BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 44, 629—637 (1971)

Electronic States of Diphenylamine and Its Related Compounds

Tadao HINOHARA,* Seikichi CHO, and Toshifumi MORITA
Department of Chemistry, Faculty of Engineering, Gunma University, Tenjincho, Kiryu

(Received July 27, 1970)

For the analysis of the characteristic nature of the first absorption band of diphenylamine (DPA), calculations of the electronic states of DPA and its analogous compounds, diphenylether (DPE) and diphenylmethane (DPM), were carried out and the solvent effects on the fluorescence spectra of these compounds were investigated. The calculated results show that the first excited states of these three compounds are mainly benzene B_{2u}. However, in DPA, the ionic state (CTs^-) is located very closely to the B_{2u} state. It seems reasonable to say, therefore, that, in solution, the ionic state lowers its energy down to the position of the B_{2u} state and that the first absorption band observed in the solution is a superposed band of two transitions, $G \rightarrow B_{2u}$ and $G \rightarrow CTs^-$. To confirm this assumption, the value of $\Delta\mu$, which is the dipole-moment change between the ground and excited states, is estimated from the solvent effect on the fluorescence spectrum. The observed value of $\Delta\mu$ for DPA is intermediate between the theoretical values for the lowest (B_{2u}) and the second excited state (CTs^-); from this fact it may be inferred that the mixing of CTs^- to the lowest excited state (B_{2u}) is increased in the excited equilibrium state.

The electronic absorption spectra of molecules containing two benzene rings joined by one atom having a lone pair electron (C_6H_5-X-C_6H_5) are expected to differ from that of the corresponding monophenyl compounds (C_6H_5-XH). The observed first absorption bands of diphenylether and diphenylmethane are, however, essentially the same as those of the corresponding monophenyl compounds, phenol and toluene respectively. On the other hand, the first absorption band of diphenylamine is considerably different from that of aniline (see Fig. 1).

The first absorption bands of aniline, phenol, and toluene have been assigned to the B_{2u} band of benzene perturbed by substitution.[1] Therefore, it is probable that the first excited states of diphenylether and diphenylmethane are of a B_{2u} character. On the other hand, the nature of the first excited state of diphenylamine should be different from pure B_{2u}, because the intensity of the first band is too high to attribute it to the B_{2u}-band. In this connection, the chemical reaction in the excited state (photochemical reaction) of diphenylamine has been found to be different from those of diphenylether and diphenylmethane.[2] From these points of view, it seemed that it would be very interesting to clarify the electronic structure of diphenylamine; this is the objective of the present investigation. In this paper, the first absorption band of diphenylamine was mainly treated, because its photochemical reaction is concerned with the first excited state.

Investigations of the electronic absorption spectra of the same type of molecules as are treated in the present investigation have already been published by several authors.[3-8] According to Matsen[6] and Bugai,[7] the

---

* Present address: Department of Chemistry, Faculty of Engineering, Toyo University, Kawagoe.

[1] For example: J. N. Murrell, *Tetrahedron*, **19**, suppl., **2**, 277 (1963).

[2] H. Stegemeyer, *Naturwissenschaften*, **53**, 583 (1966).

[3] H. H. Jaffe, *J. Chem. Phys.*, **22**, 1430 (1953).

[4] J. R. Platt, *ibid.*, **19**, 101 (1951).

[5] A. Mangini and C. Zauli, *J. Chem. Soc.*, **1950**, 4960.

[6] F. A. Matsen, *J. Amer. Chem. Soc.*, **37**, 5243 (1950).

[7] P. M. Bugai, L. M. Bazhenova, A. S. Gol'berkova, V. N. Konel'skaya, and I. I. Naidenova, *Zh. Fiz. Khim.*, **37**, 378 (1963); *Chem. Abstr.*, **58**, 13301c.

[8] L. I. Lagutskaya, *Zh. Strukt. Khim.*, **7**, 88 (1966); *Chem. Abstr.*, **63**, 13052a.

first absorption band of diphenylamine is to be attributed to the benzene B_{2u}-band.

In order to clarify the nature of the first excited state, we have measured the solvent effect on the fluorescence spectra of these molecules. We have also made calculations of the energy levels of these molecules in order to obtain more reliable knowledge about the nature of the first excited state.

Experimental

Materials. Commercially-obtained GR-grade diphenylamine and diphenylether were carefully purified by recrystallization from ethanol. GR-grade diphenylmethane was used without further purification. Cyclohexane was purified by passing it through a silica-gel column and by subsequent distillation. The other solvents were purified by the ordinary procedures.

Spectroscopy. The ultraviolet-absorption spectra were measured with a Hitachi EPS 3T and 125 model spectrophotometer. The absorption spectrum in the vapor phase was taken by the flow method, using nitrogen gas as the carrier gas. The temperature of the carrier gas was held at about 80°C.

Experimental Results

Electronic Spectra of C_6H_5-X-C_6H_5 and C_6H_5-XH. To compare the spectra of C_6H_5-X-C_6H_5 and C_6H_5-XH-type molecules, it is desirable to remeasure the absorption spectra under the same conditions, so all the absorption spectra were remeasured in cyclohexane. The observed spectra are shown in Fig. 1. The fluorescence spectra of diphenylamine, diphenylether, and diphenylmethane are also shown in Fig. 1; here, mirror-image relationships are observed. In Fig. 1, it may be seen that the band at about 280 mμ of diphenylamine observed in the solution splits into two bands, the peaks of which are at about 265 and 285 mμ, when the experimental condition is changed from a solution to a vapor.

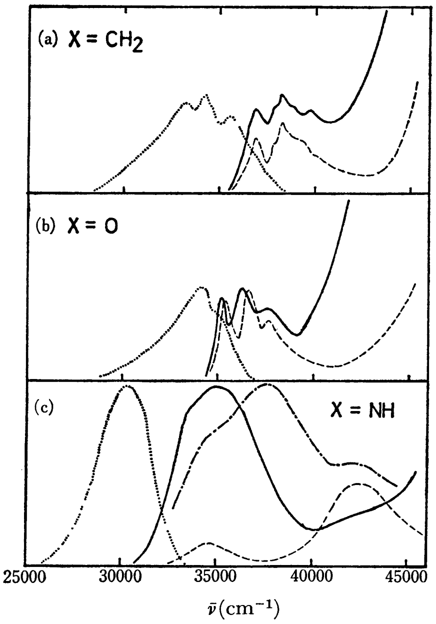

Fig. 1. Absorption and fluorescence spectra of C_6H_5-X-C_6H_5 and C_6H_5-XH. —— absorption in cyclohexane, —·—·— absorption in vapor, ······ fluorescence of C_6H_5-X-C_6H_5, ---- absorption of C_6H_5-XH in cyclohexane. Fluorescence curves are corrected.

