dichlorophosphine with 1 mole each of a mixture of ethylmagnesium bromide and n-hexylmagnesium bromide. The racemic phosphine was readily separated from the other phosphines produced, viz., diethylphenylphosphine, b.p. 72–78° (1 mm.), and di-n-hexylphenylphosphine, b.p. 162–166° (1 mm.), by fractional distillation.

Although a mixture of tertiary phosphines was produced by reaction of phenyldichlorophosphine with ethylmagnesium and isobutylmagnesium bromides, the components could not be separated easily by fractional distillation.

Reaction of phenyldichlorophosphine with a mixture of α-naphthylmagnesium bromide and p-tolylmagnesium bromide gave a predominant amount of phenyl-di-α-naphthylphosphine, m.p. 208°.

Anal. Calcd. for $C_{26}H_{19}P$: C, 86.2; H, 5.28; P, 8.60. Found: C, 85.9; H, 5.56; P, 8.61.

Ethylphenyl-n-hexylbenzylphosphonium Bromide.—Treatment of 2.22 g. (0.01 mole) of ethylphenyl-n-hexylphosphine with an excess of benzyl bromide at room temperature for 16 hr. gave an oily product which was washed with ether and crystallized from acetone. There was obtained 3.50 g. (89%) of ethylphenyl-n-hexylbenzylphosphonium bromide, m.p. 121–122°.

Anal. Calcd. for $C_{21}H_{30}PBr$: C, 64.2; H, 7.64; P, 7.88; Br, 20.3. Found: C, 64.4; H, 7.82; P, 7.99; Br, 20.3.

Di-n-hexylphenylbenzylphosphonium bromide was obtained from di-n-hexylphenylphosphine and benzyl bromide in the same manner as described for ethylphenyl-n-hexylbenzylphosphonium bromide. The di-n-hexylphenylbenzylphosphonium bromide had m.p. 134–135° after crystallization from acetone.

Anal. Calcd. for $C_{25}H_{38}PBr$: C, 66.9; H, 8.46; P, 6.90; Br, 17.8. Found: C, 67.1; H, 8.68; P, 6.99; Br, 17.9.

The Effects of Solvent and Structure on the Low Intensity (n → π*) Electronic Transition of Carboxylate Esters

BY W. D. CLOSSON AND PAT HAUG

The effects of alkyl substitution, conformation, and solvent polarity on the low intensity electronic transition of saturated carboxylate esters have been investigated. All the observed effects are in keeping with identification of the weak band as an n → π* transition. Moderate shifts to longer wave length were observed with methyl substitution either on the carbon adjacent to the carbonyl group or on the carbon adjacent to the ether oxygen. Evidence is presented indicating that the former is due to inductive effects while the latter is probably of steric origin. The solvent sensitivities of the spectra indicated that the ester carbonyl group interacts with solvent in the same way, and to approximately the same degree, as the carbonyl group in aliphatic ketones. The s-cis conformation was found to have its absorption maximum located at longer wave lengths than that of s-trans.

Introduction

While the n → π* transition of the carbonyl group in aldehydes and ketones is well known and reasonably well understood,[1] the corresponding transition in compounds in which a heteroatom is bonded directly to the carbonyl group has received little attention. The gross effects of attaching a group bearing lone-pair electrons to the carbonyl group are easily predicted.[2] Such groups most commonly met with are $-NR_2$, $-OR$, or halogen, although certain others (e.g., $-SR$, $-SCN$, $-N_3$, etc.) may be expected to bring about the same effects. An approximate energy level diagram for the ester carbonyl system is presented in Fig. 1.

As shown in Fig. 1, interaction of the nonbonding electrons on the heteroatom with the π-orbitals of the carbonyl group raises the energy of the antibonding π-orbital (π^*) and splits the bonding π-orbital into two new orbitals, π_1 and π_2,[2] the latter being essentially a nonbonding orbital located mainly on the heteroatom. The two transitions of lowest energy should be n → π_3^* and π_2 → π_3^*, as shown.

These two transitions will frequently be very close in energy, and, depending on the hetero substituent, either may appear at longer wave length. Acyl chlorides are examples where the n → π_3^* band is clearly the lowest energy transition (near 235 mμ),[3]

and the fairly intense band near 230 mμ in the spectrum of thiol esters[4] is almost surely an example of the π_2 → π_3^* transition appearing at longest wave length. In the case of carboxylic acids and esters, it is well known[1-3] that a weak absorption band occurs near 210 mμ, and this is commonly regarded as the "forbidden" n → π^* transition, analogous to that observed in ketones and aldehydes. Recently, evidence based on rotatory dispersion and circular dichroism data and, to a certain extent, direct observation has been presented that indicated the existence of n → π^* transitions near 250 mμ in α,β-unsaturated acids.[5] Distinct absorption maxima corresponding to this transition have also been observed in the spectra of acrylate esters.[6]

In the present study the effects of molecular structure and solvent on the low intensity transition of saturated carboxylate esters have been examined. These effects have been thoroughly studied in the case of aldehydes and ketones.[1,7] In particular, three effects were

(1) J. W. Sidman, Chem. Rev., **58**, 689 (1958).

(2) H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1962, pp. 179–187.

(3) H. Ley and B. Arends, Z. physik. Chem., **B17**, 177 (1932).

