Determination of the Amino and Imino Tautomer Structures of α-Quinolylamines by Analysis of Proton Magnetic Resonance Spectra

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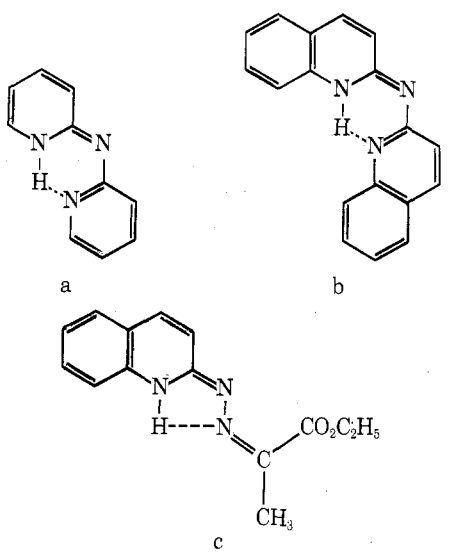
The ^{1}H NMR spectra of a series of α-quinolylhydrazones which have been isolated in the α-amino and the α-imino forms are compared. Chemical shift data of the exocyclic N–H, the azomethine C–H, and the salicylidine O–H of the amino tautomers are used to deduce the planarity of the exocyclic amino group which bridges the two π systems of the quinoline nucleus and the salicylaldimine moiety. Quinoline proton assignments in these α-amino compounds are also made with the help of 300-MHz spectra. Likewise, the ^{1}H NMR spectra of the α-imino tautomers are analyzed. Characteristic differences of (1) δN–H, (2) $J_{3,4}$ of the heterocycle, and (3) δH-8 of the quinoline nucleus are useful in determining the α-amino and α-imino tautomer structures of the α-quinolylamines.

Prototropic tautomerization of α- and γ-heteroaromatic amines to the corresponding imino forms has long been a subject of lively interest.[1] The traditional working hypothesis[1] that these imino forms are the rare tautomers is corroborated by a recent SCF MO calculation showing that the free energy barrier for isomerization is 15 kcal mol^{-1} for α-aminopyridine.[2] However, there are no lack of challenges to this view of the imino form. Thus, the broadening of the cytosine H-5 resonance observed in the ^{1}H NMR spectrum of cytosine was attributed to the presence of 15 ± 3% of the abnormal imino form,[3] but this conclusion was later retracted because the line broadening was a spurious observation.[4] While studies of the acid dissociation constants of α- and γ-aminopyridine have indicated[5] that the equilibrium constants for imino ⇄ amino forms are ca. 200 000 and 2000 respectively, a similar study of the dissociation constant of α-aminoquinoline has led to exactly the opposite conclusion, viz., α-aminoquinoline appears to exist in solution predominantly in the imino form.[6] In one ^{1}H NMR study of γ-aminoquinoline,[7] the coupling constant $J_{2,3}$ = 8 Hz was assigned to the H-2 and H-3 olefinic coupling of the γ-imino structure. This was disputed later[8] on the ground that δH-3 of 2-methyl-4-aminoquinoline at 6.50 ppm is similar to δH-3 (6.56) of 2-methyl-4-dimethylaminoquinoline but dissimilar to δH-3 (5.79) of 1,2-dimethyl-4-iminoquinoline. These contradicting and often precarious conclusions point to the need of isolating the imino tautomers for characterization under conditions which would disallow equilibration with the amino forms. Thus, in the special cases where the imino forms are chelated as in a, b, and c of Scheme I, the imino structures are more reassuring. The evidences advanced are (1) $\nu_{C=N}$ 1650 cm^{-1} for a,[9] (2) uv spectrum of b compatible with 2-(*N*-quinolylamino-1-ethyl)-1-ethylquinolinium iodide,[10] and (3) a broad singlet at δ 10.2 ascribed to the hydrogen bonded N hydrogen of c.[11] However, there has not been a comparison of a series of compounds in both the amino and imino forms under nonequilibrating conditions to decipher their major physical characteristics. In our study[12] of the photochromism of salicylaldehyde α-quinolylhydrazones (Scheme II), we have prepared a series of α-quinolylhydrazones in both the amino and the imino forms. We have now characterized these isomeric structures by the ^{1}H NMR method and found that they are distinguishable by means of (1) the chemical shift of the N hydrogen, (2) the coupling constant of H-3 and H-4 of the quinoline ring, and (3) the change in chemical shifts of the quinoline 8 hydrogen. This paper appears to be the first detailed comparative study of the ^{1}H NMR characteristics of tautomeric heteroaromatic amines in their amino and imino forms.

