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# Relative Molecular Mass Information from Aliphatic Nitro Compounds: a Chemical Ionization Study

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**The mass spectra of a number of aliphatic nitro compounds have been studied using electron ionization (EI) and a variety of chemical ionization (CI) techniques in attempts to obtain relative molecular mass information. The use of positive ion ammonia chemical ionization techniques gave very satisfactory results, providing abundant $[M + NH_4]^+$ ions, not only from both primary and secondary nitro compounds, but also from the much more labile tertiary nitro compounds. However, the use of methane and isobutane positive ion CI or EI conditions resulted in facile fragmentation with little relative molecular mass information being made available. Negative ion CI using methane, isobutane or ammonia as moderating gases all gave abundant $[M - 1]^-$ ions with primary and secondary nitro compounds but at much reduced sensitivity.**

## INTRODUCTION

Electron ionization (EI) mass spectra of nitroalkanes generally provide little information regarding relative molecular mass (RMM).[1-4] Nitromethane shows a substantial molecular ion[1,2] but other nitroalkanes show either only a very small molecular ion (for example, nitroethane) or no molecular ion peak at all.[2,4] Instead, they undergo ready loss of the elements of nitrous acid and exhibit mass spectra corresponding to the resultant alkene, or alternatively lose $NO_2$ and exhibit fragmentation of the resultant cation. Frequently, the peaks corresponding to the loss of $HNO_2$ or $NO_2$ are themselves not abundant in the mass spectra, thus hampering still further any attempts to obtain information about the whole molecule.

Aromatic nitro compounds generally provide more abundant molecular ions and several methods have been used to improve the situation further. In particular, chemical ionization (CI) using methane,[5,6] isobutane[5] or hydrogen[7] as the reagent gas has been recommended as a means of producing abundant $[M+1]^+$ peaks in the mass spectra of aromatic nitro compounds, whilst electron-capture negative ion mass spectrometry is recommended for providing RMM information of nitrated polycyclic aromatics.[8] Methane CI of polynitroaromatics gives substantial negative ion molecular ions $M^{-\cdot}$ or positive ion $[M+1]^+$ peaks.[9] Positive ion methane CI has been employed for some aliphatic nitro compounds[10] but abundant $[M+1]^+$ ions were obtained only from primary compounds.

Recently, CI using ammonia as the reagent gas has been shown to give molecular-adduct ions from 1-nitropropane.[11] Under the conditions used the $[M+H]^+$ and $[M+NH_4]^+$ peaks were each about 5-10% of the base peak ($m/z = 41$), whereas neither EI nor field ionization provided a molecular ion peak. Ammonia chemical ionization of aromatic nitro compounds has also been reported,[12] and in this case the major observed ions were $[M+NH_4]^+$ and $[M+N_2H_7]^+$.

We required a reliable method for generation of molecular (or molecular-adduct) ions of primary, secondary or tertiary aliphatic nitro compounds present in complex mixtures. Thus we have carried out a systematic study of the CI of a range of aliphatic nitro compounds with several reagent gases (methane, isobutane and ammonia) under both positive and negative ion conditions, and have compared the RMM information provided with that from EI studies. We have found that ammonia CI is a highly general and useful way of obtaining RMM information for such compounds.

## EXPERIMENTAL

### Materials

Nitromethane (**1**), 1-nitrohexane (**2**), 1-nitrododecane (**3**), nitrocyclohexane (**4**) and 2-methyl-2-nitropropane (**11**) were commercial samples obtained in better than 97% purity from Aldrich Chemical Co. Inc., and were used without further purification.

The six isomers of nitrohexylcyclohexane which were used in this study were synthesized by the following techniques.

1-*Hexyl*-1-*nitrocyclohexane* was obtained via the alcohol derivative, 1-hexylcyclohexan-1-ol, which was formed by the reaction of cyclohexanone with

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hexylmagnesium bromide. The alcohol was converted into 1-hexylcyclohexan-1-amine by the Ritter reaction[13] and the amine was then oxidized to the nitro compound using potassium permanganate.[14]

The other nitrohexylcyclohexane isomers were obtained by converting the corresponding ketone into the oxime with hydroxylamine, and then oxidizing the oxime to the nitro compound with peroxytrifluoroacetic acid using a modification of the method used by Emmons.[15]

The ketones were synthesized by the following routes.

