

Some Studies on the Novel Reaction of 2,4-Dinitrotoluene with *p*-Dimethylaminobenzaldehyde

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Received August 31, 1988; in revised form March 21, 1989

The interaction of *p*-dimethylaminobenzaldehyde and 2,4-dinitrotoluene has been studied spectroscopically both in the solid state and in solution. The product has been postulated to be a 1:1 charge transfer complex. By different methods the association constants give values of 2.30 and 3.9 liter⁻¹ mole⁻¹, showing the formation of a moderately strong molecular complex. © 1989 Academic Press, Inc.

Introduction

The solid-state reactions of organic compounds are currently of interest owing to their utility in the study of "organic metals," (1) in photographic processes and in energy conversion systems (2). These reactions find applications in stereospecific syntheses (3) and in electronic and electrostatic devices (2). Although weak charge transfer (CT) complexes are not involved, nevertheless they may reflect the mechanism of these devices.

As far as we are aware very few studies have been reported on the solid-state reactions of aromatic aldehydes with nitro compounds. Of the various solid aromatic aldehydes available, *p*-dimethylaminobenzaldehyde (pDAB) is especially important. It gives interesting color reactions with nu-

merous organic compounds and is therefore a useful chromogenic reagent (4). Its utility in organic reactions has been examined by Menzie (5).

A search of the literature shows that relatively few studies on the charge transfer complexes of 2,4-dinitrotoluene (DNT) have been reported. Buehler and Heaps (6) prepared the molecular compounds of DNT with α -naphthylamine, naphthalene, and benzidine and reported the melting points, the stoichiometry, and the color of these compounds. Giua and Marcellino (7) obtained by the freezing-point method a molecular compound of DNT with β -naphthol melting at 76.6°C. Molecular compounds of DNT with 1- and 2-naphthols (8) were prepared by heating equimolar amounts in cyclohexane. Foster and Thomson (9, 10) studied the charge transfer complexes of DNT with *N,N,N',N'*-tetramethyl-*p*-phenylenediamine (TMPD) using spectro-

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photometric methods in cyclohexane, methanol, and acetonitrile.

Qureshi *et al.* studied the analytical applications of its color reactions with nitrophenol and nitrobenzoic acids (11). However, the chemistry of these reactions was not studied at all.

An instantaneous yellow color is produced when pDAB reacts with DNT. Since pDAB and DNT have many reaction sites the DNT-pDAB solid-state reaction may give rise to interesting interactions. A study of these interactions is presented in this article.

This is perhaps the first report on the $\pi-\pi^*$ CT complexes of pDAB.

Experimental

Materials

DNT (Fluka) and pDAB (BDH Analar, BDH, Poole) were used. All other reagents were analytical grade.

Apparatus

Graduated capillaries (3 mm bore), a Cook's 400 series research microscope, Perkin-Elmer 621, Beckman DK-2A, Bausch and Lomb Spectronic 600, and Bausch and Lomb Spectronic 1001 were used for kinetics, particle size measurements, infrared spectra, reflectance spectra in the UV region, reflectance spectra in the visible region, and UV-visible studies in solution, respectively.

Procedure

i. Kinetics. The kinetics of the solid-state reaction of DNT and pDAB was studied by the capillary method of Rastogi and Dubey (12), using pDAB (40–120 μm) and DNT (100–200 μm) particle size materials at different temperatures. The substances were packed in the capillary with two clean iron rods by applying uniform pressure as far as possible as described earlier (4). The reac-

tion was followed in an electrically controlled oven at the desired temperature. The colored boundary is yellow and moves toward DNT. The distance through which the colored boundary traveled was noted to be correct to 0.01 cm and the accuracy and precision of the kinetic data were found to be 3 to 4%.

ii. Study of photoreaction. A comparative study of the photoreaction and the dark reaction was made by keeping the capillaries packed with the reactants in diffused sunlight and in absolute dark for several hours at 40°C, and the movement of the colored boundary was noted with time.

iii. Study of the spectra. The reflectance spectra of DNT, pDAB, and the DNT-pDAB complex obtained by intimately mixing the powdered samples in different mole ratios were taken in the solid state, in the visible and the UV regions, using $MgCO_3$ as the reference.

