## Theoretical studies on conformation of DPT and its nitrolysis

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The equilibrium geometries and electronic structure of DPT (dinitropentamethylenetetramine) and protonated DPT, (DPT + H<sup>+</sup>) system, have been completely optimized and calculated by MNDO method in quantum chemistry. The quantitative description of energy change from the "boat-boat" to the "chair-chair" conformation was made according to the calculated results of DPT. The selectivity of nitrolysis of DPT in various medium was discussed by comparison between the bond orders of bridge C-N and ring C-N bonds of DPT and protonated DPT.

## Introduction

DPT is an intermediate for the synthesis of the well-known explosives HMX (cyclotetramethylenetetranitramine) and RDX (cyclotrimethylenetrinitramine). Its crystal structure, conformation and the preparation of HMX and RDX through DPT nitrolysis have all along been studied theoretically and experimentally<sup> $1 \sim 5$ </sup>. However there are yet various views on such problems : why do different nitrating agents and conditions, such as temperature and reactant concentrations, cause great difference in yield ratio of HMX-RDX mixture? Does the selectivity exist in the nitrolysis of DPT at all? This paper deals with the conformation and its transition of DPT through completely optimizing calculations using MNDO energy gradient method<sup>6~7</sup>). According to obtained electronic structures of DPT and protonated DPT, i. e., (DPT + H<sup>+</sup>) system, the selective nitrolysis of DPT in different mediums was discussed by comparison between the relative strengths of bridge C-N and ring C-N bonds.

Equilibrium geometry and conformation transition of DPT

ty, the MINDO/3 calculation result is not repoted in this paper. The obtained equilibrium geometry of DPT with MNDO completely optimized calculation is shown in Fig. 1 and Table 1. The geometry parameters of DPT framework are shown in Table 2 together with the experimental values. We see from Table 1 and Table 2, the calculation result is in conformity with the crystal structure<sup>1-2)</sup> from X - ray diffraction in terms of the "chair-chair" conformation of system and the corresponding bond lengths, bond angles and torsion angles. A greater difference lies in the fact that the dihedral angles between the two  $N-NO_2$  group planes and their adjacent C-N-Cplane are approximately 34° and 26', thus making one of the nitro groups in a "axial form". On the other hand, the two corresponding torsion angles of our calculation are 10.8° and 11.5° respectively (see Table 1). This means there exist two equatorial nitro group. The "chair-chair" conformation, in general. is the stabler conformation required by bicyclo [3. 3.1] nonane system<sup>2)</sup>. The calculated dipole moment of DPT is 6.36D, which also agrees closely with the

The equilibrium geometry and electronic structure

of DPT have been calculated using the MINDO/38)

and MNDO<sup>6)</sup> methods. The results obtained with both

methods are consistent with each other. For simplici-

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reference value of  $(6.9 \pm 0.3)$  D<sup>3)</sup>. At equilibrium configuration of DPT the molecular total energy amounts to -3304.0510eV, and the heat of formation is 371.62kJ/mol. If calculating "chair-chair" conformation with one equatorial but other axial nitro group, however, the molecular total energy might account for -3304.0315eV, and the heat of formation

373.51kJ/mol. If beginning with "boat-boat" geometry as trial calculation, the MNDO program will automatically optimized into "chair-chair" conformation. Fig. 2 shows quantitatively the energy change of system from "boat-boat" conformation with two equatorial nitro groups (I) or with two axial nitro groups (II) to "chair-chair" conformation with two



Fig. 1 DPT (with two pseudo-atoms A and B)



equatorial nitro group (III). Electronic structure of DPT and  $(DPT + H^+)$  system

Fig. 3 shows the electronic structure of DPT at its equilibrium geometry. For simplicity, in the view of molecular symmetry, we only give the net charge on some atoms (left upper part) and the Wiberg bond orders between some atoms (right lower part). It can be seen from Fig. 3 that the bond order is 0.925 for bridge C-N bond (Bond b), and 0.957 for ring C-N bond (Bond a). This shows that Bond a is stronger than Bond b in DPT molecule. For the same type of bond in a molecule, the bond length and bond order could be used to measure parallel the strength of the

