AD-A143 955 THE STRUCTURAL CHEMISTRY OF ENERGETIC COMPOUNDS(U) 1/1
NAVAL RESEARCH LAB WASHINGTON DC LAB FOR THE STRUCTURE
OF MATTER R GILARDI ET AL. 06 JUL 84 LSM-84-1
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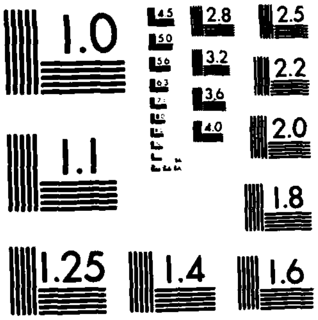
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(12)

1a. REPORT SECURITY CLAS UNCLASSIFIED

1b. RESTRICTIVE MARKINGS

2a. SECURITY CLASSIFICATION AUTHORITY

2b. DECLASSIFICATION/DOWNGRADING SCHEDULE

3. DISTRIBUTION/AVAILABILITY OF REPORT
Approved for public release;
distribution unlimited

4. PERFORMING ORGANIZATION REPORT NUMBER(S) LSM-84-1

5. MONITORING ORGANIZATION REPORT NUMBER(S) N/A

6a. NAME OF PERFORMING ORGANIZATION Lab. for Structure of Matter, Code 6030

6b. OFFICE SYMBOL *(If applicable)*

7a. NAME OF MONITORING ORGANIZATION Office of Naval Research

6c. ADDRESS *(City, State and ZIP Code)*
U.S. Naval Research Laboratory
Washington, D. C. 20375

7b. ADDRESS *(City, State and ZIP Code)*
Dr. R. S. Miller, Code 473
Office of Naval Research
Arlington, VA 22217

DTIC
AUG 6 1984
S A

8a. NAME OF FUNDING/SPONSORING ORGANIZATION ONR

8b. OFFICE SYMBOL *(If applicable)*

9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER N00014-83-WR-30130

8c. ADDRESS *(City, State and ZIP Code)*
Dept. of the Navy
Office of Naval Research
Arlington, VA 22217

10. SOURCE OF FUNDING NOS.

PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.	WORK UNIT NO.
61153N	RR024-02-01		NR093-069

11. TITLE *(Include Security Classification)* The Structural Chemistry of Energetic Compounds

12. PERSONAL AUTHOR(S) Richard Gilardi, Clifford George and Jerome Karle

13a. TYPE OF REPORT Interim

13b. TIME COVERED FROM 1/1/83 TO 12/31/83

14. DATE OF REPORT *(Yr., Mo., Day)* 7/6/84

15. PAGE COUNT 37

16. SUPPLEMENTARY NOTATION

DTIC FILE COPY

17. COSATI CODES

FIELD	GROUP	SUB. GR.

18. SUBJECT TERMS *(Continue on reverse if necessary and identify by block number)* Propellants, Explosives, X-ray Diffraction, Molecular Mechanics

19. ABSTRACT *(Continue on reverse if necessary and identify by block number)*

The molecular structures of ten materials developed in ONR-sponsored explosive/propellant research are reported. The following materials were analyzed using x-ray diffraction, and their structural parameters are reported: (1) Four nitro- and aza-adamantanes: 2-bromo-2-nitroadamantane, 2,2-dinitroadamantane, 1,3,5,7-tetranitroadamantane and 2,4,10-tribenzy-2,4,10-triaza-adamantane, (2) Two energetic nitramines: 1,4-dinitroglycoluril (DINGU) and 1,3,3-trinitroazetidine, (3) Three HMX analogs: 1-nitroso-3,3,5,7,7-pentanitro-1,5-diazacyclo-octane, 1,5-dinitroso-3,3,7,7-tetranitro-1,5-diazacyclo-octane and 1,3,3,5,7,7-hexanitro-1,5-diazacyclo-octane, and (4) One nonenergetic precursor compound, tetra-acetyl-bicyclo-HMX. Using the molecular mechanics program (MM2), modified at NRL to accommodate nitro and nitramino groups, conformational energy analyses were performed on two proposed hypothetical target compounds, octanitrocubane and hexanitrohexa-aza-adamantane. On the basis of these analyses, both molecules are relatively unstrained, and should exist in stable forms.

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT
UNCLASSIFIED/UNLIMITED XX SAME AS RPT. ☐ DTIC USERS ☐

21. ABSTRACT SECURITY CLASSIFICATION UNCLASSIFIED

22a. NAME OF RESPONSIBLE INDIVIDUAL
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22b. TELEPHONE NUMBER *(Include Area Code)* 202-767-2636

22c. OFFICE SYMBOL

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SECURITY CLASSIFICATION OF THIS PAGE

The Structural Chemistry of Energetic Compounds

ONR Annual Report

Jan 1 to Dec 31, 1983

Richard Gilardi, Clifford George,
and Jerome Karle

Laboratory for the Structure of Matter

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Washington, D.C. 20375

Contents

I. Introduction

This report summarizes the investigation of the molecular structure of a number of energetic materials or their precursors which are potentially useful in explosive or propellant formulation. The aims of this research are to determine or corroborate the exact chemical structure of newly developed materials, and to develop a library of structural parameters for groups occuring in energetic compounds. These structural parameters provide a basis for computationally modelling proposed target compounds by means of quantum chemistry and conformational energy analysis. Specific application is made in this report to the energy analyses of two proposed polynitro cage compounds, octanitrocubane and 2,4,6,8,9,10-hexanitrohexa-aza-adamantane.

(II) Molecular structures

a) Nitro- and aza- adamantanes

Adamantanes with nitro and aza substituents are potentially high density energetic compounds and are a class of compounds for which little structural information is available. X-ray diffraction analysis of compounds we have examined include: 2-bromo-2-nitroadamantane (BNA), 2,2-dinitro-adamantane (DNA)[1], 1,3,5,7-tetranitroadamantane (TNA1)[2], and 2,4,10-tribenzyl-2,4,10-triazaadamantane (TBTAA). Samples of BNA and DNA were provided by Dr. Baum of Fluorochem Inc. TNA1 was provided by Dr. Sollott of the U. S. Army Armament Research and Development Command, and TBTAA was provided by Dr. Nielsen at NWC, China Lake.

Molecular Geometry

The crystallographic data for each of the adamantane derivatives studied is listed in Table (1), with bond distances and valence angles for each given in Tables (2-4). In these materials the adamantane cage is only slightly distorted from expected values for both nitro and aza substituents. The carbon-nitrogen bond lengths seen in these compounds for $C-NO_2$ are significantly longer than a typical C-N single bond; the average C-N distances are 1.538, 1.557 and 1.528 A in BNA, DNA and TNA1 respectively. In the non-nitro compound TBTAA, the average C-N distance at the pyramidally bonded amine nitrogen is 1.47 A, which is a typical single bond length.

The $C=NO_2$ bond lengths and the O-N-O angles observed are consistent with the results of structural analysis of alicyclic nitro compounds[3] which shows a correlation of these parameters; an increase in the O-N-O angle is generally accompanied by an increase in C-N bond length.

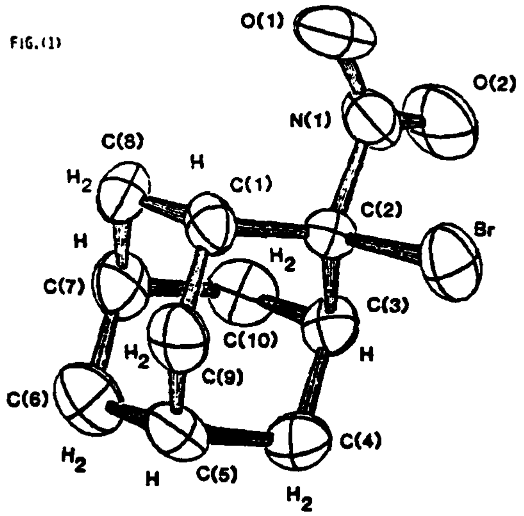
Packing

In all of these structures the intermolecular contacts are normal van der Waals' interactions. Nearest contacts in BNA and DNA are H•••H' contacts in the range 2.36 to 2.52 A; no close O•••O' or O•••Br contacts occur. In TNA1, the nearest contacts are O(1)•••H(9)' at 2.48 A and those in TBTAA are H•••H' contacts at 2.49 A.

Table 1. Crystal Data for four nitro- & aza-adamantanes.

