Electron-donating Strengths of Some Ketimines Intermolecular Charge Transfer Studies

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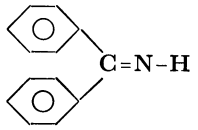
The electron-donating strengths of some ketimines have been investigated *via* the formation of charge transfer complexes with iodine as electron-acceptor. Two types of ketimines were chosen as electron-donors, namely, the =N– unsubstituted as well as the =N– substituted ketimines. With the first type of donors the "n" charge transfer complex was obtained whereas with the second type the "π" charge transfer complexes were obtained. The equilibrium constants were computed for the different types of complexes. An attempt is made to estimate the ionization potentials of the donors from the position of the charge transfer band characteristic of the specific complex.

The electron-donating properties of a Lewis-base can very well be investigated through its ability of forming an intermolecular charge transfer complex with a Lewis-acid. The more stable the complex formed, the stronger is the Lewis base. A wide variety of such complexes has been studied. Different types of electron donors are known, organic as well as inorganic molecules.[1] The donors are usually classified as either "n" or "π" donors depending on the type of their molecular orbital that overlaps with the empty molecular orbital of the acceptor.[2–6] Also, a number of electron acceptors have been used but mainly iodine, chloranil, tetracyanoethylene and maleic anhydride are well known.[7] It has been confirmed that the "n" complexes are much more stronger than the "π" ones. Literature is very rich with intermolecular charge transfer studies and many reviews are available.[8,9] Also, Drago[10–13] and his co-workers, Tamres[14–16] and his co-workers have extensively investigated a wide variety of the charge transfer complexes.

The donor properties of many, nitrogen containing, organic molecules have been investigated.[4,6,13,17] However the electron-donating properties of "Ketimines" have not yet been studied. The "Ketimine" molecule contains a C=N– group which may be called an electron sink. Hence it will be interesting to investigate the donating properties of such a group of compounds. The donating properties will essentially depend on some steric factors as well as on the planarity of the molecule.

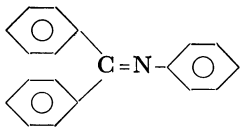
Experimental

Materials. *1,1-Diphenylmethylenimine*:



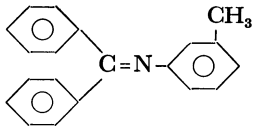
It was prepared from Grignard reaction between freshly distilled bromobenzene and phenyl cyanide. Decomposition of the complex was carried out by absolute methanol.[18] The product was purified by vaccum distillation. Refractive index of the prepared sample is the same as that reported in the literature (n_D^{19} 1.6191).[18]

N-*(Diphenylmethylene)aniline*:



It was prepared by condensation of benzophenone and aniline till the calculated volume of water is collected.[19] The sample was purified by several recrystallization. Melting point is 112—113 °C as compared with 113—114 °C found in literature.[19]

N-*(Diphenylmethylene)*m-*toluidine*.



It was prepared by the same procedure used for the *N*-phenyl derivative. Melting point is 81—82 °C as compared with 82.5 found in the literature.[20]

Solvent. Cyclohexane (Apolda Laboratory product)

