

## Deactivation channels of multidimensional S<sub>1</sub> state of some laser dyes

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**Abstract.** The photophysical properties of some donor–acceptor dye molecules such as *trans*-4-dimethylamino-4'-cyanostilbene (DCS) and its model bridged single bond derivative (DCSBS) and bridged double bond derivative (DCSBD) with different degrees of flexibility were investigated. This work reports the effect of molecular structure as well as medium viscosity on the fluorescence properties, including fluorescence quantum yields, of this class of molecules. The result could be explained on the basis of a multidimensional excited state which lead to the conclusion that *E/Z* isomerization (or double bond twisting) in the excited singlet state is the most important nonradiative deactivation channel to the ground state. Moreover, experimental results obtained by using stationary fluorescence technique reveal the formation of very weak dye-protic solvent exciplexes of different stoichiometries. Furthermore, dynamical relaxation behaviour, as reflected in the fluorescence quantum yield, is correlated with solvent viscosity/free volume. The results point to possible profitable exploitation of this class of molecules as fluorescent probes.

**Keywords.** Fluorescence; viscosity; exciplexes; twisted intramolecular charge transfer (TICT); laser dyes.

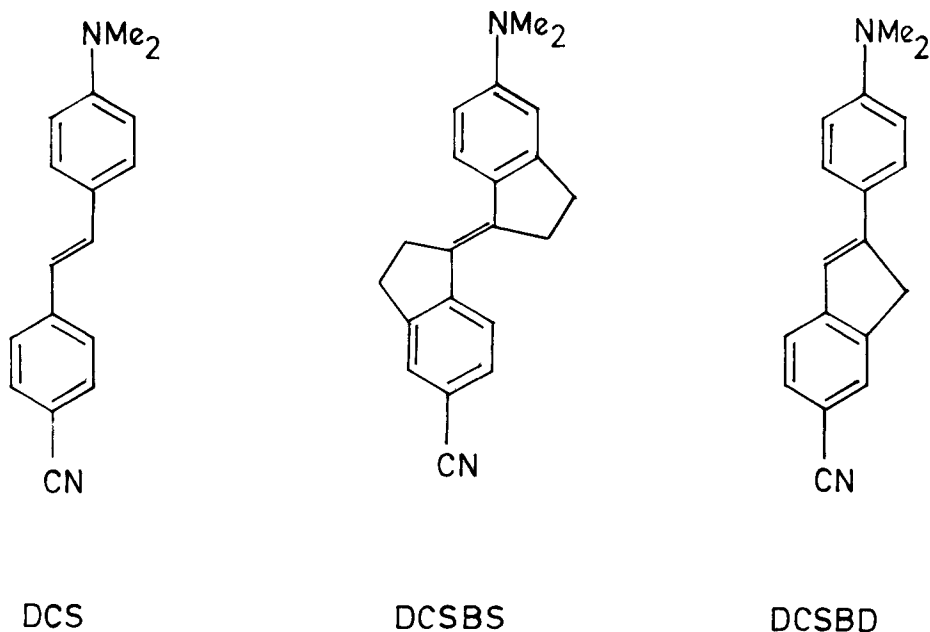
### 1. Introduction

Recently, the spectroscopic properties of a large number of donor–acceptor (D-A) intramolecular charge-transfer (ICT) complexes have received considerable attention because of their profitable applications in industry, e.g. optical recording media, switching devices, solar cells and xerographic photoreceptors.

The anomalous dual fluorescence of *N,N*-dimethylaminobenzonitrile (DMABN) observed by Lippert (Lippert *et al* 1962) in polar solvents had led Grabowski (Grabowski *et al* 1979) to introduce a twisted intramolecular charge transfer state (TICT) as an explanation for this phenomenon. The mechanism responsible for this TICT state involves a twisting relaxation around the C(Ar)–N(amino) bond. In certain molecules, as 6-aminocoumarin, the free amino group is even able to act as the donor in the TICT state (Rettig and Klock 1985). This molecule shows red shifted TICT fluorescence even in rigid environment (Rettig and Klock 1985). This is contrary to DMABN.

The TICT formation does not lead in all cases to fluorescence losses, but in a class of donor–acceptor stilbene derivatives, such as the well-known laser dye DCM, the TICT

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Scheme 1.

