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The Use of Fourier Transform Infrared (FT-IR) Spectroscopy to Study the State of Heterobifunctional Reactive Dyes

David M. Lewis* & Jian Chen Wang

Department of Colour Chemistry, University of Leeds, Leeds, UK, LS2 9JT

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ABSTRACT

The Fourier Transform Infrared (FT-IR) spectra of 12 dyes have been measured; the dyes had the same chromophore but a different side chain group. The FT-IR characteristic frequencies of vinylsulphone, sulphatoethylsulphone and hydroxyethylsulphone have been recognised in the complex conjugated molecules, especially if second derivative spectroscopy was used. © 1998 Elsevier Science Ltd. All rights reserved

Keywords: FT-IR Spectroscopy, Heterobifunctional reactive dyes, Chromophore.

INTRODUCTION

Infrared spectroscopy is the most widely used technique for the determination of molecular structure and for the identification of compounds. In this study, 12 similar structure dyes were synthesised and their FT-IR spectra obtained. The various characteristic frequencies were thus determined, so that it is possible to assess, to some extent, the likelihood of frequency shifts occurring with changes in the local environment of the group.

Derivative spectroscopy was found to be most useful and was applied in the many areas where the interpretation of conventional spectra was difficult, either because of a high background signal or where the superimposing of two or more spectral bands causes interference. The derivative mode offers the advantages of enhancing the resolution of overlapping bands, which

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*Corresponding author. Fax: 0113-233-2947; e-mail: ccddml@leeds.ac.uk facilitates quantitative assay of mixtures, suppression of background (matrix interference) to correct for systematic error, and enhancement of fine spectral features for qualitative analysis. The rate of change of the signal was recorded as a function of the wavelength or frequency. Successive differentiations of the signal obtained resolves any component peaks masked by overlapping. The differentials of simple Gaussian and Lorentzian peaks are displayed in Fig. 1

From Fig. 1 it can be seen that the odd number derivatives show a shift in the wavenumber of the peak, giving zero absorbance interception at the peak position of the original band (λ_{max}, and that the even number derivatives show the main peak which corresponds to λ_{max} of the original band. The even derivative centroid peak alternates in sign and decreases in width with increasing derivative order. Thus, as derivative order increases, fine spectral detail is enhanced, so that spectral profiles are obtained in which overlapping bands become progressively more resolved. It is more practical to use the even number derivatives when interpreting spectra, and the second derivative is preferred. The second derivative peak will be inverted compared to the original absorption or transmission band. This simple mathematical technique can also be applied to the case of two or more overlapping Gaussian bands, allowing the resolution of these peaks (Fig. 2).

EXPERIMENT

Twelve dyes, having similar structure to Sumifix Supra Brilliant Red 2BF, C.I.Reactive Red 194 (Fig. 3), were synthesised. In this study, FT-IR analysis of the 12 dyes were carried out using the Perkin-Elmer 1740 Infrared Fourier Transform Spectrometer.

Pure solid dye samples were made into discs by mixing 1 mg of sample in 200 mg of potassium bromide and pressing. The standard data collection parameters are as follows:

Resolution: 4 cm^{-1}; detector: DTGS; No. of scans: 100; scan range: 4000–400 cm^{-1}; gain: 1; mirror velocity: normal; apodisation: normal.

RESULTS AND DISCUSSION

The normalized, overlaid FT-IR spectra of the 12 dyes are shown in Fig. 4.

From these spectra, it is difficult to assign the characteristic frequencies of the vinylsulphone (VS), sulphatoethylsulphone (SES) and hydroxyethylsulphone (HES) moities, the many double bonds and sulphonate groups in the molecules and the hydroxy group on the H-acid core of the

