sociates Model A-56/60-A spectrometer equipped with a variable-temperature probe.

Cmr spectra were obtained on a Varian Associates XL-100 spectrometer equipped with a broad-band decoupler, and variable temperature probe. The instrument operates at 25.2 MHz for carbon-13 and is interfaced with a Varian 620L computer. The combined system was operated in the pulse Fourier transform mode, employing a Varian Fourier transform accessory. Typically 3000-5000 pulses, each of width 20-35 μsec, needed to be accumulated in order to give a satisfactory signal-to-noise ratio for all signals of interest. Field-frequency stabilization was maintained by locking on the fluorine-19 external sample of fluorobenzene. Chemical shifts were measured from the carbon-13 signal of 5% carbon-13 enriched tetramethylsilane in a 1.75-mm capillary held concentrically inside the standard 12-mm sample tube.

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Electron Spin Resonance Study of Heterocycles. V. Quinolyl Radicals[1]

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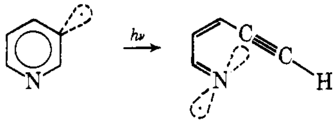
Abstract: 2-, 3-, and 4-quinolyl and 4-isoquinolyl radicals were generated in argon matrices, and their esr spectra were examined. All are found to be σ radicals, and the observed coupling constants are in good agreement with those calculated by INDO molecular orbital theory. Unlike pyridyl radicals, they are stable against uv irradiation.

Pyridyl radicals (2-, 3-, and 4-) generated in argon matrices have been all found to undergo a ring-rupture rearrangement when irradiated with uv light,[2] *e.g.*



(1)

We report here the results of matrix-isolation esr studies of 2-, 3-, and 4-quinolyl and 4-isoquinolyl radicals. All of these radicals were found to be σ radicals as in the case of pyridyls. However, unlike pyridyl radicals, they were proved to be stable against uv irradiation. The stability is attributed to the increased aromaticity of the quinolyl systems. The resolved hyperfine structures of these radicals were readily identified with those of the corresponding protons of pyridyl radicals.[2] It indicates little effect of the fused benzene ring upon the nature of the semifilled orbitals of the quinolyl and isoquinolyl radicals.

Experimental Section

Detailed descriptions of the apparatus and the method which would permit generation of molecular anions within a rare gas matrix at ~4°K and the esr investigation of the resulting anions have been presented previously.[3] In the present series of experiments, desired quinolyl radicals were generated by photolysis of the anions of quinolyl chlorides (or bromides) produced by this technique.

Argon matrices were prepared in which quinolyl halides (electron acceptors) were trapped together with Na atoms (electron donors), the composition being roughly 1000:10:1 for argon atoms, the halide molecules, and the Na atoms, respectively. Irradiation of these matrices with "red light" (λ >5800 Å) resulted in the disappearance of the esr signals due to Na atoms, and the appearance of a broad singlet signal ($\Delta H_{\text{peak-to-peak}} \simeq 20$ G) at the position corresponding to $g = 2.00$. In each case, the photoinduced broad singlet was assigned to the anions of the quinolyl halide. Subsequent irradiation of the matrix with more energetic "yellow light" (λ >5000 Å) caused the conversion of the singlet into a spectrum consisting of several hyperfine components symmetrically spaced about the position of $g = 2.00$. The final spectrum was readily recognized as that of the quinolyl (or isoquinolyl) radicals resulting from the cleavage of the C–Cl (or C–Br) bond. Let QX denote the quinolyl halide. The photoinduced reaction sequence described above can then be summarized as follows:

$$\begin{tikzcd} \mathrm{QX} + \mathrm{Na} \arrow[r, "h\nu", "\lambda > 5800\ \text{Å}"'] & (\mathrm{QX})^- + \mathrm{Na}^+ \arrow[d, "h\nu", "\lambda > 5000\ \text{Å}"'] \\ & \mathrm{Q}\cdot + \mathrm{X}^-\cdot \end{tikzcd} \qquad (2)$$

Quinolyl halides (2-chloroquinoline, 2-chloro-4-methylquinoline, 3-bromoquinoline, 4-chloroquinoline, and 4-bromoisoquinoline) were obtained from Aldrich Chemical Co. and were used as received. An Oriel xenon-mercury high-pressure arc lamp (1 kW) equipped with appropriate sharp cut-off filters was used for the irradiation of the matrices. All the esr spectra were obtained while

