

## Cyclization of Diaza[6]helicenes to Monoazacoronenes under Electron Impact †

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**Abstract:** Electron impact (EI)-induced cyclizations of 1,16-diaza[6]helicene (1), of 1,14-diaza[6]helicene (2) and of 3,14-diaza[6]helicene (3) to monoazacoronenes (abundant loss of HCN and H) were investigated through their source spectra supported by accurate mass measurements, their unimolecular metastable ion (MI) spectra, and their high-energy (8KeV) collision-induced dissociation (CID) tandem mass spectra obtained with a four-sector mass spectrometer.

High-energy collision-induced dissociation (CID) mass spectra<sup>1</sup> using the advantages<sup>2-4</sup> of tandem mass spectrometry (MS/MS) are very useful for obtaining knowledge of ion structure and fragmentation mechanisms. We have previously<sup>5-9</sup> used this technique as well as source spectra and metastable ion (MI) spectra, to establish the mechanisms of intramolecular cyclizations of sterically crowded aromatic diamines.

The present report discusses the cyclization of three crowded new diaza[6]helicenes<sup>10</sup> – 1,16-diaza[6]helicene (1), 1,14-diaza[6]helicene (2), 3,14-diaza[6]helicene (3) – to monoazacoronenes comparing their mass spectra with that of isomeric naphtho[2,1-*h*:7,6-*h'*]diquinoline 4 (Fig. 1).

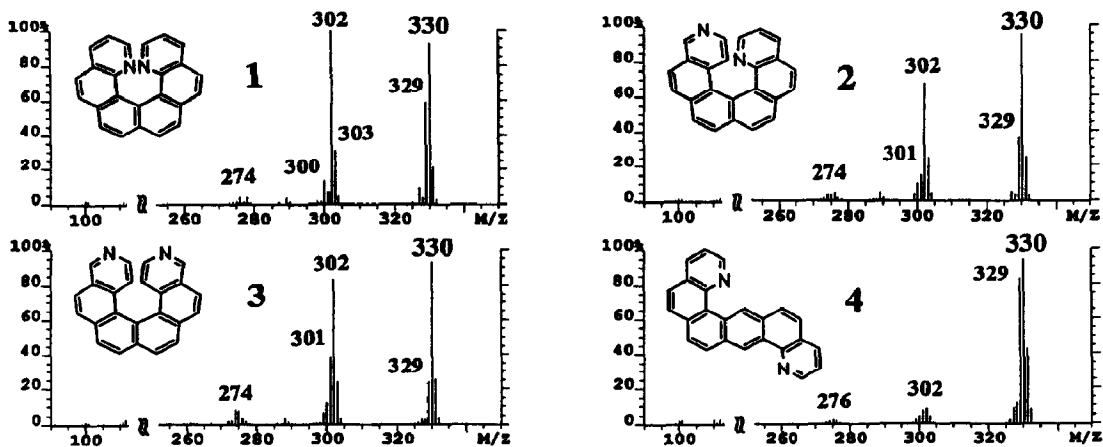
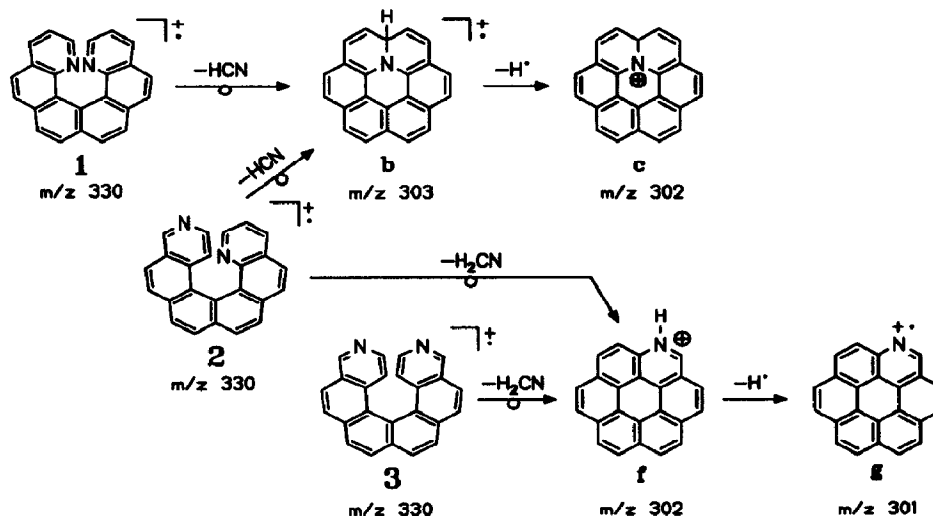


Figure 1. 70 eV EI spectra of compounds 1-4.

As expected, compounds 1-4 show abundant molecular ions at  $m/z$  330 and  $[M-H]$  ions of various intensities at  $m/z$  329 (Fig. 1). For all the molecular ions (1-4) and their fragments we also found the corresponding doubly charged ions (not shown). Compound 4 (Fig. 1) exhibits in its spectrum only the normal features to be expected in the mass spectra of polynuclear heteroaromatic hydrocarbons, losing only hydrogen.