Solvent Effects on Fluorescence Spectra. According to Mataga *et al.*[9] and Lippert,[10] the difference between the absorption maximum (σ_a) and the fluorescence maximum (σ_f) is given by the following equation:

$$\sigma_a - \sigma_f = \frac{2\Delta f}{hca^3}(\mu_e - \mu_g)^2 + \text{const.} + \text{smaller terms} \qquad (1)$$

where $\Delta f = (D-1)/(2D+1)-(n^2-1)/(2n^2+1)$,
D: dielectric constant of the solvent,
n: refractive index of the solvent,
a: Onsager's cavity radius,
μ_e: dipole moment of the solute in its excited state,
μ_g: dipole moment of the solute in its ground state,
h: Planck's constant, and
c: light velocity.

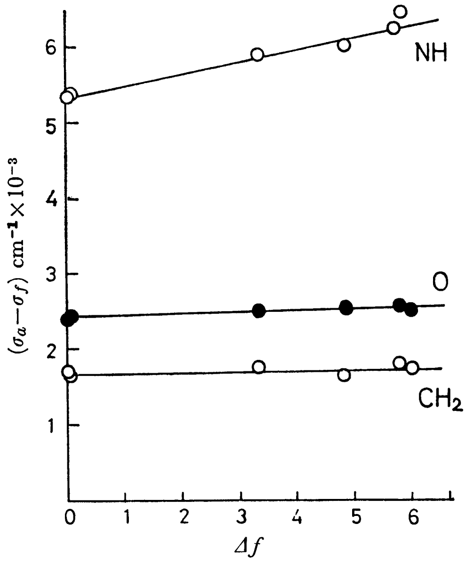

Fig. 2. Difference between absorption and fluorescence maxima, ($\sigma_a - \sigma_f$), plotted against Δf values.

If the smaller terms in the equation are small enough, the difference, $\sigma_a - \sigma_f$, measured in various solvents should be linear with respect to Δf. The experimental results are shown in Table 1 and Fig. 2. A linear relation between $\sigma_a - \sigma_f$ and Δf is observed in Fig. 2, and from the slopes of these lines, $(\mu_e - \mu_g)^2/a^3$ can be obtained. Assuming that a=4 Å[12], and using the value of μ_g given in the literature,[11] the dipole moment in the excited state can be calculated. The results are summarized in Table 2.

---

9) N. Mataga, Y. Kaifu, and M. Koizumi, This Bulletin, **29**, 465 (1956).

10) E. Lippert, *Z. Naturforsch.*, **109**, 54 (1955); *Z. Elektrochem.*, **61**, 962 (1967).

11) Values of dipole moment in the ground state used here are as follows: 1.0 D for diphenylamine (C. A. Barclay, R. J. W. LeFever, and B. H. Smyth, *Trans. Faraday Soc.*, **47**, 357 (1951)), 1.0 and 0.4 D for diphenylether and diphenylmethane respectively (I. Esterman, *Z. Phys. Chem.*, **B1**, 161 (1928).

12) a is the radius of the equivalent sphere of the molecule, or $(4/3)\pi a^3$=molecular volume. In the present case, however, the same value of a is used for diphenylamine, diphenylether, and diphenylmethane.

Table 1. Solvent effects on absorption and fluorescence maxima

solvent	diphenylamine			diphenylether			diphenylmethane		
	a (Å)	f (Å)	$a-f$ (cm^{-1})	a (Å)	f (Å)	$a-f$ (cm^{-1})	a (Å)	f (Å)	$a-f$ (cm^{-1})
CH	2820	3290	5065	2785	2900	1542	2690	2815	1651
C_6H_6	2860	3380	5380	2785	—	—	—	—	—
$(Et)_2O$	2835	3400	5862	2775	2900	1672	2692	2920	2901
CH_3CN	2820	3470	6642	2773	2910	2357	2682	2820	1825
$C_2H_4Cl_2$	2840	3400	5831	2780	2915	1666	2690	2820	1714
EtOH	2840	3480	6383	2775	2900	1672	2687	2810	2310
H_2O	2780	3800	9862	—	—	—	—	—	—

CH: cyclohexane

Table 2. Dipole moment of the excited state of C_6H_5-X-C_6H_5

X	$(\mu_e-\mu_g)/a^3$ (erg)	$\Delta\mu_{obs}$[a] (D)	μ_e (D)	$\Delta\mu_{cal}$ (D)
NH	3.2×10^{-13}	4.4	5.4	2.9, 7.7[b]
O	1.6×10^{-14}	1.0	2.0	0.9
CH_2	1.0×10^{-14}	0.8	1.0	0.7

a) $\Delta\mu=\mu_e-\mu_g$

b) calculated value for the second excited state

Theoretical

Method. The present method of calculating the electronic structure of C_6H_5-X-C_6H_5-type molecules is essentially based on that presented by Longuet-Higgins and Murrell.[13] In the present case, the interaction between three fragments, consisting of two benzene rings and the central atom, X, are taken into account by configuration interaction among the ground, charge-transfer, and locally-excited configurations. In the present calculation, the doubly-excited configurations were ignored.

The Configuration of C_6H_5-X-C_6H_5. Because of the steric hindrance of two hydrogen atoms at the *o*- and *o'*-positions of two benzene rings, the molecule cannot take the planar configuration. Although several considerations of the configurations of two benzene rings in C_6H_5-X-C_6H_5 molecules have been presented,[14-17] no detailed structural data of these molecule have yet been reported. We assume the nonplanar configuration shown in Fig. 3, where the two rings are twisted around the bond axes, NC_1 and NC'_1, at the angles of φ_1 and φ_2 respectively. When the two benzene rings are twisted in the same direction, the molecule may belong to the point group C_2, and when they are twisted in opposite directions, to C_{1h}. The distance between two hydrogen atoms, H and H', must be equal to or larger than 2.4 Å, because the van der Waals radius of the hydrogen atom is 1.2 Å. Therefore, the twisting angle for diphenylamine, satisfying the above restriction, is as follows:

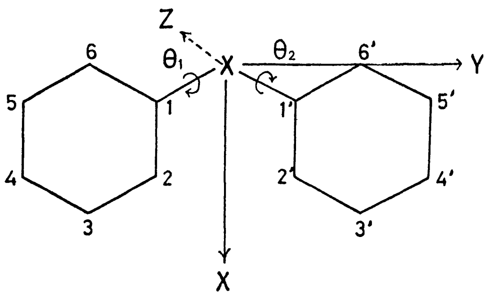

Fig. 3. Configuration of C_6H_5-X-C_6H_5 molecule.

$$\varphi_1 = \varphi_2 = 35° \text{ for } C_2$$

$$\varphi_1 = -\varphi_2 = 88° \text{ for } C_{1h}$$

These values are obtained on the assumptions that the central atom (N) is in the sp^2 hybrid valence state, that the bond length, NC_1, is 1.407 Å,[18] that CC in the benzene ring is 1.397 Å,[10] and that CH is 1.09 Å.[20] Diphenylether and diphenylmethane are assumed to be in the same configuration as diphenylamine.

