

ARTICLE

Substituent Effect on Infrared Spectra and Thermodynamic Properties of Polynitroamino Substituted Cyclopentane and Cyclohexane

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Density functional theory method was employed to study the effect of the nitroamino group as a substituent in cyclopentane and cyclohexane, which usually construct polycyclic or caged nitramines. Based on the optimized molecular structures of two groups of monocyclic nitramines at the B3LYP/6-31G** level, the infrared (IR) spectra were obtained and assigned by harmonic vibrational analysis. The calculated results agree reasonably with the available experimental data. According to the principles of statistic thermodynamics, thermodynamic properties were derived from the IR spectra, which were linearly correlated with the number of nitroamino groups as well as the temperature. The contributions of nitroamino groups to thermodynamic properties are in accord with the group additivity.

Key words: Density functional theory, Substituent effect, Monocyclic nitramine, Infrared spectrum, Thermodynamic property

I. INTRODUCTION

Cyclic nitramines, such as RDX (1,3,5-trinitro-1,3,5-triazacyclohexane) and HMX (1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane), have long played an important technological role as explosive and fuel in both civilian and military fields. There has been a significant history of interest in their structures and properties since they were first reported [1-14]. In order to obtain novel high energy density materials (HEDMs), naturally scientists have paid attention to other cyclic nitramines and have managed to attach the NO₂ group essentially needed for the combustion (so-called energetic function) to the heterocyclic rings to form energetic materials with good explosive performance [15-21]. In the past two decades, polycyclic and caged nitramines have attracted particular attention since they are expected to possess a better combination of stability, density, and detonation performances. For example, bicyclo-HMX (*cis*-2,4,6,8-tetranitro-1H,5H-2,4,6,8-tetraazabicyclooctane) [22], TNAD (*trans*-1,4,5,8-tetranitro-1,4,5,8-tetraazadecalin) [23], and HNIW (2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane, also commonly called "CL-20") [24], are the results of efforts in this direction to develop energetic materials with improved energetic properties to meet superior performance requirements. They appear to be the future candidates of HEDM to compete with RDX and HMX, which have inspired a significant history of interest [25-37].

Considering that they are all constructed by a series of monocyclic nitramines with five or six-membered ring, it is therefore of primary importance and practical significance to probe the valuable parameters of the components related to the detonation performance and to pioneer the design of new energetic materials.

As is well known, the infrared (IR) spectrum is not only a basic property of the compound, but also an effective measure to analyze or identify the substance. Besides this, the spectrum is also directly related to the thermodynamic properties of the compounds. However, to the best of our knowledge, heretofore only a little experimental data of IR spectra has been reported for the title compounds [38,39], and no systematic studies on these two series of monocyclic nitramine derivatives have been performed. Therefore, predictions of their IR spectra are of great importance for both theoretical and practical reasons. Thermodynamic properties, such as standard molar heat capacity ($C_{p,m}^{\ominus}$), standard molar entropy (S_m^{\ominus}), and standard molar enthalpy (H_m^{\ominus}), are also important parameters for the compounds and are necessary for predicting the reactive properties of chemical reactions. However, hitherto we are also not aware of any experimental results of thermodynamic properties of the title compounds.

In the present research, as an extension of the studies on the polycyclic and caged nitramines, we carried out a systematic investigation on two important types of monocyclic nitramines: the polynitroamino substituted cyclopentane and cyclohexane (Fig.1). The IR spectra were investigated by using DFT-B3LYP/6-31G** calculations and compared with the available experiments. Based on the calculated vibrational frequencies, thermodynamic properties including $C_{p,m}^{\ominus}$, S_m^{\ominus} , and H_m^{\ominus}