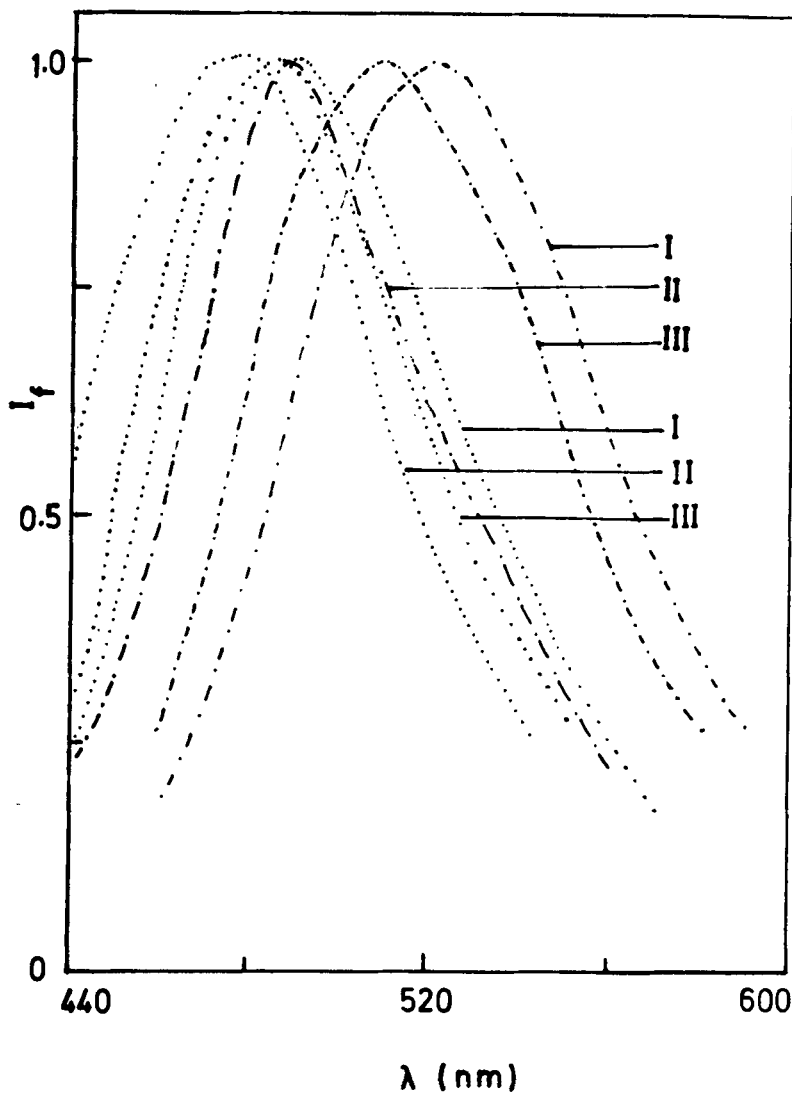
formation is the source of good fluorescence properties (Rettig and Majenz 1989). This can occur because the non-radiative decay channel of double-bond twisting cannot compete with the highly fluorescent TICT state. The internal molecular rotations of DCM and related compounds can be controlled by changing the temperature, viscosity of the surrounding medium and the free volume available for molecular relaxation.

Furthermore, changing molecular structure (molecular rigidity) plays an important role in radiative/nonradiative processes in the excited state of D-A molecules. On the basis of fluorescence properties of a series of ICT complexes of varied structure, Abdel-Mottaleb *et al* (1989) proposed a model of nonradiative decay. The model specifically describes the relative contributions of the possible internal relaxation channels to nonradiative energy dissipation of the singlet excited states via the free rotor mechanism.

The aim of the present work is to find out the relative importance of different deactivation channels operated in the  $S_1$  state of these molecules via the free rotor mechanism. Therefore, we investigate the viscosity dependence of the fluorescence quantum yield of DCS (I) and its model compounds DCSBS (II) and DCSBD (III). Further information about the excited state nature of these dyes and the established equilibrium in its excited state by the interaction with H-bonding solvents will be discussed.

## 2. Experimental

Compounds (I), (II) and (III) were obtained courtesy Dr Rafik O Loutfy, Xerox (Canada). Spectroscopically pure solvents were used for all measurements. Absorption spectral data were obtained on a SP-1800 Pye Unicam spectrophotometer. Fluorescence



**Figure 1.** Fluorescence spectra of compounds I, II and III in ethanol (—) and ethylacetate (· · ·).

spectra were recorded on a Shimadzu Rf-510 spectrofluorometer. Fluorescence quantum yields were determined by comparing with a quinine bisulfate fluorescence standard ( $\phi_f = 0.55$ ).

