A is enhanced by additives such as CCl_4, which tend to stabilize electrons, and reduced by alkenes, which trap positive charges. It has been proposed[3b,7] that the 4400-A peak may be due to RI^+, and the 7500-A peak to $(RI)_n^+$ resulting from solvation of the monomer, or to R_2I^+ resulting from an ion–molecule reaction of the type $RI^+ + RI \rightarrow R_2I^+ + I$, such as has been observed in the gas phase.[17] If the latter species exist, it is plausible that in pure alkyl iodides they would be formed from the RI^+ so rapidly that the 4400-A peak would not be observed.

The 5200-A peak in C_2H_5I glass grows following irradiation, in parallel with the growth of the 4050-A peak, whereas in n-C_4H_9I it is present immediately after irradiation and remains constant while the 4050-A peak grows. It does not appear to be due to I_2 or an $RI \cdot I_2$ complex, since iodine dissolved in C_2H_5I shows one absorption peak, with the maximum at 4800 A at 298°K and at 4400 A at 77°K. It is unlikely that an $RI \cdot I$ complex is responsible for the 5200-A absorption, since photolysis at 2500 A of alkyl iodide glasses or of dilute alkyl iodides in hydrocarbon glasses does not yield a peak in this region. A $C_2H_5I \cdot I$ complex in liquid ethyl iodide at 298°K has been reported to have λ_{max} at 4900 A.[18] By analogy to the $RI \cdot I_2$ peak, this peak may be shifted to a lower wavelength at 77°K. The fact that the 5200-A peak grows in some systems following irradiation, and its relatively high stability, are consistent with some type of complex formation. Since $RI \cdot I_2$ and $RI \cdot I$ appear to be eliminated, a charged complex (for example, $C_2H_5I \cdot I^-$) seems probable.

It is probable that a complex or complexes involving HI are responsible for the absorption in the 3500-A region which is induced in alkyl halide glasses by γ radiation, and which increases and spreads to higher wavelengths on warming. HI is known to be formed in the radiolysis of glassy C_2H_5I and it has been shown that solutions of HI in C_2H_5I in the liquid at 195°K and the glass at 80°K show intense absorption in the 3500–4000-A region,[19] the position of the maxima depending on the relative amount of I_2 present.

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[17] (17) H. A. Gillis, R. R. Williams, and W. H. Hamill, *J. Am. Chem. Soc.*, **83**, 17 (1961).

[18] (18) T. A. Gover and G. Porter, *Proc. Roy. Soc.* (London), **A262**, 476 (1961).

[19] (19) (a) T. O. Jones, R. H. Luebbe, Jr., J. R. Wilson, and J. E. Willard, *J. Phys. Chem.*, **62**, 9 (1958); (b) H. J. Arnikar and J. E. Willard, unpublished.

Spectroscopic Studies of Keto–Enol Equilibria. IX. N^{15}-Substituted Anilides[1,2]

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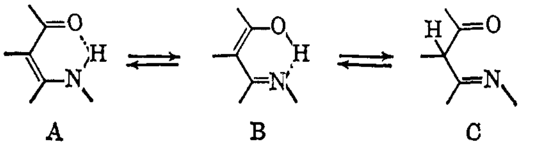
Abstract: Proton magnetic resonance (pmr) spectroscopy was used to determine the keto–enol equilibria as a function of solvent and temperature in the Schiff bases derived from the N^{15}-substituted anilines and the following aldehydes and ketones: benzoylacetone, 2-acetyldimedone, salicylaldehyde, 2-hydroxyacetophenone, 2-hydroxy-1-naphthaldehyde, and 1-hydroxy-2-acetonaphthone. The ultraviolet spectra of a number of these Schiff bases were recorded and, with the aid of the pmr data, the ultraviolet extinction coefficients were computed for the tautomers of each base. The values of the extinction coefficients indicated that the pmr and ultraviolet spectra were measuring the same phenomenon.

In a previous report[3] concerned with the keto–enol equilibria in Schiff bases derived from N^{15}-methylamine and several carbonyl compounds, it was shown that intramolecular proton exchange between the oxygen and nitrogen is rapid. The observed spin coupling therefore provides a good measure of the residence time of the proton on nitrogen. This technique has now been extended to Schiff bases derived from N^{15}-aniline to determine the effect of the N-phenyl group upon the keto–enol equilibria. Some studies on the basicities of aliphatic Schiff base anilides have appeared, but the results are ambiguous.[4]

The proton magnetic resonance (pmr) spectra of the N^{15}-anilide derivatives have been recorded in several solvents as a function of temperature. From the measured values of the N^{15}–H spin coupling, the relative amounts of the three possible tautomers have been determined for each Schiff base.[5] The ultraviolet spectra of the Schiff bases were obtained, and with the



A B C

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[1] (1) Part VIII: G. O. Dudek, *J. Org. Chem.*, **30**, 548 (1965).

