}$ (MP4SDTQ) is the $\triangle E_C$(MP4SDTQ) corrected for the zero point energy. From $E^{MP4SDTQ}$ in Table 1, it can be known that the total energy of structure **III** is 11.81 kJ·mol^{-1} lower than that of **II** and 11.97 kJ·mol^{-1} lower than that of **IV**. So the structure **III** is the most stable of three optimized structures. Though $E^{MP4SDTQ}$ is lower than E^{MP2}, for **II**, **III** and **IV** $\triangle E_C$(MP2) is nearly equal to $\triangle E_C$(MP4SDTQ), $\triangle E$(MP2) is also close to $\triangle E$(MP4SDTQ). This indicates that the MP2 interaction energy is very close to the MP4SDTQ for nitromethane dimer, which can also be concluded from previous computed results.[23, 24] These substantiate the reference's proposal.[36] Data in Table 1 show that the greatest corrected binding energy [$-\triangle E_C^{ZPEC}$ (MP4SDTQ)] of the nitromethane dimer is 17.29 kJ·mol^{-1}. For structures **II**, **III** and **IV**, $\triangle E_C^{MP4SDTQ}$ are very small (see Table 1), and the quantities of $\triangle E_C^{MP4SDTQ}/\triangle E_C^{HF}$ are −0.5%, 17% and 5.3%, respectively. Therefore, the correlation interaction energy makes a little contribution to the interaction energy. Considering that the correlation interaction energy is approximately equivalent to the dispersion energy,[16] we can conclude that the dispersion interaction in these optimized dimers is very weak.

In order to check the quality of the 6-31G* basis set, we have carried out the calculations at MP2/6-311G**//HF/6-31G* and MP2/6-311++G**//HF/6-31G* levels. The calculated results are listed in Table 1. It can be known that for structures **II**, **III** and **IV** the intermolecular interaction energies $\triangle E_C$(MP2) calculated at the MP2/6-31G*//HF/6-31G* level are very close to those at MP2/6-311G**//HF/6-31G* and MP2/6-311++G**//HF/6-31G* levels, respectively, which shows that the 6-31G* basis set may be a good basis set for the calculation of binding energy of nitromethane dimer.[10]

Conclusions

We summarize the following conclusions from our investigations: (1) The $-CH_3$ group rotates internally while two nitromethane molecules interact, and there exists no intermolecular hydrogen bond in optimized nitromethane dimers. (2) The cyclic structure **III** is the most stable of the three optimized structures, whose cor-

rected binding energy is 17.29 kJ · mol^{-1} at the MP4SDTQ/6-31G*//HF/6-31G* level. (3) In optimized nitromethane dimers, both the charge-transfer interaction and the dispersion interaction are very weak.

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(E200002038 SONG, J.P.; DONG, L.J.)