3-*Hexylcyclohexanone* was obtained by the reaction of trihexylborane with 2-cyclohexen-1-one as described by Brown.[16]

2-*Hexylcyclohexanone* was prepared by reaction 2-chlorocyclohexanone with hexylmagnesium iodide. However, this does not involve direct replacement of the chloride, but attack at the carbonyl centre followed by migration of the hexyl group.[17]

4-*Hexylcyclohexanone* was prepared by hydrogenation of 4-hexylaniline using 10% palladium on carbon, and oxidation of the resultant 4-hexylcyclohexan-1-amine with potassium permanganate.

1-*Cyclohexylhexan*-1-*one* was prepared from cyclohexanecarboxylic acid chloride by reaction with a reagent prepared from 1-hexylmagnesium iodide and cadmium chloride.[18]

1-Cyclohexylhexan-2-one was obtained by oxidation with pyridinium chlorochromate[19] of 1-cyclohexylhexan-2-ol, which was prepared by the action of cyclohexylmethylmagnesium bromide with pentanal.

### Instrumental conditions

Mass spectra were obtained using a VG Masslab 12-253 quadrupole mass spectrometer at 1200 resolution, controlled through a DEC PDP11/73J data system. All spectra were recorded using the combined EI/CI source with the packed column inlet blanked off, the CI slit being in position for all positive and negative CI measurements. Spectra were recorded by repetitive scanning over the range 33-650 u using a 1 s scan with a 0.1 s interscan delay period.

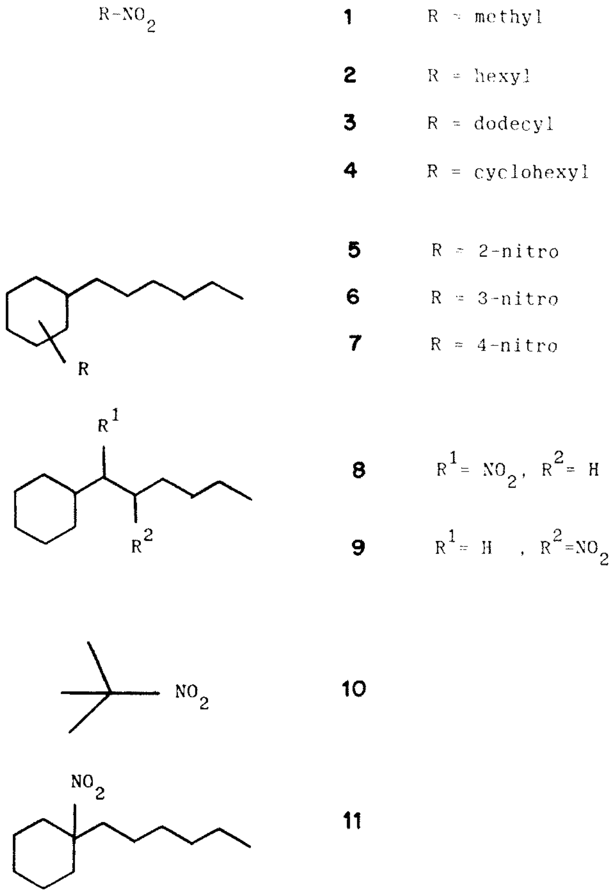
EI spectra were recorded at 70 eV electron energy (200 μA) and a source temperature of 200 °C. Positive ion CI spectra were recorded at 50 eV electron energy (500 μA) and a source temperature of 175 °C. The source pressure for methane and isobutane reagent gases was set to give a pressure in the source housing of $7.5 \times 10^{-5}$ Torr, whilst ammonia was found to give satisfactory results at the lower pressure of $4 \times 10^{-5}$ Torr. These readings correspond to pressures in the ion chamber of the order of 0.1-0.5 Torr. Negative ion CI spectra were recorded at 25 eV electron energy (800 μA) and at a source temperature of 150 °C; all reagent gases were introduced to a pressure of $2 \times 10^{-5}$ Torr.

