Studies in Nonpyridinoid Azaaromatic Systems. 7. Synthesis and Tautomeric Character of Cyclopenta[*c*]quinoline (Benzo[*c*][2]pyrindine)[1]

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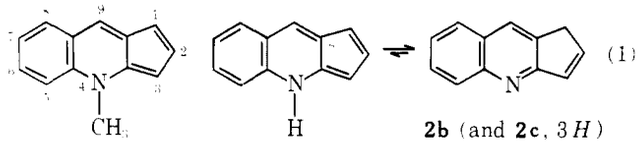
The further study of azaaromatic heterocycles isoelectronic with azulenes (the azalenes) has led to the syntheses of the tautomeric cyclopenta[*c*]quinolines (**12**) and the fully conjugated member, 5-methyl-5*H*-cyclopenta[*c*]quinoline (**14**). Compound **12** was synthesized from 4-oxo-2,3,4,5-tetrahydro-1*H*-cyclopenta[*c*]quinoline (**4**) by the following sequence: (1) reduction to 2,3-dihydro-1*H*-cyclopenta[*c*]quinoline (**5**); (2) N-oxidation of **5** to **5** *N*-oxide (**9**); (3) acetoxylation of **9** to 1-acetoxy-2,3-dihydro-1*H*-cyclopenta[*c*]quinoline (**10**); and (4) dehydroacetoxylation of **10** with sulfuric acid. Compound **12** was converted into **14** by a sequence of quaternization with methyl sulfate and dehydroacetoxylation with sulfuric acid. Spectral studies have demonstrated that **12** is a mixture of the 1*H*, 3*H*, and 5*H* tautomers, whose properties vary with physical state and the nature of solvent. In contrast to the cyclopenta[*b*]quinoline system (**1**), whose N-substituted derivatives have azulene-like visible spectra, the N–H tautomer of **12** and compound **14** do not. A resonance explanation is offered to account for the spectral differences between **1** and **14** and for the varying chromoisomerism of the cyclopentaquinolines themselves.

Heterocyclic systems formally derived from azulene by replacing CH=CH units by oxygen, sulfur, or nitrogen atoms have posed interesting challenges for both experimental and theoretical chemists.[2-6] The known number of such nitrogen analogues of azulene (azalenes) is limited,[7,8] and only recently have the unsubstituted cyclopentapyridines[9,10] and -quinolines[11-15] been reported. The properties of the most extensively studied azalene, 4-methyl-4*H*-cyclopenta[*b*]quinoline (**1**), accord well with its azulenoid character: a long wavelength maximum at 525 nm, nucleophilic attack at C_9, electrophilic attack at C_1 and C_3, and a general deshielding of the ring protons.[12-14] Hückel MO calculations on **1** and related azulene analogues give results in good agreement with the observed chemical properties, but they predict absorptions not at all in agreement with the observed visible spectra.[16,17]

A further interesting aspect of the cyclopenta[*b*]quinoline itself (**2**) is its striking chromoisomerism: depending upon physical state, temperature, and solvent, the colorless 1*H*- and 3*H*-cyclopenta[*b*]quinolines exist in equilibrium with varying small amounts of the intensely purple **2a**. Such systems thus

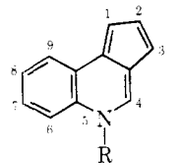


(1)

1 **2a** **2b** (and **2c**, 3*H*)

offer the opportunity for assessing the relative stability of the aromatic azalene delocalization through a study of the tautomeric equilibria.

To learn how the properties of cyclopentaquinolines change with the location of nitrogen, we have undertaken the synthesis and spectral examination of cyclopenta[*c*]quinolines (benzo[*c*][2]pyrindine) (**3**). We now wish to report that under certain conditions **3** shows a pronounced preference to exist as the NH tautomer (**3a**) and that its 5-methyl derivative (**3b**), in sharp contrast to **1**, shows no resemblance whatsoever in its visible spectrum to its azulene analogue, 4,5-benzazulene.

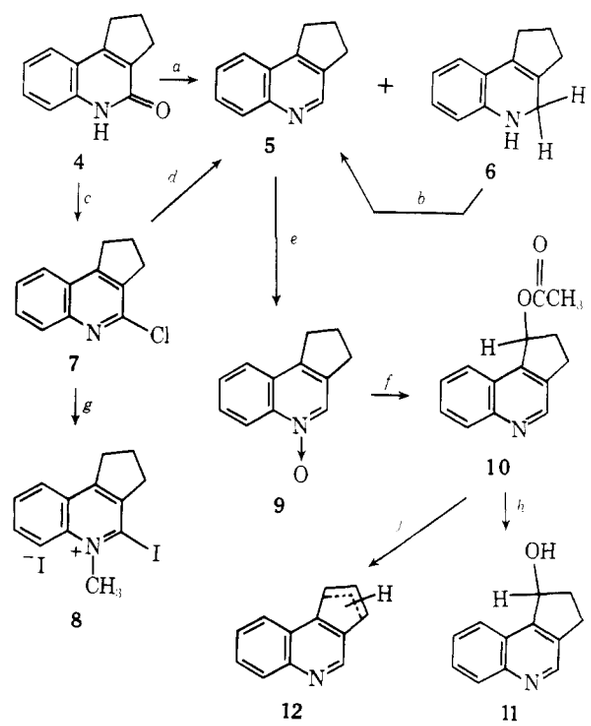


3a, R = H
b, R = CH_3

Results

Synthesis of 1*H*- (3*H*- and 5*H*-) Cyclopenta[*c*]quinoline (12). The basic heterocyclic skeleton required was obtained by the thermal condensation of ethyl cyclopentanone-2-carboxylate with aniline at 95 °C to yield the cyclic amide **4**[19] (Scheme I). This amide could be reduced to 2,3-dihydro-1*H*-cyclopenta[*c*]quinoline (**5**) in a number of reasonably efficient procedures: (1) **4** could be converted into a mixture of **5** and its 4,5-dihydro derivative **6** by means of $LiAlH_4$ in refluxing tetrahydrofuran, and then the overreduced component **6** could be reoxidized to **5** with 30% H_2O_2; (2) **4** could be treated with PCl_5 and $POCl_3$ to yield the 4-chloro derivative of **5** and the chloro derivative **4** then reduced with Raney nickel and sodium methoxide in methanol to yield **5** and some **6**; the **6** was then oxidized with picric acid to yield

Scheme I



4 **5** **6** **7** **8** **9** **10** **11** **12**

[a] $LiAlH_4$ in THF. [b] H_2O_2 or picric acid, followed by base. [c] PCL_5 and $POCl_3$. [d] Raney Ni and CH_3ONa, or Sn, $POCl_3$, and H_2O. [e] *m*-$C_6H_4ClCO_3H$. [f] $(CH_3C])_2Q$ in HOAc. [g] Excess CH_3I. [h] NaOH in CH_3OH. [j] Concentrated H_2SO_4 at 130 °C.

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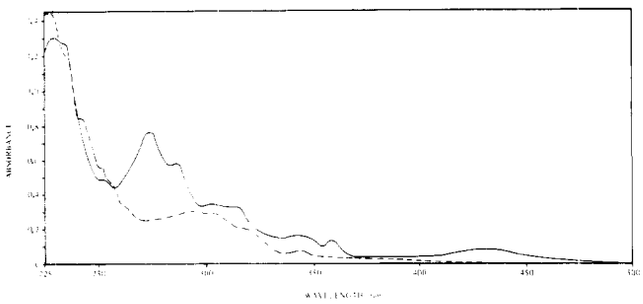


Figure 1. Ultraviolet and visible spectra of 5.3×10^{-5} M solutions of cyclopenta[*c*]quinoline (**12**): A (----) in cyclohexane and B (—) in diethyl ether.

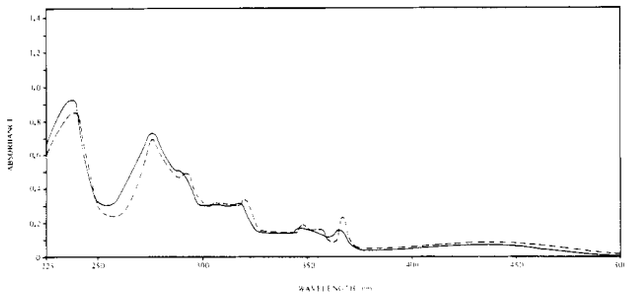


Figure 2. Ultraviolet and visible spectra of 5.0×10^{-5} M solutions of 5-methyl-5*H*-cyclopenta[*c*]quinoline (**14**): A (----) in cyclohexane and B (—) in diethyl ether.

