Infrared Examination of Rotational Isomerism in Alkyl Furan-2-carboxylates: Determination of Thermodynamic Parameters from Infrared Data

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Solutions of 66 alkyl furan-2-carboxylates in carbon tetrachloride and in acetonitrile have been examined at high dispersion in the i.r. C=O region. In carbon tetrachloride one ester shows four bands, eight show single bands, and 57 show well separated doublets. With one exception, the doublets are the consequence of rotational isomerism between *syn-s-trans-* and *anti-s-trans-*forms. The higher wavenumber component of a doublet arises from the form with the higher dipole moment and the higher enthalpy: this form is very probably the *syn-s-trans-*rotamer. The failure of attempts to obtain reliable free energy and entropy differences reveals the shortcomings of standard approaches to the determination of energy differences between rotational isomers from i.r. data.

DURING a general investigation into rotational isomerism of furan derivatives possessing a C=O group at position 2 several series of furan-2-carboxylic esters (methyl, ethyl, and t-butyl) containing deuterio-, halogeno-, and nitro-substituents were prepared; [1a-d] the present paper is concerned with the absorptions of the esters in the i.r. carbonyl region. Our main purpose was to see whether the spectra provide evidence for the occurrence of rotational isomerism in these esters and, if so, whether the absorptions could be correlated with particular conformations.[1e] This led on to an extension of earlier work [2a] on methods for obtaining energy differences between rotational isomers from i.r. data. It transpired that only the enthalpy differences could be assessed in this way. Attempts to evaluate reliable free energy differences were unsuccessful; this being so, and since the topic requires detailed theoretical treatment of a large volume of experimental results, the material dealing with free energy differences is not reported here. [It is available as Supplementary Publication No. SUP 21625 (14 pp.).†]

Origin of Multiple Absorptions in the Carbonyl Region. —Of the 66 esters (Table 1) examined in carbon tetrachloride solution one (9a) shows four bands, eight show

single bands, and 57 show well separated doublets. (Although the data in Table 1 for esters giving more than one band refer to the components obtained by curve resolution, the doublet nature of the absorptions found with most of the esters is clearly evident from the experimental traces.) Since the relative intensities of the component bands are not influenced by the concentrations of the solutions (in the range *ca.* 10—0.1 g l⁻¹) the multiplet absorptions do not arise from intermolecular interactions. Distinction between other possible causes (the occurrence of rotational isomerism, Fermi resonance, and hot transitions) was made by the approaches discussed recently in work on furan-2-carbaldehydes,[2b] *viz.*, (i) studying the spectra over a range of temperature, (ii) examining the absorptions in the fundamental and overtone regions, (iii) changing the solvent (carbon tetrachloride) to one of much higher dielectric constant (acetonitrile), and (iv) comparing the spectra of particular protio-esters with those of their deuterio- and bromo-analogues. The results ‡ of approach (i) exclude the (unlikely) possibility that the

† For details of Supplementary Publications see Notice to Authors No. 7 in *J.C.S. Perkin II*, 1975, Index Issue.

‡ A conspectus of the results appears in the Supplementary Publication; the complete set is given by R. L. Snowden, D.Phil. Thesis, Oxford, 1973.

[1] D. J. Chadwick, J. Chambers, G. D. Meakins, and R. L. Snowden, *J.C.S. Perkin I*, (a) 1973, 201; (b) 1973, 1766; (c) D. J. Chadwick, J. Chambers, P. K. G. Hodgson, G. D. Meakins, and R. L. Snowden, *ibid.*, 1974, 1141; D. J. Chadwick, J. Chambers, G. D. Meakins, and R. L. Snowden (d) *J.C.S. Perkin I*, 1975, 523; (e) *Chem. Comm.*, 1971, 625.
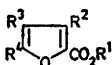[2] D. J. Chadwick, J. Chambers, G. D. Meakins, and R. L. Snowden, *J.C.S. Perkin II*, (a) 1972, 1959; (b) 1975, 13; (c) D. J. Chadwick, G. D. Meakins, and E. E. Richards, *Tetrahedron Letters*, 1974, 3183.