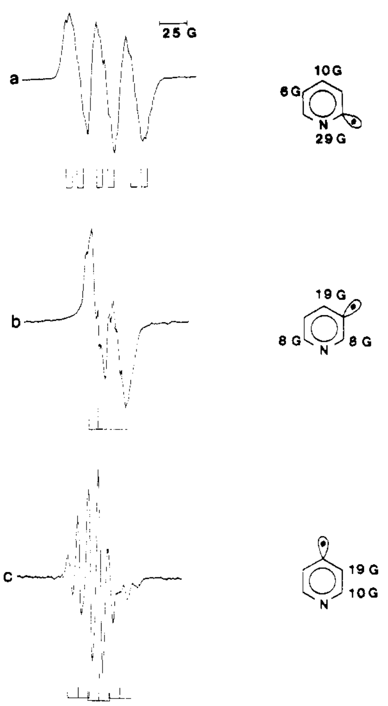


Figure 1. Esr spectra and assigned isotropic coupling constants of pyridyl radicals.

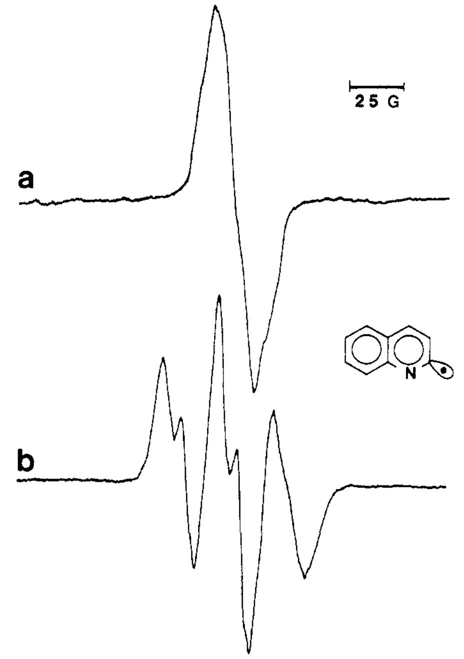


Figure 2. Esr spectra observed when an argon matrix containing 2-chloroquinoline and Na was irradiated: (a) with red light (λ >5800 Å); (b) with yellow light (λ >5000 Å).

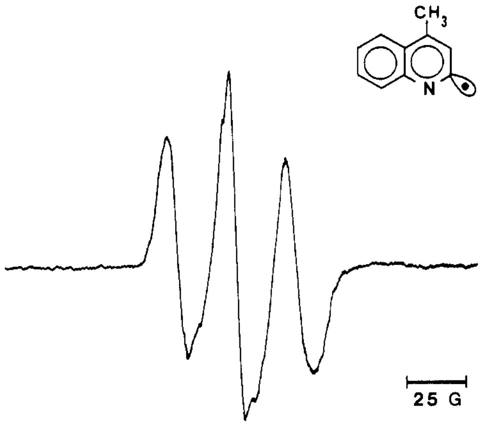


Figure 3. Esr spectrum of 4-methyl-2-quinolyl generated in an argon matrix.

the matrix was maintained at ~4°K, and the esr spectrometer frequency locked to the sample cavity was 9.430 GHz.

Spectra and Assignments

Pyridyl Radicals. Shown in Figure 1 are the esr spectra of pyridyl radicals generated and observed in argon matrices. They have already been analyzed in detail.[2] Let us discuss briefly, however, the salient features of these spectra in order to facilitate the analyses and the assignments of the spectra exhibited by quinolyl radicals.

The esr spectrum of 2-pyridyl is recognized as a triplet of doublets of doublets with the respective spacings of 29, 10, and 6 G. As indicated in the figure, the pattern is attributed to the hyperfine structure (hfs) due to the ^{14}N nucleus and the protons at 4 and 5.

The spectrum of 3-pyridyl is a doublet of triplets. The doublet (A_{iso} = 19 G) is assigned to the proton at 4 and the triplet to the protons 2 and 6 having the accidentally degenerate coupling constant of 8 G.

The spectrum of 4-pyridyl has the expected triplet-of-triplet pattern. The larger triplet (A_{iso} = 19 G) is due to the protons at 3 and 5 and the smaller (A_{iso} = 10 G) to the protons at 2 and 6.