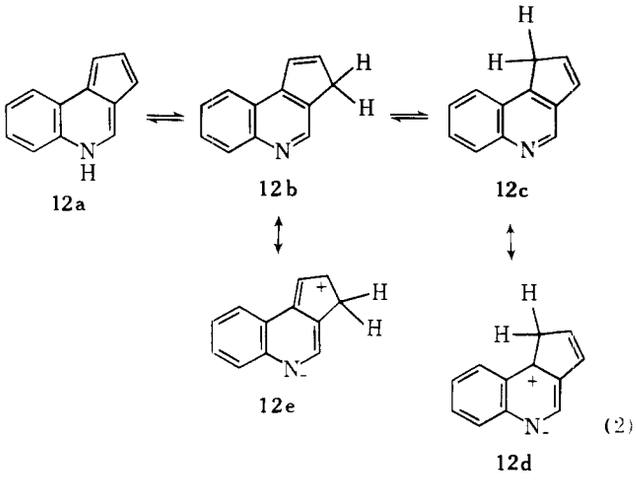
5 picrate; or (3) the chloro derivative could be reduced solely to **5** by means of tin, $POCl_3$, and water.[20]

The resulting 2,3-dihydro-1*H*-cyclopenta[*c*]quinoline (**5**) displayed the expected deshielded protons at C_4 and C_6 in its NMR spectrum and the three ultraviolet maxima characteristic of substituted quinolines.[21] Compound **5** underwent smooth quaternization with methyl iodide and almost quantitative *N*-oxide formation (**9**) with *m*-chloroperbenzoic acid in methylene chloride. It might be noted that even the chloro derivative **4** underwent quaternization with methyl iodide, albeit slowly, but the product was the 4-iodo methiodide (**8**).[22]

The acetoxylation of **9** with acetic anhydride in glacial acetic acid solution gave a moderate yield of the 1-acetoxy derivative (**10**), whose structure is assigned based upon the characteristic tendency of acetoxylation to occur on methylene groups α or γ to nitrogen in pyridine derivatives.[23-26] Saponification of **10** with methanolic sodium hydroxide yielded the 1-hydroxy derivative **11** whose NMR spectrum displayed a two-proton multiplet at 2.20–2.75 ppm, comparable to the H_2 protons in **5** (2.11), and another two-proton multiplet at 2.78–3.25 ppm, comparable to the H_3 protons in **5** (3.05). Such similarities offer direct support for assigning **10** and **11** the 1-substituted structures.

Either **10** or **11** could be subjected to an elimination reaction by means of concentrated sulfuric acid; the reaction was conducted at 130 °C for short contact times and then quenched with ice and sodium hydroxide solution at or below 0 °C. The mixture of 1*H*-, 3*H*-, and 5*H*-cyclopenta[*c*]quinolines (**12**) was isolated as an orange crystalline solid, which was quite stable if stored under nitrogen at 0 °C.

Spectral Properties of the Cyclopenta[*c*]quinolines (12). The infrared spectra of **12** in a neat condition (evaporation of solutions) or in mineral oil suspension showed intense NH bands in the 3300 cm^{-1} region, but these disappeared in solutions of **12** in $CHCl_3$ or CCl_4. The NMR spectrum in $CDCl_3$ exhibited two sharp absorptions at 8.97 and 8.99 ppm in an intensity ratio of 2:1, corresponding to the different C_4 protons in the 3*H*- and 1*H*-cyclopenta[*c*]quinolines (**12b** and **12c**). Likewise, two multiplets appeared at 3.64 and 3.75 ppm, also in a ratio of 2:1, and these could be assigned to the methylene absorptions of **12b** and **12c,** respectively. The greater magnetic deshielding of the methylene protons in **12c** can be ascribed to polar resonance contributions, such as **12d.** An analogous polar contributor to **12b,** namely **12e,** would be less important, since it involves greater charge separation. Therefore, from the infrared and NMR spectra alone, it is clear that significant proportions of all three tautomers can be present at equilibrium (eq 2).



(2)

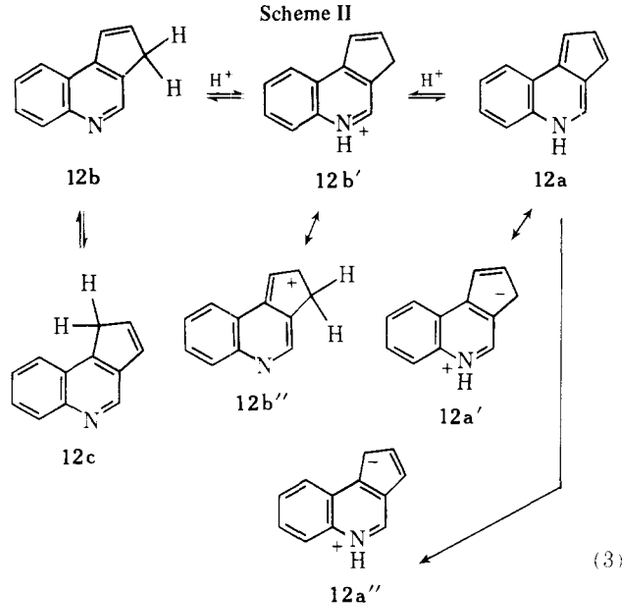
Examination of the ultraviolet and visible spectra of **12** as well as its NMR spectrum in concentrated sulfuric acid further revealed that pronounced variations in the proportions of **12a, 12b,** and **12c** could occur. As the subsequent synthesis of 5-methyl-5*H*-cyclopenta[*c*]quinoline (**14**) has established (cf. infra), the orange color of **12** is properly attributed to the chromophoric system in **12a.** The presence of the NH infrared bands in very concentrated samples of **12** and their absence in more dilute solutions show how sensitive the proportion of **12a** is to the nature of the medium. The visible spectrum of **12** in different solvents was even more indicative of drastic variations in the ratio of the tautomers: not only did **12** dissolve slowly in cyclohexane, but an almost colorless solution resulted. Its molecular spectrum (Figure 1A) shows little resemblance to the spectra of either **12** in diethyl ether (Figure 1B) or **14** in cyclohexane (Figure 2A). Although the concentration of **12** in both solvents is the same (5.3×10^{-5} mol/L), the ethereal solution is distinctly yellow. From these spectra one can conclude that very little **12a** is present at equilibrium, since almost no absorption is observable in the 410–450-nm region. The spectrum of **12** in cyclohexane is similar to that of **5,** with the kinds of bathochromic shifts to be expected from vinylquinolines, such as **12b** and **12c.**[11]

On the other hand, the almost superimposable spectra of **12** and **14** in diethyl ether solution (both 5×10^{-5} mol/L, Figure 1B) lead to the conclusion that in this solvent **12** exists almost entirely in the form of **12a.** Ethanolic solutions also favor the preponderance of **12a.**

The dissolution of orange **12** in concentrated sulfuric acid produced a light-amber colored solution, whose NMR spectrum now showed only a broad singlet at 4.35 ppm, corresponding to one methylene group. In accordance with this view, only one C_4 proton was displayed downfield, at 9.20 ppm, although it was split by the adjacent NH^+ group. Verification that this was indeed splitting, rather than two signals, was secured by observing only a singlet at 9.20 ppm, when the spectrum of **12** was recorded in D_2SO_4.

