Technical Report ARAED-TR-92026

THE CRYSTAL AND MOLECULAR STRUCTURE OF TRIETHANOL-AMMONIUM NITRATE

A. J. Bracuti

December 1992

US ARMY
ARMAMENT MUNITIONS
& CHEMICAL COMMAND
ARMAMENT RDE CENTER

U.S. ARMY ARMAMENT RESEARCH, DEVELOPMENT AND ENGINEERING CENTER

Armament Engineering Directorate

Picatinny Arsenal, New Jersey

The views, opinions, and/or findings contained in this report are those of the authors(s) and should not be construed as an official Department of the Army position, policy, or decision, unless so designated by other documentation.

The citation in this report of the names of commercial firms or commercially available products or services does not constitute official endorsement by or approval of the U.S. Government.

Destroy this report when no longer needed by any method that will prevent disclosure of its contents or reconstruction of the document. Do not return to the originator.

REPORT DOCUMENTATION PAGE	Form Approved OMB No. 0704-0188

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	December 1992	

4. TITLE AND SUBTITLE

THE CRYSTAL AND MOLECULAR STRUCTURE OF TRIETHANOL-AMMONIUM NITRATE

5. FUNDING NUMBERS

6. AUTHOR(S)

A. J. Bracuti

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESSES(S)

ARDEC, AED
Energetics and Warheads Division (SMCAR-AEE-BR)
Picatinny Arsenal, NJ 07806-5000

8. PERFORMING ORGANIZATION REPORT NUMBER

Technical Report ARAED-TR-92026

9.SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(S)

ARAED, IMD
STINFO Br (SMCAR-IMI-I)
Picatinny Arsenal, NJ 07806-5000

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION/AVAILABILITY STATEMENT

Approved for public release; distribution is unlimited.

12b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

The liquid propellant used in the 155-mm regenerative liquid propellant gun is XM46 which is a solution of 60% hydroxyl ammonium nitrate (HAN), 20% triethanolammonium nitrate (TEAN), and 20% water. This material exhibits rather unusual liquid properties that have been attributed to its being a "molten eutectic" of fused salts rather than a normal aqueous solution of two different nitrate salts. A hydrogen-bonded liquid structure for eutectic LP1946 was proposed previously based on the known structures of neat HAN and water and a best-guess estimate of the TEAN structure. To verify this estimate, the molecular structure of neat TEAN was recently determined. This investigation revealed TEAN has very unusual and interesting bifurcated intermolecular and trifurcated intramolecular hydrogen bonding configurations within the crystal. If these hydrogen bonding configurations are retained in aqueous solution, they could be responsible in some part to the observed unusual liquid properties of liquid propellant XM46.

14. SUBJECT TERMS				15. NUMBER OF PAGES
Crystal structure Triethanolammonium nitrate	X-ray diffraction	Molecular structure	TEAN	28
				16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	SAR

CONTENTS

TABLES

FIGURES

INTRODUCTION

The liquid propellant used in the 155 mm regenerative liquid propellant gun is XM46 which is a nominal homogeneous mixture of 60% hydroxyl ammonium nitrate (HAN), 20% triethanolammonium nitrate (TEAN), and 20% water. It was reported that this highly concentrated mixture of nitrate salts and water behaves as a eutectic of fused salts (ref 1) rather than a normal aqueous solution. A liquid propellant structure composed of hydrogen-bonded TEAN/water/HAN clusters surrounded by regions of unstructured water was proposed for XM46 (ref 2) based on the known molecular structures of neat HAN and liquid water and a best-guess estimate of the TEAN molecular structure.

EXPERIMENTAL

X-Ray Diffraction Data Collection

A colorless translucent crystal of TEAN having approximate dimensions of 0.50 x 0.30 x 0.30 mm was mounted on a glass fiber[1]. The preliminary examination and data collection were performed with copper (Cu) Kα X-radiation (λ = 1.54178 A) on a Rigaku ASC5r computer controlled diffractometer equipped with a graphite crystal incident-beam monochromator and a 12 kw rotating anode generator.

Cell constants presented in table 1 and orientation matrix for data collection were obtained at 23 ± 1°C from least-squares refinement using the setting angles of 25 reflections in the angular range of 78.12 deg < 2θ < 79.67 deg. Prior to data collection was a check on crystal quality, omega scans of several intense reflections were measured. The average width at reflection intensity half-height for these reflections was 0.18 (2θ) with a take-off angle of 6 deg.

The intensity data were collected at a temperature of 23 ± 1°C using the w - 2θ technique at a scan rate of 32 deg/min. (in omega). To assure good counting statistics, the intensities of weak reflections [I < 25 σ (I)] were measured by accumulating the counts from three successive rescans. Intensity data for 1,726 reflections with h = 0 to 7, k = 10 to 18, and l = -10 to 10 were collected to a maximum value of 120 deg. The scan range (in deg) was determined as a function of θ to correct for the separation of the Kα doublet. The scan width was calculated with the equation

$$\theta \text{ scan width} = (1.26 + 0.14 \tan \theta)$$

[1]X-ray diffraction data collected by Molecular Structure Corporation, The Woodlands, TX.

The background level was determined by recording the counts at a fixed position on each side of the reflection. The ratio of peak counting-time to background counting-time was 2:1. The diameter of the incident beam collimator was 0.5 mm and the crystal to detector distance was 400 mm.

Data Reduction

A total of 1,726 reflections were measured, but only 1,577 reflections were unique. The R for averaged intensities is 0.019. As a check on crystal stability, the intensities of three representative reflections were measured after every 150 reflections. A linear decay correction was applied to the reflection data-set because the intensities of these monitored reflections declined by -5.6%. This indicated that TEAN was decomposing during the x-ray diffraction experiment.

The reflections were corrected for Lorentz-polarization, absorption, and secondary extinction effects. The empirical absorption corrections made using the program DIFABS (ref 3), based on the linear absorption coefficient for Cu Kα of 10.3 cm and the azimuthal scans of several reflections, resulted in transmission factors ranging from 0.92 to 1.04. The secondary extinction coefficient applied was 0.91158E-04.

A trial structure involving all the nonhydrogen atoms was determined with direct methods (ref 4) and all the hydrogen atoms were located with different Fourier methods (ref 5). Based on this trial structure, scattering factors were calculated using the neutral scattering factors of Cromer and Waber (ref 6). Anomolous dispersion effects were also included in the calculations of the structure factors (ref 7) using Cromer's values (ref 8) for f' and f".

Nonhydrogen atoms were refined anisotropically and all hydrogen atoms were refined isotropically with full-matrix least-squares analyses. The final cycle of full-matrix least-squares refinement based on 1,180 observed reflections [$I > 3\ \sigma(I)$] and 192 variables converged with weighted agreement factor (Rw) of 0.070 and unweighted agreement factor (R) of 0.057 where

$$Rw = \left[\left(\sum w\,(|Fo| - |Fc|)^2 / \sum w\,Fo^2\right)\right]^{\frac{1}{2}}$$

$$R = \sum (|Fo| - |Fc|) / \sum |Fo|$$

The maximum and minimum peaks on the final difference Fourier map were 0.21 and -0.21 e/A^3, respectively.

