Vibrational Spectroscopic Studies of Phase Transitions in Organic Molecular Crystals and Dicarboxylic Acids*

*Chintamani Nagesha Ramachandra Rao,** Somnath Ganguly, and Humachadakatte Ramachandra Swamy*

Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore 560012, India

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Order-disorder transitions in 2,3-benzothiophene and cyclopentyl-1-thiaethane as well as the vibronic effects in the phase transitions of the alkali metal salts of TCNQ have been investigated by infrared spectroscopy. In all these cases, marked variations in band intensities accompany the transitions. Existence of two crystalline forms of methylcyclohexane has been established by infrared spectroscopy. Phase transitions of aliphatic dicarboxylic acids have been examined with particular attention to the transitions in malonic, succinic, and glutaric acids.

INTRODUCTION

Although phase transitions in organic crystals have been documented in the literature, they have not been as fully investigated as in the case of inorganic solids[1]. Eearly studies[2,3] of organic molecular solids had indicated that no structural relationships existed between the parent and the transformed phases. However, some of the recent studies have shown that phase transitions in organic crystals involve mechanisms not very different from those of inorganic solids[1]. Thus, orientational relationships have been found in the transformation of 1,8-dichloro-10-methylanthracene[4]. Martensitic as well as nucleation-growth type behaviours have been recognized in the phase transitions of some organic solids[4,5]. We considered it most worthwhile to investigate a few types of phase transitions of organic crystals by employing vibrational spectroscopy. This study was not only expected to illustrate the use of vibrational spectroscopy in investigating phase transitions of organic crystals but also to throw some light on the mechanisms of the phase transitions.

Organic crystals are known to undergo order-disorder phase transitions where the entropy change is given by $S = R \ln (w_2/w_1)$ in which w_1 and w_2 are the numbers of orientations in phases 1 and 2 respectively[6]. We felt that vibrational spectroscopy could provide a useful means of investigating such order-disorder transitions in organic molecular crystals. 2,3-Benzothiophene is reported to undergo a non-isothermal transition around 262 K where the

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molecules attain an over-all orientational disorder[6,7]. We have confirmed the occurrence of the transition with an entropy change of 11.5 J mol⁻¹ K⁻¹ which is exactly equal to $R \ln 4$ by differential scanning calorimetry. The low-temperature β phase, of benzothiophene appears to be perfectly ordered whereas in the high-temperature α-phase, $w = 4$ giving rise to the pseudosymmetry of naphthalene. Cyclopentyl-1-thiaethane is known to undergo an isothermal first-order transition at 165 K just below its melting point[6,8]. The observed entropy change is 5.46 J mol⁻¹ K⁻¹ which is just less than $R \ln 2$. It has been suggested that disorder in the high-temperature α-phase, results from the random distribution of molecules in two equivalent conformations. We have investigated the order-disorder transitions of 2,3-benzothiophene and cyclo-pentyl-1-thiaethane by recording infrared spectra through the phase transition temperatures.

The second type of phase transitions we have investigated is that exhibited by alkali metal salts of 7,7,8,8-tetracyanoquinodimethane (TCNQ). These salts undergo intracolumnar dimerziation in the TCNQ radical anion stacks below their phase transition temperature[9]. Associated with this structural change, one observes changes in properties like dc conductivity, paramagnetic susceptibility and so on. Phase transitions of these TCNQ radical anion salts seem to be accompanied by an increase in intensity of some of the forbidden A_g modes in infrared spectra[10]. We have studied intensity variations of these vibrational modes in K-TCNQ, Rb-TCNQ (I) and Cs-TCNQ through the phase transition temperatures.

We have next employed infrared spectroscopy to establish a suspected phase transition in methylcyclohexane (MCH). Based on a comparison of the Shpolskii spectra of azulene derivatives in a matrix of MCH, Olszowski[11] has reported the possible occurence of two crystalline phases of MCH. We have established the existence of these phases and the transition between them by the combined use of differential scanning calorimetry and infrared spectroscopy.

It has been known for some time that oxalic acid exists in two crystalline forms with unique H-bonded structures and these have been characterized by X-ray crystallography and vibrational spectroscopy[12]. It has also been known that among the higher alkanedioic acids, those with odd number of carbon atoms are generally polymorphic, occurring in two forms α and β, α being the high-temperature form[13-15]. Structures of both the α and β forms are known for pimelic and azlaic acids[14], whereas those of only the β form is available for glutaric acid[15]. Phase transitions from the β to the α form have been reported[16] for glutaric, pimelic and suberic acids. Polymorphism appears to be rather uncommon in the case of alkanedioic acids with an even number of carbon atoms. However, a DSC study of succinic acid in this laboratory showed the occurence of a phase transition at 395 K; the structures of the two phases are also known.[13] We have also found that malonic acid undergoes a phase transition[17] at 360 K, besides the one at 38 K reported earlier[18]. The structure of the low-temperature form of malonic acid is known[19]. We have been examining the vibrational spectra of several of these alkanedioic acids through their phase transitions in this laboratory and we report some of the results obtained hitherto in this paper.

