

## The lowest ( $n, \pi^*$ ) transition of indanetrione (anhydrous ninhydrin) in various ethers as solvents

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**Abstract.** The lowest  $S_1(n, \pi^*)$  transition (absorption) of indanetrione having a *cis*-vicinal triketo group exhibits a large blue-shift in cyclic saturated ethers compared to that in an open-chain saturated ether. This transition of indanetrione in mixed solvents containing a cyclic saturated ether (tetrahydrofuran, dioxane and tetrahydropyran) as one of the components and a non-polar or less polar solvent as the other component has been studied at room temperature. The spectra are also studied in pure cyclic saturated ethers as a function of temperature. These studies suggest a specific interaction between indanetrione and cyclic ethers in the ground state. Similar studies in open-chain saturated ethers indicate the absence of such an interaction. The nature of the specific interaction has been discussed.

**Keywords.** Indanetrione;  $n, \pi^*$  transition; *cis*-vicinal triketo group; cyclic ethers; open-chain ethers.

### 1. Introduction

In continuation of our studies (Ghosh and Chowdhury 1981, 1982; Ghosh *et al* 1985) on the photophysical characteristics of polyketones and polyazines containing more than two interacting nonbonding centres, we recently observed a dramatic blue-shift ( $1100 \text{ cm}^{-1}$ ) of the lowest ( $n, \pi^*$ ) transition of indanetrione (figure 1) in tetrahydrofuran compared to that in the open chain analogue diethylether. This observation prompted us to undertake a systematic investigation of the lowest ( $n, \pi^*$ ) transition of indanetrione in various saturated cyclic ethers and open chain ethers. The compound indanetrione (anhydrous ninhydrin,  $\text{C}_9\text{H}_4\text{O}_3$ ), a planar molecule with a *cis*-vicinal triketo group (figure 1), shows four absorption bands having  $\lambda_{\text{max}}$  at 600, 430, 330 and 250 nm (Ghosh and Chowdhury 1981a). The three lower energy bands are ( $n, \pi^*$ ) in nature (Ghosh and Chowdhury 1981a). Our earlier work (Ghosh and Chowdhury 1981) showed that the lowest ( $n, \pi^*$ ) singlet transition exhibits a large solvent effect. The large blue-shift observed for this band in solvents containing a carbonyl group or a nitrile group compared to that in relatively non-polar solvents was demonstrated to be due to the existence of a specific interaction between the  $\beta > \text{C}=\text{O}$  group of indanetrione and the carbonyl group ( $> \text{C}=\text{O}$ ) or the nitrile group ( $-\text{C} \equiv \text{N}$ ) of the solvent. In this paper, we present the unusually large solvent effect of the lowest

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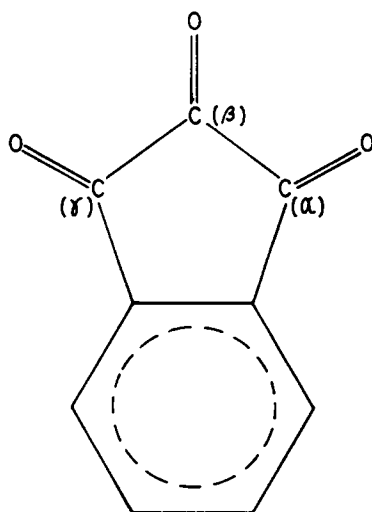


Figure 1. Structure of indanetrione.

( $n, \pi^*$ ) singlet state of indanetrione observed in various ethers as solvents. The various ethers used as solvents include open-chain ethers viz. diethyl ether (DEE), anisole, and cyclic saturated ethers, viz. tetrahydrofuran (THF), tetrahydropyran (THP), and dioxane (DX). In order to understand the large blue-shifts observed in cyclic saturated ethers compared with those in the open-chain ethers, we have studied here the absorption, emission and excitation spectra of this ( $n, \pi^*$ ) transition in various pure ethers, in mixed solvents containing an ether and a less polar or non-polar solvent like dichloromethane (DCM) or cyclohexane (CHX) over a wide range of temperature.