The infrared spectra of DNT-pDAB mixtures in different mole ratios were taken by the KBr disk technique at different time intervals; this is complemented with some solution IR studies.

Results and Discussion

The DNT-pDAB reaction follows the rate law

$$\xi = k \log t,$$

where ξ is the thickness of the colored boundary, t is the time, and k is a constant.

The energy of activation and other important parameters for the DNT-pDAB reaction are summarized in Table I.

There are four possible diffusion mechanisms in the solid-state reactions:

- i. Surface migration,
- ii. Grain-boundary diffusion,
- iii. Vapor-phase diffusion, and
- iv. Bulk diffusion.

TABLE I
ENERGY OF ACTIVATION, ENTHALPY OF ACTIVATION, FREE ENERGY OF
ACTIVATION, AND ENTROPY OF ACTIVATION FOR THE DNT-pDAB REACTION

Temperature (°K)	E_a^* (kcal mole ⁻¹)	ΔH^* (kcal mole ⁻¹)	ΔG^* (kcal mole ⁻¹)	ΔS^* (cal deg ⁻¹ mole ⁻¹)
338		9.2	0.134	26.7
333		9.2	0.332	26.6
328	9.88	9.2	0.558	26.4
323		9.2	0.644	26.6
318		9.2	0.764	26.6
308		9.3	0.966	26.9

The absence of a reaction temperature rules out the possibility of bulk diffusion and grain-boundary diffusion. The values of k increase slightly with an increase in particle size. This shows that surface migration is partly taking place in the reaction. Non-polar studies conducted using pellets of the pure reactants show that the DNT tablet is covered with a fine coating of the yellow product. When the DNT tablet is cut into pieces the yellow-colored product is found to have penetrated the surface to a significant depth. This confirms that diffusion of pDAB takes place partly by surface migration and partly through the vapor phase. Finally the positive value of ΔS^* confirms vapor-phase diffusion since vapor-phase diffusion involves a disordered state leading to a positive value of ΔS^* .

Since the methyl group in DNT is electron releasing, by the hyperconjugative effect it fortifies the electron-donating ability of DNT. The effect of the electron-withdrawing nitro group is thereby diluted and DNT is only a weak acceptor. Hence the complexes formed are rather loose. Mulliken's valence bond theory of charge transfer (13) describes the wavefunction as

$$\psi(AD) = a\psi_0(A, D) + b\psi_1(A^- - D^+),$$

where $\psi_0(A, D)$ is the "no bond function."

The extra absorption band in the electronic spectra is characteristic of the dative

function. However, in weak complexes the "no bond function" is far greater, i.e., $a \gg b$. The bonding is largely due to van der Waal/London's dispersion forces, etc., with little or no electron transfer from the donor to the acceptor. The problem is further complicated by "local excitations" in the donor and acceptor moieties which mask the CT band.

The UV-visible reflectance spectra of pDAB, DNT, and the DNT-pDAB complex are given in Fig. 1. The DNT spectrum shows a broad band around 250 nm due to $\pi-\pi^*$ transition. The pDAB spectrum shows two maxima at 245 and 340 nm due to the $\pi-\pi^*$ transition of the benzene ring and the $n-\pi^*$ transition of the C=O group. However, contrary to the UV spectra of carbonyl compounds the intensity of the band due to $n-\pi^*$ transition is much higher than that due to $\pi-\pi^*$ transition. This is perhaps due to the fact that the nonbonded electrons of the nitrogen atom of the amino group contribute appreciably to the $n-\pi^*$ transition. The charge transfer band obtained by subtracting the component absorptions shows a shift due to $\pi-\pi^*$ transitions in the complex. There is however no shift in the $n-\pi^*$ transition but there is an increase in intensity and an increase in the probability of excitation of the n -electrons to the antibonding π -orbitals.