EXPERIMENTAL

2,3-Benzothiophene was synthesized in the laboratory by adopting the procedure reported in the literature[20] and purified by repeated fractionation under vacuum. Cyclopentyl-1-thiaethane was prepared following general methods of synthesizing unsymmetrical alkyl sulphides[21] and purified by vacuum distillation. The alkali metal salts of TCNQ were made and characterized following Melby et al.[22] Methylcyclohexane and alkanedioic acids of high purity were available commercially.

Differential scanning calorimetry (d.s.c.) was carried out with a Perkin-Elmer DSC-2 instrument employing indium as standard. Infrared spectra were recorded with a Perkin-Elmer 580 spectrophotometer fitted with a Specac variable temperature cell. Liquid nitrogen was used as a coolant.

RESULTS AND DISCUSSION

2,3-Benzothiophene

Major bands in the infrared spectra of benzothiophene in the low-temperature ordered phase, β, the high-temperature disordered phase, α, and in the liquid phase are given in Table I with the band assignments made in the light of the work of Mille et al.[23]. When the ordered phase, β, is heated gradually, we find significant changes in the absorption bands across the transition to the disordered phase, α. Heating the α-phase further to the melt does not cause marked changes in the band intensities. In addition to changes in band intensities, we notice greater structure in the bands in the ordered β-phase, as can be seen from Table I.

In Figure 1, we have plotted the intensities of bands undergoing intensity changes against temperature. We see that three out-of-plane deformation bands of A″ type (at 665, 890 and 942 cm^{-1}) show decrease in intensity across the $\beta - \alpha$ transition. The skeletal mode vibration bands at 1015 and 1060 cm^{-1}
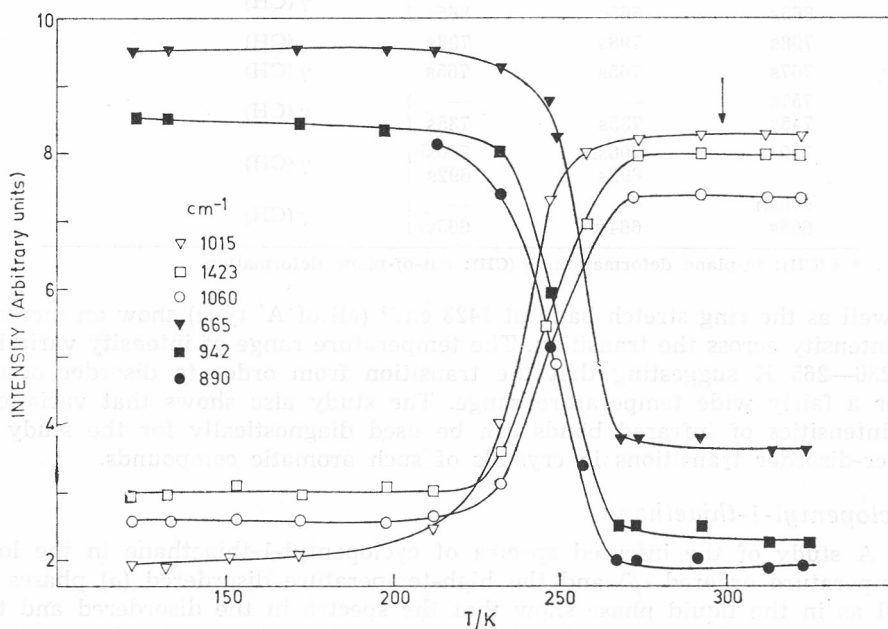

Figure 1. Temperature variation of the intensities (in arbitrary units) of some of the infrared bands of 2,3-benzothiophene.

TABLE I

*Infrared frequencies (cm⁻¹) and assignments of bands of benzothiophene in ordered,
β, disordered, α, and liquid phases*

Phase β (130 K)	Phase α (273 K)	Liquid (313 K)	Assignment[a]
1587m	1587m	1587m	ring stretching
—	1462s	1462s ⎫	skeletal ring stretching
1458s	1458s	1458s ⎭	
1446s	1446s	1446s	skeletal ring stretching
1422m	1423s	1423s ⎫	ring stretching
1414s	—	— ⎭	
1347s	1345m	1345m	ring stretching
1274m	—	— ⎫	δ (CH)
1260s	1259s	1259s ⎭	
1210s	1210m	1210m ⎫	δ (CH)
1200sh	—	— ⎭	
1155m	1155m	1155m	δ (CH)
1120m	1120m	1120m	ring skeletal
1092m	1092s	1092s	ring skeletal
1060m	1060s	1060s ⎫	ring skeletal
1050sh	1050sh	1050sh ⎭	
1025sh	1025sh	1025sh	δ (CH); γ ring stretch
1015w	1015s	1015s	
982w	982w	982w	γ (CH)
942s	940m	940m ⎫	γ (CH)
938sh	—	— ⎭	
890s	890w	890w ⎫	γ (CH)
865s	865s	865s ⎭	
798s	798s	798s	γ (CH)
767s	765s	765s	γ (CH)
757s	—	— ⎫	γ (CH)
745s	735s	735s ⎭	
700s	700sh	700sh ⎫	γ (CH)
	692s	692s ⎭	
670sh	—	— ⎫	γ (CH)
665s	664w	665w ⎭	

[a] δ (CH): in-plane deformation, γ (CH): out-of-plane deformation

as well as the ring stretch band at 1423 cm⁻¹ (all of A′ type) show an increase
in intensity across the transition. The temperature range of intensity variation
is 230—265 K suggesting that the transition from order to disorder occurs
over a fairly wide temperature range. The study also shows that variations
of intensities of infrared bands can be used diagnostically for the study of
order-disorder transitions in crystals of such aromatic compounds.

