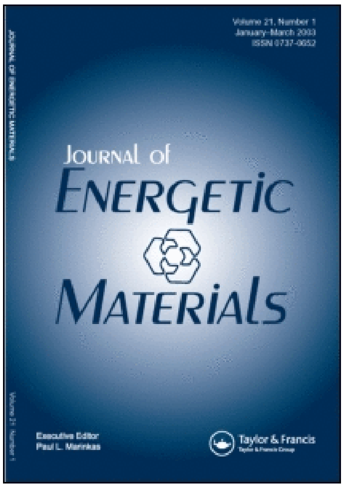

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Calculations of heats of formation for azoles with Pm3

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CALCULATIONS OF HEATS OF FORMATION FOR AZOLES WITH PM3

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ABSTRACT

We have calculated heats of formation (ΔH_f°) for azoles with the semi-empirical molecular orbital theory, PM3. SC-DSC (sealed cell differential scanning calorimetry) measurements for some azoles have been conducted and heats of reaction obtained by DSC have reflected ΔH_f°. By combining heats of sublimation obtained by the additivity rule with ΔH_f° in the gas phase obtained by PM3, ΔH_f° of azoles in the solid phase have been estimated within about ± 10 kcal/mol of observed values.

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INTRODUCTION

In order to investigate characteristics of energetic materials, their heats of formation (ΔH_f°) are indispensable. We had calculated ΔH_f° for various aromatic and aliphatic nitro compounds including nitramines and alkyl nitrates with the semi-empirical molecular orbital theory and the molecular mechanics[1-4].

Azoles are five-membered aromatic compounds with two or more heteroatoms, including at least one nitrogen. They are important compounds in chemical industries. But high-nitrogen compounds such as triazoles and tetrazoles are unstable or explosive[5]. Here we have calculated ΔH_f° of several azoles including only nitrogens as heteroatoms with semi-empirical molecular orbital theory, PM3. We have also conducted SC-DSC (sealed cell differential scanning calorimetry) measurements for some azoles and investigated the relationship between their structures and observed data.

In addition, we have attempted to estimate ΔH_f° of azoles in the solid phase by using heats of sublimation obtained by the additivity rule.

METHOD

Calculation

Molecular orbital calculations by the PM3 method were performed with MOPAC Ver. 6.01[6]. All calculations were conducted on a HITAC M-880 in the Computer Centre of the University of Tokyo.

Experiment

Azoles used here were obtained from Wako Pure Chemical Industries, Ltd., Dojin Laboratories, Ltd. and Aldrich Chem. Co.. Sample cells used were 15 μ l stainless cells made by Seiko Densi Kogyo Co. Ltd.. Shimazu DSC Model 41 was used for measuring decomposition behaviours of azoles.

About 1mg of azole was weighed in the stainless cell. A sample cell and a reference cell with Al_2O_3 were put on the cell holder and the lid of the holder was closed. The heating rate was set to 10 ℃ /minute. Flow rate of N_2 gas was adjusted to 30ml/minute. By analyzing the DSC curve using a computer, DSC on-set temperature (T_{DSC}) and DSC heat (ΔH_{DSC}) were obtained.

RESULTS AND DISCUSSION

Structure

Calculated geometries of 1H-tetrazole are shown in Table 1 with observed values for the crystal[7] and calculated values with ab initio[8]. Calculated geometries by semi-empirical MO methods except MINDO/3 correspond to those by ab initio calculations. Calculated geometries of azoles by PM3 are listed in Table 2 with observed values in the gas phase[8-9].

PM3 tends to show rather longer bond lengths for azoles, but they correspond to observed values well.

TABLE 1

Calculated Geometries for 1H-tetrazole with MO Methods

	MINDO/3	MNDO	AM1	PM3	STO-3G[8]	3-21G[8]	6-31G[8]	exp.[7]
N1-N2	1.296	1.342	1.343	1.360	1.387	1.385	1.353	1.33
N2-N3	1.230	1.275	1.282	1.276	1.310	1.278	1.270	1.30
N3-N4	1.283	1.328	1.335	1.333	1.410	1.415	1.372	1.33
N4-C5	1.331	1.352	1.360	1.351	1.320	1.299	1.304	1.30
C5-N1	1.361	1.396	1.404	1.383	1.371	1.346	1.343	1.33
N1-H1	1.038	1.004	0.992	0.989	1.025	0.994	0.989	0.98
C5-H2	1.110	1.082	1.093	1.094	1.084	1.061	1.061	1.10
N5C1N2	110.0	108.1	107.8	108.8	108.3	107.8	108.4	108.5
N1N2N3	105.5	107.4	107.5	107.5	105.8	106.5	106.6	107.6
N2N3N4	114.7	112.3	112.6	110.7	111.1	110.4	110.5	107.8
N3N4C5	106.3	107.3	106.7	109.5	105.5	105.5	106.5	109.4
N4C5N1	103.5	104.9	105.4	103.8	109.3	109.8	108.0	106.7
H-N1N2	125.5	122.6	122.8	121.5	121.7	120.6	120.7	131.0
H-C5N1	125.5	126.1	125.8	129.2	123.8	124.5	125.6	115.0
ΔH_f°	-22.0	53.8	109.7	86.3	---	---	---	80.0