### 3. Results and discussion

#### 3.1 Excited state interactions (exciplex formation)

Figure 1 shows the fluorescence spectra of compounds (I), (II) and (III) in two solvents; inert ethylacetate solvent and in ethanol. It is obvious that specific H-bonding interaction in case of ethanol results in the observed red-shift in the fluorescence of

these compounds. Upon adding increasing amounts of ethanol (H-bonding donor solvent) to the ethylacetate solutions of the compounds, red-shift of the fluorescence band is observed, (figure 2). Moreover, the fluorescence wavelength is also red-shifted upon adding the more H-bonding donor water to ethanolic solutions of the compounds (figure 2). No similar changes in the absorption spectra of the compounds were noticed indicating that no ground state complexes are practically observed.

The appearance of the isoemissive point is characteristic of excited-state hydrogen-bonding complex formation as previously reported for some other class of molecules of the electron donor-acceptor type (Abdel-Mottaleb *et al* 1992). The formation of excited state hydrogen-bonding complexes is not limited to ethylacetate/ethanol or ethanol/water mixtures but can be observed in some other mixed solvents as acetone/water. This is given in figure 3 for dye (I) as a representative example.

Analysis of the spectral data was carried out by using the relation

$$I_F = K[\text{donor}]^n,$$

where  $I_F = (F - F_0)/(F_\infty - F)$  where  $F_0, F, F_\infty$  are the intensities of fluorescence in case of absence of donor, presence of a given amount of donor, and presence of donor alone, respectively, and  $n$  is the number of donor molecules involved in complex formation. All compounds form very weak complexes in the excited state ( $K$  is of order of  $1 \text{ l.mol}^{-1}$ ) with different stoichiometries (1:1 dye:ethanol or 2:3 dye:water).

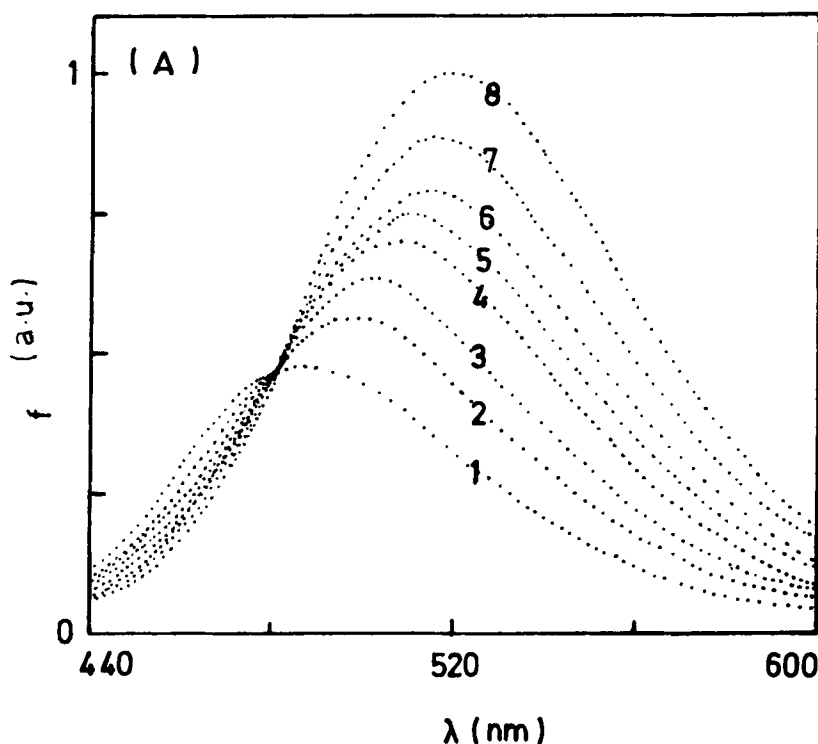
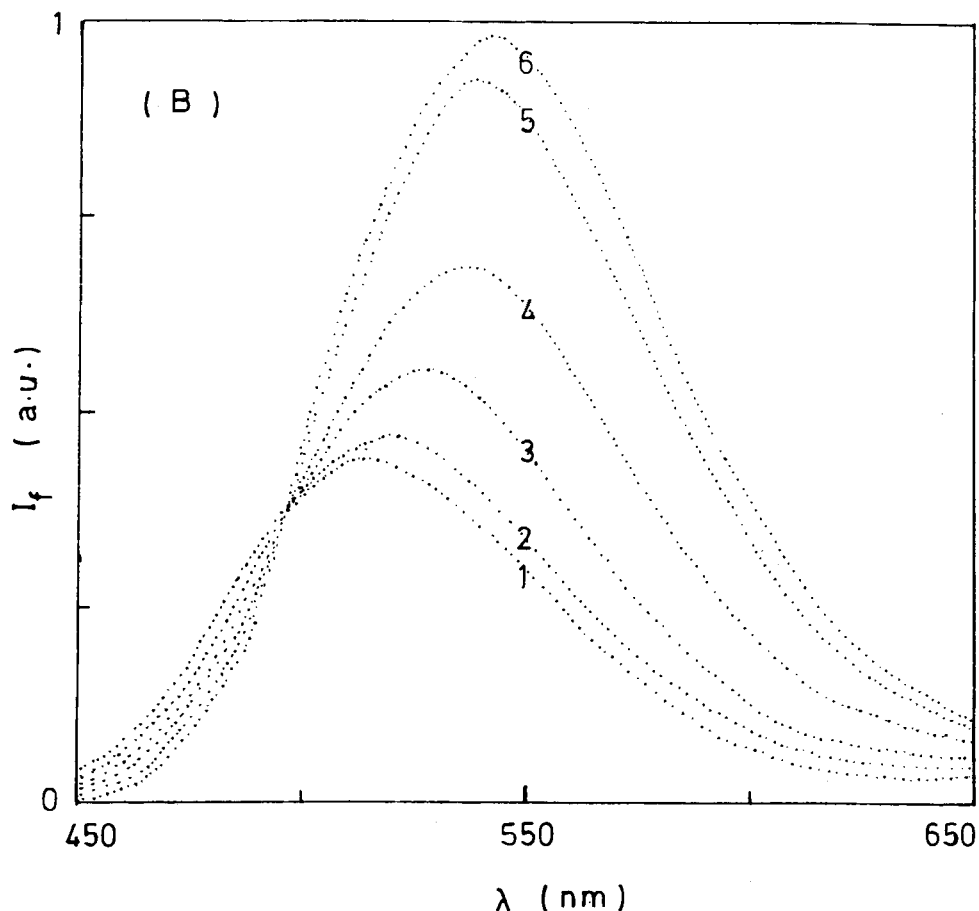


