[7](2,6)Pyridinophane and [7](2,6)Pyrylophanium Perchlorate

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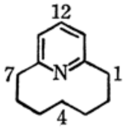
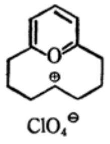
(Received February 5, 1969)

Although preparation of [10](2,6)pyridinophane and 15-methyl[10](2,6)pyrylophanium perchlorate has been reported,[1] homologs with shorter methylene bridge still remain to be synthesized. In continuing the work on heterocyclophanes,[2] we were interested in the title compounds.



(I)



(III)

[7](2,6)Pyridinophane (I) (bp 70—73°C/3 mm Hg. Anal. Found: C, 82.5; H, 9.9; N, 7.7%) was obtained in a 44% yield by treatment of cyclododecane-1,5-dione (II) with 2.5 mol equivalents of hydroxylamine hydrochloride in an autoclave at 150—175°C. The dione II (mp 66.5—67.5°C, lit.[3] 64—65°C) was conveniently prepared by the Jones oxidation of cyclododecane-1,5-diol and/or by oxidation of *B*-acetoxy-13-borabicyclo[7.3.1]-tridecane[4] with aqueous sodium dichromate in ether.

Compound I exhibited aromatic absorptions (neat) at 3060, 1588 and 1575 cm^{-1} and a UV maximum (EtOH) at 272 nm (log ε 3.50). The bathochromic shift in the UV absorption as compared with [10](2,6)pyridinophane[5] may be ascribed to the nonplanar pyridine ring bridged by the heptamethylene group. The aromatic NMR signal (3 protons) (Fig. 1) showed a typical AB$_2$ pattern (ν_A δ 7.40, ν_B δ 6.87, J_{AB} 7 Hz) which resembled the splitting pattern of 2,6-lutidine very closely. The absorptions due to the heptamethylene protons were composed of three groups of multiplets. Protons of one methylene (a quintet at δ 0.16) were unexpectedly shielded in comparison with usual paraffinic methylenes. Tentatively, we assign the absorption to C$_4$ protons[6] locating close to the pyridine ring on inspection of the Dreiding model. Since the multiplet (centered at δ 2.84) due to C$_1$ and C$_7$ protons can be regarded as a triplet approximately, the heptamethylene chain should be flexible at room temperature.[2] Heating of I with a mixture of 30% hydrogen peroxide and acetic acid failed to give the *N*-oxide, whereas similar treatment of [10](2,6)-pyridinophane afforded the corresponding *N*-oxide.[1a] This is another point of difference introduced by the shorter polymethylene chain.

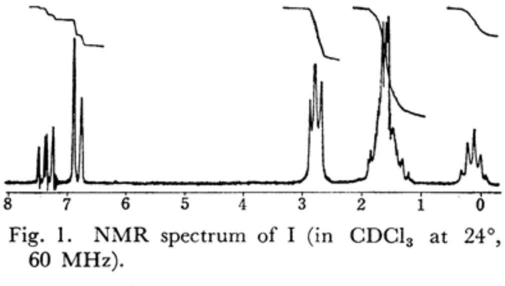


Fig. 1. NMR spectrum of I (in CDCl$_3$ at 24°, 60 MHz).

Reaction of II with trityl perchlorate in glacial acetic acid at 110—120°C afforded [7](2,6)-pyrylophanium perchlorate (III) (mp 150°C (dec.). Found: C, 52.6; H, 6.0; Cl, 12.6%) in a 65% yield. The IR spectrum (Nujol) exhibited aromatic bands at 3060, 1627 and 1498 cm^{-1} and a broad band due to the perchlorate anion at 1088 cm^{-1}. The NMR spectrum of III (in trifluoroacetic acid) consisted of an AB$_2$-type signal (3 aromatic protons, ν_A δ 8.85, ν_B δ 7.98, J_{AB} 8 Hz), a triplet at δ 3.42 (4 methylene protons on C$_1$ and C$_7$), a multiplet at δ 2.4—1.5 (8 methylene protons on C$_2$, C$_3$, C$_5$ and C$_6$) and a quintet at δ 0.82 (2 methylene protons on C$_4$). Treatment of the pyrylium salt III with ammonium acetate in glacial acetic acid yielded the pyridinophane I (66%) which was identical with the sample prepared directly from II.[7] Details of the experiments and further discussions will be presented in a paper to be published later.

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[1] a) K. Biemann, G. Büchi and B. H. Walder, *J. Am. Chem. Soc.*, **79**, 5558 (1957); b) A. T. Balaban, M. Gavat and C. D. Nenitzescu, *Tetrahedron*, **18**, 1079 (1962). See also A. T. Balaban, *Tetrahedron Letters*, 4643 (1968).

[2] H. Nozaki, T. Koyama, T. Mori and R. Noyori, *Tetrahedron Letters*, **1968**, 2181.

[3] G. S. Fonken, M. E. Merr, H. C. Murray and L. M. Reineke, *J. Am. Chem. Soc.*, **89**, 672 (1967).

[4] G. W. Rotermund and R. Köster, *Liebigs Ann. Chem.*, **686**, 153 (1965).

[5] [10](2,6)Pyridinophane exhibits UV maxima (EtOH) at 213 (log ε 3.82) 267 nm (3.62). See Ref. 1a.

[6] For this nomenclature, see B. H. Smith, "Bridged Aromatic Compounds, Academic Press, New York, N. Y. (1964), pp. 1—23.

[7] [8](2,5)Pyridinophan-1-one has recently been reported independently: H. Gerlach and E. Huber, *Helv. Chim. Acta*, **51**, 2027 (1968).