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Heat-Induced Structural Changes in Merocyanine Dyes: X-Ray and Thermal Studies

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ABSTRACT

Certain merocyanine dyes undergo heat-induced isomerisation, which is responsible for their thermovoltage generation properties. Using these dyes, our studies reveal the correlation between their thermal properties and their crystalline structure. Differential thermal analysis of hexadecyl, decyl and pentyl dyes showed reversible phase transitions at their respective characteristic temperatures (T_c*) owing to thermal isomerisation of the dyes. X-Ray diffraction patterns indicated heat-induced changes in the crystal structure of the dyes. This was also supported by the results obtained from polarising microscopy studies and thermogravimetric analysis. Further heating of these dyes caused a permanent deformation in the crystal structure, which ultimately led to total disintegration as recorded in the thermogravimetric studies.*

INTRODUCTION

Merocyanine dyes belong to a group of thermal and photosensitive compounds,[1,2] and undergo heat or light-induced isomerisation.[3–6] These dyes have symmetry in their chemical structure but differ in the nature of their functional *N*-alkyl groups,[1–7] leading to differences in their binding and crystal structure. This causes variations in the isomerisation temperature, reaction mode, and the enthalpy involved.

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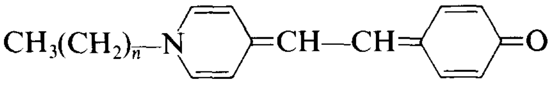
MATERIALS AND METHODS

The dyes used in the study were the hexadecyl (n = 15) decyl (n = 9) and pentyl (n = 4) derivatives **I**.



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The dyes were synthesized according to Ref. 7. AR grade acetone and chloroform supplied by E. Merck were used without further purification.

Thermal analysis was carried out in air using Shimadzu thermal analysers (Model no. DT 30 and DT 50). Dried dye crystals (30 mg) were placed in a platinum crucible and heated to different temperatures at rates varying from 3°C min^{-1} to 10°C min^{-1}.

X-ray diffraction patterns were obtained using a Philips PW 1730 X-Ray diffraction unit with nickel filtered CuK_α radiation. Thin films of dye deposited on glass plates were used to take the diffractogram.

The thermogravimetric analysis was carried out with a Shimadzu thermogravimetric analyser (Model no. TG-50). Dried dye in the form of powdered crystals was placed in a platinum crucible and heated at rates of 3°C min^{-1} to 10°C min^{-1}.

From differential thermal analysis (DTA), thermogravimetric analysis (TGA) and X-ray diffraction studies, we have obtained complete information about the thermal reactions in these merocyanine dyes. The DTA graphs revealed that merocyanine dyes undergo reversible phase transitions at their respective charcteristic temperatures (T_c), which is probably responsible for the thermal isomerisation of the dyes. This fact was further supported by the results obtained from X-ray diffractograms, polarising microscopy and TGA studies. Above T_c the DTA graphs indicated a series of endothermic and exothermic irreversible reactions, and results obtained from X-ray diffraction patterns indicated some permanent deformation in the crystal structure of these dyes. Very little weight loss in the TGA graph indicated the utilization of absorbed energy in breaking the molecular bonding in the crystal structure. At higher temperatures, a total disintegration of the merocyanine dyes takes place, as confirmed by the DTA and TGA studies.

Thus, using DTA, TGA and X-ray spectroscopy, our studies reveal the correlation between the thermal properties and the crystalline structure of the merocyanine dyes investigated. The heat-induced isomerisation of these dyes is responsible for their thermovoltage generation properties.

These results may be of value in the field of non-conventional energy sources.

RESULTS AND DISCUSSION

The X-ray diffractograms showed that the dyes exist in well defined crystalline forms at room temperature. Using de Wolffe's method,[8] the crystal structure of the decyl merocyanine dye was determined (Fig. 1, Table 1). The dyes used have a common chemical backbone but differ in the nature of the *N*-alkylsubstituent, which leads to differences in their crystallographic structure (Fig. 2), nature of intermolecular arrangement and strength of binding. As a result of this, the phase transition temperatures, mode of crystal breakdown and enthalpy involved differ for different dyes.

