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INFRARED AND RAMAN SPECTRA OF 1, 3, 5-TRINITRO-1, 3, 5-TRIAZACYCLOHEXANE (RDX)

Zafar Iqbal, et al

Picatinny Arsenal
Dover, New Jersey

October 1972

COPY NO. 21

TECHNICAL REPORT 4401

INFRARED AND RAMAN SPECTRA
OF
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OCTOBER 1972

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A

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(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY *(Corporate author)*
U.S. Army, Picatinny Arsenal, Dover, NJ

2a. REPORT SECURITY CLASSIFICATION
Unclassified

2b. GROUP

3. REPORT TITLE
Infrared and Raman Spectra of 1,3,5-Trinitro-1,3,5-Triazacyclohexane (RDX)

4. DESCRIPTIVE NOTES *(Type of report and inclusive dates)*

5. AUTHOR(S) *(First name, middle initial, last name)*
Zafar Iqbal; K. Suryanarayana; Suryanarayana Bulusu; J.R. Autera

6. REPORT DATE

7a. TOTAL NO. OF PAGES

7b. NO. OF REFS

8a. CONTRACT OR GRANT NO.
AMCMS Code 501B.11.85601

b. PROJECT NO.

c. DA Project 1T061102A32B 01

d.

9a. ORIGINATOR'S REPORT NUMBER(S)
Technical Report 4401

9b. OTHER REPORT NO(S) *(Any other numbers that may be assigned this report)*

10. DISTRIBUTION STATEMENT
Approved for public release; distribution unlimited.

11. SUPPLEMENTARY NOTES

12. SPONSORING MILITARY ACTIVITY
Picatinny Arsenal, Dover, NJ

13. ABSTRACT

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DD FORM 1 NOV 66 1473 REPLACES DD FORM 1473, 1 JAN 64, WHICH IS OBSOLETE FOR ARMY USE.

UNCLASSIFIED
Security Classification

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Infrared spectra						
Raman spectra						
Vibrational spectra						
1,3,5-trinotro-1,3,5-triazacyclohexane (RDX)						
CH_2 modes						
NO_2 modes						
Ring vibrations						
Lattice modes						
Combination and overtone modes						
N^{15} - labeled RDX						
Isotopic shift						
1,3,5-trinitroso-1,3,5-triazacyclohexane (TNTC)						

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AMCMS Code 501B.11.85601
DA Project 1T061102A32B 01

Explosives Division
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Dover, New Jersey

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ABSTRACT

The transmission infrared and the laser excited Raman spectra of polycrystalline RDX have been measured in the range of 40 to 4000 cm^{-1}. To aid assignments in the spectral region of 400 to 4000 cm^{-1}, the spectra of two types of N^{15}-labeled samples and the solution spectra in different solvents were also recorded. From these data it was possible to assign many of the observed bands to intramolecular modes of the RDX molecule. The Raman active lattice modes also were resolved and found to be comparable to the lattice mode frequencies in solid cyclohexane.

INTRODUCTION

The nitramines form an interesting group of organic compounds, which have provided structural chemists with a wide variety of problems. This report deals with RDX (1,3,5-trinitro-1, 3, 5-triazacyclohexane), a monocyclic member of the above group, consisting of three nitramine units. The molecule has 21 atoms; it was thought that it would show sufficient symmetry to allow an analysis of its vibrational spectrum. Such an analysis would permit qualitative conclusions regarding molecular bond orders and conformations in different environments. Previous studies include a detailed structural analysis of the compound by X-ray diffraction (Ref 1) as well as by neutron scattering (Ref 2), and a partial analysis of the mid-infrared part of the spectrum (Ref 3,4). While the present work has been in progress, another study of the infrared and Raman spectra of RDX has been published by Rey-Lafon (Ref 5) et al. Their data are in general agreement with ours; the purpose of the concise account presented here is only to stress the more unusual aspects of the RDX structure. The objective of this work has been to measure the infrared and Raman active vibrations in as wide a spectral range as feasible, and assign the modes by analogy with previous studies on similar but simpler molecules, and from isotopic and solution data. The results obtained may, therefore, form a starting point for a normal coordinate analysis of the molecular spectrum of RDX and the vibrational analysis of the related eight-membered ring HMX molecule (1,3,5,7-tetranitro-1,3,5,7-tetrazacyclooctane).

SYMMETRY CONSIDERATIONS AND STRUCTURE

RDX has a structure similar to the boat and chair forms of cyclohexane, and as in the latter the chair form should be of lower energy. It is, therefore, expected that RDX will exist predominantly in the chair form. The structure as determined by X-ray diffraction (Ref 1) and confirmed by neutron scattering (Ref 2) of crystalline RDX is shown in Fig 1. This does represent a chair form but, surprisingly, with an unfavorable orientation of two nitramine groups in the axial positions.

