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Note on the Electron Impact Fragmentation of Some Polycyclics Bearing Two or Three Nitrogen Heteroatoms

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Apart from the heterocyclic systems related to the alkaloids, which have been extensively studied in the course of structure determinations of these natural compounds (1), the patterns of electron impact fragmentation of nitrogen-containing heterocycles has been investigated mostly in mono- and di-cyclic systems (2), the more condensed types having scarcely been examined. Recently we investigated the benzacridines (3) and the phenarsazines (4), and this research has now been extended to five further types of nitrogen heterocycles, containing two or three nitrogen heteroatoms and from two to five rings.

The six compounds whose patterns of electron impact fragmentation (determined as previously described (3,4) with an Atlas CH4 mass spectrometer) are reported here, were:

1) Two heterocycles with their two nitrogen heteroatoms occupying *ortho* positions on a benzene ring: benzo-2,1,3-selenadiazole, and phenanthro(1′,2′)2,1,3-selenadiazole; the behavior of these was compared with that of phenazine, which carries two similarly disposed nitrogen atoms but which is known to be chemically far more stable.

2) Two analogs of benz[c]acridine, with their two nitrogen heteroatoms located in a *para* position to each other: 9,10-dimethyldibenzo[*b,h*][1,6]naphthyridine, and 2-chloro-6-methyldibenzo[*b,h*][1,6]naphthyridine.

3) Two γ-carbolines: 2-chloro-6-methyl-13*H*-dibenzo-[*a,i*]-γ-carboline, and 11*H*-pyrido[2,3-*i*]-γ-carboline. The selection of these compounds was made on the basis of the information their main fragmentation characteristics could provide in regard to relationships with their intrinsic molecular structure, and of the possibility of comparing one type of heterocycle with the other. Because of our limited objectives, no attempt will be made to identify all the fragments observed.

Benzo-2,1,3-selenadiazole and Phenanthro(1′,2′)2,1,3-selenadiazole.

Both these compounds have two nitrogen atoms located in *ortho* positions on a benzene ring, and the most interesting feature of their fragmentation patterns, *viz.* the complete splitting off of the hetero ring to give, respectively, the benzyne and the 1,2-phenanthryne species (feature that is characteristic of all benzo-2,1,3-selenadiazoles), has already been reported briefly (5). However, comparison of the two substances with each other and with phenazine (whose two nitrogen atoms are similarly disposed) is highly instructive. Thus, whilst phenazine (relevant part of mass spectrum given in Fig. 1, right-hand side) shows a very pronounced peak corresponding to the dehydrogenation species M-1 (typical of heterocycles with a marked aromatic character), benzo-2,1,3-selenadiazole (Fig. 1, left-hand side) gives only insignificant M-1 peaks. Annellation to the latter of a naphthalene nucleus to give phenanthro(1′,2′)2,1,3-selenadiazole, enhances the aromaticity and hence the probability of important M-1 peaks: this is indeed observed

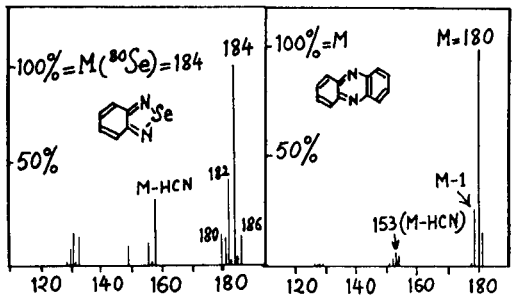

Figure 1

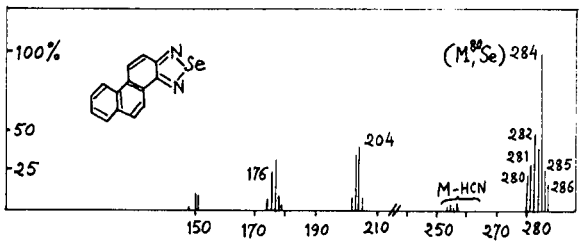

Figure 2

(Fig. 2), in the peak m/e 283, corresponding to the loss of one hydrogen by the molecular peak 284. The difference in stability between the three compounds is further expressed in the relative ease with which hydrogen cyanide is abstracted from the less stable benzo-2,1,3-selenadiazole, in contrast with phenazine and even with phenanthro(1′,2′)-