The Job plot obtained at 260 nm by subtracting the contribution of the free reac-

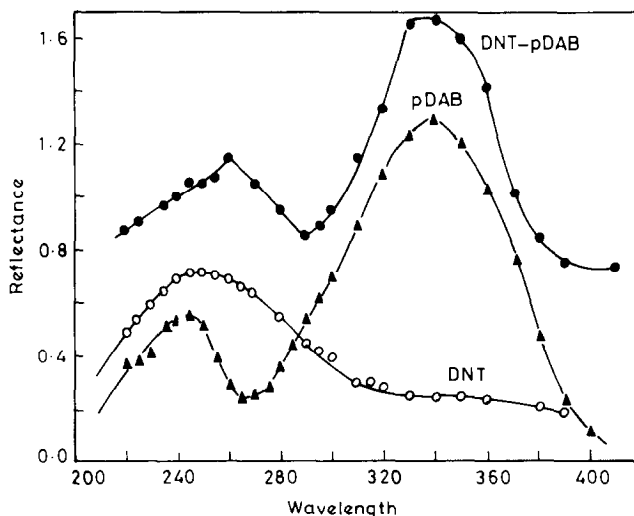


FIG. 1. Reflectance spectra of pDAB, DNT, and the pDAB-DNT charge transfer band isolated by subtracting the contribution of free reactants from the absorbance.

tants is shown in Fig. 2. It shows that a 1 : 1 charge transfer complex is formed. In this interaction we have a donor with n and π donating sites and a weak π -acceptor. The possible transitions are, therefore, $\pi-\pi^*$ and $n-\pi^*$ transitions. The UV-visible spectra in solution show similar trends (Fig. 3). The Job method obtained in solution at

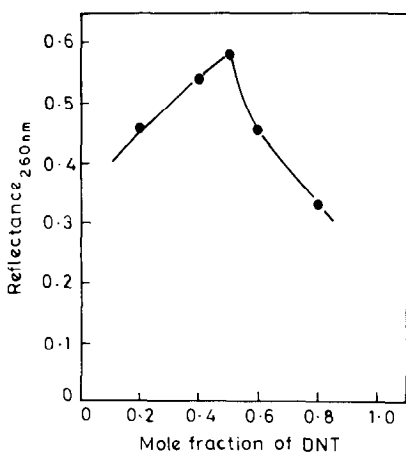


FIG. 2. Plot of the Job method for the DNT-pDAB reaction in the solid state obtained by subtracting the fractional contribution of free reactants.

440 nm confirms the 1 : 1 stoichiometry of the solid state (Fig. 4).

By working with more concentrated solutions ($\sim 0.12 M$) of DNT and pDAB in the region 340–560 nm, it was possible finally to obtain the CT band at 400 nm after compensating for DNT (Fig. 3, inset).

For homopolar diatomic acceptors such as I_2 , Br_2 , and Cl_2 the infrared forbidden stretching vibrations of the free molecules become infrared active and decrease in frequency on interaction with an electron donor (14). A similar decrease in frequency is shown by asymmetric acceptors. This fact is also observed in complexes with n -donors. Since we have an asymmetric acceptor and our electron donor has both n and π donating groups, we would also expect a decrease in frequencies of the stretching vibrations.

It was noted by Ferguson and Matsen (15–17) that the electron affinity of the acceptor changes during stretching vibration of the acceptor. This means that the interaction energy changes; consequently there will be an oscillating dipole moment with a frequency equal to the stretching frequency

