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Spectroscopic Studies on Some Ketimines

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The electronic absorption spectra of some ketimines have been investigated using different solvents. Assignment of the obtained transitions was attempted. The *N*-substituted ketimines did not show a discrete band for the n—π^* transition as was obtained with the unsubstituted molecules. Molecular orbital calculations were carried out using the PPP variant of the SCF-MO theory. Agreement between the calculated and experimental transition energies was satisfactory.

The spectra of the ketimines are rarely found in the literature, though the spectra of the related compounds, anils or Schiff's bases, are common.[1] Kaplan[2] reported the spectra of some 4-alkyldiphenylketimine hydrochlorides. It was found that the unconjugated azomethine chromophore absorbs at higher energy than the corresponding carbonyl and thiocarbonyl chromophores.[3] The n→π^* transition for the $>$C=N– group is allowed but is symmetry forbidden for the carbonyls and thiocarbonyls.

Ultraviolet spectra of *N*-(diphenylmethylene) aniline were reported in different solvents.[4] The spectra of benzanils were found to be, essentially, a superposition of the spectra of the corresponding benzal and aniline parts of the molecule,[5] the azomethine group acted as an electron acceptor when linked to a phenyl group at its end.

Alexander *et al.*[6] investigated the solvent effects on the absorption spectra of *o*-, *m*-, and *p*-hydroxybenzylidenimines. Ebara[7] showed that the spectra of benzylideneanilines cannot be explained adopting the stilbene-type planar structure.

Different studies on some ketimines as ESR,[8] rate of hydrolysis,[9] complex formation with Cu(II) ion[10] and infrared spectra[11,12] are reported in the literature. Semi-empirical molecular orbital calculations were carried out on benzalaniline and some imines.[13,14]

In this work the spectroscopic behaviour of a series of ketimines, including halo and nitro ketimines, is investigated. Bands were assigned to transitions characteristic of specific chromophores in the molecules. To be more accurate, the extended PPP method of the SCF-MO theory was used to compute the energy of the lowest π→π^* transition.

Experimental

Solvents. Methanol and cyclohexane were purified by the conventional methods found in the literature.[15]

Compounds. 1,1-Diphenylmethylenimine was prepared by Grignard reaction between freshly distilled bromobenzene and phenylcyanide, where the complex was decomposed by absolute methanol.[16] The product was purified by vacuum distillation, n_D^{19} 1.6191. The other ketimines were prepared by condensing benzophenone and the corresponding aniline derivative till the calculated volume of water was collected.[17] Compounds were purified by repetitive crystallization. The compounds prepared were: *N*-(diphenylmethylene)aniline; *N*-(diphenylmethylene)-*ortho*-, *meta*-, and *para*-chloroanilines; *N*-(diphenylmethylene)-*p*-bromoaniline; *N*-(diphenylmethylene)-*ortho*-, *meta*-, and *para*-nitroanilines; *N*-(diphenylmethylene) *p*-methoxyaniline.

Melting points corresponded well to values reported in literature.

Apparatus. Spectra were scanned on a Beckmann DK-1 spectrophotometer using 1.0 cm fused silica cells.

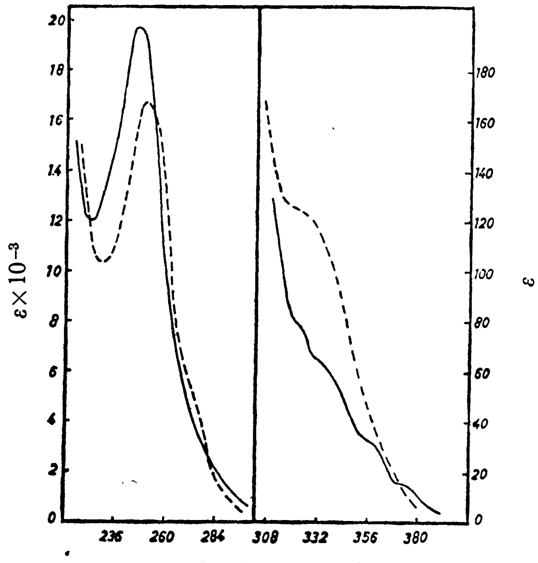
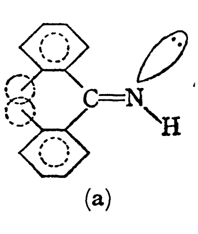