In the case of the C_{1h} symmetry, the lone-pair orbital of the central atom is almost perpendicular to the pi-electron orbitals of two benzene rings, and the resonance intraction between the central atom and the benzene rings is neglegibly small. The resonance integral, β, can be correlated with the twisting angle, φ, as follows:

$$\beta = \beta_0 \cos\varphi \qquad (2)$$

where β_0 is the resonance integral when the twisting angle is zero.

Local-excitation in a Benzene Ring and the Effect of Excitation Delocalization. Additional effects due to the phenylation of C_6H_5-XH to C_6H_5-X-C_6H_5 may be considerably more complex. Therefore, in the present investigation, our considerations are restricted to the effect necessary for the explanation of the spectral change due to the phenylation, as is shown in Fig. 1.

When the molecules are in a C_{1h} symmetry, the resonance interaction between the central atom and two benzene rings may be ignored, as has been described above, and only the effect of the excitation delocaliza-

---

[13] H. C. Longuet-Higgins and J. N. Murrell, *Proc. Phys. Soc.*, **68A**, 40 (1955); J. N. Murrell, *ibid.*, **68A**, 969 (1955).

[14] F. K. Fong, *J. Chem. Phys.*, **40**, 132 (1964).

[15] R. J. W. LeFever, A. Sundaram, and K. M. S. Sundaram, This Bulletin, **35**, 690 (1962).

[16] K. Higashi, *ibid.*, **35**, 692 (1962).

[17] M. Aroney and R. J. W. LeFevre, *J. Chem. Soc.*, **1960**, 3600.

[18] T. Sakurai, M. Sundaralingam, and G. A. Jeffery, *Acta Cryst.*, **16**, 351 (1963).

[19] K. Kimura and M. Kubo, *J. Chem. Phys.*, **32**, 1776 (1960).

[20] B. P. Stoicheff, *Can. J. Phys.*, **32**, 239, 635 (1954); G. Herzberg and B. P. Stoicheff, *Nature*, **175**, 79 (1955).

tion may be taken into account. The singly-excited states of two benzene rings can be written as follows:

$$\begin{aligned}
\Psi(\mathrm{B_{2u}}) &= 2^{-1/2}(\phi_3{}^{-1}\phi_5-\phi_2{}^{-1}\phi_4),\\
\Psi(\mathrm{B'_{2u}}) &= 2^{-1/2}(\phi'_3{}^{-1}\phi'_5-\phi'_2{}^{-1}\phi'_4)\\
\Psi(\mathrm{E_{1u'}}) &= 2^{-1/2}(\phi_3{}^{-1}\phi_5+\phi_2{}^{-1}\phi_4),\\
\Psi(\mathrm{E'_{1u'}}) &= 2^{-1/2}(\phi'_3{}^{-1}\phi'_5+\phi'_2{}^{-1}\phi'_4)\\
\Psi(\mathrm{B_{1u}}) &= 2^{-1/2}(\phi_3{}^{-1}\phi_4+\phi_2{}^{-1}\phi_5),\\
\Psi(\mathrm{B'_{1u}}) &= 2^{-1/2}(\phi'_3{}^{-1}\phi'_4+\phi'_2{}^{-1}\phi'_5)\\
\Psi(\mathrm{E_{1u}}) &= 2^{-1/2}(\phi_3{}^{-1}\phi_4-\phi_2{}^{-1}\phi_5),\\
\Psi(\mathrm{E'_{1u}}) &= 2^{-1/2}(\phi'_3{}^{-1}\phi'_4-\phi'_2{}^{-1}\phi'_5) \qquad (3)
\end{aligned}$$

where the self consistent orbitals, ϕ_i and ϕ'_i, are the same as those used by Pople.[21] The excitation of an electron within a benzene ring will give rise to two singlet states. For instance, if we take the excitation to the $\mathrm{B_{2u}}$ state, two singlet states, $\mathrm{B_{2u}}$ and $\mathrm{B'_{2u}}$, are possible, and these two will interact with each other in the manner of the exciton interaction.[22] Such interaction produces one set of exciton states, $\mathrm{B_{2u}}^+$ and $\mathrm{B_{2u}}^-$. The wave functions and energy formulae are:

$$\begin{aligned}
&\Psi(\mathrm{B^+_{2u}}) = 2^{-1/2}(\mathrm{B_{2u}}+\mathrm{B'_{2u}}),\ E(\mathrm{B^+_{2u}}) = E(\mathrm{B_{2u}})+\langle \mathrm{B_{2u}}|\mathrm{H}|\mathrm{B'_{2u}}\rangle\\
&\Psi(\mathrm{B^-_{2u}}) = 2^{-1/2}(\mathrm{B_{2u}}-\mathrm{B'_{2u}}),\ E(\mathrm{B^-_{2u}}) = E(\mathrm{B_{2u}})-\langle \mathrm{B_{2u}}|\mathrm{H}|\mathrm{B'_{2u}}\rangle \qquad (4)
\end{aligned}$$

where the interaction matrix element is given by:

$$\begin{aligned}
\langle \mathrm{B_{2u}}|\mathrm{H}|\mathrm{B'_{2u}}\rangle &= 2^{-1}\{\langle \phi_3{}^{-1}\phi_5|\mathrm{H}|\phi'_3{}^{-1}\phi'_5\rangle\\
&\quad + \langle \phi_2{}^{-1}\phi_4|\mathrm{H}|\phi'_2{}^{-1}\phi'_4\rangle\}\\
&\quad - \langle \phi_3{}^{-1}\phi_5|\mathrm{H}|\phi'_2{}^{-1}\phi'_4\rangle\\
&= (\phi_3\phi_5|\phi'_3\phi'_5) + (\phi_2\phi_4|\phi'_2\phi'_4)\\
&\quad - 2(\phi_3\phi_5|\phi'_2\phi'_4) \qquad (5)
\end{aligned}$$

The two electron integrals were evaluated under the zero-differential overlap approximation, and the two center atomic integrals of the (rr/ss)-type were equated to e^2/R_{rs}. The observed value was used for the local excitation energy in a benzene ring, $E(\mathrm{B_{2u}})$. With regard to other local excitations within a benzene ring, $\mathrm{E_{1u}}$, $\mathrm{B_{1u}}$, and $\mathrm{E_{1u}}$, the same type of equations can be derived. The splitting of locally excited states (degenerated) due to exciton delocalization are shown in Fig. 4. The interaction matrix element between $\mathrm{B_{2u}}$ and $\mathrm{B'_{2u}}$ is zero, and the exciton states, $\mathrm{B_{2u}}^+$ and $\mathrm{B_{2u}}^-$, are degenerated.