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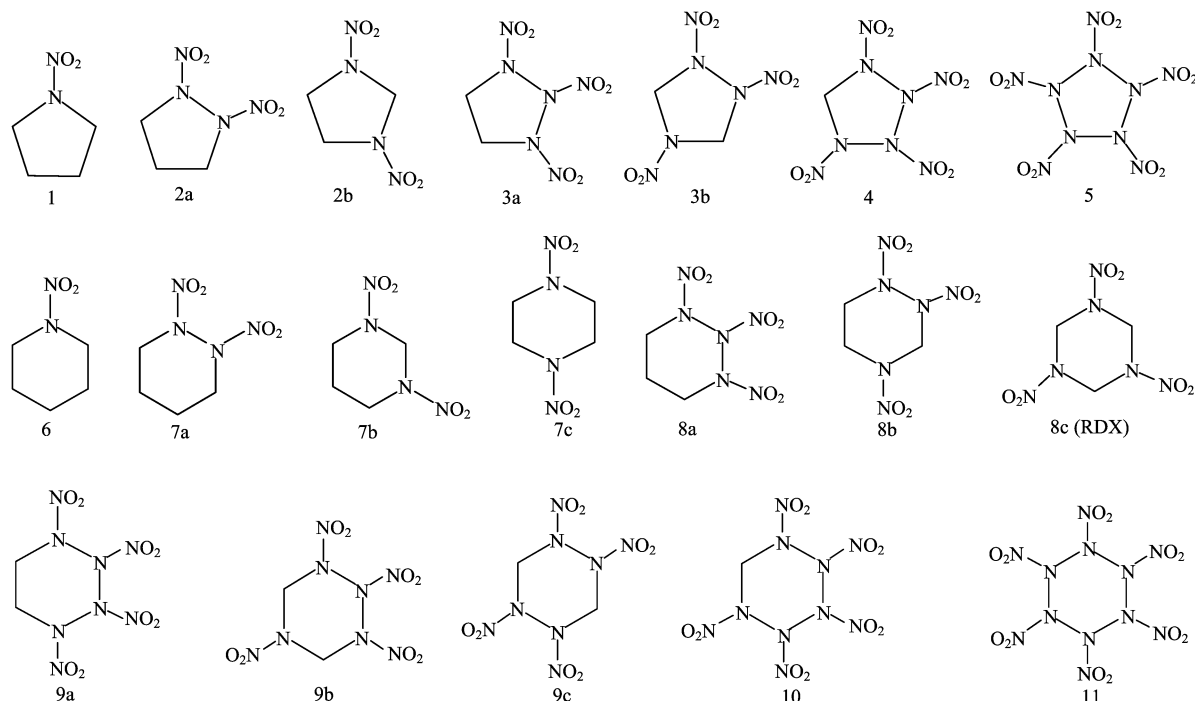


FIG. 1 The molecular structures of polynitroamino substituted cyclopentane and cyclohexane (H atoms are omitted for clarity).

were obtained from 200 K to 800 K by using the statistical thermodynamic method. The effects of the number and positions of N-NO₂ groups on the IR spectra and thermodynamic properties were studied in detail. The contributions of temperature and substituent to the thermodynamic properties were established.

II. COMPUTATIONAL METHOD

Two series of monocyclic nitramines were generated from ChemBats 3D software and fully optimized without any symmetry restrictions by the Berny method at the DFT-B3LYP level [40,41] in combination with the 6-31G** basis set [42]. To characterize the nature of stationary point and determine the zero-point vibrational energy correction, harmonic vibrational analysis was performed subsequently on each optimized structure at the same level. According to previous studies, the DFT computed harmonic vibrational frequencies are usually larger than those observed experimentally, so a scale factor of 0.96 is used uniformly to take into account the systematic overestimation of vibrational frequencies in the B3LYP/6-31G** calculations [43]. Based on the principles of statistical thermodynamics [44], thermodynamic properties ranging from 200 K to 800 K, including $C_{p,m}^{\ominus}$, S_m^{\ominus} , and H_m^{\ominus} , were derived from the scaled harmonic frequencies.

All calculations were performed with the Gaussian 03 package on a Pentium-IV personal computer using the

default convergence criteria given in the program [45].

III. RESULTS AND DISCUSSION

A. IR spectra

All the optimized structures were characterized to be true local energy minima on the potential energy surface without any imaginary frequency. The fundamental vibrational frequencies were obtained from the B3LYP/6-31G** calculations using analytical second-order derivatives at the optimized geometries, and the simulated IR spectra for the title compounds based on the scaled harmonic vibrational frequencies are presented in Fig.2, where the intensity is plotted against the frequency. Due to the complexity of vibrational modes, it is difficult to assign all bands, so only some typical vibrational modes are assigned and discussed that would facilitate assignment of the observed peaks.

Figure 2 shows that there are five main characteristic regions for both the polynitroamino substituted cyclopentane and cyclohexane excluding those without nitroamino or methylene substituent, which have two or four characteristic regions respectively. The five characteristic regions are associated with the stretching vibration of CH₂, asymmetric and symmetric stretching of NO₂, stretching of the ring skeleton, and the fingerprint region in the lower frequencies.