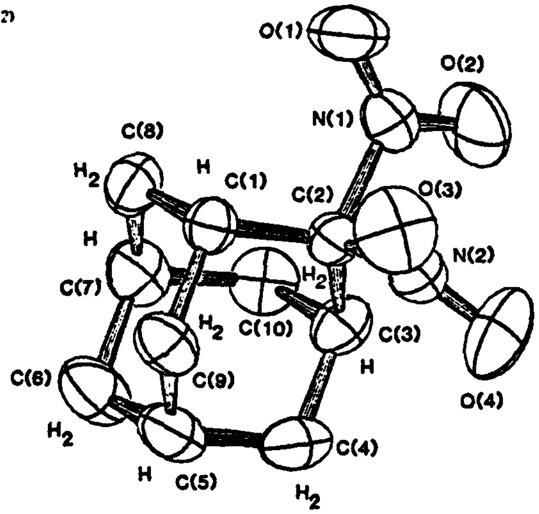
	BNA	DNA	TNA1	TBTAA
a(A)	6.583	6.586	7.874	9.542
b(A)	12.095	12.407	7.874	11.000
c(A)	13.024	12.916	10.552	21.843
	-	100.88°	-	95.24°
Vol(A^3)	1037.0	1036.3	542.2	2283.1
Z	4	4	2	4
Mol. wt.	260.1	226.2	316.2	409.6
d_x(mg/mm^3)	1.666	1.450	1.605	1.191
Space group	$P2_12_12_1$	$P2_1/n$	$P\bar{4}2_1c$	$P2_1/c$

FIG.(1)



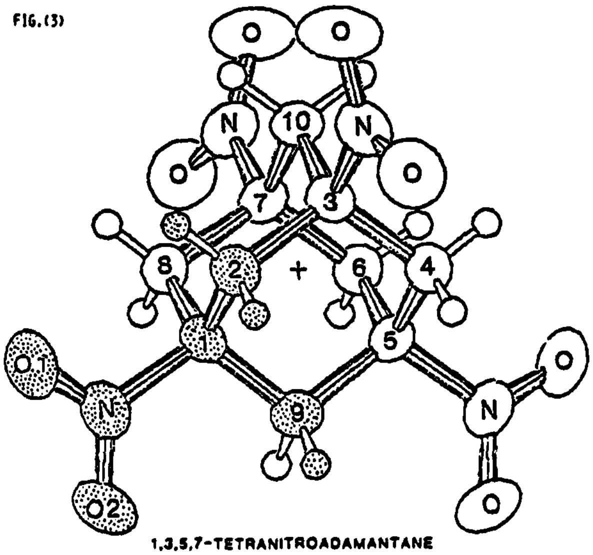
2-BROMO-2-NITROADAMANTANE

FIG.(2)



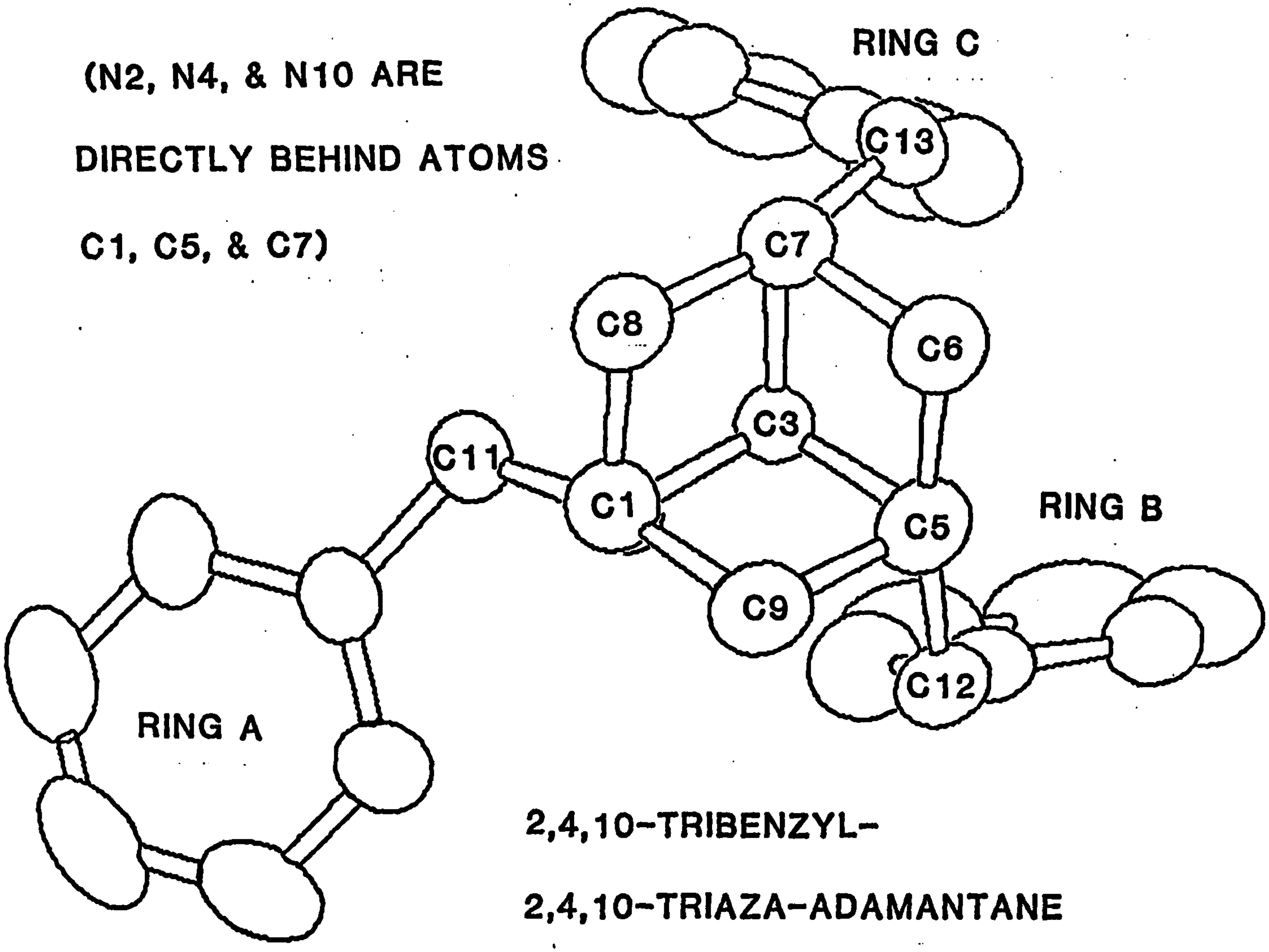
2,2-DINITROADAMANTANE

FIG.(3)



1,3,5,7-TETRANITROADAMANTANE

FIG.(4)



(N2, N4, & N10 ARE

DIRECTLY BEHIND ATOMS

C1, C5, & C7)

2,4,10-TRIBENZYL-

2,4,10-TRIAZA-ADAMANTANE

Table (2)

Bond distances (A) and bond angles (deg.) for 2-bromo-2-nitroadamantane (I), and 2,2-dinitroadamantane (II). The e.s.d.'s are listed for each distance; all angle e.s.d.'s are 0.6° (I) and 0.3° (II).

Bond Distance		
	(I)	(II)
C(1)-C(2)	1.528(8)	1.508(3)
C(1)-C(8)	1.521(11)	1.530(5)
C(1)-C(9)	1.517(10)	1.537(5)
C(2)-C(3)	1.512(8)	1.511(5)
C(3)-C(4)	1.527(9)	1.535(5)
C(3)-C(10)	1.527(9)	1.536(5)
C(4)-C(5)	1.548(10)	1.511(6)
C(5)-C(6)	1.520(11)	1.528(6)
C(5)-C(9)	1.525(9)	1.526(6)
C(6)-C(7)	1.517(11)	1.533(6)
C(7)-C(8)	1.528(9)	1.534(6)
C(7)-C(10)	1.532(9)	1.526(6)
C(2)-N(1)	1.538(7)	1.555(5)
N(1)-O(1)	1.205(7)	1.206(4)
N(1)-O(2)	1.195(6)	1.206(4)
C(2)-Br	1.979(6)	
C(2)-N(2)		1.560(5)
N(2)-O(3)		1.205(4)
N(2)-O(4)		1.206(4)

Bond Angle		
	(I)	(II)
C(2)-C(1)-C(8)	108.5	108.7
C(2)-C(1)-C(9)	109.4	108.0
C(8)-C(1)-C(9)	109.5	108.5
C(1)-C(2)-C(3)	110.6	112.3
C(2)-C(3)-C(4)	109.8	108.9
C(2)-C(3)-C(10)	107.9	107.5
C(4)-C(3)-C(10)	110.0	109.3
C(3)-C(4)-C(5)	109.2	110.4
C(4)-C(5)-C(6)	109.6	109.7
C(4)-C(5)-C(9)	109.0	109.2
C(6)-C(5)-C(9)	108.8	109.4
C(5)-C(6)-C(7)	110.8	109.2
C(6)-C(7)-C(8)	108.3	109.7
C(6)-C(7)-C(10)	110.2	110.5
C(8)-C(7)-C(10)	107.9	107.6
C(1)-C(8)-C(7)	110.3	110.3
C(1)-C(9)-C(5)	110.1	110.7
C(3)-C(10)-C(7)	110.4	110.2
C(1)-C(2)-N(1)	112.0	112.0
C(3)-C(2)-N(1)	111.4	111.4
C(1)-C(2)-Br,N(2)	110.9	110.2
C(3)-C(2)-Br,N(2)	111.2	111.4
C(2)-N(1)-O(1)	118.0	118.2
C(2)-N(1)-O(2)	117.2	116.9
O(1)-N(1)-O(2)	124.7	124.8
N(1)-C(2)-Br,N(2)	108.3	98.7

Table (3)

Bond distances (Å) and angles (deg.) for 1,3,5,7-tetranitroadamantane with e.s.d.'s in parentheses

Bond distance	
C(1)-C(2)	1.528(3)
C(1)-C(9)	1.531(3)
C(1)-C(8)	1.539(3)
C(1)-N	1.529(3)
O(1)-N	1.216(3)
O(2)-N	1.203(3)

Bond angle	
C(2)-C(1)-C(9)	111.5(2)
C(8)-C(1)-C(9)	110.3(2)
C(8)-C(1)-C(2)	110.9(2)
C(2)-C(1)-N	106.9(2)
C(8)-C(1)-N	108.0(2)
C(9)-C(1)-N	109.1(2)
C(1)-N-O1	117.1(2)
C(1)-N-O2	118.8(3)
O1-N-O2	124.1(3)
C(1)-C(2)-C(3)	106.4(2)
C(1)-C(9)-C(5)	106.6(2)

Table (4)

Bond distances (Å) and valence angles (deg.) for TBTAA with e.s.d.'s in parentheses.