1) D. Meyerstein and A. Treinin, *Trans. Faraday Soc.*, **59**, 1114 (1963).
2) G. Briegleb, J. Czekalla, and G. Reuss, *Z. Phys. Chem.* (Frankfurt am Main), **30**, 333 (1961).
3) R. P. Lange, *J. Amer. Chem. Soc.*, **84**, 4438 (1962).
4) V. G. Krishna and M. Chowdhury, *J. Phys. Chem.*, 1067 (1963).
5) M. Ashraf El-Bayoumi and O. S. Khalil, *J. Chem. Phys.*, **47**, 4863 (1967).
6) S. Nagakura, *J. Amer. Chem. Soc.*, **80**, 520 (1958).
7) Z. Yoshida and T. Kobayashi, *Tetrahedron*, **26**, 267 (1970).
8) O. Hassel and Chr. Rømming, *Quart. Rev.*, **16**, 1 (1962).
9) G. Briegleb, "Elektronen Donator-Acceptor-Komplexe," Springer Verlag. Berlin (1963).
10) R. S. Drago and D. A. Wenz, *J. Amer. Chem. Soc.*, **84**, 526 (1962).
11) R. S. Drago, B. Wayland, and R. L. Carlson, *ibid.*, **85**, 3125 (1963).
12) R. L. Middaugh, R. S. Drago, and R. J. Niedzielski, *ibid.*, **86**, 388 (1964).
13) R. S. Drago, D. W. Meek, R. Longhi, and M. Joesten, *Inorg. Chem.*, **2**, 1056 (1963).
14) M. Tamres and S. Searles, Jr., *J. Phys. Chem.*, **66**, 1099 (1962).
15) A. F. Grand and M. Tamres, *ibid.*, **74**, 208 (1970).
16) A. F. Grand and M. Tamres, *Inorg. Chem.*, **8**, 2495 (1968).
17) H. Yada, J. Tanaka and, S. Nagakura, This Bulletin, **33**, 1660 (1960).
18) P. L. Pickard and T. L. Tolbert, *J. Org. Chem.*, **26**, 4886 (1961).
19) A. W. Weston and R. J. Michaels, Jr., *J. Amer. Chem. Soc.*, **73**, 1381 (1951).
20) G. Reddelien, *Ber.*, **42**, 4761 (1909).

was purified by vigorously stirring with fuming sulphuric acid for eight hours. It was washed with water, saturated sodium carbonate and finally with water. The solvent was dried by keeping over anhydrous magnesium sulphate for 24 hr. The solvent was distilled and then used for scanning the spectra.

Apparatus. Beckman DK spectrophotometer was used. The cells were fused silica of 1.0 cm thickness.

Results and Discussion

1,1-Diphenylmethylenimine-Iodine System. Equilibrium Studies: When solutions of the ketimine (D), and iodine, in cyclohexane, are mixed the following equilibrium exists assuming that only a 1 : 1 complex is formed.

$$D + I_2 \rightleftharpoons D \cdot I_2 \quad (1)$$

The equilibrium constant K is given by:

$$K = [C_c]/[C_D - C_c][C_{I_2} - C_c] \quad (2)$$

where, C_C is the molar concentration of the charge transfer complex, C_D is the initial concentration of the ketimine and C_{I_2} is the initial concentration of iodine. If the absorbance "A" is due to complexed as well as noncomplexed iodine and A_0 corresponds to the absorbance of the initial iodine solution then, assuming Beer's law is obeyed, Eq. (2) will read, after rearrangement:[21]

$$K^{-1} = \frac{A - A_0}{\varepsilon_c - \varepsilon_{I_2}} - C_{I_2} - C_D + \frac{C_D C_{I_2}(\varepsilon_c - \varepsilon_{I_2})}{A - A_0} \quad (3)$$

This equation will be used to calculate the equilibrium constant for some "Ketimine-iodine" system from the variation of the absorbance of the iodine 520 nm band on mixing with the donor.

If at a given wavelength, the absorbance is only due to the charge transfer complex, then A_0 and ε_{I_2} are zero and Eq. (3) becomes:

$$K^{-1} = \frac{A}{\varepsilon_c} - C_{I_2} - C_D + \frac{C_D C_{I_2}}{A}\varepsilon_c \quad (4)$$

When both C_D and C_{I_2} are both small and each is much more than C_C, then Eq. (4) can be rearranged to read:

$$\frac{C_{I_2} C_D}{A} = \frac{1}{K\varepsilon_c} + \frac{C_{I_2} + C_D}{\varepsilon_c} - \frac{K C_{I_2} C_D}{\varepsilon_c} \quad (5)$$

If C_D is equal to or of the order of C_{I_2} (and both are small), the last term of (5) can be neglected and a plot of $C_{I_2} \cdot C_D/A$ *versus* $(C_{I_2} + C_D)$ will give a straight line. According to Scott,[22] the best straight line is drawn through the experimental points. From the slope and intercept ε_C and K are computed.