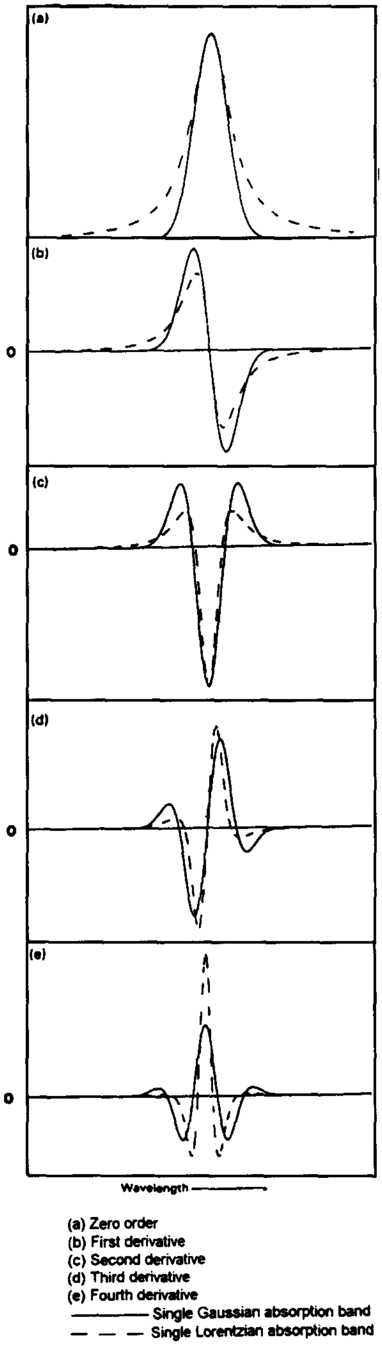


Fig. 1. Typical derivative profiles.

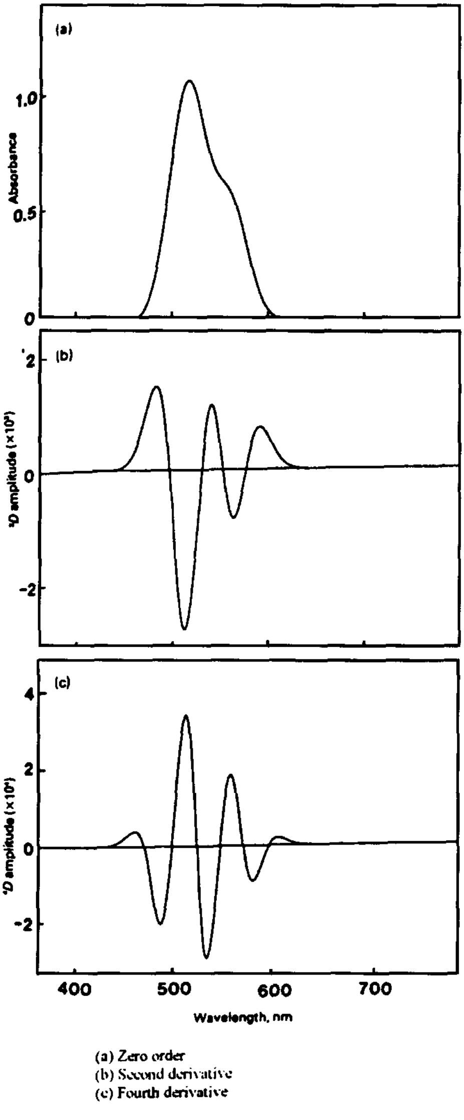


Fig. 2. Resolution of overlapping absorbance bands of equal bandwidth.

dyes lead to peak overlap. Second derivative spectroscopy was therefore carried out and the second derivative FT-IR spectra of the twelve dyes are shown in Figs 5 and 6

From these figures, it is very apparent that the characteristic frequencies of the vinylsulphone and hydroxyethylsulphone groups appear in Figs 5 and 6,

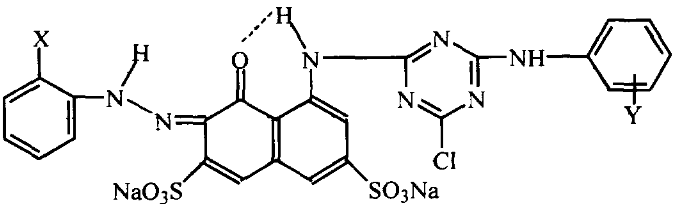


Fig. 3. Dye Structures.

as marked. The vinylsulphone dyes (B, E, H and K) show a characteristic band at 756 cm^{-1} (Fig. 5, region 900–700 cm^{-1}, black solid line). In the case of the hydroxyethylsulphone dyes (C, F, I and L) a characteristic C–C–O out-of-phase stretching frequency is seen at 1158 cm^{-1} (Fig. 5, region 1200–1000 cm^{-1}, black solid line). The various substituted sulphone groups (Y) show absorbance due to SO_2 stretching at 1150–1140 cm^{-1}; this absorbance is shifted downwards in the case of the hydroxyethylsuphone derivatives. The SO_2 stretching frequency for all the hydroxyethylsuphone derivatives is the same (Fig. 6, region 1200– 1000 cm^{-1}).