Using 70 eV EI source spectra, MI spectra (not shown) and CID MS/MS spectra, we established the fragmentation pathways of **1**, **2** and **3** (Schemes 1-3).

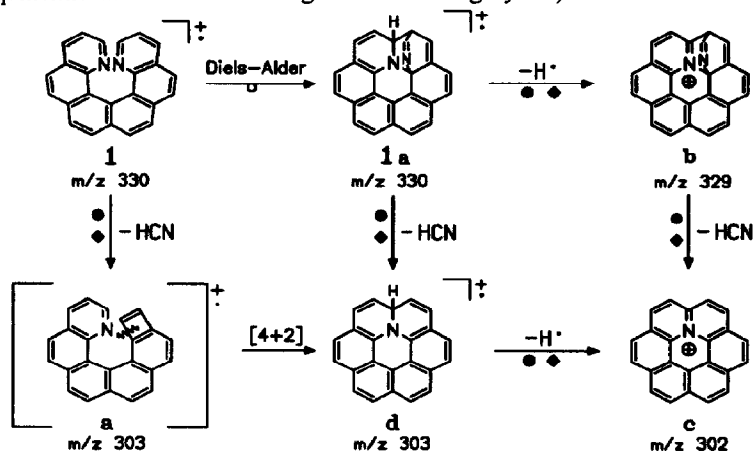
All three diaza[6]helicenes cyclize *purely* by abundant loss of HCN and H to stable strainfree heteroaromatic ions of monoazacoronene structure (**b** and **c** or **f** and **g**, Scheme 1). Neither C<sub>2</sub>H<sub>4</sub> (even from **3**) nor C<sub>2</sub>H<sub>2</sub> was released; no doublets were found in a high resolution (HR) mode of 50,000. These cyclizations to the azacoronene system very probably involve [4+2] cycloadditions.



**Scheme 1.** Cyclization of 1-3 to monoazacoronene ions under electron impact.

The question is whether these cycloadditions take place before or after the HCN elimination?

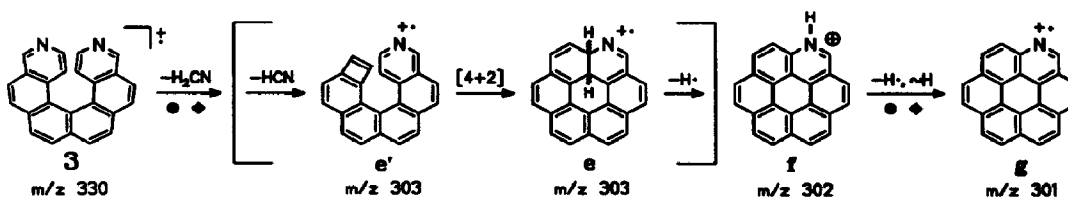
Previous EI studies on structurally similar [6]helicenes and monoaza[6]helicenes<sup>11</sup> have shown that the ethylene- and/or HCN- loss channel for the molecular radical cation is typical of the formation of coronene or of azoniacoronenones via intramolecular Diels-Alder cyclization and subsequent elimination<sup>12</sup>. On the other hand, the same energy channel and the same favourable entropy factors for the intramolecular reaction, with relief of steric strain and formation of a continuously conjugated  $\pi$ -electron system in coronenes, would also contribute to facilitate the loss of HCN *prior* to [4+2] cycloaddition (at least as easily and completely as, for example, from quinoline and isoquinoline and with the same high structural integrity<sup>13,14</sup>).



**Scheme 2.** Fragmentation pathways of compound **1**; pathways investigated and confirmed by unimolecular MI spectra (●) and CID MS/MS (◆).

Only for **1** the Diels–Alder cycloaddition probably takes place *prior* to HCN ejection since only here we found two distinct intermediate fragment ions (**d**,  $m/z$  303 and **b**,  $m/z$  329) on two distinct fragmentation routes leading to the same azoniacoronene ion **c** at  $m/z$  302 namely loss of H from the adduct **1a**  $\rightarrow$  **b** ( $m/z$  329, 70% rel. int.) followed by HCN loss to **c** or fragmentation of HCN from **1a**  $\rightarrow$  **d** ( $m/z$  303) followed by loss of H to **c**. Obviously, this fragmentation mechanism is dependent on the specific positions of the two nitrogen atoms in **1**. It would therefore be difficult to evaluate the (if any, probably modest) contribution of a fragmentation pathway **1**  $\rightarrow$  **c** via **a** (a benzocyclobutadiene intermediate<sup>15</sup> at  $m/z$  303 in which the [4+2] cycloaddition would take place *after*<sup>16</sup> HCN ejection) to the unimolecular decomposition of **1**.

On the other hand, for **3** neither the EI nor the MI spectra show any distinct H and HCN two-step fragmentations (Fig. 1, Scheme 3). From the molecular ion **3** only a simultaneous loss of H and HCN to abundant ion **f** ( $[M-H_2CN]^+$ ,  $m/z$  302) was observed. The HCN fragmentation occurs very probably *prior* to the [4+2] cycloaddition, via very short-lived transient species such as **e'**, which cyclize to **e** and lose H before they leave the source. The final stabilization of the positive charge is then achieved by subsequent loss of H to the azacoronene radical cation **g** ( $[M-H_2CN-H]^+$ ,  $m/z$  301).