The melting and decomposition temperatures for TEAN were determined using differential scanning calorimetry (DSC). The experiments were performed with a DuPont model 2100 DSC in an air atmosphere on TEAN samples weighing between 2 and 3 g.

RESULTS

The crystal data, atomic coordinates, thermal parameters, bond lengths, and bond angles of TEAN are presented in tables 1 through 5. Details of the hydrogen bonding are given in table 6. Both the triethanolammonium cation (TEA+) and nitrate anion as well as the atom numbering scheme are depicted in figure 1, and a rendering of the TEAN cation with space filled atoms is shown in figure 2. The unit cell is presented in figure 3, and a stereographic pair of unit cells drawn in the same orientation is shown in figure 4. Different orientations of the unit cells are presented in figures 5 and 6. A DSC curve of TEAN with its melting endotherm is presented in figure 7.

Crystal Structure of TEAN

TEAN crystallizes in the centrosymmetric monoclinic space group $P2_1/c$ with a = 6.592(1), b = 16.358(1), c = 9.3850(8)A, and β = 90.87(1) deg. Based on four formula weights of TEAN per unit cell, the computed density is 1.393 g/cm^3. The TEAN asymmetric unit (fig. 1) contains one TEA+ cation and one nitrate anion. The atomic coordinates for the TEA+ cation, which contains six nonequivalent carbon atoms, one nitrogen atom, and 12 nonequivalent hydrogen atoms and for the nitrate anion which contains one nitrogen atom and three nonequivalent oxygen atoms, are listed in table 2.

In this structure each ion is surrounded by four oppositely charged ions. In addition to electrostatic forces, the structure is held together by a three-dimensional network of hydrogen bonds between cations and between cations and anions. All of the hydroxyl hydrogen atoms of the cation and two of the nitrate oxygen atoms are involved in this interionic hydrogen-bond network.

In the cation-anion linkage of this network two of the hydroxyl groups from the TEA+ cation form three hydrogen bonds with two oxygen atoms of the nitrate anion (table 6). One of the hydrogen bonds is formed between a hydroxyl hydrogen atom and an oxygen atom of the nitrate ion within the same asymmetric unit [O(1)-H(1). . . .O(4) is 2.784(4) A]. The second hydroxyl hydrogen atom forms an asymmetrically bifurcated hydrogen bond between two oxygen atoms of a nitrate

anion in a different asymmetric group [0(2)--H(2). . . .O(5) and O(2)--H(2). . . .O(4) are 2.970 (5) and 3.075 (5) A, respectively]. The closest nonhydrogen bonded interionic distances between heavy atoms are 3.287 (5) A for O(1)--O(6) and 2.160 (6) A for C(4)--O(4).

In the cation-cation linkage of this hydrogen-bond network, there is a hydrogen-bond between neighboring hydroxyl groups [0(3)-H(3). . .0(1), 2.850 (4) A].

Since TEAN is usually synthesized[2] by the nitric acid neutralization of triethanolamine (TEA), the parent free-base of TEAN, both the TEA and TEAN crystal structures and molecular conformations are compared in this report.

The TEAN DSC curve at ambient pressure (fig. 7) displays only two peaks: a sharp endotherm with an onset temperature at 80°C and a broad exotherm with an onset temperature at 251°C. The sharp endotherm is caused by the melting of TEAN. The melting point of TEA is near room temperature (21°C). Although both observed low melting points suggest that neither compound has strong intermolecular binding forces, the lower melting point of TEA indicates that weaker cohesive forces bind the molecules together in TEA.

The crystal structure of TEA ($R\bar{3}$) is composed of hydrogen-bonded cage -like dimers which are held together by van der Waals' forces in a spatial arrangement approximating cubic-close packing of equal spheres (ref 9). Since these molecular lattice forces are weaker than the ionic/hydrogen bond lattice forces found in crystalline TEAN, it is not surprising that TEA melts at a lower temperature than TEAN.

The broad exotherm presented in figure 7 with a 251°C onset temperature is caused by the thermal decomposition of TEAN. The absence of a second endotherm preceding the 251°C exotherm indicates that thermal decomposition of TEAN starts before it can vaporize. Therefore, TEAN thermal decomposition initiates in the liquid state. In contrast, TEA at ambient pressure vaporizes at 360°C without any reported thermal decomposition. This relatively high boiling point for this organic compound with a molecular weight of 149 suggests that the dimer does not thermally depolymerize below its vaporization temperature.

[2]Rothgery, E., Private communication, Olin Corporation, Cheshire, CT, 1992.

Conformation of the TEA+ Cation

As mentioned before, TEA exists as a dimer in the liquid and solid states. This dimer is formed through strong hydrogen bonding of six adjacent hydroxyethyl groups of two stacked inverted TEA molecules. The nitrogen atoms of the dimer lie on the three-fold inversion c axis of the unit cell (but not on inversion centers), and the remaining atoms lie on general positions related by three-fold inversion symmetry. The dimer is held together by six strong equivalent hydrogen bonds (O-H. .H, 2.700(1) A). It has six equivalent N-C, C-C, and C-O bonds of 1.467(1), 1.520(1), and 1.430(1) A, respectively, and six equivalent bond angles C-N-C, N-C-C, and C-C-O of 110.7(1), 113.5(1), and 112.1(1) deg, respectively.

Although the free base TEA is a caged molecule, the interior volume of the dimer cage is reported to be too small for enclathration of other atoms. To form the cation, protons must enter the cage and form coordinated covalent bonds with the amino nitrogen atoms. Since there is limited volume inside the cape, salt formation should be accompanied by destruction of the cage conformation.

As expected the TEA+ cation in crystalline TEAN does, indeed, consist of a single molecule rather than a hydrogen-bonded dimer. This is illustrated in figure 1 in which the cation conformation displays approximate three-fold heavy -atom symmetry with a central ammonium nitrogen atom bonded to four atoms: three carbon atoms of three hydroxyethyl groups, and one hydrogen atom, which shall be referred to as the proton. This conformation results in three equivalent N-C bonds with an average bond length of 1.507 A, three equivalent C-C bonds with an average bond length of 1.498 A, and three equivalent C-O bonds with an average bond length of 1.477 A. These average C-N-C, N-C-C, and C-C-O bond angles are 112.2, 110.9, and 106.8 deg, respectively. These TEAN bond lengths and bond angles differ significantly from their TEA counterparts. The individual bond lengths and bond angle are listed in tables 5 and 6.