(4) C. C. Price and S. Oae, "Sulfur Bonding," The Ronald Press Co., New York, N. Y., 1962, p. 47.

(5) U. Weiss and H. Ziffer, J. Org. Chem., **28**, 1248 (1963).

(6) (a) W. D. Closson, S. F. Brady, E. M. Kosower, and P. C. Huang, ibid., **28**, 1161 (1963); (b) S. F. Brady, unpublished work carried out in these laboratories.

(7) (a) E. M. Kosower, J. Am. Chem. Soc., **80**, 3261 (1958); (b) E. M. Kosower and G.-S. Wu, ibid., **83**, 3142 (1961); (c) E. M. Kosower, G.-S. Wu, and T. S. Sorensen, ibid., **83**, 3147 (1961); (d) P. Maroni, Ann. Chim., [13] **2**, 757 (1957); R. F. Mariella, et al., J. Org. Chem., **19**, 678 (1954), (e) H. McConnel, J. Chem. Phys., **20**, 700 (1952); (f) G. C. Pimentel, J. Am. Chem. Soc., **79**, 3323 (1957); (g) H. L. McMurry, J. Chem. Phys., **9**, 231 (1947); (h) see also A. E. Gillam and E. S. Stern, "Electronic Absorp-

investigated in the present study: the effect of solvent polarity on the energy of the transition, the effect of alkyl substitution at the carbon bonded to the carbonyl group (substitution in the acyl portion), and the effect of alkyl substitution in the alkoxy portion of the ester.

Results and Discussion

The wave lengths of maximum absorption for the low intensity band were carefully determined for several esters in a series of solvents of different polarity. The data are presented in the Experimental section, along with details of measurement and estimates of reproducibility.

There are two complicating factors involved in these measurements. One is the fact that the ester function is roughly planar and may exist in s-cis and s-trans conformations, as shown in I and II. Dipole moment measurements indicate that the favored conformation

I (s-cis)　　　　　　　II (s-trans)
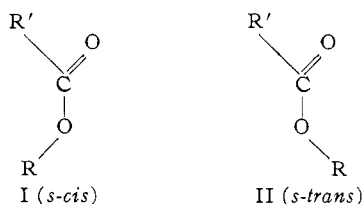
of acyclic esters is s-trans,[8] and that only when the ester function is incorporated into a ring of eight or fewer members does the less favorable (by ca. 3–4 kcal./mole) s-cis conformation appear.[9] It also appears that the alkyl group attached to oxygen is normally 20 to 30° out of the plane of the O—C=O triangle,[10] presumably a compromise between resonance and steric interactions. Although the temperature independence of the dipole moment indicates that the ester group is rather firmly fixed in the s-trans conformation,[8] this does not rule out a shift in equilibrium caused by solvation by a polar solvent, or at least change in the torsional angle of the alkoxy group.

The second complicating factor is the fact that in no case is the low intensity band completely separated from other, more intense, absorption which apparently reaches a maximum at a wave length shorter than the range of the instrument used. This means that changes in intensity and energy of the more intense band will have an effect on the measured position and intensity of the weak band. The most likely contributor to this end absorption is the $\pi_2 \rightarrow \pi_3^*$ transition. This band probably has a modest solvent sensitivity, shifting toward lower energies with increase in solvent polarity. (The effect of solvent on the related transition in n-butylthiol acetate is quite meager.[11]) It is assumed that the effects of this overlap will be similar for all esters, and that comparisons of the 210 mμ band of different esters will not suffer seriously.

Four criteria which have been used in the identification of n $\rightarrow$ π^* transitions are (a) low intensity (since it is symmetry-forbidden),[1,12] (b) "blue shift" of the

tion Spectroscopy," Edward Arnold (Publishers) Ltd., London, 1954, Chapter 5.

(8) (a) M. L. Bender, Chem. Rev., 60, 53 (1960), and references listed therein; (b) C. P. Smyth, "Dielectric Behavior and Structure," McGraw-Hill Book Co., Inc., New York, N. Y., 1955, pp. 303–309.

(9) (a) R. Huisgen and H. Ott, Tetrahedron, 6, 253 (1959); (b) N. L. Owen and N. Sheppard, Proc. Chem. Soc., 264 (1963).

(10) R. J. W. LeFevre and A. Sundaram, J. Chem. Soc., 3094 (1962).

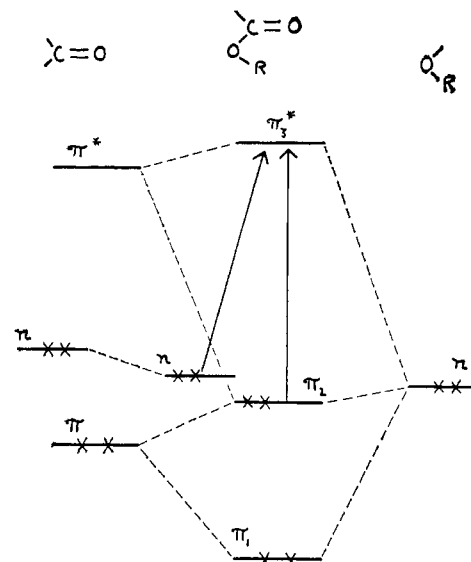(11) P. Haug; unpublished observations in these laboratories.