Esters [a] were examined as described previously [b] at a spectral slitwidth of 1.5 cm^{-1} on a spectrometer purged continuously with dry air. Solutes and solvents were dried immediately before use, and solutions were made up in a dry box. Band positions (at 303 K) are in cm^{-1}; where more than one band is shown the experimental trace was resolved into symmetrical components using an analogue computer, and the component positions are followed, in parentheses, by their relative absorbances. Enthalpy differences (ΔH^0 J mol^{-1}, statistical error ± 300 J mol^{-1}) between the forms giving doublet absorptions are for the direction form with higher cm^{-1} $\longrightarrow$ form with lower cm^{-1}.

TABLE 1

Series of alkyl furan-2-carboxylates

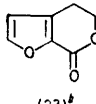| Ester	R¹	R²	R³	R⁴	CO Fundamental region CCl₄		MeCN		CO Overtone region CCl₄			ΔH⁰
(1a)	Me	H	H	H	1 740 (1)	1 725 (0.94)	1 733 (1)	1 725 (0.77)	3 469 (1)	3 437 (1)	3 424 (0.91)	—900
(2a)	Me	H	H	D	1 740 (1)	1 725(0.91)						
(3a)	Me	H	D	H	1 742 (1)	1 727 (0.98)	1 733 (1)	1 723 (0.71)	3 467 (0.81)	3 438 (1)		
(4a)	Me	D	H	H	1 741 (1)	1 727 (0.93)	1 732 (1)	1 722 (0.70)	3 468 (0.83)	3 436 (1)		
(5a)	Me	H	D	D	1 743 (1)	1 728 (0.95)	1 733 (1)	1 724 (0.73)	3 468 (0.81)	3 440 (1)		
(6a)	Me	D	D	H	1 738 (1)	1 725 (0.97)	1 731 (1)	1 722 (0.69)	3 468 (0.82)	3 435 (1)		
(7a)	Me	D	H	D	1 741 (1)	1 726 (0.94)	1 732 (1)	1 723 (0.72)	3 468 (0.82)	3 438 (1)		
(8a)	Me	D	D	D	1 742 (1)	1 727 (1)	1 735 (1)	1 724 (0.77)	3 468 (0.80)	3 438 (1)		
(1b)	Et	H	H	H	1 734 (0.90)	1 718 (1)	1 726 (1)	1 717 (0.83)	3 453 (0.83)	3 422 (1)		—1 900
(2b)	Et	H	H	D	1 734 (0.90)	1 718 (1)						
(3b)	Et	H	D	H	1 737 (0.83)	1 721 (1)	1 729 (1)	1 717 (0.84)	3 452 (0.82)	3 420 (1)		
(4b)	Et	D	H	H	1 734 (0.85)	1 720 (1)	1 727 (1)	1 715 (0.83)	3 448 (0.85)	3 422 (1)		
(5b)	Et	H	D	D	1 738 (0.85)	1 722 (1)	1 729 (1)	1 717 (0.82)	3 454 (0.83)	3 424 (1)		
(6b)	Et	D	D	H	1 735 (0.89)	1 718 (1)	1 726 (1)	1 715 (0.81)	3 448 (0.84)	3 420 (1)		