Usually, as the atomic mass increases, the corresponding vibrational frequency shifts toward the lower

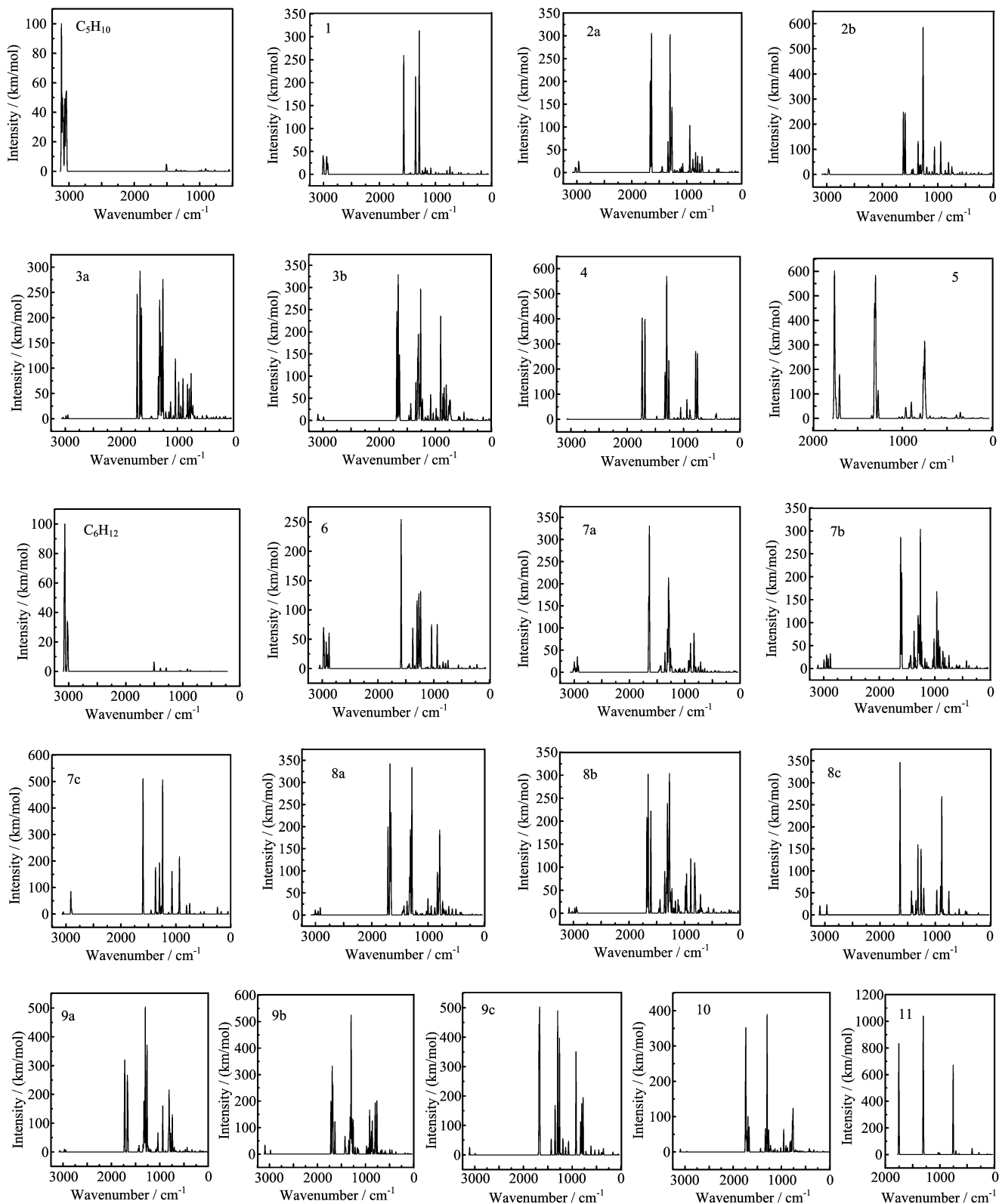


FIG. 2 IR spectra of the title compounds simulated at the B3LYP/6-31G** level.

TABLE I Comparison between theoretical and experimental IR spectra of compounds 7c and 8c^a.

	Wavenumber/cm ⁻¹	Assignment
7c	3025w(3049), 2967w(3049), 2965w(3048), 2891w(2912), 2883w(2909), 2875w(2901), 2857w(2899)	Stretching vibration of CH ₂
	1571vs(1597)	Asymmetric stretching vibration of NO ₂
	1471w(1462), 1458w(1452), 1439w(1445), 1425w(1440)	Bending vibration of CH ₂
	1386m(1382), 1384m(1370)	Symmetric stretching vibration of NO ₂
	1280m(1297), 1279m(1265), 1259s(1241), 1251m(1228)	Bending vibration of CH ₂ and stretching vibration of NO ₂
	1066w-949m (1069-934)	Stretching vibration of the ring skeleton
8c	3065vw(2959-3091)	Stretching vibration of CH ₂
	1584vs(1637)	Asymmetric stretching vibration of N-NO ₂
	1444m(1430), 1420m(1412)	Bending vibration of CH ₂
	1374m(1314), 1319s(1259), 1268s(1256)	Symmetric stretching vibration of NO ₂
	1218w(1209), 1014w(973), 910s(903), 880m(882), 845w(857), 782m(753)	Stretching vibration of the ring skeleton

