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MS/MS of energetic compounds. A collision induced dissociation (CID) study of some polynitrobiphenyl-2-amines

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MS/MS OF ENERGETIC COMPOUNDS. A COLLISION INDUCED DISSOCIATION (CID) STUDY OF SOME POLYNITROBIPHENYL-2-AMINES*

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ABSTRACT

In an effort to design energetic materials with improved properties, polyaminopolynitroaromatic compounds have become the subject of renewed investigation. As part of this effort we have investigated the fragmentation processes of a series of polynitrobiphenyl-2-amines, previously synthesized, using tandem mass spectrometry (MS/MS) with collision induced dissociation (CID). Major fragmentations included loss of OH from the molecular ion, second loss of OH from the $(M-OH)^+$ ion, loss of NO and loss of NO_2. Fragmentation processes in relation to molecular structure are discussed.

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INTRODUCTION

Although polyaminopolynitroaromatic compounds have been used as explosives for many years, only recently have they become the subject of renewed interest. Amino substitution has been used as a way of modifying the properties of nitroaromatic compounds in an effort to decrease the impact sensitivity[1-4]. It was found that the amino group can raise the melting point[1-4] and density[2,4] of a nitroaromatic compound, because of its ability to undergo strong hydrogen bonding with a neighboring nitro group and its ability to strengthen the C-NO_2 bond of an ortho or para nitro group[5]. As part of this effort to design energetic materials with improved properties, a series of polynitrobiphenyl-2-amines were synthesized[5].

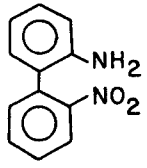
In order to better understand the mass spectral fragmentation reactions and pathways of these compounds a collision induced dissociation (CID) study was carried out using a tandem mass spectrometer (MS/MS).

In CID, when using magnetic sector instruments, a beam of precursor ions having translational kinetic energies of several keV collides with an inert gas, which transforms some of the translational energy of the ions into internal excitation energy. The products of these reactions arise from simple bond cleavages and therefore are useful for ion structure elucidation. It is assumed that the CID mass spectrum is related to the precursor ion struc-

ture in the same way as the EI mass spectrum is related to the molecular structure. Hence the similarity between CID and EI spectra[6].

Fragmentation pathways of several energetic compounds have been previously determined by MS/MS CID[7-13].

Thus, we have studied the MS/MS CID spectra of a series of polynitrobiphenyl-2-amines in order to determine the fragmentation processes of these compounds. The investigated compounds included 2'-nitrobiphenyl-2-amine (1), 2',4',6'-trinitrobiphenyl-2-amine (2), 2',3,4',5-tetranitrobiphenyl-2-amine (3), 2',3,5,6'-tetranitrobiphenyl-2-amine (4), 2',4,4',6,6'-pentanitrobiphenyl-2-amine (5), and 2',3,4',5,6'-pentanitrobiphenyl-2-amine (6).



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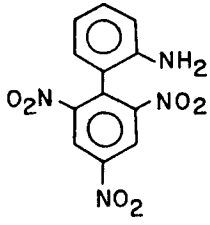

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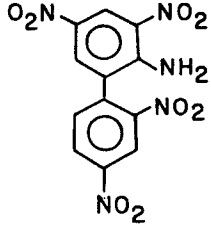

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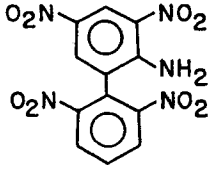

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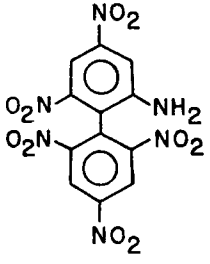

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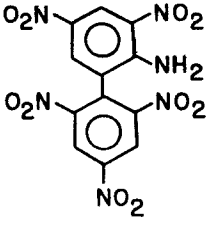

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EXPERIMENTAL

The tandem mass spectrometer (MS/MS) consists of two magnetic sector analyzers with a collision cell located in the region between the two analyzers. A full description of the instrument is given elsewhere[11]. Argon was used as collision gas. The pressure of the argon was adjusted so that the precursor ion beam intensity was reduced to half of its initial value.