Effect of Interaction among the Exciton States. The exciton states can interact with each other. The elements of the matrix for calculating the interaction between the four exciton states are as follows:

For the plus state:

$$\begin{array}{c}
\mathrm{B^+_{2u}}\\ \mathrm{E^+_{1u'}}\\ \mathrm{B^+_{1u}}\\ \mathrm{E^+_{1u}}
\end{array}
\begin{pmatrix}
E(\mathrm{B^+_{2u}}) & 0 & 0 & 0\\
0 & E(\mathrm{E^+_{1u'}}) & H_{\mathrm{E_{1u'},B_{1u}}} & H_{\mathrm{E_{1u'},E_{1u}}}\\
0 & H_{\mathrm{B_{1u},E_{1u'}}} & E(\mathrm{B^+_{1u}}) & H_{\mathrm{B_{1u},E_{1u}}}\\
0 & H_{\mathrm{E_{1u},E_{1u'}}} & H_{\mathrm{E_{1u},B_{1u}}} & E(\mathrm{E^+_{1u}})
\end{pmatrix}$$

and for the minus state:

$$\begin{array}{c}
\mathrm{B^-_{2u}}\\ \mathrm{E^-_{1u'}}\\ \mathrm{B^-_{1u}}\\ \mathrm{E^-_{1u}}
\end{array}
\begin{pmatrix}
E(\mathrm{B^-_{2u}}) & 0 & 0 & 0\\
0 & E(\mathrm{E^-_{1u'}}) & -H_{\mathrm{E_{1u'},B_{1u}}} & -H_{\mathrm{E_{1u'},E_{1u}}}\\
0 & -H_{\mathrm{B_{1u},E_{1u'}}} & E(\mathrm{B^-_{1u}}) & -H_{\mathrm{B_{1u},E_{1u}}}\\
0 & -H_{\mathrm{E_{1u},E_{1u'}}} & -H_{\mathrm{E_{1u},B_{1u}}} & E(\mathrm{E^-_{1u}})
\end{pmatrix}$$

Diagonal elements are given by Eq. (4) and so on. The off-diagonal elements were evaluated under the same approximation as those used in calculating Eq. (5).

Since all the matrix elements involving $\mathrm{B_{2u}}\pm$ are zero, the degeneracy of $\mathrm{B_{2u}}\pm$ exciton states is not removed; moreover, $\mathrm{B_{2u}}\pm$ does not mix with any of the other exciton states. These results indicate that the $\mathrm{B_{2u}}$-band in the absorption spectrum of $\mathrm{C_6H_5}$-XH will not be essentially changed by the phenylation. This is the case for diphenylether and diphenylmethane, as is shown in Fig. 1 (b) and Fig. 1 (c) respectively. The ground state can not interact with any of the exciton states. The calculated results are shown in Fig. 4 and Table 3.

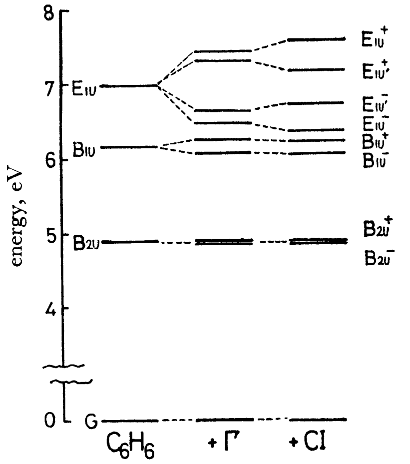

Fig. 4. Change of energy levels due to the exciton interaction (Γ) and configuration interaction (CI).

TABLE 3. THE WAVE FUNCTIONS AND ENERGIES OF $\mathrm{C_6H_5}$-X-$\mathrm{C_6H_5}$ IN $\mathrm{C_{1\mathit{h}}}$ SYMMETRY

Energy (eV)	Wave function		
$W_1=4.89$,	$\Psi_1=B^-_{2u}$		
$W_2=4.89$,	$\Psi_2=B^+_{2u}$		
$W_3=5.86$,	$\Psi_3=-0.270B^-_{1u}$	$+0.802E^-_{1u}$	$+0.532E^-_{1u'}$
$W_4=6.06$,	$\Psi_4=0.998B^+_{1u}$	$+0.041E^+_{1u}$	$+0.041E^+_{1u'}$
$W_5=6.29$,	$\Psi_5=0.963B^-_{1u}$	$+0.232E^-_{1u}$	$+0.139E^-_{1u'}$
$W_6=6.82$,	$\Psi_6=-0.012B^+_{1u}$	$-0.552E^+_{1u}$	$+0.834E^+_{1u'}$
$W_7=7.17$,	$\Psi_7=0.011B^-_{1u}$	$-0.550E^-_{1u}$	$+0.835E^-_{1u'}$
$W_8=8.07$,	$\Psi_8=-0.057B^+_{1u}$	$+0.833E^+_{1u}$	$+0.550E^+_{1u'}$

Effect of Charge-resonance Interaction. Effect of resonance interaction between the central atom and the two benzene rings must be taken into account if the molecule is in $\mathrm{C_2}$ symmetry, for, in this case, the resonance interaction can not be ignored.

Unlike the benzene excited state, eight ionic states do not interact with each other. However, we can take, for convenience, these ionic configurations in the sym-

---

[21] J. A. Pople, *Proc. Phys. Soc.*, **68A**, 81 (1955).

[22] J. N. Murrell, "The Theory of the Electronic Spectra of Organic Molecules," Methuen Co. Ltd., London (1963), p. 135.

metry combination:[23)]

$$(\mathrm{CTs}^{\pm}) = 2^{-1/2}(\theta^{-1}\phi_5 \pm \theta^{-1}\phi'_5)$$
$$(\mathrm{CTa}^{\pm}) = 2^{-1/2}(\theta^{-1}\phi_4 \pm \theta^{-1}\phi'_5)$$
$$(\mathrm{CT}_{ij}{}^{\pm}) = 2^{-1/2}(\phi_i{}^{-1}\phi'_j \pm \phi'_i{}^{-1}\phi_j) \tag{6}$$

As for CT_{ij}, we take the following four configurations into account: CT_{24}, CT_{25}, CT_{34}, and CT_{35}. The corresponding energies are given by the following equations:

$$E(\mathrm{CTs}^{\pm}) = E(\theta^{-1}\phi_5) = (I-A) - Qs,\quad Qs = (\theta\theta|\phi_5\phi_5)$$
$$E(\mathrm{CTa}^{\pm}) = E(\theta^{-1}\phi_4) = (I-A) - Qa,\quad Qa = (\theta\theta|\phi_4\phi_4)$$
$$E(\mathrm{CT}_{ij}^{\pm}) = E(\phi_i{}^{-1}\phi_j) = (I'-A) - Q_{ij},\quad Q_{ij} = (\phi_i\phi_i|\phi_j\phi_j)$$

where A is the electron affinity of benzene and where I and I' the ionization potentials of the central atom, X, and benzene respectively. The $(\phi_i\phi_i/\phi_j\phi_j)$-type integrals were evaluated using the approximation of zero differential overlap and the point charge. Qs and Qa may be expanded as follows:

$$Qs = 3^{-1}\{(\mathrm{C_1C_1}|\theta\theta) + 1/2(\mathrm{C_2C_2}|\theta\theta) + 1/2(\mathrm{C_3C_3}|\theta\theta) + (\mathrm{C_4C_4}|\theta\theta)\}$$
$$Qa = 2^{-1}\{(\mathrm{C_2C_2}|\theta\theta) + (\mathrm{C_3C_3}|\theta\theta)\} \tag{8}$$