Intra-ionic interactions probably cause the bond length and bond angle differences observed between TEAN and TEA. In TEAN, the proton forms an approximately symmetric trifurcated intramolecular hydrogen bond with the oxygen atoms of the three hydroxyethyl groups. The combined attractive forces of hydrogen bonding and electropolar interactions between the electronegative oxygen atoms and the positive cationic charge on the proton pull each hydroxethyl chain around to the same side of the central nitrogen atom. The total attractive force causes the C-N-C bond angle to become more obtuse while making both the N-C-C and C-C-O bond angles more acute than their respective TEA counterparts.

This intramolecular hydrogen bonding effectively encloses the proton within a nest of carbon, nitrogen, and oxygen atoms. This nested configuration of the proton, which is clearly illustrated in the space-filled atom diagram presented in figure 2, could possibly shield the proton from interaction with other molecules.

If this nested proton configuration is maintained in solution, it could affect the solution properties of TEAN such as hydrolysis or solvation. An NMR investigation of aqueous TEAN may resolve this question.

The proposed XM46 liquid structure (ref 2) consists of large globally neutral molecules which are multi-ion clusters of TEAN, water, and HAN surrounded by regions of unstructured or disordered water. One proposed ion cluster of many other possible ion clusters depicted in reference 2 contains one dissociated TEAN, three water molecules, and four associated HAN molecules. In dissociated TEAN, the TEA+ cation and nitrate anion are isolated by relatively large distances from each other. In contrast, an associated HAN molecule has its hydroxyl ammonium cation and nitrate anion hydrogen bonded to each other in much the same way as they are in the crystalline phase.

Situated at the center of the ion cluster is TEA+ whose three hydroxyl group hydrogen atoms form hydrogen bonds with the oxygen atoms of three water molecules. The hydrogen atoms of the three water molecules are also hydrogen bonded to the oxygen atoms of nitrate ions of three associated HAN molecules. Essentially these water molecules act as bridges. The nitrate anion from dissociated TEAN is hydrogen bonded to two of the water molecule bridges. In addition, the cluster contains an associated HAN molecule which is hydrogen bonded through one of its nitrate oxygen atoms to the TEAN proton.

Not much, if anything, is known about the structure of TEAN in solution, but if the TEA+ nested proton configuration is preserved in solution, it possibly could impede solvent proton interaction. This suggests that solvation and resultant dissociation of the TEAN proton decreases as the molecular size of the solvent molecule increases. If this is true, then it would seen more likely that in the liquid propellant mixture the TEAN proton would be hydrogen bonded by the small polar water molecule rather than by the larger associated HAN molecule. On the other hand, the TEAN hydroxyl hydrogen atoms, by virtue of the intra-ionic hydrogen bonding of the proton, would be optimally oriented to hydrogen bond oxygen atoms of water molecules or nitrate anions of associated HAN molecules.

Although little is actually known about the configuration of TEA+ in solution, nothing can be culled from the crystalline TEA+ conformation that refutes or weakens the theory of a liquid propellant structure containing clusters of hydrogen bonded anions and cations.

Conformation of the Nitrate Anion

The nitrate ion shown in figure 1 is planar as verified by the least-squares-plane calculations which show that N(2) has the largest deviation from the plane with a value of 0.0001(31). The planar nitrate ion usually displays D_{3h} symmetry with three equal angles of 120 deg and three equivalent N--O bonds. In this case, the bond angles do not vary significantly from each other [118.8(4), 119.9(4), and 121.3(4) deg] and have an average value of 120.4(4). However, only two of the three N-O bonds are equivalent [N(1)-O(4) and N(2)-O(5) are 1.238(4) and 1.234 (4)A, respectively], while the third N-O bond is significantly shorter [N(2)-O(6), 1.207(4) A]. The oxygen atoms [O(4) and O(5)] of the longer equivalent N-O bonds take part in hydrogen bonding with the cation, but in the oxygen atom [O(6)] of the shorter N-O bond does not participate in hydrogen bonding.

CONCLUSIONS

The proton in the TEA+ is hydrogen bonded to three hydroxyl group oxygen atoms (trifurcation). This conformation may cause unusual or atypical solvation effects and may impact some reactions.

The molecular structure of crystalline TEAN does not refute the ion-cluster theory for the structure of liquid propellant XM46.

Table 1. TEAN crystal data collected at 23 + 1°C

Monoclinic, space group $P2_1/c$ (#14), a = 6.592(1), b = 16.358(1), c = 9.3850(8) A, β = 90.87(1), Z = 4, V = 1011.9(2) A^3, DX = 1.393 g/cm^3, u = 10.30 cm^{-1}, Fw = 2.2.20, F(000) = 456 Systematic Absences: h0l, l = 2n + 1; 0k0, k = 2n + 1

Table 2. Atomic coordinates and equivalent thermal parameters and their estimated standard deviations in paraentheses for TEAN

Atom	x/a	y/b	z/c	Beq
O(1)	0.6474(5)	0.1053(2)	0.4604(3)	5.8(2)
O(2)	1.0060(5)	0.2504(2)	0.6451(3)	6.5(2)
O(3)	1.1060(5)	0.0238(2)	0.6448(4)	6.4(2)
N(1)	0.7920(6)	0.1173(2)	0.7496(3)	4.2(1)
C(1)	0.5815(7)	0.0912(3)	0.7049(5)	5.1(2)
C(2)	0.5166(7)	0.1325(3)	0.5690(5)	5.3(2)
C(3)	0.7958(7)	0.1990(3)	0.8225(5)	5.2(2)
C(4)	0.9895(8)	0.2430(3)	0.7951(5)	5.6(2)
C(5)	0.9001(8)	0.0528(3)	0.8382(4)	5.3(2)
C(6)	0.9780(8)	-0.0143(3)	0.7444(3)	5.7(2)
H(1)	0.593(8)	0.117(3)	0.375(6)	9(1)
H(2)	1.113(8)	0.279(3)	0.628(6)	10(2)
H(3)	1.153(7)	-0.010(3)	0.596(5)	9(2)
H(4)	0.855(5)	0.121(2)	0.673(4)	3.5(8)
H(5)	0.588(5)	0.029(2)	0.691(4)	5.1
H(6)	0.499(6)	0.104(2)	0.783(4)	6(1)
H(7)	0.533(5)	0.194(3)	0.583(4)	6(1)
H(8)	0.373(7)	0.114(3)	0.547(5)	8(1)
H(9)	0.668(6)	0.232(3)	0.782(5)	8(1)
H(10)	0.773(5)	0.189(2)	0.919(4)	4.6(8)
H(11)	1.109(6)	0.209(2)	0.837(4)	6(1)
H(12)	0.983(5)	0.295(2)	0.842(4)	4.8(8)
H(13)	1.020(6)	0.085(3)	0.894(4)	7(1)
H(14)	0.798(5)	0.032(2)	0.903(4)	4.3(8)
H(15)	0.861(7)	-0.046(3)	0.688(5)	9(1)
H(16)	1.044(7)	-0.054(3)	0.811(5)	8(1)
O(4)	0.4017(5)	0.1646(2)	0.2394(3)	7.0(2)
O(5)	0.3283(6)	0.1464(2)	0.0200(3)	8.3(2)
O(6)	0.5883(6)	0.0892(3)	0.1132(4)	9.2(2)
N(2)	0.4413(6)	0.1327(2)	0.1234(4)	5.1(2)