The ionization mode was EI at 70 eV. The ion source was operated at a temperature of 150–250°C. Samples were introduced through the solid probe inlet, using the in-beam EI technique[14,15]. To obtain in-beam EI spectra, the sample was loaded on the tip of the modified solid probe[16]. The probe was not heated separately.

The synthesis of the investigated compounds is described in Reference 5.

RESULTS AND DISCUSSION

Table 1 lists the abundances of the major ions observed in the CID spectra of the molecular ions as well as of the highly abundant fragment ions. The daughter ion abundances are expressed as a percentage of the abundance of the largest daughter ion. Six examples of CID spectra are shown in Figures 1-6, which depict the CID spectra of the molecular ions of the six investigated compounds.

All six compounds are characterized by a molecular ion in their EI mass spectrum. Loss of OH from the molecular ion is typical to all 6 compounds, and is probably due to a reaction of the amino group with the ortho nitro group on the adjacent aryl ring. Second loss of OH from the $(M-OH)^+$ ion occurs only in the 2'-nitro and the 2',3,4',5-tetranitro derivatives. These two compounds are the only ones which do not have a nitro group in the 6' position, which might be the reason of the exclusion of this process in the other compounds.

Loss of NO occurs sometimes after loss of OH as in the 2',4,4',6,6'-pentanitro compound, sometimes after loss of NO_2 as in the 2',3,4',5,6'-pentanitro compound, and sometimes after loss of both, as in the two tetranitro isomers. The loss of NO might be a measure of the C-NO_2 to C-ONO rearrangement. Isotopic labeled compounds could give an indication concerning the origin of the NO loss.

Loss of NO_2 (or loss of HNO_2 in the 2'-nitro compound) is a major loss in most of the investigated compounds. Loss of a second nitro group (either simultaneously with the first one or consecutively after loss of the first one) is a minor process in these compounds.

The interest of mass spectrometry of energetic materials from the point of view of characteristics of these materials as explosives is that there are some parallels between the early stages of

decomposition by explosive shock and fragmentation in the mass spectrometer[17,18].

From the CID results it can be concluded that the fragmentation of these molecules is a stepwise fragmentation: First we observe loss of OH from the molecular ion, which occurs due to the presence of the amino group and its reaction with an ortho nitro group. The next step is loss of an NO_2 group and consequently additional NO_2 groups. Very little fragment ions due to the carbon structure have been observed. The possible implication in explosives is that these compounds are relatively stable due to the presence of the amino group and the numerous nitro groups.

The results reported herein are only preliminary results. More work on CID of amino nitro biphenyls has to be carried out in order to come to quantitative conclusions regarding the stability of these molecules as function of amino and nitro groups.

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TABLE 1. CID Ions of Polynitrobiphenyl-2-amines