[2] (2) Part of the work on the phenols has appeared previously: G. Dudek and E. P. Dudek, *Chem. Comm.*, 464 (1965).

[3] (3) G. O. Dudek and E. P. Dudek, *J. Am. Chem. Soc.*, **86**, 4283 (1964).

[4] (4) D. F. Martin, G. A. Janusonis, and B. B. Martin, *ibid.*, **83**, 73 (1961).

[5] (5) Although C is a possible tautomer, there is no evidence for the presence of any detectable amount of this nonconjugated species in the pmr spectra of the N^{15}-aniline Schiff bases. Similarly, in all our previous studies of Schiff bases, this tautomer has not been observed.[3,6]

[6] (6) G. O. Dudek and R. H. Holm, *J. Am. Chem. Soc.*, **84**, 2691 (1962).

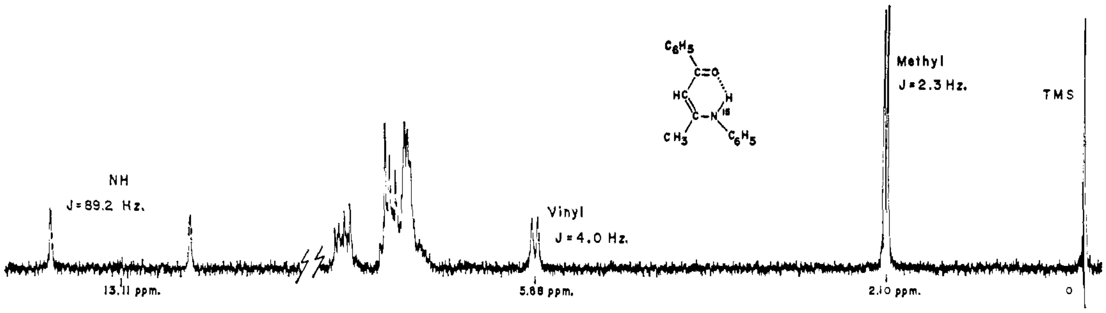
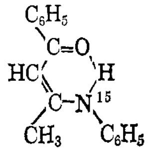
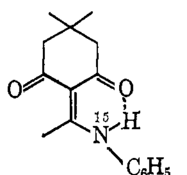


Figure 1. The pmr spectrum of 3-(N^{15}-phenylamino)crotonophenone at 60.00 Mhertz in $CDCl_3$ solution.

aid of the pmr data the extinction coefficients for the tautomers could be calculated. The simultaneous consideration of the ultraviolet and pmr data have clarified certain problems which have arisen in the interpretation of the ultraviolet spectra.[7-9]

Proton Magnetic Resonance Data. The data in Table I indicate that the N^{15}–H spin coupling for the N^{15}-aniline Schiff bases exceeds 80 hertz for the β-diketone derivatives, I and II (see Figure 1).[10] The spin coupling for these two compounds is comparable to the coupling of 88–90 hertz observed for the other N^{15}-substituted Schiff bases and amides which exist primarily in the ketoamine form.[3,11,12] The new splitting in II is noticeably smaller than in compound I. The decrease in coupling suggests that there may be some exchange of the proton between nitrogen and oxygen. An alternative explanation would be that the reduced coupling is due to a change in s character of the bonding to the nitrogen.[12] The change in s character could be attributed to electron delocalization into the second carbonyl group. Nevertheless, the value of $J_{N^{15}H}$ indicates that in both compounds I and II and their N-methyl analogs, the hybridization of the nitrogen orbitals is similar to that of an ordinary amide, approximately sp^3.