The absence of any significant color and the presence of only one methylene group rule out the formation of any N-

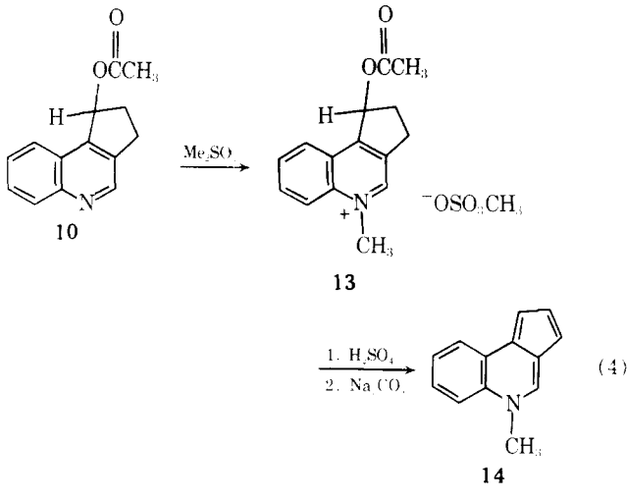
Scheme II



(3)

protonated cation of **12a.** The generation of one methylene group supports the preferential protonation of **12b** or **12c.** Because its cation (**12b'**) has the more advantageous delocalization of charge, **12b** would seem to be more basic than **12c** and thus undergo preferential protonation (Scheme II). Any component **12a** present in the initial tautomeric mixture could also lead to cation **12b'** by undergoing protonation exclusively at C_3. Consideration of the polar resonance structures **12a'** and **12a''** suggests that **12a'** would contribute more to the ground state stabilization of **12a** because of: (1) smaller charge separation and (2) superior conjugation of the exocyclic vinyl group when γ rather than β substituted on the pyridinoid nucleus.[27]

5-Methyl-5*H*-cyclopenta[*c*]quinoline (14). In order to determine the spectral properties of the azalene nucleus present in tautomer **12a** (or **3a**), the *N*-methyl derivative (**14**) was synthesized from the 1-acetoxy derivative **10.** This transformation was readily achieved by quaternizing **10** to **13** with methyl sulfate, dehydroacetoxylating **13** in hot, concentrated sulfuric acid, and neutralizing the reaction mixture to release **14** (eq 4).



(4)

The resulting orange product **14** lacked any infrared absorption in the NH region. Its electronic spectrum in either cyclohexane or diethyl ether closely resembled the spectrum of **12** in diethyl ether or ethanol. The spectrum of **12** in cyclohexane, however, was quite different from that of **14** in the same solvent (cf. Figure 1). This finding supports the above-mentioned conclusion that in cyclohexane **12** exists largely in the form of tautomers **12b** and **12c,** but that in ether or ethanol **12** exists chiefly as **12a.**

The spectrum of **14** in diethyl ether was identical with that in methanol, but the addition of one drop of 0.1 N hydrochloric acid to the latter solution caused pronounced spectral changes. No absorption occurred over 380 nm and spectral peaks were now at 322, 275, 244, 239, and 204. In general features, this latter spectrum resembles the spectra of other protonated vinylquinolines.[11]

Finally, the NMR spectrum of **14** displays all its nuclear protons between 6.95 and 8.24 ppm, an observation more consistent with aromatic deshielding of protons by ring current than with the shielding to be expected of C–H protons vinylogously β to an enamine nitrogen (i.e., those at C_1, C_2, or C_3).[28]

Discussion

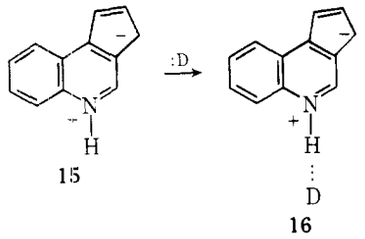
The properties of the cyclopenta[*b*]quinoline (**2**) and the cyclopenta[*c*]quinoline (**3**) nuclei provide a striking and instructive contrast. Although the N-substituted derivatives are isoelectronic with the 5,6-benzazulene (long wavelength λ_{max} 557 nm) and the 4,5-benzazulene (λ_{max} 575 nm) systems, respectively, only **1** and **2a** show a close similarity to their azulene counterpart in their visible spectra. Their purple color (λ_{max} at ca. 510 nm) contrasts sharply with the yellow-orange of **3a** and **3b** (λ_{max} at ca. 430 nm).

Even the tautomeric equilibria existing among the cyclopenta[*c*]quinolines (**12a–c,** eq 2) offer some unusual aspects when compared with similar equilibria established among the cyclopenta[*b*]quinolines (**2a–c,** eq 1). It is true that with both systems the ratio of the two C–H tautomers (C_1:C_3 in **2** and C_3:C_1 in **12**) is 2:1 in $CDCl_3$ or CCl_4 solution. The relative amounts of the N–H tautomers, (**2a** and **12a**), however, are clearly different. Although liquid samples of **2** are purple, solidified **2** is essentially colorless. Solutions of **2,** 2 M in benzene, are estimated to contain ca. 5% of tautomer **2a,** but dilute solutions in 95% ethanol or cyclohexane are colorless and do not absorb above 350 nm. On the other hand, samples of **12** in the solid state and in ethanolic or ethereal solution are distinctly yellow or orange; in fact, the visible spectra of **12** and **14** in diethyl ether are superimposable. These observations support the conclusion that **12** exists largely or exclusively as tautomer **12a** under these conditions. It is readily apparent that the NH tautomer is much more stable (relative to its C–H tautomers) in the cyclopenta[*c*]quinoline system than in the cyclopenta[*b*]quinoline system.

Yet with both heterocycles, the solvent employed can reduce the content of the N–H tautomer to a negligible amount. Already in dilute solutions the percentage of **2a** in **2** has fallen under 1%. More remarkable, however, is the dramatic change in the electronic spectrum of **12** when recorded in cyclohexane. The content of **12a** is now 1% or less. The spectral behavior of **12** (and less so, **2**) in various solvents seems to be another vivid example of how solvents can influence tautomeric equilibria.[29] As explicated by Hammett, a solvent in which one tautomer is relatively more soluble than the other tautomer(s) will favor that tautomer at equilibrium. Such changes in the K_{eq} are due to variations in the activity coefficient of the tautomer as the solvent is varied.[30] The observed spectral changes of **12** in ether and in cyclohexane can be interpreted to mean, therefore, that **12a** is more soluble than **12b** and **12c** in ether (and in ethanol), while **12b** and **12c** are more soluble than **12a** in cyclohexane. The slow dissolution of the orange solid **12** in cyclohexane thus seems to be due to the necessity of the dominant isomer **12a** to rearrange slowly to the more soluble isomers **12b** and **12c.**

Since tautomer **12a** is more soluble in polar solvents than **12b** and **12c,** it appears reasonable to ascribe its heightened

solubility to its greater dipolar character (**15**) and its ability to form hydrogen-bonded solvates (**16**) (eq 5). The behavior



(5)

15 16

of **12** in strong acids is, in part, also related to the polar character of **12a** (**15**), whereby C_3 protonation should yield the more stable cation (cf. supra).

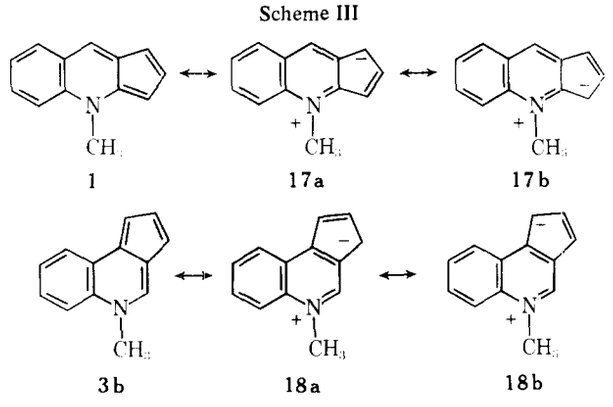
Some attempt should now be made to understand both the visible spectra of the methyl derivatives, **1** and **3b**, as well as the relative stability of the N–H tautomers, **2a** and **12a**. A common explanation underlies, we believe, both phenomena. In the introduction we have already mentioned how inadequate Hückel MO treatments are in reproducing the spectra of these azalenes. Hence, we shall attempt a qualitative analysis in the terms of resonance theory.

The long wavelength absorptions of **1** and **3b** can be viewed as the lowest π–π^* transitions of these systems.[31] The energy of this transition is clearly lower for **1** (510 nm) than for **3b** (430 nm). The difference could be ascribed to a greater stabilization of one of the ground states, of one of the two first excited states, or some combination of the two energy perturbations. Without claiming to have made a definitive choice, we believe that relative ground-state stabilization can be invoked to explain both the spectra and the N–H tautomer stability.

