greater excitation intensity. The area under the recorded output was calibrated before and after each run using a standard solution of α-naphthalene-d_1 whose quantum yield for exchange had been carefully determined using apparatus I.

Fluorescence Quenching. The apparatus for measuring fluorescence consisted of a high-pressure Hg light source focused through a Bausch and Lomb high-intensity grating monochromator and a Corning CS-7-54 visible filter. A 1-cm rectangular quartz cell was used, which was maintained at a desired temperature by submersion in a constant-temperature water bath. The fluorescence was monitored at right angles using a Jarrell-Ash 0.75-m, *f*/6.3 grating spectrometer.

Delayed Emission. Delayed fluorescence and excimer emission were observed upon direct excitation with the high-pressure Hg lamp with the aid of a phosphoroscope. The phosphoroscope consisted of two rapidly rotating chopper blades situated on the entrance and exit sides of the sample cell and offset sufficiently to completely suppress normal fluorescence. The emission was recorded using the 0.75-m spectrometer.

Degassing was achieved by repeated freeze–thaw cycles, and the observation of delayed emission was used as the criterion for oxygen removal. As many as 20 cycles were necessary in some cases to effect removal.

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On the Interaction of Electron Pairs at Peri Positions. Base-Catalyzed Hydrogen–Deuterium Exchange of Quinoline and 1,5-Naphthyridine

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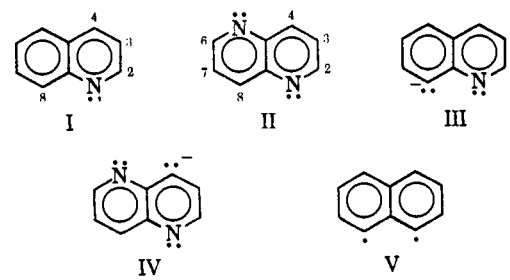
Abstract: Rate constants for hydrogen–deuterium exchange of quinoline and 1,5-naphthyridine in CH_3ONa–CH_3OD at 190.6° were obtained by an nmr method. Values for quinoline are 4.5×10^{-5} (H-2), 3.0×10^{-4} (H-3), 9.4×10^{-4} (H-4), and 4.5×10^{-5} (H-8) M^{-1} sec^{-1}. For 1,5-naphthyridine the values are 2.5×10^{-4} (H-2,6), 2.1×10^{-3} (H-3,7), and 9.2×10^{-3} (H-4,8) M^{-1} sec^{-1}. Isotope exchange is believed to take place by deprotonation of the substrates. H-3 and H-8 of quinoline have similar reactivities, and the H-4 to H-3 rate constant ratios are nearly the same for both compounds. Therefore, it is concluded that the effect of electron pair interactions on the rate of formation of a carbanion at a position peri to an annular nitrogen atom is not significantly different from the effect on a carbanion at a position meta to an annular nitrogen atom.

Recent molecular orbital calculations[1-3] and photoelectron spectra[4] indicate that the "unshared" electron pairs of the annular nitrogen atoms of diazabenzenes and diazanaphthalenes interact. Pair–pair interaction is not found to be limited to adjacent pairs as was once thought; widely separated pairs may also interact strongly. The interaction is transmitted both through space and through σ bonds, the latter mode of transmission being of major importance for pairs separated by large distances.

In view of these new results it becomes of interest to examine new systems and even to reconsider old results in order to seek chemical evidence of such interactions, particularly for widely separated electron pairs. At this infant stage in the search for chemical evidence of pair–pair interactions it is not yet clear what kinds of reactions will be sensitive to this effect and how large any effect will be. Many different systems will have to be examined for pair–pair repulsion effects before the chemical significance of this effect can be revealed.

We here consider the interaction of electron pairs at peri positions and employ base-catalyzed hydrogen–deuterium exchange as the chemical probe. Two molecules were examined, quinoline (I) and 1,5-naphthyridine (II). The reactivities of H-8 in I and of H-4 in II which are located in positions peri to an annular nitrogen atom are of special interest. It is expected that both these molecules will undergo H–D exchange by a mechanism involving cleavage of a CH bond to give carbanions such as III and IV where pair–pair interactions are possible at the peri positions.