The results have been interpreted in terms of a specific interaction involving indanetrione and a five- or six-membered cyclic saturated ether. Recognition of such an interaction is important since formation of such a weak complex may act as a precursor in thermal and photochemical changes of vicinal polyketones.

## 2. Experimental section

The thin red needles of the triketo compound were obtained by the sublimation of ninhydrin,  $C_9H_4O_2(OH)_2$ , (EM) under vacuum at  $150^\circ\text{--}160^\circ\text{C}$ . The solvents used were purified by standard procedures after special precautions were taken to remove any trace of moisture. As the triketo compound is highly sensitive (Rubin 1975) to a trace of moisture, the preparation of solutions was carried out in a desiccated chamber immediately before the experiment.

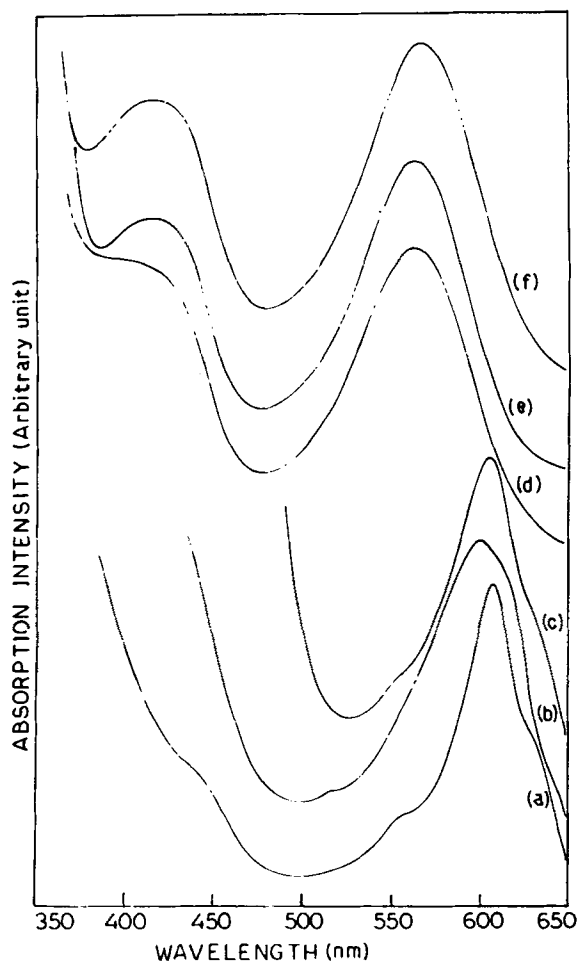
Absorption measurements were made on a Hitachi model U 3210 spectrophotometer using a stoppered cell. The temperature was controlled within  $\pm 1^\circ\text{C}$  by circulating water from a thermostatted water-bath (Techno model C-85A).

Emission and excitation spectra were recorded on a Hitachi F 3010 fluorescence spectrophotometer using a stoppered cell. The lifetime of singlet emission was measured as described in our earlier work (Ghosh and Chowdhury 1981).