Evidence has been offered above on the polar character of the azalene ring (**15**) in the ground state. If those polar resonance structures are now considered for **1** and **3b** that do not disrupt the quinoline 10π-electron set, then it is apparent that **18a** and **18b** retain aromatic sextets in all rings, while **17a** and **17b** do not (Scheme III). Therefore, either by the intuitive Fries rule or more rational MO–structure enumeration techniques[32] canonical structures **18a** and **18b** should be of lower energy than **17a** and **17b** and thus should stabilize the ground state of **3b**, more than **17a** and **17b** should stabilize that of **1**.[33a] Furthermore, the more energy-rich structures **17a** and **17b** should contribute more to stabilizing the first excited state of **1** than **18a** and **18b** do to the excited state of **3b** (because of the lower energy of the latter contributors) (Figure 3). Hence, the hypsochromic shift in the π–π^* transition of **3b** is accounted for satisfactorily.

Clearly it remains highly desirable to seek a theoretical interpretation of these unusual spectral changes in the language of molecular orbital theory. Although large molecules (>15–20 atoms) of low symmetry lie at the border of quantitative MO calculations (cf. Bock's discussion[33b]), approximations may provide insights. Thus, the ω technique of HMO theory has been used to rationalize the spectral differences between 1- and 2-pyrindines.[33c]

Scheme III



1 17a 17b

3b 18a 18b

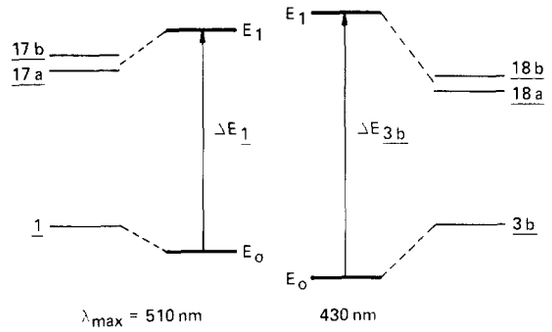


Figure 3. Relative contributions of resonance canonical structures, **1**, **17a**, and **17b** for 4-methyl-4*H*-cyclopenta[*b*]quinoline and **3b**, **18a**, and **18b** for 5-methyl-5*H*-cyclopenta[*c*]quinoline, to the ground-state (E_0) and first excited-state (E_1) energies of these heterocylces. The energies ΔE_1 and ΔE_{3b} represent those of the longest wavelength π-π^* absorptions of the cyclopenta[*b*]quinoline and the cyclopenta[*c*]-quinoline, respectively.

This suggested stabilization of **3b** over **1** should also be reflected in the tautomeric equilibria of **12** (eq 2) and of **2** (eq 1). Thus, it is expected that, in competition with various C–H tautomers of similar energy (N.B., ratio of CH tautomers, 2:1 in both cases), the greater azalene stabilization of **12a** over **2a** should shift the equilibrium in eq 2 farther to the left than that in eq 1.

By such resonance considerations, a consistent interpretation of the properties of these tautomeric cyclopentaquinolines can be formulated. It is clear, however, that chromoisomerism in heterocyclic compounds is a complex and significant phenomenon, deserving of further study.

Experimental Section

Melting points were determined with a Thomas-Hoover "Unimelt" apparatus and are uncorrected. Infrared spectra of samples were recorded on Perkin-Elmer spectrophotometer, Model 457, as solutions in pure solvents (spectral grade) or as mineral oil suspensions. Proton magnetic resonance spectra were measured with Varian spectrometers, Model A-60 (60 MHZ) or V-3521A (100 MHZ), on samples dissolved in pure solvents containing tetramethylsilane as an internal standard. Signals are reported using the δ scale in parts per million, followed by the integrated intensities of the proton signals and the coupling constants (J) in hertz. Ultraviolet and visible spectral data were obtained with a Perkin-Elmer spectrophotometer, Model 202, on samples in solvents of spectral grade purity. Mass spectra of samples were recorded at Baker Laboratories, Cornell University, Ithaca, N.Y., either on Associated Electrical Industries, Model AEI MS902, or Perkin-Elmer, Model 270, mass spectometer. TLC was run on a plate made up of silica gel with 10% calcium sulfate as binder. Iodine was used as a spot developer. Silica gel, supplied by Baker Chemicals, was used for all column chromatography. Elemental analyses were carried out by the Spang Microanalytical Laboratory, Ann Arbor, Mich.

All preparations and reactions involving sensitive, reactive heterocyclic intermediates were conducted under an atmosphere of dry, oxygen-free nitrogen. Appropriate techniques for such manipulations, including the necessary purification of solvents, have already been described.[20]

4-Oxo-2,3,4,5-tetrahydro-1*H*-cyclopenta[*c*]quinoline (4). The preparation of **4** was carried out by a slightly modified procedure of Blount et al.[19] In a 250-mL, three-neck, round-bottom flask, fitted with a thermometer and a Dean-Stark trap, were placed ethyl cyclopentanone-2-carboxylate (39.0 g, 250.0 mmol) and freshly distilled (over zinc dust) aniline (23.25 g, 250.0 mmol). The mixture was heated to reflux (~95 °C) with magnetic stirring. With the distillation of ethanol the temperature of the reaction mixture rose slowly at first and sharply at the end. By the time ca. 11 mL of distillate was collected, the temperature reached 170 °C. The heating was discontinued and the reaction mixture was allowed to stand at room temperature for 18 h. The resulting light-brown oil was slowly added to 75 mL of

36 N H_2SO_4 with cooling. The reddish-brown syrup was heated on a steam bath (80–90 °C) for 15 min. The dark-red liquid was poured into 1 L of ice-chilled water. The light-yellow solid that separated was filtered and thoroughly washed (neutral to litmus) with water. The crude product (mp >250 °C) was recrystallized from boiling ethanol to yield[34] 16.3 g (35%) of the pure crystalline product: mp 262–264 °C dec (with previous blackening) (lit.[19] 256 °C, 259–61 °C); IR (Nujol) 1660 (vs, C=O), 1622 (vw), 1612 (vw), 1568 (m), 1510 (m), 1480 (w), 1441 (s), 1438 (s), 1408 (w), 1402 (w), 1350 (w), 1308 (vw), 1288 (vw), 1280 (vw), 1270 (w), 1258 (w), 1165 (m), 1155 (w), 1122 (w), 1030 (vw), 940 (m), 960 (sh), 950 (m), 852 (vw), 765 (vw), 760 (s), 755 (s), 642 cm^{-1} (m).

2,3-Dihydro-1*H*-cyclopenta[*c*]quinoline (5). Method A. Step 1. Lithium Aluminum Hydride Reduction of 4-Oxo-2,3,4,5-tetrahydro-1*H*-cyclopenta[*c*]quinoline (4). To a magnetically stirred solution of lithium aluminum hydride[35] under a nitrogen atmosphere (4.45 g, 117.0 mmol) in 800 mL of absolute tetrahydrofuran was added carefully, in small portions (frothing, H_2 evolution), powdered **4** (21.40 g, 116.0 mmol). As the reaction mixture was heated at gentle reflux, the color of the reaction mixture gradually changed from gray to green (18 h) and finally to pale green (40 h). After 6 days of reflux (color change pale green to green at 18 h to pale green at 40 h), 4.5 mL of H_2O and then 4.5 mL of NaOH and 13.5 mL of H_2O were added. Upon further stirring, the hydrolyzed mixture formed a white granular precipitate which was filtered off. The precipitate was thoroughly washed with methylene chloride. The filtrate was dried ($MgSO_4$), and the solvent was evaporated under reduced pressure to yield 17.7 g of a brownish solid (crude yield ca. 90%). The NMR of the crude product showed it to be a mixture of **5** and 2,3,4,5-tetrahydro-1*H*-cyclopenta[*c*]quinoline (**6**).

