



reference value of  $(6.9 \pm 0.3)D^9$ . At equilibrium configuration of DPT the molecular total energy amounts to  $-3304.0510\text{eV}$ , and the heat of formation is  $371.62\text{kJ/mol}$ . If calculating "chair-chair" conformation with one equatorial but other axial nitro group, however, the molecular total energy might account for  $-3304.0315\text{eV}$ , and the heat of formation

$373.51\text{kJ/mol}$ . 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

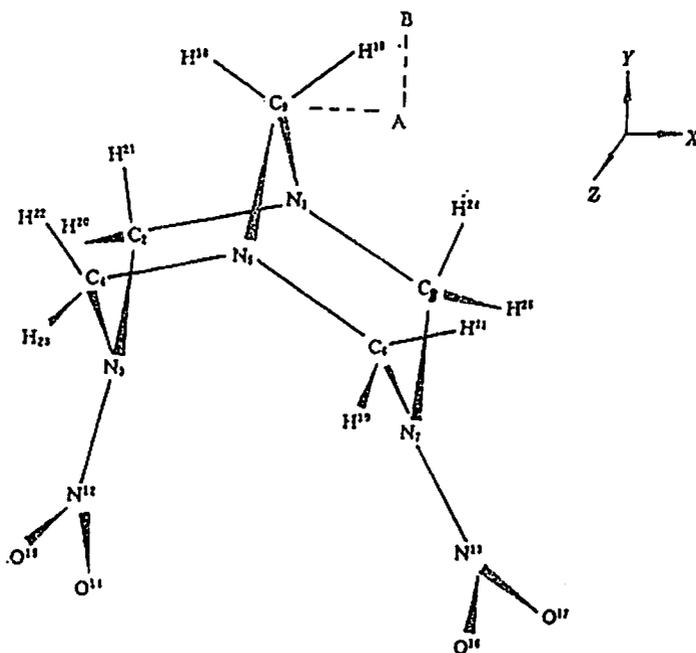
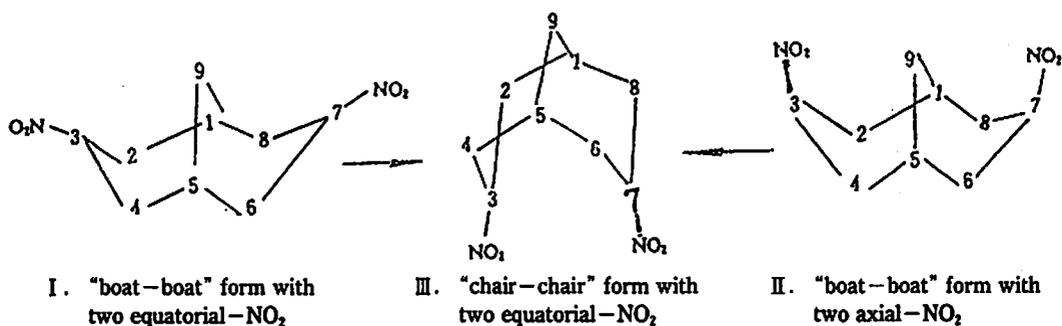


Fig. 1 DPT (with two pseudo-atoms A and B)



equatorial nitro group (III).

Electronic structure of DPT and  $(\text{DPT} + \text{H}^+)$  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

Table 1 Equilibrium geometry of DPT from MNDO calculation.

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

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

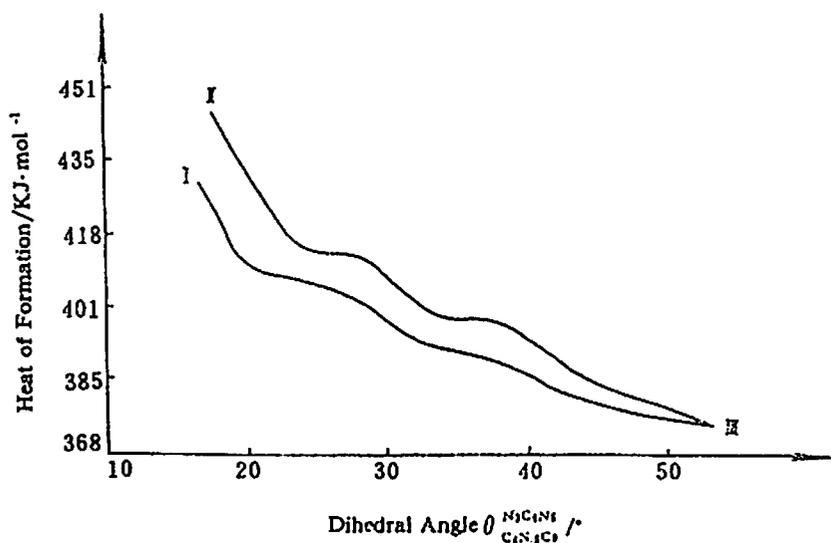


Fig. 2 Conformation transition of DPT.

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

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			

(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 Table 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<sup>+</sup>) system, the protonated DPT, has also

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.

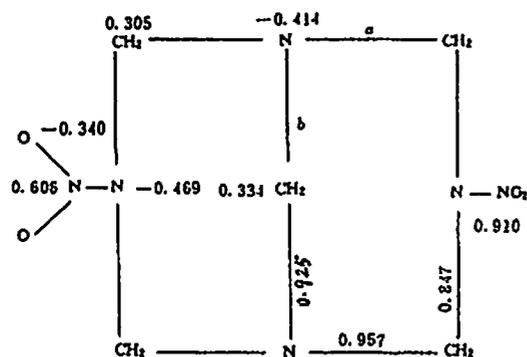


Fig. 3 Net charge (left upper part) and bond order (right lower part) of DPT from MNDO calculation.

