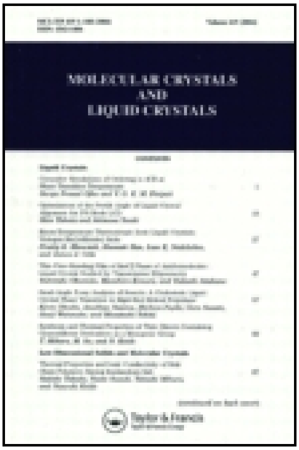

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A Survey of the Thermoluminescence of Organic Crystalline Solids

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A Survey of the Thermoluminescence of Organic Crystalline Solids

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Abstract—A survey of the thermoluminescence of 42 organic crystalline solids is described and the data obtained is tabulated. The curves are found to consist of a number of distinct peaks not further resolvable by partial annealing and were usually precisely repeatable between different samples of the same material and could not be modified by doping. The majority of the peaks were found to be of low emission intensity and occurred at low temperatures.

1. Introduction

In the last 30 years interest in thermoluminescence has centred on inorganic phosphors(1,2) while very few studies have been made using the great variety of organic crystalline materials. Only a few substances have been examined, chiefly amino acids and proteins,(3) polymers,(4) some solid solutions in rigid organic glasses,(5,6) and a few isolated compounds.(7,8) Because thermoluminescence is a potentially useful means of investigation of materials which are difficult to examine using many other methods, it was decided to undertake a survey of this phenomenon in organic materials prior to making a more detailed study of selected compounds.

2. Experimental

The samples were prepared in the form of 1.25 cm diameter tablets by subjecting the material to a pressure of 180 kg/cm^2 for one minute in a stainless steel die. They were then placed on the tip of a type of cold finger held in an evacuated chamber attached to the X-ray tube housing, cooled to liquid air temperature, irradiated for 10 minutes with X-rays from a Mo target tube to give a dose of approxi-

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mately 20 K rad and warmed at a linear heating rate of 20 °C/minute to 0 °C, the temperature being measured using a chromel-alumel thermocouple. The emitted light was observed through quartz windows using a 1P28 photomultiplier with an S5 spectral response, which was mounted in a liquid air cooled housing. The photocathode of the detector subtended a solid angle of 0.025 steradians at the sample. After amplification the signal was traced out on a pen recorder. The results obtained are summarized in Table 1. The relative intensities refer to the maximum luminosity of the brightest peak, one unit representing a photomultiplier current of 10^{-11} amps, i.e. approximately 2×10^3 photons per second striking the photocathode.

3. Results

The glow curves of the organic materials studied were found to consist of up to 6 separate peaks (Fig. 1) which were not resolvable in

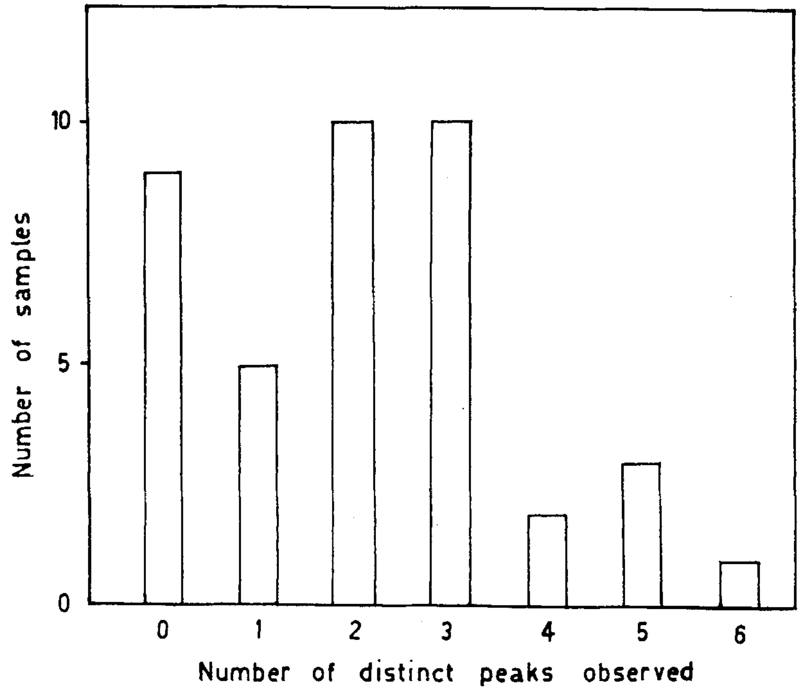


Figure 1. Frequency distribution of numbers of observed peaks.