The crude product from the reduction of **4** gave, after six recrystallizations from ethanol, a fairly pure sample of 2,3,4,5-tetrahydro-1*H*-cyclopenta[*c*]quinoline (**6**): mp 89–92 °C; NMR ($CHCl_3$) δ 6.42–7.08 (complex m, 4, H_6, H_7, H_8, and H_9), 4.25 (br s, 2, H_4), 3.30 (br s, 1, NH, chemical shift varied with concentration and signal disappeared upon shaking with D_2O), 1.67–2.83 (complex m, 6, H_1, H_2, and H_3); picrate, mp 196–197 °C dec (orange, from ethanol).

Step 2. Hydrogen Peroxide Oxidation of 6 to 5. Usually after the workup of lithium aluminum hydride reduction, the aluminum hydroxide precipitate was filtered off and the tetrahydrofuran solution was treated directly with 1 equiv of 30% hydrogen peroxide[37] (13.3 mL, 116 mmol), whereupon a mild exotherm occurred. Since the reaction mixture yielded a positive KI starch test, it was heated at gentle reflux for 6 h. The completion of the reaction could be easily followed with NMR by observing the disappearance of the complex multiplet at 7.08–6.42 ppm and the increase in integrated intensity of H_4 singlet absorption at 8.73.

Most of the solvent was evaporated under reduced pressure and at low temperature (~40 °C). The residual orange thick oil was taken upon methylene chloride and washed twice with saturated sodium bicarbonate solution, then with water, and finally by sodium sulfite solution and water. After the organic layer was dried ($MgSO_4$) and the solvent removed in vacuo, the remaining thick brownish oil was vacuum distilled [113–115 °C (0.1 mm)] to give 14.2 g of **5** (yield 72% based on starting compound **4**), mp 55–56 °C. The distillate yielded a white solid upon recrystallization from ether–petroleum ether, tiny sugar-like cubes: mp 58–59 °C; IR (CCl_4) 3061 (m), 3030 (2), 3000 (w), 2955 (vbr vs), 2864 (vw), 2950 (s), 1616 (w), 1600 (m), 1582 (s), 1561 (s), 1500 (vs), 1456 (s), 1432 (s), 1428 (sh), 1415 (sh), 1382 (vs), 1366 (w), 1354 (m), 1306 (vs), 1298 (s), 1290 (sh), 1275 (vw), 1254 (m), 1200 (w), 1178 (vw), 1152 (vs), 1031 (m), 1020 (s), 1000 (vw), 955 (s), 927 (s), 902 (w), 885 (w), 852 (m), 680 (w), 632 cm^{-1} (m); UV (cyclohexane) λ_{max} (log ϵ) 233 (3.35), 277 (3.28), 308 (3.22), 310, 317 (3.25). These absorptions are close to those of other cycloalkenoquinolines reported earlier[11] and can be compared with quinoline values:[21] λ_{max} (ϵ_{max}) 228 (40 000), 270 (3162), 315 (2500) in cyclohexane; NMR ($CDCl_3$) 8.73 (s, 1, H_4), 8.17 (m of d, 1, H_6), 7.73–7.17 (complex m, 3, H_7, H_8, and H_9), 3.05 (q, 4, H_1 and H_3), 2.11 (m resembling a quintet, 2, H_2); mass spectrum (70 eV) *m/e* (rel intensity) 169 (M^+, 100).

Anal. Calcd for $C_{12}H_{11}N$: C, 85.21; H, 6.51; N, 8.29. Found: C, 85.26; H, 6.46; N, 8.22. Picrate: a yellow crystalline powder (EtOH), mp 205 °C dec (with previous blackening) (lit. 216–217 °C dec, 212–215 °C dec).

Anal. Calcd for $C_{18}H_{14}N_4O_7$: C, 54.27; H, 3.54. Found: C, 54.26; H, 3.77.

Method B. Step 1. 4-Chloro-2,3-dihydro-1*H*-cyclopenta[*c*]quinoline (7). A mixture of 2.0 g (10.8 mmol) of **4**, 3.0 g of phosphorus pentachloride, and 30 mL of phosphorus oxychloride was heated at reflux for 30 min, the excess phosphorus oxychloride was distilled off, and the residue was poured into ice-water. The colorless solid product was filtered off and recrystallized from methanol, 70%: mp 120–120.5 °C (lit.[38] 118–120 °C); IR (mineral oil) absence of C=O; NMR δ 2.1–2.4 (m, 2, CH_2), 3.0–3.5 (m, 4, C_1 and C_3), and 7.5–8.0 (m, 4). Heating **7** with an excess of methyl iodide in benzene solution slowly (>24 h) led to the deposition of a yellow solid, mp 220–222 °C dec, that by mass spectrometry proved to be the methiode of 4-iodo-2,3-dihydro-1*H*-cyclopenta[*c*]quinoline (**8**): mass spectrum (70 eV) *m/e* (rel intensity) 310 ($C_{13}H_{13}IN^+$, 46), 309 (37), 295 ($M^+ - CH_3$, 37), and 168 (100).

Step 2. Raney Nickel Reduction of 7. In a hydrogenation pressure bottle was placed a mixture of 5.5 g (27 mmol) of **7**, 5.4 g of fresh Raney nickel catalyst, and a solution of sodium methoxide in methanol (prepared from 3.2 g of sodium metal and 50 mL of methanol). After the mixture was shaken at room temperature and pressure for 48 h, the catalyst was filtered off and the filtrate freed of solvent. The residue was dissolved in ethyl ether, and the extracts were washed with water, dried, and then evaporated. Distillation of the residue yielded a mixture of **5** and **6**, bp 95–100 °C (0.65 mm). The distillate was treated directly with an excess of ethanolic picric acid to yield the picrate of **5**, mp 212–215 °C dec, after recrystallization from acetone (lit.[39] 216–217 °C dec). Treatment of an aqueous suspension of the picrate with a 20% NaOH solution yielded **5**, which formed colorless platelets from petroleum ether (bp 30–60 °C), mp 36.5–37.5 °C, but mp 58–59 °C from ether–petroleum ether pair, in an overall 55% yield.

Anal. Calcd for $C_{12}H_{11}N$: C, 85.21; H, 6.51; N, 8.29. Found: C, 85.26; H, 6.46; N, 8.29.

Warming **5** (850 mg) and 3 mL of methyl iodide in 25 mL of 95% ethanol for 30 min on a steam bath and cooling deposited 800 mg of the dull-green methiodide, mp 225–228 °C dec, from ethanol. Heating **5** methiodide with ethanolic picric acid and cooling yielded thick yellow needles of the methopicrate, mp 171–172 °C dec, from ethanol.

2,3-Dihydro-1*H*-cyclopenta[*c*]quinoline *N*-Oxide (9). To an ice-cooled solution of **5** (8.79 g, 52.0 mmol) in 200 mL of methylene chloride was added, in small portions, 10.5 g (52.2 mmol) of 85% *m*-chloroperbenzoic acid with cooling and stirring. An exothermic reaction occurred as the solution became yellow.[41] An excess of the peracid was confirmed by starch–iodide test paper. The reaction mixture was heated at reflux for 6 h under a nitrogen atmosphere. Completion of reaction was monitored by starch–iodide test paper and by NMR (upfield shift of H_4 absorption from 8.73 ppm in **5** to 8.47). The reaction mixture was chilled in ice and then excess peracid was destroyed by the addition of 10% aqueous sodium sulfite solution until a test with starch–iodide paper was negative. The layers of the reaction mixture were then separated, and the organic layer was vigorously shaken with 1.5 equiv of 2 N sodium hydroxide solution (ca. 39 mL) to extract the *m*-chlorobenzoic acid. The organic layer was washed with water and finally with saturated sodium chloride solution. The clear organic layer was dried ($MgSO_4$) and stripped of solvent to yield 9.15 g of a light-brown solid (yield ca. 95%): mp 148–50 °C dec. An analytical sample was prepared by recrystallization with ethanol–ether–pentane to yield a light-brownish crystalline material: mp 150–151.5 °C dec (previously black); IR (mineral oil) 1568 (m), 1512 (w), 1428 (2), 1420 (vw), 1402 (s), 1398 (m), 1365 (w), 1325 (m), 1295 (m), 1260 (w), 1222 (w), 1203 (w), 1188 (vw), 1160 (w), 1148 (m), 1141 (m), 1082 (s), 1018 (w), 1004 (vw), 962 (m), 872 (m), 865 (m), 782 (m), 775 (s), 760 cm^{-1} (w); NMR ($CDCl_3$) δ 8.88–8.57 (m of d, 1, H_6), 8.47 (S, 1, H_4), 7.87–7.33 (m, 3, H_7, H_8 and H_9), 3.10 (q, 4, H_1 and H_3, J = 7.0 Hz), 2.25 (q, 2, H_2, J = 7.0 Hz); mass spectrum (70 eV) *m/e* (rel intensity) 185 (M^+, 100), 184 (30), 169 (M − O, 14), 168 (M − OH, 31), 167 (M − H_2O, 35), 156 (M − C_2H_5, 37), 130 (30), 129 (45).