Figure 1 show the absorption spectra of mixtures of the ketimine and iodine solutions in the 465—330 nm region. Cyclohexane is used as the solvent and as the blank. The best experimental conditions for studying this CT system were found to use equal concentrations of both the donor and the acceptor. In the 465—330 nm region neither iodine nor the ketimine has an absorption band and their absorbance in this region is quite negligible. However, the spectra of the "iodine-ketimine" mixtures show a discrete and well defined band with λ_{max} at 398 nm. This band is assigned to a charge transfer transition characteristic of the charge transfer complex $(C_6H_5)_2C{=}NH \cdot I_2$ obtained on mixing the ketimine with iodine. The spectra of a number of "donor-acceptor" mixtures were scanned. Equation (5) is used to compute ε_C and K. Figure 2 shows a

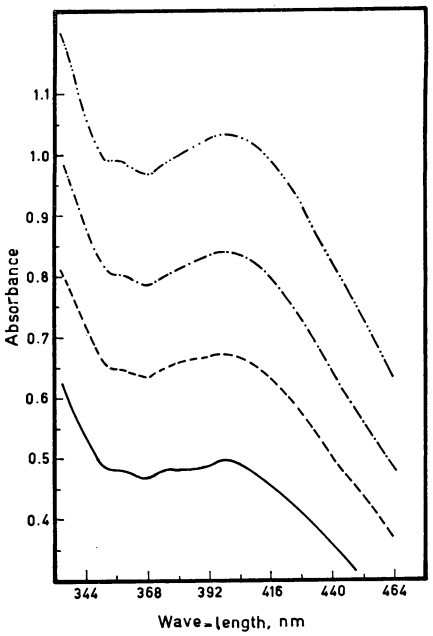


Fig. 1. Absorbance spectra of ketimine-iodine mixtures in cyclohexane.
—— $[I_2]=[\text{Ketimine}]=1.7728\times10^{-3}$ M
----- $[I_2]=[\text{Ketimine}]=2.0682\times10^{-3}$ M
— · — $[I_2]=[\text{Ketimine}]=2.3637\times10^{-3}$ M
— ·· — $[I_2]=[\text{Ketimine}]=2.6592\times10^{-3}$ M

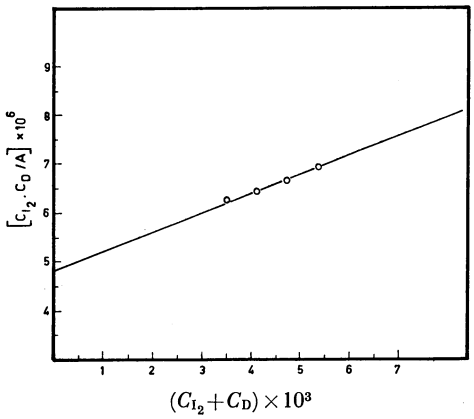


Fig. 2. Variation of $C_{I_2} \cdot C_D/A$ with $C_{I_2}+C_D$ at 398 nm.

Table 1. Variation of absorbance, at $\lambda=398$ nm, with concentration of 1,1-diphenylmethylenimine and iodine

$C_{I_2}=C_D$	Absorbance A	$C_{I_2} \cdot C_D/A$	$C_{I_2}+C_D$
1.7728×10^{-3}	0.50	6.28×10^{-6}	3.5456×10^{-3}
2.0682×10^{-3}	0.67	6.38×10^{-6}	4.1364×10^{-3}
2.3637×10^{-3}	0.84	6.65×10^{-6}	4.7274×10^{-3}
2.6592×10^{-3}	1.03	6.86×10^{-6}	5.3184×10^{-3}

21) N. J. Rose and R. S. Drago, *J. Amer. Chem. Soc.*, **81**, 6138 (1959).
22) R. L. Scott, *Rec. Trav. Chim.*, **75**, 787 (1956).

