

# Mass Spectra of Unlabeled and Isotopically Labeled Hexamethylene Triperoxide Diamine (HMTD)

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## Massenspektren von unmarkiertem und mit Isotopen markiertem Hexamethylentriperoxididiamin

Elektronenimpakt(EI)-Massenspektren wurden von unmarkiertem und  $^{13}\text{C}/^{15}\text{N}$  markiertem Hexamethylentriperoxididiamin mit direkter Probeneinbringung erhalten. Die stärksten Peaks ergaben die Molekülonen ( $m/z$  208 bzw.  $m/z$  216). Ein EI-Fragmentierungspfad wird auf Grund der massenspektrometrischen Beobachtungen vorgeschlagen.

## Spectre de masse de l'Hexaméthylène triperoxide diamine non marqué et marqué par des isotopes

Les spectres de masse d'impact d'électron (EI) ont été obtenus pour l'hexaméthylène triperoxide diamine non marqué et marqué  $^{13}\text{C}/^{15}\text{N}$  en utilisant une éprouvette d'insertion directe. Les ions moléculaires  $m/z$  208 et 216 ont donné les pics les plus importants. On propose un processus de fragmentation EI sur la base des observations par spectrométrie de masse.

## Summary

Electron impact (EI) mass spectra of unlabeled and  $^{13}\text{C}/^{15}\text{N}$  labeled hexamethylene triperoxide diamine were obtained using a direct insertion probe. The most prominent peaks were the molecular ions ( $m/z$  208 and  $m/z$  216, respectively). An EI fragmentation pathway is proposed based on the mass spectral evidence.

## 1. Introduction

We report the first electron impact (EI) mass spectra of unlabeled and carbon-13/nitrogen-15 ( $^{13}\text{C}/^{15}\text{N}$ ) labeled hexamethylene triperoxide diamine (HMTD). Although HMTD was first synthesized in 1885, it has found little practical application, even as a primary explosive, due to its extreme sensitivity to heat, friction, and impact<sup>(1)</sup>. It remains of interest today because of its unique planar structure about the bridgehead nitrogens<sup>(2)</sup> and because of the recent emergence of terrorist threats from peroxide functionalized explosives.

## 2. Experimental Section

### 2.1 Reagents

Unlabeled hexamethylenetetramine (hexamine; Aldrich Chemical Co., #39,816-0) was purified via bulb-to-bulb sublimation (165–175 °C at 3.0 mm). Unlabeled hexamethylene triperoxide diamine (HMTD) was prepared according to

the literature<sup>(2)</sup>. Isotopically labeled HMTD was prepared as detailed below. Starting materials were purchased from Isotec Incorporated ( $^{15}\text{NH}_4\text{OH}$ ) and Cambridge Isotope Laboratory (paraformaldehyde,  $^{-13}\text{CH}_2\text{O}$ –).

### 2.2 Synthesis of $^{13}\text{C}/^{15}\text{N}$ labeled hexamethylenetetramine ( $^{13}\text{C}/^{15}\text{N}$ hexamine)

In a modification of literature procedures<sup>(3)</sup>, to 0.4990 g (16 mmol) of  $^{13}\text{C}$  (99%) paraformaldehyde contained in a small vial with micro stir-bar was added 6 mg  $\text{NaHCO}_3$  and 0.7 ml distilled water. The vial was capped with a septum and purged gently with argon gas. The vial was heated with stirring in a warm-water bath (75–80 °C) until a clear solution resulted ( $\sim 45$  min). With constant stirring, the solution was cooled slowly and maintained at  $\sim 40$  °C. To the stirred solution was added dropwise 4.3 ml (3.3N; 14 mmol) of  $^{15}\text{N}$  ( $>98\%$ )  $\text{NH}_4\text{OH}$  via a gas-tight syringe, followed sequentially by 1 ml water and one additional drop of concentrated  $\text{NH}_4\text{OH}$  (reagent grade). With stirring, the water-bath temperature was slowly increased to  $\sim 80$  °C over the course of two hours. The solution was cooled, and the bulk of the aqueous solvent removed via rotary evaporation (full  $\text{H}_2\text{O}$  aspirator vacuum). To the remaining slurry was added 15 ml anhydrous  $\text{CH}_3\text{OH}$ , and the resultant solution re-evaporated; after three repetitions a white solid remained. The product was purified via bulb-to-bulb sublimation (165–170 °C at 3.0 mm) to afford 0.3749 g (2.53 mmol; 94%) of crystalline material, mp 263–264 °C;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$ 4.73 ( $\delta$ ,  $^1\text{J} = 150$  Hz);  $^{13}\text{C}$  NMR: 74.99 ( $^1\text{H}$  dec.;  $J_{\text{C-N}} < 0.5$  Hz).