Results and Discussion

Planarity of the Exocyclic Amino Group. The resonances of N, O, and azomethine hydrogens in the α-quinolylhydrazones shown in Table I permit the deduction of the electronic and stereochemical nature of the amino hydrogen. These absorptions are readily recognizable. The former two signals appear as a broad singlet in Me_2SO-d_6 which readily exchange in D_2O. The azomethine proton appears as a sharp singlet at lower field from the aromatic region. Using salicylaldehyde phenylhydrazone (**2**) as a point of departure, the deshielding effect of the quinoline ring as opposed to the benzene ring, viz., Δδ **5,2** is found to be additive of the shift due to both the ring nitrogen, Δδ **3,2**, and the fused benzene ring,

Scheme I



Scheme II

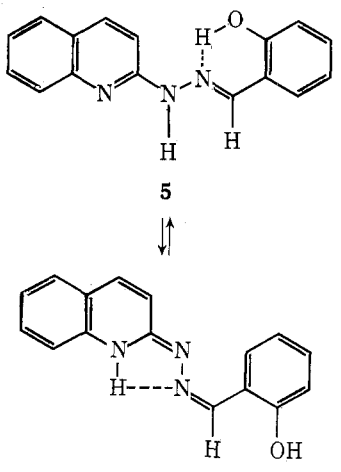


Table I. Comparison of ^{1}H NMR Spectra of α-Quinolylhydrazones and Derivatives in the Amino Form[a]

No.	Compd[b]	Chemical shift, δ			Compd	Comparison (Δδ)		
		N–H	O–H	N=C–H		N–H	O–H	N=C–H
1	Ph—NH—N=CH—C_6H_5	9.97		7.62				
2	Ph—NH—N=CH—C_6H_4—2—OH	10.43	10.70	8.27	**2,1**	0.46		0.65
3	Py—NH—N=CH—C_6H_4—2—OH	10.73	10.73	8.35	**3,2**	0.30	0.03	0.08
4	Py—CH_2—N=CH—C_6H_4—2—OH		12.27	8.92	**4,3**		1.54	0.57
5	Q—NH—N=CH—C_6H_4—2—OH	11.10	11.10	8.50	**5,2**	0.67	0.40	0.23
					5,3	0.37	0.37	0.15
6	Q—NH—N=CH—C_6H_5	10.97		8.33	**6,1**	1.00		0.71
					5,6	0.13		0.17
7	Q^3—NH—N=CH—C_6H_4—2—OH	10.75	11.12	8.62	**5,7**	0.35	−0.02	−0.12
8	Q—NH—N=CMe—C_6H_4—2—OH	10.58	13.43		**5,8**	0.52	−2.33	

[a] 60-MHz spectra, 1 M in Me_2SO-d_6. [b] Ph = phenyl, Q = 2-quinolyl, Q^3 = 3-quinolyl, Py = 2-pyridyl.

