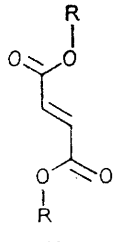
Conformations of Some αβ-Unsaturated Carbonyl Compounds. Part VII.[1] Assignments of Raman and Infrared Spectra of Dimethyl, Diethyl, and Di-n-butyl Fumarates and Maleates

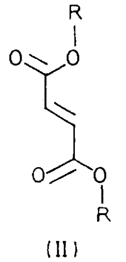
By **David A. C. Compton, William O. George,*** and **Alan J. Porter,** School of Chemical and Physical Sciences, Kingston Polytechnic, Kingston-upon-Thames, Surrey

Raman and i.r. spectra of dimethyl, diethyl, and di-n-butyl fumarates and maleates in the liquid (or solid) state at room temperature (or above) and as frozen solids are reported together with vibrational assignments for conformers (*trans,trans* $\rightleftharpoons$ *trans,cis* for the fumarates, *cis,trans* only for the maleates). Measurement of intensities of selected Raman bands at various low temperatures leads to calculation of enthalpy differences (ΔH^0 ± standard deviation) of 396 ± 42 and 219 ± 28 cal mol^{-1} between the high and low energy forms of the di-n-butyl and diethyl fumarates, respectively. Dimethyl fumarate is a solid at room temperature; measurement of Raman band intensities at higher temperatures leads to a corresponding value of 774 ± 184 cal mol^{-1}. These results provide general support for a previous result based on i.r. measurements.

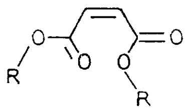
VARIABLE-TEMPERATURE i.r. studies of dimethyl, diethyl, and di-n-butyl fumarates and maleates have been interpreted [2] on the basis of *trans,trans* (I) and *trans,cis* (II) forms of the fumarates and *cis,trans* (III) forms of the maleates. As in the case of esters of monocarboxylic acids [3,4] there is a need to obtain additional evidence for the presence of these conformers and to evaluate the enthalpy differences between them, and Raman measurements may be regarded as independent of i.r. measurements in terms of experimental errors. Detailed Raman and i.r. assignments of vibrational modes in fumarates and maleates are presented here for the first time. Values of ΔH^0 for the equilibria (I) $\rightleftharpoons$ (II) based on Raman measurements are reported for comparison with values of ΔH^0 from i.r. measurements.


(I)

trans , *trans*


(II)

trans , *cis*


(III)

cis , *trans*

EXPERIMENTAL

Samples were obtained as described [2] previously and purities checked by g.l.c. and i.r. measurements. Raman and i.r. studies involving use of variable-temperature sample equipment were carried out as before.[4] Some difficulties were encountered in recording Raman spectra of methyl fumarate as a heated liquid. A sample prepared by acid-catalysed esterification was recrystallized from methanol and dried in a vacuum oven (m.p. 103·5°; lit., 101°). This was sensitive to blue and green Argon ion laser lines and was studied at low laser power (100 mW) by using wide spectrometer slits (14 cm^{-1}). On cooling the sample no time-dependent spectral changes were observed and the i.r. spectrum of a solution in CS_2 agreed with that in the literature.[5]

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[1] Part VI, J. R. Cowles, W. G. Fateley, and W. O. George, preceding paper.

[2] W. O. George and A. J. Porter, *J.C.S. Perkin II*, 1973, 954.

[3] W. O. George, D. V. Hassid, and W. F. Maddans, *J.C.S. Perkin II*, 1972, 400.

[4] W. O. George, W. C. Harris, D. V. Hassid, and W. F. Maddams, *J.C.S. Perkin II*, 1974, 392.

[5] 'Documentation of Molecular Spectroscopy,' Butterworths, London, No. 1912.