### 3. Results and discussion

#### 3.1 Absorption in pure solvents

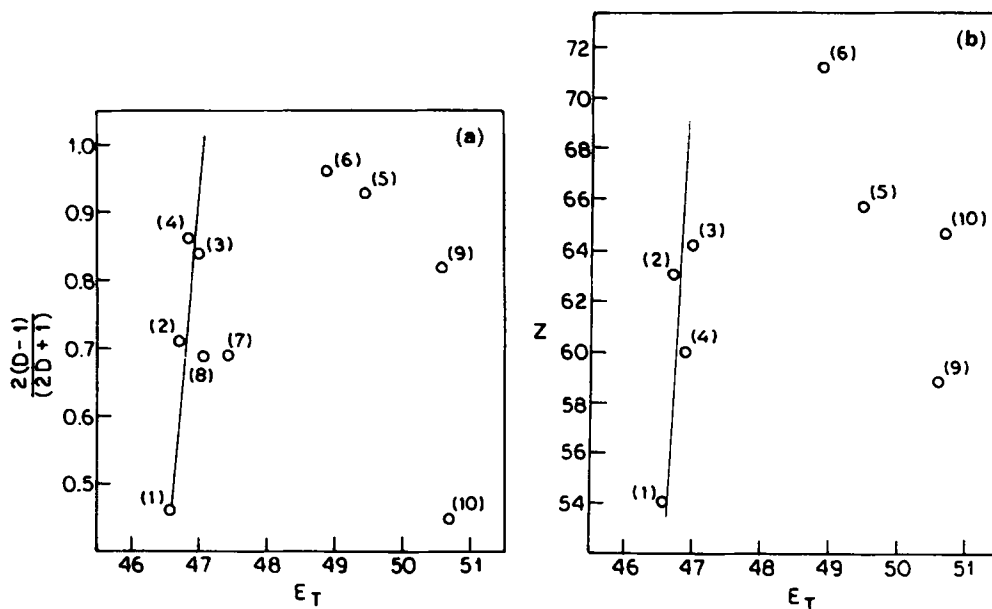
The absorption spectra of the  $n, \pi^*$  state at 300 K in various ethers, namely DEE, anisole, THF, THP and DX are shown in figure 2. Figure 2 also includes the absorption spectra in DCM at 300 K for comparison. The positions of  $\lambda_{\max}$  of the lowest  $n, \pi^*$  state and the values of  $E_T$  (transition energy, calculated by converting the  $\lambda_{\max}$  into kcal/mol) in different ethers, acetone, acetonitrile and several non-polar or less polar solvents together with solvent parameters are given in table 1. The  $\epsilon_{\max}$  of the lowest  $n, \pi^*$  band in various solvents used are  $15\text{--}17 \text{ mol}^{-1} \text{ cm}^{-1}$ . When the values of  $E_T$  are plotted against  $f(D)$  [ $f(D) = 2(D - 1)/(2D + 1)$ ], where  $D$  is the dielectric constant of the solvent or  $Z$ -value (Kosower 1968; Foster 1969) of the solvents studied, deviation from linearity has been observed for acetone, acetonitrile and cyclic saturated ethers



**Figure 2.** Absorption spectra of indanetrione in different solvents using suitable concentration at 300 K: in (a) DCM, (b) DEE, (c) anisole, (d) THF, (e) DX and (f) THP (at 295 K). Spectra are displaced vertically for clarity.

**Table 1.** Values of absorption maxima  $S_0 \rightarrow S_1(n, \pi^*)$  transition in different solvents at 300 K along with solvent parameters.

Solvents	$\lambda_{\max}$ (nm)	$E_T$ (kcal/mol)	$D$ (at 298 K)	$\frac{2(D-1)}{2D+1}$	$Z$ values (kcal/mol)
1,4-Dioxane	562.0	50.7	2.2	0.45	64.6
Tetrahydrofuran	563.0	50.6	7.6	0.82	58.8
Tetrahydropyran	566.0	50.3	—	—	—
Diethyl ether	601.0	47.4	4.3	0.69	—
Anisole	605.0	47.1	4.3	0.69	—
Dichloromethane	606.0	47.0	8.8	0.84	64.2
Chloroform	610.0	46.7	4.6	0.71	63.2
Benzene	612.0	46.6	2.3	0.46	54.0
Ortho-dichlorobenzene	608.0	46.9	9.9	0.86	60.0
Acetone	576.0	49.5	20.7	0.93	65.7
Acetonitrile	583.0	48.9	36.2	0.96	71.3

**Figure 3.** (a) Plot of  $E_T$  (kcal/mol) vs.  $f(D) = 2(D-1)/(2D+1)$ ; (b) plot of  $E_T$  (kcal/mol) vs.  $Z$ -values in various solvents at 300 K. (1) Benzene, (2) chloroform, (3) DCM, (4) *o*-dichlorobenzene, (5) acetone, (6) acetonitrile, (7) DEE, (8) anisole, (9) THF and (10) DX.