themselves by partial annealing, and appeared to be each due to one species of centre (e.g., Fig. 2). In the cases where there was one broad feature with no distinct maximum, careful partial annealing of the sample invariably indicated that this was due to a large number of overlapping peaks. The glow curves produced by different samples of the same compound were found in general to be reproducible, there being only three exceptions to this statement. A specimen of glycine was found which gave an easily detectable glow curve, while all other samples were non-luminous. When different samples of hexamine were studied a selection of the same five peaks with varying relative intensities were found. However repeated irradiations, at least at dose levels up to 0.5 M rad., using a given sample produced identical curves in all cases except that of urea. This implies that there is usually no effect arising as a consequence of the total cumulative dose received, and also that the past history of the sample as regards exposure to radiation can be ignored. Visual observation of thermoluminescing single crystals with the eyes dark adapted and with the aid of a wide aperture long focus microscope shows the emission to be uniformly distributed throughout the crystal.

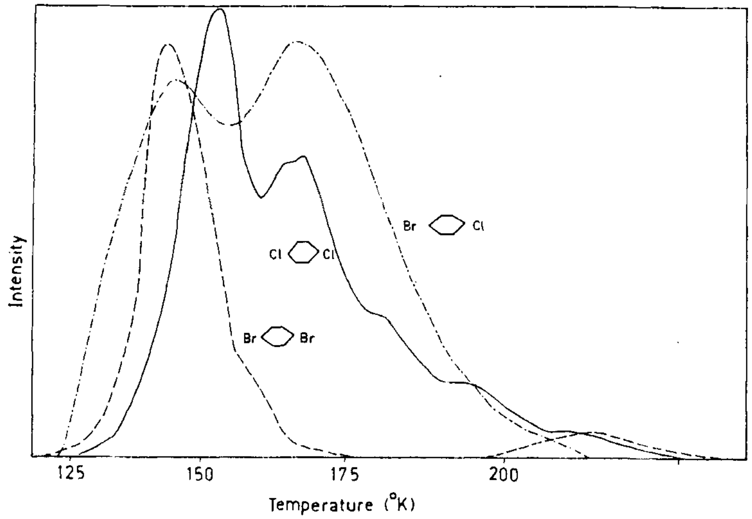
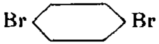
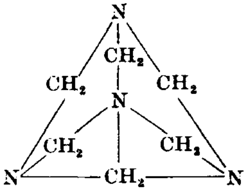
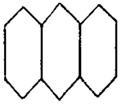
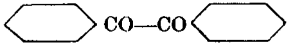
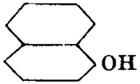
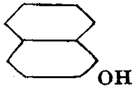
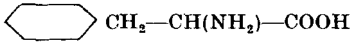
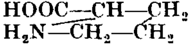
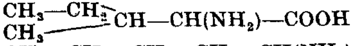


Figure 2. Glow curves of isomorphous dihalogenated benzenes.

