Conformations of Some Saturated Carbonyl Compounds. Part II.[1] Infrared Spectra of Ethyl Formate, Acetate, Propionate, and n-Butyrate, and $[^2H_5]$Ethyl n-Butyrate

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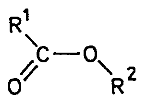
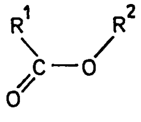
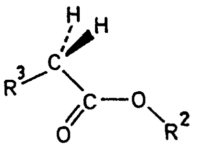
Infrared spectra of ethyl formate, acetate, propionate, and n-butyrate, and $[^2H_5]$ethyl n-butyrate are reported. The effects on these spectra of cooling solutions in carbon disulphide to −100 °C and of solidification are reported and are interpreted in terms of conformational equilibria. Evidence for the presence of one pair of conformers, derived probably from rotation about the O–Et bond, has been found in all the esters examined; an enthalpy difference ($\Delta H°$) of 315 ± 25 cal mol^{-1} between high- and low-energy conformers has been obtained for ethyl acetate. Evidence has also been obtained for the presence of an additional equilibrium in ethyl and $[^2H_5]$ethyl n-butyrates associated with rotations within the n-butyl chain.

IN Part I[1] we summarised the evidence for the more stable form of simple saturated esters being (I) rather than (II), except when R^2 is bulky which causes destabilisation of (I) relative to (II). In the cases of methyl propionate and n-butyrate we reported evidence for the equilibrium (III) $\rightleftharpoons$ (IV), and discussed temperature effects on the spectra of methyl and $[^2H_3]$methyl n-butyrates in terms of a further equilibrium involving the n-butyl chain. Related studies have been made in αβ-unsaturated esters.[2] We now report the corresponding spectra of ethyl esters in relation to the additional conformational equilibrium associated with internal rotation of the O–Et bond (V) $\rightleftharpoons$ (VI). Because four separate conformational equilibria are possible in ethyl n-butyrate, with consequent spectral complexity, a study of $[^2H_5]$ethyl n-butyrate was also included. This study further supports the conformational equilibria suggested.


(I)


(II)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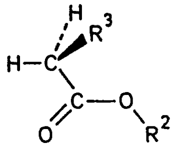
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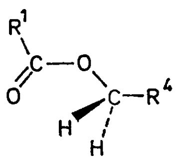
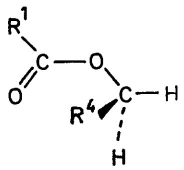

(V)


(VI)

EXPERIMENTAL

Commercial ethyl formate, acetate, propionate, and n-butyrate were fractionally distilled through a 25 cm packed column, a 1 °C cut being collected in each case. $[^2H_5]$Ethyl n-butyrate was made[1] from $[^2H_6]$ethanol (1 ml) and n-butyryl chloride (4 ml). The distillate from the mixture was purified with a Wilkins Autoprep 705 chromatograph equipped with a 6 m Carbowax 20 M column at 100 °C, the $[^2H_5]$ethyl n-butyrate being extracted from the trapping vessel as a solution in carbon disulphide. The structure of the $[^2H_5]$ethyl n-butyrate was checked by ^{1}H n.m.r. and i.r. spectroscopy.

The purity of all samples was checked on a 2 m 5% polyethylene glycol adipate and 1·5 m 10% Apiezon L column in a Perkin-Elmer F11 chromatograph.

I.r. spectra were obtained by use of the methods and conditions described.[1,2] Samples were examined as solutions in carbon disulphide with, in general, a concentration of 10% at 0·2 mm path-length except for ethyl propionate where a 5% solution at 0·2 mm path-length was used. For the more intense bands a concentration range of 1·5—2·5% at 0·1 mm path-length was used. In addition the 650—900 cm^{-1} region of the spectra of ethyl and $[^2H_5]$ethyl n-butyrates was observed by use of a 15% solution at 0·2 mm path-length. Samples were also observed as thin films of liquid and frozen liquid. These studies enabled changes of the solution spectra with temperature to be confirmed.