2-Quinolyl Radicals. Figure 2a shows the spectrum obtained when an argon matrix containing 2-chloroquinoline and Na atoms was irradiated with red light. The spectrum is assigned to the anions of 2-chloroquinoline. The peak-to-peak separation of ~20 G is consistent with the expected π state of the anion, the extra electron being accommodated in the lowest unoccupied π orbital of the neutral molecule. As mentioned earlier, the spectra with similar appearance were obtained from the argon matrices containing other quinolyl halides and Na atoms also. Since these spectra reveal little other information, they shall not be discussed any further.

Figure 2b shows the spectrum observed when the matrix showing the spectrum of 2-chloroquinoline anions (Figure 2a) was irradiated with yellow light for 30 min. If one asserts that the fusion of a benzene ring to a pyridyl radical has little effect upon the localized, semifilled σ orbital of the radical, one would predict from the known assignment of 2-pyridyl (Figure 1a) that the spectrum of 2-quinolyl should have a triplet-of-doublet pattern with the respective spacings of ~29 and ~10 G. The spectral pattern clearly discernible in Figure 2b is in close agreement with this prediction. It is, therefore, assigned to the 2-quinolyl radicals. They must result from the photolysis of the anion radicals as shown in eq 2. The isotropic hfs constants determined from the spectrum are shown in Figure 7.

Bower, *et al.*,[4] showed by deuterium substitution that the proton 4 in 2-pyridyl indeed has the largest proton coupling constant. Shown in Figure 3 is the spectrum of 4-methyl-2-quinolyl radicals generated in an argon matrix by photolysis of the anions of 4-methyl-2-chloroquinoline. The simpler triplet pattern (A_{iso} = 26 G) observed here is a strong substantiation of the assignment that the proton 4 in 2-quinolyl also has the largest proton coupling constant.

3-Quinolyl Radicals. Figure 4a shows the spectrum of 3-quinolyl radicals generated in an argon matrix from the anions of 3-bromoquinoline. It has a doublet-of-doublet pattern as would be predicted from the assignment of 3-pyridyl (Figure 1b). The larger doublet with the spacing of 19 G is thus ascribed to the proton 4 and the smaller doublet with the spacing of 6 G to the proton 2. The broadness and the

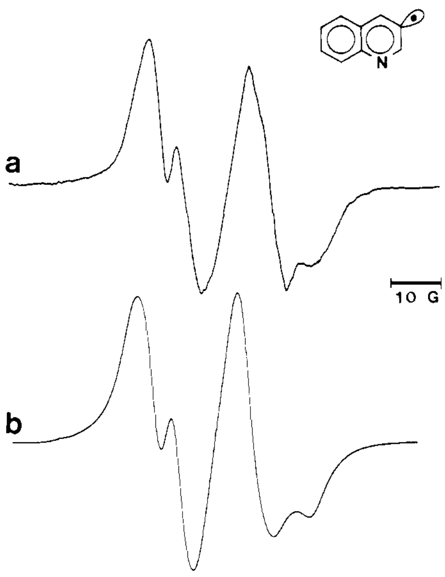


Figure 4. (a) Esr spectrum of 3-quinolyl generated in an argon matrix. (b) A computer-simulated spectrum of 3-quinolyl (see text).

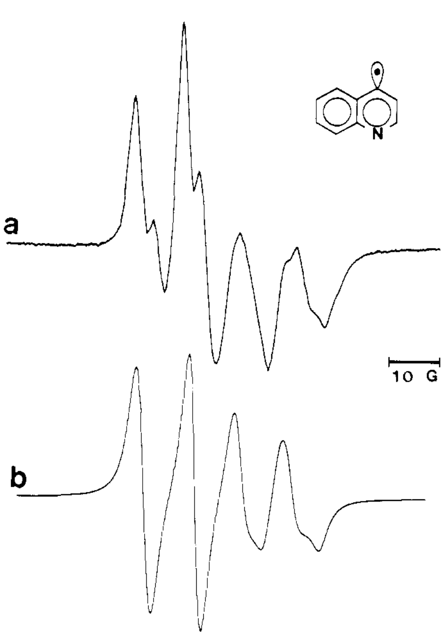


Figure 5. (a) Esr spectrum of 4-quinolyl generated in an argon matrix. (b) A computer-simulated spectrum of 4-quinolyl (see text).

asymmetry of the overall pattern are due to the anisotropy of the hyperfine coupling tensors and that of the g tensor as shall be shown later.