Cyclopentyl-1-thiaethane

A study of the infrared spectra of cyclopentyl-1-thiaethane in the low-
-temperature ordered (β) and the high-temperature disordered (α) phases as
well as in the liquid phase show that the spectra in the disordered and the
molten states are very similar. The most marked changes in the spectrum
occur in the 860—800 cm⁻¹ region where the bands at 857 and 800 cm⁻¹ show

splittings in the low-temperature β-phase. The intensity of the 857 cm^{-1} band decreases markedly as we go from the ordered to the disordered phase. The changes in the band at 857 cm^{-1} are likely to be related to the disorder brought about by the presence of two equivalent conformations of the C—S—CH$_3$ group. The other bands that show striking changes in intensity are the C—S stretching and the ring modes at 720 cm^{-1} and 660 cm^{-1} which develop an additional peak or shoulder in the β-phase. In addition to these changes, we see marked changes in some other bands accompanying the β — α transition, of which the intensity change in the 515 cm^{-1} band (due to a ring deformation vibration mode) is noteworthy.

In Figure 2, we have shown the variation in the intensities of the 515 and 857 cm^{-1} bands with temperature. We see that as the ordered phase, β, is heated, the intensities of the bands decrease, reaching constancy as β transforms to α. There is a further decrease in intensity when the α-phase transforms to the melt. This behaviour is reversible in the cooling cycle (from the melt to β via α). Figure 2 also shows evidence for slight hysterisis
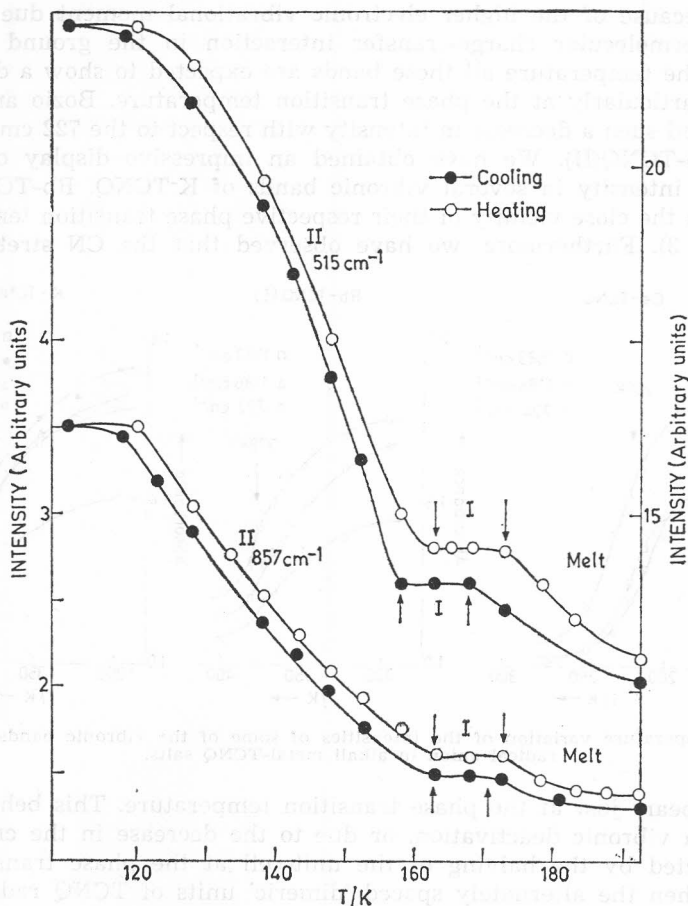

Figure 2. Temperature variation of the intensities (in arbitrary unts) of some of the infrared bands of cyclopentyl-1-thiaethane.

in the phase transition. The decrease in band intensitioes occurs over a temperature range of about 40 °C which may be due to the sluggishness of the transition[8]. The nature of the variation of band intensity in the $\beta - \alpha$ transition of cyclopentyl 1-thiaethane is quite different from that of benzothiophene shown in Figure 1. The more marked changes in intensity accompanying the order-disorder transition of benzothiophene may be related to the larger entropy change of the transition in this compound.