Table II. Quinoline Proton Assignments of α-Quinolylhydrazones and Derivatives in the Amino Form

No.	Compd	Chemical shift, δ						$J_{3,4}$, Hz
		H–3	H–4	H–5	H–6	H–7	H–8	
9	Quinoline[a,b]	7.27	8.00	7.69	7.44	7.62	8.06	8.3
10	2-Aminoquinoline[c]	6.90	7.90	7.48–7.80	7.17	7.51	7.48–7.80	8.8
11	2,7-Dimethylquinoline[d]	7.06	7.81	7.49	7.16		7.68	
5	Q—NH—N=CH—C_6H_4—2—OH[e]	6.841	8.100	7.604 or 7.537	7.263–7.150	7.604 or 7.537	7.712	8.5
12	Q—NH—N=CH—C_6H_4—2—OCH_3[e]	7.000	8.091	7.580	7.303–7.193	7.544–7.490	7.700	9.0
13	Q—NH—N=CH—C_6H_2—2—OH—4,6-diOMe[f,g]	7.280	7.983	7.620	7.308	7.581	7.674	8.0
14	Q—NH—N=CH—C_6H_2—2—OH—3,6-diMe[h,i]	7.15	8.30	7.95–7.37	7.95–7.37	7.95–7.37	7.95–7.37	8.5

[a] See ref 14. [b] H–2 observed at δ 8.81. [c] "Sadtler Indices", Sadtler Research Laboratories, Philadelphia, Pa., 1967, Spectrum No. 6041. [d] R. Pastor, J. Musso, and A. Cambon, *Bull. Soc. Chim. Fr.*, 3009 (1973). [e] 300-MHz spectrum, 1 M in Me_2SO-d_6. [f] 300-MHz spectrum, 1 M in $CDCl_3$. [g] The chemical shifts for N–H, O–H, N=C–H (1 M in Me_2SO-d_6) are respectively 10.83, 10.83, 8.53. [h] 60-MHz spectrum, 1 M in Me_2SO-d_6. [i] The chemical shifts for N–H, OH, N=CH are respectively 11.50, 12.10, 8.65.

Δδ **5,3**. This additive effect operates for all the three hydrogens, although the deshielding by the quinoline ring is most pronounced at the amino hydrogen site. Hence, considerable conjugation of the amino lone pair electrons with the ring must exist. This observation is substantiated by the higher field N-hydrogen absorption of the isomeric 3-quinolylhydrazone **7**. Here the upfield shift due to the loss of the α-nitrogen effect, Δδ **5,7**, is comparable to that between the pyridyl and phenyl hydrazone, Δδ **3,2**. The phenolic signal merges with the amino hydrogen of pyridyl and quinolyl hydrazones **3** and **5** as one broad singlet. However, the phenylhydrazone **2** and 3-quinolylhydrazone **7** show two separate singlets for these heteroatom hydrogens. The lower field of the two is attributed to the phenolic group in view of the well-known chelation of salicylaldimines. Such chelation imposes a positive character on the azomethine carbon, hence the extent of chelation is indicated by the shift of the azomethine hydrogen to lower field, e.g., Δδ **2,1**. In this respect, Δδ **5,6** being only 23% of that of Δδ **2,1** denotes much weaker chelation strength, a result of decreased azomethine nitrogen basicity via conjugation with the inductively withdrawing quinoline system. When the azomethine hydrogen is replaced by a methyl, chelation is enhanced as displayed by the acetophenone quinolylhydrazone **8** where δOH is shifted 2.33 ppm downfield from that in **5**. That the salicylaldimine chelation is sensitive to inductive effects is also shown by Δδ **4,3**. Here, replacement of the exocyclic amino group by the methylene has shifted the phenolic OH downfield by 1.54 ppm. Since the quinoline ring exerts pronounced deshielding effect on the amino hydrogen and the salicylaldimine chelation is progressively weakened by the attachment of the hydrazone nitrogen and the quinoline ring, it is probable that the exocyclic amino nitrogen is sp^2 hybridized and planar, thereby bridging the two π systems of the quinoline nucleus and the salicylaldimine moiety.