Figure 2. A. (Caption on facing page.)



**Figure 2.** Fluorescence spectra of compound I in (A) ethylacetate/ethanol and (B) in ethanol/water.

### 3.2 Excited state relaxation mechanism; Molecular structure effect

The fluorescence quantum yields,  $\phi_f$ , of the compounds under consideration were found to be solvent dependent. In ethanol,  $\phi_f$ , was found to be 0.163, 0.044 and 0.600 for compounds I, II, III, respectively. In other words, the fluorescence quantum yield increases in the order  $II < I < III$ . This must reflect a decrease in the non-radiative decay rate in the order  $II > I > III$  which is in complete agreement with the data reported by Rettig (Rettig *et al* 1992) (the reported values of the nonradiative rate constant in diethylether,  $k_{nr}$  ( $10^9 \text{ s}^{-1}$ ) of II, I and III are 1320, 15 and 0, respectively).

The possible decay mechanism (Rettig *et al* 1992) for compound I which possesses one double and three flexible single bonds may be through twisting about the double bond which is commonly believed to constitute the main non-radiative decay channel, whereas twisting about the different single bonds can lead to TICT states. If one or more of these TICT states are sufficiently low-lying, they can act as photochemical traps, thus reducing intramolecular fluorescence quenching and leading to efficient fluorescence properties.