RESULTS AND DISCUSSION

Fumarate Assignments.—The existence of a conformational equilibrium has consequences in the Raman and i.r. activity of fumarates. If the alkyl groups are considered as single units, the vibrational spectrum of each fumarate can be separated into two parts: first the normal modes of the skeletons (I) and (II), which should be approximately the same in all three fumarates, and secondly, the normal modes internal to the alkyl group. The latter are not discussed because they are standard to all substituted CH compounds. The skeletal modes of the fumarates depend on the conformations, which may have different symmetries and hence different Raman and i.r. activities.

In the case of the *trans,trans* conformer (I) the symmetry corresponds to the C_{2h} point group and the normal modes divide as $11a_g$ (R.pol.) + $5a_u$ (R.depol.) + $4b_g$ (i.r.) + $10b_u$ (i.r.). In the case of the *cis,trans* conformer (II) the symmetry corresponds to the C_s point group and the normal modes divide as $21a'$ (R.pol., i.r.) + $9a''$ (R.depol., i.r.). Discussion of assignments follows the considerations used for acrylates and *trans*-crotonates. The fundamental modes of the three fumarates and the observed vibrational spectra are shown in Table 1, the assignments are discussed briefly for particular spectral regions.

TABLE 1

Vibrational spectra of alkyl fumarates (ν/cm^{-1})

Methyl fumarate			Ethyl fumarate			n-Butyl fumarate			
I.r.	Raman	p †	I.r.	Raman	p †	I.r.	Raman	p †	Assignment
3440w			3430w			3430w			2 × 1730 = 3460
3055w, sh	3061m	sp	3060w	3060m	sp	3100w	3057m	sp	CH str., a_g and b_u
2990w			2975m	2975s	sp	2955m	2957s, sh	mp	Alkyl CH str.
2950m	2959m	sp	2930sh	2936s	sp	2930sh	2932s	mp	
			2920w	2910w, sh	sp		2910s	mp	
2900sh			2895sh			2890sh			
2840w	2851w	sp	2880w	2873w, sh	sp	2870w	2871s	sp	
			2865w						
1731s	1730s	sp	1720s	1726s	sp	1721s	1730s	sp	C=O str., a_g and b_u
	1655s↑	sp		1663s↑	sp		1662s↑	sp	C=C str., a_g
1640w↓	1640s↓	sp	1641w↓	1644m, sh↓	sp	1640w↓	1645sh↓	sp	C=C str., a′
			1472sh	1477w	dp	1470m	1470m		Alkyl CH bend
			1642w	1460w	dp	1460m	1462m		
	1456w	dp							
1438m	1435w	sp	1443w	1450m	dp		1450	dp	
			1388sh	1390w	mp	1380w	1380w	sp	
			1364m	1363w	sp		1365w	sp	
1302s↑	1302w↑	dp	1292s↑	1300m, sh↑	dp	1291s↑	1300m↑	dp	C–O as. str., b_u
1270sh	1275m↓	sp		1275m	mp	1265sh	1277w↓		C–H as. bend, b_u
1260m↓	1261m↓	sp	1256s↓	1259m↓	sp	1255s↓	1261m↓	sp	C–O as. str., a'
1225w↓			1221w↓			1220w↓			C–O s. str., a'
							1230	dp	
	1215m↑	sp		1203m↑	sp		1200m↑	sp	C–O s. str., a_g
1190sh	1182w	mp					1175w	sp	Alkyl rock
1170sh	1177w	mp	1174sh	1175w	sp	1171m, sh	1150w	sp	C–H s. bend, a_g
1154s↓			1151s↓			1151s↓			C–H s. bend, a'
			1100sh	1110w	sp	1125w	1122w	sp	Alkyl CH rock
			1090w↓	1092sh↓	sp	1058m	1061w	dp	Alkyl CH rock
1028m	1031w↓	mp	1033m	1032sh↓	dp	1021m	1025w↓	mp	O–R as. str., b_u
	1000m↓	dp		1025w↓	dp		1010vw	dp	
1015sh	995w↑	mp		980w↑	sp		985w↑	mp	O–R s. str., a_g
976m			975m			975m			C–H def., a_u
	950m↑	sp		935vw			949w	sp	Alkyl C–C str.
915w	912m↓	sp							Alkyl C–C str.
	902w, sh								
	888m↑	dp		890w	dp		890w	dp	C–H def., b_g
850sh	851m↓	sp	856w	864m↓	sp	835w	840m↓	sp	C–C s. str., a_g
							808w	mp	
770w	780w	dp	771w	782vw		771w	760vw		C–C as. str., b_u
	745w	sp		730vw	sp	734w	735vw	mp	C=O bend, a_g and b_g
661w			665w			667w			C=O bend, a_u and b_u
			650w	650vw	dp		650vw	mp	C–C–O bend, a_g and b_u
				555vvw			545vw	sp	Alkyl C–C bend
			520w	525vw			510w	mp	Alkyl C–C bend
390vw	389vw	sp		384vw	sp		420w	sp	C=C–C bend, a_g
	330vw	sp		348vw	sp		340w	sp	C–O–R bend, a_g
	275vw, sh	dp		250w	sp		225m	sp	Alkyl C–C bend:
	204w	dp		172w	dp				C–OR torsion, b_g

