Proton Magnetic Resonance Data for Some Intermediates and Products of Nitrolysis of Hexamethylenetetramine

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Proton chemical shifts are reported for 14 products and intermediates involved in the formation of 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane (HMX) from the nitrolysis of hexamethylenetetramine (hexamine). These include three hexamine derivatives and six cyclic and five linear nitramines. Geminal proton spin coupling is observed in three cases.

In the present work, we obtained proton magnetic resonance (pmr) spectral data on several compounds which have been characterized as products or intermediates in the formation of 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane (HMX) from the nitrolysis of hexamethylenetetramine (hexamine). This reaction was discussed by Urbanski (*3*) and Wright (*4*), among others.

The proton chemical shifts, as well as the structures of the compounds in question, are given in Table I. The pmr spectra of most of these compounds are simplified by high-molecular symmetry, which reduces the number and multiplicity of the spectral bands, and by the absence of vicinal spin coupling of the protons of methylene groups (—CH_2—), which are always separated by either the amino group (>N—) or the nitramino group (>N—NO_2). AB-type quartets associated with spin coupling of nonequivalent geminal protons were observed for dinitropentamethylenetetramine (DPT), methyl dinitropentamethylenetetramine (MeDPT), and methyl hexamine dinitrate (MHDN), since rapid pseudorotation is restricted in these molecules.

The data in Table I permit the assignment of about 85% of the lines in the pmr spectrum of a hexamine nitrolysis reaction mixture and are thus useful in determining the composition of the mixture.

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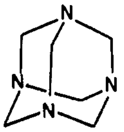
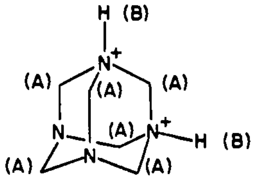
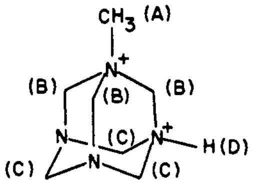
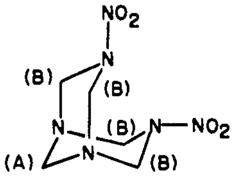
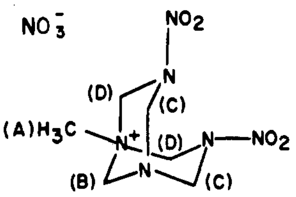
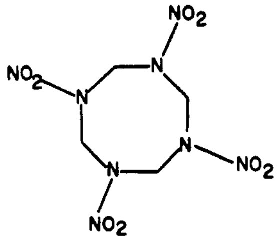
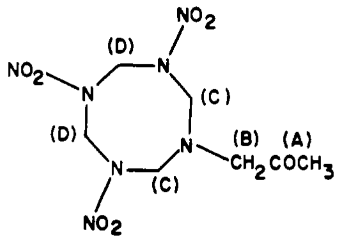
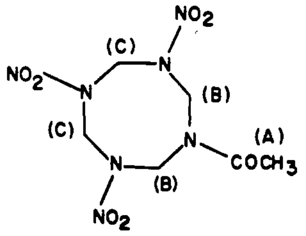
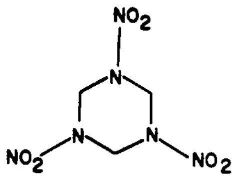
Table I. Proton Chemical Shifts of Some Hexamines and Nitramines

Compounds	Structure	Chemical shift δ, ppm[a]	Coupling constant *J*, Hz
Hexamines Hexamethylenetetramine (hexamine)		4.55	
Hexamine dinitrate (HADN)	2NO$_3^-$ 	(A) 4.85 (B) 8.7	
Methyl hexamine dinitrate (MHDN)	2NO$_3^-$ 	(A) 2.49 (B) 4.48 q (C) 5.02 (D) 8.7	(B) 13.0
Cyclic nitramines Dinitropentamethylenetetramine (DPT)		(A) 4.16 m (B) 5.25 q	(B) 12.9

(Continued on page 340)

Table I. Continued

Compounds	Structure	Chemical shift δ, ppm^a	Coupling constant J, Hz
Methyl dinitropentamethylenetetramine (MeDPT)		(A) 3.27 (B) 5.06 (C) 5.40 q (D) 5.90 q	(C) 12.7 (D) 11.2
1,3,5,7-Tetranitro-1,3,5,7-tetraazacyclooctane (HMX)		6.03 6.07^b 6.35^c	
1-Acetoxymethyl-3,5,7-trinitro-1,3,5,7-tetraazacyclooctane (PHX)		(A) 1.81 (B) 5.13 (C) 5.27 (D) 6.00	
1-Aceto-3,5,7-trinitro-1,3,5,7-tetraazacyclooctane (SEX)		(A) 2.24 (B) 5.56 (C) 5.98	
1,3,5-Trinitro-1,3,5-triazacyclohexane (RDX)		6.10 6.12^b 6.14^c	
Linear nitramines			
Methylene dinitramine (medina)	(B) (A) $[HN(NO_2)]_2CH_2$	(A) 5.10 (B) 13.0	
1,3,5-Trinitro-1,3,5-triazapentane (TTP)	(B) (A) $[HN(NO_2)CH_2]_2N(NO_2)$	(A) 5.45 (B) 12.7	
1,9-Dinitroxy-2,4,6,8-tetranitro-2,4,6,8-tetraazanonane	(C) (B) (A) $[O_2NOCH_2N(NO_2)CH_2N(NO_2)]_2CH_2$	(A) 5.90 (B) 5.90 (C) 6.29	
1,7-Diacetoxy-2,4,6-trinitro-2,4,6-triazaheptane (BSX)	(A) (B) (C) $[CH_3CO_2CH_2N(NO_2)CH_2]_2N(NO_2)$	(A) 2.07 1.98^c (B) 5.80 6.13^c (C) 5.89 6.30^c	
1,9-Diacetoxy-2,4,6-tetranitro-2,4,6,8-tetraazanonane (AcAn)	(A) (B) (C) (D) $[CH_3CO_2CH_2N(NO_2)CH_2N(NO_2)]_2CH_2$	(A) 2.08 (B) 5.78 (C) 5.85 (D) 5.85	