From DTA studies it was observed that the dyes undergo a reversible phase transition arising from a reversible heat-induced isomerisation

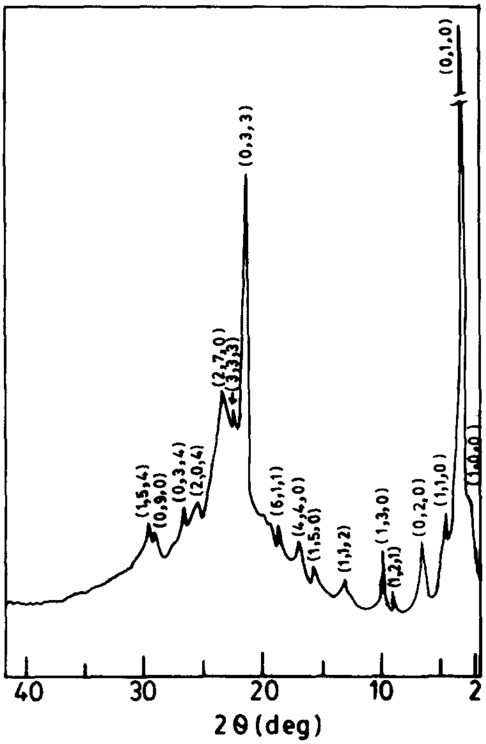


Fig. 1. X-Ray diffraction pattern of decyl merocyanine dye.

TABLE 1
Crystal Structure of Decyl Merocyanine Dye

d (A°)	*I/I*$_1$	*h k l*	*d (A°)*	*I/I*$_1$	*h k l*
31·26	20	1 0 0	4·82	7	6 1 1
27·59	100	0 1 0	4·222	72	0 3 3
20·69	25	1 1 0	3·913	32	3 3 3
13·79	23	0 2 0	3·821	51	2 7 0
9·45	4	1 2 1	3·475	10	2 0 4
8·82	21	1 3 0	3·323	9	0 3 4
6·74	7	1 1 2	3·065	5	0 9 0
5·43	5	1 5 0	2·980	12	1 5 4
5·17	9	4 4 0			

Radiation CuK$_{\alpha 1}$: $\lambda = 1{\cdot}5408$ Å; filter = Ni.
System orthorhombic: $a_0 = 31{\cdot}264$ Å, $b_0 = 27{\cdot}587$ Å, $c_0 = 14{\cdot}257$ Å.

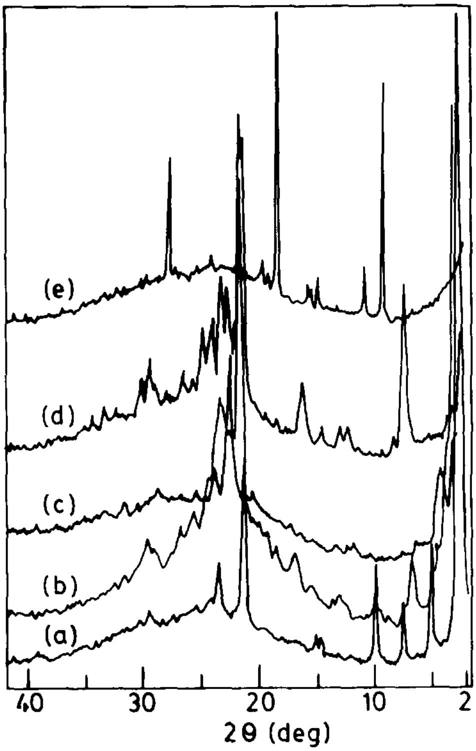


Fig. 2. X-Ray diffractograms of: (a) hexadecyl; (b) decyl; (c) octyl; (d) pentyl; (e) di-*tert* butyl merocyanine dyes.