† sp = strongly polarized; mp = moderately polarized; dp = depolarized.

3500—2000 cm^{-1}.—The a_g and b_u olefinic CH stretching modes are assigned to bands near 3060 cm^{-1} in both Raman and i.r. The alkyl CH stretching modes occur between 2800 and 3000 cm^{-1}.

2000—1500 cm^{-1}.—The a_g and the b_u C:O stretching modes are at similar wavenumber values, also indicating little mechanical or electrical interaction between groups. The a_g C:C mode is assigned to strong polarized Raman bands near 1660 cm^{-1}, and the absence of corresponding bands in the i.r. is consistent with the centrosymmetric C_{2h} structure. The satellites at 15 cm^{-1} below these Raman bands do however have i.r. counterparts. These satellites are absent, or in some cases reduced to very weak bands, in the Raman and i.r. spectra for the solid state. They are, therefore, assigned to the C:C stretching mode of the high energy conformer which is both i.r. and Raman active.

TABLE 2

Vibrational spectra of maleates (ν/cm^{-1})

Methyl maleate			Ethyl maleate			n-Butyl maleate			
I.r.	Raman	p †	I.r.	Raman	p †	I.r.	Raman	p †	Assignment
3440w			3435w			3440w			
3055w	3056m	sp	3055w	3052m	sp	3055w	3050w	sp	CH str.
2995w	3004uw	mp	2975m	2968m	mp	2960m	2955m sh	sp	Alkyl CH str.
2950w	2952s	sp	2930sh	2932s	sp	2930sh	2924s	sp	
2895sh	2900vw	sp	2895sh	2898w, sh	sp	2890sh	2909s	sp	
2840w	2848w	sp	2870sh	2868w, sh	sp	2870sh	2868s	sp	
1730s	1730vs	sp	1725s	1725vs	sp	1728s	1725s	sp	C=O str.
				1660m, sh	sp				
1642w	1645vs	sp	1640w	1645s	sp	1640w	1645s	sp	C=C str.
			1470sh			1462w			Alkyl CH bend
	1450w	dp		1450m	mp		1445m	dp	
1435m	1438w, sh	mp	1441w				1430m, sh	dp	
			1440m	1400m	mp	1402m	1400w	mp	
1387m	1387w	mp	1380m	1380w, sh	mp	1375sh	1370w, sh	sp	
			1364w	1363w, sh	mp	1375sh	1370w, sh	sp	
1296m	1298vw	sp	1294m	1296w	mp	1290m	1298m	mp	C–O as. str.
				1270w	mp		1260w, sh	mp	C–H as. bend
1246m			1244m			1243m			
							1224w, sh	dp	
1215s	1215vvw		1208s	1209w	mp	1207s	1204w, sh		C–O s. str.
	1182w, sh	mp							
1160s	1160m	mp	1156s	1160w	mp	1161s	1160m	mp	C–H s. bend, OR as. str.
			1108sh	1109m	sp		1116w	sp	Alkyl C–H rock
			1090w	1096m, sh	sp	1060w	1056w	dp	
1004w	1002w	mp	1025m	1025w	dp	1020w	1016w	mp	O–R s. str.
						1002sh			Alkyl C–C str.
						980w			
990w	987w	mp	970w	975w	mp	960w	964w	mp	Alkyl C–H rock
935w	938vw	mp				945w	942sh	mp	Alkyl C–H rock
			910w	908w, sh	sp		904m	sp	
880w	885vvw			880w, sh	sp		875w, sh	sp	Alkyl C–C str.
860w	862vs	sp	860w	861s	sp	840w	836s	sp	C–C s. str.
			834w	833w	sp			sp	
812w	815w	mp	802w	800w	sp	809w	805w, sh	sp	C–C as. str.