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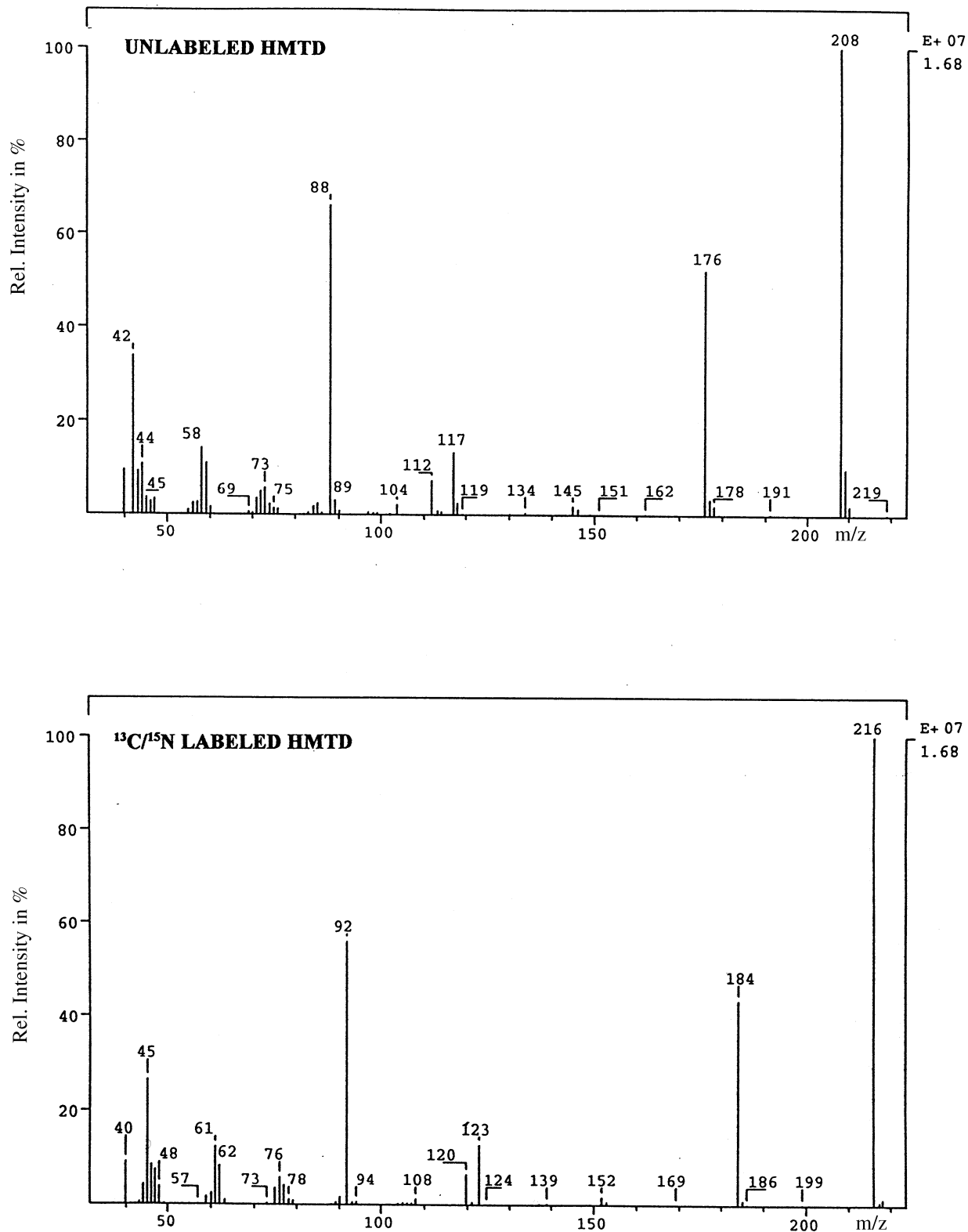
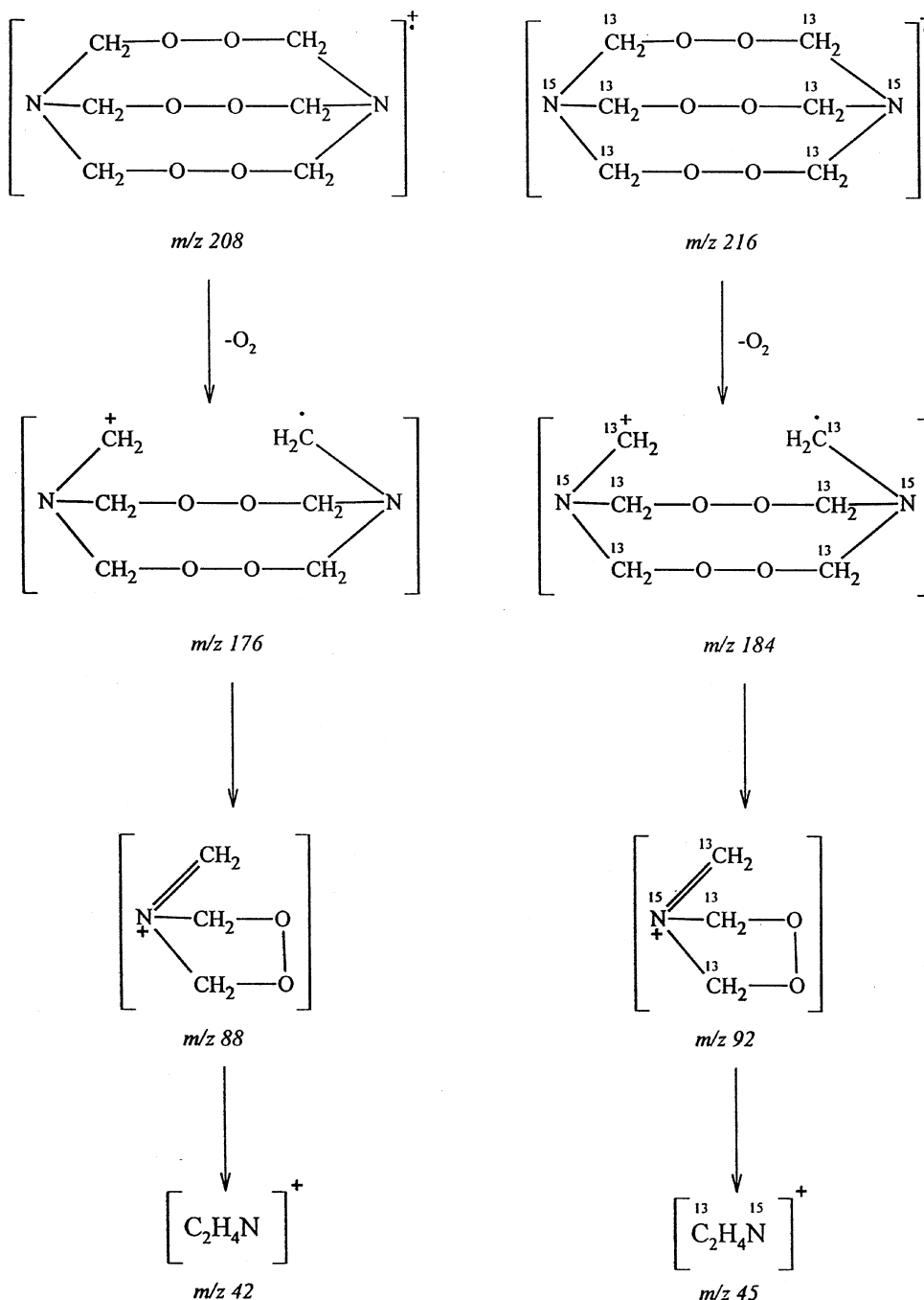