units: angstrom, degree, kcal/mol

TABLE 2
Calculated Structure of Azoles with PM3

pyrrole		N1-C2	C2-C3	C3-C4	C4-C5	C5-N1	N1-H	C2-H	C3-H	C4-H	C5-H	N1C2C3	C2C3C4	C3C4C5	C4N5C1	C5N1C2
	PM3	1.396	1.389	1.421	1.390	1.397	0.985	1.089	1.086	1.086	1.089	106.9	108.3	108.0	107.0	109.8
	obs.[8]	1.370	1.382	1.417	1.382	1.370	0.996	1.076	1.077	1.077	1.076	107.7	107.4	107.4	107.7	109.8
		(angstrom)										(degree)				
pyrazole		N1-N2	N2-C3	C3-C4	C4-C5	C5-N1	N1-H		C3-H	C4-H	C5-H	N1N2C3	N2C3C4	C3C4C5	C4C5N1	C5N1N2
	PM3	1.354	1.359	1.419	1.394	1.390	0.986		1.088	1.086	1.089	107.2	108.9	106.8	105.9	111.2
	obs.[8]	1.349	1.331	1.416	1.372	1.359	0.999		1.087	1.082	1.084	104.1	111.9	104.5	106.4	113.1
imidazole		N1-C2	C2-N3	N3-C4	C4-C5	C5-N1	N1-H	C2-H		C4-H	C5-H	N1C2N3	C2N3C4	N3C4C5	C4C5N1	C5N1C2
	PM3	1.393	1.348	1.393	1.385	1.402	0.987	1.092		1.088	1.089	107.7	108.9	108.7	105.7	109.0
	obs.[8]	1.364	1.314	1.382	1.364	1.377	0.998	1.079		1.078	1.079	112.0	104.9	110.7	105.5	106.9
1H-1,2,3-triazole		N1-N2	N2-N3	N3-C4	C4-C5	C5-N1	N1-H			C4-H	C5-H	N1N2N3	N2N3C4	N3C4C5	C4C5N1	C5N1N2
	PM3	1.355	1.282	1.398	1.387	1.396	0.988			1.089	1.089	108.2	110.5	106.9	104.1	110.2
	obs.[9]	1.355	1.309	1.370	1.378	1.356						108.2	108.2	109.9	104.4	110.2
2H-1,2,3-triazole		N1-N2	N2-N3	N3-C4	C4-C5	C5-N1		N2-H		C4-H	C5-H	N1N2N3	N2N3C4	N3C4C5	C4C5N1	C5N1N2
	PM3	1.339	1.339	1.364	1.414	1.364		0.987		1.089	1.089	111.8	107.0	107.1	107.1	107.0
	obs.[9]	1.323	1.323	1.346	1.405	1.346		1.017		1.105	1.105	117.1				
1H-1,2,4-triazole		N1-N2	N2-C3	C3-N4	N4-C5	C5-N1	N1-H		C3-H		C5-H	N1N2C3	N2C3N4	C3N4C5	C4C5N1	C5N1N2
	PM3	1.360	1.351	1.387	1.353	1.383	0.987		1.092		1.093	106.5	108.8	108.4	106.0	110.3
	obs.[6]	1.381	1.328	1.354	1.280	1.375	0.998		1.078		1.078	102.7	113.0	106.8	109.0	108.5
4H-1,2,4-triazole		N1-N2	N2-C3	C3-N4	N4-C5	C5-N1			C3-H	N4-H	C5-H	N1N2C3	N2C3N4	C3N4C5	C4C5N1	C5N1N2
	PM3	1.336	1.348	1.396	1.396	1.348			1.093	0.988	1.093	110.0	106.0	108.0	106.0	110.0
1H-tetrazole		N1-N2	N2-N3	N3-N4	N4-C5	C5-N1	N1-H				C5-H	N1N2N3	N2N3N4	N3N4C5	N4C5N1	C5N1N2
	PM3	1.360	1.276	1.333	1.351	1.383	0.989				1.094	107.5	110.7	109.5	103.8	108.8
2H-tetrazole		N1-N2	N2-N3	N3-N4	N4-C5	C5-N1		N2-H			C5-H	N1N2N3	N2N3N4	N3N4C5	N4C5N1	C5N1N2
	PM3	1.340	1.278	1.333	1.278	1.340		0.990			1.093	110.4	107.5	109.4	106.5	106.1
1H-pentazole		N1-N2	N2-N3	N3-N4	N4-N5	N5-N1	N1-H					N1N2N3	N2N3N4	N3N4N5	N4N5N1	N5N1N2
	PM3	1.340	1.278	1.333	1.278	1.340	0.992					106.6	109.2	109.2	106.6	108.4

