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A Novel Spectroscopic Method for the Investigation of Structural Phase Transitions in Molecular Crystals

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A simple experimental technique for the investigation of structural phase transitions in molecular crystals in the temperature range 77–300 K has been developed and applied to a wide variety of organic molecular crystals. The 'Photokinematical Approach', as the method has been termed, utilizes the responsiveness of photoluminescence of guest aromatic ketone molecules to the changes in crystalline structure of host molecular crystals as sensitive probe for the identification of structural phase transformations in host molecular crystals. In this method the prediction of the number of distinct polymorphs a given molecular crystal may exist, their corresponding optimum temperatures of existence and the transition temperatures is based on the observation of characteristic changes in the luminescence intensity of the guest ketone molecules that occur in response to host crystalline modifications. The reliability of the method has been established from the conformity and reproducibility of the results the technique yields in case of its application to a number of well characterized molecular crystals. The results reveal close correlation between the occurrence of structural phase transitions and the occurrence of noncoplanar molecular conformation in polymorphic crystals.

I INTRODUCTION

Polymorphism is a common phenomenon in molecular crystals and the elucidation of the structural phase transition of organic molecular crystals has been the subject of numerous studies. There are several crystallographic, spectroscopic and calorimetric methods, including the diffraction of X-rays,[1-4] electrons[5] and neutrons;[6] infrared and Raman spectroscopy;[7] and differential thermal analysis (DTA) and differential scanning calorimetric (DSC) techniques[8-10] which have been widely employed for investigating structural phase transitions in crystalline solids. The methods have been reviewed in detail[1-11] and the experimental techniques are now well known.

Unfortunately, so far as the investigation of thermal phase transitions in polymorphic solid is concerned, both the crystallographic and spectroscopic methods have severe limitations. The identification of structural modifications by these methods is primarily based on the analyses of experimental data obtained at a limited number of ambient temperatures, and it is impracticable to scan the entire temperature range over which the substance under investigation may exist as a solid. Therefore, the identification of each of the distinct crystalline phases and the corresponding transition temperatures can not readily be ascertained. A further difficulty is encountered with the IR and Raman spectroscopic method in which the identification of structural modifications is based on the observation of the instability of some normal vibrational modes of the lattice. However, there is no guarantee that soft modes will be Raman active or, indeed, IR active in either phase of a polymorphic solid. Although neutron and X-ray diffraction techniques are widely applicable and are the most powerful tools for the determination of structural details of crystalline solids, the kind of information these crystallographic techniques provide largely depends on the quality of the single crystal specimen available for the study. Various kinds of structural defects, e.g., the coexistent phases and the statistical disorderliness in the molecular arrangement in the lattices are commonly encountered in polymorphic solids[5,11-19] (particularly those exhibiting a wide range of polymorphs or plastic phases), and the precise determination of structural details is often handicapped by the poor diffraction patterns these materials yield.[5,11,20-24]

It is nevertheless possible to improve the quality of the crystalline specimen to a significant extent if the solid under consideration is subjected to a prolonged heat treatment (such as, annealing) at a temperature optimum† (T_{OP}) for the existence of a distinct phase of interest.

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† The crystal packing and the structural stability of a given crystalline phase of a polymorphic molecular crystal vary significantly in the entire temperature range the phase may exist; the nearer the ambient temperature of the solid to its transition point, the more probable is the existence of structural disorder in the crystal. It is surmisable, therefore, that corresponding to each distinct polymorphic form of such solids, there should be a characteristic temperature (or a narrow temperature range, well removed from the transition point) at which the phase may exist in a most stable form. This thermodynamically most favorable temperature might be called the optimum temperature for the crystalline phase.

This would however necessitate a prior knowledge of the corresponding T_{op} values of the polymorphs of the solid.

Although the continuous scanning calorimetric methods, such as DSC and DTA, are widely employed for the experimental determination of the energetics of phase transformations and the transition temperature (T_c) of polymorphic solids, they are incapable of providing information about the T_{op} temperatures for the various polymorphs of these solids. Moreover, these calorimetric techniques also suffer from certain disadvantages, particularly at low temperatures.[8-10,25]

Since precise structural determination of different crystalline phases of a polymorphic molecular crystal is essential for a detailed understanding of the transitional properties, it is of corollary interest to obtain information about the T_{op} value of each distinct phases of such solids. Accordingly, it is desirable that some method be developed which would provide the desired information (regarding both T_{op} and T_c values) and to this end the present work is directed.

A. The "photokinematical approach": principle

Studies of the luminescence of aromatic organic molecules in crystalline environments have shown that the crystal field effects of the host molecular crystals can exert profound influences upon luminescence spectral properties of the guest molecules. This is especially so in cases of molecules with closely spaced electronic states (e.g. the heteroaromatic and aromatic carbonyl compounds) where a favorable situation for strong vibronic interaction of the pseudo Jahn-Teller type exists.[26-29] The bulk crystal field is known to affect the guest spectral properties in a number of ways: (i) it may modify the vibronic coupling between the electronic states by changing their energies[26-28] and thereby reinforcing or nullifying the effects of pseudo Jahn-Teller distortion,[28-29] (ii) it may impose severe restriction on the intramolecular motion, especially of the torsional type,[29] and (iii) in cases of molecules possessing distortable geometries, it may potentially distort the molecular conformation[26-29] modifying the Franck-Condon factor. Since the extent to which the spectral properties of a luminescent guest will be modified depends on the effectiveness of these crystal field effects in changing the properties of the guest emitting state, it is expected that the emission characteristics of the guest molecules will be different for different crystalline hosts, or, alternatively, for different stable crystalline phases of the same polymorphic host.