Table 3. Thermal parameters and their estimated standard deviations in parentheses for TEAN

Atom	U11	U22	U33	U12	U13	U23
N(2)	0.077(2)	0.060(2)	0.00562)	0.001(2)	0.016(2)	0.007(12
O(4)	0.102(2)	0.102(2)	0.063(2)	0.011(2)	0.008(2)	-0.010(2)
O(5)	0.120(3)	0.137(3)	0.058(2)	0.019(2)	-0.015(2)	-0.000(2)
O(6)	0.108(3)	0.139(3)	0.105(3)	0.052(3)	0.026(2)	0.013(2)
O(1)	0.088(2)	0.081(2)	0.052(2)	0.013(2)	0.007(2)	-0.001(1)
O(2)	0.100(2)	0.088(2)	0.058(2)	-0.03092)	0.003(2)	0.011(2)
O(3)	0.100(2)	0.068(2)	0.077(2)	0.010(2)	0.028(2)	-0.001(2)
N(1)	0.066(2)	0.049(2)	0.044(2)	-0.001(2)	0.012(2)	0.003(2)
C(1)	0.066(3)	0.072(3)	0.057(3)	-0.011(2)	0.009(2)	0.003(2)
C(2)	0.073(3)	0.068(3)	0.061(3)	-0.000)2)	0.010(2)	-0.001(2)
C(3)	0.090(3)	0.054(2)	0.055(2)	-0.002(2)	0.01692)	-0.007(2)
C(4)	0.097(4)	0.054(2)	0.062(3)	-0.008(3)	0.006(2)	-0.001(2)
C(5)	0.093(3)	0.059(2)	0.051(2)	0.003(2)	0.01392)	0.010(2)
C(6)	0.096(3)	0.052(2)	0.069(3)	0.005(3)	0.016(3)	0.006(2)
H(1)	0.11(2)					
H(2)	0.12(2)					
H(3)	0.11(2)					
H(4)	0.04(1)					
H(5)	0.07(1)					
H(6)	0.07(1)					
H(7)	0.07(1)					
H(8)	0.10(2)					
H(9)	0.10(2)					
H(10)	0.06(1)					
H(11)	0.08(1)					
H(12)	0.06(1)					
H(13)	0.09(1)					
H(14)	0.06(1)					
H(15)	0.11(2)					
H(16)	0.10(2)					

Table 4. TEAN bond lengths in angstroms (A) and their estimated standard deviations in parentheses

Atom	Atom	Distance	Atom	Atom	Distance
O(1)	C(2)	1.417(5)	C(1)	H(5)	1.03(4)
O(1)	H(1)	0.89(5)	C(1)	H(6)	0.94(4)
O(2)	C(4)	1.419(5)	C(2)	H(7)	1.02(4)
O(2)	H(2)	0.86(5)	C(2)	H(8)	1.00(4)
O(3)	C(6)	1.414(5)	C(3)	C(4)	1.491(6)
O(3)	H(3)	0.78(5)	C(3)	H(9)	1.07(4)
O(4)	N(2)	1.238(4)	C(3)	H(10)	0.94(4)
O(5)	N(2)	1.235(4)	C(4)	H(11)	1.04(4)
O(6)	N(2)	1.207(4)	C(4)	H(12)	0.95(4)
N(1)	C(1)	1.505(5)	C(5)	C(6)	1.502(6)
N(1)	C(3)	1.503(5)	C(5)	H(13)	1.08(4)
N(1)	C(5)	1.513(5)	C(5)	H(14)	0.98(3)
N(1)	H(4)	0.84(3)	C(6)	H(15)	1.07(5)
C(1)	C(2)	1.501(6)	C(6)	H(16)	0.99(5)

Table 5. TEAN bond angles in degrees and their estimated standard deviations in parentheses

Atom	Atom	Atom	Angle	Atom	Atom	Atom	Angle
O(4)	N(2)	O(5)	118.8(4)	N(1)	C(3)	C(4)	111.1(4)
O(4)	N(2)	O(6)	119.6(4)	N(1)	C(3)	H(9)	106(2)
O(5)	N(2)	O(6)	121.3(4)	N(1)	C(3)	H(10)	107(2)
C(2)	O(1)	H(1)	110(3)	C(4)	C(3)	H(9)	112(2)
C(4)	O(2)	H(2)	108(4)	C(4)	C(3)	H(10)	113(2)
C(6)	O(3)	H(3)	109(4)	H(9)	C(3)	H(10)	107(3)
C(1)	N(1)	C(3)	112.8(3)	O(2)	C(4)	C(3)	106.9(4)
C(1)	N(1)	C(5)	112.3(3)	O(2)	C(4)	H(11)	110(2)
C(1)	N(1)	H(4)	105(2)	O(2)	C(4)	H(12)	113(2)
C(3)	N(1)	C(5)	111.4(3)	C(3)	C(4)	H(11)	109(2)
C(3)	N(1)	H(4)	108(2)	C(3)	C(4)	H(12)	108(2)
C(5)	N(1)	H(4)	107(2)	H(11)	C(4)	H(12)	110(3)
N(1)	C(1)	C(2)	111.0(4)	N(1)	C(5)	C(6)	110.5(3)
N(1)	C(1)	H(5)	106(2)	N(1)	C(5)	H(13)	105(2)
N(1)	C(1)	H(6)	105(2)	N(1)	C(5)	H(14)	105(2)
C(2)	C(1)	H(5)	110(2)	C(6)	C(5)	H(13)	113(2)
C(2)	C(1)	H(6)	113(2)	C(6)	C(5)	H(14)	110(2)
H(5)	C(1)	H(6)	110(3)	H(13)	C(5)	H(14)	112(30
O(1)	C(2)	C(1)	107.5(4)	O(3)	C(6)	C(5)	106.1(4)
O(1)	C(2)	H(7)	111(2)	O(3)	C(6)	H(15)	109(3)
O(1)	C(2)	H(8)	109(3)	O(3)	C(6)	H(16)	116(3)
C(1)	C(2)	H(7)	107(2)	C(5)	C(6)	H(15)	113(3)
C(1)	C(2)	H(8)	107(3)	C(5)	C(6)	H(16)	105(3)
H(7)	C(2)	H(8)	116(3)	H(15)	C(6)	H(16)	107(4)

Table 6. TEAN hydrogen bond distances in angstroms (A) and angles in degrees and their estimated standard deviations in parentheses

D-H...A*	D-H	H...A	D....A	Angle
O(1)-H(1)..O(4)	0.89(5)	1.94(5)	2.784(4)	157(5)
O(2)-H(2)..O(5)	0.86(5)	2.14(5)	2.970(5)	161(5)
O(2)-H(2)..O(4)	0.86(5)	2.35(5)	3.075(5)	142(5)
O(3)-H(3)..O(1)	0.78(5)	2.12(5)	2.850(4)	157(5)
N(1)-H(4)..O(1)	0.84(3)	2.42(3)	2.870(4)	115(3)
N(1)-H(4)..O(2)	0.84(3)	2.35(3)	2.781(4)	113(3)
N(1)-H(4)..O(3)	0.84(3)	2.32(3)	2.766(4)	114(3)

* D is the hydrogen donor atom and A is the hydrogen acceptor atom.