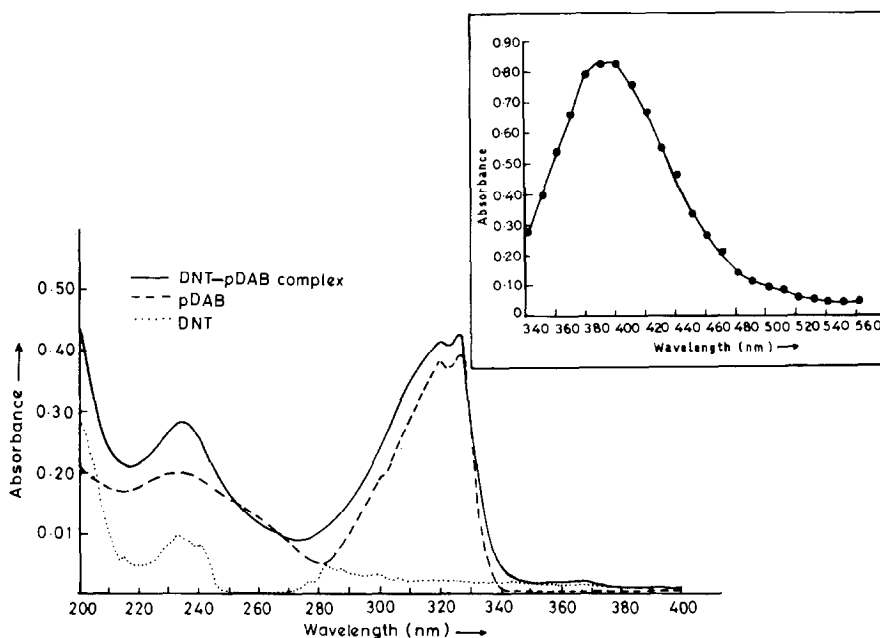


FIG. 3. Solution spectra of DNT, pDAB, and the DNT-pDAB complex in spectroscopic grade cyclohexane. Inset shows the spectra between 340 and 560 nm in concentrated solutions of 0.12 *M* DNT and 0.12 *M* pDAB.

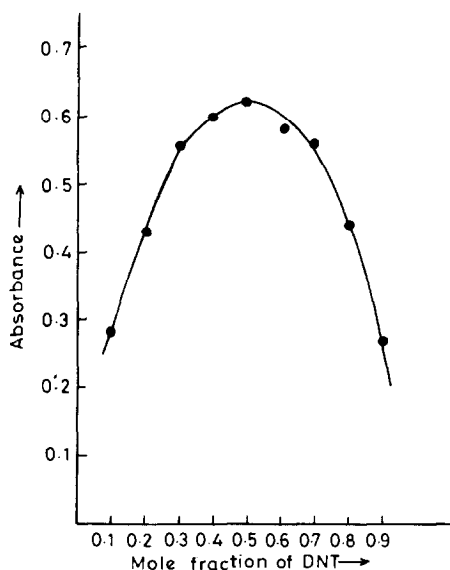


FIG. 4. Complementary Job's plot for the DNT-pDAB complex in solution at 440 nm.

of the acceptor. This changing dipole will potentiate the absorption by the acceptor. The forbidden A_{1g} benzene band at 992 cm^{-1} was accounted for in the complex by a change in the vertical ionization of benzene during the vibration (14). We have also noted that in the DNT molecule and in the pDAB molecule there is no vibration at 992 cm^{-1} but in the complex there is a small peak showing that the formation of the complex causes an oscillating dipole moment.

A possible reason for the paucity of studies on the CT complexes of pDAB is due to the uncertainty of the site of electron donation from pDAB. Since both the carbonyl oxygen and the amine nitrogen have non-bonded electrons, both are capable of participating in either $n-\pi^*$ complexes or a localized molecular interaction.

Our IR studies show clearly that the amine nitrogen is the donor atom participat-

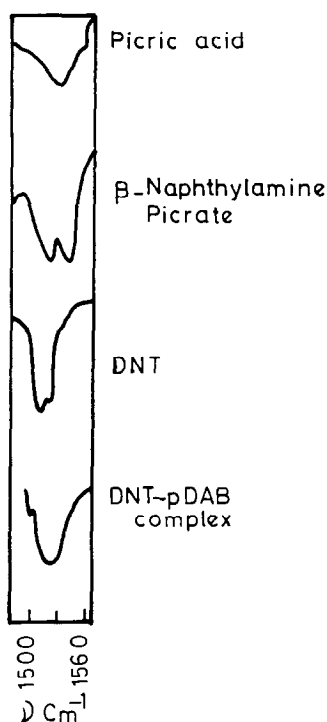


FIG. 5. The $NO_{2(as)}$ stretching vibration in the infrared spectra of DNT and the DNT-pDAB complex compared with picric acid and the picric acid- β -naphthylamine picrate.

ing in a CT interaction, whereas the carbonyl oxygen is not appreciably involved. Evidence pertaining to the proposed charge transfer will be discussed.