Note that clear chemical evidence does exist for the interaction of electrons in peri positions in the case of aryne V. The evidence is found in the stereochemistry



I II III IV V

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of its cycloaddition products.[5] Indeed, the unusual chemistry of this intermediate played an important early role in the formulation of the concept that electrons in σ orbitals at nonadjacent positions may interact strongly.[2]

Results

Deuterodeprotonation of I and II in CH_3OD is catalyzed by CH_3ONa, but it is a pseudo-first-order reaction because only the hydrogen content of the substrate changes. The hydrogen content was measured by nmr.[6] Determination of rate constants for the hydrogen exchange reactions is complicated by reverse reactions, proteodedeuterations, because the deuterium content of the solvent is not "infinitely" large. This presents no real difficulty, however. A knowledge of the H–D content of a position at equilibrium exchange along with a knowledge of the amounts of exchangeable H and D in the solvent and substrate allows the observed rate constants to be corrected for the reverse reaction.[6,7] The amount of the two isotopes is known from the composition of the reaction mixture. The H–D content of a position at equilibrium was established in two ways. Experimental values were obtained in some cases. Where it was not practical to obtain an experimental value, owing to long reaction times or to complications resulting from other positions in the molecule undergoing exchange and thereby changing the composition of the solvent, equilibrium values were obtained by calculations. These calculations of mole fraction of H assume no equilibrium isotope effect is present. This assumption was shown to be valid in the case of II; calculated and experimental values agreed to within the limits of the nmr measurements, ~4%. The mole fraction of H present at equilibrium was always <15%. Since the equilibrium values are small, uncertainties in their estimation only result in small changes in rate constants.

An additional complication was present in the case of quinoline, signal overlap. The signal for H-3 overlapped part of the H-6 signal, even at 100 MHz. However, correction factors were applied to remove from integrations the unwanted additional peak areas; these factors were obtained from integrations of the proteo substrate. Additional information is given in the Experimental Section.

The relative chemical shifts of H-4 and H-8 of I are solvent dependent.[8] Consideration of coupling constants and reactivities in the exchange reactions allowed us to conclude that H-4 is at lower field than H-8. Other signal assignments are straightforward and are consistent with other reports.[8,9]

Second-order rate constants for exchange at the three nonequivalent positions of II and at positions 2, 3, 4, and 8 of I are given in Table I; they refer to reaction at a single position. The concentrations of CH_3ONa employed are low enough so that it is unnecessary to make corrections of the acidity function type.[6,10] A fivefold change in the CH_3ONa concentration results in no change in second-order rate constants for II, other than a small (<10%) random error.

Table I. Rate Constants for the Deuteration of 1,5-Naphthyridine and Quinoline in CH_3ONa–CH_3OD at 190.6° [a]

Compd	Position	M, CH_3ONa[b]	k_2, M^{-1} sec^{-1}
1,5-Naphthyridine[c]	2,6	0.0733	2.5×10^{-4}
	3,7		2.05×10^{-3}
	4,8		9.2×10^{-3}
	2,6	0.367	2.6×10^{-4}
	3,7		2.2×10^{-3}
	4,8		9.3×10^{-3}
Quinoline[d]	2	0.367	4.5×10^{-5}
	3		3.0×10^{-4}
	4		9.4×10^{-4}
	8		4.5×10^{-5}

[a] ±0.5°. [b] Concentrations corrected for thermal expansion. [c] 0.26 *M*. [d] 0.6 *M*.

The ratio of the second-order rate constants[11] for H-2,6, H-3,7, and H-4,8 of II at 190.6° is 1.0:8.1:35. For H-2, H-3, H-4, and H-8 of I under the same conditions the ratio is 1.0:6.7:21:1. By comparison, pyridine which undergoes H–D exchange under the same conditions shows a ratio of 1.0:8.4:12 for H-2,6, H-3,5, and H-4.[6] In these comparisons, that position of each substrate which undergoes H–D exchange at the slowest observed rate is taken as the rate standard for that molecule. Since the three compounds show the same reactivity pattern, it is likely that they react by a common mechanism. This is likely to be base-catalyzed deprotonation of a CH bond.[6]

A check on the results for quinoline is obtained by a comparison with the rate constants for H–D exchange of pyridine under the same conditions. The benzolog is expected to be slightly more reactive, just as naphthalene is slightly more reactive than benzene in hydrogen exchange reactions.[13,14] The H-2 ratio (quinoline to pyridine) is 1.45, H-3 is 1.15, and H-4 is 2.9. Those positions (H-2 and H-3) β to the benzene ring are activated less than that (H-4) α to the ring. The α:β ratio is 2.2 (the results for the two β positions are averaged). The α and β factors and the α:β ratio are similar to those reported for a comparison of naphthalene and benzene.[13,14] Hence the quinoline–pyridine results are self-consistent. Moreover, the mechanisms of deprotonation of the arenes and hetarenes are likely to be similar because the comparisons reveal such similar values.