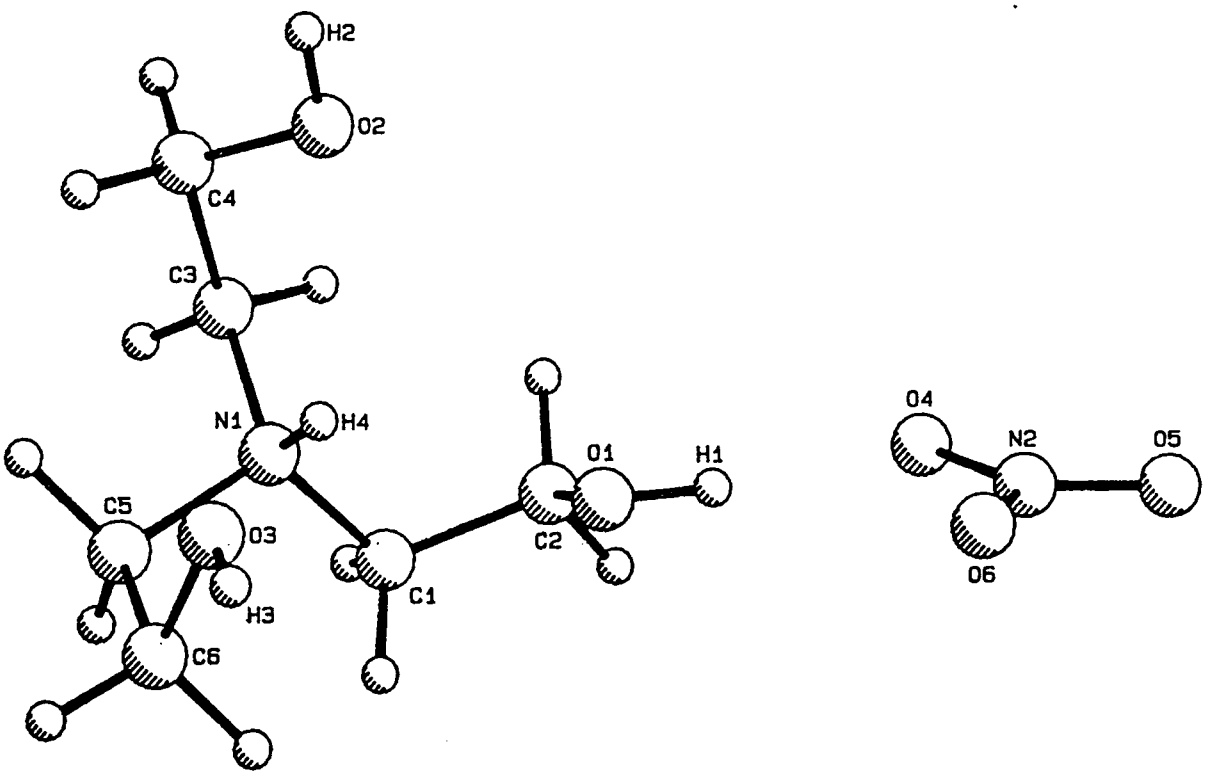

Figure 1. TEAN with atom numbering scheme

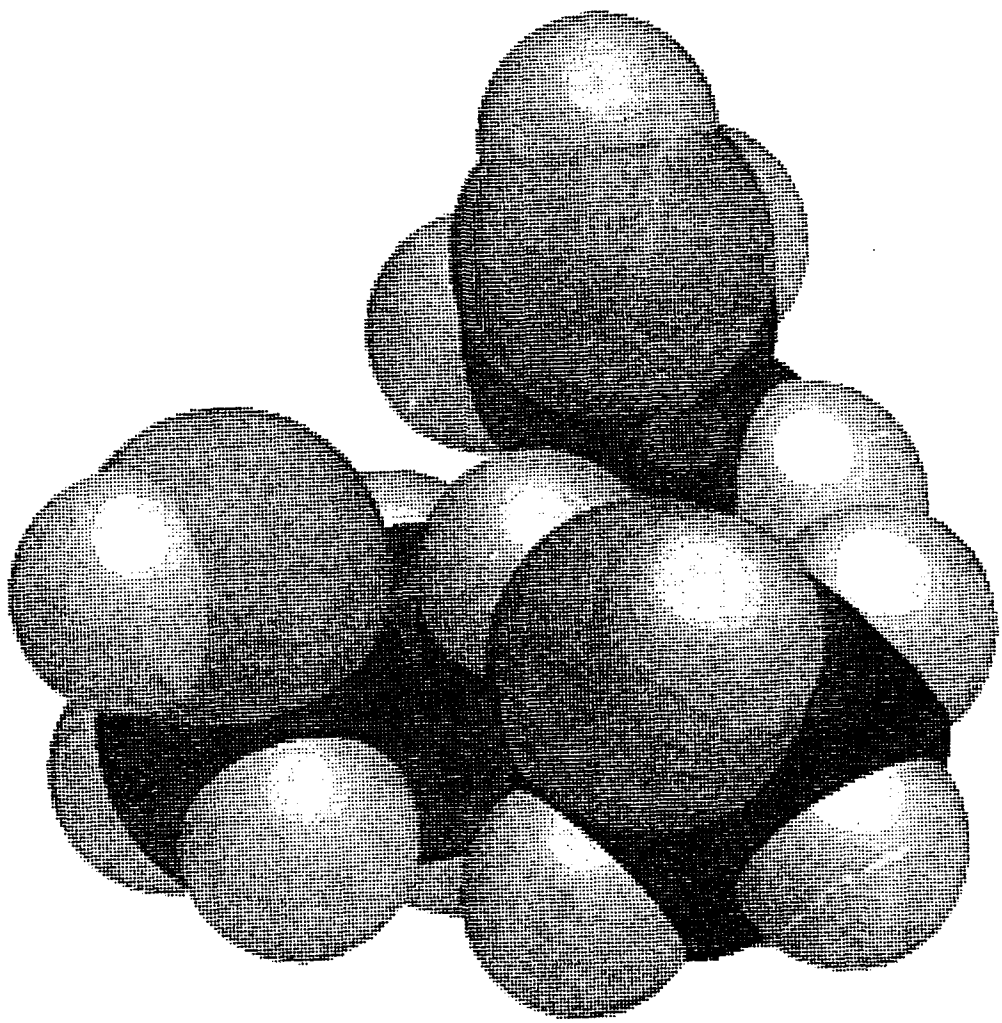

Figure 2. TEA+ with space filled atoms

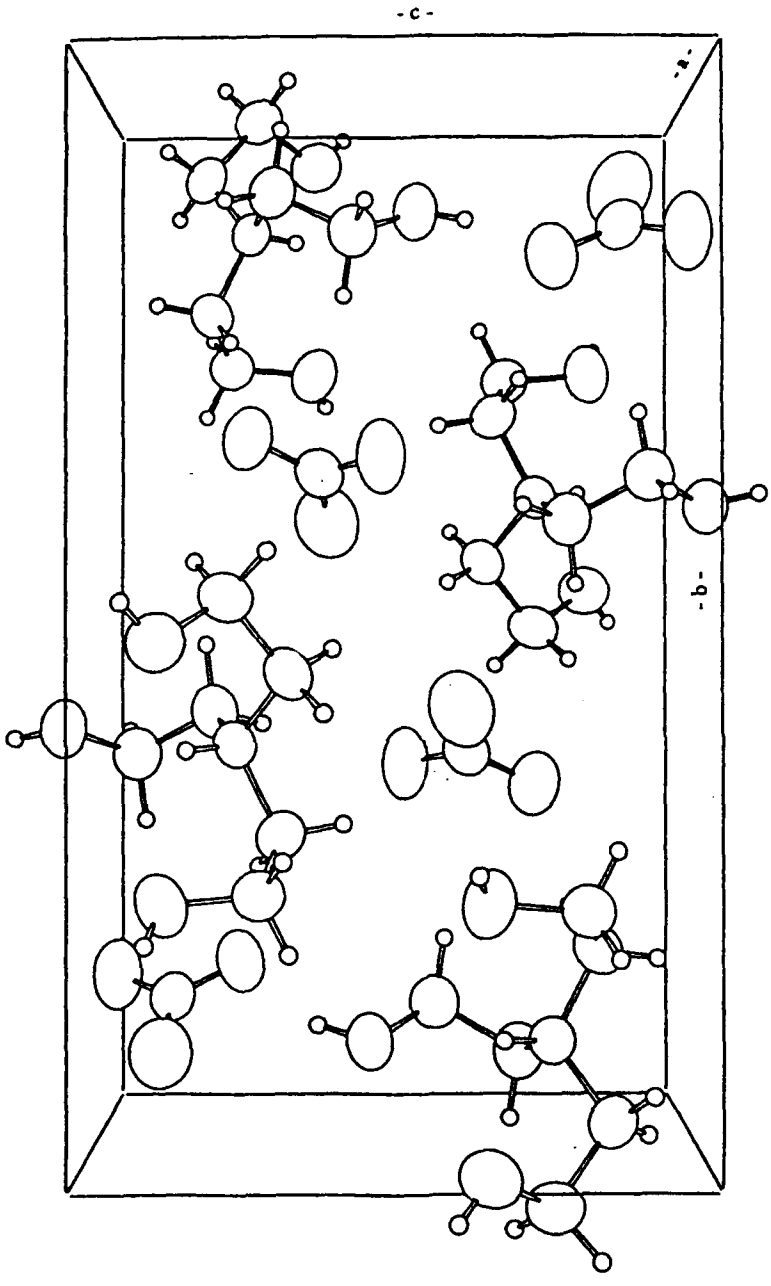

Figure 3. TEAN unit cell viewed down the a axis

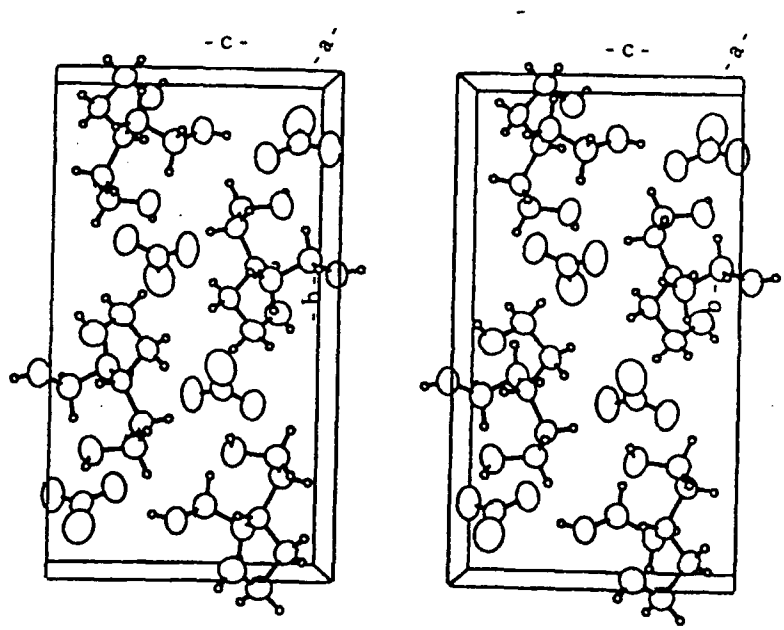

Figure 4. Stereographic pair of unit cells of TEAN viewed down the a axis

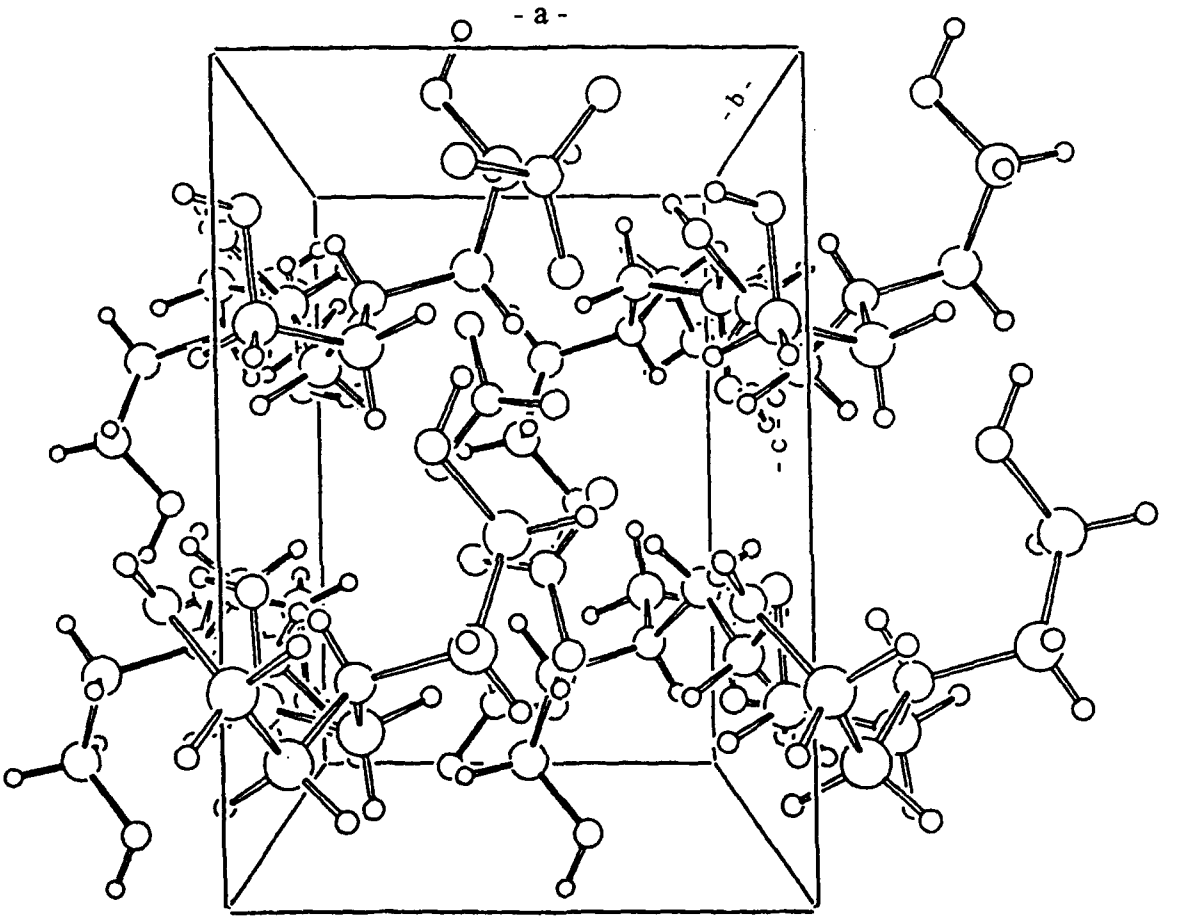

Figure 5. TEAN unit cell viewed down the b axis

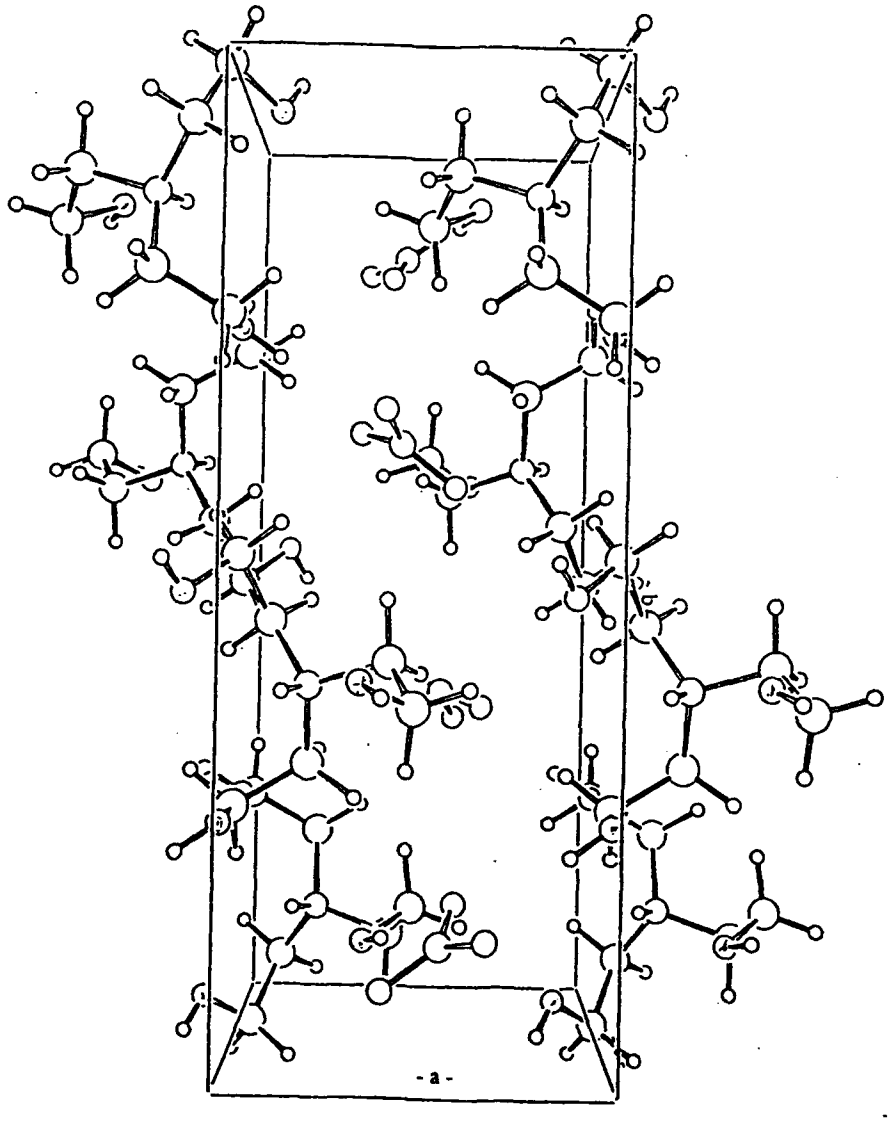

Figure 6. TEAN unit cell viewed down the c axis

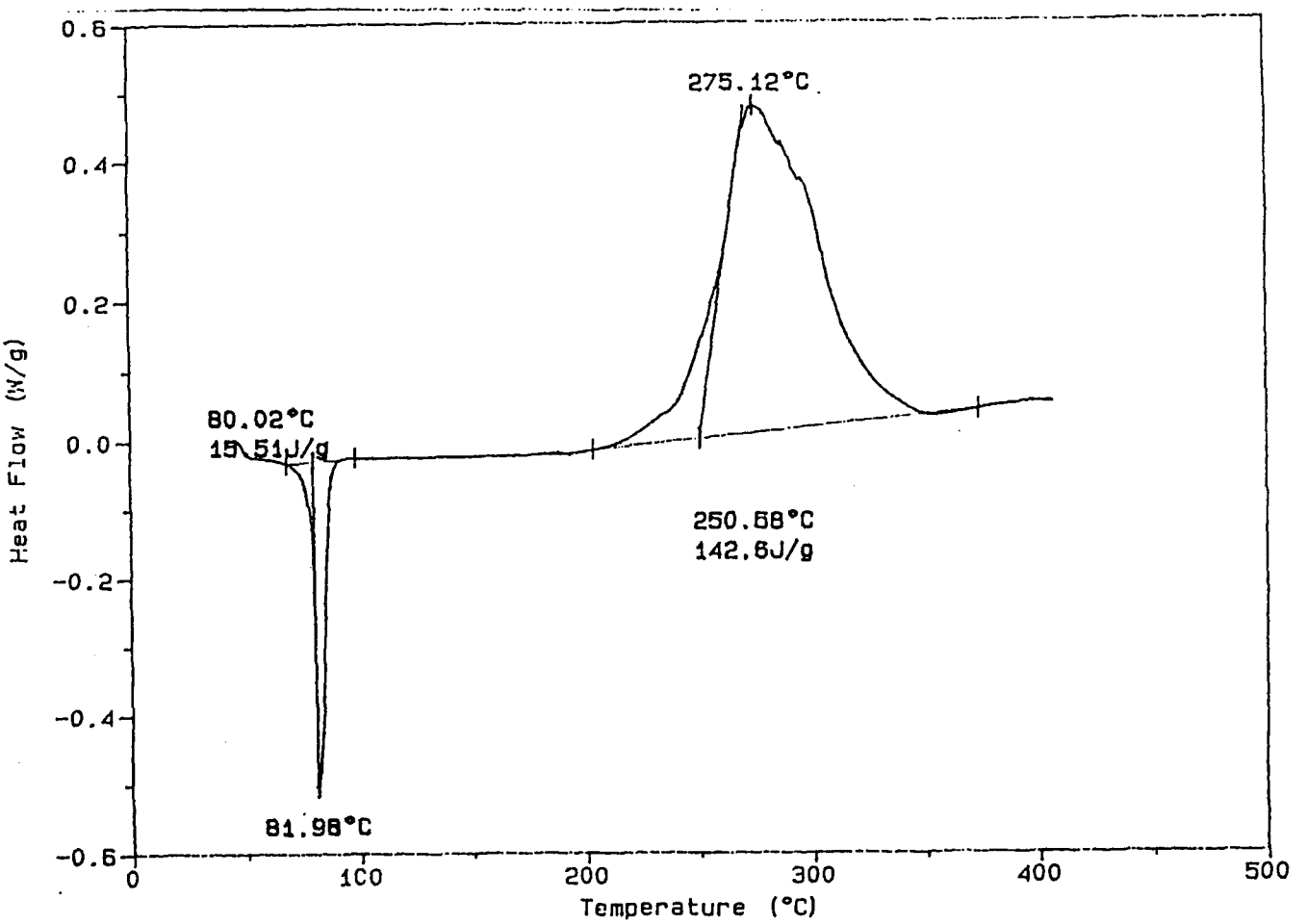

Figure 7. DSC curve of TEAN

REFERENCES

1. Klein, Nathan, "Liquid Propellants for Use in Guns - A Review," BRL-TR-2641, U.S. Army Ballistic Research Laboratory, Aberdeen, MD, February 1985.

2. Klein, Nathan, "The Molecular Structure of the HAN-Based Liquid Propellant," BRL-TR-3139, U.S. Army Ballistic Research Laboratory, Aberdeen Proving Ground, MD, August 1990.

3. Walker, N. and Steward, D., "An Empirical Method for Correcting Diffractometer Data for Absorption Effects," Acta Cryst. A39, pp 158 - 166, 1983.