I


II

It has been previously shown[3] that changes in the N^{15}–H coupling due to temperature or solvent variations may be attributed to rapid proton exchange between oxygen and nitrogen (A $\leftrightarrows$ B). The observed spin coupling (J_{obsd}) could be given as the weighted average of J_O (the oxygen–proton spin coupling constant) and J_N (the N^{15}–proton spin coupling constant).

$$J_{obsd} = J_O P_O + J_N P_N$$

Since $J_O = 0$, and only two sites for the proton were involved ($P_O + P_N = 1$), the observed coupling of the acidic proton could be used as a measure of the oxygen–nitrogen equilibrium (K). If it is assumed that $J_N = 89$ hertz in the pure N^{15}-amine form (compound I), then

$$K = P_O/P_N = (89 - J_{obsd})/J_{obsd} \qquad (1)$$

Table I. Proton Magnetic Resonance Data for the N^{15}-Substituted Schiff Bases (ppm, from Tetramethylsilane)

Compound	Solv	Temp, °C	NH signal: δ, ppm[a]	NH signal: J, hertz
3-(N^{15}-Phenylamino)crotonophenone (I)	$CDCl_3$	29.5	13.11	89.2
		10	13.12	89.1
		−20	13.16	89.2
	CCl_4	29.5	13.17	88.5
2-(N^{15}-Phenylacetimidoyl)-5,5-dimethylcyclohexane-1,3-dione (II)	$CDCl_3$	29.5	15.03	85.5
		0	15.04	85.5
		−30	15.06	85.5
	CCl_4	29.5	15.13	84.7
2-(N^{15}-Phenylacetimidoyl)-1-naphthol (IV)	$CDCl_3$	31	16.99	27.5
		−1	17.21	31.7
		−11	17.28	33.7
		−20	17.35	35.1
		−30	17.41	36.5
1-(N^{15}-Phenylformimidoyl)-2-naphthol (III)	$CDCl_3$	29.5	15.44	33
		15	15.51[c]	36.1, 5.2
		0	15.58[c]	39.4, 5.6
		−10	15.61[c]	41.1, 5.9
		−20	15.64[c]	43.8, 6.1
		−30	15.68[c]	46.5, 6.3
		−40	15.69[c]	49.4, 6.9
	CCl_4	29.5	14.95	12.3
		15	14.98	13.3
		0	15.03[c]	13.8, 2
		−10	15.07[c]	14.1, 2.1
		−20	15.09[c]	14.3, 2.1
	CH_3CN	15	14.79[c]	27.8, 4.0
		30	14.74[c]	27.7, 3.9
		40	14.70[c]	27.5, 3.6
		50	14.67	27
	CS_2	29.5	14.9[d]	
		15	14.98	11.5
		0	15.03	12.1, 2
2-(N^{15}-Phenylacetimidoyl)-phenol (V)	$CDCl_3$	29.5	14.59[d]	
		0	14.74	
		−20	14.87	
		−40	15.01	
2-(N^{15}-Phenylformimidoyl)-phenol (VI)	$CDCl_3$	29.5	13.22[b]	
		0	13.37	
		−20	13.47	
		−50	13.61	
	C_2H_5OH	29	...	
		0	15.02[c]	13.1, 2
		−10	15.05[c]	14.0, 2

[a] From tetramethylsilane as internal reference. [b] Broad. [c] Quartet. [d] About 1.5 cps wide.

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(7) H. E. Smith, S. L. Cook, and M. E. Warren, *J. Org. Chem.*, **29**, 2265 (1964); M. E. Warren and H. E. Smith, *J. Am. Chem. Soc.*, **87**, 1757 (1965).

(8) L. A. Kazitsyna, *et al.*, *J. Gen. Chem. USSR*, **31**, 286 (1961).

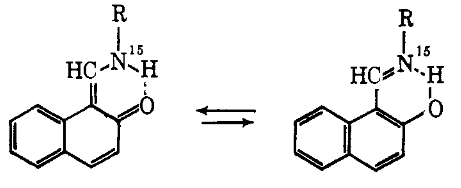
(9) (a) D. G. Anderson and G. Wettermark, *J. Am. Chem. Soc.*, **87**, 1433 (1965); (b) J. Charette, G. Falthansl, and Ph. Teyssie, *Spectrochim. Acta*, **20**, 597 (1964), (c) V. I. Minkin, *et al.*, *Zh. Fiz Khim.*, **38**, 938 (1964).

(10) The 2.3 hertz coupling of the N^{15} nucleus to the methyl group indicates that the structure is the isomer given in I, and not the reverse isomer (Figure 1). The same was found true of the N-methyl adduct.[3]

(11) B. Sunners, L. H. Piette, and W. G. Schneider, *Can. J. Chem.*, **38**, 681 (1960).