(figure 3). Cyclic ethers exhibit largest deviations. Absorption bands in cyclic ethers are also broad compared to those observed in DEE and anisole. Furthermore, two vibrations around  $600$  and  $1500 \text{ cm}^{-1}$  which are discernible in DCM and open-chain ethers in spite of the broadness of the band are not present in cyclic ethers. These facts clearly indicate that something other than the general solvent effect is operating in the case of cyclic ethers.

## 3.2 Absorption in mixed solvents

In order to understand the large blue-shift in the case of cyclic ethers we studied the absorption spectra in mixed solvents containing a cyclic ether and a solvent like DCM or CHX at 298 K. Figure 4 shows the spectra in mixed solvents containing DX and DCM, DX and CHX, THF and DCM. The concentration of the triketo compound in each mixture of each pair of mixed solvents was kept constant. The observation of a clear isosbestic point in each case indicates the existence of a specific interaction of the triketo compound with cyclic ethers, since the triketo compound

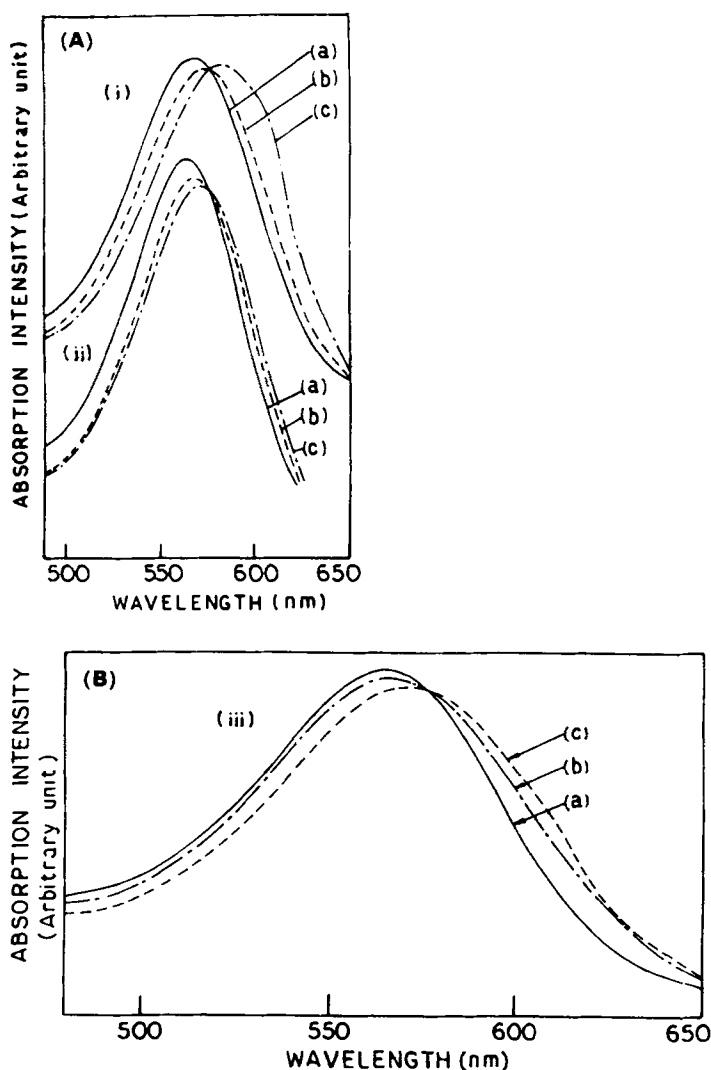


Figure 4. Absorption spectra of indanetrione at 300 K in mixed solvents containing (A) (i) DX and DCM in the ratio (a) 1:1, (b) 1:2, (c) 1:5; (ii) (a) pure DX, (b) DX and CHX (1:1), (c) DX and CHX (1:2), (Spectra are displaced vertically for clarity); (B) (iii) (a) pure THF, (b) THF and DCM (1:1), (c) THF and DCM (1:2) - (concentration of indanetrione is kept constant in different mixtures of each pair).

has no specific interaction with DCM (*vide* § 3.4). However, it was not possible to obtain reliable values of equilibrium constants because of the difficulty faced in handling the moisture-sensitive triketo compound.