	COMPOUND	PRECURSOR ION m/z	DAUGHTER IONS							
			$(P\text{-}OH)^+$	$(P\text{-}NO)^+$	$(P\text{-}2OH)^+$	$(P\text{-}NO_2)^+$	$(P\text{-}HNO_2)^+$	$(P\text{-}OH\text{-}NO_2)^+$	$(P\text{-}2NO_2)^+$	OTHER IONS
1	2'-NITROBIPHENYL-2-AMINE M.W. 214	$214(M)^{+\cdot}$ $197(M\text{-}OH)^+$ $167(M\text{-}HNO_2)^{+\cdot}$	197(42) 180(100)		180(14)		167(100)			152(5) 166(5),139(100)
2	2',4',6'-TRINITROBIPHENYL-2-AMINE M.W. 304	$304(M)^{+\cdot}$ $287(M\text{-}OH)^+$ $258(M\text{-}NO_2)^+$	287(100) 241(100)			258(71) 241(100) 212(73)		241(28)		
3	2',3,4',5-TETRANITROBIPHENYL-2-AMINE M.W. 349	$349(M)^{+\cdot}$ $332(M\text{-}OH)^+$ $303(M\text{-}NO_2)^+$ $286(M\text{-}OH\text{-}NO_2)^+$	332(100) 315(35) 286(100)	256(100)		303(16) 286(100) 240(27)		286(12)	240(27)	
4	2',3,5,6'-TETRANITROBIPHENYL-2-AMINE M.W. 349	$349(M)^{+\cdot}$ $332(M\text{-}OH)^+$ $303(M\text{-}NO_2)^+$ $286(M\text{-}OH\text{-}NO_2)^+$	332(100) 286(100)	256(100)		303(42) 286(100) 257(11) 240(45)		286(68)	257(11) 240(10)	
5	2',4,4',6,6'-PENTANITROBIPHENYL-2-AMINE M.W. 394	$394(M)^{+\cdot}$ $377(M\text{-}OH)^+$	377(100)	347(100)		348(38)			302(11)	
6	2',3,4',5,6'-PENTANITROBIPHENYL-2-AMINE M.W. 394	$394(M)^{+\cdot}$ $377(M\text{-}OH)^+$ $348(M\text{-}NO_2)^+$	377(100)	364(21) 318(100)		348(25) 331(100) 302(80)		331(35)	302(9) 285(37)	

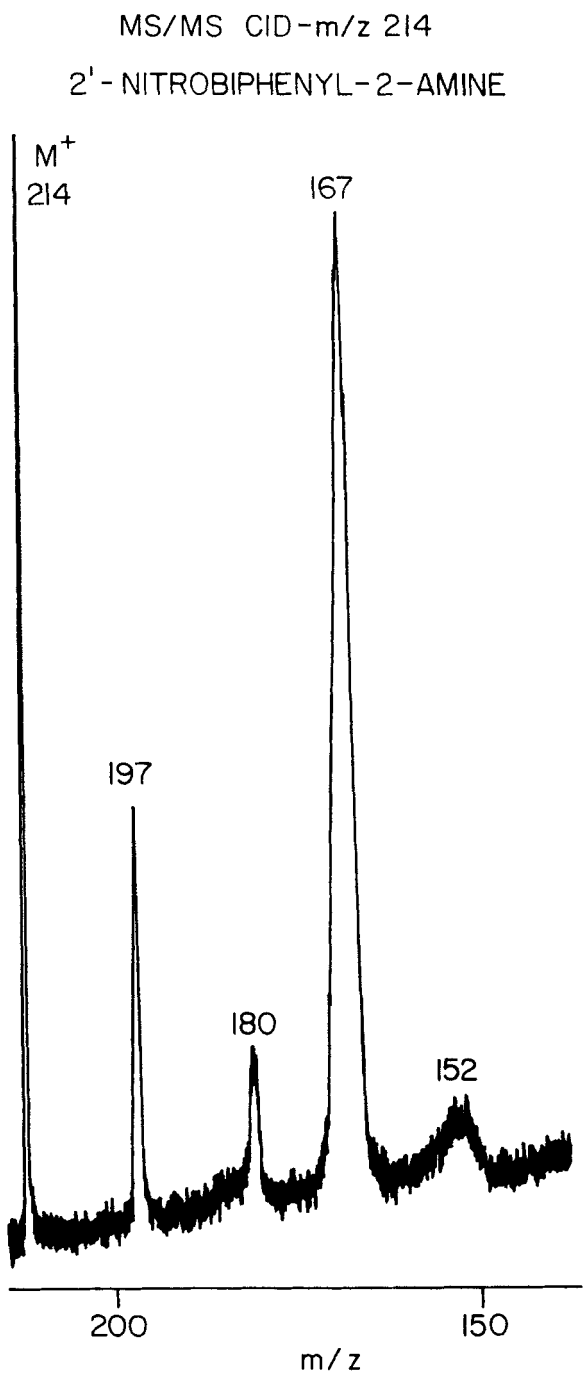

FIGURE 1
CID spectrum of the molecular ion of 2'-nitrobiphenyl-2-amine.