After studying 40 molecular complexes of picric acid, Kross and Fassel have given an important and useful classification (18), which includes some broad generalities which can be applied to other polynitroaromatics such as DNT.

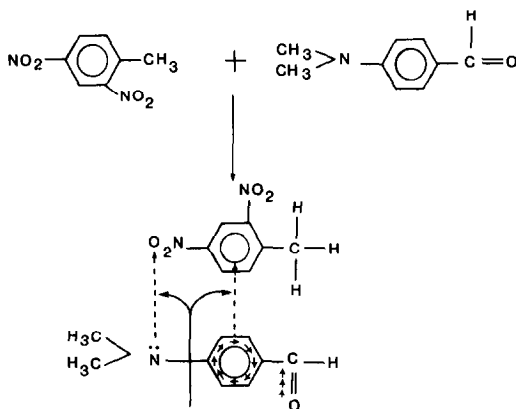
Picric acid contains three nitro groups whose stretching frequencies are not expected to be equivalent. One nitro group *ortho* to the phenolic OH is involved in a hydrogen bond with that group. As a result of this interaction, the asymmetric stretching frequency of the nitro group is decreased. The other nonbonded *ortho* nitro group is rotated out-of-plane of the ring be-

cause of the steric effect of the hydroxyl group. the *para* nitro group is coplanar with the ring. The three nitro asymmetric stretching frequencies are not resolved and appear as one broad band with a maxima at 1525 cm^{-1} .

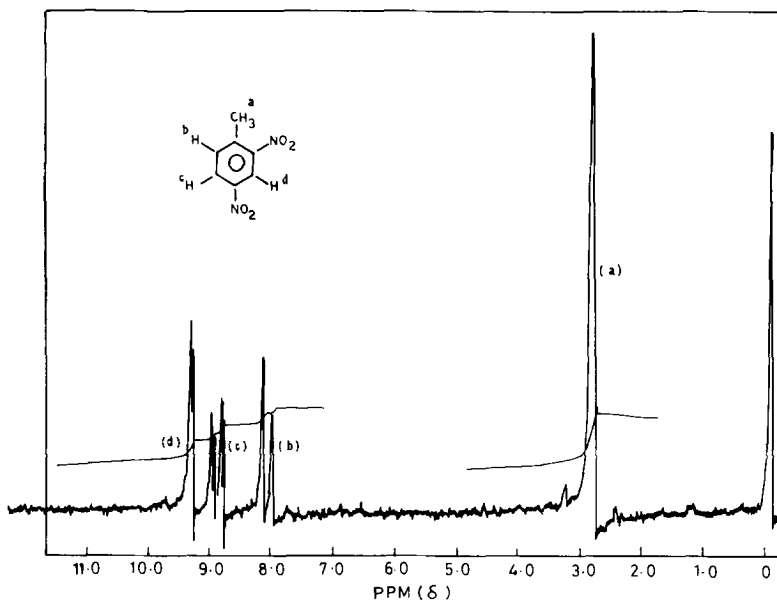
The electron densities on the two nitro groups of the DNT are not the same due to the electron releasing effect of the CH_3 group. Hence the two nitro groups are not equivalent and we get a peak which has been split into a doublet at 1515 and 1530 cm^{-1} . Hydrogen bonding is a possible reason for the nonresolution of the peaks in picric acid.

As a result of Kross' generalization the following conclusions may be reached. The band due to the CH out-of-plane bending occurs at 790 cm^{-1} in DNT and is shifted to 780 cm^{-1} in the complex as a result of a $\pi-\pi^*$ interaction. The $(CH_3)_2N$ peak from 2810 cm^{-1} in the free donor is shifted to 2830 cm^{-1} in the complex. This is due to an appreciable decrease in the charge density on the nitrogen atom. The $\nu_{as} NO_2$ at 1515 and 1530 cm^{-1} in the free acceptor merges to a singlet at 1520 cm^{-1} .

