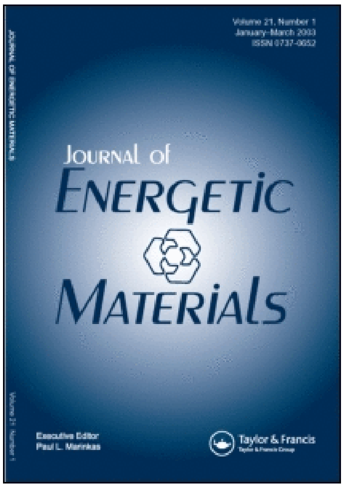

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CALCULATIONS OF HEATS OF FORMATION FOR NITRO COMPOUNDS BY SEMI-EMPIRICAL MO METHODS AND MOLECULAR MECHANICS

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ABSTRACT

Heats of formation (ΔH_f°) for nitro compounds have been calculated with the semi-empirical molecular orbital theory and the molecular mechanics. Semi-empirical MO method PM3 and molecular mechanics MM2 can estimate ΔH_f° accurately enough for practical use. However, accurate ΔH_f° can't be calculated by MM2 for tetranitromethane which has spatially very crowded structure.

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INTRODUCTION

Energetic materials decompose, ignite and explode by the heat and the impact. In order to investigate characteristics of energetic materials, it is indispensable to obtain their heats of formation(ΔH_f°). For example, heats of explosion are calculated with ΔH_f°. In addition to experimental measurements, ΔH_f° can be estimated with several calculation methods such as the additivity rule[1]. Experiments for measuring ΔH_f° of energetic materials are sometimes not so precise. Calculative methods are helpful in that case. We attempted to calculate ΔH_f° for nitro compounds by the semi-empirical molecular orbital theory and the molecular mechanics, and results of two methods are compared.

METHOD

The programs used are MOPAC(Molecular Orbital Package) version 5.0 and MM2[2](Molecular Mechanics 2). For semi-empirical MO calculation, AM1[3] and PM3[4] methods are selected from MOPAC.

In MM2, parameters for the nitro group are not prepared. Tanabe et al.[5] decided these parameters in MM2'(partly revised version of MM2) from the experimental data of some nitro compounds. We applied their parameters to MM2. For the parameters they have not determined, we used similar ones in MM2.

For the initial geometry, standard structures calculated by CHEMOGRAM[6] were used. Then the structure is optimized by each program and the geometry with minimum energy is found.

All calculations were conducted on a HITAC M-682H in the Computer Centre of the University of Tokyo. We used MM2 program installed by Prof. E.Osawa of Hokkaido University. Calculations are done for nine nitro paraffins and nine nitro aromatics.

RESULTS and DISCUSSION

Structure

Calculated bond length and bond angle for p-nitrotoluene are shown in Table 1. Fairly good molecular geometry is

TABLE 1

Calculated Geometry of p-Nitrotoluene with Several Methods

method	C-CH_3	C-N	N-O(A)	C-N-O	O-N-O(degree)
obs.[7]	1.528	1.482	1.243	118.5	122.8
AM 1	1.480	1.484	1.203	119.0	122.0
PM 3	1.485	1.495	1.216	119.5	121.0
MM 2	1.509	1.495	1.224	118.1	123.8

obtained by all three methods. Especially, MM2 can predict good geometry with less calculation time.

Heat of Formation

Gas-phase heats of formation at 298K are calculated for 18 nitro compounds with three methods. Results are summarized in Table 2. Observed values are quoted from references[7-9].

Fig.1 shows ΔH_f^0 calculated by semi-empirical MO methods. For all the compounds calculated here, values obtained by PM3 are closer to observed ones than those by AM1. Davis et al.[10] calculated physical properties for 105 nitro compounds by semi-empirical MO methods MINDO/3, MNDO and AM1. They investigated the performance of each method in detail and concluded that MINDO/3 predicts ΔH_f^0 more accurately than MNDO and AM1. Stewart[4] calculated properties of 763 compounds to estimate the performance of PM3. For 26 nitro-organic compounds and three organic nitrates, the average differences between calculated and observed ΔH_f^0 are 5.2 kcal/mol for PM3 and 15.7 for AM1.