Alkali Metal Salts of TCNQ

The TCNQ radical anion exhibits five vibronic bands in the solid state infrared spectrum, besides fifteen bands due to the various intramolecular modes. The five vibronic bands are due to infrared-inactive, totally symmetric, in-plane A_g-type vibrational modes which become active in the infrared due to a vibronic interaction mechanism. These bands, observed around 2187, 1583, 1353, 1186 and 722 cm^{-1}, are assigned to ν_{CN}, $\nu_{C=C}$ (ring), $\nu_{C=C}$ (external), δ_{CCH} and ν_{C-C} respectively. Intensities of these bands increase appreciably in the dimeric structure because of the higher electronic vibrational moment due to an increased intermolecular charge-transfer interaction in the ground state. On increasing the temperature all these bands are expected to show a decrease in intensity, particularly at the phase transition temperature. Bozio and Pecile[10] have reported such a decrease in intensity with respect to the 722 cm^{-1} vibronic band of Rb-TCNQ(II). We have obtained an impressive display of a sharp decrease in intensity in several vibronic bands of K-TCNQ, Rb-TCNQ(I) and Cs-TCNQ in the close vicinity of their respective phase transition temperatures (see Figure 3). Furthermore, we have observed that the CN stretching (A_g)
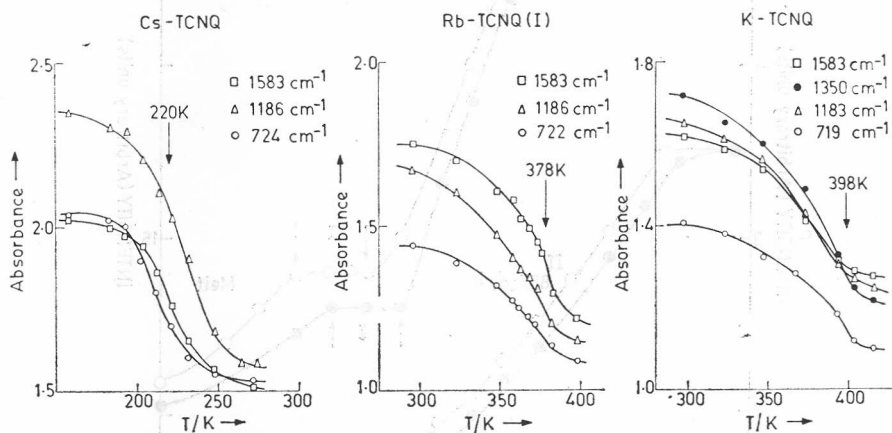

Figure 3. Temperature variation of the intensities of some of the vibronic bands of the TCQ radical anion in alkali metal-TCNQ salts.

band disappears just at the phase transition temperature. This behaviour can be due to a vibronic deactivation, or due to the decrease in the crystal field forces effected by the halving of the unit-cell at the phase transition temperature when the alternately spaced 'dimeric' units of TCNQ radical anions readjust themselves to become uniformly stacked monomeric units. The latter appears to be a more plausible explanation of the phenomenon.

Methylcyclohexane (MCH)

When liquid methylcyclohexane is quenched rapidly to 77 K and the glass thus formed is warmed up to 123 K, in about 15 minutes, a crystalline β-phase is obtained. This crystal form is different from that of another phase, α which crystallizes when a glass obtained by slow cooling is warmed from 113 K to 143 K in about 10 minutes. By subjecting the two different MCH glasses to differential scanning calorimetry, we have been able to establish the occurrence of two distinct crystalline phases; we estimate the β—α transition enthalpy to be 3.2 kJ mol^{-1}. Phase transition was also achieved in the infrared cell, by maintaining the β-phase at 128 K for about an hour. We have recorded the infrared spectra of both α- and β-phases of MCH, relevant excerpts from which are shown in Figure 4. Marked differences are discernible in the C—H
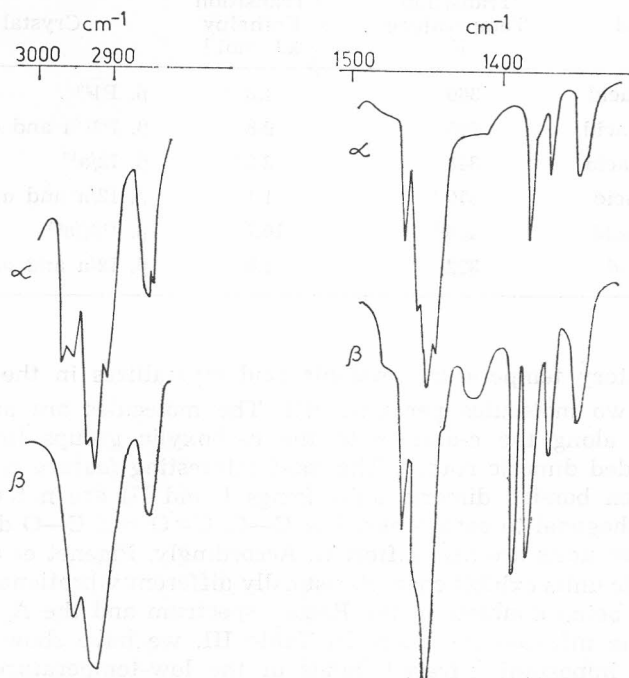

Figure 4. Infrared spectra of the α- and β-phases of methylcyclohexane (the C—H stretching and bending regions).

stretching as well as in the C—H bending regions, the spectrum of the α-phase being more structured in both regions than that of the β-phase. Thus, in the α-phase, both the methylene and the methyl C—H stretching vibrational bands show splittings and become doublets. Similarly, the CH$_3$ asymmetric bending vibration shows evidence for splitting in the α-phase. We also see differences in the CH$_3$ symmetric deformation band between the two phases. The changes in the spectra seem to suggest that the differences mainly arise from factor group splittings, although the presence of an additional band in the β-phase at 1388 cm^{-1} could be due to site group splitting. The present study clearly shows that infrared spectroscopy can be effectively employed to characterize

new phase transitions in organic molecular crystals. The conformation of MCH is likely to be the same in both the crystalline phases as suggested by Hankin et al.[24] based on changes in the lattice mode region in the Raman spectra.