In Fig. 6 the spectra are grouped as the four VS dyes (region 900—700 cm^{-1}) and the four HES dyes (region 1200–1000 cm^{-1}); in this case the spectral shifts in the 1200–680 cm^{-1} region are much less obvious, since Y is the same in each group of spectra. However, since X is different and Y is in a different position, the spectral peaks of each of the four dyes in Fig. 6 show different frequencies in the region 1650∼1200 cm^{-1} and 680∼400 cm^{-1}; this contrasts with Fig. 5 region 1650∼1200 cm^{-1} , since X is the same and Y is in the same position. The spectral peaks of each of the four dyes in Fig. 5 show quite tidy frequencies in the region 1650–1200 cm^{-1} and 680–400 cm^{-1}.

The 756 cm^{-1} $CH=CH_2$ band and 1157 cm^{-1} C_2H_4OH band in Fig. 6 are very clear and accurately distinguish VS and HES dyes respectively.

The characteristic frequencies of the important groups in the dyes are listed in Table 1.

The O–H stretching band in the IR spectrum is by far the most characteristic IR band of alcohols and phenols. The free O–H vibration occurs as a sharp band above 3600 cm^{-1}, while for the majority of condensed-phase (liquid or solid) samples, this O–H band is broadened and shifted to 3500–2500 cm^{-1} due to various types of hydrogen bond formation. The primary alcohol band cannot be found in this range. The intense band in the 1260–1000 cm^{-1} region, which is referred to as C–O stretching in some works, is assigned to the out-of-phase C–C–O stretching mode by the normal coordinate analysis method [7, 8]. This vibration also gives rise to a medium to strong intensity band in the Raman spectra [9]. Primary alcohols absorb strongly at 1075–1000 cm^{-1}, secondary alcohols at 1150–1075 cm^{-1}, tertiary

