

THE FAR-ULTRAVIOLET SPECTRA OF SOME SIMPLE AZOMETHINES

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Evidence has recently been presented which indicates that the absorption band of simple azomethines occurring at 230-250 m μ is due to an $n \rightarrow \pi^*$ transition (1)(2). We have also been interested in the spectroscopic analogies of azomethines and carbonyl compounds, and wish to report here the results of our studies of the absorption band of azomethines which occurs around 180 m μ . The values of the absorption maxima and molar absorptivities for a number of simple azomethines are given in Table I. Values found for the $n \rightarrow \pi^*$ band are also listed.

With the view of extending the spectroscopic analogies of the carbonyl and azomethine chromophores, it is of interest to consider the possible origin of the transition around 180 m μ . Carbonyl compounds show two additional maxima at shorter wavelengths than the $n \rightarrow \pi^*$ band, one around 185 m μ , and one around 150-170 m μ . These bands have been assigned to either $\pi \rightarrow \pi^*$ or $n \rightarrow \sigma^*$ transitions by various authors, and some uncertainty seems to persist concerning these assignments. Recent reviews (3)(4) consider the 185 m μ band as due to an $n \rightarrow \sigma^*$ transition, and the more intense 150-170 m μ band as due to a $\pi \rightarrow \pi^*$ transition. If the azomethine chromophore were completely analogous to the carbonyl,

TABLE I

| Solvent Com- pound ^a | Vapor ^b | | | n-Heptane ^c | | Cyclohexane ^d | | Ethanol ^d | |
|---------------------------------------|----------------------------|----------------------------|-------------------|----------------------------|-------------------|----------------------------|-------------------|----------------------------|-------------------|
| | λ_{\max} , m μ | λ_{\max} , m μ | ϵ_{\max} | λ_{\max} , m μ | ϵ_{\max} | λ_{\max} , m μ | ϵ_{\max} | λ_{\max} , m μ | ϵ_{\max} |
| I | 177 | 181 | 5980 | 244 | 160 | 231 | 160 | 231 | 160 |
| II | 174 | 179 | 8900 | 246 | 140 | 232 | 200 | 232 | 200 |
| III | 172 | 179 | 9450 | 240 _s | -- | 235 | 200 | 235 | 200 |
| IV | 177 | 180 | 9470 | 247 | 196 | 235 | 180 | 235 | 180 |
| V | 173 | 178 | 7100- 8350 | 252 | 296 | 235 | 300 | 235 | 300 |
| VI | 181 | 181 | 9275 | 250 | 246 | 240 | 290 | 240 | 290 |
| VII | 178 | 180 | 9600 | 245 _s | -- | 238 | 230 | 238 | 230 |
| VIII | 176 | 180 | 10475 | 250 | 192 | 240 | 202 | 240 | 202 |

^aI, N-isopropylidinemethylamine; II, N-isopropylidenebutylamine; III, N-cyclohexylidinemethylamine; IV, N-isopropylidene-cyclohexylamine; V, 2-butyl-3, 4, 5, 6-tetrahydropyridine; VI, N-cyclopentylidenebutylamine; VII, N-cyclohexylidenebutylamine; VIII, N-cycloheptylidenebutylamine. run in 100 mm. cells. run in 0.1 mm. cells. run in 10.0 mm. cells. All spectra were recorded using a Beckman DK2-A Far Ultraviolet Spectrophotometer.

it would appear reasonable to assign the 180 m μ band in the former to an n \rightarrow σ^* transition. However, the molar absorptivities range from 6×10^3 to 10^4 , and these are more nearly what would be expected for a $\pi \rightarrow \pi^*$ transition. In order to obtain some evidence as to the nature of this transition, we have run spectra of II, V, VII and acetone in trimethyl phosphate (TMP), which is transparent (in 0.1 mm. cells) to 176 m μ , and compared the results with those obtained in hydrocarbon solvents. These results are given in Table II.

It would be anticipated that the more polar trimethyl phosphate solvent would cause a blue shift in transitions involving non-bonding electrons. This shift is observed in the n \rightarrow π^* band of the azomethines

TABLE II
 $\lambda_{\max}(\text{m}\mu)$ in Different Solvents

| Compound | n-Heptane | TMP | Δ , m μ | Cyclohexane | TMP | Δ , m μ |
|----------|-----------|-----|--------------------|------------------|------------------|--------------------|
| II | 179 | 183 | +4 | 246 | 236 | -10 |
| V | 178 | 184 | +6 | 252 | 242 | -10 |
| VII | 180 | 185 | +5 | 245 _g | 238 | - 7 |
| Acetone | 185 | 182 | -4 | 279 | 270 _g | - 9 |

and acetone and these results are entirely consistent with those already reported by Bonnett (1)(2). In the case of the band around 180 m μ , however, the results are not the same. In trimethyl phosphate the 186 m μ band of acetone shows a blue shift of 4 m μ , as would be expected for an $n \rightarrow \sigma^*$ band. On the contrary, the 180 m μ band of the azomethines show a red shift of 4-6 m μ , and this is presented as evidence for this band being due to a $\pi \rightarrow \pi^*$ transition. We hope to present more evidence as to the nature of this transition in the near future.

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