(7b)	Et	D	H	D	1 737 (0.86)	1 721 (1)	1 728 (1)	1 717 (0.83)	3 452 (0.85)	3 421 (1)		
(8b)	Et	D	D	D	1 736 (0.89)	1 720 (1)	1 728 (1)	1 716 (0.90)	3 454 (0.86)	3 422 (1)		
(1c)	Bu^t	H	H	H	1 729 (1)	1 711 (1)	1 719 (1)	1 710 (0.83)	3 440 (0.87)	3 408 (1)		—2 500
(2c)	Bu^t	H	H	D	1 729 (1)	1 711 (1)						
(3c)	Bu^t	H	D	H	1 731 (1)	1 714 (0.95)	1 722 (1)	1 709 (0.87)	3 438 (0.87)	3 406 (1)		
(4c)	Bu^t	D	H	H	1 730 (1)	1 712 (1)	1 721 (1)	1 708 (0.77)	3 436 (0.90)	3 408 (1)		
(5c)	Bu^t	H	D	D	1 732 (1)	1 715 (0.97)	1 722 (1)	1 709 (0.81)	3 442 (0.90)	3 407 (1)		
(6c)	Bu^t	D	D	H	1 729 (1)	1 712 (0.94)	1 720 (1)	1 707 (0.79)	3 436 (0.88)	3 404 (1)		
(7c)	Bu^t	D	H	D	1 731 (1)	1 714 (0.98)	1 720 (1)	1 707 (0.82)	3 438 (0.87)	3 406 (1)		
(8c)	Bu^t	D	D	D	1 729 (1)	1 712 (0.98)	1 719 (1)	1 707 (0.84)	3 438 (0.95)	3 405 (1)		
(9a)	Me	H	H	Br	⎰1 748 0.59) ⎱1 731 (1)	1 738 (0.94) 1 720 (0.88) †	1 731 (1)	1 719 (0.67)	3 466 (0.71)	3 431 (1)		
(10a)	Me	D	D	Br	1 743 (0.77)	1 729 (1)	1 731 *					
(11a)	Me	H	H	Cl	1 745 (0.69)	1 728 (1)	1 736 (1)	1 725 (0.98)	3 468 (0.65)	3 436 (1)		-2 500
(12a)	Me	H	H	I	1 743 (0.76)	1 727 (1)	1 736 (1)	1 725 (1)	3 466 (0.77)	3 432 (1)		—1 500
(13a)	Me	H	H	NO₂	1 756 (0.46)	1 737 (1)	1 744 (1)	1 735 (0.98)	3 490 (0.50)	3 454 (1)		—1 100
(14a)	Me	H	Br	H	1 746 (1)	1 728 (1)	1 738 (0.83)	1 727 (1)				—1 200
(15a)	Me	H	Br	D	1 747 (1)	1 729 (0.88)	1 739 (1)	1 726 (0.72)	3 470 (1)	3 442 (0.89)		
(16a)	Me	H	Br	Br	1 745 (0.89)	1 730 (1)	1 737 (1)	1 726 (0.60)	3 476 (0.90)	3 444 (1)		—1 600
(17a)	Me	H	Br	Cl	1 746 (1)	1 729 (0.90)	1 739 (1)	1 726 (0.68)	3 474 (1)	3 438 (1)		—1 500
(18a)	Me	H	I	H	1 746 (1)	1 728 (0.84)	1 737 (1)	1 725 (0.69)	3 472 (1)	3 440 (0.92)		—1 500
(19a)	Me	H	I	D	1 744 (1)	1 727 (0.85)	1 735 (1)	1 724 (0.71)	3 472 (1)	3 440 (0.88)		
(20a)	Me	Br	H	H	1 733 *		1 727 *					
(21a)	Me	Br	H	Br	1 732 *		1 726 *					
(22a)	Me	I	H	H	1 731 *		1 726 *					
(9b)	Et	H	H	Br	1 735 (0.67)	1 719 (1)	1 726 (1)	1 716 (0.83)	3 455 (0.68)	3 423 (1)		—700
(10b)	Et	D	D	Br	1 736 (0.63)	1 719 (1)	1 727 (1)	1 716 (0.83)				
