

[10b,10c]DIAZAPYRACEHEPTYLENE¹⁾

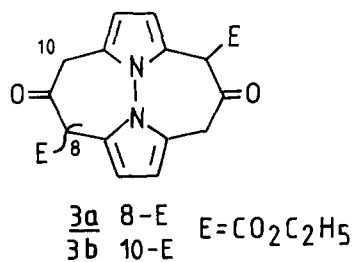
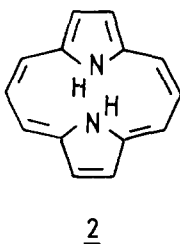
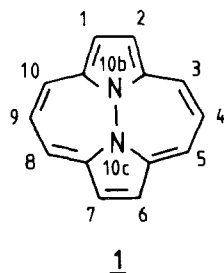
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Summary: The labile [10b,10c]diazapyraceheptylene **1** was obtained by thermo-flash dehydrogenation of a mixture of olefins **5a/b**. The ¹H NMR spectrum indicates a strong influence of the 14π-electron periphery. A by-product of the synthesis of **1**, i.e., pyrazino[2,1,6-cd:5,4,3-c'd']dipyrrolizine **6**, points to a rearrangement of the diazapyraceheptylene system, which may be frontier orbital controlled.

Previous investigations of [10b,10c]diazapyraceheptylene derivatives did not reveal informations concerning the properties of the parent compound **1**²⁾. From a frontier orbital model described in the preceding paper³⁾ a destabilization of **1** as compared with the bis-imino[14]annulene **2**⁴⁾ may be deduced. This conclusion, however, may be uncertain because differences of MO-parameters of nitrogen atoms resulting from a splitting of the (N-N)-bond are difficult to evaluate²⁾.

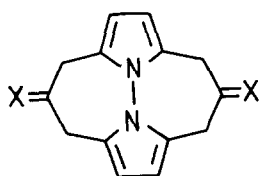


We synthesized **1** which, according to the frontier orbital considerations mentioned above proved to be more labile in solution than **2**. The ¹H NMR properties, however, point to a strong influence of the 14π-electron periphery.

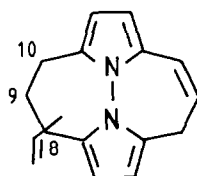
Starting from a mixture of esters **3a/b**³⁾ the olefins **5a/b** were obtained via the intermediates **4a**, **4b** and **4c** or **4d** along a route described previously⁴⁾. The yields were increased significantly by variation of the synthetic methods⁵⁾.

From a desosylation of **4d** 1% of the bridged [14]annulene **6** was obtained as a by-product⁵⁾, the structure of which follows from a comparison of spectral data⁶⁾ with those of the recently described compound⁷⁾.

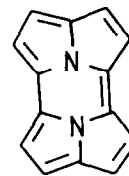
Thermoflash dehydrogenation of the mixture **5a/b** at 250°C⁵⁾ gave 13% of the parent compound **1** which is fairly stable in the crystalline state.



4a X=O
b X=H/OH
c X=H/Cl
d X=H/OTs



5a Δ-8,9
b Δ-9,10



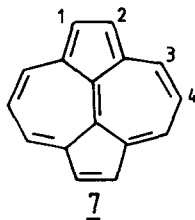
6

The chemical shifts of the protons of **1** are strongly influenced by the 14π-electron periphery. This may be deduced from a comparison with topologically equivalent bridged [14]annulenes given in the Table. It seems noteworthy that differences of shifts are negligible even compared with **7** and **8** which are not isoelectronic to **1**. No decisive influence resulting from a splitting of the (N-N)-bond can be deduced from the ¹H NMR spectra of **1** and **2**.

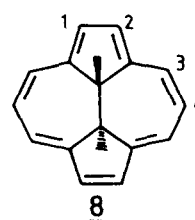
A slight deviation from planarity follows from differences of the vicinal coupling constants of the seven-membered ring protons of **1** (³J = 9.8 Hz, 9.3 Hz) and - more marked - **2** (³J = 13.0 Hz, 9.5 Hz).