4-Quinolyl Radicals. The esr spectrum of 4-pyridyl (Figure 1c) suggests that the spectrum of 4-quinolyl should appear as a doublet of doublets. 4-Quinolyl radicals generated in an argon matrix indeed showed such a pattern (Figure 5a). The larger doublet of 4-quinolyl (A_{iso} = 20 G) is therefore assigned to the proton 3 and the smaller doublet (A_{iso} = 10 G) to the proton 2. A closer inspection of the spectrum indicates an additional, partially resolved doublet feature of ~3 G. Based upon the result of the semiempirical SCF molecular orbital calculation, INDO,[5] the latter structure is assigned to the proton 8. Again the superficial inequality in the apparent intensities of the major components is the result of the anisotropies of the g tensor and the hyperfine coupling tensors.

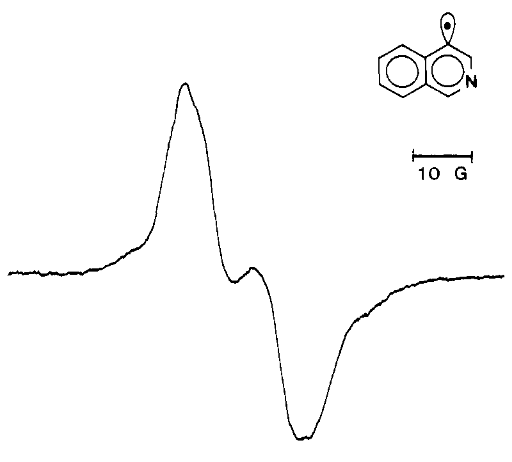


Figure 6. Esr spectrum of 4-isoquinolyl generated in an argon matrix.

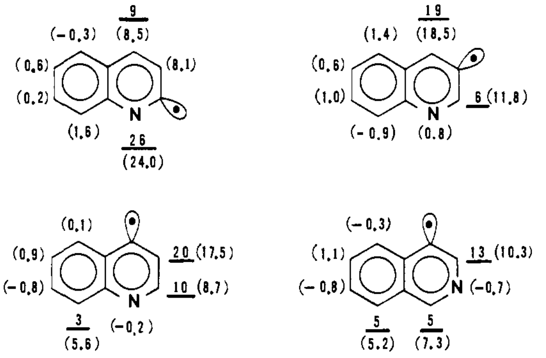
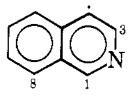


Figure 7. Observed (underlined) and calculated (in parentheses) isotropic coupling constants (given in gauss) to the H and N nuclei of quinolyl radicals. The uncertainties of the observed values are ±1 G.

4-Isoquinolyl Radicals. According to the assignment of 3-pyridyl (Figure 1b), the spectrum of 4-isoquinolyl is expected to have a triplet or a doublet-of-doublet pattern arising from the couplings to the protons 1 and 3. Figure 6 shows the spectrum of 4-isoquinolyl generated from the anions of 4-bromoisoquinoline in an argon matrix. The resolved doublet with the spacing of 13 G is assigned to the proton 3. The unusual width and shape of the spectrum are suspected to arise from the couplings of ~5 G to both the protons 1 and 8. The latter postulate is supported by the result of INDO calculation.



2-, 3-, and 4-quinolyl and 4-isoquinolyl radicals discussed above were all concluded to be stable against uv irradiation. No further change in the esr spectrum was noted when the argon matrices containing these radicals were irradiated with more energetic light (5000 Å > λ > 2500 Å).

Discussions

The isotropic coupling constants assessed from the observed spectra are compiled and shown in Figure 7. The numbers given in parentheses are the isotropic coupling constants calculated by INDO molecular orbital theory[5] using the relation $A_{\mathrm{iso}} = Q\rho_i$, where ρ_i represents the spin density at the valance s orbital of the ith atom. As for the values of Q, 508 and 552 G were used for the hydrogen 1s and the nitrogen 2s orbitals, respectively. The structural parameters used for the calculations were $r_{\mathrm{N-C}}$ = 1.34, $r_{\mathrm{C-C}}$ = 1.39, and $r_{\mathrm{C-H}}$ = 1.08 Å. The agreement between the observed and the calculated values is quite reasonable.