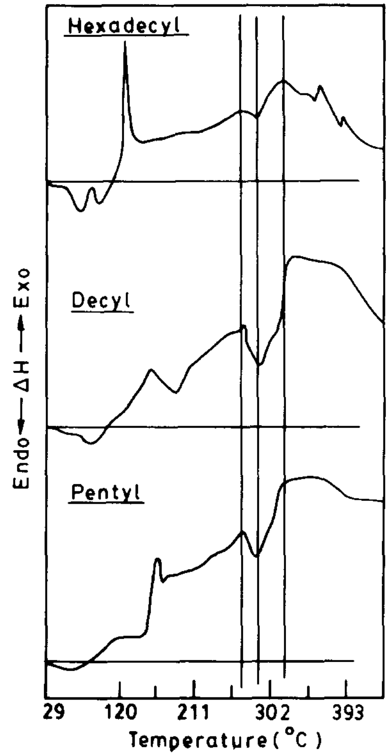


Fig. 3. DTA curves of hexadecyl, decyl and pentyl merocyanine dyes.

within their characteristic temperature range T_c (up to ~70°C).[9] For the decyl dye, the DTA exhibited two reversible endothermic reactions at 40°C and 67°C (Fig. 3).

Comparison of the X-ray diffractogram of the decyl dye at 30°C and 70°C showed that whilst the number and position of the peaks was constant, their intensity varied. In particular, the peak intensity corresponding to the 100 plane became more intense at 70°C compared with that at 30°C (Fig. 4). Such variations imply a conformational change of the *cis* → *trans* type[10] of the dye molecules within the same crystalline structure, thereby suggesting that change in the crystal structure was responsible for the reversible phase transition. The temperature ranges and amounts of heat required for these transformations were calculated from thermal analysis (Table 2). As the crystal structure was different for different dyes, the phase transition temperature and the corresponding enthalpy involved also varied.

For temperatures greater than T_c, the dye crystals underwent some

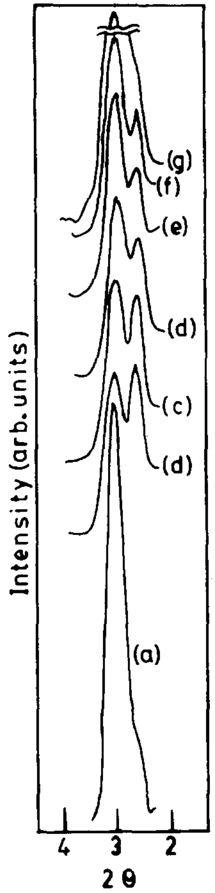


Fig. 4. X-Ray diffractogram of decyl merocyanine dye: (a) at room temperature (30°C); (b) at 65°C; (c) after 10 min of normal cooling; (d) after 20 min of normal cooling; (e) after 2·5 h of normal cooling; (f) after 3 h of normal cooling; (g) after 24 h of normal cooling.

permanent deformation through a series of irreversible endothermic and exothermic reactions. As the mode of breakdown of the dye crystal depends on the crystal structure and the strength of the molecular bonds involved, the nature of the thermal reaction was different for different dyes. The hexadecyl dye which exists in an orthorhombic crystal form[9] passes through two endothermic and one exothermic reaction at 95°C, 110°C, and 121°C, respectively (Fig. 3). X-ray diffraction patterns (Fig. 5) showed that these reactions are responsible for the permanent deformation in this dye. All the merocyanine dye crystals break below 160°C, but through different types and modes of reactions. The TGA study also showed very slow weight loss within this

TABLE 2
Thermal Analysis Data for the Hexadecyl, Decyl and Pentyl Merocyanine Dyes

Dye used	*Step no.*	*Type of reaction*	*Reaction range (°C)*		*Enthalpy (kcal X mol^{-1})*
			Start	*End*	
Hexa decyl	1	Endothermic	30	70	1·44
	2	Endothermic	70	121	20·136
	3	Exothermic	130	145	10·58
	4	Exothermic	282	400	15·82
Decyl	1	Endothermic	30	70	1·26
	2	Endothermic	70	200	19·46
	3	Exothermic	250	282	4·49
	4	Exothermic	282	400	14·58
Pentyl	1	Endothermic	30	70	1·13
	2	Exothermic	131	165	11·05
	3	Exothermic	250	282	1·25
	4	Exothermic	282	400	14·55

Step 1: Characteristic temperature range for reversible phase transition.
Steps 2 & 3: Crystal structure breaks and partial disintegration takes place.
Step 4: Total disintegration takes place for all the dyes.