Figure 1. Mass spectra of HMTD; unlabeled (top) and  $^{13}\text{C}/^{15}\text{N}$  labeled (bottom).

### 2.3 Synthesis of $^{13}\text{C}/^{15}\text{N}$ Labeled Hexamethylene Triperoxide Diamine (HMTD)

A 2 ml Craig recrystallization tube equipped with a paddle-type micro-stirrer was charged with 0.1384 g (0.9 mmol) of  $^{13}\text{C}/^{15}\text{N}$  hexamine and 0.5 ml 50%  $\text{H}_2\text{O}_2$ ,

and chilled to  $\sim 0^\circ\text{C}$  (ice/ $\text{NaCl}$ ). While stirring, 0.2493 g (1.19 mmol) citric acid monohydrate was added in eight small portions over the course of an hour. The clear solution was stirred at  $\sim 0^\circ\text{C}$  for an additional six hours before the ice-bath was removed and allowed to slowly warm to room temperature. The resultant opaque mixture was stirred for an



**Figure 2.** Proposed EI mass fragmentation pathway for HMTD; unlabeled and  $^{13}\text{C}/^{15}\text{N}$  labeled.

additional two hours; the micro-stirrer removed; and the Teflon plug inserted into the top of the Craig tube. After chilling the Craig tube and contained  $^{13}\text{C}/^{15}\text{N}$  HMTD product in ice for 30 minutes, the tube was gently centrifuged for one minute. The wet crystalline material was rinsed with 1 ml ice water, re-centrifuged, and finally rinsed with 0.5 ml ice-cold  $\text{CH}_3\text{OH}$  and again gently centrifuged. The crystalline material contained in the Craig tube along with the Teflon plug was dried in a vacuum desiccator ( $\text{CaSO}_4$ ) overnight to afford 0.0864 g (0.40 mmol; 44%) product, mp 153–154°C (dec);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$ 4.80 ( $\delta$ ;  $^1\text{J} = 154\text{ Hz}$ ;  $^2\text{J} = 4.9\text{ Hz}$ );  $^{13}\text{C}$  NMR:  $\delta$ 90.44 ( $^1\text{H}$  dec.;  $\delta$ ,  $\text{J}_{\text{C-N}} = -12\text{ Hz}$ ).

#### 2.4 Mass Spectrometry

The EI spectra of HMTD were obtained using a Finnigan TSQ 700 mass spectrometer with direct insertion probe. The electron energy was 70 eV and the emission current was 200  $\mu\text{A}$ . The ion source temperature was 150°C, and the scan range was  $m/z$  35–220. Trace amounts of HMTD solid were loaded into aluminum crucibles and inserted directly into the source. The probe temperature was ramped from 50°C to 200°C at 15 K/min. Data acquisition was started immediately following insertion. Spectra were observed at the initial temperature and total ion current intensities increased with temperature until about 90°C.

### 3. Results and Discussion

The mass spectra of unlabeled and  $^{13}\text{C}/^{15}\text{N}$  labeled HMTD are given in Figure 1. The base peak was also the molecular ion ( $m/z$  208 and  $m/z$  216). The comparison of the two spectra suggested the fragmentation pathways shown in Figure 2. The initial step is loss of a peroxide functionality as oxygen ( $\text{O}_2$ ). The resulting fragments of  $m/z$  176 and  $m/z$  184 indicate that no label has been lost. The following step appeared to be a symmetrical splitting of the  $m/z$  176 (or  $m/z$  184) fragment to yield a  $m/z$  88 or the  $m/z$  92 fragment with half numbers of the labeled atoms in the structure. The  $m/z$  42 (or  $m/z$  45) is thought to have a composition of  $[\text{C}_2\text{H}_4\text{N}]^+$ .

### 4. References

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