In addition to this responsiveness of the guest molecular luminescence the phase transition dynamics of the host molecular crystal also plays an important role in determining the luminescence intensity of the guest molecules during a phase transition. It is known that in polymorphic solids there occurs extensive unpacking and repacking (building up) of the lattice structures within the solid at the phase transition temperature; and from a thermodynamic view point, the system undergoing a polymorphic transformation might be considered to be in a state of maximum disorder at this temperature. As a consequence the guest molecules suffer a maximum collision-induced radiationless deactivation of their photoexcited states at these temperatures and a marked diminution in their emission intensity would be expected when it is measured across any phase transition point. On the other hand, the emission intensity should reach its maximum value at the optimum temperature of a particular phase of the solid. This is because of the fact that a crystalline phase is expected to be thermodynamically most stable at such temperatures and the rigidity of the crystal cage enhances the luminescence either by conferring rigidity on the molecule or by suppressing diffusion-controlled quenching processes (i.e., dynamic quenching).

Such spectral manifestations of host crystalline modifications have indeed been observed in several heteroaromatic and aromatic carbonyl molecules, e.g., cyanopyridines,[28] aminopyridines,[30] acetyl pryidines,[30] *p*-chlorobenzaldehyde,[29] benzophenone[30] and benzil.[30] The results of these studies have provided the necessary support in favor of the idea that the photoluminescence of these molecules could possibly be used as a sensitive probe for investigating the structural changes in molecular crystals. Among the two types of organic compounds mentioned, the aromatic ketones were chosen as suitable probe materials because, besides having distortable geometries[31,32] and phosphorescent state unusually responsive to its environment,[32,33] they exhibit strong phosphorescence emissions in a wide variety of crystalline matrices.

Since the observation of the characteristic changes in the photoluminescence of probe molecules embeded in the host molecular crystals and submitted to the governing influences of the crystallographic constraints and dynamics of phase transformation, is at the basis for identification of structural phase transition in molecular crystals, this spectroscopic method might appropriately be termed as the "Photokinematical Approach."

In this work, the method has been applied to the examination of thermal phase transition properties of over three dozens of organic molecular crystals comprising molecules with widely varying structures. The primary objective has been the exploration of the feasibility and versatility of the method and secondly to find out if any correlation could be established between the phase transformation behavior of molecular crystals and the structural characteristics of the constituent molecules.

The details of the experimental technique are described and the results obtained are discussed in this paper.

II. EXPERIMENTAL

A. Instrument and technique

The examination of structural phase transitions in molecular crystals by the photokinematical technique involves two basic steps; (i) preparation of a dilute solid solution of a guest aromatic ketone in the molecular crystal of interest and (ii) recording, in a continuous manner, the variations in the guest phosphorescence intensity while the specimen temperature is varied progressively from 77 to 300 K or, in the reverse order. The prime experimental essentials are: an intense source of light, a set of excitation and emission monochromators, a cryostat, a photomultiplier-recorder combination for measuring the emission intensity and a temperature measuring device. The experimental arrangement employed in this work is shown schematically in Figure 1.

A quartz sample cell 2 cm long and 5 mm o.d. was filled with the experimental material and placed in a cavity in the coldfinger of the cryostat. The sample was slowly cooled to 77 K by pouring liquid nitrogen into the cryostat, while the gradual rise in its temperature from 77 K to room temperature was effected simply by allowing the system to

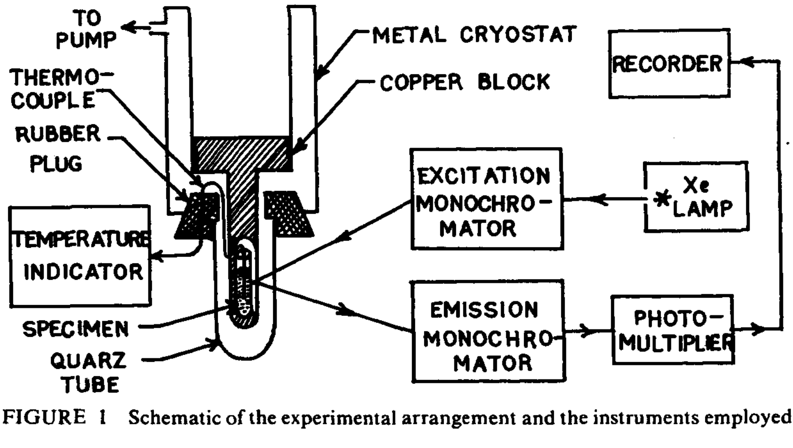

FIGURE 1 Schematic of the experimental arrangement and the instruments employed.

warm up slowly following complete evaporation of the liquid nitrogen from the cryostat. Because of the thermal inertia associated with the metal block and the coldfinger of the cryostat, the rate of change of sample temperature was slow, which was also controlled by controlling the vacuum of the cryostat. The actual temperature of the specimen was measured with a copper constantan thermocouple (one junction of which was inserted into the sample) in conjunction with a Kiethley milli-micro voltmeter. The probe ketone molecules are prepared by suitably exciting them to one of their excited singlet states with radiation of appropriate wavelengths. In this work, the Xenon lamp of the Perkin-Elmer MPF 44A Fluorescence Spectrophotometer was used as an exciting source of light; the same instrument was also used to detect and record the variations of the probe phosphorescence intensity (corresponding to λ_{max}) with changes of temperature. The gradual rise of the specimen temperature was simultaneously recorded, at regular intervals of a few degrees, on the same chart paper by means of a marker. The data pertinent to the study were then determined from the analysis of the plots of phosphorescence intensity vs. temperature.