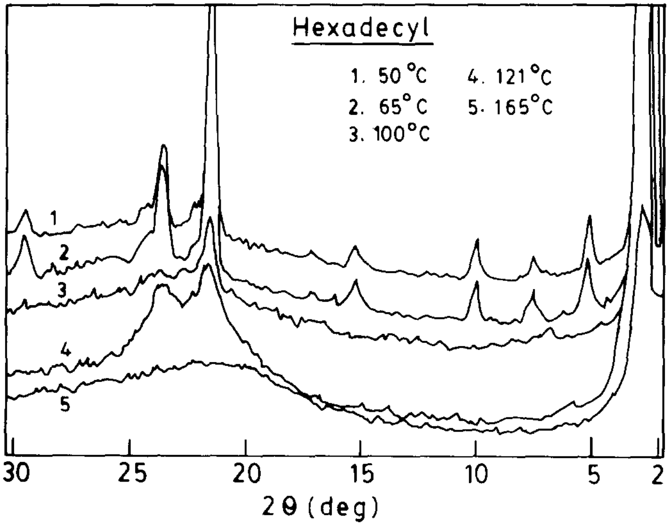


Fig. 5. X-Ray diffractogram of hexadecyl merocyanine dye at 30°C after heating to: (1) 50°C; (2) 65°C; (3) 100°C; (4) 121°C; (5) 165°C.

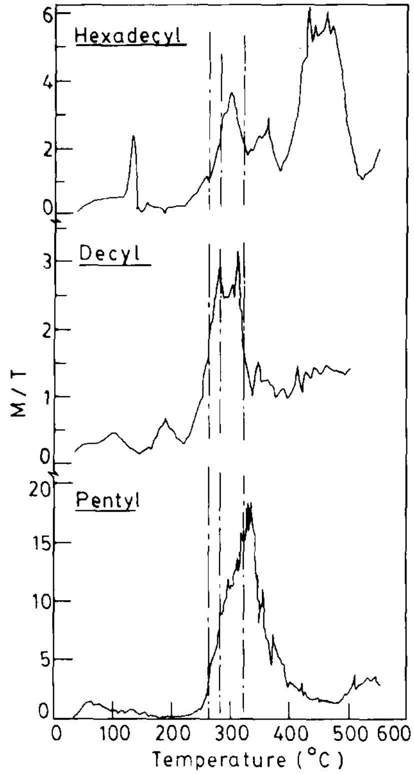


Fig. 6. TGA curves of hexadecyl, decyl and pentyl merocyanine dyes.

temperature range (Fig. 6), which indicates that heat energy is used to the crystal bonding.

Further heating of the dyes decomposed them very quickly through three identical endothermic and exothermic reactions at 260°C, 295°C and 310°C (Fig. 3). From TGA studies the rapid and total decomposition of the dyes was confirmed. Thus, above 200°C all the merocyanine dyes disintegated in a similar manner, which can be attributed to the fact that the dyes possess a common backbone structure.

When these dyes, which are optically active, were studied under a polarising microscope between two cross polarisers, it was observed that on heating the sample a reversible phase transition took place at 65°C. The various changes observed are shown in Fig. 7.

Therefore, this study not only correlates the thermal properties of the merocyanine derivative dyes with their crystalline structure, but it also reveals the molecular mechanism that is associated with their thermal transitions.