(11b)	Et	H	H	Cl	1 741 (0.76)	1 722 (1)	1 729 (1)	1 717 (0.86)	3 454 (0.75)	3 422 (1)		—2 000
(12b)	Et	H	H	I	1 737 (0.65)	1 720 (1)	1 727 (0.95)	1 715 (1)	3 450 (0.71)	3 420 (1)		—2 600
(13b)	Et	H	H	NO₂	1 747 (0.45)	1 728 (1)	1 738 (1)	1 726 (0.83)	3 478 (0.47)	3 440 (1)		—1 600
(14b)	Et	H	Br	H	1 739 (0.91)	1 724 (1)	1 730 (1)	1 722 (0.83)				—400
(15b)	Et	H	Br	D	1 740 (1)	1 725 (0.93)	1 732 (1)	1 721 (0.74)	3 458 (1)	3 430 (0.95)		
(16b)	Et	H	Br	Br	1 741 (0.92)	1 725 (1)	1 733 (1)	1 723 (0.84)	3 464 (0.94)	3 428 (1)		—1 500
(17b)	Et	H	Br	Cl	1 741 (0.82)	1 723 (1)	1 734 (1)	1 721 (0.89)	3 464 (0.79)	3 430 (1)		—1 600
(18b)	Et	H	I	H	1 740 (1)	1 724 (0.98)	1 732 (1)	1 719 (0.76)	3 458 (1)	3 430 (1)		-1 600
(19b)	Et	H	I	D	1 740 (1)	1 724 (0.95)	1 731 (1)	1 719 (0.72)	3 458 (1)	3 430 (0.98)		
(20b)	Et	Br	H	H	1 727 *		1 721 *					
(21b)	Et	Br	H	Br	1 727 *		1 721 *					
(22b)	Et	I	H	H	1 726 *		1 719 *					
(9c)	Bu^t	H	H	Br	1 729 (0.91)	1 711 (1)	1 719 (1)	1 710 (0.83)	3 446 (0.59)	3 409 (1)		—1 900
(10c)	Bu^t	D	D	Br	1 731 (0.67)	1 712 (1)	1 721 (1)	1 711 (1)				
(11c)	Bu^t	H	H	Cl	1 733 (0.80)	1 712 (1)	1 724 (1)	1 709 (0.93)	3 442 (0.81)	3 408 (1)		—2 000
(12c)	Bu^t	H	H	I	1 728 (0.64)	1 710 (1)	1 720 (1)	1 708 (0.88)	3 440 (0.64)	3 404 (1)		—1 500
(13c)	Bu^t	H	H	NO₂	1 742 (0.49)	1 722 (1)	1 731 (1)	1 718 (0.88)	3 465 (0.52)	3 425 (1)		—2 600
(14c)	Bu^t	H	Br	H	1 734 (1)	1 718 (0.91)	1 724 (1)	1 717 (0.77)				—1 500
(15c)	Bu^t	H	Br	D	1 732 (1)	1 717 (0.96)	1 724 (1)	1 714 (0.57)	3 442 (1)	3 415 (0.98)		
(16c)	Bu^t	H	Br	Br	1 735 (0.86)	1 715 (1)	1 729 (0.93)	1 714 (1)	3 450 (0.92)	3 414 (1)		—2 500
(17c)	Bu^t	H	Br	Cl	1 733 (0.81)	1 717 (1)	1 728 (0.95)	1 717 (1)	3 444 (0.90)	3 414 (1)		—1 300
(18c)	Bu^t	H	I	H	1 733 (1)	1 717 (0.88)	1 724 (1)	1 712 (0.66)	3 444 (1)	3 416 (0.88)		—700
(19c)	Bu^t	H	I	D	1 733 (1)	1 717 (0.90)	1 724 (1)	1 714 (0.63)	3 444 (1)	3 416 (1)		
(20c)	Bu^t	Br	H	H	1 723 *		1 715 *					
(21c)	Bu^t	Br	H	Br	1 722 *		1 717 *					
(22c)	Bu^t	I	H	H	1 726 (1)	1 718 (1) †	1 713		3 436			