Fig. 1.—Approximate energy level scheme for the ester carbonyl system.

maximum caused by electron-supplying substituents attached directly to the π-system,[2,7c] (c) "blue shift" of the maximum with increasing polarity of the medium,[7] and (d) obliteration of vibrational fine structure on changing from nonpolar to polar media.[1] The band near 210 mμ in the spectra of saturated carboxylate esters, as is shown below, satisfies all these requirements and thus is definitely an n $\rightarrow$ π^* transition.

Intensity.—The molar absorptivities (ϵ) of saturated esters range from 20 to 100, most of them falling between 50 and 80. In the case of a typical ester (n-butyl acetate in methanol, λ_{max} 2082 Å., ϵ_{max} 56) the oscillator strength (f) of the transition was estimated as 0.0017.[13] This is about five times that of typical aldehydes and ketones, but still well within the range of "forbidden" n $\rightarrow$ π^* transitions.[1] The greate intensity of the ester transition may be due to a variety of causes, such as greater local asymmetry of the ester carbonyl, "stealing" of intensity from the nearby intense transitions, and simply to the higher energy of the ester transition (the theoretical expression of f being directly proportional to the frequency of the transition).

Vibrational Structure.—All of the formate esters measured showed considerable fine structure in isooctane. On changing to more polar solvents this feature vanished and smooth curves with only occasional shoulders and minor asymmetries were obtained. Even relatively nonpolar acetonitrile ($Z = 71.3$[7a]) was sufficient to cause this. A typical example of this effect in the case of neopentyl formate is shown in Fig. 2. In the spectra of other esters fine structure seems limited to the ocasional occurrence of shoulders or of flattened maxima. Certain esters, such as ethyl propionate and isobutyl acetate, exhibit distinct double maxima which persist even into certain polar solvents, but these may not be vibrational effects. Most simple esters exhibited maxima with smooth, symmetrical envelopes in all solvents.

(12) Reference 2, pp. 118–124.

(13) The expression

$$f = 2 \times 4.315 \times 10^{-9} \int_{40,000 \text{ cm.}^{-1}}^{\nu_{max} \text{ (cm.}^{-1})} \epsilon \, d\nu$$

was used in order to decrease contribution of end absorption to the calculated value.
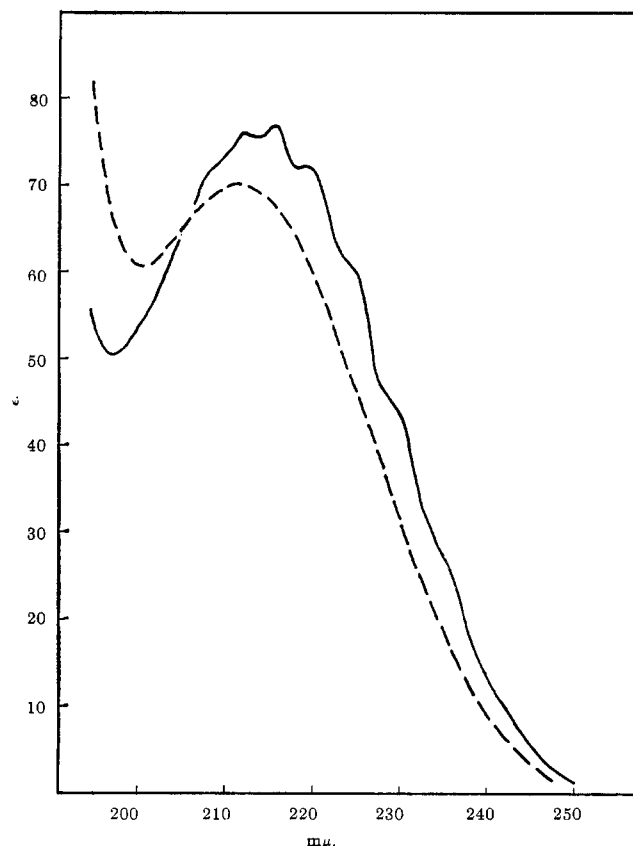
Fig. 2.—The ultraviolet absorption spectrum of neopentyl formate in: (a) isooctane, ———; (b) methanol, - - - - - - - - -.

Alkyl Substitution in the Acyl Group.—The effects of alkyl substitution in the acyl portion of methyl esters are presented in Table I. As in the case of aldehydes,[2]

TABLE I

ABSORPTION MAXIMA OF METHYL ESTERS

Ester	Isooctane λ_{max}, Å.	ϵ_{max}	Ethanol λ_{max}, Å.	ϵ_{max}	Water λ_{max}, Å.	ϵ_{max}
Formate	2152[a]	71	2130	77	2070	63
Acetate	2097	57	2072	57	2026	61
Propionate	2110	61	2087	60	2044	50
Isobutyrate	2128	77	2105	80	2063	79
Pivalate	2137	97	2116	100	2086	[b]

[a] Highest of several maxima. [b] Saturated solution.