Alkanedioic Acids

Enthalpy changes and temperatures of phase transitions of a few alkanedioic acids are given in Table II. The data on the phase transitions of malonic, succinic and azlaic acids are those obtained for the first time in this laboratory.

TABLE II

Phase Transitions of Alkanedioic Acids

Compound	Transition Temperature K	Transition Enthalpy kJ mol^{-1}	Crystal data
Malonic acid	360	1.5	β, P$\bar{1}$[19]
Succinic acid	395	0.8	β, P2$_1$/a and α, P$\bar{1}$[13]
Glutaric acid	348[a]	2.3[a]	β, I2/a[15]
Pimelic acid	370[a]	1.1[a]	β, I2/a and α, P2$_1$/a[14]
Suberic acid	406[a]	10.7[n]	β, P2$_1$/a[25]
Azlaic acid	322	1.9	β, I2/a and α, P2$_1$/a[14]

[a] From Ref.[16]

At laboratory temperature, malonic acid crystallizes in the space group P$\bar{1}$ (C$_i$) with two molecules per unit cell. The molecules are arranged in a zig-zag chain along the c-axis, with the carboxylic groups linked through hydrogen bonded dimeric rings[19]. The most interesting feature is that the two cyclic hydrogen bonded dimeric units (rings I and II) are not coplanar, but are nearly orthogonal to each other. The C—C, C=O and C—O distances with respect to these units are also different. Accordingly, Pigenet et al.[26] find that the two dimeric units exhibit characteristically different vibrational frequencies, the A$_g$ modes being doublets in the Raman spectrum and the A$_u$ modes being doublets in the infrared spectrum. In Table III, we have shown the assignments of the important infrared bands of the low-temperature β phase of malonic acid which are definitely attributable to the two unique hydrogen bonded dimeric rings I and II. Above 360 K, in the high-temperature α phase, only one set of vibrational frequencies attributable to a single type of cyclic dimeric hydrogen bonded ring is observed (Table III, Figure 5). The 180 cm^{-1} band which is mainly due to ν (OH ... O) with some possible contribution from the τ (C—C) mode in the low-temperature β phase is shifted to 165 cm^{-1} in the high-temperature α phase, the latter showing some structure (Table III). The band due to δ (CCC) mode is also shifted to a lower frequency above the transition temperature. It is interesting that one of the vibration-rotation bands at 126 cm^{-1} disappears above the phase transition. In the Raman spectrum, we have found that the high-temperature α phase has only one band at 931 cm^{-1} due to ν_a (C—C) whereas the low-temperature β phase shows two bands at 923 and 946 cm^{-1} respectively. Since the ν (O—H) and ν (C=O) frequencies are

TABLE III

Infrared frequencies (cm⁻¹) *of crystalline malonic acid above and below the phase transition temperature*

303 Kᵃ (β phase)	Assignment	Ring	368 K (α phase)
3100	ν (OH)	I	3100
2900	ν (OH)	II	—
1720	ν (C=O)	I	1720
1690	ν (C=O)	II	—
1425	δ (OH)	II	—
1400	δ (OH)	I	1400
1260	combination	II	—
—	—		1240ᵇ
965	γ (OH)	II	—
900	γ (OH)	I	900
596	γ (CCO)	II	—
580	γ (CCO)	I	583
450	δ (CCO)	II	—
438	δ (CCO)	I	440
180	ν (OH···O)	—	165 (174, 158)ᶜ
126	R¹	—	—
90	R¹	—	90

ᵃ The spectrum at 333 K gave the same bands as at 303 K.
ᵇ Combination band.
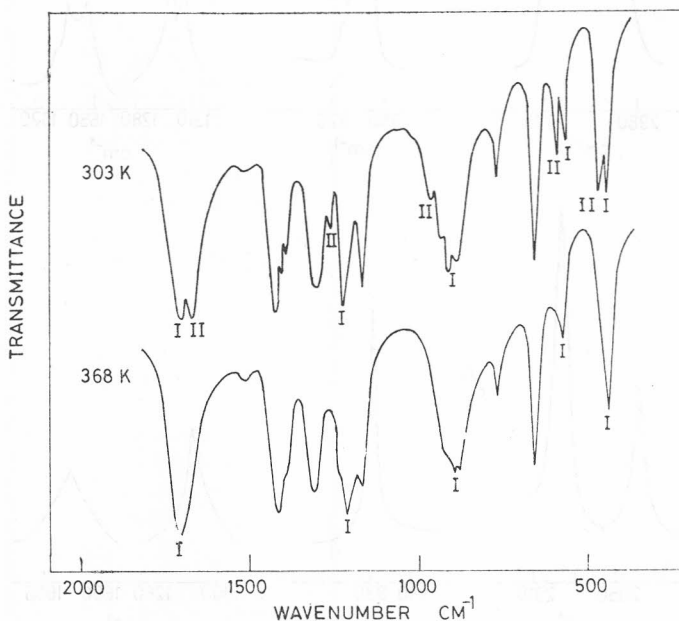ᶜ There are two weaker bands on either side at 174 and 158 cm⁻¹; these may be assigned to the τ (C—C) modes.