TABLE 1

Compound	Formula	Number of peaks	Relative intensity of brightest peak
p-dichlorobenzene		5	4450
p-bromochlorobenzene		2	1500
p-dibromobenzene		3	4000
hexamine (hexamethylenetetramine)			
urea	$(NH_2)_2CO$	3	64
anthracene (blue fl.) anthracene (green fl.)		3 3	60 60
benzil		6	4100
1-naphthol		0	
2-naphthol		2	5
sodium tartrate oxalic acid	NaOOC—CHOH—CHOH—COONa HOOC--COOH	2 1	$\overline{53}$

malonic acid	$HOOC—CH_2—COOH$	0	—
succinic acid	$HOOC—CH_2—CH_2—COOH$	3	—
adipic acid	$HOOC—CH_2—CH_2—CH_2—CH_2—COOH$	2	2
citric acid	$HOOC—CH_2—C(OH)(COOH)—CH_2—COOH$	1	7
L-aspartic acid	$HOOC—CH_2—CH(NH_2)—COOH$	2	5
DL-aspartic acid		0	—
L-glutamic acid		0	—
DL-glutamic acid		0	—
Dα alanine	$CH_3—CH(NH^2)—COOH$	1	5
β-alanine	$H_2N—CH_2—CH_2—COOH$	0	—
L-β-phenylalanine		2	400
DL-β-phenylalanine		2	15
Glycine	$H_2N—CH_2—COOH$	0	
L-proline		0	
DL-proline		4	640
L-threonine	$CH_3—CH(OH)—CH(NH_2)—COOH$	2	50
DL-threonine		3	10
DL-leucine	$(CH_3)_2CH—CH_2—CH(NH_2)—COOH$	0	—
L-isoleucine		3	20
DL-isoleucine		2	16
DL-nor-leucine	$CH_3—CH_2—CH_2—CH_2—CH(NH_2)—COOH$	1	3
p-bromoaniline		3	26
p-chloroaniline		5	127
p-nitroaniline		3	3
diphenylamine		6	22
p-aminobenzoic acid		1	—
p-aminophenol		4	4300
p-nitrophenol		3	6
dextrose	$C_6H_{12}O_6$	2	—

4. Discussion

Attempts were made to determine the effect of the presence of impurities upon the glow curves and to see if one could ascribe any particular peak to a defect arising from a given impurity centre. This was done using two techniques. Firstly, attempts were made to dope succinic acid, glycine, adipic acid, urea, malonic acid and citric acid with benzene, by making a paste of the finely powdered material and the liquid dopant, which was then allowed to evaporate. This failed to produce any change in the glow curves. Secondly, crystals of various materials were grown both from the solution and from the vapour. The glow curves produced using these were identical to those obtained from pressed tablets or a fine powder. As one would expect the crystals to have a different level of impurity as a result of the growing process it appears unlikely that this factor influences the shape of the curves.

Two experiments were performed to ascertain whether either the crystal structure or the form of the molecule had a major influence on the shape of the glow curve. The thermoluminescence of *p*-dibromobenzene and *p*-dichlorobenzene, which have isomorphous crystal structures(10) and different molecules, were examined and found to be quite dissimilar (Fig. 2). This implies that the crystal structure does not provide the dominant influence in deciding the shape of the glow curves. When the L and DL isomers of certain amino acids (aspartic acid, glutamic acid, β phenylalanine, proline, threonine and isoleucine) were examined it was found that their glow curves showed no similarity (Fig. 3). Since they have similar molecules, the only difference being in the arrangement of the radicals about the assymetric carbon atom, while their crystal structures are entirely different, it appears that the form of the individual molecules does not give rise to a dominant influence on the nature of the curve.

It is well known that the aromatic materials are generally more luminous than other organics. In the light of this it is interesting to note that all of the six compounds having four or more distinct peaks, and all of the seven substances which have intensities of over 100 in the units of Table 1 had ring structures, not necessarily benzene rings. Only one aromatic compound failed to thermoluminesce.