Bond distances (cage)	
C(1)-N(2)	1.473(3)
C(1)-C(8)	1.535(4)
C(1)-C(9)	1.526(3)
N(2)-C(3)	1.456(3)
N(2)-C(11)	1.445(3)
C(3)-N(4)	1.472(3)
C(3)-N(10)	1.459(3)
N(4)-C(5)	1.482(3)
N(4)-C(12)	1.492(3)
C(5)-C(6)	1.524(4)
C(5)-C(9)	1.529(4)
C(6)-C(7)	1.534(3)
C(7)-C(8)	1.529(4)
C(7)-N(10)	1.473(3)
N(10)-C(13)	1.475(3)

Bond angles (cage)			
N(2)-C(1)-C(8)	111.4	C(5)-C(6)-C(7)	108.1
N(2)-C(1)-C(9)	106.5	C(6)-C(7)-C(8)	109.8
C(8)-C(1)-C(9)	109.9	C(6)-C(7)-N(10)	112.0
C(1)-N(2)-C(3)	110.0	C(8)-C(7)-N(10)	106.2
C(1)-N(2)-C(11)	113.5	C(1)-C(8)-C(7)	108.2
C(3)-N(2)-C(11)	114.2	C(1)-C(9)-C(5)	108.0
N(2)-C(3)-N(4)	110.2	C(3)-N(10)-C(7)	109.6
N(2)-C(3)-N(10)	111.0	C(3)-N(10)-C(13)	112.8
N(4)-C(3)-N(10)	111.2	C(7)-N(10)-C(13)	114.9
C(3)-N(4)-C(5)	108.9		
C(3)-N(4)-C(12)	112.1		
C(5)-N(4)-C(12)	112.9		
N(4)-C(5)-C(6)	106.7		
N(4)-C(5)-C(9)	112.1		
C(6)-C(5)-C(9)	110.1		

Bond distance (ring)	i = A	i = B	i = C
C1(i)-C2(i)	1.385(4)	1.383(4)	1.382(3)
C1(i)-C6(i)	1.383(3)	1.381(4)	1.384(4)
C2(i)-C3(i)	1.381(4)	1.368(5)	1.383(4)
C3(i)-C4(i)	1.388(4)	1.381(6)	1.369(5)
C4(i)-C5(i)	1.367(4)	1.373(5)	1.367(4)
C5(i)-C6(i)	1.373(4)	1.370(4)	1.393(4)
C1(i)-C(11)	1.512(3)	-	-
C1(i)-C(12)	-	1.497(4)	-
C1(i)-C(13)	-	-	1.508(3)

Angles (ring)	A	B	C
C2(i)-C1(i)-C6(i)	118.8	118.4	117.9
C1(i)-C2(i)-C3(i)	120.8	120.8	121.1
C2(i)-C3(i)-C4(i)	119.7	120.0	121.1
C3(i)-C4(i)-C5(i)	119.3	119.8	119.5
C4(i)-C5(i)-C6(i)	121.3	119.7	120.4
C1(i)-C6(i)-C5(i)	120.3	121.2	120.6

(e.s.d.'s for all angles are 0.2°)

II.(b) 1,4-dinitroglycoluril (DINGU)

DINGU, a material provided by Dr. C. Coon of Lawrence Livermore Labs, is a nitramine explosive formed by condensing glyoxal and urea in a medium of concentrated nitric acid. The X-ray analysis[4] provided confirmation of the formation of the 1,4 dinitro derivative and also afforded the opportunity to obtain the structural parameters for a nitramine group in a five membered ring, an environment not previously reported in any nitramine crystal structure. DINGU is of interest because of its high density. Although it is substituted with only 2 nitro groups, it is more dense than HMX, primarily because of its efficient packing.

Molecular Structure

DINGU crystallized in the triclinic $P\bar{1}$ space group with a = 6.407, b = 6.991, c = 9.249 A, α = 103.35, β = 101.61 and γ = 96.70°. The cell volume is 389.0 A^3 with two molecules per cell which yields a calculated density of 1.982 mg/mm^3. Table (5) gives the bond distances and angles.

Packing

The conformation of the molecule is folded-planar. One half of each molecule participates with other molecules in the crystal in an antiparallel stack mode of packing which involves no strong hydrogen bonding while the other halves of the molecules participate in inter-stack hydrogen bonding. Hydrogen bonding links the carbonyl group C(2)=O(2) to the amino N3-H3 of a symmetry related molecule and vice versa. The N(3)•••O(2) distance is 2.906 A and the H(3)•••O(2) distance is 1.95 A. In addition, there are several close contacts between the molecule and its symmetry mates. The carbonyl C(5)=O(5) and the C(2)=O(2) carbonyl on a symmetry related molecule have an O(5)•••C(2)' approach of 2.907 A, which is significantly less than the sum of the usual van der Waals' radii (3.1 A). Additional contacts involving oxygen and hydrogen have approaches of 2.4 A which is less than the normal van der Waals O•••H contact of 2.6A .

It appears that the presence of carbonyls in this compound is essential to both modes of packing mentioned above. The close antiparallel stack involves tight intermolecular carbonyl approaches, and the hydrogen bonding involves carbonyl acceptors. The carbonyl group, which is generally considered non-energetic because it does not add to the heat of formation, may have a role in facilitating dense packing in energetic compounds. The structure and packing of the tetranitro analog of DINGU, TNGU, will be investigated in FY84 to further clarify this question. TNGU reportedly has a density significantly greater than 2.0 mg/mm^3.

FIG.(5)