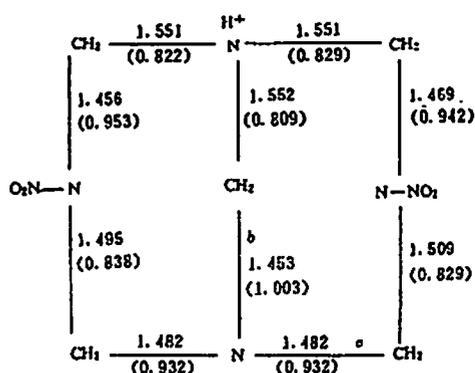
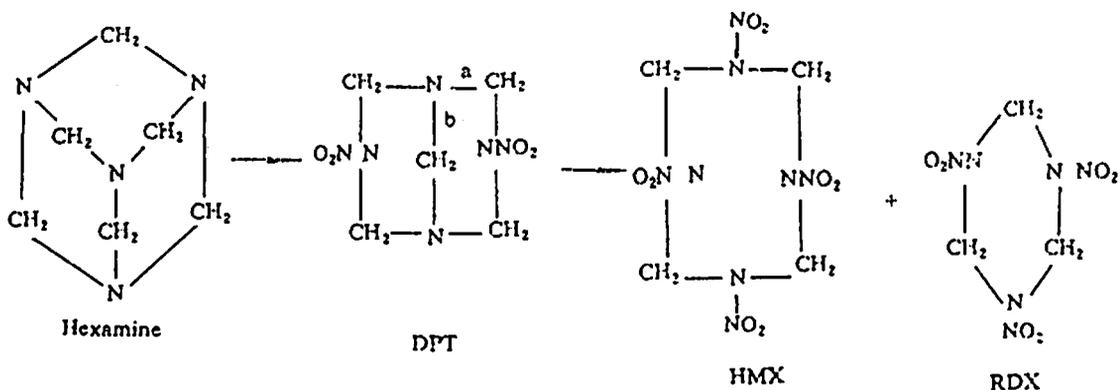


Fig. 4 Bond length (Å) and bond order (in parenthesis) of (DPT + H<sup>+</sup>) system from MNDO calculation.

#### Selectivity of nitrolysis of DPT

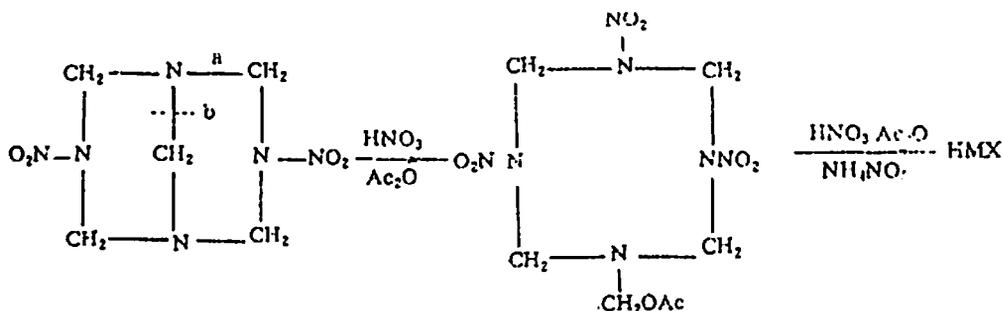
DPT can be prepared readily from the nitrolysis of

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 preferable to Bond a in DPT.

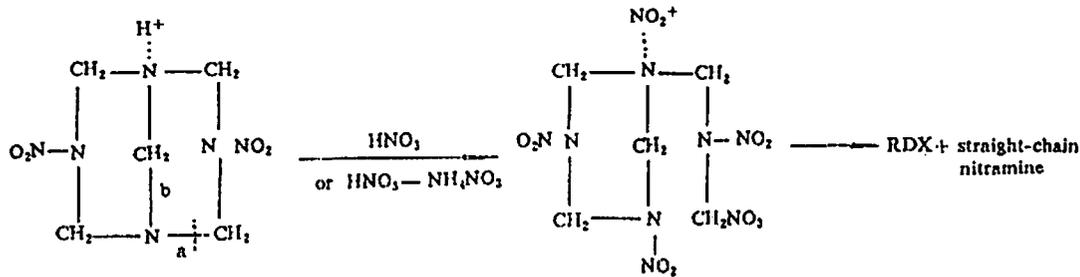


Castorina et al.<sup>5)</sup> came to the conclusion from their <sup>14</sup>C tracer studies that both the degradation of hexamine to low molecular weight species during the first stage and the degradation of DPT to cyclic methylenitramines during the second stage are nonselective. They thought that 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 :



#### References

- 1) Choi C. S., Bulusu S., *Acta Cryst.*, B30, 1576 (1974).
- 2) Bhattacharjee S. K., Chacko K. K., *Tetrahedron*, 35, 1999 (1979).
- 3) Hall P. G., Horsfall G. S., *Chem. Soc., Perkin II*, (9), 1280 (1973).
- 4) Bachmann W. E., Horton W. J., Jenner E. L., J. Amer. Chem. Soc., 73, 2773 (1973).
- 5) Castorian T. C., Holahan F. S., Graybush R., J, et al., *J. Amer. Chem. Soc.*, 82, 1617 (1960).
- 6) Dewar M. J. S., Thiel W., *J. Amer. Chem. Soc.*, 99, 4899 (1977).
- 7) Pulay P., *Theoret. Chim. Acta (Berl.)*, 50, 299 (1979).
- 8) Dewar M. J. S., *Science*, 187, 1037 (1975).

### 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(ジニトロペ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、異なる溶媒下での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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