			790sh	785w	sp				
720w	725vw	dp	715w	730w	dp	732vw	730vw	dp	C–H def.
600w	600w	sp	590w	600w	sp		588w	sp	C–C–O bend
	490w	sp		525w	sp		528vw	sp	C=O bend
				500vw			500vw	dp	
	460w	mp		465w	mp		465vw	mp	C=C–C bend
	350w	mp		385w	sp		380w	sp	Alkyl C–C bend
	333w	mp		320w	sp		320w	sp	C–O–R bend
				283w	dp		272vw	mp	Alkyl C–C bend
	245w	mp		244w	mp		244w		Alkyl C–C bend
	180vw, sh			178w	mp		178vw, sh		C–OR torsion

† sp = strongly polarized; mp = medium polarized; dp = depolarized.

associated with a pair of bands near 1300 (low energy conformer) and 1260 cm^{-1} (high energy conformer) in all three fumarates, whilst the corresponding a_g CO stretching modes are associated with a pair near 1220 (high energy conformer, i.r. active only) and 1212 cm^{-1} (low energy conformer, Raman active only). A third set of conformer pairs occurs near 1170 and 1154 cm^{-1}. The higher wavenumber band is polarized in the Raman but is only observed as a shoulder in the i.r. and is,

1500—1000 cm^{-1}.—The various CH_3 and CH_2 bending modes are assigned to bands between 1480 and 1360 cm^{-1}. As in the acrylates and *trans*-crotonates a number of pairs of conformer bands occur between 1300 and 1000 cm^{-1} for which an accurate description of assignments is not possible. Comparisons of wavenumber values and consideration of Raman and i.r. intensities amongst various fumarates, *trans*-crotonates, and acrylates suggest that the b_u CO stretching mode is therefore, assigned to the a_g CH bending mode. The lower wavenumber band is observed in the i.r. only as a high energy conformer band. It is likely to be the a' CH bending mode of the conformer with C_s symmetry. The similarity of a pattern of five i.r. bands in a range of esters of fumaric acid and of temperature dependences in the methyl, ethyl, and n-butyl compounds has been noted previously.[2] The additional Raman data in the present work assist the assignments of these bands. Of the four CO and CH modes, only the b_u CH band appears not to split into conformer bands and is assigned to a shoulder near 1270 cm^{-1} in the i.r.

A prominent pair of conformer bands is observed in the Raman spectrum of dimethyl fumarate at 1031 and 990 cm^{-1} (the latter is part of a doublet). The lower band has a weak Raman counterpart in the ethyl and n-butyl fumarates; this is also polarized and assigned to the a_u OR stretching mode. The higher band is coincident with medium intensity i.r. bands near 1030 cm^{-1} which are assigned to the b_u OR stretching mode.