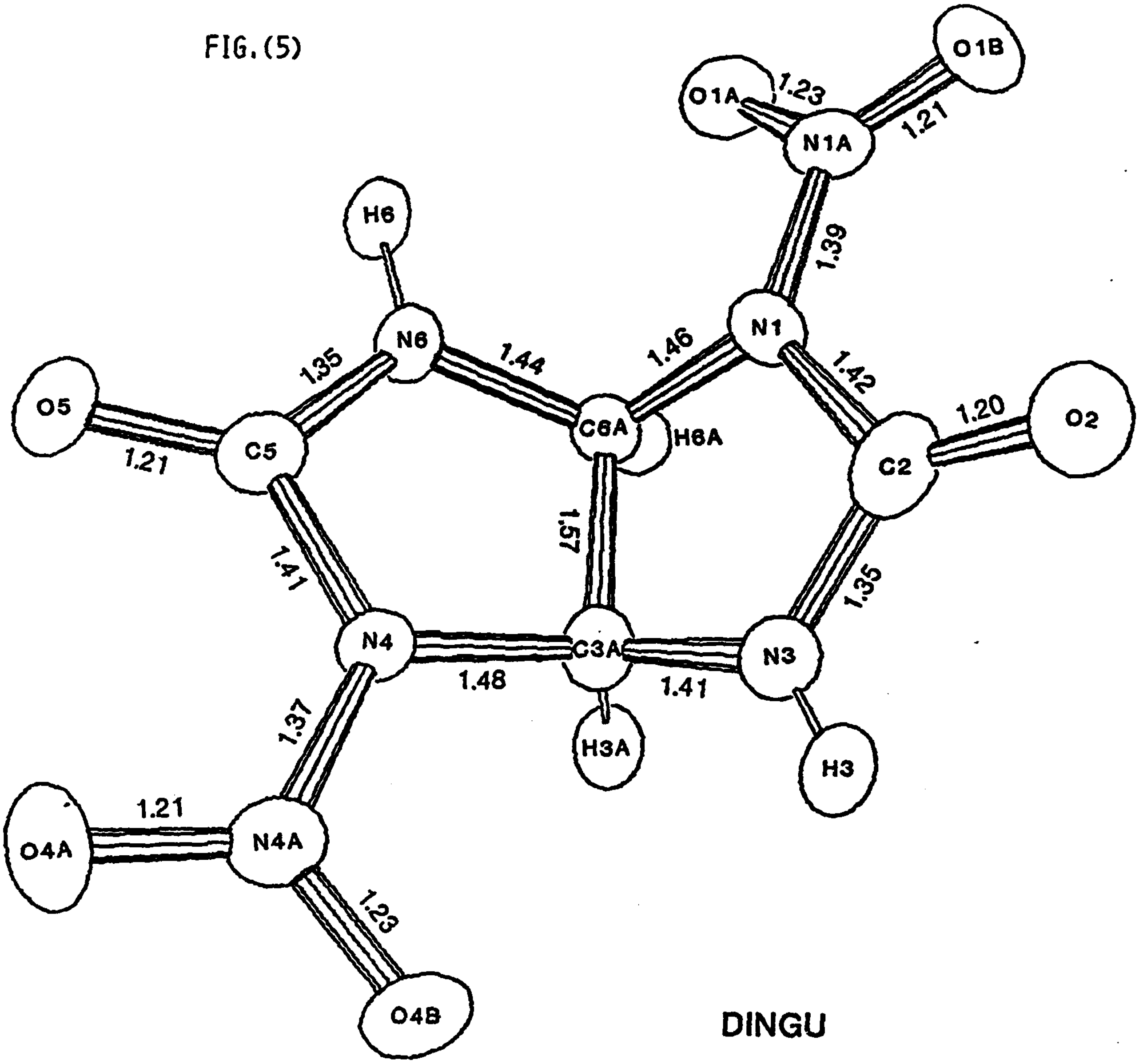

O1B
O1A
1.23
N1A
1.21
H6
1.39
N6
N1
1.35
1.44
1.46
1.42
O5
1.20
O2
C5
C6A
H6A
C2
1.21
1.57
1.41
1.35
N4
C3A
N3
1.48
1.41
1.37
H3A
H3
1.21
O4A
N4A
1.23
O4B
DINGU

Table (5)

DINGU (1,4-dinitroglycouril) Bond Distances, Angles, Torsions

Distances (Angstroms)

N1	N1A	1.369(6)	N4	N4A	1.386(6)
N1	C6A	1.475(7)	C3A	N4	1.464(7)
N1	C2	1.406(7)	N4	C5	1.423(7)
C2	02	1.214(7)	C5	05	1.201(7)
C2	N3	1.346(7)	C5	N6	1.346(8)
N3	C3A	1.442(7)	N6	C6A	1.412(7)
N3	H3	0.98(7)	N6	H6	0.76(7)
C3A	C6A	1.573(7)			
C3A	H3A	0.98(7)	C6A	H6A	1.01(7)
N1A	01A	1.233(6)	N4A	04B	1.229(6)
N1A	01B	1.206(6)	N4A	04A	1.213(6)

Angles (degrees)

C2	N1	C6A	115.2(5)	C3A	N4	C5	114.5(5)
C2	N1	N1A	124.8(5)	C5	N4	N4A	125.5(5)
C6A	N1	N1A	120.0(4)	C3A	N4	N4A	118.1(5)
N1	C2	02	127.7(5)	N4	C5	05	126.5(6)
N1	C2	N3	105.0(5)	N4	C5	N6	104.0(5)
02	C2	N3	127.3(5)	N6	C5	05	129.5(6)
C2	N3	C3A	115.4(5)	C5	N6	C6A	116.4(5)
C2	N3	H3	123(4)	C5	N6	H6	118(6)
C3A	N3	H3	121(4)	C6A	N6	H6	125(6)
N3	C3A	N4	111.9(5)	N6	C6A	N1	115.1(5)
N3	C3A	C6A	104.4(5)	N6	C6A	C3A	104.5(5)
N3	C3A	H3A	114(4)	N6	C6A	H6A	113(4)
N4	C3A	C6A	99.7(4)	N1	C6A	C3A	99.7(4)
N4	C3A	H3A	114(4)	N1	C6A	H6A	113(4)
C6A	C3A	H3A	112(4)	C3A	C6A	H6A	110(4)
N1	N1A	O1A	114.6(5)	N4	N4A	04B	113.9(5)
N1	N1A	O1B	119.2(5)	N4	N4A	04A	118.5(5)
O1A	N1A	O1B	126.2(5)	04A	N4A	04B	127.5(5)

Torsion Angles (degrees)

N1	C2	N3	C3A	-2.9(6)	N4	C5	N6	C6A	0.7(7)
C2	N3	C3A	C6A	5.1(7)	C5	N6	C6A	C3A	5.1(7)
N3	C3A	C6A	N1	-4.8(6)	N6	C6A	C3A	N4	-8.3(6)
C3A	C6A	N1	C2	3.6(6)	C6A	C3A	N4	C5	9.6(6)
C6A	N1	C2	N3	-0.8(6)	C3A	N4	C5	N6	-7.1(6)

Note: Values reported in the left and right columns are related by a non-crystallographic mol. 2-fold symmetry axis.

II.(c) 1,3,3-Trinitroazetidine (TNAZ)

This dense (1.84 mg/mm3)* energetic compound, provided by Dr. Kurt Baum of Fluorochem Inc., contains a strained nitramine group and two additional nitro groups. The x-ray analysis provides model structural parameters for nitramines in four membered rings and nitro groups in crowded molecules.

Molecular Geometry

TNAZ crystallized in the orthorhombic space group Pbca, with a = 5.734A, b = 11.127A and c = 21.497A . The cell volume is 1370.0 A^3 with 8 molecules per unit cell. The density at -30°C , the sample temperature during data collection, is 1.86 mg/mm^3. Bond distances and angles are given in Table (6) with the molecular geometry illustrated in Fig.(6). The azetidine ring is puckered with a dihedral angle, ϕ, (the angle between the C-C-C and C-N-C planes) of 13.6°. This may be compared with crystallographic data on other azetidine derivatives[5,6] for which ϕ varies from 0 to 14°, and also with the value ϕ = 33.1° for azetidine in the gas phase[7]. The out-of-plane deformation angle of the ring nitrogen (the angle between the C-N-C plane and the N-N vector) is 39.4° which is larger than that normally observed in nitramines. An examination of the previous literature shows an average of 12.2° with a range of 0 to 35° for this angle. Orientation of the $N-NO_2$ is trans with respect to C(3), while the planes of the nitro groups bonded to C(3) are mutually perpendicular (torsion angle N7-C3-N6-06A = 0.4°).

Packing.

TNAZ packs with no contacts closer than normal van der Waals' contacts. The nearest intermolecular contacts are N6···07B' of 2.90A and 06A···H4A of 2.58 A.

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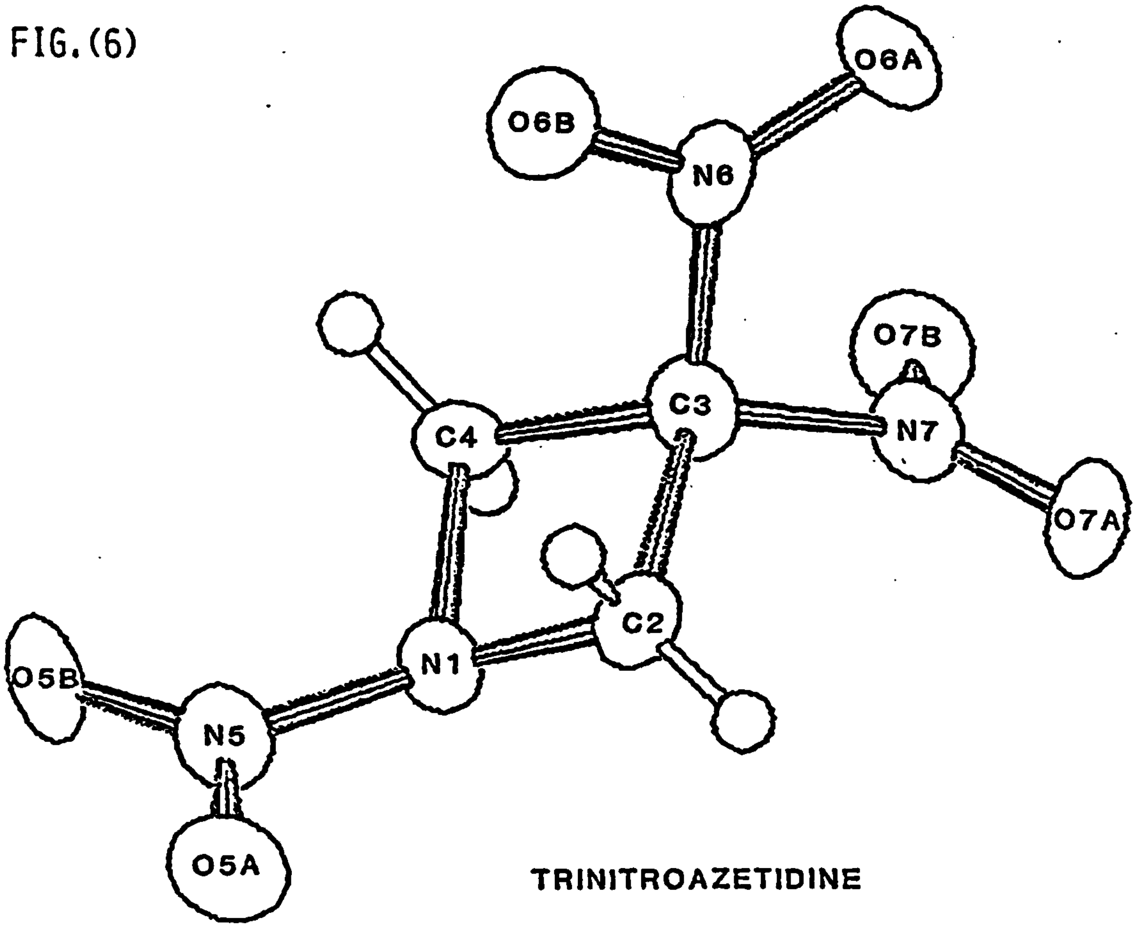
* density at 20° C

FIG.(6)



TRINITROAZETIDINE

Table (6)

1,3,3-Trinitroazetidine bond distances (Å) and angles (deg.) with distance e.s.d.'s in parentheses. All bond angle e.s.d.'s are 0.5° .