In solution, the symmetry of the molecule is, due to ring inversion, that of a symmetric top belonging to point symmetry C_{3v}. If the N and C atoms of the nitramine group in position 1 (see Fig 1) are in the same plane as the hydrogen atoms of the C atom in position 4, then the 57 normal mode vibrations of the molecule are distributed among the following symmetry species:

$$\Gamma^{I} = 13\,A_1 + 6\,A_2 + 19\,E$$

However, if the O atoms of the $N\text{-}NO_2$ group in position 1 are not in that plane, the vibrations are distributed as:

$$\Gamma^{II} = 12\,A_1 + 7\,A_2 + 19\,E$$

The vibrations of A_1 and E symmetry are active in both the infrared and Raman spectra, while vibrations of A_2 symmetry are silent in both. Thus, in structure I (symmetry species Γ^{I}), 32 modes, in structure II (symmetry species Γ^{II}), 31 modes are active. The comparatively short N-N bond length of the equatorial $N\text{-}NO_2$ group observed in the crystal (Ref 1) would favor structure II in the solid phase. This may also be true for the isolated molecule.

In the condensed phase RDX loses its threefold symmetry. A staggered chair conformation as shown in Fig 1, in which 2 axial and 1 equatorial $-NO_2$ groups are found, is suggested by the X-ray diffraction data (Ref 1). The molecules are at sites of symmetry C_1 in the space group D_{2h}^{15}-Pbca with eight formula units in the primitive cell. According to the site group approximation, the A_2 type molecular vibrations will, therefore, have both infrared and Raman active components in the solid state spectra. The external or lattice mode optic translatory (T) and libratory (R) components for the factor group D_{2h}^{15}, will be distributed as:

$$\begin{aligned}\Gamma = {} & (3T + 3R)\,A_{1g} + (3T + 3R)\,B_{1g} + (3T + 3R)\,B_{2g} + \\ & (3T + 3R)\,B_{3g} + (3T + 3R)\,A_{1u} + (2T + 3R)\,B_{1u} + \\ & (2T + 3R)\,B_{2u} + (2T + 3R)\,B_{3u}\end{aligned}$$

The factor group is centrosymmetric; hence the Raman active vibrations would be forbidden in the infrared. In principle, however, the correlation field in organic crystals is small, and hence the infrared and Raman spectra in the condensed phase would be nearly coincident. The large number of factor group splittings predicted by group theory would not be observed, either, since the splittings predicted may amount to less than 1 cm^{-1}.

EXPERIMENTAL

The infrared spectra in the region 400 to 4000 cm^{-1} were recorded in a Perkin-Elmer 621 grating spectrometer using KBr disc samples and solutions. Single crystal measurements were performed using the spectrometer with 6x beam condensing arrangement. The infrared spectra of the region 70 to 400 cm^{-1} were measured in a Beckman IR-11 spectrometer, using a thin film of the sample in Nujol oil on a polyethylene substrate.

The Raman spectra were recorded using both He-Ne (6328A, 50 mW) and Ar ion (4830 A, 300 nW) focussed radiation. The 90^o scattered radiation was analyzed by a Spex 1400 double monochromator coupled with a photon counting detection system. The powder and solution spectra were measured in glass capillaries.

The RDX samples used were purified by multiple recrystallization. Single crystals were grown from acetone solutions of the compound. The ring N^{15} -labeled RDX samples were prepared by the nitration of N^{15} -labeled hexamine, while the nitro-group labeled RDX samples were prepared by nitrating hexamine with N^{15} -labeled nitric acid. The isotopic enrichment in all samples was about 99%.

RESULTS

The infrared and Raman spectra of RDX as single crystal, powder, and solution samples, have been measured in the frequency range 400 to 4000 cm^{-1}. The tracings of the spectra are shown in Figures 2 and 3. The solution Raman spectra were recorded using saturated solutions of RDX in deuterated dimethylsulphoxide (d_6-DMSO), while the solution infrared spectra in the frequency ranges 1200 to 3200 cm^{-1} and 600 to 1200 cm^{-1}, were recorded using as solvents d_6-DMSO and acetonitrile, respectively. The powder infrared spectra of ring and nitro group N^{15} labeled RDX samples, in the spectral range 400 to 1800 cm^{-1}, also were measured; the tracings are shown in Fig 4 together with the spectrum for unlabeled RDX. The low frequency 40 to 400 cm^{-1} region of the spectrum was recorded only for solid samples of RDX and is shown in Fig 5. The infrared spectrum of 1,3,5-trinitroso-1,3,5-triazacyclohexane (TNTC), the trinitroso analog of RDX also was measured; its spectrum in the low frequency region is shown in Fig 5b.