Quinoline Proton Assignments in the α-Amino Tautomers. The ^{1}H NMR spectrum of quinoline **9** has been studied extensively.[13,14] The chemical shifts of the ring hydrogens have been assigned and, with the exception of H-8, have been correlated with the charge density on the respective carbon atoms calculated by the extended Huckel method.[13] The deshielding experienced by H-8 relative to its calculated chemical shift has been ascribed to the proximity of the quinoline nitrogen lone pair.[13] The lowest field resonance is assigned to H-2 followed by H-8 and H-4. Placing a substituent on C-2 has a marked effect upon the chemical shifts of H-3, H-4, and H-8. In the case of 2-aminoquinoline **10** and 2,7-dimethylquinoline **11**, H-8 resonates at higher field than H-4 while H-3 which is at highest field in the parent quinoline is shielded further by the 2-amino or 2-methyl substituent. The order of absorptions of H-3 and H-4 from the highest to the lowest field is expected from their meta and para relationship to the quinoline nitrogen.[14a]

Analysis of the 2-quinolylhydrazones **5**, **12**, and **13** using 300-MHz ^{1}H NMR spectra has enabled the assignments of H-3, H-4, and H-8 resonances of the α-amino form (Table II). The assignments for H-3, H-4, and H-8 resonances are in agreement with the literature values for **10** and **11**. Exact assignment of H-5, H-6, and H-7 resonances in compounds **5** and **12** could not be accomplished owing to the overlap of resonances from the aryl substituent. For **13** which has a 4,6-dimethoxyphenyl ring, these three resonances are clearly resolved, and are assigned in accordance with the quinoline assignments.[14] Applying the same pattern of assignments to the less resolved 60-MHz spectra of the 3,6-dimethyl derivative **14**, H-3 and H-4 can be assigned as shown in Table II.

Analysis of the ^{1}H NMR Spectra of α-Iminoquinolines.

