

Microanalytical Research Laboratory, Department of Chemistry, Faculty of
Science, Ain Shams University, Cairo, Egypt

Characterization of Some Gem-Dinitrilo Sneeze and Tear Gases by Electron-Impact Induced Fragmentation

By

Saad S. M. Hassan*

With 1 Figure

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Introduction

Benzal malonitrile and some of its derivatives have the effect of sneeze and tear gases besides many other physiological properties¹. Since these compounds could not be specifically identified by either chemical or spectroscopic methods, attention was turned to their behaviour during electron-impact induced fragmentation.

Search of the literature shows that nitriles have received little attention in mass spectrometric studies. Interpretation of the spectra is complicated by the presence of isobaric carbon-hydrogen and carbon-nitrogen ions and by complex fragmentation process². Nevertheless, the technique is a useful tool for identification of some nitriles^{3, 4}.

With mono-nitrile aliphatic compounds, the molecular ion peak is weak or missing with compounds higher than propionitrile. In most cases significant peaks exist at $(M - 1)$ and at m/e 41⁵⁻⁷. Branched and straight chain nitriles show peaks at m/e 54 and 55 besides that corresponding to the loss of ethylene^{6, 8-10}. On the other hand, with aromatic nitriles the C — N group is always found in the spectra and the parent peaks can usually be observed¹¹. Mass spectra of some poly nitriles as tri-nitrilo cyclopropane and, di-nitrilo hepta-fulvene have been also mentioned^{12, 13} in the literature.

* Present address: Department of Chemistry, Faculty of Science, Libya University, Tripoli, Libya.

In the present work the general characteristic behaviour of benzal malonitrile and its derivatives upon electron impact are described and used as diagnostic features for characterization of these compounds.

Experimental

The mass spectra were taken with the Hitachi-Perkin Elmer RMU-6E mass spectrometer under the following conditions:

Ion source temperature 110° ; ion source pressure 5×10^{-7} ; electron accelerating voltage 70 eV; ionising current $100 \mu\text{A}$; and temperature inlet system 110° .

The samples used were prepared from malonitrile and the corresponding aldehydes according to Corson and Stoughton¹: benzal malonitrile (m. p. 83°), *o*-chlorobenzal malonitrile (m. p. 95°) and *m*-nitrobenzal malonitrile (m. p. 104°).

Results and Discussion

A study of the spectra obtained by the electron-impact of benzal malonitrile and its derivatives shows that a large number of common fragmentation and rearrangement reactions take place. Fig. 1 shows the intensity diagrams of the fragmentation products of benzal malonitrile (A), *m*-nitrobenzal malonitrile (B), and *o*-chlorobenzal malonitrile (C). The intensities are given in % total ionisation and ions with abundance smaller than 1% have been omitted.

The total abundance of the molecular ion $[M]^+$ is 100% of the total ion current in case of benzal malonitrile as well as *m*-nitro derivative. The latter shows another strong peak of the same intensity at m/e 153 corresponding to $[M - \text{NO}_2]^+$. In case of *o*-chloro derivative, the molecular ion peak constitute 50% and the base peak appears at m/e 153 i. e., $[M - \text{Cl}]^+$. Thus fission of $\text{C} - \text{NO}_2$ and $\text{C} - \text{Cl}$ is therefore very facile. In general, the base peak of these compounds is visible at $[M\text{-substituted atom or group}]^+$.

The fragmentation pattern, spectral characterization and trend for these compounds are almost identical. The presence of substituent group have little influence on the behaviour of the parent molecule because these substituents are lost in the initial step of fragmentation. The nitro group and chlorine atom are indicated by the presence of prominent peaks at $(M - \text{NO}_2)$ and $(M - \text{Cl})$, respectively. In case of the nitro compound a very important peak, though weak, occurred at m/e 46 due to loss of NO_2 .