Samples of nitromethane (**1**), 1-nitrohexane (**2**), 1-nitrododecane (**3**), nitrocyclohexane (**4**) and 2-nitro-2-methylpropane (**11**) were introduced via the heated septum inlet (150 °C) and other samples via a quartz sample tube on the solids inlet probe (25 °C).

Accurate mass measurements were made at 10 000 resolution using a VG Analytical ZAB-E instrument in peak matching mode using PFK as reference standard for the ammonia negative ion CI (NICI) measurements, and a fatty acid methyl ester mixture (FAME1)[20] as reference standard for the ammonia positive CI ion (PICI) measurements.

## RESULTS AND DISCUSSION

The mass spectra of a series of aliphatic nitro compounds have been studied, both by EI and CI techniques using a variety of reagent gases. Three primary nitro compounds (**1-3**, Scheme 1), six secondary nitro compounds (**4-9**, Scheme 1) and two tertiary nitro compounds (**10** and **11**, Scheme 1) were examined under EI conditions and PICI and NICI conditions using ammonia, isobutane and methane as reagent gases.



**Scheme 1**

The RMM information which was obtained by each ionization procedure from the various nitro compounds is given in Table 1.

### EI mass spectra

EI of these nitro compounds resulted in ready fragmentation and molecular ions were normally absent. The only compound for which a molecular ion was observed was nitromethane (compound **1**). Fragmentation was usually extensive and it was rare to find even $[M - NO_2]^+$ ions; these were, however, significant in the

**Table 1. Abundance of ions giving RMM information using various ionization techniques. (The abundance values (%) are normalized to the base peak for ions at *m/z* values higher than the reagent gas ions)**

| | | | PICI | | | NICI | | |
|---|---|---|---|---|---|---|---|---|
| Nitro compounds | $M_r$ | EI $M^+$ | Ammonia $[M+NH_4]^+$ | Isobutane $[M+H]^+$ | Methane $[M+H]^+$ | Ammonia $[M-H]^-$ | Isobutane $[M-H]^-$ | Methane $[M-H]^-$ |
| Primary | | | | | | | | |
| **1** | 61 | 100 | 2 | 100 | 100 | 14 | 100 | 100 |
| **2** | 131 | 0 | 100 | 70 | 21 | 99 | 91 | 100 |
| **3** | 215 | 0 | 100 | 20 | 0 | 20 | 28 | 43 |
| Secondary | | | | | | | | |
| **4** | 129 | 0 | 100 | 15 | 0 | 100 | 100 | 100 |
| **5** | 213 | 0 | 100 | 0 | 0 | 11 | 46 | 32 |
| **6** | 213 | 0 | 100 | 0 | 0 | 9 | 16 | 12 |
| **7** | 213 | 0 | 100 | 0 | 0 | 20 | 20 | 43 |
| **8** | 213 | 0 | 100 | 0 | 0 | 10 | 42 | 5 |
| **9** | 213 | 0 | 100 | 0 | 0 | 8 | 29 | 0 |
| Tertiary | | | | | | | | |
| **10** | 103 | 0 | 100 | 27 | 1 | 0 | 0 | 0 |
| **11** | 213 | 0 | 60 | 0 | 0 | 0 | 0 | 0 |

mass spectra of the two tertiary nitro compounds (for example, 100% in compound **10** and 25% in compound **11**) where the resultant tertiary carbocations would be expected to be more stable than the primary or secondary species.

## Ammonia PICI mass spectra

CI with ammonia reagent gas in the positive ion mode resulted in facile addition of the ammonium ion and gave an $[M+NH_4]^+$ molecular-adduct ion as the base peak of the spectra of nearly all the nitro compounds studied. The only exceptions to this rule were nitromethane (**1**), where the $[NO_2]^+$ ion was more abundant, and the tertiary nitro compound 1-hexyl-1-nitrocyclohexane (**11**), where an elimination ion $[M-29]^+$ predominated. $[M-NO_2]^+$ ions were absent in all of these spectra.