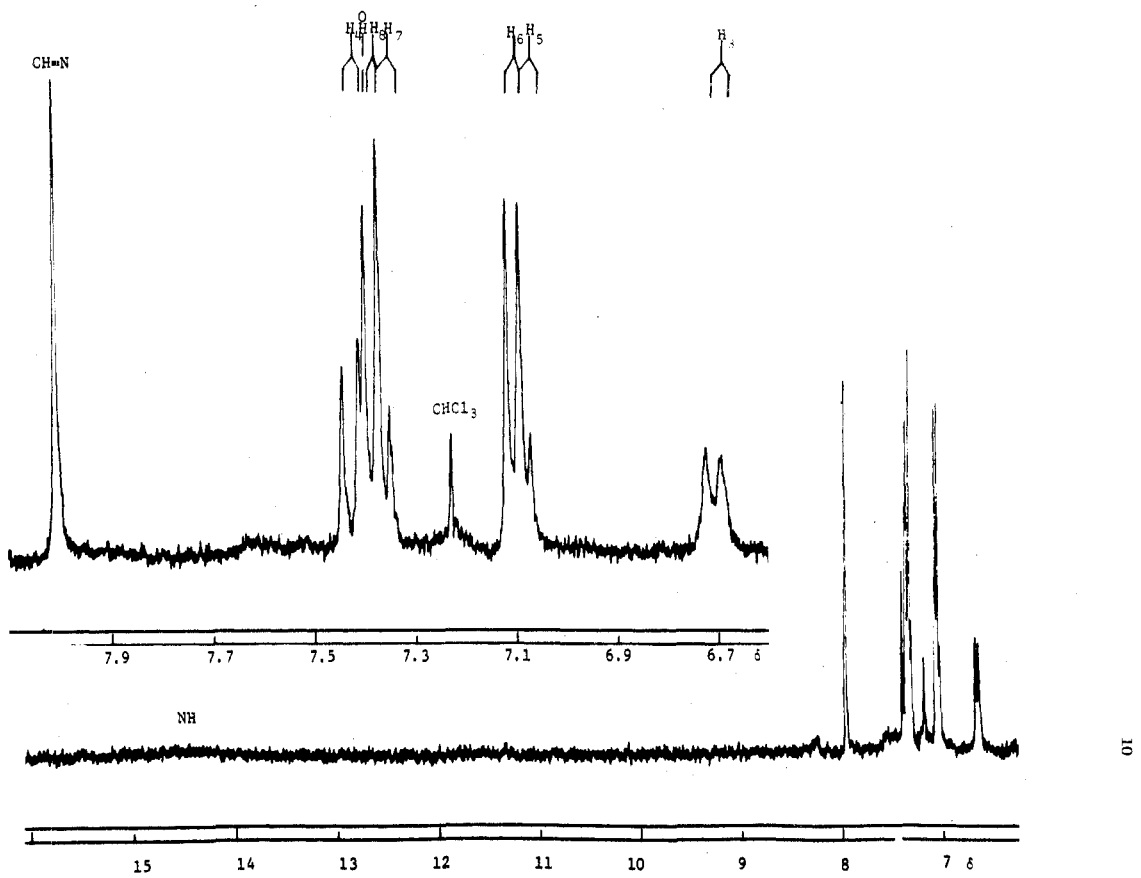


Figure 1a. 300-MHz ^{1}H NMR spectrum of **13a** in the region of δ 6.33–16.0 ppm. Sweep width 5000 Hz (sweep width 1000 Hz).

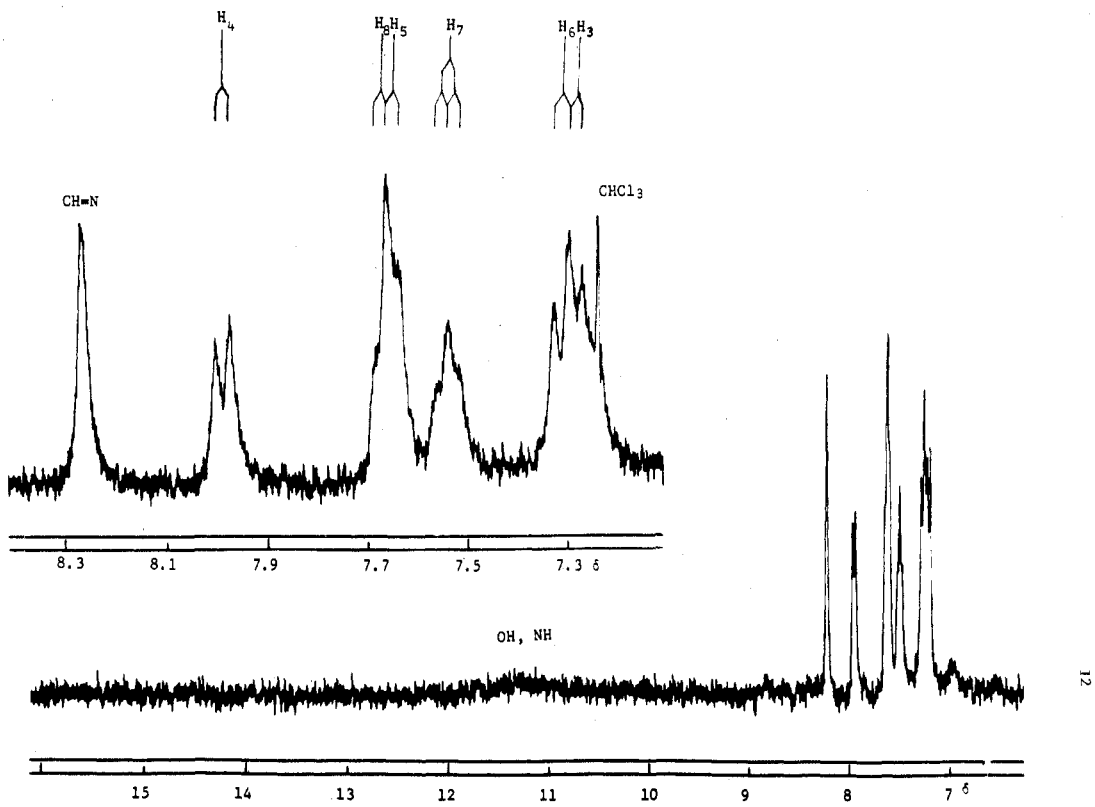
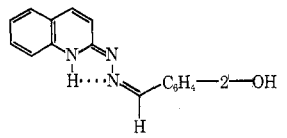
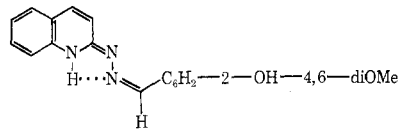
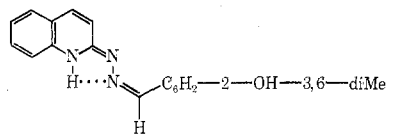
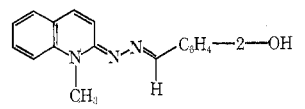


Figure 1b. 300-MHz ^{1}H NMR spectrum of **13** in the region of δ 6.33–16.0. Sweep width 5000 Hz (sweep width 1000 Hz).

