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PROXIMITY EFFECTS IN THE MASS SPECTRA OF CROWDED BIS(DIMETHYLAMINO)ARENES, I,
INTRAMOLECULAR CYCLIZATION OF 'PROTON SPONGES' UNDER ELECTRON IMPACT

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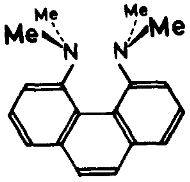
Abstract: EI mass spectra of 4,5-bis(dimethylamino)phenanthrene (1) and the related compounds 2 - 5 show base peaks corresponding to an $M^{+\cdot}$-Me_2NH-H fragmentation for which the following mechanism is proposed: intramolecular hydrogen migration from one of the methyl groups to the nitrogen of the adjacent dimethylamino group, intramolecular cyclization with ejection of dimethylamine, and aromatization involving loss of H· and leading to stable N-methyl thebenidinium and phenanthridinium ions, respectively.

The unusual basicity of 'proton sponges' such as 1,8-bis(dimethylamino)naphthalene [1], 4,5-bis(dimethylamino)fluorene [2] and 4,5-bis(dimethylamino)phenanthrene (1) [3] is a consequence of the strong destabilizing steric compression of the two dimethylamino groups in the free bases and of the formation of a very strong N---H---N hydrogen bond in their protonated salts. These interesting properties led us to examine the mass spectrometrical behaviour of such 'proton sponges' with regard to proximity effects.



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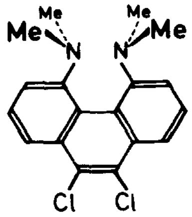

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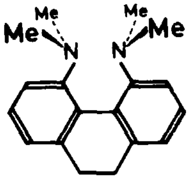

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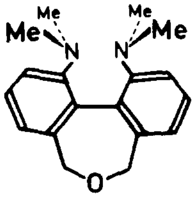

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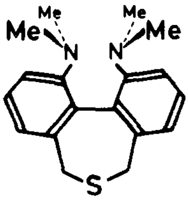
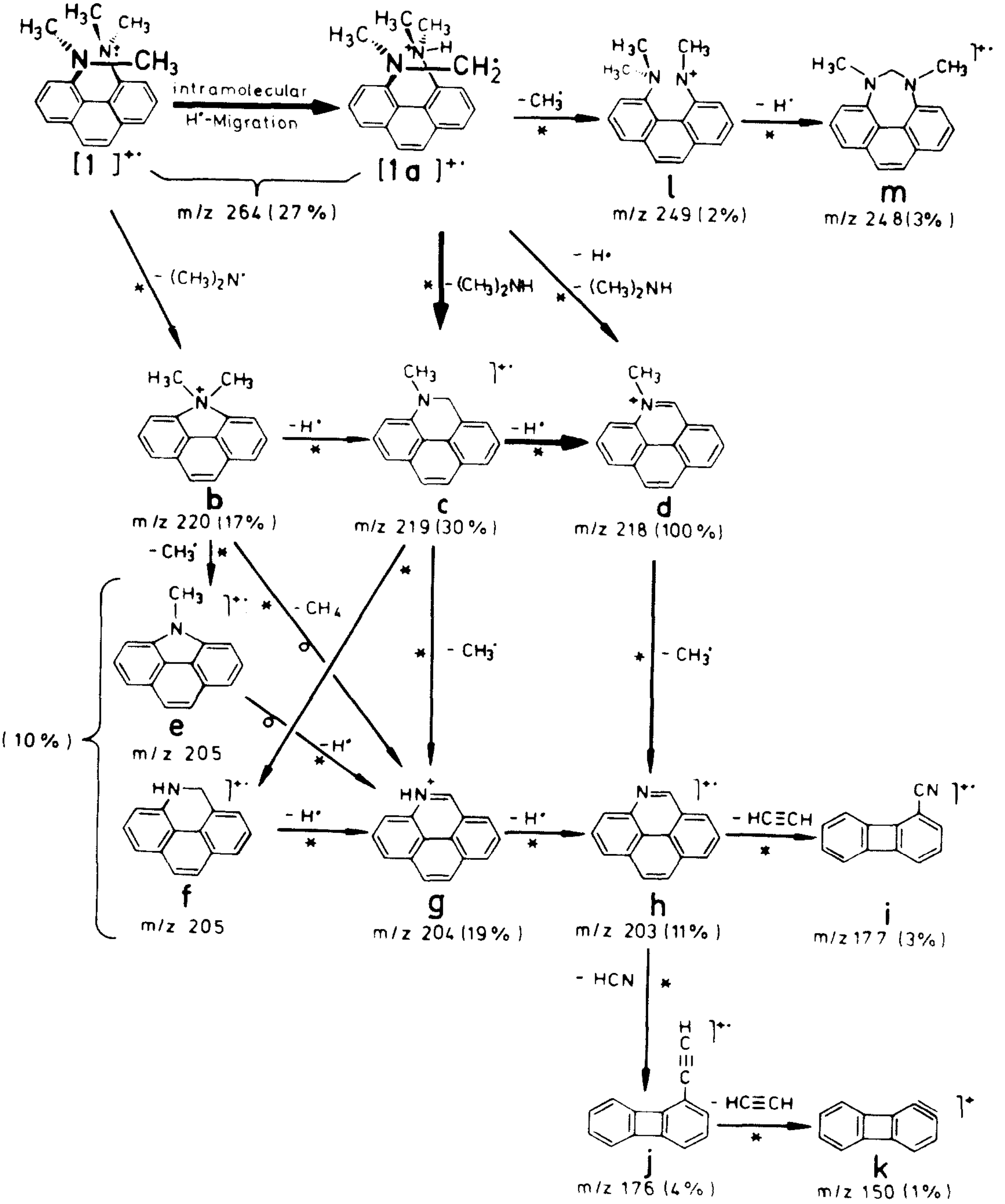