Figure 5. Infrared spectra of α- and β-phases of malonic acid showing two sets of bands becoming one above the phase transition temperature.

higher and the δ (OH) and ν (OH) frequencies are lower in the hightemperature α phase than the corresponding ones in the low-temperature β phase, we expect hydrogen bonding to be weaker in the high-temperature α phase. Accordingly, the hydrogen bond stretching frequency, ν (OH ... O), is also lower in the high--temperature α phase. Since the difference between the frequencies of rings I and II are due to a difference in the strengths of hydrogen bonds in the two dimeric rings, it is possible that the phase transition at 360 K involves a rearrangement in the molecular chain which renders the two disimmilar dimeric rings to become similar.

The vibrational assignments of succinic acid in the low-temperature β phase have been reported by Suzuki and Shimanouchi. In the Raman spectrum, we have observed marked changes in the C—H stretching, δ (OCO), C—O stretching and C=O stretching bands, all of them showing splitting in the high-temperature α phase (see Figure 6). We also notice changes in the lattice modes as shown in Figure 7. In the infrared spectrum too we see differences in the C—O stretching (1308 cm^{-1}), CH$_2$ rocking (803 cm^{-1}) and δ (C'CO) deformation (548 cm^{-1}) modes, all these bands showing splitting in the high-temperature
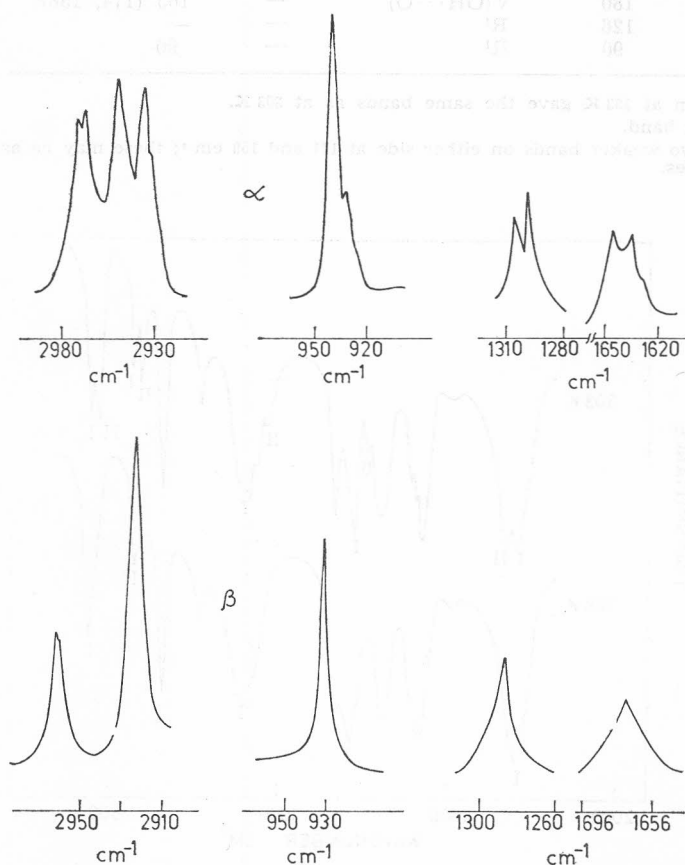

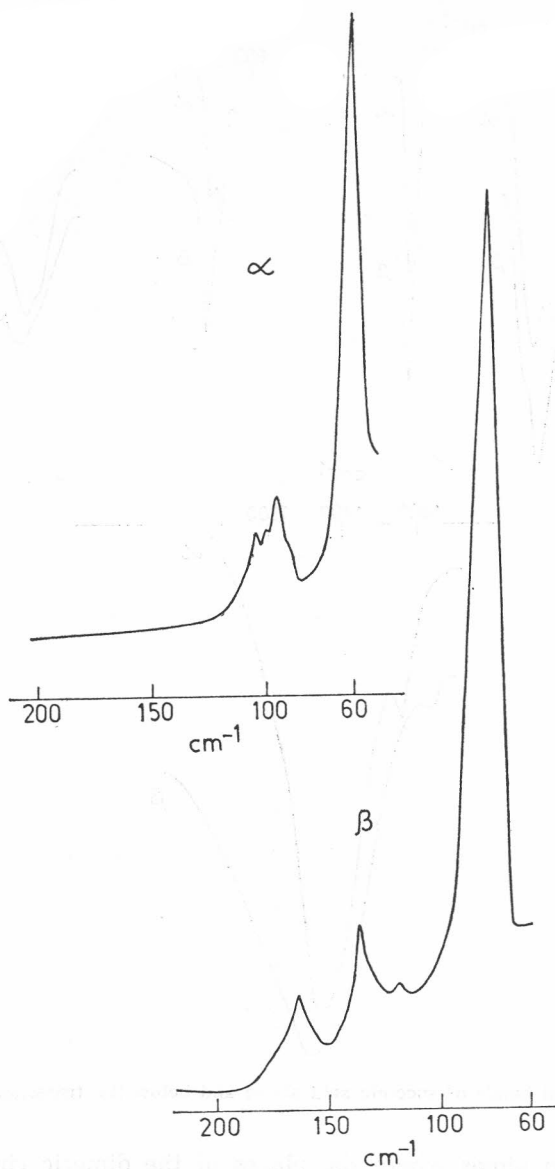Figure 6. Raman spectra of α- and β-phases of succinic acid showing significant changes.