B. Sample preparation

The use of photokinematical technique for the investigation of polymorphic properties of molecular solids requires that the guest ketone molecules must be trapped at a given crystal site, preferably the substitutional sites in the lattices of the host molecular crystals. For this condition to be satisfied and to ensure that the guest concentration remain within the solubility limit of the host crystal even at low temperatures, it is important that the mixed crystal be prepared sufficiently dilute ($10^{-5} - 10^{-6}$ M/M). Although there exists the possibility that the presence of excess amount of guest molecules in the host lattices could bring about appreciable distortions in the host lattice structure,[34] and its phase transformation properties could thereby be influenced,[35,36] it is unlikely, in view of such low concentrations of guest molecules that the changes in bulk crystalline properties of the host crystal would be more than merely marginal.[35,36] However, an essential prerequisite for obtaining reliable results with this technique is that both host and guest materials must be free from any luminescent impurity. This requirement was accomplished by following a sequence of chemical and physical purification steps.[37] Samples of dilute mixed crystals were then prepared by a procedure judiciously chosen from the following methods: (i) by slowly cooling to solidification the dilute solution or the melt; (ii) by mixed crystallization from the solution or (iii) co-sublimation. It is worth pointing out that although the samples thus prepared would be mostly polycrystalline in nature, the technique has the advantage that it does not require the samples to be sufficiently defectless or in the form of single crystals. However, care must be exercised so as to avoid formation of large concentrations of structural defects at the final stage of sample preparation, which may otherwise introduce significant errors in the results obtainable by this method.

C. Materials

The organic compounds selected for the present study can be broadly classified into various types: (i) benzene and higher condensed ring systems—naphthalene, anthracene, phenanthrene, tetracene and pyrene; (ii) the benzene derivatives—toluene, durene, *p*-dichlorobenzene, 1,3,5-trichlorobenzene, acetophenone, benzonitrile and 1,2,4,5-tetrachlorobenzene; (iii) the *N*-heterocyclic compounds pyridine, pyrazine, quinoline, *s*-triazine and 4-cyanopyridine; (iv) the plastic crystal forming compounds—cyclohexane, methylcyclohexane, carbontetrachloride, furan, thiophene and diethyl ether; (v) the so called double molecules—biphenyl, benzil, carbazole, benzophenone, benzylbenzoate, azobenzene, *p*-terphenyl, stilbene and fluorene and (vi) the hydrogen bonded compounds—benzoic acid, anthranilic acid, chloranil, 2-aminopyridine, *p*-nitrophenol, thiourea and heavy water. All the chemicals were either of spectroscopic grade or of the purest quality available from commercial firms. They were further purified by fractional distillation, recrystallization, sublimation or zone refining till no impurity emission could be detected by the Perkin-Elmer Fluorescence Spectrophotometer.

A number of compounds, e.g. anthracene, acetophenone, benzophenone, benzil, azobenzene, pyrazine, pyrene and tetracene were found to be luminescent in their pure crystalline state. The phase transition properties of these compounds were examined both by monitoring the emissions from their pure crystalline forms and also the ketonic emissions in the case of mixed crystals. Among the various aromatic ketones employed as probe materials, benzophenone and benzil proved themselves most promising.

III RESULTS AND DISCUSSION

The characteristic plots of the temperature variation of guest phosphorescence intensity (I_p) for various crystalline hosts are shown in Figures 2–8. The T_c and T_{op} values determined from these curves together with the pertinent morphological data from the literature are summarized in Table I.

TABLE I

Molecular planarity, crystal data (space group and Z, molecules per unit cell) and the T_c and T_{op} values of various crystalline form(s) of molecular crystals.

Compound	Crystalline form(s)[a]	T_c in °K		T_{op} in °K	Molecular planarity	References[c]
		This work[b]	Other studies			
Acetophenone	I: Monoclinic[81] (154 K) $P2_1/n$, $Z = 4$	140 (I–II)		I: 150 II: 88	The phenyl ring is planar with the acetyl group rotated slightly out of plane[81]	X-ray[81]
	II:					
2-Aminopyridine	I: Monoclinic[82] (RT) $P2_1/c$, $Z = 4$	120 (I–II)		I: 250 II: 120	The angle between the plane of the ring and the plane determined by the NH$_2$ group is 15°	X-ray[82]
	II:					
Anthracene	Monoclinic[43] (290 and 95 K) $P2_1/a$, $Z = 2$				Planar[43]	X-ray[43]
Anthranilic acid	I: Orthorhombic[77] (293 K) P_{bca}, $Z = 8$	203 (II–III)	352 (I–II)[76]	II: 260 III: 190 IV: 103	Benzene rings are slightly puckered and are nonregular hexagon[87]	X-ray[77] DTA, DSC[76]
	II: Orthorhombic[77] (192 K) $P2_1c_n$, $Z = 8$	127 (III–IV)				
	II:					
	IV:					
Azobenzene	I: Monoclinic[83] (RT) $P2_1/a$, $Z = 4$	85 (I–II)		I: 246	Two phenyl rings are not coplanar[83]	X-ray[83]
	II:					
Benzene	Orthorhombic[38] (218 and 138 K) Q_h^{15}, $Z = 4$				Planar[38]	ND[38]
Benzil	I: Triclinic[20] (293 and 161 K) $P3_12_1$, $Z = 3$	85 (I–II)	83.5 (I–II)[52,53]	I: 205	Crystals are built of skew molecules[40]	X-ray[20,53] DSC[52]