Scheme 3. Fragmentation pathway of **3** confirmed by MI spectra (●) and CID MS/MS (◆).

High-energy CID MS/MS spectra of helicenes **1-3** and of their fragments are very characteristic and as distinguishing as fingerprints. The bimolecular reactions, which occur in the third field-free region of the tandem mass spectrometer, give rise to peaks similar to those of the source spectra<sup>2-4</sup> and to those due to MI fragmentations<sup>1</sup>; but they provide more information due to far more peaks (product ions generated by 8keV collision with helium atoms). For structural attributions we used data from these product-ion MS/MS spectra because of their proven superior reliability in characterising organic ions<sup>4</sup>.

Our results show that small structural differences among molecular ions **1-3** produce significant differences among their CID MS/MS spectra ( Fig. 2).

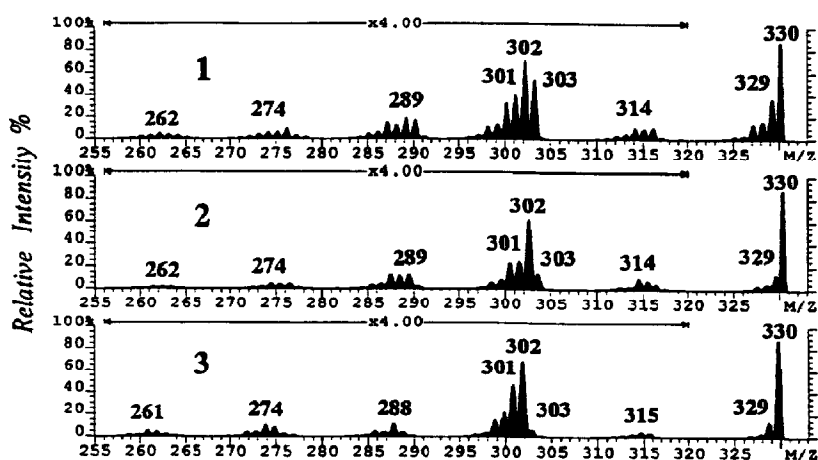


Figure 2 . Comparison of the CID MS/MS spectra of the molecular ions of isomeric compounds **1-3**.

The non-superimposable CID MS/MS spectra of ions **c** (from 1) and **f** (from 3) both at  $m/z$  302 (Fig. 3) provide clear evidence of their structural difference. The superimposability of the CID spectra of the ions at  $m/z$  301 from 2 and from 3 (Fig. 4) reflect their identical structure (ion **g**). From 2 our CID data (Fig. 4, Scheme 1) show the formation of ion **g** at  $m/z$  301 and of a mixture of ions **c** and **f** at  $m/z$  302 (not shown).

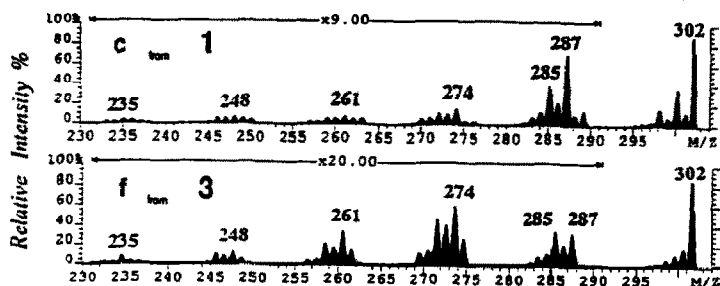


Figure 3. Comparison of the CID MS/MS spectra of monoazacoronene ions **c** and **f** ( $m/z$  302) from 1 and 3.

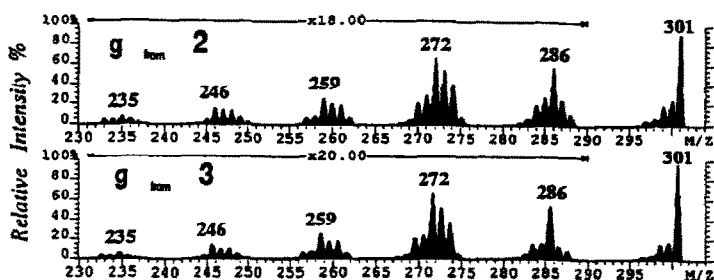


Figure 4. Comparison of the CID MS/MS spectra of monoazacoronene ion **g** ( $m/z$  301) from 2 and 3.

**Experimental.** The 8 keV CID spectra were obtained with a Fisons ZAB 2E/70 SE four-sector (BEEB) mass spectrometer equipped with PDP 11/73 and VAX data systems by admitting helium to a collision cell in the field-free region ahead of the electrical sector of the second mass spectrometer. MI spectra (unimolecular linked scans at constant  $B/E$ ), low-resolution spectra and HR EI spectra were measured with both a Fisons ZAB 2E and a JEOL SX-102A mass spectrometer using direct insertion probes.

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