The two center integrals, $(\mathrm{C}_j\mathrm{C}_j/\theta\theta)$, where C_j indicates the j'th carbon atom of the benzene ring, were calculated by the use of quadratic equations with an interatomic distance of r_{CX}.[24)]

The off-diagonal elements of the matrix for calculating the interaction between the exciton states and the electron transfer states are evaluated by the method of Pople[21)] and Murrell[13)] as follows:

$$H_{\mathrm{G,CTs}^{\pm}} = -2/\sqrt{6}(\beta-\beta'),\quad H_{\mathrm{CTs}^{\pm},\mathrm{CT}_{24}^{\pm}} = \mp 1/\sqrt{3}\beta$$
$$H_{\mathrm{CTs}^{\pm},\mathrm{B}_{1u}^{\pm}} = -1/\sqrt{6}(\beta+\beta'),\quad H_{\mathrm{CTa}^{\pm},\mathrm{CT}_{25}^{\pm}} = \mp 1/\sqrt{3}\beta$$
$$H_{\mathrm{CTs}^{\pm},\mathrm{E}_{1u}^{\pm}} = 1/\sqrt{6}(\beta+\beta')\quad H_{\mathrm{CT}_{ij}^{\pm},\mathrm{CT}_{lm}^{\pm}} = -(\phi_i\phi_l|\phi'_j\phi'_m)$$
$$H_{\mathrm{CTa}^{\pm},\mathrm{B}_{2u}^{\pm}} = 1/\sqrt{6}(\beta+\beta'),$$
$$H_{\mathrm{CTa}^{\pm},\mathrm{E}_{1u'}^{\pm}} = 1/\sqrt{6}(\beta+\beta') \tag{9}$$

where β is the resonance integral between two atomic orbitals belonging to the central atom and adjacent carbon atoms, and where β' is that belonging to the central atom and ortho carbon atoms. β' was originally taken into consideration by Kimura *et al.*[25)] in the calculation of the electronic structure of aniline and its related compounds. According to them, β' is correlated with β as follows:

$$\beta' = S'/S \times \beta = 0.116\beta \tag{10}$$

where S and S' are the overlap integrals corresponding to β and β'. In the present investigation, the transition energies and wave functions were calculated by assuming β_0 and I-A as the parameters. The transition energies, ΔW, evaluated by the use of −1.8 eV for β_0 and 35° for φ are plotted against the (I-A) values in Fig. 5. In those calculations, the CT_{34} and CT_{35} configurations were ignored, for these configurations were found to be unimportant in interpreting the nautre of the lower energy levels, as is shown in Table 4.

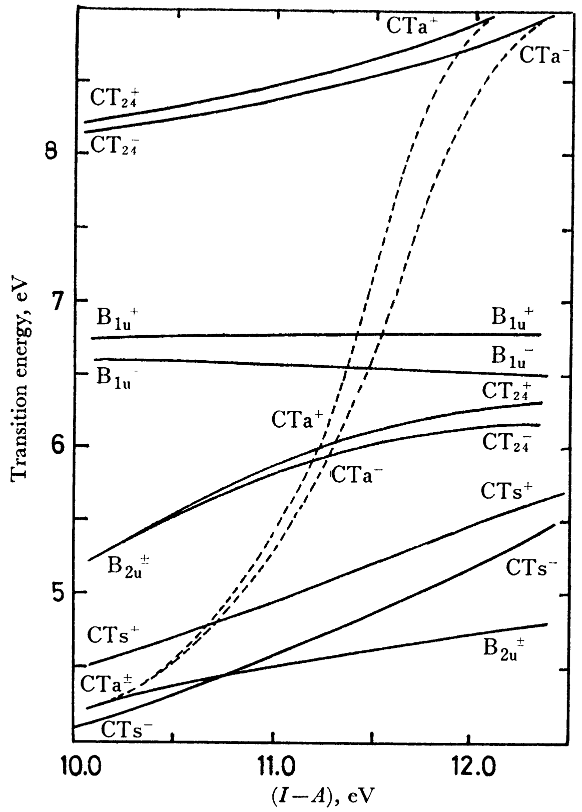

Fig. 5. The calculated transition energies plotted against ($I-A$) values. ($\beta_0 = -1.8$ eV, $\theta = 35°$)

The results calculated using different β_0 values were essentially the same as those shown in Fig. 5. Therefore, the qualitative nature of the lower excited states of $\mathrm{C_6H_5\text{-}X\text{-}C_6H_5}$ molecules may be understood from Fig. 5, in which the values of (I-A) is assumed to be about 11.0 eV for diphenylamine (X=NH), about 12.0 eV for diphenylether, (X=O), and about 14.0 eV for diphenylmethane ($\mathrm{X{=}CH_2}$). A more detailed comparison of diphenylamine and diphenylether is shown in Fig. 6, in which the relation between the electron configurations used in the present calculation and the energy levels finally obtained is shown.

Table 4 gives the energy levels and wave functions calculated using the following values for (I-A) and β_0:

$(I-A) = 11.0$ eV and $\beta_0 = -1.8$ eV for diphenylamine,[26)]

$(I-A) = 12.2$ eV and $\beta_0 = -1.64$ eV for diphenylether,[26)]

$(I-A) = 14.6$ eV and $\beta_0 = -1.52$ eV for diphenylmethane.[27)]

The correlation between the energy levels of diphenylamine and those of aniline is illustrated in Fig. 7 in comparison with the observed spectrum. The oscillator strength was calculated using the following equation:

$$f = 0.0875 \times E\sum_i Q^2_i \tag{11}$$

[23)] θ is the nonbonding orbital of the central atom, X.

[24)] R. Pariser and R. G. Parr, *J. Chem. Phys.*, **21**, 767 (1953).

[25)] K. Kimura, H. Tsubomura, and S. Nagakura, This Bulletin, **37**, 1336 (1064).

[26)] Values of (I-A) and β_0 used here are taken from the following literature; S. Nagakura and K. Kimura, *Nippon Kagaku Zasshi*, **86**, 1 (1965) and Ref. 23.

[27)] Ionization potential of $\mathrm{CH_3}$ group and the resonance integral between the central carbon atom and the adjacent carbon atoms are taken as 13.25 and −1.52 eV respectively. (H. Hanazaki, H. Hosoya, and S. Nagakura, This Bulletin, **36**, 1673 (1963)).

