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Mass Spectrometry of 10-Chloro-5, 10-dihydrophenarsazine (Adamsite) and 10-Methyl-5, 10-dihydrophenarsazine

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The mass spectrograms of 10-chloro- and 10-methyl-5,10-dihydrophenarsazine have been determined. These spectrograms show the following main characteristics of fragmentation behavior for these heterocycles: (a) a relative stability, in both compounds, of the arsenic atom within the heterocyclic framework; (b) an exceptionally facile splitting of the As-Cl bond, contrasting with the behavior of the As-CH₃ bond; and (c) an easy formation of the phenarsazine species from 10-chloro-5,10-dihydrophenarsazine.

10-Chloro-5,10-dihydrophenarsazine (I), a compound readily obtained by the Wieland-Rheinheimer reaction of arsenic trichloride upon diphenylamine (1), is notorious as a toxic "gas" used in warfare for its strong irritant and sternutatory properties. Chemically, it belongs to a group of compounds interesting for their structure, which is still a matter of some debate. Because of its yellow color, contrasting with the colorless diphenylchloroarsine, the ionic structures (II) and (III) have been suggested (1,2); but if these can explain certain features of this molecule, such as its high melting point, they cannot account for most of its reactions. For instance, Grignard reagents produce As-substitution to give 10-alkyl- or 10-aryl-5,10-dihydrophenarsazines (3), and sodium methoxide gives the corresponding As-methoxy compound (4). Most workers therefore (5) have given their preference to formula (I).

As a contribution to a better knowledge of compounds falling into this category, which our group has repeatedly investigated in the past because of their potential carcinogenic activity (6), the electron impact fragmentation of 10-chloro-5,10-dihydrophenarsazine has now been studied. The mass spectrogram, taken with a German Atlas CH₄ apparatus at 70 electron-volts (40 μ A), was a remarkably simple one (Fig. 1), showing, in the range of the m/e measured, barely ten significant peaks, which are listed in Table I. The following features call for comment: (a) The molecular peaks $m/e = 277$, corresponding to the isotope ³⁵As, and $m/e = 279$, corresponding to the isotope ³⁷As, are practically non-existent (representing barely 0.2% of the base peak). This quasi-absence of molecular ions testifies to the particular ease with which the As-Cl bond is ruptured on electron impact. (b) At $m/e = 242$, there is an important peak which corresponds to the loss of chlorine. To this same species M-Cl corresponds also the doubly charged ion $m/e = 121$. (c) The peak $m/e = 241$, which is the most pronounced and is therefore taken as the base peak, corresponds to the phenarsazine species (formula

IV). This prominent formation of phenarsazine ions is all the more interesting as in conventional organic chemistry there is no direct way to proceed from 10-chloro-5,10-dihydrophenarsazine (I) to phenarsazine (IV), and as phenarsazine is known to be a very elusive substance. The phenarsazine species can also be recognized by its doubly charged ion at $m/e = 120.5$, which attains as much as 4.5% of the base peak; this formation of a double charge is in line with what has often been observed in the electron impact fragmentation of the similarly built acridines (7). The similarity of behavior between acridine and phenarsazine points to the latter's high degree of aromaticity. (d) The peak $m/e = 167$ corresponds to the loss of the arsenic heteroatom and formation of the carbazole species (V). This attribution is confirmed by the presence, in the spectrogram, of ions which had previously been identified in the fragmentation of carbazole itself: if we take C to represent carbazole, the peak $m/e = 166$ corresponds to C-1 and the peak $m/e = 140$ corresponds to the well known loss, by carbazole, of hydrogen cyanide (8). (e) Lastly, the peak $m/e = 139$ corresponds to the loss by molecule (I) of As-Cl and CH₂N: it can be recalled in this respect that the mass spectrograms of many nitrogen heterocycles (imidazole, indole, 2-methylcarbazole, etc.) show the presence of the ion [CH₂N]⁺ ($m/e = 28$) (9).

10-Methyl-5,10-dihydrophenarsazine (VI).