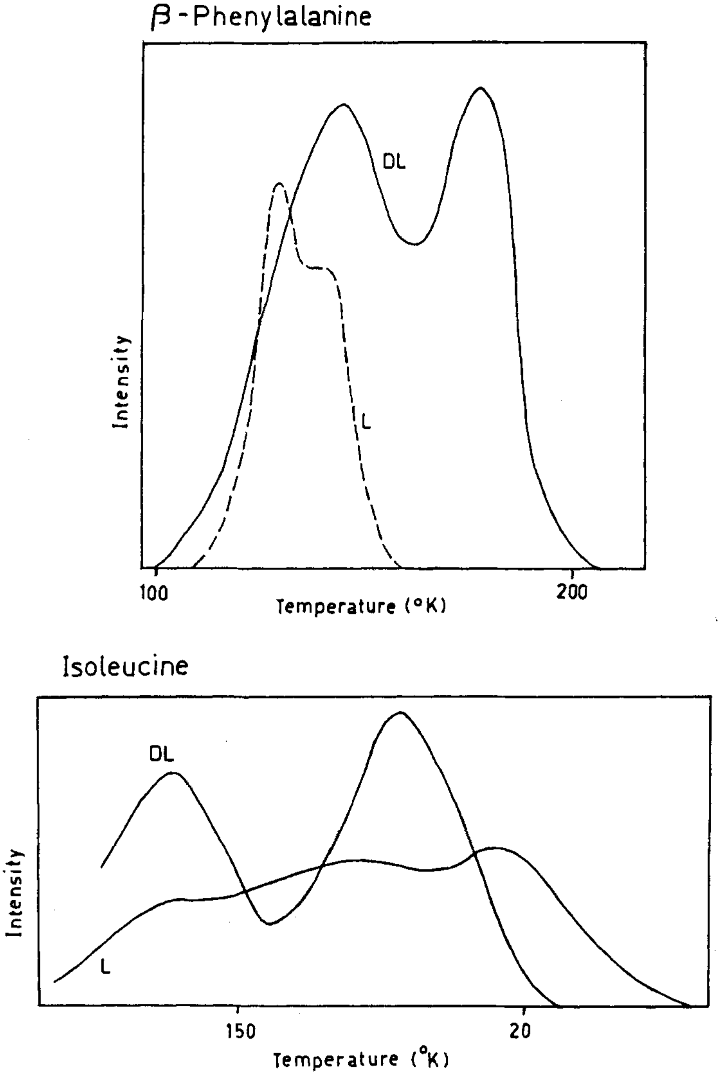


Figure 3. Glow curves of pairs of isomers.

Thus it seems that aromatic materials give a larger number of more luminous glow peaks.

When the observed parameters of the peaks are marked on a brightness versus temperature plot (Fig. 4) it will be noted that the majority occur at low temperatures (120–180 °K) and are of low