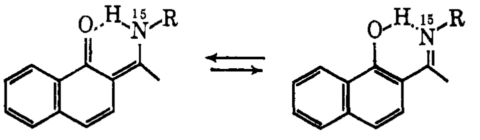
(12) G. Binsch, J. B. Lambert, B. W. Roberts, and J. D. Roberts, *J. Am. Chem. Soc.*, **86**, 5564 (1964).

There is some uncertainty[12] in the value of J_N, but at most it amounts to a few hertz and affects none of the conclusions drawn in this paper.



IIIa IIIb

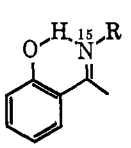
In 1-(N^{15}-phenylformimidoyl)-2-naphthol (III, R = C_6H_5)[13] the observed N^{15}–H spin coupling is only 33 hertz in chloroform (Table I). The predominance of the enolimine tautomer (IIIb) is even greater in nonpolar solvents, reaching 85% in carbon tetrachloride solution. Since the N^{15}–H spin coupling for the N^{15}-methyl analog (III, R = CH_3) was reported to be 64.5 hertz in chloroform, it is evident that, compared to an N-methyl group, an N-phenyl substituent destabilizes the ketoamine tautomer (IIIa).



IVa IVb

According to the observed spin coupling (Table I), the percentage of enolimine form B in solution is greater for the acetonaphthone derivative (IV, R = C_6H_5) than for the naphthaldehyde compound (III, R = C_6H_5). The reverse is true for the N-methyl compounds previously studied.[2,3] The slow formation of the acetonaphthone adduct (Experimental Section) and the far greater amount of the enol tautomer in IV can be attributed to steric interactions between the methyl and the N-phenyl group (*cf.* ultraviolet spectra). The limited solubility of IV prevented a determination of the keto–enol equilibrium in either carbon tetrachloride or alcoholic solution.

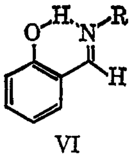
No N^{15}–H coupling is observed for 2-(N^{15}-phenylacetimidoyl)phenol (V) in chloroform solution. There-



V

fore the proton resides predominantly on oxygen in this compound. In contrast, the N-methyl analog of V possesses an appreciable amount of the nonaromatic tautomer in solution (J_{obsd} is 21.0 hertz in $CDCl_3$ at 0°).[2]

For the Schiff base formed from salicylaldehyde and



VI

aniline-N^{15} (VI), the proton is on oxygen in chloroform solution (Table I). At room temperature in ethanol, proton exchange with the solvent is large; thus no acidic proton signal can be observed. At 0°, the rate of exchange with the solvent is lowered to the extent that a 13.1-hertz N^{15}–H can be measured as well as a 2-hertz splitting due to the aldehydic proton. These data, in conjunction with the ultraviolet results presented in the next section, suggest that in the absence of solubility limitations, all the aromatic Schiff bases would exhibit detectable amounts of the nonaromatic tautomer A in alcoholic solution.

By means of eq 1, the tautomeric equilibrium constants for compounds III and IV have been calculated. From a plot of ln K *vs.* $1/T$, $-\Delta H$ values have been obtained and are listed in Table II. It should be noted that the plot for compound III in chloroform solution is linear over the entire 70° range.

Table II. Enthalpy Values for the Tautomeric Interchange

Compound	Solvent	$-\Delta H$, kcal/mole
III, R = C_6H_5	$CDCl_3$	1.5
	CCl_4	0.4
	CH_3CN	~0.08
IV, R = C_6H_5	$CDCl_3$	1.1

The enthalpy values in Table II and the equilibrium constants from Table I suggest that the hydrogen bonding ability of the medium produces a greater effect upon the keto–enol equilibrium (A $\rightleftarrows$ B) than does the polarity. Although acetonitrile (37.5 μ) has a higher dielectric constant[14] than chloroform (4.81 μ), there is more nonaromatic tautomer A in the less polar solvent. Further, the temperature dependence of the equilibrium in acetonitrile is small, being only slightly greater than the experimental error over a 35° range.[15] However the association of hydrogen bonding solvents such as chloroform with the carbonyl groups of amides is a well-known phenomenon.[16] The $-\Delta H$ for the amide–chloroform association has been estimated to be about 2 kcal/mole, similar to the values obtained in Table II.