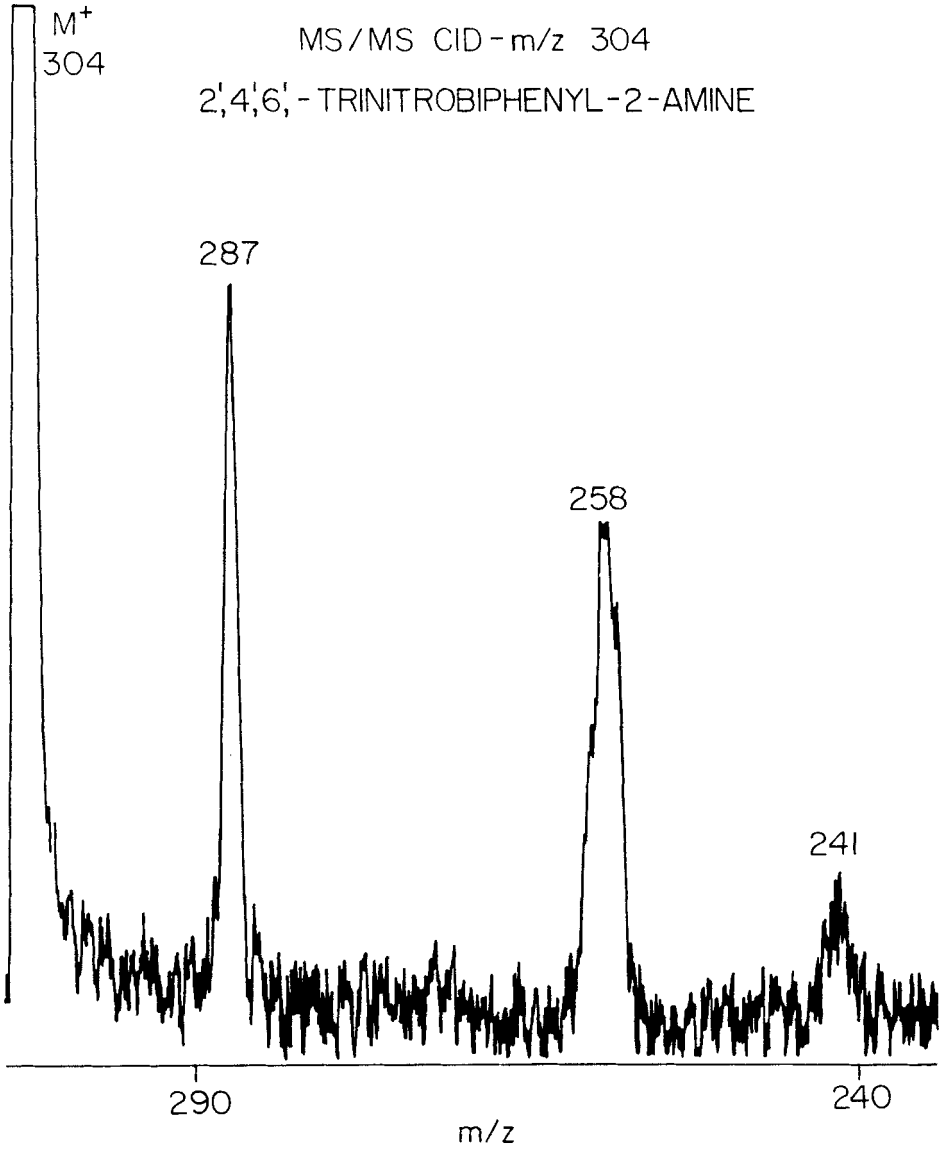

FIGURE 2
CID spectrum of the molecular ion of 2',4',6'-trinitrobiphenyl-2-amine.