[a] Singlets unless identified by q = quartet or m = multiplet.

[b] Chemical shift reported in Ref. *2*.

[c] Chemical shift reported in Ref. *1*.

Experimental

All of the spectra were recorded with a Varian A60D spectrometer at an ambient probe temperature of 34 ± 2°C. The samples were dissolved in dimethyl-d_6 sulfoxide, and tetramethylsilane (TMS) was used as the internal reference for the chemical shifts, which could be measured to within 0.04 ppm. Assignments of spectral bands were made by comparing integrated line intensities, by observing the effect of substitution of deuterium for labile hydrogen, and by comparing the spectra of a series of related compounds.

With the exception of MHDN and 1,3,5-trinitro-1,3,5-triazapentane (TTP), the compounds were prepared according to procedures described in (*3*) and (*4*). Details of the identification and preparation of MHDN and TTP will be presented in a forthcoming publication.

Acknowledgment

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Preparation and Spectra of Trimethylnaphthalene Isomers

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The collection of pure samples of 13 out of a possible 14 trimethylnaphthalene isomers and the measurement of reference spectral data on these compounds are described. Five isomers were synthesized, and five others were isolated from petroleum streams by the careful application of preparative scale, gas-liquid chromatographic techniques. Three isomers were obtained from outside sources. The only isomer that could not be obtained was 1,2,8-TMN. The properties of this isomer, however, can be predicted on the basis of the data collected for the other isomers. The nmr and ir spectra of the 13 isomers are also described. Portions of spectra from each isomer are shown along with correlation tables showing the important ir bands and nmr chemical shifts. The significance of each region of the spectrum is discussed in relationship to its usefulness in analytical identifications.

From 1964 through 1969 a major research effort of Sun Research and Development Co. was directed toward characterizing the C_{13}-alkylnaphthalenes and other dinuclear aromatics in catalytic gas oil streams. The major components of these streams were trimethylnaphthalenes (TMN) and methylethylnaphthalenes. Early in this research, it became apparent that the correct identification of individual components would depend upon the availability of adequate reference spectral data. A literature search was made to see what reference data were available at that time. Reference infrared spectra were available for seven of the 14 isomers. Three of these spectra were in the API Research Project 44 collection (*25*) and four spectra were in the Documentation of Molecular Spectroscopy (DMS) collection (*6*). Two nmr spectra were available, both in the API collection (*26*). Ultraviolet spectra for almost all of the isomers were available in scattered collections. Unfortunately, uv spectra are not extremely valuable for the characterization of compounds isolated from petroleum streams.

During this research, several more spectra became available. The DMS collection added all the ir spectra except that of 1,2,8-TMN. Yew et al. (*28, 29*) showed nmr spectra for eight of the TMN isomers and tabulated chemical shifts for two other isomers. Hume and Jenkins (*16*) published a bar chart correlation of the 8–15 μ ir region for seven TMN isomers. Two of these were from their own spectra, and the others were from Mosby (*18*) and DMS (*6*). One of the most complete spectral collections has been provided by Karr et al. (*17*). They show uv spectra for all 14 isomers and ir spectra for seven of the isomers.

Many investigators have reported spectra and other properties for TMN's thrroughout the last 30–40 years. Most of these spectra and properties resulted from the synthesis or isolation of TMN's from natural products. Although the spectra were sometimes not shown, these efforts will be reviewed to document the synthetic procedures. From 1929 through 1932, Ruzicka and coworkers (*20–24*) reported the isolation of trimethylnaphthalenes as dehydration products of sapogenins. To identify these TMN products, they undertook the synthesis of all the trimethylnaphthalenes from various known materials, by use of Freidel-Crafts acylations and other types of well-established synthetic methods. Most of these syntheses were laborious, but they did unequivocally establish the identities of the TMN products. They then obtained picrate and styphnate melting points of all the TMN isomers. Most of the data for trimethylnaphthalenes that are published in Elsevier (*9*) are that of Ruzicka.

Heilbronner et al. (*13*) published the uv spectra of all TMN's except the 1,6,7- and 2,3,6-isomers. The method of synthesizing these compounds was not given in the publication. In 1952 Mosby (*18*) reported the synthesis of four trimethylnaphthalenes by the Freidel-Crafts condensation of α-valerolactone with isomeric xylenes. Ir spec-

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