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

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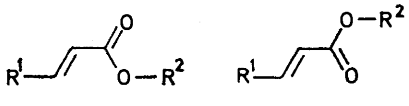
I.r. spectra of dimethyl, diethyl, and di-n-butyl fumarates and maleates are reported. The effects on these spectra of cooling the liquids and their solutions in carbon disulphide to −100 °C and of solidification have been studied. For dimethyl fumarate the effects of heating the solid and its solution in carbon disulphide to +110 °C have also been studied. Evidence is presented for a conformational equilibrium in the fumarates involving probably *trans–trans* $\rightleftharpoons$ *trans–cis*; $\Delta H^{\circ} = 372 \pm 20$ cal mol^{-1} was measured for di-n-butyl fumarate. The maleates probably exist in the *cis–trans* conformation.

IN Parts I—III we related the vibrational spectra of αβ-unsaturated aldehydes,[2] ketones,[2] and esters[1,3] to particular conformations arising from internal rotation. We have also related the i.r. spectra of saturated esters[4] to their conformations. Vibrational spectra of αβ-unsaturated esters are consistent with an equilibrium between (I) and (II) and analogies with αβ-unsaturated aldehydes and ketones together with steric considerations suggest (I) is the more stable form. On this basis the difference in enthalpy ΔH°, was measured as 326 ± 18 and 306 ± 30 cal mol^{-1} in methyl acrylate and methyl *trans*-crotonate respectively. However, Williams *et al.*[5] detect only (II) in the microwave spectrum of methyl acrylate but comment that the intensities of the rotational transitions of the *s-trans* form are likely to be very low.


(I) (II)

R^1 = H or Me
R^2 = Me or Et

SCHEME 1

A rationale of the suggested conformations of simple saturated and αβ-unsaturated esters in terms of steric effects would predict analogous equilibria in more complex systems. The purpose of the present work is to examine the i.r. spectra of various diesters of fumaric and maleic acid at different temperatures and in different states and to attempt to relate these spectra to possible conformations. Kingsland and Spedding[6] note differences between the i.r. spectra of a number of dialkyl fumarates in solid and solution states but explain only one of these differences in terms of conformations suggested in an earlier study.[7]

EXPERIMENTAL

The spectra were obtained on Perkin-Elmer 257, 457, and 521 spectrophotometers for thin films and for solutions in carbon tetrachloride and carbon disulphide. Dimethyl fumarate was examined as a KBr disc and as a Nujol mull and also as a liquid film in a heated cell. Wavenumbers are accurate to within ±3 cm^{-1}. Intensity measurements and variable temperature studies were performed by the methods described previously,[1] except that band overlap precluded any measurements of band areas; therefore, peak heights were used.

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[1] Part III, W. O. George, D. V. Hassid, and W. F. Maddams, *J.C.S. Perkin II*, 1972, 400.

[2] A. J. Bowles, W. O. George, and W. F. Maddams, *J. Chem. Soc.* (*B*), 1969, 810.

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[5] G. Williams, N. L. Owen, and J. Sheridan, *Trans. Faraday Soc.*, 1971, **67**, 922.

[6] M. Kingsland and H. Spedding, *Chem. and Ind.*, 1971, 508.

[7] W. L. Walters and R. B. Hughes, *J. Amer. Chem. Soc.*, 1957, **79**, 3985.

Samples were obtained commercially as follows: dimethyl fumarate and maleate (Eastman Kodak), diethyl fumarate (Ralph N. Emanuel), di-n-butyl fumarate and maleate (Cambrian Chemicals Ltd), and diethyl maleate (Koch-Light). G.l.c. showed dimethyl and diethyl fumarate to contain $<0{\cdot}1\%$, di-n-butyl fumarate $<0{\cdot}9\%$, and the maleates $<0{\cdot}3\%$ higher molecular weight impurity. Mass spectra and n.m.r. spectra were consistent with structures in all cases.