Benzophenone	I: Orthorhombic[84] (RT) $P2_12_12_1$, $Z = 4$ II:	102 (I–II)		I: 120 II: 88	Two phenyl rings are not coplanar[84]	X-ray[84]
Benzonitrile	Tetragonal[46] (198 K) $P4_12_12$, $Z = 4$				Planar[46]	X-ray[46]
Benzoic acid	I: Monoclinic[85] (RT) $P2_1/c$, $Z = 4$ II:	104 (I–II) 87 (II–III)		I: 118 II: 100	The —COO group deviates significantly from the plane of the benzene ring[85]	X-ray[85]
Benzylbenzoate	I: Monoclinic[86] (290 K) $P2_1/c$, $Z = 4$ II: . . . . . . III:	196 (I–II) 95 (II–III)		I: 210 II: 100	The —COO group is twisted 9.8° out of plane of the benzene ring[86]	X-ray[86]
Biphenyl	Monoclinic[41] (RT) $P2_1/a$, $Z = 2$				The molecule is perfectly planar[23]	X-ray[41]
Carbontetrachloride	I: Cubic[22] (238 K) $Z = 4$ II: Rhombohedral $Z = 21$ III: Monoclinic[49] (195 K) $C\,2/c$, $Z = 32$	235 (I–II) 226 (II–III)	234 (I–II)[25] 225 (II–III)	I: 245 II: 232 III: 126	Nonplanar, regular tetrahedral[49]	DSC[25] X-ray[49]
Chloranil	I: Monoclinic[54] (RT) $P2_1/a$, $Z = 2$ II: Monoclinic[55] (80 K) $P2_1/n$ or $P1$, $Z = 4$	94 (I–II)	90.3 (I–II)[56] 92 (I–II)[55]	I: 80 II: 200	The chlorine and oxygen atoms on the aromatic ring show 0.05 Å displacements from planarity[54]	X-ray[54] NQR[55]

TABLE I (*Continued*)

Compound	Crystalline form(s)[a]	T_c in °K This work[b]	Other studies	T_{op} in °K	Molecular planarity	References[c]
Cyclohexane	I: Cubic[21] (195 K) F_m3_m, $Z = 4$ II: Monoclinic[21] (115 K) $C2/c$, $Z = 4$	I–II: 186	I–II: 186[21]	I: 210 II: 100	Nonplanar[21]	X-ray[21] IR[47]
P-Dichlorobenzene	I: Monoclinic(α)[57] (240 K) $P2_1/a$, $Z = 2$ II: Monoclinic(γ)[57] (100 K) $P2_1/c$, $Z = 2$	I–II: 94		I: 148 II: 80	Chlorine atoms are displaced 0.045 A from the benzene plane[57]	X-ray[57,58] Raman[13]
Diethyl ether	I: Orthorhombic[59] (128 K) $P2_12_12_1$, $Z = 8$ II:	152 (I–II)		I: 154 II: 95	Significant departure from planarity[59]	X-ray[59]
Durene	Monoclinic[39] (RT) $P2_1/a$, $Z = 2$				The molecule is completely planar[39]	ND[39]
Fluorene	Orthorhombic[45] $P_{nam}(D_{2n}16)$ $Z = 4$				Planar[45]	X-ray[45]
Furan	I: Orthorhombic[50] (152 K) C_mC_a, $Z = 4$ II: Tetragonal (123 K) $P4\ 2\ 2$, $Z = 4$	152 (I–II)	*150 (I–II)*[50]	I: 200 II: 90	The molecule deviates from planarity[50]	X-ray[50]
Ice (D_2O)	I: Hexagonal[95] $P6_3/mmc$ II: Face-centered cubic[95] F_d3m, $Z = 8$ III: Amorphous[95]	210 (I–II)	203 (I–II)[97]	I: 220 II: or III: 130	The lattice consists of hexagonal rings of water molecules that have the conformation of the 'chair' form of cyclohexane[95]	X-ray[95,96]

Methylcyclohexane	I:	115 (I–II)		I: 122	Nonplanar, equitorial chair form at low temperatures[48]	Raman[48]
	II:			II: 95		
Naphthalene	Monoclinic[42] (RT) $P2_1/a$, $Z = 2$				Planar[42]	X-ray[42]
p-Nitrophenol	α: Monoclinic[98] (90 K) $P2_1/n$, $Z = 4$	170 (. . .)			The —NO_2 group is displaced from the plane of the ring[98]	X-ray[98]
	β: Monoclinic[99] (90 K) $P2_1/a$, $Z = 4$					
Phenanthrene	I:				The molecule is slightly bent around the central ring[79]	Raman[78]
	II: Monoclinic[79] (RT) $P2_1$, $Z = 2$	85 (II–III)	343 (I–II)[78]	II: 94		
	III:					
Pyrazine	I: Orthorhombic[80] (310–324 K) C_{mmm}, $Z = 8$		310 (I–II) 301.5 (II–III)[80]	III: 100 IV: 88		X-ray[80] Raman and DTA[80]
	II: Orthorhombic[80] (301.5–310 K) C_{mmm}, $Z = 2$	95 (III–IV)				
	III: Orthorhombic[80] (301.5 K) C_{mmm}, $Z = 8$					
	IV:					
Pyrene	I: Monoclinic[60] (RT) $P2_1/a$, $Z = 4$	135 (I–II) 109 (II–III)	110 (II–III)	I: 137 II: 114 III: 95	The molecule is slightly nonplanar[60]	ND[60]
	II:					
	III:					

TABLE I (*Continued*)