Hence our complex falls in Group II of the Kross classification where there is a $\pi-\pi^*$ interaction coupled with a localized interaction. A point of difference with the

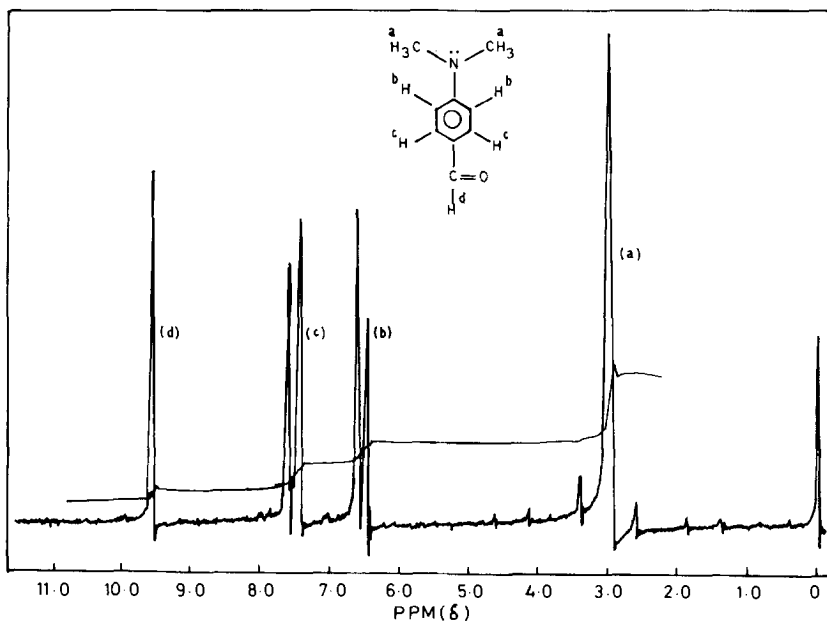


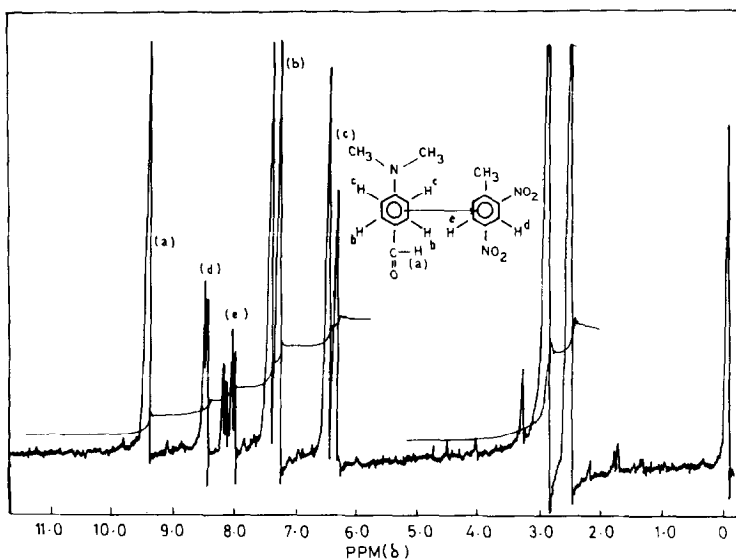
SCHEME 1

FIG. 6. NMR spectra of DNT in CCl_4 .

Kross classification: the band due to ν_{as} NO_2 appears as a singlet in picric acid and splits into a doublet in the complex; in DNT the band occurs as a doublet and merges

into a singlet. These differences can perhaps be reconciled by the magnitude of charge transfer which in the DNT-pDAB complex is fortuitously such that the elec-

FIG. 7. NMR spectra of pDAB in CCl_4 .

FIG. 8. NMR spectra of the DNT-pDAB complex in CCl_4 .

tron densities on both NO_2 groups become approximately equal (see Fig. 5 and Scheme 1).