1000—500 cm^{-1}.—Assignment of the a_u out-of-plane CH deformation is well established at 975 cm^{-1} but that of the corresponding b_g out-of-plane CH deformation is less certain. It is assigned to the medium or weak depolarized Raman band near 890 cm^{-1} in the fumarates. Both CH o.p. deformation assignments obey the mutual exclusion rule rigorously and the bands occur at somewhat higher values than the corresponding modes in the *trans*-crotonates. Other fundamentals expected in this region are the a_g and b_u C·C stretching modes. The former is assigned to the medium intensity polarized Raman band near 850 in ethyl and n-butyl fumarate. In methyl fumarate a Raman band at 851 cm^{-1} appears to be a high energy conformer band and the corresponding low energy conformer band is considered to be superimposed on that assigned to the b_g CH deformation at 888 cm^{-1}. The medium intensity Raman bands near 850 cm^{-1} all have weak i.r. counterparts, suggesting either that there is no splitting between the a_g and b_u C·C stretching motions, or, more probably, that the selection rules are not rigorously obeyed. In this case the b_u C·C stretching modes are assigned to weak i.r. bands near 770 cm^{-1} in all three fumarates. The in-plane and out-of-plane C:O bending modes of esters are normally assigned in the 600—700 cm^{-1} region. The weak i.r. band near 665 cm^{-1} may be assigned to both the a_u and b_u C:O bending modes. The weak Raman band at 745 and 730 cm^{-1} in methyl and ethyl fumarate, respectively, may be assigned to the a_g and b_g C:O bending modes.

As in the case of esters of monoacids, assignment to skeletal modes in the 600—100 cm^{-1} region is only tentative. Bands near 650, 420, and 340 cm^{-1} are likely to be associated with the various skeletal bending modes and other bands in this region are dependent on the alkyl group and are therefore associated with bending modes of these groups. A full assignment of the interesting torsion modes is postponed until a detailed study of the far-i.r. spectrum is possible in the solid and vapour states.

Maleate Assignments.—On the basis of variable-temperature i.r. studies and from considerations of molecular models, esters of maleic acid were considered to exist in the *cis,trans* form (III). This would correspond to the C_s point group if the system were planar (normally favoured in conjugated systems and in the ester group). The normal modes divide into $21a'$ (R.pol., i.r.) + $9a''$ (R.depol., i.r.) and the approximate forms of these modes together with the observed Raman and i.r. spectra are shown in Table 2. The assignments follow fairly closely from those of the corresponding fumarates except that the a_g and b_u species in the fumarates correspond to the a' species in the maleates, and the b_g and a_u species in the fumarates correspond to the a'' species in the maleates. It follows that all the modes should show i.r. and Raman coincidence and the distinction between symmetric and antisymmetric motions is best made by comparison with the fumarates. The assignments tabulated require no discussion further to the considerations outlined for the fumarates.