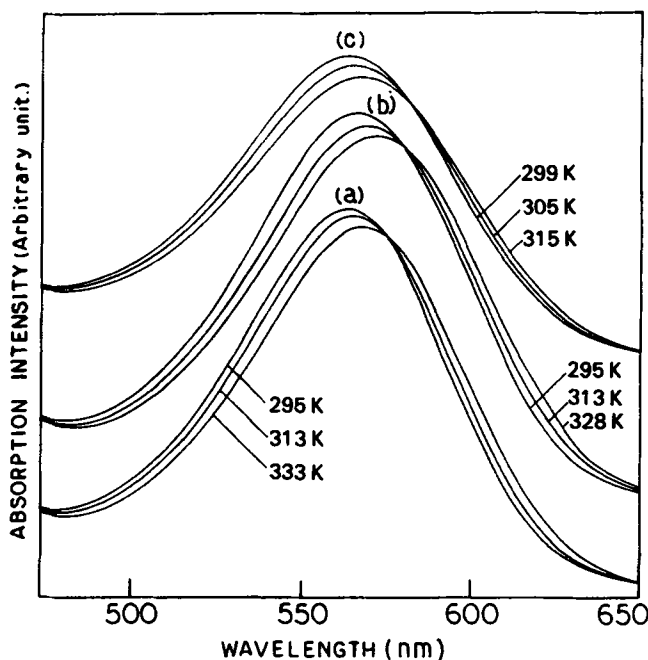
### 3.3 Effect of temperature on the $S_0 \rightarrow S_1$ ( $n, \pi^*$ ) absorption

In DCM it was observed that a very small blue-shift took place with the general shape of the curve and the intensity of the band remaining almost the same with the decrease of temperature. The small blue-shift observed was ascribed to the slight increase of the dielectric constant of the solvent as the temperature is lowered or to the depopulation of low frequency vibrations of the ground state or to both. The possibility of a simple equilibrium involving just two conformations of the triketo compound or just two species, one nonbonded and another hydrogen-bonded with DCM, was excluded due to the absence of any isosbestic point.

Absorption spectra for the lowest singlet ( $n, \pi^*$ ) transition at different temperature in pure DX, THF, THP are shown in figure 5. The temperature range chosen is within 20° to 60°C as DX freezes at 11°C. In each case we found

- $\lambda_{\max}$  increases with the increase of temperature, the shift being reversible,
- in all the cases the blue side of the spectrum becomes intensified with the decrease of temperature and a clear isosbestic point is observed.

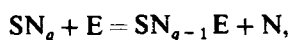
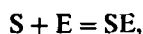
The process is reversible during cooling and heating. No such isosbestic point was observed in anisole. A very small blue shift took place with the shape of the curve



**Figure 5.** Absorption spectra of indanetrione in different cyclic saturated ethers at various temperatures using suitable concentrations. (a) DX, (b) THP, (c) THF. Spectra are displaced vertically for clarity.

remaining unchanged as the temperature was lowered. The temperature variation of the absorption spectrum was not performed in DEE (b.p. = 35°C) in the lower temperature range since the solubility of the triketo compound in DEE is very low and the compound precipitates as the temperature is lowered. Any solute-solute association or any reaction with the cyclic saturated ethers used may be ruled out since the phenomena observed are independent of the solute concentration and there is no evidence of new absorption bands.

The occurrence of isosbestic points in figures 4 and 5 suggests the existence of an equilibrium involving the cyclic ethers of the type



where S indicates the solute (the triketo compound), E, the cyclic saturated ether and N, the solvent DCM or CHX. The concomitant conformational change of the triketo compound due to a specific interaction with cyclic ethers studied is not, however, ruled out.

### 3.4 Nature of specific interaction

Indanetrione is a planar molecule with a *cis* vicinal triketo group (Bolton 1965). It is well known that  $\beta >C=O$  group of vicinal triketo, being under the inductive effect of  $\alpha$  and  $\gamma >C=O$  groups, behaves as a highly reactive centre (Rubin 1975).