Some IR studies were also carried out in solution, the solvent being carbon tetrachloride. Since the peak of interest is the $\nu_{2,asym} NO_2$ vibration, the spectra were taken after compensating for pDAB by taking pDAB in the reference cell. The spectra reveal that only one $\nu_{as} NO_2$ peak appears in solution at 1540 cm^{-1} for free DNT. In the

complex (obtained after compensating for pDAB) this peak occurs at 1530 cm^{-1} showing a shift of ca. 10 cm^{-1} . These studies in solution show a result similar to that in the solid state. Slight differences in the value of $\nu_{as} NO_2$ in the solid and solution state may be due to crystal packing effects in the solid.

TABLE II
NMR SHIFTS IN VARIOUS PROTON RESONANCES OF
REACTANTS WHEN COMPLEXED

Proton	Shifts in pDAB resonances in complex (in cycles)	Shifts in DNT resonances in complex (in cycles)
a	11.8	11.8
b	10.6	Merges with pDAB resonances in the complex
c	12.5	10.6
d	12.5	16.8

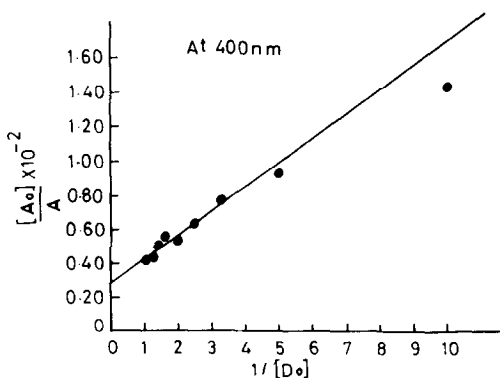


FIG. 9. The Benesi-Hildebrand plot for the evaluation of the association constant of the DNT-pDAB system at 400 nm. $[A_0]$, concentration of DNT which is kept constant; $[D_0]$, concentration of pDAB which is varied; solvent, CCl_4 .

The NMR spectra of the free reactants and the complex in carbon tetrachloride are shown in Figs. 6–8. The shifts are in consonance with a charge transfer whereby the acceptor resonances shift to high fields compared to those of the free reactant. The donor (pDAB) resonances also move up-field even though they should have moved downfield. This is perhaps due to considerable back-donation in the complex (19) and also to transfer of charge from the carbonyl group to the benzene ring depleted in π -electron density due to charge transfer. This shift of charge is designated in the postulated structure by small arrows (\rightarrow).

The $\text{—}\ddot{\text{N}}\begin{matrix} \text{CH}_3 \\ \text{CH}_3 \end{matrix}$ proton of pDAB shifts up-

field by 11.8 cycles while the carbonyl proton shows almost no shift, thereby establishing that the $\text{—}\ddot{\text{N}}\begin{matrix} \text{CH}_3 \\ \text{CH}_3 \end{matrix}$ group is the

donor group. The various shifts are tabulated in Table II.

An idea of the stability of the complex

can be gained from the measurement of the association constants by the Benesi–Hildebrand method by visible spectrophotometry. A value of $2.30 \text{ liter}^{-1} \text{ mole}^{-1}$ is obtained for the association constant. This value is essentially constant within experimental error and is wavelength independent. The results at three wavelengths are given in Figs. 9–11. This value shows that

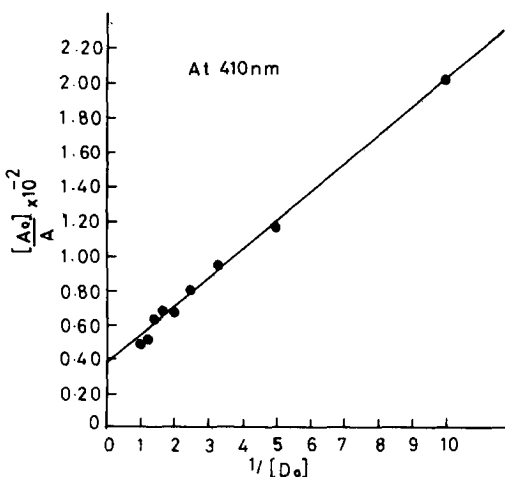


FIG. 10. The Benesi–Hildebrand plot for the evaluation of the association constant of the DNT–pDAB system of 410 nm. $[A_0]$, concentration of DNT which is kept constant; $[D_0]$, concentration of pDAB which is varied; solvent, CCl_4 .