Fig. 1. Absorption spectra of 1,1-diphenylmethylenimine at room temperature.
—— in cyclohexane, ---- in methyl alcohol

Results and Discussion

Electronic Absorption Spectra. *1,1-Diphenylmethylenimine,* N*-Phenyl and* p*-Methoxy Derivatives*: Figure 1 shows the absorption spectra of 1,1-diphenylmethylenimine (a) in polar and non-polar solvents. The extent of molecular coplanarity will be clearly reflected in its spectrum. If the distortion is maximum *i.e.*, the two benzene nuclei are perpendicular, the spectrum will be similar to that of *N*-benzylimine whereas if the distortion is slight the spectrum will be different than that of *N*-benzylimine. In benzophenone Jones[18] calculated 30° as the angle between the planes of the



(a)

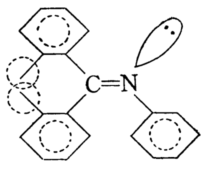
two benzene rings.

1,1-Diphenylmethylenimine is "π" isoelectronic with 1,1-diphenylethylene *i.e.* the $\pi \rightarrow \pi^*$ transitions of both compounds are expected to be energetically comparable. Korver[19] assigned the 260 nm band of 1,1-diphenylethylene to "styrene-conjugation" and the band around 230 nm to "phenyl-phenyl" interaction. Styrene[20] has O→O transition at ~290 nm, the blue shift of the O→O transition of 1,1-diphenylethylene is a result of steric hindrance.

The spectrum of 1,1-diphenylmethylenimine shows a weak shoulder ($\varepsilon_{max}=65$ in cyclohexane and 120 in methyl alcohol) at 332 nm in cyclohexane and at 323 nm in alcohol. The band shows a blue-shift in a polar solvent, and characteristic vibrational structures which are blurred in methanol, thus it may be assigned to an $n \rightarrow \pi^*$ transition. It was shown that 1,1-diphenylmethylenimine forms an n-σ charge transfer complex with iodine[21] which also supports this assignment.

In the UV region, 1,1-diphenylmethylenimine shows an intense assymetric band, with λ_{max} at 245 nm and a shoulder ~270 nm. The long wavelength shoulder is assigned to a transition corresponding to the ${}^1b_{2u} \leftarrow {}^1a_{1g}$ transition of benzene whereas the intense band is assigned to an intramolecular charge transfer transition. The donor site is a benzene nucleus, conjugated with the "π" system of the azomethine group, and the acceptor site is a free π-molecular orbital on the azomethine group. Evidences supporting this assignment will follow. The above way of transitions assignment is an approximate one, since with it, one is bisecting the same molecule to discrete chromophores. However, this approximation is not a crude one, especially if the separate chromophores are not coplanar.

Figure 2 shows the spectra of *N*-(diphenylmethylene)-aniline (b). The position and intensity of band maxima, in Figs. 1 and 2, are very much comparable. This indicates that the π system of the *N*-phenyl ring is not conjugated with the π system of the >C=N– group and may be conjugated with "n" electrons on the nitrogen atom. If this is so, an $n \rightarrow \pi^*$ transition may overlap with the $\pi \rightarrow \pi^*$ band. The bands shown in Fig. 2 are all $\pi \rightarrow \pi^*$ transitions, the 338 nm band may correspond to the intense "a" band of stilbene.[22] The significant reduction of intensity is attributed to the non-coplanarity of the molecule. The 242 nm is assigned to an intramolecular charge transfer transition.



