HETEROCYCLES, Vol. 29, No. 4, 1989

STRAINED HETEROCYCLIC SYSTEMS. 16.[1] 1-AZATRIPTYCENE

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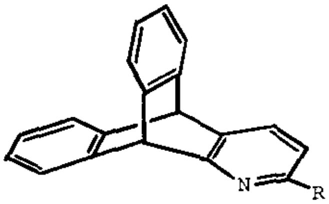
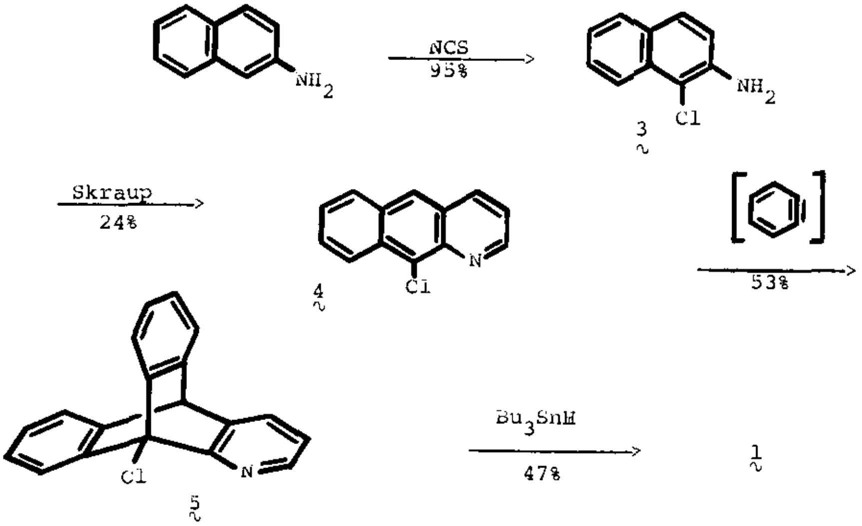
Abstract - The first synthesis of 1-azatriptycene (1) was accomplished in four steps from 2-naphthylamine. Its pK_a was determined by potentiometric titration and compared to that of diphenyl-2-pyridylmethane. The seven-fold decrease in the basicity of 1 was attributed to ring strain effects.

Relatively few heterotriptycenes are known, and only recently have azatriptycenes been described.[2] It is well established that triptycene itself is a strained molecule[3] and that ring strain perturbs the physical and chemical properties of nitrogen heterocycles.[4] 1-Azatriptycene (1) was therefore of interest in order to extend such correlations to this bicyclic framework. Herein we report the first synthesis of 1 and assess its basicity. The route to such a molecule can proceed via a suitably functionalized 9,10-dihydro-9,10-ethanoanthracene, followed by construction of the pyridine ring. Alternatively, an azaanthracene system can be prepared, followed by cycloaddition of benzyne. Both strategies were employed by Quast and Schön in their recent studies.[2] The former pathway was followed in the synthesis of 2, while the latter route was utilized for derivatives of 1,8-diazatriptycene. We chose the benzyne strategy for 1 and therefore a benzo[g]quinoline was the key intermediate. 2-Naphthylamine was converted to 1-chloro-2-naphthylamine (3) by *N*-chlorosuccinimide (NCS). Skraup cyclization by the sulfomix method[5] gave 10-chlorobenzo[g]quinoline (4). Addition of benzyne afforded



	R
1	H
2	Ph

9-chloro-1-azatriptycene (5), which was reductively dechlorinated by tributyltin hydride to yield 1.[6] The basicity of 1 was determined by potentiometric titration[7] and compared (Table) to the pK_a values reported for 2-benzylpyridine (6) and diphenyl-2-pyridylmethane (7).[8] The latter compound incorporates the benzhydryl moiety and serves as a model for the inductive effects, but not the strain effects, inherent in 1. The seven-fold difference in basicity between 7 and 1 reflects strain-induced effects observed with related systems and conforms to our earlier interpretations. Thus, to accommodate ring strain in the bicyclic system rehybridization occurs at C-9a, whereby the shaded orbitals increase in *p* character and the unshaded orbital concomitantly gains *s* character. These effects are transmitted along the sigma-bond framework, inducing analogous orbital rehybridization at nitrogen. As a result, the pair of *n* electrons occupies an orbital of higher *s* character and the basicity, therefore, is decreased.



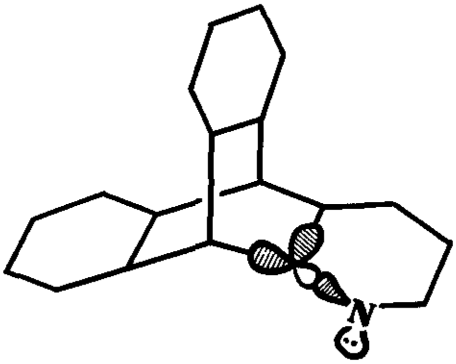


Table. Half neutralization potentials (HNP) and pK_a values

Compound	HNP[a] mv	pK_a
6	312	5.13
7	333	4.51
1	364	3.66

[a] Determined at 25°C in acetic anhydride solution by titration with perchloric acid in acetic acid.

ACKNOWLEDGEMENTS

This work was funded, in part, by a faculty research grant from Williams College. Generous support from Dr. Peter M. Wege II provided summer stipends for K.J.L., M.E.M., and C.K.M.

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Received, 2nd December, 1988