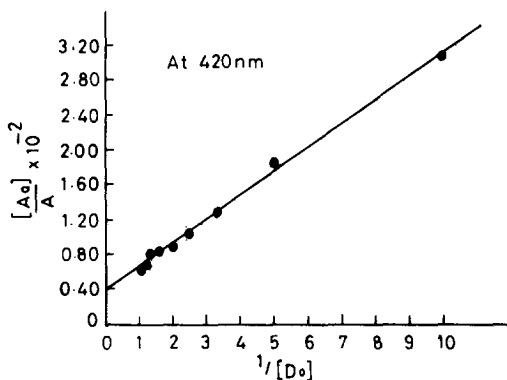


FIG. 11. The Benesi–Hildebrand plot for the evaluation of the association constant of the DNT–pDAB system at 420 nm. $[A_0]$, concentration of DNT which is kept constant; $[D_0]$, concentration of pDAB which is varied; solvent, CCl_4 .

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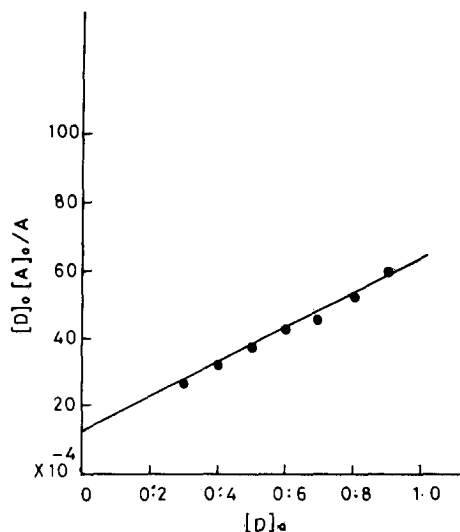


FIG. 12. A plot for the evaluation of association constants by the method of Scott (20).

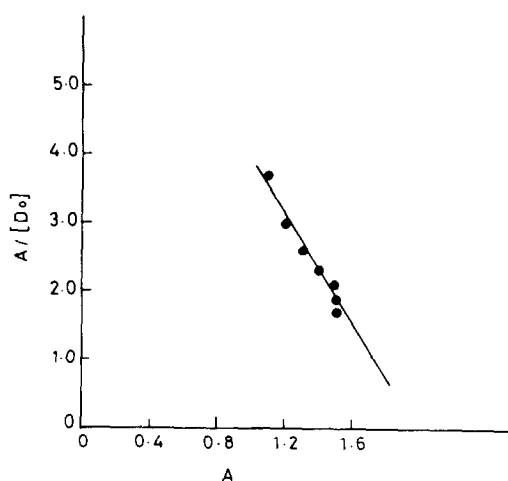


FIG. 13. A plot for the evaluation of association constants by the method of Foster *et al.* (21).

the interaction of DNT with pDAB gives rise to a moderately strong molecular complex.

The Benesi-Hildebrand procedure has been criticized (20) because the method requires an extrapolation to concentrated solutions. Therefore association constants were also evaluated by the equations of Scott (20) and Foster *et al.* (21) both of which extrapolate to dilute solutions. Both Scott's method and Foster's equation give the same value for K , i.e., $3.9 \text{ liter}^{-1} \text{ mole}^{-1}$ (Figs. 12 and 13). The difference from the Benesi-Hildebrand method is obvious in the light of the above discussion. Foster's equation has an advantage as K can be evaluated directly without evaluating ϵ . The $K\epsilon$ in the Benesi-Hildebrand procedure can be evaluated accurately but their separation presents problems.

Acknowledgments

The authors thank Professor S. M. Osman, Chairman, Department of Chemistry, for facilities, and

P. M. Q. thanks U.G.C. (India) for a minor research grant.

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