

# Benzylum Versus Tropylium-like Ion Formation: The Dissociation of Ionized 1-Methylnaphthalene

Formation des ions de type benzylum versus ions de type tropylium : la dissociation du 1-méthylnaphtalène ionisé

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## Abstract | Résumé

The formation of benzylum versus tropylium ions in the dissociation of gas-phase ions has a long and rich history. In this brief report, the possible formation of these two structurally isomeric ions in the dissociation of ionized 1-methylnaphthalene was explored. Hydrogen (H)-loss from 1-methylnaphthalene gave a distinct ion species compared to those generated by bromine (Br) atom-loss from 2-(bromomethyl)naphthalene, 1-methyl-4-bromonaphthalene, and 1-bromo-2-methylnaphthalene. The primary dissociation pathway for the tropylium ion structure [molecule (M)-H]<sup>+</sup> ion from cycloheptatriene was H-atom loss. This was also the primary reaction for [M-H]<sup>+</sup> from 1-methylnaphthalene, a result consistent with the ion-molecule reaction chemistry of Gotkis and Lifshitz, which suggested this population of ions was largely benzotropylium. The three brominated species must thus lose Br to make the naphthylmethyl cation structure as the common reacting configuration.

La formation des ions benzylum par rapport aux ions tropylium lors de la dissociation d'ions en phase gazeuse possède une longue et riche histoire. Dans ce court rapport, la formation possible de ces deux ions isomères de structure lors de la dissociation du 1-méthylnaphtalène ionisé a été étudiée. La perte d'un atome d'hydrogène (H) à partir du 1-méthylnaphtalène a produit une espèce ionique distincte de celles générées par la perte d'un atome de brome (Br) à partir du 2-(bromométhyl)naphtalène, du 1-méthyl-4-bromonaphtalène et du 1-bromo-2-méthylnaphtalène. La principale voie de dissociation menant à la structure de l'ion tropylium, c'est-à-dire l'ion [molécule (M) - H]<sup>+</sup> issu du cycloheptatriène, correspond à la perte d'un atome d'hydrogène. Cette réaction est également la voie principale pour l'ion [M - H]<sup>+</sup> issu du 1-méthylnaphtalène, un résultat cohérent avec la chimie des réactions ion-molécule décrite par Gotkis et Lifshitz, ce qui suggère que cette population d'ions est majoritairement de type benzotropylium. Ainsi, les trois composés bromés doivent perdre un atome de brome pour former la structure de cation naphthylméthyle, qui constitue la configuration réactive commune.

**Keywords:** benzylum ion; tropylium ion; benzotropylium; 1-methylnaphthalene; MIKE spectrometry; gas-phase ion chemistry; ion dissociation; naphthylmethyl cation; density functional theory; mass spectrometry

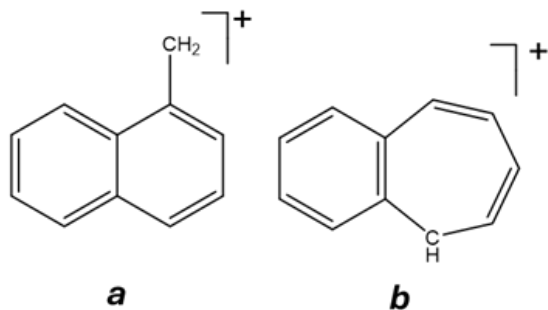
## Introduction

One of the more famous stories in gas phase ion chemistry is the formation of the benzylum versus tropylium ion structure (C<sub>7</sub>H<sub>7</sub><sup>+</sup>, mass-to-charge ratio (m/z) 91, where C is carbon). Hydrogen-loss from toluene forms a mixture of the two structures, with tropylium being the dominant one (1-4). Tropylium is formed uniquely via the H-loss reaction of cycloheptatriene radical cations. This story bled over into astrochemical interest as researchers probe the dissociative photoionization of methyl-substituted polycyclic aromatic hydrocarbon molecules, which are expected to be carriers of some of the unidentified infrared bands (5). For example, the H-loss reaction in photoionized 1-methylpyrene demonstrated the formation of only the benzylum-like structure due to the ring strain in the key transition state leading to the tropylium-like product (6). Jusko et al. concluded that the tropylium-analogue, if present, is below the detection limit