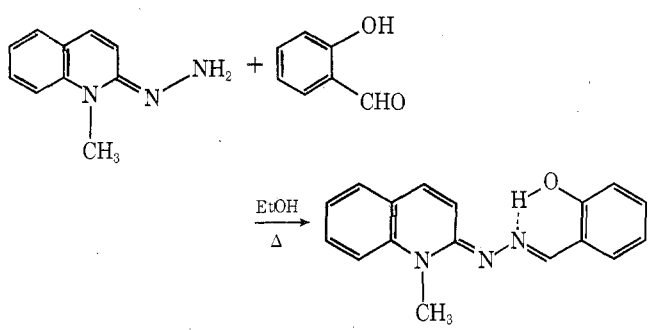
The 300-MHz ^{1}H NMR spectrum of the α-iminoquinoline **13a** has been analyzed and compared with that of the α-amino compound **13** as shown in Figure 1. As mentioned earlier, the stability of α-imino heteroaromatic compounds is usually dependent upon internal chelation. For the α-iminoquinolylhydrazones such as **5a**, stabilization of the α-imino bond is due to the formation of a new five-membered chelate ring between the quinoline N–H and the hydrazone imino nitrogen

Table III. ^{1}H NMR Spectra of the Imino Tautomers

No.	Compd	Chemical shifts, δ N–H	O–H	N=C–H	H-3	H-4	H-5	H-6	H-7	H-8	$J_{3,4}$, Hz
5a[a]		11.80	7.743[b]	7.581	6.892	8.094	7.700–7.125	7.700–7.125	7.700–7.125	7.356	10
13a[c]		14.50[d]	7.398[b]	8.017	6.705	7.431	7.110	7.138	7.391	7.418	10
14a[e]		12.23	*f*	7.97	7.26	8.00	7.83–7.42	7.83–7.42	7.83–7.42	7.83–7.42	10
15[e]			11.93	8.63	6.72	7.72	7.60–7.19	7.60–7.19	7.60–7.19	7.60–7.19	10

[a] 300-MHz spectrum, 1 M in Me_2SO-d_6. [b] δ-OH determined by D_2O exchange. [c] 300-MHz spectrum, 1 M in $CDCl_3$. [d] δ N–H 11.30 (1 M in Me_2SO-d_6). [e] 60-MHz spectrum, 1 M in Me_2SO-d_6. [f] Not resolved.

Scheme III



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(Scheme II) as evidenced by the chemical shift differences between the azomethine hydrogen and the hydroxyl hydrogen in the α-amino and α-imino forms (Tables II and III). In the case of the amino structure **13**, the azomethine hydrogen found at δ 8.53 is 0.51 ppm lower field than that of the imino tautomer **13a**, δ 8.02. This is consistent with that observed for *E* and *Z* hydrazones where the azomethine hydrogen of the *Z* form resonates 15–60 Hz higher field than that of the *E* form.[15] Furthermore, the phenolic hydrogen in the α-amino **13** (δ 10.83) is 3.43 ppm lower field than that of the α-imino **13a** (δ 7.40), indicating the loss of intramolecular hydrogen bonding. The actual stabilization of the α-imino bond due to the intramolecularly hydrogen-bonded quinoline N–H can be seen in its lower field resonance. Thus, comparing δN–H of the amino and imino forms (1 M Me_2SO-d_6), the following Δδ are observed: Δδ **5,5a** −0.7 ppm, Δδ **13,13a** −0.47, and Δδ **14,14a** −0.73. In all cases, the imino N–H resonates at lower field. It also appears that these Δδ values are indicative of the stability of the α-imino forms. Hence, from the above Δδ, the stability of **13a** should be less than that of the other two α-iminoquinolylhydrazones. Indeed, half-life determination at 56 °C in ethanol for the imino → amino conversion showed 10 h for **5a** vs. 8 h for **13a**.

