

## THE SOLVATION OF TWISTED INTRAMOLECULAR CHARGE TRANSFER FLUORESCENT STATES BY ALCOHOLS

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(Received May 20, 1982)

### Summary

The solvent-induced shift of the emission maximum of 3-( $\alpha$ -naphthyl)-benzo[*b*]thiophen was measured in a number of solvents. The correlation of the apparent specific solvation by alcohols with the  $E_T(30)$  parameter is interpreted in terms of the organization of solvent molecules around the hydrophobic solute. An alternative correlation using the dipole moment of the solvent is more suitable for such solutes.

### 1. Introduction

Many molecules undergo large changes of polarity on electronic excitation by intramolecular charge transfer. In those which have donor (D) and acceptor (A) moieties the charge transfer and modification of the geometry of the D-A molecule can occur at the same time. Such excited states are known as twisted intramolecular charge transfer (TICT) states [1]. The energy and intensity of the emission from the charge transfer state are very sensitive to solvent polarity.

In a preceding paper [2] we reported an investigation of the fluorescence of 3-( $\alpha$ -naphthyl)benzo[*b*]thiophen (1) which shows a TICT excited singlet. By analogy with the work of Kosower and Tanizawa [3] on 9,9'-bianthryl fluorescence, the emission shift in the fluorescence of 1 was correlated with Dimroth's solvent parameter  $E_T(30)$  [4]. This correlation gives two lines as the alcoholic solvents behave very differently from other solvents. In this work we investigate the solvation effects of alcohols on the excited singlet of 1 and attempt to explain their anomalous behaviour.

### 2. Experimental details

The fluorescence spectra were measured using a FICA 55000 spectrofluorometer and were corrected for excitation and emission. The solvents

were all fluorescence or spectroscopic grade and were obtained from Merck or Carlo Erba. The solutions (concentration,  $10^{-5}$  M) were flushed with dry nitrogen. The samples were contained in quartz cells of dimensions 1 cm  $\times$  1 cm and kept at a constant temperature of 298 K.

The synthesis of 1 has been described elsewhere [5]. *p*-dimethylaminobenzaldehyde (DMABA) obtained from Aldrich was recrystallized twice from ethanol.

### 3. Results

The emission maxima of 1 in a variety of solvents are given in Table 1 and Fig. 1 shows the correlation of these values against the  $E_T(30)$  parameter. As in the case of 9,9'-bianthryl [3], the values for the alcoholic solvents (except alcohols 19 and 20) lie on the same line. The primary and secondary amines lie on another line. In solvents of medium and strong polarity the DMABA fluorescence consists of two bands, of which the long wave emission  $F_A$  is assumed to be from the TICT state [7]. The values of the solvent-induced shift of the  $F_A$  band are also shown in Fig. 1. The emission maxima of 1 and of 9,9'-bianthryl [3] (expressed as shifts from the solvent-independent absorption maxima) are plotted against the dipole moment of the solvents [6] in Fig. 2. A single line including all the solvents is obtained for each compound.

### 4. Discussion

The difference between the two correlations can be explained in terms of the two different solvent parameters used.

Dimroth's  $E_T(30)$  value is a microscopic parameter, and in the case of alcoholic solvents the examination of the possibility of the formation of a hydrogen bond with the solute may be a good approach to the interpretation of the solvation. In the case of DMABA the  $F_A$  fluorescence intensity decreases with the solvent polarity and the red shift is well correlated with the  $E_T(30)$  values as the alcoholic solvents lie on the same line as the other solvents. DMABA acts as a hydrogen bond acceptor solute (via the oxygen atom in the carbonyl group). In alcoholic solvents we assume that the solvent molecules are organized around the solute with the hydroxylic groups located near DMABA. In the case of 1, which has a hydrophobic character, the organization of the solvent cage should be very different: the alkyl groups should be in contact with the solute and the hydroxylic groups should form an outer rigid sphere by hydrogen bonding. On electronic excitation the variation in the dipole moment between the excited and the ground states cannot be completely stabilized by reorientation of the molecules forming the solvent cage. Therefore 1 is more likely to be in a hydrocarbon solvent cage than in a polar alcoholic cage. The organization of

TABLE 1

Shifts in the emission maxima of 3-( $\alpha$ -naphthyl)benzo[*b*]thiophen and 9,9'-bianthryl relative to the solvent-independent absorption maxima in different solvents