Gas-phase Heat of Formation

Gas-phase heats of formation at 298K have been calculated for azoles with PM3. Results are summarized in Table 3 with observed values[10-11]. Strictly speaking, pyrrole doesn't belong to azoles, but it is included for comparison. ΔH_f° of azoles increase with the number of nitrogen atoms and nitrogen-nitrogen bonds.

TABLE 3

Calculated Heats of Formation and Dipole Moments for Azoles with PM3

	ΔH_f°(kcal/mol)		μ (debye)	
compound	calc.	obs.[10-11]	calc.	obs.[8,12]
pyrrole	27.1	25.9	2.17	1.74
pyrazole	48.8	42.9	2.37	2.21
imidazole	31.3	31.8	3.86	3.67
1H-1,2,3-triazole	67.9		4.35	4.38
2H-1,2,3-triazole	70.7		0.30	0.22
1H-1,2,4-triazole	51.8	46.1	2.98	2.72
4H-1,2,4-triazole	51.9		5.69	
1H-tetrazole	86.3	80.0	5.41	5.30
2H-tetrazole	88.4		2.34	2.19
1H-pentazole	120.7		4.10	

Dipole moments have been also calculated and shown in Table 3. Calculated values correspond to observed values[8,12] except for pyrrole.

Our results for triazoles and tetrazoles correspond with those by Fabian[12]. PM3 can hardly estimate the correct tautomerism of triazoles and tetrazoles.

DSC measurement

T_{DSC} and ΔH_{DSC} for some azoles are shown in Table 4 with calculated and observed ΔH_f°. ΔH_{DSC} of azoles increase with the number of nitrogen atoms and N-N bonds. Measured ΔH_{DSC} correspond to ΔH_f° well. These azoles contain only C,H and N atoms. Their decomposition products are presumed to be rather simple and similar, such as N_2. So ΔH_f° can reflect heats of decomposition, though the degree of decomposition depends on the thermal stability of the compound.

The more N-N bonds the azoles have, the lower T_{DSC} are, although imidazole which has no N-N bond has lower T_{DSC} than pyrazole. Its C5-N1 bond is rather longer than those of pyrazole and 1,2,3-triazole, which may show the weakness of C5-N1 bond of imidazole.

Two-center bond energies can be calculated with PM3. Absolute values of them correspond to the dissociation energies[13]. Calculated values of azoles are listed in Table

5. Absolute values of N1-N2, N-H and C-H bond energies become smaller as the number of N-N bonds. If the decomposition of azoles begins from the cleavage of these bonds, T_{DSC} correspond to their two center bond energies. About bond lengths, similar results can be obtained, too.

TABLE 4

Results of SC-DSC Measurement for Azoles

compound	T_{DSC}(°C)	ΔH_{DSC}(cal/g)	ΔH_f°(cal/g)
pyrrole	no decomposition		404(386)
pyrazole	486	238	717(630)
imidazole	405	101	460(467)
1H-1,2,3-triazole	327	492	983
1H-1,2,4-triazole	341	284	750(667)
1H-tetrazole	190	776	1231(1141)

Observed ΔH_f° are shown in parenthesis.

Thermal decomposition of tetrazole in a melt proceeds through a reversal formation of azidoazomethyne, which lead to the breakdown of N-N bond to produce N_2 and nitrene[14]. Here, N1-N2 bond cleavage occurs at first and then N3-N4 bond breaks. Calculated N1-N2 bond length is longer than those of