methyl substitution directly on the carbonyl carbon results in a considerable shift of the transition to shorter wave length and is probably due to the same reason, *i.e.*, a moderate resonance interaction between the alkyl carbon and the carbonyl system.[2] Further substitution on the methyl group of acetate esters shifts the transition energy back toward lower values. The pattern of these latter shifts persists in all the solvents used and appears to occur in fairly regular increments as each additional methyl group is attached. This is quite similar to the pattern of shifts observed by Rice for the case of methyl alkyl ketones.[14] These shifts are probably the result of inductive effects. It has been pointed out that C–C hyperconjugation should be about as effective as C–H hyperconjugation,[15] so that resonance effects should remain roughly constant for the acetate–pivalate series while electron-donating inductive effects should increase.[16] Such an
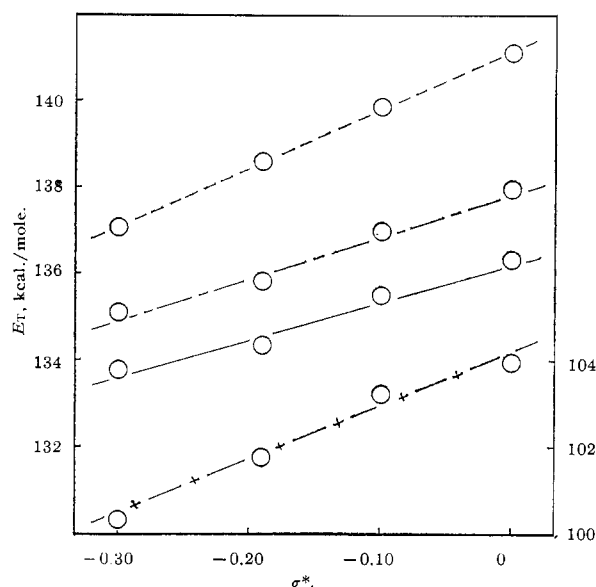
(14) F. O. Rice, *J. Am. Chem. Soc.*, **42**, 727 (1920).

(15) M. J. S. Dewar, "Hyperconjugation," The Ronald Press Co., New York, N. Y., 1962, Chapter 2.

Fig. 3.—E_T (transition energies) *vs.* σ^* for methyl acetate, propionate, isobutyrate, and pivalate in: (a) water, - - - - - - - - -; (b) ethanol, — - — - —; and (c) isooctane, ———. The bottom curve is a plot of E_T *vs.* σ^* for methyl alkyl ketones (data from ref. 14), and the ordinate scale at the right should be used with it.

inductive effect should raise the energy of the n-electrons on oxygen and shift the transition to longer wave length. In Fig. 3 are shown plots of E_T *vs.* Taft's polar substituent constants (σ^*)[16] for the esters in three different solvents, and for Rice's data on methyl alkyl ketones in chloroform.[14] The relationship between E_T and σ^* is quite linear for both esters and ketones. The slope (determined by least-squares treatment) for methyl alkyl ketones is 13.0 kcal. per σ^* unit, while that for the esters is 14.5, 10.7, and 9.7 kcal. in water, ethanol, and isooctane, respectively. The upward trend in slope of the ester plots as one moves to more polar solvents is due to a relationship between the solvent sensitivity of the n → π^* transition of individual esters and their degree of substitution in the acyl portion (see column 2 of Table III). Thus the spread in E_T between methyl pivalate and methyl acetate becomes larger, the more polar the solvent. This is probably caused by steric hindrance of solvation of the carbonyl group in the more highly alkylated esters. Assuming, therefore, that the data in isooctane are most comparable to Rice's data, one sees that acyl substitution has three-quarters the effect in esters that it has in methyl alkyl ketones.

Alkyl Substitution in the Alkoxy Group.—In Table II are shown the absorption data (in isooctane) for acetates and formates of different alcohols. Consider the sequence methyl, ethyl, isopropyl, *t*-butyl acetate. The maxima shift from 2097 to 2162 Å., with the bulk of the change coming between isopropyl and *t*-butyl acetates. A similar, but less clear, pattern is seen in the formate esters. The considerable fine structure shown by formates in isooctane makes assignment of absolute maxima difficult, and the *t*-butyl ester unfortunately possesses the most irregular spectrum. In more polar solvents *t*-butyl formate curiously develops a long flat shoulder instead of a distinct maximum. In any case, the acetate spectra are more typical since the same pattern also appears very clearly in the

(16) R. W. Taft, Jr., "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, p. 619.

TABLE II

ABSORPTION MAXIMA OF ACETATE AND FORMATE ESTERS IN ISOOCTANE

Ester	Acetate λ_{max}, Å.	Acetate ϵ_{max}	Formate λ_{max}, Å.[a]	Formate ϵ_{max}
Methyl	2097	57	2152	71
Ethyl	2110	58	2157	82
Isopropyl	2118	63	2159	75
t-Butyl	2162	53	2178	79
Isobutyl	2107[b]	. .	. . .	. .
Neopentyl	2104	63	2155	77
n-Propyl	2098	56	2157	79
2,2,3,3-Tetrafluoropropyl	2097	57	. . .	. .

[a] Highest of several maxima.   [b] Midpoint between two maxima of approximately equal height.