This compound, obtained in the reaction of methylmagnesium iodide on 10-chloro-5,10-dihydrophenarsazine, is colorless and has a low melting point, in contrast with compound (I). It was interesting to determine its mass spectrogram for comparing the pattern of its electron impact fragmentation with that described above for (I). As shown in Fig. 2, the mass spectrogram of (VI) is also a relatively simple one, and the most significant peaks are listed in Table I. The following main features appear: (a) A fundamental difference between the two compounds is that here there is an important molecular peak ($m/e = 257$); to this singly charged

molecular ion corresponds also a doubly charged molecular ion ($m/e = 128.5$). (b) The most pronounced peak, and the one considered as the base peak, is, however, the one corresponding to the loss of a methyl ($m/e = 242$), and to this species $M-CH_3$ corresponds the doubly charged ion $m/e = 121$. (c) The formation of carbazole is shown by the presence of a prominent peak $m/e = 167$; here again, taking C to represent the carbazole species, the peak $m/e = 166$ corresponds to C-1, and the peak $m/e = 140$ to the abstraction of hydrogen cyanide from C. Again, the usual formation of the $[CH_2N]^+$ ion at the expense of nitrogen heterocycles is manifested here by the presence of the peak $m/e = 139$,

corresponding to the splitting off, from (VI), of $As-CH_3$ and CH_2N . (d) Lastly, it is worth mention that the formation of the phenarsazine species (IV) from 10-methyl-5,10-dihydrophenarsazine (VI) by abstraction of the methyl group + one hydrogen, although signalled by the presence of a peak $m/e = 241$, is here considerably less pronounced than in the case of (I).

The patterns of fragmentation upon electron impact of compounds (I) and (VI) are reproduced to a greater or lesser degree in more complex dihydrophenarsazines such as the benzo derivatives of these two compounds.

