

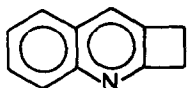
STRAINED HETEROCYCLIC SYSTEMS. II. ACENAPHTHO[1,2-b]QUINOLINE

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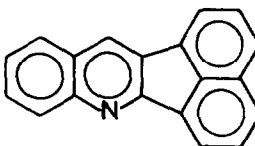
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A recent communication by Streitwieser, et al., (1) on the kinetics of base-catalyzed protodetrition of biphenylenes led to the generalization that "aryl positions adjacent to a fused strained ring have enhanced acidity and reduced reactivity toward electrophilic substitution." Our work (2) on the basicity of 1,2-dihydrocyclobuta[b]quinoline (I) was the first example of such effects observed in a heterocyclic system. We report now the extension of these studies to acenaphtho[1,2-b]quinoline (II).



I



II

Compound II [m.p. 182.8-183.8°; lit. m.p. 181° (3a), 185° (3b)] was obtained in 70% yield from a Friedlander condensation of o-aminobenzaldehyde (4) with acenaphthenone (5). Model compounds were prepared for comparison

purposes: 2-phenylquinoline (III) [m.p. 81.6-82.7°; lit. m.p. 84° (6)] and 2,3-diphenylquinoline (IV) [m.p. 88.4-89.6°; lit. m.p. 90-91° (6)]. Compounds III and IV were prepared by Pfitzinger condensations of isatin with acetophenone and deoxybenzoin, respectively, followed by thermal decarboxylation (6). The half-neutralization potentials (HNP) for the series of compounds in the Table were determined at 25° in acetic anhydride by titration with perchloric acid in acetic acid (7). The apparent acid dissociation constants (pK_a) were calculated from the known pK_a 's of quinoline and quinaldine in water and include the assumption that $HNP(Ac_2O)$ and $pK_a(H_2O)$ are linearly related (7).

TABLE
Basicities of Substituted Quinolines

Compound	HNP ^a	pK_a	Ref.
Quinaldine	331 mv	5.74	8
Quinoline	376	4.94	9
Acridine		5.60	9
2,3-Diphenylquinoline (IV)	410	4.34	<u>b</u>
2-Phenylquinoline (III)	414	4.26	<u>b</u>
Acenaphtho[1,2- <u>b</u>]quinoline (II)	451	3.61	<u>b</u>

^a Average values (± 1 mv) from duplicate titrations.

b Present work.

The basicities of compounds II-IV have not previously been reported; the HNP data clearly establish that II is the least basic of the compounds studied in the present work. The conversion to pK_a values is included for

the convenience of comparison to other heterocyclics; the significance lies in the relative basicities. The decreased basicity of III relative to quinoline is in accord with the inductive withdrawal of electrons by the phenyl group (-I effect). Both steric inhibition of solvation and the degree of coplanarity between the quinoline and phenyl rings undoubtedly influence base strength. It may be inferred, however, from the similar basicities of III and IV that these effects are not dominant in the present series.

The additional five-fold decrease in basicity of II relative to III or IV must be attributed to ring strain caused by the fused acenaphtho system. For II the orbital on nitrogen containing the lone pair of electrons is comparable to that at C-1 for biphenylene. The effect of the adjacent strained ring is transmitted via changes in hybridization analogous to those postulated by Streitwieser and co-workers (1). It should be noted that the present data involve equilibrium measurements, and a correlation between kinetic and thermodynamic scales is avoided.

Work currently in progress involves both the assessment of strain in other heterocyclic systems by this technique and the influence of such strained rings on other physical properties.

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