$n \rightarrow \pi^*$ transitions of acrylate esters.[6b] Again, hyperconjugation effects seem ruled out for the reasons stated above. Also, it seems difficult to draw reasonable valence-bond resonance structures involving the methoxyl methyl group. Another possibility would be contribution of resonance forms such as III, although theoretical considerations suggest that such electron supply would raise rather than decrease transition

III
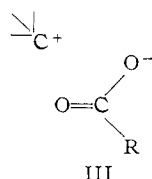
energy.[1,7c]   An explanation based on inductive effects also appears implausible, considering the fact that nearly all the shift occurs between isopropyl and t-butyl acetate. Another good argument against operation of inductive effects is the fact that n-propyl and 2,2,3,3-tetrafluoropropyl acetates have virtually identical absorption spectra in isooctane (Table II), even though inductive effects should be considerably different in the two cases. A steric origin thus seems likely. The pattern is very similar to that caused by steric effects in many other instances.[17]   (Note that movement of the branching methyl groups to a position one carbon atom away from the ether oxygen, as in neopentyl acetate and formate, results in return of the maximum to its normal wave length.) The cause of the effect is probably direct interaction between the alkyl group and the carbonyl oxygen. This could either raise the energy of the n-electrons on oxygen, or force the –OR group further out of coplanarity with the O—C=O triangle and thereby lower π_3^*. Another result of such interaction could be an increase in the C–O–C bond angle (normally about 112°)[18] which would also probably decrease π_3^*. A large deviation from coplanarity of the alkoxy group in t-butyl esters should result in increased dipole moments, but the dipole moment of t-butyl acetate (1.91 D.) is very similar to that of primary and secondary alkyl acetates (1.74–1.90 D.).[8b]   Interestingly, the solvent sensitivity of the $n \rightarrow \pi^*$ maximum in t-butyl acetate is very similar

TABLE III

SOLVENT SENSITIVITIES OF $n \rightarrow \pi^*$ TRANSITIONS

Compound	$E_T(H_2O) - E_T(isooctane)$[a]	m[b]	Ref.
Methyl formate	4.25	0.129	
Methyl acetate	4.79	.142	
Methyl propionate	4.37	.113	
Methyl isobutyrate	4.13	.152	
Methyl pivalate	3.27	.091	
Ethyl acetate	4.31	.138	
Isopropyl acetate	5.10	.062	
t-Butyl acetate	4.36	.143	
Propiolactone	4.12	.119	
Butyrolactone	6.15[e]	.183	
Cyclobutanone	2.94	.082	d
Cyclopentanone	6.58	.182	d
Cyclohexanone	5.07	.147	d
Cyclohexyl azide[e]	0.31[c,e]	.011[e]	f

[a] In kcal./mole.   [b] Slope of plot of E_T vs. Z ($E_T = mZ + b$). [c] $E_T(H_2O)$ replaced by $E_T(2,2,3,3$-tetrafluoropropanol).   [d] Data taken from ref. 7b.   [e] For the $\pi_y \rightarrow \pi_x^*$ transition near 2870 Å. [f] Data taken from ref. 24.

to that of methyl acetate (see Table III) and not at all depressed as in the case of methyl pivalate. Whatever the nature of the interaction between the t-butoxy and carbonyl groups, it does not interfere with solvation of the carbonyl oxygen.

Lactones.—As examples of esters possessing the *s-cis* conformation, propiolactone and butyrolactone were investigated. Propiolactone has its maximum at an abnormally short wave length (2072 Å. in isooctane) while the $n \rightarrow \pi^*$ band of butyrolactone is centered at 2140 Å. in isooctane, exhibiting a relatively low transition energy.

The high transition energy of propiolactone is probably due to the bond angle strain involved in placing the ester function in a four-membered ring. Reduction of the internal angles should result in an increase in s-character in the σ-bond of the carbonyl group which should shorten both the σ- and π-bond and thus raise the π_3^* level.[19] Shortening of the carbonyl bond is also indicated by the abnormally high carbonyl stretching frequency of propiolactone.[20] Cyclobutanone also shows a shift of its $n \rightarrow \pi^*$ transition (2815 as compared with 2914 Å. for cyclohexanone; both in isooctane),[7b] and its carbonyl stretching frequency also is increased.[21] The suggestion that normal ester resonance is considerably dampened in propiolactone[20] seems implausible since this would shift its $n \rightarrow \pi^*$ transition to *longer* wave lengths.

The rather low transition energy of butyrolactone is probably an indication that the unstrained *s-cis* ester conformation has its $n \rightarrow \pi^*$ band located at longer wave length than the *s-trans* form. A five-membered lactone still possesses some internal strain as indicated by its slightly higher than usual carbonyl stretching frequency.[20] Also, its dipole moment (4.09[9a] to 4.12 D.[22]) appears to be slightly lower than the value 4.30 D. which has been assigned to the strainless *s-cis* conformation.[9a] It would seem that the (lone-pair)–

(17) See, for example: A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw–Hill Book Co., Inc., New York, N. Y., 1962, p. 13; P. B. D. de la Mare, "Progress in Stereochemistry," Vol. 1, W. Klyne, Ed., Academic Press, Inc., New York, N. Y., 1954, Chapter 3; Vol. 2, Chapter 3; B. M. Wepster, *ibid.*, Chapter 4; ref. 16, p. 205; C. A. Bunton, "Nucleophilic Substitution at a Saturated Carbon Atom," Elsevier Publishing Co., New York, N. Y., 1963, Chapter 2.

(18) J. M. O'Gorman, W. Shand, and V. Schomaker, *J. Am. Chem. Soc.*, **72**, 4222 (1950).