The frequencies of the solid and solution bands of RDX together with the assignments are listed in Table 1. Since a wider frequency range has been measured with powder samples, the frequencies quoted in Table 1 have been taken from the powder spectra. The combination and overtone frequencies in the spectral region 1700 to 3000 cm^{-1} were observed in the transmission infrared spectrum of a thick single crystal. These frequencies have been compiled in Table 2.

DISCUSSION

Fundamental Molecular Vibrations

CH_2 Modes

The bands in the 2900 to 3100 cm^{-1} region can be assigned to CH_2 stretching modes. An assignment in terms of symmetric and asymmetric motions is based on the fact that the symmetric mode gives rise to strong bands in the Raman, and weaker peaks in the infrared spectrum. A number of interesting features can be noted on comparing the solution with the solid infrared and Raman spectra. The higher frequency asymmetric stretching mode in the solid shows a site group splitting of about 10 cm^{-1} (Fig 2d). This is in agreement with the presence of two types of sites in the staggered chair conformation of the molecule in the crystal. Two peaks separated by 50 cm^{-1} are observed in the solid state spectra in the region of the symmetric stretching mode. Since the second peak disappears in the spectra of RDX in d_6-DMSO solution, one can associate this band with the lowered symmetry of the molecule at the crystal site, which leads to the infrared and Raman activity of this mode. In d_6-DMSO solution, however, both the symmetric and asymmetric stretching peaks broaden out, indicating the presence of possible solvent-solute interaction in that solution.

A point worth noting is that the mode frequency for the CH_2 asymmetric stretching motion in RDX is about 100 cm^{-1} higher than in cyclohexane. This anomalous value seems to indicate considerable strain on the RDX ring in the crystalline state. This aspect of RDX structure is the subject of a more detailed study involving a group of cyclic nitramines, which will be published shortly.

The assignment of the bands between 1390 and 1460 cm^{-1} to CH_2 skeletal motions is based on the data of Wood (Ref 3) on deuterated RDX.

NO_2 Modes

The symmetric and asymmetric stretching modes of the NO_2 group can be assigned in the same manner as the corresponding motions in the CH_2 group. These bands would also show the largest shift when the nitrogen atom on the NO_2 group is labeled with N^{15}. The peaks between 1540 to 1600 cm^{-1} can be clearly identified as the asymmetric NO_2 stretching mode components. The extremely strong peak at approximately 1596 cm^{-1} shows a splitting of between 10 and 15 cm^{-1}, which can be attributed to the two types of NO_2 groups in the staggered chair conformation of the molecule in the crystal.

The symmetric-stretching NO_2 and the N-N vibrations can have mode frequencies close to one another (Ref 6). Since the peak at 1268 cm^{-1} is very strong in the solution Raman spectrum, one can probably assign this band to the NO_2 type stretching. The peak at 1310 cm^{-1} can, therefore, be associated with the symmetric stretching N-N mode. Both these modes show a site group splitting of approximately 10 cm^{-1} in the infrared absorption measurements on a solid sample.

Two bands in the 750 cm^{-1} region of the spectrum show a large shift for nitro group labeled RDX (see Fig 4) and can therefore be assigned to a NO_2 vibration, possibly the NO_2 deformation motion. The skeletal NO_2 modes lie in the low frequency region of the spectrum and are probably mixed to a large degree with torsional and bending ring vibrations. Hence, assignments on the basis of frequency shifts of the nitro group labeled RDX samples would be difficult. However, by comparison with the spectrum of TNTC one can assign the bands between 450 to 610 cm^{-1}, which do not occur in the spectrum of the trinitroso analog (see Fig 5b), to NO_2 skeletal motions. The broad bands between 128 and 150 cm^{-1} are somewhat too high in energy to be associated with lattice vibrations (see the subsection on lattice modes) and hence can be tentatively identified as due to the N-NO_2 torsional mode.

Ring Vibrations

The strongest band in the Raman spectrum of solid RDX occurs at 832 cm^{-1}. This peak can be assigned to the symmetric ring stretching mode since such a motion is likely to generate a large polarizibility change. By analogy with the work on cyclohexane (Ref 5), the bands around 200 cm^{-1} can be assigned to a ring bending and torsional motion, while the peak at 410 cm^{-1}, which corresponds closely to the strongest band in the neutron inelastic scattering (NIS) spectrum of the salt, can be assigned to an essentially ring bending vibration.