The integrated absorbances of ethyl acetate were measured in a 10% solution at 0·2 mm path-length. The bands were replotted in linear absorbance by use of transmittance values at intervals of one wavenumber and included, as far as possible, the complete band envelope. Each peak was planimetered five times, the line of demarcation being a perpendicular line drawn from the inter-peak minimum.

RESULTS AND DISCUSSION

The effects of temperature variation on the i.r. spectra of ethyl formate, acetate, propionate, and n-butyrate, and $[^2H_5]$ethyl n-butyrate will be discussed for particular spectral regions. In systems participating in conformational equilibria the same vibrational mode in each pair of conformers may or may not occur at the same

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[1] Part I, W. O. George, D. V. Hassid, and W. F. Maddams, *J.C.S. Perkin II*, 1972, 1029.

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

wavenumber. If these modes occur at different wavenumbers a pair of bands with the following properties may be observed. (1) The band associated with the low-energy form systematically increases in intensity relative to non-conformationally sensitive bands, whilst the band associated with the high-energy form systematically decreases in relative intensity, as the temperature of the system is reduced. (2) On solidification of the solution and on annealing to produce the most thermally stable solid form, the band due to the low-energy form persists and the band due to the high-energy form disappears.

A pair of bands satisfying these two criteria will be referred to as conformer bands and designated as the low-energy band and the high-energy band according to their response to cooling. Assignments are confined to particular conformers rather than to detailed normal modes of vibration for which complementary Raman data are essential.

1230—1400 *cm*$^{-1}$ *Region.*—Conformationally sensitive pairs of bands were not observed in this region of the spectra of ethyl formate, acetate, and propionate. However, weak bands near 1300 cm^{-1} weakened further or were absent on solidification of the solution spectra of these compounds; these changes may be associated with the equilibrium (V) $\rightleftharpoons$ (IV) but the evidence is not clear-cut.

For ethyl and [$^2H_5$]ethyl n-butyrates a pair of conformer bands were observed near 1260 and 1307 cm^{-1}, these being the high-energy band and low-energy band respectively. The behaviour of this pair of bands parallels that of a pair near 1262 and 1310 cm^{-1} in the spectra of methyl and [$^2H_3$]methyl n-butyrates,[1] the changes in this case being attributed to a rotation involving the n-butyl chain. The use of bands at 1260 and 1307 cm^{-1} to obtain a $\Delta H°$ value was precluded by band overlap. Other changes in the 1230—1400 cm^{-1} region of the spectra of ethyl and [$^2H_5$]ethyl n-butyrates may be associated with the same equilibrium.

1150—1250 *cm*$^{-1}$ *Region.*—The two i.r. bands at 1186 and 1155 cm^{-1} of ethyl formate appear to be the analogues of the bands at 1206 and 1158 cm^{-1} of methyl formate assigned [3,4] to two different modes in a single conformer. We find no evidence that the 1186 and 1155 cm^{-1} bands in ethyl formate are a pair of conformer bands.

In the i.r. spectra of various methyl esters of saturated and unsaturated esters [1,2] two bands near 1200 cm^{-1} of similar intensities were identified as conformer bands. It was considered that the conformational splitting is less pronounced in [$^2H_3$]methyl and ethyl esters and this conclusion is supported in the present work.

900—1150 *cm*$^{-1}$ *Region.*—Significant temperature effects were observed in all the compounds. A pair of conformer bands occurs near 1100 cm^{-1}. The low-energy band is observed in the range 1113—1118 cm^{-1} and the high-energy band in the range 1094—1100 cm^{-1} for each compound, except in the spectrum of [$^2H_5$]ethyl n-butyrate where the low- and high-energy bands occur at 1097 and 1086 cm^{-1} respectively. A second pair of conformer bands, somewhat variable in wavenumber, occurs in all cases, the higher-wavenumber band of each pair being the low-energy band. This pair of bands occur at 1012 and 1004 cm^{-1} in the spectrum of ethyl formate, 939 and 917 cm^{-1} in ethyl acetate, 1084 and 1075 cm^{-1} in ethyl propionate, 946 and 932 cm^{-1} in ethyl n-butyrate, and at 978 and 955 cm^{-1} in [$^2H_5$]ethyl n-butyrate; the band at 955 cm^{-1} in the last case persisted in the i.r. spectrum of the solidified solution.