* Unsymmetrical band.   † Fermi resonance (see text).   [a] Ref. 1.   [b] Ref. 2.

doublets arise consistently from hot transitions; those of the other approaches (Table 1) establish that rotational isomerism is generally responsible for the gross features of the band doubling. (Effects probably arising from the operation of Fermi resonance are discussed later.

absorptions is observed for only two compounds, ester (9a), which has the four component absorption in carbon tetrachloride, and ester (22c); and replacement of protium by deuterium at the 3-, 4-, and 5-positions of the ring causes little change in the form of the absorptions

TABLE 2

Comparison of the lactone (23) with ethyl furan-2-carboxylate (1b)

The figures in square brackets are the areas of component bands expressed as percentages of the total area of the doublet at 258 K;[a] the figures in parentheses are relative absorbances, as in Table 1

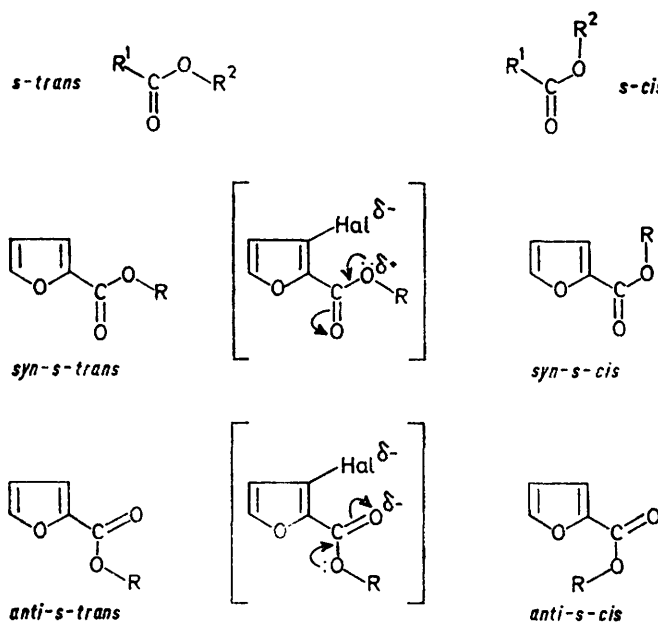|		CO Fundamental region				CO Overtone region
	$T(K)$	CCl$_4$		MeCN		CCl$_4$
(23)[b]	258	1 755 [80.0]	1 737 [20.0]			
	303	1 756 [76.5]	1 737 [13.5]	1 748 (0.58)	1 733 (1)	3 486
	348	1 758 [73.0]	1 737 [5.5]			
(1b)	258	1 733 [55.0]	1 717 [45.0]			
	303	1 734 [53.5]	1 718 [39.0]	1 726 (1)	1 717 (0.83)	3 453 (0.87) 3 422 (1)
	348	1 735 [52.5]	1 719 [34.0]			

[a] Ref. 2a.   [b] Ref. 1d.

Variable temperature ^{1}H n.m.r. measurements of the furan esters were not informative, but evidence for rotational isomerism in t-butyl furan-2-carboxylate was obtained from ^{13}C n.m.r. studies.[2c]) Thus, esters giving doublets in the fundamental region give doublets also

SCHEME   Conformations of esters

in the overtone region,[3] and for a particular ester the relative intensities of its doublet components in the two regions are similar; dramatic solvent dependence of the

except for ester (9a) where the four component absorption collapses to a doublet in the 3,4-dideuterio-derivative (10a).

Support for this attribution of the ester multiple absorptions is provided by studying the lactone [1d] (23) which for the present purpose (i.e. neglecting fluxional motions in the six-membered ring) is a 'fixed conformation ester.' The doublet absorption of the lactone (Table 2) cannot arise from rotational isomerism: detailed examination suggests that Fermi resonance is responsible for the band doubling here, and the spectrometric behaviour of the lactone is markedly different from that of a typical ester, ethyl furan-2-carboxylate (1b), shown for comparison in Table 2.