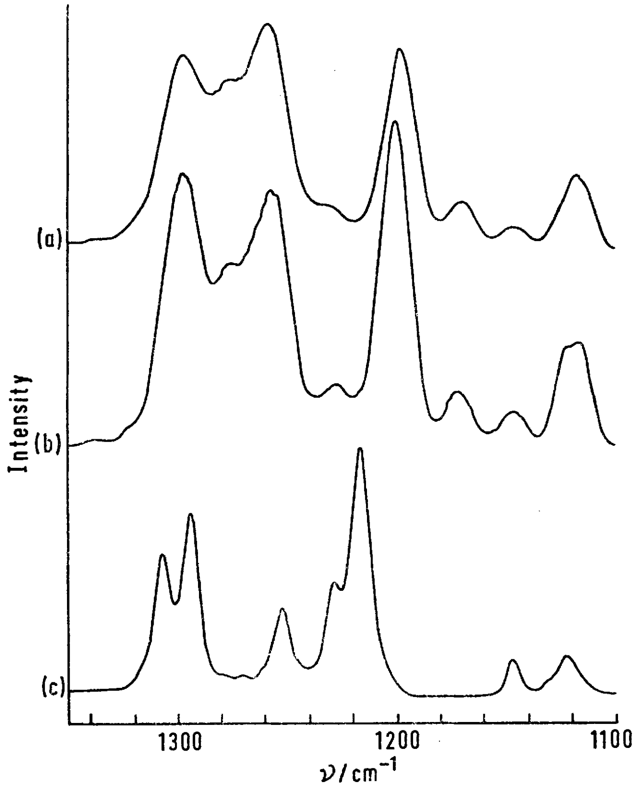

FIGURE 1 Raman spectra of butyl fumarate, 1350—1100 cm^{-1}: (a) +119 °C; (b) −8 °C; (c) annealed solid at −30 °C

Conformational Equilibria.—As in the case of esters of monocarboxylic acids, variable-temperature Raman studies are desirable to establish equilibria parameters. Comparison between the Raman spectra of the fumarates as liquids and solids (heated or frozen according to their room temperature state) reveal a number of pairs of conformer bands. High and low energy conformer bands are denoted as (↓) for bands which decrease in relative intensity on cooling and are absent in the solid state after annealing, and as (↑) for bands which increase in relative intensity on cooling. In many cases band overlap precludes accurate measurement. The Raman spectra of n-butyl fumarate in the region 1350—1100 cm^{-1} at +119°, at −8°, and as an annealed frozen solid are shown in Figure 1. In the solid certain bands are split, intensified, or shifted to increased wavenumber value. The strongest band in this region at 1261 cm^{-1} is absent in the solid. In the liquid the intensity of this band was measured over a 200° temperature range relative to that of the band at 1300 cm^{-1}. A plot of ($\log I_{1261} - \log I_{1300}$) against $1/T$ provided a value for ΔH^0 of 396 $\pm$ 42 cal mol^{-1}. This pair of bands corresponds to the conformer pair used for i.r. studies [2] to obtain a value for ΔH^0 of 372 $\pm$ 20 cal mol^{-1}. The close agreement provides good support for the existence of an equilibrium with this enthalpy difference.

The Raman spectrum of ethyl fumarate is shown in Figure 2 under similar conditions in the region and temperature ranges in which conformational changes are apparent. Bands in the spectrum of the liquid at 1259, 1092, 1032, and 1025 cm^{-1} weaken on cooling and are absent in the solid. Measurements of the intensities of the Raman bands at 1300 and 1259 cm^{-1} were made between -14 and $+152$° leading to a value for ΔH^0 of 219 $\pm$ 28 cal mol^{-1}. The Raman spectrum of methyl fumarate is shown in Figure 3 for the region 1325—825 cm^{-1}. Since this is a solid at normal temperatures comparisons are made with melts at 118 and 202°. A number of bands in the liquid spectrum are absent from that of the solid (1275, 1261, 1031, 1000, 912, and 851 cm^{-1}). Various pairs were studied in an endeavour to relate intensity changes with temperature to conformational equilibria, and the most favourable pair was found to be at 950 and 915 cm^{-1}. Intensities of this pair between $+112$ and $+202$° provided a value for ΔH^0 of 774 $\pm$ 154 cal mol^{-1}. We consider that the large value for the methyl ester in comparison with those for the ethyl and n-butyl esters may be associated with the same stabilizing features which cause this ester to exist as a solid at room temperature, but the detailed relationship between (I) $\rightleftharpoons$ (II) and solid $\rightleftharpoons$ liquid equilibria is not understood.