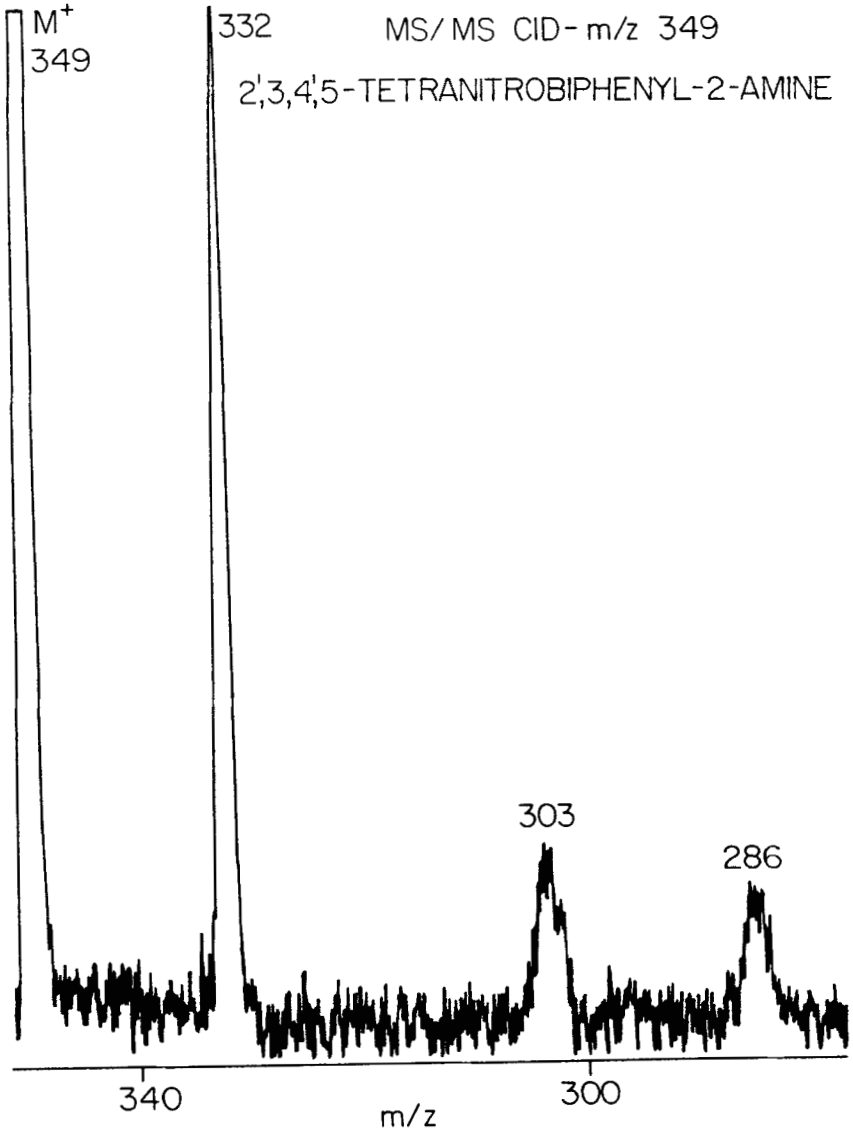

FIGURE 3
CID spectrum of the molecular ion of 2',3,4',5-tetranitrobiphenyl-2-amine.