Solvent	$E_T(30)^a$ (kcal mol <sup>-1</sup> )	$\mu \times 10^{30}{}^b$ (C m)	$(\bar{\nu}_A - \bar{\nu}_C) \times 10^{-3}$ (cm <sup>-1</sup> )	
			$I^c$	9,9'-bianthryl <sup>d</sup>
1 <i>n</i> -hexane	30.9	0.0	4.62	1.50
2 Cyclohexane	31.2	0.0	4.38	
3 Diisopropylamine	33.3		5.01	
4 Triethylamine	33.3	2.90	4.54	
5 Toluene	33.9	1.43	4.78	
6 Benzene	34.5	0.0	4.70	1.87
7 Diethyl ether	34.5	4.34	4.70	1.77
8 Diethylamine	35.4		4.85	
9 Piperidine	35.5	3.97	4.70	
10 1,4-dioxane	36.0	1.50	4.70	2.00
11 <i>tert</i> -butylamine	36.8		4.78	
12 Chlorobenzene	37.5	5.14	5.09	2.25
13 Ethyl acetate	38.1	6.27	4.85	2.25
14 Dichloromethane	41.1	5.17	5.24	3.05
15 <i>N,N</i> -dimethylformamide	43.8	12.88	5.74	
16 Acetonitrile	46.0	11.48	5.46	4.05
17 2-pentanol	46.5	5.54	5.34	
18 Cyclohexanol	46.9	6.20	5.51	
19 2-propanol	48.6	5.54	4.70	2.55
20 1-butanol	50.2	5.84	4.80	
21 1-propanol	50.7	5.54	4.78	
22 1-pentanol	50.7		5.05	
23 Acetic acid	51.2	5.60	4.86	
24 Ethanol	51.9	5.77	5.24	3.30
25 Ethanol:water (80:20 vol.%)	53.7		5.60	
26 Methanol	55.5	5.67	5.24	3.60
27 1,2-ethanediol	56.3	7.61	5.78	4.10
28 1,2,3-propanetriol	57.0		5.58	
A Bromobenzene	37.5	5.17		2.10
B Chloroform	39.1	3.84		2.55
C Pyridine	40.2	7.91		3.50
D Acetone	42.2	9.54		3.37

<sup>a</sup>From ref. 4.

<sup>b</sup>From ref. 6.

<sup>c</sup> $\bar{\nu}_A = 32.79 \times 10^3$  cm<sup>-1</sup>.

<sup>d</sup>Values estimated from ref. 3, Fig. 5.

the solvent cage for alcohols with long chains or with sterically masked hydroxylic groups (secondary and tertiary alcohols) should be less structured and less rigid. This may be the explanation for the solvation effects of 2-pentanol and cyclohexanol: the emission maxima of 1 in these two solvents are in better agreement with their  $E_T(30)$  values and lie on the first correlation line. The fact that the emission maxima measured in primary and

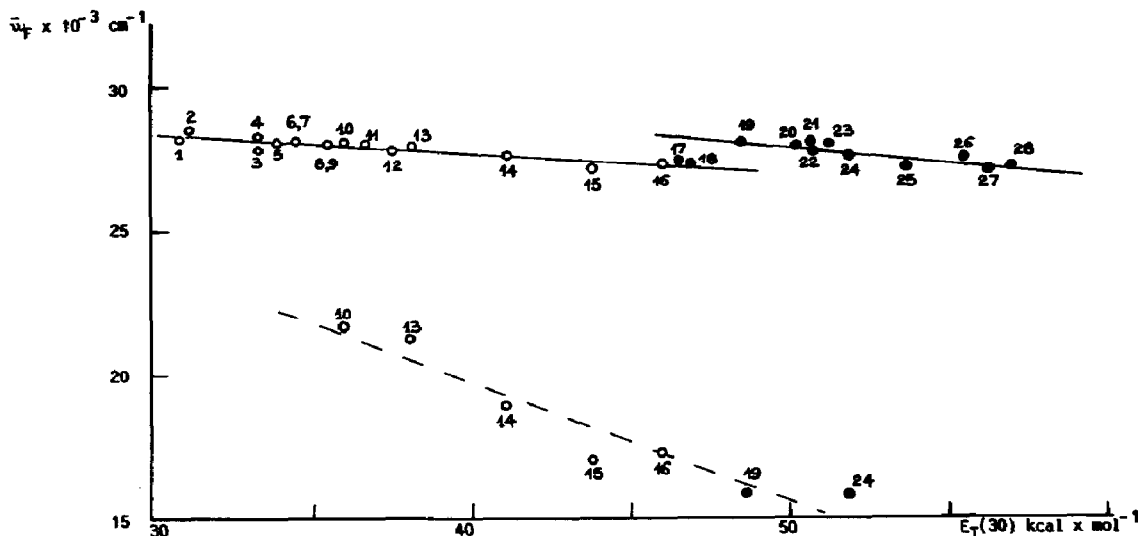


Fig. 1. Shifts in the emission maxima of 1 (—) and of DMABA ( $F_A$  band) (---) plotted against the  $E_T(30)$  solvent parameter.