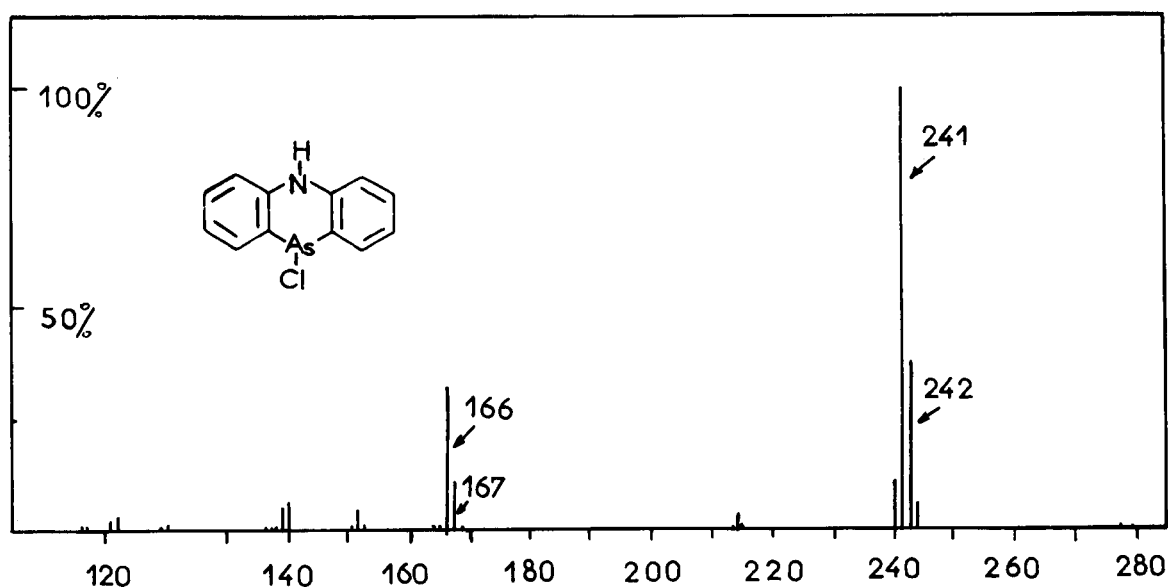


Figure 1

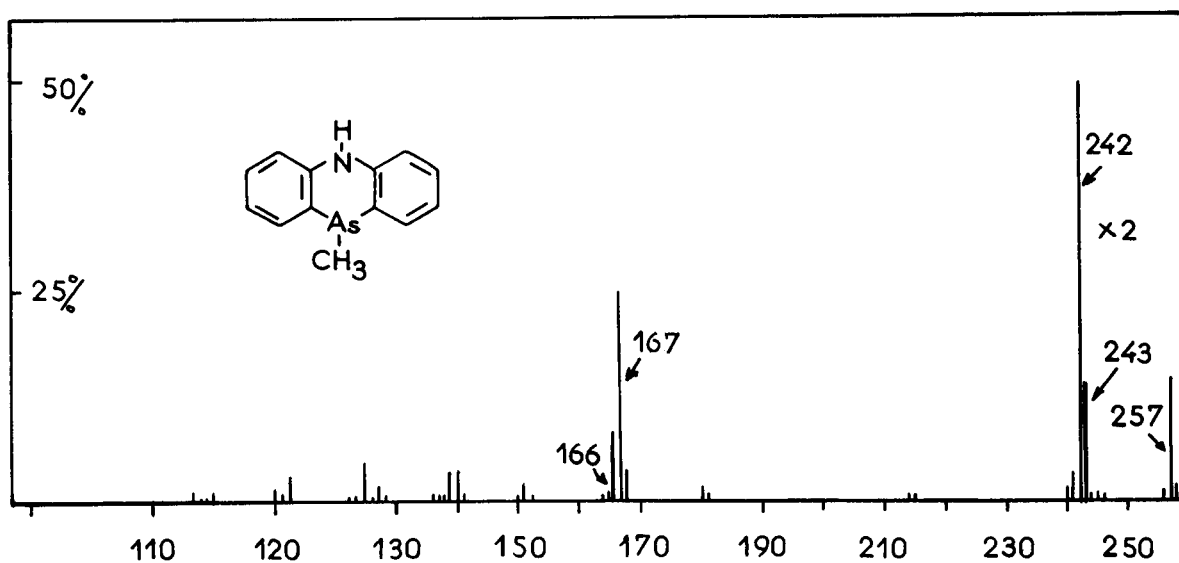
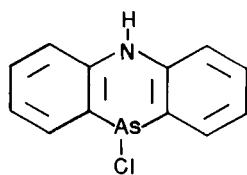
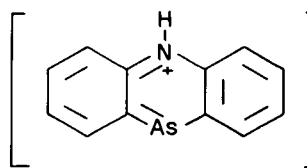


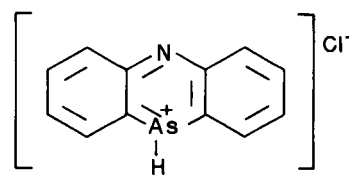
Figure 2



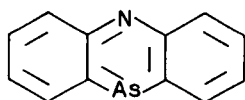
I



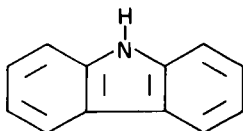
II



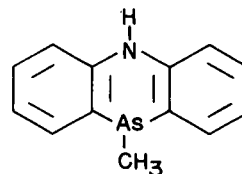
III



IV



V



VI

TABLE I

10-Chloro- 5,10-dihydrophenarsazine		10-Methyl 5,10-dihydrophenarsazine	
m/e	% of base peak	m/e	% of base peak
120.5	4.5	121	3.9
121	1	127.5	5.6
139	6.5	128.5	2.6
140	6.7	139	3.6
151	6	140	3.6
166	31.5	151	2.5
167	15	166	7.1
214	3.5	167	25
241	100	241	3.9
242	40	242	100
		243	14.6
		256	2.5
		257	14.6

EXPERIMENTAL

Preparation of 10-Chloro-5,10-dihydrophenarsazine (I).

This compound was obtained in at least 80% yield by refluxing a solution of arsenic trichloride (1 mole) and diphenylamine (0.1 mole) in *o*-dichlorobenzene, as recommended by Burton and Gibson (10); it was purified by recrystallization from xylene followed by vacuum-sublimation, to give yellow needles, m.p. 195° (lit. (1), 193°).

Preparation of 10-Methyl-5,10-dihydrophenarsazine (VI).

This was prepared by treating an ice-cooled solution of methylmagnesium iodide (2.5 moles) with the finely powdered chloro compound (I) (1 mole) in small portions with stirring; the mixture was then refluxed on a water bath for a few minutes, and after cooling, poured into an ice-cold 20% aqueous solution of ammonium chloride. The organic layer was collected, washed with water and dried over sodium sulfate, the solvent was distilled off, and the residue crystallized from a mixture of ether and hexane. Compound (VI) was thus obtained in 90% yield as colorless needles, m.p. 105° (lit. (3), 105°).

Some of the mass spectrograms were determined in the Department of Mass Spectroscopy of this Institute, and we thank the authorities in charge.

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