Compound	Crystalline form(s)[a]	T_c in °K This work[b]	 Other studies	T_{op} in °K	Molecular planarity	References[c]
Pyridine	I: Orthorhombic[15]			I: 180	The molecule attains a nonplanarity at low temperatures[16]	X-ray[15]
	(93 K)	170 (I–II)		II: 130		
	Q_h^1, $Z = 8$	95 (II–III)				
	II: Orthorhombic[15]					
	Q_h^2, $Z = 8$					
Stilbene	I: Monoclinic[93]			II: 160	The phenyl rings are slightly twisted (5°)	X-ray[92]
	(RT)	218 (I–II)		III: 85		
	$P2_1/c$, $Z = 4$	105 (II–III)				
	II:					
	III:					
p-Terphenyl	I: Monoclinic[65]			I: 211	Planar at RT[65] non-planar at 190[66,67]	X-ray[65,66]
	(300 K)	190 (I–II)	191 (I–II)	II: 164		DSC[67]
	$P2_1/a$, $Z = 2$	100 (II–III)	110 (II–III)	III: 80		ED[68]
	II: Triclinic[66]					
	(113 K)					
	$P\bar{1}$, $Z = 8$					
	III:					
Tetracene	Triclinic[44]				The molecules in the unit cell are completely planar[44]	X-ray[44]
	(RT)					
	$P\bar{1}$, $Z = 2$					
1,2,4,5-Tetrachlorobenzene	I: Monoclinic[62]			I: 230	Chlorine atoms are significantly displaced out of the benzene plane[64]	X-ray[62]
	(RT)			II: 120		Raman[63]
	$P2_1/c$, $Z = 2$	190 (I–II)	188 (I–II)[62]			
	II: Triclinic[62]					
	(150 K)					
	$P\bar{1}$, $Z = 2$					
Thiophene	I: Orthorhombic[18]	174 (I–II)	172 (I–II)[17]	I: 186		X-ray[18]
	(218 K)	140 (II–III)	138 (II–III)[17]	II: 154		IR, Raman[69,70]
	$B_{mab}(D_{2h}^{18})$	112 (III–IV)	112 (III–IV)[23]	III: 132		

	II: Orthorhombic (77 K) C_{mca}, $Z = 4$ III: Orthorhombic[57] IV: Orthorhombic[57]			IV: 81		
Thiourea	I: Orthorhombic[71] (293 K) P_{nma}, $Z = 4$ II: . . . . . . III: . . . . . . IV: . . . . . . Orthorhombic (110 K) $P2_1ms$, $Z = 4$	210 (I–II) 185 (III–IV)	202 (I–II)[72] 180 (II–III)[72] 176 (III–IV)[72] 169 (IV–V)[72]	I: 280 II: 195	Hydrogen atoms are not coplanar with the SCNN′ unit at low temperature[71]	ND[71] Raman[72]
Toluene	I: . . . . . . II: Orthorhombic[94] (93 K) C^7_{2v}, $Z = 4$	142 (I–II)		I: 171 II: 100		X-ray[94]
s-Triazene	I: Trigonal[73] (RT) $R\bar{3}c$, $Z = 2$ II: Monoclinic[75] (150 K) $C2/c$ or C_c, $Z = 2$	200 (I–II)	198 (I–II)[74–76]	I: 240 II: 150	The molecule deviates quite markedly from a regular hexagon[73]	X-ray[73,74] ND[76]
1,3,5-Trichlorobenzene	Orthorhombic[40] (RT − 77 K) $P2_12_12_1$, $Z = 4$				Planar[40]	X-ray[40]

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[a] The crystalline phases are numbered I, II, III, . . . in the order of decreasing temperature; the corresponding experimental conditions of study are given in parentheses. RT: room temperature.

[b] The T_c and T_{op} values represent the average of both forward and reverse temperature scans of at least two runs, the phases involved are indicated in parentheses. Possible experimental errors are ±2 K and ±5 K for sharp and broad minima (or, maxima), respectively.

[c] ND: Neutron diffraction; IR: Infrared; ED: Electron diffraction; NQR: Nuclear quadrupole resonance.

Figure 2 shows the nature of variation of phosphorescence intensity of benzophenone in crystalline benzene,[38] durene,[39] 1,3,5-trichlorobenzene[40] and biphenyl[41] in the temperature range 77–300 K. A noticeable feature exhibited by these curves is that, except for the difference in the rate of change of I_p with temperature for different hosts, the I_p value in each case decreases monotonically with the rise of temperature. Such monotonic decay of the I_p-T curves was also observed for several other host molecular crystals, e.g., naphthalene,[42] anthracene,[43] tetracene,[44] fluorene[45] and benzonitrile.[46] It is interesting to note that all these host compounds are known to exist in a single crystalline phase, at least, in the 77–300 K temperature range. The observed I_p decay characteristic is the expected one, since it is expected that an enhancement of host phonon field with the rise of system temperature would favor the non-radiative relaxation of the excited electronic states of the guest molecules at the expense of the radiative process. The distinct differences in the rate of fall of phosphorescence intensity with temperature for different crystalline hosts might be interpreted as signifying the varying