Two sets of frequencies at 1020 and 1220 cm^{-1} have been assigned to ring type vibrations on the basis of the observed shifts for the ring labeled RDX sample.

Lattice Modes

Five peaks have been resolved in the solid state Raman spectrum between 50 and 110 cm^{-1}, which can be assigned to the external optic or lattice modes. These peaks correspond to the broad density of states centered at 55 cm^{-1} (Ref 8).

Combination and Overtone Modes

The bands between 1700 and 3000 cm^{-1}, observed in the infrared spectrum of a thick single crystal of RDX, can be assigned to combination and overtone modes. The spectrum (see Fig 2b) is divided into four regions, as shown in the figure. Possible overtone and summation modes can be suggested for these bands in terms of the strongest infrared and Raman peaks. These are shown in Table 2.

CONCLUSION

Possible assignments of the rich infrared and Raman spectra of RDX, both in the solid and in d_6-DMSO and acetonitrile solutions, have been proposed. Site group splittings, observed in the solid state spectra for the CH_2 asymmetric stretching and the NO_2 and N-N stretching modes, support the proposed staggered chair conformation of the molecule in the crystal with two distinctive oreintations of the nitramine groups. However, solution data suggest a more symmetrical RDX conformation than in the crystal lattice and some possible solute-solvent interaction. A complete normal coordinate analysis of RDX molecule is being carried out in collaboration with Dr. George Adams of the Propellants Division, Feltman Research Laboratory. A detailed structural study of HMX polymorphs by infrared and Raman spectra also is in progress.

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TABLE 1

Frequencies and assignments of bands
in the 40 to 4000 cm^{-1} region in the spectrum of RDX

Infrared(cm^{-1})		Raman(cm^{-1})		Remarks and Assignments
Solid	Solution	Solid	Solution	
		50.3 s[a]		Lattice modes
		59.2 vs		
		71.5 s		
		85.7 m		
		107 m		
		128 m br		N-NO$_2$ torsion
		148 m br		
		183 w		
		206 m		C-N-C bend + torsion
225 ms				
		224 s		
346 s		349 s		
412 m		410 w	410 m	C-N-C bend
460 m		464 m	470 w	NO$_2^-$ skeletal
487 m		487 w br	490 w	
595 m	595 m	590 m[b]	sol.[c]	
610 m	610 m sh	605 m[b]	sol.	
675 w		671 w	sol.	
740 w sh	740 w	738 w	sol.	NO$_2$ deformation
754 m	750 m	758 w	sol.	

TABLE 1 (cont'd)

782 m	794 m	787 w	790 m	
844 m		847 m	845 m	
854 m		854 w sh	850 m sh	
882 m	885 w sh	880 vs	885 ms	Symmetric ring stretch
917 vs	910 m	916 w		
927 vs				
947 s	935 s	940 m	947 w	
1020 m	1015 s	1030 m	sol.	Ring
1040 s	1045 m sh			
1219 m		1217 s	1214 m	Ring
1232 m	1230 m sh	1232 w sh		
1267 s	1270 s	1274 s	1268 vs	NO_2 symmetric stretch
1275 s sh				
1312 m	1320 m	1313 s	1309 m	N-N symmetric stretch
1322 m				
1352 m		1344 w	1339 w	
1391 m	1392 m	1382 m sh	1384 m	CH_2 skeletal modes
		1389 m		
1424 m	1435 m	1427 m sh	1434 m	
1435 m				
1460 m	1460 m	1461 w		
		1509 w		
1535 ms	1550 m sh	1544 m	1542 m sh	NO_2 asymmetric stretch
		1574 m		
1576 s				
		1577 m sh		
1593 s	1585 s	1596 m	1582 s	

TABLE 1 (cont'd)

2950 w[b]		2948 vs		CH_2 symmetric stretch
	2980 w		2967 s	
3006 m		3004 s		
3068 ms		3067 m	3074 m	CH_2 asymmetric stretch
3078 s	3080 m	3074 m		

[a] s-strong, m-medium strong, w-weak, sh-shoulder, br-broad

[b] observed in single crystal sample only

[c] solvent interference

TABLE 2

Combination and Overtone bands observed in the 1700-3000 cm^{-1} region in the transmission infrared spectrum of a thick single crystal of RDX

Frequency (cm^{-1})	Remarks
1770 ms	2 x 885
1875 ms	1592 + 1267
1915 m br	Internal-external combination peaks; 1875 + 40, 1875 + 60, and 1875 + 80.
1935 m br	
1955 m br	
2010 m	1020 x 2, 1020 + 1219 and related peaks
2030 m	
2070 w	
2110 w	
2130 w	
2160 m	
2200 m	
2275 m sh	
2300 ms	
2350 ms	
2380 m sh	
2430 m	
2470 m	