Positions and Assignments of C=O Bands.—Extensive investigations of a variety of esters by several methods have established that planar conformations are preferred unless they involve severe steric repulsions; further, esters in general adopt the s-trans-arrangement (Scheme) exclusively or predominantly.* While it is agreed [4–6] that the s-cis-form is present to a significant extent only when the structural situation is unusual (notably with esters of formic acid), there is an unresolved conflict about the results and interpretation of some i.r. studies. Thus, Oki and Nakanishi contend that detection of the s-cis-form is restricted to formates of tertiary alcohols and examination in polar solvents,[4a] whereas Morgan and his collaborators believe that this is possible with formates in general and examination in a range of solvents.[6] Different values for the wavenumber separation of the forms (s-cis — s-trans) are also given: ca. 10 cm^{-1} in acetonitrile,[4a] and ca. 20—30 cm^{-1} in several solvents.[6] It may be noted that the positions

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* The methods used, and the main conclusions, are given in refs. 4—6.

[3] C. Goldenberg and F. Binon, *Bull. Soc. chim. belges,* 1966, **75**, 129 appear to be the first to have reported doublets in the fundamental and overtone regions of the spectra of several heterocyclic esters; we were not aware of this work at the time of our preliminary publication.[1e]

[4] M. Oki and H. Nakanishi, *Bull. Chem. Soc. Japan,* (a) 1970, **43**, 2558; (b) 1971, **44**, 3144; (c) 1971, **44**, 3197.
[5] W. O. George, D. V. Hassid, and W. F. Maddams, *J.C.S. Perkin II,* 1973, 952, and earlier papers listed there.
[6] J. S. Byrne, P. F. Jackson, and K. J. Morgan, *J.C.S. Perkin II,* 1973, 845.

of the C=O bands of six-membered lactones, which are necessarily in the s-cis-form, are very close to those of analogous acyclic esters: [7] this is difficult to reconcile with the analysis of ref. 6.

The methyl and ethyl esters involved here do not have any of the special structural features which would be expected to destabilise the s-trans-form, and even with the t-butyl esters this form should be markedly preferred (cf. t-butyl formate and acetate [4b]). Between the three types of ester there are the usual wavenumber differences (methyl > ethyl > t-butyl) but no major systematic variations in the relative intensities or the wavenumber separations of corresponding doublet components. The conformational preferences must, therefore, be common to the three types, and since the doublet components have almost equal intensities in many cases it is extremely unlikely that any of the absorptions arise from s-cis-forms. Thus, of the four possible planar conformations (Scheme) the syn-s-trans- and anti-s-trans-forms are taken to be responsible for the doublets. The positions of the higher wavenumber components of the doublets are more sensitive than those of the lower wavenumber components towards solvent polarity, and as the dielectric constant of the solvent is increased the higher wavenumber components become relatively more intense: both observations show that the rotamers responsible for the higher wavenumber bands have higher dipole moments than those associated with the lower wavenumber bands.

Introduction of halogen substituents at position 4 of the heterocyclic ring increases the wavenumbers of the C=O bands, while halogens at position 5 have little effect: bearing in mind the lower electron-withdrawing tendency of an ester group compared with that of a formyl group, these results can be interpreted as discussed earlier for furan-2-carbaldehydes.[2b] However, apart from one ester, the 3-halogenated compounds have single C=O bands.* [The results in Table 1 demonstrate that Fermi resonance operates with the exceptional ester, t-butyl 3-iodofuran-2-carboxylate (22c).] The field effect arising from almost parallel C–Hal and C=O dipoles in an anti-s-trans-form of a 3-halogeno-ester (Scheme) would be expected to increase the wavenumber

of its absorption by 20 cm^{-1} (cf. α-halogenated ketones [7]) relative to that of an anti-s-trans-5-halogenated isomer band. In contrast, with the syn-s-trans-rotamers the 3-halogenated ester (Figure 1) should have the lower wavenumber since the field effect here will enhance the $+M$ effect of the alkoxy-group. (Esters of certain 3-alkylfuran-2-carboxylic acids exhibit well defined carbonyl doublets,[1d] which shows that the appearance of only single bands with the 3-halogeno-esters is not simply a result of steric hindrance.) Thus, the positions of the 3-halogeno-ester absorptions suggest that the bands arise from syn-s-trans-conformations and correspond to the higher wavenumber components of the 4- and 5-halogeno-ester doublets; the correspondence is supported by the solvent effects, the behaviour of the single bands resembling that of the higher wavenumber components of the doublets.