(19) R. N. Jones and C. Sandorfy, "Chemical Applications of Spectroscopy, Technique of Organic Chemistry," Vol. 9, W. West, Ed., Interscience Publishers, Inc., New York, N. Y., 1956, p. 486, and references listed therein.

(20) S. Searles, M. Tamres, and G. M. Barrow, *J. Am. Chem. Soc.*, **75**, 71 (1953).

(21) S. L. Friess and P. E. Frankenburg, *ibid.*, **74**, 2679 (1952).

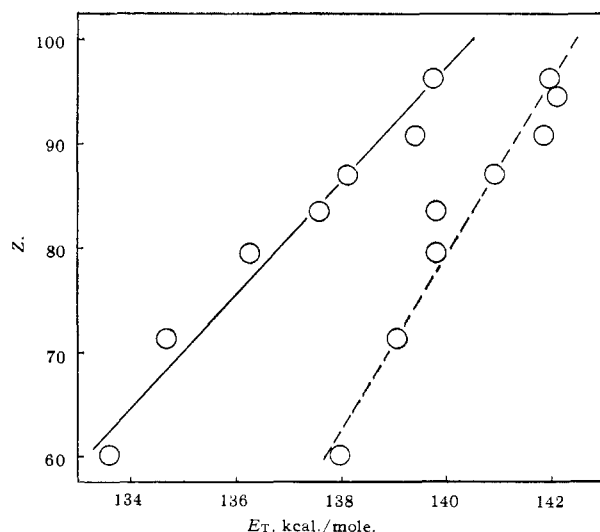(22) R. J. B. Marsden and L. E. Sutton, *J. Chem. Soc.*, 1383 (1936).

Fig. 4.—E_T (transition energies) vs. Z (solvent polarity values) for butyrolactone, ———, and propiolactone, ---------.

Fig. 5.—E_T (transition energies) vs. Z (solvent polarity values) for: t-butyl acetate, —O—; methyl pivalate, —◐—; ethyl acetate, —◔—; and methyl acetate, —◑—.

(lone-pair) electron repulsions[9b] in the s-cis conformation, which apparently account for most of the difference in ground-state energies in the s-cis and s-trans conformations,[9] will probably lead to a lowering of the n → π* transition energy by 2–4 kcal./mole in the case of 6-, 7-, and possibly 8-ring lactones. This is presently being investigated.

Effects of Solvent Polarity.—Since the solvent sensitivity of the n → π* band of ketones has been carefully studied and reasonable explanations have been advanced,[1,7] it is of considerable interest to look at similar effects in the case of esters. In Table III are presented data comparing solvent sensitivities of ester n → π* bands with those of certain other compounds. The data in the second column (E_T-(H_2O) − E_T(isooctane)) are self-explanatory; the m-values in the third column are slopes of the least-squares plots of E_T vs. Z, where Z is an empirical index of solvent polarity.[23]

In their ability to hydrogen bond to CH_3OD, it has been previously shown that lactones and cyclic ketones are roughly equal, and that their basicities both lie in the order 6- > 5- > 4-membered ring.[20,24] It was also shown that it was the carbonyl oxygen and not the ether oxygen of lactones that was involved in hydrogen bonding.[20] One would then expect that the n → π* transition of lactones would have about the same solvent sensitivity as that of cyclic ketones. (Most polar solvents are hydroxylic.[23]) When one compares either the ΔE_T or m-values of the lactones and ketones in Table III, it is seen that they are very similar. In particular, the close resemblance between the data for butyrolactone and cyclopentanone is striking. On the other hand, neither the ΔE_T nor the m-values of the esters and lactones resemble those of the 2860 Å. band of cyclohexylazide, which is known not to be an n → π* transition.[25]

In Fig. 4 are shown plots of E_T vs. Z for propiolactone and butyrolactone. There is some scatter, but a linear relationship (as observed for cyclic ketones[7b]) seems definite. In Fig. 5 similar plots for some of the acyclic esters are presented. Here the scatter is a
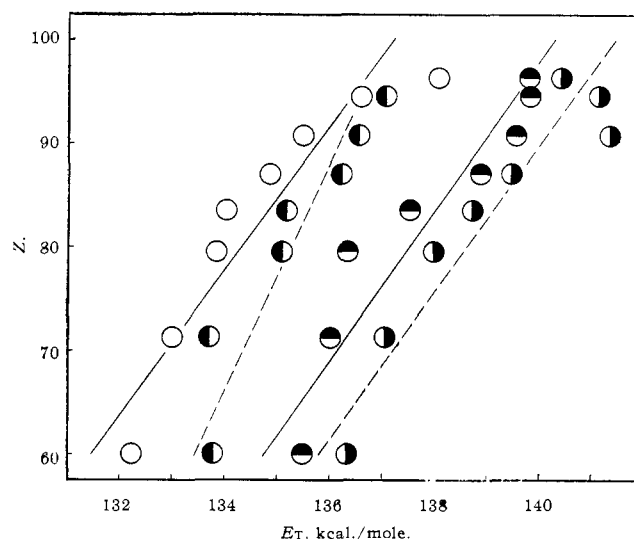
little worse and curvature appears in some instances. Causes of these deviations may include the conformational mobility of the esters, or the occurrence of ether oxygen solvation in the more polar solvents. Unfortunately, the high concentrations of solute necessary for the measurements (ca. 0.08 to 0.15 M) may have had effects on the actual polarity of the solutions, thus making more refined interpretations of little value. In any case, the m-values for acyclic esters are at least qualitatively significant. The fact that their solvent sensitivities fall in the same range as those of cyclic ketones indicates that the major factors influencing solvation of the carbonyl oxygen are the same in both cases.