Anal. Calcd for $C_{12}H_{11}NO$: C, 77.81; H, 5.99; N, 7.56. Found: C, 77.75; H, 5.94; N, 7.59. Picrate: mp 160–162 °C dec (pale green, from EtOH).

Anal. Calcd for $C_{18}H_{14}N_4O_8$: C, 52.18; H, 3.40; N, 13.52. Found: C, 52.31; H, 3.53; N, 13.41.

1-Acetoxy-2,3-dihydro-1*H*-cyclopenta[*c*]quinoline (10). Under a nitrogen atmosphere a stirred portion of acetic anhydride (3.70 mL, 4.00 g, 39.25 mmol) was treated dropwise with a solution of *N*-oxide **9** (7.23 g, 39.1 mmol) in 75 mL of glacial acetic acid over a period of 1.5 h. The brown solution was heated on a steam bath for 2 h[42] with stirring. After a few minutes of heating, the reaction mixture became deep blood-red. After heating, the deep-red reaction mixture was allowed to stand at room temperature overnight and then stripped of most of the acetic acid under reduced pressure. The remaining reddish-brown, sticky material was dissolved in ether, and the etheral layer was washed with saturated sodium bicarbonate solution and then water. The ethereal layer was dried ($MgSO_4$) and the solvent removed to yield 5.76 g of a dark reddish-brown viscous product.

The acetoxy derivative **10** was separated by chromatography on a 210-g silica gel column (95 × 3.5 cm) prepared with petroleum ether. The eluting solvent was varied from petroleum ether through mixtures with ether (mainly 1:1), as fifty 50 mL fractions were collected. The fractions were analyzed by weight curve determination and by NMR spectroscopy. Fractions 1–15, weighing together 290 mg, were discarded since they contained unidentifiable oil products. Fractions 16–25 contained a colorless crystalline solid, whereas fractions 26–34 contained crystalline product ranging from light pink to red. However, all these fractions (16–34) contained **10**, by NMR, and were combined to give 4.23 g of the product. The remaining fractions contained some polymeric material (mp 143–152 °C dec) which gave an intense bright-red solution in organic solvents, showed very broad NMR absorptions, and hence were discarded.

The product **10** was recrystallized with hexane to give 3.90 g (44%)[43] of colorless, compact crystals, mp 96–97 °C. An analytical sample was prepared by two more recrystallizations from ether–petroleum ether: mp 97–98 °C; TLC (1:1.5 mixture of petroleum ether–ether) showed a single spot with R_f 0.5; IR ($CHCl_3$) 3050 (sh), 3030 (sh), 2950 (br m), 2856 (vw), 1730 (br vs), 1592 (w), 1570 (w), 1509 (m), 1468 (w), 1450 (vw), 1430 (vw), 1372 (s), 1320 (w), 1300 (w), 1225 (vbr vs), 1158 (m), 1132 (vw), 1080 (w), 1022 (s), 978 (w), 948 (m), 922 (m), 890 (w), 864 cm^{-1} (w); NMR ($CDCl_3$) δ 8.72 (S, 1, H_2), 8.08 (m of d, 1, H_6), 7.88–7.28 (m 3, H_7, H_8, and H_9), 6.56 (q, 1, H_1), 3.38–1.90 (complex m, 4, H_2 and H_3), 2.02 (S, 3, $OCOCH_3$). Irradiation of H_1 affects the upfield part of multiplet (i.e., 2.76–1.90) which is the absorption due to $2H_2$: mass spectrum (70 eV) *m/e* (rel intensity) 227 (M^+, 1), 184 (M − CH_3CO, 6), 168 (M − CH_3CO_2, 38), and 167 (M − CH_3CO_2H, 100). For comparison, it should be noted that 3-acetoxy-2,3-dihydro-1*H*-cyclopenta[*b*]quinoline displays a similar cracking pattern: 227 (17), 184 (56), 158 (31), and 167 (100).

Anal. Calcd for $C_{14}H_{13}NO_2$: C, 73.99; H, 5.76; N, 6.16. Found: C, 74.09; H, 5.86; N, 6.35.

1-Hydroxy-2,3-dihydro-1*H*-cyclopenta[*c*]quinoline (11). The 1-acetoxy derivative **10** was saponified to yield the corresponding hydroxy derivative **11** by heating a solution of **10** (3.42 g, 15.1 mmol) in 75 mL of methanol with 16 mL of 1 N NaOH on a steam bath for 30 min and then allowing the mixture to stand at room temperature overnight. A crystalline solid thus formed was filtered and thoroughly washed with water, ether, and a small amount of methanol. The product weighed 2.20 g, mp 185–86 °C. The mother liquor was stripped of solvent, and the residue was taken up in water and extracted with four 50-mL portions of methylene chloride. The combined organic extracts were dried ($MgSO_4$), and the solvent was removed to give a grayish solid that was recrystallized with methanol–ether to yield 600 mg of the product (combined yield, quantitative). An analytical sample was prepared by two recrystallizations from methanol–ether: mp 187–188 °C; IR (mineral oil) 3120 (br m, OH), 1570 (w), 1505 (m), 1320 (sh), 1309 (m), 1270 (m), 1230 (w), 1155 (w), 1145 (w), 1078 (w), 1052 (w), 772 cm^{-1} (s); NMR (Me_2SO-d_6) δ 8.85 (s, 1, H_4), 8.45–7.43 (m, 4, H_6, H_7, H_8, and H_9), 5.73–5.40 (m, 2, H_1 and OH), 3.25–2.78 (m, 2, H_3), 2.75–2.20 (m, 2, H_2); NMR (CF_3CO_2H) δ 8.34 (br s, 1, H_4; it resembled doublet, possibly because of N-protonation: it became a doublet in concentrated H_2SO_4), 7.96 (m, 1, H_6), 7.80–6.95 (m, 3, H_7, H_8, and H_9), 5.80–5.33 (m, 1, H_1), 2.93–1.43 (m, 4, H_2 and H_3); mass spectrum (70 eV) *m/e* (rel intensity) 185 (M, 100), 184 (72), 168 (M − OH, 21), 167 (M − H_2O, 17), 156 (20), 143 (22), and 142 (22).

Anal. Calcd for $C_{12}H_{11}NO$: C, 77.81; H, 5.99; N, 7.56. Found: C, 77.69; H, 5.90; N, 7.64.

The 1-hydroxy derivative **11** can be reacetylated by the standard reaction with acetic anhydride and pyridine, but an attempted acetylation using acetic anhydride and glacial acetic acid was unsuccessful.

1*H*- (3*H*- and 5*H*-) Cyclopenta[*c*]quinoline (Benzo[*c*][*2*]-pyridine) (12). To the powdered 1-hydroxy derivative **11** (3.0 g, 16.2 mmol), or an equivalent amount of 1-acetoxy compound **10**, was added dropwise 15 mL of cooled 36 N sulfuric acid (540 mmol). The magnetically stirred, partially dissolved mixture was heated in an oil bath at 130 °C for 5 min (10–12 min in the case of **10**), and the resulting light-brown solution was immediately poured over ice (~500 g), upon which the diluted mixture displayed faint purple coloration. Then the mixture was neutralized with saturated sodium carbonate solution and the temperature of the reaction mixture was kept below 0 °C. Interestingly, neutralization occurred like a titration and was visually observable (color change from faint purple to bright lemon-yellow). The reaction mixture was thoroughly extracted with four parts of 250 mL of ether. The bright-yellow etheral extracts were combined and dried (K_2CO_3) with ice bath cooling.[44] The solvent was removed at or below room temperature under reduced pressure to yield a yellow-orange solid (~1.65 g, 61% yield) which was triturated with methanol to give an orange crystalline powder, mp 109–111 °C dec (with previous darkening; shrinks from 105 °C).