As the discrepancy between observed and calculated values has a certain bias in AM1, correction by subtracting the constant value per one nitro group from the calculated ΔH_f^0 was conducted by Hwang et al[11]. By that correction, calculated ΔH_f^0 by AM1 becomes closer to observed one.

TABLE 2

Calculated Heats of Formation for Nitro Compounds

Compound \ ΔH_f°	obs.	AM1	PM3	MM2
Nitroethane*+	-24.38	-16.80	-20.84	-23.10
1-Nitropropane*+	-29.98	-23.57	-26.30	-28.83
2-Nitropropane*	-33.21	-21.30	-26.30	-30.98
1-Nitrobutane*+	-34.39	-28.10	-31.65	-34.60
2-Nitrobutane*	-39.11	-27.56	-31.68	-36.63
1,1-Dinitropropane*	-25.84	-8.64	-20.31	-22.45
Dinitromethane*+	-14.06	3.39	-11.78	-11.11
Trinitromethane*+	-0.35	25.35	-4.32	-8.85
Tetranitromethane*	19.20	53.49	6.50	-60.91
1,3,5-Trinitrobenzene	13.40	44.98	6.95	10.21
2,4,6-Trinitrotoluene*	12.30	41.39	4.35	9.98
o-Dinitrobenzene	20.20	38.61	15.26	22.80
m-Dinitrobenzene*	11.30	33.13	9.22	11.98
p-Dinitrobenzene	13.30	33.30	10.14	11.32
o-Nitrotoluene*	9.30	21.46	9.60	8.67
m-Nitrotoluene	4.10	17.63	5.10	6.86
p-Nitrotoluene	7.40	17.28	4.70	6.88
Nitrobenzene*+	16.10	25.30	14.50	14.90

unit:kcal/mol

*:the nitrocompouds used to determine the parameters of PM3[4]

+:the nitrocompouds used to determine the parameters of MM2[5]