5

Compounds \ Ions	$[M]^{+\cdot}$	$[M-Me_2N]^+$	$[M-Me_2NH]^{+\cdot}$	$[M-Me_2NH-H]^+$
1	27	17	28	100
2	25	7	22	100
3	25	11	25	100
4	70	28	36	100
5	73	30	43	100

Table 1. Relative Intensities of the Principal Ions in the EI Mass Spectra of 1 - 5 (Corrected for ^{13}C and ^{37}Cl Contents).

For 4,5-bis(dimethylamino)phenanthrene (1) and the related compounds 2 - 5 3) the most abundant ionic species in the EI mass spectra are listed in Table 1. For 1 the fragmentation routes as determined by means of linked scans and exact mass measurements are given in detail in Scheme 1.



Scheme 1: General Fragmentation Pattern of 1.

The fragmentation pattern of 1 can be rationalized by assuming two competing fragmentation routes. The predominant route leads to an intense even-electron ion d at m/z 218 which gives rise to the base peak. To explain this consecutive loss of dimethylamine and H· the following mechanism is suggested:

a) intramolecular H· migration from an N-methyl group to an adjacent dimethylamino nitrogen leading to the isomer 1a of the molecular ion 1,
b) subsequent (or synchronous) cyclization of 1a to c involving an intramolecular substitution by $-CH_2\cdot$ with extrusion of dimethylamine, and
c) *aromatization by loss of H· leading to an N-methylthebenidinium ion d which is a stable* even-electron and aromatic ion. Demethylation, then, leads to thebenidine h.

The formation of N-methylthebenidinium ion d and of thebenidine h from 1 under electron impact is strongly supported by the comparison of the EI mass spectra of 1 with N-methylthebenidinium iodide and thebenidine (Figure 1).