Anal. Calcd for $C_{12}H_9N$: C, 86.20; H, 5.43; N, 8.38. Found: samples sent for analysis gave a low total for C, H, N, indicating uptake of oxygen but yielded the right ratio, $C_{12}H_9N$. Cf. mass spectrum (20 eV) *m/e* (rel intensity), source at 80 °C and probe at 50 °C; 168 (M + 1, 17.3), 167 (m, 100), 166 (18.2), 149 (27.3), 139 (15.5), 128 (20), 105 (18.2), and 88 (19.6) with no sign of peaks due to dimers (334) or higher oligomers; source at 80 °C and probe at 150 °C, 167 (100), with weak peak at 334, but no peaks for trimers (501) or tetramers (668); NMR ($CDCl_3$) 8.99 and 8.97 (two s, 1, for the H_4 of the isomeric 3*H*- and 1*H*-cyclopenta[*c*]quinolines in a ratio of 67:33), 7.53–8.23 (m, 4, H_6, H_7, H_8, and H_9), 6.59–7.06 (m, 2, vinylic H_1, H_2, and H_3), 3.75 and 3.64 (two t, 2, for the isomeric 1-CH_2 and 3-CH_2, respectively, in a ratio of 32:68); IR (neat) 3370 (br m), 3280 (br, m), 1625 (m), 1595 (m), 1570 (w), 1533 (w), 1500 (w), 1468 (w), 1443 (m), 1418 (w), 1358 (m), 1335 (m), 1325 (vw), 1288 (m), 1238 (vw), 1192 (w), 1160 (w), 1152 (w), 1093 (m), 1055 (vw), 1035 (w), 1018 (w), 975 (m), 940 (w), 920 (w), 870 (m), 862 (vw), 850 (w), 800 (br m), 760 (s), 756 (s), 732 (m), 685 cm^{-1} (w); IR (Mineral oil) 3370 (s, NH), 3286 (s, NH), 1630 (vs), 1625 (sh), 1598 (s), 1572 (m), 1546 (m), 1502 (w), 1445 (s), 1418 (w), 1410 (vw), 1361 (vs), 1338 (m), 1298 (w), 1288 (m), 1282 (w), 1258 (w), 1238 (w), 1192 (s), 1160 (w), 1152 (m), 1093 (vs), 1052 (w), 1034 (w), 1018 (m), 976 (s), 939 (w), 920 (w), 890 (vw), 870 (m), 864 (vw), 850 (w), 795 (m), 762 (sh), 758 (vs), 732 (s), 682 cm^{-1} (m). Although both these concentrated spectral samples showed absorptions in the NH regions, samples of **12** in either $CHCl_3$ of CCl_4 did not display such NH absorptions.

Ultraviolet Absorption Study of the 1*H*-, 3*H*-, and 5*H*-Cyclopenta[*c*]quinolines (12). Since **12** tended to discolor upon standing, a sample was prepared from **10** just prior to spectral measurements. To 1.5 mL of 36 N H_2SO_4 chilled in an ice bath was added 0.300 g of **10**, and the mixture was heated for 20 min in an oil bath held at 130 °C. Immediate cooling, followed by addition of 100 g of ice and slow neutralization with saturated $NaHCO_3$ solution, led to a bright-yellow suspension. The yellow product was taken up in ether, the solution dried over K_2CO_3, and the solvent removed. Redissolution in anhydrous ether gave an estimated concentration of **12:** 2.6×10^{-3} M (by UV absorption at 230 nm). Aliquots were introduced into volumetric flasks, and, where a different solvent was used, the ether was removed under reduced pressure. Of the solvents employed, the sample of **12** dissolved quickly in anhydrous ethyl ether or 95% ethanol but only slowly in cyclohexane. Dissolution of **12** from 1.0 mL of the 2.6×10^{-3} M ethereal stock solution in 50.0 mL of cyclohexane gave almost a colorless solution; in 50.0 mL of ethyl ether, the solution was light yellow; and in 95% ethanol, the solution was definitely yellow: UV (diethyl ether) λ_{max} 210 sh (21 500), 230 (33 000), 274 (19 500), 287 sh (14 500), 295–315 br sh (8500), 330–350 br sh (3800), and 430 (br, 410–450 nm, ϵ ca 1000); UV (95% EtOH) 210 sh (22 000), 230 (33 000), 274 (13 500), 287 sh (11 000), 292–312 sh (9000), 330–350 br sh (3100), and 430 (br 410–450 nm); UV (cyclohexane) 228 (33 000), 236 sh (27 000), 243 sh (19 000), 290–305 (6300), 315 (sh, 5000), 325 (sh, 3700), without any absorption over 400 nm.

NMR Spectral Study of the Dehydration of 1-Hydroxy-2,3-dihydro-1*H*-cyclopenta[*c*]quinoline (11) and of the Protonation of the Cyclopenta[*c*]quinolines (12). The NMR samples were prepared by treating **11** with 36 N H_2SO_4 for 0.5 h at 25 °C, 5 min at 125 °C and 24 h at 25 °C, The dehydration proceeded cleanly, for no extraneous peaks were observed: NMR (external Me_4Si) 9.20 (d, 1, H_4 split by NH^+, *J* 7.0 hz), 7.97–8.85 (m, 8, H_1, H_2, NH^+, H_6, H_7, H_8, H_9, and HSO_4^-), and 4.35 (br s, 2).

An analogous heating of a sample of **11** with 36 N D_2SO_4 gave a spectrum similar to that recorded above, except that the peak at 9.20 ppm was now a sharp singlet and the integration of the multiplet between 7.97 and 8.85 varied, with time, from 7 to almost 8. The increase in proton count may be due to the water that was lost from **11** exchanging with the DSO_4^-.

5-Methyl-5*H*-cyclopenta[*c*]quinoline (5-Methyl-5*H*-benzo[*c*][*2*]pyridine (14). A solution of 894 mg (3.94 mol) of acetate **10** (mp 96–97 °C) in 20 mL of dry benzene was allowed to stand under nitrogen with 2 mL of freshly distilled dimethyl sulfate for 12 h at 25 °C. Evaporation of volatiles in vacuo left the colorless crystalline methosulfate (**13**).

The product **13** was immediately treated with 4.4 mL of 36 N H_2SO_4 and heated for 15 min in an oil bath preheated to 130 °C (actually, however, the product **14** seemed more stable toward H_2SO_4 than **12**). The brown reaction mixture was poured over ice (no purple color as with **12**). Neutralization with saturated sodium carbonate solution, extraction with ether, and drying of the extracts over K_2CO_3 gave a bright yellow-orange ether solution, which appeared to be stable at

0 °C under nitrogen. Removal of solvent yielded a dark-orange solid, which was accompanied by varying amounts of dark-brown, insoluble, apparently polymeric material.