of their infrared multi-photon dissociation experiment. They computationally modeled both isomers and found C<sub>2</sub>H<sub>2</sub>-loss was the dominant reaction from both, making the distinction of the two structures even more difficult (7). Recently, Rossi et al. demonstrated that the two ions can be distinguished based on vacuum ultraviolet photodissociation action spectra (8). Benzylum and tropylium ions also factor in the dissociation of ions with multiple rings such as substituted coumarins (9).

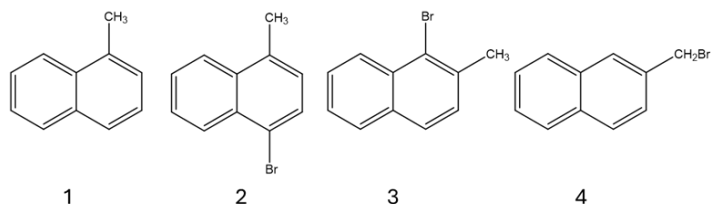
Taking a step back from this more complex system, this study focuses on the ion formed by H-loss from 1-methylnaphthalene. Gotkis and Lifshitz explored the nature of the m/z 141 ion (C<sub>11</sub>H<sub>9</sub><sup>+</sup>) formed upon photoionization of 1-methylnaphthalene, and using time-resolved measurements, they monitored the dissociative photoionization of the above-mentioned molecules on timescales from microseconds to seconds. Importantly, they observed a side reaction of a percentage of the m/z 141 ions (C<sub>11</sub>H<sub>9</sub><sup>+</sup>) with their

precursor molecule to form  $C_{12}H_{11}^+$  ( $m/z$  155) and  $C_{10}H_8$ , which is analogous to the reaction observed between the benzylium ion and toluene (10, 11). This reaction showed that H-loss from the 1-methylnaphthalene ions resulted in both 1-naphthylmethyl (a) and benzotropylium (b) ion structures (Scheme 1). The ion-molecule reactions suggested the content of 1-naphthylmethyl was about 20% across a photon energy range of 10–13 eV, corresponding to a molecular ion internal energy of up to 5 eV (10).



**Scheme 1. Chemical structures of 1-naphthylmethyl and benzotropylium ions.** The 1-naphthylmethyl ion (a) and the benzotropylium ion (b).

To probe this further, this study examines the  $C_{11}H_9^+$  ( $m/z$  141) ions formed by electron ionization of 1-methylnaphthalene and three brominated isomers (Scheme 2) with mass-analyzed ion kinetic energy (MIKE) spectrometry and theory to probe the dissociation over a narrow internal energy window for these ions.



**Scheme 2. Precursor compounds of 1-methylnaphthalene and brominated isomers.** 1-methylnaphthalene (1), 1-methyl-4-bromonaphthalene (2), 1-bromo-2-methylnaphthalene (3), and 2-bromomethylnaphthalene (4).

## Methods

Compounds 1-4 (Scheme 2) were purchased from Millipore Sigma and used without further purification. MIKE spectrometry was performed on a VG ZAB-R mass spectrometer (Manchester) (12, 13). Samples were introduced into the ion source of the instrument by thermal desorption from a solids inlet insertion probe. The ion source pressure (read above the ion source turbopump using an ion gauge) was kept below  $1.0 \times 10^{-6}$  Torr. The radical cations were generated by electron ionization with 80 eV electrons. The resulting ions were accelerated to 8 kV toward the magnetic sector where  $m/z$  141 was momentum-selected and transmitted to the second field-free region. Ions with internal energies such that their unimolecular dissociation rate constant is between  $10^4$  and  $10^6$   $s^{-1}$

can dissociate in this region, and they are coined “metastable ions.” Due to the conservation of energy and momentum, product ions from unimolecular dissociation ( $F^+$ ) have a fraction of the precursor ion’s ( $P^+$ ) translational energy,  $T_{P^+}$ , according to the equation:

$$T_{F^+} = T_{P^+} \left( \frac{M_{F^+}}{M_{P^+}} \right) \quad (\text{Eq. 1})$$