Bond distance	
N1-C2	1.484(10)
N1-C4	1.474(10)
N1-N5	1.351(9)
C2-C3	1.533(10)
C3-C4	1.545(11)
C3-N7	1.493(10)
C3-N6	1.516(10)
N5-O5A	1.217(8)
N5-O5B	1.222(8)
N6-O6A	1.214(8)
N6-O6B	1.222(8)
N7-O7A	1.216(8)
N7-O7B	1.212(8)

Bond angle	
C2-N1-C4	95.1
C2-N1-N5	120.5
C4-N1-N5	122.4
N1-C2-C3	86.6
C2-C3-C4	90.3
C2-C3-N6	114.5
C2-C3-N7	116.2
N6-C3-N7	105.5
N6-C3-C4	114.2
N1-C4-C3	86.5
N1-N5-O5A	118.4
N1-N5-O5B	116.3
O5A-N5-O5B	125.3

Bond angle	
C3-N6-O6A	118.8
C3-N6-O6B	115.2
O6A-N6-O6B	126.0
C3-N7-O7A	116.3
C3-N7-O7B	117.1
O7A-N7-O7B	126.6

Torsion angle	
C4-N1-C2-C3	-9.6
N5-N1-C2-C3	-142.2
N7-C3-N7-O6A	-0.4
N6-C3-N7-O7A	89.2
C2-N1-N5-O5A	-34.7
C4-N1-N5-O5B	29.0
C4-C3-N6-O6A	-129.2
C2-C3-N6-O6A	128.6
C2-C3-N7-O7A	-38.8
C2-C3-N7-O7B	143.0

Dihedral angles	
C2-C3-C4 plane / C2-N1-C4 plane	13.6
C2-N1-C4 plane / N1-N5 vector	39.4

II.(d) HMX Analogs

Three new HMX analogs, provided by the NSWC, 1,5-dinitroso-3,3,7,7-tetranitro-1,5-diazacyclooctane (I), 1-nitroso-3,3,5,7,7-pentanitro-1,5-diazacyclooctane (II), and 1,3,3,5,7,7-hexanitro-1,5-diazacyclooctane (III) were examined (in collaboration with Dr. H. Ammon of the U. of Md.) and their structures were determined[8]. While these materials are highly dense and energetic, they are not quite dense enough to surpass β-HMX as an explosive.

Molecular Structure

All of these molecules have a chair conformation similar to that of β-HMX. The packing and symmetry in these three crystals are identical, with each of the molecules lying on a center of symmetry at (1/2, 0, 0) coincident with the center of the eight membered ring. Molecule (II) is disordered with the occupancies of nitroso and nitramine consistent with that required for the expected symmetry. Overall similarity of the molecules is sufficiently good that only one set of bond distances and angles is provided, Table (8), and only one molecule shown in Fig. (7). The differences are at the amino-linked nitroso and nitro groups. As the oxygen substitution increases from (I) to (III) the N-N distance also increases. The N-N bond length in the NO/NO_2 disorder compound (II), 1.352 A, is near the mean of the other two [1.326 A in (I), and 1.366 A in (III)] .

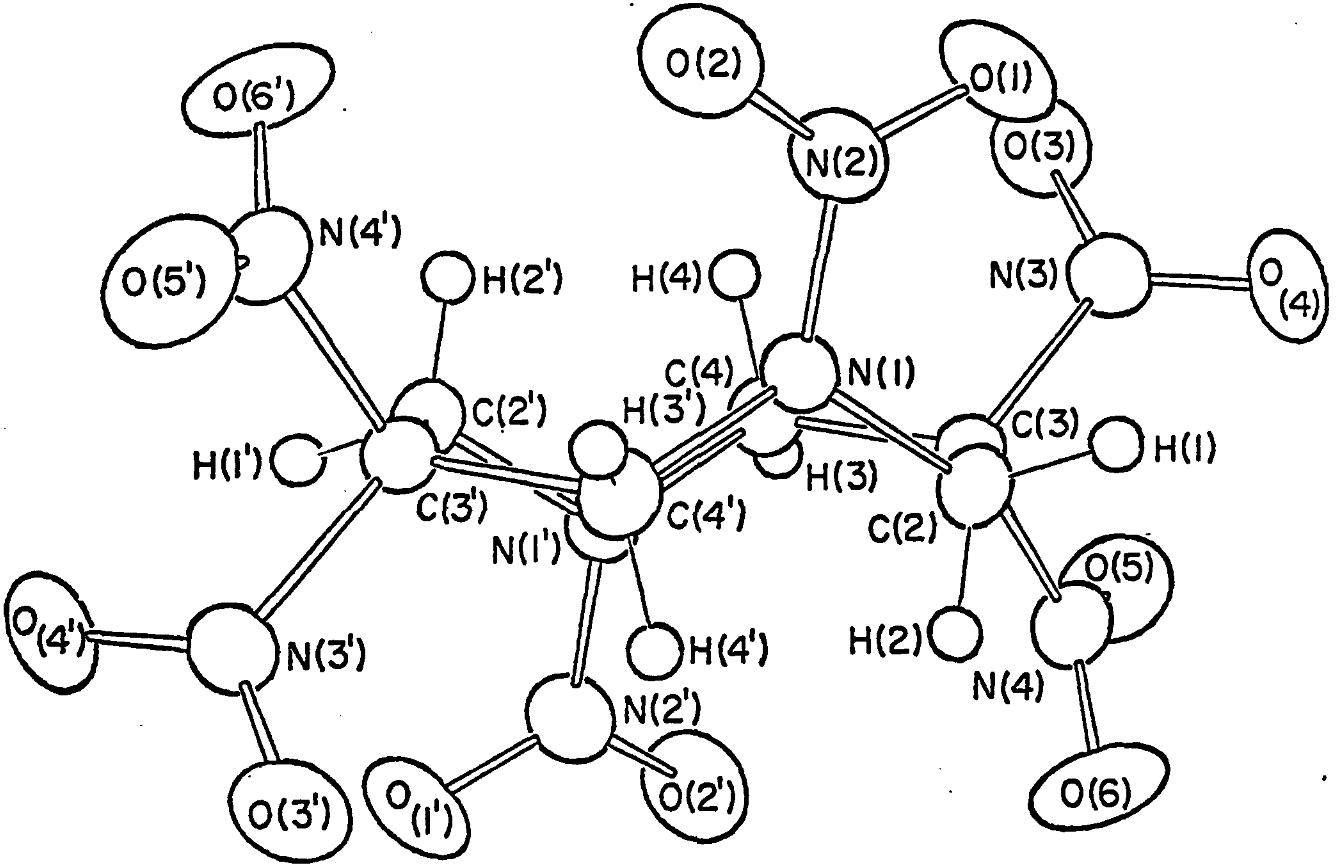
Packing

As the oxygen substitution increases from (I) to (III), a cell volume increase is expected to occur, reflecting the increase in the molecular volume. The cell dimensions a and c increase, however b decreases suggesting some extra intramolecular attraction directed along the b axis. An analysis of the packing reveals a few O•••H contacts directed along b which decrease on going from (I) to (III). Quantum chemical calculations on β-HMX[9] indicate that the hydrogens in HMX become quite strongly positive, and the nitro oxygens quite negative due to the electron-withdrawing nature of the nitro group. On going from nitroso to nitro substitution, the electron withdrawal increases and strengthens these attractive O•••H contacts, causing an actual shrinkage along the b axis.

Table (7)

	(I)	(II)	(III)
a (A)	10.695	10.955	11.289
b (A)	10.607	10.418	10.205
c (A)	11.575	11.756	11.880
Vol (A^3)	1313.1	1341.7	1368.6
Z	4	4	4
Mol. wt.	352.2	368.2	384.2
d_x(mg/mm^3)	1.781	1.823	1.864
Space group	Pbca	Pbca	Pbca

FIG.(7)



DINITRO HMX ANALOG

Table 8.

Bond lengths (Å), bond angles (deg.), torsion angles (deg.) and e.s.d.'s (in parentheses) for the dinitro HMX analog.