Table 1 provides many comparisons between 5-halogenated esters and their non-halogenated analogues in which the situation is not complicated by Fermi resonance [e.g., the pairs (1a)—(11a), (1b)—(9b), and (1c)—(9c)]. In view of the close similarity between the spectra of corresponding esters it is logical to extend to the non-halogenated esters the correlations developed for the halogenated compounds. Independent consideration of the non-halogenated esters leads to the same correlations. Thus, vector treatment incorporating the recent conclusion about the direction of the dipole moment of furan [8] indicates that the dipole moment of the syn-s-trans-form should be bigger than that of the anti-s-trans-rotamer: as the dielectric constant of the solvent is increased the syn-s-trans-form should therefore become relatively more important and, from the observed effects, it is then to be associated with the higher wavenumber component of a doublet.† The higher wavenumber of the syn-s-trans-form probably has its origin in the electrostatic repulsion that would arise from proximity of the ring oxygen and the negatively charged oxygen of dipolar canonicals, i.e. electrostatic inhibition of mesomerism reducing the single bond character of the formal C=O group.

The accumulated evidence leads to the general conclusion that where esters of furan-2-carboxylic acids show carbonyl doublets arising from rotational isomerism, the higher wavenumber band arises from the syn-s-trans-form and the lower wavenumber band from the anti-s-trans-form.

Thermodynamic Parameters.—Determination of the thermodynamic parameters of a system involving rotational isomers by variable temperature i.r. measurements is complicated by (i) the possible ' natural decrease ' of the band intensities with increasing temperature, and (ii) uncertainties in assessing the integrated absorption coefficients of the rotamer bands.[2a] Although the origin of natural decrease [9] is obscure and it is not

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* The description of these bands as unsymmetrical (Table 1) is not intended to imply any distinction between them and the components of resolved multiplets. For curve resolution the total absorption is simulated as precisely as possible by combining a number of symmetrical components; slight inflections in the experimental traces would not be represented in the resolved components. Many, possibly the majority of ' single ' ester C=O bands are not strictly symmetrical. Although the cause of this unsymmetrical profile has been established in specific cases (e.g. Fermi resonance in methyl pivalate [4c]), the generality of the phenomenon suggests that various effects may be involved.[4b]

† It might be contended that the results with the lactone (23) support this assignment. The relative intensities of the lactone bands in carbon tetrachloride over a range of temperature suggest that the C=O vibration occurs at ca. 1 758 cm^{-1}. This represents the absorption of a syn-s-cis-conformation, and if the general interpretation of ref. 7 is accepted the band of a corresponding syn-s-trans-form should be at ca. 1 730 cm^{-1}, close to the position of the higher wavenumber band of ethyl furan-2-carboxylate (1b). However, this argument involves a number of dubious assumptions.

[7] L. J. Bellamy, ' Advances in Infrared Group Frequencies,' Methuen, London, 1968.

[8] G. Marino, *J. Heterocyclic Chem.*, 1972, **9**, 817.

[9] R. Mierzecki, *Acta Phys. Polonica*, 1964, **25**, 797.

yet possible to predict whether a particular band will show this phenomenon,[10] its effect may be nullified or reduced in a rotameric system by using the relative band areas of the isomer absorptions.[2a] As explained earlier [2a] reliable enthalpy differences can be obtained without knowing, and irrespective of the values of, the band absorption coefficients. The results (Table 1) with the compounds examined over a temperature range reveal a general relationship, that for the furan esters showing rotational isomerism the *anti-s-trans*-forms are the thermochemically more stable forms. Work on attempts to assess free energy and entropy differences is described in SUP 21625.

[10] W. O. George, D. V. Hassid, and W. F. Maddams, *J.C.S. Perkin II*, 1973, 957.