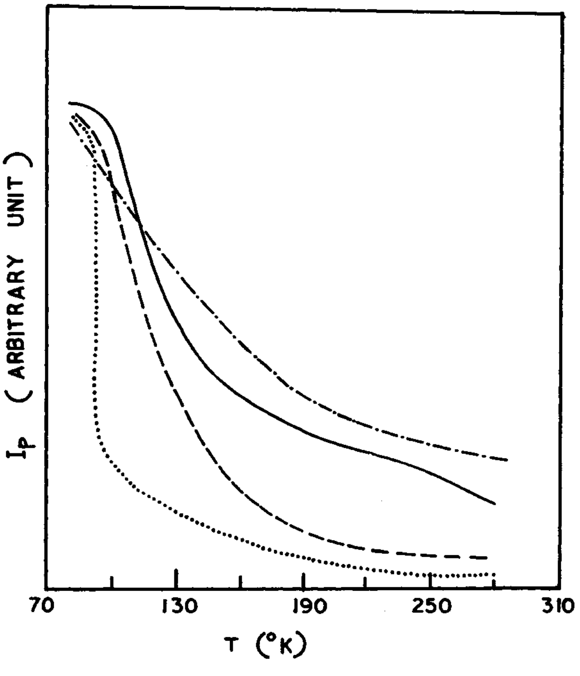

FIGURE 2 Temperature dependence of phosphorescence intensity of guest benzophenone in crystalline biphenyl (———), benzene (– – – –), durene (—·—·—) and 1,3,5-trichlorobenzene (······) hosts.

strength of intermolecular coupling between the host and guest for different host–guest systems.

The I_p-T curves (Figures 3, 5–8) for polymorphic hosts, by contrast, show a distinctly different behavior: the phosphorescence intensity of the guest molecules in these crystalline hosts, instead of decreasing monotonically with the rise of temperature, undergoes a marked variation with well defined maxima and minima. The nature of the variation of the I_p-T curves for the guest benzophenone in four typically plastic variety of crystalline matrices—cyclohexane,[21,47] methylcyclohexane,[48] carbontetrachloride[49] and furan[50] is shown in Figure 3.

In the case of cyclohexane, the I_p-T curve displays two distinct peaks, at ≈100 K and 210 K, and a minimum at ≈186 K. The occurrence of a well defined minimum at a temperature that exactly corresponds to the monoclinic–cubic phase transition temperature for the solid cyclohexane[21,47] is noteworthy. A sudden reversal of the nature of the I_p-T curve

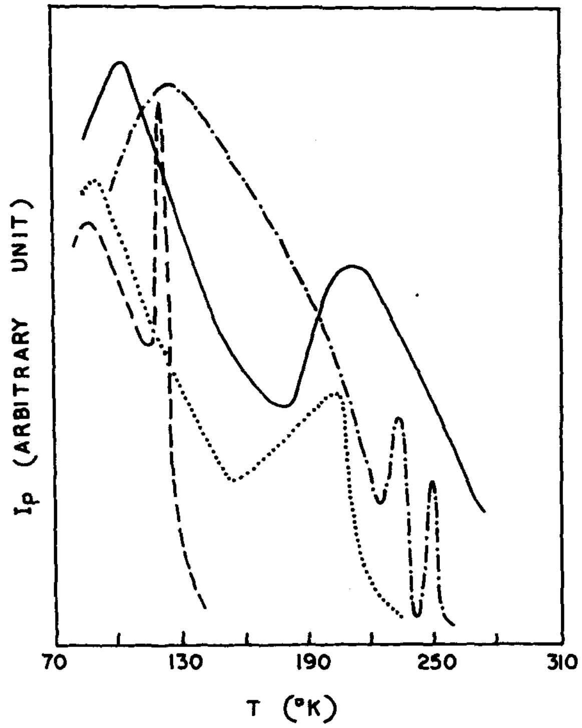

FIGURE 3 Temperature dependence of phosphorescence intensity of guest benzophenone in crystalline cyclohexane (———), methylcyclohexane (– – – –), carbontetrachloride (–·–·–) and furan (······) hosts.

apparently commencing from this point clearly signifies the occurrence of a major change in the dynamics of the system.

At $\simeq$100 K the monoclinic lattice structure of cyclohexane is effectively rigid[51] and presumably provides an environment optimal for the occurrence of a high-quantum-yield phosphorescence emission from the trapped ketone molecules, as is evidenced by the appearance of a predominant peak in the I_p-T curve at this temperature. As the temperature is raised, the reorientational freedom of the cyclohexane molecules increases and there occurs a progressive enhancement of the collisional deactivation of the photoexcited ketone molecules. This becomes maximum at the transition temperature where the system actually passes through a state of maximum disorder. A comparison of the phosphorescence spectrum of benzophenone in cyclohexane at $\simeq$100 K and at $\simeq$186 K (Figure 4) adds credence to this supposition. It can be seen that, in contrast to the sharp and structured 100 K spectrum, the spectrum at 186 K is markedly broad and diffused.

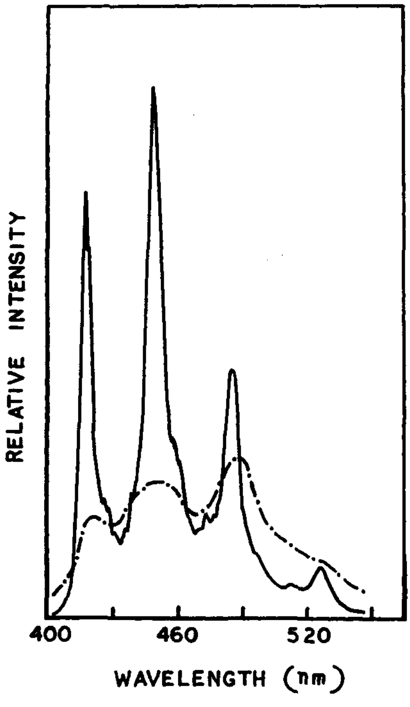

FIGURE 4 Phosphorescence spectrum of benzophenone in crystalline cyclohexane: at $\simeq$100 K (———), at $\simeq$186 K (–·–·–).