## Isobutane PICI mass spectra

CI using isobutane as reagent gas in the positive ion mode gave significant $[M+H]^+$ ions with all of the primary nitro compounds (**1**-**3**), with the simplest of the secondary nitro compounds, nitrocyclohexane (**4**), and with one of the tertiary nitro compounds, 2-methyl-2-nitropropane (**10**). Only in the case of nitromethane (**1**) was this $[M+H]^+$ ion the base peak of the spectrum. $[M-NO_2]^+$ ions were commonly observed as very abundant ions in the spectra of all of the nitro compounds and were often the base peaks.

## Methane PICI mass spectra

CI using methane as reagent gas in the positive ion mode produced significant $[M+H]^+$ ions in the spectra of only two of the primary nitro compounds, nitromethane (**1**) and 1-nitrohexane (**2**). The high proton transfer energy of this technique resulted in facile fragmentation and abundant $[M-NO_2]^+$ ions were commonly observed in the spectra of all of the nitro compounds.

## NICI mass spectra

Under the conditions used for the NICI experiments the reagent gas serves primarily to moderate the electrons to thermal energy and provides a source of molecules for collisional stabilization.[21] The spectra obtained in these NICI experiments would be expected to be virtually independent of the reagent gas type, and this was the case with most of the nitro compounds studied. However, compounds **8** and **9** did show unexpectedly higher abundances of the $[M-1]^-$ ions when isobutane was used as reagent gas.

The spectra contained substantial $[M-H]^-$ ions for nearly all the primary and secondary nitro compounds (**1**-**9**), but the overall sensitivity of the ion signals was very much reduced in comparison to the positive ion mode. The two tertiary nitro compounds (**10** and **11**) failed to give any RMM information under these conditions.

## Comparison of the mass spectra of primary, secondary and tertiary nitro compounds

The effects of the different modes of ionization can be compared directly by examination of the mass spectra in Figs 1, 2 and 3, where the different spectra of the primary nitro compound, 1-nitrohexane (**2**), are compared with those of the secondary compound, 1-hexyl-2-nitrocyclohexane (**5**), and the tertiary compound, 1-hexyl-1-nitrocyclohexane (**11**).

The primary nitro compound, 1-nitrohexane (**2**, Fig. 1), exhibited no *m/z* 131 molecular ion under EI conditions, but gave $[M+H]^+$ ions at *m/z* 132 under methane and isobutane PICI conditions, with more fragmentation being apparent with methane. Ammonia PICI conditions gave a much more abundant $[M+NH_4]^+$ ion at *m/z* 149, with a small cluster ion at *m/z* 166 corresponding to $[M+N_2H_7]^+$. NICI produced a large $[M-H]^-$ ion at *m/z* 130 and a base peak at *m/z* 46 for the $[NO_2]^-$ ion.

The secondary nitro compound, 1-hexyl-2-nitrocyclohexane (**5**, Fig. 2), failed to give molecular ions under

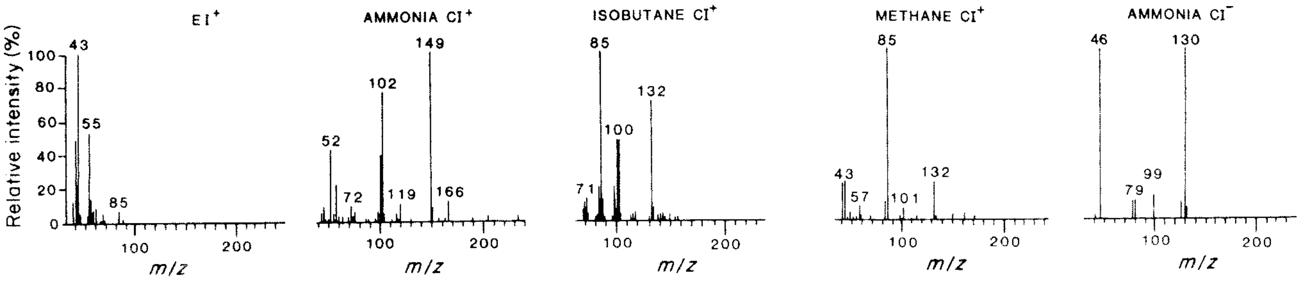


Figure 1. Mass spectra of 1-nitrohexane (compound **2**, mol. wt = 131) under EI and CI conditions.