Ultraviolet Spectra. The complimentary nature of the ultraviolet and pmr data in determining the keto–enol equilibria have been alluded to in previous papers in this series.[2,3] It has been noted by Kazitsyna and his collaborators[8] that the ultraviolet absorptions of the N-alkyl derivatives of 2-hydroxy-1-naphthaldehyde (III) were strongly solvent dependent. An intense band in the region 400–420 mμ, in associating solvents such as alcohol and chloroform, becomes weak in nonpolar solvents such as isooctane. These authors suggested that the intense absorption is due to a nonaromatic system such as IIIa. A similar, solvent-dependent absorption band exhibited by phenolic Schiff bases has also been timidly assigned to a non-

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[13] The nomenclature is not intended to specify the prevalent tautomer.

[14] J. A. Riddick and E. E. Toops, "Technique of Organic Chemistry," Vol. VII, A. Weissberger, Ed., Interscience Publishers, Inc., New York, N. Y. 1955.

[15] The lower temperature limit was determined by the solubility of the compound.

[16] (a) W. A. Klemperer, M. W. Cronyn, A. H. Maki, and G. C. Pimentel, *J. Am. Chem. Soc.*, **76**, 5846 (1954); (b) L. A. LaPlanche, H. B. Thompson, and M. T. Rogers, *J. Phys. Chem.*, **69**, 1482 (1965); (c) F. Takanashi and N. C. Li, *ibid.*, **69**, 2950 (1965).

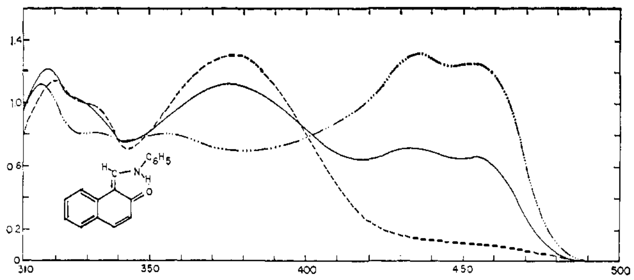

Figure 2. The ultraviolet spectra of 1-(N-phenylformimidoyl)-2-naphthol in: —···—, absolute ethanol; ———, acetonitrile; and – – – –, cyclohexane.

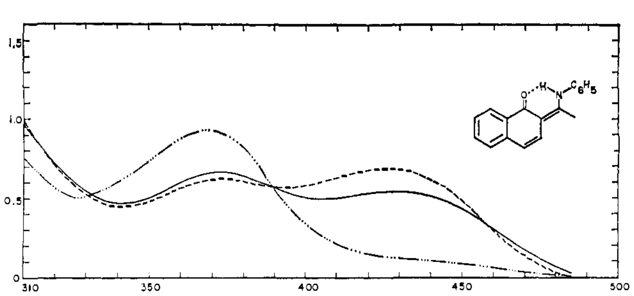

Figure 3. The ultraviolet spectra of 2-(N-phenylacetimidoyl)-1-naphthol in: – – – –, absolute ethanol; ———, chloroform; and —···—, cyclohexane.

aromatic tautomer (similar to IIIa);[7] however Minkin, *et al.*,[9c] do not agree. Although it is usually with reluctance that a nonaromatic structure is postulated for a naphthol or phenol derivative, the ultraviolet and the pmr data support the presence of this form in solution.

The ultraviolet spectra of the anilides III and IV in several solvents are presented in Figures 2 and 3, and the data listed in Table III. The compounds 2-(N-methylacetimidoyl)1-naphthol and 2-(N-methylacetimidoyl)-3-naphthol are included in the table for the purpose of comparison. The pmr spectra for these compounds have been reported,[3] yet their ultraviolet spectra have not. The extent of the tautomeric equilibrium of each Schiff base has been previously established by pmr spectroscopy. The greater the preponderance of the ketoamine species, the larger is the N^{15}–H spin coupling and presumably the more intense is the ultraviolet absorptions of this tautomer. Hence by comparing the variation of the observed N^{15}–H spin coupling and the ultraviolet absorption intensities with solvent, the ultraviolet bands of the Schiff bases have been assigned to the two tautomers. For example, the *ortho*-quinoid structure for the ketoamine tautomer is energetically unfavorable for 2-(N-methylacetimidoyl)-3-naphthol.[3] No N^{15}–H coupling is observed in the pmr spectra,[3] and only a weak imine band appears at 374 mμ. In compounds III and IV, the intensity variation of the bands in the 410–450-mμ region parallels the observed N^{15}–H spin coupling. If a small solvent dependency of the band positions did not interfere, an isosbestic point[17] would be present in the ultraviolet spectra near 400 mμ (Figures 2 and 3).