^a Data in the parentheses are theoretical results; w, m, s, and vs denote the weak, medium, strong, and very strong intensities of IR spectra, respectively.

wavenumber. Since the mass of the hydrogen atom is the smallest, the symmetric and asymmetric stretching vibrations of CH₂ occur at the higher region of approximately 3000 cm⁻¹, and the number of vibrational modes equals that of C-H bonds. As for pentanitroazacyclopentane and hexanitroazacyclohexane, there is no characteristic signal in this region since they have no hydrogen atoms. The number and relative positions of N-NO₂ groups both have significant influence on the vibrational frequencies and intensities. As the number of N-NO₂ groups increases from 0 to 4 or 5, the vibrational modes of C-H shift to the higher wavenumber, and the corresponding intensities decrease. This is mainly attributed to the increase in the strong induction effect caused by the increasing nitroamino groups, which leads to the average component of s orbital in forming the C-H bond increases and the corresponding C-H bond becomes stronger. In the range of 1567-1761 cm⁻¹, the strong characteristic peaks correspond to the stretching vibration of N-N and the asymmetric stretching vibrations of N=O in the nitro groups. It is remarkable that, in this region, the number of vibrational modes is also equal to that of the N-NO₂ groups; and as the number of nitroamino groups increases, its central position moves towards a higher region, i.e. blue shift. Also noteworthy is that, there is another strong characteristic signal in the range of 1235-1370 cm⁻¹, which is associated with the stretching motion of N-N and the symmetric stretching motion of N=O in the nitro groups. With the number of N-NO₂ groups increasing, the vibrational frequencies move to lower values, i.e. red shift. Similarly, as for the parent molecules cyclopentane and cyclohexane, there is no characteristic peak in these two regions since they possess no N-NO₂ substituent. The fourth region is located at approximately 1200 cm⁻¹, which is caused by the weak bend-

ing of CH₂ and stretching of NO₂. Finally, the region less than 1200 cm⁻¹ is the fingerprint region, which can be used to identify and distinguish the isomeric configurations; and the relatively weak peaks in this region are mainly caused by the stretching and twisting of the ring skeleton, wagging and scissoring of CH₂, torsion of N-NO₂ groups, etc.

To testify the reliability of theoretical computations, the calculated frequencies were compared with the available experimental data for the compounds 7c (1,4-dinitropiperazine, i.e. *p*-DNP) and 8c (RDX), as shown in Table I. It can be seen that the calculated results are in reasonable agreement with the experimental data although there are some inconspicuous discrepancies. This is probably due to the intermolecular interactions in the experiment, which are not presented in the DFT calculations applied here. Given the solid-state effect considered, they are rather compatible as a whole. That is to say, theoretical frequencies should be compared to the gas-phase experimental results measured under low pressure. Hitherto we are not aware of any experimental measurements of the vibrational frequencies reported for other title compounds, so we hope that the computed IR spectra will stimulate experimental investigations on the gas-phase vibrational spectroscopies of the interesting molecules, and can be used as references in their detection from the reaction mixtures.

B. Thermodynamic properties

On the basis of vibrational analysis and statistical thermodynamic method, $C_{p,m}^{\ominus}$, S_m^{\ominus} , and H_m^{\ominus} ranging from 200 K to 800 K were obtained for the title compounds and listed in Table II. Firstly, as can be seen, thermodynamic functions of the polynitroamino substituted cyclopentane and cyclohexane all increase ev-

TABLE II Thermodynamic properties of the title compounds at different temperatures^a.