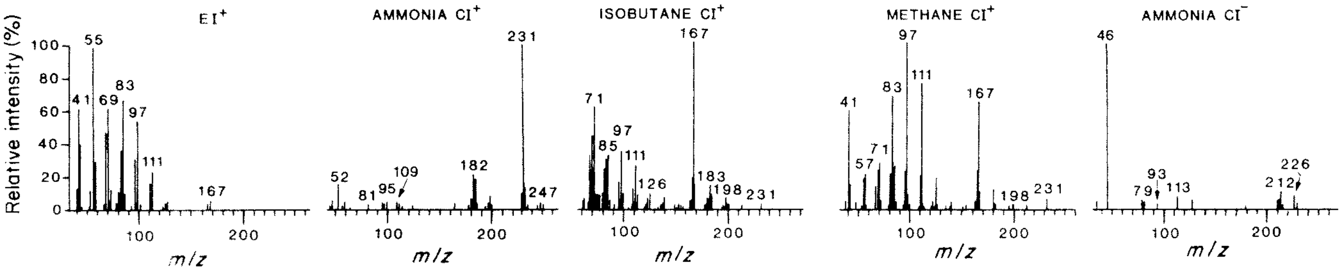


Figure 2. Mass spectra of 1-hexyl-2-nitrocyclohexane (compound **5**, mol. wt = 213) under EI and CI conditions.

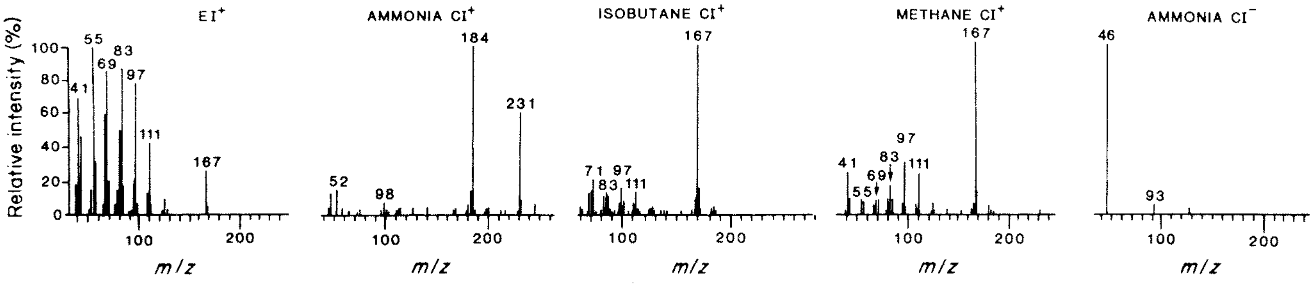


Figure 3. Mass spectra of 1-hexyl-1-nitrocyclohexane (compound **11**, mol. wt = 213) under EI and CI conditions.

EI, or molecular-adduct ions under methane PICI or isobutane PICI conditions, but furnished abundant $[M-NO_2]^+$ ions at *m/z* 167 in the two CI modes. Ammonia PICI gave a molecular-adduct $[M+NH_4]^+$ ion at *m/z* 231 as the base peak, with abundant ions at *m/z* 182 $[M-31]^+$ and *m/z* 184 $[M-29]^+$. NICI gave the usual base peak at *m/z* 46 for the $[NO_2]^-$ ion and an $[M-H]^-$ ion at *m/z* 212. There was also a small ion at *m/z* 226 corresponding to $[M+13]^-$ which was found to be common to several of the NICI spectra.

The tertiary nitro compound, 1-hexyl-1-nitrocyclohexane (**11**, Fig. 3) gave an $[M-NO_2]^+$ ion at *m/z* 167 as its highest mass ion under EI and PICI conditions with both methane and isobutane reagent gases. However, under ammonia PICI conditions a very abundant $[M+NH_4]^+$ ion was observed at *m/z* 231 with a base peak at *m/z* 184 corresponding to an $[M-29]^+$ species. NICI provided only very weak ions with higher mass than the base peak of *m/z* 46 which corresponded to the $[NO_2]^-$ ion.