The conversion from the monoclinic to the cubic lattice sets in as soon as the transition temperature is reached from low temperatures and it proceeds towards completion at temperatures attributable to the thermodynamically most favorable for the existence of cubic phase of cyclohexane. The peak at ≃210 K most likely corresponds to this temperature.

In the case of carbontetrachloride (Figure 3), the I_p-T curve comprises a series of maxima and minima in the 77–300 K temperature range. The temperatures 235 and 226 K, corresponding to the two prominant minima in the I_p-T curve, are in close agreement with the data reported for the I → II and II → III transition points respectively. A similar line of reasoning that has been offered in the case of cyclohexane might also be extended to account for the occurrence of maxima and minima in the I_p-T curve of carbontetrachloride and to all other cases of plastic molecular crystals.

The polymorphic properties of many organic molecular crystals, e.g., benzil,[52,53] chloranil,[54–56] *p*-dichlorobenzene,[13,57,58] diethyl ether,[59]

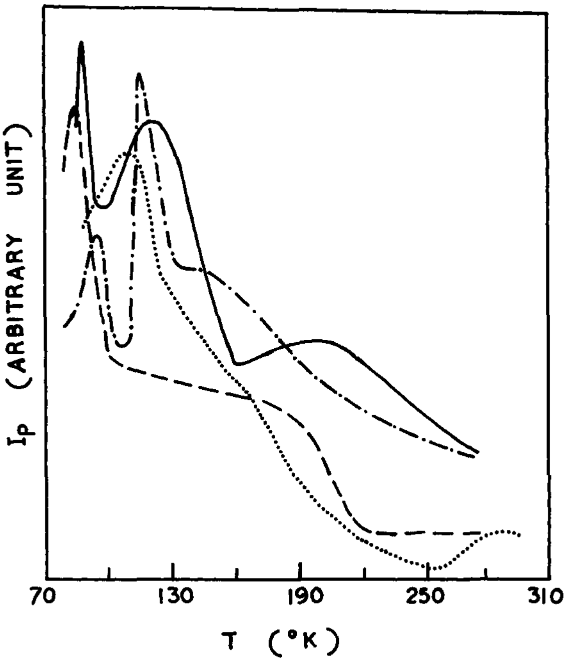

FIGURE 5 Temperature dependence of phosphorescence intensity of guest benzil in crystalline carbazole (———), stilbene (– – – –), pyrene (–·–·–) and *p*-dichlorobenzene (······) hosts.

furan,[50] pyrene,[60,61] *p*-terphenyl,[62–65] 1,2,4,5-tetrachlorobenzene,[66–68] thiophene,[69,70] thiourea[71,72] and *s*-triazine[73–75] have been studied extensively and their phase transformation characteristics are now well documented. It is worth noting again that the temperature values corresponding to the minima of the I_p-T curves (Figures 5–8) show remarkable coincidence with the reported transition temperature of these polymorphic solids (Table I). All these observations strongly suggest that, irrespective of the nature of the crystalline solid, the appearance of a well defined minimum in the I_p-T curve can be considered as a diagnostic feature indicating the occurrence of a structural phase transition. It might also be argued that a peak in the I_p-T curve should then correspond to a temperature optimum for the existence of a distinct crystalline phase of the solid under consideration.

Recent Raman studies of crystalline methylcyclohexane,[48] and *p*-dichlorobenzene[13] have indicated the existence of two distinct crystalline phases of methylcyclohexane and a α–γ phase transition in *p*-dichlorobenzene. The results of our investigations are in agreement with these findings. Organic crystals viz. anthranilic acid,[76,77] phenanthrene[78,79] and pyrazine[80] are known to undergo structural phase transitions at temperatures somewhat above room temperature. Our exper-

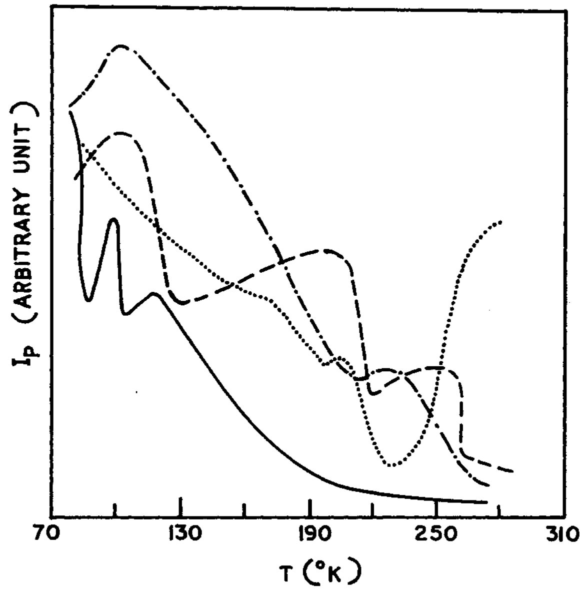

FIGURE 6 Temperature dependence of phosphorescence intensity of guest benzil in crystalline benzoic acid (———), anthranilic acid (– – – –), D₂O ice (–·–·–) and thiourea (······) hosts.

imental results indicate that phase transformations in these polymorphic solids occur also at low temperatures. Besides, the occurrence of polymorphic phase transformations in several other organic crystals such as acetophenone,[81] 2-aminopyridine,[82] azobenzene,[83] benzophenone,[84] benzoic acid,[85] benzyl benzoate,[86] carbazole,[87–89] 4-cyanopyridine,[90] quinoline,[91] stilbene[92,93] and toluene[94] at low temperatures has also been revealed in this investigation. The polymorphic properties of these compounds do not appear to have been determined previously. Thus among the over three dozens of organic crystals investigated in this work, an overwhelming majority has been found to be polymorphous.