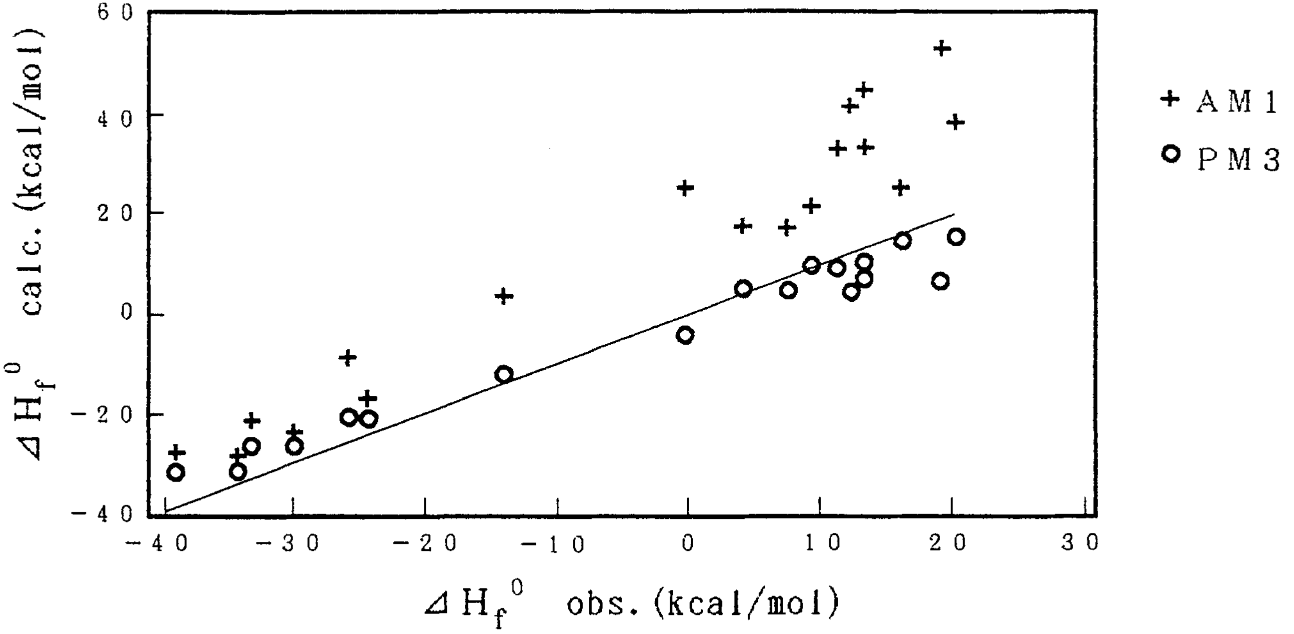

FIGURE 1
Calculated Heats of Formation by AM1 and MM2

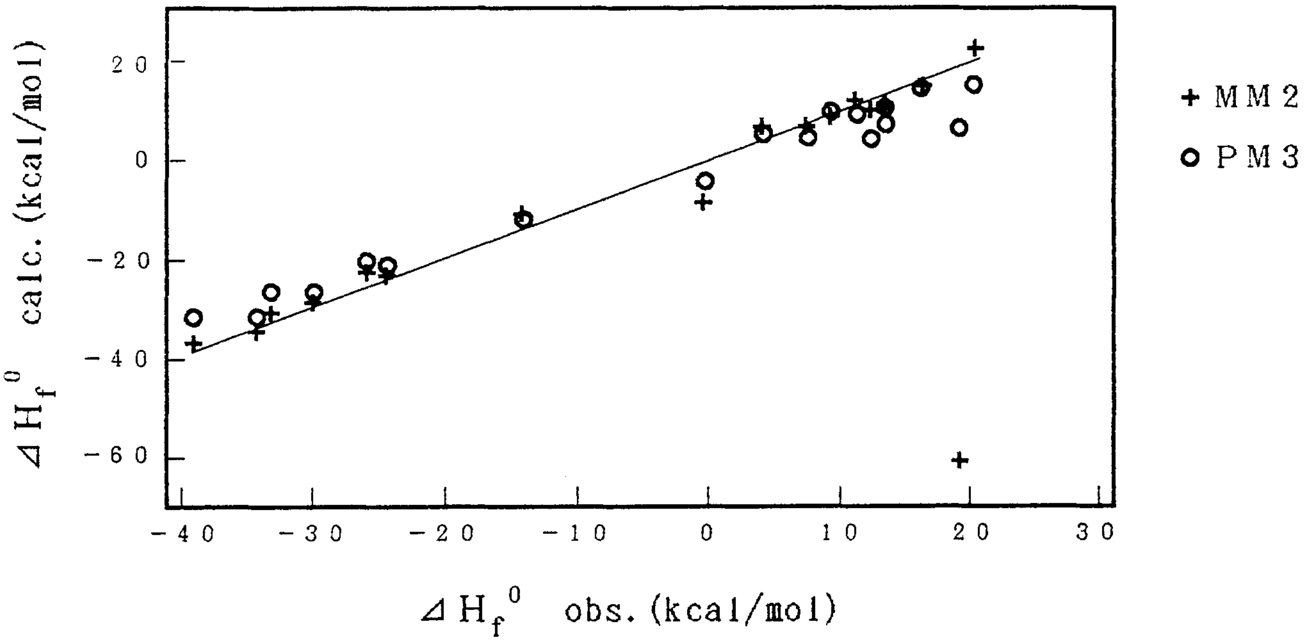

FIGURE 2
Calculated Heats of Formation by PM3 and MM2

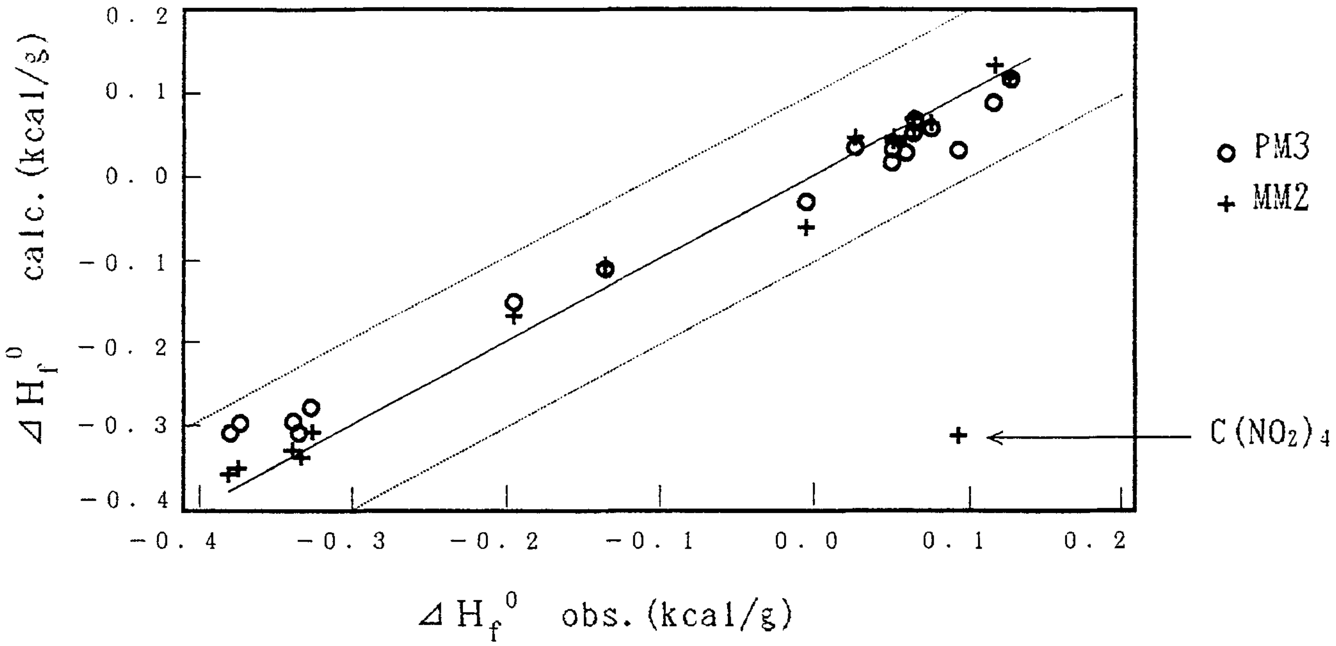

FIGURE 3
Calculated Heats of Formation by PM3 and MM2

Fig.2 shows ΔH_f° calculated by PM3 and MM2. Both methods turned out to estimate ΔH_f° very accurately. However, estimated ΔH_f° of tetranitromethane by MM2 is very much different from the observed value. Nitro groups of tetranitromethane are spatially very crowded and steric energy can't be appropriately evaluated in MM2. PM3 also predicts that ΔH_f° for tetranitromethane is most different from observed one.

In Fig.3, ΔH_f° is expressed by kcal/g, which is popularly used for explosives. ΔH_f° is calculated within ± 0.07 kcal/g from the observed value by PM3 ,and ± 0.06 kcal/g by MM2 except tetranitromethane. It shows that ΔH_f° calculated by PM3 and MM2 is accurate enough for their practical use. The number of nitro compounds used to determine parameters are 1 for AM1, 26 for PM3 and 7 for MM2'. Some of them are marked in Table 2. This reflects the advantage of PM3 in calculating ΔH_f°. Comparatively, satisfactory results are obtained by MM2 with less calculation time.

Sana et al.[12] studied the heats of formation for some nitro compounds using isodesmic procedure. They showed that ΔH_f° of nitro substituted paraffin increases quasilinearly for the number of NO_2. They introduced the concept of stabilization energy which measures the special effects due to bond interactions, electron delocalization etc. and pointed out that NO_2 substituent produces large destabilization energy. To estimate ΔH_f^0 of larger molecules, they also devised the concept of group energy, which contains the bond energies and the contribution of stabilization energy.

In general, deviation from simple additivity in ΔH_f^0 is large for nitro compounds. Steric energy estimated in MM2 calculation compensates for it. In this sense, the approach of Sana et al.[12] is similar to MM2 method.

CONCLUSIONS

Heats of formation for nitro compounds have been calculated with the semi-empirical molecular orbital theory and the molecular mechanics. Semi-empirical MO method PM3 and molecular mechanics MM2 can estimate ΔH_f^0 more accurately than AM1. But for polynitro compounds such as tetranitromethane in which multi-nitro groups are on one carbon atom, ΔH_f^0 can't be predicted accurately because of high steric energy.

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