RESULTS AND DISCUSSION

The i.r. spectra of the dimethyl, diethyl, and di-n-butyl esters of fumaric and maleic acids are given in Table 1 for samples in the liquid state. These compounds are liquids at normal temperatures except for dimethyl fumarate which is a solid and which was examined in the molten state above its m.p. (105 °C). The spectra of these esters as solids were recorded after repeated annealing to convert, as far as possible, samples to the most stable solid form. Comparisons were also made between the i.r. spectra of solutions of these esters in carbon disulphide at room temperature and in the frozen state. Spectra of frozen solutions were obtained for all diesters except dimethyl fumarate which precipitated from solution as the temperature was lowered. These spectra provide some simplications compared with spectra of pure solids presumably because in frozen solution the motions of neighbouring molecules are partially uncoupled and the interactions which give rise to correlation field splittings are diminished.

TABLE 1

I.r. spectra of diesters of fumaric and maleic acids as liquids (cm^{-1})

Dimethyl fumarate: 3440w, 2990w, 3055sh, 2950w, 2900sh, 2840sh, 1730s, 1640w, 1436m, 1300s, 1270sh, 1260m, 1225w, 1190sh, 1170msh, 1154s, 1028m, 976m, 915w, 870w, 850sh, 770w, 655w, 510w

Diethyl fumarate: 3430w, 3060w, 2975m, 2930sh, 2895sh, 2865w, 1720s, 1641w, 1472sh, 1462w, 1443w, 1388sh, 1364m, 1292s, 1256s, 1221w, 1174msh, 1151s, 1100sh, 1090w, 1033m, 975m, 856w, 771w, 622w, 650w, 520w

Di-n-butyl fumarate: 3430w, 2955m, 2930sh, 2890sh, 2870w, 1721s, 1645sh, 1640w, 1460m, 1380w, 1291s, 1265sh, 1255s, 1220w, 1171msh, 1151s, 1058m, 1021m, 975m, 835w, 771w, 734w, 667w

Dimethyl maleate: 3440w, 3055w, 2995w, 2950w, 2895sh, 2840w, 1730s, 1642w, 1435m, 1387m, 1296m, 1246m, 1215s, 1160s, 1004w, 990w, 935w, 880w, 860w, 812w, 600w

Diethyl maleate: 3435w, 3055w, 2975m, 2930sh, 2895sh, 2870sh, 1725s, 1640w, 1470sh, 1460w, 1441w, 1400m, 1380m, 1364w, 1294m, 1244m, 1208s, 1156s, 1108sh, 1090w, 1025m, 970w, 910w, 860w, 834w, 802w, 790sh, 770sh, 590w

Di-n-butyl maleate: 3440w, 3055w, 2960m, 2930sh, 2890sh, 2870sh, 1728s, 1640w, 1462w, 1402m, 1375sh, 1290m, 1243m, 1270s, 1161s, 1060w, 1020w, 1002sh, 980w, 960w, 945w, 840w, 809w

s = Strong, m = medium, w = weak, sh = shoulder.

Fumarates.—The solid state spectra of these esters exhibited the usual band sharpenings and splittings associated with the solid state. Other features present in the dimethyl, diethyl, and di-n-butyl esters were attributed to rotational isomerism. In particular a remarkable similarity occurs between the spectra of the three fumarates in the 1100—1300 cm^{-1} region. The solution and frozen solution spectra of diethyl and di-n-butyl fumarate shown in Figure 1(a) and (b), exhibit two pairs of bands in each case near 1290, 1260 and 1170, 1150 cm^{-1} in which the higher wavenumber components increase and the lower wavenumber components decrease in relative intensity with cooling. The latter are absent for the frozen solution. A fourth weaker band near 1225 cm^{-1} in the solution is also absent in the frozen solution. Precipitation of dimethyl fumarate from its solution in carbon disulphide prevented variable temperature solution studies. However, a similar relationship exists between spectra of solid and liquid states of dimethyl fumarate in the 1100—1300 cm^{-1} region [Figure 2(c)] to that found for the frozen solution and normal temperature solution states for the higher esters.