plot of $C_{I_2} \cdot C_D/A$ (at $\lambda=398$ nm) *versus* $(C_{I_2}+C_D)$. A quite satisfactory straight line relationship is obtained. Data needed to plot Fig. 2 are given in Table 1 and are obtained from Fig. 1. Several plots, as shown in Fig. 2, were drawn at different wavelengths. Results are highly reproducible as shown in Table 2. Variation of K with wavelength has been attributed to the formation of I_3^-.[23]

Table 2. Numerical values of K and ε for the 1,1-diphenylmethylenimine-iodine charge transfer complex at room temperature (18 °C)

λ, nm	K	$1/\varepsilon K$	ε
410	83.49	4.90×10^{-6}	2445
404	83.50	4.85×10^{-6}	2469
398	83.33	4.80×10^{-6}	2500
392	85.37	4.80×10^{-6}	2440
386	84.08	4.90×10^{-6}	2427

The numerical value of the equilibrium constant K of the charge transfer complex of the 1,1-diphenylmethylenimineiodine system is of the order of 84. Reproducibility of the results is quite satisfactory. The relatively high value of "K" suggests strongly that one is dealing with an "n" charge transfer complex. The π charge transfer complexes are much weaker than the n ones. The equilibrium constants for π charge transfer complexes vary between 0.15 and 1.35 for benzene or alkyl benzenes-iodine systems.[25,26]

Position of the Charge Transfer Band and Ionization Potential of 1,1-Diphenylmethylenimine. Figure 3

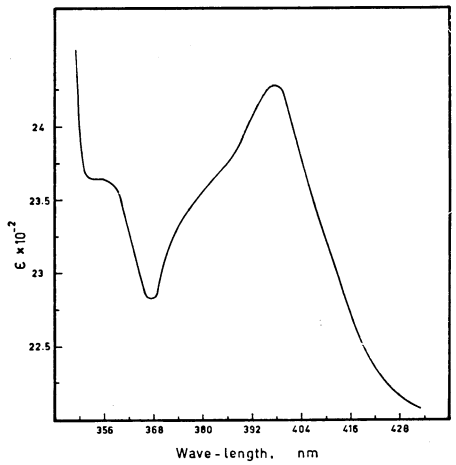


Fig. 3. Charge transfer band of "iodine-1,1-diphenylmethylenimine" System.

shows the charge transfer band of 1,1-diphenylmethylenimine-iodine complex. There are some semiempirical relations which predict the position of the charge transfer band if the ionization potential of the donor is known and others which predict the ionization potential of the donor knownig the position of the charge transfer band. Ionization potentials are determined by a number of methods but most of them cannot differentiate between n and π ionization potentials. On the other hand, ionization potentials obtained from charge transfer studies can be identified as either n or π ionization potentials.

Briegleb[9] *Equation.*

$$E_{CT} = I_D - 5.2 + 1.5/(I_D - 5.2)$$

gives the relation between the energy of the charge transfer band (E_{CT}) and the ionization potential of the donor (I_D) when iodine is the acceptor. Using 3.115 eV for E_{CT} for the 1,1-diphenylmethylenimine-iodine system the n ionization potential of 1,1-diphenylmethylenimine is found to be 7.72 eV.

N-*(Diphenylmethylene)aniline-iodine System. Equilibrium Studies*: Figures 4a and b show the absorption spectra of the pure ketimine, pure iodine and mixtures of both in the 650—350 nm region. Cyclohexane is the solvent and the blank and spectra were scanned at room temperature. Iodine concentration (in the free solution and in the mixtures) was kept constant at 8.5038×10^{-4} M whereas that of the ketimine varied between 1.8153×10^{-2} and 4.8410×10^{-2}. The spectra in Fig. 4 show only the perturbed visible iodine band. That is, no new characteristic band was obtained for the charge transfer transition. On mixing iodine solution with that of the ketimine, the 520 nm band of iodine was blue shifted and the absorbance decreased as the concentration of the ketimine increased. Figure 4a shows one clear and definite isosbestic point. These experimental observations are characteristics of a charge transfer complex. However, since the perturbation of the iodine band is slight and no characteristic charge transfer band was obtained (Fig. 4a) we conclude that we are dealing with a weak charge transfer complex,