TABLE 4. (1) CALCULATED ENERGY LEVELS AND WAVE FUNCTIONS OF DIPHENYLAMINE

Energy, eV	Wave function								
	G	B_{2u}	E_{1u}'	B_{1u}	E_{1u}	CTs	CTa	CT_{24}	CT_{25}
$W_{16}=8.46$	0.074	0.057	-0.247	0.185	-0.453	0.485	-0.248	-0.258	0.573
$W_{15}=8.25$	0.040	-0.134	0.454	0.115	-0.116	0.256	0.548	0.530	0.295
$W_{14}=8.24$		-0.074	0.136	-0.170	0.193	-0.451	0.303	-0.373	0.689
$W_{13}=8.15$		-0.137	0.315	0.103	-0.172	0.280	0.546	-0.573	-0.370
$W_{12}=7.53$	-0.003	-0.021	-0.356	0.005	-0.705	-0.019	0.066	0.310	-0.525
$W_{11}=7.17$	0.003	0.018	0.703	0.060	-0.375	0.019	-0.051	-0.524	-0.289
$W_{10}=6.87$		-0.023	0.617	0.069	-0.556	0.120	0.056	0.422	0.331
$W_9=6.72$		-0.067	0.505	-0.344	0.507	-0.269	0.150	0.344	-0.390
$W_8=6.48$	0.053	0.026	0.044	0.861	0.272	0.267	-0.050	0.039	-0.322
$W_7=6.27$		0.048	-0.148	-0.812	-0.496	-0.150	-0.080	-0.131	-0.163
$W_6=5.70$	-0.005	-0.586	-0.297	0.053	0.022	-0.022	0.580	-0.478	-0.014
$W_5=5.61$		-0.600	-0.433	-0.038	-0.078	0.010	0.526	0.409	0.030
$W_4=4.88$	0.201	-0.035	-0.011	-0.451	0.235	0.761	0.000	-0.016	-0.347
$W_3=4.54$		0.010	0.022	-0.421	0.339	0.780	0.004	0.014	0.314
$W_2=4.33$	-0.005	-0.796	0.149	0.004	-0.013	-0.016	-0.541	0.226	0.013
$W_1=4.31$		0.780	-0.195	0.000	-0.019	-0.006	0.549	0.228	0.005
$W_0=-0.29$	-0.974	0.000	-0.000	-0.027	0.023	0.219	0.000	0.000	-0.033

(2) CALCULATED WAVE FUNCTIONS OF THE LOWER ENERGY LEVELS OF DIPHENYLAMINE
(involving the configurations of CT_{34} and CT_{35})

Energy, eV	Wave function										
	G	B_{2u}	E_{1u}'	B_{1u}	E_{1u}	CTs	CTa	CT_{24}	CT_{25}	CT_{34}	CT_{35}
$W_8=6.48$	0.053	0.026	-0.042	0.861	0.270	0.266	-0.051	0.038	-0.323	-0.008	-0.038
$W_7=6.27$		0.047	-0.143	-0.812	-0.495	-0.150	-0.079	-0.132	-0.164	-0.019	-0.019
$W_6=5.70$	0.005	0.586	0.296	-0.053	-0.022	0.022	-0.578	0.479	0.014	0.031	0.009
$W_5=5.61$		-0.600	-0.432	-0.038	-0.078	0.010	0.525	0.409	0.030	0.025	0.008
$W_4=4.88$	0.201	-0.035	-0.012	-0.451	0.235	0.761	0.000	-0.016	-0.374	-0.004	-0.012
$W_3=4.54$		0.010	0.022	-0.421	0.339	0.780	0.004	0.015	0.314	0.003	0.009
$W_2=4.33$	0.005	0.795	-0.149	-0.004	0.013	0.016	0.541	-0.227	-0.014	-0.008	-0.002
$W_1=4.31$		-0.780	0.195	0.000	0.018	0.006	-0.549	-0.228	-0.005	-0.007	-0.002
$W_0=-0.29$	-0.974	0.000	0.000	-0.027	0.023	0.219	0.000	0.000	-0.033	0.000	0.000

(3) CALCULATED WAVE FUNCTIONS OF THE LOWER ENERGY LEVELS OF DIPHENYLETHER

Energy, eV	Wave function								
	G	B_{2u}	E_{1u}'	B_{1u}	E_{1u}	CTs	CTa	CT_{24}	CT_{25}
$W_8=6.59$	-0.068	-0.046	0.012	-0.714	-0.351	-0.369	0.108	-0.130	0.442
$W_7=6.32$		-0.088	0.007	0.707	0.573	0.181	0.172	0.253	0.194
$W_6=6.19$	0.002	-0.317	-0.378	0.140	0.066	0.011	0.563	-0.642	-0.062
$W_5=6.00$		0.317	0.622	0.160	0.206	-0.007	-0.483	-0.458	-0.038
$W_4=5.56$	0.135	-0.021	-0.020	-0.650	0.225	0.622	0.019	-0.036	-0.347
$W_3=5.27$		0.009	0.043	-0.579	0.405	0.636	-0.005	0.015	0.305
$W_2=4.61$	-0.001	-0.936	0.086	0.000	-0.007	-0.005	-0.315	0.133	0.007
$W_1=4.64$		0.929	-0.119	-0.002	-0.012	-0.001	0.322	0.136	0.004
$W_0=-0.21$	0.984	0.000	0.000	0.020	-0.016	-0.175	0.000	0.000	0.024

(4) CALCULATED WAVE FUNCTIONS OF THE LOWER ENERGY LEVELS OF DIPHENYLMETHANE

Energy, eV	Wave function								
	G	B_{2u}	E_{1u}'	B_{1u}	E_{1u}	CTs	CTa	CT_{24}	CT_{25}
$W_8=6.92$		0.045	-0.479	0.018	0.236	-0.016	-0.136	-0.810	-0.196
$W_7=6.72$	0.019	-0.106	-0.397	0.112	0.210	0.112	0.286	-0.780	-0.266
$W_6=6.57$		0.088	0.598	-0.275	-0.529	-0.126	-0.218	-0.423	-0.191
$W_5=6.27$		0.068	0.615	0.369	0.656	0.078	-0.138	-0.152	0.051
$W_4=6.07$	-0.045	0.002	-0.010	0.948	-0.088	-0.246	-0.003	0.020	0.175
$W_3=5.86$		-0.005	-0.060	0.860	-0.380	-0.285	0.007	-0.009	-0.175
$W_2=4.79$	0.000	0.007	-0.039	0.001	0.004	0.001	0.144	0.060	0.003
$W_1=4.79$		0.986	-0.054	-0.001	-0.006	0.000	0.146	0.061	0.002
$W_0=-0.13$	0.993	0.000	0.000	0.013	-0.011	-0.120	0.000	0.000	0.015