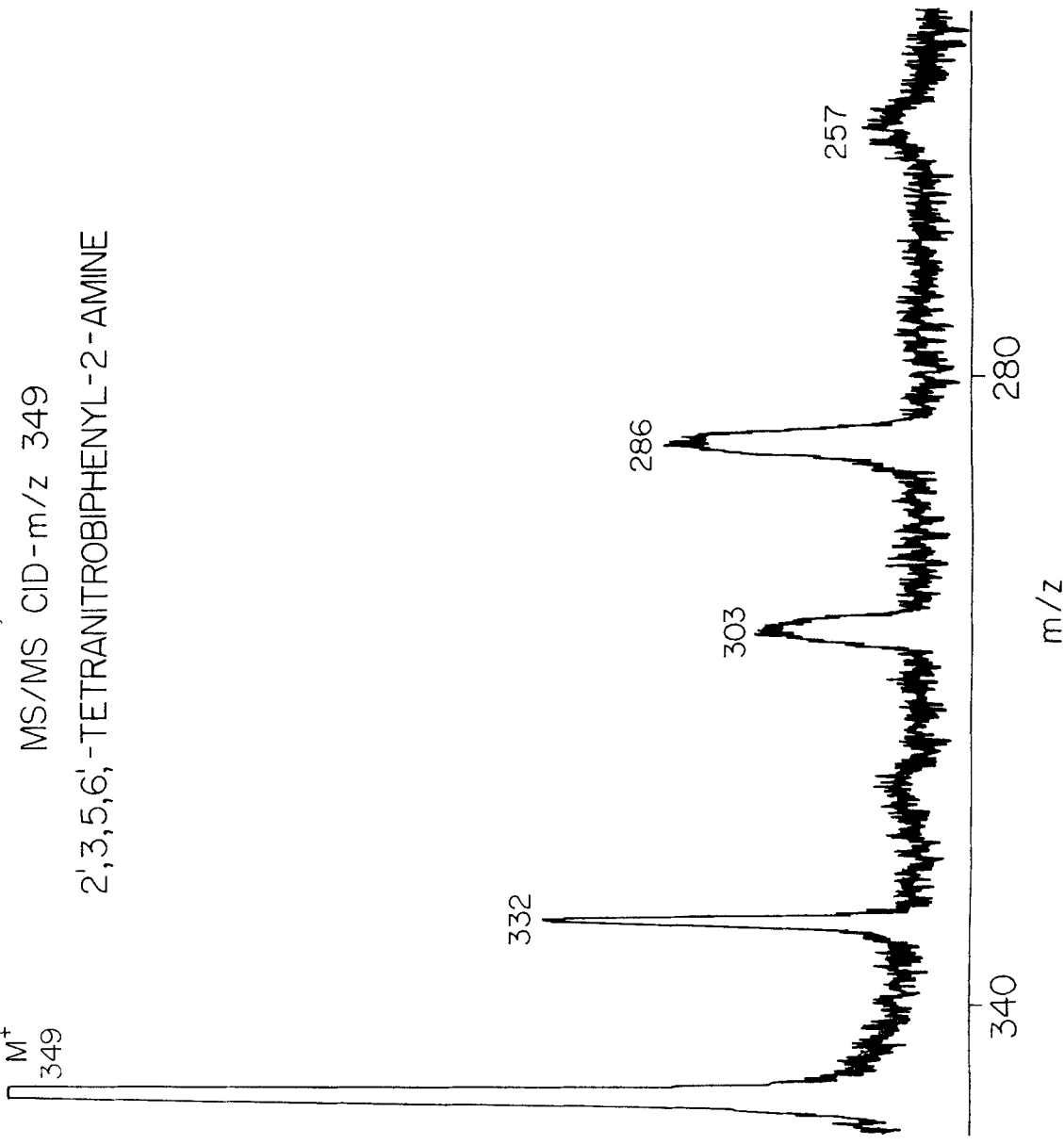

FIGURE 4
CID spectrum of the molecular ion of 2',3,5,6'-tetranitrobiphenyl-2-amine.