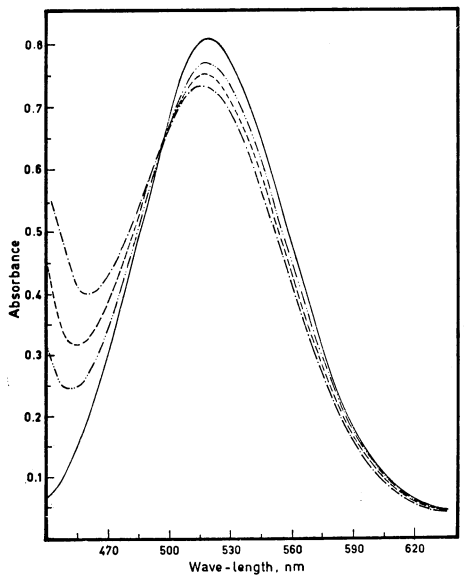


Fig. 4a. Electronic absorption spectra in cyclohexane.
—— Free iodine (8.5038×10^{-4} M)
— · — I_2+Ketimine (Ketimine=4.8410×10^{-2} M)
– – – – I_2+Ketimine (Ketimine=3.0256×10^{-2} M)
— ·· — I_2+Ketimine (Ketimine=1.8153×10^{-2} M)
Concn. of I_2 in all mixtures=8.5038×10^{-4} M

23) A. D. Autery and R. E. Connick, *J. Amer. Chem. Soc.*, **73**, 1842 (1951).
24) N. Ebara, This Bulletin, **34**, 1151 (1961).
25) N. W. Blake, H. Winston, and J. A. Patterson, *J. Amer. Chem. Soc.*, **73**, 4437 (1951).
26) L. S. Andrews and R. M. Keefer, *ibid.*, **74**, 4500 (1952).

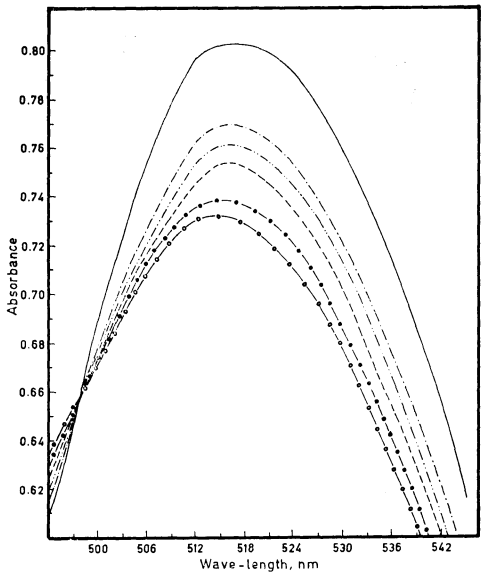


Fig. 4b. Enlarged part of the spectra of *N*-(diphenylmethylene), aniline–iodine system.
——— Free iodine (8.5038×10^{-4} M)
-o-o- I_2+Ketimine (Ketimine=4.8410×10^{-2} M)
-•-•- I_2+Ketimine (Ketimine=4.2359×10^{-2} M)
----- I_2+Ketimine (Ketimine=3.0256×10^{-2} M)
—··— I_2+Ketimine (Ketimine=2.4205×10^{-2} M)
—·— I_2+Ketimine (Ketimine=1.8153×10^{-2} M)
Concn of I_2 in all mixtures=8.5038×10^{-4} M

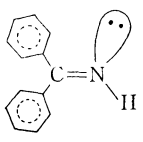
Table 3. Numerical values of K and ε for the *N*-(diphenylmethylene) aniline-iodine charge transfer complex (at 20°C)

Mixtures	K	ε_c
1,2	7.2191	610
1,3	6.3734[a)]	578[a)]
1,4	7.3980	616
1,5	7.8308	629
2,4	7.4510	618
2,5	7.9617	634
3,6	6.9783	605
Average (calculated for the 95% probability limite)	7.4731 ± 0.3875	619

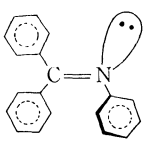
a) Excluded values

most probably a "π" one. The explicit Eq. (3) was used to calculate "K", results are given in Table 3.