Where  $M_{F^+}$  and  $M_{P^+}$  are the  $m/z$  ratios of the product and precursor ions, respectively. The electrostatic analyzer separates the ions according to their kinetic energies, and the ions are then detected by an off-axis conversion dynode/scintillator/photomultiplier assembly. By measuring  $T_{F^+}$  and  $T_{P^+}$ , and knowing  $M_{P^+}$ ,  $M_{F^+}$  can be deduced for a singly-charged ion.

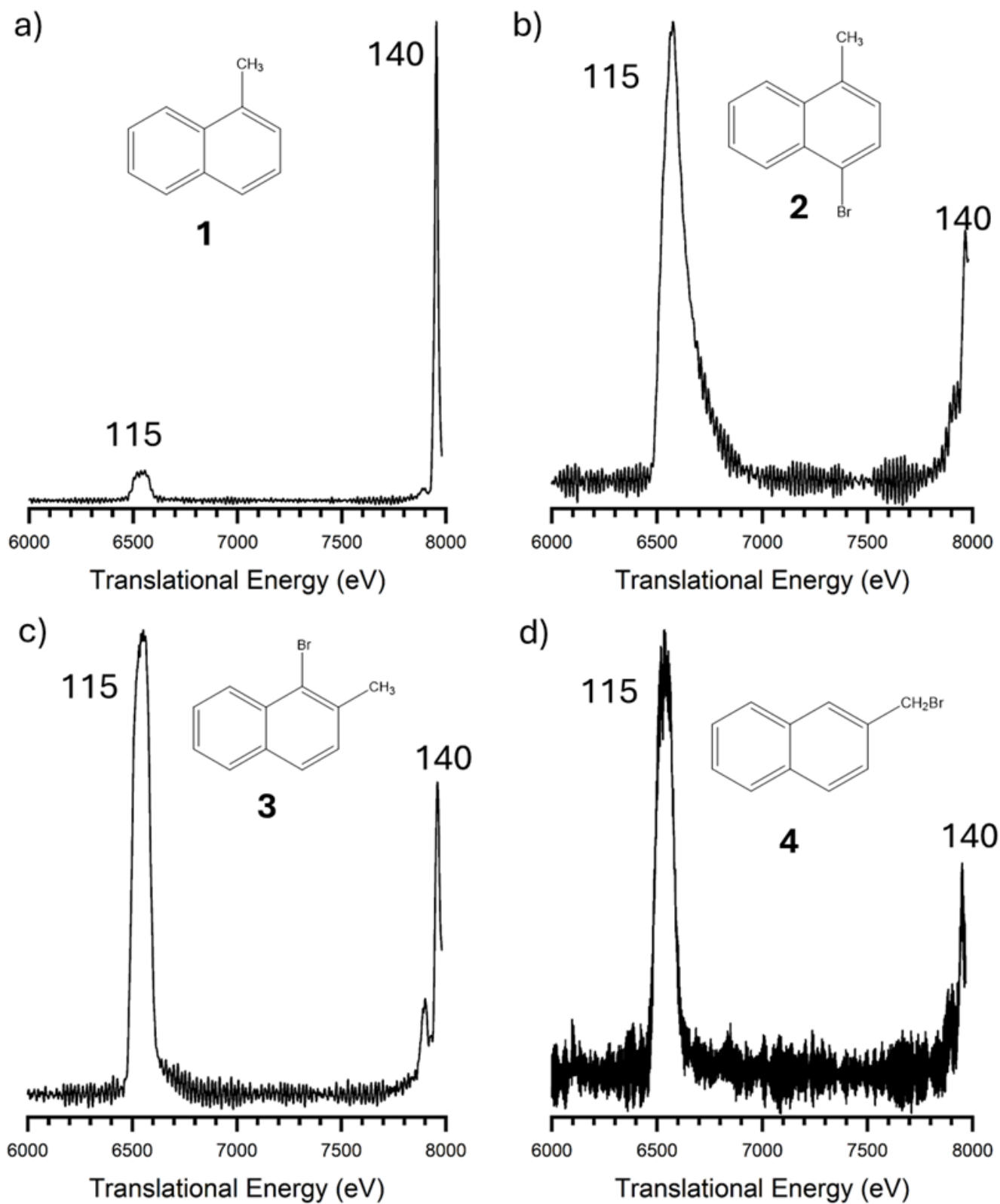
All structures were optimized using density functional theory with the B3LYP/6-311+G(d,p) level of theory using the Gaussian 16 software suite (14). Transition states were confirmed with the intrinsic reaction coordinate protocol.