Noteworthy is that the orange product **14** is much more readily soluble in cyclohexane than is **12**. Purification of **14** was effected by solution in cyclohexane, filtration, and removal of the solvent from the filtrate all under nitrogen. The orange solid was sensitive to both heat and oxygen; it turns bluish green when treated with dilute HCl; as did **12**, **14** formed bluish-green solutions with $CHCl_3$ or CCl_4; in CS_2 **14** formed a deep-red solution: IR (neat) 2964 (m), 1620 (m), 1592 (m), 1550 (w), 1490 (w), 1460 (w), 1440 (vw), 1390 (vw), 1378 (vw), 1350 (m), 1289 (m), 1260 (s), 1225 (w), 1100 (br s), 1030 (br s), 980 (vw), 800 (br s), 750 (m), 680 (m), 662 cm^{-1} (w); IR (mineral oil) 1620 (m), 1590 (m), 1550 (w), 1490 (w), 1365 (vw), 1350 (m), 1290 (m), 1287 (sh), 1280 (sh), 1260 (m), 1222 (m), 1110 (m), 1095 (sh), 1060 (vw), 1040 (w), 1020 (w), 982 (w), 800 (br m), 758 (m), 750 (m), 680 (m), 662 cm^{-1} (w); IR ($CHCl_3$) 3060 (vw), 2993 (m), 2955 (sh), 1628 (s), 1600 (m), 1550 (w), 1491 (m), 1465 (m), 1460 (sh), 1440 (vw), 1422 (vw), 1392 (w), 1378 (w), 1365 (sh), 1355 (s), 1328 (vw), 1290 (s), 1258 (s), 1214 (br m), 1110 (s), 1060 (w), 1040 (w), 1018 (w), 992 (m), 905 (w), 892 cm^{-1} (vw) (in all cases, the NH absorption, noticeable at 3280–3370 in **12**, was absent); NMR ($CDCl_3$) δ 8.10–8.24 (d of m, H_6), 7.78 (br s, H_4, J = 1.5 Hz), 7.22–7.31 (m, 3 H), 7.10–7.22 (d of d, H_2, J = 3 and 4 Hz), 6.95–7.02 (q, H_3), 6.74 (d of d, H_1, J = 1 and 4 Hz), and 3.84 ($N-CH_3$); mass spectrum (70 eV) m/e (rel intensity) 182 (7.0), 181 (M, 19.9), 168 (22.3), 167 (M − CH_3, 100), 166 (32.4), 155 (10.5), 154 (30.3), 153 (13.2), 152 (13.2), 139 (M − CH_3 and HCN), and 113 (M − CH_3 and HCN and HC≡CH); UV (cyclohexane) 238 (16 000), 276 (13 200), 292 (9300), 320 (6300), 325–358 (peak at 348) (3000), 367 (4400), and 430 (br 410–450 nm, ϵ ca. 1700); UV (diethyl ether) similar spectrum, except for peak at 212 (13 000); UV (max) (MeOH) 210, 238, 276, 296–312 (sh), 335–365 (br sh), and 410–450 (br); UV (max) (MeOH + HCl) 205, 238, 244, 270–280 (br) 320 (br) (nothing over 370 nm).

For comparison with the NMR of **14**, it should be noted that 4-methyl-4*H*-cyclopenta[*b*]quinoline displays the following NMR absorptions: 8.1 (br s, H_9), 7.84 (br d, H_5), 7.5 (m, 2*H*), 7.3 (d of d, H_2, J_{23} = 3 Hz, J_{12} = 4 Hz), 7.0–7.2 (m, H_6), 6.4 (d of d, H_3, J_{13} = 1.2 Hz, J_{12} = 4.0 Hz), 5.83 (br m, H_1), and 3.97 (s, $N-CH_3$). Previous NMR data reported for this compound inadvertently assigned the peak at 8.1 to H_5.

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Registry No.—**1**, 13038-93-2; **3a**, 35731-21-6; **3b**, 65733-50-8; **4**, 4514-03-8; **5**, 65733-51-9; **5** picrate, 65733-52-0; **5** methiodide, 65733-53-1; **5** methopicrate, 65776-59-2; **6**, 65733-54-2; **6** picrate, 65733-55-3; **7**, 15944-16-8; **8**, 65733-56-4; **9**, 65733-57-5; **9** picrate, 65733-58-6; **10**, 65733-59-7; **11**, 65733-60-0; **12b**, 19557-49-4; **12c**, 232-62-2; **13**, 65733-62-2; ethyl cyclopenlanone-2-carboxylate, 611-10-9; aniline, 62-53-3; 3-acetoxy-2,3-dihydro-1*H*-cyclopenta[*b*]-quinoline, 29411-26-5.

References and Notes

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(18) In ref 11 the proportion of **2a** in **2** is given as <1% for 10% CCl_4 and as 0.09% for a 1.94 M solution of **2** in benzene. This latter figure is actually the molar concentration of **2a**. The percentage of **2a** in **2** is ca. 5%. As the present study demonstrates, the proportion of NH tautomers like **2a** increases in more polar nonacidic media and is sharply reduced in nonpolar solvents or acidic media.
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(27) Cf. ref 11 for the similar shifting of the tautomeric equilibria of **2a**, **2b**, and **2c** in trifluoroacetic acid.
(28) For comparison, the 1,2-dihydro derivative of **1** displays a typical shielded enamine signal at C_3 (4.15) and vinylogous β enamine signal at C_9 (5.85 ppm).
(29) Cf. O. Dimroth, *Justus Liebigs Ann. Chem.*, **399**, 91 (1913), for the effect of solvents on the enol:keto ratio of benzoylcamphor.
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(33) (a) Noteworthy is the observation that, for both 4,5-benzazulene and 5,6-benzazulene, polar structures can be written that maintain an aromatic sextet in each ring. Thus, in contrast to **1** and **3b**, neither benzazulene ground state has any significantly different stabilization on these grounds. In describing the excited states of **1** and **3b** in resonance terms, obviously many other ionic structures must also be considered. Here we limit ourselves just to the polar forms, **17a**, **17b**, **18a** and **18b**, which are also important in describing the ground state. The underlying principle in describing any state by resonance is that structures contribute more significantly the closer they are in energy. (b) H. Bock, *Angew. Chem.*, **89**, 631 (1977). (c) E. M. Evleth, Jr., J. A. Berson, and S. L. Manatt, *J. Am. Chem. Soc.*, **87**, 2908 (1965).
(34) The yield varies from 13–37% with an average yield of 23% from eight reactions. For a longer, but higher-yielding procedure, *cf.* W. Ried and W. Käppeler, *Justus Liebigs Ann. Chem., 688*, 177 (1965).
(35) Instead of lithium aluminum hydride, a mixture of $LiAlH_4$-$AlCl_3$ leads to similar result. However, reduction could not be achieved with amine-stabilized aluminum hydride solution (1.06 M 1:1 AlH_3:NEt_3 in benzene; Lithium Corp.).
(36) In a separate experiment, reaction was followed by NMR and IR spectroscopy, namely by working up portions of the reaction mixture at different intervals. Initially only **5** was observed besides unreacted **4**. However, after 11 h of reaction **6** was formed and its amount increased with time. It appears that **5**, being completely soluble in tetrahydrofuran, undergoes further reduction faster with $LiAlH_4$ than the sparingly soluble **4** to form a Lansbury type of complex. This reduces the reactivity of the hydride and, therefore, a longer reaction period is required for the completion of the reduction.
(37) In initial attempts, peracids were successfully employed for dehydrogenation of **6**. Peracetic acid oxidation of **6** yielded only **5**, but trifluoroperacetic gave, besides **5**, a trace amount (<1%) of the corresponding *N*-oxide; *m*-chloroperbenzoic acid can cause complete *N*-oxide formation (cf. infra).
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(40) Perphthalic and peracetic (CH_3CO_2H–H_2O_2) acids were tried unsuccessfully. Trifluoroacetic acid (CF_3CO_2H–H_2O; 4 h reflux), however, gave a very low yield of *N*-oxide **9** as its trifluoroacetate salt.
(41) Presence of impurities can cause the color to be brown or dark brown.
(42) The reaction was observed to occur only slowly at room temperature (followed by NMR). After 70 h of reaction period 20–25% *N*-oxide **9** remained. However, the reaction was complete after 2 h on a steam bath. Also, a slight decarboxylation was observed during the heating when the nitrogen from the reaction vessel was bubbled through barium hydroxide solution.
(43) In attempts to improve the yield of the acetoxy derivative **10**, by employing different reaction conditions, the following observations were made: (a) The use of 2 equiv of acetic anhydride to *N*-oxide **9** (instead of 1:1) did not affect the yield of **10** significantly. (b) When the amount of *N*-oxide **9** in glacial acid exceeded more than 20% (w/v) a significant drop (10%) in the yield of **10** was observed. However, use of lower concentration (5%) did not affect the yield. (c) A very poor yield (9.5%) was obtained when an acetic acid solution of **9** was added to already heated acetic anhydride on a steam bath instead of at room temperature. (d) Also, a poor yield (9.2%) of **10** was obtained when the reaction was run according to a published procedure for 3-acetoxy-2,3-dihydro-1*H*-cyclopenta[*b*]quinoline. (e) A poor yield of **10** resulted when no acetic acid was used.
(44) The product **12** is quite stable if kept as a solution at a low temperature 0 °C or below.