Bond distances

N(1)-C(2)	1.454(3)	N(2)-O(1)	1.224(3)	C(3)-N(4)	1.538(3)
N(1)-N(2)	1.366(2)	N(2)-O(2)	1.214(3)	N(3)-O(3)	1.205(3)
N(1)-C(4)	1.465(3)	C(3)-C(4)	1.533(3)	N(3)-O(4)	1.214(3)
C(2)-C(3)	1.530(3)	C(3)-N(3)	1.537(3)	N(4)-O(5)	1.219(3)
				N(4)-O(6)	1.200(3)

Bond Angles

C(2)-N(1)-N(2)	117.3(2)	C(4)-C(3)-N(3)	109.6(2)
C(2)-N(1)-C(4')	121.7(2)	C(4)-C(3)-N(4)	109.7(2)
C(4')-N(1)-N(2)	117.1(2)	N(3)-C(3)-N(4)	101.4(1)
N(1)-C(2)-C(3)	113.1(2)	C(3)-N(3)-O(3)	118.6(2)
N(1)-N(2)-O(1)	116.4(2)	C(3)-N(3)-O(4)	115.8(20
N(1)-N(2)-O(2)	117.3(2)	O(3)-N(3)-O(4)	125.6(20
O(1)-N(2)-O(2)	126.2(2)	C(3)-N(4)-O(5)	115.2(2)
C(2)-C(3)-C(4)	115.7(2)	C(3)-N(4)-O(6)	118.9(2)
C(2)-C(3)-N(3)	110.2(2)	O(5)-N(4)-O(6)	125.9(2)
C(2)-C(3)-N(4)	109.2(1)	C(3)-C(4)-N(1')	112.2(2)

Torsion Angles

C(4')-N(1)-C(2)-C(3)	115.7(2)	C(2)-N(1)-N(2)-O(1)	15.0(3)
N(1)-C(2)-C(3)-C(4)	-30.7(3)	N(1)-C(2)-C(3)-N(3)	94.3(2)
C(2)-C(3)-C(4)-N(1')	-31.6(3)	N(1)-C(2)-C(3)-N(4)	-155.1(2)
C(3)-C(4)-N(1')-C(2')	115.9(2)	C(2)-C(3)-N(3)-O(3)	-126.2(2)
C(3)-C(2)-N(1)-N(2)	-87.1(2)	C(2)-C(3)-N(3)-O(5)	-163.4(2)

* The primed atoms are related to the original ones by a center of symmetry at 1/2,0,0 .

II.(e) Tetra-acetyl-bicyclo-HMX (TABHMX)

This material, provided by Dr. H. Adolph of NSWC, is not an energetic compound. Synthesis of this compound was undertaken since theoretical calculations indicated that this bicyclic backbone, when fully nitro substituted, is likely to yield higher densities than HMX. A tetra-nitro version of this compound would only differ from HMX by the added presence of a covalent bond bridging the central ring of HMX, and the loss of two methylene hydrogens. For this reason the energetic target compound is called 'bicyclo-HMX'.

Molecular Geometry

The material crystallizes in two different space groups, depending on solvent used. TABHMX1 was grown from CH_3OH and TABHMX2 from CH_3CN. The crystal data for each form is listed in Table (9). The molecular geometry of these forms is essentially identical, with differences in packing only. The $Pca2_1$ cell very closely resembles one-half of the Pbca cell. Both forms are racemic, but (1) is acentric, and (2) is centric. For that reason only one set of bond distances and angles are given, Table (10). Orientation of the two fused five membered rings with respect to one another is folded-planar. Least squares planes through each of the five-membered rings form a dihedral angle of 75.8^{o}, with the average deviation of the atoms in each ring from its least squares plane being only ± 0.1A. The orientations of the four acetyl groups are defined by the torsion angles: O17-C9-N2-C3 = 165.8°, O18-C10-N4-C3 = 15.0°, O19-C11-N6-C7 = 179.7° and O20-C12-N8-C7 = 13.4° .

Table 9. Crystal Data for Two Forms of TABHMX

	TABHMX1	TABHMX2
a (A)	17.616	17.848
b (A)	9.724	7.738
c (A)	7.977	19.682
Vol. (A^3)	1366.4	2718.2
Z	4	4
d_x (mg/mm^3)	1.372	1.379
Space group	$Pca2_1$	Pbca

Table 10. Bond distances (Å) and valence angles (deg.) with e.s.d.'s in parentheses for TABHMX2 from CH_3CN solvent.

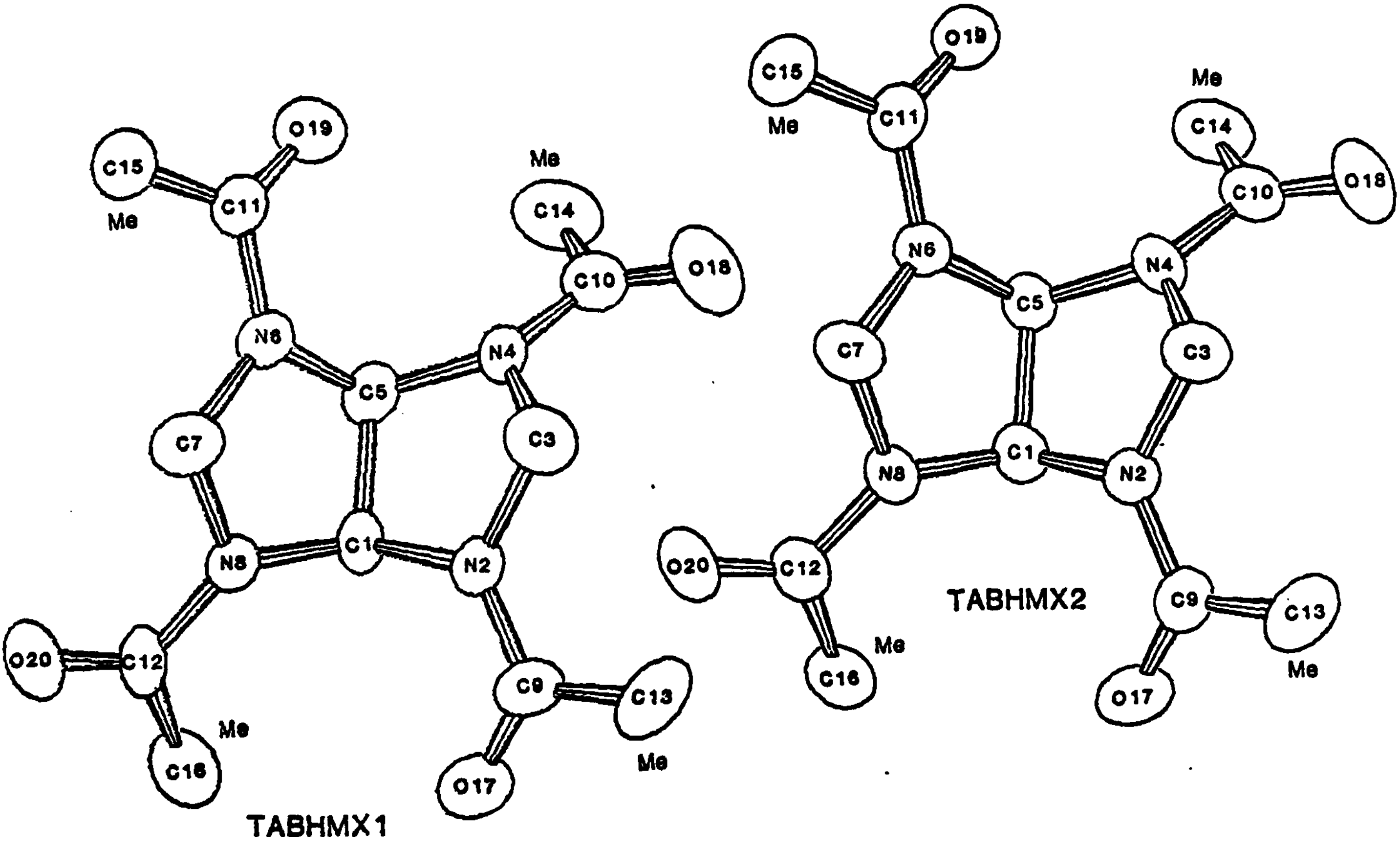
Bond distances

C(1)-N(2)	1.443(4)	N(4)-C(10)	1.352(4)	C(9)-O(17)	1.219(4)
C(1)-C(5)	1.544(4)	C(5)-N(6)	1.449(4)	C(10)-C(14)	1.499(5)
C(1)-N(8)	1.463(3)	N(6)-C(7)	1.465(4)	C(10)-O(18)	1.219(4)
N(2)-C(3)	1.451(4)	N(6)-C(11)	1.364(4)	C(11)-C(15)	1.504(5)
N(2)-C(9)	1.366(4)	C(7)-N(8)	1.460(4)	C(11)-O(19)	1.221(4)
C(3)-N(4)	1.469(4)	N(8)-C(12)	1.352(4)	C(12)-C(16)	1.497(5)
N(4)-C(5)	1.468(4)	C(9)-C(13)	1.493(5)	C(12)-O(20)	1.226(4)