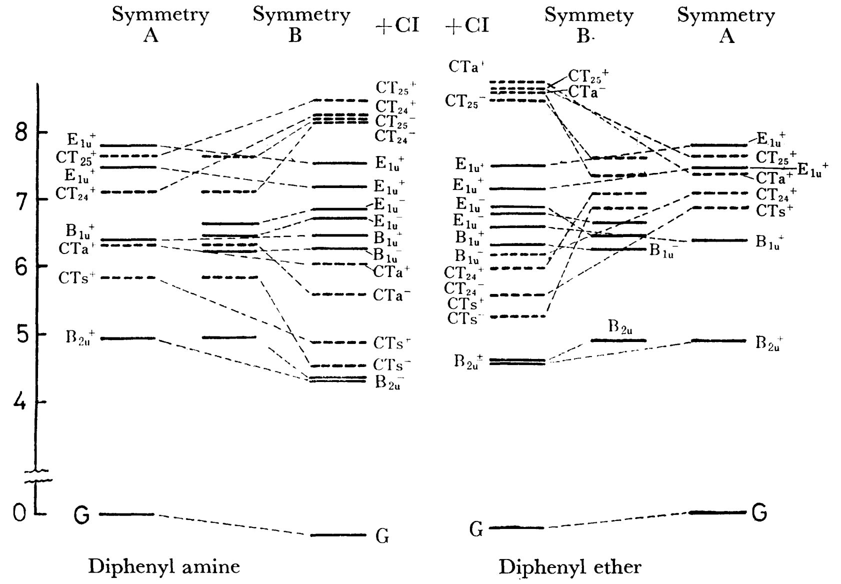

Fig. 6. Energy levels of diphenylamine and diphenylether before and after configuration interaction. (—— locally excited state of benzene; ---- charge transfer state)

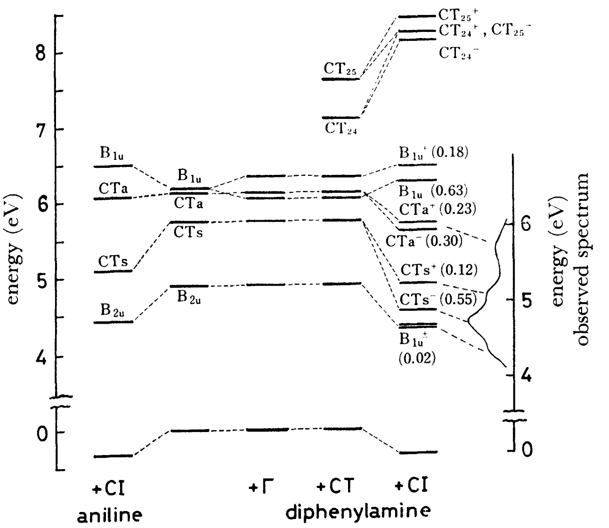

Fig. 7. Correlation among the energy levels of diphenylamine, those of aniline and the observed spectrum. Numbers in parentheses indicate the oscillater strength. The energy levels before and after introduction of excition interaction (Γ), electron transfer interaction (CT) between two benzene rings and configuration interaction (CI) are shown.

where E and Q_t are the transition energy in electron volts and the transition moment in Å respectively.

Theoretical Calculation of $\Delta\mu$ Values. The theoretical expression for $\Delta\mu$ in terms of the state function, Ψ, is given by:

$$\Delta\mu = \langle\Psi_e/M/\Psi_e\rangle - \langle\Psi_g/M/\Psi_g\rangle \tag{12}$$

where $M = \sum e_t r_t$ and where e_t and r_t are the charge and the position vector of the t'th particle respectively. In the present calculation, Ψ_e for the lowest excited state and Ψ_g are approximated as follows:

$$\Psi_g = \chi_g$$

$$\Psi_e = a\mathrm{B}_{2u}^- + b\mathrm{E}_{1u'}^- + c\mathrm{CTa}^-, \text{ for B symmetry}$$

$$\Psi_e = a'\mathrm{B}_{2u}^+ + b'\mathrm{E}_{1u'}^+ + c'\mathrm{CTa}^+, \text{ for A symmetry}$$

where χ_g is the ground-state configuration. The necessary formulae for the expansion of Eq. (12) have been presented by Pariser[28] and also by Mataga.[29] The Eq. (12) is thereby reduced to the following:

$$\Delta\mu = c^2(M_{44} + M_{4'4'})/2 \text{ for B symmetry}$$

$$\Delta\mu = c'^2(M_{55} + M_{5'5'})/2 \text{ for A symmetry}$$

where $M_{ii} = \langle\phi_i/M/\phi_i\rangle = \sum c_{ij}^2 R_j$. R_j is the position vector of the j'th particle. The calculated values of $\Delta\mu$ for the lowest excited states of diphenylamine, diphenylether, and diphenylmethane are tabulated in Table 2.

Discussion

One of the characteristic features of the calculated results shown in Fig. 5, Fig. 6, and Table 4 is that the lowest excited state of each of the compounds treated here is of a B_{2u} character. Moreover, the exciton states, B_{2u}^+ and B_{2u}^-, are degenerated, and these two states do not interact with any of the other exciton states. These facts indicate that the first absorption band of diphenyl compound, C_6H_5-X-C_6H_5, are essentially the same as that of the monophenyl compound, C_6H_5-XH, in the case of the C_2 symmetry or that of benzene in the case of the C_{1h} symmetry. As may be seen in Fig. 1, the first absorption bands of diphenylether and diphenylmethane are not identical with that of benzene, but they are identical with those of the corresponding monophenyl compounds, phenol and toluene respectively. This clearly indicates that the configurations of the two benzene rings belong to the C_2 symmetry. On the other hand, the first absorption band of diphenylamine can not be attributed solely to the B_{2u} of benzene, for its intensity is too high.

The distinctive feature of diphenylamine observed in Fig. 6 is that the CTs^- state is located very close to the B_{2u}^- states. On the contrary, the finaly CTs^- state of

---

[28] R. Pariser, *J. Chem. Phys.*, **24**, 250 (1956).

[29] N. Mataga, This Bulletin, **36**, 654 (1963).

diphenylether obtained after the configuration interaction is located at higher energy and has little effect on the lower-lying energy levels.

Unlike the benzene-excited configurations, the two charge-transfer configurations, $\theta^{-1}\phi_4$ and $\theta^{-1}\phi_4'$, do not interact with each other, and the energy of the charge-resonance state is equal to that of aniline. The origin of the distinction between the observed spectrum of diphenylamine and that of aniline must be attributed to the existence of an interaction between the two benzene rings. Two types of interaction, exciton interaction (Γ) and electron-transfer interaction (CT) between two benzene rings, were considered to explain the distinctive nature of the absorption spectrum of diphenylamine. The effect of the exciton (Γ) and electron-transfer (CT) interactions on the lower energy levels of diphenylamine are illustrated graphically in Fig. 7 and Fig. 8. The energy levels of CTs of aniline split into two levels, CTs^- and CTs^+, upon the introduction of the Γ or CT interaction, while the B_{2u} level is not affected so strongly. The final CTs^- state of diphenylamine obtained after configuration interaction is located at a lower energy than the CTs level of aniline, and the energy gap between CTs^- and B_{2u}^- in diphenylamine is considerably smaller than that in aniline, as may be seen in Fig. 7. This distinction of the calculated energy levels between diphenylamine and aniline can be correlated with that of the observed spectrum between diphenylamine and aniline.