TABLE 2 (cont'd)

2545 m	2 x 1267, 2 x 1312, 1267 + 1312 and related peaks
2590 m	
2620 m	
2680 w	2 x 1592 and related peaks
2710 w	
2760 w	
2780 w	

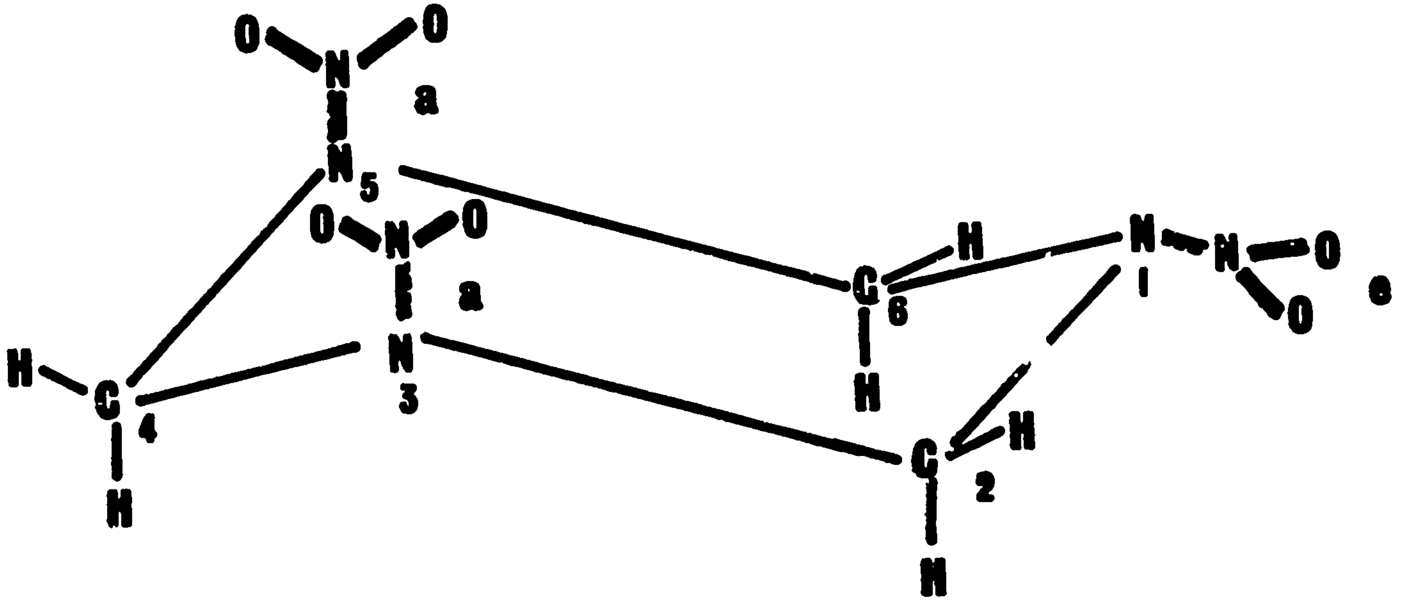

Fig 1 Structure of the molecule at a crystal site; 'a' and 'e' indicate the axial and equatorial nitramino groups. A single line represents a single bond, a single line with dots a partial double bond, a heavy line a double bond