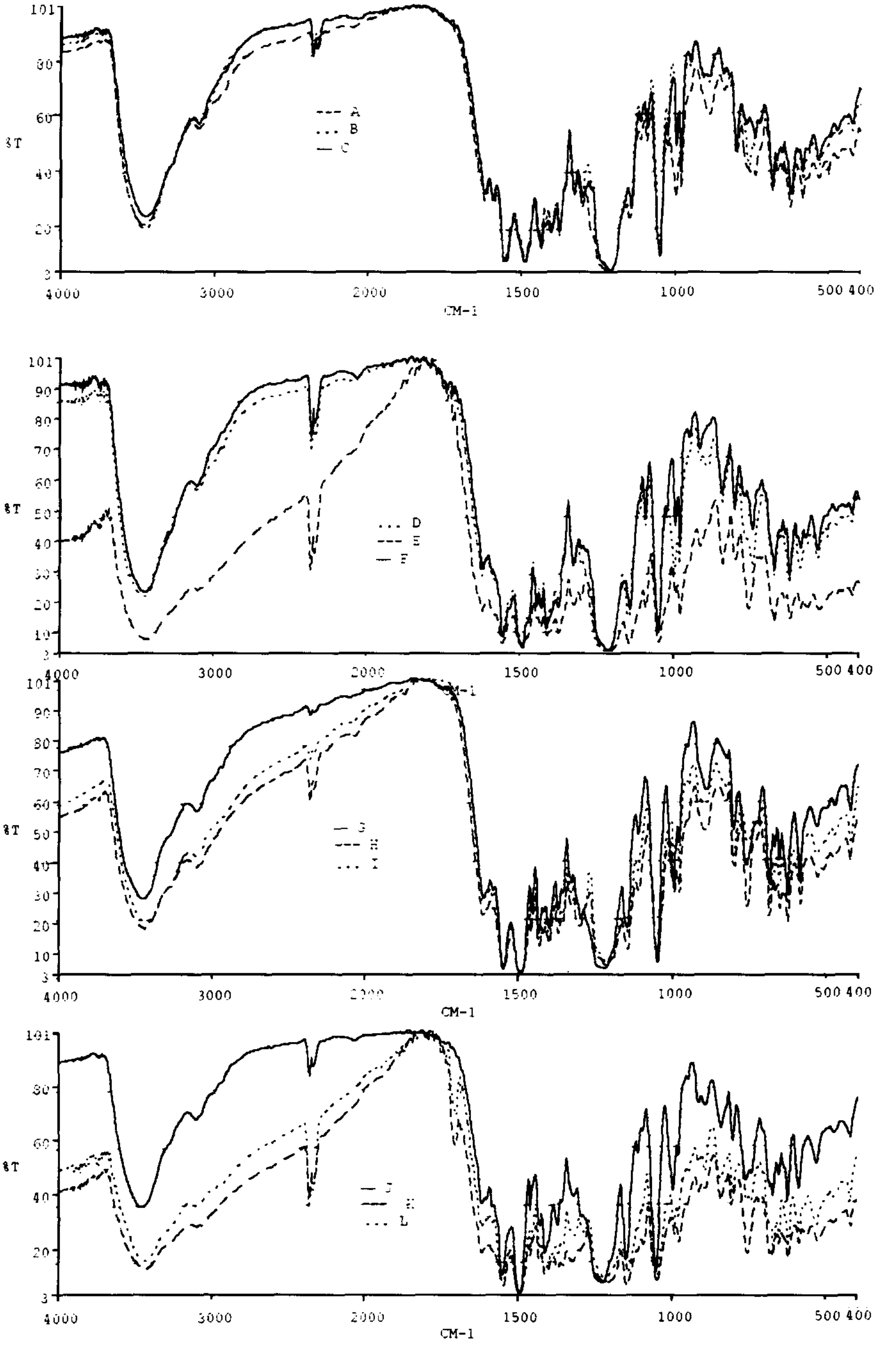


Fig. 4. Normalized, Overlaid FT-Infrared Spectra of Twelve Dyes.

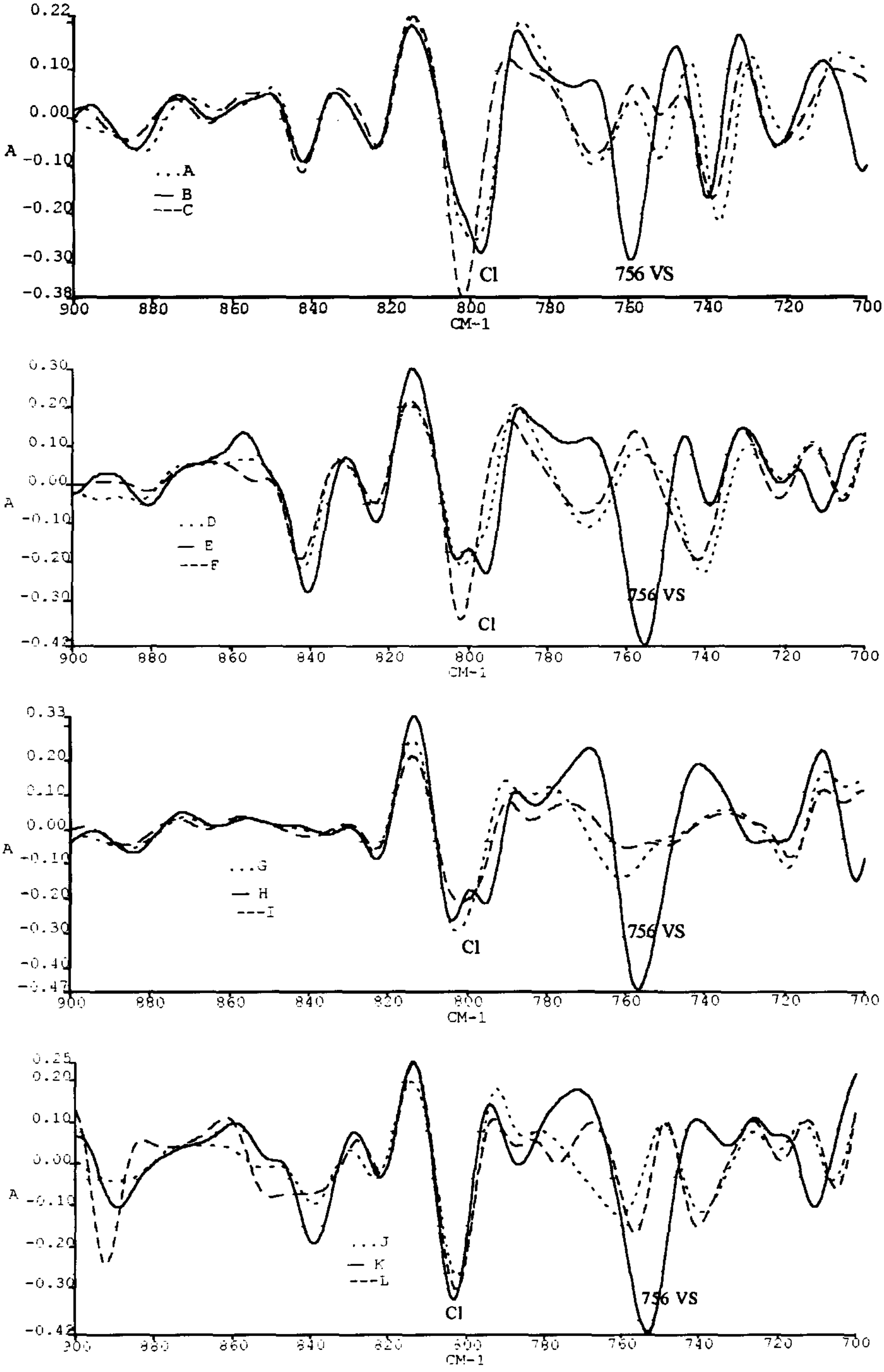


Fig. 5. Second Derivative FT-Infrared Spectra of Twelve Dyes Region 900–700 cm^{-1}.