The other diagnostic changes in proceeding from an α-aminoquinoline to an α-iminoquinoline are found in the coupling constants $J_{3,4}$ and H-8 resonance. Analysis of the coupling constant $J_{3,4}$ of 2-quinolone derivatives which are known to exist exclusively as the keto tautomer[3] provides a criterion for the presence of vinylic H-3 and H-4. As an example, the H-3 and H-4 of 6-methoxy-1-methylcarbostyril[16] are observed as doublets at δ 6.60 and 7.49 with a coupling constant of 9.6 Hz consistent with the vinylic assignment. Further confirmation of this criterion was obtained via the synthesis of a hydrazone similar to those of interest to this study which exists exclusively in the α-imino form (Scheme III).[12] As expected, ^{1}H NMR analysis of both the hydrazine and the product, **15**, revealed $J_{3,4}$ = 10 Hz. For the α-imino tautomers **5a**, **13a**, and **14a**, H-3 and H-4 possess similar vinylic character as revealed in Table III by the uniform $J_{3,4}$ of 10 Hz as opposed to $J_{3,4}$ of <9 Hz for their α-amino counterparts.

The applicability of this criterion in the determination of tautomeric forms of α-quinolylamine systems is illustrated by the analysis of the ^{1}H NMR spectra of α-aminoquinoline and α-hydrazinoquinoline. In the former compound the H-3 and H-4 resonances are observed as doublets at δ 6.90 and 7.90 ($J_{3,4}$ = 8.8 Hz), whereas in the latter they are observed at δ 6.96 and 7.92 ($J_{3,4}$ = 9 Hz). The $J_{3,4}$ values are too low to be associated with vinylic coupling; therefore both the above must exist in the α-amino form. This conclusion has been advanced on the basis of ir analysis, viz., $\nu_{C=N}$ 1622 ± 2 cm^{-1}, which is too low to be associated with an exocyclic imino group.[17]

Our attempt to use the chemical shift values of H-8 to distinguish the α-aminoquinolines from their imino tautomers is also successful. On comparing H-8 of **5a** (δ 7.356) and **13a** (δ 7.418) with H-8 of the corresponding α-aminoquinolines **5** (δ 7.712) and **13** (δ 7.674), it is apparent that H-8 of the α-imino tautomers is shifted upfield by 0.356 and 0.256 ppm, respectively. The lower field resonance of H-8 in the amino form has been attributed to the deshielding effect of the quinoline nitrogen lone pair. Thus, since the quinoline nitrogen of the α-imino form no longer contains the lone pair electrons in the sp^2 orbital, the H-8 resonance would be shifted upfield to a value more nearly approximating that calculated by the charge density on C-8. The correlation obtained by Chakrabarty and Hanrahan[13] for the carbon charge density vs. chemical shift of the quinoline ring hydrogens is linear except for H-8. Their calculated shift value of 7.35 ppm for

H-8 of quinoline is in excellent agreement with δH-8 obtained for **5a** and **13a**.

Characteristic Differences between the Amino and Imino Tautomer Structures of α-Quinolylamines. The ^1H NMR spectra of the quinolylhydrazones in the amino form differ from that of their α-imino tautomers in three basic features. In all cases, the chemical shift of the N hydrogen in proceeding from an α-amino to an α-imino form is to lower field. These Δδ values are indicative of the relative stability of the α-imino form. There is a vinylic center in the imino tautomers as evidenced by the increase in J values of H-3 and H-4 of the heterocycle. Furthermore, a pronounced upfield shift is noted in H-8 of the imino form which is no longer parallel to the nitrogen lone pair. This hydrogen in the α-imino form, unlike that in the amino form, is now correlatable with the charge density on the respective carbon atom.