Bond angles

N(2)-C(1)-C(5)	104.5(2)	N(6)-C(7)-N(8)	102.4(3)
N(2)-C(1)-N(8)	112.8(2)	C(1)-N(8)-C(7)	113.0(2)
C(5)-C(1)-N(8)	103.0(2)	C(1)-N(8)-C(12)	120.9(2)
C(1)-N(2)-C(3)	108.5(2)	C(7)-N(8)-C(12)	126.0(3)
C(1)-N(2)-C(9)	127.2(3)	N(2)-C(9)-C(13)	118.2(3)
C(3)-N(2)-C(9)	121.2(3)	N(2)-C(9)-O(17)	119.5(3)
N(2)-C(3)-N(4)	102.4(3)	C(13)-C(9)-O(17)	122.4(3)
C(3)-N(4)-C(5)	111.0(2)	N(4)-C(10)-C(14)	117.5(3)
C(3)-N(4)-C(10)	125.8(3)	N(4)-C(10)-O(18)	120.6(3)
C(5)-N(4)-C(10)	121.1(3)	C(14)-C(10)-O(18)	121.9(3)
C(1)-C(5)-N(6)	104.8(2)	N(6)-C(11)-C(15)	117.8(3)
C(1)-C(5)-N(4)	103.1(2)	N(6)-C(11)-O(19)	120.3(3)
N(4)-C(5)-N(6)	113.6(2)	C(15)-C(11)-O(19)	121.9(3)
C(5)-N(6)-C(7)	101.1(2)	N(8)-C(12)-C(16)	117.4(3)
C(5)-N(6)-C(11)	127.4(3)	N(8)-C(12)-O(20)	120.4(3)
C(7)-N(6)-C(11)	119.5(3)	C(16)-C(12)-O(20)	122.2(3)

FIG.(8)


TABHMX1

TABHMX2

III. Conformational Energy Analysis and Model-Building

(a) Energy Analysis and Structure Prediction for Octanitrocubane

Using the MM2 molecular mechanics program, modified in this lab to accommodate nitro and nitramino groups, models of isolated molecules of cubane and octanitrocubane were constructed and energy minimized. Summarizing briefly, the calculations showed no evidence of strain due to nitro-addition in the resultant distances, angles, and inter-nitro approaches. The large strain inherent in the cubic cage formation remains, but is not increased or decreased appreciably by nitro addition. However, in octanitrocubane there are sixteen N-O dipoles, all pointing outwards from the center of the molecule. This adds a certain amount of electrostatic repulsion energy which is difficult to predict well, but is estimated to be about 3.5 kcal/per molecule for each nitro group. This is very close to the dipole-dipole repulsion energy (estimated by the same program) found in gem-dinitro alkanes, which are known stable compounds.

A slightly more detailed analysis of the steric energy of cubane and octanitrocubane is provided by Table 11. Most of the strain for both molecules is in the angle-bending and torsional components. Obviously, within the cage eclipsed torsions and bond angles much smaller than tetrahedral are required for closure; somewhat less obviously, the addition of any exo-substituents is accompanied by large strain. Each substituent is torsionally eclipsed with three other substituents, and the cage-substituent bond angles are necessarily much larger than tetrahedral values. These components are roughly estimated by comparing the MM2 results for cubane with a cubane cage stripped of all hydrogens (Table 11).

In Table 11, the column labelled "van der Waals'" refers to direct electrodynamic forces between atoms which are not bonded to each other or to a common neighbor. At short distances, van der Waals' interactions are due to overlap of non-bonded electron distributions and can be massively repulsive; at longer distances, the van der Waals' potential in this program includes a weakly attractive term known as the dispersion energy. In octanitrocubane, the net van der Waals' contribution is attractive, for most of the non-bonded interatomic distances are larger than the usual van der Waals' "contact distances"; i.e., they are in the weakly attractive rather than the strongly repulsive region. These intramolecular distances (Table 12) are similar to the intermolecular distances usually observed in crystals of nitro and nitroamino compounds (RDX, HMX, tetranitroadamantane). The nitro group is actually subject to less intermolecular crowding in octanitrocubane than in HMX or RDX, because the cube formation draws the carbons away from the nitro oxygens. For example, in RDX intramolecular C•••O distances from 2.63 to 2.68 A are observed; these are much shorter than any in the octanitrocubane model.

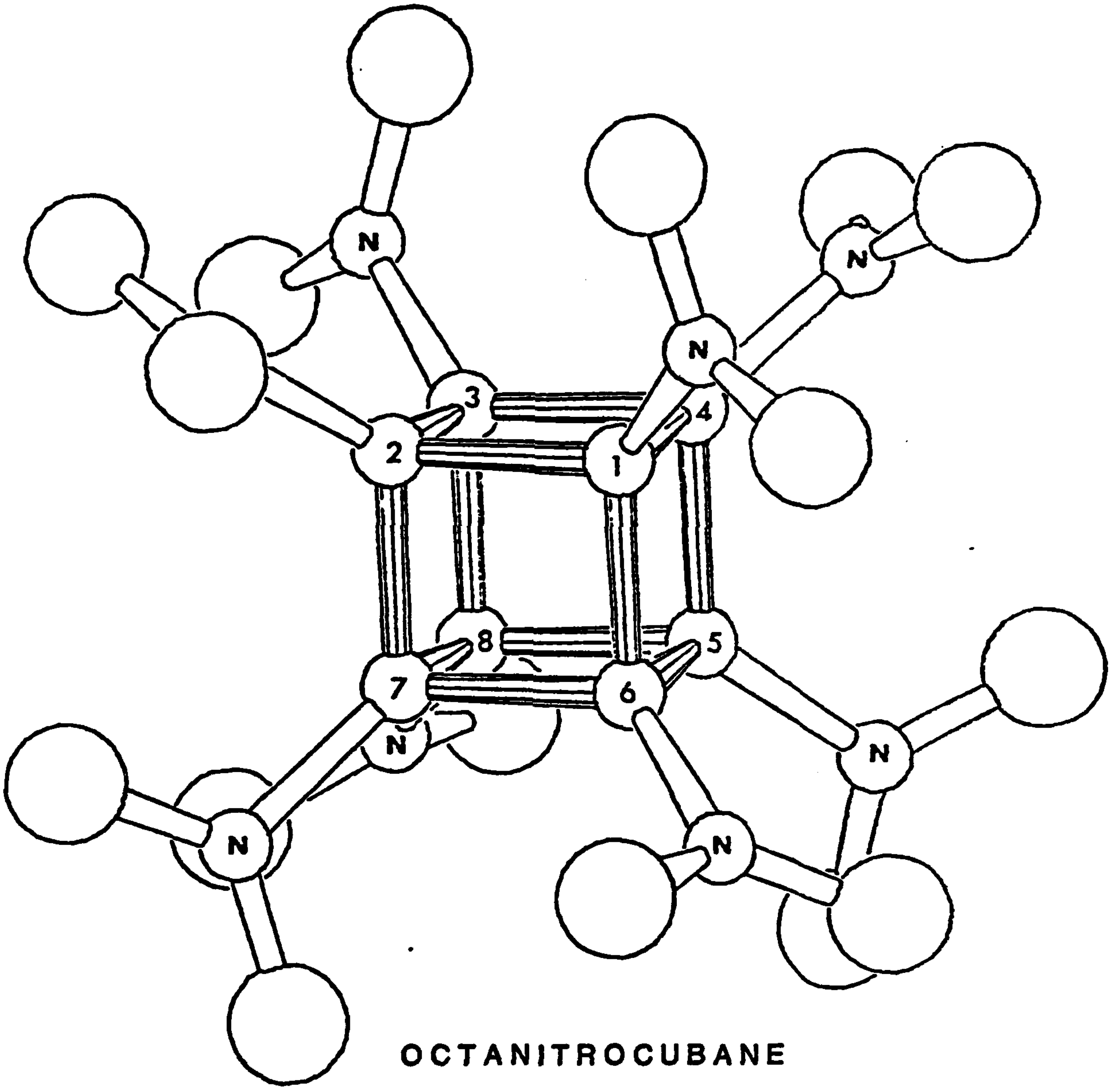
The molecular structure of octranitrocubane is pictured in Figure Nine. No symmetry was imposed during the molecular refinement, and random orientations were chosen for initial nitro orientations. Final structures which were essentially the same resulted from three independent minimizations. The final structure cannot have cubic symmetry, since a nitro is substituted on the 3-fold axis of the cube. To within a few degrees, all final conformation angles correspond to D_2 molecular symmetry, which consists of three two-fold axes of symmetry, one perpendicular to each face of the cube. This makes atoms 1, 3, 5 and 7 of the cube equivalent to each other, but slightly different from atoms 2, 4, 6 and 8 (which are equivalent to each other).

The nitro groups are rotated slightly from eclipsed torsions, so no mirrors exist, and no four-fold axes. In Figure Nine, the nitros on atoms 1, 3, 5 and 7 are approximately eclipsed with vertical cage bonds (average torsion = 14.3°, range ±1°), while atoms 2, 4, 6 and 8 are nearly eclipsed with horizontal cage bonds (average torsion = 11.7°, range ±1°).

Despite the slight differences in site symmetry, all bond distances between similar atoms were identical; these distances are C-C, 1.549A; C-N, 1.507A; and N-O, 1.205A. These distances are extremely dependent on the input potentials used, whereas the final conformational torsion angles are often more sensitive to the stereochemistry of the individual case, and only weakly potential-dependent. In this case, the potentials were fit to several nitroadamanane crystal structures; the C-C bond length may possibly be longer (1.56-1.59A) in any real cubane derivative.