The main fragmentation paths of the odd-electron molecular ion are elimination of $\text{H} - \text{C} \equiv \text{N}$ and $\text{H} - \text{C} \equiv \text{C} - \text{C} \equiv \text{N}$ mole-

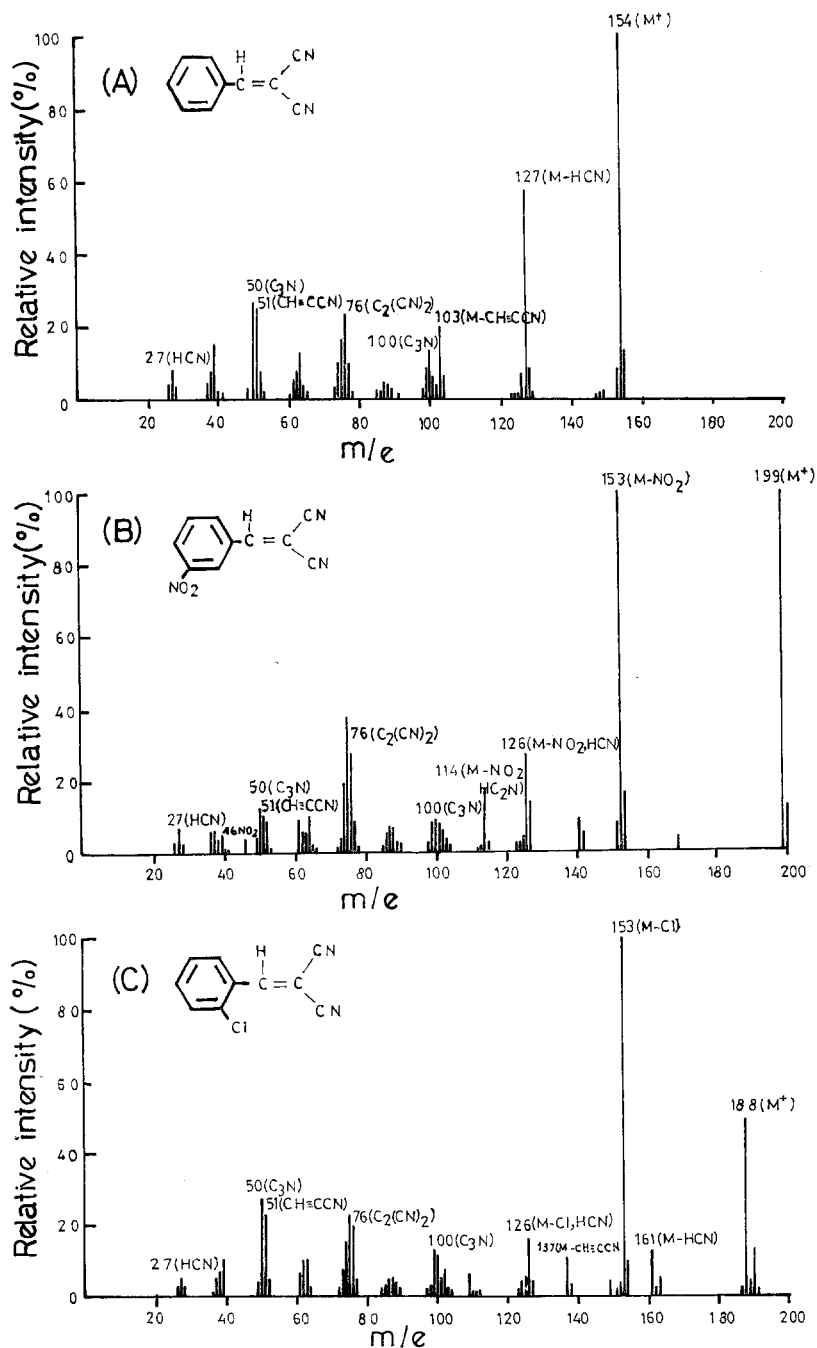


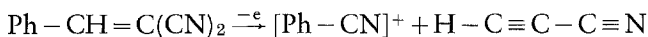
Fig. 1. Mass spectra of benzal malonitrile (A); *m*-nitro benzal malonitrile (B); and *o*-chloro benzal malonitrile (C)