Polymorphic transformations in many organic compounds, e.g., azobenzene, benzil, carbontetrachloride, methylcyclohexane, 4-cyanopyridine, pyrazine, pyrene and stilbene have been seen taking place with remarkable rapidity and almost isothermally. The corresponding I_p-T curve of these compounds displays abrupt changes in I_p and sharp minima at the transition points. On the other hand, the phase transformations in *p*-terphenyl, *s*-triazine and all hydrogen bonded compounds are found to be rather sluggish and occurring over a considerable range of temperature. Hysteresis effect has been observed in most

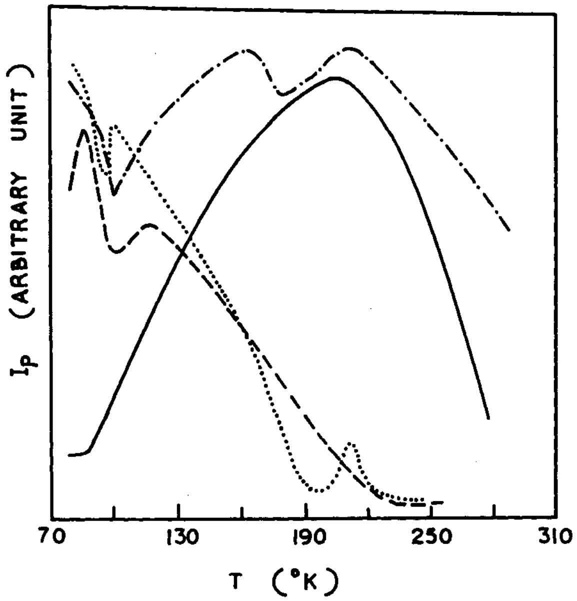

FIGURE 7 Temperature dependence of phosphorescence intensity of benzil in pure crystal (———) and as a guest in crystalline benzophenone (– – – –), *p*-terphenyl (–·–·–) and benzylbenzoate (······) hosts.

of the cases of organic compounds studied. An outstanding feature in thermal phase transformations of these compounds is that they all exhibit reversible phase transformation.

Several important interrelations between the occurrence of polymorphic phase transformations in molecular crystals and the structure and chemical composition of the molecules are evident upon inspection of the experimental data in Table I. It is seen that the compounds containing halogen atoms, or the hetero atoms(s) (e.g., nitrogen, oxygen, sulfur) either in the aromatic ring or as an exocyclic functional group, show in general a greater propensity for polymorphic transformations. Among the molecular crystals which tend to retain a single crystalline form are mostly the aromatic hydrocarbons. A close inspection of the data reveals a particularly striking fact: whereas the molecular crystals composed of strictly planar molecules do not exhibit any crystalline phase transition at least in the temperature range 77–300 K, a significant deviation from uniplanarity of the constituent molecules is found almost in every molecular crystal undergoing phase transformations in

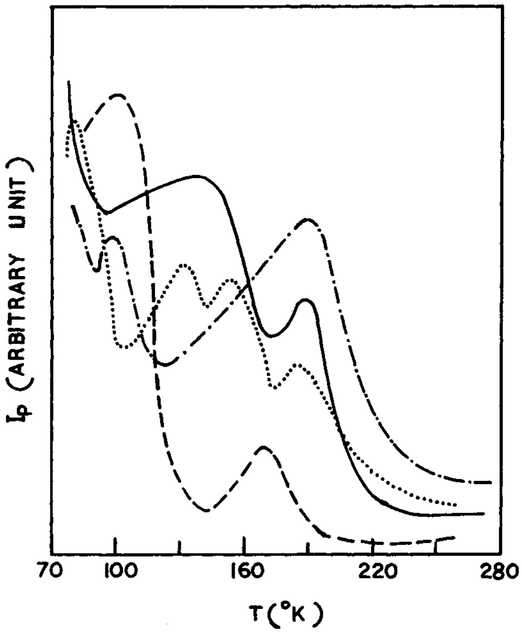

FIGURE 8 Temperature dependence of phosphorescence intensity of guest benzophenone in crystalline pyridine (———), toluene (– – – –), quinoline (–·–·–) and thiophene (·····) hosts.

this temperature range or at higher temperatures. Biphenyl and *p*-terphenyl probably afford the most interesting examples of these categories. The free biphenyl molecules exist in a markedly twisted conformation in the gas phase and are planar in the crystalline state above 77 K. No structural phase transition is known to occur in biphenyl above this temperature. The Raman[101] and X-ray diffraction[100] studies of biphenyl crystal indicate that it undergoes a second order phase transition at ≃40 K[101] and that the molecules once attain a nonplanarity below 75 K.[100] Analogously, the molecules of *p*-terphenyl are also planar in the solid at room temperature but they cease to be planar at or below its phase transition temperature (110 K). All these facts clearly reflect a close correlation between the occurrence of structural phase transitions and the flexibility and non-coplanarity of the molecules in polymorphic crystals.

IV CONCLUSIONS

In conclusion, it may be remarked that the simplicity of the technique and its widespread applicability indicate the power and usefulness of the spectroscopic method outlined here, and the likelihood of further applications as an efficient tool in the investigation of polymorphic phase transition properties of molecular crystals. We feel that the kind of information this spectroscopic method yields (e.g., the number of distinct crystalline phases a solid may exist in and their corresponding T_{op} and T_c values) can be generally valuable not only in the identification of polymorphism in molecular crystals but also for the detailed structural investigation of such solids by diffraction techniques.

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