Comparison of the reactivities of 1,5-naphthyridine and quinoline in the exchange reactions allows a rate factor to be calculated for an annular nitrogen atom. The second nitrogen atom of II activates H-4 by a factor of 9.8, H-3 by 7.0, and H-2 by 5.8. These rate factors are smaller than those resulting from a comparison of the reactivities of pyridine and the three

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(11) A value of 3 has been reported[12] for the D-3 to D-2 ratio for the proteodeuteration of quinoline in CH_3OK–CH_3OH at 180°.
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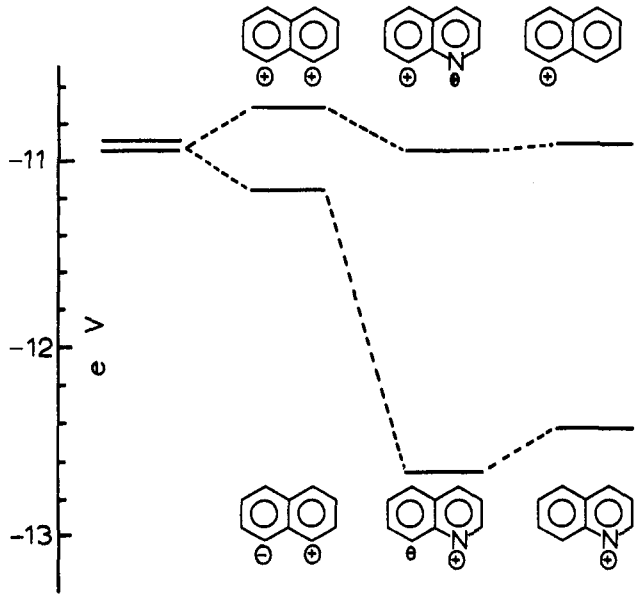
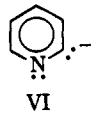


Figure 1. Correlation diagram showing the effect of a nitrogen atom on the interaction between peri orbitals.

diazines in H–D exchange reactions under the same conditions. The monocyclic compounds yield ortho (20), meta (270), and para (290) rate factors.[6] Hence the effect of a second nitrogen atom in the same ring as that undergoing reaction is greater than the effect of a second nitrogen present in an adjacent ring.

Discussion

Before the H–D exchange results for I and II are considered in terms of pair–pair interactions, it first must be established how the presence of such an effect may be discerned. This becomes clear from a consideration of the reactivity of pyridine in base-catalyzed H–D exchange reactions where pair–pair interactions are believed to have an influence.[3,6] The proton exchange reactions of pyridine are believed to take place by simple deprotonations to give intermediate carbanions such as VI.[6] Although the nitrogen atom in pyridine facil-



VI

itates H–D exchange, those positions (H-2,6) ortho to this atom are found to be less activated than those more removed. Thus, a position (H-2) ortho to the nitrogen is 8.4 times less reactive than a meta (H-3) position toward CH_3ONa–CH_3OD at 190.6.[6]

In the absence of special effects it was anticipated that an ortho would be at least 10^2 more reactive than a meta position. The pattern (ortho $\gg$ meta) follows from a consideration of the reactivities of a variety of aromatic compounds, carbocyclic[13] and heterocyclic,[15] in H–D exchange reactions which give rise to carbanionic intermediates. Clearly, the special effect operating at the ortho position is large, being at least a factor of 10^3. Note that the three diazines (diazabenzenes) show reactivity patterns similar to that in pyridine, and the effects of the two nitrogen atoms on all positions are additive.[6]

Position H-3 of I and of II will be employed as a rate standard to determine whether the interaction of peri orbitals gives rise to an unusual effect such as that found for the ortho positions in pyridine and the diazines. It should be noted that annelation is said not to significantly change the magnitudes of pair–pair interactions when the pairs are present in the same ring.[4] The effect of the nitrogen atom in I and II on an ortho (H-2) position is much the same as that in pyridine, the H-3 to H-2 rate constant ratio being 7–8 in the three cases.

Consider quinoline first. The number of σ bonds separating H-8 and H-3 from the activating nitrogen atom is the same and so the N–C distances must be about the same in both instances. Hence in the absence of special effects the reactivities of H-8 and of H-3 are expected to be about the same.[16] The observed H-8:H-3 rate constant ratio is only 1:6.7. This indicates that no important peri destabilizing effect is apparent.