cules leaving the ions $[\text{Ph} - \text{C} \equiv \text{C} - \text{C} \equiv \text{N}]^+$ and $[\text{Ph} - \text{C} \equiv \text{N}]^+$ respectively. This process is favored due to the stability of the neutral products¹⁴. The cleavage of C — C, C — N, and C — H bonds leading to the formation of ions of the masses: 26, 27, 38, 39, 50, 51, 52, 64, 65, 76, 77, 103, 126, 127, and 153 occurred in all compounds under investigation. The intense peaks (20—30% relative abundance) of $\text{C}_2(\text{CN})_2$ m/e 76 and $\text{C}_2\text{H}(\text{CN})_2$ m/e 77 are diagnostically useful for identification of the *gem* di-nitrilo group. Less intense peaks (1—10% relative abundance) of $\text{C}(\text{CN})_2$ m/e 64 and $\text{CH}(\text{CN})_2$ m/e 65 may be also useful. In addition, presence of other prominent peaks due to: $\text{M} - \text{HCN}$ at m/e 126 and 127 and that of CN at m/e 26, HCN at m/e 27, C_2N at m/e 38, C_2HN at m/e 39, C_3N at m/e 50, C_3HN at m/e 51 and $(\text{CN})_2$ at m/e 52 are used as additive confirmation of the presence of the cyano group.

While it was not possible to ascertain quantitatively the origin of the m/e 74 and 75 peaks observed with relative intensities ranged from 20 to 40% in all the compounds under investigation, it was concluded that loss of $-\text{CH} = \text{C}(\text{CN})_2$ from precursor of mass 153 and 154 is the most important route.

Considering the fragmentation pattern, a remarkable rearrangement reaction was noticed *viz* elimination of $\text{H} - \text{C} \equiv \text{C} - \text{C} \equiv \text{N}$ from the molecular ion or its derivatives. The known propensity of nitriles to undergo bond-forming reactions^{10, 15, 16} on electron-impact process is also observed. Ion corresponding to ionized phenyl cyanide (m/e 103) is frequently observed in the spectra. Such ion may vary greatly in relative abundance according to the nature of the substituents but can be identified in all compounds. The abundance attain 20, 8, and 7% relative to the base peak in case of benzal-, *m*-nitro-, and *o*-chloro-malonitriles, respectively. The latter shows another peak at m/e 137 (11% relative abundance) corresponding to *o*-chlorophenyl cyanide.

The presence of a metastable ion peak at m/e 103 in all compounds confirms that phenyl cyanide is formed in one step process (*i. e.*, synchronous mechanism):



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Summary

Characterization of Some Gem-Dinitrilo Sneeze and Tear Gases by Electron-Impact Induced Fragmentation

Reaction products obtained during the decomposition of some *gem* dinitrilo sneeze and tear gases upon electron-impact are described. The spectra of benzal, *o*-chloro, and *m*-nitro malonitriles show some common characteristics which can be used for identification and characterization of these compounds. These are: (a) a base peak at $[M\text{-substituted atom or group}]^+$; (b) diagnostic intense peak at m/e 76 and 77 due to $C_2H(CN)_2$ and $C_2(CN)_2$ besides other cyano fragmentation products; and (c) rearrangement reaction leading to the formation of phenyl cyanide.

Zusammenfassung

Bei der Zersetzung einiger *gem*-Dinitrilo-Reiz- und Tränengase durch Elektronenstoß entstehende Reaktionsprodukte wurden beschrieben. Die Massenspektren der Benzal-, *o*-Chlor- und *m*-Nitromalonitrile zeigen einige gemeinsame Charakteristika, die zu deren Identifizierung herangezogen werden können. Diese sind:

- a) ein Basepeak für das atom- oder gruppensubstituierte Molekülion;
- b) ein intensiver diagnostischer Peak bei m/e -Werten von 76 und 77 entsprechend $C_2H(CN)_2$ und $C_2(CN)_2$ neben anderen CN-haltigen Bruchstücken und
- c) der Ablauf von Umwandlungsreaktionen, die zur Bildung von Phenylcyanid führen.

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