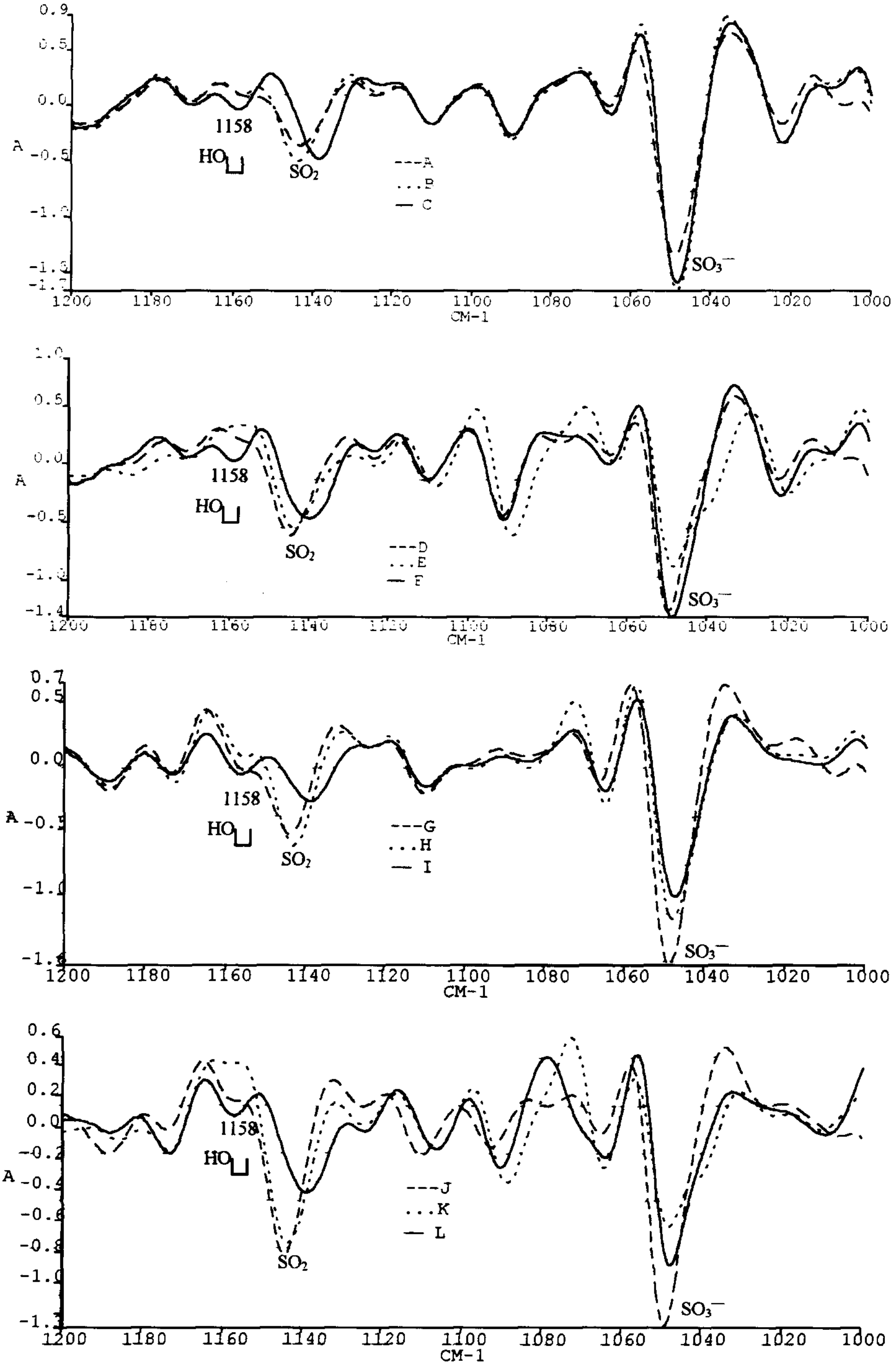


Fig. 5. *cont.* Region 1200–1000 cm^{-1}.