(b)

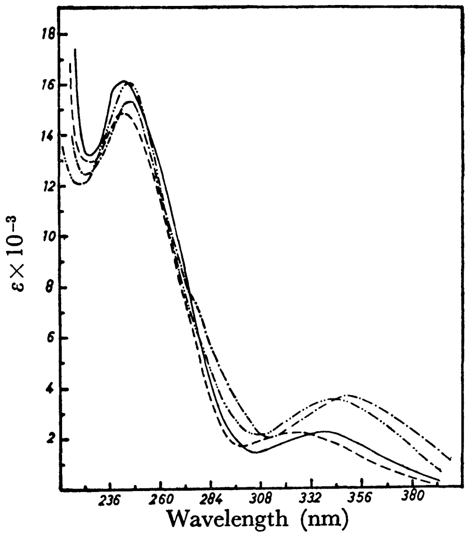


Fig. 2. Absorption spectra of *N*-(diphenylmethylene)-aniline.
—— in cyclohexane, ---- in methyl alcohol *N*-(diphenylmethylene)-*p*-methoxyaniline
····· in cyclohexane, ······· in methyl alcohol at room temperature

To confirm the above results, the spectra of *N*-(diphenylmethylene) *p*-methoxyaniline were investigated (Fig. 2). If "π" conjugation extends over the whole molecule, the –OCH$_3$ group will perturb all the π—π^* transitions, otherwise it will merely perturb the transitions localized on the benzene nucleus attached to it. Investigation of Fig. 2 indicates that the long wavelength band has been significantly red shifted and intensified on substitution by the –OCH$_3$ group whereas perturbation of the other transitions (at ~270 and 245 nm) is only slight. These results confirm that: the long wavelength transition is localized over the *N*-phenyl ring the "π" system of which is not in the same plane as the "π" system of the azomethine group. This is also confirmed by the fact that the band, ~245 nm, assigned to a charge transfer transition was not perturbed by –OCH$_3$ substitution. That is to say, the donor site is the same before and after –OCH$_3$ substitution. Anisole is of lower ionization potential than benzene, and if it were the donor, the energy of the charge transfer band would have been lowered than its value when benzene is the donor. In *N*-(diphenylmethylene) *p*-methoxyaniline, the anisole nucleus is not the donor, since its "π" system is not in the same plane as that of the acceptor site (C=N–). In Table 1 the values of the band maxima, molar extinction coefficient and oscillator strengths for the above molecules are given.

TABLE 1. NUMERICAL VALUES OF THE BAND MAXIMA, MOLAR EXTINCTION COEFFICIENTS AND THE OSCILLATOR STRENGTHS OF THE ABSORPTION BANDS OF SOME KETIMINES IN CYCLOHEXANE

Compound	λ_{max} (nm)	ε_{max}	$f \times 10^3$
1,1-Diphenylmethylenimine	332	65	0.95
	~270*	3297	—
	245	19800	456
N-(Diphenylmethylene)-aniline	338	2160	61
	~270*	8000	—
	242	16100	523
N-(Diphenylmethylene)-*p*-Methoxyaniline	350	3659	103
	~270*	8000	—
	245	15300	760

* Shoulder.