4. Gilmore, C. J., "MITHRIL - An Integrated Direct Methods Computer Program," J. Appl. Cryst. 17, pp 42 - 46, 1984.

5. Beurskens, P. T., "DIRDIF - Direct Methods for Difference Structures," Technical Report 1984/1, Crystallography Laboratory, Toernooiveld, 6525 Ed Nijmegen, Netherlands.

6. Cromer, D. T. and Waber, J. T., International Tables for X-Ray Crystallography, Vol IV, Table 2.2A, The Kynoch Press, Birmingham, England, 1974.

7. Ibers, J. A. and Hamilton, W. C., "Dispersion Corrections and Crystal Structure Refinements," Acta Cryst. 17, p 781, 1964.

8. Cromer, D. T., International Tables for X-Ray Crystallography, Vol IV, Table 2.3.1, The Kynoch Press, Birmingham, England, 1974.

9. Mootz, Deitrich, Brodalla, Dieter, Wiebcke, and Michael, "Structures of Monoethanolamine (MEAM), Diethanolamine (DEAM), and Triethanolamine (TEA)," Acta Cryst., C45, pp 754 - 757, 1989.

DISTRIBUTION LIST

Commander
Armament Research, Development and Engineering Center
U.S. Army Armament, Munitions and Chemical Command
ATTN: SMCAR-IMI-I (5)
SMCAR-AE, B. Bushey
G. Taylor
SMCAR-AEE (4)
SMCAR-AEE-B
SMCAR-AEE-BR, A. Bracuti (10)
P. Hui (2)
D. Chiu (2)
SMCAR-AEE-WE (2)
Picatinny Arsenal, NJ 07806-5000

Commander
U.S. Army Armament, Munitions and Chemical Command
ATTN: AMSMC-GCL (D)
Picatinny Arsenal, NJ 07806-5000

Administrator
Defense Technical Information Center
ATTN: Accessions Division (12)
Cameron Station
Alexandria, VA 22304-6145

Director
U.S. Army Material Systems Analysis Activity
ATTN: AMXSY-MP
Aberdeen Proving Ground, MD 21005-5066

Commander
Chemical Research, Development and Engineering Center
U.S. Army Armament, Munitions and Chemical Command
ATTN: SMCCR-MSI
Aberdeen Proving Ground, MD 21010-5423

Commander
Chemical Research, Development and Engineering Center
U.S. Army Armament, Munitions and Chemical Command
ATTN: SMCCR-RSP-A
Aberdeen Proving Ground, MD 21010-5423

Director
Ballistic Research Laboratory
ATTN: AMXBR-OD-ST, J. Fraiser
J. Rocchio
I. May
J. Knapton
Aberdeen Proving Ground, MD 21005-5066