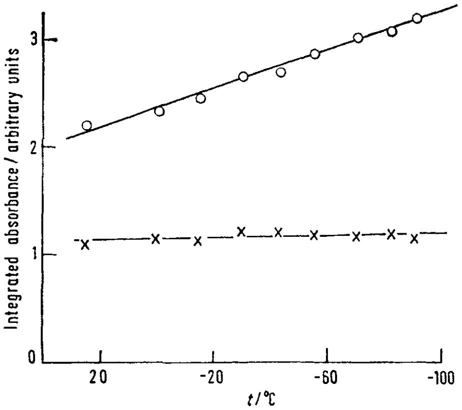

FIGURE 1 Integrated absorbances of bands in ethyl acetate at 10% (v/v) in CS_2 and 0·2 mm path-length at different temperatures: ×, 917 cm^{-1}; ○, 939 cm^{-1}

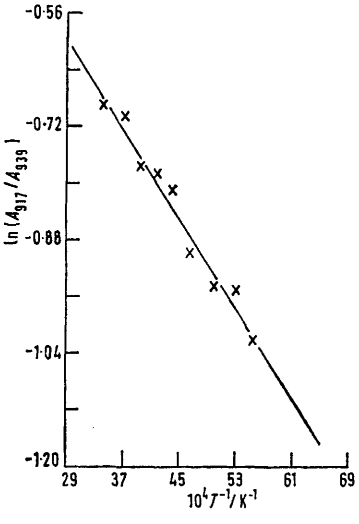

FIGURE 2 Temperature-dependence of absorbance ratios for ethyl acetate in CS_2 solution

The relative freedom from overlap of the 939 and 917 cm^{-1} pair of bands in the spectrum of ethyl acetate enabled the integrated absorbances to be obtained. These are shown in Figure 1. The intensity of the low-energy band at 939 cm^{-1} increases systematically with decreasing temperature whereas that of the high-energy band at 917 cm^{-1} increases only very slightly. However, if the effect of change in density of solvent with

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[3] J. K. Wilmshurst, *J. Mol. Spectroscopy*, 1957, **1**, 201.
[4] H. Susi and T. Zell, *Spectrochim. Acta*, 1963, **19**, 1933.

temperature is allowed for, the intensity of the high-energy band at 917 cm^{-1} does not vary significantly with temperature. Since the concentration of high-energy conformer decreases with decreasing temperature the absorption coefficient of both bands must increase with decreasing temperature. The ΔH° value was determined by assuming that the ratio of the absorption coefficients remained constant with temperature by plotting[2] ln (A_{917}/A_{939}) against $1/T$ (Figure 2). This procedure leads to a value of $\Delta H^\circ = 315 \pm 25$ cal mol^{-1}. It was not possible to determine ΔS° values by methods discussed previously.[2]

The absence of analogous changes from the 900—1150 cm^{-1} region of the spectra of the methyl esters is supporting evidence for an equilibrium of the type (V) $\rightleftharpoons$ (VI) in the ethyl esters.

650—900 cm^{-1} Region.—In the 650—900 cm^{-1} region of the spectrum of ethyl formate no pair of conformer bands was observed, although a band at 746 cm^{-1} present in the liquid-state spectrum was absent from that of the solidified solution. In ethyl acetate an overlapping pair of bands at 847 and 853 cm^{-1} was identified as conformer bands, the higher-wavenumber component being the low-energy band. In the i.r. spectrum of ethyl propionate three pairs of conformer bands were observed at 895 and 887, at 865 and 860, and at 805 and 790 cm^{-1}. In all cases the lower-wavenumber component is the high-energy band. Since no comparable data were observed in the spectra of the methyl analogues these results are probably associated with the equilibrium (V) $\rightleftharpoons$ (VI).