## Nature of the $[M-29]^+$ species in ammonia PICI spectra

When the ammonia PICI spectra of all of the nitro compounds (**1**–**11**) were compared, it was noted that the $[M-29]^+$ ion was present in nearly all of the CI spectra, being absent only in the non-representative nitromethane spectrum, and being particularly abundant in the spectra of the two tertiary nitro compounds (54% in compound **10** and 100% in compound **11**). Accurate mass measurement of the *m/z* 184 ion $[M-29]^+$ in the ammonia PICI spectrum of 1-hexyl-1-nitrohexane (**11**) established a molecular formula of $C_{12}H_{26}N$ (found 184.2029: required, 184.2065). An ion of this formula could arise from three alternative processes:

(i) by reduction of the nitro group to amine followed by protonation, as observed previously for aromatic nitro compounds under CI conditions;[7,22,23]
(ii) by substitution of $NO_2$ by $NH_3$ as observed for aromatic nitro compounds;[24–26]
(iii) by loss of $HNO_2$ from the ammonium adduct ion, a route which is similar to the $[M+H-HNO_2]^+$ ions observed by Chizhov *et al.*[10] in a methane CI study.

In an attempt to resolve these ambiguities, compound **10** was subjected to a precursor ion linked scan, focused on the $[M-29]^+$ ion at *m/z* 74 under ammonia PICI conditions using the ZAB-E instrument. No precursors of the *m/z* 74 ion were observed, although the normal CI spectrum contained an abundant $[M+NH_4]^+$ ion at *m/z* 121. Additionally, collision-assisted dissociation (CAD) of the ammonia adduct ion at *m/z* 121 gave no fragment ion at $m/z$ 74 when subjected to a mass-analysed ion kinetic energy spectrometric scan under ammonia PICI conditions. This evidence would seem to eliminate the possibility of a fragmentation corresponding to a facile elimination of $HNO_2$ from the ammonium adduct ion as in process (iii).

Process (i) involves the reduction of the nitro compound to amine in the presence of the ammonia reagent gas. It has been reported that other reagent gases such as methane, isobutane and water also participated in this type of reduction for aromatic nitro compounds.[7,22,23] However, in the case of compound **10**, the ion at $m/z$ 74 corresponding to $[RNH_3]^+$ was totally absent in the PICI spectra with both methane and isobutane reagent gases, which suggested that reduction was not a significant process in this case. We therefore favour the substitution process (ii) as the most likely method for the production of the $(RNH_3]^+$ ions in this compound.

### Nature of the $[M+13]^-$ ion in the NICI spectra

Detailed comparison of the NICI spectra of the secondary nitro compounds (**5**–**9**) indicated that they all contained an ion at $m/z$ 226, corresponding to $[M+13]^-$. The presence of this ion was independent of the reagent gas used, and it varied in abundance from 3% in compound **5** with isobutane to 29% in compound **7** with methane. All of these 15 spectra had the $m/z$ 46 ion $[NO_2]^-$ as their base peak from fragmentation of the nitro compounds, and it seemed likely that the $[NO_2]^-$ ion was involved in the production of the $[M+13]^-$ ion. Accurate mass measurement of the $m/z$ 226 ion in the ammonia NICI spectrum of 1-hexyl-4-nitrocyclohexane (**7**) established a molecular formula of $C_{12}H_{20}NO_3$ (found, 226.1449 : required, 226.1443). This formula suggested that the $m/z$ 226 ion was formed by the capture of $[NO_2]^-$ followed by the expulsion of the elements of $H_3NO$. Confirmation of this sequence was attempted by a precursor ion linked scan on the VG ZAB-E instrument, but was unsuccessful, presumably because the reactions took place rapidly in the ion source and no metastable fragmentations occurred in the field-free regions.

## CONCLUSION

These observations show that in order to obtain RMM information from aliphatic nitro compounds it is necessary to use ammonia CI in the positive ion mode, when it is to be expected that abundant $[M+NH_4]^+$ ions will be obtained, even in the case of the labile tertiary nitro compounds. Further confirmation can be obtained in the NICI mode in the case of primary and secondary nitro compounds, when $[M-H]^-$ ions will be obtained, although the spectra will have an overall reduced sensitivity.

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