Compound	Function	T/K							
		200.0	273.15	298.15	400.0	500.0	600.0	700.0	800.0
C ₅ H ₁₀	$C_{p,m}^{\circ}$	60.16	81.44	89.93	125.58	157.17	183.68	205.81	224.45
	S_m°	283.17	304.88	312.38	343.81	375.31	406.38	436.41	465.14
	H_m°	9.22	14.36	16.50	27.48	41.66	58.74	78.25	99.79
1	$C_{p,m}^{\circ}$	86.61	111.74	121.13	159.26	192.24	219.44	241.69	260.08
	S_m°	315.93	346.52	356.70	397.68	436.87	474.40	509.95	543.47
	H_m°	11.75	18.97	21.88	36.18	53.80	74.43	97.53	122.64
2a	$C_{p,m}^{\circ}$	113.15	144.36	155.21	196.97	231.27	258.69	280.56	298.21
	S_m°	356.00	395.82	408.93	460.51	508.28	552.97	594.55	633.20
	H_m°	14.69	24.10	27.84	45.82	67.30	91.85	118.85	147.82
2b	$C_{p,m}^{\circ}$	111.07	141.69	152.42	194.10	228.73	256.56	278.78	296.73
	S_m°	360.32	399.40	412.28	463.01	510.17	554.42	595.70	634.14
	H_m°	14.61	23.84	27.52	45.21	66.41	90.72	117.53	146.34
3a	$C_{p,m}^{\circ}$	145.66	180.67	192.35	235.94	270.75	298.07	319.46	336.39
	S_m°	404.25	454.83	471.16	533.96	590.49	642.37	689.99	733.80
	H_m°	18.63	30.57	35.23	57.10	82.50	111.00	141.92	174.75
3b	$C_{p,m}^{\circ}$	139.66	175.82	187.89	232.80	268.51	296.41	318.17	335.35
	S_m°	402.15	451.04	466.96	528.64	584.57	636.10	683.49	727.14
	H_m°	17.98	29.52	34.07	55.56	80.69	109.00	139.77	172.48
4	$C_{p,m}^{\circ}$	174.15	214.50	227.53	274.38	310.29	337.71	358.67	374.87
	S_m°	460.92	521.23	540.58	614.24	679.50	738.61	792.31	841.31
	H_m°	22.62	36.85	42.37	68.02	97.33	129.80	164.66	201.37
5	$C_{p,m}^{\circ}$	212.23	257.39	271.34	319.52	354.90	381.22	400.91	415.78
	S_m°	503.81	576.78	599.93	686.73	762.02	829.17	889.48	944.03
	H_m°	27.00	44.21	50.82	81.03	114.84	151.71	190.86	231.73
C ₆ H ₁₂	$C_{p,m}^{\circ}$	71.57	98.54	108.84	151.63	189.67	221.81	248.74	271.48
	S_m°	280.18	306.32	315.39	353.38	391.41	428.91	465.19	499.93
	H_m°	9.33	15.51	18.10	31.38	48.49	69.11	92.68	118.72
6	$C_{p,m}^{\circ}$	98.54	129.44	140.71	186.19	225.61	258.30	285.19	307.51
	S_m°	326.37	361.55	373.37	421.14	467.04	511.16	553.06	592.65
	H_m°	12.53	20.85	24.22	40.90	61.54	85.79	113.01	142.68
7a	$C_{p,m}^{\circ}$	126.98	162.90	175.43	224.08	264.64	297.47	323.92	345.47
	S_m°	375.81	420.64	435.44	493.93	548.44	599.70	647.61	692.31
	H_m°	16.27	26.86	31.09	51.48	75.98	104.15	135.27	168.77
7b	$C_{p,m}^{\circ}$	123.41	159.50	172.08	221.11	262.17	295.46	322.29	344.12
	S_m°	369.41	413.15	427.66	485.21	539.11	589.96	637.59	682.10
	H_m°	15.59	25.92	30.07	50.14	74.37	102.31	133.24	166.60
7c	$C_{p,m}^{\circ}$	125.63	160.45	172.70	220.90	261.70	294.96	321.84	343.76
	S_m°	370.62	414.86	429.43	487.03	540.84	591.60	639.16	683.62
	H_m°	15.82	26.27	30.44	50.52	74.72	102.61	133.49	166.81
8a	$C_{p,m}^{\circ}$	155.85	198.48	212.49	264.40	305.78	338.42	364.19	384.80
	S_m°	401.96	456.88	474.87	544.79	608.41	667.16	721.34	771.36
	H_m°	18.73	31.70	36.84	61.20	89.79	122.06	157.24	194.73
8b	$C_{p,m}^{\circ}$	154.03	194.27	207.85	259.30	301.21	334.58	361.01	382.16
	S_m°	418.86	472.81	490.41	558.87	621.40	679.38	733.02	782.65
	H_m°	19.48	32.21	37.24	61.10	89.20	121.05	155.88	193.08
8c	$C_{p,m}^{\circ}$	149.26	191.01	205.00	257.58	300.11	333.80	360.40	381.64
	S_m°	415.94	468.64	485.97	553.76	615.98	673.80	727.33	776.89
	H_m°	18.87	31.31	36.26	59.89	87.86	119.62	154.38	191.52

(To be continued.)

Table II continued.