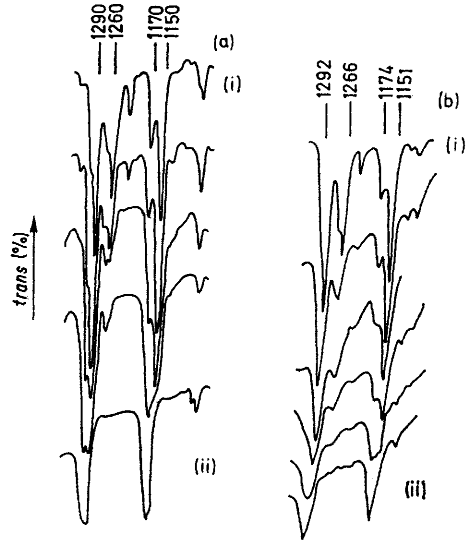


FIGURE 1 I.r. bands between 1100 and 1300 cm^{-1} at 1—3% v/v in CS_2 at 0·1 mm path-length: (i) room temperature; (ii) frozen solution, others at intermediate temperatures. (a) Di-n-butyl fumarate; (b) diethyl fumarate

Comparison of Figures 1(a) and 2(a) illustrates the similarity between spectra of frozen solid and frozen carbon disulphide solutions in the case of di-n-butyl fumarate. The same pattern of bands shown in Figures 1(a), (b), 2(a), and (c) are provided by other difumarates. The wavenumber values of these bands are given in Table 2 to show the degree of consistency.

TABLE 2

I.r. bands in diesters of fumaric acid (1100—1300 cm^{-1} region) [a]

Di-isopropyl fumarate	1300	1260	1225	1175	1160
Di-n-propyl fumarate	1290	1250	1220	1170	1150
Dipentyl fumarate	1292	1258	1222	1170	1152
Dihexyl fumarate	1292	1255	1220	1170	1150
Diheptyl fumarate	1295	1257	1220	1170	1152
Dioctyl fumarate	1295	1260	1225	1172	1155
Bis-(3,5,5-trimethylhexyl) fumarate	1290	1260	1220	1170	1150
Di-lauryl fumarate	1295	1260	1220	1175	1155

[a] From the D.M.S. Collection, Butterworths, London.

Other temperature dependent effects in fumarates were observed. In all three diesters a band near 1640 cm^{-1} in the liquid state was absent from the solid state. A sharp though weak peak at 3080 cm^{-1} in dimethyl, diethyl, and di-n-butyl fumarate was observed in the solid state. A corresponding band in the liquid state was not observed in the case of the n-butyl ester. Weak bands had been observed in the liquid state spectra of dimethyl and diethyl fumarate near 3060 cm^{-1}. All these features were also apparent in the spectra of solutions and frozen solutions. A sharp peak at 938 cm^{-1} in di-n-butyl fumarate was present in the solid and absent in the spectra of the liquid solution and frozen solution and it was concluded that this band was not associated with conformational equilibrium. No other significant temperature change was observed in the region 4000—400 cm^{-1}.

Maleates.—Considerable intensification and band splitting were observed in the i.r. spectra of the frozen solids for dimethyl, diethyl, and di-n-butyl maleates. However, comparison of solid and liquid states as well as comparison of solution and frozen solution states failed to reveal any differences attributable to conformational changes. Comparison of the temperature effects on the i.r. spectra of di-n-butyl fumarate and maleate in the 1100—1300 cm^{-1} region is shown in Figure 2(a) and (b). This illustrates the marked distinction between the corresponding esters of fumaric and maleic acid with respect to the temperature dependencies of their i.r. spectra.

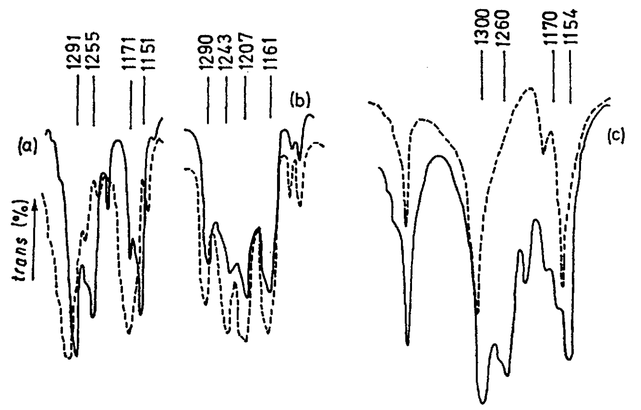
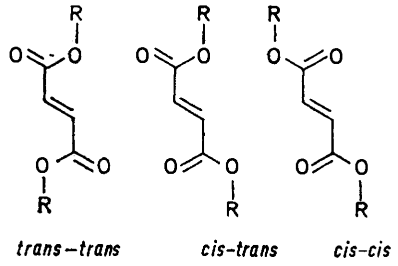