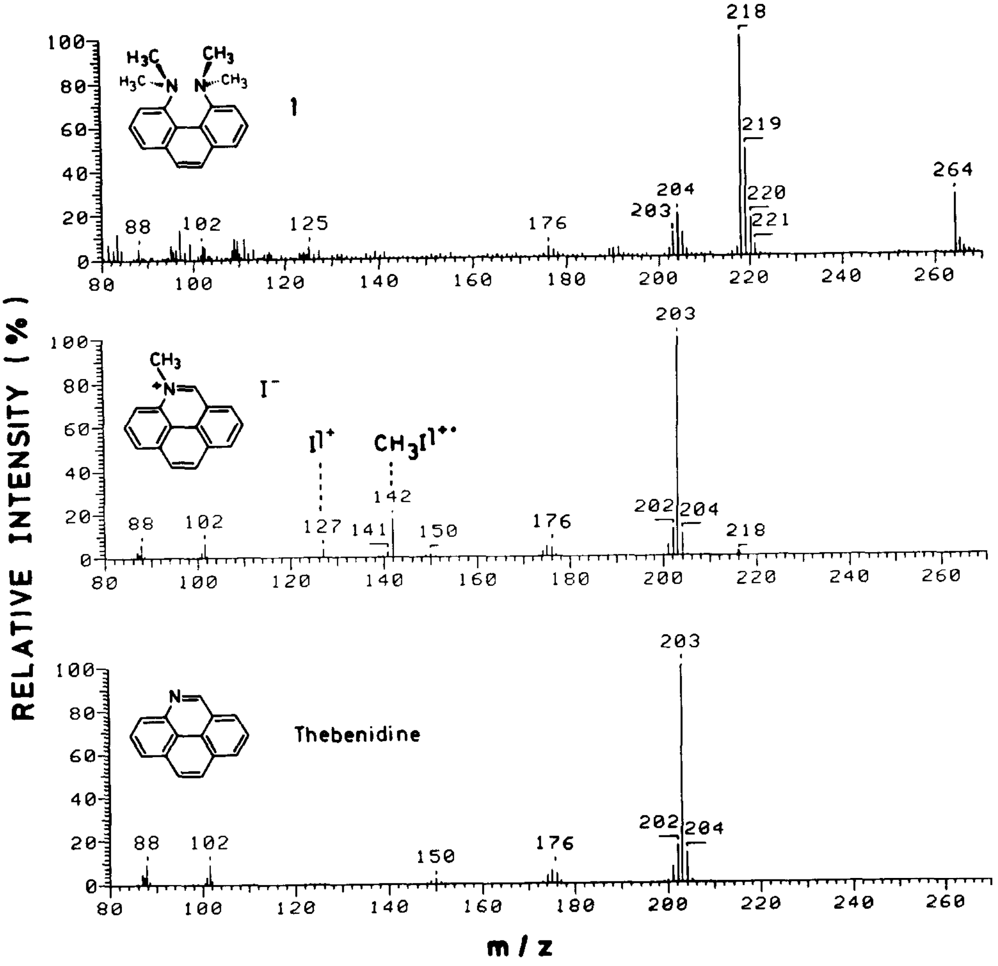


Figure 1. EI Mass Spectra of 1, N-Methylthebenidinium Iodide [4] and Thebenidine [5].

The less favoured fragmentation route of **1** probably leads by loss of $Me_2N\cdot$ and cyclization to the N,N-dimethylcarbazolium ion **b**. This latter ion **b** shows further demethylation to the thebenidinium ion **g** and thebenidine **h** itself. The corresponding rearrangement of the proper N-methylcarbazole to the phenanthridine system has recently been shown 6). Formation of perimidine radical-ions such as **m** is only a minor fragmentation process.

The fragmentations of **2** - **5** under electron impact (obtained by means of linked scans and exact mass measurements, see Table 1) follow closely the fragmentation pattern discussed for **1**. Similar results were also obtained for the 'proton sponges' 1,8-bis(dimethylamino)naphthalene and 4,5-bis(dimethylamino)fluorene 7).

CI mass spectra (isobutane) of **1** - **5** and of thebenidine showed the quasi-molecular ion $[MH]^+$ as base peak and $M^{+\cdot}$ with relative intensities between 10 and 67%; only minor fragmentations were observed.

All 70eV EI and CI mass spectra were recorded using a Finnigan MAT 212 double focussing instrument (source temperature 150 - 250°C).

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3) T. Saupe, C. Krieger, H. A. Staab, Angew. Chem. **98** (1986) 460; Angew. Chem. Int. Ed. Engl. **25** (1986) 451.

4) The mass spectrum of the intact N-methylthebenidinium cation with m/z 218 as base peak was obtained by using the thermospray technique. We thank Mr. M. A. McDowall, VG Instruments, Tudor Road, Altrincham, Cheshire WA 145RZ, for recording this spectrum on a VG20-250 LC-MS-DS mass spectrometer.

5) The authors thank Dr. M. Haenel, Max-Planck-Institut für Kohlenforschung Mülheim, and Professor Dr. M. Zander, Rütgers-Werke AG, Castrop-Rauxel, for samples of thebenidine.

6) M. Rentzea, to be published; a thermal rearrangement of N-methylcarbazole to phenanthridine has been reported: A. Pictet, Ber. Dtsch. Chem. Ges. **38** (1905) 1946; J. M. Patterson, Chyng-Yann Shiue, W. T. Smith, Jr., J. Org. Chem. **38** (1973) 2447.

7) M. Rentzea, T. Saupe, H. A. Staab, to be published.

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