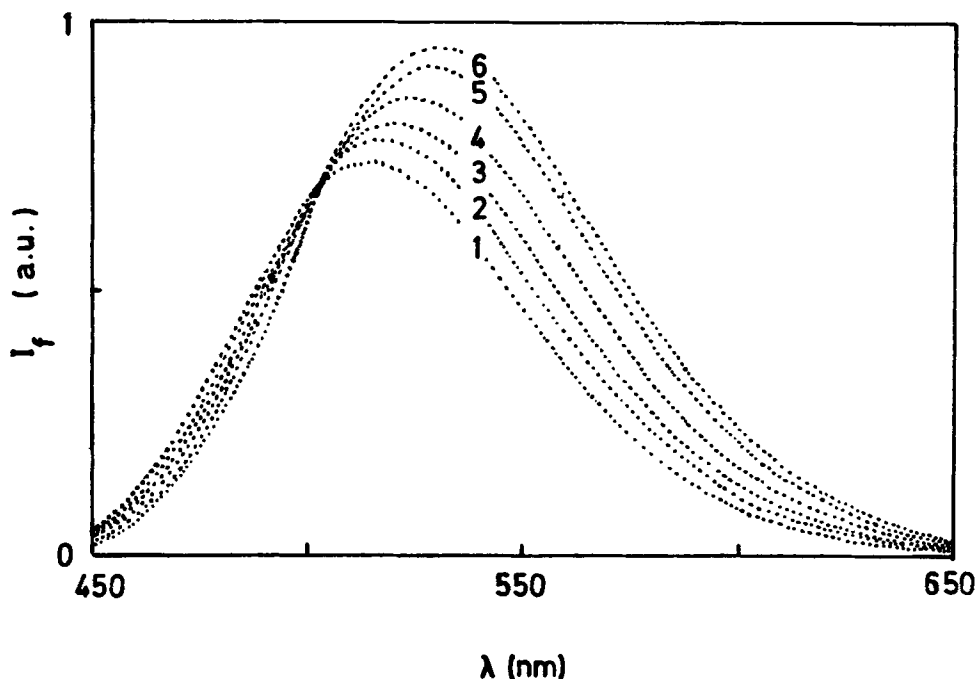


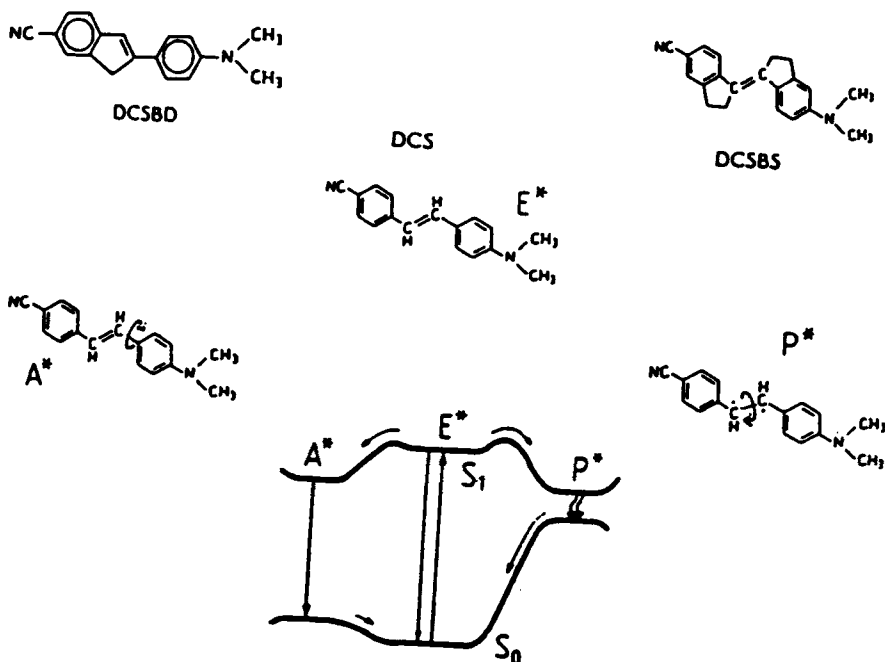
Figure 3. Fluorescence spectra of compound I in acetone/water mixed solvent.

In order to explain the importance of different deactivation pathways in these molecules, we can refer to a simple three-state kinetic scheme, figure 4, similar to that proposed earlier (Rettig *et al* 1992). In this scheme, the primarily excited state  $E^*$  can relax either to  $A^*$  (single bond twist state, can generally be emissive or non-emissive) or to  $P^*$  (twisted double bond state, non-emissive). The TICT state,  $A^*$ , is always very polar and lowered energetically by donor-acceptor substitution. The branching ratio from  $E^*$  to  $A^*$  and  $P^*$  will therefore determine the fluorescence properties. For compound I both channels  $A^*$  and  $P^*$  are possible and accordingly in high polar solvents, the non-radiative decay via  $P^*$  is disfavoured; thus leading to good fluorescence. Compound II, on the other hand, has only the  $P^*$  channel which leads to non-radiative deactivation. Compound III will have the radiative deactivation channel through  $A^*$  since the  $P^*$  channel is hindered. The fluorescence quantum yield data obtained for compounds I, II and III show that  $\phi_f$  for II is less than that for I which is due to the take-away of the  $A^*$  state while  $\phi_f$  for III is greater than for I due to the absence of the  $P^*$  state.