The bond angles in the final structure are not unusual in any way. Cage bond angles are in the range 89-91°. Exo-cage angles vary somewhat; at each carbon atom there are three C-C-N angles which are 122.7°, 125.3° and 127.6° to within 0.2°. The smallest bond angle is of the type C4-C1-N (see Fig. 9). This slight reduction in bond angle seems to indicate that the closest-approaching nitro groups, in this case on C1 and C4, are actually attracting one another. The nitro groups are planar, with CNO angles of 117 ±1° and ONO angles of 125.6 ±0.1°.

Fig. 9.



OCTANITROCUBANE

Table 11. Steric Energy of Hypothetical Nitro Cage Compounds (kcal/mole)

	Stretch	Bend	van der Waals	Torsion	Dipole	Total
Cubane-8H atoms	3.82	80.47	4.09	24.23	-	112.6
Cubane	3.18	133.77	2.54	38.01	-	177.5
Octanitrocubane	3.94	143.16	-4.58	38.19	-	180.7
Octanitrocubane 1.8 D. NO dipole	"	"	"	"	29.41	210.1
Hexa-nitro-hexa-aza adamantane	2.54	5.48	8.54	20.04	7.88	4.48

Table 12. Shortest Non-bonded Approaches in Octanitrocubane

Type	Number	Distance (A)	vdW Contact
N•••O	8	2.98	2.9
O•••O	4	3.08	2.8
O•••C	8	3.02	3.1
O•••C	8	3.06	3.1

III.(b) Energy Analysis of Hexanitro-hexa-aza-adamantane

The energetic minimization of a molecular model of hexanitrohexa-aza-adamantane (HAZA) is underway. Two minimizations with the NRL-modified MM2 program were run to convergence. After a full analysis of the results, further runs may be necessary to corroborate that a global energy minimum was indeed found. However, some important questions are already answered by our minimized model. The main point proved by this model is that a reasonable three-dimensional model of HAZA can be built which contains no impossible (or even unlikely) distortions in bond distances, angles, or non-bonded approaches.

HAZA shows much more repulsion between nitro groups, and especially between cage atoms and nitro groups, than octanitrocubane. On the other hand these non-bonded approaches are not short enough to be unprecedented or infeasible; the intramolecular crowding is very similar to that observed in HMX & RDX (see below).

The current model of HAZA contains, as a result of the energy minimization, slightly nonplanar nitramine groups. In some compounds, such as trinitroazetidine, the amino nitrogen atom is almost tetrahedral, and thus the nitramine is decidedly nonplanar; in others, such as DINGU, the amino nitrogen and the nitramine group are almost completely planar. Our current results, using soft nitramine torsional potentials, indicate that the nitramines in HAZA bend about 9° out-of-plane. In HMX & RDX crystals, similar nitramine bends vary from 0 to 25° out-of-plane.

With nonplanar amino nitrogen atoms, the possibility of conformational isomerization arises. Each nitro group can be out-of-plane in one of two directions; all combinations of bends would seem to lead to the possibility of 64 isomers. However, because of the high symmetry of the cage backbone, this large number reduces to only four energetically distinct types (i.e., neglecting mirror images which would be non-superimposable but equal in energy). These four isomers can be labelled by listing the 'axial' or 'equatorial' disposition of the three substituents on each of the four six-membered rings in the cage. The four isomers which we found to be distinct are:

(a)	aaa/aae/aee/eee	(no symmetry)
(b)	aaa/aee/aee/aee	(possible 3-fold symmetry)
(c)	aae/aae/aae/eee	(possible 3-fold symmetry)
(d)	aae/aae/eea/eea	(possible 2-fold symmetry)

Our current HAZA model, shown in Fig. 10, has the asymmetric conformation (a). The starting model for the energy minimization was a 'neutral' conformation in which all nitramines were planar (neither axial nor equatorial). In future work, we will attempt to force a model to adopt some of the more symmetrical conformations (b-d), and see if any are significantly more or less strained than the current model.

The various components of the steric energy of HAZA are shown in Table 11. In contrast to octanitrocubane, there is little angle-bend strain. The torsional component is largely due to nitro-cage eclipsed bond interactions, as it was in the nitrocubane. The overall steric energy is considerably lower than for octanitrocubane; the only component which is larger is the van der Waals energy, and this is due to numerous short nitro•••cage carbon interactions.

Bonded distances predicted for HAZA by the MM2 calculation are:

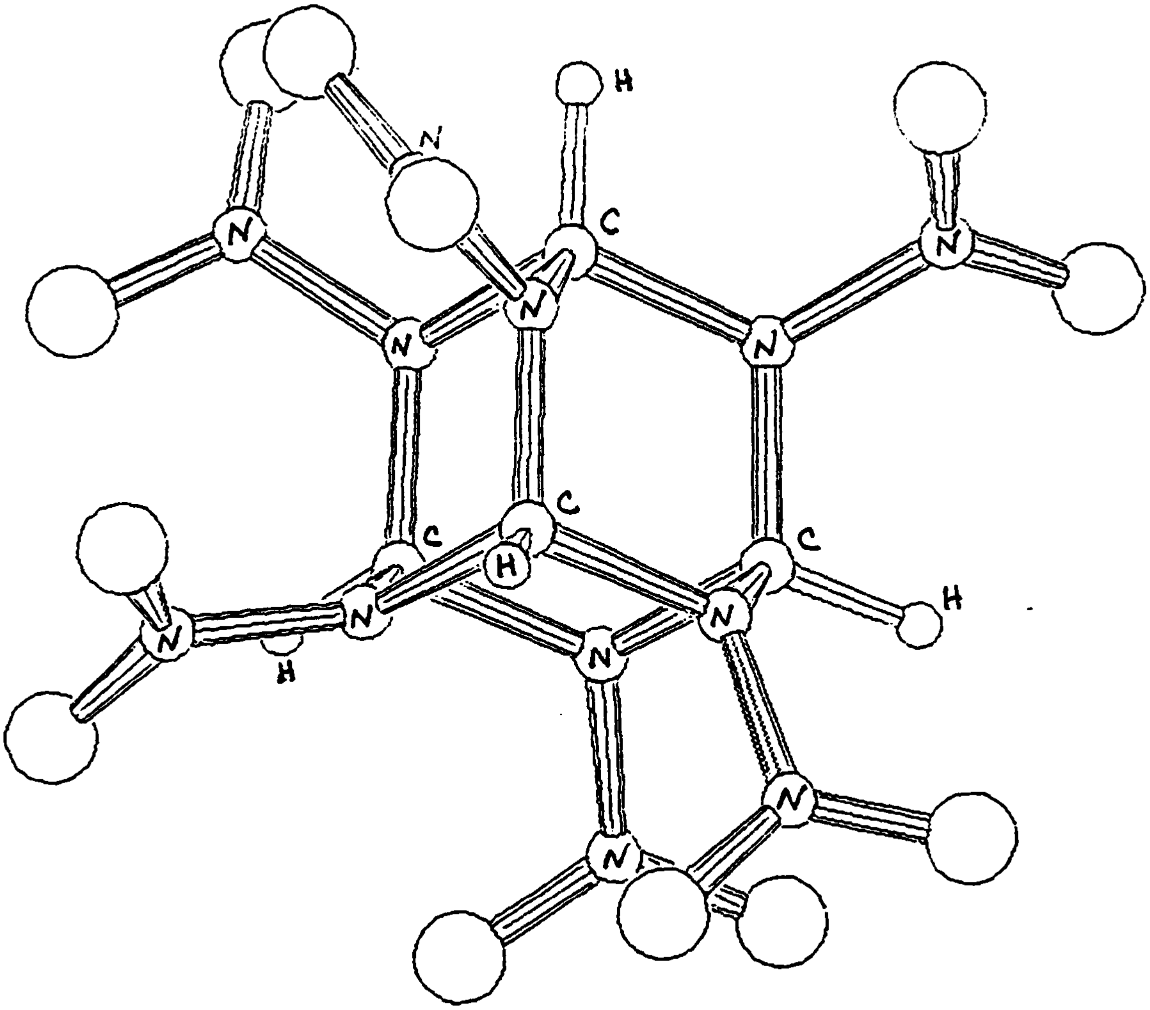
C-N	1.484(5)A	N-N	1.386(4)A
C-H	1.115(1)A	N-O	1.223(1)A

Predicted bond angles in HAZA are (to within ±2°):

NCN	108°	NCH	112°
CNC	112.5°	CNN	118°
ONO	124.5°	NNO	118°

Each carbon atom of the cage has three nonbonded nitro oxygen neighbors at distances from 2.72 to 2.90A (usual van der Waals' distance is 3.1A). Each hydrogen atom is approached by three oxygen atoms at distances from 2.43 to 2.58A (van der Waals distance is 2.6A). This indicates that HAZA is slightly crowded, but is considerably less crowded than the known stable compounds RDX and HMX, in which shorter H•••O contacts (2.19-2.30A) and C•••O contacts (2.60-2.68A) were observed [10,11]. However, the close H•••O approaches in HAZA do indicate that further nitro-substitution of the tertiary carbon atoms will be almost certainly impossible.

Fig. 10.



HEXANITRO-HEXA-AZA-ADAMANTANE

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