Experimental[26]

Solvents.—All solvents were at least of spectrograde quality. The 2,2,3,3-tetrafluoropropanol was received as a gift from D. E. O. Langerak of the Organic Chemicals Department, E. I. du Pont de Nemours and Co., and was purified by the method of Kosower and Huang.[7b] The 80% aqueous methanol was prepared by mixing 4 volumes of pure methanol and 1 volume of distilled water at 25°. The 40% aqueous ethanol was prepared from absolute ethanol and distilled water in a similar manner.

Materials.—Most of the esters were obtained commercially and redistilled prior to use. All the esters were tested for purity and homogeneity by gas chromatographic analysis, using a 6-ft. column of 20% didecyl phthalate on 60/80 mesh firebrick at an appropriate temperature. All except neopentyl formate were found to be at least 99.5% pure, the major contaminant usually being the corresponding alcohol. Traces of ether and of the corresponding carboxylic acid were occasionally observed. Minor amounts of these compounds would be unlikely to affect the values of the spectroscopic constants to a measurable extent.

2,2,3,3-Tetrafluoropropyl acetate was prepared from the alcohol by treatment with acetic anhydride in pyridine solution. To a solution of 4.2 g. (0.0411 mole) of acetic anhydride in pyridine was added 3.5 g. (0.0341 mole) of tetrafluoropropanol, and the mixture stirred briefly then heated on a steam bath for 4 hr. It was next poured into a mixture of ice and HCl. The ester was extracted with ether, washed with dilute acid and then with dilute carbonate solution, and dried with magnesium sulfate. After concentrating the solution, the crude ester was evaporatively distilled at 75° and 40 mm.; $n^{25}D$ 1.3386.

Anal. Calcd. for $C_5H_6F_4O_2$: C, 34.49; H, 3.48. Found: C, 34.66; H, 3.77.

(23) E. M. Kosower, *J. Am. Chem. Soc.*, **80**, 3253 (1958).
(24) M. Tamres and S. Searles, Jr., *ibid.*, **81**, 2100 (1959).
(25) W. D. Closson and H. B. Gray, *ibid.*, **85**, 290 (1963).

(26) The authors wish to thank Mr. M. Kassenoff and Mr. P. Orenski for preparing some of the esters used in this study.

2,2,3,3-Tetrafluoropropyl propionate was prepared in a similar manner; n^{25}D 1.3490.

Anal. Calcd. for $C_6H_8F_4O_2$: C, 38.30; H, 4.29. Found: C, 38.53; H, 4.40.

Neopentyl formate was prepared by treating 7.51 g. (0.085 mole) of neopentyl alcohol with a solution of 0.75 ml. of sulfuric acid in 51 ml. of 97% formic acid. The mixture was stirred at room temperature for 22 hr., poured into water, and extracted with ether. The ether solution was washed with dilute base and then with saturated brine before being dried with sodium sulfate. Distillation yielded 6.11 g. (0.0525 mole) of ester; b.p. 110–111°, n^{26}D 1.3899. This was shown by gas chromatographic analysis to contain about 4% of neopentyl alcohol.

Anal. Calcd. for $C_6H_{12}O_2$: C, 62.04; H, 10.41. Found: C, 62.08; H, 10.59.

Neopentyl acetate was prepared from neopentyl alcohol and acetic anhydride in a manner similar to that of tetrafluoropropyl acetate; b.p. 123–125°, n^{26}D 1.3921 (lit.[27] b.p. 127° (740 mm.), n^{25}D 1.3927).

t-**Butyl formate** was prepared by placing a mixture of 24 ml. of 97% formic acid and 75 ml. of isobutene in a pressure bottle and allowing it to stand at room temperature for 18 hr. The solution was then poured into ice water and the ester extracted with ether. The ether solution was washed with bicarbonate solution and saturated brine, then dried with sodium sulfate. The ether was removed by distillation at atmospheric pressure, and the residual ester purified by evaporative distillation at 47° (180 mm.); n^{26}D 1.3778 (lit.[28] n^{26}D 1.3783).

Measurements.—The spectra were measured with a Cary recording spectrophotometer, Model 14, using matched 0.1-cm. cells. The maxima were measured by running three to four times (at the slowest scanning speed) over the region of maximal absorption and averaging the values thus obtained. A slow flow of nitrogen was passed through the spectrophotometer during the measurements, and care was taken to ensure that the slit width did not exceed 0.3 mm. In a few cases where solubility prohibited the use of 0.1-cm. cells, 1.0-cm. cells were used and the slit widths kept within the above mentioned range by increasing the photocell voltage. The maxima could be duplicated to at least ±5 Å., and usually to ±3 Å., except in those few cases where the bands were irregularly shaped. The molar absorptivities (ϵ) are probably accurate to within ±5%, except in the cases of the more volatile esters (*e.g.*, methyl formate) where the reproducibility was rather poor. All measurements were carried out using freshly prepared solutions.