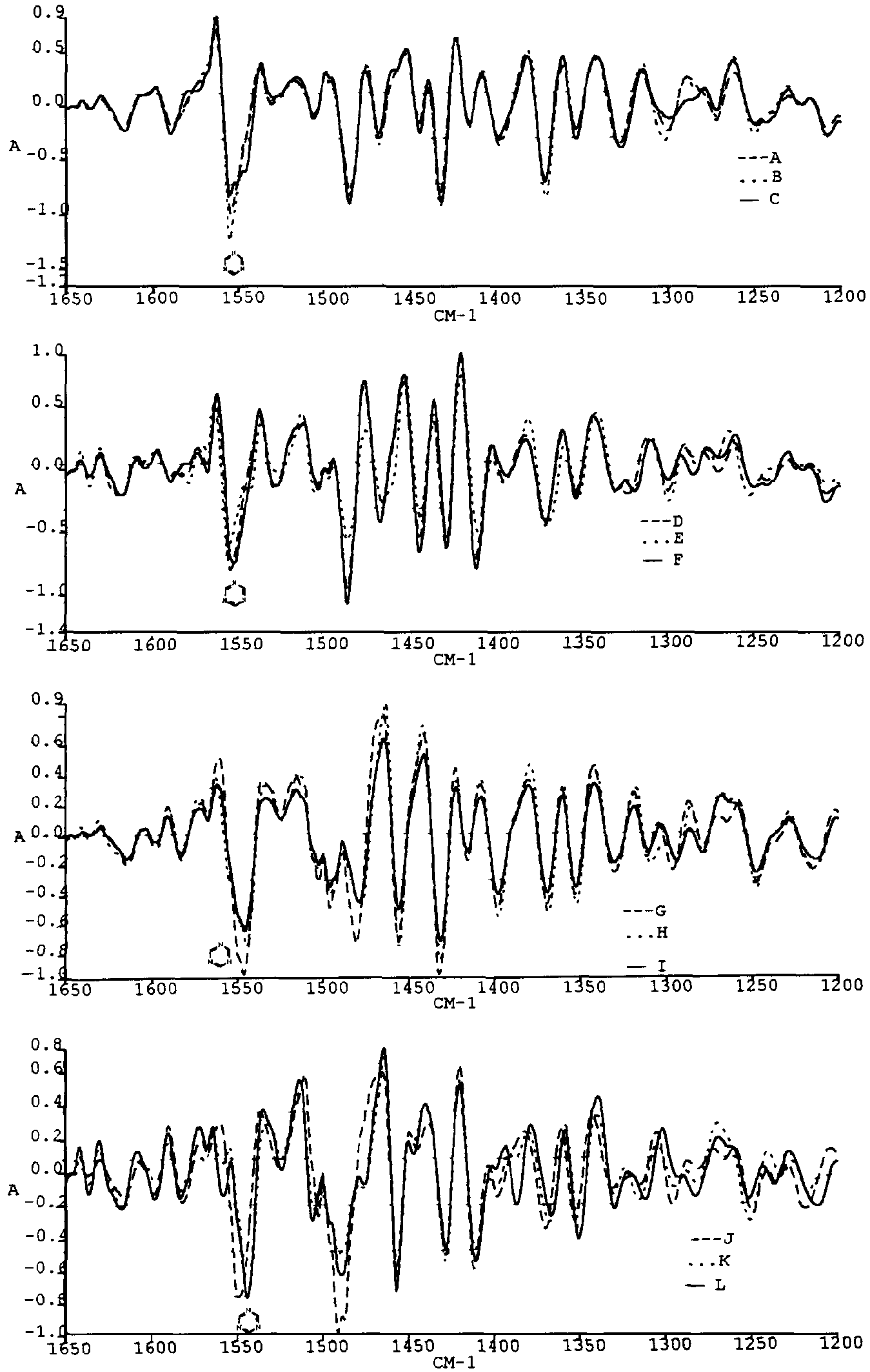
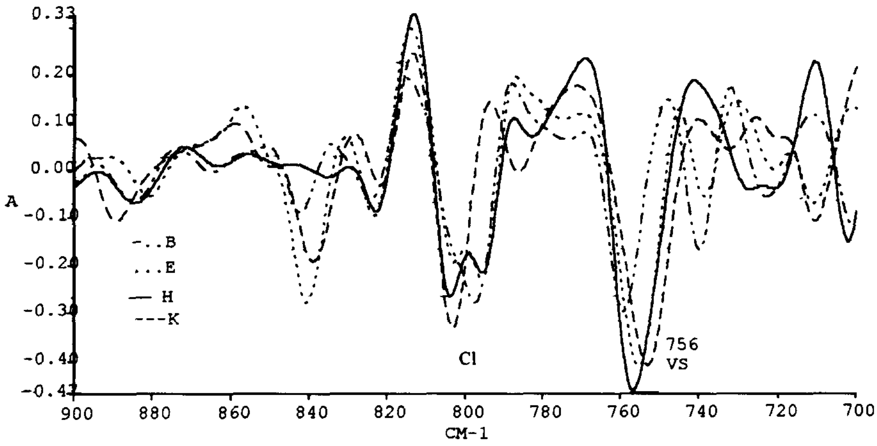