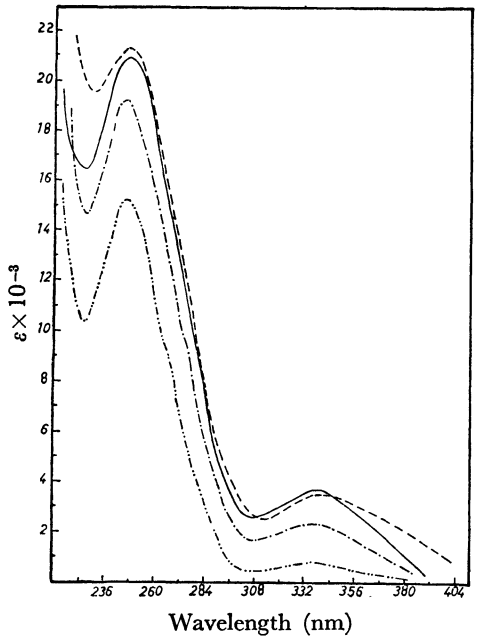


Fig. 3. Absorption spectra.
······· N-(diphenylmethylene) o-chloroaniline
-·-·- N-(diphenylmethylene) m-chloroaniline
---- N-(diphenylmethylene) p-chloroaniline
—— N-(diphenylmethylene) p-bromoaniline
in cyclohexane at room temperature

Halogenated Ketimines: Figure 3 shows the absorption spectra of *N*-(diphenylmethylene) *o*-chloroaniline in addition to the *meta* and *para* derivatives in cyclohexane. When the spectra were scanned in methanol, the long wavelength transition was slightly blue-shifted whereas the ~245 nm transition was red-shifted. The spectra are very much similar to those given in Figs. 1 and 2 indicating that the same types of electronic transitions are occurring. Chlorine substitution in the *N*-phenyl ring perturbed, mainly, the long wavelength transtion. This behaviour was also encountered with $-OCH_3$ substitution. Bands of the halogenated ketimines are assigned in a way similar to that of the previously studied ketimines. Bands of the *o*-chloro derivative are of lower intensity than those of the other, halo derivatives owing to steric hindrance in the former.

To confirm the above results the spectra of *N*-(diphenylmethylene) *p*-bromoaniline were studied (Fig. 3). Spectra of the *p*-chloro and *p*-bromo derivatives are very similar, yet one notices that though ionization potential of chlorobenzene differs from that of bromobenzene the band (248 nm) assigned to a charge transfer transition has the same λ_{max} for the two compounds. This indicates that the donor site is a benzene nucleus rather than the bromo or chlorobenzene nuclei. Rationalization of this point was given before. Numerical values of band maxima, molar extinction coefficients and oscillator strengths (Gaussian analysis was made to clarify the shape of the band and estimate its half width) of the absorption bands of halogenated derivatives are given in Table 2.

Table 2. Numerical values of the band maxima, their molar extinction coefficients and the oscillator strengths of the absorption bands of halogenated derivatives in cyclohexane

Compound	λ_{max} (nm)	ε_{max}	$f \times 10^3$
N-(Diphenylmethylene)	338	790	25
o-chloroaniline	~270*	6300	—
	246	15400	536
N-(Diphenylmethylene)	335	3200	57
m-chloroaniline	~270*	9700	—
	245	19200	711
N-(Diphenylmethylene)	338	2900	93
p-chloroaniline	~270*	8700	—
	248	17200	775
N-(Diphenylmethylene)	338	3700	100
p-bromoaniline	~270*	10800	—
	248	20800	949

* Shoulder.

Nitroketimines: To investigate fairly the spectral properties of ketimines, the spectra of the nitro derivatives were studied. Figure 4 shows the spectrum of *N*-(diphenylmethylene) *o*-nitroaniline which is quite similar to that of *N*-(diphenylmethylene) aniline. This indicates that "π" conjugation does not extend over the >C=N– group and the nitrobenzene nucleus. Here again the nitro group, mainly, perturbed the long wavelength transition. The spectra of *p*-nitroketimine (Fig. 4) indicate many overlapping bands. More than one charge transfer transition can be obtained with this molecule and this reflects the large solvent effect on its spectra. In fact, *p*-nitroaniline possesses a symmetric charge transfer transition with an energy of 3.9 eV. The *p*-nitroketimine has a shoulder at —340 nm (3.6 eV), which appears more clearly in cyclo-