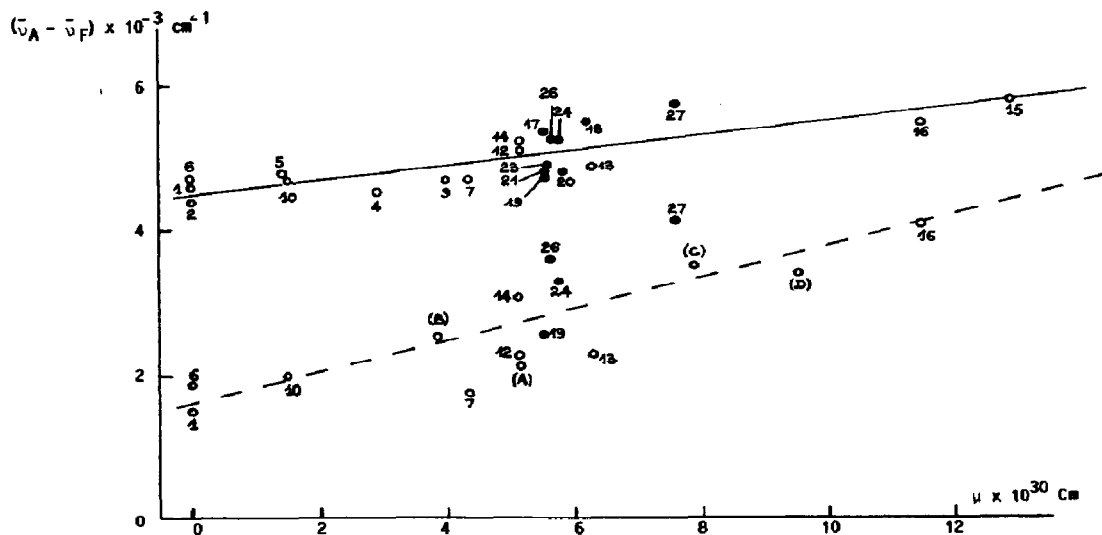


Fig. 2. Shifts in the emission maxima of 1 (—) and of 9,9'-bianthryl (---) from the solvent-independent absorption maxima plotted against the dipole moment of the solvent.

secondary amines also lie on this line is in good agreement with their less effective hydrogen bond formation.

The existence of two separate lines in the correlation of the solvent effects for the excited states of hydrophobic solutes is not limited to the shifts in the emission maxima. A similar result is obtained for the variation in the vibronic structure of pyrene fluorescence in different solvents [8]. The fact that the  $E_T(30)$  parameter for protic solvents reflects their hydro-

gen bond donor properties [4] and that pyrene is expected to be insensitive to hydrogen bonding is further support for our hypothesis.

We have developed an alternative correlation using the dipole moment  $\mu$  of the solvent which is a macroscopic parameter. Although the points are more dispersed in this correlation than in the first one, the results for all the solvents are located on the same line. Unfortunately no values of  $\mu$  have been determined for alcohols 19 and 20, but we believe that the corresponding points should be in the alcoholic range of the correlation. However, this correlation cannot be used for DMABA where microscopic solute-solvent interactions are very important and where the  $E_T(30)$  correlation is justified.

## 5. Conclusion

In the absence of a rigorous theoretical treatment of solute-solvent interactions which is applicable over a large range of very different solvents, empirical parameters are extensively used in practice. However, care must be taken in interpretations and conclusions based on these parameters.

The solvent shift induced in the emission of molecules with TICT excited states can be correlated with Dimroth's  $E_T(30)$  parameter. If a good correlation is obtained for a solute which is a hydrogen bond acceptor, in the case of a hydrophobic solute the specific line obtained for alcoholic solvents must be regarded as a consequence of the organization of the solvent cage around the solute and not as a modification of the excited state specific to these solvents. A correlation using the dipole moment of the solvent, which gives only one line, is more appropriate for such solutes.

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