Next consider 1,5-naphthyridine. The presence of a second nitrogen atom is expected and is found to have a net activating effect. In the absence of a special effect such as pair–pair interaction, the nitrogen atom in the adjacent ring is expected to activate position 4 more than position 3 but the difference in activation is not expected to be large. This conclusion follows from a consideration of the effects of substituents on the rates of formation of aryl anions.[13,15] It is observed that the H-4:H-3 rate constant ratio for II is 4.4:1. This value is similar to that (3.1:1) found for the same positions in quinoline where a peri effect cannot operate. Again the results indicate the absence of a significant peri destabilizing effect.

It should be emphasized that the comparisons employed above in no way lead to the conclusion that electron pairs in peri positions do not interact. The rate constant ratios provide a measure of differences in effects which include pair–pair interactions. Our chemical probe indicates that the effect of peri electron pairs on the reactivity of I and II in proton transfer reactions is not significantly different from that for electron pairs with a meta geometry such as that found for the reference (H-3) position.

Professor R. Gleiter has kindly provided us with the interaction diagram shown in Figure 1 which supports our findings. This diagram, based on extended Hückel theory calculations, provides an understanding of the interactions between electrons in peri orbitals. Moving from left to right across the diagram, two noninter-

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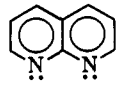
(16) A closer analysis of the H-8:H-3 ratio in I would note that H-8 is α to a ring while H-3 is β. Correcting for this difference would decrease the ratio by 2.2, the factor obtained from a comparison of pyridine and quinoline. Using an ion–dipole model to measure through space effects (field effects) to further correct the observed ratio, it is necessary to account for differences in dielectric constants inside and outside the quinoline molecule as well as differences in ion–dipole angles.[17] The net effect of all these corrections is to make the H-8:H-3 ratio even more similar.

(17) For recent discussions, see, for example, A. Streitwieser, Jr., and R. G. Lawler, *J. Amer. Chem. Soc.*, **87**, 5388 (1965); A. Streitwieser, Jr., and F. Mares, *ibid.*, **90**, 644 (1968); W. Adcock and M. J. S. Dewar, *ibid.*, **89**, 379 (1967); C. L. Liotta, W. F. Fisher, G. H. Greene, Jr., and B. L. Joyner, *ibid.*, **94**, 4891 (1972); R. Golden and L. M. Stock, *ibid.*, **94**, 3080 (1972); G. R. Haugen and S. W. Benson, *J. Phys. Chem.*, **74**, 1607 (1970).

acting carbon orbitals are indicated first. On interacting, these orbitals split in energy by 0.44 eV. Next, one of the carbon orbitals is replaced by a nitrogen orbital. This substitution, involving an atom more electronegative than carbon, results in a lowering of the energies of the two orbitals, the lower being influenced more because the nitrogen orbital makes a larger contribution to this molecular orbital. The splitting now is 1.70 eV. Finally, the energies of noninteracting orbitals for the naphthalene anion and quinoline are shown; they are separated by 1.51 eV. The key point of the diagram is this. There is a large separation in energy between the two peri orbitals for the 8-quinolyl anion. But this large difference is due only in small part (0.19 eV) to the intramolecular interaction between carbon and nitrogen orbitals. Most of the splitting (1.51 eV) reflects the inherent difference in energy between noninteracting carbon and nitrogen orbitals. A similar interaction diagram may be constructed for ortho orbitals. But in the case of the 2-quinolyl anion, orbital interaction makes a larger contribution to the splitting than in the case of the 8-quinolyl anion.

It is entirely possible that other chemical probes may uncover significant peri effects. There is evidence that 1,8-naphthyridine (VII) shows an enhanced nucleophilicity toward saturated carbon.[18] It is worth considering that the enhanced reactivity is associated with the interaction of peri electron pairs. It remains to be determined what kinds of reactions will be responsive to pair–pair effects and how large these effects will be.[19]



VII

Experimental Section

Reagents. CH_3OD–CH_3ONa was prepared and standardized as before.[6] Quinoline was heated at reflux over zinc dust and distilled at reduced pressure under nitrogen. 1,5-Naphthyridine hydrate (Aldrich Chemical Co.) was sublimed and recrystallized from hexane to give a solid which was stored over phosphorus pentoxide. The initial H content of the methanol-*O-d* was 2–6 mol %. The ^{13}C side-bands of methanol were employed as an internal standard to calculate the H content of the methanol-*O-d*.

Kinetics. The previously described method and integrated rate equation were employed.[6] *tert*-Butyl alcohol served as an nmr internal standard. A Varian A60-A spectrometer was employed in 1,5-naphthyridine studies; a Varian XL-100 was used to study quinoline.