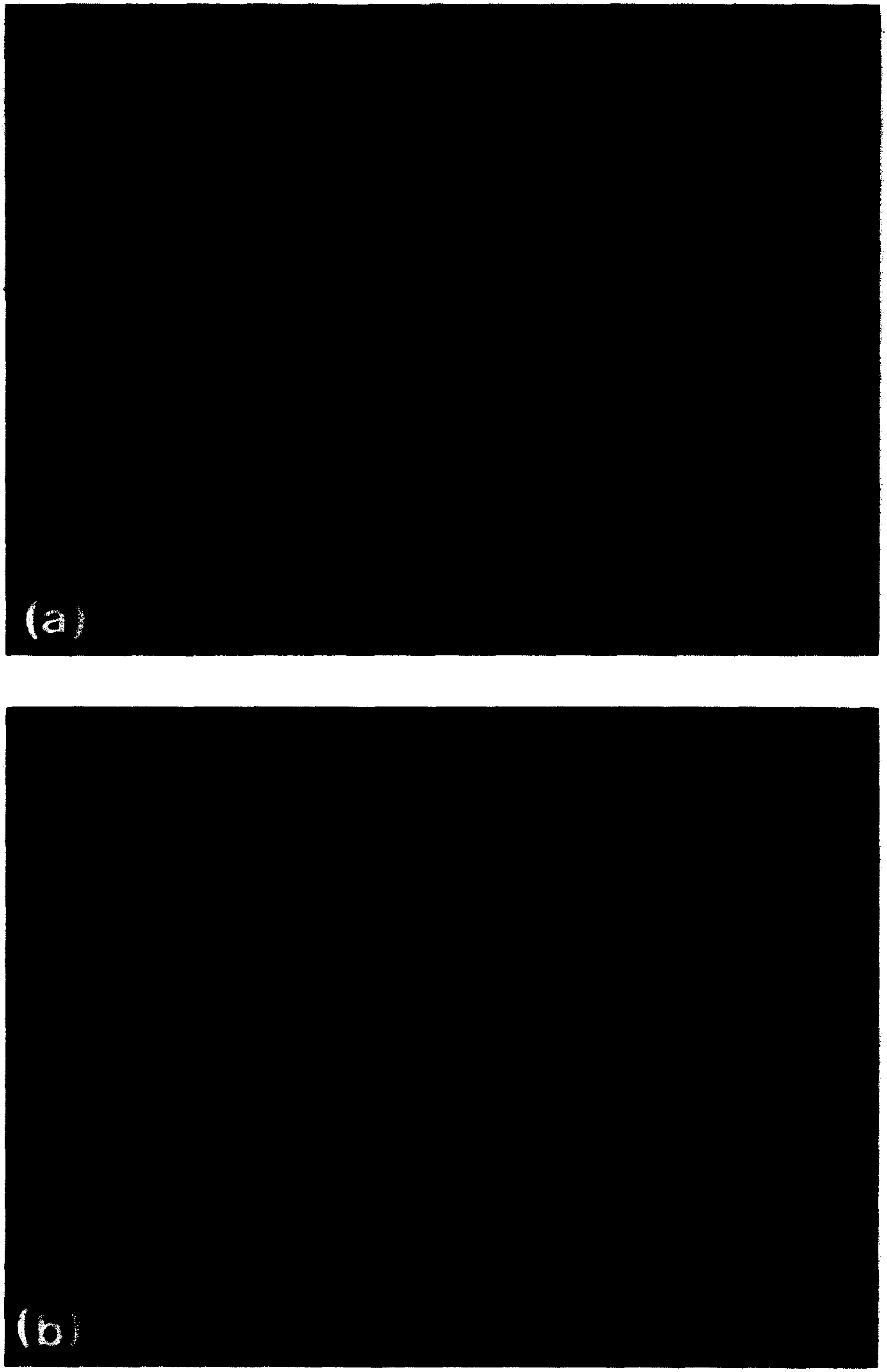
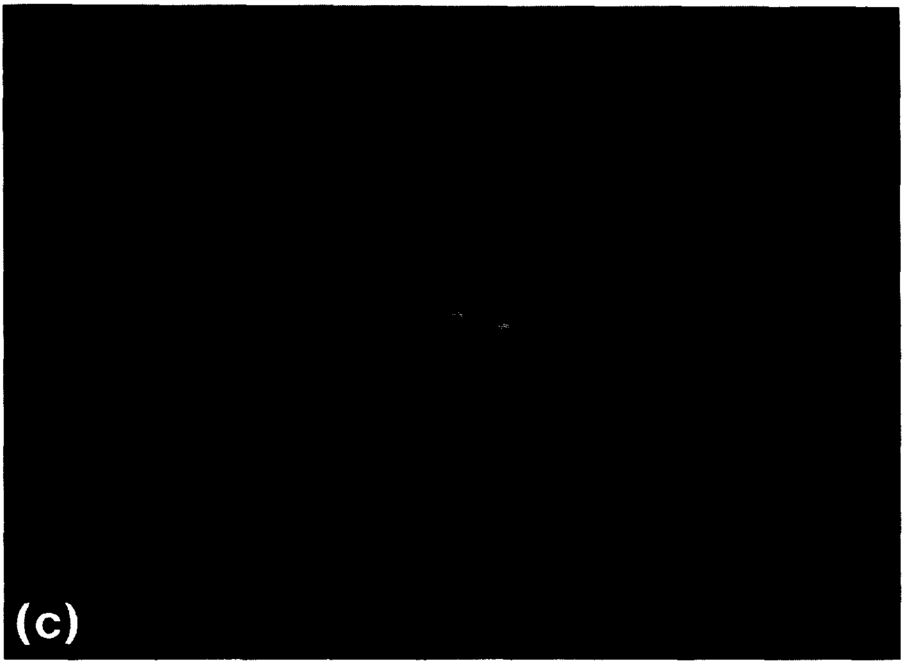