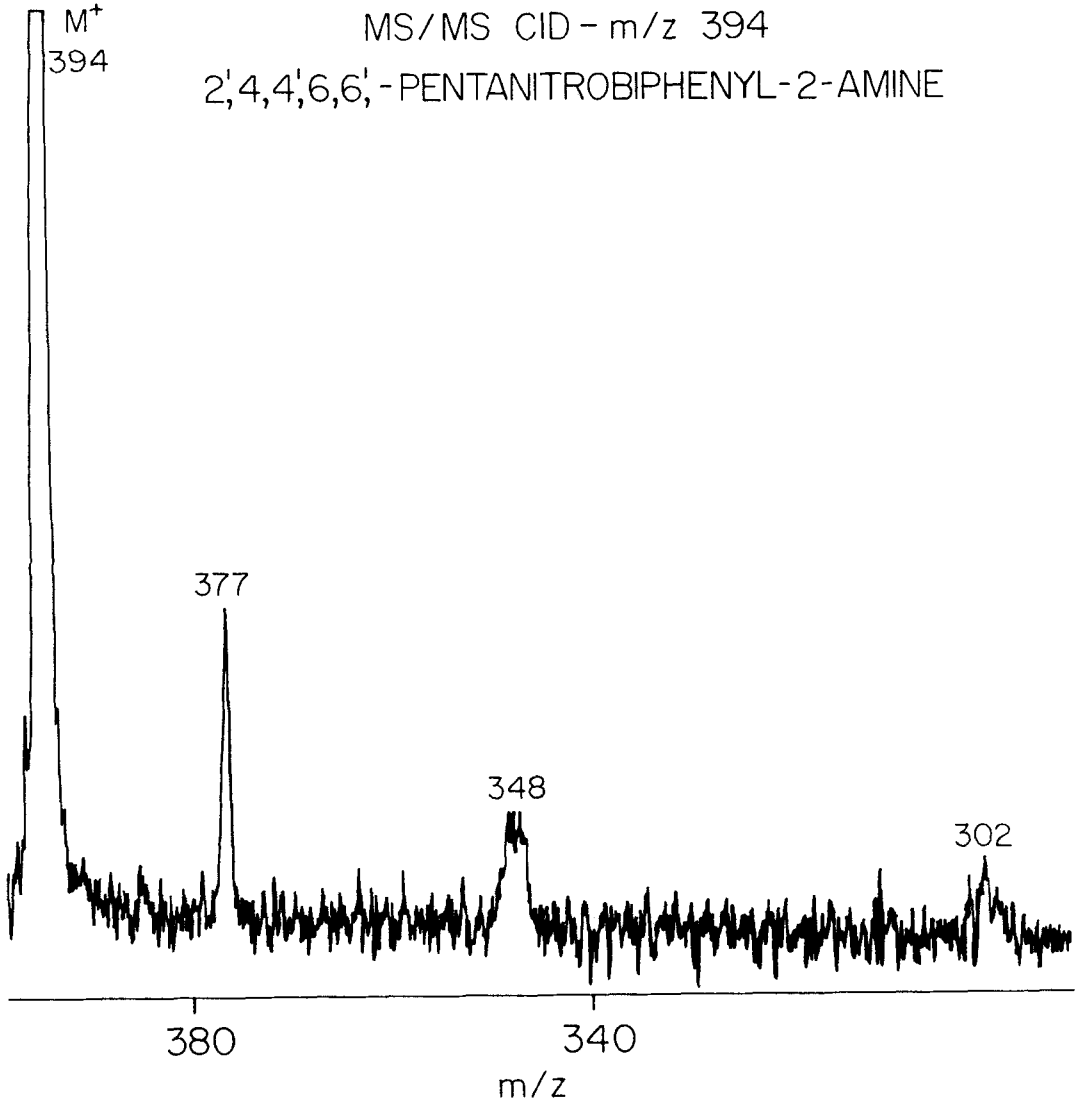

FIGURE 5
CID spectrum of the molecular ion of 2',4,4',6,6'-pentanitrobiphenyl-2-amine.