The methoxide ion concentration was monitored by nmr throughout the exchange reactions. The method relies on the fact that the chemical shift of OH is a sensitive measure of the methoxide ion concentration.[20] The difference in shifts between OH of the solvent and CH of *tert*-butyl alcohol internal standard was observed. No change in this difference was found in the case of 1,5-naphthyridine. Even with the less reactive substrate quinoline, no significant change was apparent; a quinoline sample containing 0.367 *M* CH_3ONa–CH_3OD was heated at 190.6° for 1488 min. Known densities of methanol were employed to correct concentrations for thermal expansion.[21]

1,5-Naphthyridine. The stability of 1,5-naphthyridine toward sodium methoxide was demonstrated in a control run by heating this material at 190.6° in 1 *M* CH_3ONa–CH_3OH for 1150 min, conditions surpassing those used in kinetic studies employing deuterated methanol. No change in the substrate could be detected by nmr analysis. The ratio of substrate to *tert*-butyl alcohol internal standard remained constant. The signal assignments (methanol) are τ 1.06 (H-2,5), 2.22 (H-3,6), and 1.57 (H-4,7).

At equilibrium H–D exchange, H still remains in the substrate. Control runs were carried out to determine whether there is an equilibrium isotope effect for H–D exchange. For example, when a 1,5-naphthyridine solution was heated (1300 min, 190.6°, 0.367 *M* CH_3ONa) so that all positions were at equilibrium, each position contained 13% H. Using eq 1, which assumes no equilibrium isotope effect, it was calculated that each position should contain 14% H at equilibrium. The good agreement between observed and calculated values indicates there is no important equilibrium isotope effect.

$$He = \frac{[H]}{[H] + [D]} = \frac{[CH_3OH] + y[Het]}{[CH_3OH] + [CH_3OD] + y[Het]} \quad (1)$$

He in eq 1 is the fractional amount of hydrogen present in the heterocycle (or solvent) when the six (y) positions of 1,5-naphthyridine are at equilibrium exchange.

In kinetic runs, the amount of hydrogen in the 4,8 positions, the most reactive sites of 1,5-naphthyridine, was observed to go through a minimum value and then increase as other positions underwent exchange. This minimum value was employed in calculating rate constants by the reported method.[6] This value was also used as the equilibrium exchange value to calculate rate constants for the 3,7 positions. In principle, different equilibrium exchange values should be used in calculating rate constants for positions 4,8 and 3,7, but under the conditions employed these different values are within the uncertainty of the nmr measurements, about ±4%. Moreover, the equilibrium values employed are very similar to those calculated using eq 1. For positions 2,6 of 1,5-naphthyridine the equilibrium exchange value used in obtaining a rate constant was that calculated using eq 1.

Kinetic plots which correct for approach to equilibrium hydrogen exchange were linear over 2–4 half-lives. This linearity testifies to the validity of the kinetic treatment employed.

Quinoline. Rates were corrected for approach to equilibrium hydrogen exchange using calculated, eq 1, "infinity" values. The initial H content of the methanol was 1.3%. In eq 1, y equals 1 for H-4 and 2 for H-3. For H-2 and H-8 y has the value 5, since some exchange also occurred in the H-5,6,7 multiplet. Evidence for exchange in the H-5,6,7 multiplet was found in diminished areas and spin decoupling to H-8. There was no indication of any kind of decomposition during the H–D exchange run. The reaction mixture remained clear and colorless throughout. Signal assignments (methanol) are τ 1.32 (H-2), 1.88 (H-4), 2.08 (H-8), and 2.66 (H-3).

Kinetic data for the 4 position were treated in the usual way. Analysis was more difficult for H-3 since even at 100 MHz the quartet of H-3 overlaps part of the H-6 multiplet. Rate constants for H-3 were obtained by treating the data in two ways; (a) dealt with the area under three peaks of the H-3 quartet, and (b) dealt with the area of the entire H-3 multiplet and also part of the H-6 multiplet. The three peaks for H-3 at the highest field contain only a small fraction of the H-6 signal, as evidenced by a small peak among these three. The three peaks plus the small fourth peak corresponded in area to about 0.9 of one proton. This fractional area was plotted in the usual way, correcting for approach to equilibrium hydrogen exchange. The reaction was followed for slightly more than 2 half-lives and gave a linear plot. In (b) the areas considered contained about 1.5 protons, owing to the presence of some H-6. After 0.5 of a proton was subtracted from this combined area, the resultant quantity was plotted in the usual way. The plot was linear. The rate constants obtained by the two methods were identical. All plots were linear for at least 2 half-lives.

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