In the spectra of ethyl and [^{2}H$_5$]ethyl n-butyrates a pair of conformer bands was observed at 749 and 773 and at 749 and 771 cm^{-1} respectively, the lower-wavenumber component of each pair being the low-energy band; similar results observed in the spectra of methyl and [^{2}H$_3$]methyl n-butyrates[1] are associated with an equilibrium involving the $\beta\gamma$-C–C bond on the n-butyl chain. Other changes with temperature in this region of the spectra are given in the Table. It is not possible to relate these changes to a particular equilibrium.

The i.r. wavenumbers (1400—650 cm^{-1}) of ethyl formate, acetate, propionate, and n-butyrate and [^{2}H$_5$]ethyl n-butyrate as solutions in carbon disulphide at various temperatures (+30 °C)—(−150 °C)

Ethyl formate: 1385m—1382vs, 1377w,sh—absent, 1367w,sh—1354m, 1301m—absent, 1295w,sh—absent, 1280vw,b,sh—1276w, absent—1260vw,b,sh, absent—1232m, 1186vs—1207vs, absent—1195m,sh, 1155vs—1156m, 1113m—1113vs, 1100m,sh—absent, 1050vw,sh—1050vw, 1012m—1010vs, 1004m,sh—998vw,sh, 878vw,sh—880vw, 842m—839vs, 812w—819m, 785vw—775vw, 746w—absent

Ethyl acetate: 1391m—1400m, absent—1377s,sh, 1371vs—1371s, 1358m—1360m, 1315vw,sh—1317w, 1300w—1300vw,sh, 1265m,sh—1269vs, 1241vs—1250vs, absent—1223s, absent—1167w,sh, 1158vw,b,sh—1158w,sh, 1113w,sh—1123s, 1098w—absent, 1070w,sh—1070vw,sh, absent—1049vs,sh, 1047vs—1044vs, 1003vw,sh—1006m, 939w—942m, 917w—absent, 853vw,sh—853s, 847w—absent, absent—821w, 807vw,sh—813w, 785w—absent, 635w—637s, 607w—606s

Ethyl propionate: 1389w,sh—1379w,sh, 1370s—1370s, 1345s—1345s, 1326w,sh—absent, 1301vw,sh—absent, 1271w—1265vw,sh, 1225m,sh—1229w,sh, 1187vs,b—1190vs,b, 1167m,sh—1160w,sh, 1114w,sh—1119m, 1097m,sh—absent, 1084s—1088s, 1075m,sh—absent, 1034s—1027vs, 990vw,sh—1009w, 895vw,sh—898m, 887vw,sh—absent, 865w—867s, 860vw,sh—absent, 805m—805vs, 790w,sh—absent

Ethyl n-butyrate: 1392w,sh—1398m, 1378m,sh—1382s, 1370s—1369w,sh, 1351m—absent, 1344m,sh—absent, 1335w,sh—1330vw,sh, absent—1313vs, 1303s—1306vs, absent—1291m, 1285m,sh—1285m,sh, 1265m,sh—absent, 1253s—absent, 1234m,sh—1235w,sh, absent—1208vs,sh, 1183vs,b—1188vs,b, 1166m,sh—1166m,sh, absent—1125m, 1118m,sh—1118m, 1102s,sh—1115vw,sh, 1094s—absent, 1080m,sh—absent, 1052m—absent, 1045m,sh—1042w,sh, 1028s—1036vs, 946vw,sh, 954m, 932w—absent, 921w,sh—absent, 900vw,sh—904vw, 893vw,sh—absent, 877vw,sh—879w, 869w,sh—865vs, 855w—absent, absent—822w, 807vw,sh—811vw,sh, 797w—absent, 773w—absent, absent—751s, 749w—749s, absent—717m, 675vw—absent