TABLE 5

Calculated Two Center Energies of Azoles by PM3

pyrrole	N1-C2	C2-C3	C3-C4	C4-C5	C5-N1	N1-H	C2-H	C3-H	C4-H	C5-H
	-17.63	-19.17	-17.49	-19.16	-17.62	-13.03	-13.55	-13.36	-13.37	-13.55
pyrazole	N1-N2	N2-C3	C3-C4	C4-C5	C5-N1	N1-H		C3-H	C4-H	C5-H
	-15.50	-18.39	-17.65	-18.83	-17.86	-12.92		-13.31	-13.43	-13.52
imidazole	N1-C2	C2-N3	N3-C4	C4-C5	C5-N1	N1-H	C2-H		C4-H	C5-H
	-17.35	-18.82	-16.62	-19.44	-17.27	-12.96	-13.50		-13.36	-13.59
1H-1,2,3-triazole	N1-N2	N2-N3	N3-C4	C4-C5	C5-N1	N1-H			C4-H	C5-H
	-14.91	-18.05	-16.51	-19.23	-17.37	-12.84			-13.44	-13.55
1H-1,2,4-triazole	N1-N2	N2-C3	C3-N4	N4-C5	C5-N1	N1-H		C3-H		C5-H
	-15.15	-18.63	-16.72	-18.39	-17.65	-12.84		-13.27		-13.45
1H-tetrazole	N1-N2	N2-N3	N3-N4	N4-C5	C5-N1	N1-H				C5-H
	-14.64	-18.20	-15.33	-18.49	-17.37	-12.78				-13.48

unit:eV

pyrazole and 1H-1,2,3-triazole. Absolute values of calculated two center energies for N1-N2 and N3-N4 bonds are also small. In the gaseous state N_2 eliminates from the cyclic 2H-form, and remaining intermediate decomposes to form HCN,N_2 and H_2. Here, N2-N3 bond and N4-C5 bonds break. Calculated two center energies of 2H-tetrazole are -15.39 eV for N2-N3 and -16.57 eV for N4-C5.

From these results, bond lengths and two-center energies from the energy partitioning obtained by PM3 can correspond to the bond strength for similar kinds of compounds.

Condensed-phase Heat of Formation

Various kinds of methods had been developed to estimate ΔH_f° in the condensed state[15-17]. We had attempted to estimate ΔH_f° of nitro compounds in condensed phases by combining heats of vaporization(ΔHv) and heats of sublimation(ΔHs) obtained by the additivity rule[18-19] with ΔH_f° in the gas phase obtained by PM3 and MM2$^{(')\,3-4}$. Here we adopted the same procedure. Estimated ΔH_f° of azoles in the solid phase are shown in Table 6 with observed values[10-11,20]. For tetrazoles, calculated ΔH_f° are usually a little overestimated. The uncertainty is within about ± 10 kcal/mol. These results show that ΔH_f° calculated with PM3 are accurate enough for using the estimation of heats of reaction for azoles.

TABLE 6

Calculated Heats of Formation for Azoles in the Solid Phase

Compound	ΔH_f°(kcal/mol) Calc.	Obs.[10-11, 20]
1-phenyl-1H-pyrrole	29.8	36.9
2-phenyl-1H-pyrrole	25.5	33.3
1H-pyrazole	32.6	27.7
1H-imidazole	11.4	14.0
1-acetylimidazole	-37.7	-28.6
1H-1,2,4-triazole	30.1	26.0
3-amino-1,2,4-triazole	20.8	18.4
1H-tetrazole	64.7	56.7
1,5-dimethyltetrazole	47.5	45.1
1-phenyltetrazole	84.1	86.5
1-acetyltetrazole	16.6	19.5
5-phenyl-1H-tetrazole	78.5	70.0
1-phenyl-5-methyltetrazole	72.2	69.2
2-phenyl-5-methyltetrazole	74.3	65.7
1-methyl-5-phenyltetrazole	74.9	70.0
5-amino-1H-tetrazole	55.8	50.0
5-cyano-1H-tetrazole	98.9	96.1
5-methoxy-1H-tetrazole	22.4	16.5
1,5-diphenyltetrazole	100.3	99.4
2,5-diphenyltetrazole	101.5	94.5
1-methyl-5-aminotetrazole	51.6	46.3
2-methyl-5-aminotetrazole	53.3	50.4
1-phenyl-5-aminotetrazole	76.7	74.3
1-allyl-5-aminotetrazole	68.5	63.4
2-allyl-5-aminotetrazole	70.3	67.6
2,2'-dimethyl-5,5'-azotetrazole	171.5	180.3
5,5'-bis-1H-tetrazole	137.8	127.1

CONCLUSIONS

Heats of formation for azoles have been calculated with the semi-empirical molecular orbital theory, PM3. It can estimate gas-phase ΔH_f° at 298k within ± 8 kcal/mol of the observed values. From SC-DSC measurements, ΔH_f° for azoles correspond to ΔH_{DSC} well. ΔH_f° for azoles in the solid phase can be estimated within about ± 10 kcal/mol of the observed values by using heats of sublimation calculated with the additivity rule. This method would be accurate enough to estimate energy hazards of azoles.

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