The Chemistry of Dibenzo-[*d,f*][1,3]diazepines. 4.*Sterically Determined Water Loss from Dibenzo[*d,f*][1,3]diazepines upon Electron Impact

JAN BECHER,[a] ERIK G. FRANDSEN [a]
and JØRGEN MØLLER [b]**

[a] Department of Chemistry, Odense University, DK-5000 Odense and [b] Physical Laboratory II, University of Copenhagen, The H. C. Ørsted Institute, DK-2100 Copenhagen, Denmark

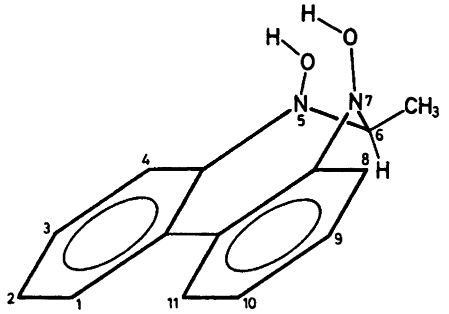

Fig. 1. I

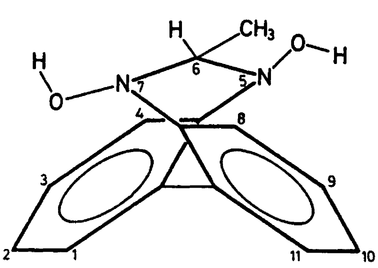

Fig. 2. II

The electron-impact-induced loss of H_2O from the molecular ion of 6-methyl-5,7-dihydroxy-6,7-dihydro-5-*H*-dibenzo[*d,f*][1,3]diazepine (*A*) was shown [2] — by deuterium labeling — preferentially to involve the loss of the hydrogen atoms from the two OH-groups. Inspection of Dreiding models of *A* further indicated, that in one of the conformations (I, Fig. 1) the two OH-groups could approach each other closely. In this conformation a hydrogen rearrangement through a six-membered ring transition

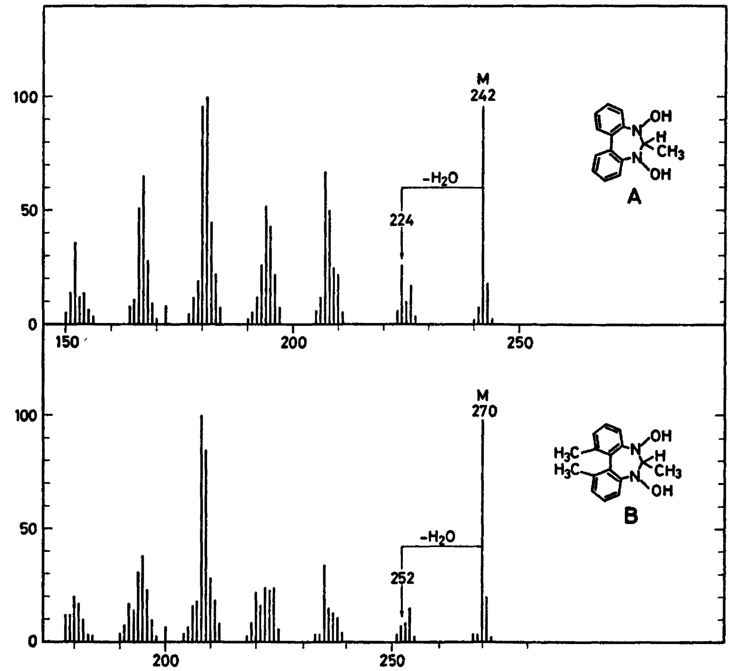

Fig. 3. The mass spectra of *A* and *B*.

---

* See Ref. 1. ** Present address as a.

state may lead to the ejection of a molecule of water.

In stereochemical studies it was found that substituted biphenyls bridged by three atoms may be resolved.[3] Furthermore, the optical stability was reported to be increased considerably when the biphenyl system was substituted in the 1- and 11-positions. Correspondingly it could be expected that conformation I is impossible when substituents – large enough to prevent the planar arrangement of the biphenyl – are introduced in the 1- and 11-positions. In those cases the two OH-groups are separated considerably (*e.g.* confirmation II, Fig. 2).

If this effect is preserved in the molecular ion formed upon electron impact a less abundant $[M-H_2O]^{+\cdot}$ ion should be expected in the mass spectrum of a 1,11-substituted compound than found in that of *A*. However, the structure of a molecular ion may differ to a great extent from that of the "ground state" due to the large amount of excess energy ($\sim$5eV [4]).

In order to investigate the influence of these factors the mass spectrum of 1,6,11-trimethyl-5,7-dihydroxy-6,7-dihydro-5*H*-dibenzo[*d,f*][1,3]diazepine[1] (*B*) was recorded. A comparison with the mass spectrum of *A*[2] (Fig. 3) shows a significant decrease in the abundance of the $[M-H_2O]^{\cdot+}$ ion (from 25 % to 7 %) and also of the daughter ions of this fragment.

This leads to the conclusion that the considerations regarding the conformation of the "ground state" of these compounds appear to be valid also for their molecular ions. Thus a relation between the stereochemistry of these compounds and ease of water elimination upon electron impact is highly probable.

1. Becher, J. and Iversen, P. E. *Acta Chem. Scand. B 28* (1974) 539. Part 3 in this series.
2. Becher, J. and Møller, J. *Acta Chem. Scand. 27* (1973) 1395. Part 2.
3. Eliel, E. L. *Stereochemistry of Carbon Compounds*, McGraw-Hill, New York 1962, p. 164.
4. Cooks, R. G. *Org. Mass Spectrom. 2* (1969) 481.

Received January 18, 1975.