## Results and Discussion

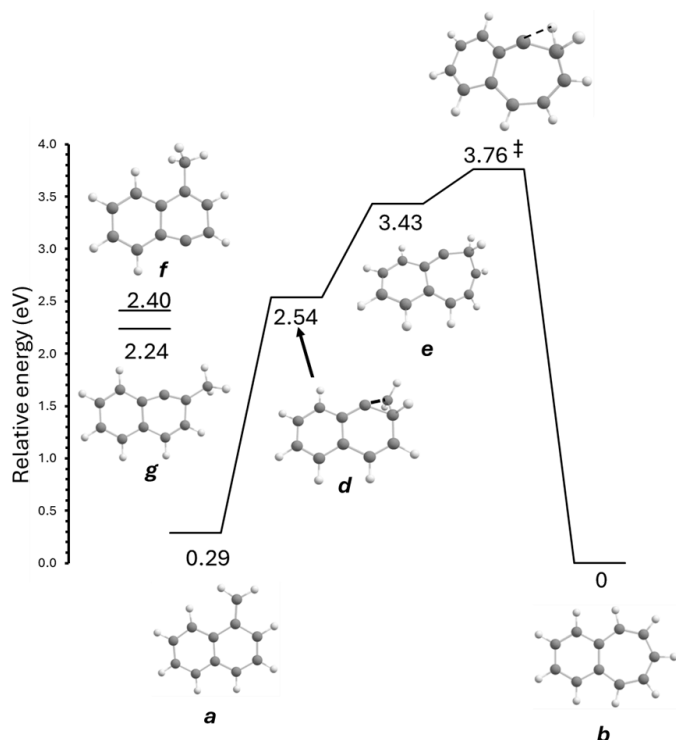
Figure 1 shows the MIKE spectra for the source-generated  $m/z$  141 ion from Scheme 2 compounds 1-4. For 2-4,  $m/z$  141 resulted from the loss of Br in the ion source upon dissociative ionization. Three fragment ions were observed. The main peaks are due to either H-loss ( $m/z$  140) or  $C_2H_2$ -loss ( $m/z$  115), with some evidence for 2H-loss in some of the spectra. The spectra appear to cluster into two types: one in which  $C_2H_2$ -loss predominates (for  $m/z$  141 from 2-4), and one where H-loss dominates (for  $m/z$  141 from 1). Interestingly, Br-loss from 4, which one would assume produced the 2-naphthylmethyl cation (c), produces an ion with the same MIKE spectrum as those formed from Br-loss from 2 and 3, suggesting that the three initially formed  $[M-Br]^+$  ions may isomerize to a common reacting configuration before metastable dissociation (it would be highly improbable for multiple reacting configurations to be formed in the same relative abundance from three precursors) (12). If this is the case, then the data suggests a minimum of two predominant reacting configurations, at least one formed from 1 and the other formed from 2-4.

### Computational investigation of the interconversion of a and b

At the presently employed level of theory, ion b is the global minimum, lying 0.3 eV below a (Figure 2). Ion a first isomerizes to d by bending the  $CH_2$  moiety over to the adjacent carbon. The  $CH_2$  group then inserts into the ring to form e, which undergoes a 1,2-H shift to form b. The reverse barriers from d to a, and from e to d are tiny with the slightest geometry change leading back to a or e, respectively. The high relative energy for e and the subsequent transition state is due to the breaking of the delocalization in a and b and the incorporation of both a carbene carbon and the  $CH_2$  moiety into the seven-member ring.