Fig. 5. *cont.* Region 1650–1200 cm^{-1}.

alcohols at 1210–1100 cm^{-1}, and phenols at 1260–1180 cm^{-1} [2]. These may be single bands or band clusters. All these bands shift somewhat when there are changes in hydrogen bonding. A study of the factors influencing the C–O stretching frequencies has been reported by Nyquist [10].

The vinyl type double bond gives rise to two strong bands near 990 and 910 cm^{-1}. The first of these is connected with the hydrogen deformation mode of the C=C structure, and is absent from asymmetrically

Region 900 - 700 cm^{-1} VS dyes



Region 1200 - 1000 cm^{-1} HES dyes

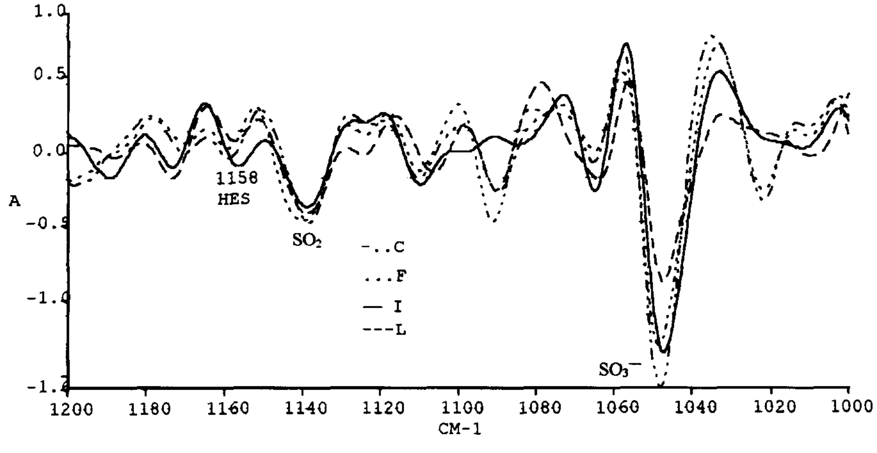


Fig. 6. Second Derivative FT-Infrared Spectra of Twelve Dyes.