From the pmr spectra the concentration in solution of each tautomer of the Schiff base can be calculated. According to eq 1, the per cent of ketoamine is given by $(J_{\text{obsd}}/89) \times 100$. From the per cent of the nonaromatic form present in solution, the extinction coefficients (ϵ_0) for that tautomer can be calculated from the observed intensities (ϵ) of its ultraviolet bands. The extinction coefficients (ϵ_0) for the enolimine form have been obtained by similar calculations and the results are given in Table III.

The acidic proton signal of 2-(N-phenylformimidoyl)-phenol (VI) in alcoholic solution could not be observed at room temperature due to rapid proton exchange with the solvent (*vide supra*). Therefore *K* for the tautomeric equilibrium was determined by plotting *K vs.* $1/T$ and extrapolating to room temperature. Fortunately compound VI was the only anilide for which such a procedure was necessary in order to obtain a value for *K*.

Since the extinction coefficients (ϵ_0) for the keto form of a Schiff base are relatively constant and of sufficient magnitude, the assumption that the pmr and ultraviolet spectra are measuring the same phenomenon seems to be a valid one. A small variation of ϵ_0 with solvent is noted, but this is not unexpected.[18] Due to the limited solubility of the Schiff bases, particularly in hydroxylic solvents, further pmr–ultraviolet comparisons were not possible.

For several Schiff bases, it was difficult to accurately determine values for ϵ and λ due to the overlap of the absorption bands. The overlap was most pronounced in 2-(N-methylacetimidoyl)-1-naphthol (IV, R = CH_3) where the band of the enol tautomer appeared only as an inflection about 370 mμ; hence no quantitative data could be obtained for the enol form of the compound. Since the keto band of 2-(N-phenylformimidoyl)phenol (VI, R = C_6H_5) in methanol solution appeared as a shoulder near 410 mμ, a value for ϵ could only be estimated.

It is obvious from the pmr results that a change of solvent may shift the keto–enol equilibrium considerably, but its effect on the ultraviolet band positions is not as large. Of the compounds listed in Table III, the spectrum of 2-(N-methylacetimidoyl)-1-naphthol (IV, R = CH_3) exhibits one of the larger solvent dependencies. There is an 11-mμ blue shift of the 433-mμ band and a 9-mμ blue shift of the 415-mμ band.[19] A blue shift is indicative of a slightly less polar excited state.[20,21]

The fact that each tautomer exhibits an ultraviolet absorption, even under conditions where the amount of keto and enol forms are nearly equal, suggests that a symmetrical hydrogen bond is not present.[22] Although the proton is exchanging rapidly between sites in the time scale of pmr spectroscopy,[3] the ultraviolet spectra reveal that the proton is either on nitrogen or oxygen.[23]

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[17] H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1962, p 562.

[18] W. P. Hayer and C. S. Timmons, *Spectrochim. Acta*, **21**, 529 (1965).

[19] This difference may be a result of band overlap (*vide supra*) or demonstrate that the two bands do not have the same origin.

[20] H. H. Jaffé and M. Orchin, ref 17, p 192.

[21] Although the solvent shift of a band has often been used to assign the origin of the absorption,we prefer not to do so. One reason is the shifts here are small, and secondly the work of Hayer and Timmons indicates that a hydrogen-bonded system may react abnormally to solvent effects.[18]

[22] (a) C. A. Coulson in "Hydrogen Bonding," D. Hadži, Ed., Pergamon Press Ltd., London, 1959, p 351. (b) G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman and Co., San Francisco, Calif., 1960, p 259.

[23] H. H. Jaffé and M. Orchin, ref 17, p 134.