Figure 7. Lattice mode region of Raman spectra of α- and β-phases of succinic acid

α-phase (Figure 8). In the C=O stretching region of the infrared spectrum, the β-phase has bands at 1730 cm^{-1} and 1697 cm^{-1} while the α-phase shows bands at 1788 cm^{-1} and 1698 cm^{-1}. It appears as though the changes observed in many of these bands may be due to factor group splitting. We should however note that the high-temperature α phase of succinic acid has a crystal structure similar to that of adipic acid and other higher homologues with an even
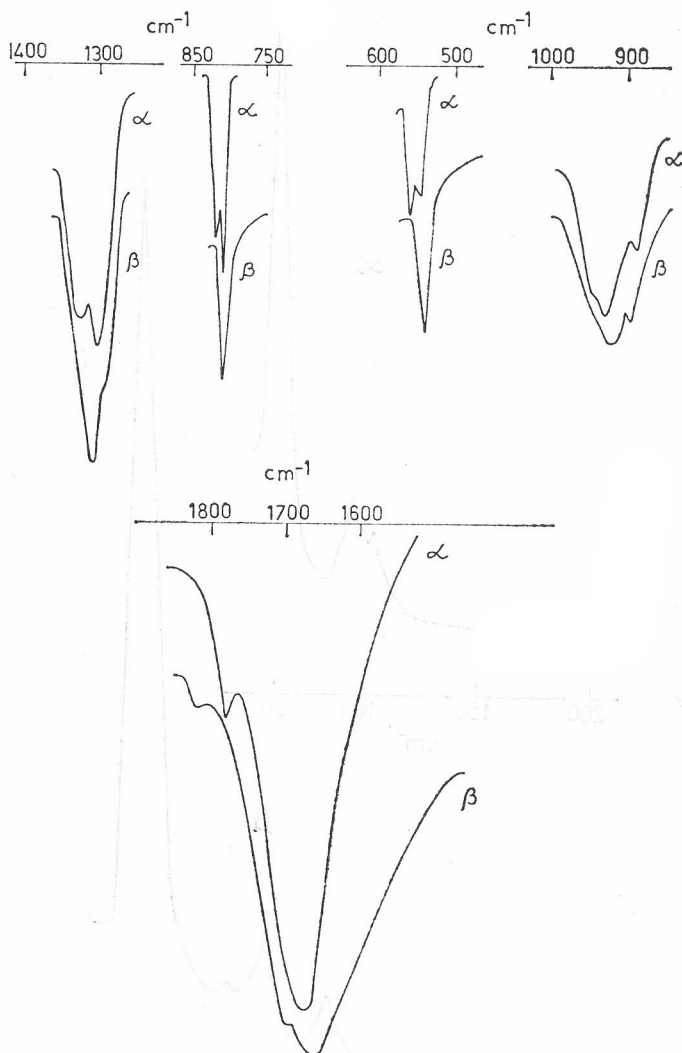
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Figure 8. Infrared bands of succinic acid above and below the transition temperature.

number of carbon atoms where the planes of the dimeric rings within each chain are parallel to each other, but tilted with respect to the planes of similar rings of neighbouring chains. The structure of the α phase of succinic acid seems to be somewhat in between the structure of oxalic acid and that of higher even homologues. Interestingly, the space group of the high-temperature α phase of succinic acid (P$\bar{1}$) is the same as that of low-temperature phase of malonic acid. The low-temperature β phase of succinic acid has the same space group (P2_1/a) as the β phase of oxalic acid. We see some evidence for weakening of hydrogen bonding in the phase as indicated by a higher frequency of the π (OH) band.