Compound	Function	T/K							
		200.0	273.15	298.15	400.0	500.0	600.0	700.0	800.0
9a	$C_{p,m}^{\ominus}$	187.05	232.76	247.56	301.50	343.74	376.56	402.07	422.12
	S_m^{\ominus}	467.18	532.31	553.34	633.89	705.89	771.59	831.63	886.68
	H_m^{\ominus}	23.61	38.98	44.98	73.04	105.38	141.47	180.45	221.70
9b	$C_{p,m}^{\ominus}$	182.31	228.71	243.76	298.61	341.54	374.86	400.72	421.01
	S_m^{\ominus}	463.59	527.34	548.02	627.58	699.02	764.37	824.17	879.06
	H_m^{\ominus}	23.07	38.12	44.03	71.74	103.84	139.73	178.56	219.69
9c	$C_{p,m}^{\ominus}$	182.85	229.11	244.06	298.67	341.52	374.82	400.66	420.94
	S_m^{\ominus}	450.78	514.68	535.40	615.01	686.45	751.79	811.59	866.47
	H_m^{\ominus}	22.56	37.64	43.56	71.29	103.39	139.28	178.10	219.22
10	$C_{p,m}^{\ominus}$	217.98	268.27	284.16	340.63	383.60	416.36	441.36	460.65
	S_m^{\ominus}	518.49	593.99	618.18	709.90	790.74	863.71	929.85	990.10
	H_m^{\ominus}	27.70	45.52	52.43	84.36	120.66	160.74	203.68	248.82
11	$C_{p,m}^{\ominus}$	252.93	307.83	324.74	383.15	426.15	458.24	482.28	500.47
	S_m^{\ominus}	568.08	655.22	682.92	786.91	877.25	957.93	1030.46	1096.10
	H_m^{\ominus}	32.23	52.79	60.70	96.89	137.45	181.75	228.84	278.01

^a Units: $C_{p,m}^{\ominus}$ in J/(mol·K), S_m^{\ominus} in J/(mol·K), and H_m^{\ominus} in kJ/mol.

idently as the temperature increases. This is because the main contributions to the thermodynamic functions come from the translations and rotations of the molecules at a lower temperature. However, with the temperature increasing, the vibrational movement is intensified and therefore makes more contributions to the thermodynamic functions. For intuitive illustration, 2b (DNCP) and 8c (RDX) were taken from the title compounds as typical examples to show the quantitative relationships between thermodynamic functions and temperature, which has been presented in Fig.3(a). The corresponding equations can be expressed as follows:

$$2b: C_{p,m}^{\ominus} = 3.5085 + 0.5851T - 2.7314 \times 10^{-4}T^2 \quad (1)$$

$$R^2 = 0.9998, \quad SD = 1.1499$$

$$S_m^{\ominus} = 246.1704 + 0.5998T - 1.4350 \times 10^{-4}T^2 \quad (2)$$

$$R^2 = 1.0, \quad SD = 0.0802$$

$$H_m^{\ominus} = -5.4865 + 0.0658T + 1.5591 \times 10^{-4}T^2 \quad (3)$$

$$R^2 = 0.9999, \quad SD = 0.6546$$

$$8c: C_{p,m}^{\ominus} = 10.1786 + 0.7693T - 3.8218 \times 10^{-4}T^2 \quad (4)$$

$$R^2 = 0.9999, \quad SD = 0.9100$$

$$S_m^{\ominus} = 261.2513 + 0.8179T - 2.1698 \times 10^{-4}T^2 \quad (5)$$

$$R^2 = 1.0, \quad SD = 0.1756$$

$$H_m^{\ominus} = -9.5291 + 0.0985T + 1.9220 \times 10^{-4}T^2 \quad (6)$$

$$R^2 = 0.9998, \quad SD = 0.9044$$

It is obvious that as the temperature increases, the increments for $C_{p,m}^{\ominus}$ and S_m^{\ominus} both decrease but that for H_m^{\ominus} increases constantly. However, since the coefficients of T^2 are very small, these correlations approximate to linear equations. In other words, thermodynamic functions of polynitroamino substituted cyclopentane and

cyclohexane increase linearly with the temperature on the whole.

On the other hand, with the increase in the number of nitroamino groups (N), thermodynamic functions of two series of cyclic nitramines all increase monotonically, as shown in Fig.3(b). The contribution of N-NO₂ groups to the thermodynamic properties matches the group additivity. With respect to the polynitroamino substituted cyclopentane, the correlation coefficients are 0.9975, 0.9965, and 0.9947 for $C_{p,m}^{\ominus}$, S_m^{\ominus} , and H_m^{\ominus} , respectively; and they increase respectively by the average values of 36.08, 58.51 J/(mol·K), and 6.86 kJ/mol with each additional nitroamino group attached. As for the polynitroamino substituted cyclohexane, the correlation coefficients of $C_{p,m}^{\ominus}$, S_m^{\ominus} , and H_m^{\ominus} are 0.9982, 0.9967, and 0.9962, respectively, and each additional nitroamino group contribute to the thermodynamic functions by 35.93, 60.51 J/(mol·K), and 7.04 kJ/mol, respectively. These correlations can be described directly by the following equations.