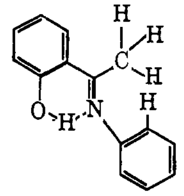
Table III. Ultraviolet Spectroscopic Data for the Aromatic Schiff Bases

Compound	Solvent	Enol λ, mμ	Enol $\epsilon \times 10^4$	Enol $\epsilon_0 \times 10^4$	Keto λ, mμ	Keto $\epsilon \times 10^4$	Keto $\epsilon_0 \times 10^4$
3-(N-Methylacetimidoyl)-2-naphthol	$CHCl_3$	374	0.187				
	$CH_3C{\equiv}N$	370	0.184				
2-(N-Methylacetimidoyl)-1-naphthol (IV, R = CH_3)	CCl_4				433	0.807	
					416	0.904	
	CH_2Cl_2				429	1.08	1.22
					412	1.15	1.29
	$CHCl_3$	Not separable[a]			431	1.06	1.18
					412	1.13	1.26
	$CH_3C{\equiv}N$				423	1.07_5	
					407	1.13	
	CH_3OH				422	1.06	
					407	1.13_5	
2-(N-Phenylacetimidoyl)-1-naphthol (IV, R = C_6H_5)	C_6H_{12}	368	0.93		425	0.14	
	CCl_4	371	0.87		425	0.20	
	$CHCl_3$	372	0.67	0.98	428	0.54	1.70
	$CH_3C{\equiv}N$	368	0.70		421	0.46	
	CH_3OH	374	0.63		425	0.70	
1-(N-Methylformimidoyl)-2-naphthol (III, R = CH_3)	CH_2Cl_2				421	0.70	1.00
					402	0.71	1.01
	$CHCl_3$[b]				420	1.09	1.48
					403		
1-(N-Phenylformimidoyl)-2-naphthol (III, R = C_6H_5)	C_6H_{12}	376	1.30		455	0.11	
	CCl_4	378	1.37	1.58	455	0.275	1.95
					435	0.316	2.24
	$C_6H_5CH_3$	378	1.30		457	0.318	
					435	0.360	
	$CHCl_3$	375	1.02	1.39	457	0.79	2.08
					438	0.86	2.25
	$CH_3C{\equiv}N$	376	1.11	1.61_5	453	0.67	2.11
					433	0.72	2.34
	CH_3OH				455	1.26	
					437	1.32_5	
2-(N-Phenylformimidoyl)phenol (VI, R = C_6H_5)	CCl_4	343	1.17				
	$CHCl_3$	341	1.16				
	CH_3CN	337	1.22				
	CH_3OH	337	1.18		434	0.183	1.46
2-(N-Phenylacetimidoyl)phenol (V, R = C_6H_5)	CCl_4	331	0.769				
	$CHCl_3$	327	0.761				
	CH_3OH	333	0.738		~410[a]	0.187	

[a] Shoulder. [b] Data from ref 8.

Hence there must be a barrier to enol–keto interconversion, albeit small.

Models indicate that both 2-(N-phenylacetimidoyl)-phenol and 2-(N-phenylacetimidoyl)-1-naphthol (IV and V, R = C_6H_5) have steric interactions between the acetylmethyl and N-phenyl groups such that the system cannot be planar. On the basis of space-filling models, the preferred conformation for the phenyl ring would be at right angles to the plane of the Schiff base aromatic system. The ultraviolet spectra of IV (R = C_6H_5) are peculiar in that the two bands normally present in the long wavelength region of the N-methyl derivatives[8] are absent (*cf.* Figures 2 and 3). The absence of fine structure could result from the lack of planarity of the system. The steric interactions could also be responsible for the very slow addition of aniline to the aromatic ketones (Experimental Section).



In summary, it is evident that an N-phenyl group destabilizes the ketoamine tautomer (A) as compared to a methyl substituent on the nitrogen of a Schiff base. The destabilizing effect of the phenyl moiety is not observed for the open-chain Schiff bases such as I for which the ketoamine form is particularly stable, but in aromatic Schiff bases the effect is so pronounced that no nonaromatic ketoamine form can be detected except in ethanol or methanol.

The utilization of pmr and ultraviolet spectroscopy provides a useful complementary technique for determining the tautomeric equilibria in Schiff bases. Each method individually possesses its own distinct advantage for the solution of this type of problem. When the amount of amine present is large, the pmr method is most applicable, whereas the ultraviolet technique serves best for the other extreme.

Experimental Section

Proton magnetic resonance spectra were taken on a Varian A-60 spectrometer operating at 60.00 Mhertz. The sample usually consisted of 40 mg of compound in 0.50 ml of solvent with tetramethylsilane as the internal reference. The chemical shifts were determined by interpolating between sidebands of tetramethylsilane generated by an audiooscillator continuously monitored by a frequency counter. The variable temperature probe was calibrated by measuring the shift between the resonances of methanol. The chemical shifts are accurate to ±0.01 ppm, the spin couplings to ±0.2 hertz, and the temperature to ±1°.