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Bond length(Å)		Bond angle(*)		Torsion angle(°)	
A*-C(9)	1.000				
B*-A	1.000	BAC(9)	90.00	N(1)C(9)AB	
N(1)-C(9)	1.478	N(1)C(9)A	127.69	N(1)C(9)AB	0.00
N(5)-C(9)	1.478	N(5)C(9)A	127.69	N(5)C(9)AB	180.00
C(2)-N(1)	1.471	C(2)N(1)C(9)	112.31	C(2)N(1)C(9)N(5)	-67.74
C(4)-N(5)	1.471	C(4)N(5)C(9)	112.31	C(4)N(5)C(9)N(1)	67.87
C(8)-N(1)	1.471	C(8)N(1)C(9)	112.31	C(8)N(1)C(9)N(5)	67.93
C(6)-N(5)	1.471	C(6)N(5)C(9)	112.31	C(6)N(5)C(9)N(1)	-67.75
N(3)-C(2)	1.505	N(3)C(2)N(1)	109.96	N(3)C(2)N(1)C(9)	52.33
N(7)-C(6)	1.505	N(7)C(6)N(5)	109.96	N(7)C(6)N(5)C(9)	52.26
N(12)-N(3)	1.387	N(12)N(3)C(2)	118.54	N(12)N(3)C(2)C(4)	202.16
N(13)-N(7)	1.387	N(13)N(7)C(6)	118.54	N(13)N(7)C(6)C(8)	202.24
O(14)-N(12)	1.211	O(14)N(12)N(3)	118.61	O(14)N(12)N(3)C(2)	10. 82
O(15)-N(12)	1.211	O(15)N(12)N(3)	118.61	O(15)N(12)N(3)C(2)	171.06
O(16)-N(13)	1.211	O(16)N(13)N(7)	118.61	O(16)N(13)N(7)C(6)	-11.47
O(17)-N(13)	1.211	O(17)N(13)N(7)	118.61	O(17)N(13)N(7)C(6)	170.61
H(18)-C(9)	1.118	H(18)C(9)N(1)	111.65	H(18)C(9)N(1)N(5)	120.98
H(19)-C(9)	1.118	H(19)C(9)N(1)	111.65	H(19)C(9)N(1)N(5)	239.11
H(20)-C(2)	1.121	H(20)C(2)N(1)	108.98	H(20)C(2)N(1)N(3)	122.06
H(21)-C(2)	1.121	H(21)C(2)N(1)	108.96	H(21)C(2)N(1)N(3)	239.37
H(22)-C(4)	1.121	H(22)C(4)N(5)	108.98	H(22)C(4)N(5)N(3)	120.48
H(23)-C(4)	1.121	H(23)C(4)N(5)	108.96	H(23)C(4)N(5)N(3)	237.88
H(24)-C(8)	1.121	H(24)C(8)N(1)	108.98	H(24)C(8)N(1)N(7)	120.55
H(25)-C(8)	1.121	H(25)C(8)N(1)	108.96	H(25)C(8)N(1)N(7)	238.02
H(10)-C(6)	1.121	H(10)C(6)N(5)	108.98	H(10)C(6)N(5)N(7)	122.05
H(11)-C(6)	1.121	H(11)C(6)N(5)	108.96	H(11)C(6)N(5)N(7)	239.41

Table 1 Equilibrium geometry of DPT from MNDO calculation.

\*A and B are pseudo-atoms for suitable calculations





Bond length(Å)			Bond angle(*)			Torsion angle(*)		
	MNDO	X-ray <sup>(b)</sup>		MNDO	X – ray <sup>(b)</sup>		MNDO	X-ray <sup>(b)</sup>
N(1) -C(2)	1.471	1.445	C(4)N(5)C(9)	112.3	109.9	C(4)N(5)C(9)N(1)	67.87	57
C(4) -N(5)	1.471	1.448	C(9)N(1)C(2)	112.3	109.8	N(5)C(9)N(1)C(2)	-67.74	- 59
C(2) - N(3)	1.505	1.485	N(1)C(2)N(3)	110.0	109.2	N(3)C(4)N(5)C(9)	-52.26	-47
N(3)-C(4)	1.504	1.493	N(3)C(4)N(5)	110.0	110.4	C(9)N(1)C(2)N(3)	52.33	50
			C(2)N(3)C(4)	119.2	118.0			
N(5)-C(6)	1.471	1.452				C(8)N(1)C(9)N(5)	67.87	55
C(8) - N(1)	1.471	1.452	C(8)N(1)C(9)	112.3	110.3	N(1)C(9)N(5)C(6)	-67.74	-57
C(6) -N(7)	1.505	1.485	C(9)N(5)C(6)	112.3	109.3	N(7)C(8)N(1)C(9)	- 52.26	-47
N(7)-C(8)	1.505	1.490	N(5)C(6)N(7)	110.0	113.4	C(9)N(5)C(6)N(7)	52.33	48
			N(7)C(8)N(1)	110.0	113.9			
N(5)-C(9)	1.479	1.471	C(6)N(7)C(8)	119.2	113.2	N(3)C(4)N(5)C(6)	80.75	72.4
C(9) - N(1)	1.479	1.465				C(4)N(5)C(6)N(7)	- 80.75	-69.0
			C(4)N(5)C(6)	117.6	114.1	N(7)C(8)N(1)C(2)	80.75	73.0
			C(8)N(1)C(2)	117.6	114.2	C(8)N(1)C(2)N(3)	- 80.75	-70.0
			N(5)C(9)N(1)	104.4	110.4			

Table 2 MNDO computed and X-ray exprimental geometory of DPT framework<sup>(a)</sup>.