Results given in Table 3 are quite reproducible. Figure 4a led to the conclusion that we are dealing with a weak complex. Table 3 confirms this conclusion. Most probably we are dealing with a π complex since K is of the order of 7 whereas that for the 1,1-diphenylmethylenimine-iodine complex K is of the order of 84. It is known that the π complexes are much weaker than those of the n ones. It is worthy to rationalize why, when 1,1-diphenylmethylenimine (a) was the donor an n charge transfer complex is obtained whereas



(a)



(b)

when *N*-(diphenylmethylene)aniline (b) was the donor a π complex was obtained. Assuming sp^2 hybridization for nitrogen atom, the lone pair of electrons occupies one of the sp^2 hybrid orbitals which is perpendicular to the π atomic orbitals of the rest of the molecule. Hence, overlap of this n orbital with the σ^* molecular orbital of iodine is not sterically hindered and a quite stable n charge transfer complex is obtained. On the other hand, in case of the *N*-(diphenylmethylene)aniline, the phenyl group attached to the -*N* atom is not coplanar with the rest of the molecule. As a result the n orbital is conjugated with the π system of the phenyl group attached to the –N atom. Hence, we have no free n orbital to overlap with the σ^* molecular orbital of iodine and only a π charge transfer complex is botained. The π charge transfer complexes are much weaker than the n ones and usually, donot show an absorption band of their own.[25,26] Overlap of transitions is commonly encountered with π complexes.

The above discussion is confirmed when we consider the electronic absorption spectra of the two donors: 1,1-diphenylmethylenimine (a) and *N*-(diphenylmethylene)aniline (b) as shown in Fig. 5. The spectra of

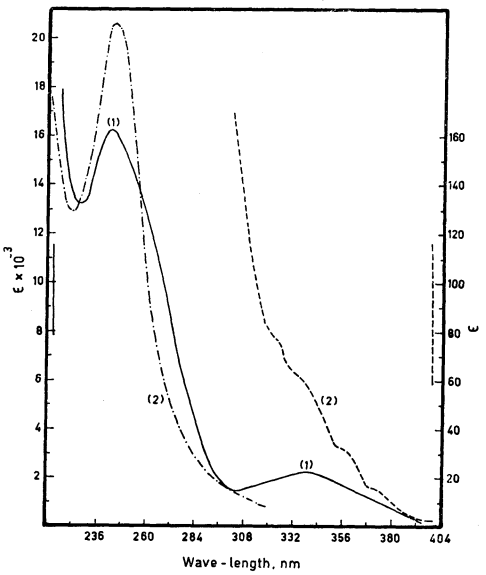


Fig. 5. Electronic absorption spectra of 1,1-(diphenylmethylenimine) (2) and *N*-(diphenylmethylene) aniline (1) in cyclohexane.

the two compounds are very much similar and each show two $\pi\rightarrow\pi^*$ electronic transitions in the ultraviolet region (discussion of the spectra of some ketimines will be subjected in a separate comunication). If conjugation extended over the whole molecule in (b) (molecule is completely planar), then its spectrum would have been significantly different from that of (a). This means that in (b), the benzene ring attached to the nitrogen atom does not lie in the plane of the molecule but may be perpendicular to it. Consequently the n orbital of the nitrogen atom is conjugated with its π cloud and is not free to form an n charge transfer complex when mixed with iodine. This is also confirmed by the fact that the spectrum of 1,1-diphenylmethylenimine shows a separate band for the $n\rightarrow\pi^*$

transition whereas the spectrum of *N*-(diphenylmethylene)aniline does not show this band (Fig. 5). Deviation from coplanarity was also indicated when the spectra of benzylidine aniline were investigated.[24] However, numerical values of the equilibrium constant of "*N*-(diphenylmethylene)aniline-iodine" charge transfer complex indicate that the lone pair of electrons on the nitrogen atom contributes substantially to the relative stability of such a complex. On the other hand, steric factors (in addition to conjugation of n electrons with the π system) inhibit strong interaction with iodine.