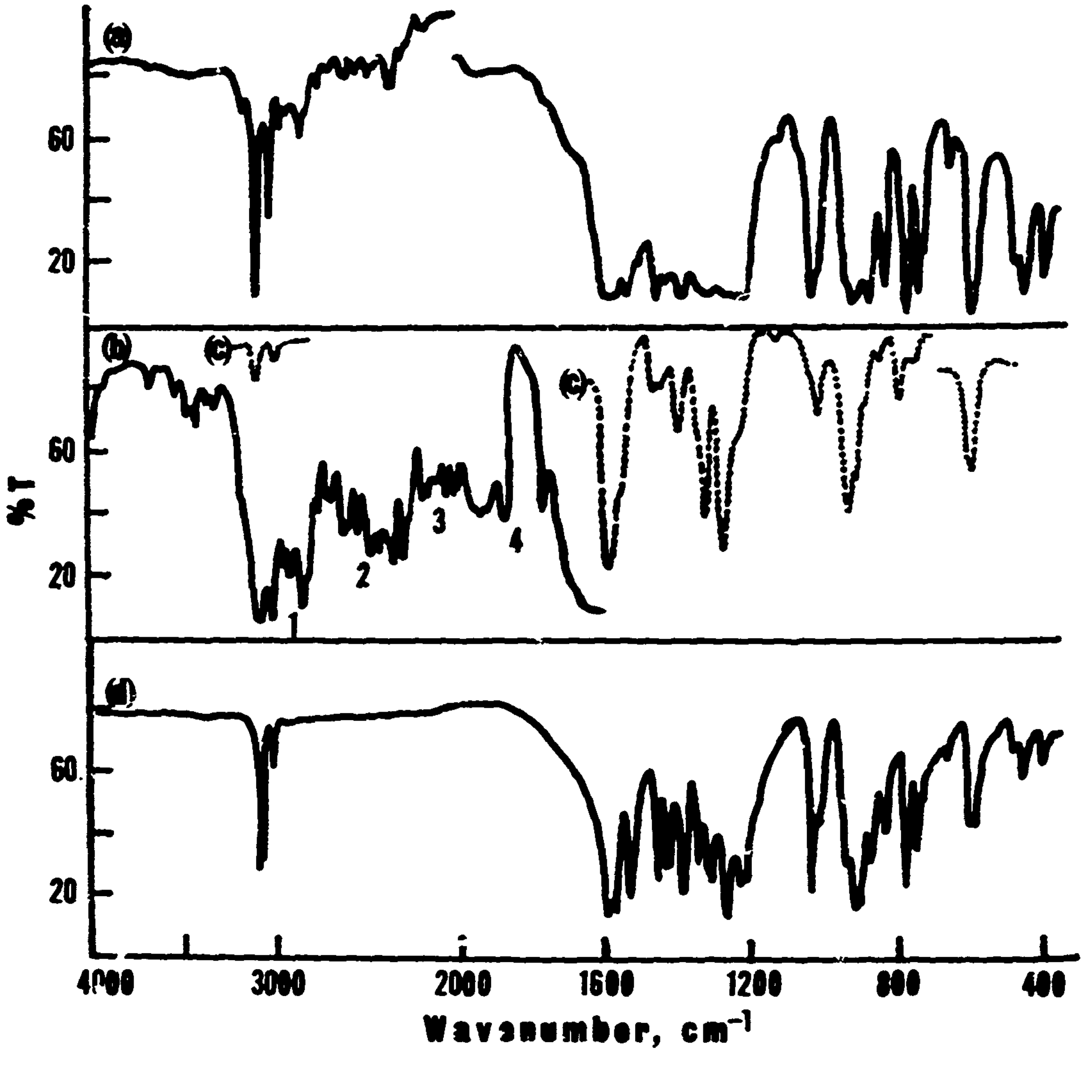

Fig 2 % Transmission (T) vs frequency traces of the infrared spectra of RDX in the 400 to 4000 cm^{-1} region: (a) Spectrum of a thin single crystal (b) Spectrum of a thick single crystal in the 1600 to 4000 cm^{-1} region (c) Spectrum of RDX in d_6-DMSO in the 1200 to 4000 cm^{-1} region and RDX in acetonitrile in the 600 to 1200 cm^{-1} region (d) Spectrum of KBr pellet of RDX