Table:
¹H NMR spectra of bridged [14]annulene derivatives⁸⁾

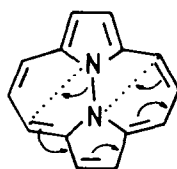
	H-1	H-3	H-4
1	8.60	8.31	8.10
2	7.74	8.23	7.98
7	8.93	8.72	7.38
8	8.74	8.77	8.04



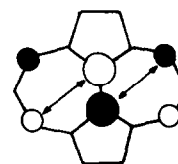
7



8



9



10

The mechanism of formation of **6** is under current investigation. An electrocyclic rearrangement of **1** (possibly frontier orbital controlled as indicated in **9** and **10**) could yield a dihydro derivative of **6** which is aromatized in a subsequent dehydrogenation step. Alternatively, a rearrangement starting from the olefins **5** seems conceivable which may be similar to the route of formation of the bisimino[14]annulene **2**⁴⁾.

ACKNOWLEDGEMENT

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REFERENCES AND NOTES

- 1) K. Rutkowski, Dissertation, Univ. Münster, 1985.
- 2) W. Flitsch, *Compreh. Heterocycl. Chem.* **4**, 492 (1984).
- 3) W. Flitsch and K. Rutkowski, *Tetrahedron Lett.*, preceding communication.
- 4) W. Flitsch and H. Peeters, *Chem. Ber.* **110**, 273 (1977).
- 5) Experimental conditions:
 - 4a:** **3a/b** was refluxed with $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ and a trace of HMPT in xylene for 2h. After evaporation in vacuo, the residue was washed with water and recrystallized from acetonitrile (93%).
 - 4b:** From **4a** with NaBH_4 in methanol at r.t. (10 min.). Neutralizing with 2N HCl and partial evaporation of the solvent gave **4b** which was washed with water and recrystallized from ethanol (64%).
 - 4c:** **4b** was refluxed with $\text{PPh}_3/\text{CCl}_4$ in $\text{C}_2\text{H}_4\text{Cl}_2$ (30 min). Evaporation of the solvent in vacuo, chromatography (silica gel, toluene/ethyl acetate = 30:1) and recrystallization from ethanol gave 99% **4c**.
 - 4d:** Stirring **4b** with $\text{TsCl}/\text{pyridine}$ for 15 h at r.t. Conventional work up, chromatography (silica gel, CHCl_3/THF = 9:1) and recrystallization gave 95%.
 - 5a/b** and **6:** Refluxing **4c** or **4d** with freshly sublimed potassium tert.-butoxide toluene for 15 min (**4c**) or 1h (**4d**). Filtration, washing with water, evaporation of the toluene and chromatography (silica gel, toluene/petrol ether = 1:5) gave **5a/b** (60% from **4c** and 40% from **4d**). From **4d** additional 1% of **6** was obtained.
 - 1:** Dehydrogenation under flash vacuum conditions ($\text{PtO}_2/\text{quartz-wool}$, 250°C , 0.01 Torr, 4 h). The product was collected at -190°C : 13%, m.p. 245°C .

6) 6: ^1H NMR spectrum (CDCl_3)⁷⁾: 7.86 (4H: $J = 4.5$ Hz), 7.93 (4H: $J = 4.5$ Hz). Mass spectrum: 205 (15%), 204 (100% M^+), 203 (11%), 176 (3%), 153 (3%), 102 (18%), 89 (3%), 75 (4%), 63 (2%), 50 (1%).

7) D. Leaver and D. Skinner, *J. Chem. Soc., Chem. Commun.* **1984**, 821. We are grateful to Dr. D. Leaver for a sample of 6

8) ^1H NMR spectra, solvents: 1: d_6 -acetone; 2: CS_2 ⁴⁾; 7: CDCl_3 ; C. Jutz and E. Schweiger, *Synthesis* **1974**, 193; 8: THF;

W. Huber, W. Irmen, J. Lex and K. Müllen, *Tetrahedron Lett.* **23**, 3889 (1982); W. Huber, J. Lex, T. Meul and K. Müllen, *Angew. Chem.* **93**, 401 (1981), *Angew. Chem., Int. Ed. Engl.* **93**, 391 (1981).

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