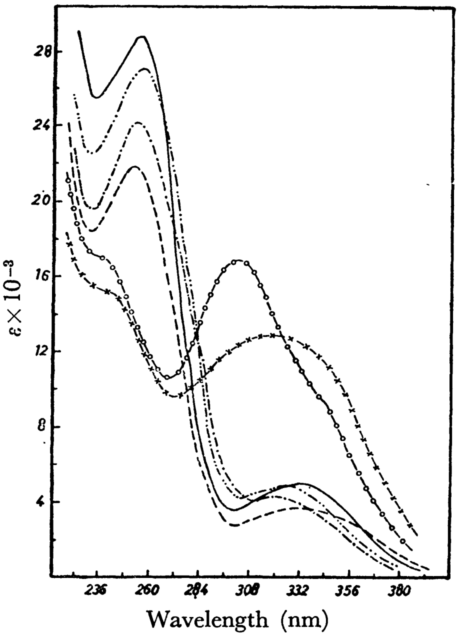


Fig. 4. Absorption spectra of *N*-(diphenylmethylene)-*o*-nitroaniline
—— in cyclohexane, ---- in methyl alcohol *N*-(diphenylmethylene) *m*-nitroaniline
······· in cyclohexane, -·-·- in methyl alcohol *N*-(diphenylmethylene) *p*-nitroaniline
-o- in cyclohexane, -×- in methyl alcohol at room temperature

hexane, could very well be assigned to a charge transfer transition.

Figure 4 shows that the *ortho*- and *meta*-nitroketimines have similar spectra to each other which differ from that of the *para*-isomer. Moreover, the *para*-isomer has its first absorption maximum at a higher energy than those of the *ortho*- and *meta*-derivatives. The same results are found on investigating the spectra of nitroanilines. Resonance theory predicts that the *ortho*- and *para*-isomers should have similar spectra that differ from that of the *meta*-isomer. Godfrey and Murrell[23] calculated the energies of the first four transitions for *ortho*-, *meta*-, and *para*-nitroanilines using the localized-orbital model. Transitions were differentiated to locally-excited and charge-transfer ones. They found that the amino group *para*- to the nitro-group lowers the energy of the first charge transfer state but will have no effect on the energy of the second charge transfer state. On the other hand an amino-group *ortho*- or *meta*- to the nitro-group lowers the energy of the second charge transfer state three times as it does to the first charge transfer state. This goes along with experimental results.

The spectra of nitroketimines are comparable to those of nitroanilines and the lone pair of electrons on the nitrogen azomethine group will play the same role as that of the amino group in nitroanilines. Similarity of the spectra of the *ortho*- and *meta*-nitroketimines and their deviation from that of the *para* isomer are due to the lowering of the energy of the charge transfer states to different extents in the different isomers.

Localized-orbital model bisects the molecule to discrete chromophores, namely donor and acceptor,transition energies are better computed when the molecule is treated as one unit. Molecular orbital calculations were performed on 1,1-diphenylmethylenimine using the PPP[24] variant of the SCF-MO theory to investigate correspondence between the theoretical and experimental values of the energy of the first transition and to investigate how far the coplanarity of the molecule is distorted. The computed value of the energy of the first transition was found to be 4.2 eV (experimental value is 4.4 eV). The semi-empirical method of calculation accounted satisfactorily for the transition energy and showed that coplanarity of the molecule is not highly distorted. Table 3 gives the values of band maxima for the studied nitro derivatives.

TABLE 3. NUMERICAL VALUES OF BAND MAXIMA, MOLAR EXTINCTION COEFFICIENTS AND OSCILLATOR STRENGTHS OF STUDIED NITRO DERIVATIVES IN CYCLOHEXANE

Compound	λ_{max} (nm)	ε_{max}	$f \times 10^3$
N-(Diphenylmethylene)	332	5100	157
o-Nitroaniline	~270*	15100	—
	251	28900	997
N-(Diphenylmethylene)	326	4900	126
m-Nitroaniline	~270*	14200	—
	257	27000	1236
N-(Diphenylmethylene)	~340	9500	—
p-Nitroaniline	302	17000	643
	~240*	17000	—

* Shoulder.

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