Polynitroamino substituted cyclopentane:

$$C_{p,m}^{\ominus} = 84.53 + 36.08N \quad (7)$$

$$R = 0.9975, \quad SD = 4.4097$$

$$S_m^{\ominus} = 299.84 + 58.51N \quad (8)$$

$$R = 0.9965, \quad SD = 8.5052$$

$$H_m^{\ominus} = 14.88 + 6.86N \quad (9)$$

$$R = 0.9947, \quad SD = 1.2292$$

Polynitroamino substituted cyclohexane:

$$C_{p,m}^{\ominus} = 102.93 + 35.93N \quad (10)$$

$$R = 0.9998, \quad SD = 3.7143$$

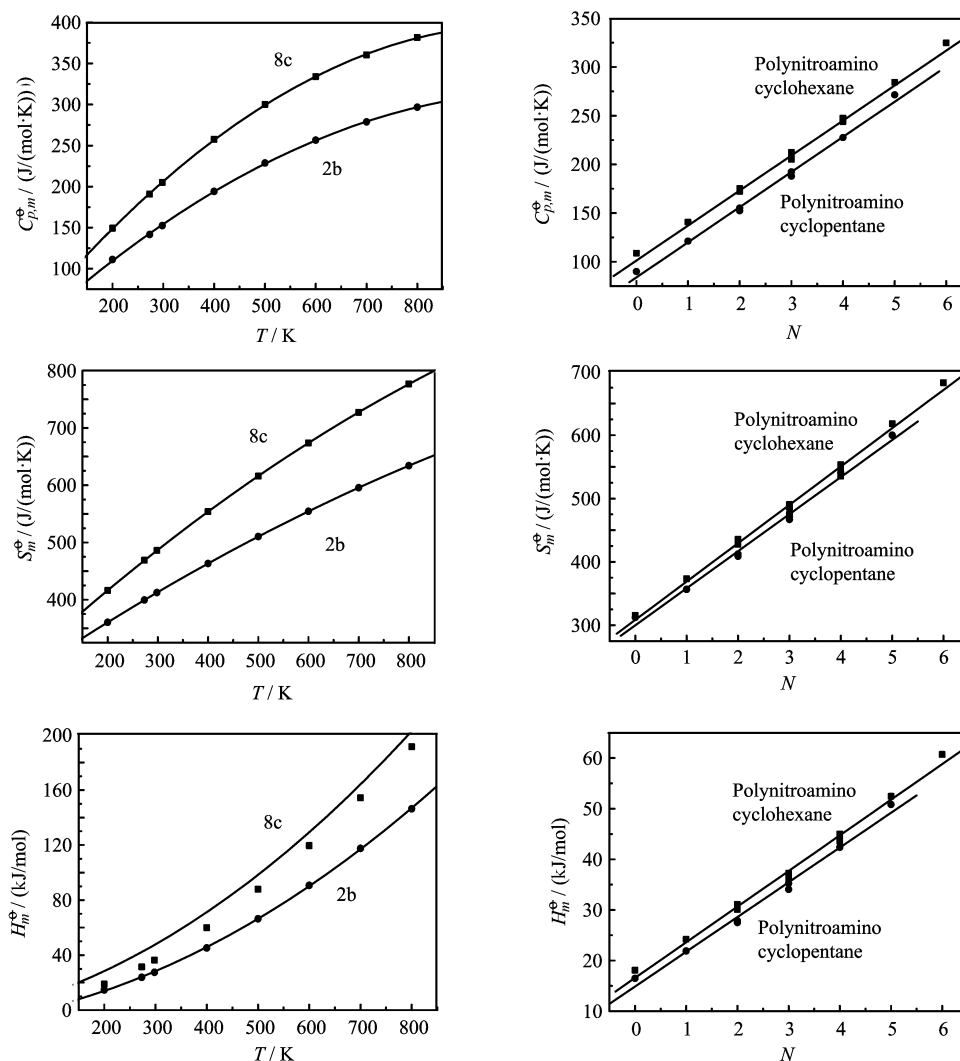


FIG. 3 Relationships between thermodynamic functions ($C_{p,m}^{\circ}$, S_m° , and H_m°) and temperature T or the number of $\text{N}-\text{NO}_2$ groups N .

$$S_m^{\circ} = 308.49 + 60.51N \quad (11)$$

$$R = 0.9967, \quad \text{SD} = 8.3923$$

$$H_m^{\circ} = 16.58 + 7.04N \quad (12)$$

$$R = 0.9962, \quad \text{SD} = 1.0525$$

Moreover, as for the isomers (such as 2a-2b, 3a-3b, 7a-7c, 8a-8c, and 9a-9c), the relative positions of $\text{N}-\text{NO}_2$ groups also have important influences on their thermodynamic properties. In general, $C_{p,m}^{\circ}$, S_m° , and H_m° all decrease as the distances between substituents increase although there is little discrepancy, which can be observed intuitively from Fig.4. This is due to the decrease in the intramolecular group interactions as the relative positions between substituents becomes farther.