[^{2}H$_5$]Ethyl n-butyrate: 1380s,sh—1388vs, 1362s—absent, 1352s,sh—absent, 1341w,sh—1343vw,sh, 1308s—1310s, 1288s,sh—1293m,sh, 1267vs—absent, 1230s,sh—absent, 1193s,sh—1219s,sh, 1180vs,b—1190vs, absent—1135vw,sh, 1109m,sh—1118s, 1097s,sh—1099vs, 1086s—absent, 1061s—1066s, 1050s—1055m,sh, absent—1044s, absent—1033m, 1020w,sh—absent, absent—995vw,sh, 978m—977vs, 955m—961w, 943w,sh—absent, 913vw—913m, 888vw,sh—899m, absent—894m, absent—883m, 872w—879m,sh, 860vw,sh—865w, 842vw,sh—absent, 791vw—absent, 771vw—absent, absent—753vs, 749w—748vs,sh, absent—738vw, 729vw—absent, absent—717vw, absent—702m

sh = Shoulder, s = strong, m = medium, w = weak, v = very, b = broad.

Conformational Equilibria.—In summary, two conformational equilibria, (I) $\rightleftharpoons$ (II) and (V) $\rightleftharpoons$ (VI), are possible in ethyl formate and acetate, a third equilibrium is possible in ethyl propionate, (III) $\rightleftharpoons$ (IV), and a fourth equilibrium is possible in ethyl and [^{2}H$_5$]-ethyl n-butyrates associated with the additional degree of freedom derived from rotation of the terminal ethyl group about the $\beta\gamma$-C–C bond on the n-butyl chain.

The equilibrium (I) $\rightleftharpoons$ (II) is undetectable in any ester studied. Calculations based on the range of values generally obtained[5-7] for the difference in energy between structures (II) and (I) indicate that the concentration of (II) is too small to be detectable in the i.r. spectra.

Evidence for the equilibrium (V) $\rightleftharpoons$ (VI) is described in the present paper for ethyl formate, acetate, propionate, and n-butyrate. This equilibrium has been detected in ethyl formate by microwave[8] studies which indicate that the more stable form is *trans* (V) with a planar skeleton of heavy atoms, whilst the less stable form is *gauche* (VI) in which the methyl group is 95° to the plane of the molecule. Relative intensity measurements[8] suggest a difference in energy of 186 ± 60 cal mol^{-1} between these two forms. Our value, $\Delta H^\circ = 315 \pm 25$ cal mol^{-1}, between structures (VI) and (V) for ethyl acetate is significantly higher than that of ethyl formate. It is hoped that further work will enable the relative stabilities of these conformers to be understood.

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[5] S. V. Subrahmanyan and J. E. Piercy, *J. Acoust. Soc. Amer.*, 1965, **37**, 340.

[6] J. E. Piercy and S. V. Subrahmanyan, *J. Chem. Phys.*, 1965, **42**, 1475.

[7] J. Bailey and A. M. North, *Trans. Faraday Soc.*, 1968, **64**, 1499.

[8] J. M. Riveros and E. B. Wilson, *J. Chem. Phys.*, 1967, **46**, 4605.

Evidence for the equilibrium (III) $\rightleftharpoons$ (IV) has been presented[1] for methyl propionate and methyl n-butyrate and the absence of conformational splitting in the corresponding [$^2H_3$]methyl and ethyl esters has been discussed[1,2] in terms of conformationally sensitive coupling between the methyl group and the C–C–O stretching vibration of the ester grouping.

The fourth equilibrium detected in ethyl and [$^2H_5$]-ethyl n-butyrate appears to be similar to that in methyl and [$^2H_3$]methyl n-butyrate.[1] There is no direct evidence for the nature of this equilibrium but it is almost certainly associated with the additional internal rotation possible in the n-butyrate chain compared with the propionate chain.

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