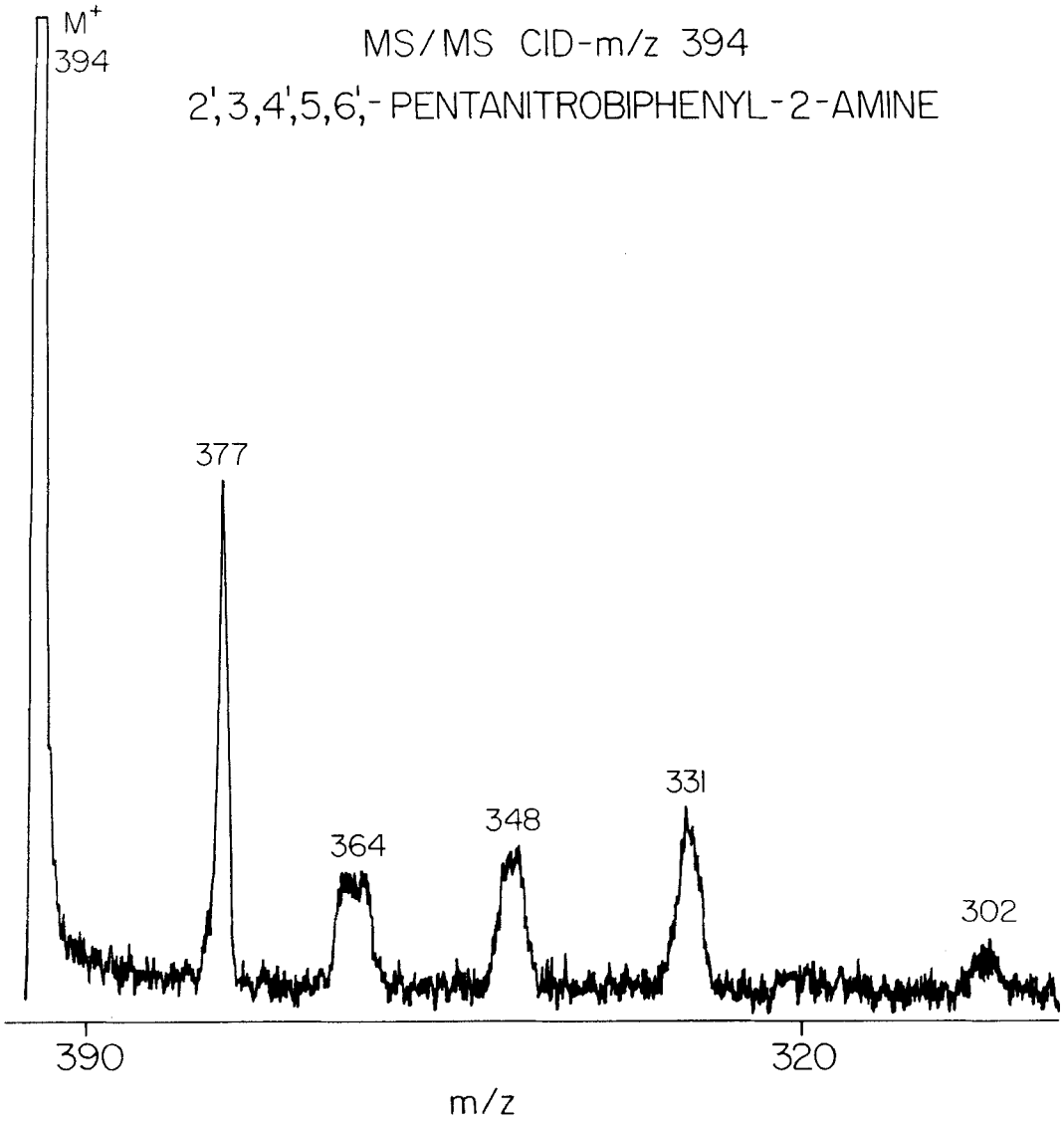

FIGURE 6
CID spectrum of the molecular ion of 2',3,4',5,6-pentanitrobiphenyl-2-amine.