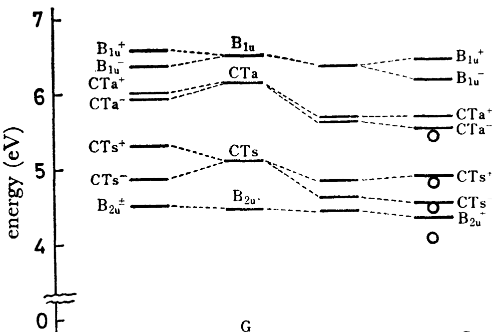

Fig. 8. Comparison of effect of exciton (Γ) and electron transfer (CT) interaction between two benzene rings on stabilizing the CTs^- level of diphenylamine. ○ indicate the observed energy levels.

The mechanism of the stabilization of the CTs^- level due to the introduction of Γ and CT interaction may be illustrated as follows. Firstly, in diphenylamine, the B_{1u} state of benzene, which is located just above the CTs state, splits through the exciton interaction, giving two exciton states, B_{1u}^+ and B_{1u}^-, as may be seen in Fig. 7. The minus state is lower in energy than the plus state, and the energy gap between the CTs^- and B_{1u}^- states is smaller than that between the CTs and B_{1u} states in aniline. Therefore, the configuration interaction will cause more stabilization of the CTs^- level of diphenylamine than the CTs level of aniline. Secondly, the introduction of another benzene ring into aniline at the N-position produces new electron configurations arising from electron transfer between the two benzene rings. One of these configurations, CT_{25}^-, which is located above the CTs^- state, interacts with the CTs^- state; moreover, the interaction matrix element between these two configurations is considerably larger than that between B_{1u}^- and CTs^-. It may be seen in Fig. 8 that the "CT" interaction has a greater effect than the "Γ" interaction in stabilizing the CTs^- level. This result indicates that the electron-transfer interaction between the two benzene rings is important in interpreting the nature of the absorption spectrum of diphenylamine.

The correspondence of the calculated energy levels to the observed absorption spectrum is shown in Fig. 7. The observed band at 260 mμ (4.74 eV) of diphenylamine is reasonably attributed to the Ψ_0—Ψ_3 transition (5.25 eV, $f=0.50$), and the broad shoulder at 275 mμ (4.49 eV) may be thought to consist of two transitions Ψ_0—Ψ_1 and Ψ_0—Ψ_2 (4.92 eV, degenerated, $f=0.016$). The nature of the former transition is that of an intramolecular charge transfer, while the later is of a B_{2u} character.

Since the band shift due to the solute-solvent interaction in a solution may be larger in the charge-transfer band than in B_{2u} band,[30] it may be assumed that in solution, these two bands are superposed upon each other, giving one broad intense band. If this assumption is valid, the solvent effects on the wave-number difference between the first absorption and fluorescence bands, $\sigma_a-\sigma_f$, may be expected to be larger than that of diphenylether or diphenylmethane. In Fig. 2, it may be seen that the slope of the straight line for diphenylamine is considerably larger than that of diphenylether or diphenylmethane. As may be seen in Table 2, the values of $\Delta\mu$ obtained from the slope of the straight lines for diphenylether and diphenylmethane are in good agreement with the theoretically-calculated values of $\Delta\mu$. Therefore, it may be said that the lowest excited states (fluorescent state) of diphenylether and diphenylmethane are mainly benzene B_{2u}. In the case of diphenylamine, the situation is somewhat more complicate. As has already been described, the first absorption band of diphenylamine does not consist of one transition, but of two transitions, $G \rightarrow B_{2u}$ and $G \rightarrow \text{CTs}^-$. The absorption due to the $G \rightarrow B_{2u}$ transition appears as a shoulder on the lower-frequency side of the absorption band attributable to the $G \rightarrow \text{CTs}^-$ transition, as may be seen in Fig. 1 (c). Therefore, the effect of the solvent on the shift of the absorption peak should concern the $G \rightarrow \text{CTs}^-$ transition.

It has been known, in general, that the fluorescent state is the lowest excited singlet state. In diphenylamine, the CTs^- state is located very close to the lowest excited singlet state (B_{2u}). However, the possibility that the second excited state (CTs^-) is the emissive state may be eliminated on the basis of the following facts. First, the absorption and fluorescence bands are not in a good mirror-image relation, as may be seen in Fig. 1 (c); the absorption band is broad, while the fluorescence is sharp. Secondly, the energy gap between the first and second excited states is about 1000 cm^{-1}, and the population of the second excited state,

---

30) E. G. McRae, *J. Phys. Chem.*, **61**, 562 (1957).

as the emissive state, can not be taken into account because of the presence of a rapid internal conversion process and the Boltzman distribution law. Therefore, the observed solvent effect on the fluorescence should be related to the $G \leftarrow B_{2u}$ transition. However, the observed shift of the fluorescence band due to the change in the solvent polarity is larger than that to be expected from the degree of the CT contribution to the lowest excited state, as may be seen in Table 1 and Table 4. One reasonable explanation for this is the resonance (or mixing) of the first and second excited states. This mixing may arise from the change in the molecular configuration in the excited equilibrium state. The interference effect of two closely-spaced excited states have been discussed by Jano[31] and Bixon.[32] In the present case, also, the fluorescent state may be a mixed state of B_{2u} and CTs^- states. The observed value for $\Delta\mu$ (the dipole-moment change between the ground and excited states) of diphenylamine listed in Table 1 may be explained well as the basis of the above conception.

Summary

As for the configuration of the molecule of the C_6H_5-X-C_6H_5 type, two possibilities may be considered. One belongs to the point group C_2, and the other, to C_{1u}. The first excited states of diphenylether and diphenylmethane, calculated theoretically, are B_{2u}, and theoretical considerations suggest that the first absorption bands of diphenylether and diphenylmethane are identical with that of benzene (in the case of C_{1h}) or those of the corresponding monophenyl compounds, phenol and toluene respectively. The observed spectra clearly indicate that these molecules belong to the C_2 symmetry.

The first absorption band of diphenylamine is quite distinctive compared with those of diphenylether and diphenylmethane. The theoretical analysis of this point indicates that the characteristic feature of the first absorption band of diphenylamine is to be ascribed to its low-lying charge-transfer configuration and to the existence of exciton and electron-exchange interaction between the two benzene rings. The first absorption band of diphenylamine in solution is illustrated by the assumption that the lowest excited state is not pure B_{2u}, but a superposed state of B_{2u} and CTs^-. This assumption is verified experimentally by the solvent effects on the absorption and emission spectra.

The authors wish to express their thanks to Professor Ikuzo Tanaka of the Tokyo Institute of Technology for his valuable suggestions and encouragement during this work.

---

[31] I. Jano, *Chem. Phys. Lett.*, **2**, 643 (1968).

[32] M. Bixon and J. Jortner, *Mol. Phys.*, **17**, 109 (1969).