As stated above, the increase in  $\phi_f$  in the sequence  $II < I < III$  reflects a decrease in the non-radiative decay rate,  $k_{nr}$ , since the only difference in structure of these three compounds arises from the hindering of the twisting around the double bond. It can be concluded that the *cis/trans* isomerization in the excited singlet state is the most important non-radiative deactivation channel to the ground state.

### 3.3 Medium viscosity effect

The obtained fluorescence quantum yield of our compounds was also found to be sensitive to solvent viscosity. This prompted us to explore the relative sensitivity of



**Figure 4.** Three-state kinetic scheme;  $E^*$  (planar, highly polar, fluorescent),  $P^*$  (twisted double bond "E/Z isomerization", weakly polar, nonfluorescent) and  $A^*$  (twisted single bond "anilino group"; TICT, polar, fluorescent).

these compounds to medium viscosity for possible use as fluorescence probes. Considerable decrease in  $\phi_f$  values can be seen by increasing the temperature of the glycerol solution of the compounds. Varying the ratio of  $T/\eta$  for glycerol by changing temperature, leads to results which fit the expression of Foerster (Foerster and Hoffmann 1971);

$$\phi_f = B(\eta/T)^x.$$

Plots of  $\ln(\phi_f)$  vs  $\ln(\eta/T)$  should yield a straight line, figure 5. The established equations are:

$$\ln(\phi_f) = \begin{array}{ll} -0.735 + 0.196 & \text{for compound I} \\ -1.450 + 0.397 \ln(\eta/T), & \text{for compound II} \\ -0.558 + 0.102 & \text{for compound III} \end{array}$$

with a correlation coefficient of 0.989 or better.

The free-volume model is operative since the relationships between  $\ln \phi_f$  and  $\ln(\eta/T)$  are linear [according to the free-volume model the fluorescence quantum yield should depend nonlinearly on the function  $\eta/T$ ]. The coefficient of  $\ln(\eta/T)$  function (or the exponent of  $\eta/T$ ) reflects a high degree of sensitivity for (II) towards viscosity/free-volume. This suggests also that excited state geometrical processes via a double bond play the major role as a non-radiative deactivation channel in molecular relaxation.

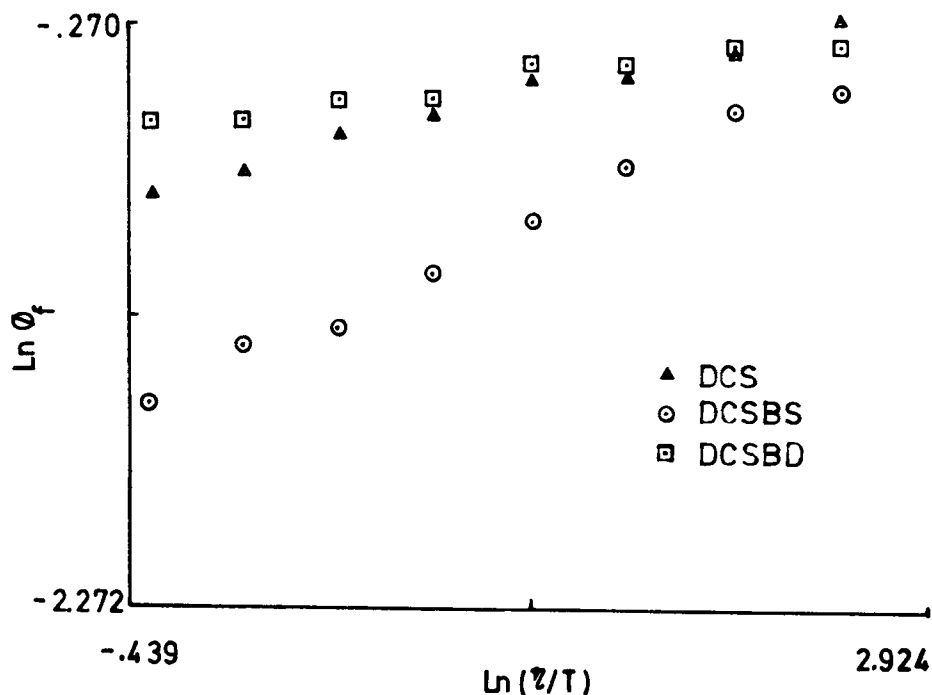


Figure 5. Plot of  $\ln \phi_f$  vs  $\ln(\eta/T)$  for compounds I, II and III.

### Acknowledgement

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