FIGURE 2 I.r. bands between 1100 and 1300 cm^{-1} as thin films; (i) liquid state (full line); (ii) solid state (dotted line). (a) Di-n-butyl fumarate; (b) di-n-butyl maleate; (c) dimethyl fumarate

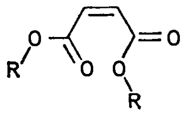
Conformational Equilibria.—The existence of marked temperature effects in the spectra of each of the three fumarates studied and the absence of these effects in the spectra of the three maleates suggests that a conformational change occurs in the fumarate series only. The marked similarity between these effects in the three fumarates suggests that this change is associated with the common skeleton rather than with the different alkyl substituents. Molecular models show the possibility of conformational changes in fumarates which are excluded in maleates by steric forces. These are shown in Scheme 2. The nature of the conformers present under particular conditions cannot be conclusively determined by vibrational spectroscopy but some tentative deductions may be made using symmetry considerations. The *trans–trans* and *cis–cis* conformers have a centre of symmetry and the totally symmetric vibrations should be absent from the i.r. spectrum. The *trans–cis* and the equivalent *cis–trans* conformers have only a plane of symmetry and all vibrations should be present in the i.r. spectrum. The band near 1640 cm^{-1} observed in the liquid state of the three fumarates is the symmetric C=C stretching vibration. This is absent from the solid state suggesting the conformation is largely *cis–trans* in the liquid (high energy conformer) but either *trans–trans* or *cis–cis* in the solid (low energy conformer). All other fundamentals occur in pairs corresponding to in-phase (symmetric) or out-of-phase (antisymmetric) vibrations. The separation between the pairs is small if the separation of groups largely associated with the vibrations is large. Only one band is observed in the olefinic C–H stretching region for each of the esters and only one band is observed in the carbonyl region in each case. This suggests the symmetric and antisymmetric vibrations are coincident for these particular modes and are, therefore, not likely to show differences attributable to conformational changes. The bands assigned to the olefinic C–H stretching mode occurs near 3060 cm^{-1} in five of the esters but is unobserved in di-n-butyl fumarate. Kingsland and Spedding [6] have noted that this band is clearly visible in the solid but did not observe the equivalent band in the liquid or solution state spectra of certain fumarates. The intensification in the solid state of bands which are weak in the liquid is typical for i.r. spectra of compounds of this type.



SCHEME 2

We may conclude, from their temperature dependence, that bands near 1640, 1260, 1225, and 1150 cm^{-1} in the three difumarates are associated with a high energy conformation (*cis–trans*) and bands near 1290 and 1170 cm^{-1} are associated with a low energy conformation. The existence of two identical conformations increases the entropy of this *cis–trans* form by $R\ln 2$. The enthalpy difference between the high and low energy conformer could be determined from intensity measurements of either the 1290, 1260 or the 1170, 1150 cm^{-1} pair. In all cases the bands are overlapped and have asymmetries suggesting several components. The pair of bands most amenable to quantitative studies are at 1291 and 1255 cm^{-1} in di-n-butyl fumarate. Using the assumptions described previously[1] a value of $\Delta H^\circ = 372 \pm 20$ cal mol^{-1} was calculated on the basis of peak height measurements at eight temperatures between -20 and -100 °C. This is the enthalpy difference between the high and low energy conformers. The standard deviation is a measure of precision but the accuracy is uncertain because of the systematic errors inherent in the assumptions used. We consider the low energy conformer is more likely to correspond to *trans–trans* than *cis–cis* since steric models suggest the π electrons are probably at greater separations in the former leading to a lower potential energy in this molecule. Microwave evidence[5] suggested the analogous *cis*-conformer was present in methyl acrylate. However, in the fumarates the *trans–trans* and *cis–cis* conformers would be inactive in the microwave region.

The absence of detectable temperature effects in the i.r. spectra of the maleates is evidence for the existence of these in a single conformation. Molecular models suggest that the *cis–trans* is likely to be the most stable conformer but it is possible that non-planar conformations exist because of the strong lone pair repulsions which would occur in all planar forms of the dimaleate esters.



cis – trans

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