IV. CONCLUSION

In this study, a detailed density functional theory study has been performed on the substituent effect on

the IR spectra and thermodynamic properties of two types of monocyclic nitramines. The major findings can be summarized as follows:

The computed IR spectra are comparable to the available experimental values, indicating that the B3LYP/6-31G** method can generate reliable geometries and properties of the polynitroamino substituted cyclopentane and cyclohexane. These fundamental data may be helpful for the identification and further studies of them.

There are five main characteristic peaks in the IR spectra of the polynitroamino substituted cyclopentane and cyclohexane excluding those with zero or five (six) $\text{N}-\text{NO}_2$ groups. They are associated with the symmetric and asymmetric stretching vibrations of $\text{C}-\text{H}$ (ca. 3000 cm^{-1}), the strong stretching of $\text{N}-\text{N}$ and asymmetric stretching of $\text{N}=\text{O}$ ($1567-1761 \text{ cm}^{-1}$), the strong symmetric stretching vibration of $\text{N}=\text{O}$ ($1235-1370 \text{ cm}^{-1}$), the weak bending of CH_2 and stretch-

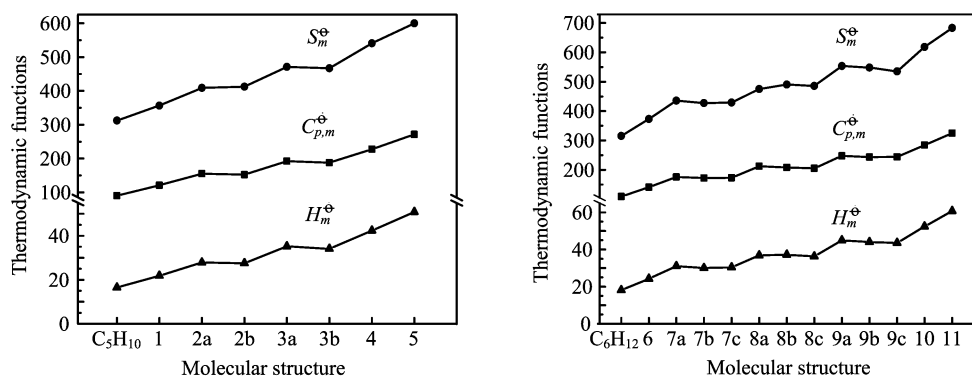


FIG. 4 Variations of thermodynamic properties with the molecular structures of the title compounds. $C_{p,m}^{\circ}$, S_m° , and H_m° in unit of J/(mol·K), J/(mol·K), and kJ/mol, respectively.

ing of NO_2 (ca. 1200 cm^{-1}), and the fingerprint region ($<1200\text{ cm}^{-1}$). As the number of N-NO_2 group increases, the vibrational modes of C-H shift to the higher wavenumber, the stretching vibration of N-N and the asymmetric stretching vibrations of N=O move towards a higher region, while the symmetric stretching motion of N=O moves to a lower region.

Thermodynamic properties ($C_{p,m}^{\circ}$, S_m° , and H_m°) of polynitroamino substituted cyclopentane and cyclohexane all increase linearly with the increasing temperature and number of nitroamino groups. The increments for heat capacities and entropies decrease while it increases constantly for enthalpies. With each additional nitroamino group attached to cyclopentane, $C_{p,m}^{\circ}$, S_m° , and H_m° increase by $36.08\text{ J}/(\text{mol}\cdot\text{K})$, $58.51\text{ J}/(\text{mol}\cdot\text{K})$, and $6.86\text{ kJ}/\text{mol}$, respectively; and those of cyclohexane increase by $35.93\text{ J}/(\text{mol}\cdot\text{K})$, $60.51\text{ J}/(\text{mol}\cdot\text{K})$, and $7.04\text{ kJ}/\text{mol}$, respectively. As for the isomers, $C_{p,m}^{\circ}$, S_m° , and H_m° decrease as the distances between substituents increase.

In conclusion, the established dependence of IR spectra and thermodynamic functions on the substituent and temperature would be helpful for further studies on the nitramine derivatives of cyclopentane and cyclohexane.

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