It was previously established that solvents containing  $>C=O$  or  $-C \equiv N$  groups exhibit specific interactions with the triketo compound (Ghosh and Chowdhury 1981b). It was also proved that no hydrogen bonding is possible with the triketo compound and the hydrogen atoms of the methyl groups of acetone or acetonitrile. It was proposed that the carbon atom of the  $>C=O$  or  $-C \equiv N$  group of the solvent is sufficiently positively charged to act as an acceptor of the nonbonding electrons of the central  $\beta$  carbonyl oxygen atom of the triketo compound forming a 1:1 loose complex. This is supported by the blue shift of the absorption spectrum in the crystal, where molecules are arranged in such a way that the carbon atom of the central carbonyl group is in close proximity (2.83 Å) to the oxygen atoms of the carbonyl groups of two other molecules, the distance being shorter than (below Van der Waals radii) that allowed by the London dispersion forces (Bolton 1965).

In the present case, the absence of a specific interaction with anisole excludes the possibility of hydrogen-bond formation between the highly active carbon atom of the  $\beta$  carbonyl group of the triketo compound and the  $\alpha$  hydrogen atoms of the ether oxygen.

The interaction should, therefore, be due to the formation of a 1:1 complex between the triketo compound and the cyclic ethers, where the ether oxygen atom having nonbonding electrons can function as a donor to the carbon atom of the  $\beta >C=O$  group in the triketo compound. The formation of such a complex is always favourable since it relieves to some extent the unfavourable electrostatic interaction present in the cyclic triketo. The presence of such an interaction in cyclic ethers and the absence of such an interaction in open-chain ethers suggest that the special geometry of the cyclic ethers is responsible for such interaction. The special geometry increases the availability of the nonbonding electrons of cyclic ethers for functioning as better

donors because of steric factors. Such a difference in the binding ability has been noticed in the case of crown ethers and the corresponding open chain analogue. Thus, 18-crown-6 has been demonstrated to bind  $t\text{-C}_4\text{H}_9\text{NH}_3^+$  more than  $10^4$  times more strongly than does its open-chain analogue (Timko *et al* 1977). The enhanced thermodynamic stability for the cyclic system relative to the open-chain systems has been ascribed to both enthalpic and entropic effects. The different solvation energies of the open-chain and cyclic ligands and the changes in conformation on complexation may play a crucial role in determining the enthalpic and entropic contribution (Clay *et al* 1979). Furthermore, the less flexible cyclic system will tend to undergo much less geometrical change on coordination than will its open-chain analogue and thus the cyclic system provides greater thermodynamic stability due to the entropic effect (Lindoy 1989).

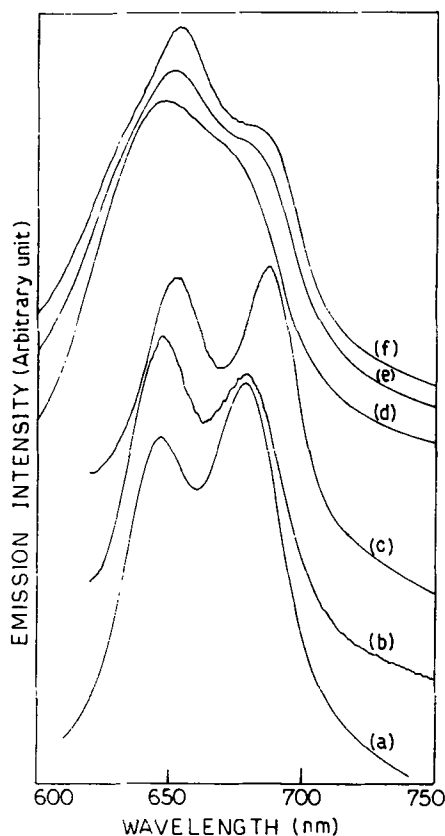
At present we have undertaken theoretical calculations to investigate the special geometry of the three cyclic ethers responsible for such strong interaction with the  $\beta$  carbonyl group of the triketo compound. The concomitant change in the conformation of the triketo compound is also taken into consideration in the calculation (to be published elsewhere).