Ultraviolet spectra were taken on a Cary Model 14 spectrometer. The cells were of 0.05-cm path length with 1.00 cm used for the weaker bands. The wavelengths are good to ±1 mμ, the extinctions to ±2%.

Solvents were commercial spectrograde materials. Normal chloroform was freed from ethanol by passing it through a column of neutral alumina. This procedure was also used to purify the $CDCl_3$ and CCl_4 used for pmr spectroscopy. Absolute ethanol for pmr use was dried with Linde molecular sieve until a sample indicated a distinct triplet for the hydroxyl resonance in the pmr spectrum.

Compounds were synthesized (unless otherwise noted) by mixing the β-diketone, etc., with aniline and warming to 80–90° for a brief period. The materials were recrystallized several times. Their properties agreed with the literature values.[24]

2-(N-Phenylacetimidoyl)-1-naphthol, not having been previously reported, was prepared by heating, under nitrogen, 1-hydroxy-2-acetonaphthone and aniline at ~160° for 36 hr. The mass was fractionally sublimed and then recrystallized from benzene–hexane and resublimed, 119.9–120.4°.

Anal. Calcd for $C_{18}H_{15}NO$: C, 82.73; H, 5.79; N, 5.36. Found: C, 82.72; H, 5.79; N, 5.44.

2-(N-Phenylacetimidoyl)phenol was prepared in a similar manner.[24e]

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The Reactions of Sulfur Atoms. VII. The Ultraviolet Spectrum, the Photolysis, and the Mercury Sensitization of Carbonyl Sulfide

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Abstract: Ultrapure gaseous COS exhibits a broad absorption continuum in the near-ultraviolet region which starts at 2550 A and extends to below 2000 A with a rounded maximum at 2225 A. Semiempirical molecular orbital calculations, with the inclusion of the sulfur d orbitals, indicate this continuum to correspond to a $\pi \rightarrow \pi^*$ transition since the lowest lying $n \rightarrow \pi^*$ type state appears at considerably higher energies. Photolysis in this region affords CO ($\Phi = 1.81$ at 2537 and 2288 A) and sulfur. The primary step yields S atoms at least 74% of which are formed in the excited (^1D) state. The mercury photosensitization at 2537 A affords only triplet-ground-state sulfur atoms. Both singlet- and triplet-state atoms abstractively attack COS to form S_2 with the rate ratio, $S(^1D)/S(^3P)$, being *ca.* 30. The condensed-phase photolysis is similar to that of the gas phase although the relative yields of triplet- and singlet-state atoms may be altered.

Over 30 years ago it was suggested on energetic grounds that the photolysis of gaseous COS in its first absorption continuum results in carbon monoxide and $S(^1D)$ atoms.[2] This postulate has been proven, however, only in recent years by trapping the atomic sulfur with hydrocarbons.[3–6] When the photolysis is carried out in the presence of an olefin or paraffin, episulfide and/or mercaptan form, respectively, in high yields. The alkyl mercaptan has been shown to arise without the intervention of free radicals, by an insertion-type mechanism, which is possible only if the S atoms produced in the primary photolytic step are in their excited singlet D state, 26.4 kcal/mole above the triplet P_2 ground level.[7] It has also been demonstrated that the insertion reaction can be effectively suppressed by collisional relaxation of the $S(^1D)$ atoms to the ground state.

In the early study of Forbes and Cline,[8] the quantum yield of CO was reported to be nearly unity. Later Kondratjev,[9] from the photooxidation of COS, concluded that S atoms attack COS, to form S_2 and CO. We reported[3,5,6] recently that Φ(CO) decreases with increasing olefin pressure to a limiting value of exactly one-half of that in the absence of olefin. Therefore the abstraction reaction at room temperature and over 50 torr of COS must go to completion. Consequently Φ(CO) for pure COS should be 2 unless the photodecomposition is inherently inefficient.

The ultraviolet absorption spectrum of COS has been reported to possess two continua,[10] with the lower energy continuum extending with maxima at 2080 and 2250 A, from 2550 down to *ca.* 1600 A. At very low pressures the first continuum was reported to resolve into several broad, diffuse bands involving a number of different electronic transitions thought to arise from an $n \rightarrow \pi^*$ type excitation. The second absorption region sets in at *ca.* 1550 A.

The spectrum has been discussed by Walsh,[11] and relevant information may be found in one of Mulliken's

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