In this series of α-iminoquinolines, the hydrazone portion stabilizes the α-imino structure from reverting to the α-amino form. The ^1H NMR characteristics deduced above pertain to the α-iminoquinoline moiety. Therefore, they should be applicable to other α-quinolylimines which may be stabilized by a different substituent.

Experimental Section

The ^1H NMR spectra of the compounds were obtained on a Varian A-60A 60-MHz nuclear magnetic resonance spectrometer. 2,2-Dimethyl-2-silapentane-5-sulfonate (DDS) was used as an internal standard in Me_2SO-d_6 and Me_4Si in $CDCl_3$. The results of the ^1H NMR spectral analyses are listed in Tables I–III. The 300-MHz ^1H NMR spectra were provided by the NMR Service of the Institute of Polymer Science at the University of Akron. Two 300-MHz ^1H NMR spectra for **13** and **13a** are given from δ 6.33 to δ 16.0 in Figure 1.

The preparation and photochromic chemistry of this series of α-quinolyl hydrazones have been described elsewhere.[12]

Registry No.—**1**, 588-64-7; **2**, 614-65-3; **3**, 2824-60-4; **4**, 2909-19-5; **5**, 2746-55-6; **5a**, 59044-15-4; **6**, 2719-72-4; **7**, 59034-55-8; **8**, 59034-56-9; **12**, 21119-45-9; **13**, 59034-57-0; **13a**, 59034-58-1; **14**, 59034-59-2; **14a**, 59034-60-5; **15**, 50984-02-6.

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Notes

High Pressure Thermal and Photosensitized Dimerizations of 2-Pyrones

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Owing to the synthetic manipulability of the resulting lactones, 2 pyrones have frequently been utilized as dienes and, more recently, as dienophiles[1] in Diels–Alder reactions. In view of their ability to act in both capacities, it is surprising that no Diels–Alder dimers of 2-pyrones have ever been reported. Seyferth[2] has postulated the intermediacy of such a dimer in the conversion of 2-pyrone to *trans*-cinnamic acid. Even earlier, Chavanne[3] reported that protracted heating of 3-acetoxy-2-pyrone or 3-hydroxy-2-pyrone afforded then unidentified $C_{11}H_8O_4$ and $C_9H_6O_3$ compounds, respectively. We have subsequently found these compounds to be 3-acetoxycoumarin and coumarilic acid and note that the formation of these products can also be rationalized as proceeding via Diels–Alder dimers.

It is well known that pressure accelerates Diels–Alder reactions and slows fragmentation reactions such as decarboxylation.[4] Accordingly, several representative 2-pyrones have been subjected to pressures of up to 7 kbar and moderate temperatures (<100 °C) to determine whether Diels–Alder dimerization of 2-pyrones can thus be effected. Synthesis of such dimers would allow one to determine whether their subsequent chemistry is consistent with their postulated intermediacy in the reactions of Seyferth and Chavanne. Moreover, dimers of suitably functionalized 2-pyrones are potentially useful as precursors of substituted coumarins and isocoumarins. Finally, the comparison of the structures of thermal dimers of 2-pyrones with those of the dimers obtained via photosensitization[5] of the same 2-pyrones would be of interest.

Dimerization of 2-Pyrones. Initially, the thermal dimerization of 2-pyrone was attempted simply by heating neat pyrone at 120 °C for 24 h. This procedure afforded only unreacted 2-pyrone and a tan, insoluble powder melting above 300 °C and presumed to be polymeric. Pressurization of 50% solutions of 2-pyrone in toluene or nitromethane at 7 kbar at 70 °C, in the presence of 1% hydroquinone to scavenge radicals, yields mostly polymer and a minor amount of a dimer, **1**. Identification of this dimer was facilitated by the earlier characterization of two [2 + 4] dimers of 2-pyrone obtained by photosensitization.[5] By means of selective spin–spin decoupling experiments and preparation of the photodimers from each of the four monodeuteriated 2-pyrones, these compounds were shown to have structures **2** and **3**.[5] While the ^1H NMR spectrum of thermal dimer **1** is not identical with