The low-temperature β phase of glutaric acid has a space group I2/a and contains linear chains of molecules hydrogen bonded through dimeric rings that are inclined by 32° in opposite directions to the plane of carbon atoms so as to have a C_2 molecular symmetry. The chains as well as the dimeric rings in them are parallel to each other[13]. The structure of the high-temperature α phase is not known, but is likely to be similar to that of the higher homologues with an odd number of carbon atoms such as pimelic and azlaic acids. The high-temperature phases of the latter acids totally lack molecular symmetry in the lattice, as the two dimeric rings are inclined to different degrees from the plane of carbon atoms. The stacking of chains is such that each dimeric ring is nearly orthogonal to every other in its vicinity[14]. We have recorded the infrared spectrum of glutaric acid across its phase transition (Figure 9). The bands that show maximum changes above the transition are
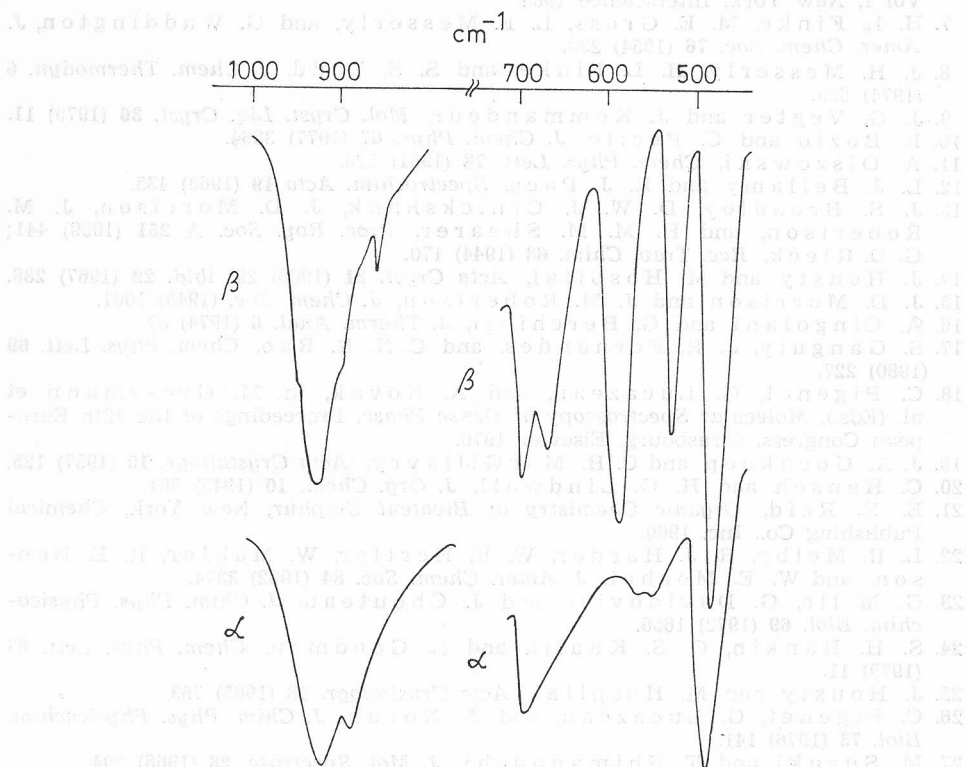

Figure 9. Infrared spectra of α- and β-phases of glutaric acid.

those associated with the bending vibrations of C=O, C′CO and COO groups which give rise to bands at 525, 585 and 665 cm⁻¹ respectively in the low-temperature β phase. The band at 665 cm⁻¹ is reduced to a shoulder in the high-temperature α phase, while the bands at 525 and 585 cm⁻¹ shift to 540 and 563 cm⁻¹ respectively with a dramatic decrease in intensity (Figure 9). The band at 853 cm⁻¹ of the low-temperature β phase completely vanishes above the phase transition temperature. Further studies on the transformations of glutaric and other acids are in progress in this laboratory.

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IZVLEČEK

Študij faznih prehodov v organskih molekulskih kristalih in dikarbonskih kislinah z vibracijsko spektroskopijo

Chintamani Nagesha Ramachandra Rao, Somnath Ganguly in Humachadakatte Ramachandra Swamy

Fazni prehodi v kristalih organskih spojin so precej manj znani kot oni v anorganskih, vendar se zdi, da so mehanizmi strukturnih transformacij podobni v obeh primerih. Raziskava kaže uporabnost infrardeče in Ramanske spektroskopije pri študiju faznih prehodov v organskih kristalih in pojasni v nekaterih primerih tudi

ustrezni mehanizem. V primeru 2,3-benzotiofena infrardeči spektri pokažejo pomembne razlike v intenzivnosti trakov, ko preide urejena nizkotemperaturna faza v neurejeno visokotemperaturno fazo med 230 in 265 K. Prehod v talino, po drugi strani, pa ne kaže več sprememb. Podobne pojave opazimo tudi pri ciklopentil-1-tiaetanu, kjer navzočnost dveh ekvivalentnih konformacij skupine C—S—CH$_3$ verjetno poskrbi za nered. Infrardeča spektroskopija pokaže nove fazne prehode metil-cikloheksana $\cdot$ α faza ima podvojene trakove v področju valenčnih in deformacijskih nihanj pri skupinah CH. V primeru malonske kisline ločimo tri trdne faze: v visokotemperaturni fazi nad 360 K so verjetno vse vodikove vezi OH—O ekvivalentne, medtem ko najdemo pri nižji temperaturi dve različni vodikovi vezi. Fazne prehode kristalov jantarjeve in glutarove kisline tudi spremljajo pomembne spremembe frekvenc in intezivnosti infrardečih in Ramanskih trakov.