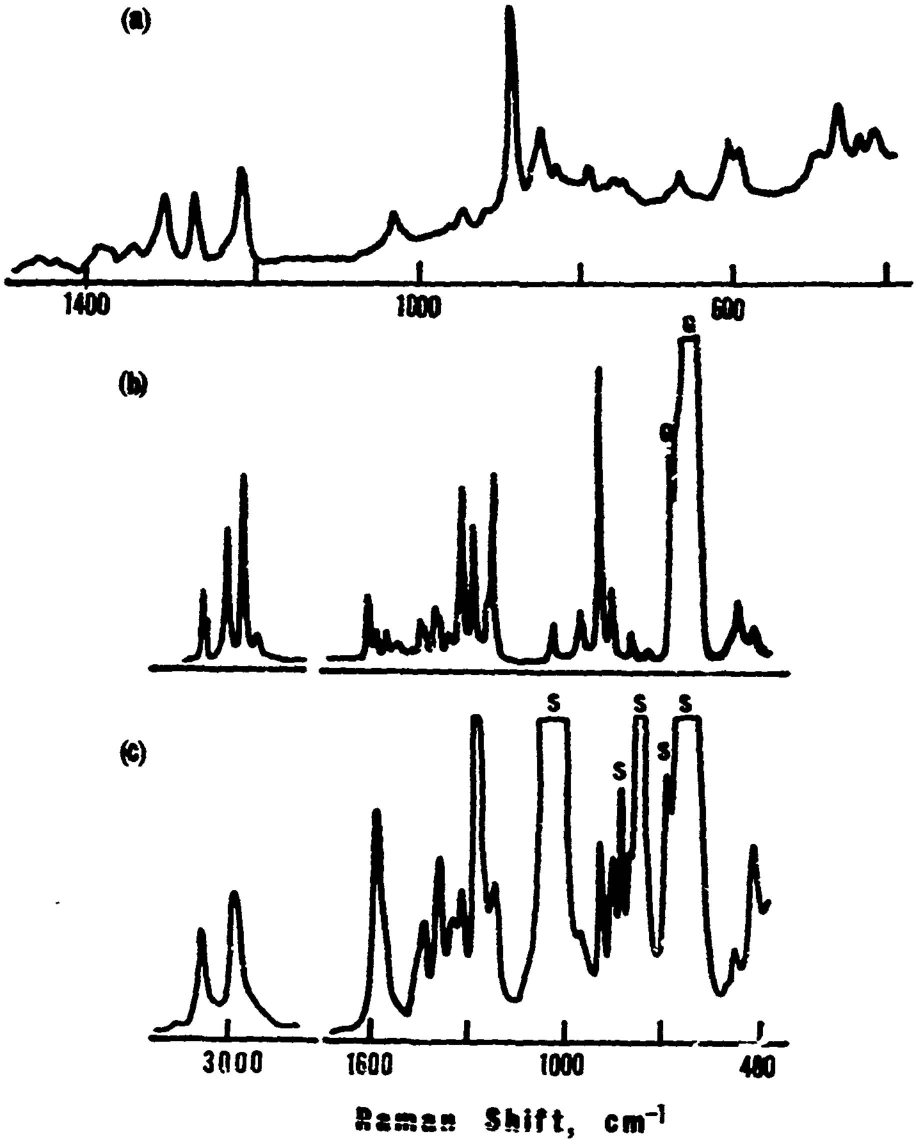

Fig 3 Traces of the Raman spectra of RDX in the 400 to 4000 cm^{-1} region: (a) Raman spectrum in the 400 to 1500 cm^{-1} region using 6328 Å excitation and slit width about 5 cm^{-1} of a single crystal of RDX (b) Raman spectrum between 400 and 4000 cm^{-1} of powdered RDX using 4880 Å excitation and slit width of about 5 cm^{-1} (bands marked G are due to the glass capillary tube) (c) Raman spectrum between 400 and 4000 cm^{-1} of d_6-DMSO solution of RDX using 4880 Å excitation and slit width of about 7 cm^{-1} (bands marked S are due to the solvent)