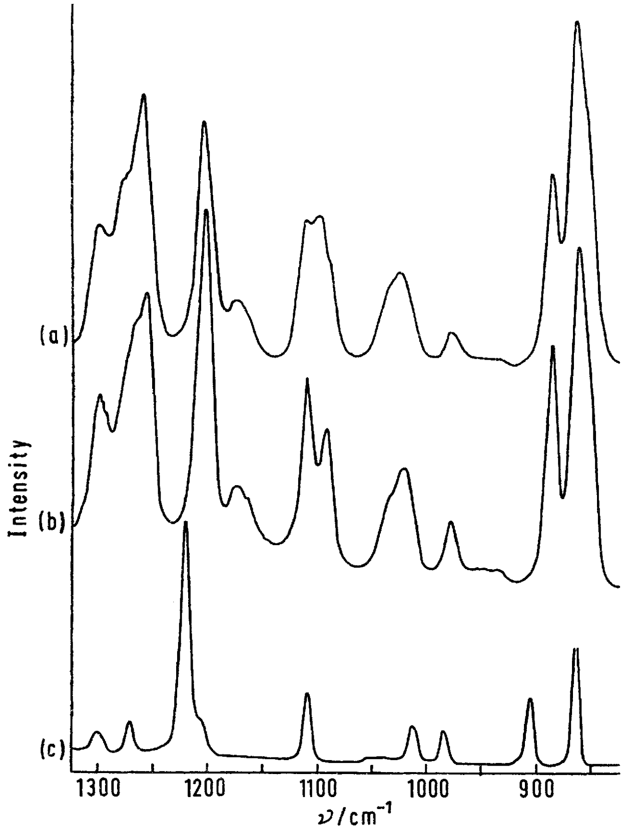

FIGURE 2 Raman spectra of ethyl fumarate, 1325—825 cm^{-1}: (a) $+126$ °C; (b) -3 °C; (c) annealed solid at -21 °C

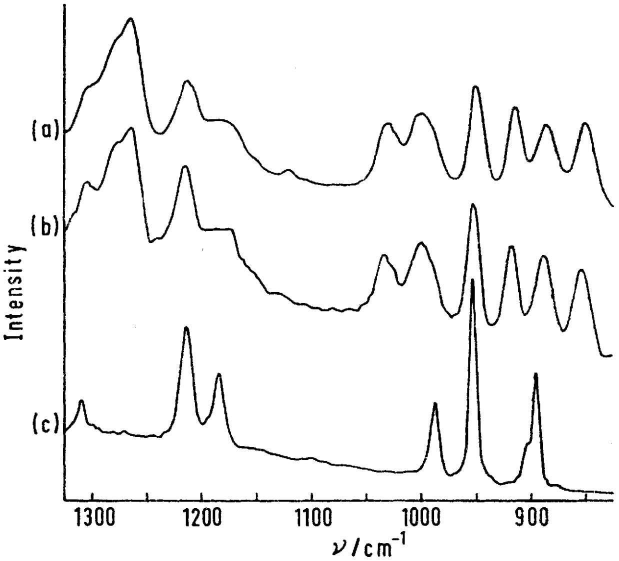

FIGURE 3 Raman spectra of methyl fumarate, 1325—825 cm^{-1}: (a) 202 °C; (b) 118 °C; (c) annealed solid at 20 °C

Variable-temperature studies of the Raman spectra of the maleates reveal notable differences from the fumarates. On freezing methyl maleate and annealing, a number of solid state spectra were obtained in which there were differences in relative intensities, splittings, and enhancement of weaker bands. Nevertheless, in terms of possible conformational changes, only one very weak liquid band is not observed in the solid (1298 cm^{-1}). In the absence of the many other changes observed in the i.r.[2] and Raman (Figure 3) spectra of methyl fumarate we assume that the 1295 cm^{-1} band is weakened owing to a phase-sensitive intensity change rather than a shift in a conformational equilibrium.

Ethyl maleate differs from the methyl compound in providing reproducible solid state spectra. In this case, no liquid bands are absent in the spectrum of the solid. n-Butyl maleate on freezing yields a Raman spectrum which is also very similar to that of the liquid. This evidence, therefore, supports the existence of these three maleate esters in a single conformation, which steric models suggest is the *cis,trans* (III).

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