(a) See Fig.1 for labeling of atoms

(b) Ref. 1) and 2)

bond. Because the results from X-ray studies and our calculations (see Talbe 1) show that the lengths of bridge C-N bonds are longer than those of ring C-N bonds, i. e., Bond b is longer than Bond a, it also proves Bond a to be stronger.

As DPT could be protonated in strong acid medium, the equilibrium geometry and electronic structure of (DPT +  $H^+$ ) system, the protonated DPT, has also



Fig. 3 Net charge (left upper part) and bond order (right lower part) of DPT from MNDO calculation.

## Selectivity of nitrolysis of DPT

DPT can be prepared readily from the nitrolysis of

been calculated. The bond lengths and the Wiberg bond orders are listed in Fig. 4. The length of bridge C-N bond (Bond b) is 1.453 Å, and the bond order 1.003. The length of ring C-N bond (Bond a), however, is 1.482 Å and its bond order, 0.932. As compared with Bond a, the bond length of Bond b is smaller, and the bond order greater, so Bond b is stronger than Bond a.



Fig. 4 Bond length (Å) and bond order (in parenthesis) os (DPT + H<sup>+</sup>) system from MNDO calculation.

hexamine and is an intermediate in the synthesis of HMX and RDX. This can be shown as follows.



Bachmann<sup>4)</sup> found that when ammonium nitrate is present in nitric acid-acetic anhydride mixture, the nitrolysis of DPT results in HMX containing a small amount of RDX. He thought that the unsymmetrical bond, i. e. bridge C-N bond (Bond b) breaks first, and that the formation of RDX may result from ring closure of a fragment containing three nitramine groups or may be attributed to Ross – Schiessler synthesis involving formaldehyde from acetoxymethyl group. Our calculation results (see Fig. 3) is in agreement with Bachmann's viewpoint that Bond b breakage is preferrable to Bond a in DPT.



Castorina et al.<sup>5)</sup> came to the conclusion from their <sup>14</sup>C tracer studies that both the degradation of hexamine to low molecular weight species during the first stage and the degradation of DPT to cyclic methylenenitramines during the second stage are nonselective. They thought that the ratio of HMX to RDX is therefore, not controlled by a selective cleavage of a large molecule, but is more likely influenced by particular conditions controlling the recombination of a common methylene-containing fragment.

The result from the nitrolysis of hexamine of DPT, especially the ratio of HMX and RDX, is influenced by some factors, such as nitrating agents, temperature and reactant concentrations, and the real nitrolysis mechanism is quite complicated. The conclusions microscopically by Bachmann and Castorina from their experiments are of opposite views, but essentially, objective reality of nitrolysis appears to have been partially revealed from different sides.

As for the nitrolysis of DPT in strong acid medium with HNO<sub>3</sub> or with HNO<sub>3</sub>-NH<sub>4</sub>NO<sub>3</sub> mixture, the electrophilic reagent H<sup>+</sup> together with NO<sub>2</sub><sup>+</sup> is likely to competitively attack nucleophilic atom N of the bridgehead. If protonated DPT is formed first, as shown in Fig. 4 the C-N bond of non-protonated edge (Bond b) might be strengthened, i. e. Bond b is stronger than Bond a, and Bond a becomes relatively easy to break. Thus RDX could be obtained in good yield with HMX reduced greatly. This is the experimental result from the nitrolysis of hexamine (via DPT) by what is called "direct method". In this case, the selective cleavage during the nitrolysis can not be neglected, and the reaction might go as follows :

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DPTのニトロ化分解におけるコンフォメーションに関する理論的研究

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DPT(ジニトロベンタメチレンテトラミン)とプロトン化DPTにつき,その最適平衡構造と電子状態を分子軌道法(MNDO法)を用いて計算した。この結果から,DPTにおける「舟-舟」コンフォメーションと「椅子-椅子」コンフォメーションのエネルギー差を定量的に評価した。また,異る溶媒下でのDPTのニトロ化分解の選択性について,分子内のbridge C-N と ring C-N の結合次数(計算値)の比較から検討した。

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