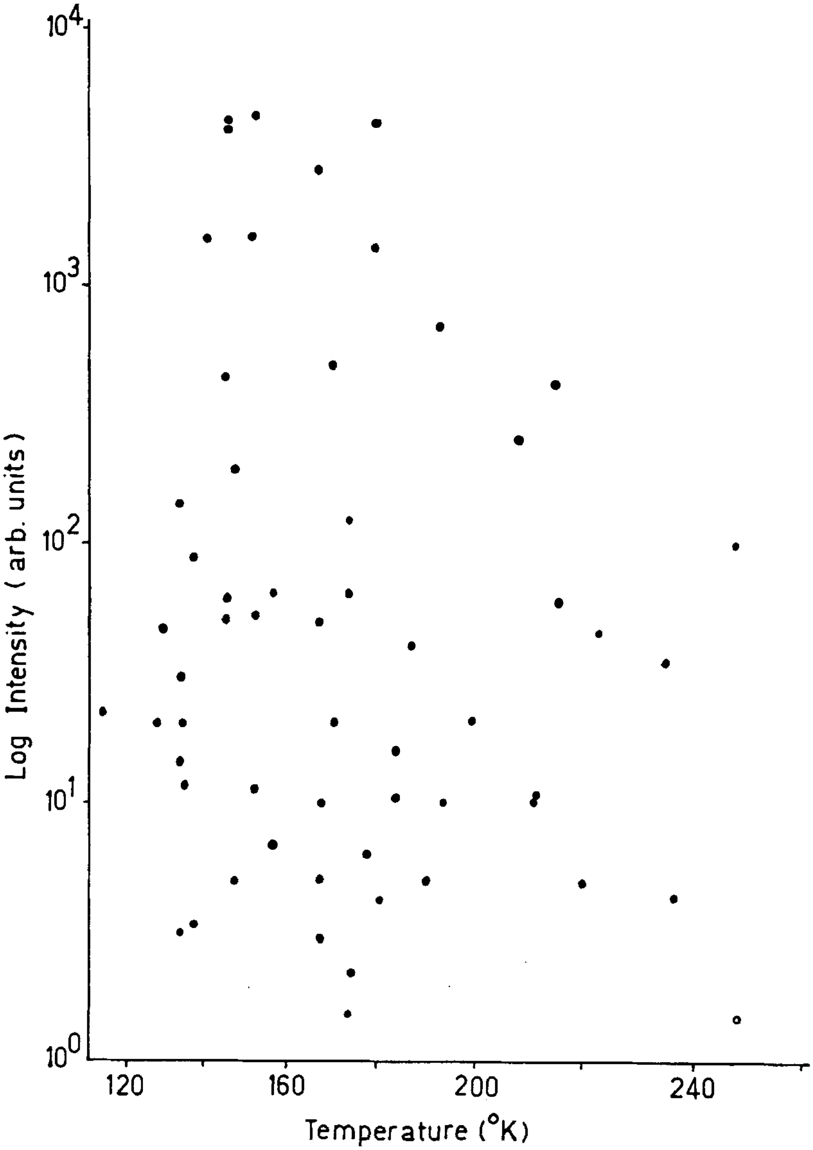


Figure 4. Brightness–temperature plot of observed peaks.

brightness. Very luminous features were never observed at the higher end of the temperature scale. This seems accountable on the basis of a progressive decrease in the efficiency with which organic materials can convert stored energy into light as the temperature rises. Other work in this laboratory supports this hypothesis. In addition the distribution of points on the plot suggests that this efficiency controls the ability of organic materials to thermoluminesce to a greater extent than does their ability to store energy. It appears possible that most or all of the materials studied are capable of storing energy by the trapping of separated charges but only those with sufficiently high luminous efficiencies (e.g. aromatics) are capable of giving glow curves.

The activation energies (E) of some of the peaks were obtained using the initial rise method as described by Garlick and Gibson(9) and are listed in Table 2, together with the temperatures (T_0) of the maximum emission intensities of the peaks when the samples were warmed at 20 °K/min. It will be noted that the peaks with lower activation energies generally occur at lower temperatures.

The emission spectra of some of the brighter peaks were found using a Bausch and Lomb f/3.5 grating monochromator and the liquid air cooled photomultiplier mentioned earlier. They were observed to generally consist of one or two broad bands up to 500 A wide.

5. Conclusions

It appears that X-ray stimulated thermoluminescence is a more widespread phenomenon in organic solids than was previously thought, and could probably be produced in almost all other organics if one could work at very low temperatures with a sufficiently sensitive detector. The observed curves usually consist of a number of homogeneous distinct peaks, each of which appears to arise a consequence of the annealing of a single species of defect. Substances with molecules in the form of rings appear to be more luminous than other organics. The shape of the curves did not appear to be affected by the physical condition of the solid or to be sensitive to the presence of impurities. It was not possible to correlate the nature of the glow curves to either the form of the molecules or the materials crystal structure. It was also found that

TABLE 2

Compound	E(eV)	T_0(°K) ($\beta = 20$°K/min)
hexamine	0.35	160
p-dichlorobenzene	0.28	154
DL-isoleucine	0.24	184
L-threonine	0.19	167
anthracene	0.28	128
	0.45	146
diphenylamine	0.27	114
	0.24	136
	0.40	153
	0.52	184
benzil	0.31	130
p-aminophenol	0.28	134
	0.52	216
	0.39	223
p-bromoaniline	0.33	139
	0.38	167
	0.46	—
succinic acid	0.26	142
	0.39	199
p-chloroaniline	0.29	126
	0.43	139
	0.55	174
	0.5	216

a given compound gave the same glow curve regardless of the origin of the sample.

Acknowledgements

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