Spectroscopic Data.—Below are listed the absorption maxima (in Å.) and the molar absorptivities of each ester in all the solvents used. In cases of more than one maxima, the principle ones are listed.

Methyl formate: isooctane, 2112 (70), 2152 (71), 2191 (66) (considerable fine structure); acetonitrile, 2117 (71); methanol, 2114 (59); TFP,[29] 2077 (63).

Ethyl formate: isooctane, 2122 (81), 2157 (82), 2196 (78) (considerable fine structure); acetonitrile, 2134 (48); ethanol, 2132 (75); methanol, 2126 (64); water, 2077 (52); TFP,[29] 2084 (64).

n-**Propyl formate:** isooctane, 2121 (78), 2157 (79), 2195 (75) (considerable fine structure); acetonitrile, 2134 (71); ethanol, 2124 (76); methanol, 2124 (71); water, 2063 (saturated solution); TFP,[29] 2047 (54).

Isopropyl formate: acetonitrile, 2137 (65); ethanol, 2136 (67); methanol, 2134 (64); water, 2082 (saturated solution); TFP,[29] 2083 (61).

t-**Butyl formate:** acetonitrile, *ca.* 210 mμ (69) (broad shoulder); ethanol, *ca.* 213 mμ (75) (broad shoulder); methanol, *ca.* 210 mμ (72) (broad shoulder); water, *ca.* 211 mμ (55) (broad shoulder).

Neopentyl formate: isooctane, 2120 (76), 2155 (77), 2195 (72) (considerable fine structure); acetonitrile, 2122 (69); ethanol, 2155 ± 5 (72) (flat peak); methanol, 2117 (70).

Methyl acetate: acetonitrile, 2086 (45); methanol, 2061 (55); 80% aqueous methanol, 2050 (56); 40% aqueous ethanol, 2023 (59); TFP,[29] 2036 (50).

Ethyl acetate: acetonitrile, 2102 (58); ethanol, 2097 (64); methanol, 2079 (56); 80% aqueous methanol, 2059 (60); 40% aqueous ethanol, 2049 (56); water, 2045 (53) (flat peak); TFP,[29] 2045 (55).

n-**Propyl acetate:** acetonitrile, 2103 (50); ethanol, 2081 (58); methanol, 2090 (55); water, 2033 (51); TFP,[29] 2044 (56).

n-**Butyl acetate:** isooctane, 2017 (51), 2138 (50); acetonitrile, *ca.* 210 mμ (71) (flat peak); ethanol, 2090 (58); methanol, 2082 (56); water, 2030 (saturated solution); TFP,[29] 2040 (60).

Isobutyl acetate: isooctane, 2078 (50), 2136 (56); acetonitrile, *ca.* 210 mμ (60) (average of 2 indistinct maxima); ethanol, 2087 (60); methanol, 2077 (57); TFP,[29] 2039 (59).

Neopentyl acetate: acetonitrile, 2074 (59); ethanol, 2067 (62); methanol, 2063 (62).

Isopropyl acetate: acetonitrile, 2101 (58); ethanol, 2091 (60); methanol, 2088 (59); water, 2041 (62); TFP,[29] 2048 (59).

t-**Butyl acetate:** acetonitrile, 2149 (59); ethanol, 2136 (61); methanol, 2133 (55); 80% aqueous methanol, 2120 (60); 40% aqueous ethanol, 2110 (60); water, 2093 (saturated solution); TFP,[29] 2071 (65).

Methyl propionate: acetonitrile, 2095 (53); methanol, 2077 (62); TFP,[29] 2057 (52).

Ethyl propionate: isooctane, 2045 (66), 2078 (67); acetonitrile, 2047 (78), 2075 (78); ethanol, 2045 (70), 2076 (70); methanol, 2046 (73), 2074 (74); water, 2042 (62), *ca.* 2065 (61); TFP,[29] 2034 (60), 2063 (59) (all the ethyl propionate spectra exhibited additional shoulders).

2,2,3,3-Tetrafluoropropyl propionate: isooctane, 2101 (64); acetonitrile, 2082 (58).

Methyl isobutyrate: acetonitrile, 2131 (73); methanol, 2106 (78); TFP,[29] 2071 (87).

Ethyl isobutyrate: isooctane, 2123 (85); acetonitrile, 2112 (86); ethanol, 2105 (89); methanol, 2103 (89); TFP,[29] 2075 (98).

Methyl pivalate: acetonitrile, 2138 (89); methanol, 2115 (100); 80% aqueous methanol, 2099 (103); 40% aqueous ethanol 2094 (102); TFP,[29] 2082 (110).

Propiolactone: isooctane,[30] 2072 (54); acetonitrile, 2056 (48); ethanol, 2045 (52); methanol, 2045 (49); 80% aqueous methanol, 2029 (52); 40% aqueous ethanol, 2016 (50); water, 2012 (52); TFP,[29] 2014 (50).

Butyrolactone: isooctane,[30] 2140 (25); acetonitrile, 2123 (35); ethanol, 2098 (39); methanol, 2078 (40); 80% aqueous methanol, 2070 (39); 40% aqueous ethanol, 2051 (41); water, *ca.* 203 mμ (42) (shoulder); TFP,[29] 2046 (28).

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(29) 2,2,3,3-Tetrafluoropropanol.

(30) Data in isooctane obtained from measurements using 1.0-cm. cells.