Chief
Benet Weapons Laboratory, CCAC
Armament Research, Development and Engineering Center
U.S. Army Armament, Munitions and Chemical Command
ATTN: SMCAR-CCB-TL
Watervliet, NY 12189-5000

Commander
U.S. Army Rock Island Arsenal
ATTN: SMCRI-TI, Technical Library
Rock Island, IL 61299-6000

Director
U.S. Army TRADOC Systems Analysis Activity
ATTN: ATAA-SL
White Sands Missile Range, NM 88002

Director of Army Research and Technology
ATTN: DAMA-AR, L. M. Cameron
Pentagon Room 3E474
Washington, DC 20004

Director
LABCOM
ATTN: R. Vitale
Harry Diamond Laboratory
2800 Powder Mill Road
Adelphia, MD 20783-1145

Chairman
DoD Explosive Safety Board
Room 856-C
Hoffman Building 1
2461 Eisenhower Avenue
Alexandria, VA 22331

Commander
U.S. Naval Ordnance Station
ATTN: E. Walsman
Technical Library
Indian Head, MD 20604

Commander
U.S. Naval Surface Weapons Center
ATTN: K. Wagman
Technical Library
Silver Springs, MD 20910

Commander
Air Force Armament Laboratory
ATTN: Munitions Division
Technical Library
Eglin AFB, FL 32542-5434