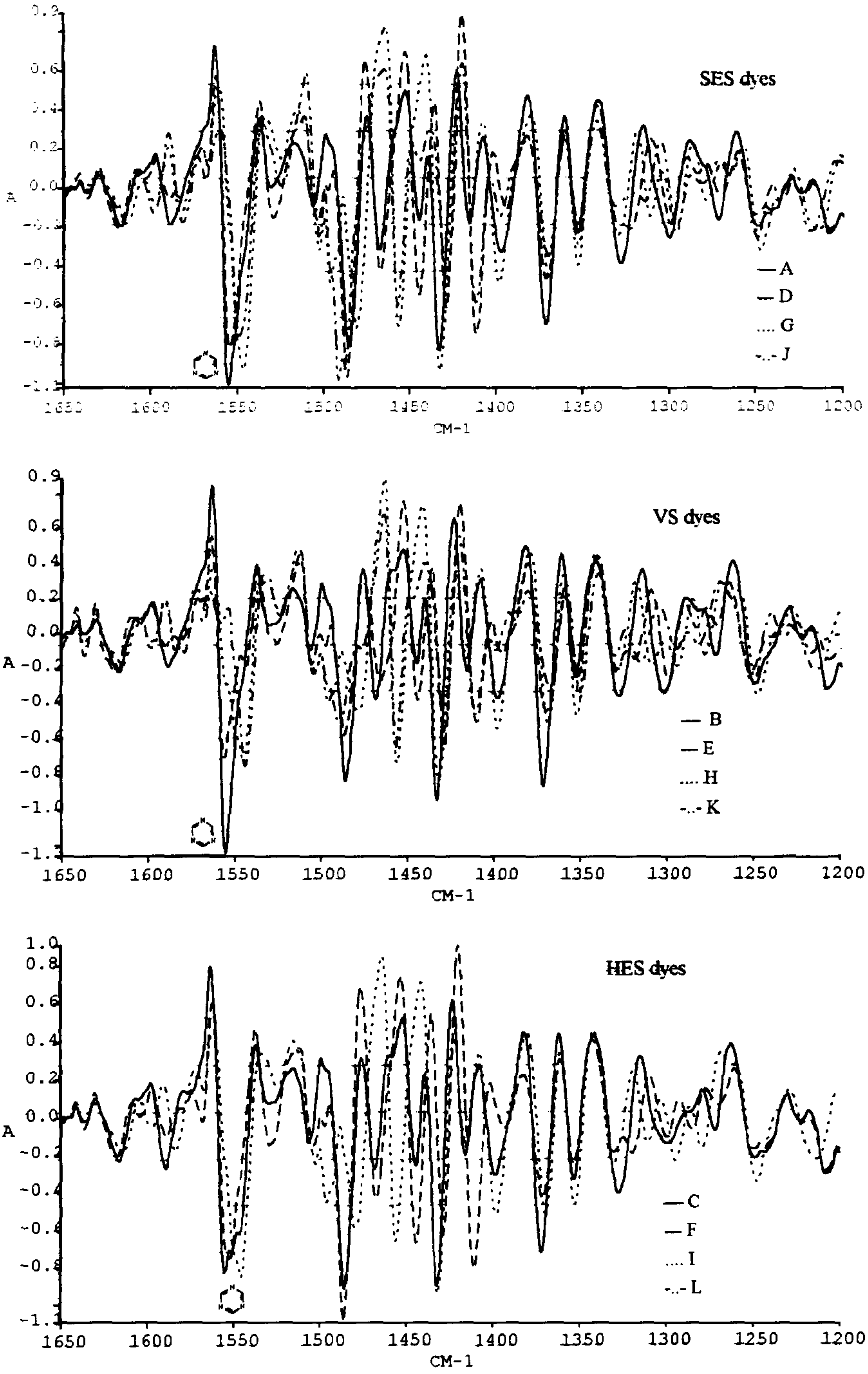
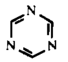


Fig. 6. *cont.* Region 1650–1200 cm^{-1}.

TABLE 1
The Characteristic IR Frequencies of Important Groups and Their Actual Frequencies in the Model Dyes (cm^{-1})

	Group	*IR*	*Reference*	*IR in the dye*
Sulphonates	Ar-SO$^-_3$	1230–1120 vs 1080–1025 vs	[1] [2]	1210 vs 1048 vs
Sulphones	Ar-SO$_2$-R	1334–1325 s 1160–1120 s	[3] [4]	1327 s 1145 s
Chlorine	Ar-Cl	850–700 s	[5]	800 s
Triazines		1550 vs 1410 vs	[6]	1550 vs 1410 m
Primary alcohol	C-C-OH	1075–1000 s	[5]	1157 m
Vinyl	$-CH=CH_2$	915–590 s	[3]	756 s

di-substituted ethylenes. The second band arises from out-of-plane deformations of the hydrogens of the $=CH_2$ group and occurs in both types of linkage. The direct attachment of polar atoms results in large downwards shifts. The 910 cm^{-1} band moves to 810 cm^{-1} in vinyl ethers, and in the vinylidene compounds with two attached oxygens the shift of the corresponding band is doubled (720 cm^{-1}). The hydrogen out-of-plane deformations in compounds of the type $R_1R_2C=CH_2$ occur at 890 cm^{-1}. The direct attachment of oxygen leads to a major shift to 795 cm^{-1}, with a further fall to 710 cm^{-1} in diethoxy compounds [3]. The vinyl group $-CH=CH_2$ in the dyes C, F, I, L is directly attached to the polar sulphone group producing the 756 cm^{-1} frequency for the vinyl moiety.

Strong bands appear in the region 1000–650 cm^{-1} in the spectra of aromatic materials due to out-of-plane deformation vibrations of the hydrogen atoms remaining on the ring. All the 12 dyes showed two bands near 995 and 979 cm^{-1}.

CONCLUSION

Dyes with the same chromophore but with different branched substituted alkylsulphone groups are complex conjugated molecules; it is thus difficult to recognise every characteristic frequency in the original FT-IR spectra. Second derivative spectroscopy must be used to separate superimposed spectral bands and enhance fine spectral detail. The FT-IR characteristic frequency of the vinylsulphone group in such dyes is 756 cm^{-1} and the FT-IR characteristic frequency of the hydroxyethylsulphone group in such dyes is 1157 cm^{-1}.

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