### 3.5 Emission in pure solvents

Figure 6 shows the emission spectra of indanetrione in various ethers at room temperature. Emission spectra in DCM at room temperature are also given for comparison. This emission is  $S_1(n, \pi^*) \rightarrow S_0$ , as discussed in earlier work (Ghosh and Chowdhury 1981). The positions of the (0,0) band and the fluorescence maxima in all the ethers are listed in table 2. The emission observed in all the ethers is independent of solute concentration. Furthermore, the excitation spectra monitored at  $(\nu_f)_{0,0}$  and at  $(\nu_f)_{\max}$  in various ethers studied coincide with the corresponding absorption spectra. The lifetime of this emission monitored at  $(\nu_f)_{\max}$  in various solvents at 300 K studied in this work ranges from 10 to 20 nanoseconds.

The large gap between the onset of the absorption and the emission in the case of cyclic ethers is noticeable relative to that found in open-chain ethers and in DCM. The closeness of the first emission band [(0,0)] in the cyclic ethers, in the open-chain ethers (tables 2) and in other polar and non-polar solvents (Ghosh and Chowdhury 1981b) indicates that  $\mu_g > \mu_e$  where  $\mu_g$  is the dipole moment of indanetrione in the ground state and  $\mu_e$  is the dipole moment of the indanetrione in the lowest excited singlet state. Since the solvent relaxation time is of the order of  $10^{-12}$  s and the lifetime of the  $S_1(n, \pi^*)$  emission of indanetrione is of the order of  $10^{-8}$  s, it is assumed that the two states involved in the emission process are the equilibrium-excited state and the Franck-Condon (FC) ground state. On the other hand, the two states involved in the absorption process are the equilibrium ground state and the FC excited state. A strong interaction with cyclic ethers in the ground state results  $(\nu_f)_{0,0} \ll (\nu_{\text{abs}})$  compared to that found in open-chain ethers. The less-resolved vibrational structures of the emission spectra in the cyclic ethers (figure 6) are indicative of a specific interaction in the  $S_1$  state. Among the three cyclic ethers used, DX exhibits the strongest interaction in the excited state (Suppan 1987).





**Figure 6.** Fluorescence spectra of indanetrione (conc.  $10^{-4}$  M) at 298 K in various solvents using 5 nm emission band pass and 10 nm excitation band pass. (a) DCM ( $\lambda_{exc} = 605$  nm), (b) anisole ( $\lambda_{exc} = 605$  nm), (c) DEE ( $\lambda_{exc} = 600$  nm), (d) DX ( $\lambda_{exc} = 560$  nm), (e) THF ( $\lambda_{exc} = 560$  nm), (f) THP ( $\lambda_{exc} = 560$  nm). Spectra are displaced vertically for clarity.

**Table 2.** Positions of fluorescence spectra in different media at 300 K.

Solvents	$\bar{\nu}_{f(0,0)}$ (nm)	$\bar{\nu}_{f(0,0)}$ ( $\text{cm}^{-1}$ )	$\bar{\nu}_{f(\text{max})}$ (nm)	$\bar{\nu}_{f(\text{max})}$ ( $\text{cm}^{-1}$ )	Separations ( $\text{cm}^{-1}$ )
Dichloromethane	647	15450	678	14750	700
Anisole	648	15440	680	14710	730
Diethylether	653	15310	688	14530	780
1,4-Dioxane	649	15410	672	14880	530
Tetrahydrofuran	652	15330	681	14680	650
Tetrahydropyran	654	15300	682	14670	630

#### 4. Conclusions

A specific interaction between indanetrione, a *cis*-vicinal triketo compound, and a five- or six-membered cyclic saturated ether in the ground state has been recognised through optical absorption and emission studies on the lowest singlet excited state of indanetrione. Open-chain ethers, e.g. DEE, and anisole do not exhibit such an interaction.

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