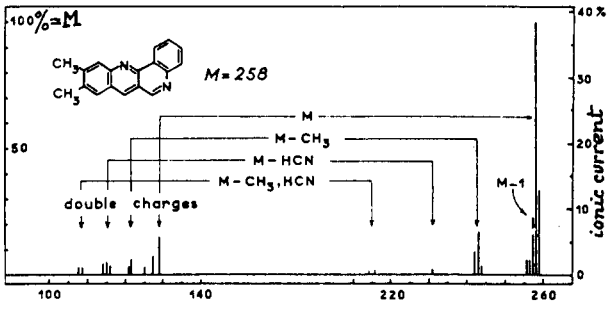

Figure 3

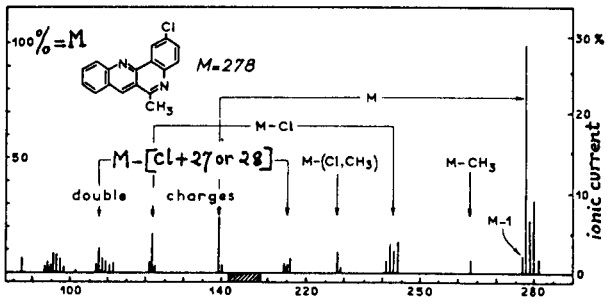

Figure 4

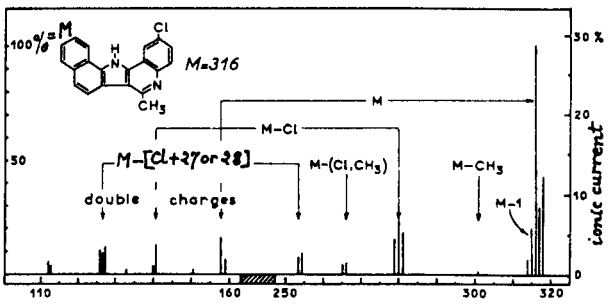

Figure 5

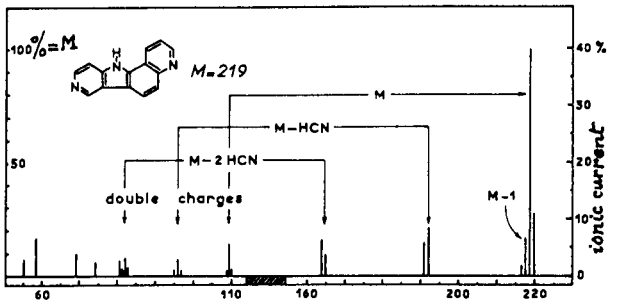

Figure 6

2,1,3-selenadiazole; the mass spectrum of this last compound shows, in fact, that loss of hydrogen cyanide is greatly facilitated once the nitrogen hetero ring has lost, along with its selenium moiety, its aromatic character (Fig. 2; the peak m/e = 177 corresponds to the loss by M (^{80}Se) of ^{80}Se and HCN).

9,10-Dimethyldibenzo[*b*,*h*][1,6]naphthyridine (6).

The fragmentation pattern, shown in Fig. 3, closely resembles those previously reported for dimethylbenz[*a*]-acridines (3): importance of dehydrogenation species and of double-charged ions, outstanding stability of the framework as shown by the very small loss of hydrogen cyanide in contrast with the relative importance of the demethylation process; in this respect it is significant that only one of the two methyl groups was removed.

2-Chloro-6-methyldibenzo[*b*,*h*][1,6]naphthyridine.

The fragmentation pattern of this compound (Fig. 4) strikingly resembles the previous one (importance of double-charged ions, insignificant loss of hydrogen cyanide contrasting with the ready loss of the substituents). Here, the simultaneous presence of a chlorine and a methyl group makes it possible to compare the respective lability of the two substituents: as expected, the chlorine was much more readily removed than the methyl group.

2-Chloro-6-methyl-13*H*-dibenzo[*a*,*i*]-γ-carboline.

As shown in Fig. 5, the mass spectrum of this carboline is strikingly like that of the foregoing compound, despite the dissimilarity of their structures: importance of double charges, insignificant loss of hydrogen cyanide, and, in contrast, ready loss of chlorine.

11*H*-Pyrido[2,3-*i*]-γ-carboline.

Although this compound has two nitrogen heteroatoms similarly disposed as in the three previous compounds, its mass spectrum (Fig. 6) is quite different: hydrogen cyanide is readily abstracted, a feature doubtless to be ascribed to the presence of the extra pyridinic nitrogen heteroatom.

REFERENCES

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(6) The synthesis of this substance and the following ones is reported in O. Roussel, N. P. Buu-Hoi, and P. Jacquignon, *J. Chem. Soc.*, 5458 (1965).

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