**Figure 1. MIKE mass spectra for compounds 1-4.** In (b), the skewed appearance of the peak at 6500 eV is due to the lag of the amplifier at high gain. Peaks are labelled with their  $m/z$  as calculated from Equation 1.

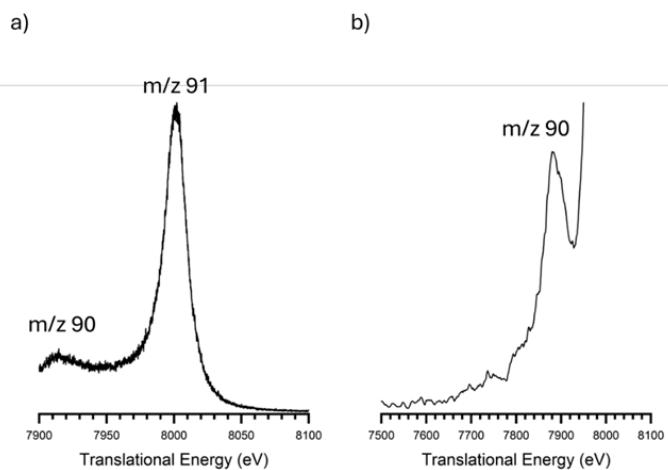


**Figure 2. The interconversion of a and b at the B3LYP/6-311+G(d,p) level of theory.** Structures f and g are included for comparison.

Br-loss from 2 and 3 will initially form distorted structures with the charge on a bare ring carbon, structures f and g (Figure 2). These lie at high relative energy (2.40 and 2.24 eV, respectively). Hydrogen migration along the ring would result in their isomerization to a (from f) and c (from g), the 2-naphthylmethyl cation. For the naphthalene radical cation, such hydrogen migration occurs below 3.5 eV (15). Combined with the fact that Br-loss from 4 should initially make c, these combined experimental and theoretical results suggest that the reactive configuration(s) for the m/z 141 ions from 2-4 are a form of naphthylmethyl cation (a and/or c). This would be consistent with the results of Gotkis and Lifshitz that showed m/z 141 from 1 is primarily b (10). The results also imply that H-loss would be the primary fragmentation pathway for b. The MIKE spectrum was obtained for m/z 91 from cycloheptatriene, which should be 100% tropylium ion, and the main peak is indeed H-loss (Figure 3). As the ring size of the polycyclic aromatic hydrocarbon increases, it seems either the predominant loss from b-type structures switches to C<sub>2</sub>H<sub>2</sub> (according to Jusko et al.) (7) or the H-loss energy was overestimated in their theoretical model.

## Conclusion

This study employed MIKE spectra to explore the structure of the C<sub>11</sub>H<sub>9</sub><sup>+</sup> ions (m/z 141) formed by H-loss from ionized 1-methylnaphthalene. The spectrum of these m/z 141 ions was dominated by the loss of an H atom together with a small amount



**Figure 3. MIKE mass spectra of ion source generated m/z 91 ([M-H]<sup>+</sup>) from cycloheptatriene.** Panel (a) illustrates the relative abundance of the precursor and fragment ion, while (b) shows the entire H-loss peak.

of C<sub>2</sub>H<sub>2</sub>-loss. By comparison, the source-generated m/z 91 ion from cycloheptatriene, which should have the tropylium structure, also exhibited primarily H-loss in its MIKE spectrum. Thus, in conclusion, ionized 1-methylnaphthalene loses H to form primarily the benzotropylium ion (b), in agreement with the ion-molecule results of Gotkis and Lifshitz (10). Three isomeric brominated ions also generated m/z 141 ions (by Br-loss) that had virtually identical MIKE spectra consistent with a naphthylmethyl cation, such as a, which exhibited a dominant reaction leading to loss of C<sub>2</sub>H<sub>2</sub>.

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