Fig. 7. Polarising micrograph of hexadecyl merocyanine dye after heating and cooling: (a) at 30°C; (b) after heating to 50°C; (c) after heating to 60°C; (d) after cooling to 40°C.



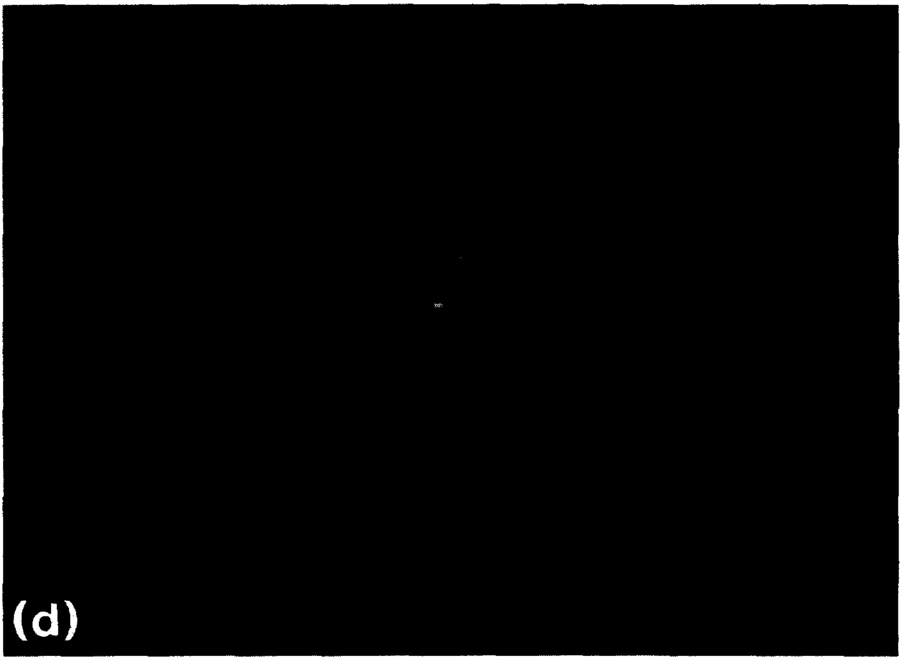


Fig. 7.—*contd.*

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