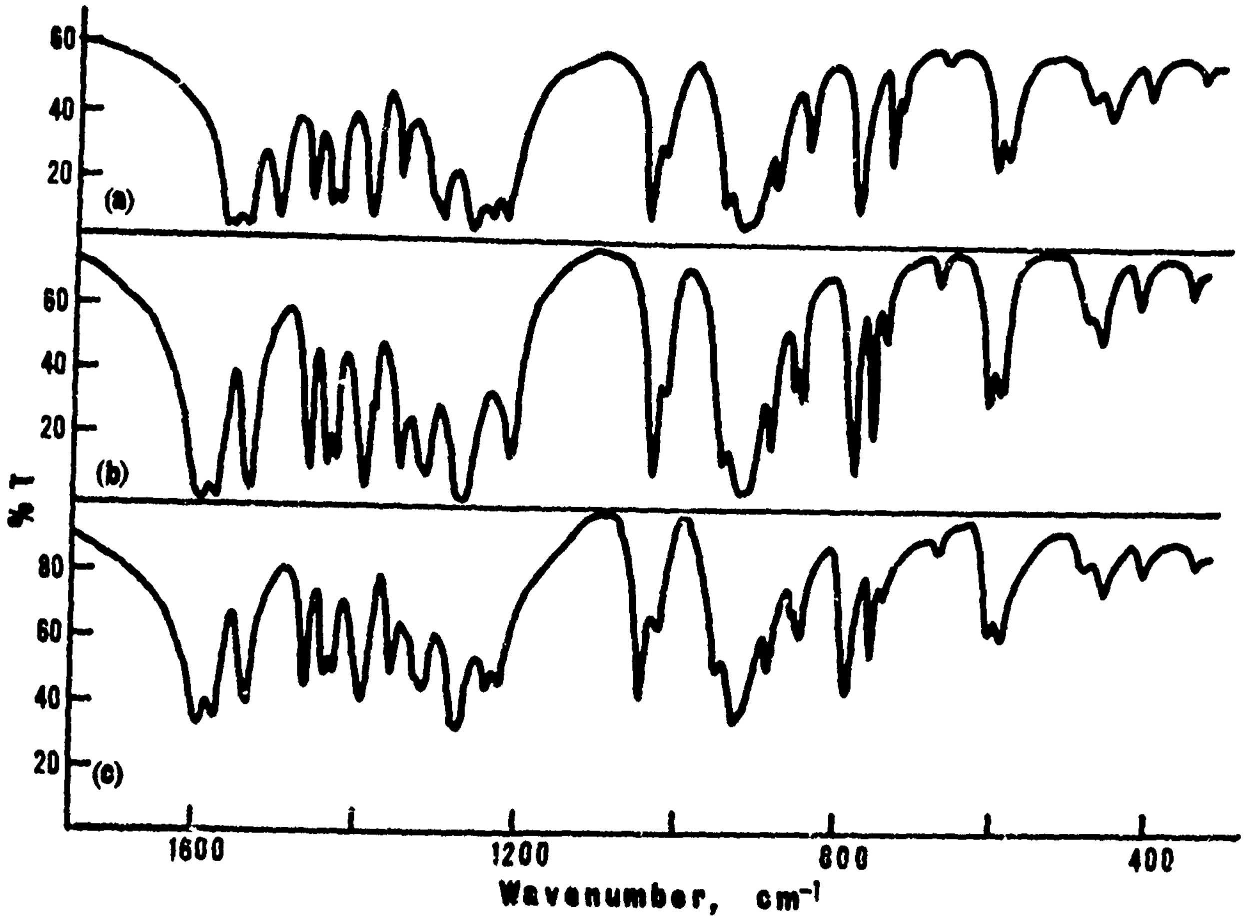

Fig 4 % Transmission (T) vs frequency traces of the KBr pellet infrared spectra between 400 and 1700 cm-1 of (a) Nitro group labeled RDX (b) Ring labeled RDX (c) Unlabeled RDX

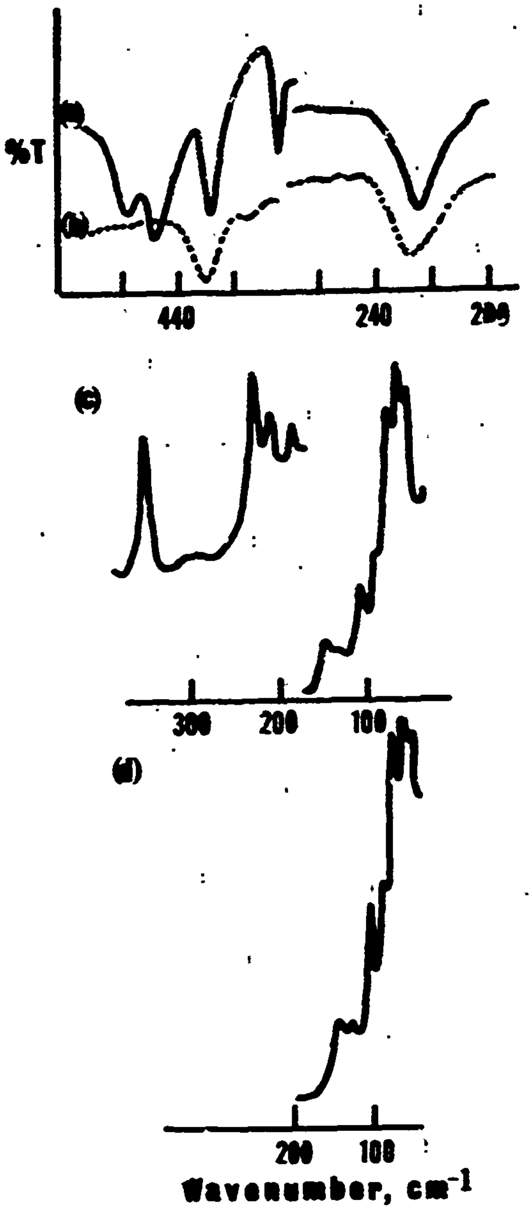

Fig 5 Traces of the low frequency infrared and Raman spectra: (a) Infrared spectra of pure RDX in Nujol mull, between 200 and 500 cm^{-1} (b) Infrared spectra of the trinitroso analog of RDX, TNTC, in Nujol mull between 200 to 500 cm^{-1} (c) Raman spectrum of an RDX single crystal using 6328 A excitation between 30 and 400 cm^{-1}. Slits of about 3 cm^{-1} were used between 30 and 200, and of about 6 cm^{-1} between 200 and 400 cm^{-1} (d) Raman spectrum of powder RDX using 4830 A radiation between 30 and 200 cm^{-1}. Slits of about 3 cm^{-1} were used .