As in the case of 2-pyridyl, the substantial and essentially isotropic coupling constant of 26 G to ^{14}N of 2-quinolyl is an evidence for the existence of a "benzyne" type interaction between the broken, nonbonding σ orbital at C-2 and the lone-pair orbital of the nitrogen. The interaction must indeed be significant since nitrogen has a greater electronegativity, and the unpaired electron must settle for the antibonding combination of the two orbitals. The isotropic coupling constant to ^{14}N in NO_2, for example, is 53 G,[6] although it cannot be compared directly because of the difference in the hybridization of nitrogen.

It is curious that, in both 2-pyridyl and 2-quinolyl, the proton 4 should possess a larger hyperfine coupling constant than that of the proton 3. The isotropic coupling constants to the ortho and meta protons of phenyl radicals have been shown to be 17.4 and 5.9 G, respectively.[7] Also curious is the large difference between the coupling constants to the protons 2 and 4 in both 3-pyridyl and 3-quinolyl radicals. Qualitatively these features can be attributed to the electronegativity of nitrogen. The increased negativity should produce polarization of the electron density of the filled orbitals toward the nitrogen end and hence the flow of the electron in the semifilled orbital toward the opposite end.

In σ radicals of the type studied here, the isotropic part of the hyperfine coupling tensor to a proton is relatively large compared with its dipolar or anisotropic part. The anisotropy is not insignificant, however. The broadness and the asymmetry of the overall pattern particularly evident in Figures 4a and 5a, for example, are due to the interplay of the anisotropies of the g tensor and the hyperfine coupling tensors. Shown in Figures 4b and 5b are computer-simulated spectra of 3- and 4-quinolyl radicals, taking into account only the g tensor and the coupling tensors to the ortho and meta protons, and assuming that their g tensors and the anisotropic parts of the coupling tensors are the same as those determined for the phenyl radicals.[7] The latter assumptions are justified since the INDO calculations show only a small difference between the semifilled orbitals of the phenyl and 3- and 4-quinolyl radicals. The overall asymmetric patterns observed in the actual spectra are clearly indicated by the simulated spectra.

In our study of pyridyl radicals,[2] it was found that irradiation of argon matrices containing pyridyl halides and Na atoms result in the immediate formation of pyridyl radicals. It was surmised that the halide anions dissociate spontaneously from the pyridyl halide anions.

$$[PX]^- \longrightarrow P\cdot + X^- \qquad (3)$$

The facility with which reaction 3 proceeds may be inferred from the energy difference $\Delta E = E_{C-X} - \Delta E_{EA}$, where E_{C-X} represents the dissociation energy of the C-X bond, and ΔE_{EA} is the difference between the electron affinities of X· and PX. The C-Cl bond energy, for example, is 3.4 eV, while the electron affinity of Cl· is ~3.8 eV.[8] The spontaneous dissociation of the anion is, therefore, expected only if the electron affinity of pyridyl chloride is less than 0.4 eV. We are thus led to conclude that, while the electron affinity of pyridyl chloride is less than 0.4 eV, that of quinolyl chloride is greater. The electron affinities of these molecules are not known. One might note, however, that the values reported for benzene and naphthalene are −0.54 and +0.65 eV, respectively.[8] The advantage of generating quinolyl radicals by way of quinolyl halide anions can still be appreciated since the energy required for the C-X bond scission is lessened by ΔE_{EA}. The C-Cl bond of neutral quinolyl chloride cannot be photolyzed even by uv light (λ 3650 Å).

It is interesting that quinolyl radicals are stable against uv irradiation and do not undergo a ring-rupture process similar to that observed with pyridyl radicals. The $n_N \rightarrow \pi^*$ transition, an excitation of an electron from the nitrogen nonbonding orbital to an antibonding π^* orbital, was proposed to be the initial step toward the observed ring rupture of pyridyl radicals.[2] The increased stability of the quinolyl radicals must result from the increased aromaticity due to the fused ring. The π^* orbitals delocalized over a larger aromatic system would be more stable and less antibonding with respect to individual skeletal bonds.

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