Position of the Charge Transfer Band and Ionization Potential of the Donor. When the spectra of pure iodine (3.4270×10^{-5} M), pure *N*-(diphenylmethylene)-aniline (2.4018×10^{-4} M) and their mixtures were scanned in the visible-near ultraviolet region 400—300 nm

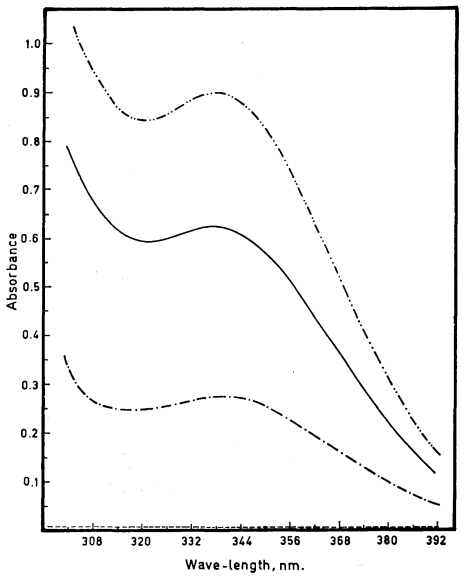


Fig. 6. Electronic absorption spectra of iodine, *N*-(diphenylmethylene) aniline and their charge transfer complex in cyclohexane.
----- Iodine [3.4270×10^{-5} M]
— · — Charg transfer complex
—— Ketimine [2.4018×10^{-4} M]
—··— Mixture of I_2 and ketimine

the absorbance of the mixture is significantly greater than the sum of the absorbances of the free ketimine (Fig. 6) and free iodine. The difference is the absorbance of the charge transfer complex. Thus, in this system, the charge transfer transition and the first $\pi\rightarrow\pi^*$ transition of the donor are overlapping. The energy of the charge transfer band, E_{CT}, is 3.67 eV ($\lambda_{max}=338$ nm) is substituted in Briegleb's equation to yield 8.40 eV as the first ionization potential of *N*-(diphenylmethylene)aniline. Results of Fig. 6 indicate clearly that the electronic transition of the donor with λ_{max} at 338 is $\pi\rightarrow\pi^*$ one ($\varepsilon=2160$). However this transition may be overlapping on the $n\rightarrow\pi^*$ one.

N-*(Diphenylmethylene)*-m-*Toluidine-iodine Systems.* To confirm the above results we used *N*-(diphenylmethylene)-*m*-toluidine as the donor and iodine as the acceptor. The same procedure used with *N*-(diphenylmethylene)aniline was followed. The results obtained with the two donors were very much similar. On mixing iodine solution with that of *N*-(diphenylmethylene) *m*-toluidine the 520 nm iodine band was slightly perturbed, a clear isosbestic point is obtained and no new charge transfer band was obtained. Equation (3) was used to calculate the equilibrium constant. Results are given in Table 4.

Table 4. Numerical values of the equilibrium constant *K* and the molar extinction coefficient ε of the *N*-(diphenylmethylene)-*m*-toluidine-iodine charge transfer complex at room temperature (25 °C)

Mixtures	*K*	ε_c
1,2	5.6895	656
1,3	5.6401	654
1,4	6.2227	676
2,3	5.5481	650
2,4	6.3645	683
3,4	6.7114	695
Average (calculated for the 95% probability limit)	6.0294 ± 0.4949	669

Results of Table 4 are quite reproducible. Also the values of *K* agree fairly well with these obtained for the *N*-(diphenylmethylene)aniline-iodine charge transfer complex. This what one expects when the two donors forms the same type of complex with iodine. The relatively small values of "*K*" as well as the slight perturbation of the iodine band on complexation suggest that we have a weak charge transfer complex.